Metalloporphyrin-based MOFs: First Cobalt Based TPPS-bipy Coordination Network

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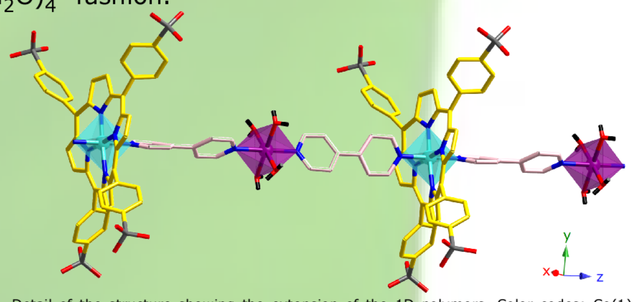
Introduction

Supramolecular entities based on self-assembly of metalloporphyrins are paradigmatic examples of the great efficiency of the nanodevices used by natural systems in photosynthesis, oxygen transport, electron transfer and catalysis.[1] Thus, porphyrin catalysts are well-known to be highly efficient and, during the last years, a great effort has been devoted to the immobilization of distinct types of catalysts on solids.[2] In this sense, recent strategy consists of the immobilization of catalysts in MOFs,[3,4] and, in our group we have started exploring the possibility of using metalloporphyrins both as structural units in MOFs and catalyst,[5] in the same compound.

The work herein presented correspond to the compound $[CoTPPS_{0.5}(bipy)(H_2O)_2]\cdot 6H_2O$, as far as we know, this is the first with Co-TPPS and bipy (TPPS=*meso*-tetra(4-sulfonatophenyl)-porphyrin and bipy=4,4`-bipyridine) , and from a crystallographic point of view, this is an unprecedented bimetallic chain for this type of systems.

Crystal structure

Crystal structure of $[CoTPPS_{0.5}(bipy)(H_2O)_2]\cdot 6H_2O$ consists of 1D polymers where CoTPPS units are axially bonded to bipy ligands along the [001] direction. The extension of the 1D polymers consists of the link between alternating metal centres according to the bipy-CoTPPS-bipy-$Co(H_2O)_4$- fashion.

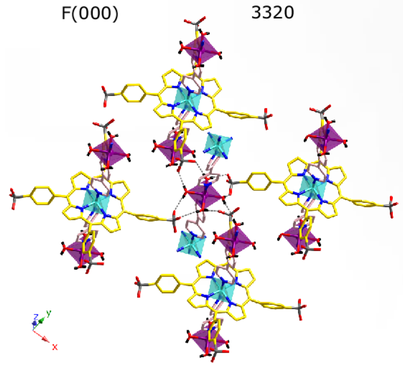


Detail of the structure showing the extension of the 1D polymers. Color codes: Co(1) (TPPS) in turquoise, Co(2) in purple, N in blue, C (TPPS) in yellow, C (bipy) in pink, O in red, S in grey.

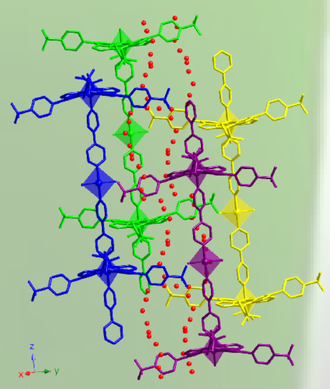
Crystal Data

Empirical formula	$C_{32}H_{36}CoN_4O_{14}S_2$
Formula weigth	811.62 g/mol
Crystal system	Tetragonal
Space group	$I4_1/a$
Cell dimensions	a=17.9776(2) Å
	c=22.3657(3) Å
Volume	7225.55(15) Å^3
Z, ρ_{calc}	8, 1.492 g/cm^3
F(000)	3320

This compound exhibits a robust system of H-bonds that reinforce the stability of the framework. This way, each chain is surrounded by another four, and multiple H-bonds are formed between the coordination molecules of water and the termonal SO_3 groups of the TPPS.



H-bond system represented by dashed grey lines

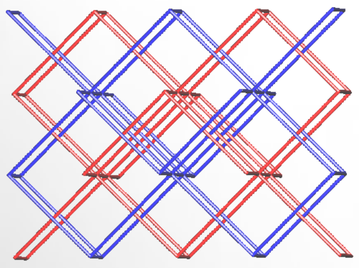


Detail of the structure showing relative position of the chains. Crystallization molecules of water are shown in red.

The relative position of the chains give rise to cavities where crystallization molecules of water are located, forming a disordered chain along the [001] direction, reinforcing the robustness of the H-bond system.

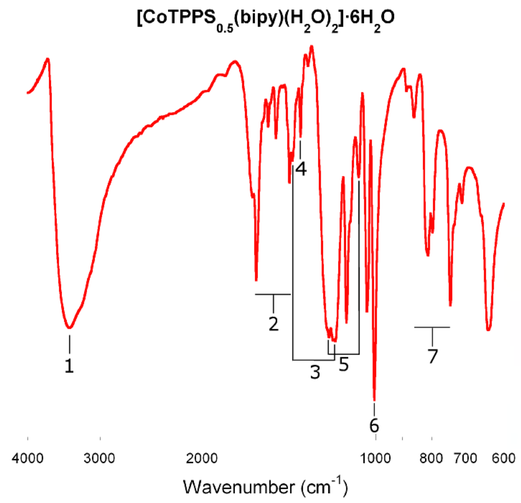
Topology

The topology for $[CoTPPS_{0.5}(bipy)(H_2O)_2]\cdot 6H_2O$ is a pcu α-Po primitive cubic net. This consists on a two-fold interpenetrated 6-c nets framework (Point Symbol= $4^{12}.6^3$)



Topology of the two-fold interpenetrated net

Infrared spectroscopy



1- 3397 cm^{-1} (OH)

2- 1624-1410 cm^{-1} (C=C)

3- 1394 and 1174 cm^{-1} (SO)

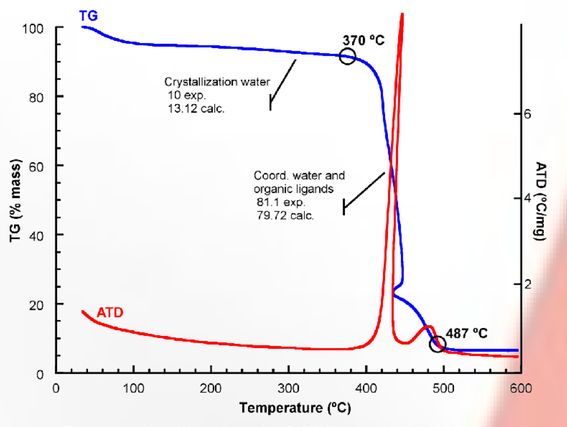
4- 1349 cm^{-1} (CN)

5- 1208 and 1076 cm^{-1} (bipy)

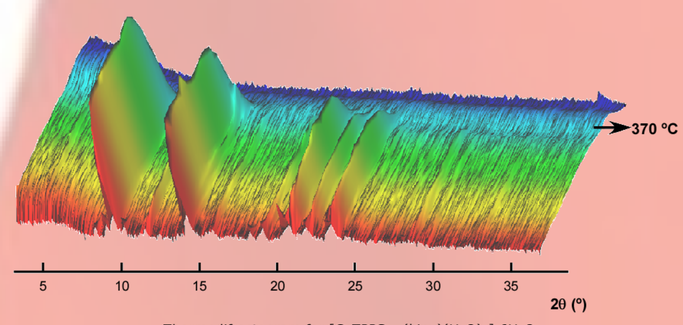
6- 1000 cm^{-1} (CoTPPS)

7- 863 and 744 cm^{-1} (CH)

Thermal characterization



Thermogravimetric analisys for $[CoTPPS_{0.5}(bipy)(H_2O)_2]\cdot 6H_2O$



Thermodifractogram for $[CoTPPS_{0.5}(bipy)(H_2O)_2]\cdot 6H_2O$

Conclusions

- $[CoTPPS_{0.5}(bipy)(H_2O)_2]\cdot 6H_2O$ is the first extended system with this metalloporphyrin combination.

- The extension of the 1D polymers, from a crystallographic point of view, is an unprecedented bimetallic chain for this type of systems.

- An extended hydrogen bond system along with an intricate topology are probably the responsible of a remarkably high thermal stability for this compound.

References

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Acknowledgements

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