Characterization of a cobalt based TPP-bipy coordination polymer

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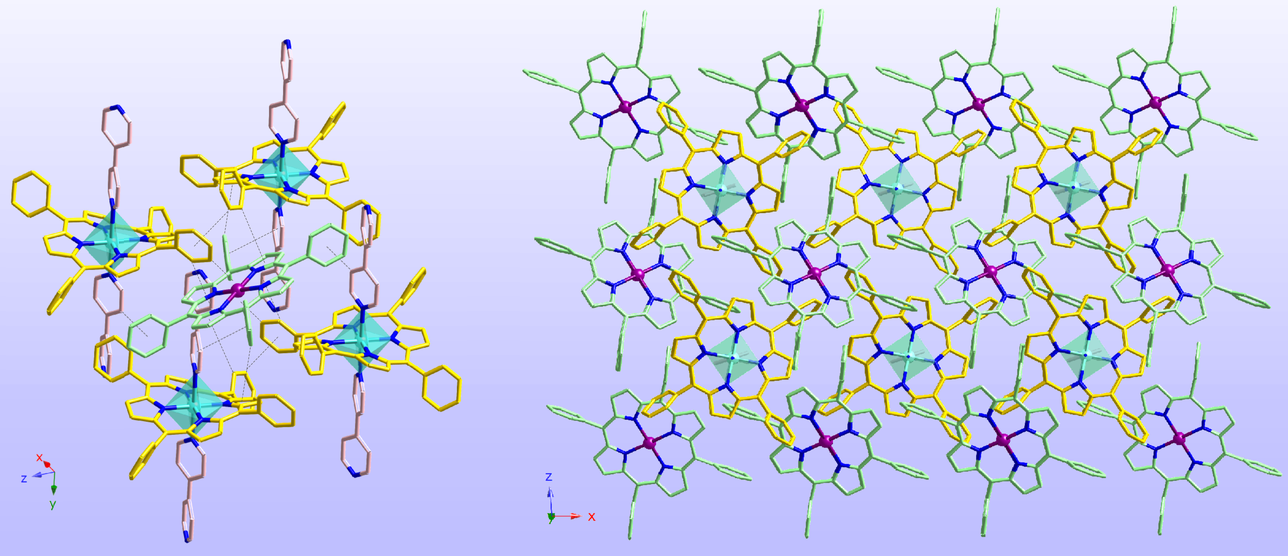
Introduction

Metalloporphyrin systems 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.[1] Cobalt porphyrins are well-known to be prominent catalysts for oxygen reduction reactions (ORR),[2] and in this context, this work was focused on the preparation of metalloporphyrin-based coordination networks where metallopophyrin (MP) is intended to act both as synthon and guest molecule. Our strategy to obtain these materials consists of the conbination of CoP, where P is TPP (TPP=*meso*-tetraphenylporphyrin) with dipyridylic ligands like 4, 4´-bipyridine (bipy).[3]

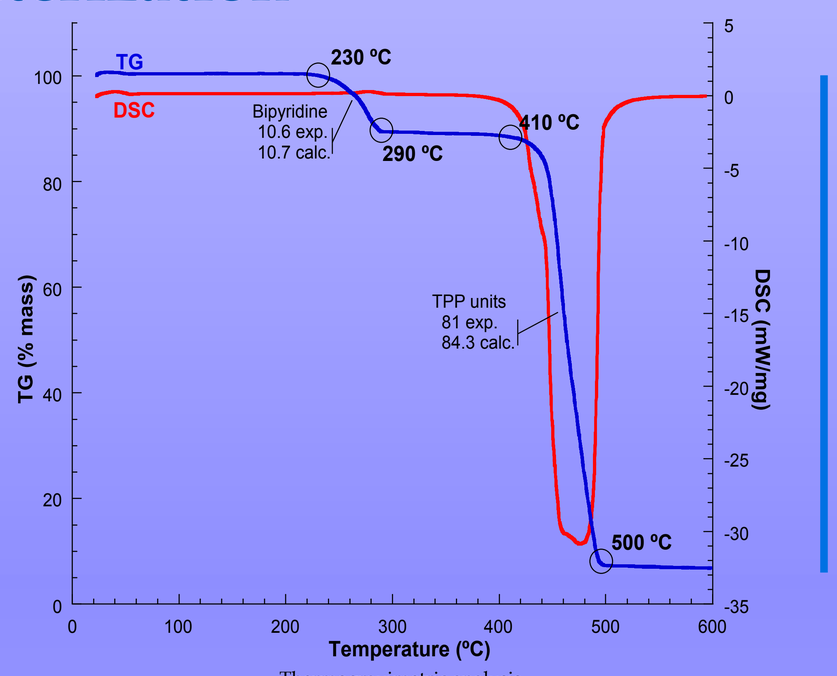
This work consists of the characterization of $[CoTPP(bipy)]\cdot[CoTPP]_{0.22}\cdot TPP_{0.78}$ compound, which can be described as 1D polymers forming cavities where CoP isolated units are immobilized trough a intricate π–π bond system.



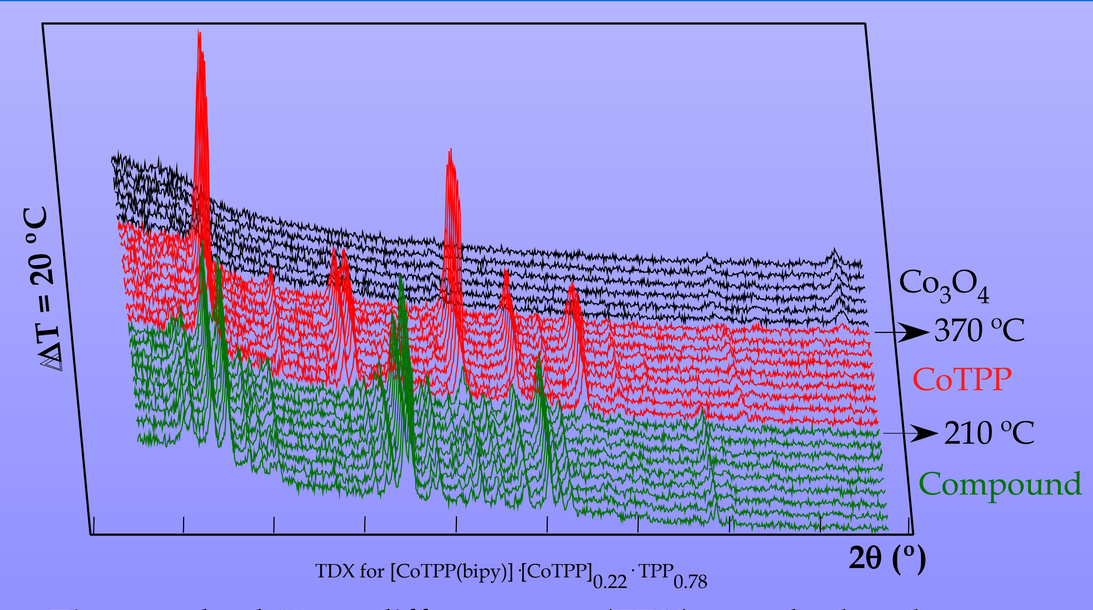
Views of the π-bonding system (dashed lines) and packing of the 1D polymers for $[CoTPP(bipy)]\cdot[CoTPP]_{0.22}\cdot TPP_{0.78}$. Colour codes: Co1 (TPP chain) in turquoise, Co2 (isolated TPP) in purple, N in blue, C (TPP chain) in yellow, C (isolated TPP) in green, C (bipy) in pink.

Thermal characterization

The thermogravimetric decomposition curve for $[CoTPP(bipy)]\cdot[CoTPP]_{0.22}\cdot TPP_{0.78}$ shows a two stage mass loss. The first step occurs between 230-290 ºC with a 10.6% weight loss, and the second from 410 ºC to 500 ºC with an 81% weight loss. These mass percentages are close to the theoretical values for bipyridine (10.7%) for the first stage and for the polymeric and isolated CoTPP and TPP molecules (84.3%) for the second stage.



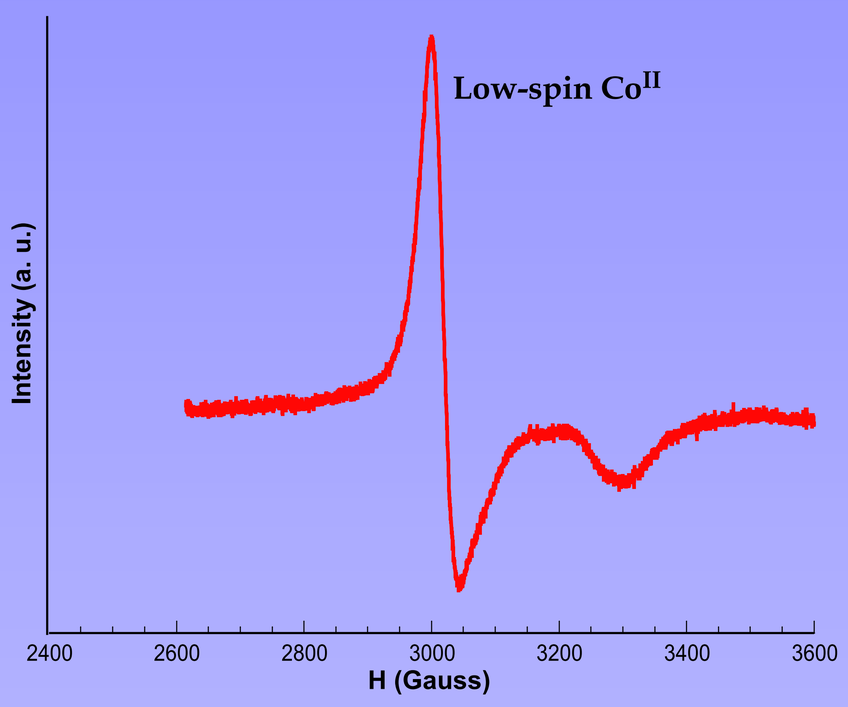
Thermogravimetric analysis



TDX for $[CoTPP(bipy)]\cdot[CoTPP]_{0.22}\cdot TPP_{0.78}$

Time-resolved X-ray diffractometry (TDX) reveals that the compound is thermally stable until 190 ºC. At 210 ºC, in accordance to the thermogravimetry, the bipy molecules abandon the network, giving rise to CoTPP.

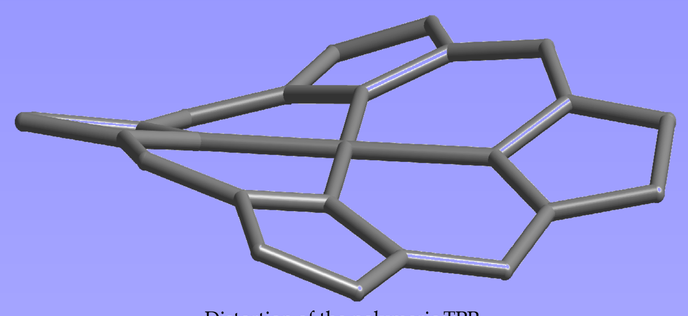
EPR



Electron Paramagnetic Resonance (EPR) X-band spectrum at 5 K shows a low-spin Co(II) typical signal with g = 2 value.

NSD analysis

The distortion of the porphyrin cores were analysed by the normal coordinate structural decomposition method (NSD) developed by Shelnutt *et. al.*[4], indicating a ruffled type (B_{1u}) distortion for the polymeric porphyrin. The contribution of this type of distortion (1.4813) to the total of out-of-plane displacements is 82 %. On the other hand, the isolated porphyrin is totally planar.



Distortion of the polymeric TPP

Conclusions

- We have obtained a CoTPP-bipy based coordination network with immobilized CoTPP units.
- The immobilization is due to a strong π–π bond system that results in a dense network.

References

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Acknowledgements

This work has been financially supported by the Ministerio de Ciencia e Innovación (MAT2010-15375) and the Gobierno Vasco (Basque University System Research Groups, IT-177-07), which we gratefully acknowledge. SGIker (UPV/EHU) technical support (MEC, GV/EJ, European Social Fund) is gratefully acknowledged. A. Fidalgo-Marijuan thanks the UPV/EHU fellowships.