Synthesis of Metal Organic Thiolate Coordination Polymers as Innovative Thermoelectric Materials

Abstract

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...

Thus, 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.

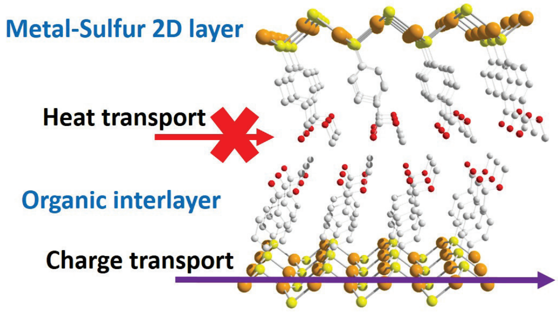

Fig. 1. Project: formation of anisotropic thiolate-based CPs for thermoelectricity.

The goal of the internship, based on the expertise of A. Demessence 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**. During this internship project, it is proposed to work with series of compounds based on multidentate thiol-based ligands associated to different functions (-NH_2, -CO_2H, -OH, -F) and copper and silver metals, in order to obtain different network dimensionalities and n- or p-type conductivities. The study involves the optimization of the synthetic procedures (combinatorial and large scale syntheses), the in-depth characterizations of the obtained products, the structural studies and their electrical 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 payed 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 internship student will be highly encouraged to contribute with his/her own skills, experience and vision of the topic to the development of the project.

Technics

Among the characterization methods available are: single crystal and powder X-Ray diffraction; IR, Raman, UV-vis and XPS spectroscopies; N_2 adsorption, SEM and TEM, NMR, TGA-DTA and DSC.
Internship will take place in collaboration with Dr Stéphane Pailhès (conductivity measurements, shaping techniques) in ILM on the Doua campus.

Required skills:

The candidate is required to have very good grades and strong knowledge in the domain of coordination chemistry and crystallography, as well as be interested and curious to work with material science and motivated to work in interdisciplinary research. Being autonomous in work organization, time management and good knowledge of English is strongly suggested.

Address and contact to apply :
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To apply, send your CV, motivation letter and grades from the first year of your master studies to Dr. Adel Mesbah (adel.mesbah@ircelyon.univ-lyon1.fr) **AND** Dr. Aude Demessence (aude.demessence@ircelyon.univ-lyon1.fr).

Starting date: January or February 2022.
A PhD grant is also available on this project from October 2022.

Salary: *550 euros per month.*

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.