Self-assembly of metalloporphyrins: first TPP-bipy coordination polymer with Co^{II} (TPP= meso-tetraphenylporphyrin and bipy= 4,4´-bipyridine)

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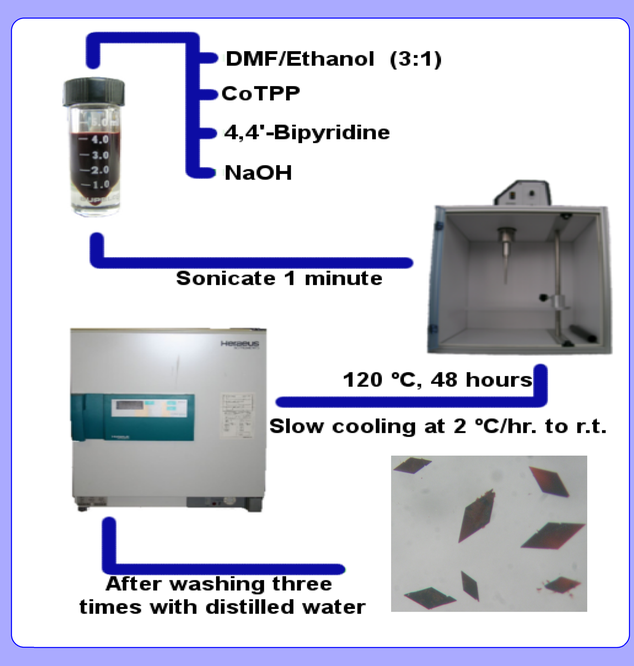
| Introduction |

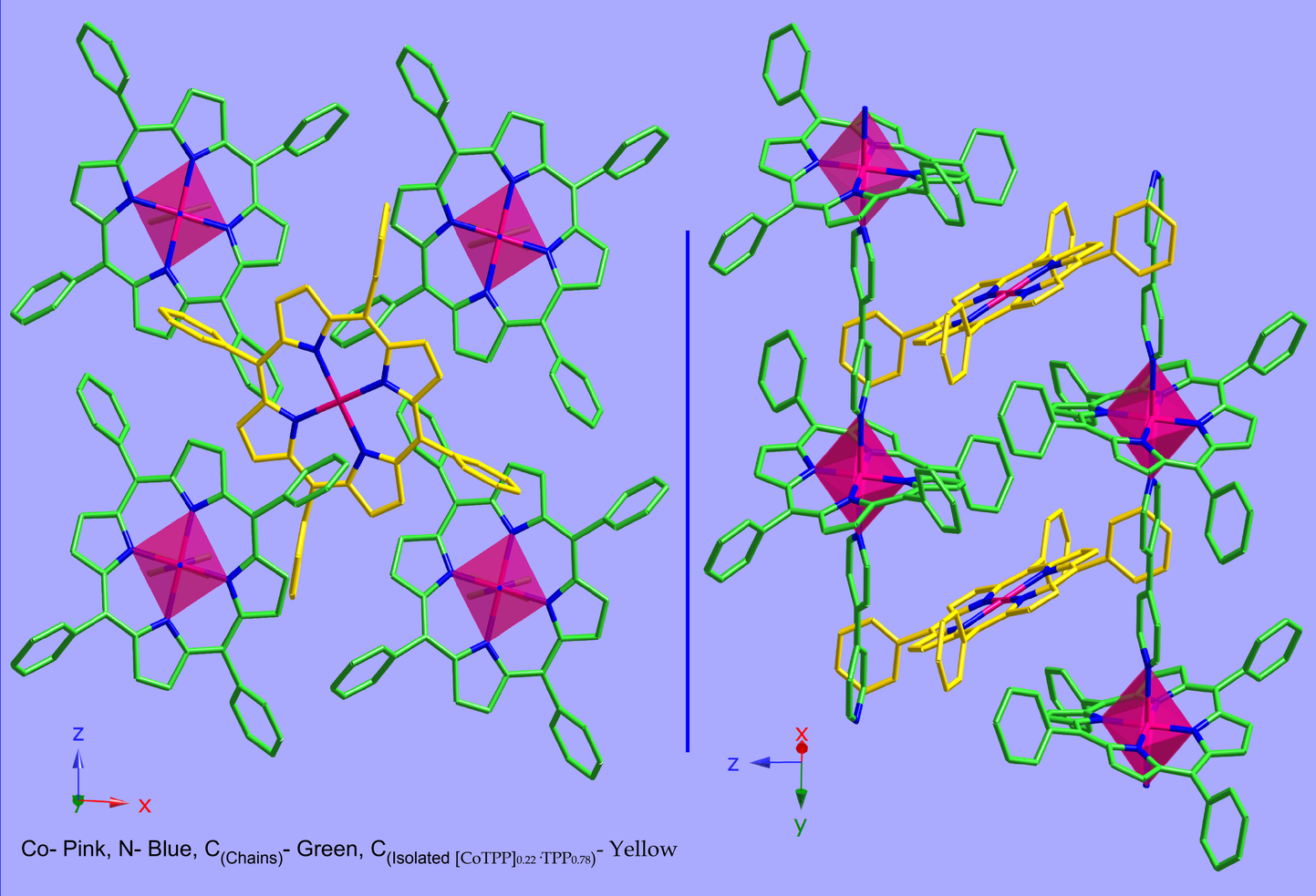
Supramolecular entities based on self-assembly of metalloporphyrins are paradigmatic examples of the great efficiency of the nanodevices used by natural systems in photosynthesis, oxygen transport, electron transfer and catalysis [1]. Therefore, they constitute reference models for the development of 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. Several strategies of synthetic design may be approached and, in this context, our research group is working with different combinations of dipyridyl ligands and metalloporphyrins [2]. The work herein presented corresponds to the compound $[CoTPP(bipy)]\cdot[CoTPP]_{0.22}\cdot TPP_{0.78}$ (TPP = meso-tetraphenylporphyrin and bipy = 4,4´-bipyridine), obtained by solvothermal synthesis.

| Synthesis |



| Crystal Structure |



Co- Pink, N- Blue, $C_{(Chains)}$- Green, $C_{(Isolated\ [CoTPP]_{0.22}\cdot TPP_{0.78})}$- Yellow

Crystal structure of $[CoTPP(bipy)]\cdot[CoTPP]_{0.22}\cdot TPP_{0.78}$ consist of chains of alternating $[CoTPP(bipy)]\cdot$ octahedra where bipy molecules are on the axial positions along the [010] direction. Within the voids between the parallel chains, isolated $[CoTPP]\cdot$ monomers and TPP units are located.

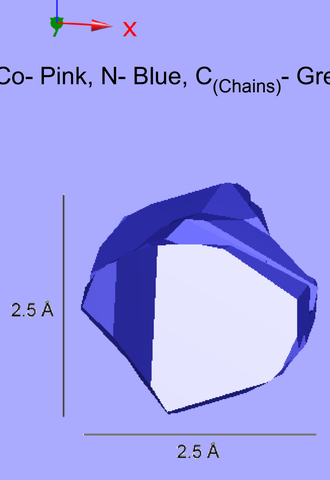
Crystallographic data

Moiety formula	$C_{54}H_{36}CoN_6$, $C_{44}H_{29.56}Co_{0.22}N_4$
Formula weight	1455.06 g/mol
Crystal system	Monoclinic
Space group	C2/c
Cell dimensions	a =25.1252(4)Å, b =11.7811(2)Å, c =23.9790(4)Å β= 93.596(1)°
Z, ρ_{calc}	4, 1.364 (g/cm^3)
Volume	7083.9(2) $Å^3$
F(000)	3026

[CoTPP(bipy)]· octahedra angles (°) and distances (Å) (in bold)

Co	N1	N1^i	N2	N2^i	N3	N4
N4	89.84(4)	89.84(4)	89.89(4)	89.89(4)	180	**2.2958(18)**
N3	90.16(4)	90.16(4)	90.11(4)	90.11(4)	**2.3573(19)**	
N2^i	89.79(6)	90.21(6)	179.77(7)	**1.9619(13)**		
N2	90.21(6)	89.79(6)	**1.9619(13)**			
N1^i	179.68(8)	**1.9660(13)**				
N1	**1.9660(13)**					

i) -x+1, y, -z+1/2



The voids occupied by the non-metallated porphyrins form channels extending along the [010] direction, with 2.5 Å average diameter.

Comparison with [FeTPP(bipy)] [2] indicates that the later compound does not exhibit any non-metallated porphyrins, giving rise to channels with slightly higher diameter (2.8 Å).

| Conclusions |

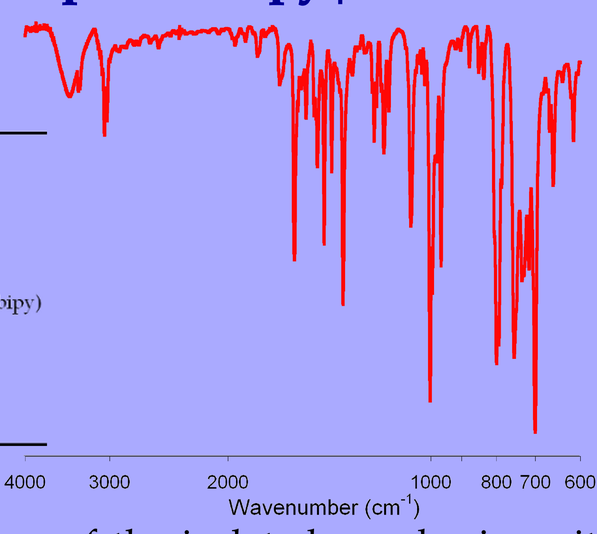
- Apart from $[CoTPP(bipy)]\cdot[CoTPP]_{0.22}\cdot TPP_{0.78}$, another 1D compound with TPP and bipy has been found in the literature [3], the dimensionality being refereed just to covalent bonds.

- As far as we know, $[CoTPP(bipy)]\cdot[CoTPP]_{0.22}\cdot TPP_{0.78}$ is the first Co-based compound with TPP and bipy exhibiting 1D extension of the framework through covalent bonds.

| Infrared spectroscopy |

IR (cm^{-1})	Assigment
3330(w)	ν_{N-H}
3052(m), 3028(m)	$\nu_{sC(sp2)-H}$
1596(s), 1532(m-w), 1490(s), 1441(m)	$\nu_{C=C}$
1349(m)	ν_{C-N}
1210(m-w)	H in plane bend (bipy)
1069(s)	Ring stretching + H bend (bipy)
1000(s)	ν_{Co-TPP}
960(m)	γ_{N-H}
795(w), 753(s), 700(s)	γ_{C-H} (H out of plane bend)
658(m)	Ring bend

s=soft, m=medium and w=weak



The unusual fact that some of the isolated porphyrin units were Co free, was corroborated by the presence of N-H bond vibrations in the IR spectra.

| Acknowledgements |

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| References |

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