PhD position in Coordination and Organic Chemistry (2023-2026) from Lyon 1 University

Metal Organic Thiolate Coordination Polymers as Innovative Thermoelectric Materials

PhD supervisor: Dr. Aude Demessence[1,2]
PhD co-supervisor: Dr. Florent Perret[1,3]

[1] *Claude Bernard Lyon 1 University*
[2] *Institute of Researches on Catalysis and Environment of Lyon (IRCELYON) - UMR CNRS 5256, C'Durable group (www.ircelyon.univ-lyon1.fr/team/cdurable), Villeurbanne, France*
[3] *Institut de Chimie et Biochimie Moléculaire et Supramoléculaire (ICBMS) - UMR CNRS 5246 –CSAp. Group (www.icbms.fr/csap), Villeurbanne, France.*

A three years PhD fellowship is proposed at Lyon University, France, for an exceptional candidate to conduct leading edge research in the new and existing domains of conducting coordination polymers and thermoelectricity. This grant is from a national research project funded by the ANR MOTIC.

Aside from our reliance on fossil fuel, one of the challenges of the energy use in our modern society is the huge untapped amount of waste heat generated, which cannot be harnessed and utilized with today thermoelectric (TE) materials. Indeed, all the industrial machineries, the combustion engines and batteries in automobiles, the thermal and nuclear power plants and most technological equipment produce heat, even our human bodies, which when being left untapped, is forever lost, counting almost 70 % of the total energy used today.[1] Therefore, to move forward and to tap this mostly unused resource, **new and efficient thermoelectric materials should be developed 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.

The power conversion efficiency of a TE material scales with a dimensionless figure of merit $ZT = (\sigma S^2 T) / \kappa$, where σ is the electrical conductivity, S the Seebeck coefficient, κ the thermal conductivity, and T the absolute temperature. 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, which are due to their limited *ZT*. Research efforts have been mostly focused in semi-conducting inorganic materials bringing on stage efficient materials like Bi_2Te_3, SiGe, skutterudites…

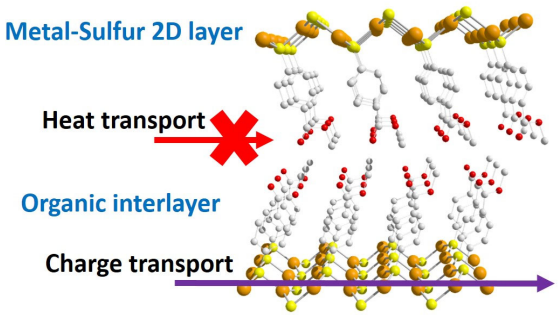

Fig. 1. Formation of anisotropic thiolate-based CPs for thermoelectricity.

Thus, in order to improve this *ZT*, novel TE materials have to be developed. Since *ZT* is inversely proportional to the thermal conductivity, it is required to have TE materials with very low thermal conductivity, close to zero, and high electrical conductivity. **Coordination polymers (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 structured materials (Fig. 1). Recent progresses show that sulfur-based CPs exhibit the best

electrical conductivity compared to oxygen one.[3] Thus, with anisotropic CPs, it is possible to build metallic layers or chains efficient for charge transport, while the organic surroundings will act as a heat insulator.

The goal of the PhD, based on the expertise of the team on thiolate-based CPs,[4] is to synthesize new **conducting thiolate-based CPs with original thiol molecules for a complete structure/electronic properties understanding**.

The PhD student will conduct two main researches: (i) the ***synthesis of original thiol molecules*** (at ICBMS) and then (ii) ***the formation of new coordination polymers*** (at IRCELYON). During the PhD, it is proposed to work with series of compounds based on multidentate aromatic thiol ligands associated to different functions (-NH_2, -CO_2H, -OH, -F) (Fig. 2) and copper and silver metals, in order to obtain different network dimensionalities and *n*- or *p*-type conductivities.

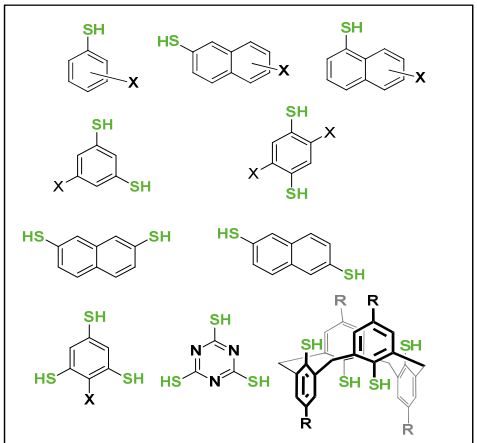

Fig. 2. Examples of target ligands

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. The conductivity studies will be carried out in close collaboration with Dr. Stéphane Pailhès at ILM on the campus. Particular attention will be paid to the stability, the reproducibility and the shaping of the materials which is a tremendous step 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.

The new compounds will be fully characterized by different techniques (PXRD, PDF, TGA, DSC, FT-IR, XPS, EXAFS, liquid and solid state NMR….) as well as their physical properties (absorption, photoluminescence and conductivity). The formation of pellets under pressure will be finally carried out to measure the conductivity.[5] This interdisciplinary and complete project is dealing with **organic synthesis, coordination chemistry**, materials solid and physics and is a new strategy towards the design of innovative and functional thermoelectric hybrid materials.

The ideal candidate for this Ph.D. degree should have a strong background in at least one of this domain: organic synthesis, coordination chemistry and/or crystallography and be comfortable with several physical characterization technics mentioned above.

To apply: Submit a cover letter, a CV, the marks of your masters and contact information for references by following this link: https://emploi.cnrs.fr/Offres/Doctorant/UMR5256-AUDDEM-004/Default.aspx?lang=EN (by email : aude.demessence@ircelyon.univ-lyon1.fr; florent.perret@univ-lyon1.fr)
Salary: 1715 € per month (after taxes).
Start and duration of the PhD: from 1st October 2023 to 30th September 2026.
Deadline to apply: 21th April 2023.

[1]. D. M. Rowe, *Thermoelectrics Handbook: Macro to Nano*, **(Taylor & Francis Ltd., 2006)**.
[2]. E. Redel; H. Baumgart, *APL Mater.*, **2020**, *8*, 060902.
[3]. Y. Kamakura; D. Tanaka, *Chem. Lett.*, **2021**, *50*, 523.
[4]. (a) O. Veselska; A. Demessence, *Coord. Chem. Rev.*, **2018**, *355*, 240; (b) S. Vaidya; O. Veselska; A. Zhadan; M. Diaz-Lopez; Y. Joly; P. Bordet; N. Guillou; C. Dujardin; G. Ledoux; F. Toche; R. Chiriac; A. Fateeva; S. Horike; A. Demessence, *Chem. Sci.*, **2020**, *11*, 6815; (c) S. Hawila; A. Abdallah; J.-L. Rukemampunzi; A. Fateeva; G. Ledoux; R. Debord; S. Paihlès; N. Guillou; F. Massuyeau; R. Gautier; A. Mesbah; A. Demessence, *Chem. Commun.*, **2022**, *58*, 8081; (d) O. Veselska; S. Vaidya; C. Das; N. Guillou; P. Bordet; A. Fateeva; F. Toche; R. Chiriac; G. Ledoux; S. Wuttke; S. Horike; A. Demessence, *Angew. Chem. Int. Ed.*, **2022**, *61*, e202117261.
[5]. O. Veselska; N. Guillou; G. Ledoux; C.-C. Huang; K. Dohnalova Newell; E. Elkaim; A. Fateeva; A. Demessence, *Nanomaterials*, **2019**, *9*, 1408.