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Metalloporphyrin-based MOFs: new strategies for catalyst immobilization

Gotzone Barandika, Begoña Bazán, Arkaitz Fidalgo-Marijuan, Miren-Karmele Urtiaga, Luis Lezama, María-Isabel Arriortua

Department of Inorganic Chemistry, Faculty of Pharmacy, University of the Basque Country (UPV/EHU), Vitoria-Gasteiz, (Spain).
Department of Mineralogy and Petrology, Faculty of Science and Technology, University of the Basque Country (UPV/EHU), Leioa, (Spain).
Department of Inorganic Chemistry, Faculty of Science and Technology, University of the Basque Country (UPV/EHU), Leioa, (Spain).

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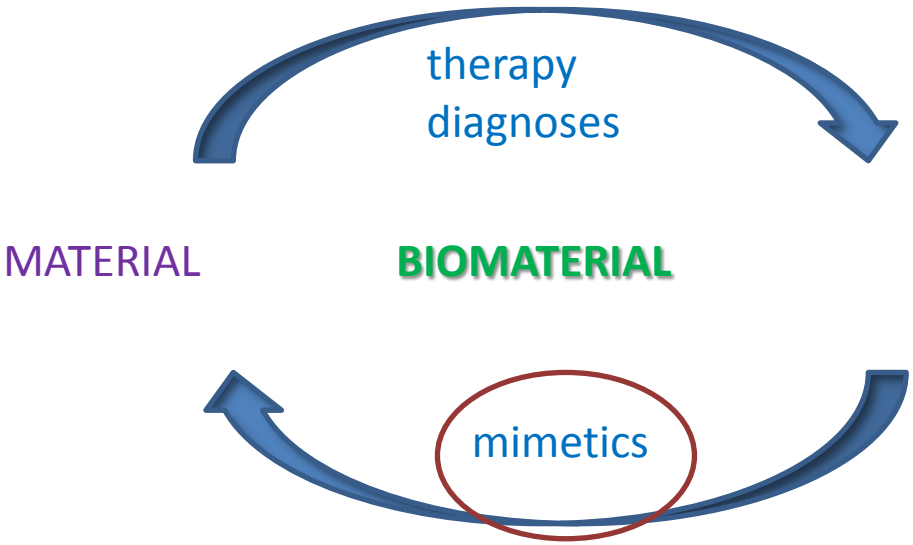
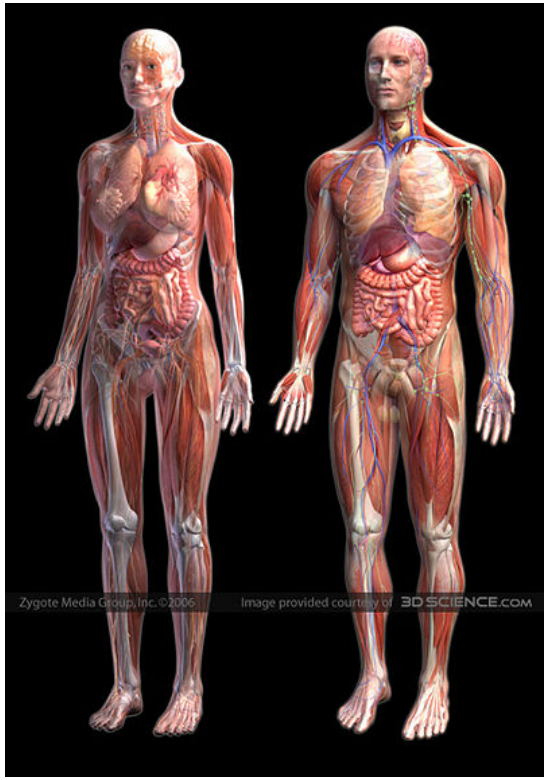
D.F. Williams / Biomaterials 30 (2009) 5897–5909

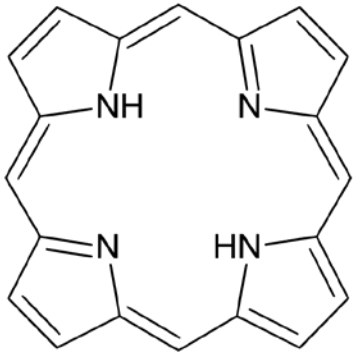
"A biomaterial is a substance that has been engineered to take a form which, alone or as part of a complex system, is used to direct, by control of interactions with components of living systems, the course of any therapeutic or diagnostic procedure, in human or veterinary medicine."



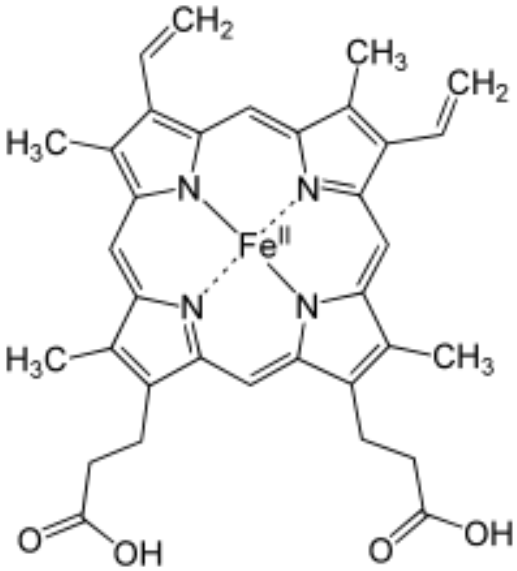


Metalloporphyrins

porphine



Porphyrins are substituted porphines



Heme group

transportation of gases
gas detection
electron transfer
chemical catalysis

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MOFs: metal organic frameworks

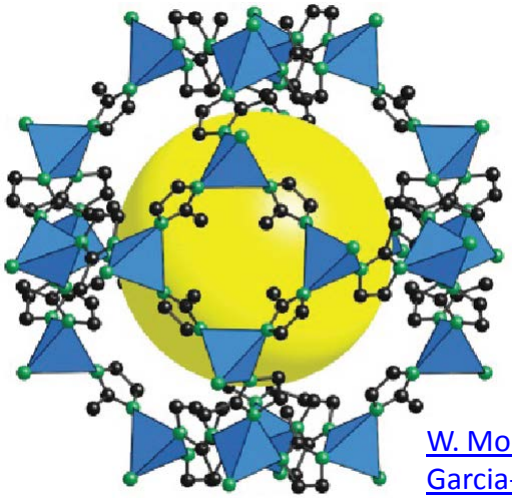
CNS: coordination network solids

Coordination polymers, metal–organic frameworks and the need for terminology guidelines

Stuart R. Batten, Neil R. Champness, Xiao-Ming Chen, Javier Garcia-Martinez, Susumu Kitagawa, Lars Öhrström, Michael O'Keeffe, Myunghyun Paik Suh and Jan Reedijk

CrystEngComm, 2012, 14, 3001-3004
DOI: 10.1039/C2CE06488J

Porous MOFs



ZIF-8 - $Zn(C_4N_2H_5)_2$

gas storage
compound separation
chemical sensing
nonlinear optics
biomedical imaging
drug delivery
heterogeneous catalysis

Host-guest chemistry

W. Morris , C. J. Stevens , R. E. Taylor , C. Dybowski , O. M. Yaghi, M. A. Garcia-Garibay, *J. Phys. Chem. C*, 2012, 116, 13307

O. M. Yaghi, G. M. Li, H. L. Li, *Nature*, 1995, **378**, 703.
G. Ferey, C. Mellot-Draznieks, C. Serre and F. Millange, *Acc. Chem. Res.*, 2005, **38**, 217.
S. Kitagawa, R. Kitaura and S.-i. Noro, *Angew. Chem., Int. Ed.*, 2004, **43**, 2334.

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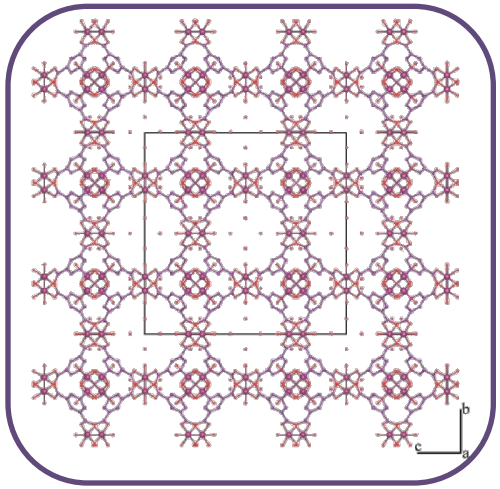
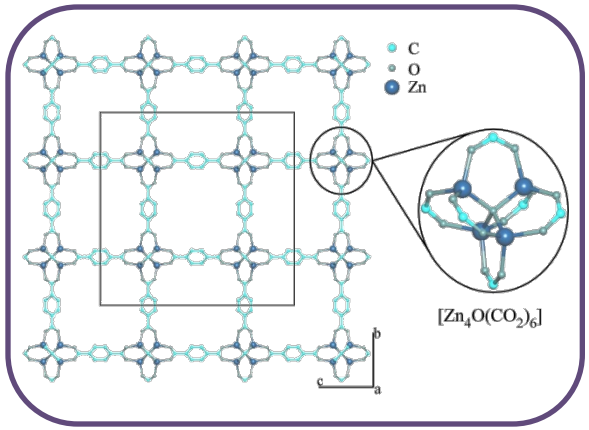
Porous MOFs based on carboxylic ligands



HKUST-1

$[Cu_3(BTC)_2(H_2O)_3]_n$

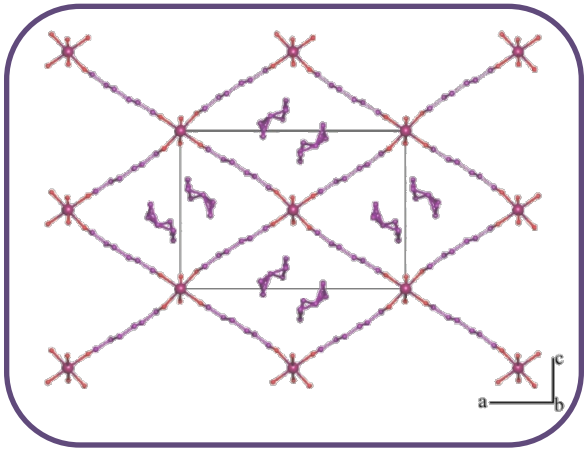
Chui S. S.-Y., Lo S. M.-F., Charmant J. P. H., Orpen A. G., Williams I. D., *Science*, **283**, 1148-1150, **1999**.



MOF-5

$[Zn_4O(BDC)_3]\cdot(DMF)_8(C_6H_5Cl)$

Li H., Eddaoudi M., O'Keeffe M., Yaghi O. M., *Nature*, **402**, 276-279, **1999**.



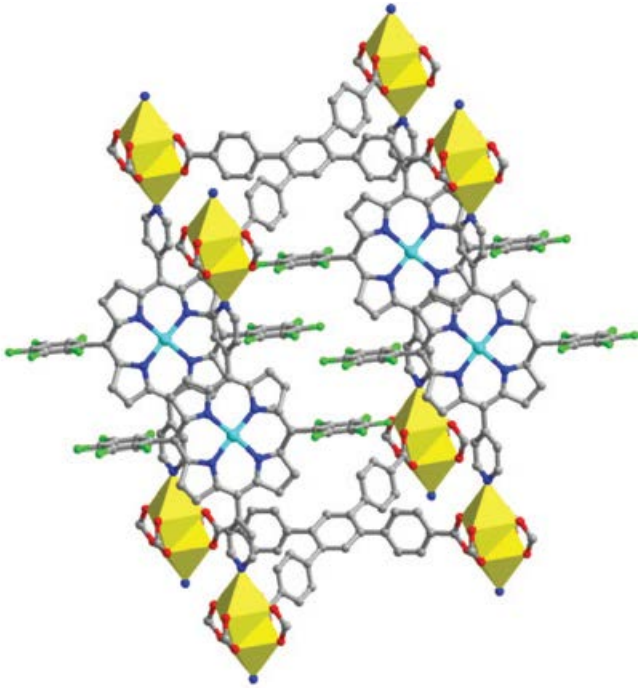
MIL-53

$[Cr(OH)(BDC)]\cdot(H_2BDC)_{0.75}$

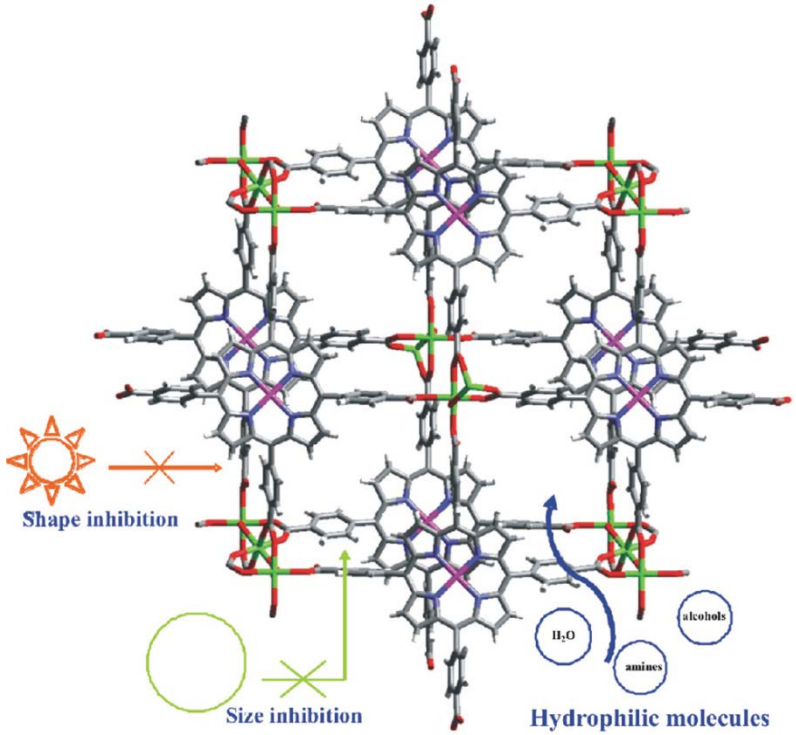
Millange F., Serre C., Férey G., *Chem. Commun.*, **8**, 822-823, **2002**.

Metalloporphyrinic porous MOFs

Functional porphyrinic metal–organic frameworks: crystal engineering and applications
Chao Zou and Chuan-De Wu. *Dalton Trans.,* 2012, 41, 3879



A. M. Shultz, O. K. Farha, J. T. Hupp and S. T. Nguyen, J. Am. Chem.Soc., 2009, 131, 4204.



M. E. Kosal, J.-H. Chou, S. R. Wilson and K. S. Suslick, Nat. Mater., 2002, 1, 118.

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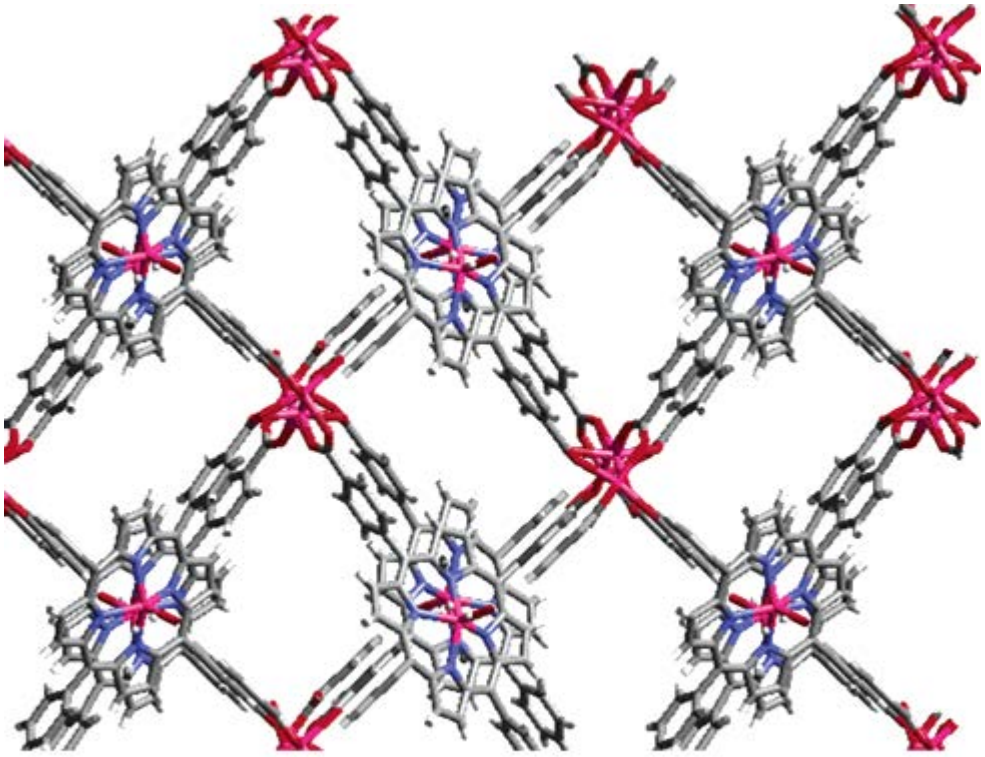
Catalytic Porphyrin Solids



Robust oxidation catalyst for the hydroxylation of a variety of linear and cyclic alkanes and the epoxidation of cyclicalkenes

PIZA-3 network, $(Mn(TpCPP)Mn_{1.5})(C_3H_7NO)\cdot 5C_3H_7NO$

KENNETH S. SUSLICK,* P. BHYRAPPA, J.-H. CHOU, MARGARET E. KOSAL, SHIRLEY NAKAGAKI,DENNIS W. SMITHENRY, SCOTT R. WILSON
Acc. Chem. Res. **2005, 38, 283**

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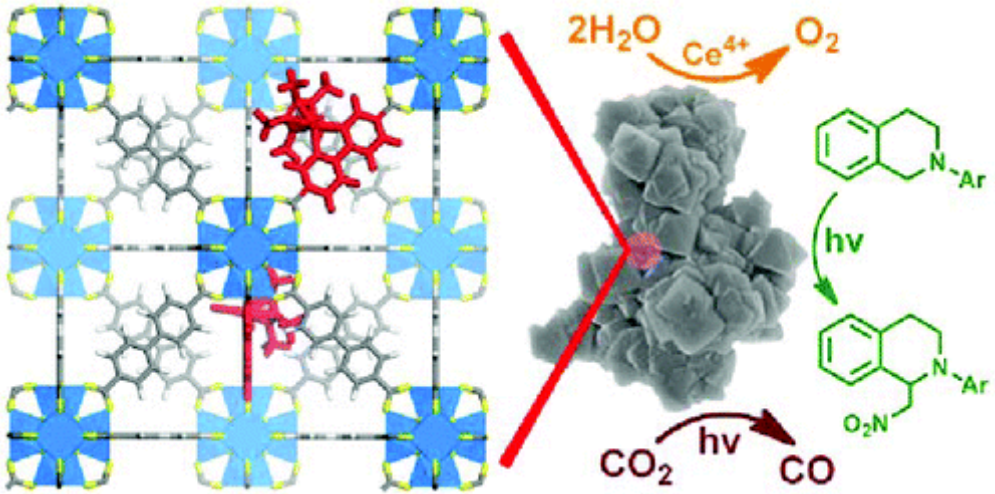
MOFs: platforms to integrate individual functional components

Anchoring a molecular catalyst without substantial change in its structure to an insoluble solid to prevent solution of the catalyst

Catalyst immobilization

Doping Metal–Organic Frameworks for Water Oxidation, Carbon Dioxide Reduction, and Organic Photocatalysis

catalytically competent Ir, Re, and Ru complexes are incorporated into a porous MOF



$Zr_6O_4(OH)_4(bpdc)_6$ (bpdc = *para*-biphenyldicarboxylic acid)

C. Wang, Z. Xie, K. E. de Krafft and W. Lin, *J. Am. Chem. Soc.*, 2011, **133**, 13445.

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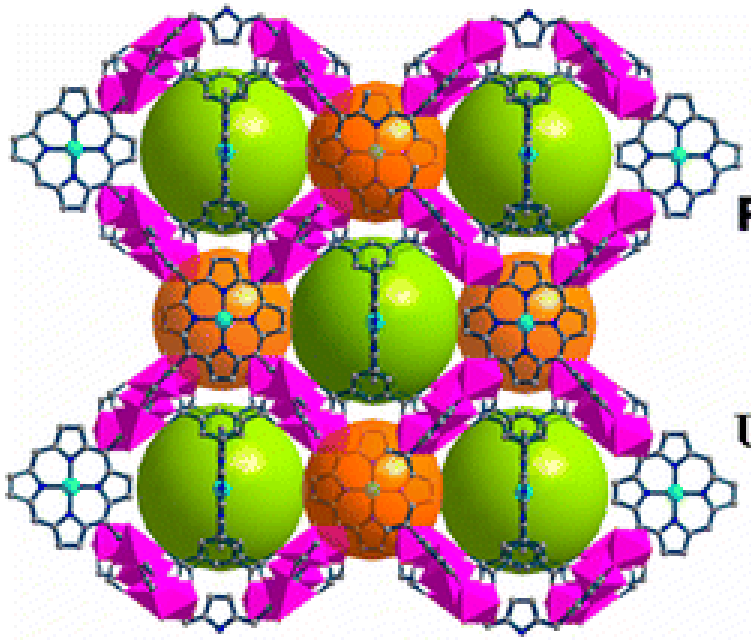
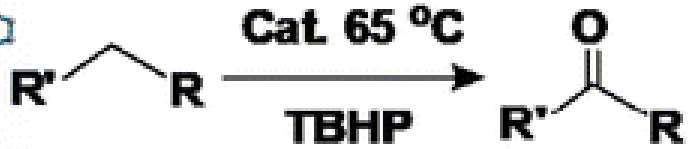
Metalloporphyrinic porous MOFs

Porous Metalloporphyrinic Frameworks Constructed from Metal 5,10,15,20-Tetrakis(3,5-biscarboxylphenyl)porphyrin for Highly Efficient and Selective Catalytic Oxidation of Alkylbenzenes

Xiu-Li Yang, Ming-Hua Xie, Chao Zou, Yabing He , Banglin Chen , Michael O'Keeffe ,Chuan-De Wu

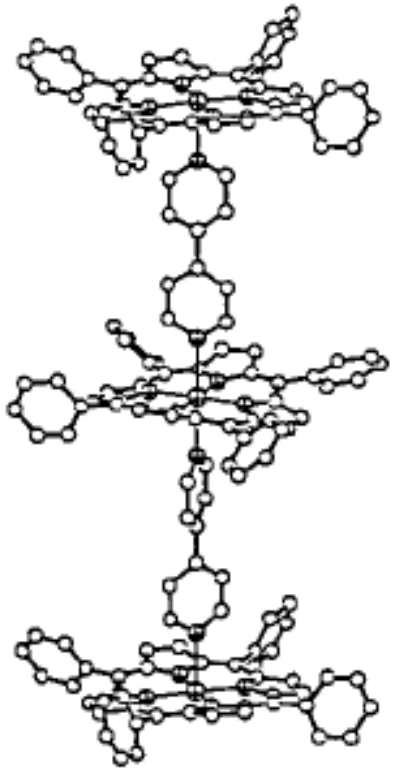
J. Am. Chem. Soc., 2012, 134, 10638





Up to >99% yield and 8076 turnovers

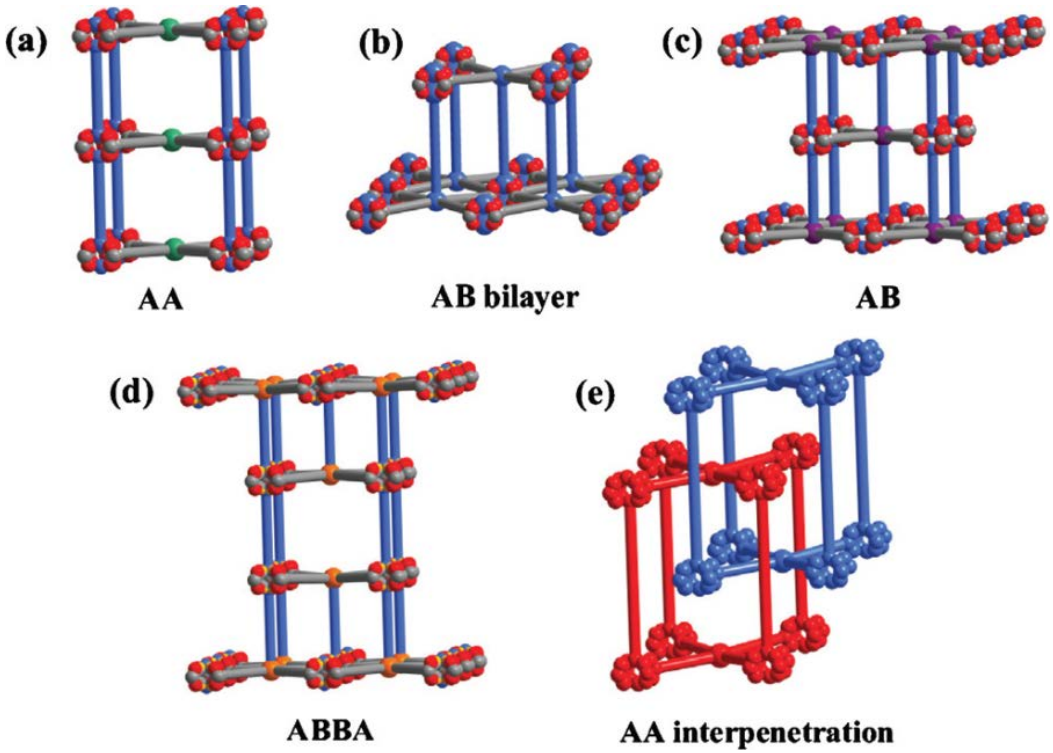
Ligand combinations for metalloporphyrinic porous MOFs



TPP (tetraphenylporphyrin)
+
bipy (4,4´-bipyridine)

Crystal engineering with tetraarylporphyrins, an exceptionally versatile building block for the design of multidimensional supramolecular structures
R. Krishna Kumar, S. Balasubramanian and Israel Goldberg
Chem. Commun., 1998, 1435

Ligand combinations in metalloporphyrinic MOFs



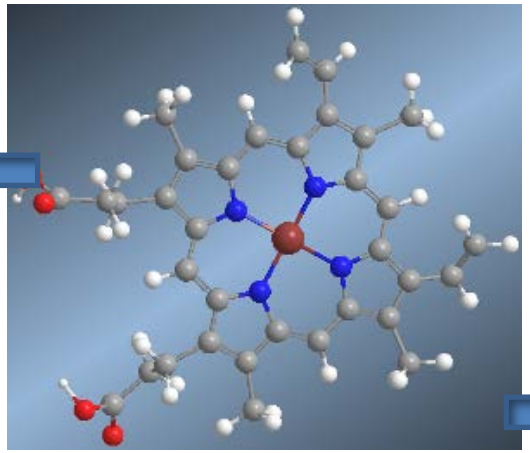
dipyridyl ligands

Classification of the stacking patterns found in the PPFs series with different dipyridyl pillars

L. D. DeVries and W. Choe, J. Chem. Crystallogr., 2009, 39, 229.

Strategy

metalloporphyrins



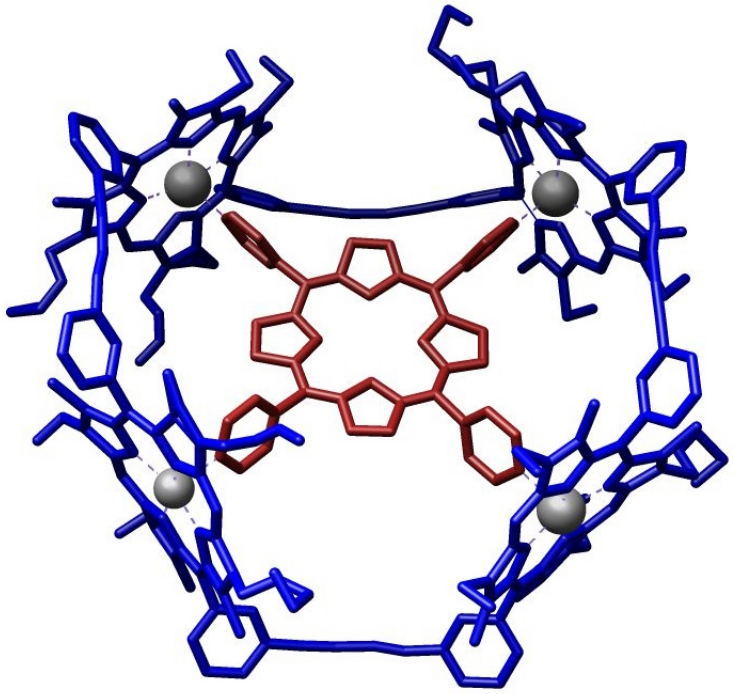
Structural unit
in porous MOFs
host

Catalyst
guest

self-doping

Host-guest chemistry

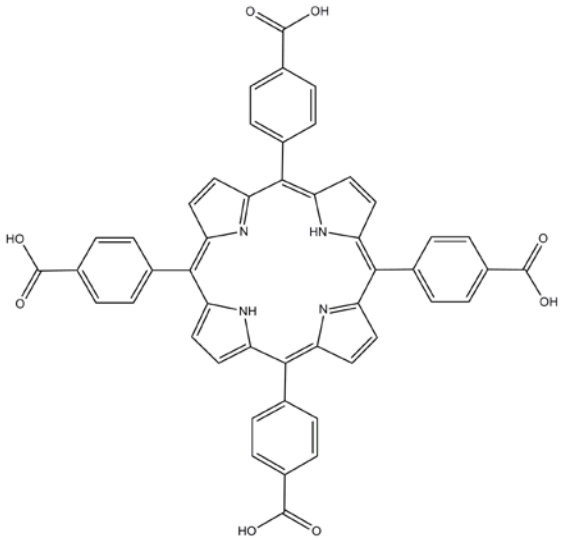
a four-porphyrin-zinc complex hosts a porphyrin guest



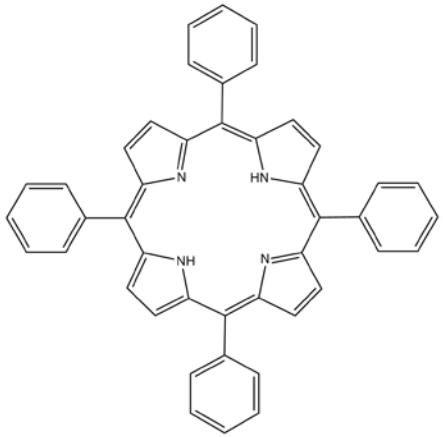
Photoactive Array of Five Porphyrins

Sally Anderson, Harry L. Anderson, Alan Bashall, Mary McPartlin, Jeremy K. M. Sanders (1995). *Angew. Chem., Int. Ed. Engl.* **34** (10): 1096–1099.

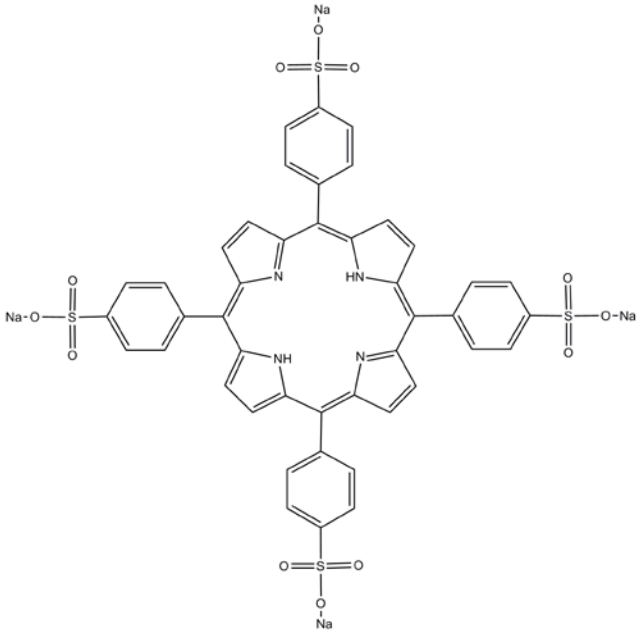
Ligand combinations for metalloporphyrinic porous MOFs



tetra(4-carboxyphenyl)porphyrin
TCPP

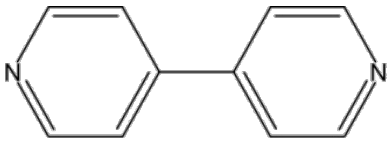


tetraphenylporphyrin
TPP



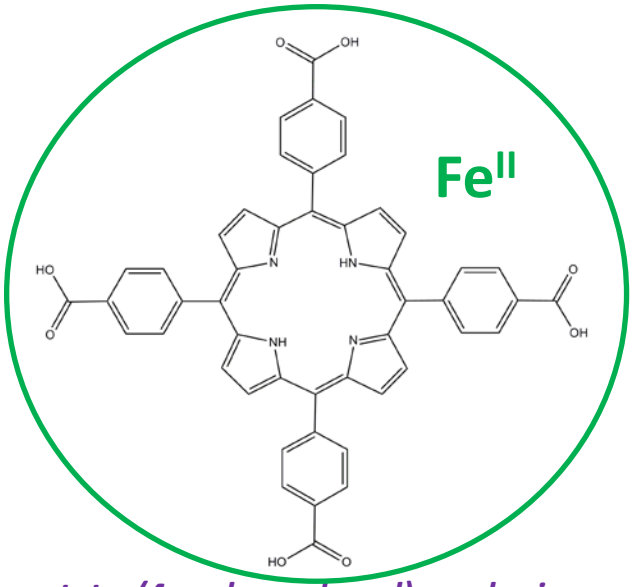
tetraphenylporphine-tetrasulfonic acid tetrasodium salt
TPPS

+

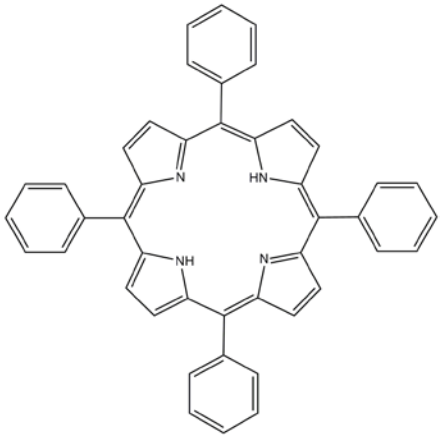


4,4´-bipyridine
bipy

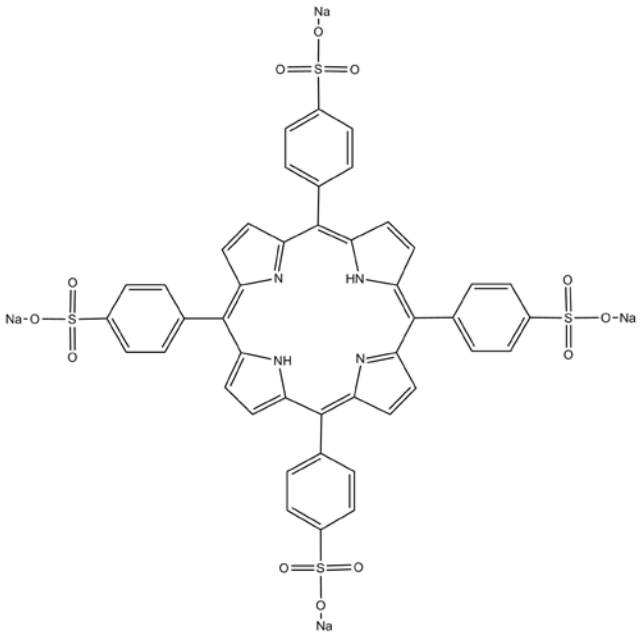
Results



tetra(4-carboxyphenyl)porphyrin
TCPP

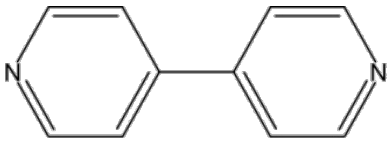


Tetraphenylporphyrin
TPP



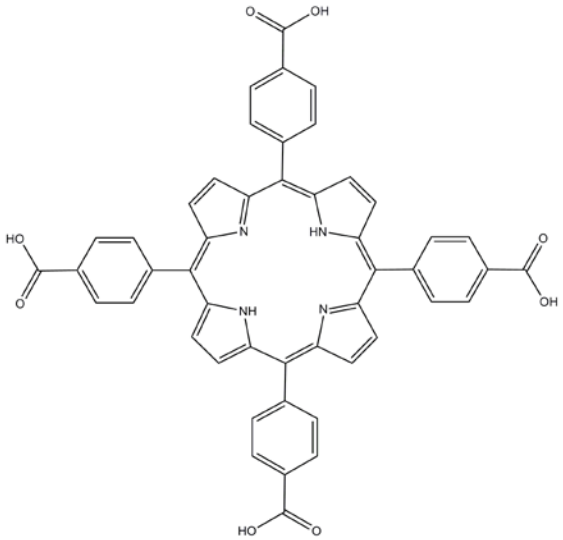
tetraphenylporphine-tetrasulfonic acid tetrasodium salt
TPPS

+

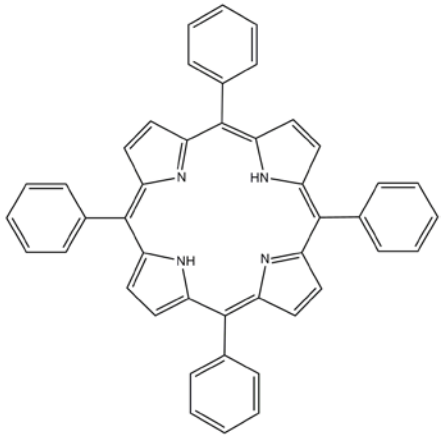


4,4´-bipyridine
bipy

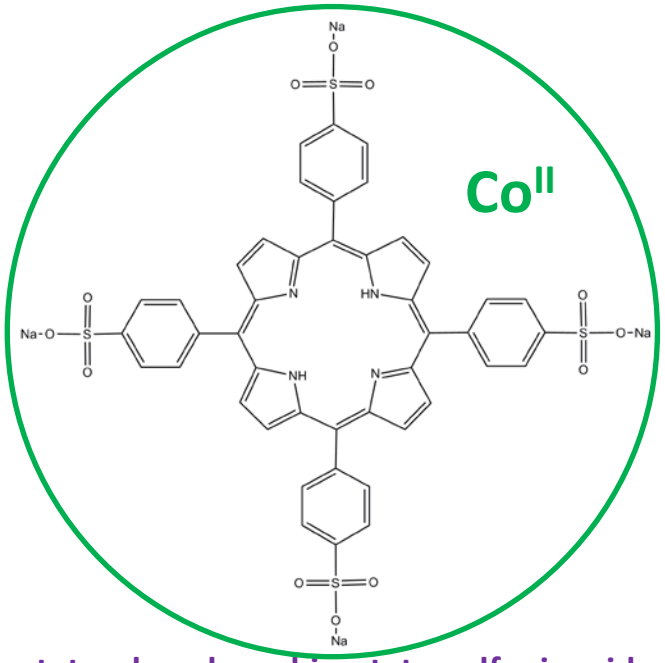
Results



tetra(4-carboxyphenyl)porphyrin
TCPP

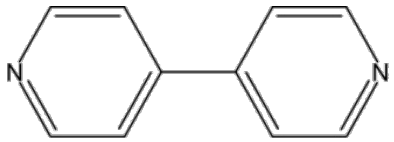


Tetraphenylporphyrin
TPP



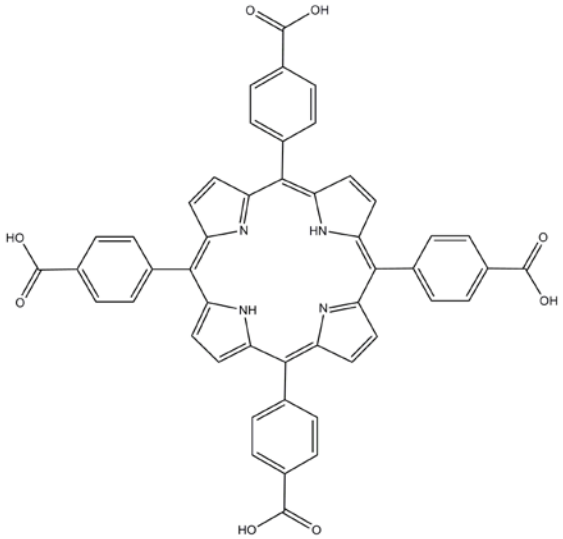
tetraphenylporphine-tetrasulfonic acid tetrasodium salt
TPPS

+

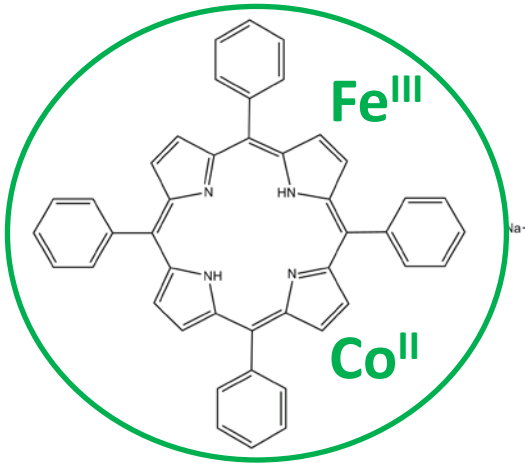


4,4´-bipyridine
bipy

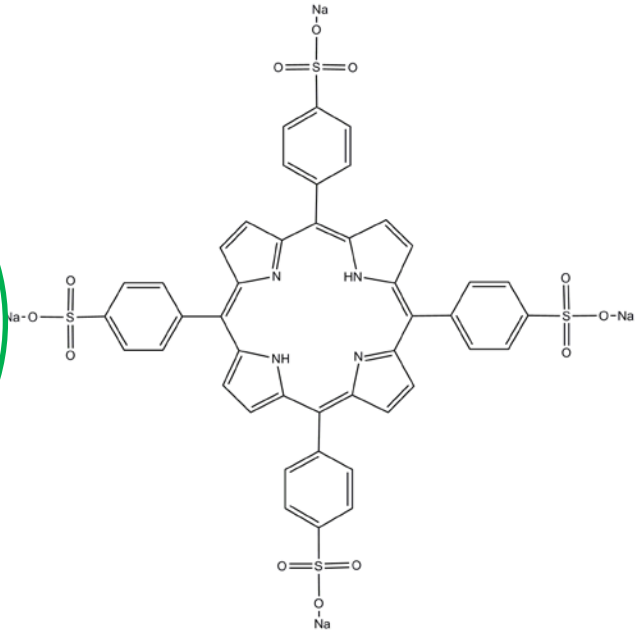
Results



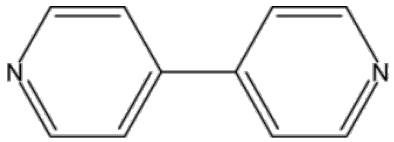
tetra(4-carboxyphenyl)porphyrin
TCPP



Tetraphenylporphyrin
TPP

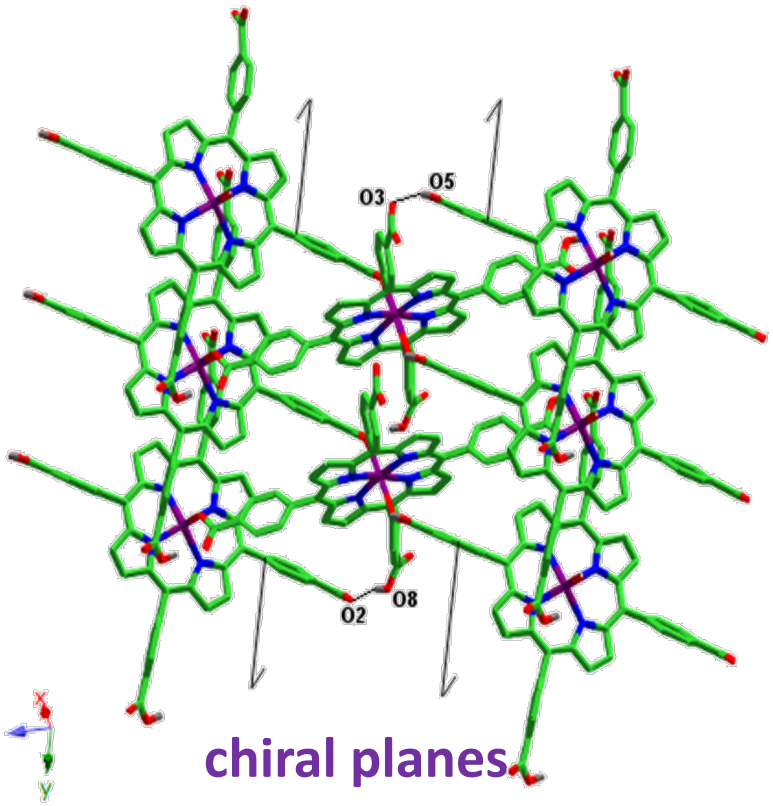


tetraphenylporphine-tetrasulfonic acid tetrasodium salt
TPPS

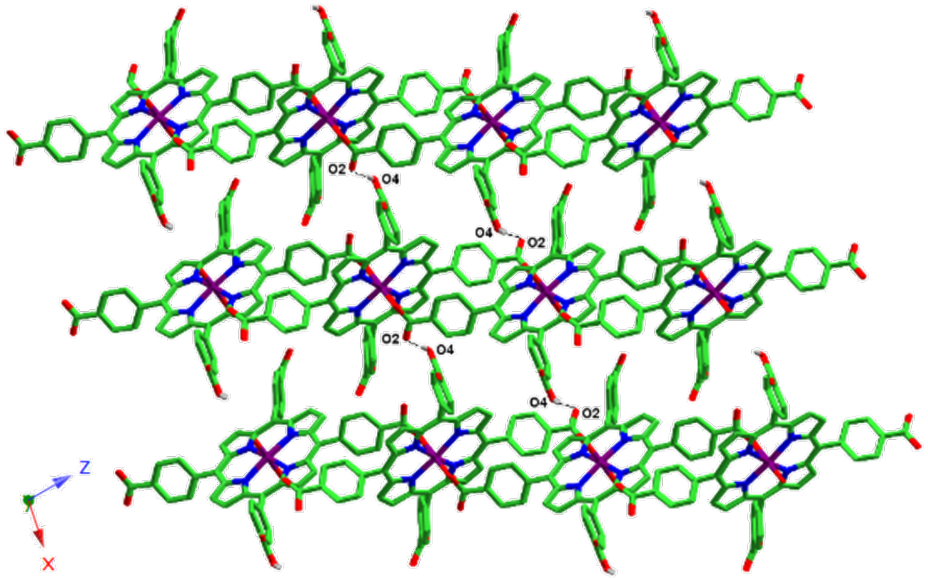


4,4´-bipyridine
bipy

Results [*FeTCPP*]



chiral planes



chiral 3D framework based on hydrogen bonds

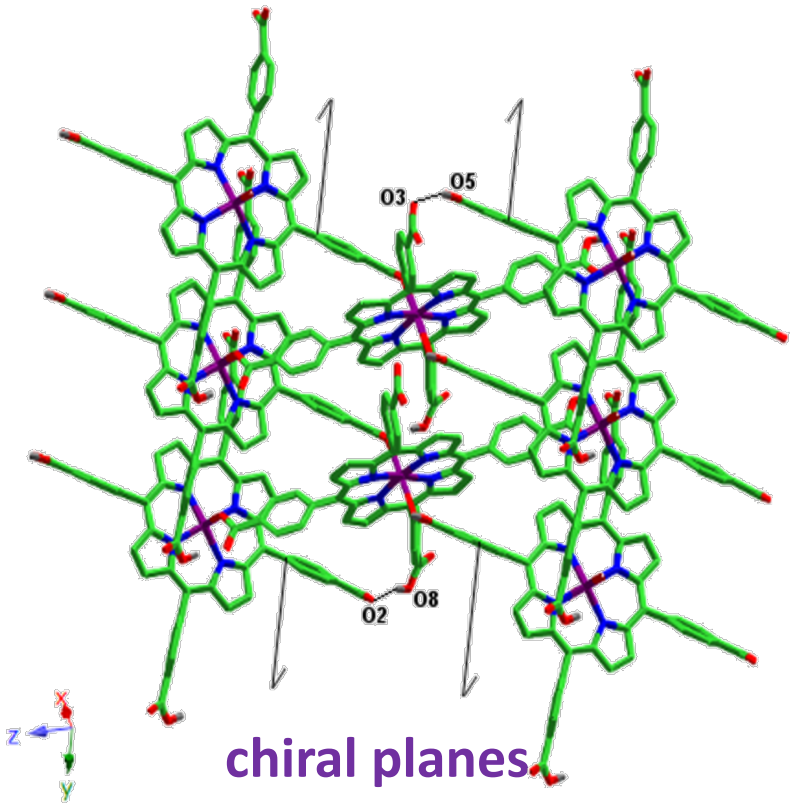
third example of a 2D coordination compound based on TCPP in which the dimensionality refers just to coordination bonds, and no other ligands are present in the structure

M. Shmilovits, M. Vinodu, I. Goldberg, New J. Chem. 28 (2004) 223.

S. George, S. Lipstman, S. Muniappan, I. Goldberg, CrystEngComm 8 (2006) 417.

Fidalgo-Marijuan A., Barandika G., Bazán B., Urtiaga M. K., Arriortua M. I., *Polyhedron*, **30**, 2711–2716, **2011**.

Results [*FeTCPP*]



chiral planes

Absence of bipy

Oxidation of the original Fe^{II} to Fe^{III}

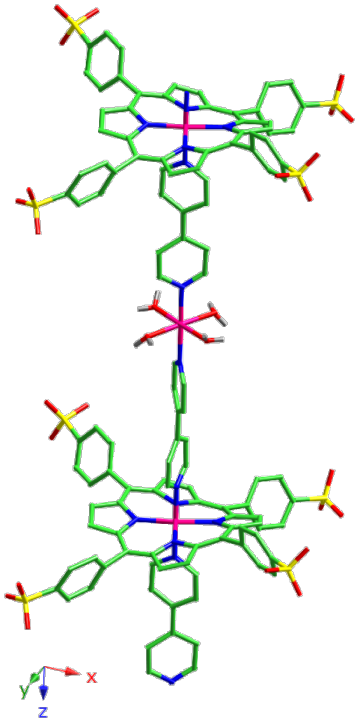
$TCPP^{-3}$: asymmetric deprotonation

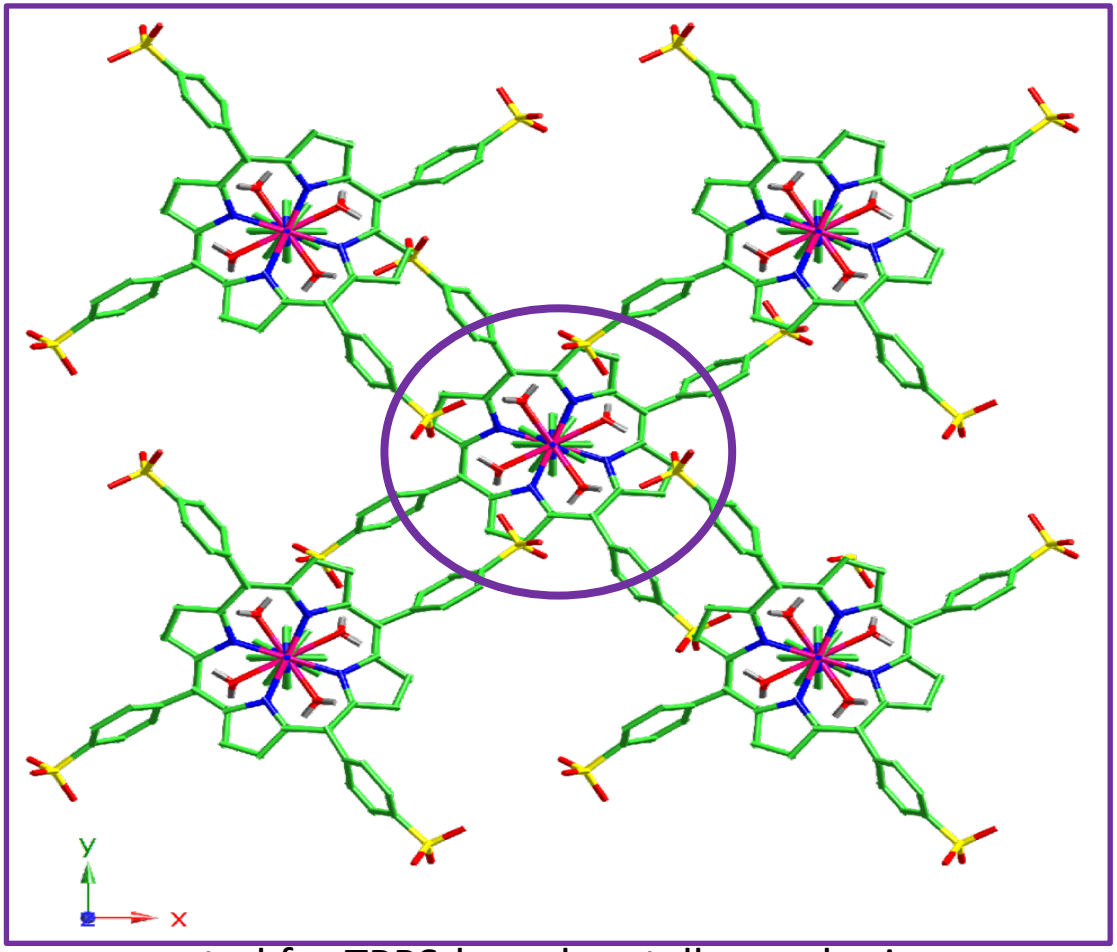
DFT calculations: Pearson acidity

Reproducibility!!!!!

Results

$[Co_2TPPS(bipy)_2(H_2O)_4]\cdot 6H_2O$



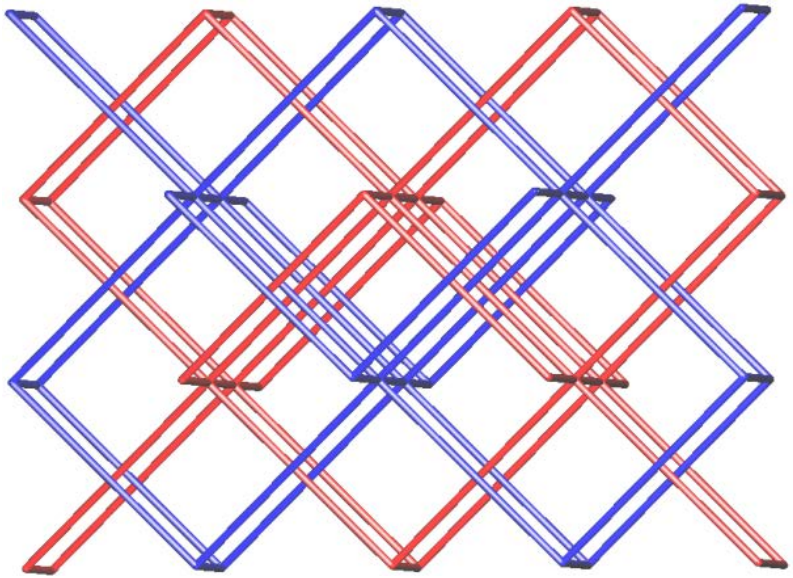


- first CoTPPS coordination network
- just 4 crystalline compounds have been reported for TPPS-based metalloporphyrins
- unprecedented extension fashion

H. Kanemitsu, R. Harada and S. Ogo, *Chem Commun*, 2010, **46**, 3083.
W.-T. Chen, Y. Yamada, G.-N. Liu, A. Kubota, T. Ichikawa, Y. Kojima, G.-C. Guo and S. Fukuzumi, *Dalton Trans.*, 2011, **40**, 12826.
W.-T. Chen, Z.-G. Luo, J.-H. Liu, H.-L. Chen and H.-M. Kuang, *J. Chem. Res.*, 2011, **35**, 571.

Results

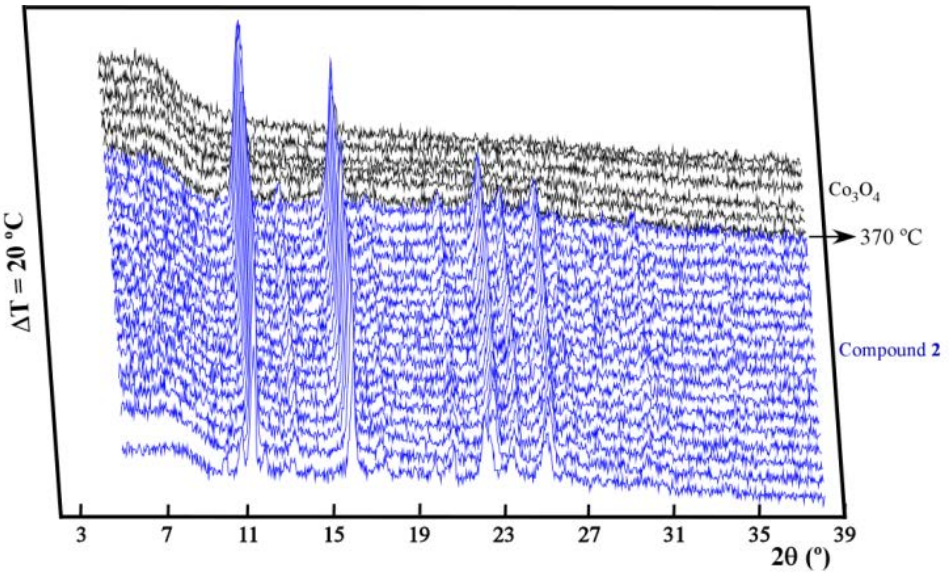
$[Co_2TPPS(bipy)_2(H_2O)_4]\cdot 6H_2O$



2-fold interpenetrated 6-c nets framework

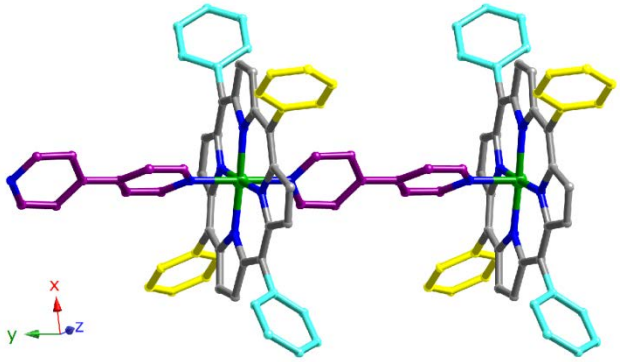
Hydrogen bond system

High thermal stability



Results

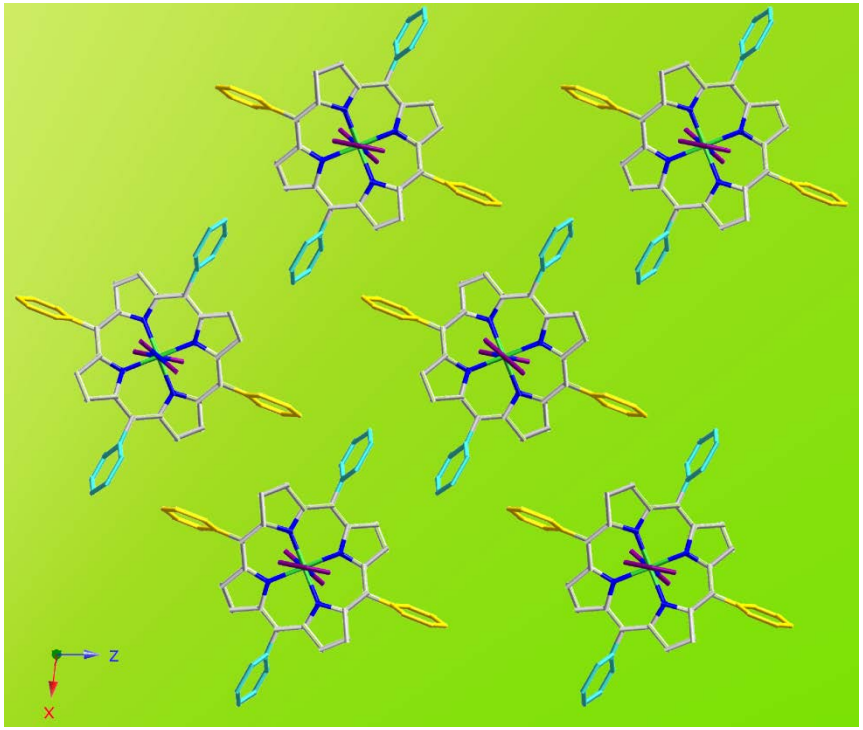
$([Fe(TPP)bipy]^{\bullet})_n$



Chemical formula suggests that the metal ion is Fe^{II}

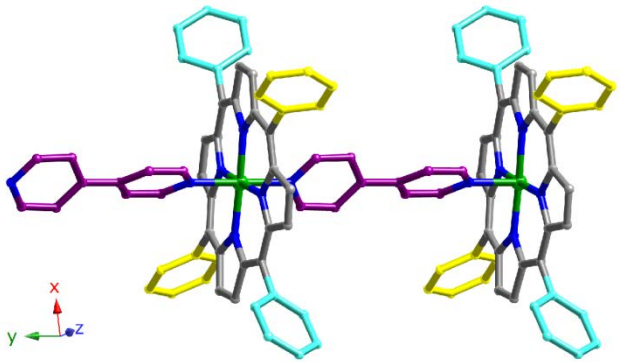
The reactant, [Fe(TPP)Cl], contains Fe^{III}

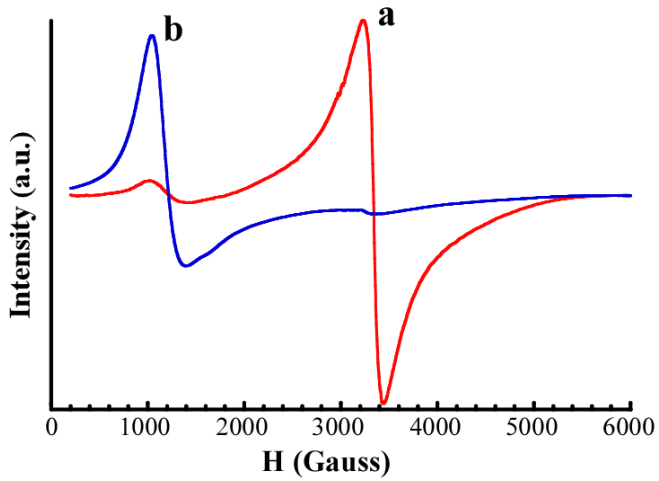
The behaviour of $([Fe(TPP)bipy]^{\bullet})_n$ is just compatible with the presence of low-spin Fe^{III}



face-to-face and *edge-to-face* π bonds

Results $([Fe(TPP)bipy]^{\bullet})_n$





X-band EPR spectrum (RT) for (a) $([Fe(TPP)bipy]^{\bullet})_n$ and (b) the reactant [Fe(TPP)Cl].

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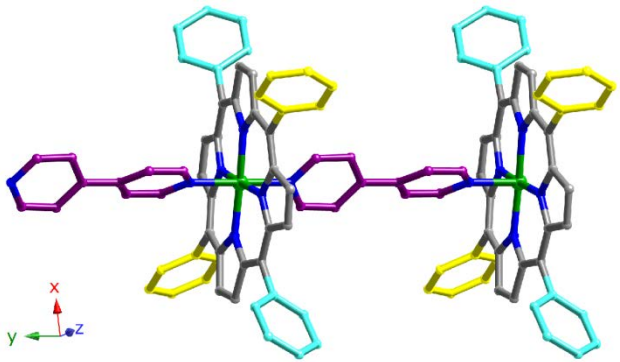
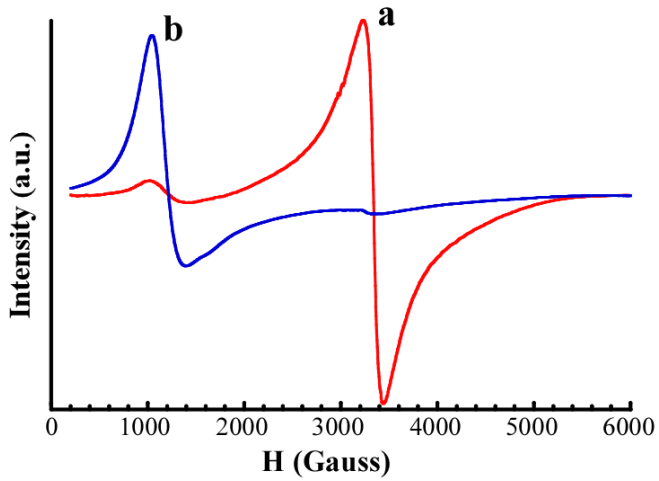
Interpretations for the principal signal (g ≈2)

1) high-spin Fe^{III} ions in very low concentration in relation to the bulk of the analysed sample

2) low-spin Fe^{III} ions with either significant magnetic interactions between metal centres having different orientations or interactions with free radicals.

Results $([Fe(TPP)bipy]^{\bullet})_n$





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Interpretations for the principal signal (g ≈2)

~~1) high-spin Fe^{III} ions in very low concentration in relation to the bulk of the analysed sample~~

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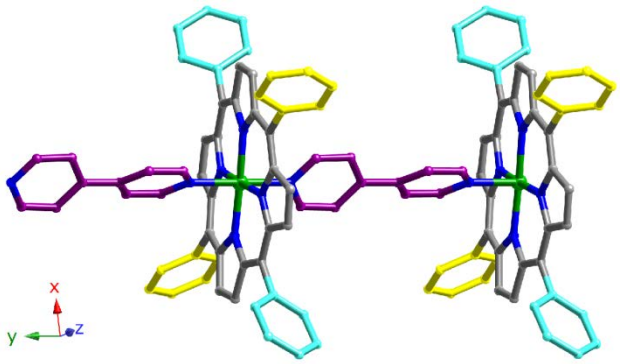
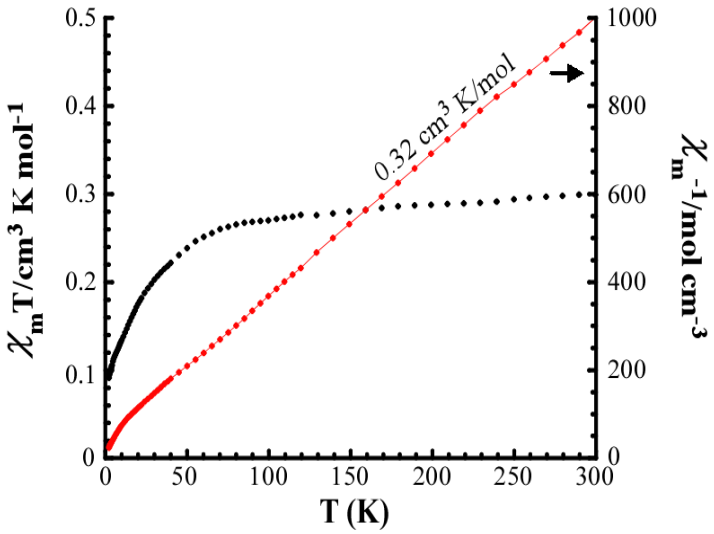
discarded by X-band EPR at 100 K that indicates the presence of antiferromagnetic interactions

Results $([Fe(TPP)bipy]^{\bullet})_n$





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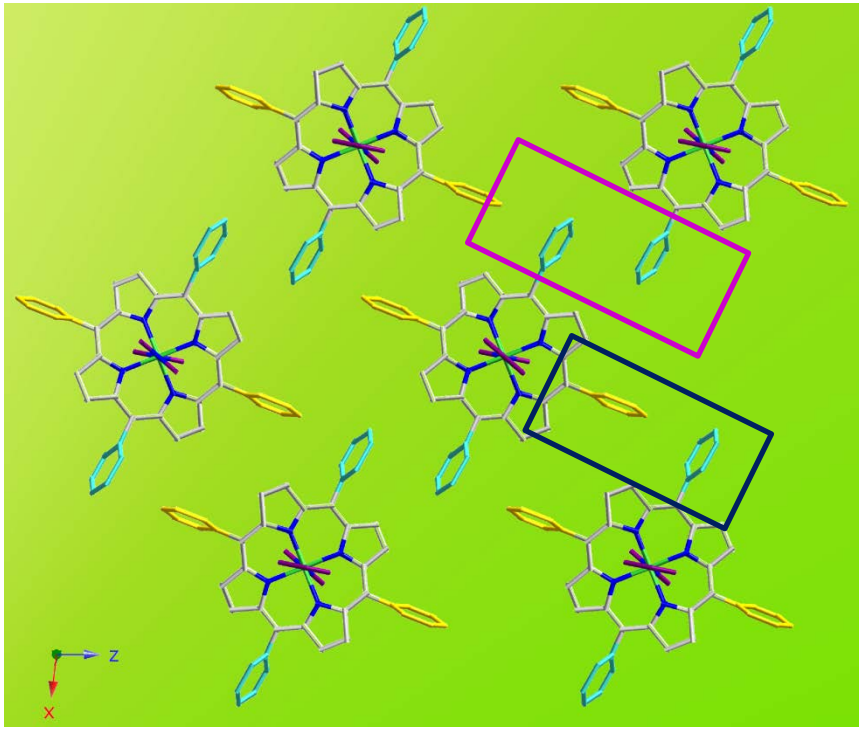
low-spin Fe^{III} ions with either significant magnetic interactions between metal centres having different orientations or interactions with free radicals.

Confirmed by magnetic susceptibility measurements

Results $([Fe(TPP)bipy]^{\bullet})_n$



Hypothesis

$TPP^{-2} + 1e \rightarrow TPP^{-3}$

Where are those electrons?

Low spin Fe^{III} (d^5): 1 e-

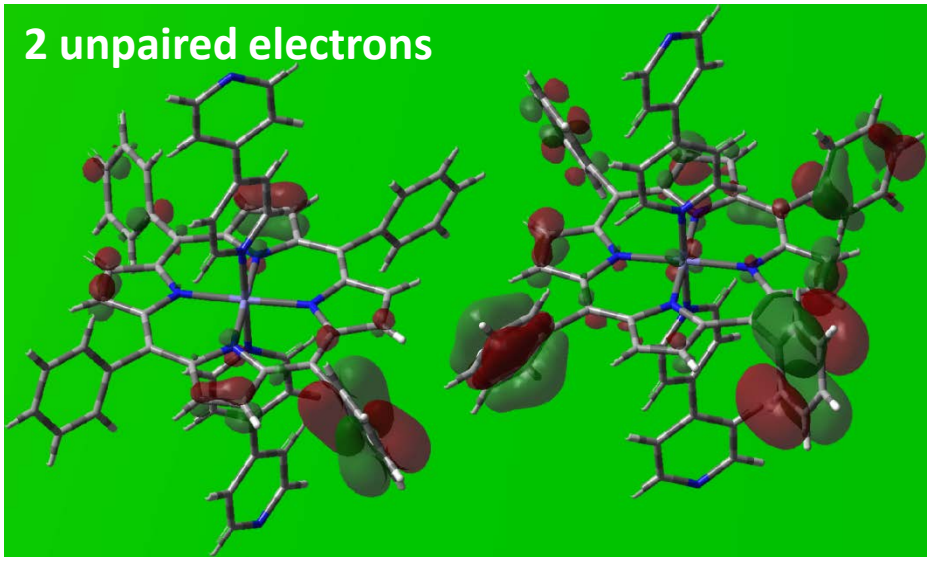
TPP^{-3}: 1 e-

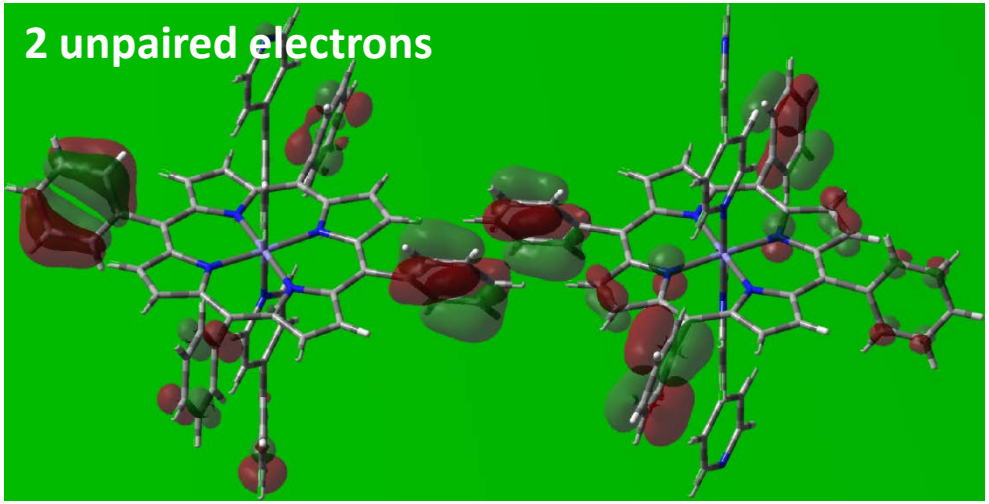
DFT calculations: $([Fe(TPP)bipy_2]^{\bullet})_2$

1) 4 unpaired electrons
2) 2 unpaired electrons

Results

$([Fe(TPP)bipy]^{\bullet})_n$

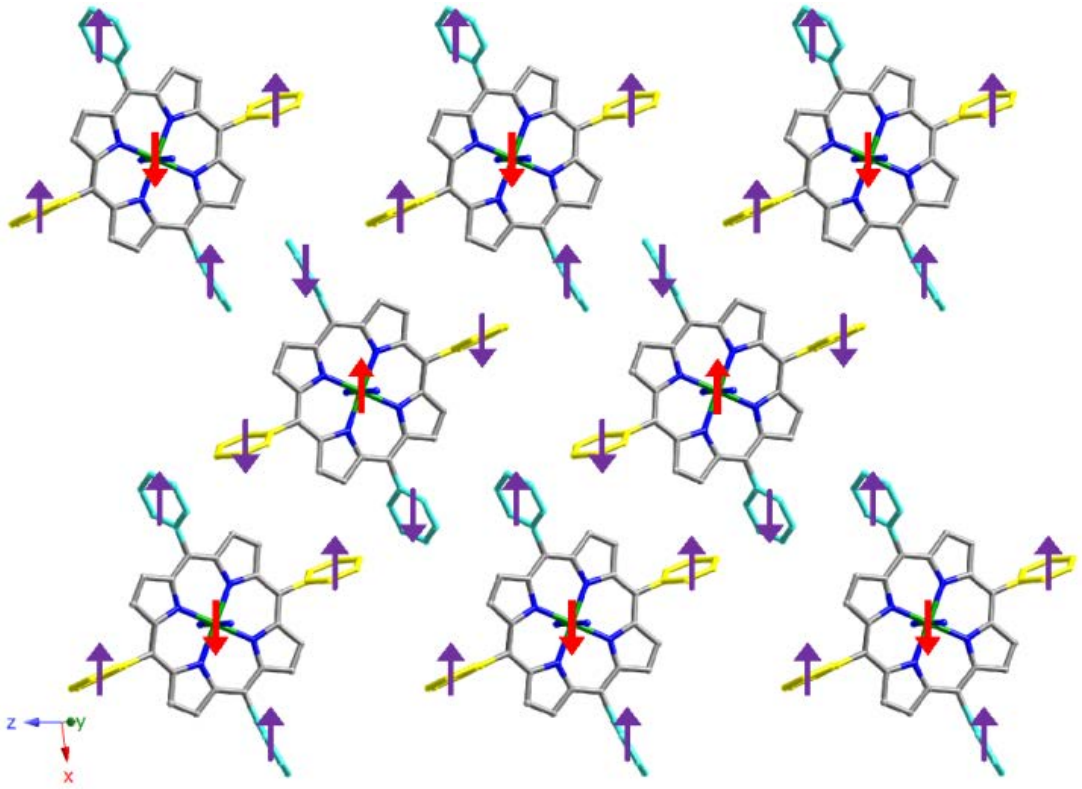




the extra electrons are paired in molecular orbitals formed by the phenyl rings

Results

$([Fe(TPP)bipy]^{\bullet})_n$

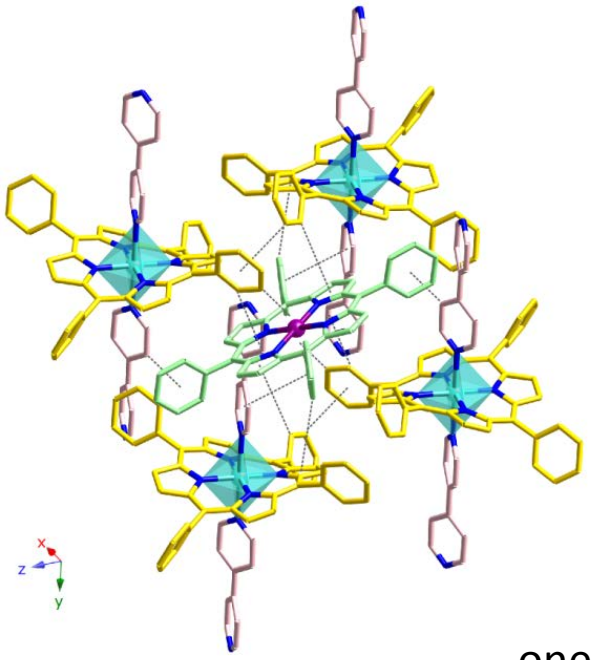


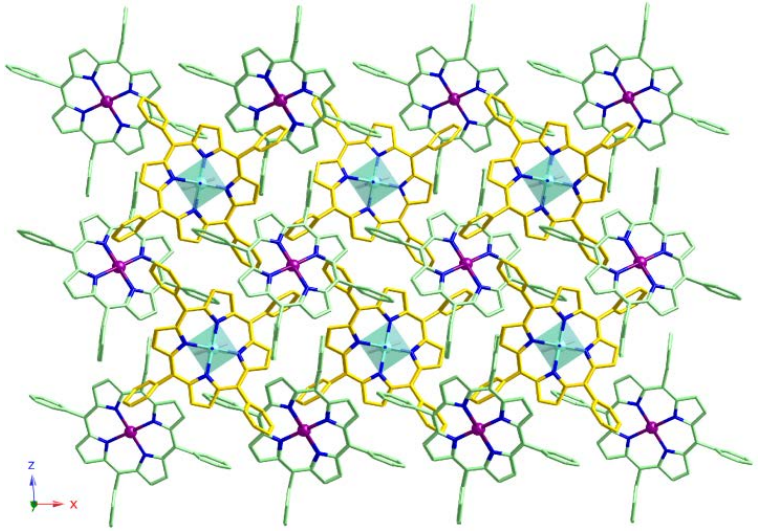
↑ 0.25 e-

↑ 1 e-

Results

$[CoTPP(bipy)]\cdot(CoTPP)_{0.22}\cdot(TPP)_{0.78}$





one-step self-doping

78% of the immobilized metalloporphyrins have lost the metal

no catalytic activity has been detected

Conclusion

Much more work must be carried out….

Acnowledments

- Ministerio de Ciencia e Innovación
- Gobierno Vasco
- UPV/EHU
- SGIker

- Xavi Sala, UAB, Barcelona
- Antoni Llobet, ICIQ, Tarragona
- Joan Aguiló, ICIQ, Tarragona

Thank you for your attention!