PhD position in Coordination Chemistry (2026-2029)

New Coordination Polymers made of Sulfur-based macrocycles for directional conductivity

Nouveaux polymères de coordination à base de macrocycles soufrés pour la conductivité anisotrope

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A three years PhD fellowship is proposed at Université Claude Bernard Lyon 1, France, for an exceptional candidate to conduct leading edge research in the new and existing domain of anisotropic and conducting coordination polymers by using coordination and supramolecular chemistries.

Conducting Metal Organic Frameworks (MOFs) or Coordination Polymers (CPs) are very promising materials thanks to the fine tuning of their structure that can generate multiple electron transport.[1]

The main goal to get highly conducting materials in this PhD project is to develop **new and efficient thermoelectric (TE) materials to convert waste heat into green and renewable electricity.** Solving this challenging problem would provide a new pathway to green energy revolution and the discovery of advanced TE materials would change our energy system and make significant contributions to lessen the reliance on fossil fuels. Although major breakthroughs have been done at the beginning of the century, all the commercially available TE generators suffer from their very low conversion efficiencies, due to the too high thermal conductivity of the inorganic materials and to the too low electrical conductivity of the organic polymers. Thus, novel TE materials have to be developed with very low thermal conductivity, high electrical conductivity and high Seebeck coefficient. **MOFs and CPs have recently appeared as a good alternative to inorganic TE materials**.[2] Indeed, their composition of metals, organic ligands and coordinating functional groups can lead to an infinite of materials with 1D, 2D, or 3D networks and be sustainable by selecting non critical raw materials. The record electrical conductivity of 1500 $S.cm^{-1}$ has been reported for a 2D copper benzenehexathiolate CP, pointing out the great performance of copper and sulfur-based linkers.[3]

In parallel, A. Demessence's team from IRCELYON has developed a series of copper thiolate CPs, called MOCs (Metal organic Chalcogenolates) with 1D and 2D structures (Fig. 1). They exhibit various properties, such as bright photoemission, luminescent thermochromism and also electrical conductivity.[4] While some of them show very high Seebeck coefficients,[4a] that is required for good thermoelectricity, their electron conduction through the copper-sulfur chains is still modest and need to be increased to afford efficient TE materials.

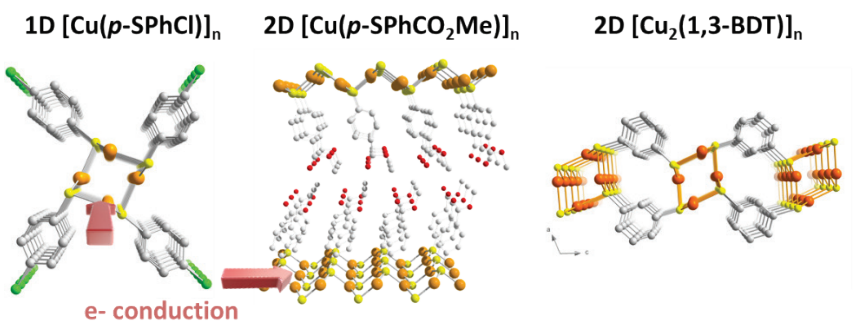

Fig. 1. Examples of copper thiolate MOCs made in IRCELYON. Orange spheres are for copper, yellow for sulfur, grey for carbon and green for chloride, hydrogen atoms are omitted for clarity.

Thus, the goal of the PhD is **to synthesize new copper-thiolate MOCs with macrocycle thiolate-based ligand to boost the electrical conductivity by generating anisotropic structures (1D or 2D) and multiple electron transport pathways, in order to develop efficient and sustainable TE materials (Fig. 2)**.

Indeed, the use of designed π-delocalized system calixarene and/or pillararene polythiol-based ligands is to form directional structures (Fig. 2). The cyclicity of these molecules and the directionality of thiol groups will allow generating original CPs, with expected tubular networks. There are two main interests of these structures: the first one is to enhance the through-space electronic pathway (π-π stacking) which has been found to contribute significantly to the conduction. The second interest is the formation of intrinsic microporosity which led to a reduction of the lattice heat transport, to reduce the heat transport, and allow the insertion of doping agents as diode or metals, to boost the electric conductivity. The team of F. Perret has long expertise in the synthesis of macrocyclic host molecules such as calixarene, cyclodextrins and dynarenes and the use of Newman Kwart rearrangement for the synthesis of thiolated derivatives.[5]

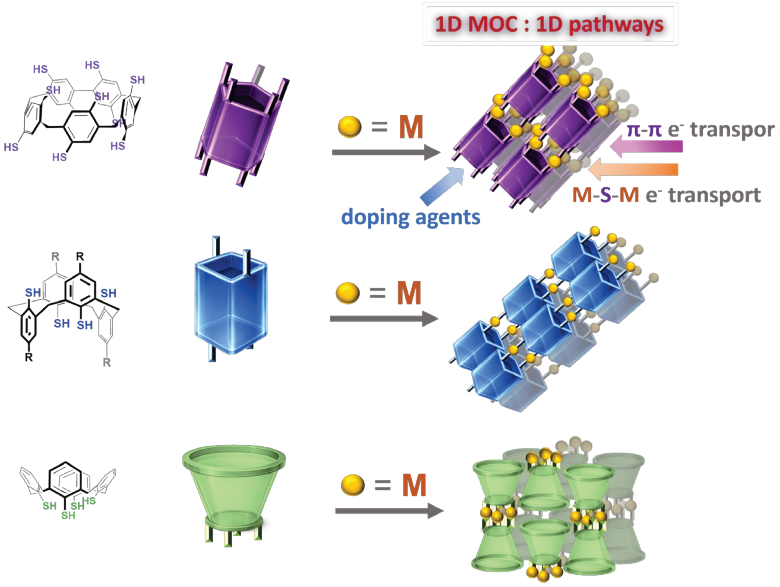

Fig. 2. PhD goal: formation of anisotropic MOCs with thiolate-based macrocycles to generate multiple electron transport pathways.

The PhD student will conduct two main researches: (i) the ***synthesis of original macrocyclic thiol molecules*** (at LCH-ENS) and then (ii) ***the formation of new MOCs*** (at IRCELYON). The study will involve the optimization of the synthetic procedures (organic, combinatorial and large-scale syntheses), the in-depth characterizations of the obtained products, the structural studies and their electrical and optical properties investigation (powder and single crystal XRD, TGA, DSC, FT-IR, SEM, XPS, liquid and solid-state NMR, UV-vis. absorption, photoluminescence…). The study of the conductivity and thermoelectricity efficiency will be done through a collaboration with Dr. Stéphane Pailhès team at ILM on the campus. Particular attention will be paid to the stability, the reproducibility and the shaping of the materials for the development of real-life applications. In the same time, the PhD student will be highly encouraged to contribute with his/her own skills, experience and vision of the topic to the development of the project.

This interdisciplinary project is dealing with **organic, supramolecular and coordination chemistries** and **materials science,** and is a new strategy towards the design of innovative, sustainable and functional TE hybrid materials. The ideal candidate for this multidisciplinary Ph.D. degree should have a strong background in at least one of these domains: organic synthesis, coordination chemistry or solid-state chemistry.

To apply: Submit a cover letter, a detailed CV, the marks of your masters and contact information for references to aude.demessence@ircelyon.univ-lyon1.fr and florent.perret@univ-lyon1.fr.

[1] L. S. Xie, G. Skorupskii, M. Dincă, *Chem. Rev.* **2020**, *120*, 8536-8580.
[2] E. Redel, H. Baumgart, *APL Mater.* **2020**, *8*, 060902.
[3] R. Tsuchikawa, N. Lotfizadeh, N. Lahiri, S. Liu, M. Lach, C. Slam, J. Louie, V. V. Deshpande, *Phys. Status Solidi A* **2020**, *217*, 2000437.
[4] a C. Andrade, S. Hawila, A. Abdallah, J.-L. Rukemampunzi, A. Mesbah, N. Guillou, F. Perret, S. Wuttke, T. Niehaus, R. Debord, O. Boisron, S. Pailhès, A. Demessence, *J. Mater. Chem. C* **2023**, *11*, 14540-14544; b A. Abdallah, S. Vaidya, S. Hawila, S.-L. Ornis, G. Nebois, A. Barnet, N. Guillou, A. Fateeva, A. Mesbah, G. Ledoux, A. Bérut, L. Vanel, A. Demessence, *iScience* **2023**, *26*, 106016; cO. Veselska, N. Guillou, M. Diaz-Lopez, P. Bordet, G. Ledoux, S. Lebègue, A. Mesbah, A. Fateeva, A. Demessence, *ChemPhotoChem* **2022**, *6*, e202200030.
[5] P.-T. Skowron, M. Dumartin, E. Jeamet, F. Perret, C. Gourlaouen, A. Baudouin, B. Fenet, J.-V. Naubron, F. Fotiadu, L. Vial, J. Leclaire, *J. Org. Chem.* **2016**, *81*, 654.