SYNTHESIS, STRUCTURAL AND SPECTROSCOPIC CHARACTERIZATIONS AND OPTIMIZATION OF COORDINATION POLYMERS BASED ON HALOGENO-CARBOXYLIC ACIDS

Metallic-based coordination polymers (CPs) 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 CPs 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 CPs.[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 at INSA Rennes) has developed an expertise in the synthesis and characterizations of metallic-based CPs with carboxylic ligands that exhibit interesting magnetic and optical properties.[4-5]

The recent studies[6-9] on CPs with halogeno-carboxylic ligands have revealed interesting and high optical properties due to the formation of 2D or 3D structures stabilized by halogen bonds in addition to the hydrogen bonds. The formation of π-staking between phenyl groups from ligands leading to rigid structures, have been shown to be responsible of the energy transfers in metallic-based CPs improvement. It would be useful to study new halogeno-carboxylic ligands (**figure 1**) and their associated CPs in order to better understand the luminescence mechanisms.

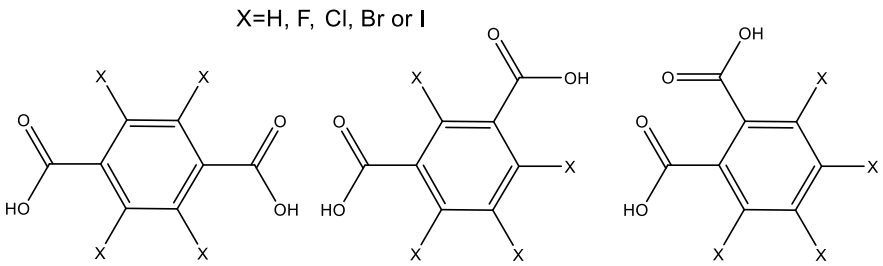

Figure 1. Halogeno-polycarboxylic ligands (we give for example the representation of bi-carboxylic ligands but halogeno-polycarboxylic with higher functionality can also be studied).

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The main point of this project is to make a fine analysis and qualitative comparison of the various halogeno-carboxylic ligands and metallic-based CPs in order to identify the best candidates by trying to optimize the antenna effect with more efficient ligands and to have a higher understanding of the photo-physical mechanisms governing the luminescence properties. A multi-disciplinary approach (chemical, physical and theoretical using DFT methods) will be used to study the carboxylic ligands and the CPs.

The project will therefore articulate around the synthesis of organic ligands such as carboxylic acids, the synthesis of homo and hetero-metallic CPs. Then all compounds will be characterized by X-ray diffraction (on powders and single-crystals), thermal analysis (TGA-TDA) 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-, low- or high-temperature (77-383 K). At last, theoretical calculations 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 Daiguebonne will participate to the supervision of the PhD student. This project will also beneficiate of close collaborations with physicists (IFOTON at INSA Rennes) and theorician chemists (ISCR-CTI).

References

[1] Y. Cui, Y. Yue, G. Qian, et al, *Chem. Rev.* 2012, 112 (2), 1126-1162.
[2] L. Meye, F. Schönfeld, K. Müller-Buschbaum, *Chem. Commun.* 2014, 50, 8093-8108.
[3] K. L. Bray, Transition Metal and Rare Earth Compounds, ed. H. Yersin, Springer, Berlin, 2001
[4] J. Wang, Y. Suffren, C. Daiguebonne, S. Freslon, K. Bernot, G. Calvez, L. Le Pollès, C. Roiland & O. Guillou., *Inorg. Chem.*, 2019, 58(4), 2659-2668.
[5] A. Abdallah, C. Daiguebonne, Y. Suffren, A. Rojo, V. Demange, K. Bernot, G. Calvez & O. Guillou, *Inorg. Chem.*, 2019, 58(2), 1317-1329.
[6] A.-M. Badiane, S. Freslon, C. Daiguebonne, Y. Suffren, K. Bernot, G. Calvez, K. Costuas, M. Camara O. Guillou, *Inorg. Chem.* 2018, *57*, 3399-3410.
[7] Y. Pointel, F. Houard, Y. Suffren, C. Daiguebonne, F. Le Natur, S. Freslon, G. Calvez, K. Bernot, O. Guillou, *Inorg. Chem.* 2020, *59*, 11028-11040
[8] Y. Pointel, Y. Suffren, C. Daiguebonne, F. Le Natur, S. Freslon, G. Calvez, K. Bernot, O. Guillou, *Inorg. Chem.* 2020, *59*, 10673-10687.
[9] Y. Pointel, C. Daiguebonne, Y. Suffren, F. Natur, F. L., S. Freslon, G. Calvez, K. Bernot, D. Jacob, O. Guillou, *Inorg. Chem. Frontiers* 2021, *8*, 2125-2135.