

SYNTHESIS, STRUCTURAL AND SPECTROSCOPIC CHARACTERIZATIONS OF COORDINATION POLYMERS

Metallic-based coordination polymers have been widely studied in the past two decades because of potentially interesting porosity, magnetic or optical properties. Compared with classical organic luminescent materials, metallic-based coordination polymers have advantages in color purity, longer lifetime and thermal/chemical stability which make them promising candidates for lighting and displays.^[1, 2] Choice of the organic part is crucial. Some transition metal ions present good affinity for oxygen donor atoms. Carboxylic ligands with aromatic rings (which enhance the intensity of luminescence by antenna effect and energy transfers) have been widely used for designing coordination polymers.^[3] Reaction of metallic ions and carboxylic ligands in water solution leads to series of compounds with general chemical formula $M_x(L)_y(H_2O)_m \cdot nH_2O$ (M = metallic ions, L = ligands, m and n = number of coordination and crystallization water molecules).

During the two last decades, our research group (ISCR/CSM-INSA Rennes) has developed an expertise in the synthesis and characterizations of metallic-based coordination polymers with carboxylic ligands that exhibit interesting magnetic and optical properties.^[4-5] Some of the ligands that have already been used by our group are drawn in **Figure 1**.

Some of the obtained coordination polymers exhibit very promising luminescent properties (**bdc**, **mip**, **dcpa**, **cpb**...). However, to date, nobody knows exactly which physical phenomena provoke high or weak luminance, high or weak color modularity. Therefore, despite a great number of reported studies, complete rationalization of these phenomena is still not possible.

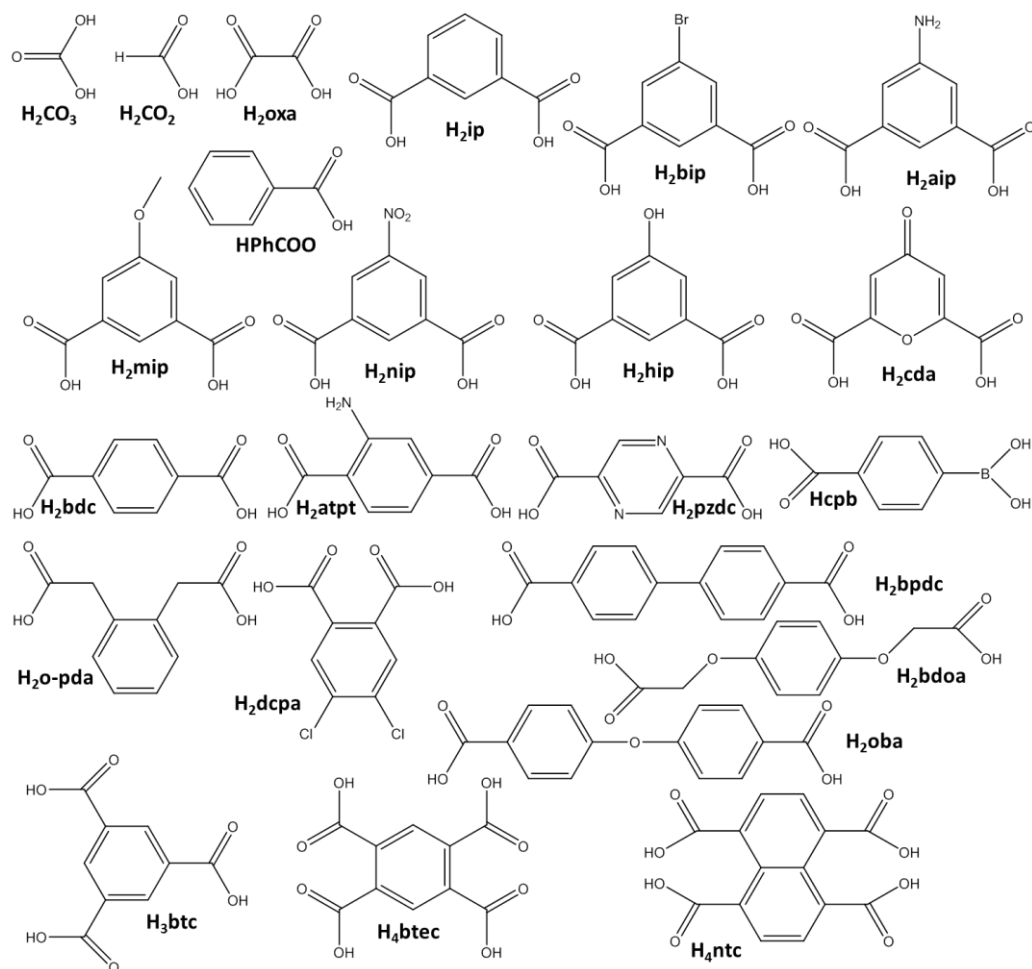


Figure 1. Ligands that have been used by our group: carbonic (H_2CO_3), methanoic (H_2CO_2), oxalic (oxa), benzoic (PhCOOH), isophthalic (ip), 5-bromoisophthalic (bip), 5-amino-isophthalic (aip), 5-methoxyisophthalic (mip), 5-nitro-isophthalic (nip), 5-hydroxy-isophthalic (hip), 4-Oxo-4*H*-pyran-2,6-dicarboxylic (cda), terephthalic (bdc), 2-aminoterephthalic (atpt), 2,5-pyrazinedicarboxylate (pzdc), 4-carboxyphenylboronic (cpb), 1,2-benzenediacetic (o-pda), 4,5-Dichlorophthalic (dcpa), 4,4'-biphenyldicarboxylic (bpdc), Benzene-1,4-dioxydiacetic (bdoa), 4,4'-oxybisbenzoate (oba), 1,3,5-benzène-tricarboxylic (btc), benzene-1,2,4,5-tetracarboxylic (btcc), 1,4,5,8-naphthalene-tetracarboxylic (ntc) acids.

Therefore, the main point of this project is to make a fine analysis and qualitative comparison of the various carboxylic ligands and metallic-based coordination polymers in order to identify the best candidates and to have a higher understanding of the photo-physical mechanisms governing the luminescence properties. For this, a multi-scale approach (chemical, physical and theoretical using DFT method) will be used to study the carboxylic ligands and the coordination polymers.

The project will therefore articulate around the synthesis of organic ligands such as carboxylic acids, the synthesis of homo and hetero-metallic coordination polymers. Then all compounds will be characterized by X-ray diffraction, TGA and scanning electron microscopy (EDS) analyzes in order to characterize the structure, the stability, the morphology and the composition of the phases that will be afterwards studied. Photo-physical properties will be studied by luminescence spectroscopy (emission spectra, excitation spectra, lifetimes and

quantum yields), luminance and colorimetry measurements. The photo-physical measurements will be realized on the solid state or in solution at room- and low-temperature. At last theoretical calculation will be performed in order to rationalize experimental results. The ultimate goal of this comprehensive study is to evidence the physical mechanisms that govern luminescence.

In our lab, Dr. Carole Daguebonne will participate to the supervision of the PhD student. This project will also beneficiate of close collaborations with physicists (FOTON-INSA Rennes) and theoretician chemists (ISCR-CTI).

References

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