Self-assembly of metallated TPP porphyrin by external dipyridyl ligands

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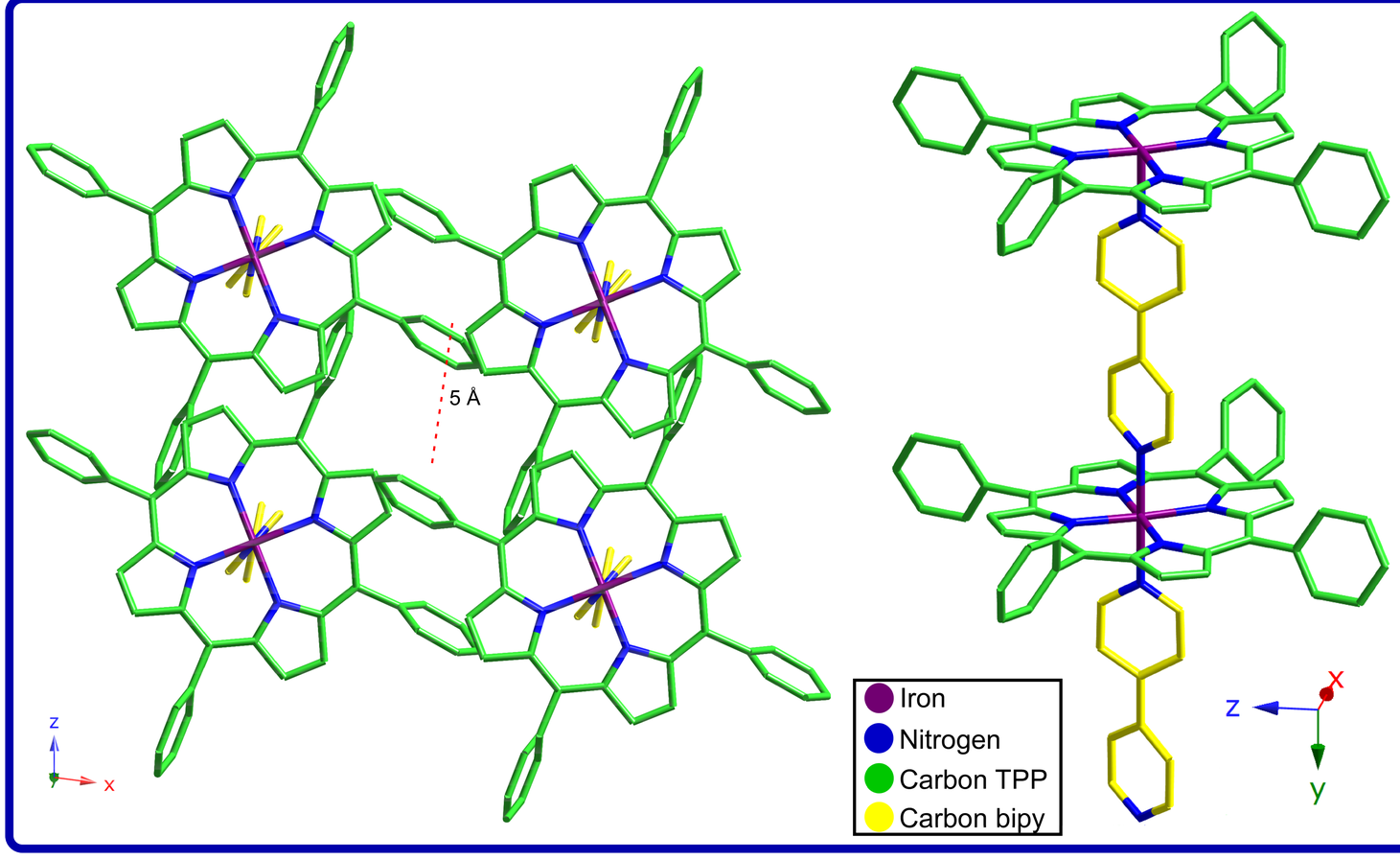
Introduction

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]. Therefore, they constitute reference models for the development of new materials that make these, and other yet unexplored, functions.

While metalloporphyrin biosystems operate in solution, the preparation of materials based on these macrocycles moves the problem to the solid state synthesis. Our research group is working on the preparation of materials based on organic ligands and metalloporphyrins, and the work herein presented corresponds to the compound [FeTPP(bipy)] (TPP=meso-tetraphenylporphyrin and bipy=4,4´-bipyridine), obtained by solvothermal synthesis.

Crystal Structure



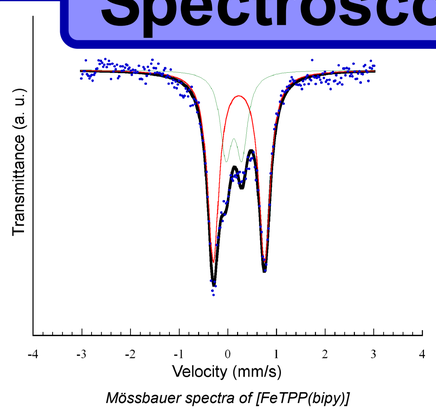
Crystal structure of [FeTPP(bipy)] consists of iron TPP units pillared by 4,4´-bipyridine ligand. The iron atom is octahedrally coordinated to four coplanar N atoms of the porphyrin core. The axial positions are occupied by the N atoms of the bipyridine to form infinite chains along the [010] direction. These chains are sustained by π–π interactions [2] between the phenyl rings of adjacent chains.

Crystallographic data

Empirical formula	$C_{54}H_{36}FeN_6$
Formula weight	824.74 g/mol
Crystal system	Monoclinic
Space group	C2/c
Cell dimensions	a = 21.6833(8)Å, b = 11.0827(4)Å, c = 17.6206(6)Å β= 97.354(3) °
Z, ρ_{calc}	4, 1.304 (gr/cm^3)
Volume	4199.6(3) Å^3
F(000)	1712

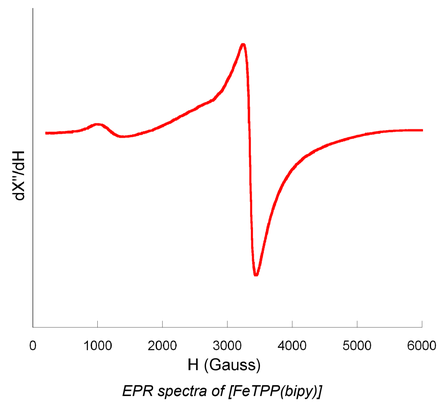
Synthesis

Spectroscopic properties



Mössbauer spectra of [FeTPP(bipy)]

A characteristic Mössbauer doublet of high-spin Fe^{III} ion in octahedral environmet [4] (left) and a same electronic configuration for iron atom by Electronic Paramagnetic Resonance (right) is observed.



EPR spectra of [FeTPP(bipy)]

Conclusions

- The resolution of the structure indicates that the oxidation state of the iron atom is +2, but EPR and Mössbauer data confirm that is Fe^{III}.

- Some other Fe-TPP coordination polymers have been already reported [3], but this is the first one containing bipy.

Acknowledgements

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