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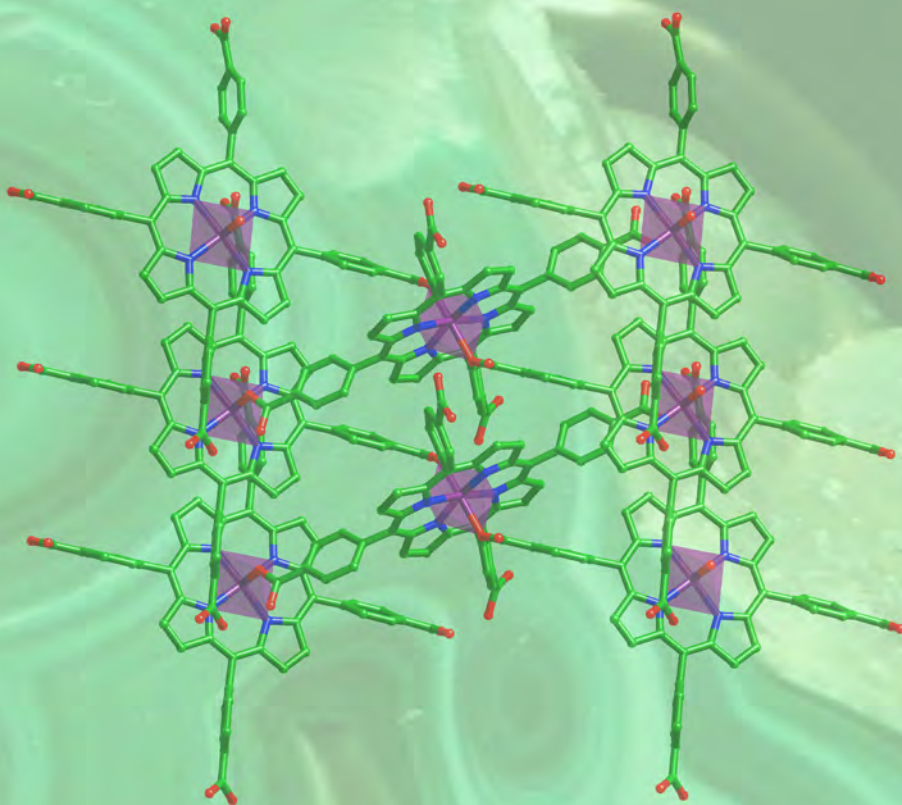


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# MOFs basados en metaloporfirinas: diseño estructural orientado a la biomimetización de sus propiedades naturales



Arkaitz Fidalgo Marijuan

Memoria para optar al grado de Doctor

Marzo 2014



EIDOS  
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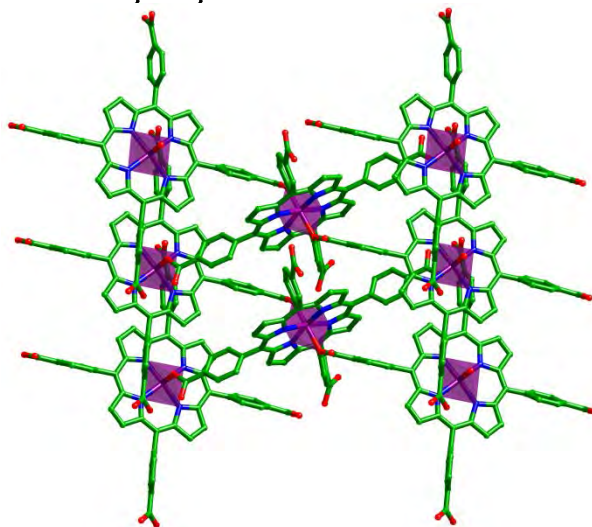
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Memoria presentada por

Arkaitz Fidalgo Marijuan

Para optar al grado de Doctor



Leioa, Marzo 2014





*Nire familiari*

*Lorenari*

*Nire inguruan dauden guztiei*





*En este espacio me gustaría mostrar mi más sincero agradecimiento a todas las personas que han hecho posible que este trabajo sea una realidad.*

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*paramagnética electrónica (EPR) y, especialmente, por la interpretación y discusión de los resultados obtenidos tanto en EPR, como en las medidas magnéticas (cuanta guerra nos ha dado el hierro). De verdad, gracias por formarme en este campo y por el interés mostrado, por haberme enseñado y por la cantidad de tiempo invertido en la realización, interpretación y redacción de los resultados. Por último, agradecer a la Dra. Marta Iglesias al acogernos en el Instituto de Ciencias Materiales del CSIC en Madrid y haber realizado las medidas de catálisis.*

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La presente memoria del trabajo de tesis Doctoral se ha escrito siguiendo el formato de publicaciones. Incluye, además de una introducción general sobre el estado actual del área de investigación en la que se enmarca el trabajo realizado, un resumen, visión global de los hallazgos, conclusiones del trabajo y una descripción de las técnicas instrumentales empleadas en la caracterización de los compuestos. Los capítulos en los que se recogen los trabajos publicados mantienen su formato original en inglés, mientras que el resto de apartados se han escrito en castellano de acuerdo con la normativa para este formato de tesis.

La memoria adjunta un CD donde se encuentra la versión electrónica de este documento, además de los artículos originales mencionados a lo largo de esta memoria separados por capítulos con los respectivos ficheros CIF de cada estructura cristalina descrita.



# Resumen

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La Ciencia y Tecnología de Materiales tiene el reto permanente de desarrollar y mejorar materiales multifuncionales y respetuosos con el medio ambiente. En este sentido, los materiales de tipo MOF (Metal-Organic Framework) están siendo objeto de un gran interés, ya que las redes sólidas de coordinación (especialmente, las porosas) presentan aplicaciones en campos en los que la sociedad manifiesta una demanda creciente de ciencia y tecnología, como el almacenamiento y transporte de energía, la captura de gases con efecto invernadero, la catálisis heterogénea y la liberación controlada de fármacos, entre otros.

En este contexto, el presente trabajo se planteó con el objetivo de desarrollar nuevos materiales de tipo MOF basados en metaloporfirinas, al objeto de mimetizar las funciones que desempeñan las mismas en los sistemas biológicos, con el fin de reproducirlas en el estado sólido. Para ello, se han escogido biometales como el hierro y el cobalto: característicos de estos sistemas, de bajo coste y medioambientalmente respetuosos. Por otra parte, las porfirinas seleccionadas han sido las siguientes: TPP (*meso*-tetra-4-fenilporfirina), TCPP (*meso*-tetra-4-carboxifenilporfirina) y TPPS (*meso*-tetra-4-sulfonatofenilporfirina). Estas tres moléculas conforman un conjunto de ligandos que difieren ligeramente en sus grupos funcionales. Asimismo, en ocasiones, se ha utilizado un ligando secundario dipiridínico (4,4'-bipiridina) que ha actuado como espaciador.

El diseño de las síntesis se ha centrado tanto en las combinaciones adecuadas de metales y ligandos como en la selección de las técnicas de síntesis. Así, se han obtenido cinco nuevos compuestos, que se han sintetizado en condiciones solvotermales suaves o mediante radiación microondas. La caracterización preliminar de los mismos se ha llevado a cabo mediante análisis cuantitativo, espectroscopia infrarroja y Raman, difracción y fluorescencia de rayos X y medidas de densidad. El estudio estructural se ha realizado mediante difracción de rayos X y el estudio térmico se ha llevado a cabo mediante termogravimetría y termodifracción.

En los casos en que ha resultado procedente, también se han caracterizado los compuestos mediante espectroscopia ultravioleta-visible (UV-Vis), Mössbauer y resonancia paramagnética electrónica (EPR) y mediante medidas de la susceptibilidad magnética. Asimismo, ocasionalmente, se han realizado cálculos mecano-cuánticos basados en la teoría del funcional de la densidad (DFT) y medidas catalíticas.

El primero de los cinco compuestos obtenidos, de fórmula [FeTCPP], es quiral y destaca por ser la tercera estructura 2D publicada basada en esta porfirina. La formación de este compuesto está condicionada por la oxidación de los iones de hierro y por la existencia de grupos carboxílicos en la porfirina.

Por otra parte, con la participación del espaciador 4,4'-bipiridina (bipy) se han obtenido tres redes 1D. Así, la estructura cristalina del compuesto  $([\text{FeTPPbipy}]^+)_n$  se explica mediante la formación de radicales neutros que se estabilizan en un empaquetamiento que permite la formación de enlaces entre los grupos fenílicos de distintas cadenas. La formación de estos enlaces queda corroborada por la existencia de significativas interacciones antiferromagnéticas. Por otra parte, en el compuesto  $[\text{CoTPP}(\text{bipy})] \cdot ([\text{CoTPP}])_{0.22} \cdot (\text{TPP})_{0.78}$ , la disposición de las cadenas deja grandes huecos en la red que se ocupan con porfirinas tanto coordinadas como sin coordinar. El tercero de estos compuestos 1D presenta la fórmula  $[\text{CoTPPS}_{0.5}(\text{bipy})(\text{H}_2\text{O})_2] \cdot 6\text{H}_2\text{O}$  y destaca porque la extensión de las cadenas se produce por la alternancia de dos tipos de octaedros de  $\text{Co}^{\text{II}}$ . La naturaleza de los grupos sulfonato de la porfirina TPPS es determinante para comprender la intrincada red de enlaces de hidrógeno de este compuesto, que propician la formación de una red interpenetrada caracterizada por su gran estabilidad térmica (hasta los 370°C).

Finalmente, con la porfirina TCPP se ha obtenido un segundo compuesto de fórmula  $\mu\text{-O}-[\text{FeTCPP}]_2 \cdot n\text{DMF}$  ( $n \approx 16$ ; DMF = dimetilformamida). El mismo presenta grandes cavidades (47% de porosidad) que diluyen la matriz magnética, caracterizada

por fuertes interacciones antiferromagnéticas intradiméricas. Todo ello revela una inusual estructura superhiperfina, observada por espectroscopia EPR.

El trabajo que se recoge en esta memoria constituye, por lo tanto, un “viaje” de mayor a menor dimensionalidad en las estructuras cristalinas. La guía de este viaje ha sido la búsqueda de propiedades catalíticas en sistemas heterogéneos. Así, el  $[\text{CoTPP}(\text{bipy})] \cdot ([\text{CoTPP}])_{0.22} \cdot (\text{TPP})_{0.78}$  obedece el enfoque de inmovilizar o anclar el catalizador en los huecos de la red. Sin embargo, la estrategia alternativa seguida para el compuesto  $\mu\text{-O-}[\text{FeTCPP}]_2 \cdot n\text{DMF}$  (es decir, que el propio MOF actúe de catalizador) es la que ha aportado mejores y más prometedores resultados en lo que a catálisis heterogénea se refiere.





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# *INTRODUCCIÓN*

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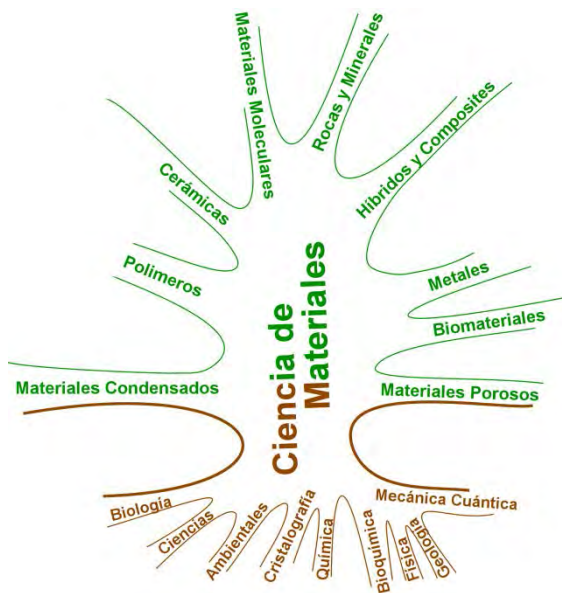
Desde los orígenes, la existencia y evolución del ser humano han estado íntimamente vinculadas al desarrollo y explotación de los materiales que ha tenido a su alcance. En parte para compensar sus limitaciones físicas, el ser humano siempre ha buscado nuevos materiales que pudieran ser de utilidad para cubrir sus carencias. Así, los materiales están íntimamente relacionados con la evolución, desde la edad de piedra; con la utilización de rocas, huesos y madera, pasando por la edad de los metales con el descubrimiento y aplicación de los mismos en el combate. Posteriormente, en la edad media, los primeros experimentos de alquimia permitieron el descubrimiento de otros nuevos materiales. Más tarde, llegó la era industrial, caracterizada por el desarrollo del acero y, por último, la era actual, en la que se debe hablar de una multitud de nuevos materiales en constante creación, desarrollo y optimización para una aplicación concreta.

La necesidad de adquirir nuevo conocimiento frente a problemáticas de distinta índole, impulsó la investigación en materiales en el campo de la metalurgia a principios del siglo XX. Sin embargo, no es hasta mediados de siglo cuando las nuevas exigencias tecnológicas provenientes de diversos sectores hacen que técnicas y teorías de muy diversas ramas del saber (química de estado sólido, física de la materia condensada, cristalografía, biología, geología, mecánica cuántica, termodinámica, ...) tiendan a interrelacionarse y confluyan en la Ciencia y Tecnología de Materiales<sup>1,2</sup> (Figura 1), permitiendo un avance simultáneo de las diferentes áreas científicas.

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<sup>1</sup> Serratos, J. M., *Bol. Soc. Esp. Ceram. V.* **2010**, 49, 129-138.

<sup>2</sup> Hutagalung, S. D., *Materials Science and Technology*. Ed. InTech, Rejika, Croatia, 2012, 324 pp.



**Figura 1.** Campos de aplicación de la Ciencia y Tecnología de Materiales.

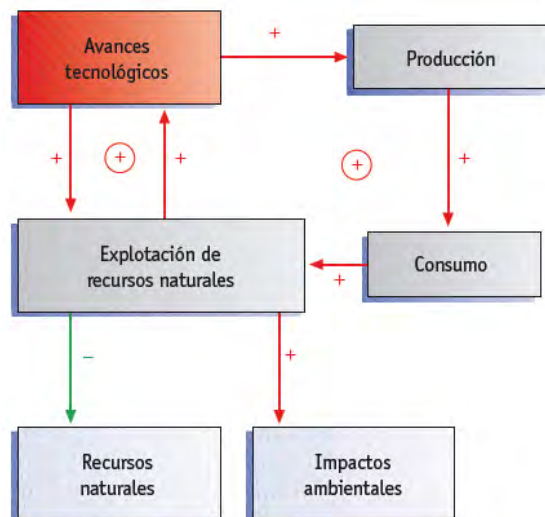
De esta manera, la Ciencia y Tecnología de Materiales se entiende como una de las áreas de conocimiento multidisciplinar más importantes y activas de la sociedad contemporánea, que tiene como objetivo el estudio de las propiedades fundamentales de los materiales en relación con su composición, textura y estructura atómico-molecular.<sup>3</sup> El progreso, en este sentido, ha sido tan vertiginoso que, en las últimas décadas, los avances en el establecimiento de correlación entre la estructura cristalina y las propiedades físico-químicas de los compuestos han permitido el diseño de nuevos materiales, átomo a átomo, previendo las propiedades de los mismos y posibilitando un masivo desarrollo de materiales aplicados a funciones inimaginables hasta ahora.

Tanto es así, que recientemente ha asomado a la bibliografía el término *materiómica* (análogo a genómica y proteómica), que trata sobre la conexión entre

<sup>3</sup> Gonzalez-Viñas, W.; Manzini, H. L., *Ciencia de los Materiales*. Ed. Ariel, Barcelona, Spain, 2003, 240 pp.

mecanismos que ocurren en múltiples escalas y que permiten estudiar el comportamiento integral de un material.<sup>4</sup>

Paralelamente a este extraordinario desarrollo, también es notorio que, desde finales del siglo XVIII, con la industrialización de las sociedades y en la trepidante carrera hacia el avance tecnológico, el ser humano se encuentra inmerso en un bucle de retroalimentación positiva, en el que los avances tecnológicos aumentan la producción y el consumo de bienes que, a su vez, imponen la utilización de una mayor cantidad de recursos naturales y el desarrollo de nuevas tecnologías (Figura 2). Éste ha sido el origen del derroche material y energético contemporáneo. Sin embargo, dichos avances tecnológicos nos mueven a alcanzar el actual reto: nuevos modelos de desarrollo más eficientes y amigables con el medio ambiente.



**Figura 2.** Diagrama causal que representa la influencia de la tecnología en las relaciones entre el ser humano y la naturaleza.

<sup>4</sup> Cranford, S. W.; de Boer, J.; van Blitterswijk, C.; Buehler, M. J., *Adv. Mater.* **2013**, 25, 802-824.

Por lo tanto, en este momento histórico es más necesario que nunca desarrollar nuevos materiales que nos ayuden a construir una sociedad en la que el avance tecnológico no signifique un deterioro del entorno, sino nuevas oportunidades tanto a nivel energético como material.

En este sentido, en los últimos años se está haciendo un esfuerzo en conseguir materiales multifuncionales; es decir, aquellos en los que se combinan dos o más propiedades de interés. Normalmente, una de estas propiedades le confiere un determinado carácter estructural y, la otra, una aplicación funcional (óptica, magnética, eléctrica, térmica, catalítica, ...). De esta manera, los últimos avances en el campo de la Ciencia y Tecnología de Materiales<sup>5</sup> apuntan hacia materiales basados en el grafeno; como por ejemplo, el aerografeno que podría utilizarse en la limpieza de vertidos tóxicos debido a su capacidad de absorber hasta 900 veces su propio peso,<sup>6</sup> materiales nanofibrosos con aplicaciones biomédicas (como la espuma de titanio que podría ser útil en la regeneración ósea)<sup>7</sup> o materiales de tipo MOF (Metal-Organic Framework) formados por compuestos de coordinación, con aplicaciones en muy diversos campos. El estudio que se presenta en esta memoria se centra en este último tipo de materiales.

Las redes metal-orgánicas (MOFs = Metal-Organic Frameworks) son materiales sólidos basados en complejos polinucleares cristalinos en los que la conexión entre los centros metálicos se da mediante ligandos orgánicos de diversa naturaleza.<sup>8</sup> Las conexiones en estas redes covalentes se extienden en una, dos o las tres dimensiones del espacio. En este tipo de compuestos, la presencia de cavidades o poros suele dotar a la red de potenciales aplicaciones en distintos campos, por lo que

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<sup>5</sup> Adams, J.; Pendlebury, D., *Global Research Report. Materials Science and Technology*. In Thomson Reuters: junio 2011.

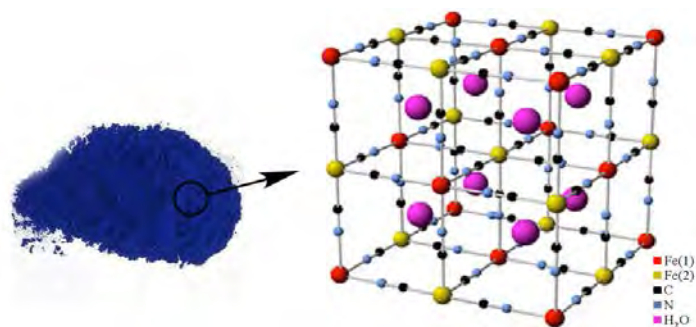
<sup>6</sup> Gao, C., *Nature* **2013**, 494, 404.

<sup>7</sup> Hannemann, C. Implant comprising foamed titanium material and process for production of same. Patent:2012-102012005293

<sup>8</sup> Batten, S. R.; Champness, N. R.; Chen, X.-M.; Garcia-Martinez, J.; Kitagawa, S.; Ohrstrom, L.; O'Keeffe, M.; Suh, M. P.; Reedijk, J., *Pure Appl. Chem.* **2013**, 85, 1715-1724.

las fuerzas cohesivas son especialmente relevantes. De hecho, en alguno de estos compuestos los enlaces de hidrógeno y otras interacciones débiles como, las interacciones  $\pi$ - $\pi$ ,<sup>9</sup> cobran una especial relevancia.

El primer compuesto tipo MOF conocido data de alrededor de 1704 y se obtuvo en Berlín, cuando el químico Alemán Heinrich Diesbach, tratando de obtener un pigmento rojo, mezcló sulfato de hierro con potasa, que estaba contaminada, y obtuvo un colorante azul oscuro. Este compuesto se denominó azul de Prusia (en alemán: Preußisch Blau o Berliner Blau) y se trata de una mezcla de cianuro ferroso y férrico, con fórmula  $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3 \cdot x\text{H}_2\text{O}$  (Figura 3).<sup>10</sup> En aquel momento, Diesbach desconocía que su inesperado descubrimiento pasaría a ser uno de los más importantes dentro del campo de la química de coordinación y también industrialmente, ya que, por su alta capacidad de tinción, el azul de Prusia ha sido muy importante en la industria textil y en la fabricación de pinturas y pigmentos.



**Figura 3.** Muestra del azul de Prusia y su estructura tridimensional.

Sin embargo, debido a la falta de la técnica adecuada necesaria para la elucidación estructural, el azul de Prusia se caracterizó 273 años después. De hecho, en 1897 los químicos Hofmann y Küspert comenzaron a ahondar dentro de la conformación estructural de los compuestos de coordinación, empleando por primera

<sup>9</sup> Cheetham, A. K.; Rao, C. N. R.; Feller, R. K., *Chem. Commun.* **2006**, 4780-4795.

<sup>10</sup> Buser, H. J.; Schwarzenbach, D.; Petter, W.; Ludi, A., *Inorg. Chem.* **1977**, *16*, 2704-2710.

vez el concepto de red, relacionándolo con el esqueleto estructural. El término polímero de coordinación, por su parte, se introdujo por primera vez en una publicación en 1916.<sup>11</sup> Sin embargo, estos incipientes conceptos no pudieron ser totalmente constatados hasta la obtención de las correspondientes estructuras cristalinas. Por tanto, el aporte de la Cristalografía de rayos X, en torno a 1930, fue el factor determinante que permitió el desarrollo y caracterización de todos los materiales cristalinos.

Aunque los compuestos de coordinación cristalinos adquirieron una elevada relevancia a raíz de los avances en las técnicas cristalográficas, el concepto MOF fue definido mucho más tarde: en 1995 en un artículo de *Yaghi y col.* en la prestigiosa revista *Nature*.<sup>12</sup> Fue a partir de ese momento cuando, debido al innovador campo que se abrió, la comunidad científica comenzó a desarrollar de manera exponencial nuevos materiales de tipo MOF.

Entre todas las familias de compuestos de este tipo cabe destacar los denominados MOF-n (n=2, 3, 4, 5...) sintetizados con ligandos tales como BDC = 1,4-benzendicarboxilato o BTC = 1,3,5-bencentricarboxilato, entre otros, y desarrollados por Yaghi y *col.*,<sup>13-15</sup> así como los compuestos denominados MIL-n y HKUST-1, en los que se utiliza el ligando BTC con diferentes centros metálicos, desarrollados por los grupos de Ferey<sup>16,17</sup> y Williams,<sup>18</sup> respectivamente (Figura 4). Éstos y otros muchos

<sup>11</sup> Shibata, Y., *J. Coll. Sci., Imp. Univ. Tokyo* **1916**, 37, 1-17.

<sup>12</sup> Yaghi, O. M.; Li, G.; Li, H., *Nature* **1995**, 378, 703-706.

<sup>13</sup> Eddaoudi, M.; Li, H.; Yaghi, O. M., *J. Am. Chem. Soc.* **2000**, 122, 1391-1397.

<sup>14</sup> Kim, J.; Chen, B.; Reineke, T. M.; Li, H.; Eddaoudi, M.; Moler, D. B.; O'Keeffe, M.; Yaghi, O. M., *J. Am. Chem. Soc.* **2001**, 123, 8239-8247.

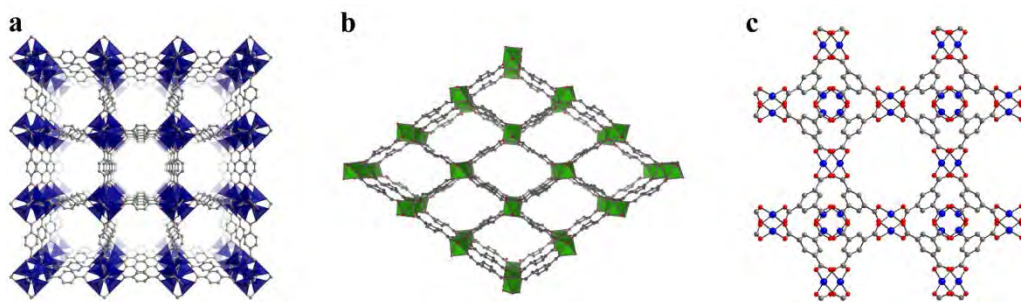
<sup>15</sup> Li, H.; Eddaoudi, M.; O'Keeffe, M.; Yaghi, M., *Nature* **1999**, 402, 276-279.

<sup>16</sup> Millange, F.; Serre, C.; Ferey, G., *Chem. Commun.* **2002**, 822-823.

<sup>17</sup> Serre, C.; Millange, F.; Thouvenot, C.; Gardant, N.; Pelle, F.; Ferey, G., *J. Mater. Chem.* **2004**, 14, 1540-1543.

<sup>18</sup> Chui, S. S. Y.; Lo, S. M. F.; Charmant, J. P. H.; Orpen, A. G.; Williams, I. D., *Science* **1999**, 283, 1148-1150.

compuestos que presentan gran variedad de arquitecturas y propiedades como materiales, son el producto de la significativa apertura de la investigación en el área de la química de coordinación.<sup>19-22</sup>



**Figura 4.** Estructuras cristalinas del (a) MOF-5, (b) MIL-53 y (c) HKUST-1.

Gran parte del éxito experimentado por este tipo de materiales se debe al amplio rango de campos de sus potenciales aplicaciones, muchas de las cuales están directamente relacionadas por el alto grado de porosidad que pueden alcanzar los MOFs. En este sentido, se destaca la gran atención que han suscitado como adsorbentes<sup>23</sup> debido a las excepcionalmente elevadas áreas superficiales que presentan, así como por sus estructuras químicas que, en algunos casos, pueden ser fácilmente modificables. En este aspecto, predominan los esfuerzos que se están llevando a cabo para el desarrollo y uso de MOFs como materiales medio ambientalmente respetuosos. Así, se han desarrollado adsorbentes de hidrógeno<sup>24</sup> para su almacenamiento como combustible, con el propósito de desarrollar portadores y

<sup>19</sup> Janiak, C., *Dalton Trans.* **2003**, 2781-2804.

<sup>20</sup> Rao, C. N. R.; Cheetham, A. K.; Thirumurugan, A., *J. Phys. Condens. Matter* **2008**, *20*, 083202/1-083202/21.

<sup>21</sup> Qiu, S.; Zhu, G., *Coord. Chem. Rev.* **2009**, *253*, 2891-2911.

<sup>22</sup> Furukawa, H.; Cordova, K. E.; O'Keeffe, M.; Yaghi, O. M., *Science* **2013**, *341*, 974.

<sup>23</sup> Eddaoudi, M.; Kim, J.; Rosi, N.; Vodak, D.; Wachter, J.; O'Keeffe, M.; Yaghi, O. M., *Science* **2002**, *295*, 469-472.

<sup>24</sup> Suh Myunghyun, P.; Park Hye, J.; Prasad Thazhe, K.; Lim, D.-W., *Chem. Rev.* **2012**, *112*, 782-835.



contenedores energéticos para su uso en medios de transporte y disminuir así la dependencia de combustibles fósiles. Del mismo modo, los adsorbentes de dióxido de carbono<sup>25</sup> permiten disminuir las emisiones de este gas a la atmósfera. En este ámbito, han suscitado gran interés los MOFs como separadores de gases, basados en una adsorción selectiva en base a la diferencia de tamaño o forma de las moléculas.<sup>26</sup>

Un ejemplo reseñable de este tipo de compuestos es el MOF-5,<sup>27</sup> que posee el mayor valor de densidad de almacenaje volumétrico publicado hasta ahora (66 g L<sup>-1</sup> de H<sub>2</sub> a 77 K). Sin embargo, el compuesto no mantiene esta capacidad a temperatura ambiente. De hecho, los compuestos IRMOF-6 e IRMOF-8<sup>28</sup> llegan a duplicar y cuadruplicar, respectivamente, la capacidad de almacenaje del MOF-5 a temperatura ambiente. En cuanto a la absorción de CO<sub>2</sub>, el MOF-74, es uno de los materiales con mayor selectividad y capacidad para absorber CO<sub>2</sub>, ya que posee una estructura con amplios canales hexagonales.<sup>29</sup>

Por otra parte, las propiedades como catalizadores heterogéneos, reutilizables y fáciles de separar tras la reacción catalítica, son otras de las aplicaciones más estudiadas. Así, la elevada área superficial, la porosidad modificable y la diversidad de centros metálicos y grupos funcionales hacen de los MOFs compuestos especialmente adecuados para su uso como catalizadores.<sup>30</sup> En este sentido, se destaca que los trabajos previos realizados en este área se centran, casi en exclusiva, en las

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<sup>25</sup> Millward, A. R.; Yaghi, O. M., *J. Am. Chem. Soc.* **2005**, *127*, 17998-17999.

<sup>26</sup> Montoro, C.; Linares, F.; Quartapelle Procopio, E.; Senkovska, I.; Kaskel, S.; Galli, S.; Masciocchi, N.; Barea, E.; Navarro, J. A. R., *J. Am. Chem. Soc.* **2011**, *133*, 11888-11891.

<sup>27</sup> Li, H.; Eddaoudi, M.; O'Keeffe, M.; Yaghi, M., *Nature* **1999**, *402*, 276-279

<sup>28</sup> Rosi, N. L.; Eckert, J.; Eddaoudi, M.; Vodak, D. T.; Kim, J.; O'Keeffe, M.; Yaghi, O. M., *Science* **2003**, *300*, 1127-1130.

<sup>29</sup> Britt, D.; Furukawa, H.; Wang, B.; Glover, T. G.; Yaghi, O. M., *Proc. Natl. Acad. Sci. U. S. A.* **2009**, *106*, 20637-20640.

<sup>30</sup> Ma, L.; Falkowski, J. M.; Abney, C.; Lin, W., *Nat. Chem.* **2010**, *2*, 838-846.

zeolitas.<sup>31,32</sup> De las reacciones en las que se ha investigado el potencial catalítico de los MOFs despuntan la cianosilación de aldehídos (investigación pionera llevada a cabo por Fujita y *col.*),<sup>33</sup> la oxidación de alcoholes,<sup>34</sup> la hidrogenación de olefinas,<sup>35</sup> y diversas acetilaciones<sup>36</sup> e hidrodesulfuraciones,<sup>37</sup> entre muchas otras.

Otras de las aplicaciones más estudiadas se encuentran en el campo de la biomedicina, ya que muchos MOFs son excelentes candidatos para su uso en sistemas de liberación controlada de fármacos,<sup>38</sup> y en otros campos del tratamiento y diagnóstico médico, como las técnicas de creación de imágenes.<sup>39</sup> Es decir, los MOFs se están utilizando también como biomateriales.

Estos compuestos pueden presentar, además, otras interesantes propiedades físicas, que permiten su aplicación en campos como el magnetismo,<sup>40</sup> la ferroelectricidad<sup>41</sup> o la luminiscencia,<sup>42</sup> entre otros. La movilidad de carga es otra de las propiedades estudiadas en los MOFs, debido a la importancia de los materiales conductores en aplicaciones ópticas.<sup>43</sup> Por otra parte, se conocen ejemplos de MOFs que presentan conductividad iónica a través de moléculas orgánicas o moléculas de

<sup>31</sup> Corma, A., *Chem. Rev.* **1997**, *97*, 2373-2419.

<sup>32</sup> Perez-Ramirez, J.; Christensen, C. H.; Egeblad, K.; Christensen, C. H.; Groen, J. C., *Chem. Soc. Rev.* **2008**, *37*, 2530-2542.

<sup>33</sup> Fujita, M.; Kwon, Y. J.; Washizu, S.; Ogura, K., *J. Am. Chem. Soc.* **1994**, *116*, 1151-1152.

<sup>34</sup> Chen, G.; Wu, S.; Liu, H.; Jiang, H.; Li, Y., *Green Chem.* **2013**, *15*, 230-235.

<sup>35</sup> Llabres i Xamena, F. X.; Abad, A.; Corma, A.; Garcia, H., *J. Catal.* **2007**, *250*, 294-298.

<sup>36</sup> Singh, S. J.; Kale, S. R.; Gawande, M. B.; Velhinho, A.; Jayaram, R. V., *Catal. Commun.* **2014**, *44*, 24-28.

<sup>37</sup> Peralta, D.; Chaplais, G.; Simon-Masseron, A.; Barthelet, K.; Pirngruber, G. D., *Energy Fuels* **2012**, *26*, 4953-4960.

<sup>38</sup> Horcajada, P.; Chalati, T.; Serre, C.; Gillet, B.; Sebrie, C.; Baati, T.; Eubank, J. F.; Heurtaux, D.; Clayette, P.; Kreuz, C.; Chang, J.-S.; Hwang, Y. K.; Marsaud, V.; Bories, P.-N.; Cynober, L.; Gil, S.; Ferey, G.; Couvreur, P.; Gref, R., *Nat. Mater.* **2010**, *9*, 172.

<sup>39</sup> Liu, D.; Huxford, R. C.; Lin, W., *Angew. Chem., Int. Ed.* **2011**, *50*, 3696.

<sup>40</sup> Kurmoo, M., *Chem. Soc. Rev.* **2009**, *38*, 1353-1379.

<sup>41</sup> Zhang, W.; Xiong, R.-G., *Chem. Rev.* **2012**, *112*, 1163-1195.

<sup>42</sup> Cui, Y.; Yue, Y.; Qian, G.; Chen, B., *Chem. Rev.* **2012**, *112*, 1126-1162.

<sup>43</sup> Wang, C.; Zhang, T.; Lin, W., *Chem. Rev.* **2012**, *112*, 1084-1104.

agua presentes en los poros,<sup>44</sup> y, aunque en menor grado, también se han desarrollado compuestos con conductividad electrónica;<sup>45</sup> propiedad, en muchos casos atribuible, al apilamiento de moléculas aromáticas con alta densidad electrónica.<sup>46</sup>

La obtención de MOFs con las propiedades deseadas comienza por un diseño racional de la síntesis, donde es primordial, tanto la elección de los ligandos, como su combinación con los iones metálicos. En este sentido, dentro de la gran variedad de ligandos orgánicos disponibles, las porfirinas destacan por ser unidades estructurales sumamente versátiles para la obtención de sólidos moleculares.<sup>47</sup>

Las porfirinas son un grupo de compuestos orgánicos, muchas de ellas de origen natural, formadas por macrociclos tetrapirrólicos, que pueden estar funcionalizados en diferentes posiciones (Figura 5). De hecho, las porfirinas pertenecen a una clase de biomoléculas claramente multifuncionales que juegan un papel fundamental en multitud de sistemas biológicos.

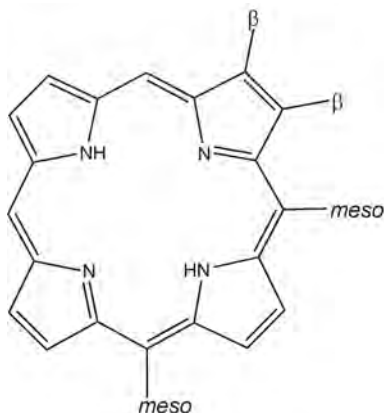
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<sup>44</sup> Bureekaew, S.; Horike, S.; Higuchi, M.; Mizuno, M.; Kawamura, T.; Tanaka, D.; Yanai, N.; Kitagawa, S., *Nat. Mater.* **2009**, *8*, 831-836.

<sup>45</sup> Kobayashi, Y.; Jacobs, B.; Allendorf, M. D.; Long, J. R., *Chem. Mater.* **2010**, *22*, 4120-4122.

<sup>46</sup> Xiao, S.; Tang, J.; Beetz, T.; Guo, X.; Tremblay, N.; Siegrist, T.; Zhu, Y.; Steigerwald, M.; Nuckolls, C., *J. Am. Chem. Soc.* **2006**, *128*, 10700-10701.

<sup>47</sup> Suslick, K. S.; Bhyrappa, P.; Chou, J. -H.; Kosal, M. E.; Smithenry, D. W.; Wilson, S. R., *Acc. Chem. Res.* **2005**, *38*, 283-291.



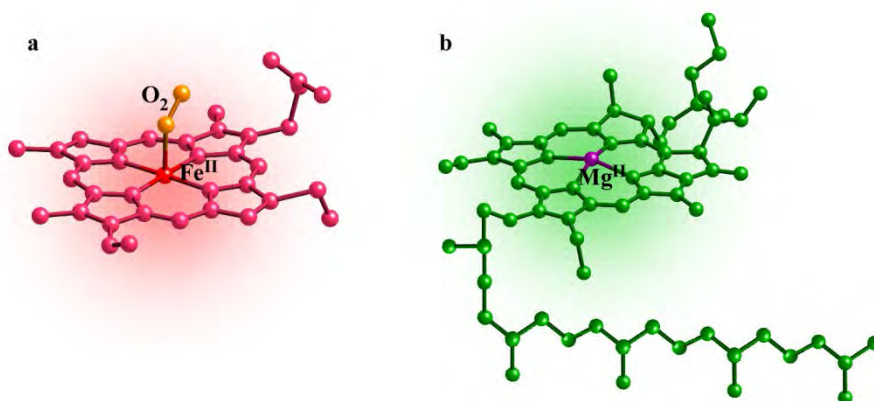
**Figura 5.** Macrocielo porfirínico mostrando las posiciones *meso* y  $\beta$ . La funcionalización de estas posiciones da lugar a una gran variedad de porfirinas.

Los procesos naturales en los que el anillo porfirínico juega un papel fundamental son bien conocidos. De hecho, el ligando porfirínico, perfeccionado a lo largo del curso de la evolución, proporciona el cromóforo para una multitud de complejos que son metabolitos primarios, sin los cuales la vida misma no podría mantenerse.

Quizá uno de los procesos más conocidos sea el transporte de oxígeno por el cuerpo humano. La responsable de dicho transporte es la protoporfirina IX, que se encuentra en los grupos hemo de la hemoglobina (Figura 6a). En un complejo mecanismo, un átomo de hierro unido en el centro de la porfirina regula el transporte de oxígeno desde los pulmones hasta la última célula del ser humano. El estado de oxidación de ese átomo de hierro posibilita el anclaje de oxígeno cuando se encuentra como ion  $\text{Fe}^{\text{II}}$ , siendo una enzima la responsable de reactivarlo una vez libera el oxígeno y se encuentra como ion trivalente.

En la plantas, la clorofila es el pigmento de color verde encargada de la fotosíntesis; proceso que permite a las plantas absorber energía a partir de la luz. La

estructura de la porfirina implicada en este proceso está formada por una larga cadena llamada *fitol*, unida por uno de los extremos a un anillo de porfirina con un ion  $Mg^{II}$  en su interior (Figura 6b). El sistema de dobles enlaces conjugados de la porfirina es el encargado de absorber determinados picos del espectro de radiación, dando comienzo al proceso fotosintético.



**Figura 6.** a) Porfirina encargada del transporte de  $O_2$  en la hemoglobina y b) porfirina de la clorofila.

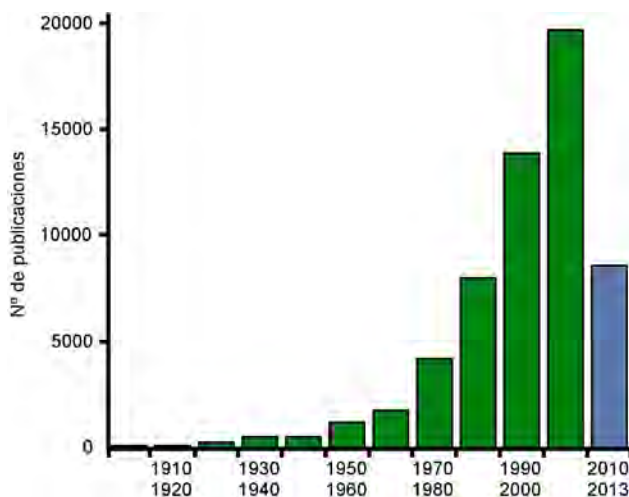
Además de en estos conocidos procesos, las porfirinas intervienen en multitud de mecanismos esenciales. En la vitamina B12, la cobalamina contiene una porfirina de cobalto y es la responsable de numerosas funciones como la síntesis de ADN y ARN y la formación de glóbulos rojos, entre otras. El citocromo P450, con porfirinas de hierro, es una oxidasa esencial en la biotransformación de sustratos químicos a biológicos y otras porfirinas, como la uroporfirina y la coproporfirina, son importantes en multitud de actividades metabólicas fundamentales.

En definitiva, las porfirinas son una clase de biomoléculas distintivamente multifuncionales que juegan un papel central en procesos naturales en los que se produce la transferencia de fotones, electrones, iones y moléculas. Así, los sistemas

basados en metaloporfirinas se inspiran en las funciones desempeñadas por estos complejos para mimetizarlos y trasladarlos a sistemas estructurados tanto a nivel molecular, como a dispositivos nanotecnológicos.

Las primeras publicaciones científicas sobre el grupo hemo y la clorofila datan de 1871<sup>48</sup> y 1872,<sup>49</sup> respectivamente. Sin embargo Zaleski<sup>50</sup> comenzó a relacionar las propiedades de dichos sistemas con moléculas porfirínicas en 1902 y, en 1940, los primeros estudios de rayos X realizados por Woodward<sup>51</sup> permitieron elucidar la estructura cristalina de compuestos basados en porfirinas.

A partir de ese momento, como se observa en la Figura 7, el número de publicaciones relacionadas con estos macrociclos tetrapirrólicos ha crecido de manera exponencial. De hecho, es probable que en la presente década se vayan a superar con creces las 20.000 publicaciones respecto a la década anterior.



**Figura 7.** Número de publicaciones por década sobre porfirinas (fuente: SciFinder®).

<sup>48</sup> Hoppe-Seyler, F., *Med. Chem. Untersuch.* **1871**, 523-550.

<sup>49</sup> Hartsen, F. A., *Chem. Centr.* **1872**, 524.

<sup>50</sup> Zaleski, J., *Ztschr. Physiol. Ch.* **1902**, 37, 54-74.

<sup>51</sup> Woodward, I., *J. Chem. Soc.* **1940**, 601-603.

Muchas de las investigaciones realizadas en el campo de las porfirinas, atienden únicamente a estudios relacionados con la caracterización de sus propiedades como unidades estructurales aisladas. En 1954<sup>52</sup>, sin embargo, aparecen los primeros trabajos en los que las porfirinas pasan a formar parte de estructuras más complejas dentro de los denominados compuestos de coordinación. No obstante, tuvieron que transcurrir dos décadas para que las porfirinas comenzaran a tomar un papel significativo en el campo de la química de coordinación.<sup>53,54</sup>

En los últimos años, y dentro de la gran expectación levantada por los materiales porosos de tipo MOF, las porfirinas se han introducido como ligandos multifuncionales, siendo pieza clave en la estructura cristalina y, al mismo tiempo, otorgando a este tipo de materiales alguna de las propiedades que ya desempeñan en la naturaleza. De esta manera, bien mimetizando las propiedades intrínsecas de estos ligandos orgánicos, bien explorando nuevas funciones, se han conseguido materiales con interesantes propiedades para el transporte de energía,<sup>55,56</sup> materiales fluorescentes,<sup>57</sup> captadores de luz,<sup>58,59</sup> electrocatalíticos<sup>60</sup> y otros con propiedades

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<sup>52</sup> George, P.; Irvine, D. H., *Nature* **1954**, *173*, 1148-1149.

<sup>53</sup> Hambright, P., *Usp. Khim.* **1977**, *46*, 1207-1232.

<sup>54</sup> Berezin, B. D., *Coordination Compounds of Porphyrins and Phthalocyanine*. Nauka, Moscu, USSR: 1978, 300 pp.

<sup>55</sup> Jin, S.; Son, H.-J.; Farha, O. K.; Wiederrecht, G. P.; Hupp, J. T., *J. Am. Chem. Soc.* **2013**, *135*, 955-958.

<sup>56</sup> Patwardhan, S.; Jin, S.; Son, H.-J.; Schatz, G. C., *MRS Online Proc. Libr.* **2013**, *1539*, opl 2013 987/1-opl 2013 987/6.

<sup>57</sup> Jiang, H.-L.; Feng, D.; Wang, K.; Gu, Z.-Y.; Wei, Z.; Chen, Y.-P.; Zhou, H.-C., *J. Am. Chem. Soc.* **2013**, *135*, 13934-13938.

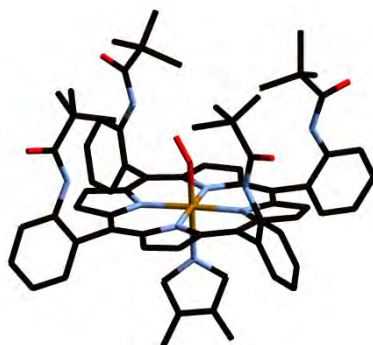
<sup>58</sup> Demel, J.; Kubat, P.; Millange, F.; Marrot, J.; Cisarova, I.; Lang, K., *Inorg. Chem.* **2013**, *52*, 2779-2786.

<sup>59</sup> Son, H.-J.; Jin, S.; Patwardhan, S.; Wezenberg, S. J.; Jeong, N. C.; So, M.; Wilmer, C. E.; Sarjeant, A. A.; Schatz, G. C.; Snurr, R. Q.; Farha, O. K.; Wiederrecht, G. P.; Hupp, J. T., *J. Am. Chem. Soc.* **2013**, *135*, 862-869.

<sup>60</sup> Jahan, M.; Bao, Q.; Loh, K. P., *J. Am. Chem. Soc.* **2012**, *134*, 6707-6713.

catalíticas en novedosas reacciones,<sup>61-63</sup> así como los que mimetizan el funcionamiento del citocromo P-450.<sup>64</sup>

Dentro de la diversidad de los compuestos porfirínicos sintetizados, cabe destacar los que presentan las mejores propiedades o han marcado un hito por sus peculiares características. Así, por ejemplo, las denominadas “*picket fence porphyrins*”, que deben su nombre a los sustituyentes verticales en forma de enrejado alrededor de una molécula de O<sub>2</sub> (Figura 8), fueron unos de los primeros sistemas análogos a la hemoglobina. Fueron desarrolladas por Collman y col.,<sup>65</sup> y son monómeros metaloporfirínicos de hierro o cobalto capaces de anclar una molécula de O<sub>2</sub> al centro metálico de la porfirina. Hoy en día se siguen estudiando en éste y otros campos.



**Figura 8.** Modelo de porfirina *picket fence* de Collman y col.

<sup>61</sup> Ferreira, G. K. B.; Castro, K. A. D. d. F.; Machado, G. S.; Ribeiro, R. R.; Ciuffi, K. J.; Ricci, G. P.; Marques, J. A.; Nakagaki, S., *J. Mol. Catal. A Chem.* **2013**, *378*, 263-272.

<sup>62</sup> Takaishi, S.; DeMarco, E. J.; Pellin, M. J.; Farha, O. K.; Hupp, J. T., *Chem. Sci.* **2013**, *4*, 1509-1513.

<sup>63</sup> Feng, D.; Gu, Z.-Y.; Li, J.-R.; Jiang, H.-L.; Wei, Z.; Zhou, H.-C., *Angew. Chem., Int. Ed.* **2012**, *51*, 10307-10310.

<sup>64</sup> Xie, M.-H.; Yang, X.-L.; He, Y.; Zhang, J.; Chen, B.; Wu, C.-D., *Chem. -Eur. J.* **2013**, *19*, 14316-14321.

<sup>65</sup> Collman, J. P.; Gagne, R. R.; Reed, C.; Halbert, T. R.; Lang, G.; Robinson, W. T., *J. Am. Chem. Soc.* **1975**, *97*, 1427-1439.



Otros compuestos porfirínicos destacables son los conocidos como porfirinas “*Pacman*” y “*Hangman*” y las “ $\mu$ -oxo/nitro bridged porphyrins”. Tanto las porfirinas *Pacman* como las *Hangman* han sido desarrolladas por Nocera y col.,<sup>66</sup> aunque se basan en las propiedades de compuestos previamente sintetizados por Shi y Anson<sup>67</sup> Son compuestos que destacan por su capacidad para catalizar las reacciones de reducción de oxígeno inspirándose en las biomoléculas presentes en bacterias fotosintéticas.

Las porfirinas *Pacman* se pueden describir como agregados en los que dos porfirinas se unen mediante un espaciador externo (Figura 9a). De esta manera, las porfirinas quedan enfrentadas posibilitando la transferencia de electrones y el anclaje de una molécula de O<sub>2</sub> entre los dos centros metálicos. Sin embargo, en las de tipo *Hangman* un grupo con base ácida sustituye a una de las porfirinas (Figura 9b). Estas configuraciones posibilitan la reducción del oxígeno molecular dando como resultado dos moléculas de agua y la mayor cantidad de energía posible, evitando intermediarios tóxicos como el H<sub>2</sub>O<sub>2</sub>.<sup>68</sup> Numerosos estudios señalan a estos compuestos como excelentes catalizadores para la reducción del oxígeno en el cátodo de las pilas de combustible de membrana de intercambio de protones (PEMFC), sustituyendo el caro y tóxico platino que se utiliza actualmente.<sup>69</sup>

En cuanto a los  $\mu$ -oxo/nitro bridged porphyrins, se trata de compuestos diméricos en los que la unión entre las dos porfirinas tiene lugar mediante un átomo de oxígeno o de nitrógeno (Figura 9c). Son compuestos ampliamente estudiados; especialmente los que poseen un átomo de hierro en el centro de la porfirina, ya que

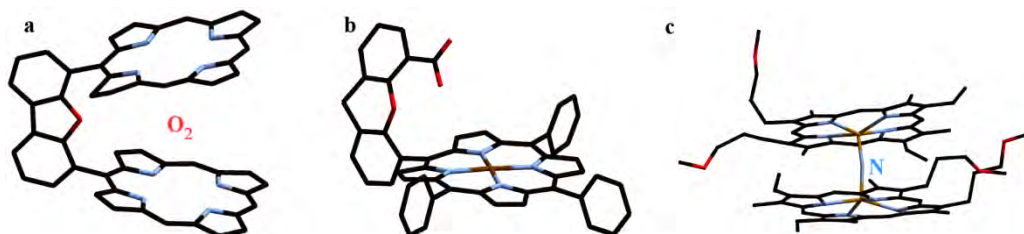
<sup>66</sup> McGuire Jr, R.; Dogutan, D. K.; Teets, T. S.; Suntivich, J.; Shao-Horn, Y.; Nocera, D. G., *Chem. Sci.* **2010**, *1*, 411-414.

<sup>67</sup> Shi, C.; Anson, F. C., *Inorg. Chem.* **1996**, *35*, 7928-7931.

<sup>68</sup> Rosenthal, J.; Nocera, D. G., *Acc. Chem. Res.* **2007**, *40*, 543-553.

<sup>69</sup> Kiros, Y., *Int. J. Electrochem. Sci.* **2007**, *2*, 285-300.

son los que mejores resultados catalíticos han aportado mimetizando la acción del citocromo P-450 en las reacciones llevadas a cabo en la naturaleza.<sup>70</sup>



**Figura 9.** Modelos de porfirinas (a) *Pacman*, (b) *Hangman* y (c)  $\mu$ -oxo/nitro bridged porphyrin.

Cabe destacar que los polímeros de coordinación basados en porfirinas que presenten estructuras cristalinas de mayor dimensionalidad que los monómeros y dímeros mencionados no son abundantes. Teniendo en cuenta que las unidades estructurales tienden a ordenarse en el mínimo espacio posible y dado que las porfirinas son ligandos con un volumen considerable, resulta complicado obtener arquitecturas moleculares que se extiendan en una (1D), dos (2D) o tres (3D) dimensiones. No obstante, existen ejemplos de este tipo de compuestos en los que bien mediante la unión directa entre porfirinas, bien añadiendo un ligando espaciador adicional, bien insertando clústeres metálicos, se consiguen estructuras con mayor dimensionalidad.

En este sentido, podemos resaltar los compuestos monodimensionales (1D) obtenidos por Goldberg y *col.*<sup>71,72</sup> y Miller y *col.*<sup>73,74</sup> en los que una gran variedad de

<sup>70</sup> Jiao, X. D.; Huang, J. W.; Ji, L. N.; Luo, B. S.; Chen, L. R., *J. Inorg. Biochem.* **1997**, *65*, 229.

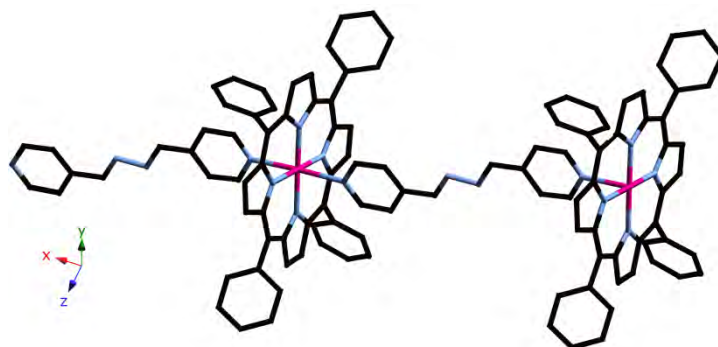
<sup>71</sup> Kumar, R. K.; Balasubramanian, S.; Goldberg, I., *Chem. Commun.* **1998**, 1435-1436.

<sup>72</sup> Lipstman, S.; Goldberg, I., *Cryst. Growth Des.* **2010**, *10*, 4596-4606.

<sup>73</sup> Dawe, L. N.; Miglioi, J.; Turnbow, L.; Taliaferro, M. L.; Shum, W. W.; Bagnato, J. D.; Zakharov, L. N.; Rheingold, A. L.; Arif, A. M.; Fourmigue, M.; Miller, J. S., *Inorg. Chem.* **2005**, *44*, 7530-7539.

<sup>74</sup> Hibbs, W.; Rittenberg, D. K.; Sundaralingam, M.; Epstein, A. J.; Miller, J. S. *et al.*, *Inorg. Chem.* **2001**, *40*, 1915-1925.

ligandos espaciadores bidentados conectados a los centros metálicos de las porfirinas dan lugar a cadenas que se extienden en una dimensión (Figura 10). Los enlaces más débiles, desde interacciones  $\pi$ - $\pi$  hasta enlaces de hidrógeno, son los encargados de estabilizar las redes cristalinas.



**Figura 10.** Estructura monodimensional en la que un espaciador bidentado enlaza las porfirinas.<sup>75</sup>

Por otra parte, la estrategia más extendida para conseguir estructuras bidimensionales consiste en enlazar las diferentes unidades porfirínicas utilizando un clúster metálico que hace de conector en los sustituyentes laterales de la porfirina. De esta manera autores como Wu y *col.*,<sup>76,77</sup> Goldberg y *col.*<sup>78,79</sup> y Choe y *col.*<sup>80</sup> destacan por la variedad y cantidad de compuestos obtenidos empleando esta estrategia (Figura 11a). Sin embargo, investigadores como Rogers y *col.*,<sup>81</sup> Chen y *col.*<sup>82</sup> y Suslick y

<sup>75</sup> Diskin-Posner, Y.; Patra, G. K.; Goldberg, I., *J. Chem. Soc., Dalton Trans.* **2001**, 2775-2782.

<sup>76</sup> Xie, M.-H.; Yang, X.-L.; Zou, C.; Wu, C.-D., *Inorg. Chem.* **2011**, *50*, 5318-5320.

<sup>77</sup> Zou, C.; Xie, M.-H.; Kong, G.-Q.; Wu, C.-D., *CrystEngComm* **2012**, *14*, 4850-4856.

<sup>78</sup> Muniappan, S.; Lipstman, S.; George, S.; Goldberg, I., *Inorg. Chem.* **2007**, *46*, 5544-5554.

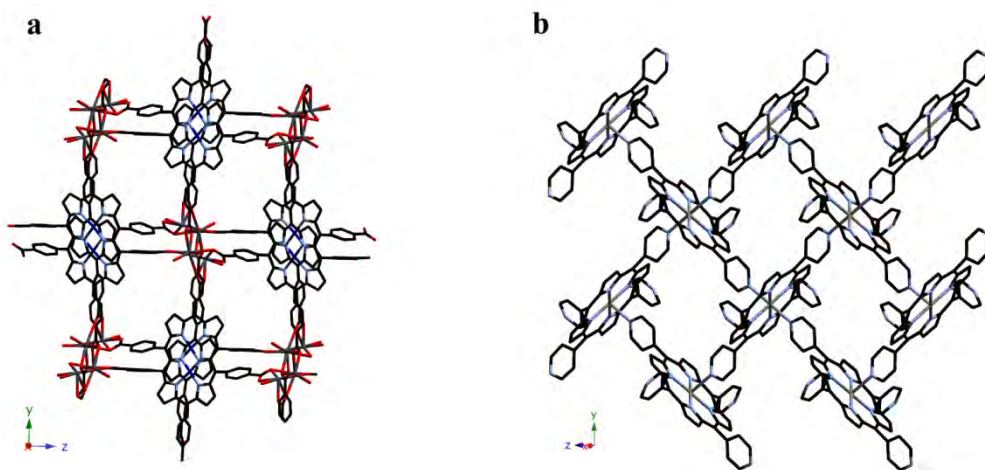
<sup>79</sup> Diskin-Posner, Y.; Dahal, S.; Goldberg, I., *Angew. Chem., Int. Ed.* **2000**, *39*, 1288-1292.

<sup>80</sup> DeVries, L. D.; Barron, P. M.; Hurley, E. P.; Hu, C.; Choe, W., *J. Am. Chem. Soc.* **2011**, *133*, 14848-14851.

<sup>81</sup> Sharma, C. V. K.; Broker, G. A.; Huddleston, J. G.; Baldwin, J. W.; Metzger, R. M.; Rogers, R. D., *J. Am. Chem. Soc.* **1999**, *121*, 1137-1144.

<sup>82</sup> Chen, W.; Luo, Z.; Chen, H.; Kuang, H.; Liu, D., *J. Chem. Res.* **2012**, *36*, 72-74.

col.<sup>83</sup> apuestan por la obtención de estructuras 2D en las que los propios sustituyentes laterales de las porfirinas son los que se conectan a los centros metálicos de las porfirinas adyacentes (Figura 11b).



**Figura 11.** Estructura 2D con clústeres metálicos entre porfirinas (a) y sin ellos (b).<sup>84</sup>

En cuanto a las estructuras 3D basadas en moléculas porfirínicas, Kosal y col.,<sup>85</sup> Hupp y col.<sup>86</sup> y Choe y col.<sup>87-89</sup> son pioneros con las familias de compuestos porfirínicos PIZA-n ( $n = 1, 2, 3, \dots$ ), ZnPO-MOF y las PPF-n ( $n = 1, 2, 3, \dots$ ), respectivamente. Hay que poner de relieve que las estructuras cristalinas de este tipo, donde los ligandos actúan como pilares uniendo las capas porfirínicas 2D formadas por clústeres metálicos, son realmente escasas (Figura 12).<sup>90</sup> La presencia de amplios

<sup>83</sup> Smithenry, D. W.; Wilson, S. R.; Suslick, K. S., *Inorg. Chem.* **2003**, *42*, 7719-7721.

<sup>84</sup> Lipstman, S.; Goldberg, I., *CrystEngComm* **2010**, *12*, 52-54.

<sup>85</sup> Kosal, M. E.; Chou, J.-H.; Wilson, S. R.; Suslick, K. S., *Nat. Mater.* **2002**, *1*, 118-121.

<sup>86</sup> Farha, O. K.; Shultz, A. M.; Sarjeant, A. A.; Nguyen, S. T.; Hupp, J. T., *J. Am. Chem. Soc.* **2011**, *133*, 5652-5655.

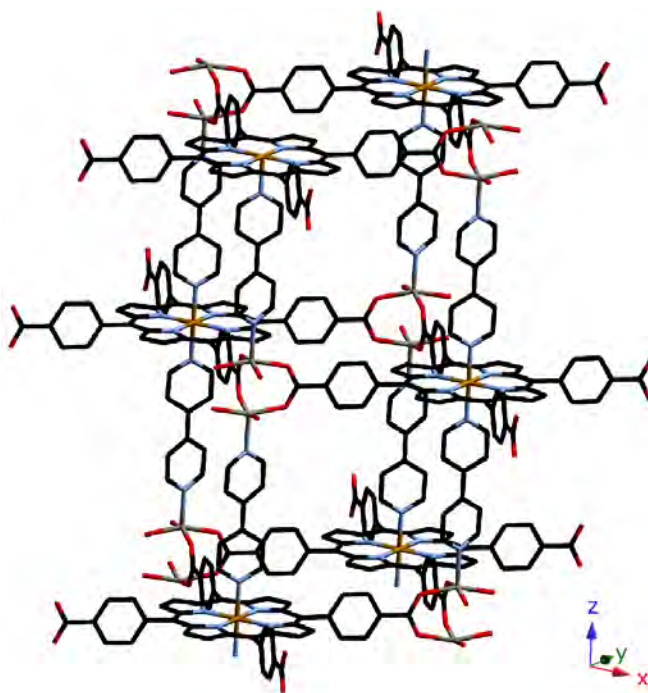
<sup>87</sup> Barron, P. M.; Son, H.-T.; Hu, C.; Choe, W., *Cryst. Growth Des.* **2009**, *9*, 1960-1965.

<sup>88</sup> Burnett, B. J.; Barron, P. M.; Hu, C.; Choe, W., *J. Am. Chem. Soc.* **2011**, *133*, 9984-9987.

<sup>89</sup> Barron, P. M.; Wray, C. A.; Hu, C.; Guo, Z.; Choe, W., *Inorg. Chem.* **2010**, *49*, 10217-10219.

<sup>90</sup> Choi, E.-Y.; Barron, P. M.; Novotny, R. W.; Son, H.-T.; Hu, C.; Choe, W., *Inorg. Chem.* **2009**, *48*, 426-428.

canales en este tipo de estructuras permite abordar el diseño de redes para el almacenamiento de sustancias como, por ejemplo combustibles, que pueden ser transportadas y liberadas en el lugar y momento apropiado.<sup>91</sup>



**Figura 12.** Estructura 3D basada en unidades porfirínicas.<sup>92</sup>

En definitiva, los antecedentes bibliográficos muestran que los sistemas supramoleculares metaloporfirínicos presentan prometedoras características para su uso como dispositivos destinados al almacenamiento de energía y masa, así como para catalizar numerosas reacciones.

<sup>91</sup> Vriezema, D. M.; Aragonés, M. C.; Elemans, J. A. A. W.; Cornelissen, J. J. L. M.; Rowan, A. E.; Nolte, R. J. M., *Chem. Rev.* **2005**, *105*, 1445-1489.

<sup>92</sup> Barron, P. M.; Son, H.-T.; Hu, C.; Choe, W., *Cryst. Growth Des.* **2009**, *9*, 1960-1965.

En este sentido, es necesario considerar que los sistemas porfirínicos operan en los seres vivos fundamentalmente en disolución: medio en el que el soluto cobra especial relevancia en lo que a la dinámica molecular se refiere. Sin embargo, el desarrollo de dispositivos de distinta dimensionalidad como los prometedores nanodispositivos, lleva el enfoque de su preparación al estado sólido. Este aspecto es especialmente reseñable, ya que supone una de las mayores dificultades asociadas a la preparación de este tipo de compuestos.

Entre los distintos métodos de síntesis empleados para la obtención de este tipo de estructuras se encuentran desde los más clásicos, como la evaporación lenta o la síntesis hidrotermal, hasta los más recientes como la síntesis por microondas o en ultrasonidos. Además, en algunos casos también se aplica la síntesis electroquímica o la mecanoquímica.

La síntesis hidrotermal es una técnica en la que se intentan imitar las condiciones de formación de ciertos minerales y rocas, bajo altas presiones y temperaturas y en un medio acuoso. Esta propuesta se debe a los geólogos De Senarmot, Spezia y *col.*, quienes abrieron la posibilidad de reproducir en el laboratorio condiciones similares con el fin de confirmar dichas hipótesis y de sintetizar nuevas especies.<sup>93</sup> La extensión de este tipo de planteamiento a otros disolventes conduce al concepto genérico de síntesis solvotermal.

El empleo de ultrasonidos o microondas permite reproducir condiciones similares a las de la técnica hidrotermal, con la ventaja añadida de la drástica reducción de los tiempos de síntesis. En el caso de los ultrasonidos la tendencia observada es la obtención de monocristales más pequeños, con morfologías de mayor área superficial.

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<sup>93</sup> Alario-Franco, M. A.; Morán-Miguélez, E., *Anales de la Real Sociedad Española de Química* **2002**, *2*, 5-15.

En relación a la técnica del microondas, se destaca su reducido impacto ambiental al minimizar o evitar el uso de disolventes y ácidos minerales.

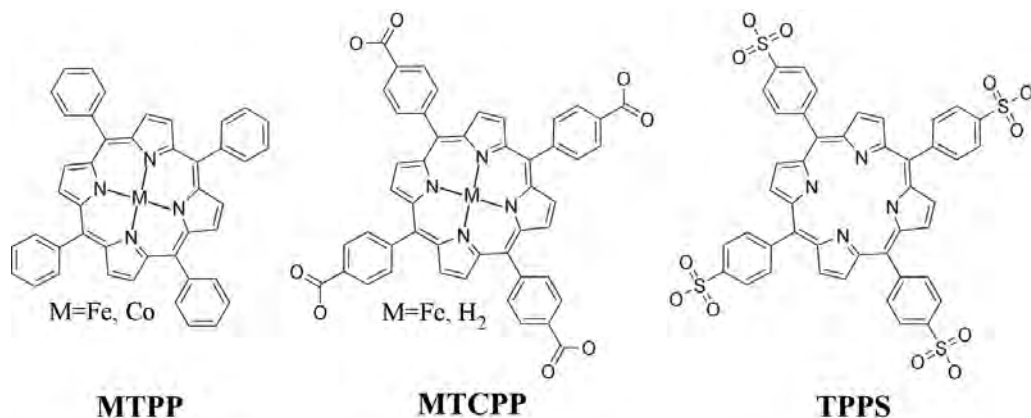
Los antecedentes descritos enmarcan el trabajo desarrollado que se refleja en esta memoria. Así, se detectó un ámbito en el que se podía desarrollar una investigación encaminada a profundizar en el conocimiento existente sobre sistemas de tipo MOF basados en metaloporfirinas y a generar nuevo conocimiento sobre su diseño, síntesis y posterior caracterización y aplicación.

Una de las mayores dificultades asociadas a la preparación de sólidos cristalinos basados en metaloporfirinas es la elucidación estructural. Esto se refleja en el hecho de que de las aproximadamente 60.000 publicaciones encontradas en la base de datos SciFinder® sobre porfirinas, solo en torno a un 10% refieren la estructura cristalina de estos compuestos.

A la hora de definir la estrategia sintética, entre la amplia variedad de porfirinas disponibles, se escogieron una serie de diferentes porfirinas *meso* sustituidas, es decir con diferentes grupos funcionales en las posiciones *meso* del macrociclo tetrapirrólico (Figura 5). Así, se han utilizado la *meso*-tetra-4-fenilporfirina cloruro de hierro (III) (FeTPP), la *meso*-tetra-4-fenilporfirina cobalto (II) (CoTPP) y la *meso*-tetra-4-carboxifenilporfirina cloruro de hierro (III) (FeTCPP) como ejemplos de porfirinas con el átomo metálico ya insertado en el centro porfirínico y la *meso*-tetra-4-carboxifenilporfirina (TCPP) y la *meso*-tetra-4-sulfonatofenilporfirina (TPPS) sin coordinar para poder alojar el ion metálico deseado (Figura 13).

Como se puede observar, las tres porfirinas escogidas difieren en la naturaleza del grupo funcional en la posición *meso*: un fenilo (TPP), un carboxifenilo (TCPP) y un sulfonatofenilo (TPPS). Más adelante, se comentarán otros aspectos relacionados

con los sólidos cristalinos encontrados en la bibliografía, que han motivado su elección.



**Figura 13.** Estructura molecular de las porfirinas escogidas para el desarrollo de este trabajo.

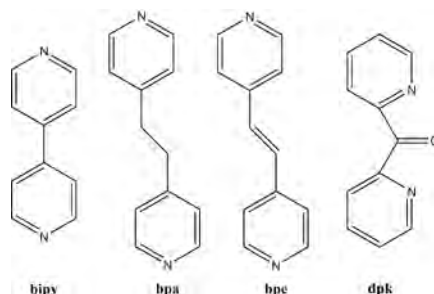
Además de los iones  $\text{Fe}^{\text{III}}$  y  $\text{Co}^{\text{II}}$ , presentes en las porfirinas comerciales ya coordinadas, se han utilizado los iones divalentes  $\text{Mn}^{\text{II}}$ ,  $\text{Fe}^{\text{II}}$  y  $\text{Ni}^{\text{II}}$ . Todos ellos son bioiones de conocida funcionalidad en los seres vivos. Por otra parte, se trata de iones metálicos de bajo coste y medioambientalmente respetuosos.

Otro aspecto importante en la estrategia sintética, ha sido la utilización ocasional de un ligando secundario, destinado a actuar como separador entre las unidades porfirínicas. En este sentido, el grupo de investigación en el que se ha desarrollado esta tesis cuenta con una amplia experiencia en el uso de los ligandos dipiridínicos N-dadores mostrados en la Figura 14: la 4,4'-bipiridina (bipy), el 1,2-



bis(4-piridil)etano (bpa), el 1,2-bis(4-piridil)eteno (bpe) y la di-2-piridilcetona (dpk).<sup>94-</sup>

<sup>100</sup> Por lo tanto, se proyectó utilizar estos ligandos como espaciadores.



**Figura 14.** Estructura molecular de los ligandos dipiridínicos escogidos para el desarrollo de este trabajo.

El análisis bibliográfico realizado al inicio de esta tesis doctoral, reveló que el 25% de las estructuras cristalinas con porfirinas publicadas correspondían a la TPP. Sin embargo, únicamente 150 correspondían a clústeres o sistemas extendidos, siendo el resto unidades monoméricas aisladas. La inmensa mayoría se correspondían a unidades diméricas o triméricas y la mayor dimensionalidad observada en la bibliografía para esta porfirina era 1D. En la Tabla 1 se recogen los escasos compuestos 1D encontrados con ligandos piridínicos como nexo entre porfirinas. Como se puede observar, todos ellos a excepción de uno de Zn, son de Mn.

<sup>94</sup> Barandika, M. G.; Serna, Z. E.; Urriaga, M. K.; De Larramendi, J. I. R.; Arriortua, M. I.; Cortes, R., *Polyhedron* **1999**, *18*, 1311-1316.

<sup>95</sup> Barandika, M. G.; Hernandez-Pino, M. L.; Urriaga, M. K.; Cortes, R.; Lezama, L.; Arriortua, M. I.; Rojo, T., *J. Chem. Soc., Dalton Trans.* **2000**, 1469-1473.

<sup>96</sup> Hernandez, M. L.; Barandika, M. G.; Urriaga, M. K.; Cortes, R.; Lezama, L.; Arriortua, M. I., *Dalton* **2000**, 79-84.

<sup>97</sup> Martin, S.; Barandika, M. G.; Lezama, L.; Pizarro, J. L.; Serna, Z. E.; Ruiz de Larramendi, J. I.; Arriortua, M. I.; Rojo, T.; Cortes, R., *Inorg. Chem.* **2001**, *40*, 4109-4115.

<sup>98</sup> Fernandez de Luis, R.; Urriaga, M. K.; Mesa, J. L.; Gomez de Segura, J. O.; Rojo, T.; Arriortua, M. I., *CrystEngComm* **2011**, *13*, 6488.

<sup>99</sup> Fernandez de Luis, R.; Urriaga, M. K.; Mesa, J. L.; Larrea, E. S.; Iglesias, M.; Rojo, T.; Arriortua, M. I., *Inorg. Chem.* **2013**, *52*, 2615-2626.

<sup>100</sup> Calderon-Casado, A.; Barandika, G.; Bazan, B.; Urriaga, M. K.; Vallcorba, O.; Rius, J.; Miravittles, C.; Arriortua, M. I., *CrystEngComm* **2011**, *13*, 6831-6838.

**Tabla 1.** Compuestos con TPP existentes al inicio de este trabajo formando estructuras monodimensionales (1D).

| Fórmula  | Metal  | Ligando piridínico                            | Ref. |
|--|--|---|------|
| $[(\text{MnTPP} \cdot \text{ClO}_4) \cdot (\text{C}_{12}\text{H}_8\text{N}_4) \cdot 3(\text{PhNO}_2)]$   | $\text{Mn}^{\text{III}}$                             | N,N'-bis((4-piridil)metileno)hidrazina        | 101  |
| $[(\text{ZnTPP})_3 \cdot (\text{C}_{26}\text{H}_{20}\text{N}_6)]_n \cdot (\text{DMF})_{2n}$  | $\text{Zn}^{\text{II}}$                              | N,N,N',N'-tetra(4-piridil)-1,4-fenilendiamina | 102  |
| $[\text{MnTPP}(\text{bipy})] \cdot 2(\text{ClO}_4) \cdot 2(\text{PhNO}_2)$   | $\text{Mn}^{\text{III}}$                             | bipy=4,4'-bipiridina                          | 103  |
| $[\text{MnTPP}]_n[\text{Ni}_3(\text{dpa})_4(4\text{-PyCOO})_2] \cdot (\text{ClO}_4)_n$<br>$[\text{MnTPP}]_n[\text{Ni}_3(\text{dpa})_4(3\text{-PyCOO})_2] \cdot (\text{ClO}_4)_n$ | $\text{Mn}^{\text{III}}$<br>$\text{Mn}^{\text{III}}$ | dpa=di( $\alpha$ -piridil)amida               | 104  |
| $[\text{MnTPP}(\text{BPU})_3]_n \cdot (\text{H}_2\text{O})_n \cdot (\text{PhNO}_2)$  | $\text{Mn}^{\text{II}}$                              | BPU=N,N'-bis(3-piridil)urea                   | 105  |

En cuanto a la TCPP, se trata de una porfirina muy versátil, ya que además del ion metálico, presenta grupos O-dadores en los carboxifenilos de las posiciones *meso* favoreciendo la extensión de estructuras en las tres dimensiones. De esta manera, la variedad estructural que presentan los compuestos publicados es mayor, aunque el número total de estructuras recogidas en la Cambridge Structural Database (CSD)<sup>106</sup> es muy inferior, con apenas 100 estructuras cristalinas. Aunque la mayoría de compuestos cristalizan en monómeros, es notorio que existe un significativo conjunto de estructuras 3D con la TCPP (Tabla 2), quizá una de las pocas que permita dicha circunstancia.

<sup>101</sup> Diskin-Posner, Y.; Patra, G. K.; Goldberg, I., *J. Chem. Soc., Dalton Trans.* **2001**, 2775-2782.

<sup>102</sup> Wang, Q.-G.; Xie, Y.-S.; Zeng, F.-H.; Ng, S.-W.; Zhu, W.-H., *Inorg. Chem. Commun.* **2010**, *13*, 929-931.

<sup>103</sup> Kumar, R. K.; Balasubramanian, S.; Goldberg, I., *Chem. Commun.* **1998**, 1435-1436.

<sup>104</sup> Tsao, T.-B.; Lee, G.-H.; Yeh, C.-Y.; Peng, S.-M., *Dalton Trans.* **2003**, 1465-1471.

<sup>105</sup> Kumar, D. K.; Das, A.; Dastidar, P., *Inorg. Chem.* **2007**, *46*, 7351-7361.

<sup>106</sup> Allen, F. H., *Acta Crystallogr., Sect. B Struct. Sci.* **2002**, *B58*, 380-388.

**Tabla 2.** Compuestos con TCPP existentes al inicio de este trabajo, formando estructuras tridimensionales (3D).

| Fórmula  | Metal  | Ligando piridínico                   | Ref. |
|--|--|--------------------------------------|------|
| [M <sub>3</sub> TCPP]·DMF                        | M=Zn/Fe, Mn, Pd  | -----                                | 107  |
| [M <sub>3</sub> TCPP·(dmbpy)(H <sub>2</sub> O)]  | M=Zn, Co   | dmbpy=2,2'-dimetil-4,4'-bipiridina   | 108  |
| [Zn <sub>3</sub> TCPP(bipy)]                     | Zn <sup>II</sup>   | bipy=4,4'-bipiridina                 | 109  |
| [M <sub>2</sub> M <sub>1</sub> TCPP(bipy)]       | Mn/Zn<br>Mn/Co<br>Fe/Zn<br>Fe/Co<br>V/Zn<br>Pt/Co<br>Ni/Zn | bipy=4,4'-bipiridina                 | 110  |
| [M <sub>3</sub> TCPP(bipy)]                      | Zn, Co, Pd/Co  | bipy=4,4'-bipiridina                 | 111  |
| [Zn <sub>3</sub> TCPP(DPT)]                      | Zn <sup>II</sup>   | 3,6-bis-4-piridil--1,2,4,5-tetracina | 112  |
| [Co <sub>3</sub> TCPP]·14(Py)·(H <sub>2</sub> O) | Co <sup>II</sup>   | -----                                | 113  |

Finalmente, la TPPS es una de las porfirinas menos estudiadas. De hecho, únicamente se han encontrado en la CSD<sup>114</sup> 5 estructuras cristalinas conteniendo esta porfirina. Tras observar que contenían metales no habituales en la bioquímica de las porfirinas o que presentaban estructuras cristalinas en forma de simples monómeros, se

<sup>107</sup> Farha, O. K.; Shultz, A. M.; Sarjeant, A. A.; Nguyen, S. T.; Hupp, J. T., *J. Am. Chem. Soc.* **2011**, *133*, 5652-5655.

<sup>108</sup> Barron, P. M.; Wray, C. A.; Hu, C.; Guo, Z.; Choe, W., *Inorg. Chem.* **2010**, *49*, 10217-10219.

<sup>109</sup> Burnett, B. J.; Barron, P. M.; Hu, C.; Choe, W., *J. Am. Chem. Soc.* **2011**, *133*, 9984-9987.

<sup>110</sup> Barron, P. M.; Son, H.-T.; Hu, C.; Choe, W., *Cryst. Growth Des.* **2009**, *9*, 1960-1965.

<sup>111</sup> Choi, E.-Y.; Barron, P. M.; Novotny, R. W.; Son, H.-T.; Hu, C.; Choe, W., *Inorg. Chem.* **2009**, *48*, 426-428.

<sup>112</sup> Chung, H.; Barron, P. M.; Novotny, R. W.; Son, H.-T.; Hu, C.; Choe, W., *Cryst. Growth Des.* **2009**, *9*, 3327-3332.

<sup>113</sup> Kosal, M. E.; Chou, J.-H.; Wilson, S. R.; Suslick, K. S., *Nat. Mater.* **2002**, *1*, 118-121.

<sup>114</sup> Allen, F. H., *Acta Crystallogr., Sect. B Struct. Sci.* **2002**, *B58*, 380-388.

escogió esta porfirina como última candidata para la obtención de estructuras extendidas.

La amplia experiencia en la síntesis y caracterización de materiales porosos y muchos otros que atesora el grupo de investigación en el que se ha desarrollado este trabajo basado en compuestos de coordinación, ha sido vital para la consecución del mismo. Así, el grupo ha estudiado ampliamente diversos materiales con estructura abierta basados en vanadatos<sup>115-117</sup> y otros oxoaniones de los grupos selenito,<sup>118</sup> fosfito,<sup>119</sup> arseniato,<sup>120</sup> así como mezclas fosfato-arseniato<sup>121</sup> o fosfato-fosfito.<sup>122</sup> Por otra parte, también ha sido explorado el empleo de conectores magnéticos como el aziduro,<sup>123</sup> el cianato<sup>124</sup> y el tiocianato,<sup>125</sup> en combinación con los ligandos piridínicos anteriormente mencionados. En estas fases se combinan propiedades potenciales, como

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<sup>115</sup> Larrea, E. S.; Fernández de Luis, R.; Mesa, J. L.; Pizarro, J. L.; Urriaga, M. K.; Rojo, T.; Arriortua, M. I., *Hybrid Vanadates, Towards Metal-Organic Frameworks*. Coordination Polymers and Metal-Organic Frameworks: Properties, Types and Applications, Nova-Publishers, USA, 1-58: 2012.

<sup>116</sup> Larrea, E. S. Nuevos Vanadatos Híbridos de Metales de Transición. Síntesis Hidrotermal, Estudio Estructural y de sus Propiedades Espectroscópicas y Magnéticas. Tesis Doctoral UPV/EHU, Leioa, 2009.

<sup>117</sup> Fernández de Luis, R. Auto-Ensamblaje de Vanadatos Heterometálicos Basados en Redes Metal Orgánicas con Ligandos Bipodales. Tesis Doctoral UPV/EHU, Leioa, 2009.

<sup>118</sup> Larrañaga, A. Selenitos de Metales de Transición (Mn, Co, Ni, Fe, Cu, Zn y Cd) Sintetizados en Condiciones Hidrotermales. Estudio Estructural y de las Propiedades Físicas. Tesis Doctoral UPV/EHU, Leioa, 2004.

<sup>119</sup> Fernández, S. Nuevos Fosfitos con Estructura Abierta de Metales de Transición y Diaminas Orgánicas: Síntesis, Estructura y Propiedades. Tesis Doctoral, UPV/EHU, Leioa, 2003.

<sup>120</sup> Bazán, B. Arseniatos Porosos de Hierro (III) y Diaminas Orgánicas con Estructura Abierta. Nuevos Polimorfos de la Fase, Fe(ASO<sub>4</sub>). Tesis Doctoral, UPV/EHU, Leioa, 2003.

<sup>121</sup> Berrocal, T. Arseniatos y/o Fosfatos de Hierro y Vanadio con Cationes Orgánicos y Estructura Abierta. Tesis Doctoral, UPV/EHU, Leioa, 2008.

<sup>122</sup> Orive, J. Materiales Condensados y con Estructura Abierta Basados en Fosfitos de Metales 3d. Tesis Doctoral, UPV/EHU, Leioa, 2011.

<sup>123</sup> Serna, Z. F.; Lezama, L.; Urriaga, M. K.; Arriortua, M. I.; Barandika, M. G.; Cortes, R.; Rojo, T., *Angew. Chem., Int. Ed.* **2000**, *39*, 344-347.

<sup>124</sup> Barandika, M. G.; Cortes, R.; Serna, Z.; Lezama, L.; Rojo, T.; Urriaga, M. K.; Arriortua, M. I., *Chem. Commun.* **2001**, 45-46.

<sup>125</sup> Serna, Z. E.; Cortes, R.; Urriaga, M. K.; Barandika, M. G.; Lezama, L.; Arriortua, M. I.; Rojo, T., *Eur. J. Inorg. Chem.* **2001**, 865-872.

las magnéticas, ópticas, luminiscentes y catalíticas, con las típicas de los materiales microporosos como el intercambio iónico, la absorción y la catálisis heterogénea. De este modo, en nuestro grupo de investigación se han obtenido nuevos compuestos con propiedades catalíticas<sup>126-129</sup>, luminiscentes<sup>130</sup> y adsorbentes,<sup>131</sup> de gran interés.

Con los antecedentes mencionados, se procedió a desarrollar el trabajo de investigación que queda reflejado en esta memoria, en el que se recogen cinco compuestos con las siguientes fórmulas: [FeTCPP], [CoTPP(bipy)]·([CoTPP])<sub>0.22</sub>·(TPP)<sub>0.78</sub>, ([FeTPPbipy]<sup>+</sup>)<sub>n</sub>,  $\mu$ -O-[FeTCPP]<sub>2</sub>·nDMF y [CoTPPS<sub>0.5</sub>(bipy)(H<sub>2</sub>O)<sub>2</sub>]·6H<sub>2</sub>O. Todos ellos se han preparado por síntesis solvotermal y microondas.

Además de la caracterización estructural por medio de la difracción de rayos X de los compuestos obtenidos, también se han estudiado sus propiedades térmicas, magnéticas y catalíticas mediante diferentes técnicas espectroscópicas, termogravimétricas y cromatográficas. Asimismo, se han realizado cálculos DFT (Teoría del Funcional de la Densidad) para estudiar la estabilidad de diferentes fases, así como para analizar la estructura electrónica de los compuestos. Por último, también ha sido objeto de análisis la topología que presentan las redes cristalinas obtenidas

<sup>126</sup> Berrocal, T.; Mesa, J. L.; Pizarro, J. L.; Bazan, B.; Iglesias, M.; Vilas, J. L.; Rojo, T.; Arriortua, M. I., *Dalton Trans.* **2010**, 39, 834-846.

<sup>127</sup> Berrocal, T.; Mesa, J. L.; Pizarro, J. L.; Bazan, B.; Iglesias, M.; Aguayo, A. T.; Arriortua, M. I.; Rojo, T., *Chem. Commun.* **2008**, 4738-4740.

<sup>128</sup> Berrocal, T.; Larrea, E. S.; Iglesias, M.; Arriortua, M. I., *J. Mol. Catal. A Chem.* **2011**, 335, 176-182.

<sup>129</sup> Larrea, E. S.; Mesa, J. L.; Pizarro, J. L.; Iglesias, M.; Rojo, T.; Arriortua, M. I., *Dalton Trans.* **2011**, 40, 12690-12698.

<sup>130</sup> Orive, J.; Mesa, J. L.; Balda, R.; Fernandez, J.; Rodriguez Fernandez, J.; Rojo, T.; Arriortua, M. I., *Inorg. Chem.* **2011**, 50, 12463-12476.

<sup>131</sup> Arriortua Marcaida, M. I.; Barandika Argoitia, M. G.; Bazan Blau, B.; Calderon Casado, A.; Urtiaga Greaves, M. K. Alcohol and water sensor compounds, detection method and device. Patente: 2012-ES070723

durante el transcurso de esta investigación y la distorsión de los poliedros metálicos, así como las distorsiones que presentan las propias porfirinas.



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# ***INTERÉS Y OBJETO DEL TRABAJO***

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El avance de la sociedad está estrechamente ligado a la obtención, estudio, desarrollo y optimización de nuevos materiales y la investigación es crucial para comprender la relación entre la síntesis, la estructura cristalina y las propiedades fisicoquímicas de los materiales. La posterior modificación de diferentes variables en este proceso interactivo puede llevar, siempre que el sistema lo permita, a la obtención de materiales con las propiedades deseadas para su directa aplicación.

Los MOFs (Metal-Organic Frameworks) constituyen una amplia familia de compuestos de coordinación en continuo desarrollo en el campo de la Ciencia y Tecnología de Materiales. Las atractivas propiedades que presentan este tipo de materiales en procesos como el almacenamiento de gases, la liberación controlada de sustancias (como combustibles ligeros y fármacos), en sensores o como catalizadores, explican el creciente interés que ha suscitado su desarrollo. En este sentido, los MOFs basados en metaloporfirinas intentan recrear, en el estado sólido, las propiedades asociadas a estos compuestos en los sistemas biológicos, como la transferencia de carga y las propiedades catalíticas.

En este contexto, el trabajo que se presenta en esta memoria se ha centrado en la obtención y caracterización de redes cristalinas basadas en metaloporfirinas, orientando el diseño de la estructura a la mimetización de sus funciones intrínsecas; con especial interés en las propiedades catalíticas. Para ello, atendiendo a la responsabilidad medioambiental inherente a la actividad investigadora actual, se decidió emplear biometales de la primera serie de transición. Asimismo, se escogieron tres porfirinas *meso* sustituidas con anillos fenílicos funcionalizados: TPP (*meso*-tetra-4-fenilporfirina), TCPP (*meso*-tetra-4-carboxifenilporfirina) y TPPS (*meso*-tetra-4-sulfonatofenilporfirina). Adicionalmente, se contempló la posibilidad de usar ligandos secundarios dipiridínicos como espaciadores. El trabajo también contempla el estudio estructural y fisicoquímico de los compuestos obtenidos.



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***VISIÓN GLOBAL DE LOS  
HALLAZGOS***

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En esta memoria se presentan los resultados de la investigación realizada y su discusión mediante los artículos científicos publicados (o en vías de estarlo). Por ello, antes de los cuatro capítulos correspondientes a cada uno de los artículos, se pretende ofrecer una visión global de los hallazgos que conforman el cuerpo de esta tesis doctoral.

Como se ha comentado previamente, el objetivo de esta investigación ha sido la búsqueda de nuevos materiales de tipo MOF basados en biometales y ligandos porfirínicos y orientados a mimetizar las funciones que las metaloporfirinas llevan a cabo en los sistemas biológicos; con especial interés en la función catalítica. Uno de los aspectos más importantes en la obtención de este tipo de materiales radica en el diseño de una correcta estrategia sintética, basada tanto en la selección de metales y ligandos como en las técnicas de síntesis. Estos aspectos se han comentado en la introducción de esta memoria.

Así, se han estudiado combinaciones de los biometales hierro y cobalto con las porfirinas TPP (*meso*-tetra-4-fenilporfirina), TCPP (*meso*-tetra-4-carboxifenilporfirina) y TPPS (*meso*-tetra-4-sulfonatofenilporfirina). Ocasionalmente, se ha utilizado un ligando secundario dipiridínico (4,4'-bipiridina) que actúa como espaciador. De este modo, se han obtenido cinco nuevos compuestos, que se han sintetizado en condiciones solvotermales suaves o mediante radiación microondas. A este respecto, es necesario subrayar la dificultad inherente a la disolución de las porfirinas y los inconvenientes que ello acarrea para la obtención de monocristales de calidad adecuada para la elucidación estructural mediante difracción de rayos X.

Como en cualquier otro trabajo de investigación dedicado a la síntesis de nuevos compuestos, esta memoria recoge sólo parte de los productos obtenidos. De las síntesis realizadas, se obtuvieron algunos compuestos que fueron descartados: en

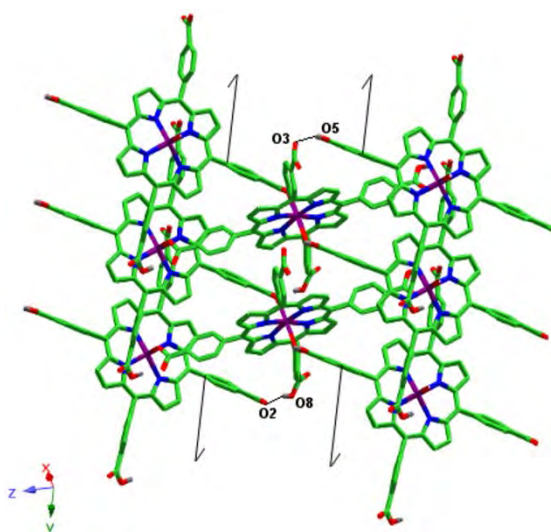
algunos casos por la imposibilidad de reproducirlos, en otros, por dificultades en la correcta elucidación estructural y también porque los compuestos no eran inéditos.

En esta memoria se recogen los resultados y la discusión relativos a la síntesis y caracterización de los cinco compuestos mencionados. En el Anexo A se detallan las técnicas correspondientes. Todos los compuestos fueron sometidos a una caracterización preliminar mediante análisis cuantitativo, espectroscopia infrarroja y Raman, difracción y fluorescencia de rayos X y medidas de densidad. Posteriormente, se elucidó mediante difracción de rayos X la estructura cristalina de los compuestos de interés y se estudió su estabilidad térmica mediante termogravimetría y termodifracción. En los casos en los que resultó procedente, también se caracterizaron los compuestos mediante espectroscopia ultravioleta-visible (UV-Vis), Mössbauer y de resonancia paramagnética electrónica (EPR) y mediante medidas de la susceptibilidad magnética. Asimismo, ocasionalmente, se realizaron análisis de la topología y la distorsión, cálculos mecano-cuánticos basados en la teoría del funcional de la densidad (DFT) y medidas catalíticas.

Los compuestos recogidos en esta memoria se presentan en orden cronológico a su estudio, ya que ello coincide con el re-enfoque que se iba dando al diseño sintético, en función de los resultados obtenidos. En este sentido, es importante subrayar que este trabajo es la primera incursión en los MOFs basados en metaloporfirinas del grupo de investigación en el que se ha desarrollado esta tesis doctoral. Así, la primera aproximación al tema se hizo desde la perspectiva de tratar de obtener redes porosas de la mayor dimensionalidad posible, al objeto de maximizar su estabilidad térmica. Ello representaba un reto significativo ya que las metaloporfirinas tienden a cristalizar como monómeros o en *clusters* de baja dimensionalidad (generalmente, dímeros). De este modo, la porfirina TCPP fue la primera molécula con las que se abordó el trabajo. Esta elección se explica por el hecho de que la formación de conexiones intermoleculares podía verse favorecida por los átomos de oxígeno

presentes en los grupos carboxifenílicos que funcionalizan las posiciones *meso* del anillo tetrapirrólico.

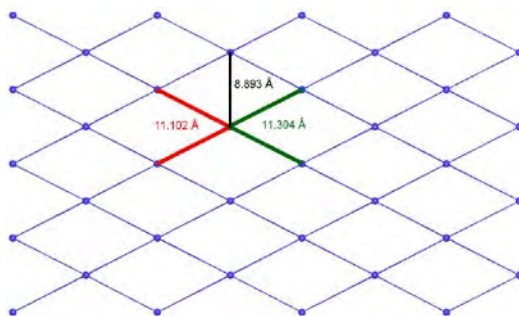
Así, el primero de los compuestos obtenidos, mostrado en el Capítulo I, es el resultado de esta primera estrategia. Se trata de una fase laminar, de fórmula [FeTCPP], que presenta una compleja red cristalina en la que las porfirinas se unen saturando la esfera de coordinación octaédrica del hierro, dando lugar a la extensión 2D de la estructura (Figura 1).



**Figura 1.** Vista de una de las capas en el compuesto [FeTCPP] (Fe: púrpura, C: verde, N: azul, O: rojo). Se han marcado los átomos de oxígeno entre los que se producen enlaces de hidrógeno intralaminares (los átomos de hidrógeno se han omitido). Los ejes binarios helicoidales ( $2_1$ ) se disponen a lo largo del eje b.

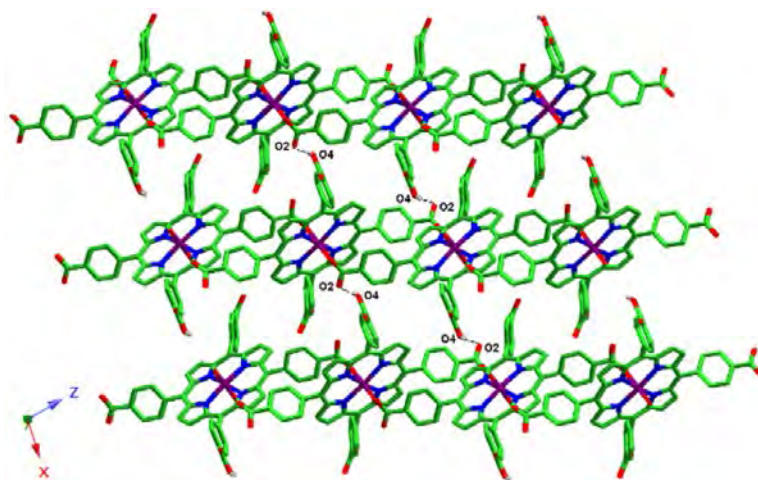
A pesar de la complejidad estructural de estas capas, su topología se basa en un modelo de conectividad muy sencillo: una red uninodal 4-c de tipo Shubnikov (Figura 2).





**Figura 2.** Topología de las capas en el compuesto [FeTCPP].

Estas capas presentan la particularidad de ser quirales. Además, destaca el hecho de que la quiralidad se mantiene en el entramado 3D (Figura 3), basado en enlaces de hidrógeno. Ello se refleja en el hecho de que el grupo espacial de este compuesto ( $P2_1$ ) es no centrosimétrico.



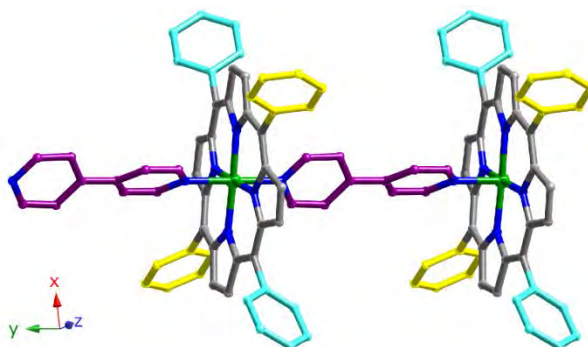
**Figura 3.** Proyección [010] del entramado 3D en el compuesto [FeTCPP] (Fe: púrpura, C: verde, N: azul, O: rojo). Se han marcado los átomos de oxígeno entre los que se producen enlaces de hidrógeno interlaminares (los átomos de hidrógeno se han omitido).

El hecho de que el ion  $\text{Fe}^{\text{II}}$  de partida se oxide a  $\text{Fe}^{\text{III}}$  es determinante en la formación de este compuesto, por sus consecuencias sobre la acidez de Pearson. Además, todo ello se relaciona con la desprotonación asimétrica de los átomos de nitrógeno del anillo tetrapirrólico, dirigida por los cambios de pH. La hipótesis propuesta fue avalada por cálculos teóricos DFT. Cabe destacar el hecho de que este compuesto es uno de los escasos ejemplos registrados en la bibliografía de redes 2D con metaloporfirinas; de hecho, es la tercera estructura 2D publicada con TCPP.

Desafortunadamente, no se pudo profundizar en la caracterización de este compuesto porque no pudo ser reproducido. La falta de reproducibilidad es una de las dificultades habituales en este tipo de sistemas.

Las potenciales aplicaciones de los MOFs basados en metaloporfirinas pasan porque la red cristalina sea accesible a moléculas externas. Por ello, se reorientó la síntesis hacia la obtención de estructuras menos compactas. Para ello, se introdujo la 4, 4'-bipiridina: un ligando rígido que actuaría como espaciador entre las unidades porfirínicas coordinándose en las posiciones axiales de las esferas de coordinación octaédricas. Asimismo, se optó por las porfirinas TPP y TPPS con grupos funcionales fenilo y sulfonatofenilo, respectivamente. De esta manera, se consiguieron tres compuestos 1D: en el Capítulo II se presenta el de fórmula  $([\text{FeTPPbipy}]^+)_n$  y en el Capítulo III, los de fórmula  $[\text{CoTPP}(\text{bipy})] \cdot ([\text{CoTPP}])_{0.22} \cdot (\text{TPP})_{0.78}$  y  $[\text{CoTPPS}_{0.5}(\text{bipy})(\text{H}_2\text{O})_2] \cdot 6\text{H}_2\text{O}$ .

En el primero de ellos,  $([\text{FeTPPbipy}]^+)_n$ , los polímeros de coordinación 1D (Figura 4) cristalizan en una estructura 3D sustentada por enlaces  $\pi$  entre los grupos fenilos.

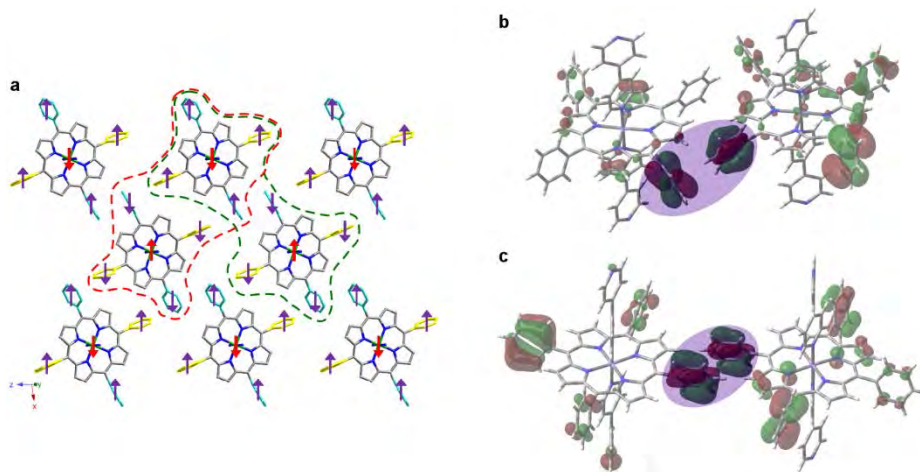


**Figura 4.** Polímeros de coordinación 1D en el compuesto  $([\text{FeTPPbipy}]^{\cdot})_n$  (Fe: verde; N: azul; C(porfirina): gris, amarillo, turquesa; C(bipy): púrpura). Los átomos de hidrógeno se han omitido.

La estequiometría de este compuesto es acorde al siguiente reparto de cargas:  $\text{Fe}^{+2}\text{-TPP}^{-2}\text{-bipy}^0$ . Sin embargo, el reactivo de partida  $[\text{FeTPP}]\text{Cl}$  contiene iones férricos y tanto las propiedades magnéticas como las espectroscópicas son consistentes con la presencia de iones  $\text{Fe}^{\text{III}}$  de bajo espín. Ésta aparente falta de coherencia fue objeto de un intenso estudio, dificultado por el hecho de que las muestras policristalinas se amorfizaban como consecuencia de su molienda; lo que añadía más dificultad a la interpretación de los resultados magnéticos y espectroscópicos. Finalmente, se formuló una propuesta coherente con todos los datos experimentales, en base a la cual el catión original  $[\text{FeTPP}]^{+1}$  se reduce aceptando un electrón, dando lugar a radicales neutros  $[\text{FeTPP}]^{\cdot}$ . Estos monómeros radicalarios polimerizan conectándose a través del ligando secundario bipy. Los cálculos DFT realizados permitieron localizar estos electrones sobre los anillos aromáticos de los grupos fenilos ( $0,25 e^-$  sobre cada uno de los cuatro grupos fenilos).

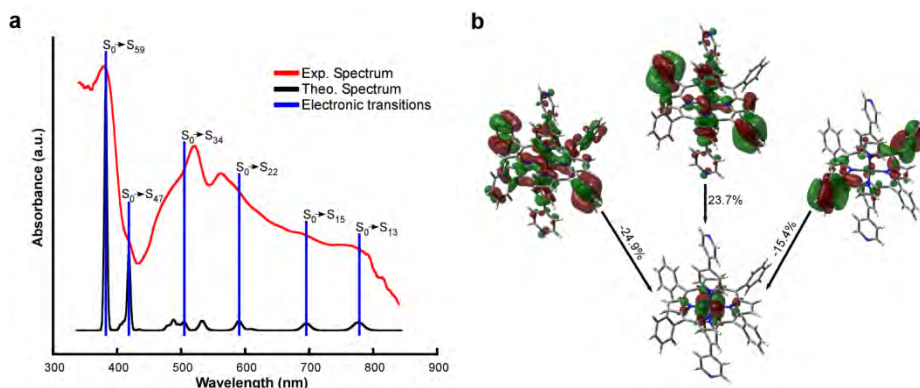
El empaquetamiento de las cadenas en este compuesto es un factor clave para comprender su comportamiento. Así, la presencia de importantes interacciones  $\pi\text{-}\pi$  (tanto de tipo *face-to-face* como *edge-to-face*) entre los grupos fenilos estabiliza estos

radicales permitiendo el apareamiento de electrones pertenecientes a diferentes cadenas. Todo ello lleva a proponer una distribución de espín como la que se muestra en la Figura 5.



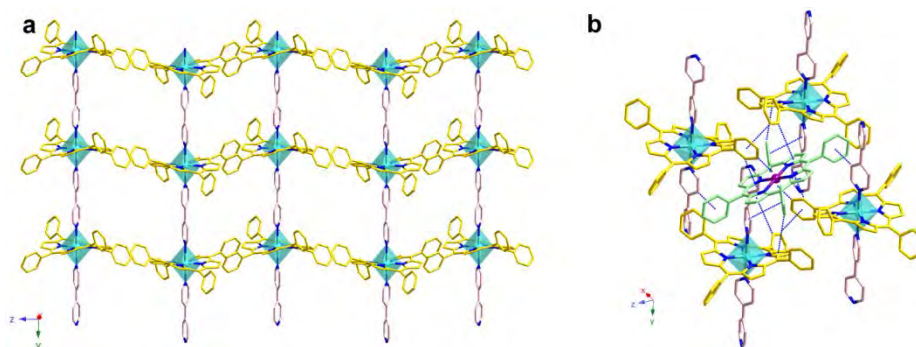
**Figura 5.** a) Empaquetamiento de las cadenas en el compuesto  $([\text{FeTPPbipy}]^n)_n$ . Las flechas rojas representan el espín de los iones  $\text{Fe}^{\text{III}}$  de bajo espín ( $d^5$ ); y las moradas, el de los electrones localizados sobre los grupos fenilos. Las líneas roja y verde marcan los fragmentos diméricos escogidos para los cálculos DFT correspondientes a cadenas conectadas por interacciones *edge-to-face* y *face-to-face*, respectivamente. Los orbitales moleculares de b) y c) corresponden a las interacciones *edge-to face* y *face-to-face*, respectivamente.

La distribución de espín mostrada en la Figura 5 es coherente con la existencia de significativas interacciones antiferromagnéticas. Por otra parte, el espectro UV-Vis del compuesto (Figura 6) reveló una banda Soret desplazada a azul, indicativa de especies radicalarias. El espectro fue simulado mediante cálculos TD-DFT, que revelaron una importante transferencia de carga entre los grupos fenilo y los centros metálicos. El conocimiento de esta transferencia fue fundamental para interpretar las medidas magnéticas.



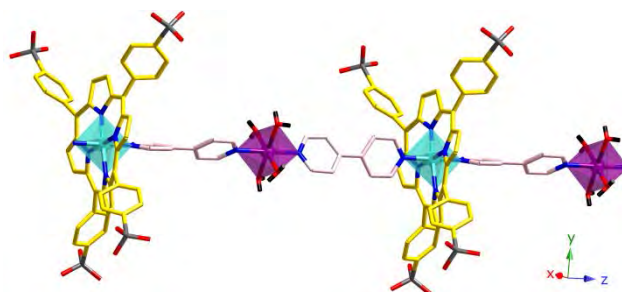
**Figura 6.** a) Espectros UV-Vis experimental y calculado del compuesto  $([\text{FeTPPbipy}]^*)_n$ . b) Orbitales moleculares implicados en la transición Soret ( $S_0$ - $S_{59}$ ).

La porfirina TPP ha permitido obtener otro compuesto con grandes similitudes respecto a  $([\text{FeTPPbipy}]^*)_n$ . Así, el compuesto  $[\text{CoTPP}(\text{bipy})] \cdot ([\text{CoTPP}])_{0.22} \cdot (\text{TPP})_{0.78}$ , que se describe en el Capítulo III, también consta de polímeros lineales en los que el ligando bipy actúa de espaciador. Sin embargo, en este compuesto de cobalto y TPP las cadenas (Figura 7) se disponen de forma que dejan grandes huecos en los que se localizan porfirinas tanto coordinadas (22% del total) como sin coordinar (78% del total). En este compuesto se ha alcanzado el reto de inmovilizar o anclar el catalizador en los huecos de un MOF. Ésta es una aproximación que está siendo objeto de gran interés en la comunidad científica, por sus implicaciones en la catálisis heterogénea. Así, el compuesto con cobalto y TPP no sólo es uno de los escasos ejemplos hasta ahora publicados, sino que cuenta con la peculiaridad de que la propia metaloporfirina cumple con la doble función de ser el soporte estructural y el potencial catalizador. Desafortunadamente, los estudios catalíticos realizados no fueron satisfactorios, lo que se explica por el bajo número de complejos potencialmente activos y por la limitada accesibilidad de la red a los mismos.



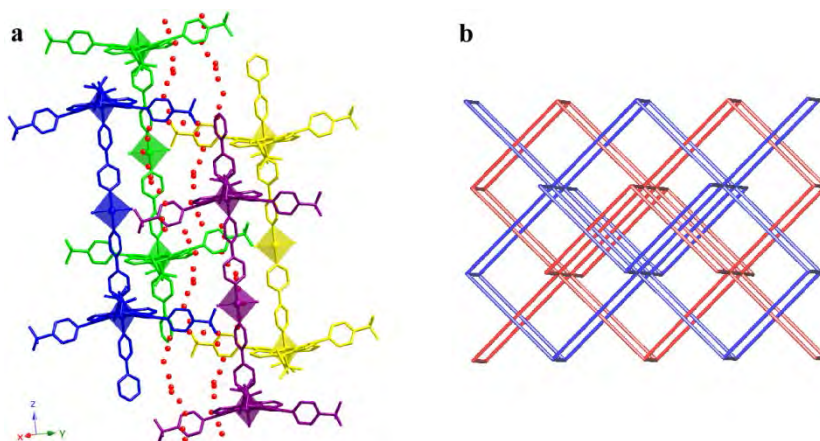
**Figura 7.** a) Empaquetamiento de los polímeros de coordinación 1D en el compuesto  $[\text{CoTPP}(\text{bipy})]\cdot([\text{CoTPP})]_{0.22}\cdot(\text{TPP})_{0.78}$  y b) detalle de una metaloporfirina de cristalización conectada a cuatro cadenas adyacentes mediante enlaces de hidrógeno (Co(1) (TPP en la cadena): turquesa; Co(2) (TPP de cristalización): púrpura; N: azul; C (TPP en la cadena): amarillo; C (TPP de cristalización): verde; C (bipy): rosa). Los átomos de hidrógeno se han omitido.

En el Capítulo III también se describe el compuesto 1D de fórmula  $[\text{CoTPPS}_{0.5}(\text{bipy})(\text{H}_2\text{O})_2]\cdot 6\text{H}_2\text{O}$ . A este respecto, es necesario recordar que la porfirina TPPS cuenta con la posición *meso* funcionalizada por un grupo sulfonatofenilo y que se trata de un ligando con el que se han dilucidado muchas menos estructuras cristalinas que con las porfirinas TCPP y TPP. De hecho, el compuesto  $[\text{CoTPPS}_{0.5}(\text{bipy})(\text{H}_2\text{O})_2]\cdot 6\text{H}_2\text{O}$  es el primero en combinar TPPS y Co. En este compuesto la extensión 1D de la estructura tiene lugar mediante la polimerización de dos unidades alternadas (Figura 8), consistentes en dos esferas de coordinación octaédricas, con el ión  $\text{Co}^{\text{II}}$  coordinado ecuatorialmente a la porfirina y a cuatro moléculas de agua, respectivamente. Estos octaedros se unen axialmente mediante el espaciador bipy.



**Figura 8.** Polímero de coordinación 1D en el compuesto  $[\text{CoTPPS}_{0.5}(\text{bipy})(\text{H}_2\text{O})_2] \cdot 6\text{H}_2\text{O}$  (Co(1) (TPPS): turquesa; Co(2): púrpura; N: azul; C (TPPS): amarillo; C (bipy): rosa; O: rojo; S: gris). Los átomos de hidrógeno se han omitido.

El empaquetamiento de las cadenas en este compuesto se produce mediante un intrincado sistema de enlaces de hidrógeno (Figura 9) que genera una topología de redes interpenetradas, responsable de la elevada estabilidad térmica que presenta el compuesto (hasta  $370^\circ\text{C}$ ).



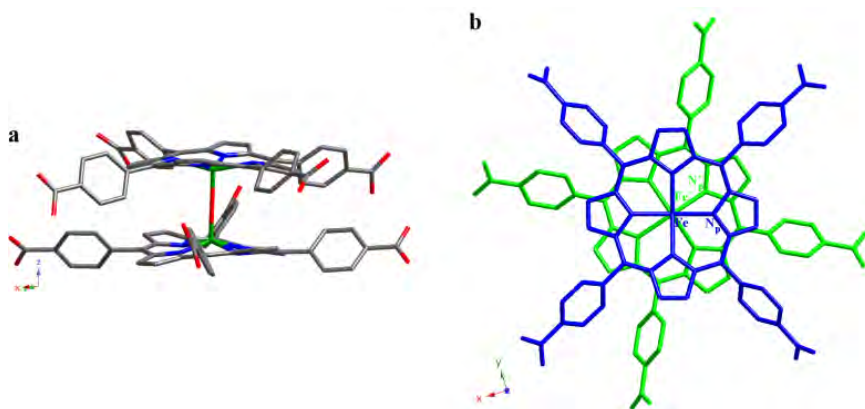
**Figura 9.** (a) Detalle del empaquetamiento de las cadenas en el compuesto  $[\text{CoTPPS}_{0.5}(\text{bipy})(\text{H}_2\text{O})_2] \cdot 6\text{H}_2\text{O}$ . Las moléculas de agua de cristalización se muestran en rojo. (b) Topología de redes interpenetradas.

El hecho de que las cadenas, cristalográficamente bimetalicas, posean centros catalíticamente activos, ha permitido explorar diferentes reacciones en las que el compuesto  $[\text{CoTPPS}_{0.5}(\text{bipy})(\text{H}_2\text{O})_2]\cdot 6\text{H}_2\text{O}$  muestra prometedores resultados. Estos ensayos necesitan ser analizados en mayor detalle y, por ello, no se han incluido en esta memoria.

La distorsión de los macrociclos es muy relevante biológicamente y en la bibliografía se encontró un análisis dedicado a las metaloporfirinas de  $\text{Co}^{\text{III}}$ . En el momento del estudio, se encontraron en la Cambridge Structural Database (CSD) 221 metaloporfirinas de cobalto; 124 de las cuáles contenían  $\text{Co}^{\text{III}}$ . Sin embargo, no se había analizado la distorsión de las 97 restantes, correspondientes al ion  $\text{Co}^{\text{II}}$ . Así, en el Capítulo III se incluye este análisis del que se deduce que la mayoría de las metaloporfirinas de  $\text{Co}^{\text{II}}$  presentan los modos de distorsión *saddle* y *ruffle*. De hecho, los compuestos de  $\text{Co}^{\text{II}}$  con TPP y TPPS mostrados en esta tesis doctoral presentan la segunda de ellas. El análisis ha permitido establecer una clara correlación entre el grado de distorsión y las distancias de enlace.

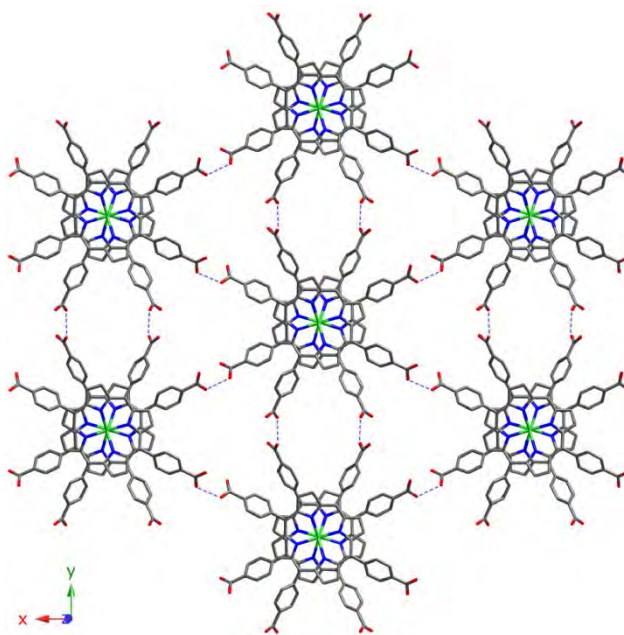
Por último, el Capítulo IV se dedica al compuesto  $\mu\text{-O}-[\text{FeTCPP}]_2\cdot n\text{DMF}$  ( $n\approx 16$  y DMF = dimetilformamida). Nuevamente se utiliza la porfirina TCPP, pero el cambio de reactivo de partida,  $[\text{FeTCPP}]\text{Cl}$ , evita la formación de las capas que dan origen al compuesto  $[\text{FeTCPP}]$  (Capítulo I), en el que el  $\text{Fe}^{\text{II}}$  libre se incorpora a la porfirina oxidado a  $\text{Fe}^{\text{III}}$ . Así, la formación del compuesto  $\mu\text{-O}-[\text{FeTCPP}]_2\cdot n\text{DMF}$  se explica por la presencia en disolución de cationes  $[\text{FeTCPP}]^+$ , que dimerizan a través de un puente oxo (Figura 10).



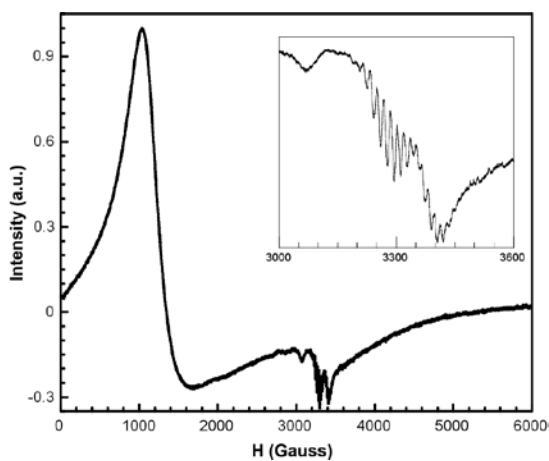


**Figura 10.** Vistas de los dímeros del compuesto  $\mu\text{-O-[FeTCPP]}_2 \cdot n\text{DMF}$ . Los códigos de colores en la vista a) son los siguientes: (Fe: verde, N: azul, C: gris and O: rojo). Los átomos de hidrógeno se han omitido.

El empaquetamiento de los dímeros en este compuesto (Figura 11), da lugar a una porosidad muy elevada (47%). Las moléculas de DMF presentes en estos huecos estabilizan el entramado 3D. Estas características estructurales dan lugar a fuertes interacciones antiferromagnéticas intradiméricas ( $J = -132 \text{ cm}^{-1}$ ) y a la aparición de una inusual estructura superhiperfina en la espectroscopia EPR (Figura 12). Esta señal se debe a la interacción entre el espín electrónico del ion  $\text{Fe}^{\text{III}}$  y los espines nucleares ( $I=1$ ) de los átomos de nitrógeno del anillo tetrapirrólico, por una parte, y al efecto de desdoblamiento a campo cero (ZFS, zero-field splitting), por otra.



**Figura 11.** Empaquetamiento de los dímeros mediante enlaces de hidrógeno (líneas discontinuas) en el compuesto  $\mu\text{-O-}[\text{FeTCPP}]_2 \cdot n\text{DMF}$  (Fe: verde, N: azul, C: gris, O: rojo). Los átomos de hidrógeno se han omitido.



**Figura 12.** Espectro EPR en banda X (temperatura ambiente) del compuesto  $\mu\text{-O-}[\text{FeTCPP}]_2 \cdot n\text{DMF}$ .

El compuesto  $\mu$ -O-[FeTCPP]<sub>2</sub>·nDMF destaca principalmente por sus propiedades catalíticas en estado sólido. De hecho, se ha probado con éxito en reacciones de oxidación y acetilación de distintos sustratos. Además, se debe destacar que este compuesto es uno de los escasos MOFs metaloporfirínicos publicados en los que el propio MOF actúa como catalizador heterogéneo.

En definitiva, la experiencia obtenida del estudio realizado en esta investigación corrobora que las porfirinas son excelentes candidatas para la obtención de redes metal-orgánicas con interesantes propiedades. Asimismo, la diversidad estructural obtenida, asociada a las propiedades fisicoquímicas de los compuestos logrados, viene a subrayar, una vez más, la importancia de la red cristalina en el comportamiento de los materiales. De hecho, en este trabajo se concluye que la mayor accesibilidad a potenciales moléculas huésped observada en las redes más sencillas da lugar a materiales con mayor proyección tecnológica.

# *CAPÍTULO I*

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## Compuesto [FeTCPP]

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*“Self-assembly of iron TCPP (meso-tetra(4-carboxyphenyl) porphyrin) into a chiral 2D coordination polymer”*

*Polyhedron 2011, 30 (16), 2711-2716*

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**Resumen**

Los complejos formados por metaloporfirinas sintéticas se utilizan, en muchas ocasiones, como análogos de los sistemas naturales aunque también pueden emplearse en la preparación de polímeros de coordinación de alta dimensionalidad. En este trabajo se muestra la síntesis y caracterización estructural del nuevo compuesto quiral con fórmula Fe-TCPP (TCPP es la meso-tetra-(4-carboxifenil)porfirina). Se trata de un compuesto 2D formado por enlaces de coordinación en el que los fuertes enlaces de hidrógeno conectan las capas formando una red 3D. Durante la formación de estas capas la oxidación de los iones originales de  $Fe^{II}$  a  $Fe^{III}$  es de crucial importancia. Es destacable el hecho de que la topología muestre una elevada conectividad que se basa en una extensión sencilla de la estructura. Además, para estudiar la estabilización del compuesto de  $Fe^{III}$ , también se han realizado cálculos DFT. Éste es el tercer ejemplo recogido en la bibliografía de un compuesto de coordinación basado en la TCPP sin otros ligandos secundarios, donde la dimensionalidad se refiere únicamente a enlaces de coordinación.

**Abstract**

*Synthetic metalloporphyrin complexes are often used as analogues of natural systems, and they can be used for the preparation of high-dimensional coordination polymers. In this work, a new chiral Fe-TCPP (TCPP is meso-tetra-(4-carboxyphenyl)porphyrin) coordination compound has been synthesised and structurally characterized. The compound is 2D via coordination bonds, and it exhibits strong hydrogen bonds that connect the planar arrays forming the 3D framework. The oxidation of the original Fe<sup>II</sup> ions to Fe<sup>III</sup> accounts for the formation of this array, in which the topological analysis reveals a very high connectivity based on a simple extension fashion of the structure. DFT calculations have been also carried out to study the stabilisation of the Fe<sup>III</sup>-compound. This is the third example of a 2D coordination compound based on TCPP in which the dimensionality refers just to coordination bonds, and no other ligands are present in the structure.*

## Laburpena

Sarritan metaloporfirinen konplexu sintetikoak sistema naturalen erara erabiltzen dira, eta gainera, dimentsio altuko koordinazio polimeroak sortzeko erabil daitezke. Lan honetan, Fe-TCPP (TCPP=meso-tetra-(4-karboxifenil)porfirina) koordinazio konposatu kiral berriaren sintesia eta kristal-egituraren karakterizazioa aurkezten dira. Koordinazio loturen bidez konposatu hau bi dimentsiokoa da, eta horrela sortutako geruzak paketatzen dira hiru dimentsioko sarea eratzen delarik hidrogeno lotura sendoen bidez. Konposatu hau era dadila ezinbestekoa da gertatzen den jatorrizko  $Fe^{II}$ -a  $Fe^{III}$ -ra oxidazioa. Bestalde, analisi topologikoak adierazten du sarearen eraketa sinplea dela, konektibitatea altua izan arren.  $Fe^{III}$  duen konposatu honen egonkortasuna aztertzeko DFT kalkuluak ere egin dira. Hots, ligando sekundariorik gabeko eta TCPP duten konposatuen artean, hauxe da hirugarren adibidea.



## I.1. Introduction

Coordination polymers are also known as MOFs (metal organic frameworks), and the work devoted to this field in the last decades is huge. In this context, metalloporphyrins are remarkable precursors in supramolecular chemistry, giving rise to various architectures and properties.<sup>1-4</sup> To illustrate this point, several examples can be cited as photodynamic therapy, information storage devices, photoelectrical devices as photocells and light-emitting diodes (that transform energy in both directions), and receptors (exploiting their ability to selectively form complexes which can sharply change the spectral properties).<sup>5-8</sup>

Metalloporphyrins are one of the cornerstones on which the existence of life is based and major biochemical, enzymatic, and photochemical functions depend on the special properties of a tetrapyrrolic macrocycle. This is the reason why synthetic metalloporphyrin complexes are often used as analogues of natural systems found in photosynthesis, oxygen carriers, and catalysts.<sup>5,9-14</sup> For instance, these systems are

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<sup>4</sup> Goldberg, I., *CrystEngComm* **2008**, *10*, 637-645.

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used to understand the mechanism of electron transfer through intermolecular interactions, and some works show that efficient energy transfer may occur across the intermolecular bonds.<sup>15-19</sup>

From the point of view of coordination chemistry, the dimensionality of metalloporphyrin frameworks is defined by the extension of a structural unit in one, two or the three dimensions of the space via coordination bonds. Thus, axial coordination of metalloporphyrins represents a limiting factor for high dimensionality as it gives only one or two binding sites with other structural units. Therefore, additional binding centers are required for high dimensional frameworks, and one way to create them consists of incorporating additional donors at the periphery of a porphyrinic cycle. An illustrative example of the later is tetra-(4-carboxyphenyl)porphyrin (TCPP) (Scheme 1) for which the presence of carboxylic groups at the 4-positions of the phenyl ring increases the possibilities of obtaining a high dimensional framework.

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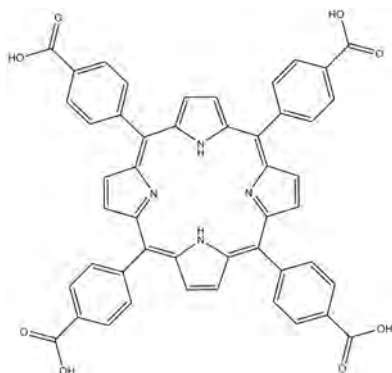
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**Scheme 1.** Lewis structure of TCPP.

TCPP coordination polymers with different structures have been prepared. For example, 2D porphyrin frameworks have been reported exhibiting square grid structure sustained by characteristic  $\pi$ - $\pi$  stacking interactions and multiple hydrogen bonds.<sup>20-23</sup> Similarly, a 2D complex with  $Mn^{II}$ <sup>24</sup> must be cited as the dimensionality is based on coordination bonds. Additionally, the combination of TCPP with other components gives rise to a variety of 2D and 3D structures.<sup>25</sup> Some of these combinations are specially remarkable as they include fullerene,<sup>26</sup> silica<sup>27</sup> and 4,4'-bipyridine.<sup>28,29</sup>

During the last years, our research has been focused on the preparation of coordination polymers with increasing dimensionality with a variety of metal-ligand combinations, and we have prepared several high dimensional structures with 4,4'-

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bipyridine, including interpenetrated networks.<sup>30-35</sup> In this sense, it is worth mentioning that, when combining an O-donor ligand like TCPP, with a N-donor one, like 4,4'-bipyridine, the Pearson acidity is one of the leading forces to be considered in the extension of the structure, as it is in relationship with the affinity of the metal centre, which is influenced by its oxidation state. The most popular example of a natural system where the oxidation state of the metal is crucial is the oxygen transport in haemoglobin.

Taking into account the above mentioned aspects, we intended to prepare Fe<sup>II</sup>-porphyrin frameworks with TCPP and 4,4'-bipyridine. In particular, the goal of this work was to study the influence of the synthesis conditions on the structural features of the framework. In this way, this work presents the microwave-assisted hydrothermal synthesis of the new compound [FeTCPP], and its X-ray structural characterisation. From the point of view of the coordination binding, the structure is 2D, and exhibits robust hydrogen bonds that connect the planar moieties giving rise to the 3D framework. A topological analysis and DFT calculations have been also carried out in order to analyze the self-assembly process.

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## I.2. Experimental Section

### I.2.1. Materials and methods

The porphyrin compound TCPP (Sigma-Aldrich) and all the others solvents and reagents (Sigma-Aldrich) were obtained commercially and used without further purification. [FeTCPP] compound was synthesized by using microwave-assisted hydrothermal synthesis. Free ligand TCPP (4.7 mg, 0.006 mmol) was dissolved in a mixture of deionised water (10 mL) and acetone (15 mL), then under continuous stirring NaOH (1M) was added until pH=14 (to cause the porphyrin deprotonation). FeCl<sub>2</sub> (7.6 mg, 0.06 mmol) dissolved in deionised water (5 mL) was added to porphyrin solution and after 10 minutes of stirring, 4,4'-bipyridine (2.8 mg, 0.018 mmol) dissolved in deionised water (10 mL) was added drop by drop. The solution was heated at 140 °C (800W) for 2h in a CEM MARS5 microwave and after that, at the same temperature in a PTFE-lined stainless steel pressure vessel for 5 days in a conventional heater, yielding diffraction quality dark red crystals.

### I.2.2. Infrared spectroscopy

The IR spectrum was collected on a JASCO FT/IR-6100 at room temperature at the range of 4000 to 400 cm<sup>-1</sup>, in KBr pellets (1%).

### I.2.3. Single-crystal X-ray diffraction

Rhombohedral single-crystals with dimensions given in Table 1 were selected under polarizing microscope and mounted on MicroMounts. Single-crystal X-ray diffraction data were collected at 100K on a Bruker X8 Prospector equipped with a high brilliance Cu-IMS (microfocus source) and APEX II detector. Details of crystal data and some features of the structure refinement are reported in Table 1. Lattice constants were obtained by using a standard program belonging to the software of the diffractometer, confirming at the same time the good quality of the single-crystal.



The Lorentz-polarization and absorption corrections were made with the diffractometer software, taking into account the size and shape of the crystals.<sup>36</sup> The structure of [FeTCPP] was solved by direct methods with the SHELXS-97 program,<sup>37</sup> in the monoclinic  $P 2_1$  space group, which allowed us to obtain the position of the Fe atom, as well as oxygen and nitrogen atoms and some of the carbon atoms of the TCPP molecule. The refinement of the crystal structures was performed by full matrix least-squares based on  $F^2$ , using the SHELXL-97 program,<sup>37</sup> obtaining the remaining carbon atoms. Anisotropic thermal parameters were used for all non-hydrogen atoms. All the hydrogen atoms, both the connected to de aromatic rings (C-H 0.95Å), such as the carboxylic groups (O-H 0.84Å) were fixed geometrically after having detected their existence on the density map and were refined using a riding model with common isotropic displacements. Final R-factors are given in Table 1 together with other crystallographic data, the conditions employed at the measurement of diffracted intensities and others characteristics of the refinement. (See Table S1, Supplementary Information for bond distances and angles).

The diffraction data (intensity statistics and systematic absences), as well as the phase determination and structure solution processes, were consistent only with the non-centrosymmetric space group  $P 2_1$ , with two screw-related porphyrin molecules per unit-cell.

<sup>36</sup> Yinghua, W., *J. Appl. Crystallogr.* **1987**, *20*, 258-259.

<sup>37</sup> Sheldrick, G. M., *Acta Crystallogr., Sect. A Found. Crystallogr.* **2008**, *A64*, 112-122.

**Table 1.** Crystal data and structure refinement for [FeTCPP].

|   | [FeTCPP]  |
|---|---|
| Formula   | C <sub>48</sub> H <sub>27</sub> FeN <sub>4</sub> O <sub>8</sub> |
| FW/g mol <sup>-1</sup>                              | 843.59  |
| Crystal system                                      | Monoclinic  |
| Space group   | <i>P</i> 2 <sub>1</sub>   |
| <i>a</i> /Å   | 11.0195(2)  |
| <i>b</i> /Å   | 8.8470(2)   |
| <i>c</i> /Å   | 20.0191(4)  |
| $\beta$ /°  | 102.902(2)  |
| <i>V</i> /Å <sup>3</sup>                            | 1902.38(7)  |
| <i>Z</i> , <i>F</i> (000), <i>T</i> /K              | 2, 866, 100(2)  |
| $\mu$ /mm <sup>-1</sup>                             | 3.728   |
| $\rho_{calc}$ , $\rho_{obs}$ / gr cm <sup>-3</sup>  | 1.473, 1.478(4)   |
| Crystal size/ mm, colour                            | 0.36 x 0.15 x 0.01, dark red                                    |
| Radiation ( $\lambda$ /Å)                           | 1.54178   |
| No. of reflections, Independent reflections         | 20868, 6320   |
| Limiting indices <i>h</i> , <i>k</i> , <i>l</i>     | -13 ≤ <i>h</i> ≤ 13; -9 ≤ <i>k</i> ≤ 10;<br>-23 ≤ <i>l</i> ≤ 23 |
| R <sub>int</sub> , R <sub>σ</sub>                   | 0.0480, 0.0489  |
| R1, wR2(obs) ( <i>I</i> > 2σ( <i>I</i> ))           | R1 = 0.0378, wR2 = 0.0877                                       |
| R1, wR2(all)  | R1 = 0.0475, wR2 = 0.0921                                       |
| GOF <i>S</i>  | 1.026   |
| No. of parameters/restraints                        | 554, 1  |
| Largest diffraction peak and hole/e Å <sup>-3</sup> | 0.281, -0.235   |

#### I.2.4. Computational details

Density functional calculations were carried out by using the GAUSSIAN 03 package<sup>38</sup> and the hybrid density functional B3LYP. The split-valence basis set 6-31G was used for all the calculations.

<sup>38</sup> Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A.; Vreven, J., T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; *et al.*, *GAUSSIAN 03, (Revision D.02)*. Gaussian, Inc., Wallingford CT, 2004.

### I.3. Results and Discussion

Microwave-assisted synthesis was employed for the preparation of a new coordination polymer. Its chemical formula is [FeTCPP], where the oxidation state of iron is 3, and TCPP<sup>3-</sup> is the trivalent anion formed from deprotonation of *meso*-tetra-(4-carboxyphenyl)porphyrin (C<sub>48</sub>H<sub>30</sub>N<sub>4</sub>O<sub>8</sub>). The fact that the original Fe<sup>II</sup> has suffered oxidation to Fe<sup>III</sup> will be discussed latter. The absence of the ligand 4,4'-bipyridine in the structure will be also commented. Structural characterization of [FeTCPP] was carried out by means of IR spectroscopy and X-ray diffraction.

#### I.3.1. Structural characterization

##### I.3.1.1. Infrared spectroscopy

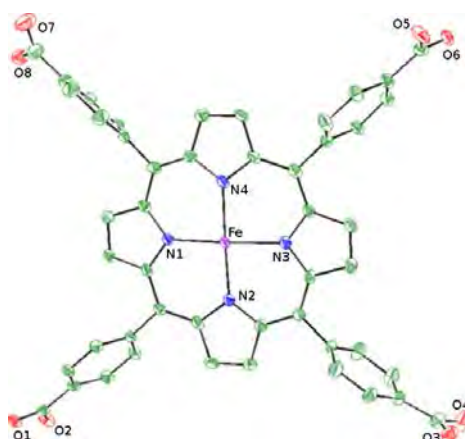
IR data show significant differences between the free ligand TCPP and the metallated [FeTCPP] compound. The N-H bond stretching and bending frequencies of TCPP located at 3200 cm<sup>-1</sup> and 970 cm<sup>-1</sup> disappeared when iron ion was inserted into the porphyrin ring, and a characteristic Fe-N band appears at 1000 cm<sup>-1</sup>, which indicates the formation of an iron porphyrin compound.<sup>39</sup> The bands at about 3415 cm<sup>-1</sup>, 1740 cm<sup>-1</sup> and 1200 cm<sup>-1</sup> were assigned to the O-H, C=O and C-O bonds of the carboxylic groups, respectively. The band at 2940 cm<sup>-1</sup> was assigned to the C-H bond of the benzene and pyrrole rings. The bands at 1690-1540 cm<sup>-1</sup> and 1380 cm<sup>-1</sup> were assigned to C=C stretching mode and the C-N stretching vibration, respectively. A weak band corresponding to the Fe-O bond stretching mode was observed at about 820 cm<sup>-1</sup>. Finally, the band at 790 cm<sup>-1</sup> was assigned to the H out of plane bending of the C-H bond (Figure S1, Supplementary Information).

<sup>39</sup> Sun, Z.-C.; She, Y.-B.; Zhou, Y.; Song, X.-F.; Li, K., *Molecules* **2011**, *16*, 2960-2970.



## I.3.1.2. Crystal structure of [FeTCPP]

The crystal structure of [FeTCPP] consists of tetrapyrrole units containing the Fe atoms as shown in Figure 1. The metal atoms are octahedrally coordinated to four N atoms (N1, N2, N3 and N4) that are coplanar. The axial positions are occupied by two O atoms (O1 and O6) that belong to the carboxylate groups of adjacent porphyrin units. Table 2 summarizes the most significant bond parameters for [FeTCPP]. As observed, the values lie among the typical ones for octahedral iron (III). In fact, the only remarkable feature is that Fe-O6 bond is slightly longer than the others.

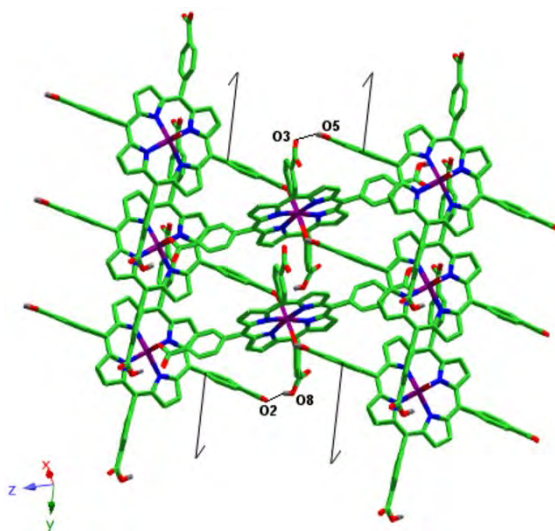


**Figure 1.** ORTEP detail of the equatorial plane for the octahedral coordination sphere in [FeTCPP]. (Fe: purple, C: green, N: blue and O: red).

**Table 2.** Most significant angles ( $^{\circ}$ ) and distances ( $\text{\AA}$ ) for [FeTCPP] (distances in bold).

| Fe        | N1              | N2              | N3              | N4              | O1              | O6              |
|-----------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| <b>O6</b> | 85.44(10)       | 89.98(10)       | 86.91(11)       | 84.09(10)       | 178.34(11)      | <b>2.220(3)</b> |
| <b>O1</b> | 95.62(11)       | 88.74(11)       | 92.03(11)       | 97.18(11)       | <b>1.988(2)</b> |                 |
| <b>N4</b> | 90.15(11)       | 174.07(13)      | 89.35(11)       | <b>2.060(3)</b> |                 |                 |
| <b>N3</b> | 172.34(13)      | 90.17(11)       | <b>2.039(3)</b> |                 |                 |                 |
| <b>N2</b> | 89.54(11)       | <b>2.067(3)</b> |                 |                 |                 |                 |
| <b>N1</b> | <b>2.030(3)</b> |                 |                 |                 |                 |                 |

Taking the structural fragment on Figure 1 as reference, the polymer extends through the formation of four new bonds with adjacent porphyrin groups, involving O1 and O6 atoms. Thus, the reference porphyrin uses its own O1 and O6 atoms to connect with another two porphyrin units. This is, each unit is connected to four equivalent units, and the result is a 2D array (Figure 2).



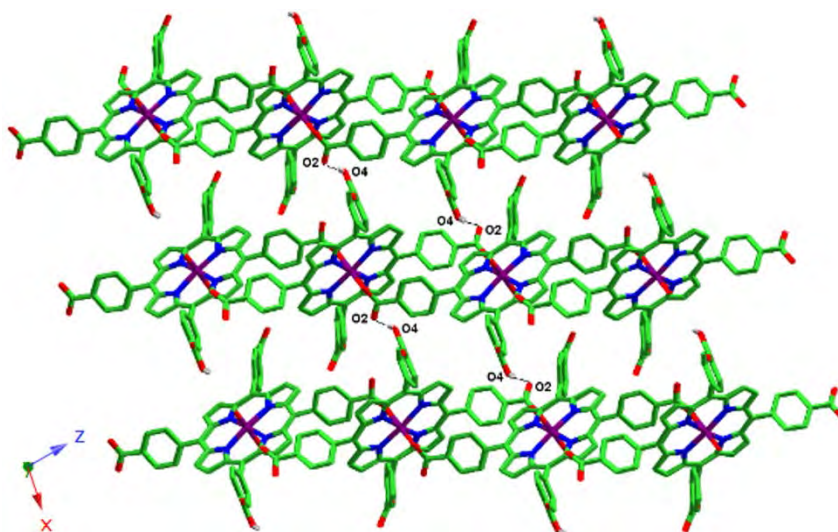
**Figure 2.** View of a layer for [FeTCPP] (Fe: purple, C: green, N: blue, O: red, H: grey). Intralayer hydrogen bonds are marked as black lines. Twofold screw axes are located along the *b*-axis.

This planar array is based on the fact that octahedral spheres are rotated forming planes that are perpendicular to the [10-1] direction, the extension of the structure taking place through coordination bonds. It is worth pointing out that this array is chiral. Additionally, there are several hydrogen bonds (Table 3) between atoms on the same plane, (O5-H50...O3) and (O8-H80...O2), that reinforce the robustness of the 2D moiety.

**Table 3.** Intra- and interlayer hydrogen bond parameters

| O-H        | A(O)                 | O-H (Å) | H...A (Å) | O...A (Å) | O-H...A (°) |
|------------|----------------------|---------|-----------|-----------|-------------|
| O(4)-H(40) | O(2) (2-x,-3/2+y,-z) | 0.84    | 1.78      | 2.614(4)  | 171         |
| O(5)-H(50) | O(3) (2-x,1/2+y,1-z) | 0.84    | 2.00      | 2.718(4)  | 144         |
| O(8)-H(80) | O(2) (1-x,1/2+y,-z)  | 0.84    | 1.91      | 2.740(4)  | 169         |

As shown in Figure 3, packing on the planes along the [10-1] direction gives rise to the 3D framework. These planes are chemically connected through strong hydrogen bonds between O2 and O4 atoms where  $d(\text{O4-H40}\cdots\text{O2})=2.614(4)$  Å. As a consequence of this packing fashion, the 3D framework keeps chirality. Undoubtedly, this is a remarkable fact for [FeTCPP], since this property is not usual for structures based on porphyrin blocks exhibiting  $D_{4h}$  molecular symmetry. Obviously, the fact that the structure extends through both axial sites and two of the equatorial ones is responsible for the later.

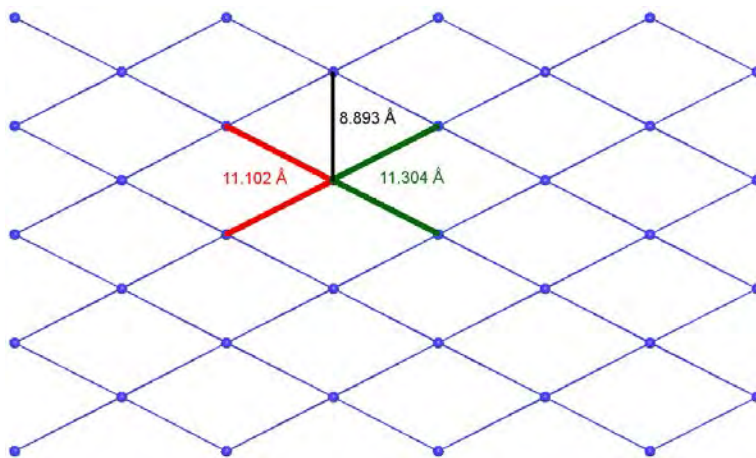


**Figure 3.** [010] projection of the 3D covalent array for [FeTCPP] (Fe: purple, C: green, N: blue, O: red, H: grey). Hydrogen bonds between the layers are marked as black lines.

### 1.3.2. Topological analysis

The topological analysis has been carried out by means of TOPOS software.<sup>40</sup> First of all, the topology of the planes has been determined just considering the node connections taking place through coordination bonds (Figure 4). The result is a uninodal 4-c net (sql/Shubnikov tetragonal plane net  $4^4;6^2$ ). Several examples of compounds exhibiting the same topology can be found in literature.<sup>41-46</sup>

The fact that such a complicated structure extends in that simple fashion is remarkable, as well as the fact that for [FeTCPP] the extension of the structure takes place through two of the four equatorial positions and both axial ones.



**Figure 4.** Topology of the 2D layer.

<sup>40</sup> Blatov, V. A., *IUCr CompComm Newsl.* 7 **2006**, 4-38. <http://www.topos.ssu.samara.ru>.

<sup>41</sup> Xu, Y.; Chen, P.-K.; Che, Y.-X.; Zheng, J.-M., *Eur. J. Inorg. Chem.* **2010**, 5478-5483.

<sup>42</sup> Kanoo, P.; Maji, T. K., *Eur. J. Inorg. Chem.* **2010**, 3762-3769.

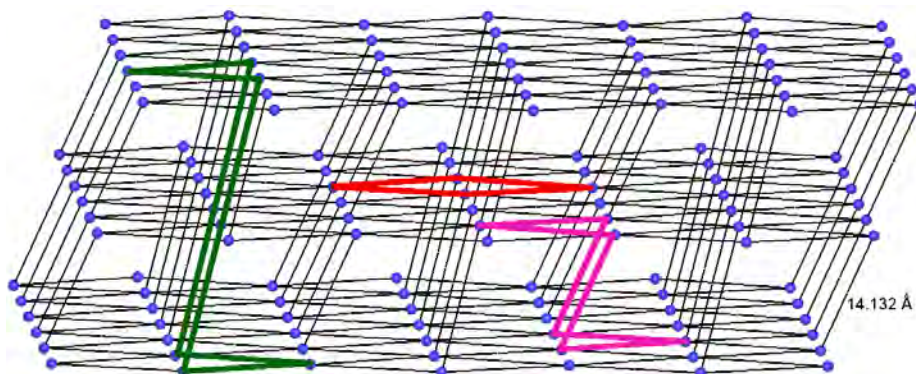
<sup>43</sup> Batten, S. R.; Murray, K. S., *Coord. Chem. Rev.* **2003**, 246, 103-130.

<sup>44</sup> Li, F.; Luo, S.; Li, X.; Li, T., *Inorg. Chem. Commun.* **2010**, 13, 656-658.

<sup>45</sup> Sokolov, M. N.; Peresyphkina, E. V.; Kalinina, I. V.; Virovets, A. V.; Korenev, V. S.; Fedin, V. P., *Eur. J. Inorg. Chem.* **2010**, 5446-5454.

<sup>46</sup> Fernandez de Luis, R.; Urriaga, M. K.; Mesa, J. L.; Aguayo, A. T.; Rojo, T.; Arriortua, M. I., *CrystEngComm* **2010**, 12, 1880-1886.

If considering now the extension of the structure in the third dimension of the space, the topology shown in Figure 5 includes connections between hydrogen bonds that take place for Fe atoms at a distance of 14.132 Å. The resulting uninodal net is 6-c type (mab 4<sup>4</sup>;6<sup>10</sup>;8). This net has been reported for just one compound.<sup>47</sup>



**Figure 5.** Topology of the 3D net. Four-, six-, and eight-member circuits are shown in red, pink and green, respectively.

It is worth mentioning that there is a shorter interlayer distance between iron atoms at 11.092 Å, but these atoms remain unconnected. Additionally, if considering the intralayer connections through hydrogen bonds, the net connectivity increases since there are two more links for each iron node at 8.893 Å. The resulting uninodal net is 8-c (3<sup>6</sup>;4<sup>10</sup>;5<sup>11</sup>;6), and no examples have been found in literature illustrating this new topology.

### 1.3.3. Stability of the metallated TCPP

The stability of the metallated monomers cannot be separated from two facts: the oxidation of the iron ions, and the pH variation along the synthesis.

<sup>47</sup> Braverman, M. A.; LaDuca, R. L., *CrystEngComm* **2008**, *10*, 117-124.

The oxidation state of iron atoms in [FeTCPP] was corroborated by using the PLATON<sup>48</sup> software (Brown method).<sup>49,50</sup> A calculated value of 2.954 was obtained that is in accordance with the presence of Fe<sup>III</sup> ions (Table S2, Supplementary Information). However, Fe<sup>II</sup> was used for the synthesis, indicating that the metal ions have suffered oxidization.

Additionally, an asymmetric location of hydrogen atoms is observed for porphyrin in [FeTCPP]. This is, both hydrogen atoms in pyrrole groups have been removed, as well as one of the four hydrogen atoms on the carboxylates. This is a striking location that results in the TCPP<sup>-3</sup> anion. In order to understand this process, the charges on the electronegative atoms in isolated porphyrin were calculated by means of the Hückel method. The results indicate that, as expected, the most acid hydrogen atoms are those located on the carboxylate groups. In fact, values close to -0.70 and -0.15 have been calculated for the O atoms on -CO and -OH groups, respectively. On the other hand, iminic N atoms exhibit negative charges (-0.41 for N2 and -0.41 for N4), and pyrrolic ones positive values (+0.39 for N1 and +0.38 for N3). Nevertheless, in [FeTCPP] the ligand keeps three of the four most acid hydrogen atoms.

In order to understand these two facts, HF energies were calculated. The selected structural unit consists of a [FeTCPP]<sup>n</sup> monomer, where n is the charge that depends on the oxidation state of the metal ion and the charge of TCPP. Obviously, at high pH values, TCPP is completely deprotonated (TCPP<sup>-6</sup>). The as-done DFT calculations (B3LYP / 6-31G) were carried out by using the GAUSSIAN 03 software.<sup>38</sup> The results (Table 4) suggest that the oxidation takes place at basic pH,

<sup>48</sup> Spek, A. L. *PLATON, A Multipurpose Crystallographic Tool*, Utrech University, Utrecht, The Netherlands, 1998.

<sup>49</sup> Brese, N. E.; O'Keeffe, M., *Acta Crystallogr., Sect. B Struct. Sci.* **1991**, B47, 192-197.

<sup>50</sup> Brown, I. D.; Altermatt, D., *Acta Crystallogr., Sect. B Struct. Sci.* **1985**, B41, 244-247.

when TCPP is completely deprotonated. Then, as pH goes to neutral values, the porphyrin recovers three of the acid protons that get located on the carboxylates. Additionally, the fact that  $[\text{FeTCPP}]^{-1}$  (with  $\text{Fe}^{\text{II}}$ ) is more stable than  $[\text{FeTCPP}]$  (with  $\text{Fe}^{\text{III}}$ ) also indicates that the  $\text{Fe}^{\text{III}}$ -monomers should not exist at neutral pH values. In other words, the  $[\text{FeTCPP}]^n$  unit with  $\text{Fe}^{\text{III}}$  becomes neutral at a higher pH value than the unit with  $\text{Fe}^{\text{II}}$ , provoking the precipitation of the final product with  $\text{Fe}^{\text{III}}$ . The later is in complete agreement with the Pearson theory. Therefore, if admitting that the presence of  $\text{Fe}^{\text{III}}$  accounts for the polymerization of the monomers via carboxylate groups, it is easy to understand that 4,4'-bipyridine is not a component of the final product.

**Table 4.** Energy values (Hartree) for the selected structural units.

| Metal ion                | Ligand             | Monomer                | HF energy     |
|--------------------------|--------------------|------------------------|---------------|
| $\text{Fe}^{\text{II}}$  | TCPP <sup>-3</sup> | $[\text{FeTCPP}]^{-1}$ | -3928.5387399 |
| $\text{Fe}^{\text{III}}$ | TCPP <sup>-3</sup> | $[\text{FeTCPP}]$      | -3928.4125033 |
| $\text{Fe}^{\text{II}}$  | TCPP <sup>-6</sup> | $[\text{FeTCPP}]^{-4}$ | -3926.7601369 |
| $\text{Fe}^{\text{III}}$ | TCPP <sup>-6</sup> | $[\text{FeTCPP}]^{-3}$ | -3926.8414566 |

Finally, it must be pointed out that this is the third example<sup>51,52</sup> of a 2D coordination compound based on TCPP in which the dimensionality refers just to coordination bonds, and no other ligands are present in the structure.

#### I.4. Conclusions

A new Fe-TCPP coordination polymer has been prepared in which 2D arrays are formed via coordination bonds. The stabilization of the metallated monomers at a

<sup>51</sup> Shmilovits, M.; Vinodu, M.; Goldberg, I., *New J. Chem.* **2004**, 28, 223-227.

<sup>52</sup> George, S.; Lipstman, S.; Muniappan, S.; Goldberg, I., *CrystEngComm* **2006**, 8, 417-424.

basic pH value accounts for the oxidation of Fe<sup>II</sup> to Fe<sup>III</sup>, and explains the polymerization of the monomers via carboxylate groups. As a result, a rare framework has been obtained in which the 2D topology follows a very simple extension fashion. The three-dimensionality is raised via hydrogen bonds that keep the chirality found for the 2D coordination array. This is the third example of a 2D coordination compound based on TCPP in which the dimensionality refers just to coordination bonds, and no other ligands are present in the structure.



## Supplementary Information

Table S1. Selected bond length (Å) and angles (°) for FeTCPP

| Distances                 |          |             |          |
|---------------------------|----------|-------------|----------|
| Fe(1)-O(1) <sup>i</sup>   | 1.988(2) | C(16)-C(17) | 1.434(5) |
| Fe(1)-N(1)                | 2.030(3) | C(17)-C(18) | 1.346(5) |
| Fe(1)-N(3)                | 2.039(3) | C(17)-H(17) | 0.9500   |
| Fe(1)-N(4)                | 2.060(3) | C(18)-C(19) | 1.441(5) |
| Fe(1)-N(2)                | 2.067(3) | C(18)-H(18) | 0.9500   |
| Fe(1)-O(6) <sup>ii</sup>  | 2.220(3) | C(19)-C(20) | 1.389(5) |
| N(1)-C(1)                 | 1.381(4) | C(20)-C(42) | 1.499(5) |
| N(1)-C(4)                 | 1.382(4) | C(21)-C(22) | 1.397(4) |
| N(2)-C(9)                 | 1.374(5) | C(21)-C(26) | 1.407(5) |
| N(2)-C(6)                 | 1.381(4) | C(22)-C(23) | 1.381(5) |
| N(3)-C(14)                | 1.370(4) | C(22)-H(22) | 0.9500   |
| N(3)-C(11)                | 1.380(4) | C(23)-C(24) | 1.387(5) |
| N(4)-C(16)                | 1.370(4) | C(23)-H(23) | 0.9500   |
| N(4)-C(19)                | 1.383(5) | C(24)-C(25) | 1.399(5) |
| O(1)-C(27)                | 1.273(4) | C(24)-C(27) | 1.496(5) |
| O(1)-Fe(1) <sup>iii</sup> | 1.988(2) | C(25)-C(26) | 1.386(5) |
| O(2)-C(27)                | 1.258(4) | C(25)-H(25) | 0.9500   |
| O(3)-C(34)                | 1.234(5) | C(26)-H(26) | 0.9500   |
| O(4)-C(34)                | 1.315(4) | C(28)-C(33) | 1.383(5) |
| O(4)-H(40)                | 0.8400   | C(28)-C(29) | 1.388(5) |
| O(5)-C(41)                | 1.313(4) | C(29)-C(30) | 1.386(5) |
| O(5)-H(50)                | 0.8400   | C(29)-H(29) | 0.9500   |
| O(6)-C(41)                | 1.232(4) | C(30)-C(31) | 1.395(5) |
| O(6)-Fe(1) <sup>iv</sup>  | 2.220(3) | C(30)-H(30) | 0.9500   |
| O(7)-C(48)                | 1.213(4) | C(31)-C(32) | 1.384(5) |
| O(8)-C(48)                | 1.340(5) | C(31)-C(34) | 1.489(5) |
| O(8)-H(80)                | 0.8400   | C(32)-C(33) | 1.393(5) |

|             |          |             |          |
|-------------|----------|-------------|----------|
| C(1)-C(20)  | 1.406(5) | C(32)-H(32) | 0.9500   |
| C(1)-C(2)   | 1.439(5) | C(33)-H(33) | 0.9500   |
| C(2)-C(3)   | 1.341(5) | C(35)-C(40) | 1.381(5) |
| C(2)-H(2)   | 0.9500   | C(35)-C(36) | 1.394(5) |
| C(3)-C(4)   | 1.440(5) | C(36)-C(37) | 1.376(5) |
| C(3)-H(3)   | 0.9500   | C(36)-H(36) | 0.9500   |
| C(4)-C(5)   | 1.400(5) | C(37)-C(38) | 1.386(4) |
| C(5)-C(6)   | 1.397(5) | C(37)-H(37) | 0.9500   |
| C(5)-C(21)  | 1.482(4) | C(38)-C(39) | 1.401(5) |
| C(6)-C(7)   | 1.444(5) | C(38)-C(41) | 1.483(5) |
| C(7)-C(8)   | 1.354(5) | C(39)-C(40) | 1.389(5) |
| C(7)-H(7)   | 0.9500   | C(39)-H(39) | 0.9500   |
| C(8)-C(9)   | 1.435(5) | C(40)-H(40) | 0.9500   |
| C(8)-H(8)   | 0.9500   | C(42)-C(47) | 1.392(5) |
| C(9)-C(10)  | 1.411(5) | C(42)-C(43) | 1.394(5) |
| C(10)-C(11) | 1.389(5) | C(43)-C(44) | 1.392(5) |
| C(10)-C(28) | 1.498(5) | C(43)-H(43) | 0.9500   |
| C(11)-C(12) | 1.447(5) | C(44)-C(45) | 1.396(6) |
| C(12)-C(13) | 1.345(5) | C(44)-H(44) | 0.9500   |
| C(12)-H(12) | 0.9500   | C(45)-C(46) | 1.380(5) |
| C(13)-C(14) | 1.438(5) | C(45)-C(48) | 1.501(5) |
| C(13)-H(13) | 0.9500   | C(46)-C(47) | 1.377(5) |
| C(14)-C(15) | 1.398(5) | C(46)-H(46) | 0.9500   |
| C(15)-C(16) | 1.407(5) | C(47)-H(47) | 0.9500   |
| C(15)-C(35) | 1.501(5) |             |          |

**Angles**

|                               |            |                   |          |
|-------------------------------|------------|-------------------|----------|
| O(1) <sup>i</sup> -Fe(1)-N(1) | 95.62(11)  | C(20)-C(19)-C(18) | 125.2(3) |
| O(1) <sup>i</sup> -Fe(1)-N(3) | 92.03(11)  | C(19)-C(20)-C(1)  | 125.6(3) |
| N(1)-Fe(1)-N(3)               | 172.34(13) | C(19)-C(20)-C(42) | 118.8(3) |
| O(1) <sup>i</sup> -Fe(1)-N(4) | 97.18(11)  | C(1)-C(20)-C(42)  | 115.5(3) |
| N(1)-Fe(1)-N(4)               | 90.15(11)  | C(22)-C(21)-C(26) | 118.6(3) |

|   |            |                   |          |
|---|------------|-------------------|----------|
| N(3)-Fe(1)-N(4)                             | 89.35(11)  | C(22)-C(21)-C(5)  | 119.5(3) |
| O(1) <sup>i</sup> -Fe(1)-N(2)               | 88.74(11)  | C(26)-C(21)-C(5)  | 121.8(3) |
| N(1)-Fe(1)-N(2)                             | 89.54(11)  | C(23)-C(22)-C(21) | 120.5(3) |
| N(3)-Fe(1)-N(2)                             | 90.17(11)  | C(23)-C(22)-H(22) | 119.8    |
| N(4)-Fe(1)-N(2)                             | 174.07(13) | C(21)-C(22)-H(22) | 119.8    |
| O(1) <sup>i</sup> -Fe(1)-O(6) <sup>ii</sup> | 178.34(11) | C(22)-C(23)-C(24) | 120.5(3) |
| N(1)-Fe(1)-O(6) <sup>ii</sup>               | 85.44(10)  | C(22)-C(23)-H(23) | 119.7    |
| N(3)-Fe(1)-O(6) <sup>ii</sup>               | 86.91(11)  | C(24)-C(23)-H(23) | 119.7    |
| N(4)-Fe(1)-O(6) <sup>ii</sup>               | 84.09(10)  | C(23)-C(24)-C(25) | 120.0(3) |
| N(2)-Fe(1)-O(6) <sup>ii</sup>               | 89.98(10)  | C(23)-C(24)-C(27) | 119.8(3) |
| C(1)-N(1)-C(4)                              | 106.9(3)   | C(25)-C(24)-C(27) | 120.2(3) |
| C(1)-N(1)-Fe(1)                             | 126.7(2)   | C(26)-C(25)-C(24) | 119.4(3) |
| C(4)-N(1)-Fe(1)                             | 126.3(2)   | C(26)-C(25)-H(25) | 120.3    |
| C(9)-N(2)-C(6)                              | 106.3(3)   | C(24)-C(25)-H(25) | 120.3    |
| C(9)-N(2)-Fe(1)                             | 125.9(2)   | C(25)-C(26)-C(21) | 120.9(3) |
| C(6)-N(2)-Fe(1)                             | 126.4(2)   | C(25)-C(26)-H(26) | 119.5    |
| C(14)-N(3)-C(11)                            | 107.2(3)   | C(21)-C(26)-H(26) | 119.5    |
| C(14)-N(3)-Fe(1)                            | 127.1(2)   | O(2)-C(27)-O(1)   | 123.3(3) |
| C(11)-N(3)-Fe(1)                            | 125.3(2)   | O(2)-C(27)-C(24)  | 120.0(3) |
| C(16)-N(4)-C(19)                            | 106.5(3)   | O(1)-C(27)-C(24)  | 116.7(3) |
| C(16)-N(4)-Fe(1)                            | 127.3(2)   | C(33)-C(28)-C(29) | 119.5(3) |
| C(19)-N(4)-Fe(1)                            | 126.0(2)   | C(33)-C(28)-C(10) | 121.2(3) |
| C(27)-O(1)-Fe(1) <sup>iii</sup>             | 130.9(2)   | C(29)-C(28)-C(10) | 119.0(3) |
| C(34)-O(4)-H(4O)                            | 109.5      | C(30)-C(29)-C(28) | 121.2(3) |
| C(41)-O(5)-H(5O)                            | 109.5      | C(30)-C(29)-H(29) | 119.4    |
| C(41)-O(6)-Fe(1) <sup>iv</sup>              | 131.6(3)   | C(28)-C(29)-H(29) | 119.4    |
| C(48)-O(8)-H(8O)                            | 109.5      | C(29)-C(30)-C(31) | 119.1(4) |
| N(1)-C(1)-C(20)                             | 125.6(3)   | C(29)-C(30)-H(30) | 120.4    |
| N(1)-C(1)-C(2)                              | 109.0(3)   | C(31)-C(30)-H(30) | 120.4    |
| C(20)-C(1)-C(2)                             | 125.4(3)   | C(32)-C(31)-C(30) | 119.7(4) |
| C(3)-C(2)-C(1)                              | 107.5(3)   | C(32)-C(31)-C(34) | 121.7(3) |

|                   |          |                   |          |
|-------------------|----------|-------------------|----------|
| C(3)-C(2)-H(2)    | 126.3    | C(30)-C(31)-C(34) | 118.1(4) |
| C(1)-C(2)-H(2)    | 126.3    | C(31)-C(32)-C(33) | 120.7(3) |
| C(2)-C(3)-C(4)    | 108.1(3) | C(31)-C(32)-H(32) | 119.6    |
| C(2)-C(3)-H(3)    | 126.0    | C(33)-C(32)-H(32) | 119.6    |
| C(4)-C(3)-H(3)    | 126.0    | C(28)-C(33)-C(32) | 119.7(3) |
| N(1)-C(4)-C(5)    | 126.8(3) | C(28)-C(33)-H(33) | 120.2    |
| N(1)-C(4)-C(3)    | 108.5(3) | C(32)-C(33)-H(33) | 120.2    |
| C(5)-C(4)-C(3)    | 124.7(3) | O(3)-C(34)-O(4)   | 123.0(3) |
| C(6)-C(5)-C(4)    | 124.9(3) | O(3)-C(34)-C(31)  | 122.8(3) |
| C(6)-C(5)-C(21)   | 118.7(3) | O(4)-C(34)-C(31)  | 113.9(3) |
| C(4)-C(5)-C(21)   | 116.4(3) | C(40)-C(35)-C(36) | 119.4(3) |
| N(2)-C(6)-C(5)    | 125.1(3) | C(40)-C(35)-C(15) | 120.5(3) |
| N(2)-C(6)-C(7)    | 109.2(3) | C(36)-C(35)-C(15) | 120.1(3) |
| C(5)-C(6)-C(7)    | 125.7(3) | C(37)-C(36)-C(35) | 120.6(3) |
| C(8)-C(7)-C(6)    | 107.4(3) | C(37)-C(36)-H(36) | 119.7    |
| C(8)-C(7)-H(7)    | 126.3    | C(35)-C(36)-H(36) | 119.7    |
| C(6)-C(7)-H(7)    | 126.3    | C(36)-C(37)-C(38) | 120.4(3) |
| C(7)-C(8)-C(9)    | 107.0(3) | C(36)-C(37)-H(37) | 119.8    |
| C(7)-C(8)-H(8)    | 126.5    | C(38)-C(37)-H(37) | 119.8    |
| C(9)-C(8)-H(8)    | 126.5    | C(37)-C(38)-C(39) | 119.4(3) |
| N(2)-C(9)-C(10)   | 124.8(3) | C(37)-C(38)-C(41) | 122.1(3) |
| N(2)-C(9)-C(8)    | 110.1(3) | C(39)-C(38)-C(41) | 118.4(3) |
| C(10)-C(9)-C(8)   | 125.0(3) | C(40)-C(39)-C(38) | 119.7(3) |
| C(11)-C(10)-C(9)  | 125.8(3) | C(40)-C(39)-H(39) | 120.1    |
| C(11)-C(10)-C(28) | 115.7(3) | C(38)-C(39)-H(39) | 120.1    |
| C(9)-C(10)-C(28)  | 118.5(3) | C(35)-C(40)-C(39) | 120.5(3) |
| N(3)-C(11)-C(10)  | 126.7(3) | C(35)-C(40)-H(40) | 119.8    |
| N(3)-C(11)-C(12)  | 108.6(3) | C(39)-C(40)-H(40) | 119.8    |
| C(10)-C(11)-C(12) | 124.7(3) | O(6)-C(41)-O(5)   | 123.5(3) |
| C(13)-C(12)-C(11) | 107.3(3) | O(6)-C(41)-C(38)  | 122.7(3) |
| C(13)-C(12)-H(12) | 126.4    | O(5)-C(41)-C(38)  | 113.9(3) |

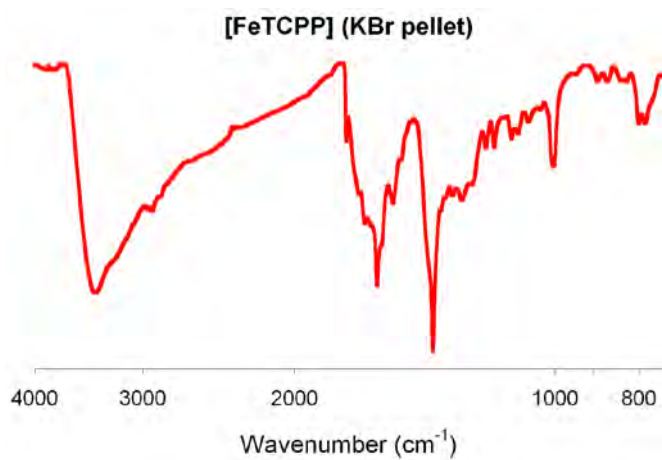
|                   |          |                   |          |
|-------------------|----------|-------------------|----------|
| C(11)-C(12)-H(12) | 126.4    | C(47)-C(42)-C(43) | 119.4(3) |
| C(12)-C(13)-C(14) | 107.8(3) | C(47)-C(42)-C(20) | 119.5(3) |
| C(12)-C(13)-H(13) | 126.1    | C(43)-C(42)-C(20) | 121.1(3) |
| C(14)-C(13)-H(13) | 126.1    | C(44)-C(43)-C(42) | 119.7(4) |
| N(3)-C(14)-C(15)  | 125.9(3) | C(44)-C(43)-H(43) | 120.2    |
| N(3)-C(14)-C(13)  | 109.1(3) | C(42)-C(43)-H(43) | 120.2    |
| C(15)-C(14)-C(13) | 124.9(3) | C(43)-C(44)-C(45) | 120.2(3) |
| C(14)-C(15)-C(16) | 125.5(3) | C(43)-C(44)-H(44) | 119.9    |
| C(14)-C(15)-C(35) | 116.9(3) | C(45)-C(44)-H(44) | 119.9    |
| C(16)-C(15)-C(35) | 117.6(3) | C(46)-C(45)-C(44) | 119.5(4) |
| N(4)-C(16)-C(15)  | 124.8(3) | C(46)-C(45)-C(48) | 120.4(4) |
| N(4)-C(16)-C(17)  | 110.0(3) | C(44)-C(45)-C(48) | 120.0(3) |
| C(15)-C(16)-C(17) | 125.2(3) | C(47)-C(46)-C(45) | 120.5(4) |
| C(18)-C(17)-C(16) | 107.0(3) | C(47)-C(46)-H(46) | 119.7    |
| C(18)-C(17)-H(17) | 126.5    | C(45)-C(46)-H(46) | 119.7    |
| C(16)-C(17)-H(17) | 126.5    | C(46)-C(47)-C(42) | 120.6(3) |
| C(17)-C(18)-C(19) | 107.8(3) | C(46)-C(47)-H(47) | 119.7    |
| C(17)-C(18)-H(18) | 126.1    | C(42)-C(47)-H(47) | 119.7    |
| C(19)-C(18)-H(18) | 126.1    | O(7)-C(48)-O(8)   | 120.8(4) |
| N(4)-C(19)-C(20)  | 125.9(3) | O(7)-C(48)-C(45)  | 122.4(4) |
| N(4)-C(19)-C(18)  | 108.7(3) | O(8)-C(48)-C(45)  | 116.8(3) |

Symmetry transformations used to generate equivalent atoms:

- i)  $-x+1, y-1/2, -z$ ; ii)  $-x+2, y+1/2, -z+1$ ; iii)  $-x+1, y+1/2, -z$ ; iv)  $-x+2, y-1/2, -z+1$

**Table S2.** Bond valence analysis for the octahedra [FeN<sub>4</sub>O<sub>2</sub>].

| Fe   | r      | r <sub>0</sub> | B    | s            |
|------|--------|----------------|------|--------------|
| O(1) | 1.9880 | 1.759          | 0.37 | 0.538        |
| N(1) | 2.0299 | 1.815          | 0.37 | 0.559        |
| N(3) | 2.0385 | 1.815          | 0.37 | 0.547        |
| N(4) | 2.0599 | 1.815          | 0.37 | 0.516        |
| N(2) | 2.0671 | 1.815          | 0.37 | 0.506        |
| O(6) | 2.2195 | 1.759          | 0.37 | 0.288        |
|      |        |                |      | <b>2.954</b> |

**Figure S1.** IR spectra for [FeTCPP].



## CAPÍTULO II

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### Compuesto ([FeTPPbipy]<sub>n</sub>)

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*“Fe-TPP Coordination Network with Metalloporphyrinic Neutral Radicals and Face-to-Face and Edge-to-Face  $\pi$ - $\pi$  Stacking”*

*Inorg. Chem. 2013, 52 (14), 8074-8081*

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**Resumen**

El compuesto  $[\text{FeTPPbipy}]^{\cdot-}_n$  (TPP=meso-tetrafenilporfirina, y bipy= 4,4'-bipiridina) es el primer ejemplo de una red de coordinación formada por Fe-TPP-bipy y consiste en polímeros 1D estabilizados por interacciones  $\pi$ - $\pi$  de tipo face-to-face y edge-to-face. Éste se ha estudiado mediante difracción de rayos X, espectroscopias IR, Mössbauer, UV-Vis y EPR, termogravimetría, susceptibilidad magnética y cálculos mecano-cuánticos de tipo DFT y TD-DFT. La fórmula del compuesto puede resultar confusa, ya que es compatible con iones  $\text{Fe}^{\text{II}}$  y  $\text{TPP}^{2-}$ . Sin embargo, las propiedades espectroscópicas y magnéticas de este compuesto son consistentes únicamente con la presencia de iones  $\text{Fe}^{\text{III}}$  de bajo espín y radicales neutros  $[\text{FeTPPbipy}]^{\cdot-}$ . Estos radicales se forman por la reducción de la metaloporfirina y los cálculos mecano-cuánticos son consistentes con el hecho de que el electrón captado se localice en los grupos fenilos de la TPP.

**Abstract**

*Compound  $([FeTPPbipy]^*)_n$  (TPP=meso-tetraphenylporphyrin, and bipy=4,4'-bipyridine) is the first example of Fe-TPP-bipy coordination network, and it consists of 1D polymers packed through face-to-face and edge-to-face  $\pi$ - $\pi$  interactions. The compound has been investigated by means of X-ray diffraction, IR, Mössbauer, UV-vis and EPR spectroscopies, thermogravimetry, magnetic susceptibility measurements, and quantum mechanical DFT and TD-DFT calculations. The chemical formula for this compound can be confusing as it is compatible with  $Fe^{II}$  and  $TPP^2$  anions. However, the spectroscopic and magnetic properties of this compound are consistent with the presence of low-spin  $Fe^{III}$  ions and  $[FeTPPbipy]^*$  neutral radicals. These radicals are proposed to be formed by reduction of metalloporphyrin, and the quantum mechanical calculations are consistent with the fact that the acquired electrons are located on phenyl groups of TPP.*

## Laburpena

$([FeTPPbipy]^*)_n$  (TPP=meso-tetrafenil porfirina eta bipy=4,4'bipiridina) konposatua Fe-TPP-bipy konbinaketan oinarritutako koordinazio-sare baten lehenengo adibidea da. Honetan face-to-face eta edge-to-face motatako  $\pi$ - $\pi$  elkarrekintzei esker paketatzen diren dimentsio bakarreko polimeroak daude. Konposatua aztertu da ondoko tekniken bidez: X izpien bidezko difrakzioa, hainbat espektroskopia (infragorri, Mössbauer, ultramore-ikusgai eta erresonantzia paramagnetiko elektronikoa), termograbitmetria, suszeptibilitate magnetiko eta DFT eta TD-DFT motako kalkulu mekano-kuantikoak. Konposatu honen formula kimikoa nahasgarria izan daiteke. Izan ere,  $Fe^{II}$  eta  $TPP^2$  espezieekin bateragarria bada ere, konposatu honen propietate espektroskopiko zein magnetikoek adierazten dute espina baxuko  $Fe^{III}$  ioiak eta  $[FeTPPbipy]^*$  erradikal neutroak daudela. Erradikal hauek metaloporfirinaren erredukzioaren ondorioz eratu dira, eta burututako kalkulu mekano-kuantikoek azaltzen dute bereganatutako elektroiak TPP-aren fenil taldeetan kokatuta daudela.

## II.1. Introduction

Metalloporphyrins are one of the cornerstones on which the existence of life is based, as major biochemical, enzymatic and photochemical functions depend on the special properties of the tetrapyrrolic macrocycle.<sup>1</sup> Thus, porphyrin catalysts are well-known to be highly efficient for oxidative reactions,<sup>2</sup> and during the last years a great effort has been devoted to the immobilization of distinct types of catalysts on solid surfaces,<sup>3-5</sup> porphyrins having been also investigated in this field.<sup>6-16</sup> Thus, these compounds can also be used for coordination networks where the assembly of metalloporphyrinic structural units can be achieved by coordination bonds and other

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weaker cohesion forces.<sup>17,18</sup> There are many examples of metalloporphyrinic 3D frameworks, but most of them consist of the crystallization of monomeric complexes, the cohesion forces being hydrogen bonds and  $\pi$ -stacking. In fact, if thinking of high dimensionality in terms of the formation of coordination polymers, metalloporphyrins exhibit important limitations. To illustrate this point, the case of TPP porphyrin can be cited (TPP=*meso*-tetraphenylporphyrin). A CSD research indicates the existence of monomers, dimers, trimers, and other types of aggregates. However, the highest dimensionality achieved with pyridil ligands connected on axial positions for octahedral specimens corresponds to 1D coordination polymers, and just seven of them have been prepared so far.<sup>19-24</sup> It is also worth mentioning that none of them has iron as metal center. In fact, as we are aware, the highest dimensionality found for Fe-TPP-dipyridyl systems consists of dimers. However, it must be pointed out that there are two previous examples in literature for 1D Fe-TPP polymers with cyanide-based ligands.<sup>25,26</sup>

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The work herein presented was inspired by previously reported metalloporphyrinic frameworks exhibiting bipyridyl ligands.<sup>27-34</sup> Our intention was the synthesis of high-dimensional frameworks in which metalloporphyrins play two roles: as building blocks in porous networks, and as catalysts immobilized in the pores. We still have not achieved this goal but instead we have synthesized and characterized the compound  $([\text{FeTPPbipy}]^+)_n$ , where bipy is 4,4'-bipyridine. The compound exhibits 1D coordination polymers that crystallize in a 3D framework in which both *face-to-face* and *edge-to-face*  $\pi$ -stacking of phenyl groups provide stability to the lattice. The main interest of this compound lies on the fact that it is the first Fe-TPP-bipy compound characterized so far. Additionally, the special characteristics of this compound have produced an intricate discussion based on an exhaustive characterization (X-ray diffraction, IR, Mössbauer, UV-vis and EPR spectroscopies, thermogravimetry, magnetic susceptibility measurements, and quantum mechanical DFT and TD-DFT calculations).

<sup>27</sup> Calderon-Casado, A.; Barandika, G.; Bazan, B.; Urtiaga, M. K.; Vallcorba, O.; Rius, J.; Miravittles, C.; Arriortua, M.-I., *CrystEngComm* **2011**, *13*, 6831-6838.

<sup>28</sup> Barandika, M. G.; Hernandez-Pino, M. L.; Urtiaga, M. K.; Cortes, R.; Lezama, L.; Arriortua, M. I.; Rojo, T., *J. Chem. Soc., Dalton Trans.* **2000**, 1469-1473.

<sup>29</sup> Barandika, M. G.; Cortes, R.; Serna, Z.; Lezama, L.; Rojo, T.; Urtiaga, M. K.; Arriortua, M. I., *Chem. Commun.* **2001**, 45-46.

<sup>30</sup> de la Pinta, N.; Martin, S.; Urtiaga, M. K.; Barandika, M. G.; Arriortua, M. I.; Lezama, L.; Madariaga, G.; Cortes, R., *Inorg. Chem.* **2010**, *49*, 10445-10454.

<sup>31</sup> Hernandez, M. L.; Urtiaga, M. K.; Barandika, M. G.; Cortes, R.; Lezama, L.; de la Pinta, N.; Arriortua, M. I.; Rojo, T., *J. Chem. Soc., Dalton Trans.* **2001**, 3010-3014.

<sup>32</sup> Serna, Z. F.; Lezama, L.; Urtiaga, M. K.; Arriortua, M. I.; Barandika, M. G.; Cortes, R.; Rojo, T., *Angew. Chem., Int. Ed.* **2000**, *39*, 344-347.

<sup>33</sup> Fidalgo-Marijuan, A.; Barandika, G.; Bazan, B.; Urtiaga, M. K.; Arriortua, M. I., *Polyhedron* **2011**, *30*, 2711-2716.

<sup>34</sup> DeVries, L. D.; Choe, W., *J. Chem. Crystallogr.* **2009**, *39*, 229-240.

## II.2. Experimental Section

### II.2.1. Materials

All solvents and chemicals were used as received from reliable commercial sources. The reagents 5,10,15,20-tetraphenyl-porphine iron(III) chloride (FeTPP-Cl) and 4,4'-bipyridine 98% and the solvent *N,N*-dimethylformamide (DMF) 99.8% were purchased from Sigma-Aldrich Co.; ethanol absolute was purchased from Panreac.

### II.2.2. Physicochemical characterization techniques

The IR spectrum was collected on a JASCO FT/IR-6100 spectrometer at room temperature at the range of 4000 to 400  $\text{cm}^{-1}$ , in KBr pellets (1% of the sample). C, H and N elemental analyses were measured using a Euro EA 3000 elemental analyzer. UV-visible Diffuse-reflectance measurements were carried out on a Cary 5000 UV-Vis-NIR spectrophotometer in the range of 2500 to 200 nm. Thermogravimetric analyses were carried out using a NETZSCH STA 449F3 thermobalance. A crucible containing 10 mg of sample was heated at 5  $^{\circ}\text{C min}^{-1}$  in the temperature range of 30-500  $^{\circ}\text{C}$ . Mössbauer spectra were obtained at room temperature using a constant acceleration Mössbauer spectrometer with a  $^{57}\text{Co/Rh}$  source. Velocity calibration was done using a metallic Fe foil. Electron paramagnetic resonance (EPR) spectra were measured with a Bruker ESP-300 spectrometer operating at X band and equipped with a nitrogen and helium cryostat. Magnetic susceptibility measurements were measured in the range of 4-300 K with a MPMS-7T, Quantum Design SQUID magnetometer.

### II.2.3. X-ray structure determinations

Prismatic dark blue single-crystal of  $([\text{FeTPPbipy}]^+)_n$  with dimensions given in Table 1 was selected under polarizing microscope and mounted on MicroMounts. Single-crystal X-ray diffraction data was collected at 100 K on an Xcalibur 2 automatic diffractometer with graphite-monochromated Mo- $\text{K}\alpha$  radiation ( $\lambda=0.71073 \text{ \AA}$ ). The



Lorentz-polarization and absorption corrections were made with the diffractometer software, taking into account the size and shape of the crystals.<sup>35</sup> The structure was solved in the monoclinic  $C2/c$  space group by direct methods with SHELXS-97 program.<sup>36</sup> The refinement of the crystal structure was performed by full matrix least-squares based on  $F^2$ , using the SHELXL-97 program.<sup>36</sup> Anisotropic thermal parameters were used for all non-hydrogen atoms (Figure S1, Supplementary Information). All the hydrogen atoms, connected to the aromatic rings (C-H 0.95 Å) were fixed geometrically and were refined using a riding model with common isotropic displacements. Brief crystal data is listed in Table 1. (See Tables S1-S4, Supplementary Information, for bond distances and angles, atomic coordinates, and anisotropic displacement).

<sup>35</sup> Yinghua, W., *J. Appl. Crystallogr.* **1987**, *20*, 258-259.

<sup>36</sup> Sheldrick, G. M., *Acta Crystallogr., Sect. A Found. Crystallogr.* **2008**, *A64*, 112-122.

**Table 1.** Crystallographic Data for  $([\text{FeTPPbipy}]^+)_n$ 

| Compound  | $([\text{FeTPPbipy}]^+)_n$  |
|---|---|
| Formula   | $\text{C}_{54}\text{H}_{36}\text{FeN}_6$                            |
| FW, $\text{g}\cdot\text{mol}^{-1}$  | 824.74  |
| Crystal system  | Monoclinic  |
| Space group (no. 15)  | $C2/c$  |
| $a$ , Å   | 21.6833(8)  |
| $b$ , Å   | 11.0827(4)  |
| $c$ , Å   | 17.6206(6)  |
| $\beta$ , deg   | 97.354(3)   |
| $V$ , Å <sup>3</sup>  | 4199.6(3)   |
| $Z$   | 4   |
| $\rho_{\text{obs}}$ , $\rho_{\text{cal}}$ , $\text{g}\cdot\text{cm}^{-3}$                                       | 1.309(5), 1.304   |
| $F(000)$  | 1712  |
| $\mu$ , $\text{mm}^{-1}$  | 0.405   |
| Crystal size, mm  | 0.34 x 0.077 x 0.072  |
| Absorption correction   | Analytical  |
| Radiation, $\lambda$ , Å  | 0.71073   |
| Temperature, K  | 100(2)  |
| Reflections collected, unique   | 10334, 3907 ( $R_{\text{int}} = 0.04$ )                             |
| Limiting indices  | $-26 \leq h \leq 26$<br>$-7 \leq k \leq 13$<br>$-21 \leq l \leq 19$ |
| Refinement method   | Full-matrix least-squares on $F^2$                                  |
| Final $R$ indices [ $I > 2\sigma(I)$ ] <sup>a</sup>   | $R1 = 0.0351$ , $wR2 = 0.0714$                                      |
| $R$ indices (all data) <sup>a</sup>   | $R1 = 0.0513$ , $wR2 = 0.0738$                                      |
| Goodness of fit on $F^2$  | 0.909   |
| Parameters /restraints  | 279 /0  |
| <sup>a</sup> $R1 = [( F_o  -  F_c ) /  F_o ]$ . $wR2 = [(\sum w( F_o ^2 -  F_c ^2)^2) / (\sum w(F_o)^2)]^{1/2}$ |   |

## II.3. Results and Discussion

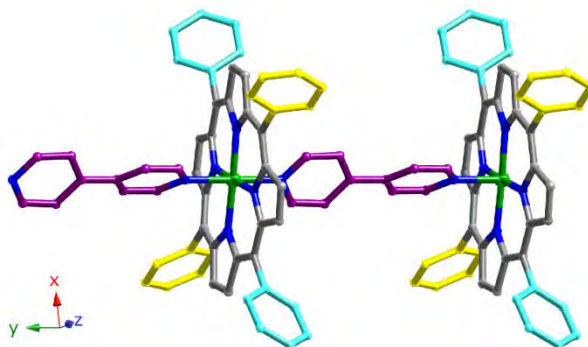
### II.3.1. Synthesis of $([\text{FeTPPbipy}]^+)_n$

5,10,15,20-tetraphenyl-porphine iron (III) chloride (7 mg, 0.01 mmol), 4,4'-bipyridine (9.4 mg, 0.06 mmol) and 40  $\mu\text{L}$  NaOH (3M) were added to a mixture of *N,N*-dimethylformamide (3 mL) and ethanol (1 mL) in a small capped vial, sonicated to ensure homogeneity and heated to 120 °C for 48 h, following by slow cooling to

room temperature at 2 °C/h, yielding diffraction quality dark blue prismatic crystals. (Found: C, 78.45(8); H, 4.31(10); N, 9.86(6). Calc. for  $C_{54}H_{36}FeN_6$ : C, 78.64; H, 4.39; N, 10.18%).  $\nu_{\max}/\text{cm}^{-1}$  3051, 3022 and 2964 (C(sp<sup>2</sup>)H), 1600-1440 (CC), 1348 (CN), 1204 and 1070 (bipy), 1000 (FeTPP) and 750 (CH) (Figure S2, Supplementary Information).

### II.3.2. Crystal structure

Crystal structure of  $([\text{FeTPPbipy}]^+)_n$  was determined by means of X-ray single crystal diffraction. The structure consists of 1D coordination polymers extending along the [010] where metallated porphyrins are axially bonded to two bipy ligands (Figure 1).



**Figure 1.** 1D coordination polymers extending along the [010] directions for  $([\text{FeTPPbipy}]^+)_n$ . Colour codes: Fe: green; N: blue; C(porphyrin): grey, yellow, turquoise; C(bipy): purple. H atoms are omitted for clarity.

The resulting octahedral coordination sphere exhibits bond angles and distances that are typical for this type of compounds (Table 2).<sup>37</sup> These coordination polymers crystallize as shown in Figure 2. The connections between chains take place through *edge-to-face*  $\pi$ -stacking along the [10-1] direction (centroid-to centroid

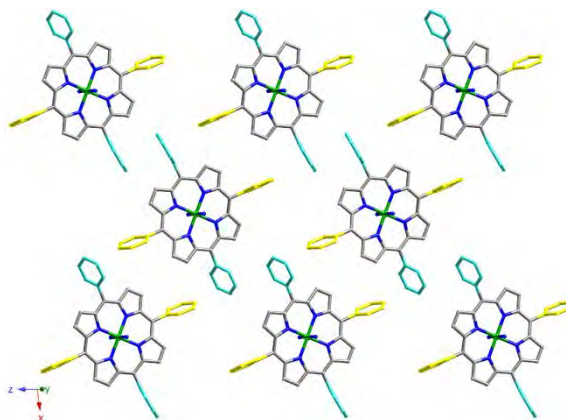
<sup>37</sup> Scheidt, W. R.; Geiger, D. K.; Haller, K. J., *J. Am. Chem. Soc.* **1982**, *104*, 495-499.

distance of 3.662 Å and angle of 83.94°). Additionally, there is a *face-to-face*  $\pi$ -stacking along the [101] direction (centroid-to centroid distance 5.067 Å and angle 0.02°). Therefore, the cohesion between 1D coordination polymers is based on a robust net of  $\pi$ -bonds.

**Table 2.** Selected bond angles (°) and distances (Å) for  $[(\text{FeTPPbipy})^+]_n$  (distances in bold).

| Octahedron [FeN <sub>6</sub> ] |                 |                 |                 |                 |                 |                 |
|--------------------------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Fe                             | N1              | N1 <sup>i</sup> | N2              | N2 <sup>i</sup> | N3              | N4              |
| N4                             | 88.46(4)        | 88.46(4)        | 91.16(4)        | 91.16(4)        | 180             | <b>1.998(2)</b> |
| N3                             | 91.54(4)        | 91.54(4)        | 88.84(4)        | 88.84(4)        | <b>1.985(2)</b> |                 |
| N2 <sup>i</sup>                | 90.14(6)        | 89.92(6)        | 177.69(8)       | <b>1.996(1)</b> |                 |                 |
| N2                             | 89.92(6)        | 90.14(6)        | <b>1.996(1)</b> |                 |                 |                 |
| N1 <sup>i</sup>                | 176.93(8)       | <b>1.983(1)</b> |                 |                 |                 |                 |
| N1                             | <b>1.983(1)</b> |                 |                 |                 |                 |                 |

Symmetry code: i) -x, y, -z+1/2



**Figure 2.** View of a (101) plane for  $[(\text{FeTPPbipy})^+]_n$ . Colour codes are the same as in Figure 1.

Bipy ligands and H atoms are omitted for clarity. *Face-to-face*  $\pi$ -stacking occurs between turquoise phenyl groups and *edge-to-face*  $\pi$ -stacking occurs between turquoise and yellow phenyl groups.

In principle, chemical formula could be interpreted in terms of the presence of Fe<sup>II</sup> and TPP<sup>2-</sup> ions. However, as explained below, the behavior of ([FeTPPbipy]<sup>+</sup>)<sub>n</sub> is consistent with the presence of Fe<sup>III</sup>. Therefore, since no further deprotonation is observed for organic ligands, reduction of TPP<sup>2-</sup> must be assumed to keep neutrality.<sup>38,39</sup>

Distortion of porphyrin was analyzed by the normal-coordinate structural decomposition method developed by Shelnutz *et al.* (NSD)<sup>40,41</sup> indicating a low saddle-type distortion (*sad*, B<sub>2u</sub>). The contribution of this type of distortion (0.5967) to the total displacements is 67%, a usual feature on low-spin Fe<sup>III</sup> porphyrins.<sup>42</sup>

It is worth mentioning that, as we are aware, ([FeTPPbipy]<sup>+</sup>)<sub>n</sub> is the first Fe-TPP-dipyridyl coordination network exhibiting 1D polymers, and it has been formed by assembly of neutral radical units. More details about the later will be discussed below.

### II.3.3. Purity of the measured samples

In order to determine the purity of the samples used for further characterization, the grinding effect on single crystals has been evaluated by means of X-ray diffraction. The results (Figure S3, Supplementary Information) indicate that a significant rate of amorphization takes place. Taking this into consideration, magnetic susceptibility measurements and UV-visible spectra were performed by using non-ground single crystals introduced into a capillary in order to guarantee the purity of the

<sup>38</sup> Saffari, J.; Khorasani-Motlagh, M.; Noroozifar, M., *Synth. React. Inorg., Met.-Org., Nano-Met. Chem.* **2010**, *40*, 899-904.

<sup>39</sup> Mezger, M.; Hanack, M.; Hirsch, A.; Kleinwaechter, J.; Mangold, K. M.; Subramanian, L. R., *Chem. Ber.* **1991**, *124*, 841-847.

<sup>40</sup> Jentzen, W.; Song, X.-Z.; Shelnutz, J. A., *J. Phys. Chem. B* **1997**, *101*, 1684-1699.

<sup>41</sup> Jentzen, W.; Ma, J.-G.; Shelnutz, J. A., *Biophys. J.* **1998**, *74*, 753-763.

<sup>42</sup> Ohgo, Y.; Hoshino, A.; Okamura, T.; Uekusa, H.; Hashizume, D.; Ikezaki, A.; Nakamura, M., *Inorg. Chem.* **2007**, *46*, 8193-8207.

sample. Unfortunately, the crystal features for  $([\text{FeTPPbipy}])_n$  were absolutely inadequate for the performance of EPR and Mössbauer spectroscopy on single crystal.

#### II.3.4. UV-visible (diffuse reflectance) spectroscopy

UV-visible spectroscopy was performed on non-ground single crystals and as observed in Figure 3a the spectrum exhibits a Soret band ( $\gamma$ ) at 377 nm and the Q bands ( $\beta$  and  $\alpha$ ) at 517 nm and 557 nm, respectively. The fact that the Soret band is blue shifted and reduced in intensity compared to typical six-coordinate low-spin ferric porphyrin complexes,<sup>43,44</sup> is justified by assuming the presence of a radical species.<sup>45,46</sup> The low-spin  $\text{Fe}^{\text{III}}$  porphyrin characteristic  $L_1$  and  $L_2$  bands<sup>47</sup> appear at 815(sh) nm and 770 nm, respectively. A broad and weak band at 690 nm is in accordance with the presence of a porphyrinic radical.<sup>44</sup> These results were compared with the theoretical spectra (Figure 3a) obtained by TD-DFT calculations, performed by means of Gaussian 03<sup>48</sup> (B3LYP<sup>49,50</sup> functional and 6-31G valence). In addition to the good concordance between both spectra, the most remarkable fact is that the molecular orbitals involved

<sup>43</sup> Mikami, S.; Sugiura, K.-i.; Maruta, T.; Maeda, Y.; Ohba, M.; Usuki, N.; Okawa, H.; Akutagawa, T.; Nishihara, S.; Nakamura, T.; Iwasaki, K.; Miyazaki, N.; Hino, S.; Asato, E.; Miller, J. S.; Sakata, Y., *J. Chem. Soc., Dalton Trans.* **2001**, 448-455.

<sup>44</sup> Quinn, R.; Strouse, C. E.; Valentine, J. S., *Inorg. Chem.* **1983**, 22, 3934-3940.

<sup>45</sup> Ikezaki, A.; Tukada, H.; Nakamura, M., *Chem. Commun.* **2008**, 2257-2259.

<sup>46</sup> Gans, P.; Buisson, G.; Duee, E.; Marchon, J. C.; Erler, B. S.; Scholz, W. F.; Reed, C. A., *J. Am. Chem. Soc.* **1986**, 108, 1223-1234.

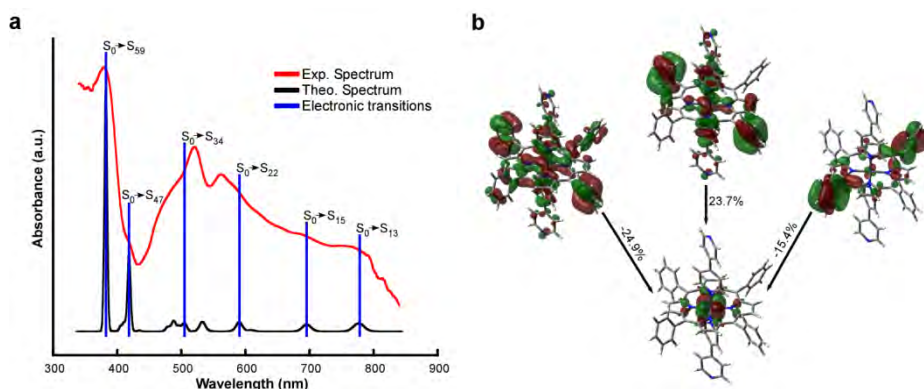
<sup>47</sup> Ochiai, E.-i., *Bioinorganic Chemistry: An Introduction*. Allyn and Bacon: Inc., Boston, USA, 1977, ch. 5, 515 pp.

<sup>48</sup> Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A.; Vreven, J., T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A., *et al.* *GAUSSIAN 03, (Revision D.02)*. gaussian, Inc., Wallingford CT, 2004.

<sup>49</sup> Becke, A. D., *J. Chem. Phys.* **1993**, 98, 5648-5652.

<sup>50</sup> Lee, C.; Yang, W.; Parr, R. G., *Phys. Rev. B Condens. Matter* **1988**, 37, 785-789.

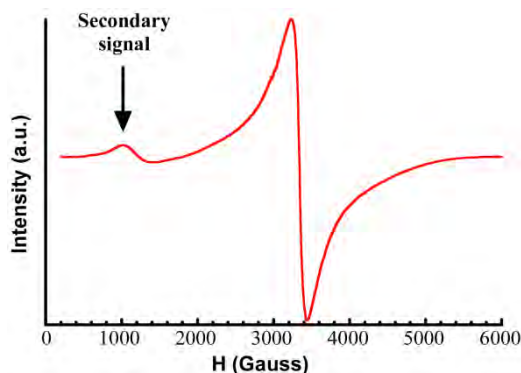
in the Soret transition ( $S_0$ - $S_{59}$ ) represent an important charge transfer between the phenyl rings and the metal center (Figure 3b). This fact will be mentioned below when discussing the magnetic behavior.



**Figure 3.** a) Experimental and theoretical UV-vis spectra for  $([\text{FeTPPBipy}]^+)_n$  and b) Molecular orbitals involved in  $S_0$ - $S_{59}$  transition.

### II.3.5. Electron paramagnetic resonance (EPR)

X-band EPR spectroscopy was performed on ground single crystals of  $([\text{FeTPPBipy}]^+)_n$ . As observed, the spectrum shows two signals (Figure 4). The weakest of them (with  $g$  close to 6) is typical for magnetically isolated  $\text{Fe}^{\text{III}}$  systems in axial symmetry. Therefore, it is supposed to have been formed by crystal grinding. Unfortunately, the fact that grinding produces amorphization (Figure S3, Supplementary Information) results in the impossibility of identifying this second phase by X-ray diffraction.



**Figure 4.** X-band EPR spectrum (room temperature) for  $([\text{FeTPPbipy}]^3)_n$ .

On the other hand, the principal signal (with  $g$  close to 2) can be interpreted in terms of the following two possibilities: a) high-spin  $\text{Fe}^{\text{III}}$  ions in very low concentration in relation to the bulk of the analyzed sample, and b) low-spin  $\text{Fe}^{\text{III}}$  ions with either significant magnetic interactions between metal centers having different orientations or interactions with free radicals. In the later case, radicals should be either delocalized or localized in such a way that they could relax in a short period of time. The first hypothesis does have sense just for the case of high-spin  $\text{Fe}^{\text{III}}$  ions diluted in a low-spin  $\text{Fe}^{\text{II}}$ -framework. This means that compound  $([\text{FeTPPbipy}]^3)_n$  should contain  $\text{Fe}^{\text{II}}$  ions, and that there are three contributions to the signal: the compound itself, the amorphous secondary phase, and a third unknown compound. This hypothesis has been discarded by X-band EPR spectroscopy at 100 K (Figure S4, Supplementary Information) as it shows a broadening of the signal and a rapid decrease of the intensity (it mostly disappears below 50 K). This clearly indicates the presence of antiferromagnetic interactions, therefore pointing to the second explanation. Thus, the second explanation could just be feasible if admitting the presence of free electrons, because the structural characteristics of  $([\text{FeTPPbipy}]^3)_n$  are not compatible with significant magnetic interactions between metal centers (the magnetic paths through the bipy ligands are too long). As explained below, these magnetic interactions were

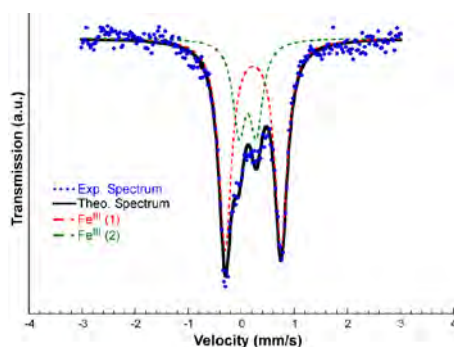


analyzed through measurements of the magnetic susceptibility and by DFT calculations.

### II.3.6. Mössbauer spectroscopy

Mössbauer spectroscopy was performed on ground single crystals. The spectrum has been simulated with the NORMOS program<sup>51</sup>, and indicates the presence of two doublets: both of them corresponding to Fe<sup>III</sup> ion signals. The presence of two Fe<sup>III</sup> centers has been explained already in the EPR section and it has been associated to the amorphization of the sample as a consequence of the grinding, discarding the presence of a previous impurity.

The most significant signal is assigned to the metal ions in ([FeTPPbipy])<sub>n</sub>, while the second one is assumed to be due to the secondary phase coming from grinding. Quantitative analysis reveals that the sample contained 70.5% weight corresponding to ([FeTPPbipy])<sub>n</sub>. This is in accordance with the significant rate of amorphization observed by X-ray diffraction (Figure S3, Supplementary Information). Isomer shift ( $\delta$ ) and quadrupolar splitting ( $\Delta E$ ) values are 0.337(1) and 1.054(2) for the first signal, and 0.235(2) and 0.326(7) for the second one, in the range usually observed for Fe<sup>III</sup> ions (Figure 5).

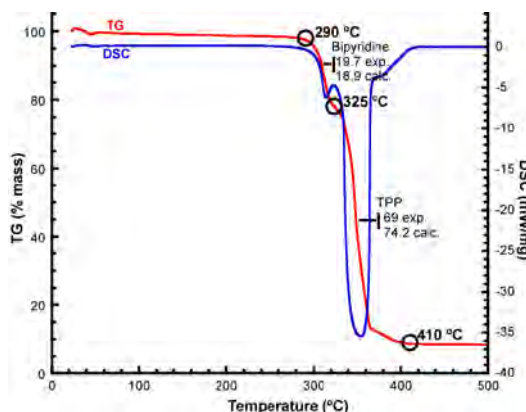


**Figure 5.** Mössbauer spectra for ([FeTPPbipy])<sub>n</sub>.

<sup>51</sup> Brand, R. A.; Lauer, J.; Herlach, D. M., *J. Phys. F: Met. Phys.* **1983**, *13*, 675-683.

### II.3.7. Thermogravimetry

Thermogravimetry analysis was carried out on non-ground single crystals. The thermogravimetric decomposition curve of the compound shows an overlapped two stage mass loss, from approximately 290 °C to 410 °C. As shown in Figure 6, the first step occurs between 290-325 °C with a 19.7% weight loss, and the second from 325 °C to 410 °C with a 69% weight loss. These mass percentages are close to the theoretical percentages of bipyridine (18.9%) and TPP (74.2%) molecules. The calcinations product was identified by X-ray powder diffraction analysis and it consists of Fe<sub>2</sub>O<sub>3</sub> [S.G. *R*-3 $c$ ,  $a$  = 5.0248 Å,  $c$  = 13.7163 Å,  $\gamma$  = 120°].<sup>52</sup>



**Figure 6.** Thermal analysis for ([FeTPPbipy']<sub>n</sub>).

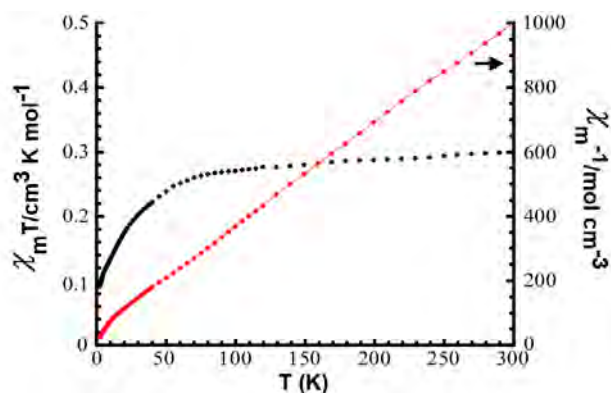
### II.3.8. Magnetic measurements

We have also performed magnetic susceptibility ( $\chi_m$ ) measurements for ([FeTPPbipy']<sub>n</sub>) in the range 4–300 K (Figure 7). It is worth mentioning that non-ground single crystals were used for this analysis, but original crystals were introduced into a capillary. The  $\chi_m T$  value at room temperature is 0.30 cm<sup>3</sup>K/mol which is much

<sup>52</sup> Tsirel'son, V. G.; Antipin, M. Y.; Strel'tsov, V. A.; Ozerov, R. P.; Struchkov, Y. T., *Dokl. Akad. Nauk SSSR* **1988**, 298, 1137-1141.

lower than the  $4.37 \text{ cm}^3\text{K/mol}$  expected for a high-spin  $\text{Fe}^{\text{III}}$  compound. On the contrary, it is close to the  $0.37 \text{ cm}^3\text{K/mol}$  value expected for low-spin  $\text{Fe}^{\text{III}}$  complexes. As explained below (DFT calculations), the one-electron reduction of metalloporphyrin is analyzed, the acquired electrons having been determined to be located on the phenyl groups. On the other hand, TD-DFT calculations carried out to analyze the UV-vis spectroscopy (Figure 3b) indicate that there is an important charge transfer between the phenyl rings and the metal centers (Figure 3b). Thus, the slight discrepancy between the expected ( $0.30 \text{ cm}^3\text{K/mol}$ ) and observed ( $0.37 \text{ cm}^3\text{K/mol}$ )  $\chi_{\text{m}}T$  values for low-spin  $\text{Fe}^{\text{III}}$  can be explained if considering this charge transfer.

The thermal evolution of the reciprocal susceptibility follows the Curie-Weiss law with  $C_{\text{m}}=0.32 \text{ cm}^3\text{K/mol}$ , and  $\theta=-18.7 \text{ K}$ . (Figure 7). The product  $\chi_{\text{m}}T$  continuously decreases upon cooling reaching a value of  $0.09 \text{ cm}^3\text{Kmol}$  at  $5.0 \text{ K}$ , indicating the presence of antiferromagnetic interactions, as expected from EPR characterization. As mentioned, these interactions cannot be attributed to magnetic exchange between metal centers. Therefore, coupling between metal ions and free electrons should be admitted.



**Figure 7.** Thermal evolution of  $\chi_{\text{m}}T$  and  $\chi_{\text{m}}^{-1}$  for  $([\text{FeTPPbipy}]^+)_n$ . and the corresponding theoretical Curie-Weiss law (red line).

### II.3.9. DFT calculations

As previously mentioned, the structural characterization of this compound could make think that the metal ion is Fe<sup>II</sup>, in accordance with the presence of TPP<sup>2-</sup> ligands and neutral bipy molecules. However, the commercial reactant, [FeTPPCI], contains Fe<sup>III</sup>, and its reduction to Fe<sup>II</sup> does not seem to be feasible. On the other hand, bond distances and angles are typical for Fe<sup>III</sup>-porphyrins, and the rest of the characterization techniques clearly indicate that the metal ion is Fe<sup>III</sup>. Therefore, the best of our hypothesis is that the compound has been formed by assembly of [FeTPP]<sup>•</sup> radical structural units, that extend producing 1D polymers by means of the axial coordinations of the metal center to bipy ligands. Thus, the [FeTPP]<sup>•</sup> structural units should be thought to be the result of the one-electron reduction of the metalloporphyrin (reactions 1-2).

1. [FeTPPCI] → [FeTPP]<sup>+</sup> + Cl<sup>-</sup>
2. [FeTPP]<sup>+</sup> + 1e<sup>-</sup> → [FeTPP]<sup>•</sup>

Admitting that the reduction must have been taken place for the metalloporphyrin, we have tried to identify the reductant agent. Even if they are some calculated redox potentials in literature,<sup>53</sup> they are not useful in our case due to the non standard conditions for solvothermal synthesis. Even so, there are several possible reductant agents like residues of bipy and DMF.<sup>54</sup>

Thus, next question about ([FeTPPbipy]<sup>•</sup>)<sub>n</sub> consists of determining the localization of the electron providing the metalloporphyrins with its radical nature. In the case of ([FeTPPbipy]<sup>•</sup>)<sub>n</sub>, the presence of low-spin Fe<sup>III</sup> and an extra unpaired electron should

<sup>53</sup> Ou, Z.; E, W.; Zhu, W.; Thordarson, P.; Santic, P. J.; Crossley, M. J.; Kadish, K. M., *Inorg. Chem.* **2007**, *46*, 10840-10849.

<sup>54</sup> Pereira, M. M.; Abreu, A. R.; Goncalves, N. P. F.; Calvete, M. J. F.; Simoes, A. V. C.; Monteiro, C. J. P.; Arnaut, L. G.; Eusebio, M. E.; Canotilho, J., *Green Chem.* **2012**, *14*, 1666-1672.

result in two unpaired electrons per metalloporphyrin. Therefore, we could think of two explanations. As previously proposed,<sup>55</sup> the extra unpaired electron could be delocalized on the aromatic porphyrinic system. If analyzing the compound from the point of view of isolated structural units (1D polymers), this could be an effective explanation. However, magnetic measurements are not consistent with the later. Besides, there is an intricate  $\pi$ -stacking system in  $([\text{FeTPPbipy}])_n$  according to which analyzing the framework from such a point of view does not seem to be adequate. Thus, a second explanation is that the electrons acquired by reduction are paired in the 3D framework (Scheme 1). This idea is strongly supported by the  $\pi$ -stacking, as it provides the opportunity of electron coupling.

**Scheme 1.** Possibilities for the number of unpaired electrons depending on the occurrence of antiferromagnetic coupling through  $\pi$  stacking.

| Possible interactions between 1D polymers per two Fe <sup>III</sup> centers |              |     |              |    |  |
|---|--------------|-----|--------------|----|--|
|   | 1D polymer 1 |     | 1D polymer 2 |    | $\pi$ -stacking producing antiferromagnetic interactions |
|   | Fe           | TPP | TPP          | Fe |  |
| 4 unpaired electrons per two Fe <sup>III</sup> centers                      | ↑            | ↑   | ↑            | ↑  | No   |
| 2 unpaired electrons per two Fe <sup>III</sup> centers                      | ↓            | ↑↓  |              | ↑  | Yes  |

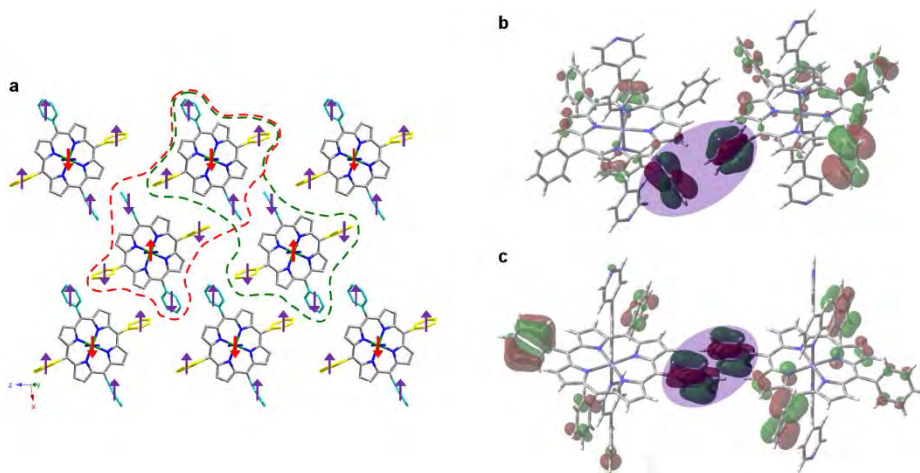
In order to provide theoretical support to the above mentioned aspects, both hypotheses were analyzed by means of quantum-mechanical DFT calculations (Gaussian 03 program).<sup>56</sup> Calculations were performed using Becke's<sup>57</sup> three

<sup>55</sup> Scheidt, W. R.; Brancato-Buentello, K. E.; Song, H.; Reddy, K. V.; Cheng, B., *Inorg. Chem.* **1996**, *35*, 7500-7507.

<sup>56</sup> Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A.; Vreven, J., T.; Kudin, K. N.; Burant, J. C.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, *et al.*, *GAUSSIAN 03*, (Revision D.02). gaussian, Inc., Wallingford CT, 2004.

<sup>57</sup> Becke, A. D., *J. Chem. Phys.* **1993**, *98*, 5648-5652.

parameter hybrid functional with the correlation functional of Lee, Yang and Parr (B3LYP)<sup>58</sup> with a split-valence basis set of 6-31G. This functional does not consider the dispersive interactions. However, it has been selected since our objective was not obtaining an accurate value for the energy but representative values for the comparison between both hypotheses. In fact, the goal was to investigate the effect of the  $\pi$ -stacking on the stability of the framework. To this purpose, two dimeric fragments ( $\text{Fe-TPP-bipy}_2$ )<sub>2</sub> were selected. In dimer 1, the interdimer connection is due to the *edge-to-face*  $\pi$ -bond along the [10-1] direction, while in dimer 2 the connection takes place by *face-to-face*  $\pi$ -bond along the [101] direction (Figure 8a).



**Figure 8.** a) Selected dimeric fragments for the DFT calculations according to *edge-to-face* (red line) and *face-to-face* (green line)  $\pi$  interactions. Scheme for the spin distribution proposal is also shown: red arrows are the unpaired electrons corresponding to LS  $\text{Fe}^{\text{III}}$  ( $d^5$ ), and each group of four purple arrows corresponds to a single electron localized on phenyl groups belonging to the same metalloporphyrin. b) Calculated MOs involving the *edge-to face* and c) the *face-to-face*  $\pi$ -stackings.

<sup>58</sup> Lee, C.; Yang, W.; Parr, R. G., *Phys. Rev. B Condens. Matter* **1988**, 37, 785-789.

For each dimer, two calculations (Table 3) were carried out: in calculation 1, the dimer has four unpaired electrons (2 per monomer), and in calculation 2, the dimer has two unpaired electrons (1 per monomer). Therefore, calculation 1 accounts for the first hypothesis (this is, analysis from the point of view of isolated 1D polymers) while calculation 2 explores the possibility of electron coupling through interpolymer  $\pi$  stacking. Obviously, the extension of the framework through the three directions of the space should have been considered for more accurate calculations. However, the large amount of atoms involved makes this very expensive.

**Table 3.** Calculated energy for  $(\text{Fe-TPP-bipy}_2)_2$  dimers.

| Dimer | $\pi$ interactions | Coupling through $\pi$ interactions | Number of unpaired electrons per dimer | Calculated energy (Hartree) |
|-------|--------------------|-------------------------------------|--|-----------------------------|
| 1     | Edge-to-face       | Yes                                 | 2                                      | -8331.1805358               |
| 1     | Edge-to-face       | No                                  | 4                                      | -8331.1309928               |
| 2     | Face-to-face       | Yes                                 | 2                                      | -8331.1814716               |
| 2     | Face-to-face       | No                                  | 4                                      | -8331.1533709               |

At this point of the discussion, claiming that the  $\pi$ -stacking is responsible for the stabilization of the framework seems to be obvious. Nevertheless, the remarkable point is that calculations strongly support the idea that the extra electrons have not been delocalized on the TPP pyrrolic system but there are paired in molecular orbitals (MOs) formed by the  $\pi$ -stacking. In fact, as observed in Figure 8b and 8c the calculations provided MOs for these interactions.

### II.3.10. Self-assembly of neutral radicals

As the  $\pi$ -stacking is extended on (101) planes, extrapolation of DFT calculations to the 3D network can be done. As observed in Figure 8b and 8c, the contribution of the phenyl MOs to the  $\pi$  stacking is consistent with this extrapolation.

First of all, the electron acquired by the porphyrin could be thought to be delocalized on the four phenyl groups. On the other hand, if considering that magnetic measurements are consistent with the presence of a value close to one unpaired electron per monomer, the spin distribution proposed in Figure 8a could be a reasonable explanation for the behavior of this compound. This spin distribution is based on the occurrence of antiferromagnetic coupling not only between electrons belonging to the metal center and the phenyl groups (as previously mentioned in the magnetic measurements section) but also between phenyl electrons localized on adjacent 1D polymers as seen in Figure 8b and 8c.

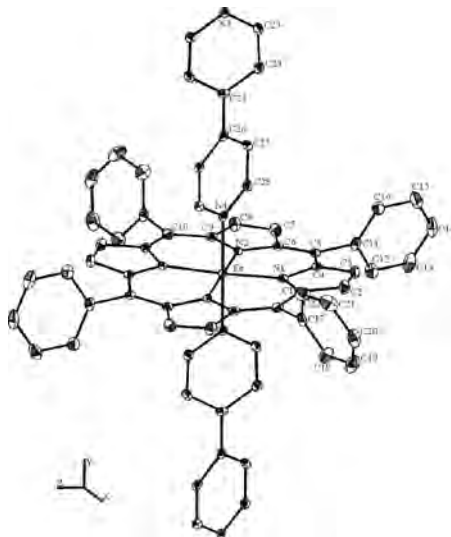
In summary, identification of the localization of the acquired electrons is the key point that supports the idea of neutral radicals having been able to self-assemble producing such a 3D framework.

## II.4. Conclusions

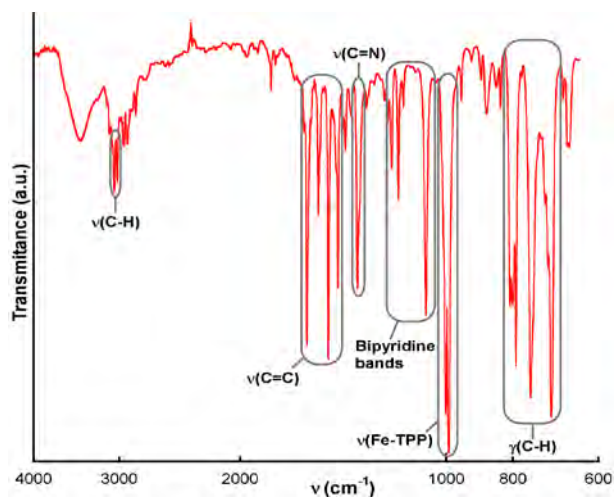
The compound  $([\text{FeTPPbipy}]^{\bullet})_n$  has been formed by assembly of metalloporphyrinic neutral radicals that have been formed by the one-electron reduction of the original  $[\text{FeTPP}]^{+1}$  cations as suggested by the presence of low-spin  $\text{Fe}^{\text{III}}$  ions. The as-acquired electrons are proposed to be paired in the MOs formed by  $\pi$ - $\pi$  interactions between the phenyl groups of different 1D polymers. The resulting packing is the first Fe-TPP-bipy coordination network exhibiting 1D polymers.



## Supplementary Information

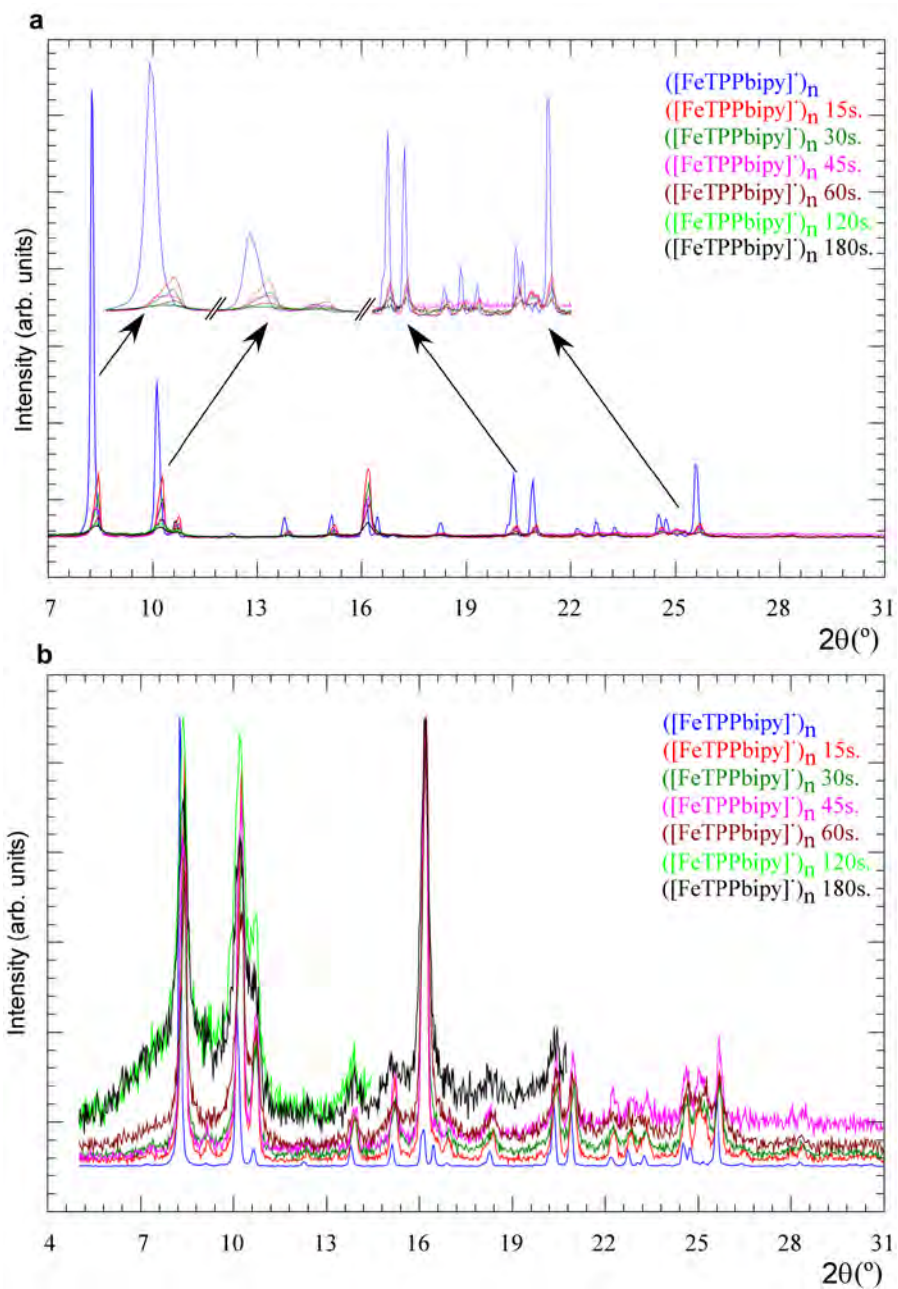


**Figure S1.** ORTEP<sup>59</sup> detail of  $[(\text{FeTPPbipy})]_n$ . The thermal ellipsoids correspond to 50% probability. Hydrogen atoms have been omitted.

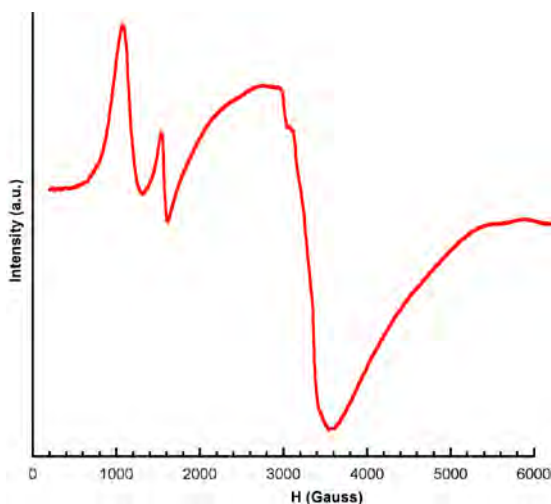


**Figure S2.** IR spectra for  $[(\text{FeTPPbipy})]_n$ .

<sup>59</sup> Farrugia, L. J., *J. Appl. Crystallogr.* **1997**, 30, 565.



**Figure S3.** a) X-ray patterns for  $([\text{FeTPPBipy}])_n$  with different time of grinding and b) with normalized intensities.



**Figure S4.** X-band EPR spectrum at 100 K for  $([\text{FeTPPbipy}]^+)_n$ .

**Table S1.** Bond distances (Å) and angles (°) for  $([\text{FeTPPbipy}]^+)_n$ .

**Distances**

|            |          |                          |          |
|------------|----------|--------------------------|----------|
| C(1)-N(1)  | 1.384(2) | C(17)-C(22)              | 1.389(3) |
| C(1)-C(10) | 1.391(2) | C(18)-C(19)              | 1.385(3) |
| C(1)-C(2)  | 1.436(2) | C(18)-H(18)              | 0.9500   |
| C(2)-C(3)  | 1.338(3) | C(19)-C(20)              | 1.370(3) |
| C(2)-H(2)  | 0.9500   | C(19)-H(19)              | 0.9500   |
| C(3)-C(4)  | 1.442(2) | C(20)-C(21)              | 1.385(3) |
| C(3)-H(3)  | 0.9500   | C(20)-H(20)              | 0.9500   |
| C(4)-N(1)  | 1.385(2) | C(21)-C(22)              | 1.387(3) |
| C(4)-C(5)  | 1.391(2) | C(21)-H(21)              | 0.9500   |
| C(5)-C(6)  | 1.395(2) | C(22)-H(22)              | 0.9500   |
| C(5)-C(11) | 1.501(2) | C(23)-N(3)               | 1.348(2) |
| C(6)-N(2)  | 1.386(2) | C(23)-C(24)              | 1.373(2) |
| C(6)-C(7)  | 1.434(2) | C(23)-H(23)              | 0.9500   |
| C(7)-C(8)  | 1.342(2) | C(24)-C(25)              | 1.389(2) |
| C(7)-H(7)  | 0.9500   | C(24)-H(24)              | 0.9500   |
| C(8)-C(9)  | 1.436(2) | C(25)-C(24) <sup>i</sup> | 1.389(2) |

|                         |          |                            |          |
|-------------------------|----------|----------------------------|----------|
| C(8)-H(8)               | 0.9500   | C(25)-C(26)                | 1.474(3) |
| C(9)-N(2)               | 1.376(2) | C(26)-C(27) <sup>ii</sup>  | 1.387(2) |
| C(9)-C(10) <sup>i</sup> | 1.399(2) | C(26)-C(27) <sup>iii</sup> | 1.388(2) |
| C(10)-C(9) <sup>i</sup> | 1.399(2) | C(27)-C(28)                | 1.379(2) |
| C(10)-C(17)             | 1.500(2) | C(27)-C(26) <sup>iv</sup>  | 1.388(2) |
| C(11)-C(12)             | 1.382(3) | C(27)-H(27)                | 0.9500   |
| C(11)-C(16)             | 1.393(3) | C(28)-N(4)                 | 1.346(2) |
| C(12)-C(13)             | 1.391(3) | C(28)-H(28)                | 0.9500   |
| C(12)-H(12)             | 0.9500   | Fe(1)-N(1)                 | 1.983(1) |
| C(13)-C(14)             | 1.379(3) | Fe(1)-N(1) <sup>i</sup>    | 1.983(1) |
| C(13)-H(13)             | 0.9500   | Fe(1)-N(3)                 | 1.985(2) |
| C(14)-C(15)             | 1.377(3) | Fe(1)-N(2) <sup>i</sup>    | 1.996(1) |
| C(14)-H(14)             | 0.9500   | Fe(1)-N(2)                 | 1.996(1) |
| C(15)-C(16)             | 1.388(2) | Fe(1)-N(4)                 | 1.998(2) |
| C(15)-H(15)             | 0.9500   | N(3)-C(23) <sup>i</sup>    | 1.348(2) |
| C(16)-H(16)             | 0.9500   | N(4)-C(28) <sup>i</sup>    | 1.346(2) |
| C(17)-C(18)             | 1.388(3) |                            |          |

### Angles

|                 |          |                   |          |
|-----------------|----------|-------------------|----------|
| N(1)-C(1)-C(10) | 125.8(2) | C(18)-C(19)-H(19) | 119.8    |
| N(1)-C(1)-C(2)  | 110.1(2) | C(19)-C(20)-C(21) | 120.0(2) |
| C(10)-C(1)-C(2) | 124.1(2) | C(19)-C(20)-H(20) | 120.0    |
| C(3)-C(2)-C(1)  | 107.6(2) | C(21)-C(20)-H(20) | 120.0    |
| C(3)-C(2)-H(2)  | 126.2    | C(20)-C(21)-C(22) | 119.4(2) |
| C(1)-C(2)-H(2)  | 126.2    | C(20)-C(21)-H(21) | 120.3    |
| C(2)-C(3)-C(4)  | 107.3(2) | C(22)-C(21)-H(21) | 120.3    |
| C(2)-C(3)-H(3)  | 126.3    | C(21)-C(22)-C(17) | 121.2(2) |
| C(4)-C(3)-H(3)  | 126.3    | C(21)-C(22)-H(22) | 119.4    |
| N(1)-C(4)-C(5)  | 125.8(2) | C(17)-C(22)-H(22) | 119.4    |
| N(1)-C(4)-C(3)  | 109.9(2) | N(3)-C(23)-C(24)  | 123.4(2) |
| C(5)-C(4)-C(3)  | 124.2(2) | N(3)-C(23)-H(23)  | 118.3    |
| C(4)-C(5)-C(6)  | 123.8(2) | C(24)-C(23)-H(23) | 118.3    |

|                                |          |   |           |
|--------------------------------|----------|---|-----------|
| C(4)-C(5)-C(11)                | 118.0(2) | C(23)-C(24)-C(25)                               | 120.2(2)  |
| C(6)-C(5)-C(11)                | 118.2(2) | C(23)-C(24)-H(24)                               | 119.9     |
| N(2)-C(6)-C(5)                 | 124.8(2) | C(25)-C(24)-H(24)                               | 119.9     |
| N(2)-C(6)-C(7)                 | 110.6(2) | C(24) <sup>i</sup> -C(25)-C(24)                 | 116.6(2)  |
| C(5)-C(6)-C(7)                 | 124.4(2) | C(24) <sup>i</sup> -C(25)-C(26)                 | 121.7(1)  |
| C(8)-C(7)-C(6)                 | 106.9(2) | C(24)-C(25)-C(26)                               | 121.7(1)  |
| C(8)-C(7)-H(7)                 | 126.5    | C(27) <sup>ii</sup> -C(26)-C(27) <sup>iii</sup> | 116.7(2)  |
| C(6)-C(7)-H(7)                 | 126.5    | C(27) <sup>ii</sup> -C(26)-C(25)                | 121.7(1)  |
| C(7)-C(8)-C(9)                 | 107.3(2) | C(27) <sup>iii</sup> -C(26)-C(25)               | 121.7(1)  |
| C(7)-C(8)-H(8)                 | 126.4    | C(28)-C(27)-C(26) <sup>iv</sup>                 | 120.2(2)  |
| C(9)-C(8)-H(8)                 | 126.4    | C(28)-C(27)-H(27)                               | 119.9     |
| N(2)-C(9)-C(10) <sup>i</sup>   | 125.2(2) | C(26) <sup>iv</sup> -C(27)-H(27)                | 119.9     |
| N(2)-C(9)-C(8)                 | 110.6(2) | N(4)-C(28)-C(27)                                | 123.1(2)  |
| C(10) <sup>i</sup> -C(9)-C(8)  | 124.2(2) | N(4)-C(28)-H(28)                                | 118.5     |
| C(1)-C(10)-C(9) <sup>i</sup>   | 123.7(2) | C(27)-C(28)-H(28)                               | 118.5     |
| C(1)-C(10)-C(17)               | 117.1(2) | N(1)-Fe(1)-N(1) <sup>i</sup>                    | 176.93(8) |
| C(9) <sup>i</sup> -C(10)-C(17) | 119.1(2) | N(1)-Fe(1)-N(3)                                 | 91.54(4)  |
| C(12)-C(11)-C(16)              | 118.8(2) | N(1) <sup>i</sup> -Fe(1)-N(3)                   | 91.54(4)  |
| C(12)-C(11)-C(5)               | 121.3(2) | N(1)-Fe(1)-N(2) <sup>i</sup>                    | 90.14(6)  |
| C(16)-C(11)-C(5)               | 119.9(2) | N(1) <sup>i</sup> -Fe(1)-N(2) <sup>i</sup>      | 89.92(6)  |
| C(11)-C(12)-C(13)              | 120.6(2) | N(3)-Fe(1)-N(2) <sup>i</sup>                    | 88.84(4)  |
| C(11)-C(12)-H(12)              | 119.7    | N(1)-Fe(1)-N(2)                                 | 89.92(6)  |
| C(13)-C(12)-H(12)              | 119.7    | N(1) <sup>i</sup> -Fe(1)-N(2)                   | 90.14(6)  |
| C(14)-C(13)-C(12)              | 120.3(2) | N(3)-Fe(1)-N(2)                                 | 88.84(4)  |
| C(14)-C(13)-H(13)              | 119.9    | N(2) <sup>i</sup> -Fe(1)-N(2)                   | 177.69(8) |
| C(12)-C(13)-H(13)              | 119.9    | N(1)-Fe(1)-N(4)                                 | 88.46(4)  |
| C(15)-C(14)-C(13)              | 119.6(2) | N(1) <sup>i</sup> -Fe(1)-N(4)                   | 88.46(4)  |
| C(15)-C(14)-H(14)              | 120.2    | N(3)-Fe(1)-N(4)                                 | 180.0     |
| C(13)-C(14)-H(14)              | 120.2    | N(2) <sup>i</sup> -Fe(1)-N(4)                   | 91.16(4)  |
| C(14)-C(15)-C(16)              | 120.4(2) | N(2)-Fe(1)-N(4)                                 | 91.16(4)  |
| C(14)-C(15)-H(15)              | 119.8    | C(1)-N(1)-C(4)                                  | 105.2(1)  |
| C(16)-C(15)-H(15)              | 119.8    | C(1)-N(1)-Fe(1)                                 | 127.3(1)  |

|                   |          |                                |          |
|-------------------|----------|--------------------------------|----------|
| C(15)-C(16)-C(11) | 120.4(2) | C(4)-N(1)-Fe(1)                | 127.4(1) |
| C(15)-C(16)-H(16) | 119.8    | C(9)-N(2)-C(6)                 | 104.6(1) |
| C(11)-C(16)-H(16) | 119.8    | C(9)-N(2)-Fe(1)                | 127.6(1) |
| C(18)-C(17)-C(22) | 118.2(2) | C(6)-N(2)-Fe(1)                | 127.7(1) |
| C(18)-C(17)-C(10) | 120.9(2) | C(23) <sup>i</sup> -N(3)-C(23) | 116.3(2) |
| C(22)-C(17)-C(10) | 120.7(2) | C(23) <sup>i</sup> -N(3)-Fe(1) | 121.9(1) |
| C(19)-C(18)-C(17) | 120.7(2) | C(23)-N(3)-Fe(1)               | 121.8(1) |
| C(19)-C(18)-H(18) | 119.6    | C(28)-N(4)-C(28) <sup>i</sup>  | 116.7(2) |
| C(17)-C(18)-H(18) | 119.6    | C(28)-N(4)-Fe(1)               | 121.6(1) |
| C(20)-C(19)-C(18) | 120.4(2) | C(28) <sup>i</sup> -N(4)-Fe(1) | 121.6(1) |
| C(20)-C(19)-H(19) | 119.8    |                                |          |

Symmetry codes: i)  $-x, y, -z+1/2$ ; ii)  $x, y-1, z$ ; iii)  $-x, y-1, -z+1/2$ ; iv)  $x, y+1, z$

**Table S2.** Fractional atomic coordinates ( $\times 10^4$ ) and equivalent thermal factors ( $\times 10^3$ ) for  $[\text{FeTPPbipy}]^+$ .

| Atoms | X        | Y       | Z        | $U_{\text{eq}}, \text{\AA}^2$ |
|-------|----------|---------|----------|-------------------------------|
| C(1)  | 956(1)   | 2790(2) | 1392(1)  | 12(1)                         |
| C(2)  | 1004(1)  | 2907(2) | 590(1)   | 16(1)                         |
| C(3)  | 427(1)   | 2880(2) | 217(1)   | 15(1)                         |
| C(4)  | 6(1)     | 2760(2) | 782(1)   | 11(1)                         |
| C(5)  | -636(1)  | 2652(2) | 611(1)   | 12(1)                         |
| C(6)  | -1041(1) | 2573(2) | 1163(1)  | 11(1)                         |
| C(7)  | -1706(1) | 2531(2) | 996(1)   | 16(1)                         |
| C(8)  | -1934(1) | 2579(2) | 1669(1)  | 16(1)                         |
| C(9)  | -1413(1) | 2649(2) | 2259(1)  | 12(1)                         |
| C(10) | 1464(1)  | 2751(2) | 1960(1)  | 13(1)                         |
| C(11) | -909(1)  | 2649(2) | -216(1)  | 13(1)                         |
| C(12) | -1123(1) | 1597(2) | -580(1)  | 20(1)                         |
| C(13) | -1361(1) | 1604(2) | -1351(1) | 25(1)                         |
| C(14) | -1383(1) | 2663(2) | -1764(1) | 25(1)                         |

|              |          |          |          |       |
|--------------|----------|----------|----------|-------|
| <b>C(15)</b> | -1173(1) | 3718(2)  | -1406(1) | 23(1) |
| <b>C(16)</b> | -933(1)  | 3715(2)  | -637(1)  | 19(1) |
| <b>C(17)</b> | 2097(1)  | 2858(2)  | 1709(1)  | 14(1) |
| <b>C(18)</b> | 2350(1)  | 1914(2)  | 1333(1)  | 23(1) |
| <b>C(19)</b> | 2907(1)  | 2057(2)  | 1037(1)  | 27(1) |
| <b>C(20)</b> | 3217(1)  | 3135(2)  | 1110(1)  | 25(1) |
| <b>C(21)</b> | 2984(1)  | 4081(2)  | 1501(1)  | 27(1) |
| <b>C(22)</b> | 2427(1)  | 3934(2)  | 1800(1)  | 21(1) |
| <b>C(23)</b> | -109(1)  | 233(2)   | 1847(1)  | 13(1) |
| <b>C(24)</b> | -109(1)  | -1006(2) | 1826(1)  | 14(1) |
| <b>C(25)</b> | 0        | -1664(2) | 2500     | 11(1) |
| <b>C(26)</b> | 0        | -2995(2) | 2500     | 12(1) |
| <b>C(27)</b> | 364(1)   | 6348(2)  | 3059(1)  | 12(1) |
| <b>C(28)</b> | 347(1)   | 5105(2)  | 3049(1)  | 12(1) |
| <b>Fe(1)</b> | 0        | 2665(1)  | 2500     | 9(1)  |
| <b>N(1)</b>  | 338(1)   | 2713(1)  | 1507(1)  | 9(1)  |
| <b>N(2)</b>  | -863(1)  | 2629(1)  | 1947(1)  | 9(1)  |
| <b>N(3)</b>  | 0        | 875(2)   | 2500     | 11(1) |
| <b>N(4)</b>  | 0        | 4468(2)  | 2500     | 10(1) |

$$U_{eq} = 1/3[U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{13}aca^*c^* \cos\beta]$$

**Table S3.** Anisotropic displacement parameters ( $\text{Å}^2 \times 10^3$ ) for  $([\text{FeTPPBipy}])_n$ .

| Atoms       | U11   | U22   | U33   | U23  | U13  | U12   |
|-------------|-------|-------|-------|------|------|-------|
| <b>C(1)</b> | 14(1) | 9(1)  | 12(1) | 1(1) | 5(1) | 1(1)  |
| <b>C(2)</b> | 17(1) | 19(1) | 14(1) | 1(1) | 7(1) | -2(1) |
| <b>C(3)</b> | 20(1) | 16(1) | 9(1)  | 0(1) | 3(1) | -1(1) |
| <b>C(4)</b> | 15(1) | 6(1)  | 12(1) | 0(1) | 3(1) | -1(1) |
| <b>C(5)</b> | 17(1) | 6(1)  | 12(1) | 0(1) | 2(1) | -1(1) |

|              |       |       |       |        |       |       |
|--------------|-------|-------|-------|--------|-------|-------|
| <b>C(6)</b>  | 14(1) | 7(1)  | 12(1) | 0(1)   | 1(1)  | 0(1)  |
| <b>C(7)</b>  | 16(1) | 19(1) | 13(1) | 0(1)   | -3(1) | -2(1) |
| <b>C(8)</b>  | 12(1) | 22(1) | 16(1) | 1(1)   | 3(1)  | -2(1) |
| <b>C(9)</b>  | 14(1) | 7(1)  | 14(1) | 1(1)   | 2(1)  | 0(1)  |
| <b>C(10)</b> | 14(1) | 11(1) | 15(1) | -1(1)  | 5(1)  | 0(1)  |
| <b>C(11)</b> | 8(1)  | 20(1) | 13(1) | -1(1)  | 5(1)  | 0(1)  |
| <b>C(12)</b> | 21(1) | 22(1) | 17(1) | 0(1)   | 2(1)  | -4(1) |
| <b>C(13)</b> | 21(1) | 36(1) | 18(1) | -10(1) | 1(1)  | -9(1) |
| <b>C(14)</b> | 14(1) | 50(2) | 10(1) | 1(1)   | 1(1)  | -1(1) |
| <b>C(15)</b> | 18(1) | 36(1) | 17(1) | 9(1)   | 4(1)  | 4(1)  |
| <b>C(16)</b> | 20(1) | 21(1) | 16(1) | 1(1)   | 3(1)  | 2(1)  |
| <b>C(17)</b> | 13(1) | 23(1) | 8(1)  | 3(1)   | -1(1) | 1(1)  |
| <b>C(18)</b> | 19(1) | 26(1) | 24(1) | -5(1)  | 7(1)  | -3(1) |
| <b>C(19)</b> | 20(1) | 39(2) | 24(1) | -5(1)  | 9(1)  | 5(1)  |
| <b>C(20)</b> | 14(1) | 42(1) | 20(1) | 8(1)   | 7(1)  | 2(1)  |
| <b>C(21)</b> | 17(1) | 28(1) | 36(1) | 10(1)  | 4(1)  | -3(1) |
| <b>C(22)</b> | 17(1) | 22(1) | 25(1) | 3(1)   | 4(1)  | 2(1)  |
| <b>C(23)</b> | 19(1) | 11(1) | 10(1) | 1(1)   | 2(1)  | 0(1)  |
| <b>C(24)</b> | 20(1) | 12(1) | 10(1) | -3(1)  | 2(1)  | -1(1) |
| <b>C(25)</b> | 9(1)  | 7(1)  | 17(1) | 0      | 3(1)  | 0     |
| <b>C(26)</b> | 12(1) | 13(2) | 11(1) | 0      | 8(1)  | 0     |
| <b>C(27)</b> | 16(1) | 10(1) | 10(1) | -4(1)  | 3(1)  | 0(1)  |
| <b>C(28)</b> | 15(1) | 11(1) | 10(1) | 1(1)   | 2(1)  | 2(1)  |
| <b>Fe(1)</b> | 11(1) | 7(1)  | 9(1)  | 0      | 2(1)  | 0     |
| <b>N(1)</b>  | 11(1) | 7(1)  | 10(1) | -1(1)  | 1(1)  | -1(1) |
| <b>N(2)</b>  | 13(1) | 6(1)  | 9(1)  | 1(1)   | 2(1)  | 0(1)  |
| <b>N(3)</b>  | 11(1) | 10(1) | 11(1) | 0      | 2(1)  | 0     |
| <b>N(4)</b>  | 13(1) | 10(1) | 10(1) | 0      | 6(1)  | 0     |

$$U_{ij} = \exp(-2\pi^2[h^2(a^*)^2 U_{11} + k^2(b^*)^2 U_{22} + \dots + 2hka^*b^* U_{12}])$$



**Table S4.** Fractional atomic coordinates ( $\times 10^4$ ) and isotropic thermal factors ( $\times 10^3$ ) of hydrogen atoms for  $([\text{Fe}(\text{TPP})\text{bipy}]^n)_n$ .

| Atoms | X     | Y     | Z     | $U_{\text{iso}}, \text{\AA}^2$ |
|-------|-------|-------|-------|--------------------------------|
| H(2)  | 1378  | 2989  | 366   | 19                             |
| H(3)  | 315   | 2931  | -322  | 18                             |
| H(7)  | -1940 | 2479  | 504   | 20                             |
| H(8)  | -2360 | 2569  | 1741  | 19                             |
| H(12) | -1108 | 862   | -300  | 24                             |
| H(13) | -1508 | 876   | -1595 | 30                             |
| H(14) | -1543 | 2666  | -2291 | 30                             |
| H(15) | -1192 | 4451  | -1688 | 28                             |
| H(16) | -785  | 4445  | -397  | 23                             |
| H(18) | 2139  | 1162  | 1278  | 27                             |
| H(19) | 3075  | 1402  | 782   | 32                             |
| H(20) | 3593  | 3235  | 892   | 30                             |
| H(21) | 3204  | 4823  | 1565  | 32                             |
| H(22) | 2268  | 4581  | 2071  | 26                             |
| H(23) | -191  | 659   | 1377  | 16                             |
| H(24) | -184  | -1413 | 1348  | 17                             |
| H(27) | 627   | 6756  | 3450  | 14                             |
| H(28) | 591   | 4677  | 3447  | 14                             |

$$U_{\text{iso}} = \exp[-8\pi^2 U(\sin\theta/\lambda)^2]$$

## *CAPÍTULO III*

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### **Compuestos**



*“Thermal stability and crystallochemical analysis for Co<sup>II</sup>-based coordination polymers with TPP and TPSS porphyrins”*

*CrystEngComm. 2013, 15 (20), 4181-4188*

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**Resumen**

*En este trabajo se muestra la síntesis y caracterización de dos nuevos compuestos de CoP-bipy, donde P es TPP para el compuesto 1 (TPP= meso-tetrafenilporfirina) y TPPS para el compuesto 2 (TPPS= meso-tetrasulfonatofenilporfirina), y bipy es la 4,4'-bipiridina. El compuesto 1 consiste en polímeros 1D estabilizados en una red donde, porfirinas aisladas quedan inmovilizadas mediante un extenso sistema de enlaces  $\pi$ - $\pi$ . Por otra parte, hasta el alcance de la bibliografía, el compuesto 2 es el primero con Co-TPPS encontrado. Éste también consiste en polímeros 1D, pero en este caso están formados por la alternancia de dos centros metálicos diferentes. Este polímero sin precedentes cristaliza formando cavidades donde se localizan las moléculas de agua de cristalización. La fortaleza del sistema de enlaces de hidrógeno y una topología basada en redes interpenetradas son las responsables de la elevada estabilidad térmica que presenta el compuesto 2. Adicionalmente, el estudio cristaloquímico realizado para las porfirinas de Co<sup>II</sup> encontradas en la bibliografía, confirma la existencia de una correlación entre el grado de distorsión de tipo ruffled del macrociclo porfirínico y varias distancias y ángulos diedros seleccionados.*

**Abstract**

*Two new CoP-bipy compounds have been synthesised and characterised, where P is TPP for compound 1 (TPP= meso-tetraphenylporphyrin) and TPPS for compound 2 (TPPS= meso-tetraphenylporphine-tetrasulfonic acid), and bipy is 4,4'-bipyridine. Compound 1 consists of 1D polymers packed in a network where isolated porphyrin units are immobilized by an extended  $\pi$ -bond system. On the other hand, as we are aware, compound 2 is the first Co-TPPS compound in literature. It also consists of 1D polymers that are formed by the alternation of two distinct metal centres. These unprecedented polymers are packed forming cavities where crystallization molecules of water are located. The robustness of the hydrogen bond system and a topology based on interpenetrated nets are responsible for the high thermal stability of compound 2. Additionally, a crystallochemical study confirmed the existence of a correlation between the degree of ruffled distortion of the porphyrin macrocycle and some selected dihedral angles and distances for Co<sup>II</sup> porphyrins in literature.*

## Laburpena

*Bi CoP-bipy konposatu berri sintetizatu eta karakterizatu dira, non P=TPP baita 1 konposatuan (TPP= meso-tetrafenil porfirina), P=TPPS baita 2 konposatuan (TPPS= meso-tetrafenil porfirina gatz tetrasodikoaren azido tetrasulfonikoa) eta bipy=4,4'-bipiridina baita. 1 konposatua dimentsio bakarreko polimeroen bidez eratutako sare bat da. Sare honetan, porfirinaren unitate isolatuak daude ainguratuak  $\pi$  motako elkarrekintzei esker. Bestalde, 2 konposatua, guk dakiguneraino, Co-TPPS konbinaketan oinarritutako lehenengo konposatua da. Hau ere dimentsio bakarreko polimeroa da, eta kristalografikoki ezberdinak diren bi atomo metaliko txandakatuta agertzen dira horretan. Aurrekaririk gabeko polimero hauek paketatzean hainbat hutsune sortzen dira, eta horietan ur kristaltze-molekulak daude. 2 konposatuaren egonkortasun termikoa oso altua da, eta hori azaltzeko kontuan izan behar da bai hidrogeno loturen sistema trinkoa eta baita ere elkar zeharkatutako sareen topologia. Gainera, bibliografian aurkitutako  $\text{Co}^{\text{II}}$  porfirinak kristalokimikoki analizatu dira, eta ondorioztatu da ruffled motako distortsioaren maila harremanetan dagoela aukeratutako hainbat angelu diedro zein distantziekin.*

### III.1. Introduction

Metal-Organic Frameworks (MOFs) have emerged as an interesting class of porous solids that can be constructed from a variety of molecular complexes<sup>1-4</sup> and explored for a range of applications in gas storage,<sup>5,6</sup> compound separation,<sup>7,8</sup> chemical sensing,<sup>9-12</sup> nonlinear optics,<sup>13</sup> biomedical imaging,<sup>14-16</sup> drug delivery,<sup>17-19</sup> and heterogeneous catalysis.<sup>20-23</sup> On the other hand, it is worth mentioning that facile

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chemical modification, high thermal and chemical stability allow metalloporphyrins to be remarkable catalysts for numerous reactions.<sup>24-26</sup> In particular, porous metalloporphyrinic frameworks have great potential to act as heterogeneous catalysts with shape- and size-selectivity. In this sense, Suslick *et al.* must be cited as they first demonstrated the catalytic property of a porphyrinic MOF.<sup>27</sup>

In this context, metalloporphyrins are remarkable precursors in supramolecular chemistry, giving rise to a variety of materials because of their unique chemical, physical and biological properties.<sup>28-30</sup> In order to enhance the connectivity between metal centres, a secondary ligand can be used in porphyrinic systems. In fact, the Choe group demonstrated that a range of metalloporphyrinic frameworks can be generated by using porphyrin metallo-ligands and bipyridyl molecules.<sup>31</sup> However, it must be pointed out that research on the applications of porphyrinic MOFs is just in the initial stage.<sup>32</sup>

Taking into account the above mentioned aspects, this work was focused on the preparation of metalloporphyrin-based coordination networks. Our strategy also includes the use of different bipyridyl ligands, as they have been observed to produce a variety of porphyrin-based MOFs.<sup>33</sup> In addition, we have a large experience with these

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connectors.<sup>34-39</sup> In this context, we have been exploring CoP-bipy combinations where P is either TPP (TPP=*meso*-tetraphenylporphyrin) or TPPS (TPPS=*meso*-tetraphenylporphine-tetrasulfonic acid), and bipy is 4,4'-bipyridine. It is worth mentioning that just four crystalline compounds have been reported for TPPS-based metalloporphyrins,<sup>40-42</sup> and none of them has cobalt. On the other hand, even if the number of TPP-based metalloporphyrins is higher, the number of Co-based compounds exhibiting extended networks is also significantly low.<sup>43,44</sup>

Thus, the work herein presented consists of the synthesis and characterisation of two new CoP-bipy compounds where the metal ion is Co<sup>II</sup> and P is TPP for compound **1**, and TPPS for compound **2**. Both of them have been structurally characterised by single-crystal X-ray diffraction (XRD) and IR and EPR spectroscopies. Thermal stability has been explored by means of thermogravimetry (TGA), and X-ray thermodiffractometry (TDX).

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Distortion of macrocycles is biologically relevant<sup>45</sup> and influences physical<sup>46,47</sup> and chemical<sup>48,49</sup> properties of porphyrin complexes. In this sense, we have also analysed the out-of-plane displacement of porphyrin backbones for both compounds. In order to contextualise this analysis the study was extended to all the Co<sup>II</sup> porphyrins found in the CSD. A similar study has been previously reported for Co<sup>III</sup> porphyrins.<sup>50</sup>

## III.2. Experimental Section

### III.2.1. General

All solvents and chemicals were used as received from reliable commercial sources. The reagents *meso*-tetraphenyl-porphine cobalt (II) (CoTPP), *meso*-tetraphenyl porphine-4,4',4'',4'''-tetrasulfonic acid tetrasodium salt (TPPS), Cobalt (II) nitrate hexahydrate 99% and 4,4'-bipyridine 98% (bipy) and the solvent *N,N*-dimethylformamide (DMF) 99.8% were purchased from Sigma-Aldrich Co.; ethanol absolute was purchased from Panreac.

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<sup>50</sup> Iimura, Y.; Sakurai, T.; Yamamoto, K., *Bull. Chem. Soc. Jpn.* **1988**, *61*, 821-826.

### III.2.2. Synthesis of compounds 1 and 2

**[CoTPP(bipy)]·([CoTPP])<sub>0.22</sub>·(TPP)<sub>0.78</sub> (1).** *meso*-tetraphenyl-porphine cobalt (II) (6.7 mg, 0.01 mmol), 4,4'-bipyridine (9.4 mg, 0.06 mmol) and 40  $\mu$ L NaOH (3M) were added to a mixture of DMF (3 mL) and ethanol (1 mL) in a small capped vial, sonicated to ensure homogeneity and heated to 120  $^{\circ}$ C for 48 h, following by slow cooling to room temperature at 2  $^{\circ}$ C/h, yielding diffraction quality prismatic dark blue crystals. (Found: C, 79.5(3); H, 4.60(4); N, 10.00(2). Calc. for C<sub>98</sub>H<sub>65.56</sub>Co<sub>1.22</sub>N<sub>10</sub>: C, 80.89; H, 4.54; N, 9.62).  $\nu_{\max}/\text{cm}^{-1}$  3052 and 3028 (C(sp<sup>2</sup>)H), 1596-1441 (CC), 1349 (CN), 1210 and 1069 (bipy), 1000 (CoTPP) and 795-700 (CH) (Figure S1, Supplementary Information).

**[CoTPPS<sub>0.5</sub>(bipy)(H<sub>2</sub>O)<sub>2</sub>]-6H<sub>2</sub>O (2).** *meso*-tetraphenyl porphine-4,4',4'',4'''-tetrasulfonic acid (10.2 mg, 0.01 mmol) and Co(NO<sub>3</sub>)·6H<sub>2</sub>O (5.8 mg, 0.02 mmol) were dissolved in distilled water (10 mL) and the solution was stirred for 30 min. Then, 4,4'-bipyridine (9.4 mg, 0.06 mmol) was dissolved in hot (70  $^{\circ}$ C) distilled water (5 mL) and added to the mixture in a 100 mL CEM EasyPrep microwave vessel. The mixture was heated by microwave under autogenous pressure at 160  $^{\circ}$ C for 2 h, and then cooled naturally to room temperature, yielding diffraction quality prismatic dark blue crystals. (Found: C, 45.8(3); H, 4.47(3); N, 6.89(2); S, 7.80(3). Calc. for C<sub>32</sub>H<sub>36</sub>CoN<sub>4</sub>O<sub>14</sub>S<sub>2</sub>: C, 46.66; H, 4.40; N, 6.80; S, 7.79).  $\nu_{\max}/\text{cm}^{-1}$  3397 (OH), 1624-1410 (CC), 1394 and 1174 (SO), 1349 (CN), 1208 and 1076 (bipy), 1000 (CoTPPS) and 863-744 (CH) (Figure S2, Supplementary Information).

### III.2.3. Single-crystal X-ray diffraction

Prismatic dark blue single-crystals of compounds **1** and **2** with dimensions given in Table 1 were selected under polarizing microscope and mounted on MicroMounts. Single-crystal X-ray diffraction data were collected at 100 K on a SuperNova single source diffractometer with Cu-K $\alpha$  radiation ( $\lambda=1.54184$   $\text{\AA}$ ). The

Lorentz-polarization and absorption corrections were made with the diffractometer software, taking into account the size and shape of the crystals.<sup>51</sup>

The structure of compound **1** was solved in the monoclinic  $C2/c$  space group with SIR-92<sup>52</sup> program, which allowed us to obtain the position of Co atoms, as well as nitrogen and some of the carbon atoms of the TPP and bipyridine molecules. The refinement of the crystal structure was performed by full matrix least-squares based on  $F^2$ , using the SHELXL-97 program<sup>53</sup> obtaining the remaining carbon atoms. Anisotropic thermal parameters were used for all non-hydrogen atoms (Figure S3, Supplementary Information). All the hydrogen atoms, connected to the aromatic rings (C-H 0.95 Å) were fixed geometrically and were refined using a riding model with common isotropic displacements.

Compound **2** was solved in the tetragonal  $I 4_1/a$  space group with Superflip<sup>54</sup> program, which allowed us to obtain the position of Co atoms, as well as nitrogen and some of the carbon atoms of the TPPS and bipyridine molecules. The refinement of the crystal structure was performed by full matrix least-squares based on  $F^2$ , using the SHELXL-97 program<sup>53</sup> obtaining the remaining carbon atoms and the oxygen and sulphur atoms of the porphyrin and water molecules. Anisotropic thermal parameters were used for all non-hydrogen atoms (Figure S4, Supplementary Information). All the hydrogen atoms, connected to the aromatic rings (C-H 0.95 Å) were fixed geometrically and were refined using a riding model with common isotropic displacements. The position of the hydrogen atoms bonded to the coordination water molecule were fixed using DFIX and DANG instructions in the refinement to adjust the O-H distance to 0.82 Å and the H-O-H angle to 112°, respectively. All of the

<sup>51</sup> Yinghua, W., *J. Appl. Crystallogr.* **1987**, *20*, 258-259.

<sup>52</sup> Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A., *J. Appl. Crystallogr.* **1993**, *26*, 343-350.

<sup>53</sup> Sheldrick, G. M., *Acta Crystallogr., Sect. A Found. Crystallogr.* **2008**, *A64*, 112-122.

<sup>54</sup> Palatinus, L.; Chapuis, G., *J. Appl. Crystallogr.* **2007**, *40*, 786-790.

crystallization molecules of water for compound **2** were disordered in two groups of three water molecules. The hydrogen atoms of these water molecules were not considered due to the lack of density in the residual density map. Crystal data for both structures are listed in Table 1. Atomic coordinates, anisotropic thermal parameters and hydrogen atom coordinates for both compounds are given in Tables S1-S6, Supplementary Information.

**Table 1.** Details of the crystal data, structural resolution and refinement procedure for **1** and **2**.

|  | <b>1</b>  | <b>2</b>  |
|--|---|---|
| Formula  | C <sub>98</sub> H <sub>65.56</sub> Co <sub>1.22</sub> N <sub>10</sub> | C <sub>32</sub> H <sub>36</sub> CoN <sub>4</sub> O <sub>14</sub> S <sub>2</sub> |
| FW, g·mol <sup>-1</sup>                          | 1455.06   | 811.62  |
| <i>a</i> , Å                                     | 25.1252(4)  | 17.9776(2)  |
| <i>b</i> , Å                                     | 11.7811(2)  |   |
| <i>c</i> , Å                                     | 23.9790(4)  | 22.3567(3)  |
| $\beta$ , deg                                    | 93.5960(10)   |   |
| <i>V</i> , Å <sup>3</sup>                        | 7083.9(2)   | 7225.55(15)   |
| Space group                                      | <i>C</i> 2/ <i>c</i>  | <i>I</i> 4 <sub>1</sub> / <i>a</i>  |
| <i>Z</i>   | 4   | 8   |
| $\rho_{obs}$ , $\rho_{cal}$ , g·cm <sup>-3</sup> | 1.371(6), 1.364   | 1.488(4), 1.492   |
| <i>F</i> (000)                                   | 3026  | 3320  |
| $\mu$ , mm <sup>-1</sup>                         | 2.761   | 5.445   |
| Crystal size, mm                                 | 0.26 x 0.19 x 0.06  | 0.12 x 0.12 x 0.021   |
| Absorption correction                            | Multi-scan  | Analytical  |
| Radiation, $\lambda$ , Å                         | 1.54184   | 1.54184   |
| Temperature, K                                   | 100(2)  | 100(2)  |
| Reflections collected, unique                    | 25120, 7352<br>( <i>R</i> <sub>int</sub> = 0.0405)                    | 23662, 3774<br>( <i>R</i> <sub>int</sub> = 0.096)                               |
| Limiting indices                                 | -29 ≤ <i>h</i> ≤ 31<br>-14 ≤ <i>k</i> ≤ 14<br>-30 ≤ <i>l</i> ≤ 23     | -22 ≤ <i>h</i> ≤ 22<br>-14 ≤ <i>k</i> ≤ 22<br>-28 ≤ <i>l</i> ≤ 25               |
| Refinement method                                | Full-matrix least-squares on <i>F</i> <sup>2</sup>                    | Full-matrix least-squares on <i>F</i> <sup>2</sup>                              |
| R1,  | R1 = 0.0416,  | R1 = 0.0669,  |
| wR2 [ <i>I</i> > 2σ( <i>I</i> )]                 | wR2 = 0.1095  | wR2 = 0.1845  |
| R1,  | R1 = 0.0438,  | R1 = 0.0856,  |
| wR2 (all data)                                   | wR2 = 0.1115  | wR2 = 0.2040  |
| Goodness of fit on <i>F</i> <sup>2</sup>         | 1.056   | 1.051   |
| Parameters /restraints                           | 504 / 0   | 274 / 3   |

#### III.2.4. Physicochemical characterisation techniques

The IR spectra were collected on a JASCO FT/IR-6100 spectrometer at room temperature at the range of 4000-400  $\text{cm}^{-1}$ , in KBr pellets (1% of the sample). C, H, N and S elemental analyses were measured using a Euro EA 3000 elemental analyser. Electron paramagnetic resonance (EPR) spectra were measured with a Bruker ESP-300 spectrometer operating at X band and equipped with a nitrogen and helium cryostat.

The thermal analyses were carried out in air atmosphere using a NETZSCH STA 449F3 instrument for compound **1** and SDT 2960 Simultaneous DSC-TGA TA Instruments for **2**. A crucible containing approximately 10 mg of sample was heated at 5  $^{\circ}\text{C min}^{-1}$  in the temperature range 30-600  $^{\circ}\text{C}$ . The thermal behaviour was also studied using X-ray thermodiffraction. A Bruker D8 Advance Vantec diffractometer (Cu-K $\alpha$  radiation) equipped with a variable-temperature stage (Anton Paar HTK2000) with a Pt sample holder was used in the experiments. The powder patterns were recorded in  $2\theta$  steps of 0.0333 $^{\circ}$  in the 5-38 $^{\circ}$  range, counting for 0.8 s per step and increasing the temperature at 10  $^{\circ}\text{C}\cdot\text{min}^{-1}$  from room temperature to 550  $^{\circ}\text{C}$ .

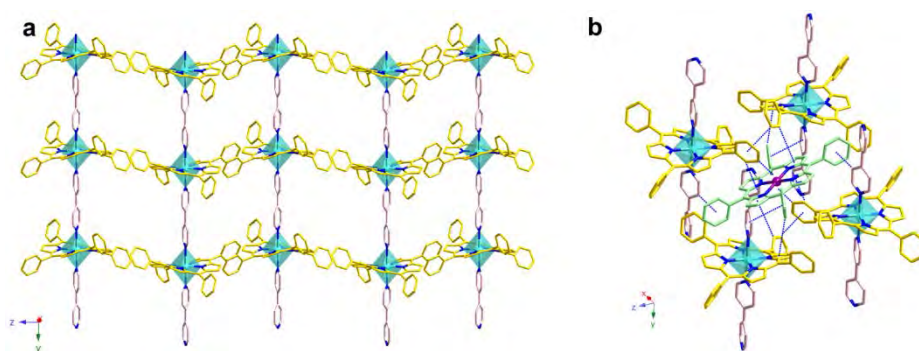
### III.3. Results and Discussion

#### III.3.1. Crystal structures

The crystal structure for compound **1** consists of 1D polymers extending along the [010] direction where CoTPP units are axially bonded to two bipy ligands resulting in a porous coordination network (Figure 1a).

Additionally, isolated TPP units are located in the voids (3.4 x 3.4  $\text{Å}$ ) generated by the packing of these chains, due to an intricate system of  $\pi$  bonds (Figure 1b). 78% of these isolated porphyrin units are metal-free, while the remaining 22% are metallated, in accordance with the chemical formula obtained by single crystal X-ray

diffraction and elemental analysis  $[\text{CoTPP}(\text{bipy})] \cdot ([\text{CoTPP}])_{0.22} \cdot (\text{TPP})_{0.78}$ . Therefore, most of the CoTPP units have lost the metal ion during the synthesis. Each isolated TPP unit is surrounded by four 1D polymers producing a dense network. As observed, there are multiple *edge-to-face*  $\pi$ -interactions stabilising the crystal structure. These are robust interactions (distances from 2.45 Å to 2.97 Å, and angles from 73.96° to 89.16°), that are accompanied by weaker *face-to-face* ones (centroid-to-centroid distance 4.04 Å, and angle is 10.77°). (Table S7, Supplementary Information).



**Figure 1.** View of the structure for compound **1** where the packing of the 1D polymers is observed (a). Detail of the structure showing a single crystallization molecule of TPP connected to four 1D polymers through the  $\pi$ -bonding system (dashed lines) (b). Color codes: Co(1) (TPP chain): turquoise, Co(2) (isolated TPP): purple, N: blue, C (TPP chain): yellow, C (isolated TPP): green, C (bipy): pink. H atoms have been omitted for clarity.

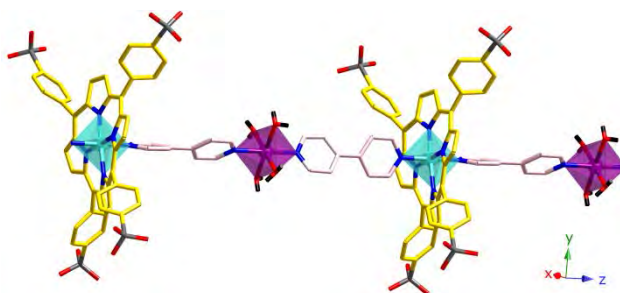
The bond distances and angles for Co(1) and Co(2) coordination spheres in compound **1** and **2** lie among typical values (Table S8, Supplementary Information). It must be pointed out that Co(1) atom lies on a two-fold axis, and Co(2) on an inversion centre. As a result, both polyhedra are close to ideal.

Topological features for compound **1** have been analysed by means of the

TOPOS software.<sup>55</sup> The simplification shows the connectivity due to the  $\pi$ -bond system (Figure S5, Supplementary Information). Due to the nature of these intermolecular interactions no classification of the topology is provided.

Considering the isolated molecules of porphyrin in compound **1**, it was tested in order to explore its capability as a catalyst for the oxidation of water. Unfortunately, these tests demonstrated no catalytic activity (Figure S6, Supplementary Information).

Compound **2** has the chemical formula  $[\text{CoTPPS}_{0.5}(\text{bipy})(\text{H}_2\text{O})_2] \cdot 6\text{H}_2\text{O}$ , and exhibits some similarities with compound **1**. In fact, compound **2** also consists of 1D polymers where CoTPPS units are axially bonded to bipy ligands. However, the extension of the 1D polymers for compound **2** consists of the link between alternating metal centres along the [001] direction. These links take place through the bipy ligands according to the bipy-CoTPPS-bipy-Co( $\text{H}_2\text{O}$ )<sub>4</sub>- fashion. From a crystallographic point of view, this is an unprecedented bimetallic chain for this type of systems (Figure 2).



**Figure 2.** Detail of the structure for compound **2** showing the extension of the 1D polymers. Color codes: Co(1) (TPPS): turquoise, Co(2): purple, N: blue, C (TPPS): yellow, C (bipy): pink, O: red, S: grey. H atoms have been omitted for clarity.

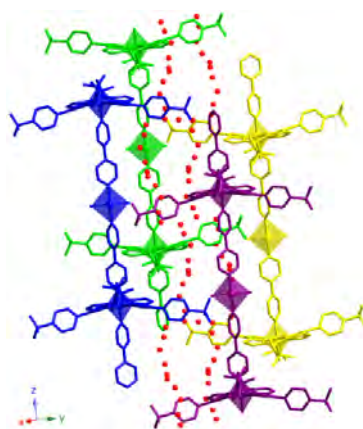
Compound **2** exhibits a robust system of hydrogen bonds that reinforce the stability of the framework (Table S9, Supplementary Information). This way, each

<sup>55</sup> Blatov, V. A., *IUCr CompComm Newsl.* **2006**, 4 <http://www.topos.ssu.samara.ru>.



chain is surrounded by another four, and multiple hydrogen bonds are formed between the coordination molecules of water and the terminal  $\text{SO}_3$  groups of the TPPS molecules.

As observed in Figure 3, the relative position of the chains give rise to cavities where crystallisation molecules of water are located. These molecules form a disordered chain along the [001] direction, reinforcing the robustness of the hydrogen-bond system.

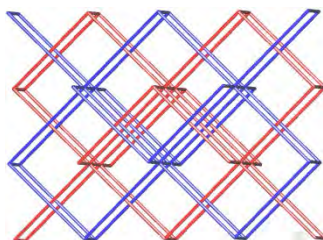


**Figure 3.** Detail of the structure showing relative position of the chains for compound **2**. Crystallisation molecules of water are shown in red. H atoms have been omitted for clarity.

As mentioned below, compound **2** exhibits a remarkable thermal stability that is related to its crystal structure. Therefore, topological features for compound **2** were analysed by means of the TOPOS software,<sup>56</sup> revealing a pcu  $\alpha$ -Po primitive cubic 6/4/c1 sqc1 net.<sup>57</sup> As shown in Figure 4 this consists on a two-fold interpenetrated 6-c nets framework (Point Symbol=  $4^{12}.6^3$  and Vertex Symbol= 4.4.4.4.4.4.4.4.4.4.4.4.\*.\*.\*).

<sup>56</sup> Blatov, V. A., *IUCr CompComm Newsl.* **2006**, 4 <http://www.topos.ssu.samara.ru>.

<sup>57</sup> Chung, H.; Barron, P. M.; Novotny, R. W.; Son, H.-T.; Hu, C.; Choe, W., *Cryst. Growth Des.* **2009**, 9, 3327-3332.



**Figure 4.** Topology of the two-fold interpenetrated net for compound **2**.

### III.3.2. Distortion of coordination spheres for metal centers

Distortion of coordination polyhedra as been evaluated according to Avnir<sup>58,59</sup> method, based on the continuous symmetry measures (CSM), by means of SHAPE program,<sup>60</sup> and the results can be seen on Table 2.

**Table 2** Distortion values calculated for the hexacoordinated and tetraordinated spheres (calculated by means of SHAPE software).

|                   | Hexacordinate | $S(O_h)$    | $S(D_{3h})$ |
|-------------------|---------------|-------------|-------------|
| Compound <b>1</b> | Co(1)         | 0.68        | 17.25       |
| Compound <b>2</b> | Co(1)         | 0.07        | 15.76       |
|                   | Co(2)         | 0.02        | 16.33       |
|                   | Tetraordinate | $S(D_{4h})$ | $S(T_d)$    |
| Compound <b>1</b> | Co(2)         | 0.004       | 33.34       |

*S*= symmetry

The projection of the as-calculated values on the distortion diagram<sup>61</sup> can be seen in Figure 5. As observed, for compound **1** there is a weak Jahn-Teller distortion for Co(1), in fact the axial Co(1)–N(3) distance is longer than equatorial ones, and the

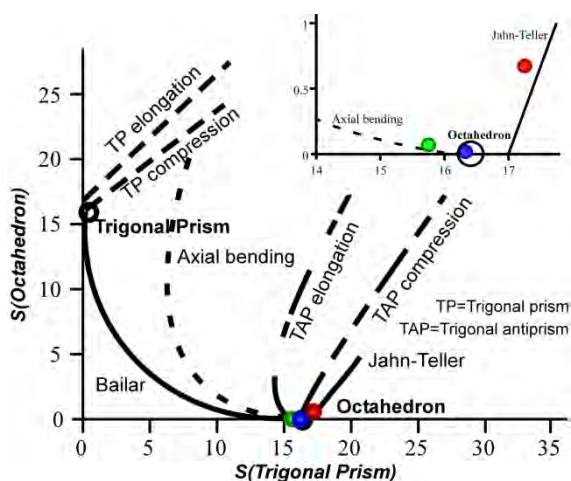
<sup>58</sup> Zabrodsky, H.; Peleg, S.; Avnir, D., *J. Am. Chem. Soc.* **1992**, *114*, 7843-7851.

<sup>59</sup> Pinsky, M.; Avnir, D., *Inorg. Chem.* **1998**, *37*, 5575-5582.

<sup>60</sup> Llunel, M.; Casanova, D.; Cirera, J.; Bofill, J. M.; Alemany, P.; Álvarez, S.; Pinsky, M.; Yatonir, D. *SHAPE v1.1a*, "Program for Continuous Shape Measure Calculations of Polyhedral  $X_n$  and  $ML_n$  Fragments", *SHAPE v1.1a*, 2003.

<sup>61</sup> Álvarez, S.; Alemany, P.; Casanova, D.; Cirera, J.; Llunel, M.; Avnir, D., *Coord. Chem. Rev.* **2005**, *249*, 1693-1708.

*cis* and *trans* N-Co(1)-N angles go from 89.79(6) to 90.21(6)°, and from 179.68(8) to 180.00(4)°, respectively. For the tetracoordinated cobalt centre, the Co(2)-N distances go from 2.032(1) to 2.055(1) Å and the *cis* and *trans* angles are close to 90 and 180°, respectively. Thus, the distortion values indicate that the coordination geometry is close to an ideal square planar sphere for Co(2). All bond distances and angles are reported in Table S10, Supplementary Information.



**Figure 5.** Distortion modes diagram of an octahedron. In the upper right is a zoom of the distortion for compound **1** Co(1) octahedra (red circle), and for compound **2** Co(1) (green circle) and Co(2) (blue circle) spheres.

Distortion of coordination polyhedra was also evaluated for compound **2** (Table 2), and the results indicate that, while Co(2) octahedra is nearly ideal, the Co(1) sphere exhibits weak axial bending distortion. Both metal atoms lie on a four-fold inversion, where all Co(1)-N are equal (1.963(3) Å). Obviously, the same occurs for Co(2)-O equatorial distances (2.092(3) Å). On the other hand, *cis* and *trans* angles for Co(1) go from 88.20(7) to 91.80(7)° and for 176.4(1) to 180.0°, respectively. For Co(2) octahedra these angles vary from 89.24(6) to 90.76(6)° and from 178.05(1) to 180.0° resulting in a perfect octahedra (Figure 2). All bond distances and angles are reported

in Table S11, Supplementary Information.

### III.3.3. Distortion of porphyrins

Distortion of macrocycles has been also analysed for compounds **1** and **2**. There are six types of distortion defined for non-planar porphyrins: saddle (*sad*), ruffle (*ruf*), dome (*dom*), wavy(x) (*wav(x)*), wavy(y) (*wav(y)*) and propeller (*pro*).

The out-of-plane distortion of the porphyrin macrocycles was analysed by the normal-coordinate structural decomposition method developed by Shelnut *et al.* (NSD).<sup>62,63</sup>

For compound **1** the results indicate a ruffle-type distortion (*ruf*, B<sub>1u</sub>) for the coordinated porphyrin, and a slight wavy one (*wav(y)*, [E<sub>g(y)</sub>]) for the crystallisation complex. The contribution of the ruffled porphyrin (1.4813) to the total displacements is 82.5%, while the wavy porphyrin shows a principal contribution of *wav(y)* (-0.1910) mixed with a small amount of the *wav(x)* (0.0884) deformation. The contribution of each type is 68.3% and 31.6%, respectively.

In compound **2** the principal distortion corresponds to the ruffled type (1.3203 and 67.8% of the total displacements), but the saddle-type (*sad*, B<sub>2u</sub>) is also observed (0.6261 and 32.2%).

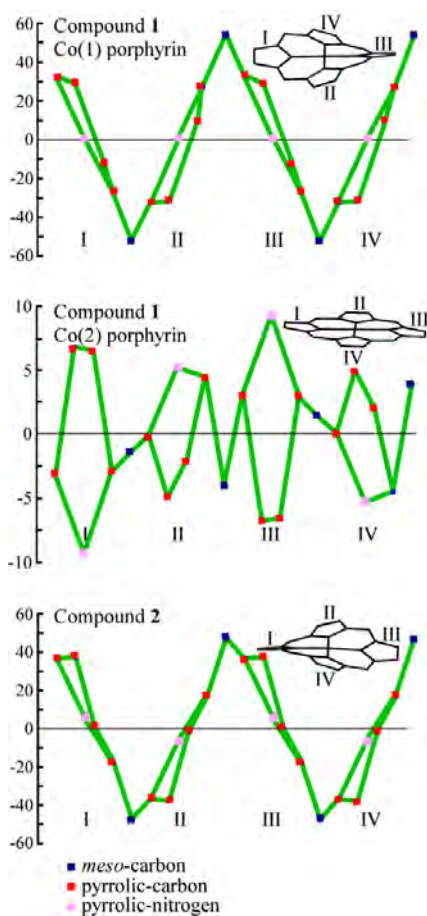
As shown in Figure 6, for compounds **1** and **2**, the occurrence of ruffled-type deformation for the polymeric porphyrins, means that the *meso* carbons (non-pyrrolic carbon atoms) are alternatively above and below the porphyrin mean plane, while the pyrrole nitrogens are placed on the plane. In compound **2**, the saddle contribution is observed by the distribution of the pyrrole rings. In fact, an opposing pair of pyrrole

<sup>62</sup> Jentzen, W.; Song, X.-Z.; Shelnut, J. A., *J. Phys. Chem. B* **1997**, *101*, 1684-1699.

<sup>63</sup> Jentzen, W.; Ma, J.-G.; Shelnut, J. A., *Biophys. J.* **1998**, *74*, 753-763.

rings tilts up, while the other pair tilts down.

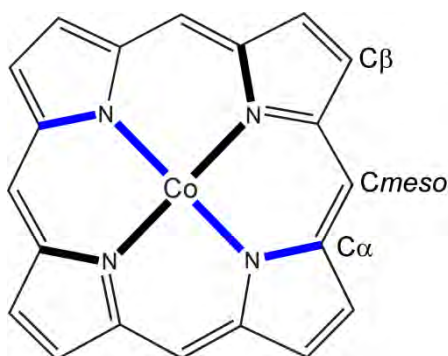
The crystallisation molecule of porphyrin in compound **1** shows the two opposing pyrrole rings tilted up and down with respect to the porphyrin mean plane, indicating a wavy distortion. However, due to the small out-of-plane displacement this porphyrin is nearly planar.



**Figure 6.** Out-of-plane displacements (in units of 0.01 Å) of the porphyrin core atoms from the mean porphyrin plane (of 24 atom). Co(1) coordinated porphyrin and Co(2) crystallization porphyrin.

There are some studies in literature exploring the relationships between the ruffle distortion and some structural parameters. However, they are referred to  $\text{Co}^{\text{III}}$  compounds.

Cullen *et al.*<sup>64</sup> proposed the use of the *cis* and *trans*  $\text{C}_\alpha\text{-N-N-C}_\alpha$  torsion angles as a quantitative measure of ruffling. Inspired by this work, we have analysed the *cis* and *trans*  $\text{C}_\alpha\text{-N-N-C}_\alpha$  dihedral angles ( $\text{C}_\alpha$  is a pyrrolic carbon atom bonded to a nitrogen atom) (Figure 7) for our ruffled porphyrins.



**Figure 7.** Porphyrin macrocycle and nomenclature used. *Cis*  $\text{C}_\alpha\text{-N-N-C}_\alpha$  dihedral angle is shown in bold and *trans*  $\text{C}_\alpha\text{-N-N-C}_\alpha$  dihedral angle in blue.

The average value for *cis* dihedral angles of **1** ( $31.6^\circ(1)$ ) is higher than for **2** ( $28.4^\circ(1)$ ). This is in accordance for the conclusions for  $\text{Co}^{\text{III}}$  compounds, since the higher the *cis* dihedral angle is, the higher ruffle distortion is expected.

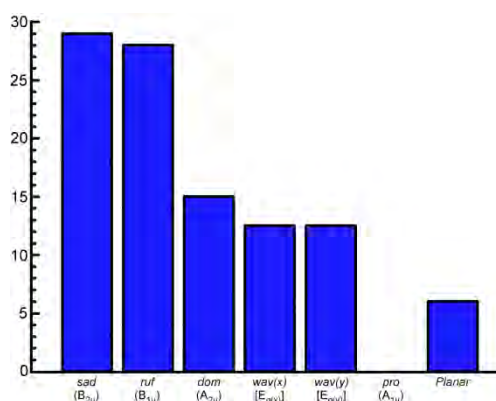
The average value for *trans* dihedral angles are  $145.7^\circ(1)$ , for **1**; and  $151.6^\circ(1)$ , for **2**. Distortion values found for compounds **1** and **2** are expected to produce values of ( $145^\circ(1)$ ) and ( $148.7^\circ(1)$ ), respectively, for  $\text{Co}^{\text{III}}$  compounds.<sup>64</sup> As observed, the prediction for **2** is not that good, probably due to the occurrence of saddle distortion.

<sup>64</sup> Cullen, D. L.; Desai, L. V.; Shelnut, J. A.; Zimmer, M., *Struct. Chem.* **2001**, *12*, 127-136.

Therefore, conclusions by Cullen *et al.* seem to be effective for Co<sup>II</sup> compounds.

On the other hand, Iimura *et al.*<sup>65</sup> found a linear relationship between the ruffled distortion and the Co-N<sub>p</sub> distances (N<sub>p</sub> are the pyrrolic nitrogen atoms) for Co<sup>III</sup> porphyrins.

Due to the lack of correlation studies for Co<sup>II</sup> compounds, we have performed a search on the Cambridge Structural Database (CSD)<sup>66</sup> v5.33 to find all the Co porphyrin complexes. This research indicated the existence of 221 cobalt-based metalloporphyrins, 124 of them containing Co<sup>III</sup>. We have analysed the remaining 97 Co<sup>II</sup> compounds (Figure 8).



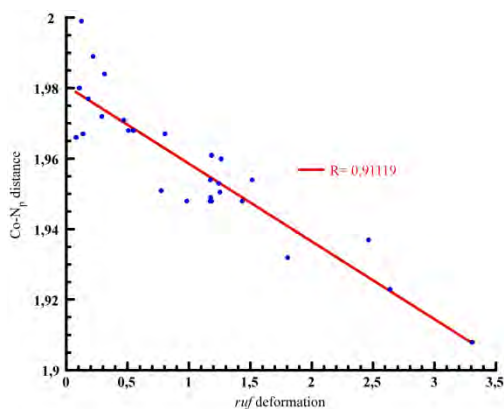
**Figure 8.** Out-of-plane distortion distribution for Co<sup>II</sup> porphyrins.

As observed in Figure 8 the most typical distortion for Co<sup>II</sup> porphyrins are *sad* and *ruf*. As the main distortion observed for compounds **1** and **2** is the ruffle-type, we have performed a study with the 28 compounds found in literature exhibiting the same type of distortion, to establish the relationship with Co-N<sub>p</sub> distances (N<sub>p</sub> are the pyrrolic nitrogen atoms).

<sup>65</sup> Iimura, Y.; Sakurai, T.; Yamamoto, K., *Bull. Chem. Soc. Jpn.* **1988**, *61*, 821-826.

<sup>66</sup> Allen, F. H., *Acta Crystallogr., Sect. B Struct. Sci.* **2002**, *B58*, 380-388.

Figure 9 shows a linear relationship between ruffle distortion and Co-N<sub>p</sub> distances for Co<sup>II</sup> compounds. As observed for Co<sup>III</sup> compounds, we have also found that the presence of low ruffled distortion leads to longer Co-N<sub>p</sub> distances. In particular, for compounds **1** and **2**, with distances of 1.964(1) and 1.963(3) Å, respectively, a value of 1 is expected for the distortion. Therefore, real values (1.4813 and 1.3203, respectively) lie among the typical ones.



**Figure 9.** Plot of the average Co<sup>II</sup>-N<sub>p</sub> distance vs. the amount of ruffled (B<sub>1u</sub>) deformation.

#### III.3.4. Electronic paramagnetic resonance

Electron paramagnetic resonance (EPR) measurements were performed for compounds **1** (Figure S7, Supplementary Information) and **2**. (Figure S8, Supplementary Information). The simulation of the EPR spectrum for both compounds gave us the following set of values:  $g_{\perp}=2.232$  and  $g_{\parallel}=2.030$  for compound **1**, and  $g_1=5.7$ ,  $g_2=3.95$  and  $g_3=3.42$  for **2**. The main signal for compound **1** is due to Co(1) atom, and it is in accordance with an octahedral low-spin Co<sup>II</sup> ion. For compound **2**, the signal is the sum of the contribution of both metal centres. The observed value for the sum of the three orthogonal  $g$  values ( $g_s=13.07$ ) is in excellent agreement with the



theoretical value near 13 proposed by Abragam and Pryce<sup>67</sup>, in accordance with an octahedral high-spin Co<sup>II</sup>.

### III.3.5. Thermogravimetry

The thermogravimetric decomposition curve for compound **1** shows a two-stage mass loss. The first step occurs between 230-290 °C with 10.6 % weight loss, and the second one from 410 °C to 500 °C with 81 % weight loss. These values have been attributed to bipyridine (10.7 %) and to isolated and polymeric TPP units (84.3 %) (Figure S9, Supplementary Information). The residue has been identified by X-ray powder diffraction as Co<sub>3</sub>O<sub>4</sub> [S.G. *Fd-3m*, a = 8.11 Å].<sup>68</sup>

Compound **2** shows a two-stage mass loss. The first of them starting at RT and finishing at about 370 °C, is a smooth decrease of mass, and has been assigned to the removal of the crystallisation molecules of water (10 % weight loss). On the contrary, the second one (approximately 81 %) is abrupt, and corresponds to the removal of the coordination molecules of water, and both organic ligands (Figure S10, Supplementary Information). The calcination product was also Co<sub>3</sub>O<sub>4</sub>.

### III.3.6. X-ray thermodiffractometry (TDX)

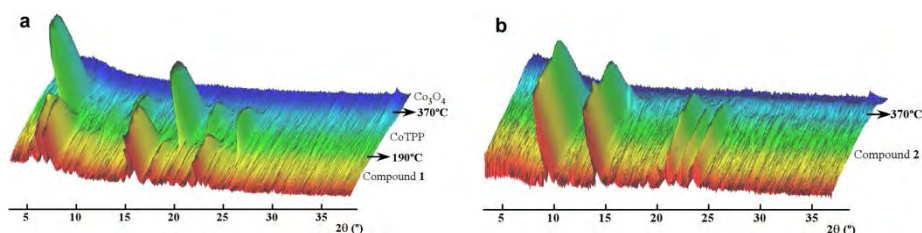
The thermal behaviour of compounds **1** and **2** was also studied by X-ray thermodiffractometry (Figure 10a). Compound **1** is thermally stable until 190 °C. At higher temperatures, the removal of the bipy ligands provokes the formation of CoTPP<sup>69</sup> (Figure S11, Supplementary Information). This phase is stable until 370 °C, temperature at which Co<sub>3</sub>O<sub>4</sub> is formed.

<sup>67</sup> Abragam, A.; Pryce, M. H. L., *Proc. R. Soc. London, Ser. A* **1951**, *206*, 173-191.

<sup>68</sup> Hanawalt, J. D.; Rinn, H. W.; Frevel, L. K., *Ind. Eng. Chem., Anal. Ed.* **1938**, *10*, 457-512.

<sup>69</sup> Nascimento, B. F. O.; Pineiro, M.; Rocha Gonsalves, A. M. d. A.; Silva, M. R.; Beja, A. M.; Paixao, J. A., *J. Porphyrins Phthalocyanines* **2007**, *11*, 77-84.

The thermal stability of compound **2** is remarkably high. In fact, TDX analysis reveals that it is stable up to 370°C (Figure 10b). Above this temperature an amorphous phase is formed. The robust hydrogen bond network and the fact that the structure is two-fold interpenetrated are thought to be responsible for the high thermal stability of this compound.



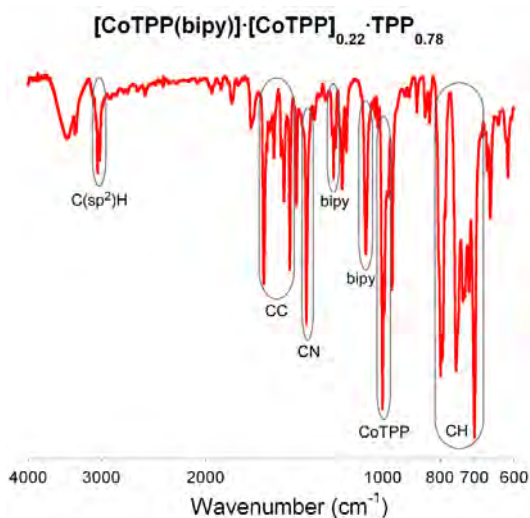
**Figure 10.** Thermodiffractogram of compound **1** (a) and for compound **2** (b).

### III.4. Conclusions

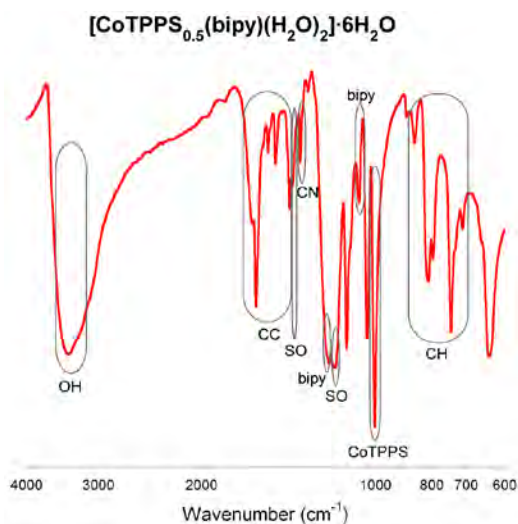
TPP and TPPS porphyrins produce 1D polymers with  $\text{Co}^{\text{II}}$ . Stabilisation of the network for Co-TPP compound takes place through crystallisation metalloporphyrins and molecules of porphyrin, *via* an extended  $\pi$ -bond system. For Co-TPPS compound an extended hydrogen bond system along with an intricate topology yields the first compound with this metalloporphyrin combination. In addition, this Co-TPPS compound exhibits an unprecedented bimetallic chain and shows a remarkably high thermal stability.

For both compounds, the distortion of the porphyrins has been observed to be ruffled-type. A crystallochemical study confirmed the existence of a correlation between the degree of ruffled distortion and  $\text{Co-N}_p$  distances not only for both compounds, but also for all the  $\text{Co}^{\text{II}}$  porphyrins found in the CSD.

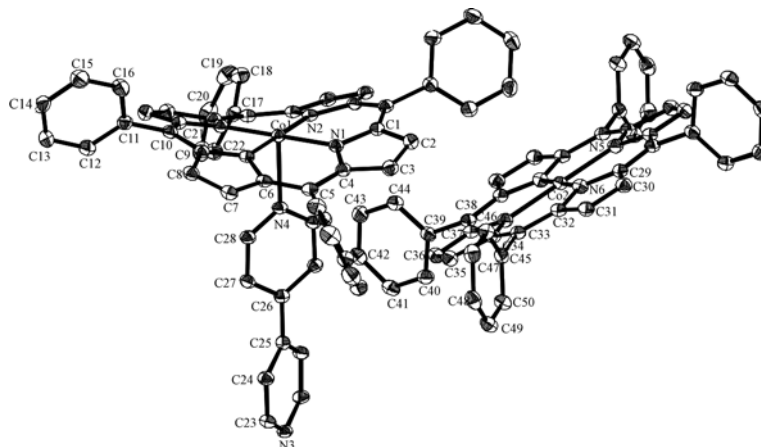
## Supplementary Information



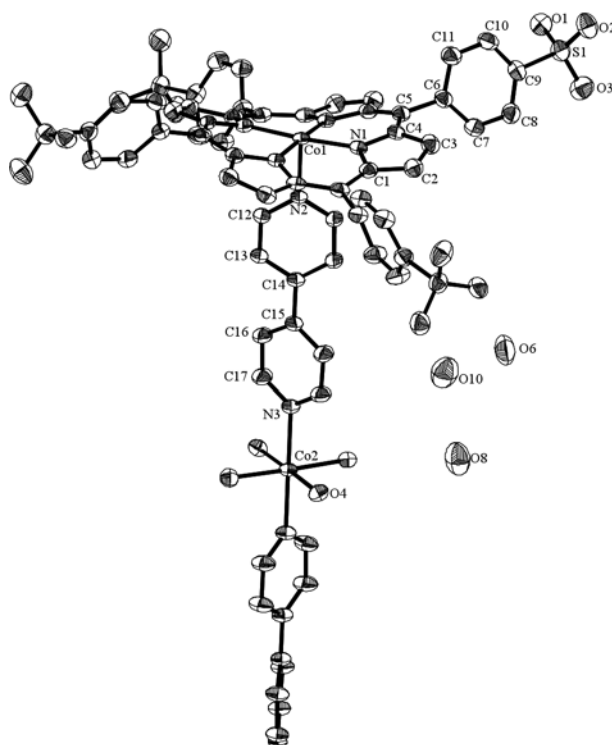
**Figure S1.** IR spectra for compound 1. The following bands ( $\text{cm}^{-1}$ ) are marked: 3052 and 3028 ( $\text{C}(\text{sp}^2)\text{H}$ ), 1596-1441 (CC), 1349 (CN), 1210 and 1069 (bipy), 1000 (CoTPP) and 795-700 (CH).



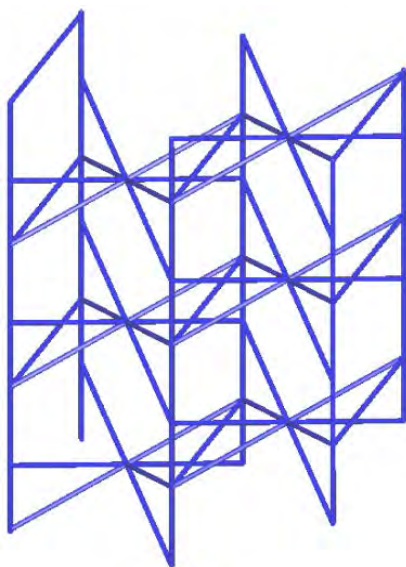
**Figure S2.** IR spectra for compound 2. The following bands ( $\text{cm}^{-1}$ ) are marked: 3397 (OH), 1624-1410 (CC), 1394 and 1174 (SO), 1349 (CN), 1208 and 1076 (bipy), 1000 (CoTPPS) and 863-744 (CH).



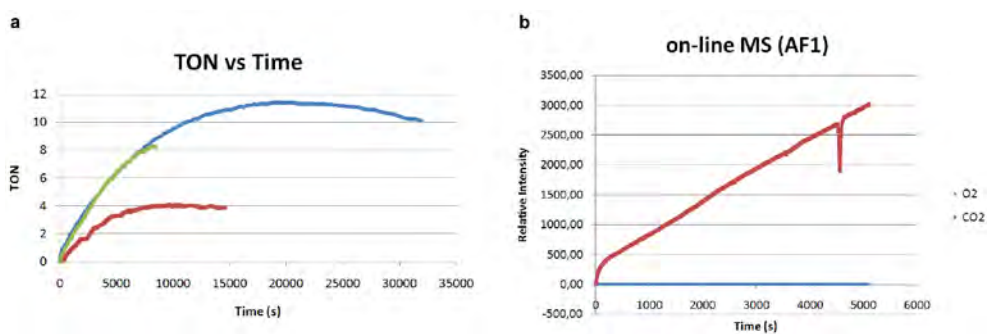
**Figure S3.** Thermal ellipsoid plot (50% of probability) for compound **1**.



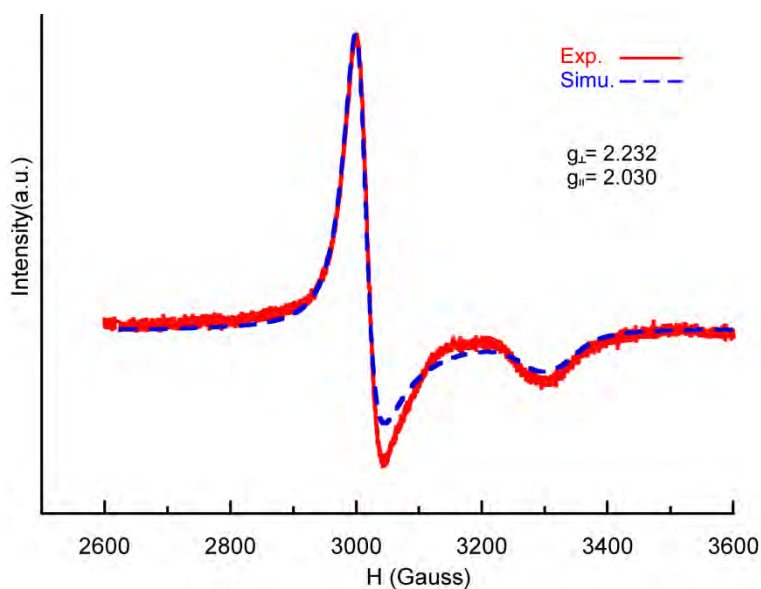
**Figure S4.** Thermal ellipsoid plot (50% of probability) for compound **2**.



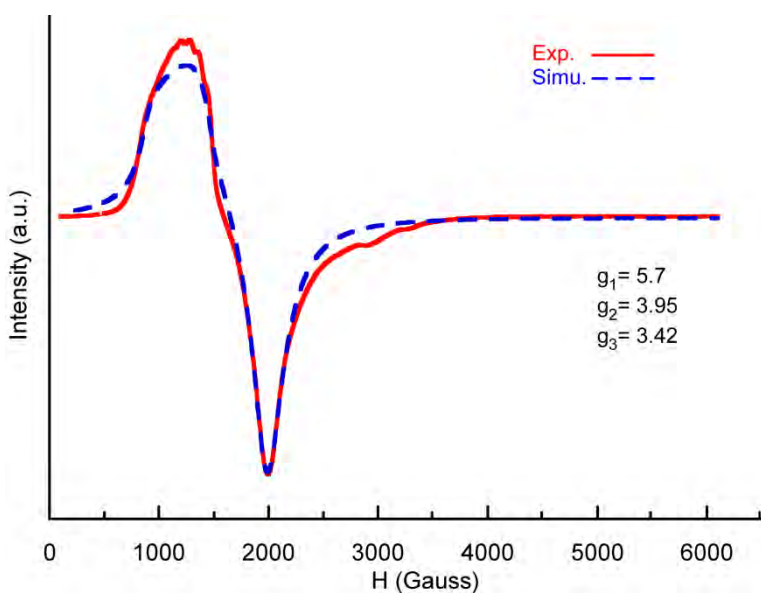
**Figure S5.** Topology of the net for compound **1**.



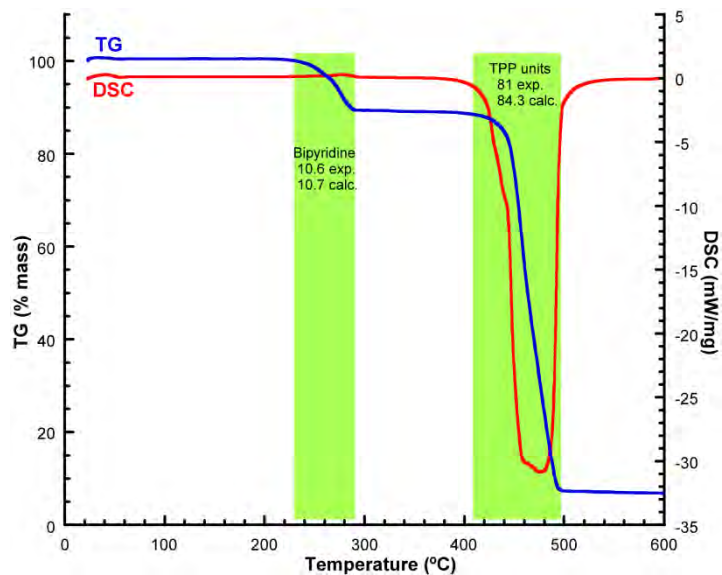
**Figure S6.** Three gas generation manometry experiments (a) and on-line-MS study (b) for compound **1**.



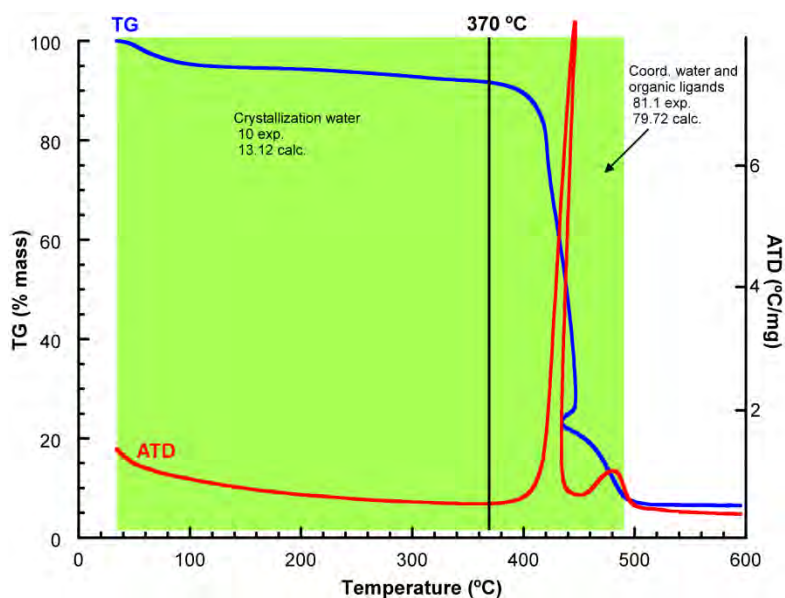
**Figure S7.** X-band EPR spectrum at 5° K for compound **1**. Red line corresponds to the observed spectra and blue dashed line to the simulated one.



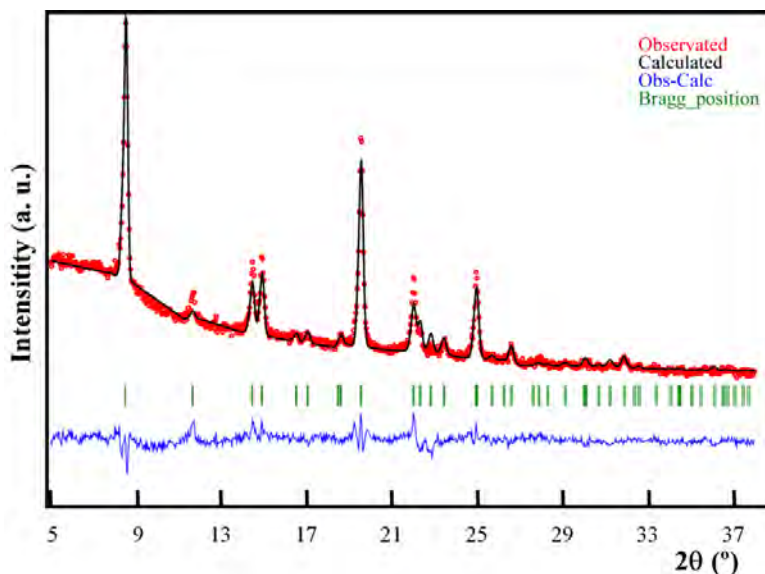
**Figure S8.** X-band EPR spectrum at 5° K for compound **2**. Red line corresponds to the observed spectra and blue dashed line to the simulated one.



**Figure S9.** Thermogravimetric analysis for compound **1**. Green ranges show the weight loss intervals.



**Figure S10.** Thermogravimetric analysis for compound **2**. Green ranges show the weight loss intervals.



**Figure S11.** Observed (red), calculated (black) and difference (blue) X-ray powder diffraction patterns for CoTPP.

**Table S1.** Fractional atomic coordinates ( $\times 10^4$ ) and equivalent thermal factors ( $\times 10^3$ ) for compound **1**.

| Atoms | X       | Y       | Z       | $U_{eq}, \text{\AA}^2$ |
|-------|---------|---------|---------|------------------------|
| C(1)  | 4305(1) | 4398(1) | 1441(1) | 20(1)                  |
| C(2)  | 4327(1) | 4363(1) | 840(1)  | 23(1)                  |
| C(3)  | 4826(1) | 4015(1) | 735(1)  | 23(1)                  |
| C(4)  | 5119(1) | 3889(1) | 1270(1) | 20(1)                  |
| C(5)  | 5667(1) | 3676(1) | 1336(1) | 20(1)                  |
| C(6)  | 5965(1) | 3844(1) | 1839(1) | 19(1)                  |
| C(7)  | 6539(1) | 3850(1) | 1907(1) | 22(1)                  |
| C(8)  | 6674(1) | 4204(1) | 2434(1) | 21(1)                  |
| C(9)  | 6183(1) | 4351(1) | 2706(1) | 18(1)                  |
| C(10) | 6157(1) | 4580(1) | 3277(1) | 20(1)                  |
| C(11) | 6656(1) | 4997(1) | 3583(1) | 21(1)                  |
| C(12) | 6966(1) | 4326(2) | 3952(1) | 28(1)                  |
| C(13) | 7440(1) | 4745(2) | 4207(1) | 30(1)                  |
| C(14) | 7610(1) | 5835(2) | 4100(1) | 28(1)                  |
| C(15) | 7303(1) | 6508(2) | 3736(1) | 32(1)                  |
| C(16) | 6829(1) | 6100(2) | 3479(1) | 28(1)                  |
| C(17) | 5945(1) | 3307(1) | 832(1)  | 21(1)                  |
| C(18) | 6325(1) | 3981(2) | 593(1)  | 27(1)                  |



|       |         |          |         |       |
|-------|---------|----------|---------|-------|
| C(19) | 6579(1) | 3596(2)  | 127(1)  | 33(1) |
| C(20) | 6455(1) | 2540(2)  | -101(1) | 33(1) |
| C(21) | 6075(1) | 1864(2)  | 131(1)  | 31(1) |
| C(22) | 5821(1) | 2247(2)  | 595(1)  | 26(1) |
| C(23) | 5431(1) | 6731(1)  | 2382(1) | 21(1) |
| C(24) | 5451(1) | 7913(1)  | 2378(1) | 21(1) |
| C(25) | 5000    | 8530(2)  | 2500    | 19(1) |
| C(26) | 5000    | -212(2)  | 2500    | 19(1) |
| C(27) | 4539(1) | 405(1)   | 2349(1) | 21(1) |
| C(28) | 4560(1) | 1587(1)  | 2351(1) | 21(1) |
| C(29) | 7373(1) | 3488(1)  | 6166(1) | 20(1) |
| C(30) | 6992(1) | 3545(1)  | 6587(1) | 22(1) |
| C(31) | 6529(1) | 3085(1)  | 6368(1) | 22(1) |
| C(32) | 6612(1) | 2729(1)  | 5808(1) | 20(1) |
| C(33) | 6236(1) | 2182(1)  | 5453(1) | 21(1) |
| C(34) | 6332(1) | 1755(1)  | 4923(1) | 21(1) |
| C(35) | 5926(1) | 1236(1)  | 4549(1) | 24(1) |
| C(36) | 6167(1) | 935(1)   | 4082(1) | 24(1) |
| C(37) | 6721(1) | 1270(1)  | 4169(1) | 21(1) |
| C(38) | 7097(1) | 1139(1)  | 3769(1) | 21(1) |
| C(39) | 6941(1) | 597(1)   | 3217(1) | 20(1) |
| C(40) | 6931(1) | -584(1)  | 3162(1) | 24(1) |
| C(41) | 6848(1) | -1082(2) | 2639(1) | 25(1) |
| C(42) | 6765(1) | -414(2)  | 2165(1) | 25(1) |
| C(43) | 6755(1) | 760(2)   | 2218(1) | 26(1) |
| C(44) | 6848(1) | 1261(1)  | 2742(1) | 24(1) |
| C(45) | 5697(1) | 2003(1)  | 5672(1) | 21(1) |
| C(46) | 5351(1) | 2914(2)  | 5746(1) | 24(1) |
| C(47) | 4857(1) | 2731(2)  | 5964(1) | 28(1) |
| C(48) | 4706(1) | 1646(2)  | 6111(1) | 27(1) |
| C(49) | 5048(1) | 740(2)   | 6045(1) | 26(1) |
| C(50) | 5541(1) | 916(1)   | 5825(1) | 24(1) |
| Co(1) | 5000    | 4129(1)  | 2500    | 16(1) |
| Co(2) | 7500    | 2500     | 5000    | 17(1) |
| N(1)  | 4794(1) | 4125(1)  | 1695(1) | 18(1) |
| N(2)  | 5756(1) | 4126(1)  | 2338(1) | 18(1) |
| N(3)  | 5000    | 6130(2)  | 2500    | 19(1) |
| N(4)  | 5000    | 2181(2)  | 2500    | 19(1) |
| N(5)  | 6813(1) | 1771(1)  | 4683(1) | 21(1) |
| N(6)  | 7129(1) | 2993(1)  | 5700(1) | 21(1) |

$$U_{eq} = 1/3[U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{13}aca^*c^* \cos\beta]$$

**Table S2.** Anisotropic displacement parameters ( $\text{Å}^2 \times 10^3$ ) for compound **1**.

| Atoms        | U11   | U22   | U33   | U23   | U13   | U12   |
|--------------|-------|-------|-------|-------|-------|-------|
| <b>C(1)</b>  | 22(1) | 14(1) | 22(1) | 1(1)  | -1(1) | 0(1)  |
| <b>C(2)</b>  | 24(1) | 23(1) | 23(1) | 1(1)  | -1(1) | 1(1)  |
| <b>C(3)</b>  | 24(1) | 22(1) | 23(1) | -1(1) | 2(1)  | 1(1)  |
| <b>C(4)</b>  | 22(1) | 16(1) | 21(1) | -1(1) | 2(1)  | 0(1)  |
| <b>C(5)</b>  | 23(1) | 14(1) | 23(1) | 1(1)  | 3(1)  | -1(1) |
| <b>C(6)</b>  | 20(1) | 13(1) | 24(1) | 1(1)  | 4(1)  | 0(1)  |
| <b>C(7)</b>  | 21(1) | 18(1) | 26(1) | 2(1)  | 3(1)  | 2(1)  |
| <b>C(8)</b>  | 20(1) | 17(1) | 27(1) | 3(1)  | 1(1)  | 0(1)  |
| <b>C(9)</b>  | 16(1) | 13(1) | 26(1) | 2(1)  | 0(1)  | -1(1) |
| <b>C(10)</b> | 21(1) | 14(1) | 25(1) | 1(1)  | 0(1)  | 1(1)  |
| <b>C(11)</b> | 19(1) | 19(1) | 23(1) | -2(1) | 1(1)  | 0(1)  |
| <b>C(12)</b> | 29(1) | 21(1) | 32(1) | 0(1)  | -4(1) | 1(1)  |
| <b>C(13)</b> | 26(1) | 30(1) | 34(1) | -3(1) | -8(1) | 6(1)  |
| <b>C(14)</b> | 20(1) | 30(1) | 34(1) | -9(1) | -2(1) | -2(1) |
| <b>C(15)</b> | 26(1) | 25(1) | 45(1) | 1(1)  | -1(1) | -7(1) |
| <b>C(16)</b> | 24(1) | 23(1) | 36(1) | 6(1)  | -3(1) | -3(1) |
| <b>C(17)</b> | 21(1) | 21(1) | 22(1) | 1(1)  | 1(1)  | 4(1)  |
| <b>C(18)</b> | 29(1) | 25(1) | 29(1) | 3(1)  | 6(1)  | 1(1)  |
| <b>C(19)</b> | 33(1) | 37(1) | 32(1) | 8(1)  | 11(1) | 5(1)  |
| <b>C(20)</b> | 36(1) | 42(1) | 23(1) | 1(1)  | 7(1)  | 14(1) |
| <b>C(21)</b> | 36(1) | 30(1) | 27(1) | -6(1) | -1(1) | 9(1)  |
| <b>C(22)</b> | 26(1) | 24(1) | 26(1) | -1(1) | 1(1)  | 2(1)  |
| <b>C(23)</b> | 20(1) | 16(1) | 26(1) | 1(1)  | 4(1)  | 2(1)  |
| <b>C(24)</b> | 21(1) | 16(1) | 26(1) | 1(1)  | 2(1)  | -2(1) |
| <b>C(25)</b> | 20(1) | 18(1) | 19(1) | 0     | 0(1)  | 0     |
| <b>C(26)</b> | 22(1) | 16(1) | 19(1) | 0     | 3(1)  | 0     |
| <b>C(27)</b> | 20(1) | 16(1) | 26(1) | -1(1) | -1(1) | -2(1) |
| <b>C(28)</b> | 21(1) | 15(1) | 28(1) | 0(1)  | 0(1)  | 1(1)  |
| <b>C(29)</b> | 23(1) | 16(1) | 22(1) | 0(1)  | 1(1)  | 0(1)  |
| <b>C(30)</b> | 24(1) | 18(1) | 24(1) | -2(1) | 2(1)  | 1(1)  |
| <b>C(31)</b> | 23(1) | 19(1) | 23(1) | -1(1) | 2(1)  | 0(1)  |
| <b>C(32)</b> | 22(1) | 15(1) | 23(1) | 0(1)  | 3(1)  | -1(1) |
| <b>C(33)</b> | 23(1) | 16(1) | 24(1) | 2(1)  | 2(1)  | -1(1) |
| <b>C(34)</b> | 22(1) | 17(1) | 23(1) | 2(1)  | 1(1)  | -2(1) |
| <b>C(35)</b> | 22(1) | 24(1) | 26(1) | 0(1)  | 2(1)  | -2(1) |
| <b>C(36)</b> | 23(1) | 23(1) | 24(1) | -1(1) | 0(1)  | -3(1) |
| <b>C(37)</b> | 23(1) | 16(1) | 23(1) | 1(1)  | 0(1)  | -2(1) |
| <b>C(38)</b> | 23(1) | 15(1) | 24(1) | 0(1)  | 1(1)  | 0(1)  |
| <b>C(39)</b> | 18(1) | 19(1) | 24(1) | -1(1) | 2(1)  | -2(1) |
| <b>C(40)</b> | 25(1) | 19(1) | 27(1) | 1(1)  | 2(1)  | -1(1) |
| <b>C(41)</b> | 25(1) | 19(1) | 32(1) | -5(1) | 3(1)  | -2(1) |

|       |       |       |       |       |      |       |
|-------|-------|-------|-------|-------|------|-------|
| C(42) | 24(1) | 28(1) | 24(1) | -6(1) | 3(1) | -4(1) |
| C(43) | 26(1) | 27(1) | 24(1) | 1(1)  | 1(1) | -2(1) |
| C(44) | 25(1) | 20(1) | 26(1) | 0(1)  | 0(1) | -1(1) |
| C(45) | 21(1) | 23(1) | 19(1) | -2(1) | 0(1) | -2(1) |
| C(46) | 24(1) | 24(1) | 26(1) | 1(1)  | 0(1) | -1(1) |
| C(47) | 23(1) | 31(1) | 29(1) | -3(1) | 1(1) | 4(1)  |
| C(48) | 21(1) | 36(1) | 25(1) | -3(1) | 3(1) | -6(1) |
| C(49) | 27(1) | 26(1) | 26(1) | -3(1) | 3(1) | -8(1) |
| C(50) | 24(1) | 21(1) | 26(1) | -3(1) | 3(1) | -3(1) |
| Co(1) | 16(1) | 14(1) | 19(1) | 0     | 1(1) | 0     |
| Co(2) | 18(1) | 16(1) | 18(1) | -1(1) | 2(1) | -2(1) |
| N(1)  | 19(1) | 14(1) | 22(1) | 0(1)  | 1(1) | 0(1)  |
| N(2)  | 20(1) | 13(1) | 21(1) | 1(1)  | 2(1) | 0(1)  |
| N(3)  | 23(1) | 13(1) | 20(1) | 0     | 1(1) | 0     |
| N(4)  | 22(1) | 13(1) | 23(1) | 0     | 1(1) | 0     |
| N(5)  | 22(1) | 18(1) | 22(1) | 0(1)  | 2(1) | -1(1) |
| N(6)  | 21(1) | 20(1) | 23(1) | 0(1)  | 1(1) | -2(1) |

$$U_{ij} = \exp(-2\pi^2[h^2(a^*)^2 U_{11} + k^2(b^*)^2 U_{22} + \dots + 2hka^*b^* U_{12}])$$

**Table S3.** Fractional atomic coordinates ( $\times 10^4$ ) and isotropic thermal factors ( $\times 10^3$ ) of hydrogen atoms for compound **1**.

| Atoms | X    | Y    | Z    | $U_{iso}, \text{\AA}^2$ |
|-------|------|------|------|-------------------------|
| H(2)  | 4047 | 4547 | 571  | 28                      |
| H(3)  | 4957 | 3879 | 379  | 28                      |
| H(7)  | 6779 | 3644 | 1633 | 26                      |
| H(8)  | 7024 | 4331 | 2593 | 25                      |
| H(12) | 6854 | 3576 | 4031 | 33                      |
| H(13) | 7649 | 4276 | 4458 | 36                      |
| H(14) | 7933 | 6116 | 4275 | 34                      |
| H(15) | 7416 | 7259 | 3660 | 39                      |
| H(16) | 6622 | 6575 | 3230 | 34                      |
| H(18) | 6412 | 4704 | 748  | 33                      |
| H(19) | 6837 | 4060 | -35  | 40                      |
| H(20) | 6630 | 2279 | -416 | 40                      |
| H(21) | 5989 | 1142 | -26  | 37                      |
| H(22) | 5560 | 1783 | 752  | 31                      |
| H(23) | 5743 | 6327 | 2296 | 25                      |
| H(24) | 5769 | 8294 | 2293 | 25                      |
| H(27) | 4214 | 24   | 2247 | 25                      |
| H(28) | 4245 | 1994 | 2239 | 25                      |
| H(30) | 7052 | 3849 | 6953 | 26                      |

|       |      |       |      |    |
|-------|------|-------|------|----|
| H(31) | 6207 | 3012  | 6553 | 26 |
| H(35) | 5562 | 1127  | 4619 | 29 |
| H(36) | 6005 | 575   | 3760 | 28 |
| H(40) | 6981 | -1049 | 3485 | 28 |
| H(41) | 6849 | -1886 | 2606 | 30 |
| H(42) | 6714 | -757  | 1807 | 31 |
| H(43) | 6685 | 1222  | 1897 | 31 |
| H(44) | 6847 | 2064  | 2774 | 28 |
| H(46) | 5454 | 3660  | 5648 | 29 |
| H(47) | 4624 | 3352  | 6012 | 33 |
| H(48) | 4368 | 1523  | 6258 | 33 |
| H(49) | 4945 | -3    | 6149 | 32 |
| H(50) | 5774 | 292   | 5780 | 28 |
| H(1N) | 7279 | 2860  | 5401 | 32 |

$$U_{iso} = \exp[-8\pi^2 U(\sin\theta/\lambda)^2]$$

**Table S4.** Fractional atomic coordinates ( $\times 10^4$ ) and equivalent thermal factors ( $\times 10^3$ ) for compound **2**.

| Atoms | X        | Y       | Z        | Ueq, Å <sup>2</sup> |
|-------|----------|---------|----------|---------------------|
| C(1)  | 8891(2)  | 1260(2) | 1328(2)  | 31(1)               |
| C(2)  | 8833(2)  | 471(2)  | 1244(2)  | 36(1)               |
| C(3)  | 9508(2)  | 219(2)  | 1082(2)  | 37(1)               |
| C(4)  | 10003(2) | 844(2)  | 1086(1)  | 31(1)               |
| C(5)  | 8297(2)  | 1728(2) | 1461(1)  | 32(1)               |
| C(6)  | 7579(2)  | 1366(2) | 1603(2)  | 34(1)               |
| C(7)  | 7019(2)  | 1305(2) | 1178(2)  | 38(1)               |
| C(8)  | 6406(2)  | 863(3)  | 1278(2)  | 41(1)               |
| C(9)  | 6343(2)  | 492(2)  | 1815(2)  | 37(1)               |
| C(10) | 6863(2)  | 601(3)  | 2267(2)  | 45(1)               |
| C(11) | 7480(2)  | 1034(3) | 2154(2)  | 43(1)               |
| C(12) | 10637(2) | 2513(2) | 56(2)    | 34(1)               |
| C(13) | 10655(2) | 2486(2) | -560(2)  | 36(1)               |
| C(14) | 10000    | 2500    | -886(2)  | 32(1)               |
| C(15) | 10000    | 2500    | -1548(2) | 32(1)               |
| C(16) | 9446(2)  | 2860(3) | -1869(2) | 42(1)               |
| C(17) | 9469(2)  | 2846(2) | -2483(2) | 41(1)               |
| Co(1) | 10000    | 2500    | 1250     | 24(1)               |
| Co(2) | 10000    | 2500    | -3750    | 28(1)               |
| N(1)  | 9612(2)  | 1480(2) | 1222(1)  | 28(1)               |
| N(2)  | 10000    | 2500    | 366(2)   | 27(1)               |
| N(3)  | 10000    | 2500    | -2794(2) | 32(1)               |

|              |         |          |          |        |
|--------------|---------|----------|----------|--------|
| <b>S(1)</b>  | 5616(1) | -156(1)  | 1947(1)  | 40(1)  |
| <b>O(1)</b>  | 5997(2) | -842(2)  | 2111(1)  | 44(1)  |
| <b>O(2)</b>  | 5156(2) | 120(2)   | 2432(2)  | 51(1)  |
| <b>O(3)</b>  | 5218(2) | -212(2)  | 1381(2)  | 57(1)  |
| <b>O(4)</b>  | 9417(2) | 3507(2)  | -3762(1) | 34(1)  |
| <b>O(6)</b>  | 3638(5) | 9557(6)  | 2426(5)  | 77(3)  |
| <b>O(8)</b>  | 3705(5) | 10413(6) | 1359(6)  | 85(3)  |
| <b>O(5)</b>  | 5000    | 10000    | 0        | 122(4) |
| <b>O(7)</b>  | 3565(5) | 10001(7) | 1957(6)  | 102(4) |
| <b>O(9)</b>  | 3637(5) | 10076(5) | 628(5)   | 84(3)  |
| <b>O(10)</b> | 3541(5) | 10118(5) | 126(5)   | 87(3)  |

$$U_{eq} = 1/3 [U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2]$$

**Table S5.** Anisotropic displacement parameters ( $\text{Å}^2 \times 10^3$ ) for compound **2**.

| Atoms        | U11   | U22   | U33   | U23   | U13    | U12    |
|--------------|-------|-------|-------|-------|--------|--------|
| <b>C(1)</b>  | 37(2) | 35(2) | 21(1) | 0(1)  | -1(1)  | -3(1)  |
| <b>C(2)</b>  | 39(2) | 37(2) | 33(2) | -2(1) | -2(1)  | -6(2)  |
| <b>C(3)</b>  | 42(2) | 35(2) | 34(2) | -5(2) | -6(2)  | 0(2)   |
| <b>C(4)</b>  | 41(2) | 34(2) | 16(1) | -3(1) | -2(1)  | 0(2)   |
| <b>C(5)</b>  | 36(2) | 41(2) | 19(2) | -3(1) | 1(1)   | -3(2)  |
| <b>C(6)</b>  | 34(2) | 40(2) | 27(2) | -3(1) | 4(1)   | -2(2)  |
| <b>C(7)</b>  | 40(2) | 46(2) | 29(2) | -1(2) | 4(1)   | 1(2)   |
| <b>C(8)</b>  | 36(2) | 49(2) | 37(2) | -6(2) | 1(1)   | -2(2)  |
| <b>C(9)</b>  | 34(2) | 38(2) | 39(2) | -3(2) | 7(2)   | -5(2)  |
| <b>C(10)</b> | 47(2) | 59(3) | 30(2) | 7(2)  | 1(2)   | -14(2) |
| <b>C(11)</b> | 44(2) | 54(2) | 31(2) | 0(2)  | -1(2)  | -11(2) |
| <b>C(12)</b> | 30(2) | 52(2) | 21(2) | 3(1)  | 1(1)   | 1(2)   |
| <b>C(13)</b> | 32(2) | 56(2) | 20(2) | 4(1)  | 1(1)   | -1(2)  |
| <b>C(14)</b> | 35(2) | 42(3) | 18(2) | 0     | 0      | -1(2)  |
| <b>C(15)</b> | 33(2) | 45(3) | 18(2) | 0     | 0      | -4(2)  |
| <b>C(16)</b> | 40(2) | 65(3) | 22(2) | -3(2) | 0(2)   | 10(2)  |
| <b>C(17)</b> | 43(2) | 60(2) | 21(2) | 2(2)  | 0(2)   | 10(2)  |
| <b>Co(1)</b> | 30(1) | 30(1) | 12(1) | 0     | 0      | 0      |
| <b>Co(2)</b> | 35(1) | 35(1) | 15(1) | 0     | 0      | 0      |
| <b>N(1)</b>  | 33(1) | 33(2) | 16(1) | -3(1) | -1(1)  | 0(1)   |
| <b>N(2)</b>  | 30(2) | 36(2) | 15(2) | 0     | 0      | -1(2)  |
| <b>N(3)</b>  | 35(2) | 43(2) | 18(2) | 0     | 0      | 0(2)   |
| <b>S(1)</b>  | 40(1) | 35(1) | 45(1) | -1(1) | 1(1)   | -6(1)  |
| <b>O(1)</b>  | 50(2) | 38(2) | 43(2) | -7(1) | 0(1)   | -3(1)  |
| <b>O(2)</b>  | 46(2) | 41(2) | 66(2) | -3(1) | 11(1)  | -3(1)  |
| <b>O(3)</b>  | 57(2) | 50(2) | 65(2) | 9(2)  | -16(2) | -17(2) |
| <b>O(4)</b>  | 39(1) | 35(1) | 29(1) | -2(1) | -7(1)  | 0(1)   |

|              |        |        |         |        |        |        |
|--------------|--------|--------|---------|--------|--------|--------|
| <b>O(6)</b>  | 44(4)  | 97(7)  | 89(7)   | -6(5)  | 6(4)   | -14(4) |
| <b>O(8)</b>  | 57(5)  | 65(6)  | 132(10) | 8(6)   | -15(5) | 7(4)   |
| <b>O(5)</b>  | 110(7) | 75(5)  | 181(10) | -9(6)  | 56(7)  | -12(5) |
| <b>O(7)</b>  | 61(5)  | 120(9) | 125(9)  | -44(8) | -15(5) | 22(5)  |
| <b>O(9)</b>  | 79(6)  | 68(5)  | 105(7)  | 2(5)   | -19(5) | 1(4)   |
| <b>O(10)</b> | 73(5)  | 78(6)  | 110(8)  | -13(5) | -10(5) | -9(4)  |

$$U_{ij} = \exp(-2\pi^2[h^2(a^*)^2 U_{11} + k^2(b^*)^2 U_{22} + \dots + 2hka^*b^* U_{12}])$$

**Table S6.** Fractional atomic coordinates ( $\times 10^4$ ) and isotropic thermal factors ( $\times 10^3$ ) of hydrogen atoms for compound **2**.

| Atoms        | X       | Y       | Z        | $U_{iso}, \text{\AA}^2$ |
|--------------|---------|---------|----------|-------------------------|
| <b>H(2)</b>  | 8397    | 179     | 1293     | 44                      |
| <b>H(3)</b>  | 9633    | -279    | 984      | 44                      |
| <b>H(7)</b>  | 7059    | 1573    | 812      | 46                      |
| <b>H(8)</b>  | 6032    | 814     | 980      | 49                      |
| <b>H(10)</b> | 6793    | 380     | 2649     | 54                      |
| <b>H(11)</b> | 7841    | 1105    | 2460     | 52                      |
| <b>H(12)</b> | 11093   | 2542    | 269      | 41                      |
| <b>H(13)</b> | 11120   | 2457    | -763     | 43                      |
| <b>H(16)</b> | 9057    | 3114    | -1667    | 51                      |
| <b>H(17)</b> | 9088    | 3096    | -2698    | 50                      |
| <b>H(20)</b> | 9660(2) | 3885(2) | -3758(2) | 34(1)                   |
| <b>H(21)</b> | 9100(2) | 3510(3) | -4022(2) | 65(2)                   |

$$U_{iso} = \exp[-8\pi^2 U(\sin\theta/\lambda)^2]$$

**Table S7.**  $\pi$ - $\pi$  interactions parameters for compound **1**.

*Face-to-face*

| $Cg^I$ | $Cg^{II}$ | $Cg^I-Cg^{II}$ ( $\text{\AA}$ ) | $Cg^I \cdots Cg^{II}$ ( $^\circ$ ) |
|--------|-----------|---------------------------------|------------------------------------|
| Cg(7)  | Cg(17)    | 4.041(9)                        | 10.77                              |

*Edge-to-face*

| $X-H$       | $Cg$   | $H-Cg$ ( $\text{\AA}$ ) | $X-H \cdots Cg$ ( $^\circ$ ) |
|-------------|--------|-------------------------|------------------------------|
| C(12)-H(12) | Cg(13) | 2.51                    | 88.10                        |
| C(13)-H(13) | Cg(12) | 2.45                    | 88.10                        |
| C(18)-H(18) | Cg(11) | 2.94                    | 87.35                        |
| C(19)-H(19) | Cg(8)  | 2.90                    | 89.16                        |
| C(27)-H(27) | Cg(16) | 2.68                    | 73.96                        |
| C(47)-H(47) | Cg(1)  | 2.97                    | 83.64                        |

**Table S8.** Most significant bond angles (°) and distances (Å) for compound **1** and **2** (distances in bold).

| Compound 1                                  |                 |                 |                 |                 | Compound 2  |                 |                 |
|---|-----------------|-----------------|-----------------|-----------------|---|-----------------|-----------------|
| <b>Co(1). CoN<sub>6</sub> octahedra</b>     |                 |                 |                 |                 | <b>Co(1). CoN<sub>6</sub> octahedra</b>                         |                 |                 |
| <b>Co1</b>                                  | <b>N1</b>       | <b>N2</b>       | <b>N3</b>       | <b>N4</b>       | <b>Co1</b>  | <b>N1</b>       | <b>N2</b>       |
| <b>N4</b>                                   | 89.84(4)        | 89.89(4)        | 180             | <b>2.296(2)</b> | <b>N2</b>   | 88.20(7)        | <b>1.976(4)</b> |
| <b>N3</b>                                   | 90.16(4)        | 90.11(4)        | <b>2.357(2)</b> |                 | <b>N1</b>   | <b>1.963(3)</b> |                 |
| <b>N2</b>                                   | 90.21(6)        | <b>1.962(1)</b> |                 |                 |   |                 |                 |
| <b>N1</b>                                   | <b>1.966(1)</b> |                 |                 |                 |   |                 |                 |
| <b>Co(2). CoN<sub>4</sub> square planar</b> |                 |                 |                 |                 | <b>Co(2). CoN<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub> octa.</b> |                 |                 |
| <b>Co2</b>                                  | <b>N5</b>       | <b>N6</b>       |                 |                 | <b>Co2</b>  | <b>O4</b>       | <b>N3</b>       |
| <b>N6</b>                                   | 90.38(5)        | <b>2.055(1)</b> |                 |                 | <b>N3</b>   | 90.76(6)        | <b>2.137(4)</b> |
| <b>N5</b>                                   | <b>2.032(1)</b> |                 |                 |                 | <b>O4</b>   | <b>2.092(3)</b> |                 |

**Table S9.** Hydrogen bond parameters for compound **2**.

| <i>D-H</i> | <i>A</i>           | <i>D-H</i> (Å) | <i>H...A</i> (Å) | <i>O-H...A</i> (°) |
|------------|--------------------|----------------|------------------|--------------------|
| O(4)-H(20) | O(3) <sup>i</sup>  | 0.81(3)        | 1.93(3)          | 173(4)             |
| O(4)-H(21) | O(1) <sup>ii</sup> | 0.82(4)        | 1.89(4)          | 178(4)             |

i) -1/2+x, 1/2+y, 1/2+z; ii) -1/4-y, -1/4+x, 3/4-z

**Table S10.** Bond distances (Å) and angles (°) for compound **1**.**Distances**

|                         |          |                           |          |
|-------------------------|----------|---------------------------|----------|
| C(1)-N(1)               | 1.375(2) | C(29)-N(6)                | 1.370(2) |
| C(1)-C(10) <sup>i</sup> | 1.396(2) | C(29)-C(38) <sup>iv</sup> | 1.401(2) |
| C(1)-C(2)               | 1.446(2) | C(29)-C(30)               | 1.436(2) |
| C(2)-C(3)               | 1.357(2) | C(30)-C(31)               | 1.358(2) |
| C(2)-H(2)               | 0.9500   | C(30)-H(30)               | 0.9500   |
| C(3)-C(4)               | 1.445(2) | C(31)-C(32)               | 1.433(2) |
| C(3)-H(3)               | 0.9500   | C(31)-H(31)               | 0.9500   |

|                         |          |                           |          |
|-------------------------|----------|---------------------------|----------|
| C(4)-N(1)               | 1.374(2) | C(32)-N(6)                | 1.376(2) |
| C(4)-C(5)               | 1.400(2) | C(32)-C(33)               | 1.390(2) |
| C(5)-C(6)               | 1.395(2) | C(33)-C(34)               | 1.402(2) |
| C(5)-C(17)              | 1.496(2) | C(33)-C(45)               | 1.498(2) |
| C(6)-N(2)               | 1.376(2) | C(34)-N(5)                | 1.371(2) |
| C(6)-C(7)               | 1.441(2) | C(34)-C(35)               | 1.449(2) |
| C(7)-C(8)               | 1.353(2) | C(35)-C(36)               | 1.353(2) |
| C(7)-H(7)               | 0.9500   | C(35)-H(35)               | 0.9500   |
| C(8)-C(9)               | 1.442(2) | C(36)-C(37)               | 1.448(2) |
| C(8)-H(8)               | 0.9500   | C(36)-H(36)               | 0.9500   |
| C(9)-N(2)               | 1.372(2) | C(37)-N(5)                | 1.372(2) |
| C(9)-C(10)              | 1.401(2) | C(37)-C(38)               | 1.398(2) |
| C(10)-C(1) <sup>i</sup> | 1.396(2) | C(38)-C(29) <sup>iv</sup> | 1.401(2) |
| C(10)-C(11)             | 1.495(2) | C(38)-C(39)               | 1.498(2) |
| C(11)-C(12)             | 1.388(2) | C(39)-C(44)               | 1.390(2) |
| C(11)-C(16)             | 1.397(2) | C(39)-C(40)               | 1.397(2) |
| C(12)-C(13)             | 1.395(2) | C(40)-C(41)               | 1.388(2) |
| C(12)-H(12)             | 0.9500   | C(40)-H(40)               | 0.9500   |
| C(13)-C(14)             | 1.381(3) | C(41)-C(42)               | 1.388(3) |
| C(13)-H(13)             | 0.9500   | C(41)-H(41)               | 0.9500   |
| C(14)-C(15)             | 1.379(3) | C(42)-C(43)               | 1.390(2) |
| C(14)-H(14)             | 0.9500   | C(42)-H(42)               | 0.9500   |
| C(15)-C(16)             | 1.392(2) | C(43)-C(44)               | 1.393(2) |
| C(15)-H(15)             | 0.9500   | C(43)-H(43)               | 0.9500   |
| C(16)-H(16)             | 0.9500   | C(44)-H(44)               | 0.9500   |
| C(17)-C(18)             | 1.393(2) | C(45)-C(50)               | 1.394(2) |
| C(17)-C(22)             | 1.399(2) | C(45)-C(46)               | 1.399(2) |
| C(18)-C(19)             | 1.397(3) | C(46)-C(47)               | 1.393(2) |
| C(18)-H(18)             | 0.9500   | C(46)-H(46)               | 0.9500   |
| C(19)-C(20)             | 1.386(3) | C(47)-C(48)               | 1.385(3) |
| C(19)-H(19)             | 0.9500   | C(47)-H(47)               | 0.9500   |
| C(20)-C(21)             | 1.385(3) | C(48)-C(49)               | 1.385(3) |
| C(20)-H(20)             | 0.9500   | C(48)-H(48)               | 0.9500   |
| C(21)-C(22)             | 1.391(2) | C(49)-C(50)               | 1.392(2) |
| C(21)-H(21)             | 0.9500   | C(49)-H(49)               | 0.9500   |
| C(22)-H(22)             | 0.9500   | C(50)-H(50)               | 0.9500   |



|                            |          |                          |          |
|----------------------------|----------|--------------------------|----------|
| C(23)-N(3)                 | 1.340(2) | Co(1)-N(2)               | 1.962(1) |
| C(23)-C(24)                | 1.393(2) | Co(1)-N(2) <sup>i</sup>  | 1.962(1) |
| C(23)-H(23)                | 0.9500   | Co(1)-N(1) <sup>i</sup>  | 1.966(1) |
| C(24)-C(25)                | 1.394(2) | Co(1)-N(1)               | 1.966(1) |
| C(24)-H(24)                | 0.9500   | Co(1)-N(4)               | 2.296(2) |
| C(25)-C(24) <sup>i</sup>   | 1.394(2) | Co(1)-N(3)               | 2.357(2) |
| C(25)-C(26) <sup>ii</sup>  | 1.482(3) | Co(2)-N(5)               | 2.032(1) |
| C(26)-C(27)                | 1.396(2) | Co(2)-N(5) <sup>iv</sup> | 2.032(1) |
| C(26)-C(27) <sup>i</sup>   | 1.396(2) | Co(2)-N(6)               | 2.055(1) |
| C(26)-C(25) <sup>iii</sup> | 1.482(3) | Co(2)-N(6) <sup>iv</sup> | 2.055(1) |
| C(27)-C(28)                | 1.393(2) | Co(2)-H(1N)              | 1.22(3)  |
| C(27)-H(27)                | 0.9500   | N(3)-C(23) <sup>i</sup>  | 1.340(2) |
| C(28)-N(4)                 | 1.338(2) | N(4)-C(28) <sup>i</sup>  | 1.338(2) |
| C(28)-H(28)                | 0.9500   | N(6)-H(1N)               | 0.85(3)  |

### Angles

|                               |          |                                  |          |
|-------------------------------|----------|----------------------------------|----------|
| N(1)-C(1)-C(10) <sup>i</sup>  | 124.7(1) | C(29) <sup>iv</sup> -C(38)-C(39) | 115.3(1) |
| N(1)-C(1)-C(2)                | 110.2(1) | C(44)-C(39)-C(40)                | 118.8(2) |
| C(10) <sup>i</sup> -C(1)-C(2) | 124.9(2) | C(44)-C(39)-C(38)                | 120.3(2) |
| C(3)-C(2)-C(1)                | 106.7(1) | C(40)-C(39)-C(38)                | 120.7(2) |
| C(3)-C(2)-H(2)                | 126.7    | C(41)-C(40)-C(39)                | 120.5(2) |
| C(1)-C(2)-H(2)                | 126.7    | C(41)-C(40)-H(40)                | 119.8    |
| C(2)-C(3)-C(4)                | 106.9(1) | C(39)-C(40)-H(40)                | 119.8    |
| C(2)-C(3)-H(3)                | 126.5    | C(42)-C(41)-C(40)                | 120.4(2) |
| C(4)-C(3)-H(3)                | 126.5    | C(42)-C(41)-H(41)                | 119.8    |
| N(1)-C(4)-C(5)                | 125.4(1) | C(40)-C(41)-H(41)                | 119.8    |
| N(1)-C(4)-C(3)                | 110.1(1) | C(41)-C(42)-C(43)                | 119.5(2) |
| C(5)-C(4)-C(3)                | 124.2(2) | C(41)-C(42)-H(42)                | 120.3    |
| C(6)-C(5)-C(4)                | 122.9(1) | C(43)-C(42)-H(42)                | 120.3    |
| C(6)-C(5)-C(17)               | 119.2(1) | C(42)-C(43)-C(44)                | 120.1(2) |
| C(4)-C(5)-C(17)               | 117.8(1) | C(42)-C(43)-H(43)                | 120.0    |
| N(2)-C(6)-C(5)                | 124.9(1) | C(44)-C(43)-H(43)                | 120.0    |
| N(2)-C(6)-C(7)                | 109.6(1) | C(39)-C(44)-C(43)                | 120.7(2) |
| C(5)-C(6)-C(7)                | 125.2(1) | C(39)-C(44)-H(44)                | 119.6    |
| C(8)-C(7)-C(6)                | 107.2(1) | C(43)-C(44)-H(44)                | 119.6    |
| C(8)-C(7)-H(7)                | 126.4    | C(50)-C(45)-C(46)                | 118.9(2) |

|                                |          |  |           |
|--------------------------------|----------|--|-----------|
| C(6)-C(7)-H(7)                 | 126.4    | C(50)-C(45)-C(33)                          | 119.8(2)  |
| C(7)-C(8)-C(9)                 | 106.8(1) | C(46)-C(45)-C(33)                          | 121.3(2)  |
| C(7)-C(8)-H(8)                 | 126.6    | C(47)-C(46)-C(45)                          | 120.3(2)  |
| C(9)-C(8)-H(8)                 | 126.6    | C(47)-C(46)-H(46)                          | 119.9     |
| N(2)-C(9)-C(10)                | 125.8(1) | C(45)-C(46)-H(46)                          | 119.9     |
| N(2)-C(9)-C(8)                 | 109.9(1) | C(48)-C(47)-C(46)                          | 120.2(2)  |
| C(10)-C(9)-C(8)                | 123.9(1) | C(48)-C(47)-H(47)                          | 119.9     |
| C(1) <sup>1</sup> -C(10)-C(9)  | 122.2(1) | C(46)-C(47)-H(47)                          | 119.9     |
| C(1) <sup>1</sup> -C(10)-C(11) | 120.7(1) | C(49)-C(48)-C(47)                          | 120.0(2)  |
| C(9)-C(10)-C(11)               | 117.1(1) | C(49)-C(48)-H(48)                          | 120.0     |
| C(12)-C(11)-C(16)              | 118.4(2) | C(47)-C(48)-H(48)                          | 120.0     |
| C(12)-C(11)-C(10)              | 123.1(2) | C(48)-C(49)-C(50)                          | 120.1(2)  |
| C(16)-C(11)-C(10)              | 118.6(1) | C(48)-C(49)-H(49)                          | 119.9     |
| C(11)-C(12)-C(13)              | 120.5(2) | C(50)-C(49)-H(49)                          | 119.9     |
| C(11)-C(12)-H(12)              | 119.7    | C(49)-C(50)-C(45)                          | 120.5(2)  |
| C(13)-C(12)-H(12)              | 119.7    | C(49)-C(50)-H(50)                          | 119.7     |
| C(14)-C(13)-C(12)              | 120.8(2) | C(45)-C(50)-H(50)                          | 119.7     |
| C(14)-C(13)-H(13)              | 119.6    | N(2)-Co(1)-N(2) <sup>1</sup>               | 179.77(7) |
| C(12)-C(13)-H(13)              | 119.6    | N(2)-Co(1)-N(1) <sup>1</sup>               | 89.79(6)  |
| C(15)-C(14)-C(13)              | 119.1(2) | N(2) <sup>1</sup> -Co(1)-N(1) <sup>1</sup> | 90.21(6)  |
| C(15)-C(14)-H(14)              | 120.5    | N(2)-Co(1)-N(1)                            | 90.21(6)  |
| C(13)-C(14)-H(14)              | 120.5    | N(2) <sup>1</sup> -Co(1)-N(1)              | 89.79(6)  |
| C(14)-C(15)-C(16)              | 120.7(2) | N(1) <sup>1</sup> -Co(1)-N(1)              | 179.68(8) |
| C(14)-C(15)-H(15)              | 119.7    | N(2)-Co(1)-N(4)                            | 89.89(4)  |
| C(16)-C(15)-H(15)              | 119.7    | N(2) <sup>1</sup> -Co(1)-N(4)              | 89.89(4)  |
| C(15)-C(16)-C(11)              | 120.6(2) | N(1) <sup>1</sup> -Co(1)-N(4)              | 89.84(4)  |
| C(15)-C(16)-H(16)              | 119.7    | N(1)-Co(1)-N(4)                            | 89.84(4)  |
| C(11)-C(16)-H(16)              | 119.7    | N(2)-Co(1)-N(3)                            | 90.11(4)  |
| C(18)-C(17)-C(22)              | 118.8(2) | N(2) <sup>1</sup> -Co(1)-N(3)              | 90.11(4)  |
| C(18)-C(17)-C(5)               | 122.2(2) | N(1) <sup>1</sup> -Co(1)-N(3)              | 90.16(4)  |
| C(22)-C(17)-C(5)               | 119.0(2) | N(1)-Co(1)-N(3)                            | 90.16(4)  |
| C(17)-C(18)-C(19)              | 120.3(2) | N(4)-Co(1)-N(3)                            | 180.0     |
| C(17)-C(18)-H(18)              | 119.9    | N(5)-Co(2)-N(5) <sup>IV</sup>              | 180.00(4) |
| C(19)-C(18)-H(18)              | 119.9    | N(5)-Co(2)-N(6)                            | 90.38(5)  |
| C(20)-C(19)-C(18)              | 120.3(2) | N(5) <sup>IV</sup> -Co(2)-N(6)             | 89.62(5)  |
| C(20)-C(19)-H(19)              | 119.9    | N(5)-Co(2)-N(6) <sup>IV</sup>              | 89.62(5)  |

|  |          |  |           |
|--|----------|--|-----------|
| C(18)-C(19)-H(19)                              | 119.9    | N(5) <sup>IV</sup> -Co(2)-N(6) <sup>IV</sup> | 90.38(5)  |
| C(21)-C(20)-C(19)                              | 120.1(2) | N(6)-Co(2)-N(6) <sup>IV</sup>                | 179.9(1)  |
| C(21)-C(20)-H(20)                              | 120.0    | N(5)-Co(2)-H(1N)                             | 91.4(1)   |
| C(19)-C(20)-H(20)                              | 120.0    | N(5) <sup>IV</sup> -Co(2)-H(1N)              | 88.6(1)   |
| C(20)-C(21)-C(22)                              | 119.8(2) | N(6)-Co(2)-H(1N)                             | 4.1(1)    |
| C(20)-C(21)-H(21)                              | 120.1    | N(6) <sup>IV</sup> -Co(2)-H(1N)              | 176.0(1)  |
| C(22)-C(21)-H(21)                              | 120.1    | C(4)-N(1)-C(1)                               | 106.0(1)  |
| C(21)-C(22)-C(17)                              | 120.9(2) | C(4)-N(1)-Co(1)                              | 126.6(1)  |
| C(21)-C(22)-H(22)                              | 119.6    | C(1)-N(1)-Co(1)                              | 127.4(1)  |
| C(17)-C(22)-H(22)                              | 119.6    | C(9)-N(2)-C(6)                               | 106.2(1)  |
| N(3)-C(23)-C(24)                               | 124.0(2) | C(9)-N(2)-Co(1)                              | 126.8(1)  |
| N(3)-C(23)-H(23)                               | 118.0    | C(6)-N(2)-Co(1)                              | 126.9(1)  |
| C(24)-C(23)-H(23)                              | 118.0    | C(23)-N(3)-C(23) <sup>I</sup>                | 116.2(2)  |
| C(23)-C(24)-C(25)                              | 119.4(2) | N(2) <sup>I</sup> -Co(1)-N(1) <sup>I</sup>   | 90.21(6)  |
| C(23)-C(24)-H(24)                              | 120.3    | N(2)-Co(1)-N(1)                              | 90.21(6)  |
| C(25)-C(24)-H(24)                              | 120.3    | N(2) <sup>I</sup> -Co(1)-N(1)                | 89.79(6)  |
| C(24)-C(25)-C(24) <sup>I</sup>                 | 117.0(2) | N(1) <sup>I</sup> -Co(1)-N(1)                | 179.68(8) |
| C(24)-C(25)-C(26) <sup>II</sup>                | 121.5(1) | N(2)-Co(1)-N(4)                              | 89.89(4)  |
| C(24) <sup>I</sup> -C(25)-C(26) <sup>II</sup>  | 121.5(1) | N(2) <sup>I</sup> -Co(1)-N(4)                | 89.89(4)  |
| C(27)-C(26)-C(27) <sup>I</sup>                 | 117.2(2) | N(1) <sup>I</sup> -Co(1)-N(4)                | 89.84(4)  |
| C(27)-C(26)-C(25) <sup>III</sup>               | 121.4(1) | N(1)-Co(1)-N(4)                              | 89.84(4)  |
| C(27) <sup>I</sup> -C(26)-C(25) <sup>III</sup> | 121.4(1) | N(2)-Co(1)-N(3)                              | 90.11(4)  |
| C(28)-C(27)-C(26)                              | 119.3(2) | N(2) <sup>I</sup> -Co(1)-N(3)                | 90.11(4)  |
| C(28)-C(27)-H(27)                              | 120.4    | N(1) <sup>I</sup> -Co(1)-N(3)                | 90.16(4)  |
| C(26)-C(27)-H(27)                              | 120.4    | N(1)-Co(1)-N(3)                              | 90.16(4)  |
| N(4)-C(28)-C(27)                               | 123.6(1) | N(4)-Co(1)-N(3)                              | 180.0     |
| N(4)-C(28)-H(28)                               | 118.2    | N(5)-Co(2)-N(5) <sup>IV</sup>                | 180.00(4) |
| C(27)-C(28)-H(28)                              | 118.2    | N(5)-Co(2)-N(6)                              | 90.38(5)  |
| N(6)-C(29)-C(38) <sup>IV</sup>                 | 126.7(2) | N(5) <sup>IV</sup> -Co(2)-N(6)               | 89.62(5)  |
| N(6)-C(29)-C(30)                               | 108.1(1) | N(5)-Co(2)-N(6) <sup>IV</sup>                | 89.62(5)  |
| C(38) <sup>IV</sup> -C(29)-C(30)               | 125.2(2) | N(5) <sup>IV</sup> -Co(2)-N(6) <sup>IV</sup> | 90.38(5)  |
| C(31)-C(30)-C(29)                              | 107.5(1) | N(6)-Co(2)-N(6) <sup>IV</sup>                | 179.9(1)  |
| C(31)-C(30)-H(30)                              | 126.2    | N(5)-Co(2)-H(1N)                             | 91.4(1)   |
| C(29)-C(30)-H(30)                              | 126.2    | N(5) <sup>IV</sup> -Co(2)-H(1N)              | 88.6(1)   |
| C(30)-C(31)-C(32)                              | 107.9(1) | N(6)-Co(2)-H(1N)                             | 4.1(1)    |
| C(30)-C(31)-H(31)                              | 126.0    | N(6) <sup>IV</sup> -Co(2)-H(1N)              | 175.9(1)  |

|                                 |          |                                |           |
|---------------------------------|----------|--------------------------------|-----------|
| C(32)-C(31)-H(31)               | 126.0    | C(4)-N(1)-C(1)                 | 106.0(1)  |
| N(6)-C(32)-C(33)                | 127.0(1) | C(4)-N(1)-Co(1)                | 126.6(1)  |
| N(6)-C(32)-C(31)                | 107.7(1) | C(1)-N(1)-Co(1)                | 127.4(1)  |
| C(33)-C(32)-C(31)               | 125.2(2) | C(9)-N(2)-C(6)                 | 106.2(1)  |
| C(32)-C(33)-C(34)               | 124.9(2) | C(9)-N(2)-Co(1)                | 126.8(1)  |
| C(32)-C(33)-C(45)               | 116.5(1) | C(6)-N(2)-Co(1)                | 126.9(1)  |
| C(34)-C(33)-C(45)               | 118.5(1) | C(23)-N(3)-C(23) <sup>i</sup>  | 116.2(2)  |
| N(5)-C(34)-C(33)                | 125.6(2) | C(23)-N(3)-Co(1)               | 121.91(9) |
| N(5)-C(34)-C(35)                | 110.5(1) | C(23) <sup>i</sup> -N(3)-Co(1) | 121.91(9) |
| C(33)-C(34)-C(35)               | 123.9(2) | C(28)-N(4)-C(28) <sup>i</sup>  | 117.0(2)  |
| C(36)-C(35)-C(34)               | 106.7(1) | C(28)-N(4)-Co(1)               | 121.5(2)  |
| C(36)-C(35)-H(35)               | 126.6    | C(28) <sup>i</sup> -N(4)-Co(1) | 121.5(2)  |
| C(34)-C(35)-H(35)               | 126.6    | C(34)-N(5)-C(37)               | 105.5(1)  |
| C(35)-C(36)-C(37)               | 106.6(2) | C(34)-N(5)-Co(2)               | 126.8(1)  |
| C(35)-C(36)-H(36)               | 126.7    | C(37)-N(5)-Co(2)               | 127.5(1)  |
| C(37)-C(36)-H(36)               | 126.7    | C(29)-N(6)-C(32)               | 108.8(1)  |
| N(5)-C(37)-C(38)                | 125.5(2) | C(29)-N(6)-Co(2)               | 125.7(1)  |
| N(5)-C(37)-C(36)                | 110.7(1) | C(32)-N(6)-Co(2)               | 125.0(1)  |
| C(38)-C(37)-C(36)               | 123.8(2) | C(29)-N(6)-H(1N)               | 125(2)    |
| C(37)-C(38)-C(29) <sup>iv</sup> | 124.6(2) | C(32)-N(6)-H(1N)               | 127(2)    |
| C(37)-C(38)-C(39)               | 120.2(1) |                                |           |

Symmetry codes: i)  $-x+1, y, -z+1/2$ ; ii)  $x, y+1, z$ ; iii)  $x, y-1, z$ ; iv)  $-x+3/2, -y+1/2, -z+1$

**Table S11.** Bond distances (Å) and angles (°) for compound **2**.

#### Distances

|           |          |                            |          |
|-----------|----------|----------------------------|----------|
| C(1)-N(1) | 1.376(5) | C(14)-C(15)                | 1.481(8) |
| C(1)-C(5) | 1.391(5) | C(15)-C(16) <sup>iii</sup> | 1.388(5) |
| C(1)-C(2) | 1.436(5) | C(15)-C(16)                | 1.388(5) |
| C(2)-C(3) | 1.344(6) | C(16)-C(17)                | 1.374(5) |
| C(2)-H(2) | 0.9500   | C(16)-H(16)                | 0.9500   |
| C(3)-C(4) | 1.433(5) | C(17)-N(3)                 | 1.335(5) |
| C(3)-H(3) | 0.9500   | C(17)-H(17)                | 0.9500   |

|                            |          |                           |          |
|----------------------------|----------|---------------------------|----------|
| C(4)-N(1)                  | 1.377(5) | Co(1)-N(1) <sup>iii</sup> | 1.963(3) |
| C(4)-C(5) <sup>i</sup>     | 1.388(5) | Co(1)-N(1)                | 1.963(3) |
| C(5)-C(4) <sup>ii</sup>    | 1.388(5) | Co(1)-N(1) <sup>i</sup>   | 1.963(3) |
| C(5)-C(6)                  | 1.481(5) | Co(1)-N(1) <sup>ii</sup>  | 1.963(3) |
| C(6)-C(11)                 | 1.381(5) | Co(1)-N(2) <sup>ii</sup>  | 1.976(4) |
| C(6)-C(7)                  | 1.388(6) | Co(1)-N(2)                | 1.976(4) |
| C(7)-C(8)                  | 1.378(6) | Co(2)-O(4)                | 2.092(3) |
| C(7)-H(7)                  | 0.9500   | Co(2)-O(4) <sup>iii</sup> | 2.092(3) |
| C(8)-C(9)                  | 1.377(6) | Co(2)-O(4) <sup>iv</sup>  | 2.092(3) |
| C(8)-H(8)                  | 0.9500   | Co(2)-O(4) <sup>v</sup>   | 2.092(3) |
| C(9)-C(10)                 | 1.390(6) | Co(2)-N(3) <sup>iv</sup>  | 2.137(4) |
| C(9)-S(1)                  | 1.776(4) | Co(2)-N(3)                | 2.137(4) |
| C(10)-C(11)                | 1.378(6) | N(2)-C(12) <sup>iii</sup> | 1.339(4) |
| C(10)-H(10)                | 0.9500   | N(3)-C(17) <sup>iii</sup> | 1.335(5) |
| C(11)-H(11)                | 0.9500   | S(1)-O(2)                 | 1.451(3) |
| C(12)-N(2)                 | 1.339(4) | S(1)-O(3)                 | 1.458(4) |
| C(12)-C(13)                | 1.379(5) | S(1)-O(1)                 | 1.457(3) |
| C(12)-H(12)                | 0.9500   | O(4)-H(20)                | 0.81(1)  |
| C(13)-C(14)                | 1.384(4) | O(4)-H(21)                | 0.81(1)  |
| C(13)-H(13)                | 0.9500   | O(9)-O(10)                | 1.14(1)  |
| C(14)-C(13) <sup>iii</sup> | 1.384(4) |                           |          |

### Angles

|                |          |   |           |
|----------------|----------|---|-----------|
| N(1)-C(1)-C(5) | 125.9(3) | N(3)-C(17)-H(17)                              | 118.3     |
| N(1)-C(1)-C(2) | 109.2(3) | C(16)-C(17)-H(17)                             | 118.3     |
| C(5)-C(1)-C(2) | 124.8(4) | N(1) <sup>iii</sup> -Co(1)-N(1)               | 176.4(1)  |
| C(3)-C(2)-C(1) | 107.6(3) | N(1) <sup>iii</sup> -Co(1)-N(1) <sup>i</sup>  | 90.058(5) |
| C(3)-C(2)-H(2) | 126.2    | N(1)-Co(1)-N(1) <sup>i</sup>                  | 90.057(5) |
| C(1)-C(2)-H(2) | 126.2    | N(1) <sup>iii</sup> -Co(1)-N(1) <sup>ii</sup> | 90.054(5) |
| C(2)-C(3)-C(4) | 107.2(3) | N(1)-Co(1)-N(1) <sup>ii</sup>                 | 90.057(5) |
| C(2)-C(3)-H(3) | 126.4    | N(1) <sup>i</sup> -Co(1)-N(1) <sup>ii</sup>   | 176.4(1)  |

|                               |          |   |           |
|-------------------------------|----------|---|-----------|
| C(4)-C(3)-H(3)                | 126.4    | N(1)-Co(1)-N(2) <sup>ii</sup>                 | 91.80(7)  |
| N(1)-C(4)-C(5) <sup>i</sup>   | 125.1(3) | N(1) <sup>i</sup> -Co(1)-N(2) <sup>ii</sup>   | 88.20(7)  |
| N(1)-C(4)-C(3)                | 109.6(3) | N(1) <sup>ii</sup> -Co(1)-N(2) <sup>ii</sup>  | 88.20(7)  |
| C(5) <sup>i</sup> -C(4)-C(3)  | 124.8(3) | N(1) <sup>iii</sup> -Co(1)-N(2)               | 88.20(7)  |
| C(4) <sup>ii</sup> -C(5)-C(1) | 122.6(3) | N(1)-Co(1)-N(2)                               | 88.20(7)  |
| C(4) <sup>ii</sup> -C(5)-C(6) | 120.4(3) | N(1) <sup>ii</sup> -Co(1)-N(2)                | 91.80(7)  |
| C(1)-C(5)-C(6)                | 116.7(3) | N(1) <sup>ii</sup> -Co(1)-N(2)                | 91.80(7)  |
| C(11)-C(6)-C(7)               | 119.0(4) | N(2) <sup>ii</sup> -Co(1)-N(2)                | 180.0     |
| C(11)-C(6)-C(5)               | 119.5(3) | O(4)-Co(2)-O(4) <sup>iii</sup>                | 178.5(1)  |
| C(7)-C(6)-C(5)                | 121.4(3) | O(4)-Co(2)-O(4) <sup>iv</sup>                 | 90.009(2) |
| C(8)-C(7)-C(6)                | 120.9(4) | O(4) <sup>iii</sup> -Co(2)-O(4) <sup>iv</sup> | 90.014(2) |
| C(8)-C(7)-H(7)                | 119.5    | O(4)-Co(2)-O(4) <sup>v</sup>                  | 90.010(2) |
| C(6)-C(7)-H(7)                | 119.5    | O(4) <sup>iii</sup> -Co(2)-O(4) <sup>v</sup>  | 90.008(2) |
| C(7)-C(8)-C(9)                | 119.1(4) | O(4) <sup>iv</sup> -Co(2)-O(4) <sup>v</sup>   | 178.5(1)  |
| C(7)-C(8)-H(8)                | 120.5    | O(4)-Co(2)-N(3) <sup>iv</sup>                 | 89.24(6)  |
| C(9)-C(8)-H(8)                | 120.5    | O(4) <sup>iii</sup> -Co(2)-N(3) <sup>iv</sup> | 89.24(6)  |
| C(8)-C(9)-C(10)               | 120.7(4) | O(4) <sup>iv</sup> -Co(2)-N(3) <sup>iv</sup>  | 90.76(6)  |
| C(8)-C(9)-S(1)                | 121.5(3) | O(4) <sup>v</sup> -Co(2)-N(3) <sup>iv</sup>   | 90.76(6)  |
| C(10)-C(9)-S(1)               | 117.7(3) | O(4)-Co(2)-N(3)                               | 90.76(6)  |
| C(11)-C(10)-C(9)              | 119.2(4) | O(4) <sup>iii</sup> -Co(2)-N(3)               | 90.76(6)  |
| C(11)-C(10)-H(10)             | 120.4    | O(4) <sup>iv</sup> -Co(2)-N(3)                | 89.24(6)  |
| C(9)-C(10)-H(10)              | 120.4    | O(4) <sup>v</sup> -Co(2)-N(3)                 | 89.24(6)  |
| C(10)-C(11)-C(6)              | 120.7(4) | N(3) <sup>iv</sup> -Co(2)-N(3)                | 180.0     |
| C(10)-C(11)-H(11)             | 119.7    | C(1)-N(1)-C(4)                                | 106.3(3)  |
| C(6)-C(11)-H(11)              | 119.7    | C(1)-N(1)-Co(1)                               | 126.7(2)  |
| N(2)-C(12)-C(13)              | 122.4(3) | C(4)-N(1)-Co(1)                               | 127.0(2)  |
| N(2)-C(12)-H(12)              | 118.8    | C(12) <sup>iii</sup> -N(2)-C(12)              | 117.7(4)  |
| C(13)-C(12)-H(12)             | 118.8    | C(12) <sup>iii</sup> -N(2)-Co(1)              | 121.2(2)  |
| C(12)-C(13)-C(14)             | 120.4(3) | C(12)-N(2)-Co(1)                              | 121.2(2)  |
| C(12)-C(13)-H(13)             | 119.8    | C(17) <sup>iii</sup> -N(3)-C(17)              | 117.3(5)  |
| C(14)-C(13)-H(13)             | 119.8    | C(17) <sup>iii</sup> -N(3)-Co(2)              | 121.4(2)  |

|                                   |          |                  |          |
|-----------------------------------|----------|------------------|----------|
| C(13)-C(14)-C(13) <sup>iii</sup>  | 116.5(5) | C(17)-N(3)-Co(2) | 121.4(2) |
| C(13)-C(14)-C(15)                 | 121.7(2) | O(2)-S(1)-O(3)   | 113.0(2) |
| C(13) <sup>iii</sup> -C(14)-C(15) | 121.7(2) | O(2)-S(1)-O(1)   | 111.7(2) |
| C(16) <sup>iii</sup> -C(15)-C(16) | 117.7(5) | O(3)-S(1)-O(1)   | 113.0(2) |
| C(16) <sup>iii</sup> -C(15)-C(14) | 121.1(2) | O(2)-S(1)-C(9)   | 108.6(2) |
| C(16)-C(15)-C(14)                 | 121.2(2) | O(3)-S(1)-C(9)   | 105.2(2) |
| C(17)-C(16)-C(15)                 | 119.1(4) | O(1)-S(1)-C(9)   | 104.6(2) |
| C(17)-C(16)-H(16)                 | 120.4    | Co(2)-O(4)-H(20) | 117(3)   |
| C(15)-C(16)-H(16)                 | 120.4    | Co(2)-O(4)-H(21) | 112(4)   |
| N(3)-C(17)-C(16)                  | 123.4(4) | H(20)-O(4)-H(21) | 112(3)   |

Symmetry codes: i)  $-y+5/4, x-3/4, -z+1/4$ ; ii)  $y+3/4, -x+5/4, -z+1/4$ ; iii)  $-x+2, -y+1/2, z+0$ ; iv)  $y+3/4, -x+5/4, -z-3/4$ ; v)  $-y+5/4, x-3/4, -z-3/4$

## CAPÍTULO IV

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### Compuesto $\mu$ -O-[FeTCPP]<sub>2</sub>·nDMF

*“Heterogeneous catalytic properties of a metalloporphyrinic MOF based on unprecedented  $\mu$ -O-[FeTCPP]<sub>2</sub> dimers: porosity revealing an unusual superhyperfine EPR structure”*

*J. Am. Chem. Soc. (enviada).*

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## Resumen

Durante los últimos años, con el objetivo de conseguir catalizadores heterogéneos, se ha realizado un gran esfuerzo en anclar catalizadores en los MOFs. En este sentido, un enfoque innovador consiste en utilizar las unidades de la red como unidades estructurales y catalizadores. Considerando lo anterior, las metaloporfirinas resultan candidatas apropiadas y así se recoge en los trabajos de MOFs metaloporfirínicos publicados. Por otra parte, los oxo-dímeros de hierro altamente distorsionados con electrones deslocalizados apuntan hacia los modelos de catalizadores más efectivos. De esta manera, el reto de esta investigación ha sido la obtención de MOFs basados en porfirinas de hierro que mostraran estas características. Por ello, en este trabajo se muestra la síntesis y caracterización del compuesto  $\mu$ -O-[FeTCPP]<sub>2</sub>·nDMF (TCPP = meso-tetra(4-carboxifenil)porfirina, DMF = N,N-dimetilformamida, y n≈16). Este MOF es el primer ejemplo de un oxo-dímero con TCPP, donde las conexiones interdiméricas dan lugar a una estructura laminar. Las propiedades estructurales, espectroscópicas y magnéticas de este compuesto son coherentes con la presencia de iones de Fe<sup>III</sup> de alto spin, mostrando fuertes interacciones antiferromagnéticas intradiméricas ( $J = -132 \text{ cm}^{-1}$ ). Mediante espectroscopia EPR se puede observar una inusual señal superhiperfina, hecho relacionado con la porosidad del mismo. Las características estructurales de los dímeros y la naturaleza porosa de la red son los responsables del prometedor comportamiento de este compuesto como catalizador heterogéneo para la oxidación y acetilación de sustratos orgánicos. Por lo tanto, éste es un nuevo ejemplo de los pocos compuestos metaloporfirínicos donde las unidades estructurales actúan como catalizadores.

**Abstract**

During the past years, a great effort has been devoted to the anchoring of catalysts into MOFs in order to achieve heterogeneous catalysts. In this sense, an innovative approach consists on using the coordination-network synthons both as structural units and as catalysts. Regarding the latter, metalloporphyrins are suitable candidates for synthons. In fact, a few works report on MOFs based on metalloporphyrins exhibiting these features. On the other hand, highly distorted di-iron oxo dimers containing electron withdrawing groups rank amongst the most-effective catalyst models. Thus, the aim of this work was obtaining MOFs based on iron porphyrins exhibiting those characteristics. This way, this work reports on the synthesis and characterization of the  $\mu$ -O-[FeTCPP]<sub>2</sub>·nDMF compound (TCPP = meso-tetra(4-carboxyphenyl)porphyrin, DMF = N,N-dimethylformamide, and  $n \approx 16$ ). This MOF is the first example of  $\mu$ -oxo dimer with TCPP. The inter-dimer connections give rise to a laminar structure. The structural, spectroscopic and magnetic properties of this compound are consistent with the presence of high-spin Fe<sup>III</sup> ions, exhibiting a strong antiferromagnetic coupling in the  $\mu$ -oxo dimer ( $J = -132 \text{ cm}^{-1}$ ). An unusual superhyperfine structure has been observed in EPR that is related to the porosity of the compound. The structural features of the dimers and the porous network are responsible for the promising behavior of the compound as an heterogeneous catalyst for the oxidation and acetylation of organic substrates. Therefore, this compound is a new of the very few examples of metalloporphyrins where structural units play as catalysts.

## Laburpena

Azken urteetan, izugarriko ahaleginak egiten ari dira katalizatzaileak ainguratzeko MOF materialetan, katalizatzaile heterogeneoak lortzeko asmotan. Horretarako, koordinazio-sarearen unitateak erabil daitezke aldi berean egitura-unitate zein katalizatzaile modura, hauxe ikuspuntu berritzailea izanik. Hau kontuan hartuz, metaloporfirinak hautagai egokiak dira, eta horrela diote MOF metaloporfirinikoei buruz argitaratu diren artikuluek. Bestalde, lekutu gabeko elektroiak dituzten di-burdin oxo-dimero distortsionatutakoek katalizatzaile eraginkorrenetarikoak dira. Beraz, lan honen helburua izan da ezaugarri hauek dituzten burdin-porfirinetan oinarritutako MOFak lortzea. Horrela, lan honetan aurkezten dira  $\mu$ -O-[FeTCPP]<sub>2</sub>·nDMF (TCPP= meso-tetra(4-carboxifenil)porfirina, DMF = N,N-dimetilformamida, eta n≈16) konposatuaren sintesia eta karakterizazioa. MOF hau TCPP porfirina duen lehenengo  $\mu$ -oxo dimeroa da, non dimeroen arteko kohesio-indarrek geruzak sortzen baitituzte. Egitura eta ezaugarri espektroskopiko zein magnetikoek adierazten dute espin altuko Fe<sup>III</sup> ioiak daudela, eta horien artean akoplamendu antiferromagnetiko sendoa dagoela  $\mu$ -oxo dimeroan (J= -132 cm<sup>-1</sup>). Gainera, EPRan ezohiko egitura superhiperrestua ikus daiteke, konposatuaren poroduntasunarekin erlazionatua dagoena. Beraz, dimeroen egitura-ezaugarriak eta sarearen izaera poroduna direla medio azaltzen da konposatu honen etorkizun handiko portaera, katalizatzaile heterogeneo bezalakoa, substratu organikoen oxidazio zein azetilazioan. Hots, konposatu berri honetan egitura-unitateek jokatzen dute katalizatzaile gisa, eta ezaugarri hori duten konposatuak gutxi dira, Fe-TCPP konposatua horietako adibide bat delarik.

## IV.1. Introduction

Metal-Organic Frameworks (MOFs), also known as coordination networks, are porous solids consisting of metal complexes that are packed in a variety of frameworks.<sup>1,2</sup> They have been thoroughly explored in many fields, such as gas storage and separation,<sup>3,4</sup> nonlinear optics,<sup>5,6</sup> ferroelectricity,<sup>7</sup> conductivity,<sup>8</sup> magnetism,<sup>9</sup> luminescence,<sup>10</sup> biomedical imaging,<sup>11</sup> chemical sensing,<sup>12</sup> drug delivery<sup>13</sup> and heterogeneous catalysis.<sup>14-16</sup> Among the different organic ligands that can be used in these coordination networks, metalloporphyrins can be highlighted as they can produce coordination networks exhibiting unique properties attached to biochemical, enzymatic and photochemical functions.<sup>17</sup> Thus, an efficient synthesis strategy gives rise to compounds capable to mimic its behavior.

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Biomimetic catalysts such as metalloporphyrins have been used as cytochrome P-450 models, and their potential for substrate oxidation has been the subject of several studies.<sup>18-20</sup> The similarity between metalloporphyrins and the active center of many natural enzymes, along with the high reactivity and selectivity towards oxidation of organic substrates, have stimulated the use of iron porphyrins as models of natural catalysts.<sup>21</sup> In this sense, a large number of model systems have been explored,<sup>22-25</sup> and the use of highly distorted di-iron oxo dimers containing electron withdrawing groups rank amongst the most-effective catalyst models attracting considerable attention on the last years.<sup>26-28</sup> Some  $\mu$ -oxo dimers of FeTPP have been used as model compounds of cytochromes P-450, and they exhibit greater catalytic activity than the FeTPP monomers.<sup>29</sup>

In order to achieve heterogeneous catalysts, there are successful approaches consisting of anchoring the catalyst into the cavities of porous MOFs,<sup>30-32</sup> doping the

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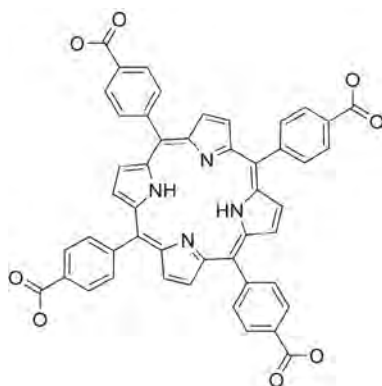
MOF with the catalyst<sup>33</sup> or post functionalizing the MOF.<sup>34,35</sup> Thus, our proposal is using the catalyst as a structural units. As concluded by several recent works,<sup>36- 46</sup> this approach has been observed to be effective. However, the number of metalloporphyrinic compounds in which the MOF itself plays as a catalyst is very low. In fact, as we are concerned, there are about 10 articles on the matter.

In this sense, our previous research on metalloporphyrins<sup>47-49</sup> has had the same goal. However, we have not been successful until now. The selection of TCPP (TCPP=*meso*-tetra(4-carboxyphenyl)porphine) must be underlined in this sense

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(Scheme 1).

**Scheme 1.** Molecular structure for TCPP.



There are many TCPP-based coordination networks in literature, and they exhibit different types of packing.<sup>50-52</sup> On the other hand, most of the reported  $\mu$ -oxo dimers are of the FeTPP type<sup>53-60</sup> (TPP = *meso*-tetra(4-phenyl)porphine, or

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octaethylporphyrins (OEP).<sup>61- 75</sup> However, as far as we are concerned, no dimers of the  $\mu$ -oxo FeTCPP-type have been reported so far.

Taking into account the above mentioned aspects, this work reports on the first TCPP based  $\mu$ -oxo dimer with formula  $\mu$ -O-[FeTCPP]<sub>2</sub>·nDMF (DMF = N,N-dimethylformamide and n≈16). The X-ray single crystal analysis reveals that the dimers crystallize producing a 2D array via hydrogen bonds, sustained by interlayer  $\pi$ - $\pi$  interactions. Additionally, the compound has been exhaustively characterized by means of IR, Raman, UV-Vis, Mössbauer and EPR (Electron Paramagnetic Resonance) spectroscopies, thermogravimetric analysis, magnetic susceptibility measurements and catalytic tests.

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## IV.2. Experimental Section

### IV.2.1. Materials

All solvents and chemicals were used as received from reliable commercial sources. The reagent iron (III) *meso*-tetra(4-carboxyphenyl)porphine chloride (FeTCPP-Cl) was purchased from Frontier Scientific, and Isophthalic acid 99% and the solvent N,N-dimethylformamide (DMF) 99.8% were purchased from Sigma-Aldrich Co.

### IV.2.2. X-ray structure determination

Prismatic black single-crystals of  $\mu$ -O-[FeTCPP]<sub>2</sub>·nDMF with dimensions given in Table 1 were selected under polarizing microscope and mounted on MicroMounts™. Single-crystal X-ray diffraction data were collected at 100 K on an Agilent Technologies SuperNova single source diffractometer with Cu-K $\alpha$  radiation ( $\lambda$ =1.54184 Å). Data frames were processed (unit cell determination, intensity data integration, correction for Lorentz and polarization effects,<sup>76</sup> and analytical absorption correction) using the CrysAlis software package.<sup>77</sup> The structure of  $\mu$ -O-[FeTCPP]<sub>2</sub>·nDMF was solved in the monoclinic *C*2/*c* space group with Superflip program,<sup>78</sup> which allowed us to obtain the position of iron atom, as well as nitrogen, oxygen and some of the carbon atoms of the TCPP molecule. The refinement of the crystal structure was performed by full matrix least-squares based on  $F^2$ , using the SHELXL-97 program<sup>79</sup> in OLEX<sup>80</sup> obtaining the remaining carbon atoms. Anisotropic thermal parameters were used for all non-hydrogen atoms (Figure S1, Supplementary

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<sup>77</sup> *CrysAlisPro Software System*, Agilent Technologies UK Ltd.: Oxford, U. K., 2012.

<sup>78</sup> Palatinus, L.; Chapuis, G., *J. Appl. Crystallogr.* **2007**, *40*, 786-790.

<sup>79</sup> Sheldrick, G. M., *Acta Crystallogr., Sect. A Found. Crystallogr.* **2008**, *A64*, 112-122.

<sup>80</sup> Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H., *J. Appl. Crystallogr.* **2009**, *42*, 339-341.

Information). All the hydrogen atoms connected to the aromatic rings (C-H 0.95Å) were fixed geometrically, and were refined using a riding model with common isotropic displacements. The hydrogen atoms of the carboxylic groups were not considered due to the lack of density in the residual density map; however they are included in the formula. DMF molecules were disordered in the crystal and the resulting electron density was found to be uninterpretable. The solvent contribution to the structure factors was taken into account by back-Fourier transformation of all density found in the disordered area using a solvent mask in OLEX. Neither formula mass, nor calculated density takes account of the solvent. Bond distances and angles, atomic coordinates, anisotropic thermal parameters and hydrogen atom coordinates are given in Tables S1-S4, Supplementary Information.

**Table 1.** Crystallographic Data for  $\mu$ -O-[FeTCPP]<sub>2</sub>·nDMF.

| Compound  | $\mu$ -O-[FeTCPP] <sub>2</sub> ·nDMF   |
|---|--|
| Formula   | C <sub>96</sub> H <sub>56</sub> Fe <sub>2</sub> N <sub>8</sub> O <sub>17</sub> |
| FW, g·mol <sup>-1</sup>   | 1705.21  |
| Crystal system  | Monoclinic   |
| Space group (no. 15)  | C2/c   |
| <i>a</i> , Å  | 39.3340(4)   |
| <i>b</i> , Å  | 19.8329(2)   |
| <i>c</i> , Å  | 16.0292(2)   |
| $\beta$ , deg   | 98.4180(10)  |
| <i>V</i> , Å <sup>3</sup>   | 12369.8(2)   |
| <i>Z</i>  | 4  |
| $\rho_{obs}$ , $\rho_{cal}$ , g·cm <sup>-3</sup>                          | 1.575(5), 0.911  |
| <i>F</i> (000)  | 3472   |
| $\mu$ , mm <sup>-1</sup>  | 2.304  |
| Crystal size, mm  | 0.21 x 0.12 x 0.05   |
| Absorption correction   | Analytical   |
| Radiation, $\lambda$ , Å  | 1.54184  |
| Temperature, K  | 100(2)   |
| Reflections collected, unique   | 50744, 12049 ( $R_{int}$ =0.04)  |
| Limiting indices  | -48<= <i>h</i> <=47, 0<= <i>k</i> <=24, 0<= <i>l</i> <=19                      |
| Refinement method   | Full-matrix least-squares on <i>F</i> <sup>2</sup>                             |
| Final <i>R</i> indices [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )] <sup>a</sup> | <i>R</i> 1 = 0.0608, w <i>R</i> 2 = 0.1867                                     |
| <i>R</i> indices (all data) <sup>a</sup>                                  | <i>R</i> 1 = 0.0788, w <i>R</i> 2 = 0.2025                                     |
| Goodness of fit on <i>F</i> <sup>2</sup>                                  | 1.063  |
| Parameters/restraints   | 555 / 0  |

#### IV.2.3. Physicochemical characterization techniques

The IR spectra were collected on a JASCO FT/IR-6100 spectrometer at room temperature at the range of 4000–400  $\text{cm}^{-1}$ , in KBr pellets (1% of the sample). Raman spectra of the solid samples were recorded using a Renishaw InVia spectrometer equipped with a 785 nm laser at the range of 3500–150  $\text{cm}^{-1}$ . UV-visible diffuse-reflectance measurements were carried out on a Cary 5000 UV-Vis-NIR spectrophotometer in the range of 2500 to 200 nm. C, H, N and O elemental analyses were measured using a Euro EA 3000 elemental analyzer. The thermal analyses were carried out in air atmosphere using a NETZSCH STA 449F3 instrument. A crucible containing approximately 10 mg of sample was heated at 5  $^{\circ}\text{C min}^{-1}$  in the temperature range 30–600  $^{\circ}\text{C}$ . Mössbauer spectra were obtained at room temperature using a constant-acceleration Mössbauer spectrometer with a  $^{57}\text{Co/Rh}$  source. The velocity calibration was done using a metallic Fe foil. Electron paramagnetic resonance (EPR) spectra were measured with a Bruker ESP-300 spectrometer operating at X band and equipped with a nitrogen and helium cryostat. Magnetic susceptibility measurements were measured in the range of 4–300 K with a Quantum Design SQUID MPMS-7T magnetometer.

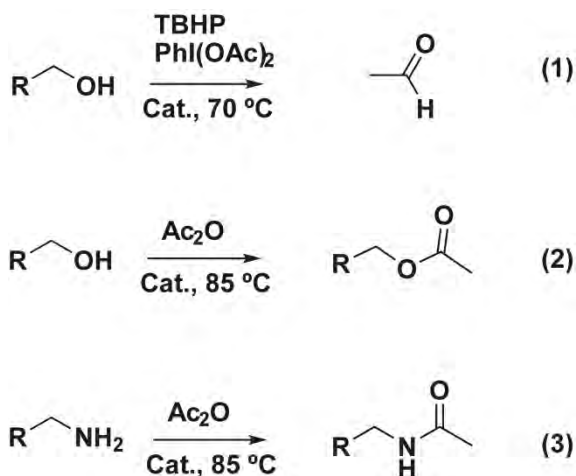
#### IV.2.4. Catalytic tests

The oxidation reactions of benzyl alcohol (Scheme 2, top) were carried out at 70  $^{\circ}\text{C}$  using acetonitrile as solvent. Before the reactions, dried compound (0.0032 mmol) was activated by stirring it with the oxidizing agent *tert*-butyl hydroperoxide (TBHP) or iodobenzene diacetate ( $\text{PhI}(\text{OAc})_2$ ) in acetonitrile, for 30 min at 70  $^{\circ}\text{C}$ . After this activation stage, the catalyst was separated from the liquid media by centrifugation. The reactor with the activated catalyst was then charged with 0.12 mmol of benzyl alcohol in 2 mL of solvent.

The acetylation of alcohols (Scheme 2, middle) and amines (Scheme 2, bottom) were carried out at 85 °C using acetonitrile as solvent. Acetic anhydride was used as acetyl source and the reactor was charged with 0.12 mmol of the corresponding alcohol or amine (phenol and aniline), 0.0059 mmol of catalyst and 0.24 mmol of acetic anhydride in 1 mL of solvent.

Reaction samples were taken at regular times and analyzed on a Hewlett-Packard 5890 II GC-MS gas chromatograph-mass spectrometer. After the reactions, the catalysts were filtered and characterized by IR and Raman spectroscopies. Due to the low crystallinity of  $\mu$ -O-[FeTCPP]<sub>2</sub>·nDMF, X-ray powder diffraction was rejected as a characterization technique for the recovered catalyst.

**Scheme 2.** Catalytic tests reaction schemes.



### IV.3. Results and Discussion

#### IV.3.1. Synthesis of $\mu$ -O-[FeTCPP]<sub>2</sub>·nDMF

Iron (III) *meso*-tetra(4-carboxyphenyl)porphine chloride (8.8 mg, 0.01 mmol)

and isophthalic acid (9.9 mg, 0.06 mmol) were dissolved in DMF (4 mL) in a small capped vial, sonicated to ensure homogeneity and heated to 80 °C for 72 h, following by slow cooling to room temperature, yielding diffraction quality prismatic black crystals. (Found: C, 66.91; H, 3.17; N, 6.54; O, 16.40. Calc. for C<sub>96</sub>H<sub>56</sub>Fe<sub>2</sub>N<sub>8</sub>O<sub>17</sub>: C, 67.62; H, 3.31; N, 6.57; O, 15.95).

#### IV.3.2. Crystal structure

Crystal structure of  $\mu$ -O-[FeTCPP]<sub>2</sub>·nDMF was determined by means of X-ray single crystal diffraction. The structure shows that two FeTCPP rings are bonded together by a bridging O atom in a Fe-O-Fe bond system (Figure 1a). The iron atom is on a five-coordinated square pyramidal environment, displaced by 0.445 Å from the mean porphyrin plane (24 atoms) towards the oxo oxygen atom, and forms a nearly lineal Fe-O-Fe angle (179.78°). The Fe-N<sub>p</sub> distances are in the narrow range of 2.077(2) to 2.087(2) Å, while the Fe-O distance is 1.7597(4) Å. These distances and angles are typical for high-spin iron (III)  $\mu$ -oxo dimers.<sup>81- 93</sup> The macrocyclic rings are

<sup>81</sup> Patra, R.; Bhowmik, S.; Ghosh, S. K.; Rath, S. P., *Eur. J. Inorg. Chem.* **2009**, 654-655.

<sup>82</sup> Jiao, X. D.; Huang, J. W.; Ji, L. N.; Luo, B. S.; Chen, L. R., *J. Inorg. Biochem.* **1997**, *65*, 229.

<sup>83</sup> Strauss, S. H.; Pawlik, M. J.; Skowrya, J.; Kennedy, J. R.; Anderson, O. P.; Spartalian, K.; Dye, J. L., *Inorg. Chem.* **1987**, *26*, 724-730.

<sup>84</sup> Konarev, D. V.; Khasanov, S. S.; Lyubovskaya, R. N., *J. Porphyrins Phthalocyanines* **2010**, *14*, 293-297.

<sup>85</sup> Li, M.; Shang, M.; Duval, H. F.; Scheidt, W. R., *Acta Crystallogr., Sect. C Cryst. Struct. Commun.* **2000**, *C56*, 1206-1207.

<sup>86</sup> Kadish, K. M.; Autret, M.; Ou, Z.; Tagliatesta, P.; Boschi, T.; Fares, V., *Inorg. Chem.* **1997**, *36*, 204-207.

<sup>87</sup> Lay, K. L.; Buchler, J. W.; Kenny, J. E.; Scheidt, W. R., *Inorg. Chim. Acta* **1986**, *123*, 91-97.

<sup>88</sup> Da Silva, C.; Bonomo, L.; Solari, E.; Scopelliti, R.; Floriani, C.; Re, N., *Chem. -Eur. J.* **2000**, *6*, 4518-4531.

<sup>89</sup> Li, A.-R.; Wei, H.-H.; Gang, L.-L., *Inorg. Chim. Acta* **1999**, *290*, 51-56.

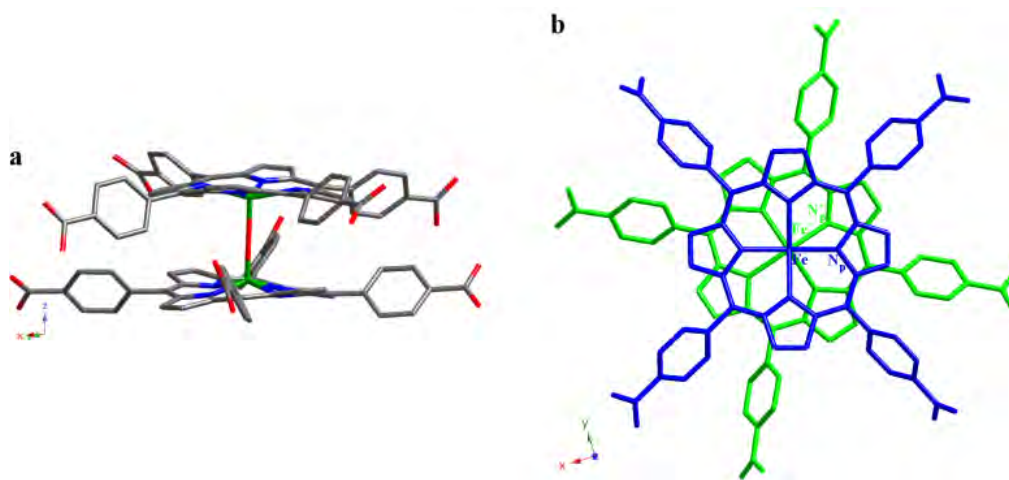
<sup>90</sup> Gold, A.; Jayaraj, K.; Doppelt, P.; Fischer, J.; Weiss, R., *Inorg. Chim. Acta* **1988**, *150*, 177.

<sup>91</sup> Karlin, K. D.; Nanthakumar, A.; Fox, S.; Murthy, N. N.; Ravi, N.; Huynh, B. H.; Orosz, R. D.; Day, E. P., *J. Am. Chem. Soc.* **1994**, *116*, 4753-4763.

<sup>92</sup> Johnson, M. R.; Seok, W. K.; Ma, W.; Sledobnick, C.; Wilcoxon, K. M.; Ibers, J. A., *J. Org. Chem.* **1996**, *61*, 3298-3303.

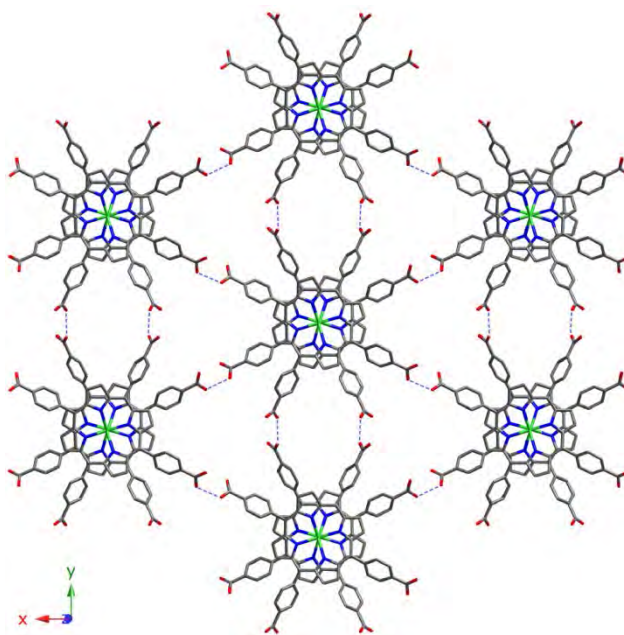
<sup>93</sup> Suzuki, M.; Tsuge, K.; Sasaki, Y.; Imamura, T., *Chem. Lett.* **2003**, *32*, 564-565.

essentially parallel to each other, the angle between the two central N<sub>4</sub> planes being 0.31°. The relative orientations of the two porphyrin rings make an average N<sub>p</sub>-Fe-Fe'-N'<sub>p</sub> dihedral angle (torsional angle) of 33.62° (Figure 1b) to accommodate the peripheral carboxylic groups.



**Figure 1.** (a) Dimeric unit for  $\mu\text{-O-[FeTCPP]}_2 \cdot n\text{DMF}$ . Color code: Fe: green, N: blue, C: grey and O: red. H atoms have been omitted for clarity and (b) top view of the dimer.

These coordination entities crystallize as shown in Figure 2. Each dimer is surrounded by another six producing an H-bonded 2D layer on the  $xy$  plane. The robust intralayer H-bonding system is generated from O8 to O4 (2.411 Å) and from O7 to O2 (2.470 Å) maintaining the stability of the layers.



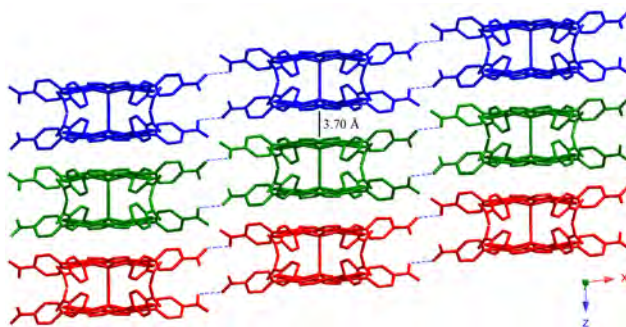
**Figure 2.** View of the H-bonded 2D layer for  $\mu$ -O-[FeTCPP]<sub>2</sub>·nDMF. Color code: Fe: green, N: blue, C: grey, O: red and H-bonds: dashed lines. H atoms have been omitted for clarity.

The H-bonded 2D layers are stacked along the (001) direction, sustained by  $\pi$ - $\pi$  interactions (3.5~3.9 Å) among the dimers of each layer (Figure 3). Crystallization DMF molecules are located in the voids generated between dimers. Unfortunately, these molecules have not been located in the structure refinement process. The resulting voids without DMF molecules were analyzed with PLATON program,<sup>94</sup> showing a 5836.2 Å<sup>3</sup> potential solvent volume (47.2% of the unit cell) and a calculated 2470.1 Å<sup>3</sup> effective volume. Taking into account the single crystal experimental density, the initial weight loss observed in the thermogravimetric analysis and the calculated free effective volume we have estimated the presence of 16 DMF molecules

<sup>94</sup> Spek, A. L. *PLATON, A Multipurpose Crystallographic Tool*, Utrecht University, Utrecht, The Netherlands, 1998.



per unit cell. These DMF molecules are located on the two types of voids on the crystal structure (along the  $c$  axis and interweaving the 2D layers).



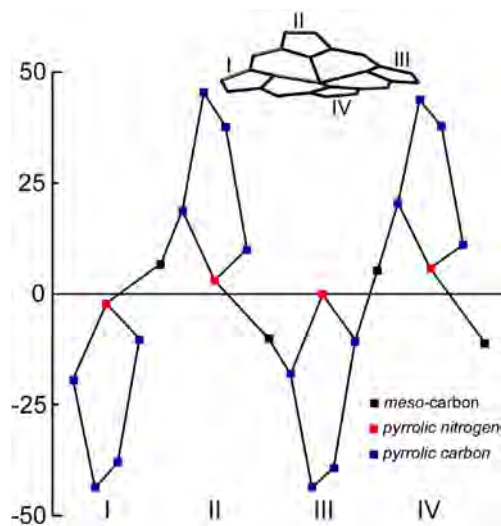
**Figure 3.** Stacking of the 2D layers for  $\mu$ -O-[FeTCPP] $_2$ ·nDMF, where each layer is shown in a different color. Intralayer H-bonds are shown as dashed lines. H atoms have been omitted for clarity.

The out-of-plane distortion of the porphyrin macrocycle was analyzed by the normal-coordinate structural decomposition method developed by Shelnutz *et al.* (NSD).<sup>95,96</sup> In a saddle conformation, alternate pyrrole rings tilt up and down with respect to the porphyrin mean plane (24 atoms), and the *meso* carbon atoms lie on the least-square plane. As is evident from Figure 4, the results indicate a main saddle type distortion (*sad*,  $B_{2u}$ ), with a contribution of the 82% to the total displacement of the porphyrin (1.502). This nonplanarity of the porphyrin core is the consequence of significant steric congestion in the periphery of the molecule. The slight saddle distortion on the two porphyrin cores and the value of the Fe atom displacement from the mean porphyrin plane (0.445 Å) is consistent with the presence of high spin

<sup>95</sup> Jentzen, W.; Song, X.-Z.; Shelnutz, J. A., *J. Phys. Chem. B* **1997**, *101*, 1684-1699.

<sup>96</sup> Jentzen, W.; Ma, J.-G.; Shelnutz, J. A., *Biophys. J.* **1998**, *74*, 753-763.

( $S=5/2$ )  $\text{Fe}^{\text{III}}$  ions.<sup>97,98</sup> This fact, as will be seen later, was corroborated by EPR and Mössbauer spectroscopies and by magnetic measurements.



**Figure 4.** Out-of-plane displacements (in units of 0.01 Å) of the porphyrin core atoms from the mean porphyrin plane (of 24 atom) for  $\mu\text{-O-}[\text{FeTCPP}]_2 \cdot n\text{DMF}$ .

#### IV.3.3. Infrared and Raman spectroscopies

The most significant IR spectral changes from the reactant FeTCPPCl porphyrin to the final dimer account for the formation of the  $\mu\text{-oxo}$  diiron(III) bond, with the appearance of two new strong absorptions at 870 and 827  $\text{cm}^{-1}$ . It is well known that the antisymmetric stretching mode ( $\nu_3$ ), specifically the  $\nu_{\text{as}}(\text{Fe-O-Fe})$ , of a linear or bent Fe-O-Fe system usually occurs in the range 900-800  $\text{cm}^{-1}$ .<sup>99</sup> Thus, these two absorptions, at 870 and 827  $\text{cm}^{-1}$ , indicate the presence of a Fe-O-Fe bond. The rest of the observed absorptions are the usual ones for porphyrin compounds:  $\nu_{\text{max}}/\text{cm}^{-1}$

<sup>97</sup> Bhowmik, S.; Ghosh, S. K.; Layek, S.; Verma, H. C.; Rath, S. P., *Chem. -Eur. J.* **2012**, *18*, 13025-13037.

<sup>98</sup> Weiss, R.; Gold, A.; Turner, J., *Chem. Rev.* **2006**, *106*, 2550-2579.

<sup>99</sup> Ercolani, C.; Gardini, M.; Monacelli, F.; Pennesi, G.; Rossi, G., *Inorg. Chem.* **1983**, *22*, 2584-2589.

3414 and 1433 (OH), 3031 (C(sp<sup>2</sup>)H), 1705 and 1202 (CO), 1632 (DMF), 1606-1476 (CC), 1383 (CN), 999 (FeTCPP) (Figure S2, Supplementary Information).

While for IR spectra the dominant feature is the antisymmetric Fe-O-Fe absorption, Raman spectra are expected to show a greater contribution of the symmetric Fe-O-Fe vibration. Previous works<sup>100,101</sup> have identified that the vibrations around 363 cm<sup>-1</sup> in Raman spectra correspond to the out-of-plane symmetric Fe-O-Fe stretching mode. Thus,  $\mu$ -O-[FeTCPP]<sub>2</sub>·nDMF shows Raman spectral band at 363.3 cm<sup>-1</sup>, which is identified as the  $\nu_{as}$ (Fe-O-Fe) mode. Furthermore, the additional bands observed in the Raman spectra are mainly porphyrin skeletal vibration modes including  $\nu_{as}$ (C<sub>α</sub>C<sub>m</sub>) (1608),  $\nu$ (C<sub>β</sub>C<sub>β</sub>) (1550),  $\nu_s$ (pyrrole half-ring) (1360),  $\delta$ (C<sub>m</sub>H) (1233) and  $\delta_{as}$ (pyrrole deform) (991) (Figure S3, Supplementary Information).

#### IV.3.4. UV-Visible (Diffuse-Reflectance) spectroscopy

The UV-Vis spectrum of  $\mu$ -O-[FeTCPP]<sub>2</sub>·nDMF shows Soret and Q bands at 361, 576 and 623 nm, respectively (Figure S4, Supplementary Information). The evident blueshift of the Soret band, compared to other iron (III) non-dimeric porphyrin compounds and to the monomeric Fe(TCPP),<sup>102</sup> reflects the short interporphyrin ring separation, whereas the Q bands are redshifted by the presence of carboxylic groups on the periphery of the porphyrin.

#### IV.3.5. Thermogravimetry

The thermogravimetric decomposition curve of the compound shows an initial two-stage mass loss from RT to 360 °C, assigned to the removal of DMF molecules (40.95% weight loss) from the two types of voids on the crystal structure. Afterwards,

<sup>100</sup> Li, A.-R.; Wei, H.-H.; Gang, L.-L., *Inorg. Chim. Acta* **1999**, 290, 51-56.

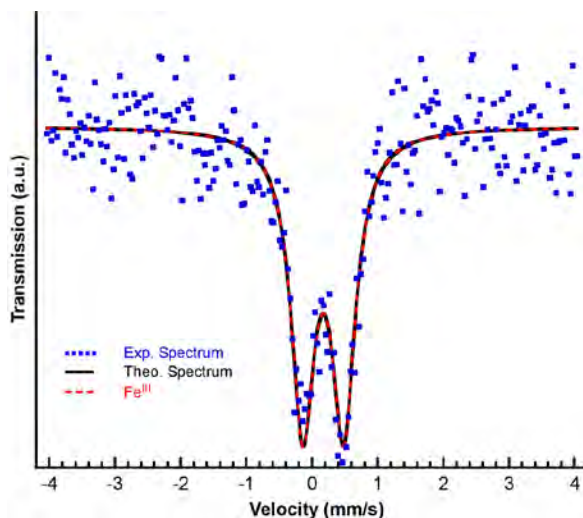
<sup>101</sup> Burke, J. M.; Kincaid, J. R.; Spiro, T. G., *J. Am. Chem. Soc.* **1978**, 100, 6077-6083.

<sup>102</sup> Benedito, F. L.; Nakagaki, S.; Saczk, A. A.; Peralta-Zamora, P. G.; Costa, C. M. M., *Appl. Catal., A* **2003**, 250, 1-11.

a second mass loss occurs from 360 °C to 400 °C, assigned to both porphyrin units (51.5% weight loss) (Figure S5, Supplementary Information). The calcination product has been identified by powder X-ray diffraction analysis, and it consists of Fe<sub>2</sub>O<sub>3</sub> [space group *R-3c*, *a* = 5.0142 Å, *c* = 13.6733 Å and  $\gamma = 120^\circ$ ].<sup>103</sup>

#### IV.3.6. Mössbauer spectroscopy

Compound  $\mu\text{-O-}[\text{FeTCPP}]_2\cdot n\text{DMF}$  has been studied by Mössbauer spectroscopy. The spectrum has been simulated with the NORMOS program,<sup>104</sup> and indicates the presence of a doublet corresponding to Fe<sup>III</sup> ions signals. The signal is assigned to the metal ions in  $\mu\text{-O-}[\text{FeTCPP}]_2\cdot n\text{DMF}$ . The isomer shift ( $\delta$ ) and quadrupolar splitting ( $\Delta E$ ) values are 0.270(6) and 0.623(9), respectively, in the range usually observed for high spin Fe<sup>III</sup> porphyrins<sup>105</sup> (Figure 5).



**Figure 5.** Mössbauer spectra for  $\mu\text{-O-}[\text{FeTCPP}]_2\cdot n\text{DMF}$ .

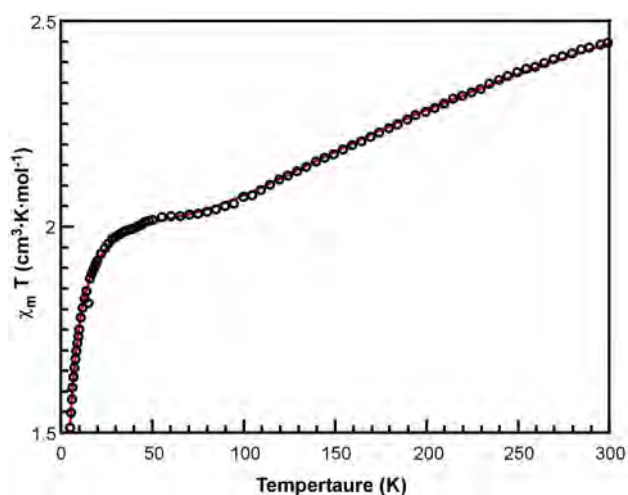
<sup>103</sup> Finger, L. W.; Hazen, R. M., *J. Appl. Phys.* **1980**, *51*, 5362-5367.

<sup>104</sup> Brand, R. A.; Lauer, J.; Herlach, D. M., *J. Phys. F: Met. Phys.* **1983**, *13*, 675-683.

<sup>105</sup> Bhowmik, S.; Ghosh, S. K.; Layek, S.; Verma, H. C.; Rath, S. P., *Chem. - Eur. J.* **2012**, *18*, 13025-13037.

## IV.3.7. Magnetic measurements

Variable temperature magnetic susceptibility measurements have been carried out between 5 and 300 K for  $\mu$ -O-[FeTCPP]<sub>2</sub>·nDMF, and the plot of  $\chi_m T$  versus  $T$  is shown in Figure 6. The effective magnetic moment decreases from 4.43  $\mu_B$  at 300 K to 4.03  $\mu_B$  at 75 K. After a slow decrease, down to 15 K, the effective magnetic moment suffers another abrupt decrease, reaching the value of 3.47  $\mu_B$  at 5 K.



**Figure 6.** Thermal evolution of the  $\chi_m T$  product for  $\mu$ -O-[FeTCPP]<sub>2</sub>·nDMF compound.

The high-temperature behavior is the expected for a strong antiferromagnetic coupling in a  $S = 5/2$  dimer. However, the plateau between 75 and 15 K, and the further abrupt decrease cannot be explained by the sole contribution of this coupling. X-ray analysis discards the presence of impurities in the required high concentration as to account for the observed curve. However, we can think of the presence of broken dimers that are expected to be paramagnetic. The dimers are expected to be broken because the magnetic measurements were performed by using ground single crystals, producing monomeric units. Thus, the decrease in the effective magnetic moment

observed at low temperatures can be explained by means of the Zero Field Splitting effect (ZFS) on the  $S = 5/2$  state.

In order to confirm this hypothesis, experimental data have been adjusted according to equation 1 where  $\chi_{dim}$  and  $\chi_{mon}$  are the contribution of the dimeric and monomeric (broken dimers) species, respectively.

$$\chi_m = (1-\delta) \chi_{dim} + \delta \chi_{mon} \quad \text{equation 1}$$

In order to evaluate the exchange constant  $J$  due to the contribution of the dimeric species ( $\chi_{dim}$ ), the van Vleck equation has been used for a spin Hamiltonian  $H = -2JS_1S_2$  (equation 2).

$$\chi_m = \frac{2Ng^2\beta^2}{kT} \frac{\exp(2x) + 5\exp(6x) + 14\exp(12x) + 30\exp(20x) + 55\exp(30x)}{1 + 3\exp(2x) + 5\exp(6x) + 7\exp(12x) + 9\exp(20x) + 11\exp(30x)}$$

where  $x = J/kT$  equation 2

The van Vleck equation has been also used to estimate the exchange constant  $J$  due to the contribution of the monomeric species ( $\chi_{mon}$ ), but in this case for  $S = 1/2$  in an axially distorted octahedral environment (equation 3). In equation 3,  $D$  is the axial parameter related to the ZFS effect, The E rhombic one has been considered negligible.

$$\chi_{\parallel} = \frac{Ng_{\parallel}^2\beta^2}{4kT} \frac{1 + 9\exp(-2x) + 25\exp(-6x)}{1 + \exp(-2x) + \exp(-6x)}$$

$$\chi_{\perp} = \frac{Ng_{\perp}^2\beta^2}{4kT} \frac{9 + 8/x - 11\exp(-2x)/2x - 5\exp(-6x)/2x}{1 + \exp(-2x) + \exp(-6x)}$$

where  $x = D/kT$  equation 3

Taking into account that the orbital contribution for  $S = 5/2$  ions is habitually negligible, the  $g$  value was considered to be  $g=2$ . This way, the number of parameters to be adjusted was lower, producing estimated values of  $J = -132 \text{ cm}^{-1}$ ;  $D = 6.9 \text{ cm}^{-1}$  and  $\delta = 0.23$ . These values were obtained by minimizing the R error (equation 4).

$$R = \frac{\sum[\chi_m T^{\text{exp}} - \chi_m T^{\text{cal}}]^2}{\sum[\chi_m T^{\text{exp}}]^2} \quad \text{equation 4}$$

Figure 6 shows that experimental and calculated values are in very good accordance ( $R=1.2 \times 10^{-5}$ ). The  $J$  value is comparable to other ones found for similar systems.<sup>106-108</sup> It is worth mentioning that the  $\delta$  value indicates a significant amount of monomeric species.

#### IV.3.8. Electronic paramagnetic resonance (EPR)

As occurs with other similar compounds that exhibit strong antiferromagnetic couplings through two high-spin iron(III) centers,<sup>108</sup> we did not expect to obtain EPR signal for this compound. However, the X-band EPR spectral measurements carried out for  $\mu\text{-O-[FeTCPP]}_2 \cdot n\text{DMF}$  at room temperature in solid state show an axially symmetric spectra with  $g_{\perp}$  and  $g_{\parallel}$  values close to 6 and 2, respectively; unequivocal evidence of high spin  $\text{Fe}^{\text{III}}$  ( $S = 5/2$ ) ions (Figure 7). The observed signal should therefore be caused by the monomeric species detected by magnetic measurements.

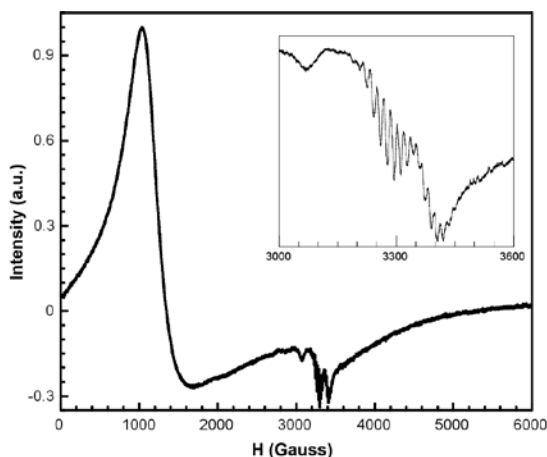
As observed in Figure 7, the parallel component exhibits a superhyperfine structure ( $A_{\parallel} = 17 \text{ Gauss}$ ) that is not habitual for this type of compounds. This superhyperfine structure can be explained by the interaction between the  $\text{Fe}^{\text{III}}$  electronic spin and the nuclear spins ( $I=1$ ) of the four pyrrolic nitrogen atoms bonded

<sup>106</sup> Hoffman, A. B.; Collins, D. M.; Day, V. W.; Fleischer, E. B.; Srivastava, T. S.; Hoard, J. L., *J. Am. Chem. Soc.* **1972**, *94*, 3620-3626.

<sup>107</sup> Da Silva, C.; Bonomo, L.; Solari, E.; Scopelliti, R.; Floriani, C.; Re, N., *Chem. - Eur. J.* **2000**, *6*, 4518-4531.

<sup>108</sup> Ghosh, S. K.; Patra, R.; Rath, S. P., *Inorg. Chem.* **2010**, *49*, 3449-3460.

to each Fe<sup>III</sup> ion on the equatorial plane. This interaction should produce a nine-line structure. However, taking into account the ZFS effect confirmed for  $\mu$ -O-[FeTCPP]<sub>2</sub>·nDMF, this structure should be repeated at least in two different transitions within the  $S = 5/2$  state. The fact that this superhyperfine structure has not been previously observed in similar compounds can be explained if considering that the magnetic matrix is very diluted for  $\mu$ -O-[FeTCPP]<sub>2</sub>·nDMF, due to the fact that 47% of the unit cell is occupied by DMF molecules. Therefore, the dilution of the magnetic matrix, induced by the porous nature of the compound, allows the unusual observance of electronic and nuclear spin interactions between different atoms.



**Figure 7.** X-band EPR spectrum for  $\mu$ -O-[FeTCPP]<sub>2</sub>·nDMF registered at room temperature.

#### IV.3.9. Catalytic properties

Synthetic metalloporphyrins complexes have been largely used for a variety of catalytic transformations,<sup>109</sup> and a special emphasis is put on the single atom bridged diiron complexes as an emerging class of catalysts.<sup>110</sup> In this sense,  $\mu$ -O-[FeTCPP]<sub>2</sub>·nDMF exhibits two additional characteristics that make one think of its

<sup>109</sup> Meunier, B., *Chem. Rev.* **1992**, *92*, 1411-1456.

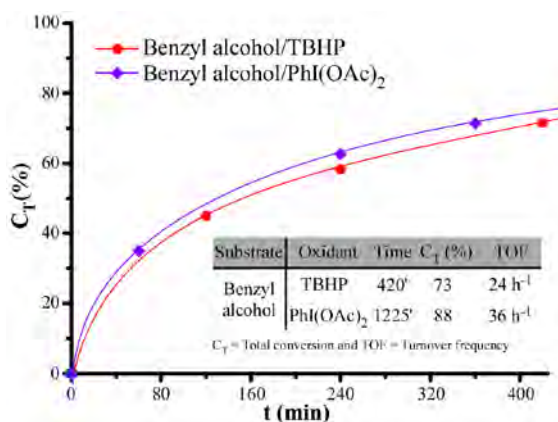
<sup>110</sup> Sorokin, A. B., *Chem. Rev.* **2013**, *113*, 8152-8191.



potential as a catalyst. Firstly,  $\text{Fe}^{\text{III}}$  centers are five-coordinated square pyramidal polyhedra. Secondly, the network is significantly porous, with mobile DMF molecules located in the cavities. Therefore, virtually approaching to the metal ion by other molecules in dissolution seems to be easy. The above mentioned aspects were considered to proceed with the study of the catalytic properties of  $\mu\text{-O-}[\text{FeTCPP}]_2\cdot\text{nDMF}$ . Thus, the catalytic activity of  $\mu\text{-O-}[\text{FeTCPP}]_2\cdot\text{nDMF}$  was tested towards oxidation of alcohols and acetylation of amines and alcohols.

#### IV.3.9.1. Oxidation of alcohols

The oxidation of alcohols is of great importance on organic synthesis and, in this sense, many iron porphyrins have been tested for this reaction.<sup>111,112</sup> The scope of the oxidation reaction was analyzed with benzyl alcohol and two oxidizing agents, TBHP (1.5 eq.) and  $\text{PhI}(\text{OAc})_2$  (2 eq.). Once the reaction conditions were established, the best conversion rates (Figure 8) were obtained when using 5% of catalyst at 70 °C. In Figure 8, the kinetic profiles of the oxidation reactions can be observed.



**Figure 8.** Kinetic profiles for the benzyl alcohol oxidation with TBHP and  $\text{PhI}(\text{OAc})_2$ .

<sup>111</sup> Zou, C.; Zhang, T.; Xie, M.-H.; Yan, L.; Kong, G.-Q.; Yang, X.-L.; Ma, A.; Wu, C.-D., *Inorg. Chem.* **2013**, 52, 3620-3626.

<sup>112</sup> Machado, G. S.; Jose de Lima, O.; Ciuffi, K. J.; Wypych, F.; Nakagaki, S., *Catal. Sci. Technol.* **2013**, 3, 1094-1101.

When using  $\text{PhI}(\text{OAc})_2$  as oxidant, the conversion rates slightly increased. Reutilization is one of the greatest advantages of heterogeneous catalysts and can also provide useful information about the anchoring process and catalyst stability along the catalytic cycle. Thus, recycling tests were carried out over  $\mu\text{-O-}[\text{FeTCPP}]_2 \cdot n\text{DMF}$  for the oxidation of benzyl alcohol and, as observe in Table 2, during the three cycles an increase of catalytic activity is observed up to 98%. This means that the catalyst is activated during the reaction. One simple explanation can be based on the fact that DMF is progressively being removed from the cavities. This way, the increasing accessible area would permit the presence of an increasing number of active centers.

**Table 2.** Recyclability of compound  $\mu\text{-O-}[\text{FeTCPP}]_2 \cdot n\text{DMF}$  for benzyl alcohol oxidation.

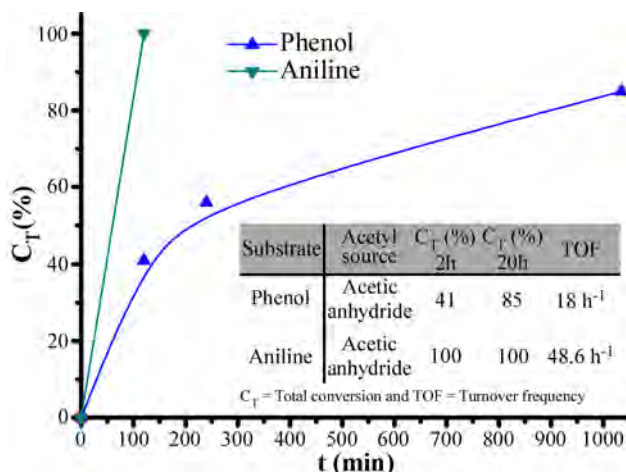
| Cycles | $C_T$ (4h) |
|--------|------------|
| 1      | 58 %       |
| 2      | 77 %       |
| 3      | 98 %       |

$C_T$  = Total conversion

After the oxidation reactions, the solid catalyst was recovered by centrifugation, washed with acetonitrile and ethanol, and then characterized by IR spectroscopy. The IR spectra of the residues for the tested oxidation reactions show that the original compound breaks down when using  $\text{PhI}(\text{OAc})_2$  as oxidant, after three cycles. In contrast, when using TBHP as oxidant, the structural units remain, in fact, the solid shows the same characteristic vibration modes of the original compound. As shown in Figure S6, Supplementary Information the characteristic vibrations of the porphyrin macrocycle are present, although the intensity of the Fe-TCPP and Fe-O-Fe vibrations at  $1000\text{ cm}^{-1}$ ,  $870\text{ cm}^{-1}$  and  $824\text{ cm}^{-1}$  is lower.

## IV.3.9.2. Acetylation of amines and alcohols

The acetylation reaction of amine and hydroxyl groups is very useful in organic synthesis, since in many occasions the protection of those functional groups is necessary to avoid the reaction at these points. Thus,  $\mu$ -O-[FeTCPP]<sub>2</sub>·nDMF was tested with aniline and phenol, and acetic anhydride (2 equivalents) as acetyl source. In all cases, acetonitrile was used as solvent, and once the reaction conditions were established, the best conversion rates (Figure 9) were obtained when using 10% of catalyst at 85 °C. All the reactions were carried out by reflux. In Figure 9 the kinetic profiles of the acetylation reactions can be observed.



**Figure 9.** Kinetic profiles for the phenol and aniline acetylation reactions.

As observed in Figure 9, the phenol acetylation conversion rates are very good with a value close to 85% for a reaction time of 20h. In the case of aniline, the rapid conversion is especially remarkable.

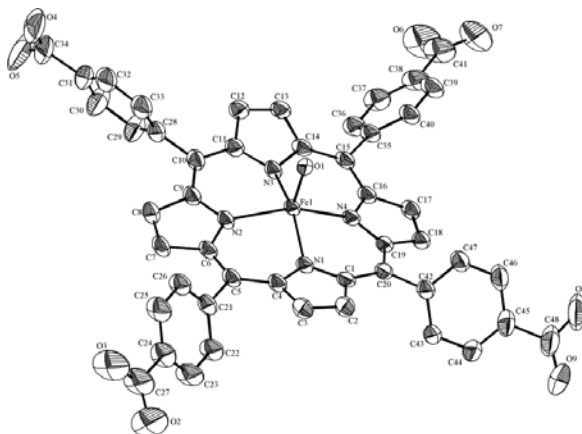
After the acetylation reactions, the solid catalyst was recovered by centrifugation, washed with acetonitrile and ethanol and then characterized by IR and Raman spectroscopies. The compound recovers the original purple color in all cases,

and IR spectra confirm the presence of the original solids (Figure S7, Supplementary Information). Additionally, Raman spectroscopy also confirms the recovery of the original catalyst. In fact, the very characteristic vibration mode of the Fe-O-Fe dimers is visible at about  $370\text{ cm}^{-1}$ . (Figure S8, Supplementary Information).

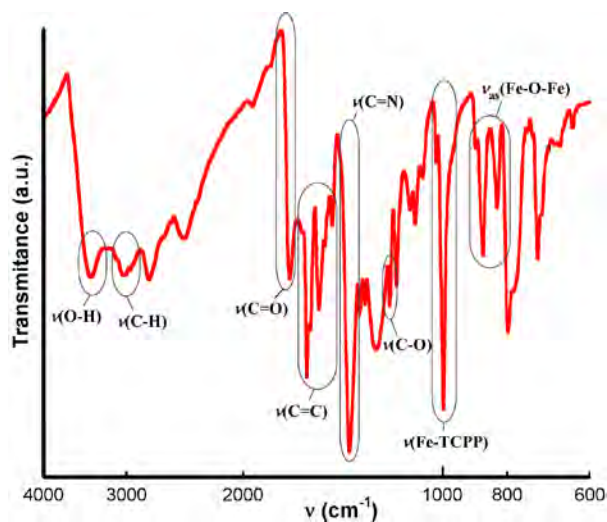
#### IV.4. Conclusions

FeTCPP metalloporphyrin has been used to produce a new porous MOF based on unprecedented  $\mu$ -oxo-FeTCPP dimers. The coordination network exhibits significant porosity, that is related to the unusual appearance of a superhyperfine EPR structure. Additionally, the porous nature of the compound, along with the structural features of the dimers, are responsible for its catalytic properties. Those characteristics allow FeTCPP to be playing a double role, as a catalyst and as a synthon. This is an innovative approach to achieve heterogeneous catalyst as an alternative to the anchoring of effective catalyst into solid frameworks. Compound  $\mu$ -O-[FeTCPP]<sub>2</sub>·nDMF is one of the very few porphyrinic systems where the MOF itself plays as a catalyst, achieving heterogeneous catalysis.

## Supplementary Information

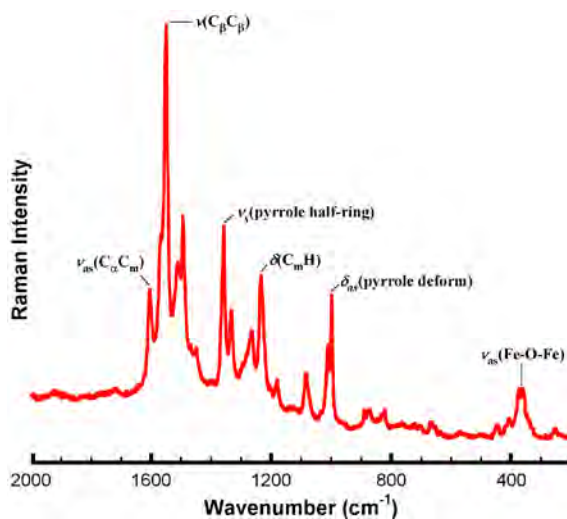


**Figure S1.** ORTEP<sup>113</sup> detail of  $\mu$ -O-[FeTCPP]<sub>2</sub>·nDMF. The thermal ellipsoids correspond to 50% probability. Hydrogen atoms have been omitted.

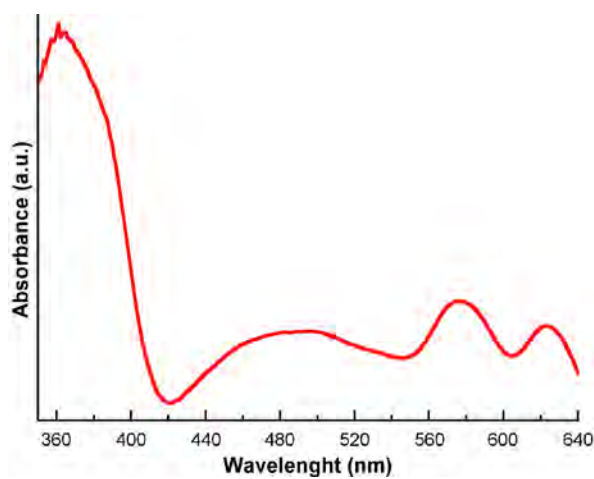


**Figure S2.** IR spectra for  $\mu$ -O-[FeTCPP]<sub>2</sub>·nDMF.

<sup>113</sup> Farrugia, L. J., *J. Appl. Crystallogr.* **1997**, *30*, 565.



**Figure S3.** Raman spectra for  $\mu\text{-O-}[\text{FeTCPP}]_2 \cdot n\text{DMF}$ .



**Figure S4.** UV-Visible spectra for  $\mu\text{-O-}[\text{FeTCPP}]_2 \cdot n\text{DMF}$ .

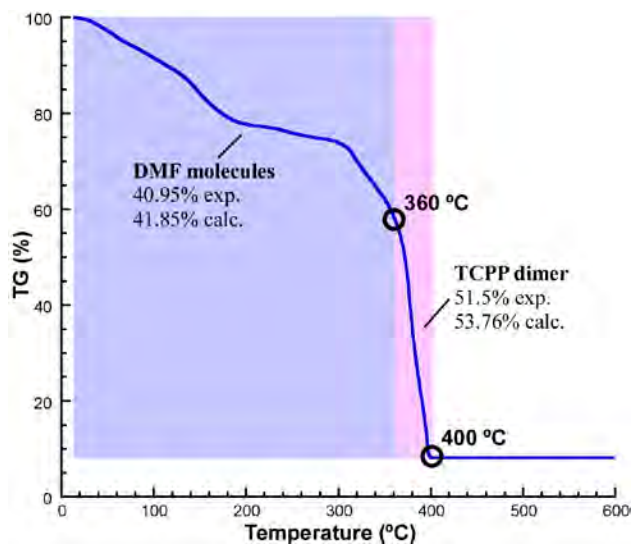


Figure S5. Thermal analysis for  $\mu$ -O-[FeTCPP]<sub>2</sub>·nDMF.

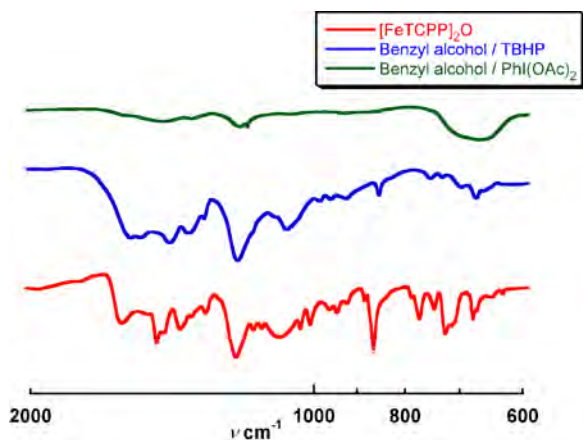
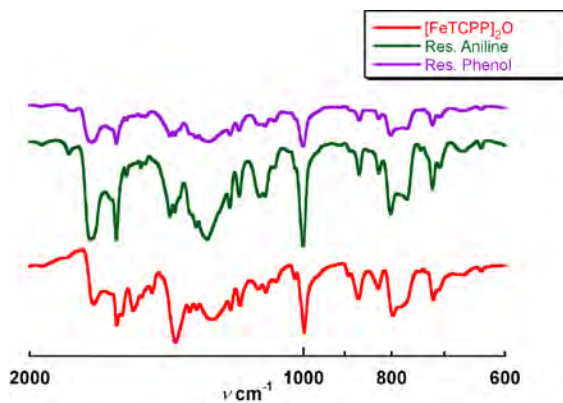
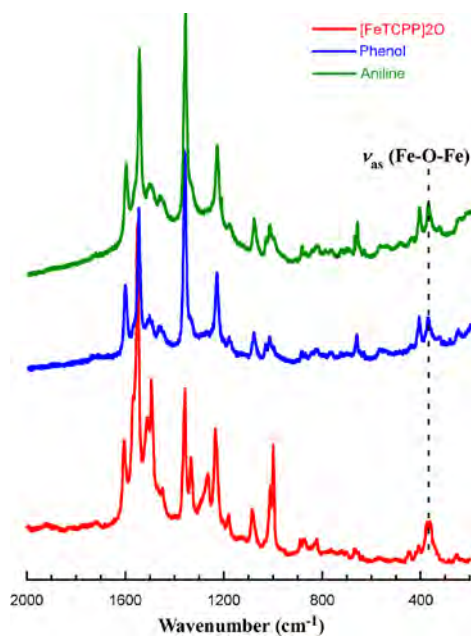


Figure S6. IR spectrums for the residues of the oxidation of benzyl alcohol and the original for  $\mu$ -O-[FeTCPP]<sub>2</sub>·nDMF.



**Figure S7.** IR spectra for the residues of the acetylation of phenol and aniline, and the original for  $\mu$ -O-[FeTCPP]<sub>2</sub>·nDMF.



**Figure S8.** Raman spectra for the residues of the acetylation of phenol and aniline, and the original for  $\mu$ -O-[FeTCPP]<sub>2</sub>·nDMF.



**Table S1.** Bond distances (Å) and angles (°) for  $\mu$ -O-[FeTCPP]<sub>2</sub>·nDMF.**Distances**

|                         |           |             |          |
|-------------------------|-----------|-------------|----------|
| Fe(1)-O(1)              | 1.7597(4) | C(40)-C(39) | 1.390(4) |
| Fe(1)-N(1)              | 2.077(2)  | C(40)-H(40) | 0.9500   |
| Fe(1)-N(4)              | 2.083(2)  | C(37)-C(38) | 1.376(6) |
| Fe(1)-N(2)              | 2.084(2)  | C(37)-C(36) | 1.386(4) |
| Fe(1)-N(3)              | 2.087(2)  | C(37)-H(37) | 0.9500   |
| O(1)-Fe(1) <sup>i</sup> | 1.7597(4) | C(7)-C(8)   | 1.348(4) |
| N(4)-C(19)              | 1.370(4)  | C(7)-H(7)   | 0.9500   |
| N(4)-C(16)              | 1.374(3)  | C(13)-C(12) | 1.354(4) |
| N(2)-C(9)               | 1.368(4)  | C(13)-H(13) | 0.9500   |
| N(2)-C(6)               | 1.376(3)  | C(12)-H(12) | 0.9500   |
| N(1)-C(1)               | 1.366(4)  | C(2)-C(3)   | 1.343(4) |
| N(1)-C(4)               | 1.376(3)  | C(2)-H(2)   | 0.9500   |
| N(3)-C(11)              | 1.365(4)  | C(3)-H(3)   | 0.9500   |
| N(3)-C(14)              | 1.376(3)  | C(28)-C(29) | 1.374(5) |
| O(8)-C(48)              | 1.284(6)  | C(28)-C(33) | 1.407(5) |
| O(3)-C(27)              | 1.217(6)  | C(8)-H(8)   | 0.9500   |
| O(7)-C(41)              | 1.260(7)  | C(35)-C(36) | 1.399(5) |
| O(9)-C(48)              | 1.220(6)  | C(33)-C(32) | 1.365(5) |
| C(16)-C(15)             | 1.407(4)  | C(33)-H(33) | 0.9500   |
| C(16)-C(17)             | 1.440(4)  | C(26)-C(25) | 1.374(4) |
| C(6)-C(5)               | 1.383(4)  | C(26)-C(21) | 1.406(4) |
| C(6)-C(7)               | 1.441(4)  | C(26)-H(26) | 0.9500   |
| O(6)-C(41)              | 1.248(7)  | C(21)-C(22) | 1.381(5) |
| C(20)-C(1)              | 1.397(4)  | C(36)-H(36) | 0.9500   |
| C(20)-C(19)             | 1.421(4)  | C(24)-C(23) | 1.371(5) |
| C(20)-C(42)             | 1.476(4)  | C(24)-C(25) | 1.395(6) |

|             |          |             |          |
|-------------|----------|-------------|----------|
| C(19)-C(18) | 1.427(4) | C(24)-C(27) | 1.504(4) |
| C(1)-C(2)   | 1.452(4) | C(22)-C(23) | 1.396(4) |
| C(9)-C(10)  | 1.396(4) | C(22)-H(22) | 0.9500   |
| C(9)-C(8)   | 1.446(4) | C(23)-H(23) | 0.9500   |
| C(11)-C(10) | 1.407(4) | C(44)-C(45) | 1.380(5) |
| C(11)-C(12) | 1.430(4) | C(44)-H(44) | 0.9500   |
| C(17)-C(18) | 1.350(4) | C(46)-C(45) | 1.410(5) |
| C(17)-H(17) | 0.9500   | C(46)-H(46) | 0.9500   |
| C(15)-C(14) | 1.403(4) | C(45)-C(48) | 1.502(5) |
| C(15)-C(35) | 1.498(3) | C(39)-C(38) | 1.390(6) |
| C(4)-C(5)   | 1.410(4) | C(39)-H(39) | 0.9500   |
| C(4)-C(3)   | 1.439(4) | C(38)-C(41) | 1.514(5) |
| C(43)-C(44) | 1.384(4) | C(29)-C(30) | 1.389(5) |
| C(43)-C(42) | 1.398(4) | C(29)-H(29) | 0.9500   |
| C(43)-H(43) | 0.9500   | C(25)-H(25) | 0.9500   |
| C(10)-C(28) | 1.489(4) | C(32)-C(31) | 1.357(6) |
| C(42)-C(47) | 1.401(4) | C(32)-H(32) | 0.9500   |
| C(14)-C(13) | 1.429(4) | C(31)-C(30) | 1.407(6) |
| C(5)-C(21)  | 1.498(4) | C(31)-C(34) | 1.494(5) |
| C(18)-H(18) | 0.9500   | C(30)-H(30) | 0.9500   |
| C(47)-C(46) | 1.377(5) | C(27)-O(2)  | 1.283(6) |
| C(47)-H(47) | 0.9500   | C(34)-O(5)  | 1.187(7) |
| C(40)-C(35) | 1.384(4) | C(34)-O(4)  | 1.285(7) |

**Angles**

|                 |            |                   |          |
|-----------------|------------|-------------------|----------|
| O(1)-Fe(1)-N(1) | 102.84(7)  | C(12)-C(13)-H(13) | 126.4    |
| O(1)-Fe(1)-N(4) | 103.42(9)  | C(14)-C(13)-H(13) | 126.4    |
| N(1)-Fe(1)-N(4) | 87.17(8)   | C(13)-C(12)-C(11) | 107.0(3) |
| O(1)-Fe(1)-N(2) | 103.77(10) | C(13)-C(12)-H(12) | 126.5    |

|                                |            |                   |          |
|--------------------------------|------------|-------------------|----------|
| N(1)-Fe(1)-N(2)                | 87.27(9)   | C(11)-C(12)-H(12) | 126.5    |
| N(4)-Fe(1)-N(2)                | 152.81(9)  | C(3)-C(2)-C(1)    | 106.3(3) |
| O(1)-Fe(1)-N(3)                | 101.24(7)  | C(3)-C(2)-H(2)    | 126.8    |
| N(1)-Fe(1)-N(3)                | 155.92(9)  | C(1)-C(2)-H(2)    | 126.8    |
| N(4)-Fe(1)-N(3)                | 87.05(9)   | C(2)-C(3)-C(4)    | 108.0(2) |
| N(2)-Fe(1)-N(3)                | 87.27(9)   | C(2)-C(3)-H(3)    | 126.0    |
| Fe(1) <sup>i</sup> -O(1)-Fe(1) | 179.79(15) | C(4)-C(3)-H(3)    | 126.0    |
| C(19)-N(4)-C(16)               | 106.5(2)   | C(29)-C(28)-C(33) | 118.5(3) |
| C(19)-N(4)-Fe(1)               | 125.73(17) | C(29)-C(28)-C(10) | 122.3(3) |
| C(16)-N(4)-Fe(1)               | 127.11(18) | C(33)-C(28)-C(10) | 119.2(3) |
| C(9)-N(2)-C(6)                 | 107.1(2)   | C(7)-C(8)-C(9)    | 107.2(3) |
| C(9)-N(2)-Fe(1)                | 125.50(17) | C(7)-C(8)-H(8)    | 126.4    |
| C(6)-N(2)-Fe(1)                | 126.99(19) | C(9)-C(8)-H(8)    | 126.4    |
| C(1)-N(1)-C(4)                 | 106.4(2)   | C(40)-C(35)-C(36) | 118.9(3) |
| C(1)-N(1)-Fe(1)                | 123.72(16) | C(40)-C(35)-C(15) | 120.2(3) |
| C(4)-N(1)-Fe(1)                | 124.44(18) | C(36)-C(35)-C(15) | 120.8(3) |
| C(11)-N(3)-C(14)               | 106.3(2)   | C(32)-C(33)-C(28) | 121.2(4) |
| C(11)-N(3)-Fe(1)               | 123.26(17) | C(32)-C(33)-H(33) | 119.4    |
| C(14)-N(3)-Fe(1)               | 124.06(18) | C(28)-C(33)-H(33) | 119.4    |
| N(4)-C(16)-C(15)               | 125.1(2)   | C(25)-C(26)-C(21) | 119.8(3) |
| N(4)-C(16)-C(17)               | 109.1(2)   | C(25)-C(26)-H(26) | 120.1    |
| C(15)-C(16)-C(17)              | 125.7(2)   | C(21)-C(26)-H(26) | 120.1    |
| N(2)-C(6)-C(5)                 | 125.6(2)   | C(22)-C(21)-C(26) | 119.1(3) |
| N(2)-C(6)-C(7)                 | 108.9(3)   | C(22)-C(21)-C(5)  | 120.6(3) |
| C(5)-C(6)-C(7)                 | 125.5(2)   | C(26)-C(21)-C(5)  | 120.2(3) |
| C(1)-C(20)-C(19)               | 123.7(3)   | C(37)-C(36)-C(35) | 120.1(3) |
| C(1)-C(20)-C(42)               | 119.0(2)   | C(37)-C(36)-H(36) | 120.0    |
| C(19)-C(20)-C(42)              | 117.3(2)   | C(35)-C(36)-H(36) | 120.0    |
| N(4)-C(19)-C(20)               | 125.7(2)   | C(23)-C(24)-C(25) | 119.2(3) |

|                   |          |                   |          |
|-------------------|----------|-------------------|----------|
| N(4)-C(19)-C(18)  | 109.9(2) | C(23)-C(24)-C(27) | 120.6(4) |
| C(20)-C(19)-C(18) | 124.4(3) | C(25)-C(24)-C(27) | 120.1(4) |
| N(1)-C(1)-C(20)   | 125.7(3) | C(21)-C(22)-C(23) | 120.3(3) |
| N(1)-C(1)-C(2)    | 110.0(2) | C(21)-C(22)-H(22) | 119.8    |
| C(20)-C(1)-C(2)   | 124.3(3) | C(23)-C(22)-H(22) | 119.8    |
| N(2)-C(9)-C(10)   | 126.1(2) | C(24)-C(23)-C(22) | 120.6(3) |
| N(2)-C(9)-C(8)    | 109.1(2) | C(24)-C(23)-H(23) | 119.7    |
| C(10)-C(9)-C(8)   | 124.7(3) | C(22)-C(23)-H(23) | 119.7    |
| N(3)-C(11)-C(10)  | 125.1(2) | C(45)-C(44)-C(43) | 121.6(3) |
| N(3)-C(11)-C(12)  | 110.0(2) | C(45)-C(44)-H(44) | 119.2    |
| C(10)-C(11)-C(12) | 124.9(3) | C(43)-C(44)-H(44) | 119.2    |
| C(18)-C(17)-C(16) | 107.2(2) | C(47)-C(46)-C(45) | 120.8(3) |
| C(18)-C(17)-H(17) | 126.4    | C(47)-C(46)-H(46) | 119.6    |
| C(16)-C(17)-H(17) | 126.4    | C(45)-C(46)-H(46) | 119.6    |
| C(14)-C(15)-C(16) | 124.7(2) | C(44)-C(45)-C(46) | 118.1(3) |
| C(14)-C(15)-C(35) | 117.6(3) | C(44)-C(45)-C(48) | 120.9(3) |
| C(16)-C(15)-C(35) | 117.6(2) | C(46)-C(45)-C(48) | 121.0(3) |
| N(1)-C(4)-C(5)    | 125.3(3) | C(38)-C(39)-C(40) | 120.1(3) |
| N(1)-C(4)-C(3)    | 109.2(2) | C(38)-C(39)-H(39) | 119.9    |
| C(5)-C(4)-C(3)    | 125.5(2) | C(40)-C(39)-H(39) | 119.9    |
| C(44)-C(43)-C(42) | 120.3(3) | C(37)-C(38)-C(39) | 119.4(3) |
| C(44)-C(43)-H(43) | 119.8    | C(37)-C(38)-C(41) | 120.2(4) |
| C(42)-C(43)-H(43) | 119.8    | C(39)-C(38)-C(41) | 120.4(4) |
| C(9)-C(10)-C(11)  | 124.4(3) | C(28)-C(29)-C(30) | 120.5(4) |
| C(9)-C(10)-C(28)  | 117.5(2) | C(28)-C(29)-H(29) | 119.7    |
| C(11)-C(10)-C(28) | 117.9(3) | C(30)-C(29)-H(29) | 119.7    |
| C(43)-C(42)-C(47) | 118.4(3) | C(26)-C(25)-C(24) | 120.9(3) |
| C(43)-C(42)-C(20) | 122.2(2) | C(26)-C(25)-H(25) | 119.5    |
| C(47)-C(42)-C(20) | 119.3(3) | C(24)-C(25)-H(25) | 119.5    |

|                   |          |                   |          |
|-------------------|----------|-------------------|----------|
| N(3)-C(14)-C(15)  | 125.1(3) | O(9)-C(48)-O(8)   | 124.1(4) |
| N(3)-C(14)-C(13)  | 109.6(2) | O(9)-C(48)-C(45)  | 121.0(4) |
| C(15)-C(14)-C(13) | 125.3(2) | O(8)-C(48)-C(45)  | 114.8(4) |
| C(6)-C(5)-C(4)    | 124.8(2) | C(31)-C(32)-C(33) | 120.2(4) |
| C(6)-C(5)-C(21)   | 118.8(2) | C(31)-C(32)-H(32) | 119.9    |
| C(4)-C(5)-C(21)   | 116.5(3) | C(33)-C(32)-H(32) | 119.9    |
| C(17)-C(18)-C(19) | 107.2(2) | C(32)-C(31)-C(30) | 120.1(3) |
| C(17)-C(18)-H(18) | 126.4    | C(32)-C(31)-C(34) | 121.4(4) |
| C(19)-C(18)-H(18) | 126.4    | C(30)-C(31)-C(34) | 118.5(5) |
| C(46)-C(47)-C(42) | 120.7(3) | O(6)-C(41)-O(7)   | 125.1(4) |
| C(46)-C(47)-H(47) | 119.6    | O(6)-C(41)-C(38)  | 119.5(5) |
| C(42)-C(47)-H(47) | 119.6    | O(7)-C(41)-C(38)  | 115.3(5) |
| C(35)-C(40)-C(39) | 120.6(3) | C(29)-C(30)-C(31) | 119.4(4) |
| C(35)-C(40)-H(40) | 119.7    | C(29)-C(30)-H(30) | 120.3    |
| C(39)-C(40)-H(40) | 119.7    | C(31)-C(30)-H(30) | 120.3    |
| C(38)-C(37)-C(36) | 120.8(4) | O(3)-C(27)-O(2)   | 125.1(4) |
| C(38)-C(37)-H(37) | 119.6    | O(3)-C(27)-C(24)  | 121.7(4) |
| C(36)-C(37)-H(37) | 119.6    | O(2)-C(27)-C(24)  | 113.1(4) |
| C(8)-C(7)-C(6)    | 107.5(2) | O(5)-C(34)-O(4)   | 122.3(4) |
| C(8)-C(7)-H(7)    | 126.3    | O(5)-C(34)-C(31)  | 122.3(5) |
| C(6)-C(7)-H(7)    | 126.3    | O(4)-C(34)-C(31)  | 115.4(5) |
| C(12)-C(13)-C(14) | 107.2(2) |                   |          |

Symmetry code: i)  $-x+1, y, -z+1/2$

**Table S2.** Fractional atomic coordinates ( $\times 10^4$ ) and equivalent thermal factors ( $\times 10^3$ ) for  $\mu$ -O-[FeTCPP]<sub>2</sub>·nDMF.

| Atoms | X       | Y        | Z       | $U_{eq}, \text{\AA}^2$ |
|-------|---------|----------|---------|------------------------|
| Fe(1) | 5001(1) | 865(1)   | 3598(1) | 29(1)                  |
| O(1)  | 5000    | 864(1)   | 2500    | 34(1)                  |
| N(4)  | 5154(1) | -111(1)  | 3956(1) | 33(1)                  |
| N(2)  | 4853(1) | 1844(1)  | 3853(1) | 35(1)                  |
| N(1)  | 4504(1) | 569(1)   | 3712(1) | 32(1)                  |
| N(3)  | 5506(1) | 1162(1)  | 4029(1) | 33(1)                  |
| O(8)  | 4007(1) | -3549(1) | 2286(2) | 106(1)                 |
| O(3)  | 2844(1) | 3526(2)  | 2943(3) | 113(2)                 |
| O(7)  | 7117(1) | -1761(2) | 3786(3) | 107(1)                 |
| O(9)  | 3764(1) | -3516(2) | 3447(3) | 95(1)                  |
| C(16) | 5485(1) | -347(1)  | 4145(2) | 36(1)                  |
| C(6)  | 4523(1) | 2076(1)  | 3853(2) | 37(1)                  |
| O(6)  | 7357(1) | -1062(2) | 4790(3) | 114(1)                 |
| C(20) | 4582(1) | -660(1)  | 3675(2) | 33(1)                  |
| C(19) | 4944(1) | -663(1)  | 3923(2) | 35(1)                  |
| C(1)  | 4384(1) | -73(1)   | 3566(2) | 35(1)                  |
| C(9)  | 5066(1) | 2392(1)  | 3959(2) | 37(1)                  |
| C(11) | 5622(1) | 1804(1)  | 3953(2) | 36(1)                  |
| C(17) | 5476(1) | -1063(1) | 4286(2) | 38(1)                  |
| C(15) | 5783(1) | 44(1)    | 4142(2) | 36(1)                  |
| C(4)  | 4221(1) | 986(1)   | 3578(2) | 37(1)                  |
| C(43) | 4148(1) | -1541(1) | 3928(2) | 38(1)                  |
| C(10) | 5420(1) | 2390(1)  | 3943(2) | 39(1)                  |
| C(42) | 4412(1) | -1319(1) | 3498(2) | 36(1)                  |
| C(14) | 5787(1) | 747(1)   | 4045(2) | 34(1)                  |

|              |         |          |         |       |
|--------------|---------|----------|---------|-------|
| <b>C(5)</b>  | 4228(1) | 1691(1)  | 3687(2) | 37(1) |
| <b>C(18)</b> | 5143(1) | -1254(1) | 4150(2) | 37(1) |
| <b>C(47)</b> | 4508(1) | -1728(2) | 2860(2) | 46(1) |
| <b>C(40)</b> | 6166(1) | -830(2)  | 3648(2) | 44(1) |
| <b>C(37)</b> | 6712(1) | -450(2)  | 4841(2) | 56(1) |
| <b>C(7)</b>  | 4535(1) | 2789(1)  | 4025(2) | 43(1) |
| <b>C(13)</b> | 6083(1) | 1143(1)  | 3957(2) | 39(1) |
| <b>C(12)</b> | 5982(1) | 1796(2)  | 3901(2) | 41(1) |
| <b>C(2)</b>  | 4015(1) | -63(1)   | 3304(2) | 40(1) |
| <b>C(3)</b>  | 3919(1) | 587(2)   | 3313(2) | 44(1) |
| <b>C(28)</b> | 5590(1) | 3052(1)  | 3857(2) | 43(1) |
| <b>C(8)</b>  | 4865(1) | 2986(1)  | 4077(2) | 43(1) |
| <b>C(35)</b> | 6120(1) | -319(1)  | 4209(2) | 39(1) |
| <b>C(33)</b> | 5510(1) | 3418(2)  | 3101(2) | 54(1) |
| <b>C(26)</b> | 3806(1) | 2562(2)  | 3025(2) | 49(1) |
| <b>C(21)</b> | 3886(1) | 2038(1)  | 3611(2) | 43(1) |
| <b>C(36)</b> | 6396(1) | -134(2)  | 4818(2) | 46(1) |
| <b>C(24)</b> | 3245(1) | 2667(2)  | 3447(3) | 67(1) |
| <b>C(22)</b> | 3645(1) | 1843(2)  | 4108(3) | 57(1) |
| <b>C(23)</b> | 3324(1) | 2157(2)  | 4020(3) | 71(1) |
| <b>C(44)</b> | 3991(1) | -2158(2) | 3733(2) | 45(1) |
| <b>C(46)</b> | 4350(1) | -2340(2) | 2670(2) | 56(1) |
| <b>C(45)</b> | 4088(1) | -2569(2) | 3114(2) | 53(1) |
| <b>C(39)</b> | 6483(1) | -1144(2) | 3675(2) | 56(1) |
| <b>C(38)</b> | 6758(1) | -951(2)  | 4274(3) | 61(1) |
| <b>C(29)</b> | 5825(1) | 3320(2)  | 4488(2) | 59(1) |
| <b>C(25)</b> | 3489(1) | 2866(2)  | 2946(3) | 63(1) |
| <b>C(48)</b> | 3931(1) | -3255(2) | 2949(3) | 74(1) |
| <b>C(32)</b> | 5665(1) | 4019(2)  | 2987(3) | 62(1) |

|              |         |          |         |        |
|--------------|---------|----------|---------|--------|
| <b>C(31)</b> | 5892(1) | 4290(2)  | 3617(3) | 67(1)  |
| <b>C(41)</b> | 7106(1) | -1281(3) | 4297(4) | 82(2)  |
| <b>C(30)</b> | 5979(1) | 3938(2)  | 4381(3) | 72(1)  |
| <b>C(27)</b> | 2903(1) | 3018(3)  | 3368(4) | 91(2)  |
| <b>C(34)</b> | 6051(2) | 4965(2)  | 3527(4) | 90(2)  |
| <b>O(5)</b>  | 6226(2) | 5235(2)  | 4096(3) | 137(2) |
| <b>O(2)</b>  | 2692(1) | 2736(2)  | 3798(4) | 142(2) |
| <b>O(4)</b>  | 5980(2) | 5238(2)  | 2795(3) | 127(2) |

$$U_{eq} = 1/3[U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{13}aca^*c^* \cos\beta]$$

**Table S3.** Anisotropic displacement parameters ( $\text{Å}^2 \times 10^3$ ) for  $\mu\text{-O-}[\text{FeTCPP}]_2 \cdot n\text{DMF}$ .

| <b>Atoms</b> | <b>U11</b> | <b>U22</b> | <b>U33</b> | <b>U23</b> | <b>U13</b> | <b>U12</b> |
|--------------|------------|------------|------------|------------|------------|------------|
| <b>Fe(1)</b> | 28(1)      | 26(1)      | 37(1)      | 3(1)       | 13(1)      | 10(1)      |
| <b>O(1)</b>  | 35(1)      | 24(1)      | 44(1)      | 0          | 15(1)      | 0          |
| <b>N(4)</b>  | 30(1)      | 30(1)      | 41(1)      | 6(1)       | 17(1)      | 11(1)      |
| <b>N(2)</b>  | 36(1)      | 30(1)      | 41(1)      | 0(1)       | 14(1)      | 13(1)      |
| <b>N(1)</b>  | 29(1)      | 30(1)      | 41(1)      | 4(1)       | 15(1)      | 11(1)      |
| <b>N(3)</b>  | 31(1)      | 30(1)      | 39(1)      | 1(1)       | 10(1)      | 11(1)      |
| <b>O(8)</b>  | 188(4)     | 34(1)      | 98(2)      | -19(1)     | 34(3)      | -4(2)      |
| <b>O(3)</b>  | 75(2)      | 119(3)     | 153(3)     | 59(3)      | 42(2)      | 71(2)      |
| <b>O(7)</b>  | 59(2)      | 106(3)     | 164(4)     | 6(3)       | 43(2)      | 51(2)      |
| <b>O(9)</b>  | 120(3)     | 45(2)      | 125(3)     | -10(2)     | 34(2)      | -28(2)     |
| <b>C(16)</b> | 36(1)      | 34(1)      | 40(1)      | 5(1)       | 15(1)      | 14(1)      |
| <b>C(6)</b>  | 35(1)      | 34(1)      | 44(1)      | 3(1)       | 16(1)      | 16(1)      |
| <b>O(6)</b>  | 43(2)      | 143(3)     | 155(4)     | 23(3)      | 8(2)       | 41(2)      |
| <b>C(20)</b> | 36(1)      | 32(1)      | 34(1)      | 4(1)       | 14(1)      | 7(1)       |
| <b>C(19)</b> | 38(1)      | 29(1)      | 43(1)      | 5(1)       | 21(1)      | 9(1)       |
| <b>C(1)</b>  | 34(1)      | 35(1)      | 39(1)      | 4(1)       | 18(1)      | 9(1)       |



|              |       |       |        |       |       |       |
|--------------|-------|-------|--------|-------|-------|-------|
| <b>C(9)</b>  | 39(1) | 33(1) | 40(1)  | 0(1)  | 12(1) | 11(1) |
| <b>C(11)</b> | 33(1) | 36(1) | 42(1)  | 3(1)  | 10(1) | 7(1)  |
| <b>C(17)</b> | 40(2) | 35(1) | 39(1)  | 5(1)  | 12(1) | 16(1) |
| <b>C(15)</b> | 35(1) | 37(1) | 40(1)  | 4(1)  | 14(1) | 16(1) |
| <b>C(4)</b>  | 33(1) | 35(1) | 44(2)  | 4(1)  | 14(1) | 14(1) |
| <b>C(43)</b> | 39(1) | 32(1) | 44(2)  | 2(1)  | 12(1) | 6(1)  |
| <b>C(10)</b> | 44(2) | 33(1) | 41(1)  | 1(1)  | 9(1)  | 11(1) |
| <b>C(42)</b> | 36(1) | 32(1) | 42(1)  | 4(1)  | 10(1) | 9(1)  |
| <b>C(14)</b> | 28(1) | 39(1) | 37(1)  | 3(1)  | 10(1) | 10(1) |
| <b>C(5)</b>  | 35(1) | 36(1) | 44(2)  | 2(1)  | 14(1) | 15(1) |
| <b>C(18)</b> | 42(2) | 31(1) | 42(1)  | 5(1)  | 17(1) | 10(1) |
| <b>C(47)</b> | 58(2) | 37(2) | 46(2)  | 3(1)  | 19(1) | 13(1) |
| <b>C(40)</b> | 42(2) | 42(2) | 53(2)  | 6(1)  | 18(1) | 18(1) |
| <b>C(37)</b> | 36(2) | 63(2) | 70(2)  | 20(2) | 9(2)  | 14(1) |
| <b>C(7)</b>  | 45(2) | 34(1) | 52(2)  | -1(1) | 15(1) | 18(1) |
| <b>C(13)</b> | 34(1) | 40(1) | 47(2)  | 6(1)  | 17(1) | 10(1) |
| <b>C(12)</b> | 36(1) | 39(1) | 51(2)  | 5(1)  | 14(1) | 7(1)  |
| <b>C(2)</b>  | 32(1) | 38(1) | 51(2)  | 1(1)  | 8(1)  | 6(1)  |
| <b>C(3)</b>  | 29(1) | 42(2) | 62(2)  | 0(1)  | 12(1) | 13(1) |
| <b>C(28)</b> | 47(2) | 32(1) | 51(2)  | 3(1)  | 16(1) | 11(1) |
| <b>C(8)</b>  | 47(2) | 32(1) | 52(2)  | -3(1) | 13(1) | 12(1) |
| <b>C(35)</b> | 31(1) | 39(1) | 51(2)  | 7(1)  | 16(1) | 14(1) |
| <b>C(33)</b> | 65(2) | 43(2) | 58(2)  | 8(1)  | 17(2) | 18(2) |
| <b>C(26)</b> | 43(2) | 46(2) | 60(2)  | 9(1)  | 16(1) | 20(1) |
| <b>C(21)</b> | 37(2) | 37(1) | 56(2)  | 1(1)  | 15(1) | 16(1) |
| <b>C(36)</b> | 36(2) | 47(2) | 58(2)  | 10(1) | 15(1) | 11(1) |
| <b>C(24)</b> | 45(2) | 60(2) | 101(3) | 17(2) | 24(2) | 33(2) |
| <b>C(22)</b> | 45(2) | 52(2) | 78(2)  | 16(2) | 26(2) | 25(2) |
| <b>C(23)</b> | 47(2) | 70(2) | 104(3) | 23(2) | 37(2) | 33(2) |

|              |        |        |        |       |       |        |
|--------------|--------|--------|--------|-------|-------|--------|
| <b>C(44)</b> | 48(2)  | 34(1)  | 55(2)  | 4(1)  | 12(1) | 1(1)   |
| <b>C(46)</b> | 84(3)  | 31(1)  | 54(2)  | -1(1) | 19(2) | 11(2)  |
| <b>C(45)</b> | 69(2)  | 29(1)  | 60(2)  | 2(1)  | 5(2)  | 8(1)   |
| <b>C(39)</b> | 52(2)  | 54(2)  | 68(2)  | 9(2)  | 28(2) | 25(2)  |
| <b>C(38)</b> | 37(2)  | 65(2)  | 86(3)  | 26(2) | 24(2) | 23(2)  |
| <b>C(29)</b> | 76(2)  | 37(2)  | 64(2)  | 9(1)  | 6(2)  | -7(2)  |
| <b>C(25)</b> | 58(2)  | 59(2)  | 76(2)  | 16(2) | 19(2) | 33(2)  |
| <b>C(48)</b> | 100(3) | 33(2)  | 89(3)  | -2(2) | 13(3) | 1(2)   |
| <b>C(32)</b> | 87(3)  | 40(2)  | 65(2)  | 13(2) | 29(2) | 21(2)  |
| <b>C(31)</b> | 91(3)  | 29(2)  | 89(3)  | 11(2) | 42(2) | 8(2)   |
| <b>C(41)</b> | 48(2)  | 91(3)  | 113(4) | 37(3) | 29(2) | 38(2)  |
| <b>C(30)</b> | 99(3)  | 44(2)  | 73(3)  | 6(2)  | 9(2)  | -20(2) |
| <b>C(27)</b> | 59(3)  | 87(3)  | 136(4) | 29(3) | 40(3) | 49(2)  |
| <b>C(34)</b> | 150(5) | 30(2)  | 104(4) | 8(2)  | 59(4) | -1(2)  |
| <b>O(5)</b>  | 205(5) | 59(2)  | 144(4) | 18(2) | 17(3) | -64(3) |
| <b>O(2)</b>  | 72(2)  | 104(3) | 269(6) | 75(3) | 90(3) | 63(2)  |
| <b>O(4)</b>  | 246(5) | 34(2)  | 116(3) | 15(2) | 79(3) | -4(2)  |

$$U_{ij} = \exp(-2\pi^2[h^2(a^*)^2 U_{11} + k^2(b^*)^2 U_{22} + \dots + 2hka^*b^* U_{12}])$$

**Table S4.** Fractional atomic coordinates ( $\times 10^4$ ) and isotropic thermal factors ( $\times 10^3$ ) of hydrogen atoms for  $\mu$ -O-[FeTCPP]<sub>2</sub>·nDMF.

| Atoms        | X    | Y     | Z    | $U_{iso} \text{ \AA}^2$ |
|--------------|------|-------|------|-------------------------|
| <b>H(17)</b> | 5669 | -1349 | 4445 | 45                      |
| <b>H(43)</b> | 4075 | -1267 | 4355 | 45                      |
| <b>H(18)</b> | 5058 | -1698 | 4195 | 45                      |
| <b>H(47)</b> | 4684 | -1582 | 2554 | 55                      |
| <b>H(40)</b> | 5978 | -968  | 3241 | 53                      |
| <b>H(37)</b> | 6899 | -319  | 5253 | 67                      |

|              |      |       |      |    |
|--------------|------|-------|------|----|
| <b>H(7)</b>  | 4344 | 3069  | 4089 | 52 |
| <b>H(13)</b> | 6309 | 978   | 3940 | 47 |
| <b>H(12)</b> | 6123 | 2176  | 3840 | 49 |
| <b>H(2)</b>  | 3870 | -440  | 3155 | 48 |
| <b>H(3)</b>  | 3691 | 754   | 3170 | 53 |
| <b>H(8)</b>  | 4950 | 3432  | 4174 | 52 |
| <b>H(33)</b> | 5345 | 3242  | 2663 | 65 |
| <b>H(26)</b> | 3971 | 2706  | 2684 | 58 |
| <b>H(36)</b> | 6368 | 208   | 5216 | 56 |
| <b>H(22)</b> | 3697 | 1494  | 4512 | 68 |
| <b>H(23)</b> | 3158 | 2017  | 4361 | 85 |
| <b>H(44)</b> | 3813 | -2302 | 4032 | 54 |
| <b>H(46)</b> | 4418 | -2611 | 2235 | 67 |
| <b>H(39)</b> | 6512 | -1491 | 3283 | 67 |
| <b>H(29)</b> | 5883 | 3079  | 5002 | 71 |
| <b>H(25)</b> | 3435 | 3218  | 2546 | 76 |
| <b>H(32)</b> | 5614 | 4250  | 2464 | 75 |
| <b>H(30)</b> | 6140 | 4122  | 4820 | 87 |

$$U_{iso} = \exp[-8\pi^2 U(\sin\theta/\lambda)^2]$$

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# *CONCLUSIONES*

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- 1.- Los grupos funcionales de las porfirinas son un factor clave para comprender su versatilidad como ligandos en la obtención de compuestos de tipo MOF, ya que estos grupos condicionan la extensión de la polimerización de los complejos metaloporfirínicos y la naturaleza de las interacciones de la red cristalina.
- 2.- Las dificultades sintéticas asociadas al empleo de porfirinas para la obtención de sólidos cristalinos pueden superarse con la combinación adecuada de codisolventes y el empleo de radiación microondas.
- 3.- Los fenómenos de oxidación-reducción están muy favorecidos en las porfirinas y la posibilidad de que se produzcan se incrementa en las metaloporfirinas de hierro, lo que da lugar a procesos poco predecibles que dificultan el diseño sintético.
- 4.- La distorsión de las metaloporfirinas de  $\text{Co}^{\text{II}}$  muestra una correlación lineal con las distancias de enlace entre los átomos de cobalto y los átomos de nitrógeno pirrólicos, para todas las porfirinas de  $\text{Co}^{\text{II}}$  encontradas en la CSD.
- 5.- Las interacciones intermoleculares de tipo Van der Waals son determinantes en los MOFs basados en metaloporfirinas, tanto en la estabilización de la red cristalina 3D como en las propiedades fisico-químicas.
- 6.- De las redes sólidas metaloporfirínicas recogidas en esta tesis doctoral se deduce que la accesibilidad a moléculas externas aumenta con el descenso en la extensión estructural de la polimerización.



# *ANEXO A*

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## *Técnicas Instrumentales*

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### ***A.1. Síntesis hidrotermal***

El término síntesis hidrotermal engloba una serie de técnicas de síntesis en las cuales las reacciones se llevan a cabo en disolución acuosa y en condiciones de presión y temperatura mayores que las condiciones ambientales, 25 °C y 1 atm. Esto supone una gran variedad de condiciones de reacción. En general, la síntesis hidrotermal se suele agrupar en dos tipos, en función de las condiciones de presión y temperatura: 1) síntesis hidrotermal en condiciones moderadas (presión de 5 a 50 atm y temperatura de 100 a 200 °C); 2) síntesis hidrotermal a alta presión y temperatura (presión de 50 a 1400 atm y temperatura de 200 a 700 °C). Según cuál sea el objetivo sintético será más recomendable la utilización de una u otra metodología. También es importante definir el término síntesis solvotermal, con el que se generaliza este tipo de síntesis para cualquier otro disolvente distinto del agua.

Este método de síntesis consiste en calentar un líquido, en un recipiente cerrado, por encima de su punto de ebullición, lo cual genera una presión superior a la atmosférica (normalmente moderada). De este modo, se han preparado una gran variedad de nuevos materiales y minerales.

Una característica de interés de la síntesis hidro o solvotermal es que los reactivos que no se disuelven fácilmente en agua pasan a la disolución por acción del propio disolvente, de la  $T^a$  o debido al empleo de agentes mineralizadores tanto básicos (carbonatos, hidróxidos...) como ácidos (nitríco, clorhídrico...), oxidantes o reductores, complejantes, etc., que actúan como disgregantes. Por lo tanto, se logran disolver o hacer reaccionar reactivos muy poco solubles en condiciones habituales.

Las variables controlables de este tipo de síntesis son la temperatura, el tiempo de reacción, la concentración de los reactivos, el pH y el factor de llenado de los

recipientes de reacción. La elección de las condiciones óptimas de temperatura y tiempo de reacción se ha realizado tras diversos ensayos.

La instrumentación necesaria para llevar a cabo la síntesis es diferente dependiendo de las condiciones de presión y temperatura que se desee utilizar. El compuesto [FeTCPP] se ha obtenido mediante síntesis solvotermal en condiciones suaves de presión y temperatura, utilizando recipientes herméticos. Estos reactores de una capacidad máxima de 40 mL, están fabricados de politetrafluoroetileno (teflón), material que se caracteriza por ser inerte (libre de metales y silicio) y por presentar unas características mecánicas, como es el grado de expansión térmica, bien conocidas. El recipiente de teflón se introduce dentro de un recipiente cilíndrico fabricado en una aleación de acero inoxidable, que posee una alta capacidad calorífica, para evitar su deformación (Figura A.1). La presión que se alcanza dentro del teflón depende del grado de llenado del mismo. De esta manera, pueden generarse condiciones de  $T^a$  y presión moderadas al aumentar la  $T^a$ , mediante el empleo de estufas, y alcanzar presiones de entre 5 y 30 atm. con porcentajes de llenado del recinto del 75 al 90%.



**Figura A.1.** Recipiente de teflón y carcasa de acero empleados en la síntesis a presión y temperatura moderadas.

Para los compuestos  $([\text{FeTPPbipy}]^n)_n$ ,  $[\text{CoTPP}(\text{bipy})] \cdot ([\text{CoTPP}])_{0.22} \cdot (\text{TPP})_{0.78}$  y  $[\text{FeTCPP}]_2 \cdot \text{O} \cdot n\text{DMF}$  se han utilizado pequeños viales tapados (Figura A.2). Estos viales de vidrio de 5 ml de capacidad se han probado para trabajar hasta temperaturas de 120 °C, y al igual que en los recipientes de teflón, el grado de llenado determina la presión.



**Figura A.2.** Viales empleados en las síntesis a presión y temperatura moderadas.

Este tipo de síntesis conlleva un desconocimiento de los procesos que se dan en su interior. El método de síntesis es, por lo tanto, un método de prueba-error, del que únicamente se conocerán las condiciones iniciales y el resultado final. El alto número de variables que se pueden modificar, implica el desarrollo de una gran cantidad de ensayos para la obtención de las condiciones óptimas de síntesis.

En general, el proceso ha consistido en mezclar disoluciones de los reactivos en el recipiente de reacción, basificar con hidróxido de sodio, someterlo a ultrasonidos para homogeneizar y cerrar el sistema, manteniéndolo a 80-140 °C durante 3-5 días y llevándolo, lentamente, a temperatura ambiente 2 °C/h. Luego los cristales obtenidos se han lavado varias veces con agua destilada o etanol.

## A.2. Síntesis asistida por microondas

La síntesis en microondas se basa en la activación de una reacción química mediante la calefacción dieléctrica del microondas, que utiliza la posibilidad que tienen algunos sólidos o líquidos en transformar la energía electromagnética en calor.

A diferencia de en la calefacción convencional, en la radiación microondas la transferencia de energía no ocurre por convección o conducción, sino por pérdidas dieléctricas. La región de microondas del espectro electromagnético está asociada a longitudes de onda desde 1cm hasta 1m, aunque para las aplicaciones químicas, la frecuencia está regulada en 2450MHz.

Existen diversas técnicas y montajes instrumentales según las condiciones bajo las cuales se lleve a cabo la síntesis. Para los compuestos [FeTCPP] y [CoTPPS<sub>0.5</sub>(bipy)(H<sub>2</sub>O)<sub>2</sub>] $\cdot$ 6H<sub>2</sub>O se ha utilizado un microondas CEM MARS 5 (Microwave Accelerated Reaction System) (Figura A.3) equipado con sensor de presión (ESP -1500 Plus) y temperatura (RTP -300 Plus).



**Figura A.3.** Microondas CEM MARS 5 empleado en la síntesis asistida por microondas.

Los recipientes utilizados (EasyPrep y OMNI-XP 1500) tienen una capacidad máxima de 100 ml y están fabricados en politetrafluoroetileno (PTFE, teflón), un material inerte con propiedades mecánicas conocidas. Los recipientes de teflón se introducen en una carcasa plástica de elevada capacidad calorífica para prevenir deformaciones. Por último, al igual que en la síntesis hidrotermal, el grado de llenado del vaso determinara la presión del interior.

En general, el proceso ha consistido en mezclar disoluciones de los reactivos en el recipiente de reacción, basificar con hidróxido de sodio y cerrar el sistema, manteniendolo a 140-160 °C durante 2 horas. Tras enfriar a temperatura ambiente, los cristales obtenidos se han lavado varias veces con agua destilada o etanol.

### ***A.3. Análisis cuantitativo***

El análisis elemental ha permitido determinar el contenido de N, C, S, O e H de los compuestos estudiados. Éste se ha realizado en un analizador elemental Euro AE Elemental Analyzer (CHNS), disponible en el Servicio Central de Análisis, SGIker, de la Universidad del País Vasco (UPV/EHU).

La técnica se basa en la combustión, en una atmosfera de oxígeno pura, de la muestra a analizar. La oxidación completa de la molécula orgánica da lugar a gases simples, CO<sub>2</sub>, H<sub>2</sub>O, N<sub>2</sub>..., que se presurizan y separan en función de su conductividad térmica. La separación de los gases se lleva a cabo en una columna cromatográfica.

#### A.4. Densidad del material

Las medidas de densidad se han llevado a cabo por flotación<sup>1</sup> (Figura A.4). Las medidas según el método de flotación se basan en obtener un líquido de densidad semejante al de la muestra problema, de forma que se realice el cálculo de la densidad del líquido. Se emplean mezclas de líquidos de densidades relativamente altas como, bromoformo ( $2.89 \text{ g/cm}^3$ ), yoduro de metileno ( $3.33 \text{ g/cm}^3$ ), añadidos a líquidos ligeros como la acetona ( $0.79 \text{ g/cm}^3$ ). El límite de medida será por tanto la densidad del líquido más pesado empleado. Se introduce el cristal en un líquido pesado y la solución se completa hasta que el cristal ni ascienda ni descienda. Para calcular la densidad se usa una balanza analítica a través de la cual se pesa una bola de cristal recubierta de mercurio en aire, en la mezcla de líquidos y en un medio de densidad conocida.



**Figura A.4.** Método de flotación.

<sup>1</sup> Hurlburt, C.S.; Klein, C., “*Manual de Mineralogía*”, Ed. Reverte, Barcelona, 1996.

### ***A.5. Espectroscopia infrarroja***

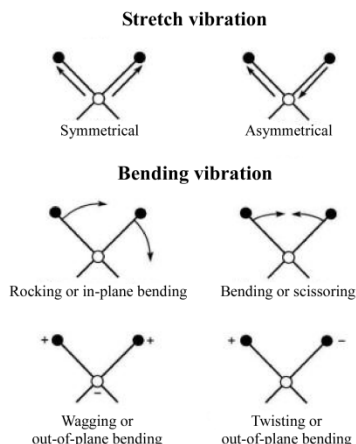
La espectroscopia infrarroja puede resultar de gran ayuda en el estudio de un compuesto para la caracterización del mismo. Esta técnica permite identificar grupos funcionales específicos o moléculas orgánicas presentes en las estructuras cristalinas.

En esta técnica la muestra se irradia con radiación infrarroja, haciendo un barrido de número de onda. La radiación infrarroja es poco energética, por lo que no es capaz de producir transiciones electrónicas. La absorción de la radiación se limita a especies moleculares para las que existen pequeñas diferencias energéticas entre los distintos estados vibracionales.

Para absorber en el infrarrojo una molécula debe sufrir un cambio neto en el momento dipolar como consecuencia de su movimiento de vibración o de rotación. En estas circunstancias el campo eléctrico alterno de la radiación puede interactuar con la molécula, y provocar cambios en la amplitud de alguno de sus movimientos. Si la frecuencia de la radiación coincide exactamente con la frecuencia de vibración natural de la molécula, tiene lugar una transferencia neta de energía que origina un cambio en la amplitud de la vibración molecular. La consecuencia es la absorción de radiación.

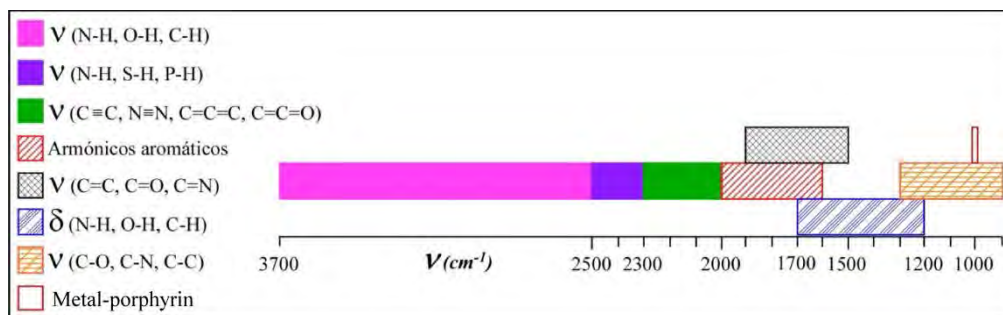
Pueden distinguirse dos categorías básicas de vibraciones: de tensión y de flexión. Las vibraciones de tensión son cambios en la distancia interatómica a lo largo del eje del enlace entre dos átomos. Las vibraciones de flexión están originadas por cambios en el ángulo que forman dos enlaces. En la Figura A.5 se representan los tipos de vibraciones moleculares.





**Figura A.5.** Tipos de vibraciones moleculares (+ indica movimiento hacia arriba, - indica movimiento hacia abajo).

El empleo de esta técnica ha resultado muy útil para la identificación de la existencia de uno o los dos ligandos orgánicos introducidos en los sistemas a estudiar. En la Figura A.6 se muestra un esquema de las zonas donde aparecen las frecuencias de enlaces más importantes para los compuestos estudiados.



**Figura A.6.** Diferenciación de las distintas zonas de vibración para los enlaces indicados en un espectro IR.

Los espectros infrarrojos de los compuestos estudiados se han realizado en un espectrofotómetro con transformada de Fourier JASCO FT/IR-6100. Los equipos con

transformada de Fourier presentan una relación señal/ruido mejor que la mayoría de instrumentos que funcionan en el intervalo espectral infrarrojo. También se caracterizan por sus altas resoluciones y por su elevada exactitud y reproducibilidad en la determinación de las frecuencias. Esto se debe a que su óptica permite la llegada al detector de mayor intensidad de radiación. Sin embargo, los detectores de respuesta rápida requeridos para estos instrumentos tienen poca sensibilidad, con lo que se compensa la llegada de mayor intensidad.

Para realizar los espectros de infrarrojo de las fases estudiadas se han preparado previamente pastillas en bromuro potásico con las muestras al 1%. El bromuro potásico, de calidad espectroscópica MERCK, se ha secado previamente y las pastillas se han obtenido aplicando una presión aproximada de 10 Pa. Los espectros se han registrado en el intervalo de número de onda de 4000 a 400  $\text{cm}^{-1}$ .

## ***A.6. Fluorescencia de rayos X***

La fluorescencia de rayos X se basa en la emisión que se produce en una muestra cuando es irradiada con radiación X. El método más habitual utiliza tubos de rayos X para excitar las muestras, que al absorber el haz primario emiten sus propios rayos X característicos. Este método es uno de los más utilizados para la identificación cualitativa de elementos con números atómicos superiores a 8. También se utiliza, a menudo, para el análisis semicuantitativo y cuantitativo. Una de las ventajas importantes de este método es que no es destructivo como la mayoría de las técnicas de análisis elemental.

Un espectro de fluorescencia de rayos X (FRX) utiliza como fuente de radiación un tubo de rayos X para provocar la emisión de rayos X secundarios de una muestra. La radiación emitida por la muestra contiene las líneas de rayos X

características de los elementos que la componen. La dispersión de estos rayos X secundarios en un espectro permite identificar los elementos presentes en la muestra. La intensidad de la línea característica de rayos X está relacionada con la concentración del elemento que las produce en la muestra analizada. Esto permite hacer análisis cuantitativos de la mayoría de los elementos.

Para producir la emisión de rayos X de una muestra es preciso excitarla previamente con radiación X primaria. En el proceso de excitación se crean huecos en las capas más internas del átomo que pasan a ser ocupados por electrones de capas superiores. Las transiciones electrónicas que se producen para ocupar las vacantes creadas conllevan la emisión de rayos X secundarios.

La fuente de radiación primaria más común en FRX es un tubo de rayos X. Los componentes principales de estos tubos son un filamento de wolframio y un ánodo o anticátodo metálico introducidos en un tubo de vidrio a alto vacío. El filamento se calienta mediante el paso de una corriente eléctrica, lo que produce una nube de electrones. Estos son acelerados mediante un potencial negativo hacia el ánodo. La rápida deceleración de estos electrones al interactuar con los átomos del ánodo libera energía en forma de rayos X, lo que produce un espectro continuo. El impacto de los electrones puede también ionizar los átomos del ánodo expulsando electrones de las capas más internas. Los electrones de capas más externas tienden a reemplazar las vacantes creadas emitiendo así rayos X con longitudes de onda características del material del ánodo. El espectro de rayos X generado consiste en un continuo y un conjunto de líneas características ( $K_{\alpha}$  y  $K_{\beta}$ ). La radiación sale del tubo a través de una ventana, que normalmente es de berilio.

Las medidas de fluorescencia de rayos X sobre los compuestos porfirínicos obtenidos se han realizado en un equipo FISCHERSCOPE X-RAY XDAL, utilizando monocristales de los materiales de estudio.

### ***A.7. Análisis termogravimétrico***

Para llevar a cabo el estudio de la evolución térmica de los compuestos sintetizados se han utilizado la termogravimetría (ATG) y el análisis térmico diferencial (ATD).

En un análisis termogravimétrico se registra, de forma continua, la masa de una muestra, colocada en una atmósfera controlada, al ir aumentando la temperatura. La representación de la masa o del porcentaje de masa en función de la temperatura se denomina termograma. En el análisis térmico diferencial (ATD) se mide la diferencia de temperatura entre una sustancia y un material de referencia inerte cuando la sustancia y el patrón se someten a un programa de temperatura controlado de calentamiento. Esto proporciona un termograma diferencial.

En el presente trabajo se han hecho ambos análisis, ATG y ATD, de manera simultánea. Los instrumentos comerciales empleados en termogravimetría constan de: una balanza analítica sensible, un horno, un sistema de gas de purga para proporcionar la atmósfera requerida, inerte o reactiva, y un microprocesador para el control del instrumento y la adquisición y visualización de los datos.

La información que proporciona la termogravimetría se limita a los procesos que producen un cambio en la masa del compuesto analizado. Éstos son básicamente reacciones de descomposición, oxidación y procesos tales como la vaporización, sublimación y la desorción. El ATD proporciona información sobre el carácter exotérmico o endotérmico de los procesos y reacciones que sufre la muestra con la variación de temperatura, por lo que complementa la información obtenida por termogravimetría.

Los análisis térmicos presentados en este trabajo se han realizado, indistintamente, en una Termobalanza SDT 2960 Simultaneous DSC-TGA TA Instruments (Departamento de Química Inorgánica) y en una Termobalanza NETZSCH STA 449 F3 Simultaneous DSC-TGA (Grupo Eidos). En todos los análisis se ha utilizado una atmósfera de aire sintético y una velocidad de calentamiento de 5 °C/min hasta una temperatura de 600°C.

## ***A.8. Difracción de rayos X***

Los rayos X son una radiación electromagnética con una longitud de onda,  $\lambda$ , del mismo orden que los parámetros de celda de los cristales. Esto hace que las sustancias cristalinas sean capaces de difractar los rayos X. Cuando esta radiación incide sobre la nube electrónica de los átomos de una red cristalina, éstos se convierten en emisores puntuales de esa radiación. La radiación emitida por cada átomo se expande en forma de onda esférica e interfiere con la creada por los átomos del entorno. Esta interferencia puede ser destructiva o constructiva. Las direcciones en las que la interferencia es constructiva son la que cumplen la Ley de Bragg:

$$\lambda = 2 d_{hkl} \text{ sen } \theta$$

donde  $\lambda$  es la longitud de onda de los rayos X utilizados,  $\theta$  es el ángulo de incidencia de la radiación y  $d_{hkl}$  es la distancia entre dos planos consecutivos definidos por un vector de componentes  $hkl$ .

### ***A.8.1. Difracción de rayos X sobre monocristal***

La difracción de rayos X sobre monocristal es una técnica muy poderosa para la determinación de la estructura cristalina de los materiales. Un experimento de difracción de rayos X sobre una muestra monocristalina permite obtener datos sobre la

distribución espacial de los máximos de difracción, que contienen información acerca de la geometría de la celda unidad y orientación del monocristal, así como medir la intensidad de esos máximos de difracción, relacionada con el tipo y distribución de los átomos en la celda unidad.

Para llevar a cabo un experimento de difracción de rayos X sobre monocristal es preciso disponer de un cristal único con un tamaño que se encuentre dentro de los límites de capacidad resolutive del difractómetro utilizado para el experimento y de buena calidad, es decir, sin defectos visibles.

Los equipos de difracción de rayos X de monocristal utilizados para realizar la toma de datos de los compuestos descritos en este trabajo, son difractómetros automáticos, con detector de áreas CCD. Se han empleado tres de los cuatro difractómetros existentes en el Servicio General de Rayos X: Moléculas y Materiales (SGIker) de la Universidad del País Vasco (UPV/EHU): Oxford Diffraction Xcalibur2 y dos Oxford Diffraction Xcalibur Supernova con anticátodo de cobre y molibdeno. Estos equipos están dotados de un monocromador primario, por lo que la radiación utilizada corresponde a la línea  $K_{\alpha}$  del anticátodo empleado, molibdeno ( $\lambda_{\text{Mo-K}_{\alpha}} = 0.71073 \text{ \AA}$ ) para el Oxford Diffraction Xcalibur2 y uno de los Supernova, y cobre ( $\lambda_{\text{Cu-K}_{\alpha}} = 1.54018 \text{ \AA}$ ), para el otro. Además, dos de ellos, Xcalibur2 y Xcalibur Supernova de cobre, disponen de sistema de baja temperatura Helojet (desde 15 K) y de alta temperatura RKD Hotjet (hasta 259°C).

#### *Selección del monocristal*

Se han seleccionado los monocristales por observación en lupa binocular bajo luz polarizada, de tal manera que los mismos carezcan de defectos visibles. Se ha procurado, en la medida de lo posible, que los ejemplares seleccionados tengan un tamaño mínimo de 0.1 mm en todas sus dimensiones, con el fin de que la intensidad de

rayos X difractados pueda ser lo suficientemente alta como para asegurar una buena estadística en las tomas de datos. A continuación, se ha fijado cada monocristal sobre el extremo de una fibra de vidrio o sobre un MicroMount<sup>®</sup> cubierto de aceite y éstos sobre una base metálica con forma de cilindro. Esta base permite situar el monocristal sobre la cabeza goniométrica empleada en el difractor.

#### *Toma y reducción de datos*

Se ha realizado una primera toma de intensidades mediante un programa estándar de cinco minutos, con el fin de determinar la calidad de los cristales y los posibles parámetros de celda unidad, a partir de un número reducido de imágenes. Posteriormente, se ha realizado una toma de datos completa de cada uno de los cristales midiendo máximos de difracción de toda la esfera de Ewald. Una vez finalizados los procesos de toma de datos, se ha procedido a la reducción de los mismos, aplicando las correcciones de Lorentz y polarización,<sup>2</sup> así como las correcciones de absorción, en función de la forma y el tamaño del cristal.

#### *Resolución estructural*

La resolución de la estructura cristalina de las fases se ha llevado a cabo empleando los programas SHELXS-97,<sup>3</sup> SIR92<sup>4</sup> o Superflip.<sup>5</sup> Los dos primeros se basan en métodos directos, mientras que el último se basa en el *Charge flipping*.<sup>6</sup> Ésto ha permitido localizar los átomos metálicos y gran parte de los átomos de oxígeno, nitrógeno y carbono, presentes en cada una de las estructuras.

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<sup>2</sup> Yinghua, W., *J. Appl. Crystallogr.* **1987**, *20*, 258-259.

<sup>3</sup> Sheldrick, G. M., *Acta Crystallogr., Sect. A Found. Crystallogr.* **2008**, *A64*, 112-122.

<sup>4</sup> Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A., *J. Appl. Crystallogr.* **1993**, *26*, 343-350.

<sup>5</sup> Palatinus, L.; Chapuis, G., *J. Appl. Crystallogr.* **2007**, *40*, 786-790.

<sup>6</sup> Oszlányi, G.; Sütö, A., *Acta Crystallogr.*, **2008**, *A64*, 123-134.

A continuación, se ha procedido al afinamiento estructural, empleando el programa SHELXL-97<sup>7</sup>, que utiliza el método de mínimos cuadrados de matriz completa. De este modo, tras varios afinamientos, se han localizado las posiciones de los átomos ligeros de carbono, nitrógeno y carbono en los mapas de densidad residual. Los átomos de hidrógeno de las moléculas orgánicas se han posicionado geoméricamente. Por el contrario, los átomos de hidrógeno pertenecientes a las moléculas de agua de coordinación se han localizado en el mapa de densidades electrónicas residuales, siendo necesario introducir restricciones suaves para obtener las distancias O-H. En el caso de la estructura de [FeTCPP]<sub>2</sub>O·nDMF, ha sido necesario utilizar la herramienta *Use Solvent Mask* del programa OLEX<sup>8</sup> para recalcular el fichero *hkl* sin la contribución del disolvente, ya que éste no se pudo localizar en el mapa de densidades.

Todos los átomos se han afinado utilizando factores térmicos anisotrópicos, excepto los átomos de hidrógeno y los átomos de oxígeno de las moléculas de agua de cristalización.

Por último, se han llevado a cabo cálculos geoméricos de las estructuras con el programa PLATON<sup>9</sup> y se han analizado las mismas con el programa TOPOS 4.0<sup>10</sup> y Crystal Maker.

El proceso de resolución de estructuras cristalinas en monocristal se muestra resumido en la Figura A.7.

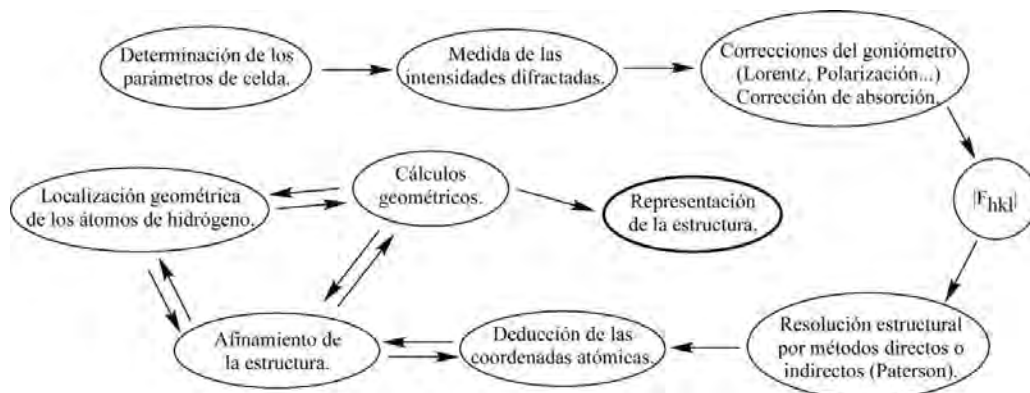
<sup>7</sup> Yinghua, W., *J. Appl. Crystallogr.* **1987**, *20*, 258-259.

<sup>8</sup> Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H., *J. Appl. Crystallogr.* **2009**, *42*, 339-341.

<sup>9</sup> Spek A. L., *Acta Crystallogr.*, **2009**, *D65*, 148-155, "Program for the Automated Analysis of Molecular Geometry", University of Utrecht, The Netherlands.

<sup>10</sup> Blatov, V. A., *IUCr CompComm Newsl.* **2006**, *7*, 4-38. <http://www.topos.ssu.samara.ru>





**Figura A.7.** Proceso de resolución de estructuras cristalinas por difracción de rayos X en monocristal.

### A.8.2. Difracción de rayos X sobre muestra policristalina

La difracción de rayos X sobre muestra policristalina se ha utilizado, en general, para el análisis cualitativo de las fases presentadas en esta memoria. Estos experimentos han sido útiles tanto para la identificación de las fases como para la determinación de su pureza química, ya que todos los sólidos cristalinos tienen un difractograma característico.

Un material policristalino está formado por un gran número de cristales diminutos dispuestos al azar, unos con respecto a otros. Una muestra de estas características, al ser irradiada con un haz de rayos X, siempre presentará un determinado número de cristalitos que satisfagan la ley de Bragg. Los difractómetros permiten determinar con precisión la dirección en la que se produce la difracción. La geometría más habitual de los difractómetros, y la que poseen los difractómetros utilizados en este trabajo, se denomina Bragg-Brentano. En este tipo de geometría, el goniómetro incorpora dos giros coaxiales: uno para la muestra y otro para el detector. Estos giros están acoplados, de tal forma que si la muestra se desplaza un ángulo  $\theta$ , el

detector recorre, en el mismo tiempo, un ángulo  $2\theta$ . La representación de la intensidad de la radiación X que llega al detector con respecto al ángulo de giro  $2\theta$  es lo que se denomina difractograma.

Para obtener información de los difractogramas es preciso hacer un análisis de los mismos, en el que se deben tener en cuenta la posición de los máximos de difracción, su forma y su intensidad.

Todos los difractómetros empleados pertenecen al Servicio General de Rayos X: Rocas y Minerales (SGIker), de la Universidad del País Vasco (UPV/EHU). Los difractogramas presentados se han medido en un difractómetro Brucker D8 Advance Vario o en un Philips X'Pert MD, ambos con geometría  $\theta$ - $2\theta$ . El primero dispone de un monocromador primario Vario ( $\text{CuK}\alpha_1$ ) y un detector de estado sólido SolX, con una ventana de discriminación de energías optimizada para dicha radiación, mientras que el segundo dispone de un monocromador secundario. Los intervalos angulares medidos, el tamaño y el tiempo por paso varían en función del compuesto estudiado.

Los difractogramas empleados para la caracterización inicial de las fases se han registrado en un difractómetro Philips PW1710, con geometría Bragg-Brentano y anticátodo de cobre. Las medidas se han realizado desde  $5$  hasta  $70^\circ$  en  $2\theta$ , con un paso de  $0.02$  y un tiempo de contaje por paso de  $1$  s. Los difractogramas así obtenidos para las fases estudiadas se emplearon para realizar el *Patern Maching* de las mismas.

También, se han realizado mediante termodiffractometría de rayos X, en muestra policristalina, los estudios de la evolución de la cristalinidad con la temperatura de las fases. Este método permite conocer los intervalos de estabilidad térmica de las fases estudiadas, identificar las fases originadas por la descomposición térmica y caracterizar los procesos de cambio de fase, siendo una técnica complementaria a los análisis termogravimétricos. Los termodifractogramas se han

llevado a cabo en un difractómetro Bruker D8 Advance Vantec, el cual opera con geometría Theta-Theta y tiene una cámara HTK2000 de alta temperatura con portamuestras de Pt. Dispone de un detector ultrarápido Vantec de 6° de apertura máxima. Las medidas se han realizado, en atmósfera de aire, entre temperatura ambiente y 550 °C, en distintos intervalos de temperatura, empleando una velocidad de calentamiento de 10 °C/min en diferentes intervalos angulares, dependiendo del compuesto. Todos los difractogramas se han registrado empleando un paso de 0.033° en 2θ y un tiempo de contaje de 0.8 s por paso.

### A.9. Estudio de la distorsión de los poliedros

El análisis de la distorsión de los poliedros de coordinación de las fases presentadas en esta memoria, se ha llevado a cabo por el método de medida continua de la simetría (CSM, Continuous Symmetry Measure). Este método cuantifica la mínima distancia que deben desplazarse los puntos de un poliedro para transformarse en otro.<sup>11</sup> Es decir, la CSM de una estructura original es la desviación normalizada de la media cuadrática de la estructura con simetría deseada más próxima. Por lo tanto, dada una estructura distorsionada compuesta por N vértices, las coordenadas de los cuales vienen dadas por los vectores  $Q_k$  ( $k= 1, 2, \dots, N$ ), y la estructura ideal más cercana, cuyas coordenadas de los vértices están descritas por los vectores  $P_k$  ( $k= 1, 2, \dots, N$ ), se define la medida de simetría como:

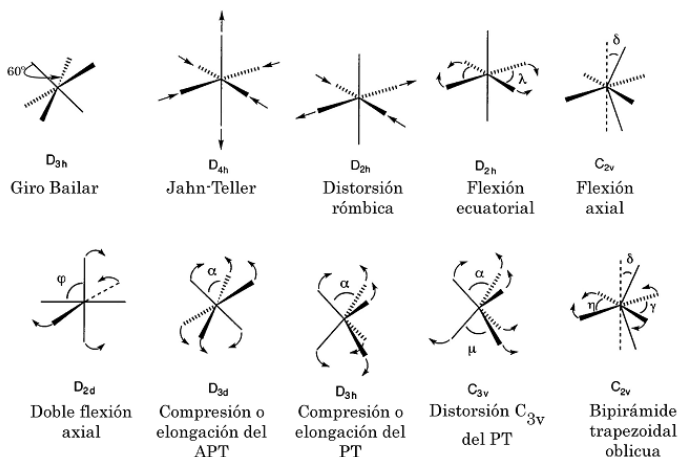
$$S = \min \frac{\sum_{k=1}^N |Q_k - P_k|^2}{\sum_{k=1}^N |Q_k - Q_d|^2} \times 100$$

<sup>11</sup> Zabrodsky, H.; Peleg, S.; Avnir, D., *J. Am. Chem. Soc.* **1992**, *114*, 7843-7851.

Donde  $Q_0$  es el vector del centro del poliedro estudiado. La CSM definida en la ecuación anterior, es independiente de la posición, de la orientación y del tamaño del poliedro estudiado.

Los cálculos de medida continua de la simetría se han realizado con el programa Shape v 1.1a, desarrollado en la Universidad de Barcelona por Álvarez y col.<sup>12</sup>

En las estructuras estudiadas se han observado poliedros de coordinación seis y cuatro. Un octaedro puede presentar diferentes distorsiones debidas a las variaciones de las distancias y ángulos de enlace (Figura A.8). La distorsión más característica del octaedro es el giro Bailar,<sup>13</sup> por el que se transforma en un prisma trigonal al girar las caras opuestas  $60^\circ$ .



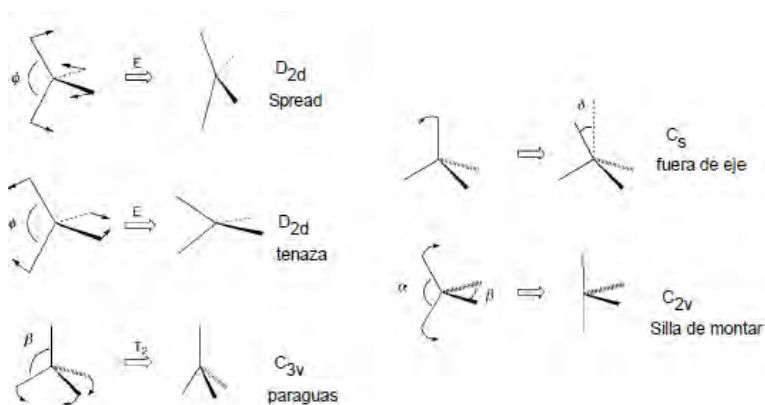
**Figura A.8.** Algunos de los posibles modos de distorsión de un octaedro.

<sup>12</sup> Llunel, M.; Casanova, D.; Cirera, J.; Bofill, J. M.; Alemany, P.; Álvarez, S.; Pinsky, M.; Yatunir, D. SHAPE v1.1a, "Program for Continuous Shape Measure Calculations of Polyhedral  $X_n$  and  $ML_n$  Fragments", **2003**.

<sup>13</sup> Álvarez, S.; Avnir, D.; Llunell, M.; Pinsky, M., *New J. Chem.* **2002**, 26, 996-1009.

Álvarez y *col.* han estudiado, ampliamente, la distorsión de los octaedros lo que les ha llevado a la elaboración de un mapa de simetría de distorsión del octaedro (Figuras presentadas en los Capítulos de la memoria), que sirve para clasificar el tipo de distorsión que presenta un octaedro en función de los valores de  $S(O_h)$  y  $S(D_{3h})$ , siendo  $S(O_h)$  la medida continua de simetría con respecto al octaedro ideal, y  $S(D_{3h})$  la medida continua de simetría para un prisma trigonal.

En la Figura A.9 se muestran los diferentes modos de distorsión que puede presentar un tetraedro.



**Figura A.9.** Algunos modos de distorsión para un poliedro  $ML_4$ .

En este caso, la distorsión más característica es la de tipo Spread,<sup>14</sup> que se basa en la conversión de la geometría tetraédrica ( $T_d$ ) en la plano cuadrada ( $D_{4h}$ ).

<sup>14</sup> Cirera, J.; Alemany, P.; Álvarez, S., *Chem. Eur. J.* **2004**, *10*, 190-207.

### ***A.10. Estudio de la distorsión de las porfirinas***

El análisis de la distorsión de las moléculas porfirínicas de los compuestos presentados en esta memoria, se ha llevado a cabo por el método NSD (Normal-coordinate Structural Decomposition) desarrollado por Shelnut y *col.*<sup>15,16</sup> Este método describe las estructuras porfirínicas no planares en términos de los desplazamientos equivalentes a lo largo de las coordenadas normales de menor frecuencia de los macrociclos porfirínicos. La descripción de la estructura de la porfirina en términos de las coordenadas normales es una forma única y útil de caracterizar la estructura macrocíclica.

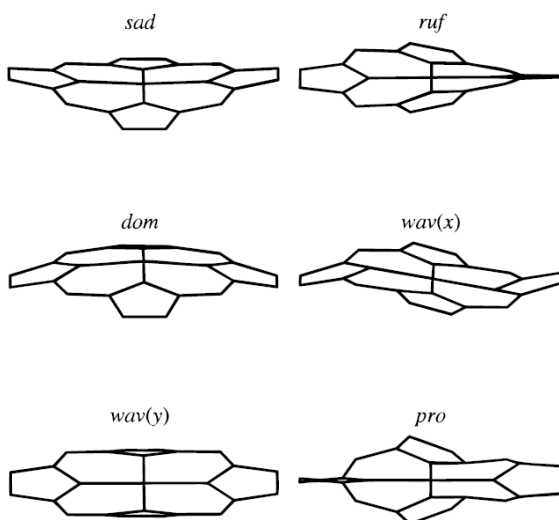
A diferencia de otras descripciones, este método ocupa una posición especial debido a la singular relación entre las energías de distorsión macrocíclicas y los desplazamientos a lo largo de las coordenadas normales de vibración. En otras palabras, si se conoce el desplazamiento para cada deformación de coordenadas normales, entonces la energía total de distorsión del macrociclo puede estimarse fácilmente como la suma de las energías para cada modo, suponiendo que las frecuencias vibratorias son conocidas. Quizás lo más importante sea la gran simplificación que se produce cuando la distorsión de la porfirina se expresa en términos de coordenadas normales. Los resultados de dicha simplificación hacen que sólo unos pocos desplazamientos (seis fuera de plano) a lo largo de los modos de frecuencia más bajos del macrociclo sean necesarios para caracterizar adecuadamente la distorsión.

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<sup>15</sup> Jentzen, W.; Song, X.-Z.; Shelnut, J. A., *J. Phys. Chem. B* **1997**, *101*, 1684-1699.

<sup>16</sup> Jentzen, W.; Ma, J.-G.; Shelnut, J. A., *Biophys. J.* **1998**, *74*, 753-763.

Los seis desplazamientos fuera del plano o distorsiones que puede experimentar la porfirina se denominan: saddle (*sad*), ruffle (*ruf*), dome (*dom*), wavy(x) (*wav(x)*), wavy(y) (*wav(y)*) y propeller (*pro*) (Figura A.10).



**Figura A.10.** Modos de distorsión del macrociclo porfirínico.

El análisis de las distorsiones de los macrociclos porfirínicos estudiados se ha realizado con el programa NSD 3.0<sup>®</sup> (versión web) desarrollado por Sun y Shelnut.<sup>17</sup>

### A.11. Estudio de la topología

La simplificación de las estructuras cristalinas y el análisis topológico de las redes obtenidas se ha realizado con el programa TOPOS 4.0.<sup>18</sup> En las fases discutidas en esta memoria se han seguido dos pautas diferentes para obtener las redes simplificadas:

<sup>17</sup> Sun, L.; Shelnut, J. A. <http://jasheln.unm.edu/jasheln/content/nsd/NSDengine/start.htm>

<sup>18</sup> Blatov, V. A., *IUCr CompComm Newsl.* **2006**, *7*, 4-38. <http://www.topos.ssu.samara.ru>

**I.- Estándar:** se han considerado los centros metálicos como nodos de la red, y los ligandos orgánicos que conectan a más de dos nodos entre sí, como un segundo tipo de nodo, denominado baricentro. Por último, todo ligando orgánico que conecte a dos nodos se define como conector entre los mismos.

**II.- Contract to:** se han seleccionando los centros metálicos como nodos de la red, y todos los ligandos orgánicos como conectores entre centros metálicos.

Usualmente, la topología de los polímeros de coordinación se ha determinado empleando el primero de los criterios. Pero, en ocasiones, debido a la complejidad de algunas estructuras cristalinas se emplea el segundo para poder observar, de forma rápida y fácil, el edificio cristalino de los compuestos. Siempre hay que tener en cuenta que la red simplificada debe ser reflejo de la estructura cristalina de partida, conteniendo la información básica de la conectividad entre nodos a través del ligando.<sup>19</sup>

Las redes obtenidas se describen en base a las invariantes topológicas. Antes de comenzar con la descripción de las mismas, se detallarán algunos conceptos de la descripción de las estructuras cristalinas en base a gráficos simplificados.<sup>20</sup>

Se define el gráfico de una red como una serie de vértices (i, j, k...) unidos mediante enlaces (i,j). Si los enlaces (i,j) y el (j,i) son diferentes se denomina al enlace entre vértices como directo. Mientras que si la unión (i,j) y (j,i) es igual, el enlace es indirecto. Un gráfico simple es aquel que tiene solamente enlaces indirectos.

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<sup>19</sup> Yaghi, O. M.; O'Keeffe, M.; Ockwig, N. W.; Chae, H. K.; Eddaoudi, M.; Kim, J., *Nature*, **2003**, *423*, 705-714.

<sup>20</sup> Delgado-Friedrichs, O.; O'Keeffe, M., *J. Solid State Chem.*, **2005**, *178*, 2480-2485.



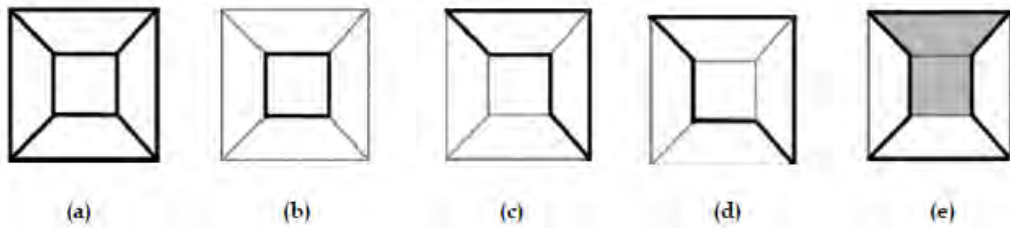
Los vértices a los cuales está enlazado un vértice central definen su entorno de coordinación y el número de coordinación. Si todos los vértices de un gráfico poseen el mismo número de coordinación,  $n$ , se define el gráfico como  $n$ -regular.

Una cadena es una secuencia de vértices enlazados mediante enlaces indirectos. Un ciclo se define como una cadena cerrada. El ciclo es elemental si solo posee un tipo de vértices y un tipo de enlace.

Una red se define como un gráfico simple conectado. Una red  $n$ -periódica es aquella generada por simetría traslacional en  $n$ -dimensiones.

A continuación se definirán los términos anillo fuerte, anillo y ciclo. Un anillo fuerte es un ciclo que no es la suma de diferentes ciclos. Un anillo es la suma de tres o más anillos fuertes que no contiene atajos en su interior. Definido de otra forma, un anillo se define como aquel ciclo en el interior del cual no existe un camino más corto entre nodos que el que une nodos entre sí, en el propio anillo. Un ciclo es aquel circuito cerrado que no cumple las condiciones mencionadas para los anillos fuertes o anillos.

Dado que la terminología es confusa, se mostrará mediante un ejemplo. En la Figura A.11a se muestra el gráfico de un cubo. La Figura A.11b representa mediante líneas gruesas uno de los anillos fuertes contenidos en el gráfico. La Figura A.11c muestra, mediante líneas gruesas, un ciclo de seis miembros que es la suma de dos anillos fuertes y, por lo tanto, no es un anillo. Es decir, podemos unir los nodos del ciclo (línea gruesa), mediante un solo enlace que atraviesa el ciclo (línea delgada en el interior de la línea gruesa). Es decir existe un atajo. En la Figura A.11d se muestra un ciclo de seis miembros que es un anillo, ya que no podemos unir los nodos de anillo mediante un solo enlace. Por último, en la Figura A.11e se observa un ciclo de ocho miembros que no es un anillo, dado que podemos unir mediante un enlace nodos que forman parte del ciclo de ocho miembros.



**Figura A.11.** (a) Gráfico de un cubo, (b) uno de los anillos fuertes del cubo, (c) ciclo de seis nodos que es la suma de dos anillos fuertes y, por lo tanto, no es un anillo, (d) ciclo de seis miembros que es la suma de tres anillos fuertes, pero no de dos, por lo tanto es un anillo, pero no un anillo fuerte, (e) ciclo de ocho nodos que es la suma de tres ciclos fuertes, pero se considera como la suma de un ciclo de seis (suma de dos anillos fuertes de cuatro (zona sombreada)) más un anillo fuerte, por lo tanto, no es un anillo.

Los términos definidos con anterioridad son de gran importancia, porque las invariantes topológicas que describen las redes están definidas en base a anillos ó ciclos.

Partiendo de las definiciones previas, una red se describe en base a cuatro invariantes topológicas, el símbolo puntual (símbolo de Schläfli) (SP), el símbolo puntual extendido (SPE), el símbolo de los vértices (SV), y la secuencia de coordinación (SC).

El símbolo puntual (SP) y símbolo puntual extendido se basan en los ciclos existentes en cada ángulo asociado a un nodo determinado. El símbolo de los vértices (SV) se define en base al mismo criterio pero solamente considera los anillos (es decir ciclos que no son la suma de otros ciclos). En una red tridimensional n-coordinada existen  $n(n-1)/2$  ángulos, asociados a cada vértice o nodo.

Las invariantes topológicas se denotan como:

**I.- Símbolo puntual (SP):** Viene dado por  $Aa.Bb.Cc\dots$ , donde  $A < B < C\dots$  y  $a+b+c\dots = n(n-1)/2$ . A, B, C... definen el tamaño de los ciclos más cortos, mientras que a, b, c... hacen referencia al número de ángulos en los cuales están incluidos los ciclos. Sin embargo, redes que poseen conectividades diferentes pueden tener el mismo símbolo puntual, por lo que se debe complementar esta información con la del símbolo extendido y la secuencia de coordinación.

**II.- Símbolo puntual extendido (SPE):** Es el mismo que el símbolo puntual, pero, en este caso, se detalla el tamaño de los ciclos más cortos para cada uno de los ángulos asociado a un nodo determinado. El símbolo extendido se nota como  $Aa.Bb.Cc\dots$ , donde A, B, C... es el tamaño de los ciclos más cortos en cada uno de los ángulos del vértice considerado, mientras que a, b, c... son el número de dichos ciclos en el ángulo dado.

**III.- Símbolo de los vértices (SV):** Determina los anillos más cortos (ciclos que no son la suma de otros ciclos) coincidentes en cada ángulo. La notación es la misma que en el caso del símbolo extendido. El número de miembros máximos de los anillos que calcula el programa TOPOS 4.0 es de 10, pero se puede incrementar si es necesario. En el caso de que para un ángulo dado no exista un anillo de diez o menos miembros, el símbolo para ese ángulo se define con un asterisco ó el símbolo de infinito.

**IV.- Secuencia de coordinación (SC):** Número de nodos, incluido el central, en las diez primeras esferas de coordinación.

Resumiendo, hay dos principios básicos que hay que tener en cuenta a la hora de visualizar una topología, la diferencia entre ciclo y anillo, y que para definir las

invariantes topológicas se analizan los ciclos o anillos más cortos posibles asociados a un ángulo determinado.

Una vez obtenidas las invariantes topológicas, el programa TOPOS las compara con las topologías que contienen las bases de datos RCSR<sup>21</sup> y EPINET.<sup>22</sup> En el caso de existir una red simplificada con la misma conectividad, el programa identifica la topología con un código “abc-d”. Las tres primeras letras del código hacen referencia al símbolo del compuesto del cual se ha obtenido la topología; por ejemplo, “dia” de diamante ó “sod” de sodalita, ó bien a tres letras que son el código del autor que ha reportado la topología a la base de datos correspondiente. El código “-d” después de las tres primeras letras, hace referencia al tipo de red:

**-a (red aumentada):** Los vértices de la red original son sustituidos por polígonos o poliedros que poseen la misma coordinación que los vértices originales.

**-b (red binaria):** Una red con dos tipos de vértices, A y B, y en la cual los vértices A solamente están unidos a los vértices B, y viceversa.

**-c (catenada):** Dos o más redes catenadas, en las cuales los conectores de una red atraviesan los huecos de la otra. La simetría de las redes catenadas es diferente a la de las redes individuales.

**-e (red de los vértices):** Los conectores de la red original se sustituyen por nodos, considerando la nueva conectividad entre nodos, y descartando los nodos y conectores originales.

**-f, -g (decorada):** Los vértices de la red son grupos de átomos, o poliedros.

<sup>21</sup> RCSR, <http://rcsr.anu.edu.au>; O'Keeffe, M.; Peskov, M. A.; Ramsden, S. J.; Yaghi, O. M.; *Accts. Chem. Res.*, **2008**, *41*, 1782-1789.

<sup>22</sup> EPINET, <http://epinet.anu.edu.au/>; *Data on the sphere packings derived by Fischer, Koch & Sowa*, Sowa, H.; Koch, E., *Acta Crystallogr.*, **2005**, *A61*, 331-342.

**-x (coordinación extendida):** Cuando se considera la unión con los vértices que no son de la primera esfera de coordinación.

**-z:** configuraciones alternativas.

### A.11.1. Poliedros VDP y análisis de la porosidad estructural

Un poliedro VDP (Voronoi-Dirichlet polyhedra) consiste en una geometría cerrada formada por las caras perpendiculares a los enlaces de un átomo determinado. Esta descripción geométrica del espacio ocupado por un átomo tiene una relación directa con el volumen ó radio iónico del mismo, así como con la fuerza de los enlaces a través de los cuales se conecta.

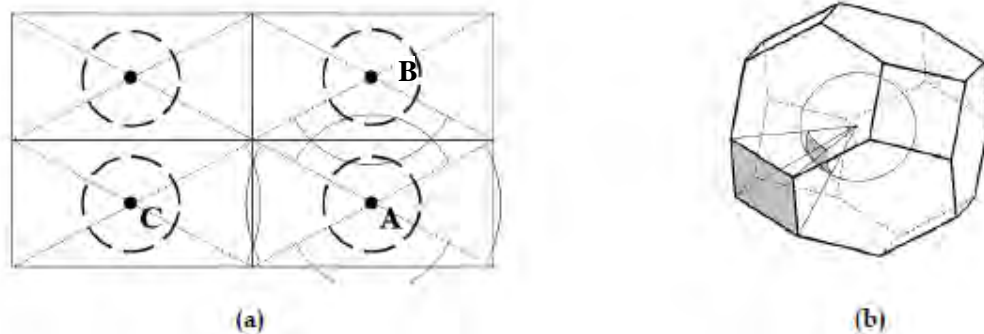
Los poliedros VDP se han construido a partir del programa TOPOS. En primer lugar, y mediante el programa AutoCN (incluido en TOPOS), se establece la conectividad entre los átomos de la estructura cristalina. Para ello, se utiliza el algoritmo Sectors (método de los sectores esféricos), en el cual la esfera de radio Rsd (átomo central del poliedro VDP) se reemplaza por una serie de sectores esféricos que corresponden a los contactos interatómicos (Figura A.12a). El radio rsec, de los diferentes sectores, viene determinado por la fórmula:

$$r_{sec} = (3V_i/\Omega_i)^{1/3}$$

donde  $V_i$  y  $\Omega_i$  son el volumen y el ángulo sólido de la pirámide formada por la cara del poliedro VDP y el centro del átomo. La sección de la esfera que representa el átomo, y que es atravesada por la pirámide, define el ángulo sólido (Figura A.12b).

En función de cuantos cortes se produzcan entre los sectores esféricos de átomos adyacentes, el contacto será covalente, ó de carácter débil. Por ejemplo, el sector esférico exterior del átomo A (Figura A.12a) corta tanto al sector esférico interior como exterior del átomo B, luego el enlace será de tipo fuerte (covalente ó

iónico). En cambio, entre los átomos A y C únicamente se cortan los sectores esféricos exteriores, por lo que el enlace entre éstos será de tipo débil. Para los átomos B y C no existe contacto y, por lo tanto, no hay enlace.



**Figura A.12.** (a) Método de los sectores esféricos para determinar el contacto entre átomos. (b) Poliedros VDP.

El área de las caras del poliedro VDP (Figura A.12b) y, por lo tanto, la sección de la esfera del átomo que corta la pirámide construida a partir de la cara ( $\Omega_i$ ) (Figura A.12b), es reflejo de la fortaleza del enlace entre el átomo central, y con el que comparte la cara del poliedro VDP.

Los poliedros VDP son una partición del espacio cristalino que ha dado lugar a diferentes descriptores cristalocímicos de gran utilidad, dado que tanto el volumen como el radio del poliedro están en relación directa con los radios y volúmenes atómicos. De hecho, los mismos criterios se han aplicado a nivel de las moléculas, determinándose el radio y volumen de las mismas en diferentes entornos cristalinos, así como otras características asociadas a ellas.

En las Tablas A.1, A.2 y A.3 se resumen los diferentes descriptores cristalocímicos que se pueden calcular en base a los poliedros VDP. Entre los

estudios realizados, resultan de gran interés, los desarrollados para determinar la geometría de los canales en los cuales se aloja el solvente de las estructuras cristalinas.

**Tabla A.1.** Significado fisico-químico de los parámetros calculados a partir de los poliedros VDP.

| Parámetro  | Dimensionalidad         | Significado   |
|------------|-------------------------|---|
| $V_{VDP}$  | $\text{Å}^3$            | Tamaño relativo del átomo en el entorno cristalino.   |
| $R_{sd}$   | $\text{Å}$              | Radios atómicos cristaloquímicos generalizados.   |
| $G_3$      | Adimensional            | Grado de esfericidad del entorno de coordinación más cercano del átomo. A menor valor de $G_3$ , más se aproxima el entorno de coordinación a una esfera. |
| $\Omega_i$ | Porcentaje de la esfera | Fuerza de la interacción atómica.   |
| $D_A$      | $\text{Å}$              | Distancia entre los centros de carga positiva y negativa en los dominios atómicos.  |
| $N_f$      | Adimensional            | Número de átomos en el entorno de coordinación más cercano para el átomo del poliedro VDP.  |

**Tabla A.2.** Significado fisico-químico de los parámetros calculados a partir de los parámetros de la partición Voronoi-Dirichlet del espacio cristalino.

| Parámetro   | Dimensionalidad                       | Significado  |
|---|---------------------------------------|--|
| $\langle G_3 \rangle$                               | Adimensional                          | Uniformidad de la estructura cristalina.               |
| <b>Coordenadas de los vértices del poliedro VDP</b> | Fracciones de los parámetros de celda | Coordenadas de los huecos en la estructura cristalina. |
| <b>Longitud de los lados del poliedro VDP</b>       | Adimensional                          | Longitud de los canales entre los huecos.              |

**Tabla A.3.** Significado físico-químico de los parámetros calculados a partir de los poliedros VDP moleculares.

| Parámetro   | Dimensionalidad                                 | Significado  |
|---|---|--|
| $V_{VDP}(\text{mol})$   | $\text{Å}^3$                                    | Tamaño relativo de la molécula u otra subunidad estructural en su entorno de coordinación.                                 |
| $R_{sd}(\text{mol})$  | $\text{Å}$                                      | Radio efectivo de la molécula o subunidad estructural.   |
| $G_3(\text{mol})$   | Adimensional                                    | Grado de esfericidad de la molécula o subunidad estructural secundaria.  |
| <b>MCN (número de caras del poliedro VDP molecular)</b>           | Adimensional                                    | Número de moléculas ó subunidades estructurales que contactan con la subunidad estructural central.                        |
| $\Omega_i(\text{mol})$  | Porcentaje de la suma de $\Omega_i(\text{mol})$ | Fortaleza de la interacción intermolecular.  |
| <b>Número de caras de la celda definida por los poliedros VDP</b> | Adimensional                                    | Número de moléculas ó subunidades estructurales que rodean a la central, considerando un empaquetamiento ideal de esferas. |

A este respecto, la construcción de los poliedros VDP de puntos equidistantes localizados a lo largo del canal, permite calcular la variación del radio y la sección eficaz de los mismos.

### ***A.12. Espectroscopia de reflectancia difusa***

Los iones y complejos de los metales de transición poseen la propiedad de absorber determinadas longitudes de onda del espectro electromagnético. En el intervalo ultravioleta-visible-infrarrojo cercano, las bandas de absorción de los espectros de iones y complejos de metales de transición son, con frecuencia, anchas y están enormemente influenciadas por los factores químicos del entorno. Los espectros



de absorción de este tipo de radiación nos permiten obtener información sobre la estructura y el enlace de los compuestos.

La absorción de los complejos de metales de transición está originada por la excitación de un electrón de un orbital d del átomo metálico, que pasa del estado fundamental a un estado excitado. El espectro de absorción que presenta un compuesto depende del estado de oxidación del metal, del número y la clase de átomos o iones que se enlazan directamente a él y de la geometría de coordinación. Por otra parte, es habitual que las porfirinas, debido a la característica estructura con electrones- $\pi$  altamente conjugados, presenten dos intervalos de absorción; uno, en la región de 380 a 500 nm denominadas bandas B o *Soret*, y un grupo de absorciones más débiles de 500 a 750 nm, conocidas como bandas Q.

Para obtener los espectros de absorción de los compuestos mostrados en el presente trabajo, se ha utilizado la espectroscopia de reflectancia difusa. Esta técnica permite medir espectros de absorción de muestras policristalinas. Un haz de radiación que incide sobre una superficie rugosa se ve reflejado difusamente. La radiación reflejada difusamente se detecta a través de una célula fotosensible. Comparando esta intensidad con la de un patrón de referencia, se obtiene el porcentaje de reflectancia.

Las medidas de reflectancia difusa de los compuestos presentados en este trabajo, se han realizado en el Servicio Central de Análisis de los Servicios Generales de Investigación (SGIker) de la UPV/EHU, en un espectrofotómetro Cary 5000 (version 1.12).

Los espectros se han registrado a temperatura ambiente en un intervalo de número de onda comprendido entre 45000 y 5000  $\text{cm}^{-1}$ .

### ***A.13. Espectroscopia Mössbauer***

La espectroscopia Mössbauer es una técnica que facilita el estudio de las transiciones entre los diferentes estados de energía de los núcleos de un material a través de la radiación electromagnética que es emitida o absorbida por el material.<sup>23</sup> El efecto Mössbauer, también conocido como Fluorescencia de Resonancia Nuclear fue descubierto por L. Rudolf Mössbauer en 1957. La espectroscopia Mössbauer es muy similar a otras formas típicas de espectroscopia y está probablemente más cercana a la espectroscopia de resonancia magnética nuclear, debido a que ambas involucran transiciones entre estados nucleares.<sup>24</sup>

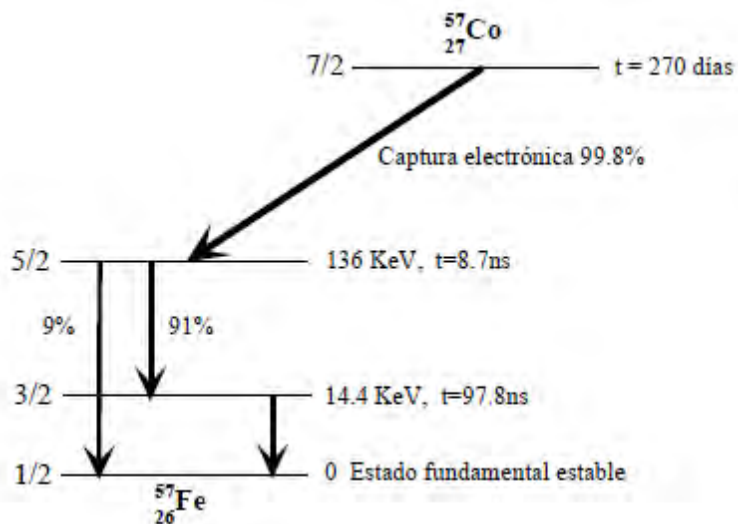
Muchos isotopos presentan el efecto Mössbauer, pero el <sup>57</sup>Fe tiene las mejores ventajas para nuestros propósitos. La fuente utilizada para la espectroscopia Mössbauer de <sup>57</sup>Fe es <sup>57</sup>Co, cuyos átomos están colocados en una matriz de rodio con estructura cúbica para dotar a los núcleos de un entorno lo más simétrico posible. De este modo, la línea de emisión es única y estrecha. En la Figura A.13 se muestra el esquema del decaimiento radioactivo y la correspondiente radiación emitida por esta fuente.

El cobalto tiene una carga nuclear positiva de 27. El núcleo captura un electrón de la capa K, reduciendo la carga a 26 y decae al nuevo estado fundamental, emitiendo tres rayos  $\gamma$  a energías de 14.4 KeV, 122 KeV y 136 KeV. La captura del electrón deja un hueco en la capa electrónica, el cual se llena, inmediatamente, produciendo rayos X de energía 6 KeV y menores. Los rayos  $\gamma$  de 14.4 KeV son los utilizados en el efecto Mössbauer. La transición con energía de 122 KeV no finaliza en el nivel fundamental, y los rayos  $\gamma$  de 136 KeV son muy energéticos para el efecto deseado.

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<sup>23</sup> Gibb, T. C., “*Principles of Mössbauer Spectroscopy*”, Chapman & Hall, Londres, 1976.

<sup>24</sup> Cranshaw, T. E.; Dale, B. W.; Longworth, G. O.; Johnson, C. E., “*Mössbauer Spectroscopy and its Applications*”, Cambridge University Press, Londres, 1985.



**Figura A.13.** Esquema de la desintegración radiactiva del  $^{57}\text{Co}$ .

Para observar el efecto Mössbauer, debemos cambiar la energía de los rayos  $\gamma$  en una pequeña cantidad. Podemos usar para ello el efecto Doppler. En lugar de un ensanchamiento Doppler debido a la agitación térmica, podemos utilizar un cambio Doppler coherente o modulación Doppler, proporcionando a la fuente una velocidad conocida. La anchura de línea de la fuente y la anchura de línea del absorbente se solapan en una cantidad diferente para cada velocidad.

La espectroscopia Mössbauer se utilizó en geometría de transmisión en la región paramagnética, usando un espectrómetro convencional de aceleración constante con una fuente de  $^{57}\text{Co}$ -Rh. La velocidad fue calibrada mediante una lamina de  $\alpha$ -Fe como material estándar. Las medidas se han realizado en el Servicio General de Espectroscopia Mössbauer (SGIker) de la UPV/EHU, en Leioa.

### ***A.14. Espectroscopia de resonancia paramagnética electrónica***

La espectroscopia de resonancia paramagnética electrónica (RPE) es una técnica utilizada para el estudio de compuestos con electrones desapareados (aquellos que no están en estado singlete). Esta técnica puede usarse para definir la distribución de un electrón desapareado en una molécula y, en cierta medida, decidir la extensión en que los electrones están desapareados. Asimismo, la espectroscopia de RPE puede proporcionar información sobre los niveles de energía de los compuestos estudiados.

Esta técnica se basa en el hecho de que el espín de un electrón puede adoptar dos orientaciones a lo largo de la dirección definida por el campo magnético aplicado,  $H$ . Esta ruptura de la degeneración de espín da lugar a una diferencia de energía entre los estados  $m_s = +1/2$  y  $-1/2$  (estados Zeeman) y siendo su valor:

$$\Delta E = g \mu_B H$$

donde:  $\mu_B$  es el magnetón de Bohr electrónico,  $H$  es el campo magnético exterior aplicado y  $g$  es el factor de Lande.

El valor de  $g$  es una constante característica para cada sustancia. Para un electrón libre tiene el valor  $g_e = 2.0023$ , siendo una de las constantes físicas conocidas más precisas. El símbolo  $g$  se utiliza cuando los electrones interactúan con otras partículas, en cuyo caso  $g \neq g_e$ .

Para la mayoría de los sistemas simples, con un solo electrón desapareado, la resonancia tiene lugar en un campo de unos 3000G, si  $\nu$  vale aproximadamente 9GHz. Las energías de los dipolos magnéticos en un campo magnético considerado como típico son tales que requieren frecuencias de radiación en la región de microondas.

El factor  $g$  de una sustancia difiere del valor  $g_e$  en una cantidad que depende de la capacidad de campo aplicado para inducir campos magnéticos locales. De esta forma, puede considerarse la cantidad  $(g/g_e)B$  como una modificación del campo aplicado que tiene en cuenta cualquier campo inducido localmente. Si  $g > g_e$ , el campo local es mayor que el aplicado; mientras que si  $g < g_e$ , dicho campo es menor. El signo y la magnitud de los campos locales inducidos dependen de la separación de los niveles de energía del compuesto a estudio. Cuanto menor sea la separación entre ellos, más fácil le resultará al campo aplicado inducir la circulación de los electrones y, en consecuencia, producir el campo magnético local.

El valor de  $g$  puede medirse teniendo en cuenta el valor del campo aplicado necesario para alcanzar la absorción de resonancia a una determinada frecuencia de microondas. Si la muestra es un monocristal, el valor de  $g$  se puede medir a lo largo de las diferentes direcciones y, por lo tanto, puede utilizarse para deducir la simetría del compuesto. La anisotropía de  $g$  proviene, fundamentalmente, del acoplamiento del momento angular de espín con el momento asociado a los electrones que se mueven en los orbitales moleculares. Así, los efectos del momento orbital se incorporan al valor de  $g$ , que, consecuentemente, varía con la dirección de medida y que, además, es anisotrópico.

Los estudios de RPE proporcionan información sobre la geometría del entorno de los iones paramagnéticos, así como sobre la existencia de posibles interacciones magnéticas entre los mismos.

El espectro de RPE, sobre muestra tanto policristalina, como en forma de monocristal de los compuestos estudiados, se ha registrado en un espectrómetro Bruker ESP300, operando en banda Q y banda X, equipado con un criostato de nitrógeno y de helio de flujo continuo. Los espectros se obtuvieron variando el campo magnético a frecuencia constante cuyo valor se ha medido mediante un frecuencímetro de

microondas Hewlett-Packard 5352B. El campo magnético se midió con un Gaussómetro Bruker ERO35M NMR. Estos equipos están adscritos a los Servicios Generales de Investigación (SGiker) de la UPV/EHU.

### ***A.15. Susceptibilidad magnética***

La estructura cristalina de los materiales está en el origen de determinados comportamientos magnéticos, no solo como soporte de la estructura magnética (disposición en cuanto a posiciones y direcciones de los momentos magnéticos en la red cristalina), sino influyendo en los mecanismos de imanación, mediante la anisotropía cristalina y, por lo tanto, condicionando el carácter magnético de los materiales.

La caracterización magnética a nivel macroscópico la proporcionan la imanación  $\mathbf{M}$  y la susceptibilidad magnética  $\chi$  que indican cómo responde un material a la acción de un campo magnético externo  $\mathbf{H}$ . La susceptibilidad magnética se define como la imanación de un material por unidad de campo aplicado.

Debido a los efectos anisotrópicos en un material cristalino, la susceptibilidad dependerá de la dirección del campo aplicado  $H$  con respecto a los ejes cristalográficos.

En todos los átomos existe un efecto diamagnético que proviene de la acción del campo sobre las orbitas electrónicas y es varios órdenes de magnitud inferior a otros efectos, por lo que solo es reseñable cuando éstos no existen, es decir, cuando no existe momento magnético intrínseco, dando lugar a un valor de  $\chi < 0$ . En cierto modo, el diamagnetismo se manifiesta por la ausencia de magnetismo.

El material paramagnético, ( $\chi > 0$ ), es aquel que teniendo los momentos inicialmente desordenados, tiende a ordenarse bajo la acción del campo magnético que debe vencer los efectos térmicos que tenderán a desordenar el material al aumentar la temperatura. El comportamiento general viene dado por las expresiones:

$$\chi = \frac{M}{H} = \frac{N_v \mu^2}{3k_B T} \kappa_m \mu_0$$

donde:  $N_v$  es el número de dipolos por unidad de volumen,  $\mu$  es el momento bipolar magnético,  $k_B$  es la constante de Boltzman,  $\kappa_m = 1 + c_m$  es la permeabilidad relativa comparada con el espacio libre, y  $\mu_0$  es la permeabilidad en el vacío ( $\mu_0 = 4\pi \cdot 10^{-7} \text{ JC}^{-2}\text{s}^2 \rightarrow \text{m}^{-1}\text{T}^2\text{J}^{-1}\text{m}^3$ ).

Cuando el campo magnético externo  $\mathbf{H}$  es pequeño y la temperatura  $T$  es elevada, se obtiene la conocida ley de Curie:

$$\chi_m = \frac{C}{T} \geq 0$$

siendo  $C$  la constante de Curie ( $C = NV\mu_{\text{ef}}^2/3k_B$ ). La determinación de esta constante permite una estimación inmediata del momento efectivo  $\mu_{\text{ef}}$ , a partir de las medidas experimentales. En muchos casos, en ausencia de campo magnético existe un orden entre momentos magnéticos debido a la existencia de la interacción de canje. Este ordenamiento permanece en tanto en cuanto la temperatura sea suficientemente baja para que el desorden térmico no supere el ordenamiento. Esta temperatura es la temperatura de Curie (si el ordenamiento es paralelo, ferromagnetismo), o de Neel (si el ordenamiento es antiparalelo, antiferromagnetismo).

Un compuesto ferromagnético se comporta para  $T > T_c$  según la ley de Curie-Weiss:

$$\chi = \frac{C}{T - \theta}$$

donde  $\theta$ , de signo positivo en este caso, es la constante de Weiss y está relacionada con la intensidad de las interacciones de canje.

Análogamente, la susceptibilidad magnética  $\chi_m$  de una sustancia antiferromagnética se ajusta a la ley de Curie-Weiss por encima de la temperatura de Neel, siendo  $\theta$  de signo negativo. Los compuestos antiferromagnéticos muestran un máximo de susceptibilidad ligeramente por encima de la temperatura de Neel. Por debajo de este valor,  $\chi_m$  decrece según disminuye la temperatura.

Las medidas de susceptibilidad magnética se han llevado a cabo entre 2 o 5 K y 300 K, utilizando un magnetómetro SQUID (MPMS-7T, Quantum Design), que suministra el campo magnético mediante una bobina superconductora que alcanza un campo máximo de 7 Teslas. El sistema de regulación de temperatura, permite trabajar hasta 1.4 K, con una estabilidad de hasta  $\pm 0.02$  K (Servicio General de Medidas Magnéticas, SGIker, UPV/EHU).

### ***A.16. Cálculos teóricos***

La Química Teórica y Computacional juega un papel de primer orden en el desarrollo de la Química Moderna. La investigación en este área requiere una amplia formación en fundamentos matemáticos y físicos, en metodología mecanocuántica, en programación y en métodos estadísticos de simulación molecular por ordenador, entre otros.



Se denomina Química Computacional (o Teórica) a la obtención de información estructural de sistemas químicos por medio de cálculos matemáticos basados en leyes fundamentales de la física. Se puede utilizar la Mecánica Clásica para realizar cálculos, siempre con la ayuda de modelos. Pero, la única teoría capaz de dar una interpretación a las ecuaciones de movimiento en sistemas del tamaño de las moléculas es la Mecánica Cuántica. Se pueden encontrar dos áreas principales para realizar los cálculos, la mecánica molecular y la teoría de estructura electrónica, gracias a los cuales se podrán realizar:

**I.-** cálculos de la energía de una estructura particular.

**II.-** optimización de la geometría.

**III.-** cálculos de frecuencia vibracionales.

La *mecánica molecular* utiliza las leyes de la física clásica para predecir estructuras y propiedades moleculares. No trata los electrones de un sistema molecular, sino que optimiza el cálculo basado en la interacción electrón-núcleo. Esta teoría se encuentra limitada debido a que:

**I.-** no todos los campos de fuerza pueden usarse para los sistemas de interés.

**II.-** los efectos electrónicos no son los predominantes, por lo que no se pueden hacer estudios sobre procesos que involucren formación o rotura de enlaces.

**III.-** las propiedades moleculares que dependan del ambiente electrónico no son reproducibles.

Por otra parte, *los métodos de estructura electrónica* están basados en las leyes de la mecánica cuántica y se caracterizan por las aproximaciones matemáticas para resolver la ecuación de Schrödinger. Se pueden encontrar tres tipos de métodos:

- métodos semiempíricos:
  - utilizan parámetros experimentales para simplificar.
  - son de bajo coste.
  - se realiza una descripción cualitativa razonable.
  - la exactitud en la predicción depende de cuan buenos sean los conjuntos de parámetros, el tamaño del sistema y el tipo de átomos que lo conformen.
  
- métodos ab-initio:
  - basados únicamente en las leyes de la mecánica cuántica y valores de las constantes físicas fundamentales.
  - mayor exactitud.
  - mayor coste.
  - se pueden estudiar sistemas en estado base y estados excitados, y en fase gaseosa o en solución.
  
- métodos de Funcional de la Densidad (DFT):
  - basados en el modelo molecular teniendo en cuenta la correlación electrónica como un funcional general de la densidad electrónica.
  - similar a los métodos ab-initio.

Los cálculos teóricos presentados en la memoria están basados en esta última teoría. De esta forma, se han calculado las energías de distintas entidades, empleando el programa Gaussian 03 mediante métodos DFT. Los mismos se han realizado en el superordenador Arina perteneciente al Servicio de Informática Aplicada a la Investigación (SGIker), de la Universidad del País Vasco (UPV/EHU).

Para realizar estos cálculos es preciso disponer de un modelo químico, el cual consiste en la combinación de un método teórico con un conjunto base (descripción matemática de los orbitales de un sistema molecular). Cada par único método/conjunto base representa una aproximación diferente a la ecuación de Schrödinger. Hay que tener en cuenta que las energías predichas por cualquiera de los métodos, resultarán en un valor mayor al real debido a las aproximaciones realizadas.

En los métodos DFT se define la correlación electrónica por medio de funcionales de la densidad electrónica, siendo éstos, la energía cinética, las interacciones electrón-núcleo, las repulsiones coulombicas y los términos de correlación-intercambio. Los funcionales que se han definido y que se distinguen por la forma en que tratan los componentes de intercambio y correlación son:

**a. Funcionales de intercambio local y de correlación:** Sólo involucran los valores de las densidades de espín de electrón; los más utilizados son Slater,  $X\alpha$  y el tratamiento de densidad de espín Vosko Wilk y Nusair (VWN).

**b. Funcionales de correlación-corregidos (no locales):** Tienen en cuenta los valores de las densidades de espín de electrón y sus gradientes; entre ellos, los más conocidos son Becke, LYP y una combinación de ambos conocida por B-LYP.

**c. Funcionales híbridos:** Resultan de la combinación lineal de términos de intercambio Hartree-Fock, local y gradiente-corregido, siendo la mejor combinación conocida la B3LYP y B3PW91.

Una vez vistos los diferentes métodos, hay que evaluar las distintas posibilidades que se tienen en los conjuntos base, para así poder elegir un modelo correcto, método/conjunto base, para realizar los cálculos que se pretendan. Existen tres tipos de funciones base:

*a. Base mínima:* únicamente incluye los orbitales internos y de valencia.

*b. Base de valencia:* describe a cada átomo utilizando bases para los orbitales de valencia.

*c. Base extendida:* además de los orbitales internos y de valencia, tiene en cuenta un conjunto de orbitales no ocupados llamados orbitales virtuales. Dentro de este tipo de base existen tres posibilidades diferentes:

*i. Conjunto base splits valence.*

*ii. Conjunto base polarizada.*

*iii. Funciones difusas.*

El modelo químico empleado para la realización de los cálculos se basa en el funcional híbrido B3LYP junto con la base extendida 6-31G, donde se añaden funciones de polarización a todos los átomos del sistema, incluyéndose, en alguno de los casos, los átomos de hidrógeno.

Todos los archivos de entrada, para los cálculos, se han preparado con el programa GaussView05, instalado en la máquina virtual de Guinness, dentro del superordenador Arina.

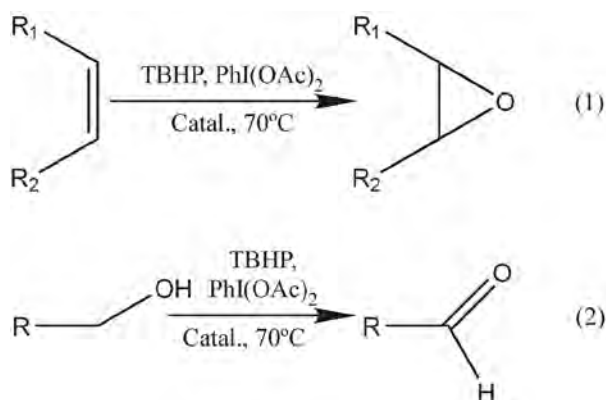
## A.17. Catálisis

Dada la importancia que la catálisis tiene en la industria química (tanto a gran escala como en química fina) y la capacidad que han demostrado poseer las porfirinas con metales de transición como el Fe, Co o Mn para catalizar diversas reacciones orgánicas, algunos de los compuestos que se presentan en esta memoria se han probado como catalizadores.

### A.17.1 Oxidación de alquenos y alcoholes

Las porfirinas sintéticas se han utilizado ampliamente en numerosas reacciones catalíticas y desde finales de 1970 se han empleado como catalizadoras en reacciones de oxidación de diferentes moléculas orgánicas.

Se han probado las propiedades catalíticas para la oxidación de alquenos y alcoholes (Figura A.14) de varios de los compuestos presentados en esta memoria. De esta manera, se han empleado diferentes sustratos (estireno, 1-octeno,  $\beta$ -metilestireno y alcohol bencílico) y *tert*-butilhidroperóxido (TBHP) o diacetato de yodobenceno ( $\text{PhI}(\text{OAc})_2$ ) como agentes oxidantes.

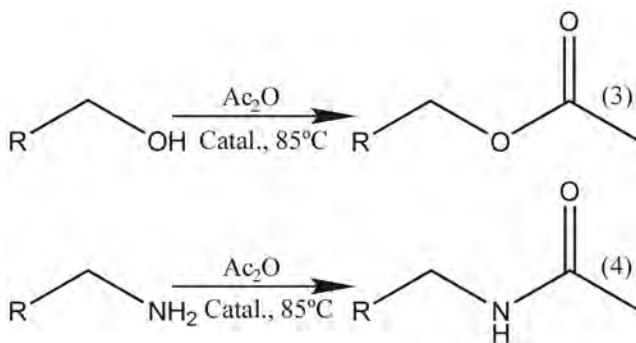


**Figura A.14.** Esquema de las reacciones de oxidación de alquenos (1) y alcoholes (2).

### ***A.17.2 Acetilación de alcoholes y aminas***

Las reacciones de acetilación de grupos hidroxilo y aminas son muy útiles en síntesis orgánica, ya que en numerosas ocasiones la protección de estos grupos funcionales es necesaria para evitar reacciones en esos puntos.

Se han probado las propiedades catalíticas para la acetilación de alcoholes y aminas (Figura A.15) de varios de los compuestos presentados en esta memoria. De esta manera, se han empleado diferentes sustratos (alcohol bencílico, 1-hexanol, fenol y anilina) y anhídrido acético como fuente de acetilo.



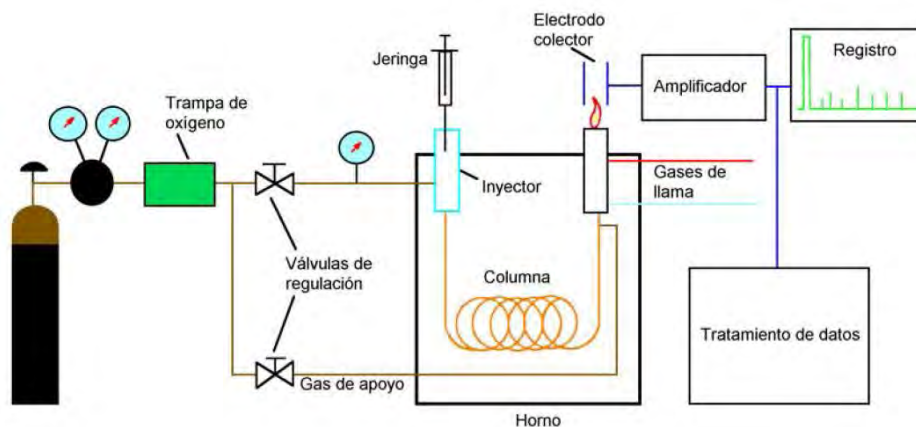
**Figura A.15.** Esquema de las reacciones de acetilación de alcoholes (3) y aminas (4).

### ***A.18. Cromatografía de gases***

En la cromatografía de gases, la muestra se volatiliza y se inyecta en la cabeza de una columna cromatográfica. La elusión se produce por flujo de una fase móvil de un gas inerte, y a diferencia de la mayor parte de los tipos de cromatografía, la fase móvil no interacciona con las moléculas de analito: su única función es la de transportar el analito a través de la columna. Existen dos tipos de cromatografía de gases, la de gas-sólido (GSC) y la de gas-líquido (GLC). La que se ha empleado en este

trabajo ha sido esta última, que presenta un gran número de aplicaciones en todos los campos de la ciencia y su denominación se abrevia normalmente de gases (GC).

La cromatografía de gas-liquido, se basa en la distribución del analito entre una fase móvil y una fase liquida inmovilizada sobre la superficie de un sólido inerte (Figura A.16). El concepto de cromatografía gas-liquido fue enunciado por primera vez en 1941 por Martin y Singe, quienes fueron también los responsables del desarrollo de la cromatografía de distribución liquido-liquido. Sin embargo, tuvo que pasar más de una década para que se demostrara, experimentalmente, la importancia de la cromatografía gas-liquido.<sup>25</sup> Tres años más tarde, en 1955, apareció en el mercado el primer aparato comercial para cromatografía gas-liquido y desde entonces las aplicaciones de esta técnica han crecido de manera espectacular.<sup>26-29</sup>



**Figura A.16.** Esquema de un cromatógrafo de gases.

<sup>25</sup> Jones, A.; Marin, A. J., *Analys.*, **1952**, 77, 915

<sup>26</sup> Willet, J., “*Gas Chromatography*”, Wiley, 1987.

<sup>27</sup> Jennings, W.; Mittleheldt, E.; Stremple, P., “*Analytical Gas Chromatography*”, Academic Press, San Diego (California), 1997.

<sup>28</sup> Mohseni-Mehran, S. M.; Golshani, B., *Journal of Clinical and Diagnostic Research*, **2013**, 7, 1004-1007.

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Para evaluar la importancia de la GLC, es necesario distinguir entre los dos papeles que desempeña esta técnica. El primero, como herramienta para realizar separaciones: resulta inmejorable cuando se aplica a muestras orgánicas complejas, a organometálicas o a sistemas bioquímicos. El segundo, una función claramente distinta, es la de proporcionar un medio para llevar a cabo un análisis. En este caso, se emplean los tiempos o volúmenes de retención para la identificación cualitativa, mientras que las alturas de los picos o sus áreas dan información cuantitativa. Esta última ha sido la finalidad con la que se ha utilizado esta técnica en el desarrollo del trabajo que se presenta.

Con fines cualitativos, la cromatografía gas-líquido es una técnica mucho más limitada que la mayoría de los métodos espectroscópicos. En consecuencia, existe una tendencia importante en este campo a combinar la capacidad de fraccionamiento de la GLC con las propiedades para la identificación que tienen otras técnicas como la espectroscopia de masas, el infrarrojo y la resonancia magnética nuclear.

Para los experimentos realizados durante esta investigación se ha utilizado un cromatógrafo Hewlett-Packard 5980 II, con un detector de ionización de llama y una columna cross-linked de metilsilicona (mezcla de metilsilicona (ov-170) y permetilcicloextrina como fases estacionarias),<sup>30</sup> perteneciente al Instituto de Ciencia de Materiales de Madrid, CSIC (Dra. M. Iglesias).

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# **ANEXO B**

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# **ANEXO C**

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## ***Trabajos Publicados***

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**PUBLICACIONES**

1.- Arkaitz Fidalgo-Marijuan, Gotzone Barandika, Begoña Bazán, Miren-Karmele Urtiaga, María-Isabel Arriortua, “*Self-assembly of iron TCPP (meso-tetra(4-carboxyphenyl) porphyrin) into a chiral 2D coordination polymer*”, *Polyhedron* **2011**, *30 (16)*, 2711-2716.

2.- Arkaitz Fidalgo-Marijuan, Gotzone Barandika, Begoña Bazán, Miren-Karmele Urtiaga, Luis Lezama, María-Isabel Arriortua, “*Fe-TPP Coordination Network with Metalloporphyrinic Neutral Radicals and Face-to-Face and Edge-to-Face  $\pi$ - $\pi$  Stacking*”, *Inorg. Chem.* **2013**, *52 (14)*, 8074-8081.

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4.- Arkaitz Fidalgo-Marijuan, Gotzone Barandika, Begoña Bazán, Miren-Karmele Urtiaga, Edurne S. Larrea, Marta Iglesias, Luis Lezama, María-Isabel Arriortua, “*Heterogeneous catalytic properties of a metalloporphyrinic MOF based on unprecedented  $\mu$ -O-[FeTCPP]<sub>2</sub> dimers: porosity revealing an unusual superhyperfine EPR structure*”, *enviada al J. Am. Chem. Soc.*

**COMUNICACIONES A CONGRESOS**

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## Self-assembly of iron TCPP (*meso*-tetra(4-carboxyphenyl)porphyrin) into a chiral 2D coordination polymer

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### ABSTRACT

Synthetic metalloporphyrin complexes are often used as analogues of natural systems, and they can be used for the preparation of high-dimensional coordination polymers. In this work, a new chiral Fe-TCPP (TCPP is *meso*-tetra-(4-carboxyphenyl)porphyrin) coordination compound has been synthesized and structurally characterized. The compound is 2D via coordination bonds, and it exhibits strong hydrogen bonds that connect the planar arrays forming the 3D framework. The oxidation of the original Fe<sup>II</sup> ions to Fe<sup>III</sup> accounts for the formation of this array, in which the topological analysis reveals a very high connectivity based on a simple extension fashion of the structure. DFT calculations have been also carried out to study the stabilization of the Fe<sup>III</sup>-compound. This is the third example of a 2D coordination compound based on TCPP in which the dimensionality refers just to coordination bonds, and no other ligands are present in the structure.

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### 1. Introduction

Coordination polymers are also known as MOFs (metal organic frameworks), and the work devoted to this field in the last decades is huge. In this context, metalloporphyrins are remarkable precursors in supramolecular chemistry, giving rise to various architectures and properties [1–4]. To illustrate this point, several examples can be cited as photodynamic therapy, information storage devices, photoelectrical devices as photocells and light-emitting diodes (that transform energy in both directions), and receptors (exploiting their ability to selectively form complexes which can sharply change the spectral properties) [5–8].

Metalloporphyrins are one of the cornerstones on which the existence of life is based and major biochemical, enzymatic, and photochemical functions depend on the special properties of a tetrapyrrolic macrocycle. This is the reason why synthetic metalloporphyrin complexes are often used as analogues of natural systems found in photosynthesis, oxygen carriers, and catalysts [5,9–14]. For instance, these systems are used to understand the mechanism of electron transfer through intermolecular interactions, and some works show that efficient energy transfer may occur across the intermolecular bonds [15–19].

From the point of view of coordination chemistry, the dimensionality of metalloporphyrin frameworks is defined by the extension of a structural unit in one, two or the three dimensions of the space via coordination bonds. Thus, axial coordination of metalloporphyrins represents a limiting factor for high dimensionality as it gives only one or two binding sites with other structural units. Therefore, additional binding centers are required for high dimensional frameworks, and one way to create them consists of incorporating additional donors at the periphery of a porphyrinic cycle. An illustrative example of the later is tetra-(4-carboxyphenyl)porphyrin (TCPP) (Scheme 1) for which the presence of carboxylic groups at the 4-positions of the phenyl ring increases the possibilities of obtaining a high dimensional framework.

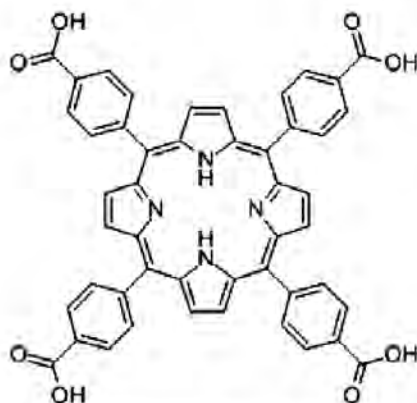
TCPP coordination polymers with different structures have been prepared. For example, 2D porphyrin frameworks have been reported exhibiting square grid structure sustained by characteristic  $\pi$ - $\pi$  stacking interactions and multiple hydrogen bonds [20–23]. Similarly, a 2D complex with Mn<sup>II</sup> [24] must be cited as the dimensionality is based on coordination bonds. Additionally, the combination of TCPP with other components gives rise to a variety of 2D and 3D structures [25]. Some of these combinations are especially remarkable as they include fullerene [26], silica [27] and 4,4'-bipyridine [28,29].

During the last years, our research has been focused on the preparation of coordination polymers with increasing dimensionality with a variety of metal–ligand combinations, and we have prepared several high dimensional structures with 4,4'-bipyridine,

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Scheme 1. Lewis structure of TCPP.

including interpenetrated networks [30–35]. In this sense, it is worth mentioning that, when combining an O-donor ligand like TCPP, with a N-donor one, like 4,4'-bipyridine, the Pearson acidity is one of the leading forces to be considered in the extension of the structure, as it is in relationship with the affinity of the metal centre, which is influenced by its oxidation state. The most popular example of a natural system where the oxidation state of the metal is crucial is the oxygen transport in haemoglobin.

Taking into account the above mentioned aspects, we intended to prepare Fe<sup>II</sup>–porphyrin frameworks with TCPP and 4,4'-bipyridine. In particular, the goal of this work was to study the influence of the synthesis conditions on the structural features of the framework. In this way, this work presents the microwave-assisted hydrothermal synthesis of the new compound [Fe-TCPP], and its X-ray structural characterization. From the point of view of the coordination binding, the structure is 2D, and exhibits robust hydrogen bonds that connect the planar moieties giving rise to the 3D framework. A topological analysis and DFT calculations have been also carried out in order to analyze the self-assembly process.

## 2. Experimental

### 2.1. Materials and methods

The porphyrin compound TCPP (Sigma–Aldrich) and all the other solvents and reagents (Sigma–Aldrich) were obtained commercially and used without further purification. [FeTCPP] compound was synthesized by using microwave-assisted hydrothermal synthesis. Free ligand TCPP (4.7 mg, 0.006 mmol) was dissolved in a mixture of deionised water (10 mL) and acetone (15 mL), then under continuous stirring NaOH (1 M) was added until pH 14 (to cause the porphyrin deprotonation). FeCl<sub>2</sub> (7.6 mg, 0.06 mmol) dissolved in deionised water (5 mL) was added to porphyrin solution and after 10 min of stirring, 4,4'-bipyridine (2.8 mg, 0.018 mmol) dissolved in deionised water (10 mL) was added drop by drop. The solution was heated at 140 °C (800 W) for 2 h in a CEM MAR55 microwave and after that, at the same temperature in a PTFE-lined stainless steel pressure vessel for 5 days in a conventional heater, yielding diffraction quality dark red crystals.

### 2.2. Infrared spectroscopy

The IR spectrum was collected on a JASCO FT/IR-6100 at room temperature at the range of 4000 to 400 cm<sup>-1</sup>, in KBr pellets (1%).

### 2.3. Single-crystal X-ray diffraction

Rhombohedral single-crystals with dimensions given in Table 1 were selected under polarizing microscope and mounted on MicroMounts. Single-crystal X-ray diffraction data were collected at 100 K on a Bruker X8 Prospector equipped with a high brilliance Cu-KMS (microfocus source) and APEX II detector. Details of crystal data and some features of the structure refinement are reported in Table 1. Lattice constants were obtained by using a standard program belonging to the software of the diffractometer, confirming at the same time the good quality of the single-crystal.

The Lorentz-polarization and absorption corrections were made with the diffractometer software, taking into account the size and shape of the crystals [36]. The structure of [FeTCPP] was solved by direct methods with the SHELXS-97 [37] program, in the monoclinic *P*2<sub>1</sub> space group, which allowed us to obtain the position of the Fe atom, as well as oxygen and nitrogen atoms and some of the carbon atoms of the TCPP molecule. The refinement of the crystal structures was performed by full matrix least-squares based on *F*<sup>2</sup>, using the SHELXL-97 program [37], obtaining the remaining carbon atoms. Anisotropic thermal parameters were used for all non-hydrogen atoms. All the hydrogen atoms, both the connected to de aromatic rings (C–H 0.95 Å), such as the carboxylic groups (O–H 0.84 Å) were fixed geometrically after having detected their existence on the density map and were refined using a riding model with common isotropic displacements. Final R-factors are given in Table 1 together with other crystallographic data, the conditions employed at the measurement of diffracted intensities and others characteristics of the refinement.

The diffraction data (intensity statistics and systematic absences), as well as the phase determination and structure solution processes, were consistent only with the non-centrosymmetric space group *P*2<sub>1</sub>, with two screw-related porphyrin molecules per unit-cell.

Table 1  
Crystal data and structure refinement for [FeTCPP].

|  | [FeTCPP]   |
|--|--|
| Formula  | C <sub>48</sub> H <sub>27</sub> FeN <sub>4</sub> O <sub>8</sub>    |
| Formula weight/g mol <sup>-1</sup>   | 843.59   |
| Crystal system   | monoclinic   |
| Space group  | <i>P</i> 2 <sub>1</sub>  |
| <i>a</i> (Å)   | 11.0195(2)   |
| <i>b</i> (Å)   | 8.8470(2)  |
| <i>c</i> (Å)   | 20.0191(4)   |
| $\beta$ (°)  | 102.902(2)   |
| <i>V</i> (Å <sup>3</sup> )   | 1902.38(7)   |
| <i>Z</i>   | 2  |
| <i>F</i> (0 0 0)   | 866  |
| <i>T</i> (K)   | 100(2)   |
| $\mu$ (mm <sup>-1</sup> )  | 3.728  |
| $\rho_{\text{calc}}$ (g cm <sup>-3</sup> )   | 1.473  |
| $\rho_{\text{obs}}$ (g cm <sup>-3</sup> )  | 1.478(4)   |
| Crystal size (mm) color  | 0.36 × 0.15 × 0.01, dark red                                       |
| Radiation ( $\lambda$ /Å)  | 1.54178  |
| No. of reflections   | 20 868   |
| Independent reflections  | 6320   |
| Limiting indices <i>h</i> , <i>k</i> , <i>l</i>  | -13 ≤ <i>h</i> ≤ 13,<br>-9 ≤ <i>k</i> ≤ 10,<br>-23 ≤ <i>l</i> ≤ 23 |
| <i>R</i> <sub>int</sub> , <i>R</i> <sub><math>\sigma</math></sub>                          | 0.0480, 0.0489   |
| <i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> (obs) ( <i>I</i> > 2 $\sigma$ ( <i>I</i> )) | <i>R</i> <sub>1</sub> = 0.0378,<br><i>wR</i> <sub>2</sub> = 0.0877 |
| <i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> (all)                                       | <i>R</i> <sub>1</sub> = 0.0475,<br><i>wR</i> <sub>2</sub> = 0.0921 |
| Goodness-of-fit (GOF) on <i>F</i> <sub>2</sub>   | 1.026  |
| No. of parameters/restraints   | 554/ 1   |
| Largest diffraction peak and hole (e Å <sup>-3</sup> )                                     | 0.281 and -0.235   |

## 2.4. Computational details

Density functional calculations were carried out by using the GAUSSIAN03 package [38] and the hybrid density functional B3LYP. The split-valence basis set 6-31G was used for all the calculations.

## 3. Results and discussion

Microwave-assisted synthesis was employed for the preparation of a new coordination polymer. Its chemical formula is [FeTCPP], where the oxidation state of iron is 3, and TCPP<sup>3-</sup> is the trivalent anion formed from deprotonation of *meso*-tetra-(4-carboxyphenyl)porphyrin (C<sub>48</sub>H<sub>30</sub>N<sub>4</sub>O<sub>8</sub>). The fact that the original Fe<sup>II</sup> has suffered oxidation to Fe<sup>III</sup> will be discussed later. The absence of the ligand 4,4'-bipyridine in the structure will be also commented. Structural characterization of [FeTCPP] was carried out by means of IR spectroscopy and X-ray diffraction.

### 3.1. Structural characterization

#### 3.1.1. IR spectroscopy

IR data show significant differences between the free ligand TCPP and the metallated [FeTCPP] compound. The N–H bond stretching and bending frequencies of TCPP located at 3200 cm<sup>-1</sup> and 970 cm<sup>-1</sup> disappeared when iron ion was inserted into the porphyrin ring, and a characteristic Fe–N band appears at 1000 cm<sup>-1</sup>, which indicates the formation of an iron porphyrin compound [39]. The bands at about 3415 cm<sup>-1</sup>, 1740 cm<sup>-1</sup> and 1200 cm<sup>-1</sup> were assigned to the O–H, C=O and C–O bonds of the carboxylic groups, respectively. The band at 2940 cm<sup>-1</sup> was assigned to the C–H bond of the benzene and pyrrole rings. The bands at 1690–1540 cm<sup>-1</sup> and 1380 cm<sup>-1</sup> were assigned to C=C stretching mode and the C–N stretching vibration, respectively. A weak band corresponding to the Fe–O bond stretching mode was observed at about 820 cm<sup>-1</sup>. Finally, the band at 790 cm<sup>-1</sup> was assigned to the H out of plane bending of the C–H bond.

#### 3.1.2. Crystal structure of [FeTCPP]

The crystal structure of [FeTCPP] consists of tetrapyrrole units containing the Fe atoms as shown in Fig. 1. The metal atoms are octahedrally coordinated to four N atoms (N1, N2, N3 and N4) that are coplanar. The axial positions are occupied by two O atoms (O1 and O6) that belong to the carboxylate groups of adjacent porphyrin units. Table 2 summarizes the most significant bond parameters for [FeTCPP]. As observed, the values lie among the typical ones for octahedral iron(III). In fact, the only remarkable feature is that Fe–O6 bond is slightly longer than the others.

Taking the structural fragment on Fig. 1 as reference, the polymer extends through the formation of four new bonds with adjacent porphyrin groups, involving O1 and O6 atoms. Thus, the reference porphyrin uses its own O1 and O6 atoms to connect with another two porphyrin units. This is, each unit is connected to four equivalent units, and the result is a 2D array (Fig. 2). This planar array is based on the fact that octahedral spheres are rotated forming planes that are perpendicular to the [10–1] direction, the extension of the structure taking place through coordination bonds. It is worth pointing out that this array is chiral. Additionally, there are several hydrogen bonds (Table 3) between atoms on the same plane. (O5–H50···O3) and (O8–H80···O2), that reinforce the robustness of the 2D moiety.

As shown in Fig. 3, packing on the planes along the [10–1] direction gives rise to the 3D framework. These planes are chemically connected through strong hydrogen bonds between O2 and O4 atoms where d(O4–H40···O2) = 2.614(4) Å. As a consequence of this packing fashion, the 3D framework keeps chirality. Undoubt-

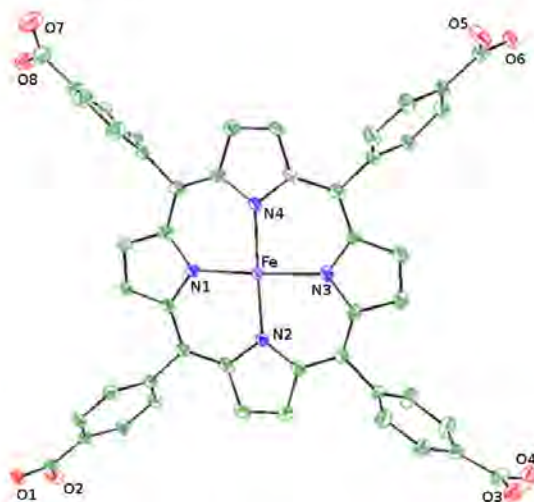


Fig. 1. ORTEP detail of the equatorial plane for the octahedral coordination sphere in [FeTCPP] (Fe–purple, C–green, N–blue and O–red). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 2  
Most significant angles (°) and distances (Å) for [FeTCPP] (distances in bold).

| Fe | N1              | N2              | N3              | N4              | O1              | O6              |
|----|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| O6 | 85.44(10)       | 89.98(10)       | 86.91(11)       | 84.09(10)       | 178.34(11)      | <b>2.220(3)</b> |
| O1 | 95.62(11)       | 88.74(11)       | 92.03(11)       | 97.18(11)       | <b>1.988(2)</b> |                 |
| N4 | 90.15(11)       | 174.07(13)      | 89.35(11)       | <b>2.060(3)</b> |                 |                 |
| N3 | 172.34(13)      | 90.17(11)       | <b>2.039(3)</b> |                 |                 |                 |
| N2 | 89.54(11)       | <b>2.067(3)</b> |                 |                 |                 |                 |
| N1 | <b>2.030(3)</b> |                 |                 |                 |                 |                 |

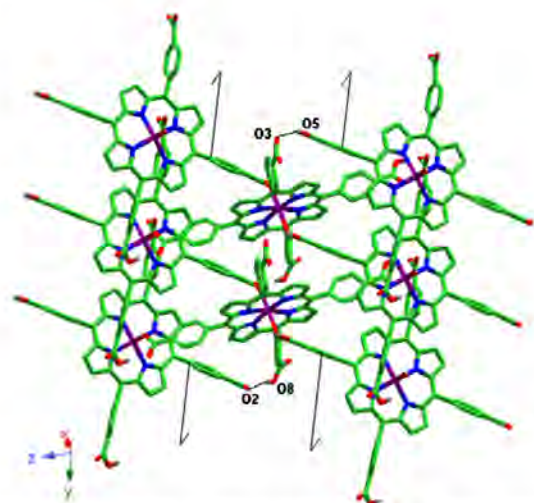
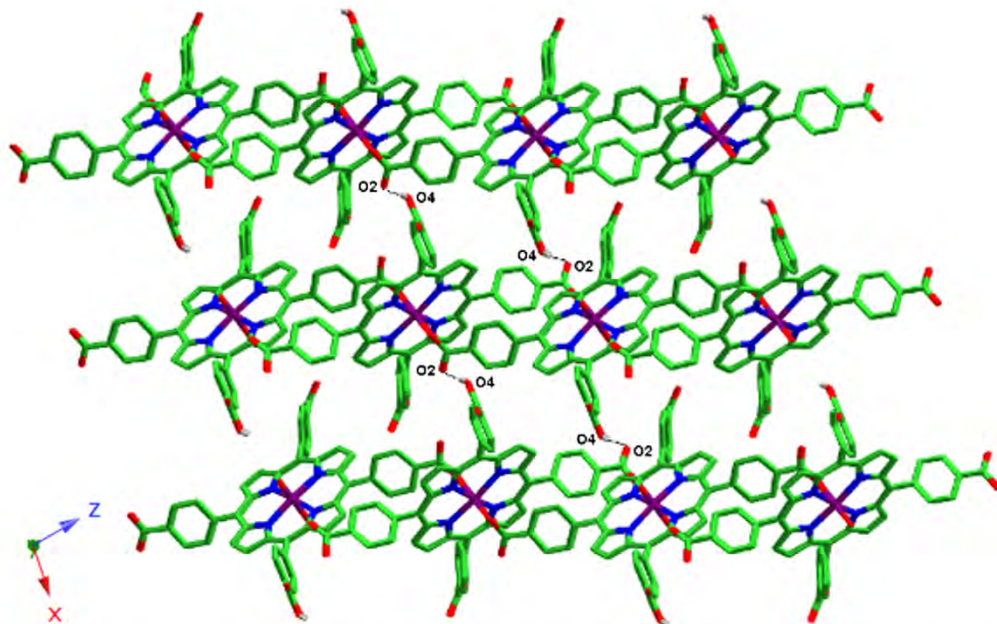


Fig. 2. View of a layer for [FeTCPP] (Fe–purple, C–green, N–blue, O–red, H–grey). Intralayer hydrogen bonds are marked as black lines. Twofold screw axes are located along the *b*-axis. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

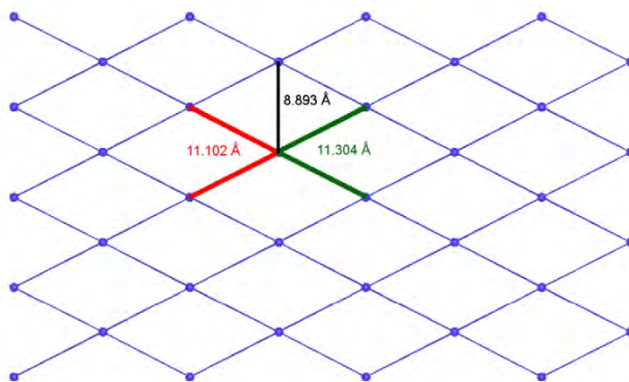
**Table 3**

Intra- and interlayer hydrogen bond parameters.

| O–H        | A(O)                         | O–H (Å) | H–A (Å) | O–A (Å)  | O–H–A (°) |
|------------|------------------------------|---------|---------|----------|-----------|
| O(4)–H(40) | O(2) (2 – x, –3/2 + y, –z)   | 0.84    | 1.78    | 2.614(4) | 171       |
| O(5)–H(50) | O(3) (2 – x, 1/2 + y, 1 – z) | 0.84    | 2.00    | 2.718(4) | 144       |
| O(8)–H(80) | O(2) (1 – x, 1/2 + y, –z)    | 0.84    | 1.91    | 2.740(4) | 169       |



**Fig. 3.** [0 1 0] Projection of the 3D covalent array for [FeTCPP] (Fe–purple, C–green, N–blue, O–red, H–grey). Hydrogen bonds between the layers are marked as black lines. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



**Fig. 4.** Topology of the 2D layers.

edly, this is a remarkable fact for [FeTCPP], since this property is not usual for structures based on porphyrin blocks exhibiting  $D_{4h}$  molecular symmetry [5]. Obviously, the fact that the structure extends through both axial sites and two of the equatorial ones is responsible for the later.

### 3.2. Topological analysis

The topological analysis has been carried out by means of TOPOS software [40]. First of all, the topology of the planes has been determined just considering the node connections taking place through

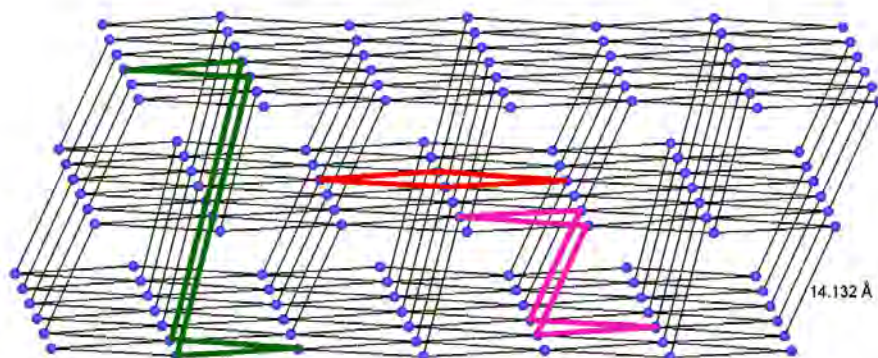


Fig. 5. Topology of the 3D net. Four-, six-, and eight-member circuits are shown in red, pink, and green, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 4  
Energy values (Hartree) for the selected structural units.

| Metal ion         | Ligand             | Monomer               | HF energy     |
|-------------------|--------------------|-----------------------|---------------|
| Fe <sup>II</sup>  | TCPP <sup>3-</sup> | [FeTCPP] <sup>1</sup> | -3928.5387399 |
| Fe <sup>III</sup> | TCPP <sup>3-</sup> | [FeTCPP]              | -3928.4125033 |
| Fe <sup>II</sup>  | TCPP <sup>2-</sup> | [FeTCPP] <sup>2</sup> | -3926.7601369 |
| Fe <sup>III</sup> | TCPP <sup>2-</sup> | [FeTCPP] <sup>3</sup> | -3926.8414566 |

All data have been obtained by considering high spin configuration, as concluded by preliminary calculations.

coordination bonds (Fig. 4). The result is a uninodal 4-c net (sql/Shubnikov tetragonal plane net {4<sup>4</sup>;6<sup>2</sup>}). Several examples of compounds exhibiting the same topology can be found in literature [41–46].

The fact that such a complicated structure extends in that simple fashion is remarkable, as well as the fact that for [FeTCPP] the extension of the structure takes place through two of the four equatorial positions and both axial ones.

If considering now the extension of the structure in the third dimension of the space, the topology shown in Fig. 5 includes connections between hydrogen bonds that take place for Fe atoms at a distance of 14.132 Å. The resulting uninodal net is 6-c type (mab {4<sup>4</sup>;6<sup>10</sup>;8}). This net has been reported for just one compound [47].

It is worth mentioning that there is a shorter interlayer distance between Fe atoms at 11.092 Å, but these atoms remain unconnected. Additionally, if considering the intralayer connections through hydrogen bonds, the net connectivity increases since there are two more links for each iron node at 8.893 Å. The resulting uninodal net is 8-c (3<sup>6</sup>;4<sup>10</sup>;5<sup>11</sup>;6), and no examples have been found in literature illustrating this new topology.

### 3.3. Stability of the metallated TCPP

The stability of the metallated monomers cannot be separated from two facts: the oxidation of the iron ions, and the pH variation along the synthesis.

The oxidation state of iron atoms in [FeTCPP] was corroborated by using the PLATON [48] software (Brown method) [49,50]. A calculated value of 2.954 was obtained that is in accordance with the presence of Fe<sup>III</sup> ions. However, Fe<sup>II</sup> was used for the synthesis, indicating that the metal ions have suffered oxidation.

Additionally, an asymmetric location of hydrogen atoms is observed for porphyrin in [FeTCPP]. This is both hydrogen atoms in pyrrole groups have been removed, as well as one of the four hydrogen atoms on the carboxylates. This is a striking location that

results in the TCPP<sup>3-</sup> anion. In order to understand this process, the charges on the electronegative atoms in isolated porphyrin were calculated by means of the Hückel method. The results indicate that, as expected, the most acid hydrogen atoms are those located on the carboxylate groups. In fact, values close to -0.70 and -0.15 have been calculated for the O atoms on -CO and -OH groups, respectively. On the other hand, iminic N atoms exhibit negative charges (-0.41 for N2 and -0.41 for N4), and pyrrolic ones positives values (+0.39 for N1 and +0.38 for N3). Nevertheless, in [FeTCPP] the ligand keeps three of the four most acid hydrogen atoms.

In order to understand these two facts, HF energies were calculated. The selected structural unit consists of a [FeTCPP]<sup>n</sup> monomer, where *n* is the charge that depends on the oxidation state of the metal ion and the charge of TCPP. Obviously, at high pH values, TCPP is completely deprotonated (TCPP<sup>3-</sup>). The as-done DFT calculations (B3LYP/6-31G) were carried out by using the GAUSSIAN 03 software [38]. The results (Table 4) suggest that the oxidation takes place at basic pH, when TCPP is completely deprotonated. Then, as pH goes to neutral values, the porphyrin recovers three of the acid protons that get located on the carboxylates. Additionally, the fact that [FeTCPP]<sup>-1</sup> (with Fe<sup>II</sup>) is more stable than [FeTCPP] (with Fe<sup>III</sup>) also indicates that the Fe<sup>III</sup>-monomers should not exist at neutral pH values. In other words, the [FeTCPP]<sup>n</sup> unit with Fe<sup>III</sup> becomes neutral at a higher pH value than the unit with Fe<sup>II</sup>, provoking the precipitation of the final product with Fe<sup>III</sup>. The later is in complete agreement with the Pearson theory. Therefore, if admitting that the presence of Fe<sup>III</sup> accounts for the polymerization of the monomers via carboxylate groups, it is easy to understand that 4,4'-bipyridine is not a component of the final product.

Finally, it must be pointed out that this is the third example [24] [51] of a 2D coordination compound based on TCPP in which the dimensionality refers just to coordination bonds, and no other ligands are present in the structure.

## 4. Conclusions

A new Fe-TCPP coordination polymer has been prepared in which 2D arrays are formed via coordination bonds. The stabilization of the metallated monomers at a basic pH value accounts for the oxidation of Fe<sup>II</sup> to Fe<sup>III</sup>, and explains the polymerization of the monomers via carboxylate groups. As a result, a rare framework has been obtained in which the 2D topology follows a very simple extension fashion. The three-dimensionality is raised via hydrogen bonds that keep the chirality found for the 2D coordination array. This is the third example of a 2D coordination compound based on TCPP in which the dimensionality refers just to

coordination bonds, and no other ligands are present in the structure.

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### Appendix A. Supplementary data

CCDC 825599; contains the supplementary crystallographic data for [FeTCPP]. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk). Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.poly.2011.08.008](https://doi.org/10.1016/j.poly.2011.08.008).

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# Fe–TPP Coordination Network with Metalloporphyrinic Neutral Radicals and *Face-to-Face* and *Edge-to-Face* $\pi$ – $\pi$ Stacking

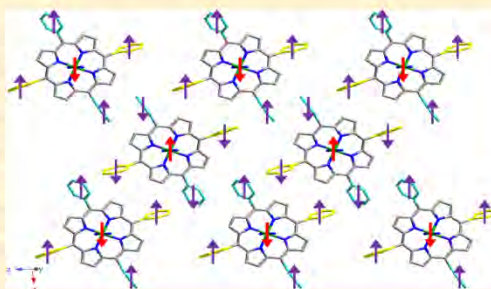
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## Supporting Information

**ABSTRACT:** Compound  $([\text{FeTPPbipy}]^*)_n$  (TPP = *meso*-tetraphenylporphyrin and bipy = 4,4'-bipyridine) is the first example of a Fe–TPP–bipy coordination network, and it consists of 1D polymers packed through *face-to-face* and *edge-to-face*  $\pi$ – $\pi$  interactions. The compound has been investigated by means of X-ray diffraction, IR, Mössbauer, UV–visible, and EPR spectroscopies, thermogravimetry, magnetic susceptibility measurements, and quantum-mechanical density functional theory (DFT) and time-dependent DFT calculations. The chemical formula for this compound can be confusing because it is compatible with Fe<sup>II</sup> and TPP<sup>2-</sup> anions. However, the spectroscopic and magnetic properties of this compound are consistent with the presence of low-spin Fe<sup>III</sup> ions and  $[\text{FeTPPbipy}]^*$  neutral radicals. These radicals are proposed to be formed by the reduction of metalloporphyrin, and the quantum-mechanical calculations are consistent with the fact that the acquired electrons are located on the phenyl groups of TPP.



## INTRODUCTION

Metalloporphyrins are one of the cornerstones on which the existence of life is based because major biochemical, enzymatic, and photochemical functions depend on the special properties of the tetrapyrrolic macrocycle.<sup>1</sup> Thus, porphyrin catalysts are well-known to be highly efficient for oxidative reactions,<sup>2</sup> and during the last years, great effort has been devoted to the immobilization of distinct types of catalysts on solid surfaces,<sup>3–5</sup> with porphyrins also having been investigated in this field.<sup>6–16</sup> Thus, these compounds can also be used for coordination networks where the assembly of metalloporphyrinic structural units can be achieved by coordination bonds and other weaker cohesion forces.<sup>17,18</sup> There are many examples of metalloporphyrinic three-dimensional (3D) frameworks, but most of them consist of the crystallization of monomeric complexes, with the cohesion forces being hydrogen bonds and  $\pi$  stacking. In fact, if thinking of high dimensionality in terms of the formation of coordination polymers, metalloporphyrins exhibit important limitations. To illustrate this point, the case of *meso*-tetraphenylporphyrin (TPP) can be cited. CSD research indicates the existence of monomers, dimers, trimers, and other types of aggregates. However, the highest dimensionality achieved with pyridyl ligands connected on axial positions for octahedral specimens corresponds to one-dimensional (1D) coordination polymers, and just seven of them have been prepared so far.<sup>19–24</sup> It is also worth mentioning that none of them has iron (Fe) as the metal

center. In fact, as far as we are aware, the highest dimensionality found for Fe–TPP–dipyridyl systems consists of dimers. However, it must be pointed out that there are two previous examples in the literature for 1D Fe–TPP polymers with cyanide-based ligands.<sup>25,26</sup>

The work herein presented was inspired by previously reported metalloporphyrinic frameworks exhibiting bipyridyl ligands.<sup>27–34</sup> Our intention was the synthesis of high-dimensional frameworks in which metalloporphyrins play two roles: as building blocks in porous networks and as catalysts immobilized in the pores. We still have not achieved this goal, but instead we have synthesized and characterized the compound  $([\text{FeTPPbipy}]^*)_n$ , where bipy is 4,4'-bipyridine (bipy). The compound exhibits 1D coordination polymers that crystallize in a 3D framework in which both *face-to-face* and *edge-to-face*  $\pi$  stacking of the phenyl groups provide stability to the lattice. The main interest of this compound lies in the fact that it is the first Fe–TPP–bipy compound characterized so far. Additionally, the special characteristics of this compound have produced an intricate discussion based on an exhaustive characterization [X-ray diffraction, IR, Mössbauer, UV–visible, and EPR spectroscopies, thermogravimetry, magnetic susceptibility measurements, and quantum-mechanical

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density functional theory (DFT) and time-dependent DFT (TD-DFT) calculations].

## EXPERIMENTAL SECTION

**Materials.** All solvents and chemicals were used as received from reliable commercial sources. The reagents 5,10,15,20-tetraphenylporphyriniron(III) chloride (FeTPP-Cl) and 4,4'-bipyridine (bipy; 98%) and the solvent *N,N*-dimethylformamide (DMF; 99.8%) were purchased from Sigma-Aldrich Co.; absolute ethanol was purchased from Panreac.

**Physicochemical Characterization Techniques.** The IR spectrum was collected on a JASCO FT/IR-6100 spectrometer at room temperature in the range of 4000–400  $\text{cm}^{-1}$  in KBr pellets (1% of the sample). C, H, and N elemental analyses were measured using a Euro EA 3000 elemental analyzer. UV–visible diffuse-reflectance measurements were carried out on a Cary 5000 UV–visible–near-IR spectrophotometer in the range of 200–2500 nm. Thermogravimetric analyses were carried out using a NETZSCH STA 449F3 thermobalance. A crucible containing 10 mg of sample was heated at 5  $^{\circ}\text{C min}^{-1}$  in the temperature range of 30–500  $^{\circ}\text{C}$ . Mössbauer spectra were obtained at room temperature using a constant-acceleration Mössbauer spectrometer with a  $^{57}\text{Co/Rh}$  source. The velocity calibration was done using a metallic Fe foil. Electron paramagnetic resonance (EPR) spectra were measured with a Bruker ESP-300 spectrometer operating at X band and equipped with a nitrogen and helium cryostat. Magnetic susceptibility measurements were measured in the range of 4–300 K with a Quantum Design SQUID MPMS-7T magnetometer.

**X-ray Structure Determination.** Prismatic dark-blue single crystals of  $([\text{FeTPPbipy}]^+)_n$  with dimensions given in Table 1 were

performed by full-matrix least squares based on  $F^2$ , using the SHELXL-97 program.<sup>36</sup> Anisotropic thermal parameters were used for all non-H atoms (Figure S1, Supporting Information). All H atoms connected to the aromatic rings (C–H 0.95 Å) were fixed geometrically and were refined using a riding model with common isotropic displacements. Brief crystal data are listed in Table 1. (See Tables S1–S4, Supporting Information, for bond distances and angles, atomic coordinates, and anisotropic displacement.)

## RESULTS AND DISCUSSION

**Synthesis of  $([\text{FeTPPbipy}]^+)_n$ .** FeTPP-Cl (7 mg, 0.01 mmol), bipy (9.4 mg, 0.06 mmol), and 40  $\mu\text{L}$  of NaOH (3M) were added to a mixture of DMF (3 mL) and ethanol (1 mL) in a small capped vial, sonicated to ensure homogeneity, and heated to 120  $^{\circ}\text{C}$  for 48 h, following by slow cooling to room temperature at 2  $^{\circ}\text{C h}^{-1}$ , yielding diffraction-quality dark-blue prismatic crystals. Anal. Calcd for  $\text{C}_{54}\text{H}_{36}\text{FeN}_6$ : C, 78.64; H, 4.39; N, 10.18%. Found: C, 78.45(8); H, 4.31(10); N, 9.86(6).  $\nu_{\text{max}}/\text{cm}^{-1}$ : 3051, 3022, and 2964 [C(sp<sup>3</sup>)H], 1600–1440 (CC), 1348 (CN), 1204 and 1070 (bipy), 1000 (FeTPP), 750 (CH) (Figure S2, Supporting Information).

**Crystal Structure.** The crystal structure of  $([\text{FeTPPbipy}]^+)_n$  was determined by means of single-crystal X-ray diffraction. The structure consists of 1D coordination polymers extending along the [010] direction, where metalated porphyrins are axially bonded to two bipy ligands (Figure 1).

The resulting octahedral coordination sphere exhibits bond angles and distances that are typical for these types of compounds (Table 2).<sup>37</sup> These coordination polymers crystallize as shown in Figure 2. The connections between chains take place through *edge-to-face*  $\pi$  stacking along the [10–1] direction (centroid-to-centroid distance of 3.662 Å and angle of 83.94 $^{\circ}$ ). Additionally, there is a *face-to-face*  $\pi$  stacking along the [101] direction (centroid-to-centroid distance 5.067 Å and angle 0.02 $^{\circ}$ ). Therefore, the cohesion between 1D coordination polymers is based on a robust network of  $\pi$  bonds.

In principle, the chemical formula could be interpreted in terms of the presence of Fe<sup>II</sup> and TPP<sup>2-</sup> ions. However, as explained below, the behavior of  $([\text{FeTPPbipy}]^+)_n$  is consistent with the presence of Fe<sup>III</sup>. Therefore, because no further deprotonation is observed for the organic ligands, reduction of TPP<sup>2-</sup> must be assumed to maintain neutrality.<sup>38,39</sup>

Distortion of the porphyrin was analyzed by the normal-coordinate structural decomposition method developed by Sheltnitt et al.,<sup>40,41</sup> indicating a low saddle-type distortion (*sad*,  $B_{2g}$ ). The contribution of this type of distortion (0.5967) to the total displacements is 67%, a usual feature on low-spin iron(III) porphyrins.<sup>42</sup>

It is worth mentioning that, as far as we are aware,  $([\text{FeTPPbipy}]^+)_n$  is the first Fe–TPP–dipyridyl coordination network exhibiting 1D polymers, and it has been formed by the assembly of neutral radical units. More details about the latter will be discussed below.

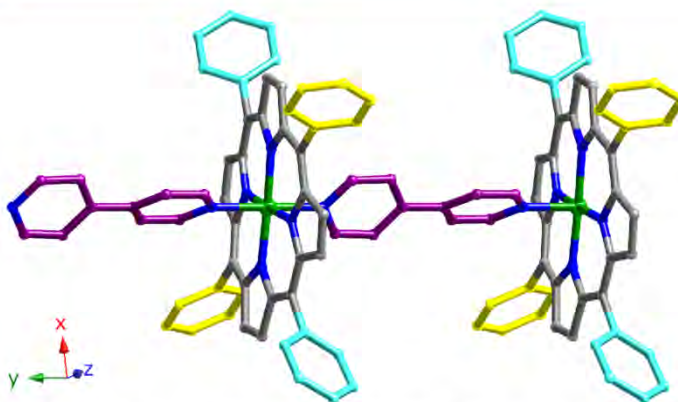
**Purity of the Measured Samples.** In order to determine the purity of the samples used for further characterization, the grinding effect on single crystals has been evaluated by means of X-ray diffraction. The results (Figure S3, Supporting Information) indicate that a significant rate of amorphization takes place. Taking this into consideration, magnetic susceptibility measurements and UV–visible spectroscopy were performed by using nonground single crystals introduced into a capillary in order to guarantee the purity of the sample. Unfortunately, the crystal features for  $([\text{FeTPPbipy}]^+)_n$  were absolutely inadequate for the

**Table 1.** Crystallographic Data for  $([\text{FeTPPbipy}]^+)_n$

|   |   |
|---|---|
| compound  | $([\text{FeTPPbipy}]^+)_n$  |
| formula   | $\text{C}_{54}\text{H}_{36}\text{FeN}_6$                          |
| fw, g mol <sup>-1</sup>                                     | 824.74  |
| cryst syst  | monoclinic  |
| space group   | $\text{C2}/c$ (No. 15)  |
| <i>a</i> , Å  | 21.6833(8)  |
| <i>b</i> , Å  | 11.0827(4)  |
| <i>c</i> , Å  | 17.6206(6)  |
| $\beta$ , deg   | 97.354(3)   |
| $V$ , Å <sup>3</sup>  | 4199.6(3)   |
| <i>Z</i>  | 4   |
| $\rho_{\text{obs}}/\rho_{\text{calc}}$ , g cm <sup>-3</sup> | 1.309(5), 1.304   |
| <i>F</i> (000)  | 1712  |
| $\mu$ , mm <sup>-1</sup>                                    | 0.405   |
| crystal size, mm  | 0.34 × 0.077 × 0.072  |
| abs corr.   | analytical  |
| radiation $\lambda$ , Å                                     | 0.71073   |
| temperature, K  | 100(2)  |
| reflex collected, unique                                    | 10334, 3907 ( $R_{\text{int}} = 0.04$ )                           |
| limiting indices  | $-26 \leq h \leq 26$ , $-7 \leq k \leq 13$ , $-21 \leq l \leq 19$ |
| refinement method   | full-matrix least squares on $F^2$                                |
| final <i>R</i> indices [ $I > 2\sigma(I)$ ] <sup>a</sup>    | $R_1 = 0.0351$ , $wR_2 = 0.0714$                                  |
| <i>R</i> indices (all data) <sup>a</sup>                    | $R_1 = 0.0513$ , $wR_2 = 0.0738$                                  |
| GOF on $F^2$  | 0.909   |
| parameters/restraints                                       | 279/0   |

$$^a R_1 = [(|F_o| - |F_c|)/|F_o|], wR_2 = [w(F_o - F_c)^2]/[w(F_o)^2]^{1/2}.$$

selected under a polarizing microscope and mounted on MicroMounts. Single-crystal X-ray diffraction data were collected at 100 K on an Xcalibur 2 automatic diffractometer with graphite-monochromated Mo *K* $\alpha$  radiation ( $\lambda = 0.71073$  Å). The Lorentz polarization and absorption corrections were made with the diffractometer software, taking into account the size and shape of the crystals.<sup>35</sup> The structure was solved in the monoclinic space group  $\text{C2}/c$  by direct methods with the SHELXS-97 program.<sup>36</sup> Refinement of the crystal structure was

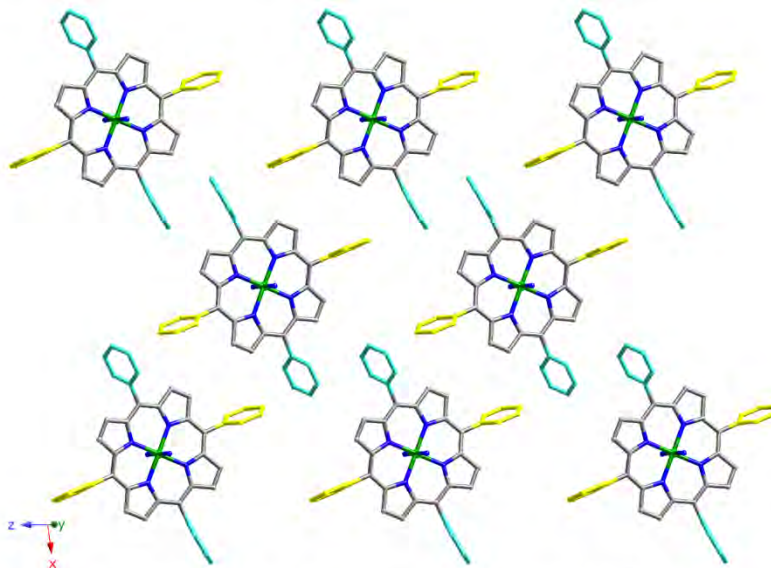


**Figure 1.** 1D coordination polymers extending along the [010] direction for  $([\text{FeTPPBipy}]^+)_n$ . Color code: green, Fe; blue, N; gray, yellow, turquoise, C(porphyrin); purple, C(bipy). H atoms are omitted for clarity.

**Table 2.** Selected Bond Angles (deg) and Distances (Å) for  $([\text{FeTPPBipy}]^+)_n$  (Distances in Bold)<sup>a</sup>

| Fe              | Octahedron [FeN <sub>6</sub> ] |                 |                 |                 |                 |                 |
|-----------------|--------------------------------|-----------------|-----------------|-----------------|-----------------|-----------------|
|                 | N1                             | N1 <sup>i</sup> | N2              | N2 <sup>i</sup> | N3              | N4              |
| N4              | 88.46(4)                       | 88.46(4)        | 91.16(4)        | 91.16(4)        | 180             | <b>1.998(2)</b> |
| N3              | 91.54(4)                       | 91.54(4)        | 88.84(4)        | 88.84(4)        | <b>1.985(2)</b> |                 |
| N2 <sup>i</sup> | 90.14(6)                       | 89.92(6)        | 177.69(8)       | <b>1.996(1)</b> |                 |                 |
| N2              | 89.92(6)                       | 90.14(6)        | <b>1.996(1)</b> |                 |                 |                 |
| N1 <sup>i</sup> | 176.93(8)                      | <b>1.983(1)</b> |                 |                 |                 |                 |
| N1              | <b>1.983(1)</b>                |                 |                 |                 |                 |                 |

<sup>a</sup>Symmetry code:  $i, -x, y, -z + 1/2$ .



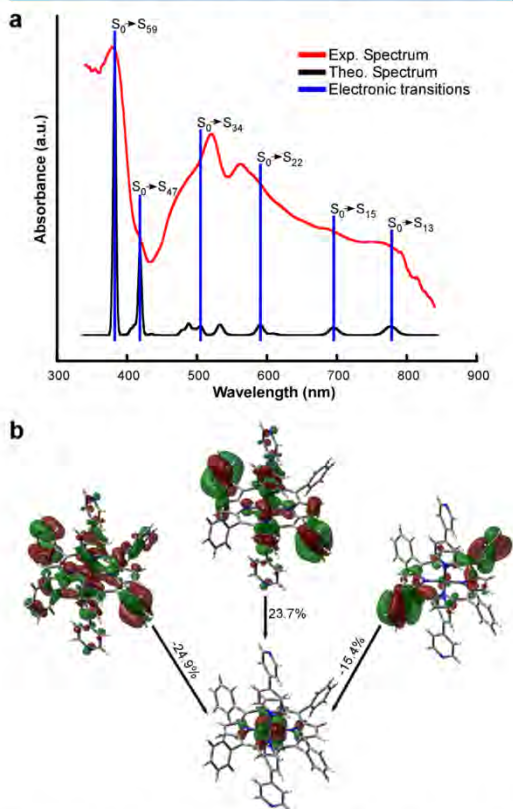
**Figure 2.** View of a (101) plane for  $([\text{FeTPPBipy}]^+)_n$ . Color codes are the same as those in Figure 1. The bipy ligands and H atoms are omitted for clarity. *Face-to-face*  $\pi$  stacking occurs between the turquoise phenyl groups, and *edge-to-face*  $\pi$  stacking occurs between the turquoise and yellow phenyl groups.

performance of EPR and Mössbauer spectroscopies on single crystals.

**UV–Visible (Diffuse-Reflectance) Spectroscopy.** UV–visible spectroscopy was performed on nonground single



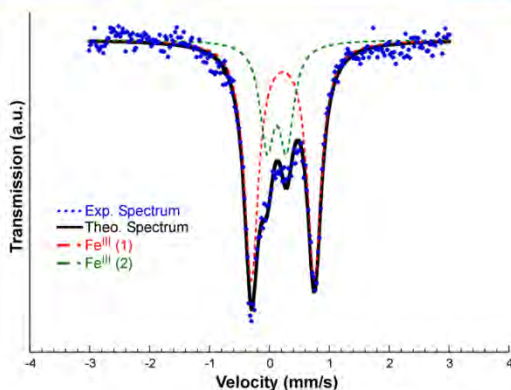
crystals, and as observed in Figure 3a, the spectrum exhibits a Soret band ( $\gamma$ ) at 377 nm and Q bands ( $\beta$  and  $\alpha$ ) at 517 and



**Figure 3.** (a) Experimental and theoretical UV–visible spectra for  $([\text{FeTPPBipy}]^*)_n$  and (b) molecular orbitals involved in the  $S_0$ – $S_{99}$  transition.

557 nm, respectively. The fact that the Soret band is blue-shifted and reduced in intensity compared to typical six-coordinate low-spin ferric porphyrin complexes<sup>25,43</sup> is justified by assuming the presence of a radical species.<sup>44,45</sup> The low-spin iron(III) porphyrin characteristic  $L_1$  and  $L_2$  bands<sup>46</sup> appear at 815 (sh) and 770 nm, respectively. A broad and weak band at 690 nm is in accordance with the presence of a porphyrinic radical.<sup>44</sup> These results were compared with the theoretical spectra (Figure 3a) obtained by TD-DFT calculations, performed by means of *Gaussian 03*<sup>47</sup> (B3LYP<sup>48,49</sup> functional and 6-31G valence). In addition to the good concordance between both spectra, the most remarkable fact is that the molecular orbitals involved in the Soret transition ( $S_0$ – $S_{99}$ ) represent an important charge transfer between the phenyl rings and the metal center (Figure 3b). This fact will be mentioned below during a discussion of the magnetic behavior.

**EPR.** X-band EPR spectroscopy was performed on ground single crystals of  $([\text{FeTPPBipy}]^*)_n$ . As observed, the spectrum shows two signals (Figure 4). The weakest of them (with  $g$  close to 6) is typical for magnetically isolated  $\text{Fe}^{\text{III}}$  systems in axial



**Figure 4.** X-band EPR spectrum (room temperature) for  $([\text{FeTPPBipy}]^*)_n$ .

symmetry. Therefore, it is supposed to have been formed by crystal grinding. Unfortunately, the fact that grinding produces amorphization (Figure S3, Supporting Information) results in the impossibility of identifying this second phase by X-ray diffraction.

On the other hand, the principal signal (with  $g$  close to 2) can be interpreted in terms of the following two possibilities: (a) high-spin  $\text{Fe}^{\text{III}}$  ions in very low concentration in relation to the bulk of the analyzed sample and (b) low-spin  $\text{Fe}^{\text{III}}$  ions with either significant magnetic interactions between metal centers having different orientations or interactions with free radicals. In the latter case, radicals should be either delocalized or localized in such a way that they could relax in a short period of time. The first hypothesis does have a sense just for the case of high-spin  $\text{Fe}^{\text{III}}$  ions diluted in a low-spin  $\text{Fe}^{\text{II}}$  framework. This means that compound  $([\text{FeTPPBipy}]^*)_n$  should contain  $\text{Fe}^{\text{II}}$  ions and that there are three contributions to the signal: the compound itself, the amorphous secondary phase, and a third unknown compound. This hypothesis has been discarded by X-band EPR spectroscopy at 100 K (Figure S4, Supporting Information) because it shows a broadening of the signal and a rapid decrease of the intensity (it mostly disappears below 50 K). This clearly indicates the presence of antiferromagnetic interactions, therefore pointing to the second explanation. Thus, the second explanation could just be feasible if the presence of free electrons is admitted because the structural characteristics of  $([\text{FeTPPBipy}]^*)_n$  are not compatible with significant magnetic interactions between metal centers (the magnetic paths through the bipy ligands are too long). As explained below, these magnetic interactions were analyzed through measurements of the magnetic susceptibility and by DFT calculations.

**Mössbauer Spectroscopy.** Mössbauer spectroscopy was performed on ground single crystals. The spectrum has been simulated with the *NORMOS* program<sup>50</sup> and indicates the presence of two doublets: both of them corresponding to  $\text{Fe}^{\text{III}}$  signals. The presence of two  $\text{Fe}^{\text{III}}$  centers has been explained already in the EPR section, and it has been associated with amorphization of the sample as a consequence of the grinding, discarding the presence of a previous impurity.

The most significant signal is assigned to the metal ions in  $([\text{FeTPPBipy}]^*)_n$ , while the second one is assumed to be due to the secondary phase coming from grinding. Quantitative analysis reveals that the sample contained 70.5% by weight corresponding to  $([\text{FeTPPBipy}]^*)_n$ . This is in accordance with the significant

rate of amorphization observed by X-ray diffraction (Figure S3, Supporting Information). Isomer shift ( $\delta$ ) and quadrupolar splitting ( $\Delta E$ ) values are 0.337(1) and 1.054(2) for the first signal and 0.235(2) and 0.326(7) for the second one, in the range usually observed for Fe<sup>III</sup> ions (Figure S).

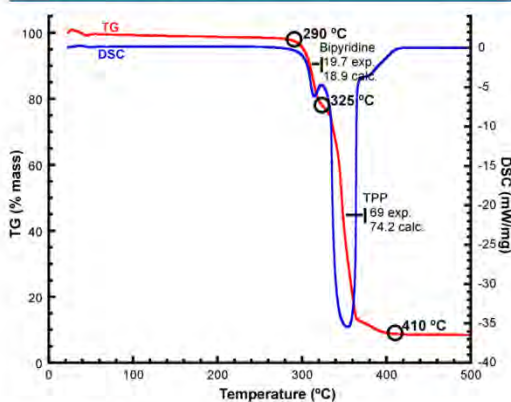


Figure 5. Mössbauer spectra for  $([\text{FeTPPBipy}]^*)_n$ .

**Thermogravimetry.** Thermogravimetry analysis was carried out on nonground single crystals. The thermogravimetric decomposition curve of the compound shows an overlapped two-stage mass loss, from approximately 290 to 410 °C. As shown in Figure 6, the first step occurs between 290 and 325 °C with a

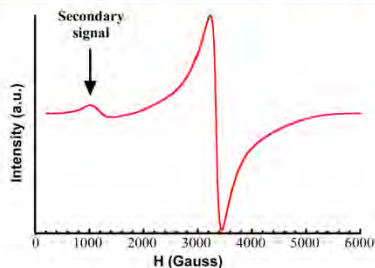


Figure 6. Thermal analysis for  $([\text{FeTPPBipy}]^*)_n$ .

19.7% weight loss and the second step from 325 to 410 °C with a 69% weight loss. These mass percentages are close to the theoretical percentages of bipyridine (18.9%) and TPP (74.2%) molecules. The calcination product was identified by powder X-ray diffraction analysis, and it consists of Fe<sub>2</sub>O<sub>3</sub> [space group R3c,  $a = 5.0248$  Å,  $c = 13.7163$  Å, and  $\gamma = 120^\circ$ ].<sup>51</sup>

**Magnetic Measurements.** We have also performed magnetic susceptibility ( $\chi_m$ ) measurements for  $([\text{FeTPPBipy}]^*)_n$  in the range 4–300 K (Figure 7). It is worth mentioning that nonground single crystals were used for this analysis, but the original crystals were introduced into a capillary. The  $\chi_m T$  value at room temperature is  $0.30 \text{ cm}^3 \text{ K mol}^{-1}$ , which is much lower than the  $4.37 \text{ cm}^3 \text{ K mol}^{-1}$  value expected for a high-spin Fe<sup>III</sup> compound. On the contrary, it is close to the  $0.37 \text{ cm}^3 \text{ K mol}^{-1}$  value expected for low-spin Fe<sup>III</sup> complexes. As explained below (DFT calculations), the one-electron reduction of metalloporphyrin is analyzed, with the acquired electrons having been determined to

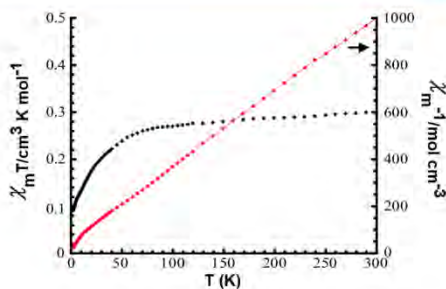
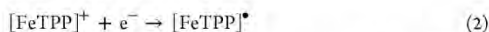
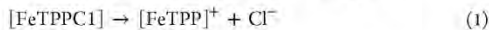


Figure 7. Thermal evolution of  $\chi_m T$  and  $\chi_m^{-1}$  for  $([\text{FeTPPBipy}]^*)_n$  and the corresponding theoretical Curie–Weiss law (red line).

be located on the phenyl groups. On the other hand, TD-DFT calculations carried out to analyze the UV–visible spectroscopy (Figure 3b) indicate that there is an important charge transfer between the phenyl rings and metal centers (Figure 3b). Thus, the slight discrepancy between the expected ( $0.30 \text{ cm}^3 \text{ K mol}^{-1}$ ) and observed ( $0.37 \text{ cm}^3 \text{ K mol}^{-1}$ )  $\chi_m T$  values for low-spin Fe<sup>III</sup> can be explained if considering this charge transfer.

The thermal evolution of the reciprocal susceptibility follows the Curie–Weiss law with  $C_m = 0.32 \text{ cm}^3 \text{ K mol}^{-1}$  and  $\theta = -18.7 \text{ K}$  (Figure 7). The product  $\chi_m T$  continuously decreases upon cooling, reaching a value of  $0.09 \text{ cm}^3 \text{ K mol}^{-1}$  at 5.0 K, indicating the presence of antiferromagnetic interactions, as expected from EPR characterization. As mentioned, these interactions cannot be attributed to magnetic exchange between metal centers. Therefore, coupling between metal ions and free electrons should be admitted.

**DFT Calculations.** As previously mentioned, the structural characterization of this compound could make one think that the metal ion is Fe<sup>II</sup>, in accordance with the presence of TPP<sup>2-</sup> ligands and neutral bipy molecules. However, the commercial reactant, [FeTPPCL], contains Fe<sup>III</sup>, and its reduction to Fe<sup>II</sup> does not seem to be feasible. On the other hand, the bond distances and angles are typical for iron(III) porphyrins, and the rest of the characterization techniques clearly indicate that the metal ion is Fe<sup>III</sup>. Therefore, the best of our hypothesis is that the compound has been formed by the assembly of [FeTPP]<sup>•</sup> radical structural units, which extend, producing 1D polymers by means of the axial coordination of the metal center to bipy ligands. Thus, the [FeTPP]<sup>•</sup> structural units should be thought of as being the result of one-electron reduction of the metalloporphyrin (reactions 1 and 2).



Admitting that reduction must have taken place for the metalloporphyrin, we tried to identify the reductant agent. Even if there are some calculated redox potentials in the literature,<sup>52</sup> they are not useful in our case because of the nonstandard conditions for solvothermal synthesis. Even so, there are several possible reductant agents like residues of bipy and DMF.<sup>53</sup>

Thus, next question about  $([\text{FeTPPBipy}]^*)_n$  consists of determining the localization of the electron providing the metalloporphyrins with its radical nature. In the case of  $([\text{FeTPPBipy}]^*)_n$ , the presence of low-spin Fe<sup>III</sup> and an extra unpaired electron should result in two unpaired electrons per metalloporphyrin. Therefore, we could think of two explanations. As previously proposed,<sup>54</sup> the extra unpaired electron could be delocalized on the aromatic

**Scheme 1. Possibilities for the Number of Unpaired Electrons Depending on the Occurrence of Antiferromagnetic Coupling through  $\pi$  Stacking**

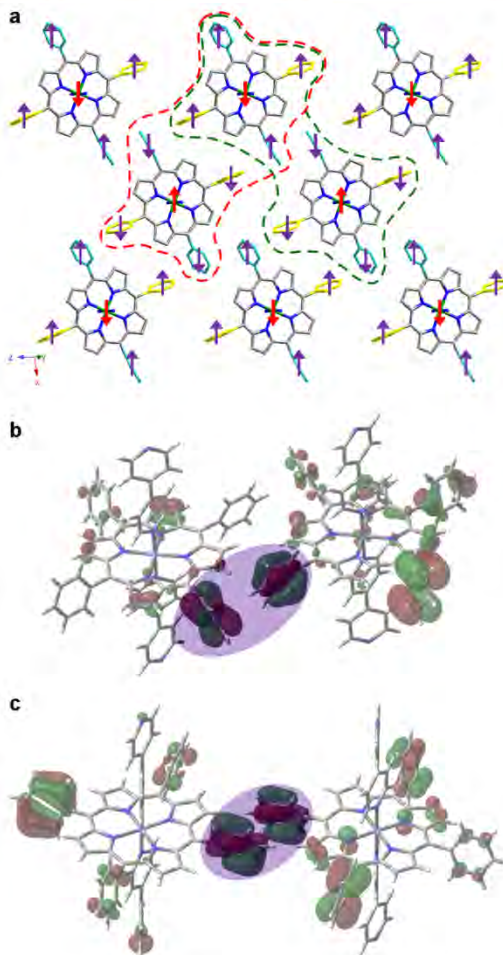
|  | Possible interactions between 1D polymers per two Fe <sup>III</sup> centers |     |              |    | $\pi$ -stacking producing antiferromagnetic interactions |
|--|---|-----|--------------|----|--|
|  | 1D polymer 1  |     | 1D polymer 2 |    |  |
|  | Fe  | TPP | TPP          | Fe |  |
| <b>4 unpaired electrons per two Fe<sup>III</sup> centers</b> | ↑   | ↑   | ↑            | ↑  | No   |
| <b>2 unpaired electrons per two Fe<sup>III</sup> centers</b> | ↓   | ↑↓  |              | ↑  | Yes  |

porphyrinic system. If analysis of the compound is done from the point of view of isolated structural units (1D polymers), this could be an effective explanation. However, magnetic measurements are not consistent with the latter. Besides, there is an intricate  $\pi$ -stacking system in  $([\text{FeTPPBipy}]^*)_n$ , according to which analysis of the framework from such a point of view does not seem to be adequate. Thus, a second explanation is that the electrons acquired by reduction are paired in the 3D framework (Scheme 1). This idea is strongly supported by  $\pi$  stacking because it provides the opportunity of electron coupling.

In order to provide theoretical support to the above-mentioned aspects, both hypotheses were analyzed by means of quantum-mechanical DFT calculations (*Gaussian 03* program).<sup>47</sup> Calculations were performed using Becke's three-parameter hybrid functional with the correlation functional of Lee, Yang, and Parr (B3LYP)<sup>48,49</sup> with a split-valence basis set of 6-31G. This functional does not consider the dispersive interactions. However, it has been selected because our objective was not obtaining an accurate value for the energy but representative values for a comparison between both hypotheses. In fact, the goal was to investigate the effect of  $\pi$  stacking on the stability of the framework. To this purpose, two dimeric fragments ( $\text{FeTPPBipy}_2$ )<sub>2</sub> were selected. In dimer 1, the interdimer connection is due to the *edge-to-face*  $\pi$  bond along the [10–1] direction, while in dimer 2, the connection takes place by the *face-to-face*  $\pi$  bond along the [101] direction (Figure 8a). For each dimer, two calculations (Table 3) were carried out: in calculation 1, the dimer has four unpaired electrons (two per monomer), and in calculation 2, the dimer has two unpaired electrons (one per monomer). Therefore, calculation 1 accounts for the first hypothesis (that is, analysis from the point of view of isolated 1D polymers), while calculation 2 explores the possibility of electron coupling through interpolymer  $\pi$  stacking. Obviously, extension of the framework through the three directions of space should have been considered for more accurate calculations. However, the large amount of atoms involved makes this very expensive.

Table 3 summarizes the as-calculated values. As observed, the values show that for both dimers the situation with one unpaired electron per monomer (two per dimer) is more stable than the situation with two unpaired electrons per monomer (four per dimer), supporting the idea that  $\pi$  stacking is responsible for stabilization of the framework.

At this point of the discussion, claiming that  $\pi$  stacking is responsible for stabilization of the framework seems to be obvious. Nevertheless, the remarkable point is that calculations strongly support the idea that the extra electrons have not been delocalized on the TPP pyrrolic system but they are paired in molecular orbitals formed by  $\pi$  stacking. In fact, as observed in Figure 8b,c, the calculations provided molecular orbitals for these interactions.



**Figure 8.** (a) Selected dimeric fragments for the DFT calculations according to *edge-to-face* (red line) and *face-to-face* (green line)  $\pi$  interactions. A scheme for the spin distribution proposal is also shown: red arrows are the unpaired electrons corresponding to low-spin Fe<sup>III</sup> ( $d^5$ ), and each group of four purple arrows corresponds to a single electron localized on the phenyl groups belonging to the same metalloporphyrin. (b) Calculated molecular orbitals involving the *edge-to-face* and (c) *face-to-face*  $\pi$  stackings.

Table 3. Calculated Energy for (FeTPPBipy)<sub>2</sub> Dimers

| dimer | $\pi$ interactions | coupling through $\pi$ interactions | no. of unpaired electrons per dimer | calculated energy (hartree) |
|-------|--------------------|-------------------------------------|-------------------------------------|-----------------------------|
| 1     | edge-to-face       | yes                                 | 2                                   | -8331.1805358               |
| 1     | edge-to-face       | no                                  | 4                                   | -8331.1309928               |
| 2     | face-to-face       | yes                                 | 2                                   | -8331.1814716               |
| 2     | face-to-face       | no                                  | 4                                   | -8331.1533709               |

**Self-Assembly of Neutral Radicals.** As  $\pi$  stacking is extended on the (101) planes, extrapolation of the DFT calculations to the 3D network can be done. As observed in Figure 8b,c, the contribution of the phenyl molecular orbitals to  $\pi$  stacking is consistent with this extrapolation. First of all, the electron acquired by the porphyrin could be thought of as delocalized on the four phenyl groups. On the other hand, if considering that magnetic measurements are consistent with the presence of a value close to one unpaired electron per monomer, the spin distribution proposed in Figure 8a could be a reasonable explanation for the behavior of this compound. This spin distribution is based on the occurrence of antiferromagnetic coupling not only between electrons belonging to the metal center and phenyl groups (as previously mentioned in the Magnetic Measurements section) but also between phenyl electrons localized on adjacent 1D polymers, as seen in Figure 8b,c.

In summary, identification of the localization of the acquired electrons is the key point that supports the idea of neutral radicals having been able to self-assemble, producing such a 3D framework.

## CONCLUSIONS

The compound  $[(\text{FeTPPBipy})^*]_n$  has been formed by the assembly of metalloporphyrinic neutral radicals that have been formed by one-electron reduction of the original  $[\text{FeTPP}]^+$  cations, as suggested by the presence of low-spin  $\text{Fe}^{\text{II}}$  ions. The as-acquired electrons are proposed to be paired in the molecular orbitals formed by  $\pi$ - $\pi$  interactions between the phenyl groups of different 1D polymers. The resulting packing is the first Fe-TPP-bipy coordination network exhibiting 1D polymers.

## ASSOCIATED CONTENT

### Supporting Information

ORTEP detail of the structure, IR and EPR spectra, X-ray measurements, crystallographic data, and a CIF file for CCDC 888109. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. All authors contributed equally.

### Notes

The authors declare no competing financial interest.

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## Thermal stability and crystallochemical analysis for Co<sup>II</sup>-based coordination polymers with TPP and TPPS porphyrins†

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Two new CoP–bipy compounds have been synthesised and characterised, where P is TPP for compound 1 (TPP = *meso*-tetraphenylporphyrin) and TPPS for compound 2 (TPPS = *meso*-tetraphenylporphyrine-tetrasulfonic acid tetrasodium salt), and bipy is 4,4′-bipyridine. Compound 1 consists of 1D polymers packed in a network where isolated porphyrin units are immobilized by an extended  $\pi$ -bond system. On the other hand, as we are aware, compound 2 is the first Co–TPPS compound in literature. It also consists of 1D polymers that are formed by the alternation of two distinct metal centres. These unprecedented polymers are packed forming cavities where crystallization molecules of water are located. The robustness of the hydrogen bond system and a topology based on interpenetrated nets are responsible for the high thermal stability of compound 2. Additionally, a crystallochemical study confirmed the existence of a correlation between the degree of ruffled distortion of the porphyrin macrocycle and some selected dihedral angles and distances for Co<sup>II</sup> porphyrins in literature.

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### Introduction

Metal–organic frameworks (MOFs) have emerged as an interesting class of porous solids that can be constructed from a variety of molecular complexes<sup>1–4</sup> and explored for a range of applications in gas storage,<sup>5,6</sup> compound separation,<sup>7,8</sup> chemical sensing,<sup>9–12</sup> nonlinear optics,<sup>13</sup> biomedical imaging,<sup>14–16</sup> drug delivery,<sup>17–19</sup> and heterogeneous catalysis.<sup>20–23</sup> On the other hand, it is worth mentioning that facile chemical modification, high thermal and chemical stability allow metalloporphyrins to be remarkable catalysts for numerous reactions.<sup>24–26</sup> In particular, porous metalloporphyrinic frameworks have great potential to act as heterogeneous catalysts with shape- and size-selectivity. In this sense, Suslick *et al.* must be cited as they first demonstrated the catalytic property of a porphyrinic MOF.<sup>27</sup>

In this context, metalloporphyrins are remarkable precursors in supramolecular chemistry, giving rise to a variety of materials because of their unique chemical, physical and

biological properties.<sup>28–30</sup> In order to enhance the connectivity between metal centres, a secondary ligand can be used in porphyrinic systems. In fact, the Choe group demonstrated that a range of metalloporphyrinic frameworks can be generated by using porphyrin metallo-ligands and bipyridyl molecules.<sup>31</sup> However, it must be pointed out that research on the applications of porphyrinic MOFs is just in the initial stage.<sup>32</sup>

Taking into account the above mentioned aspects, this work was focused on the preparation of metalloporphyrin-based coordination networks. Our strategy also includes the use of different bipyridyl ligands, as they have been observed to produce a variety of porphyrin-based MOFs.<sup>33</sup> In addition, we have a large experience with these connectors.<sup>34–39</sup> In this context, we have been exploring CoP–bipy combinations where P is either TPP (TPP = *meso*-tetraphenylporphyrin) or TPPS (TPPS = *meso*-tetraphenylporphyrine-tetrasulfonic acid tetrasodium salt), and bipy is 4,4′-bipyridine. It is worth mentioning that just four crystalline compounds have been reported for TPPS-based metalloporphyrins,<sup>40–42</sup> and none of them has cobalt. On the other hand, even if the number of TPP-based metalloporphyrins is higher, the number of Co-based compounds exhibiting extended networks is also significantly low.<sup>43,44</sup>

Thus, the work herein presented consists of the synthesis and characterisation of two new CoP–bipy compounds where the metal ion is Co<sup>II</sup> and P is TPP for compound 1, and TPPS for compound 2. Both of them have been structurally

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characterised by single crystal X ray diffraction (XRD) and IR and EPR spectroscopies. Thermal stability has been explored by means of thermogravimetry (TGA), and X-ray thermomodification (TDX).

Distortion of macrocycles is biologically relevant<sup>45</sup> and influences physical<sup>46,47</sup> and chemical<sup>48,49</sup> properties of porphyrin complexes. In this sense, we have also analysed the out-of-plane displacement of porphyrin backbones for both compounds. In order to contextualise this analysis the study was extended to all the Co<sup>II</sup> porphyrins found in the CSD. A similar study has been previously reported for Co<sup>III</sup> porphyrins.<sup>50</sup>

## Experimental section

### General

All solvents and chemicals were used as received from reliable commercial sources. The reagents *meso*-tetraphenyl-porphine cobalt(II) (CoTPP), *meso*-tetraphenyl porphine 4,4',4'',4'''-tetrasulfonic acid tetrasodium salt (TPPS), cobalt(II) nitrate hexahydrate 99% and 4,4'-bipyridine 98% (bipy) and the solvent *N,N*-dimethylformamide (DMF) 99.8% were purchased from Sigma-Aldrich Co.; ethanol absolute was purchased from Panreac.

### Synthesis of compounds 1 and 2

[CoTPP(bipy)] ([CoTPP]<sub>0.22</sub>(TPP)<sub>0.78</sub> (1). *meso*-Tetraphenylporphine cobalt(II) (6.7 mg, 0.01 mmol), 4,4'-bipyridine (9.4 mg, 0.06 mmol) and 40  $\mu$ L NaOH (3 M) were added to a mixture of DMF (3 mL) and ethanol (1 mL) in a small capped vial, sonicated to ensure homogeneity and heated to 120 °C for 48 h, following by slow cooling to room temperature at 2 °C h<sup>-1</sup>, yielding diffraction quality prismatic dark blue crystals. (Found: C, 79.5(3); H, 4.60(4); N, 10.00(2). Calc. for C<sub>28</sub>H<sub>65.56</sub>Co<sub>1.22</sub>N<sub>10</sub>: C, 80.89; H, 4.54; N, 9.62.)  $\nu_{\text{max}}$ /cm<sup>-1</sup> 3052 and 3028 (C(sp<sup>3</sup>)H), 1596–1441 (CC), 1349 (CN), 1210 and 1069 (bipy), 1000 (CoTPP) and 795–700 (CH) (Fig. S1, ESI†).

[CoTPPS<sub>0.5</sub>(bipy)](H<sub>2</sub>O)<sub>3</sub>·6H<sub>2</sub>O (2). *meso*-Tetraphenylporphine-4,4',4'',4'''-tetrasulfonic acid tetrasodium salt (10.2 mg, 0.01 mmol) and Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (5.8 mg, 0.02 mmol) were dissolved in distilled water (10 mL) and the solution was stirred for 30 min. Then, 4,4'-bipyridine (9.4 mg, 0.06 mmol) was dissolved in hot (70 °C) distilled water (5 mL) and added to the mixture in a 100 mL CEM EasyPrep microwave vessel. The mixture was heated by microwave under autogenous pressure at 160 °C for 2 h, and then cooled naturally to room temperature, yielding diffraction quality prismatic dark blue crystals. (Found: C, 45.8(3); H, 4.47(3); N, 6.89(2); S, 7.80(3). Calc. for C<sub>32</sub>H<sub>36</sub>CoN<sub>4</sub>O<sub>14</sub>S<sub>2</sub>: C, 46.66; H, 4.40; N, 6.80; S, 7.79.)  $\nu_{\text{max}}$ /cm<sup>-1</sup> 3397 (OH), 1624–1410 (CC), 1394 and 1174 (SO), 1349 (CN), 1208 and 1076 (bipy), 1000 (CoTPPS) and 863–744 (CH) (Fig. S2, ESI†).

### Single-crystal X-ray diffraction

Prismatic dark blue single crystals of compounds 1 and 2 with dimensions given in Table 1 were selected under polarizing microscope and mounted on MicroMounts. Single-crystal

X-ray diffraction data were collected at 100 K on a SuperNova single source diffractometer with Cu K $\alpha$  radiation ( $\lambda$  = 1.5418 Å). The Lorentz-polarization and absorption corrections were made with the diffractometer software, taking into account the size and shape of the crystals.<sup>51</sup>

The structure of compound 1 was solved in the monoclinic *C2/c* space group with SIR-92<sup>52</sup> program, which allowed us to obtain the position of Co atoms, as well as nitrogen and some of the carbon atoms of the TPP and bipyridine molecules. The refinement of the crystal structure was performed by full matrix least-squares based on  $F^2$ , using the SHELXL97 program<sup>53</sup> obtaining the remaining carbon atoms. Anisotropic thermal parameters were used for all non-hydrogen atoms (Fig. S3, ESI†). All the hydrogen atoms, connected to the aromatic rings (C–H 0.95 Å) were fixed geometrically and were refined using a riding model with common isotropic displacements.

Compound 2 was solved in the tetragonal *I4<sub>1</sub>/a* space group with Superflip<sup>54</sup> program, which allowed us to obtain the position of Co atoms, as well as nitrogen and some of the carbon atoms of the TPPS and bipyridine molecules. The refinement of the crystal structure was performed by full matrix least-squares based on  $F^2$ , using the SHELXL97 program<sup>53</sup> obtaining the remaining carbon atoms and the oxygen and sulphur atoms of the porphyrin and water molecules. Anisotropic thermal parameters were used for all non-hydrogen atoms (Fig. S4, ESI†). All the hydrogen atoms, connected to the aromatic rings (C–H 0.95 Å) were fixed geometrically and were refined using a riding model with common isotropic displacements. The position of the hydrogen atoms bonded to the coordination water molecule were fixed using DFIX and DANG instructions in the refinement to adjust the O–H distance to 0.82 Å and the H–O–H angle to 112°, respectively. All of the crystallization molecules of water for compound 2 were disordered in two groups of three water molecules. The hydrogen atoms of these water molecules were not considered due to the lack of density in the residual density map. Crystal data for both structures are listed in Table 1. Atomic coordinates, anisotropic thermal parameters and hydrogen atom coordinates for both compounds are given in Tables S1–S6, ESI†.

### Physicochemical characterisation techniques

The IR spectra were collected on a JASCO FT/IR-6100 spectrometer at room temperature at the range of 4000–400 cm<sup>-1</sup>, in KBr pellets (1% of the sample). C, H, N and S elemental analyses were measured using a Euro EA 3000 elemental analyser. Electron paramagnetic resonance (EPR) spectra were measured with a Bruker ESP-300 spectrometer operating at X band and equipped with a nitrogen and helium cryostat.

The thermal analyses were carried out in air atmosphere using a NETZSCH STA 449F3 instrument for compound 1 and SDT 2960 Simultaneous DSC-TGA TA Instruments for 2. A crucible containing approximately 10 mg of sample was heated at 5 °C min<sup>-1</sup> in the temperature range 30–600 °C. The thermal behaviour was also studied using X-ray thermomodification. A Bruker D8 Advance Vantec diffractometer (Cu K $\alpha$  radiation) equipped with a variable-temperature stage (Anton Paar HTK2000) with a Pt sample holder was used in the

**Table 1** Details of the crystal data, structural resolution and refinement procedure for **1** and **2**

|  | <b>1</b>  | <b>2</b>  |
|--|---|---|
| Formula  | C <sub>98</sub> H <sub>65.56</sub> Co <sub>1.22</sub> N <sub>20</sub> | C <sub>72</sub> H <sub>36</sub> CoN <sub>4</sub> O <sub>12</sub> S <sub>2</sub> |
| FW, g mol <sup>-1</sup>  | 1455.06   | 811.62  |
| <i>a</i> , Å   | 25.1252(4)  | 17.9776(2)  |
| <i>b</i> , Å   | 11.7811(2)  |   |
| <i>c</i> , Å   | 23.9790(4)  | 22.3567(3)  |
| $\beta$ , °  | 93.5960(10)   |   |
| <i>V</i> , Å <sup>3</sup>                                      | 7083.9(2)   | 7225.55(15)   |
| Space group  | <i>C2/c</i>   | <i>I4<sub>1</sub>/a</i>   |
| <i>Z</i>   | 4   | 8   |
| $\rho_{\text{obs}}$ , $\rho_{\text{cal}}$ , g cm <sup>-3</sup> | 1.371(6), 1.364   | 1.488(4), 1.492   |
| <i>I</i> (000)   | 3026  | 3320  |
| $\mu$ , mm <sup>-1</sup>                                       | 2.761   | 5.445   |
| Crystal size, mm   | 0.26 × 0.19 × 0.06  | 0.12 × 0.12 × 0.021   |
| Absorption correction  | Multi-scan  | Analytical  |
| Radiation, $\lambda$ , Å                                       | 1.54184   | 1.54184   |
| Temperature, K   | 100(2)  | 100(2)  |
| Reflections collected, unique                                  | 25 120, 7352 ( $R_{\text{int}} = 0.0405$ )                            | 23 662, 3774 ( $R_{\text{int}} = 0.096$ )                                       |
| Limiting indices   | -29 ≤ <i>h</i> ≤ 31<br>-14 ≤ <i>k</i> ≤ 14<br>-30 ≤ <i>l</i> ≤ 23     | -22 ≤ <i>h</i> ≤ 22<br>-14 ≤ <i>k</i> ≤ 22<br>-28 ≤ <i>l</i> ≤ 25               |
| Refinement method  | Full-matrix least-squares on <i>F</i> <sup>2</sup>                    | Full-matrix least-squares on <i>F</i> <sup>2</sup>                              |
| <i>R</i> <sub>1</sub>  | <i>R</i> <sub>1</sub> = 0.0416  | <i>R</i> <sub>1</sub> = 0.0669  |
| <i>wR</i> <sub>2</sub> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]   | <i>wR</i> <sub>2</sub> = 0.1095                                       | <i>wR</i> <sub>2</sub> = 0.1845   |
| <i>R</i> <sub>1</sub>  | <i>R</i> <sub>1</sub> = 0.0438  | <i>R</i> <sub>1</sub> = 0.0856  |
| <i>wR</i> <sub>2</sub> (all data)                              | <i>wR</i> <sub>2</sub> = 0.1115                                       | <i>wR</i> <sub>2</sub> = 0.2040   |
| Goodness of fit on <i>F</i> <sup>2</sup>                       | 1.056   | 1.051   |
| Parameters/restraints  | 504/0   | 274/3   |

experiments. The powder patterns were recorded in  $2\theta$  steps of  $0.0333^\circ$  in the  $5\text{--}38^\circ$  range, counting for 0.8 seconds per step and increasing the temperature at  $10^\circ\text{C min}^{-1}$  from room temperature to  $550^\circ\text{C}$ .

## Results and discussion

### Crystal structures

The crystal structure for compound **1** consists of 1D polymers extending along the [010] direction where CoTPP units are axially bonded to two bipy ligands resulting in a porous coordination network (Fig. 1a).

Additionally, isolated TPP units are located in the voids ( $3.4 \times 3.4 \text{ \AA}$ ) generated by the packing of these chains, due to an intricate system of  $\pi$  bonds (Fig. 1b). 78% of these isolated porphyrin units are metal-free, while the remaining 22% are metallated, in accordance with the chemical formula obtained by single crystal X-ray diffraction and elemental analysis [CoTPP(bipy)]<sub>0.22</sub>·([CoTPP])<sub>0.78</sub>(TPP)<sub>0.78</sub>. Therefore, most of the CoTPP units have lost the metal ion during the synthesis. Each isolated TPP unit is surrounded by four 1D polymers producing a dense network. As observed, there are multiple edge-to-face  $\pi$ -interactions stabilising the crystal structure. These are robust interactions (distances from 2.45 Å to 2.97 Å, and angles from  $73.96^\circ$  to  $89.16^\circ$ ), that are accompanied by weaker face-to-face ones (centroid-to-centroid distance 4.04 Å, and angle is  $10.77^\circ$ ) (Table S7, ESI†).

The bond distances and angles for Co(1) and Co(2) coordination spheres in compound **1** lie among typical values

(Table S8, ESI†). It must be pointed out that Co(1) atom lies on a two-fold axis, and Co(2) on an inversion centre. As a result, both polyhedra are close to ideal.

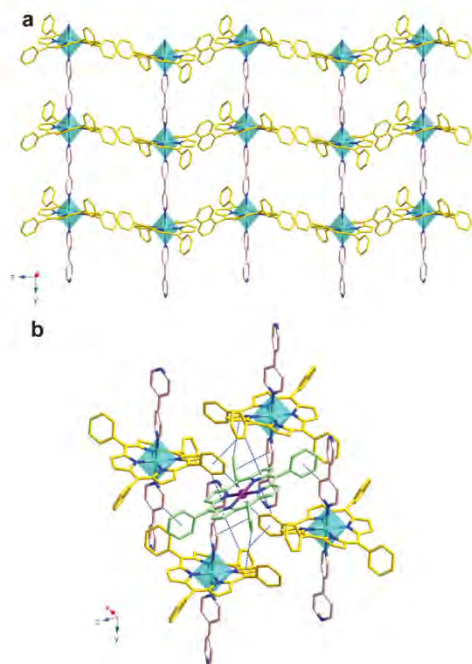
Topological features for compound **1** have been analysed by means of the TOPOS software.<sup>55</sup> The simplification shows the connectivity due to the  $\pi$ -bond system (Fig. S5, ESI†). Due to the nature of these intermolecular interactions no classification of the topology is provided.

Considering the isolated molecules of porphyrin in compound **1**, it was tested in order to explore its capability as a catalyst for the oxidation of water. Unfortunately, these tests demonstrated no catalytic activity (Fig. S6, ESI†).

Compound **2** has the chemical formula [CoTPPS<sub>0.5</sub>(bipy)(H<sub>2</sub>O)<sub>2</sub>]<sub>2</sub>·6H<sub>2</sub>O, and exhibits some similarities with compound **1**. In fact, compound **2** also consists of 1D polymers where CoTPPS units are axially bonded to bipy ligands. However, the extension of the 1D polymers for compound **2** consists of the link between alternating metal centres along the [001] direction. These links take place through the bipy ligands according to the bipy-CoTPPS-bipy-Co(H<sub>2</sub>O)<sub>4</sub>-fashion. From a crystallographic point of view, this is an unprecedented bimetallic chain for this type of systems (Fig. 2).

Compound **2** exhibits a robust system of hydrogen bonds that reinforce the stability of the framework (Table S9, ESI†). This way, each chain is surrounded by another four, and multiple hydrogen bonds are formed between the coordination molecules of water and the terminal SO<sub>3</sub> groups of the TPPS molecules.

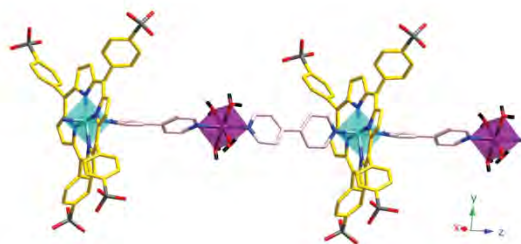




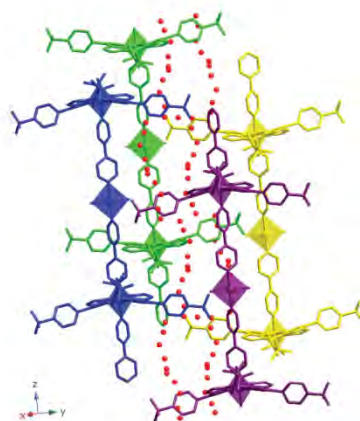
**Fig. 1** View of the structure for compound **1** where the packing of the 1D polymers is observed (a). Detail of the structure showing a single crystallization molecule of TPP connected to four 1D polymers through the  $\pi$ -bonding system (dashed lines) (b). Color codes: Co(1) (TPP chain) in turquoise, Co(2) (isolated TPP) in purple, N in blue, C (TPP chain) in yellow, C (isolated TPP) in green, C (bipy) in pink. H atoms have been omitted for clarity.

As observed in Fig. 3, the relative position of the chains give rise to cavities where crystallisation molecules of water are located. These molecules form a disordered chain along the [001] direction, reinforcing the robustness of the hydrogen-bond system.

As mentioned below, compound **2** exhibits a remarkable thermal stability that is related to its crystal structure. Therefore, topological features for compound **2** were analysed



**Fig. 2** Detail of the structure for compound **2** showing the extension of the 1D polymers. Color codes: Co(1) (TPPS) in turquoise, Co(2) in purple, N in blue, C (TPPS) in yellow, C (bipy) in pink, O in red, S in grey. H atoms have been omitted for clarity.



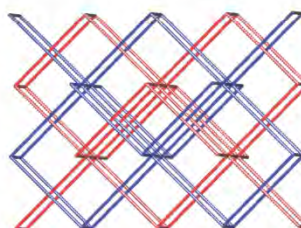
**Fig. 3** Detail of the structure showing relative position of the chains for compound **2**. Crystallisation molecules of water are shown in red. H atoms have been omitted for clarity.

by means of the TOPOS software,<sup>55</sup> revealing a *pcu*  $\alpha$ -Po primitive cubic  $6/4/c1$  *sqc1* net.<sup>56</sup> As shown in Fig. 4 this consists on a two-fold interpenetrated 6-c nets framework (point symbol =  $4^{12}.6^3$  and vertex symbol =  $4.4.4.4.4.4.4.4.4.4.4.4.*.*$ ).

#### Distortion of coordination spheres for metal centers

Distortion of coordination polyhedra as been evaluated according to Avnir<sup>57,58</sup> method, based on the continuous symmetry measures (CSM), by means of SHAPE program,<sup>59</sup> and the results can be seen on Table 2.

The projection of the as-calculated values on the distortion diagram<sup>60</sup> can be seen in Fig. 5. As observed, for compound **1** there is a weak Jahn-Teller distortion for Co(1), in fact the axial Co(1)–N(3) distance is longer than equatorial ones, and the *cis* and *trans* N–Co(1)–N angles go from 89.79(6) to 90.21(6)°, and from 179.68(8) to 180.00(4)°, respectively. For the tetracoordinated cobalt centre, the Co(2)–N distances go from 2.032(1) to 2.055(1) Å and the *cis* and *trans* angles are close to 90 and 180°, respectively. Thus, the distortion values indicate that the coordination geometry is close to an ideal square planar sphere for Co(2). All bond distances and angles are reported in Table S10, ESI†



**Fig. 4** Topology of the two-fold interpenetrated net for compound **2**.

**Table 2** Distortion values calculated for the hexacoordinated and tetra-coordinated spheres (calculated by means of SHAPE software)

| Hexacoordinate   |       | S ( $O_h$ )    | S ( $D_{3h}$ ) |
|------------------|-------|----------------|----------------|
| Compound 1       | Co(1) | 0.68           | 17.25          |
| Compound 2       | Co(1) | 0.07           | 15.76          |
|                  | Co(2) | 0.02           | 16.33          |
| Tetra-coordinate |       | S ( $D_{4h}$ ) | S ( $T_d$ )    |
| Compound 1       | Co(2) | 0.004          | 33.34          |

S = symmetry.

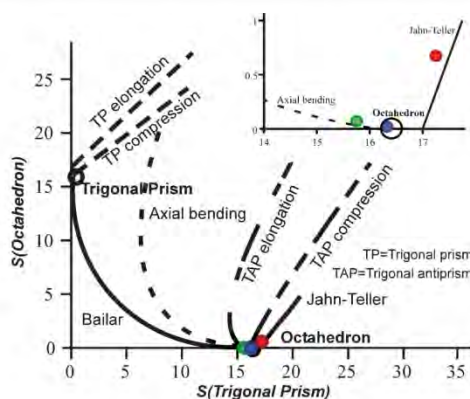
Distortion of coordination polyhedra was also evaluated for compound **2** (Table 2), and the results indicate that, while Co(2) octahedra is nearly ideal, the Co(1) sphere exhibits weak axial bending distortion. Both metal atoms lie on a four-fold inversion, where all Co(1)-N are equal (1.963(3) Å). Obviously, the same occurs for Co(2)-O equatorial distances (2.092(3) Å). On the other hand, *cis* and *trans* angles for Co(1) go from 88.20(7) to 91.80(7)° and for 176.4(1) to 180.0°, respectively. For Co(2) octahedra these angles vary from 89.24(6) to 90.76(6)° and from 178.05(1) to 180.0° resulting in a perfect octahedra (Fig. 2). All bond distances and angles are reported in Table S11, ESI†

### Distortion of porphyrins

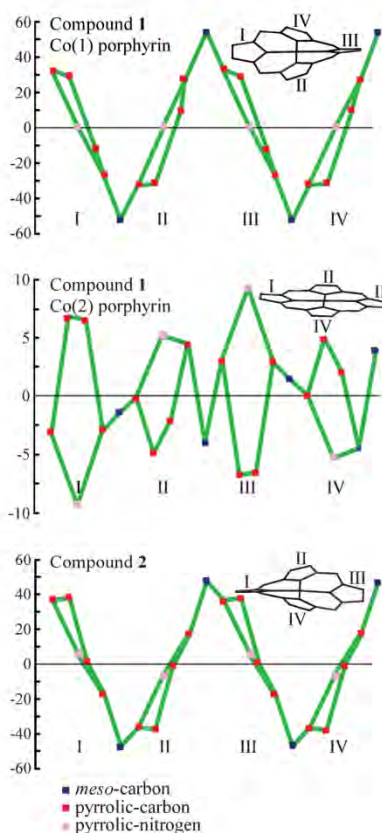
Distortion of macrocycles has been also analysed for compounds **1** and **2**. There are six types of distortion defined for non-planar porphyrins: saddle (*sad*), ruffle (*ruf*), dome (*dom*), wavy(x) (*wav(x)*), wavy(y) (*wav(y)*) and propeller (*pro*).

The out-of-plane distortion of the porphyrin macrocycles was analysed by the normal-coordinate structural decomposition method developed by Shelnut *et al.* (NSD).<sup>61,62</sup>

For compound **1** the results indicate a ruffle-type distortion (*ruf*,  $B_{1u}$ ) for the coordinated porphyrin, and a slight wavy one



**Fig. 5** Distortion modes diagram of an octahedron. In the upper right is a zoom of the distortion for compound **1** Co(1) octahedra (red circle), and for compound **2** Co(1) (green circle) and Co(2) (blue circle) spheres.



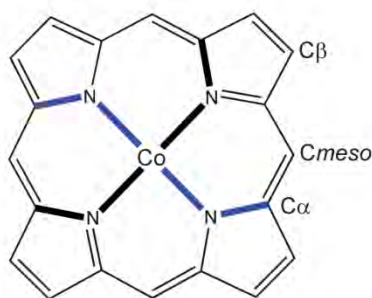
**Fig. 6** Out-of-plane displacements (in units of 0.01 Å) of the porphyrin core atoms from the mean porphyrin plane (of 24 atoms). Co(1) coordinated porphyrin and Co(2) crystallization porphyrin.

(*wav(y)*,  $[E_{g(y)}]$ ) for the crystallisation complex. The contribution of the ruffled porphyrin (1.4813) to the total displacements is 82.5%, while the wavy porphyrin shows a principal contribution of *wav(y)* (-0.1910) mixed with a small amount of the *wav(x)* (0.0884) deformation. The contribution of each type is 68.3% and 31.6%, respectively.

In compound **2** the principal distortion corresponds to the ruffled type (1.3203 and 67.8% of the total displacements), but the saddle-type (*sad*,  $B_{2u}$ ) is also observed (0.6261 and 32.2%).

As shown in Fig. 6, for compounds **1** and **2**, the occurrence of ruffled-type deformation for the polymeric porphyrins, means that the *meso* carbons (non-pyrrolic carbon atoms) are alternatively above and below the porphyrin mean plane, while the pyrrole nitrogens are placed on the plane. In compound **2**, the saddle contribution is observed by the distribution of the pyrrole rings. In fact, an opposing pair of pyrrole rings tilts up, while the other pair tilts down.

The crystallisation molecule of porphyrin in compound **1** shows the two opposing pyrrole rings tilted up and down with respect to the porphyrin mean plane, indicating a wavy



**Fig. 7** Porphyrin macrocycle and nomenclature used. *Cis*  $C_2-N-N-C_\alpha$  dihedral angle is shown in bold and *trans*  $C_2-N-N-C_\alpha$  dihedral angle in blue.

distortion. However, due to the small out-of-plane displacement this porphyrin is nearly planar.

There are some studies in literature exploring the relationships between the ruffle distortion and some structural parameters. However, they are referred to  $Co^{III}$  compounds.

Cullen *et al.*<sup>63</sup> proposed the use of the *cis* and *trans*  $C_2-N-N-C_\alpha$  torsion angles as a quantitative measure of ruffling. Inspired by this work, we have analysed the *cis* and *trans*  $C_2-N-N-C_\alpha$  dihedral angles ( $C_\alpha$  is a pyrrolic carbon atom bonded to a nitrogen atom) (Fig. 7) for our ruffled porphyrins.

The average value for *cis* dihedral angles of **1** ( $31.6^\circ(1)$ ) is higher than for **2** ( $28.4^\circ(1)$ ). This is in accordance for the conclusions for  $Co^{III}$  compounds, since the higher the *cis* dihedral angle is, the higher ruffle distortion is expected.

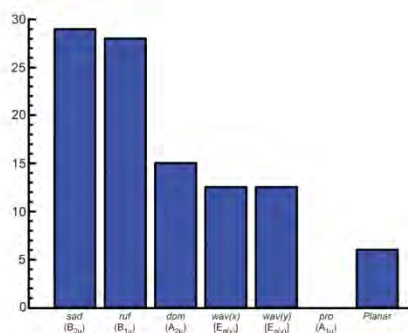
The average value for *trans* dihedral angles are  $145.7^\circ(1)$ , for **1**; and  $151.6^\circ(1)$ , for **2**. Distortion values found for compounds **1** and **2** are expected to produce values of ( $145^\circ(1)$ ) and ( $148.7^\circ(1)$ ), respectively, for  $Co^{III}$  compounds.<sup>63</sup> As observed, the prediction for **2** is not that good, probably due to the occurrence of saddle distortion. Therefore, conclusions by Cullen *et al.* seem to be effective for  $Co^{II}$  compounds.

On the other hand, Iimura *et al.*<sup>50</sup> found a linear relationship between the ruffled distortion and the  $Co-N_p$  distances ( $N_p$  are the pyrrolic nitrogen atoms) for  $Co^{III}$  porphyrins.

Due to the lack of correlation studies for  $Co^{II}$  compounds, we have performed a search on the Cambridge Structural Database (CSD)<sup>64</sup> v5.33 to find all the  $Co$  porphyrin complexes. This research indicated the existence of 221 cobalt-based metalloporphyrins, 124 of them containing  $Co^{III}$ . We have analysed the remaining 97  $Co^{II}$  compounds (Fig. 8).

As observed in Fig. 8 the most typical distortion for  $Co^{II}$  porphyrins are *sad* and *ruf*. As the main distortion observed for compounds **1** and **2** is the ruffle-type, we have performed a study with the 28 compounds found in literature exhibiting the same type of distortion, to establish the relationship with  $Co-N_p$  distances ( $N_p$  are the pyrrolic nitrogen atoms).

Fig. 9 shows a linear relationship between ruffle distortion and  $Co-N_p$  distances for  $Co^{II}$  compounds. As observed for  $Co^{III}$  compounds, we have also found that the presence of low ruffled distortion leads to longer  $Co-N_p$  distances. In particular, for compounds **1** and **2**, with distances of  $1.964(1)$  and  $1.963(3)$  Å, respectively, a value of 1 is expected for the



**Fig. 8** Out-of-plane distortion distribution for  $Co^{II}$  porphyrins.

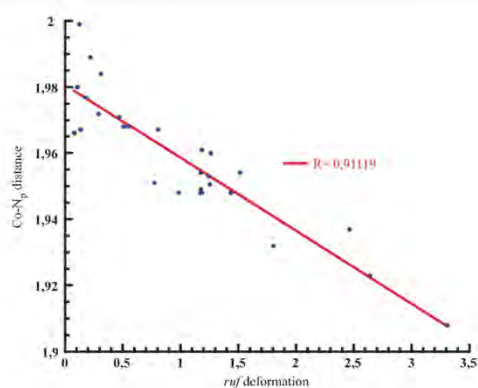
distortion. Therefore, real values (1.4813 and 1.3203, respectively) lie among the typical ones.

### Electronic paramagnetic resonance

Electron paramagnetic resonance (EPR) measurements were performed for compounds **1** (Fig. S7, ESI†) and **2** (Fig. S8, ESI†). The simulation of the EPR spectrum for both compounds gave us the following set of values:  $g_\perp = 2.232$  and  $g_\parallel = 2.030$  for compound **1**, and  $g_1 = 5.7$ ,  $g_2 = 3.95$  and  $g_3 = 3.42$  for **2**. The main signal for compound **1** is due to  $Co(1)$  atom, and it is in accordance with an octahedral low-spin  $Co^{II}$  ion. For compound **2**, the signal is the sum of the contribution of both metal centres. The observed value for the sum of the three orthogonal  $g$  values ( $g_s = 13.07$ ) is in excellent agreement with the theoretical value near 13 proposed by Abragam and Pryce,<sup>65</sup> in accordance with an octahedral high-spin  $Co^{II}$ .

### Thermogravimetry

The thermogravimetric decomposition curve for compound **1** shows a two-stage mass loss. The first step occurs between  $230-290$  °C with 10.6% weight loss, and the second one from  $410$  °C to  $500$  °C with 81% weight loss. These values have been



**Fig. 9** Plot of the average  $Co^{II}-N_p$  distance vs. the amount of ruffled ( $B_{1u}$ ) deformation.

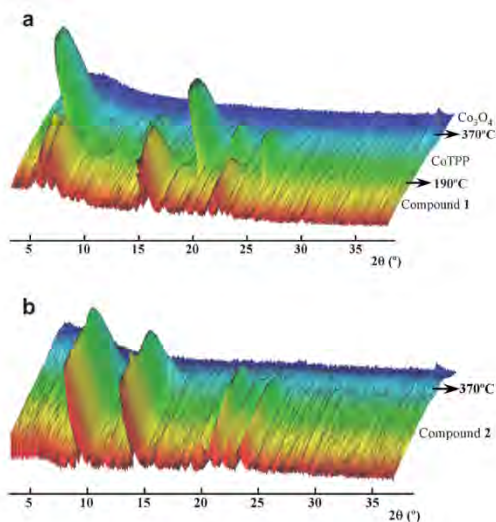


Fig. 10 Thermodiffractogram of compound 1 (a) and for compound 2 (b).

attributed to bipyridine (10.7%) and to isolated and polymeric TPP units (84.3%) (Fig. S9, ESI†). The residue has been identified by X-ray powder diffraction as  $\text{Co}_3\text{O}_4$  [S. G.  $Fd\bar{3}m$ ,  $a = 8.11 \text{ \AA}$ ].<sup>66</sup>

Compound 2 shows a two-stage mass loss. The first of them starting at RT and finishing at about 370 °C, is a smooth decrease of mass, and has been assigned to the removal of the crystallisation molecules of water (10% weight loss). On the contrary, the second one (approximately 81%) is abrupt, and corresponds to the removal of the coordination molecules of water, and both organic ligands (Fig. S10, ESI†). The calcination product was also  $\text{Co}_3\text{O}_4$ .

#### X-ray thermodiffractometry (TDX)

The thermal behaviour of compounds 1 and 2 was also studied by X-ray thermodiffractometry (Fig. 10a). Compound 1 is thermally stable until 190 °C. At higher temperatures, the removal of the bipy ligands provokes the formation of  $\text{CoTPP}$ <sup>67</sup> (Fig. S11, ESI†). This phase is stable until 370 °C, temperature at which  $\text{Co}_3\text{O}_4$  is formed.

The thermal stability of compound 2 is remarkably high. In fact, TDX analysis reveals that it is stable up to 370 °C (Fig. 10b). Above this temperature an amorphous phase is formed. The robust hydrogen bond network and the fact that the structure is two-fold interpenetrated are thought to be responsible for the high thermal stability of this compound.

## Conclusions

TPP and TPPS porphyrins produce 1D polymers with  $\text{Co}^{\text{II}}$ . Stabilisation of the network for  $\text{Co}$ -TPP compound takes place through crystallisation metalloporphyrins and molecules of porphyrin, *via* an extended  $\pi$ -bond system. For  $\text{Co}$ -TPPS

compound an extended hydrogen bond system along with an intricate topology yields the first compound with this metalloporphyrin combination. In addition, this  $\text{Co}$ -TPPS compound exhibits an unprecedented bimetallic chain and shows a remarkably high thermal stability.

For both compounds, the distortion of the porphyrins has been observed to be ruffled-type. A crystallochemical study confirmed the existence of a correlation between the degree of ruffled distortion and  $\text{Co-N}_p$  distances not only for both compounds, but also for all the  $\text{Co}^{\text{II}}$  porphyrins found in the CSD.

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**Heterogeneous catalytic properties of a metalloporphyrinic MOF based on unprecedented  $\mu$ -O-[FeTCPP]<sub>2</sub> dimers: porosity revealing an unusual superhyperfine EPR structure**

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3 During the past years, a great effort has been devoted to the anchoring of catalysts into  
4 MOFs in order to achieve heterogeneous catalysts. In this sense, an innovative approach  
5 consists on using the coordination-network synthons both as structural units and as  
6 catalysts. Regarding the latter, metalloporphyrins are suitable candidates for synthons.  
7  
8 In fact, a few works report on MOFs based on metalloporphyrins exhibiting these  
9 features. On the other hand, highly distorted di-iron oxo dimers containing electron  
10 withdrawing groups rank amongst the most-effective catalyst models. Thus, the aim of  
11 this work was obtaining MOFs based on iron porphyrins exhibiting those  
12 characteristics. This way, this work reports on the synthesis and characterization of the  
13  $\mu$ -O-[FeTCPP]<sub>2</sub>nDMF compound (TCPP = *meso*-tetra(4-carboxyphenyl)porphyrin,  
14 DMF = N,N-dimethylformamide, and n $\approx$ 16). This MOF is the first example of  $\mu$ -oxo  
15 dimer with TCPP. The inter-dimer connections give rise to a laminar structure. The  
16 structural, spectroscopic and magnetic properties of this compound are consistent with  
17 the presence of high-spin Fe<sup>III</sup> ions, exhibiting a strong antiferromagnetic coupling in  
18 the  $\mu$ -oxo dimer ( $J = -132 \text{ cm}^{-1}$ ). An unusual superhyperfine structure has been observed  
19 in EPR that is related to the porosity of the compound. The structural features of the  
20 dimers and the porous network are responsible for the promising behavior of the  
21 compound as an heterogeneous catalyst for the oxidation and acetylation of organic  
22 substrates. Therefore, this compound is a new of the very few examples of  
23 metalloporphyrins where structural units play as catalysts.  
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## 48 Introduction

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51 Metal-organic frameworks (MOFs), also known as coordination networks, are porous  
52 solids consisting of metal complexes that are packed in a variety of frameworks.<sup>1,2</sup> They  
53 have been thoroughly explored in many fields, such as gas storage and separation,<sup>3,4</sup>  
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3 nonlinear optics,<sup>5,6</sup> ferroelectricity,<sup>7</sup> conductivity,<sup>8</sup> magnetism,<sup>9</sup> luminescence,<sup>10</sup>  
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5 biomedical imaging,<sup>11</sup> chemical sensing,<sup>12</sup> drug delivery<sup>13</sup> and heterogeneous  
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7 catalysis.<sup>14-16</sup> Among the different organic ligands that can be used in these coordination  
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9 networks, metalloporphyrins can be highlighted as they can produce coordination  
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11 networks exhibiting unique properties attached to biochemical, enzymatic and  
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13 photochemical functions.<sup>17</sup> Thus, an efficient synthesis strategy gives rise to compounds  
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15 capable to mimic its behavior.  
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19 Biomimetic catalysts such as metalloporphyrins have been used as cytochrome P-450  
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21 models, and their potential for substrate oxidation has been the subject of several  
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23 studies.<sup>18-20</sup> The similarity between metalloporphyrins and the active center of many  
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25 natural enzymes, along with the high reactivity and selectivity towards oxidation of  
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27 organic substrates, have stimulated the use of iron porphyrins as models of natural  
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29 catalysts.<sup>21</sup> In this sense, a large number of model systems have been explored,<sup>22-25</sup> and  
30  
31 the use of highly distorted di-iron oxo dimers containing electron withdrawing groups  
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33 rank amongst the most-effective catalyst models attracting considerable attention on the  
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35 last years.<sup>26-28</sup> Some  $\mu$ -oxo dimers of FeTPP have been used as model compounds of  
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37 cytochromes P-450, and they exhibit greater catalytic activity than the FeTPP  
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39 monomers.<sup>29</sup>  
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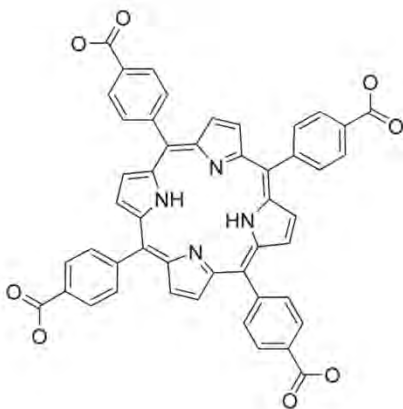
45 In order to achieve heterogeneous catalysts, there are successful approaches consisting  
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47 of anchoring the catalyst into the cavities of porous MOFs,<sup>30-32</sup> doping the MOF with  
48  
49 the catalyst<sup>33</sup> or post functionalizing the MOF.<sup>34,35</sup> Thus, our proposal is using the  
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51 catalyst as a structural units. As concluded by several recent works,<sup>36-47</sup> this approach  
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53 has been observed to be effective. However, the number of metalloporphyrinic  
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3 compounds in which the MOF itself plays as a catalyst is very low. In fact, as we are  
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5 concerned, there are about 10 articles on the matter.  
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9 In this sense, our previous research on metalloporphyrins<sup>48-50</sup> has had the same goal.  
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11 However, we have not been successful until now. The selection of TCPP (TCPP =  
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13 *meso*-tetra(4-carboxyphenyl)porphine) must be underlined in this sense (Scheme 1).  
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15  
16 There are many TCPP-based coordination networks in literature, and they exhibit  
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18 different types of packing.<sup>48,51,52</sup> On the other hand, most of the reported  $\mu$ -oxo dimers  
19  
20 are of the FeTPP type<sup>53-60</sup> (TPP = *meso*-tetra(4-phenyl)porphine, or octaethylporphyrins  
21  
22 (OEP)).<sup>27,61-74</sup> However, as far as we are concerned, no dimers of the  $\mu$ -oxo FeTCPP-  
23  
24 type have been reported so far.  
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29 **Scheme 1.** Molecular structure for TCPP  
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50  
51 Taking into account the above mentioned aspects, this work reports on the first TCPP  
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53 based  $\mu$ -oxo dimer with formula  $\mu$ -O-[FeTCPP]<sub>2</sub>nDMF (DMF = N,N-  
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55 dimethylformamide and n $\approx$ 16). The X-ray single crystal analysis reveals that the  
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57 dimers crystallize producing a 2D array via hydrogen bonds, sustained by interlayer  $\pi$ - $\pi$   
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3 interactions. Additionally, the compound has been exhaustively characterized by means  
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5 of IR, Raman, UV-Vis, Mössbauer and EPR (Electron Paramagnetic Resonance)  
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7 spectroscopies, thermogravimetric analysis, magnetic susceptibility measurements and  
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9 catalytic tests.  
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### 11 12 13 **Experimental section**

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16 **Materials.** All solvents and chemicals were used as received from reliable commercial  
17  
18 sources. The reagent iron (III) *meso*-tetra(4-carboxyphenyl)porphine chloride (FeTCPP-  
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20 Cl) was purchased from Frontier Scientific, and Isophthalic acid 99% and the solvent  
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22 N,N-dimethylformamide (DMF) 99.8% were purchased from Sigma-Aldrich Co.  
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26 **X-ray structure determination.** Prismatic black single-crystals of  $\mu$ -O-  
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28 [FeTCPP]<sub>2</sub>·nDMF with dimensions given in Table 1 were selected under polarizing  
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30 microscope and mounted on MicroMounts™. Single-crystal X-ray diffraction data were  
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32 collected at 100 K on an Agilent Technologies SuperNova single source diffractometer  
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34 with Cu-K $\alpha$  radiation ( $\lambda$ =1.5418 Å). Data frames were processed (unit cell  
35  
36 determination, intensity data integration, correction for Lorentz and polarization  
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38 effects,<sup>75</sup> and analytical absorption correction) using the CrysAlis software package.<sup>76</sup>  
39  
40 The structure of  $\mu$ -O-[FeTCPP]<sub>2</sub>·nDMF was solved in the monoclinic *C*2/*c* space group  
41  
42 with Superflip program,<sup>77</sup> which allowed us to obtain the position of iron atom, as well  
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44 as nitrogen, oxygen and some of the carbon atoms of the TCPP molecule. The  
45  
46 refinement of the crystal structure was performed by full matrix least-squares based on  
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48  $F^2$ , using the SHELXL-97 program<sup>78</sup> in OLEX<sup>79</sup> obtaining the remaining carbon atoms.  
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50 Anisotropic thermal parameters were used for all non-hydrogen atoms (Figure S1,  
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52 ESI†). All the hydrogen atoms connected to the aromatic rings (C-H 0.95Å) were fixed  
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54 geometrically, and were refined using a riding model with common isotropic  
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displacements. The hydrogen atoms of the carboxylic groups were not considered due to the lack of density in the residual density map; however they are included in the formula. DMF molecules were disordered in the crystal and the resulting electron density was found to be uninterpretable. The solvent contribution to the structure factors was taken into account by back-Fourier transformation of all density found in the disordered area using a solvent mask in OLEX.<sup>79</sup> Neither formula mass, nor calculated density takes account of the solvent. Bond distances and angles, atomic coordinates, anisotropic thermal parameters and hydrogen atom coordinates are given in Tables S1, S2, S3 and S4, ESI†.

**Table 1.** Crystallographic Data for  $\mu$ -O-[FeTCPP]<sub>2</sub>·nDMF.

| Compound  | $\mu$ -O-[FeTCPP] <sub>2</sub> ·nDMF   |
|---|--|
| Formula   | C <sub>50</sub> H <sub>50</sub> Fe <sub>2</sub> N <sub>6</sub> O <sub>17</sub> |
| FW, g·mol <sup>-1</sup>   | 1705.21  |
| Crystal system  | Monoclinic   |
| Space group (no. 15)  | C2/c   |
| <i>a</i> , Å  | 39.3340(4)   |
| <i>b</i> , Å  | 19.8329(2)   |
| <i>c</i> , Å  | 16.0292(2)   |
| $\beta$ , deg   | 98.4180(10)  |
| <i>V</i> , Å <sup>3</sup>   | 12369.8(2)   |
| <i>Z</i>  | 4  |
| $\rho_{\text{obs}}$ , $\rho_{\text{calc}}$ , g·cm <sup>-3</sup>           | 1.575(5), 0.911  |
| <i>F</i> (000)  | 3472   |
| $\mu$ , mm <sup>-1</sup>  | 2.304  |
| Crystal size, mm  | 0.21 × 0.12 × 0.05   |
| Absorption correction   | Analytical   |
| Radiation, $\lambda$ , Å  | 1.54184  |
| Temperature, K  | 100(2)   |
| Reflections collected, unique   | 50744, 12049 ( <i>R</i> <sub>int</sub> =0.04)                                  |
| Limiting indices  | -48 < <i>h</i> < 47<br>0 < <i>k</i> < 24<br>0 < <i>l</i> < 19                  |
| Refinement method   | Full-matrix least-squares on <i>F</i> <sup>2</sup>                             |
| Final <i>R</i> indices [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )] <sup>a</sup> | <i>R</i> 1 = 0.0608, <i>wR</i> 2 = 0.1867                                      |
| <i>R</i> indices (all data) <sup>b</sup>                                  | <i>R</i> 1 = 0.0788, <i>wR</i> 2 = 0.2025                                      |
| Goodness of fit on <i>F</i> <sup>2</sup>                                  | 1.063  |
| Parameters/restraints   | 555 / 0  |

$$^a R1 = \frac{(\sum |F_o| - \sum |F_c|)}{\sum |F_o|}, \quad ^b wR2 = \frac{[\sum w(F_o - F_c)^2]}{[\sum w(F_o)^2]}^{1/2}$$

**Physicochemical characterization techniques.** The IR spectra were collected on a JASCO FT/IR-6100 spectrometer at room temperature at the range of 4000-400 cm<sup>-1</sup>, in KBr pellets (1% of the sample). Raman spectra of the solid samples were recorded using a Renishaw InVia spectrometer equipped with a 785 nm laser at the range of

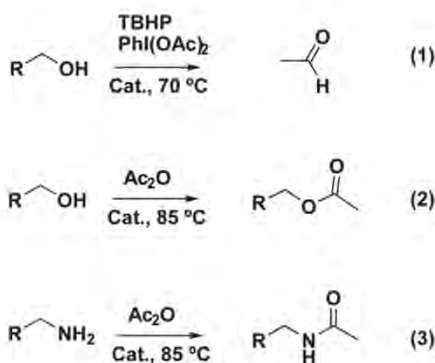
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3 3500-150  $\text{cm}^{-1}$ . UV-visible diffuse-reflectance measurements were carried out on a  
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5 Cary 5000 UV-Vis-NIR spectrophotometer in the range of 2500 to 200 nm. C, H, N and  
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7 O elemental analyses were measured using a Euro EA 3000 elemental analyzer. The  
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9 thermal analyses were carried out in air atmosphere using a NETZSCH STA 449F3  
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11 instrument. A crucible containing approximately 10 mg of sample was heated at 5  $^{\circ}\text{C}$   
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13  $\text{min}^{-1}$  in the temperature range 30-600  $^{\circ}\text{C}$ . Mössbauer spectra were obtained at room  
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15 temperature using a constant-acceleration Mössbauer spectrometer with a  $^{57}\text{Co}/\text{Rh}$   
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17 source. The velocity calibration was done using a metallic Fe foil. Electron  
18  
19 paramagnetic resonance (EPR) spectra were measured with a Bruker ESP-300  
20  
21 spectrometer operating at X band and equipped with a nitrogen and helium cryostat.  
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23 Magnetic susceptibility measurements were measured in the range of 4–300 K with a  
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25 Quantum Design SQUID MPMS-7T magnetometer.  
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31 **Catalytic Tests.** The oxidation reactions of benzyl alcohol (Scheme 2, top) were carried  
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33 out at 70  $^{\circ}\text{C}$  using acetonitrile as solvent. Before the reactions, dried compound (0.0032  
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35 mmol) was activated by stirring it with the oxidizing agent *tert*-butyl hydroperoxide  
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37 (TBHP) or iodobenzene diacetate ( $\text{PhI}(\text{OAc})_2$ ) in acetonitrile, for 30 min at 70  $^{\circ}\text{C}$ . After  
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39 this activation stage, the catalyst was separated from the liquid media by centrifugation.  
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41 The reactor with the activated catalyst was then charged with 0.12 mmol of benzyl  
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43 alcohol in 2 mL of solvent.  
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48 The acetylation of alcohols (Scheme 2, middle) and amines (Scheme 2, bottom) were  
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50 carried out at 85  $^{\circ}\text{C}$  using acetonitrile as solvent. Acetic anhydride was used as acetyl  
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52 source and the reactor was charged with 0.12 mmol of the corresponding alcohol or  
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54 amine (phenol and aniline), 0.0059 mmol of catalyst and 0.24 mmol of acetic anhydride  
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56 in 1 mL of solvent.  
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3 Reaction samples were taken at regular times and analyzed on a Hewlett–Packard 5890  
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5 II GC-MS gas chromatograph-mass spectrometer. After the reactions, the catalysts were  
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7 filtered and characterized by IR and Raman spectroscopies. Due to the low crystallinity  
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9 of  $\mu$ -O-[FeTCPP]<sub>2</sub>·nDMF, X-ray powder diffraction was rejected as a characterization  
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11 technique for the recovered catalyst.  
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15 **Scheme 2.** Catalytic tests reaction schemes.  
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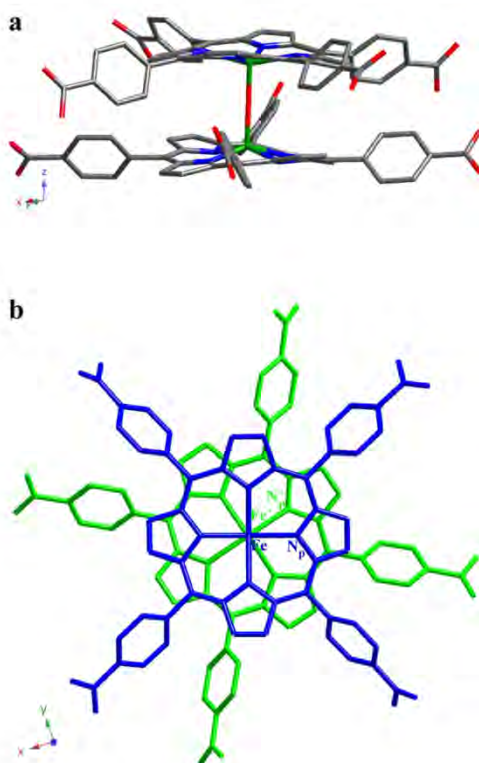


## Results and Discussion

**Synthesis of  $\mu$ -O-[FeTCPP]<sub>2</sub>·nDMF.** Iron (III) *meso*-tetra(4-carboxyphenyl)porphine chloride (8.8 mg, 0.01 mmol) and isophthalic acid (9.9 mg, 0.06 mmol) were dissolved in DMF (4 mL) in a small capped vial, sonicated to ensure homogeneity and heated to 80 °C for 72 h, following by slow cooling to room temperature, yielding diffraction quality prismatic black crystals. (Found: C, 66.91; H, 3.17; N, 6.54; O, 16.40. Calc. for C<sub>96</sub>H<sub>56</sub>Fe<sub>2</sub>N<sub>8</sub>O<sub>17</sub>: C, 67.62; H, 3.31; N, 6.57; O, 15.95).

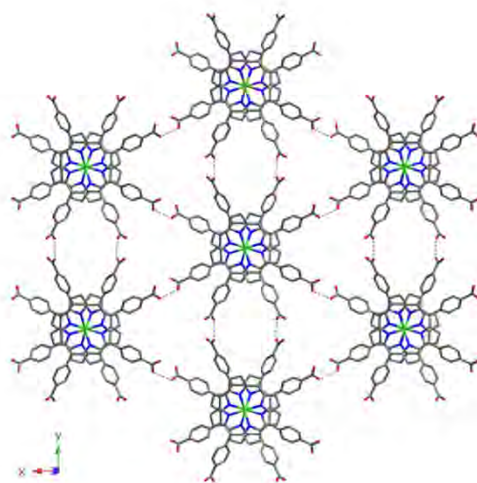
**Crystal structure.** Crystal structure of  $\mu$ -O-[FeTCPP]<sub>2</sub>·nDMF was determined by means of X-ray single crystal diffraction. The structure shows that two FeTCPP rings are bonded together by a bridging O atom in a Fe-O-Fe bond system (Figure 1a). The

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3 iron atom is on a five-coordinated square pyramidal environment, displaced by 0.445 Å  
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5 from the mean porphyrin plane (24 atoms) towards the oxo oxygen atom, and forms a  
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7 nearly linear Fe-O-Fe angle (179.78°). The Fe-N<sub>p</sub> distances are in the narrow range of  
8  
9 2.077(2) to 2.087(2) Å, while the Fe-O distance is 1.7597(4) Å. These distances and  
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11 angles are typical for high-spin iron (III)  $\mu$ -oxo dimers.<sup>27,29,53-56,61,66,80-84</sup> The  
12  
13 macrocyclic rings are essentially parallel to each other, the angle between the two  
14  
15 central N<sub>4</sub> planes being 0.31°. The relative orientations of the two porphyrin rings make  
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17 an average N<sub>p</sub>-Fe-Fe'-N'<sub>p</sub> dihedral angle (torsional angle) of 33.62° (Figure 1b) to  
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19 accommodate the peripheral carboxylic groups.  
20  
21 to accommodate the peripheral carboxylic groups.  
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3 **Figure 1.** (a) Dimeric unit for  $\mu\text{-O-}[\text{FeTCPP}]_2\text{nDMF}$ . Color code: Fe= Green, N= Blue,  
4 C= Grey and O= red. H atoms have been omitted for clarity and (b) top view of the  
5 dimer.  
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11 These coordination entities crystallize as shown in Figure 2. Each dimer is surrounded  
12 by another six producing an H-bonded 2D layer on the  $xy$  plane. The robust intralayer  
13 H-bonding system is generated from O8 to O4 (2.411 Å) and from O7 to O2 (2.470 Å)  
14 maintaining the stability of the layers.  
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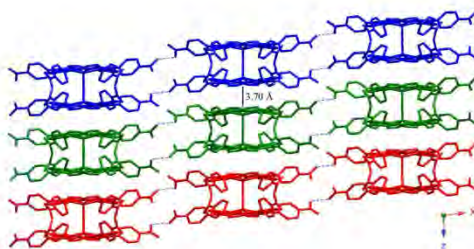


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42 **Figure 2.** View of the H-bonded 2D layer for  $\mu\text{-O-}[\text{FeTCPP}]_2\text{nDMF}$ . Color code: Fe=  
43 Green, N= Blue, C= Grey, O= red and H-bonds= Dashed lines. H atoms have been  
44 omitted for clarity.  
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49 The H-bonded 2D layers are stacked along the (001) direction, sustained by  $\pi$ - $\pi$   
50 interactions (3.5~3.9 Å) among the dimers of each layer (Figure 3). Crystallization  
51 DMF molecules are located in the voids generated between dimers. Unfortunately, these  
52 molecules have not been located in the structure refinement process. The resulting voids  
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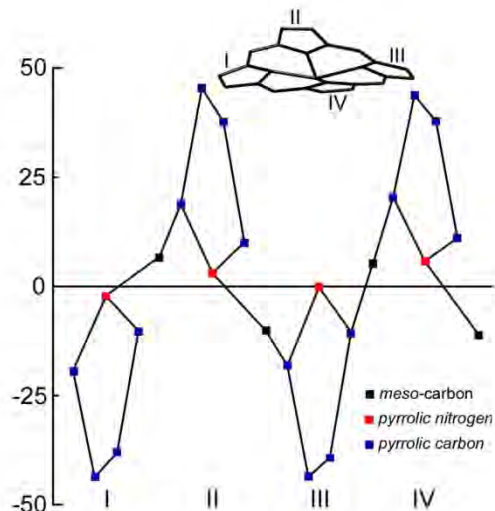
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3 without DMF molecules were analyzed with PLATON program,<sup>85</sup> showing a 5836.2 Å<sup>3</sup>  
4 potential solvent volume (47.2% of the unit cell) and a calculated 2470.1 Å<sup>3</sup> effective  
5 volume. Taking into account the single crystal experimental density, the initial weight  
6 loss observed in the thermogravimetric analysis and the calculated free effective volume  
7 we have estimated the presence of 16 DMF molecules per unit cell. These DMF  
8 molecules are located on the two types of voids on the crystal structure (along the *c* axis  
9 and interweaving the 2D layers).  
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31 **Figure 3.** Stacking of the 2D layers for  $\mu$ -O-[FeTCPP]<sub>2</sub>·nDMF, where each layer is  
32 shown in a different color. Intralayer H-bonds are shown as dashed lines. H atoms have  
33 been omitted for clarity.  
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39 The out-of-plane distortion of the porphyrin macrocycle was analyzed by the normal-  
40 coordinate structural decomposition method developed by Shelnutz *et al.* (NSD).<sup>86,87</sup> In  
41 a saddle conformation, alternate pyrrole rings tilt up and down with respect to the  
42 porphyrin mean plane (24 atoms), and the *meso* carbon atoms lie on the least-square  
43 plane. As is evident from Figure 4, the results indicate a main saddle type distortion  
44 (*sad*, B<sub>2u</sub>), with a contribution of the 82% to the total displacement of the porphyrin  
45 (1.502). This nonplanarity of the porphyrin core is the consequence of significant steric  
46 congestion in the periphery of the molecule. The slight saddle distortion on the two  
47 porphyrin cores and the value of the Fe atom displacement from the mean porphyrin  
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plane (0.445 Å) is consistent with the presence of high spin ( $S=5/2$ )  $\text{Fe}^{\text{III}}$  ions.<sup>73,88</sup> This fact, as will be seen later, was corroborated by EPR and Mössbauer spectroscopies and by magnetic measurements.



**Figure 4.** Out-of-plane displacements (in units of 0.01 Å) of the porphyrin core atoms from the mean porphyrin plane (of 24 atom) for  $\mu\text{-O-[FeTCPP]}_2 \cdot n\text{DMF}$ .

**Infrared and Raman spectroscopies.** The most significant IR spectral changes from the reactant FeTCPPCl porphyrin to the final dimer account for the formation of the  $\mu\text{-oxo diiron(III)}$  bond, with the appearance of two new strong absorptions at 870 and 827  $\text{cm}^{-1}$ . It is well known that the antisymmetric stretching mode ( $\nu_3$ ), specifically the  $\nu_{\text{as}}(\text{Fe-O-Fe})$ , of a linear or bent Fe-O-Fe system usually occurs in the range 900-800  $\text{cm}^{-1}$ .<sup>89</sup> Thus, these two absorptions, at 870 and 827  $\text{cm}^{-1}$ , indicate the presence of a Fe-O-Fe bond. The rest of the observed absorptions are the usual ones for porphyrin compounds:  $\nu_{\text{max}}/\text{cm}^{-1}$  3414 and 1433 (OH), 3031 ( $\text{C}(\text{sp}^2)\text{H}$ ), 1705 and 1202 (CO), 1632 (DMF), 1606-1476 (CC), 1383 (CN), 999 (FeTCPP) (Figure S2, ESI†).

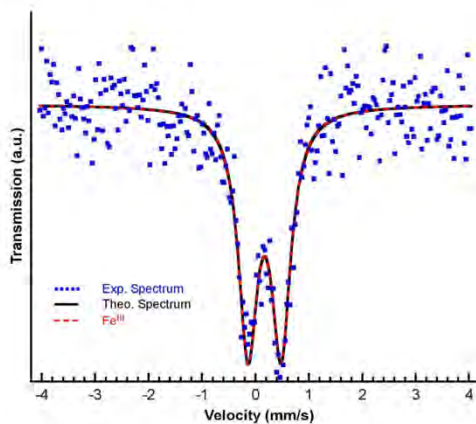
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3 While for IR spectra the dominant feature is the antisymmetric Fe-O-Fe absorption,  
4  
5 Raman spectra are expected to show a greater contribution of the symmetric Fe-O-Fe  
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7 vibration. Previous works<sup>80,90</sup> have identified that the vibrations around 363 cm<sup>-1</sup> in  
8  
9 Raman spectra correspond to the out-of-plane symmetric Fe-O-Fe stretching mode.  
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11 Thus,  $\mu$ -O-[FeTCPP]<sub>2</sub>·nDMF shows Raman spectral band at 363.3 cm<sup>-1</sup>, which is  
12  
13 identified as the  $\nu_{as}(\text{Fe-O-Fe})$  mode. Furthermore, the additional bands observed in the  
14  
15 Raman spectra are mainly porphyrin skeletal vibration modes including  $\nu_{as}(\text{C}_\alpha\text{C}_m)$   
16  
17 (1608),  $\nu(\text{C}_\beta\text{C}_\beta)$  (1550),  $\nu_s(\text{pyrrole half-ring})$  (1360),  $\delta(\text{C}_m\text{H})$  (1233) and  $\delta_{as}(\text{pyrrole}$   
18  
19  $\text{deform})$  (991) (Figure S3, ESI<sup>†</sup>).  
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25 **UV-Visible (Diffuse-Reflectance) spectroscopy.** The UV-Vis spectrum of  $\mu$ -O-  
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27 [FeTCPP]<sub>2</sub>·nDMF shows Soret and Q bands at 361, 576 and 623 nm, respectively  
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29 (Figure S4, ESI<sup>†</sup>). The evident blueshift of the Soret band, compared to other iron (III)  
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31 non-dimeric porphyrin compounds and to the monomeric Fe(TCPP),<sup>91</sup> reflects the short  
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33 interporphyrin ring separation, whereas the Q bands are redshifted by the presence of  
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35 carboxylic groups on the periphery of the porphyrin.  
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39 **Thermogravimetry.** The thermogravimetric decomposition curve of the compound  
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41 shows an initial two-stage mass loss from RT to 360 °C, assigned to the removal of  
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43 DMF molecules (40.95% weight loss) from the two types of voids on the crystal  
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45 structure. Afterwards, a second mass loss occurs from 360 °C to 400 °C, assigned to  
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47 both porphyrin units (51.5% weight loss) (Figure S5, ESI<sup>†</sup>). The calcination product has  
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49 been identified by powder X-ray diffraction analysis, and it consists of Fe<sub>2</sub>O<sub>3</sub> [space  
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51 group *R*-3*c*, *a* = 5.0142 Å, *c* = 13.6733 Å and  $\gamma = 120^\circ$ ].<sup>92</sup>  
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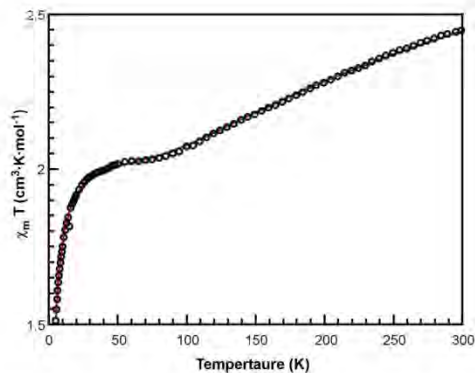
55  
56 **Mössbauer spectroscopy.** Compound  $\mu$ -O-[FeTCPP]<sub>2</sub>·nDMF has been studied by  
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58 Mössbauer spectroscopy. The spectrum has been simulated with the NORMOS  
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3 program,<sup>93</sup> and indicates the presence of a doublet corresponding to Fe<sup>III</sup> signals. The  
4 signal is assigned to the metal ions in  $\mu$ -O-[FeTCPP]<sub>2</sub>·nDMF. The isomer shift ( $\delta$ ) and  
5 quadrupolar splitting ( $\Delta E$ ) values are 0.270(6) and 0.623(9), respectively, in the range  
6 usually observed for high spin Fe<sup>III</sup> porphyrins<sup>73</sup> (Figure 5).  
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**Figure 5.** Mössbauer spectra for  $\mu$ -O-[FeTCPP]<sub>2</sub>·nDMF.

**Magnetic measurements.** Variable temperature magnetic susceptibility measurements have been carried out between 5 and 300 K for  $\mu$ -O-[FeTCPP]<sub>2</sub>·nDMF, and the plot of  $\chi_m T$  versus  $T$  is shown in Figure 6. The effective magnetic moment decreases from 4.43  $\mu_B$  at 300 K to 4.03  $\mu_B$  at 75 K. After a slow decrease, down to 15 K, the effective magnetic moment suffers another abrupt decrease, reaching the value of 3.47  $\mu_B$  at 5 K.



**Figure 6.** Thermal evolution of the  $\chi_m T$  product for  $\mu\text{-O-}[\text{FeTCPP}]_2\cdot n\text{DMF}$  compound.

The high-temperature behavior is the expected for a strong antiferromagnetic coupling in a  $S = 5/2$  dimer. However, the plateau between 75 and 15 K, and the further abrupt decrease cannot be explained by the sole contribution of this coupling. X-ray analysis discards the presence of impurities in the required high concentration as to account for the observed curve. However, we can think of the presence of broken dimers that are expected to be paramagnetic. The dimers are expected to be broken because the magnetic measurements were performed by using ground single crystals, producing monomeric units. Thus, the decrease in the effective magnetic moment observed at low temperatures can be explained by means of the Zero Field Splitting effect (ZFS) on the  $S = 5/2$  state.

In order to confirm this hypothesis, experimental data have been adjusted according to equation 1 where  $\chi_{dim}$  and  $\chi_{mon}$  are the contribution of the dimeric and monomeric (broken dimers) species, respectively.

$$\chi_m = (1-\delta)\chi_{dim} + \delta\chi_{mon} \quad \text{equation 1}$$

In order to evaluate the exchange constant  $J$  due to the contribution of the dimeric species ( $\chi_{dim}$ ), the van Vleck equation has been used for a spin Hamiltonian  $H = -2JS_1S_2$  (equation 2).

$$\chi_m = \frac{2Ng^2\beta^2}{kT} \frac{\exp(2x) + 5\exp(6x) + 14\exp(12x) + 30\exp(20x) + 55\exp(30x)}{1 + 3\exp(2x) + 5\exp(6x) + 7\exp(12x) + 9\exp(20x) + 11\exp(30x)}$$

where  $x = J/kT$  equation 2

The van Vleck equation has been also used to estimate the exchange constant  $J$  due to the contribution of the monomeric species ( $\chi_{mon}$ ), but in this case for  $S = 1/2$  in an axially distorted octahedral environment (equation 3). In equation 3,  $D$  is the axial parameter related to the ZFS effect, The  $E$  rhombic one has been considered negligible.

$$\chi_{||} = \frac{Ng^2\beta^2}{4kT} \frac{1 + 9\exp(-2x) + 25\exp(-6x)}{1 + \exp(-2x) + \exp(-6x)}$$

$$\chi_{\perp} = \frac{Ng^2\beta^2}{4kT} \frac{9 + 8/x - 11\exp(-2x)/2x - 5\exp(-6x)/2x}{1 + \exp(-2x) + \exp(-6x)}$$

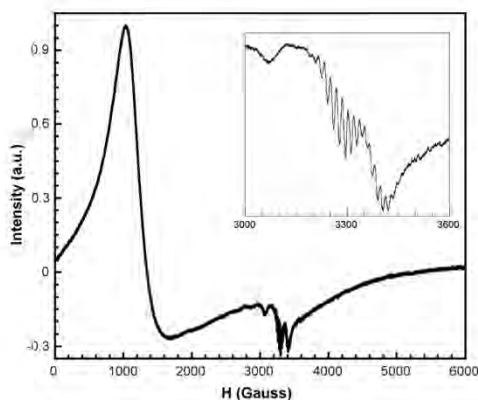
where  $x = D/kT$  equation 3

Taking into account that the orbital contribution for  $S = 5/2$  ions is habitually negligible, the  $g$  value was considered to be  $g = 2$ . This way, the number of parameters to be adjusted was lower, producing estimated values of  $J = -132 \text{ cm}^{-1}$ ;  $D = 6.9 \text{ cm}^{-1}$  and  $\delta = 0.23$ . These values were obtained by minimizing the  $R$  error (equation 4). Figure 6 shows that experimental and calculated values are in very good accordance ( $R = 1.2 \times 10^{-5}$ ). The  $J$  value is comparable to other ones found for similar systems.<sup>60,66,94</sup> It is worth mentioning that the  $\delta$  value indicates a significant amount of monomeric species.

$$R = \frac{\sum[\chi_m T^{\text{exp}} - \chi_m T^{\text{cal}}]^2}{\sum[\chi_m T^{\text{exp}}]^2}$$
 equation 4

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3 Electronic paramagnetic resonance (EPR). As occurs with other similar compounds  
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5 that exhibit strong antiferromagnetic couplings through two high-spin iron(III)  
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7 centers,<sup>94</sup> we did not expect to obtain EPR signal for this compound. However, the X-  
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9 band EPR spectral measurements carried out for  $\mu$ -O-[FeTCPP]<sub>2</sub>nDMF at room  
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11 temperature in solid state show an axially symmetric spectra with  $g_{\perp}$  and  $g_{\parallel}$  values  
12  
13 close to 6 and 2, respectively; unequivocal evidence of high spin Fe<sup>III</sup> ( $S = 5/2$ ) ions  
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15 (Figure 7). The observed signal should therefore be caused by the monomeric species  
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17 detected by magnetic measurements.  
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22 As observed in Figure 7, the parallel component exhibits a superhyperfine structure ( $A_{\parallel}$   
23  
24 =17 Gauss) that is not habitual for this type of compounds. This superhyperfine  
25  
26 structure can be explained by the interaction between the Fe<sup>III</sup> electronic spin and the  
27  
28 nuclear spins ( $I=1$ ) of the four pyrrolic nitrogen atoms bonded to each Fe<sup>III</sup> ion on the  
29  
30 equatorial plane. This interaction should produce a nine-line structure. However, taking  
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32 into account the ZFS effect confirmed for  $\mu$ -O-[FeTCPP]<sub>2</sub>nDMF, this structure should  
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34 be repeated at least in two different transitions within the  $S = 5/2$  state. The fact that this  
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36 superhyperfine structure has not been previously observed in similar compounds can be  
37  
38 explained if considering that the magnetic matrix is very diluted for  $\mu$ -O-  
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40 [FeTCPP]<sub>2</sub>nDMF, due to the fact that 47% of the unit cell is occupied by DMF  
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42 molecules. Therefore, the dilution of the magnetic matrix, induced by the porous nature  
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44 of the compound, allows the unusual observance of electronic and nuclear spin  
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46 interactions between different atoms.  
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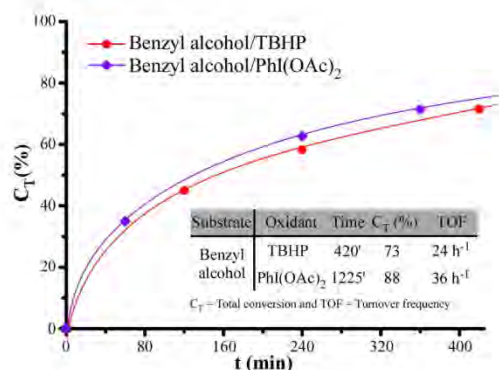
**Figure 7.** X-band EPR spectrum for  $\mu$ -O-[FeTCPP]<sub>2</sub>·nDMF registered at room temperature.

**Catalytic properties.** Synthetic metalloporphyrins complexes have been largely used for a variety of catalytic transformations,<sup>18</sup> and a special emphasis is put on the single atom bridged diiron complexes as an emerging class of catalysts.<sup>95</sup> In this sense,  $\mu$ -O-[FeTCPP]<sub>2</sub>·nDMF exhibits two additional characteristics that make one think of its potential as a catalyst. Firstly, Fe<sup>III</sup> centers are five-coordinated square pyramidal polyhedra. Secondly, the network is significantly porous, with mobile DMF molecules located in the cavities. Therefore, virtually approaching to the metal ion by other molecules in dissolution seems to be easy. The above mentioned aspects were considered to proceed with the study of the catalytic properties of  $\mu$ -O-[FeTCPP]<sub>2</sub>·nDMF. Thus, the catalytic activity of  $\mu$ -O-[FeTCPP]<sub>2</sub>·nDMF was tested towards oxidation of alcohols and acetylation of amines and alcohols.

**Oxidation of alcohols.** The oxidation of alcohols is of great importance on organic synthesis and, in this sense, many iron porphyrins have been tested for this reaction.<sup>45,96</sup> The scope of the oxidation reaction was analyzed with benzyl alcohol and two oxidizing



agents, TBHP (1.5 eq.) and  $\text{PhI}(\text{OAc})_2$  (2 eq.). Once the reaction conditions were established, the best conversion rates (Figure 8) were obtained when using 5% of catalyst at 70 °C. In Figure 8, the kinetic profiles of the oxidation reactions can be observed.



**Figure 8.** Kinetic profiles for the benzyl alcohol oxidation with TBHP and  $\text{PhI}(\text{OAc})_2$ .

When using  $\text{PhI}(\text{OAc})_2$  as oxidant, the conversion rates slightly increased. Reutilization is one of the greatest advantages of heterogeneous catalysts and can also provide useful information about the anchoring process and catalyst stability along the catalytic cycle. Thus, recycling tests were carried out over  $\mu\text{-O-}[\text{FeTCPP}]_2\cdot\text{nDMF}$  for the oxidation of benzyl alcohol and, as observe in Table 2, during the three cycles an increase of catalytic activity is observed up to 98%. This means that the catalyst is activated during the reaction. One simple explanation can be based on the fact that DMF is progressively being removed from the cavities. This way, the increasing accessible area would permit the presence of an increasing number of active centers.

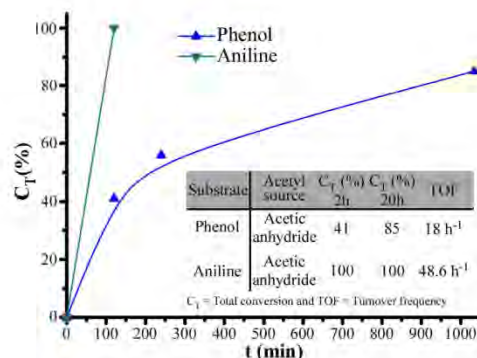
**Table 2.** Recyclability of compound  $\mu\text{-O-}[\text{FeTCPP}]_2\cdot\text{nDMF}$  for benzyl alcohol oxidation.

| Cycles | C <sub>T</sub> (4h) |
|--------|---------------------|
| 1      | 58 %                |
| 2      | 77 %                |
| 3      | 98 %                |

C<sub>T</sub> = Total conversion

After the oxidation reactions, the solid catalyst was recovered by centrifugation, washed with acetonitrile and ethanol, and then characterized by IR spectroscopy. The IR spectra of the residues for the tested oxidation reactions show that the original compound breaks down when using PhI(OAc)<sub>2</sub> as oxidant, after three cycles. In contrast, when using TBHP as oxidant, the structural units remain, in fact, the solid shows the same characteristic vibration modes of the original compound. As shown in Figure S6, ESI† the characteristic vibrations of the porphyrin macrocycle are present, although the intensity of the Fe-TCPP and Fe-O-Fe vibrations at 1000 cm<sup>-1</sup>, 870 cm<sup>-1</sup> and 824 cm<sup>-1</sup> is lower.

**Acetylation of amines and alcohols.** The acetylation reaction of amine and hydroxyl groups is very useful in organic synthesis, since in many occasions the protection of those functional groups is necessary to avoid the reaction at these points. Thus,  $\mu$ -O-[FeTCPP]<sub>2</sub>·nDMF was tested with aniline and phenol, and acetic anhydride (2 equivalents) as acetyl source. In all cases, acetonitrile was used as solvent, and once the reaction conditions were established, the best conversion rates (Figure 9) were obtained when using 10% of catalyst at 85 °C. All the reactions were carried out by reflux. In Figure 9 the kinetic profiles of the acetylation reactions can be observed.



**Figure 9.** Kinetic profiles for the phenol and aniline acetylation reactions.

As observed in Figure 9, the phenol acetylation conversion rates are very good with a value close to 85% for a reaction time of 20h. In the case of aniline, the rapid conversion is especially remarkable.

After the acetylation reactions, the solid catalyst was recovered by centrifugation, washed with acetonitrile and ethanol and then characterized by IR and Raman spectroscopies. The compound recovers the original purple color in all cases, and IR spectra confirm the presence of the original solids (Figure S7, ESI<sup>†</sup>). Additionally, Raman spectroscopy also confirms the recovery of the original catalyst. In fact, the very characteristic vibration mode of the Fe-O-Fe dimers is visible at about 370 cm<sup>-1</sup>. (Figure S8, ESI<sup>†</sup>).

## Conclusions

FeTCPP metalloporphyrin has been used to produce a new porous MOF based on unprecedented  $\mu$ -oxo-FeTCPP dimers. The coordination network exhibits significant porosity, that is related to the unusual appearance of a superhyperfine EPR structure. Additionally, the porous nature of the compound, along with the structural features of

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3 the dimers, are responsible for its catalytic properties. Those characteristics allow  
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5 FeTCPP to be playing a double role, as a catalyst and as a synthon. This is an innovative  
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7 approach to achieve heterogeneous catalyst as an alternative to the anchoring of  
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9 effective catalyst into solid frameworks. Compound  $\mu$ -O-[FeTCPP]<sub>2</sub>·nDMF is one of  
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11 the very few porphyrinic systems where the MOF itself plays as a catalyst, achieving  
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13 heterogeneous catalysis.  
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#### 21 ASSOCIATED CONTENT

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23  
24 **Supporting Information.** ORTEP detail of the structure, IR, Raman and UV/Vis  
25  
26 spectra, thermogravimetry, IR and Raman of the catalysis residues, crystallographic  
27  
28 data and CIF file. CCDC 981624. This material is available free of charge via the  
29  
30 Internet at <http://pubs.acs.org>.  
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#### 8 Author Contributions

9  
10 The manuscript was written through contributions of all authors. All authors have given  
11 approval to the final version of the manuscript. †, ‡, † and § authors contributed  
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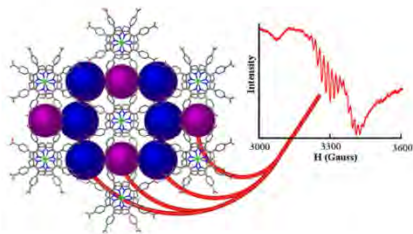
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Porosity of the  $\mu$ -O-[FeTCPP]<sub>2</sub>·nDMF dimer revealing an unusual superhyperfine EPR structure.













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