

## Luminescent Coinage metal thiolate coordination polymers, $[M(SR)]_n$ ( $M = Au(I), Ag(I), Cu(I)$ ), for optoelectronics

### Abstract:

Hybrid compounds of the composition  $[M(SR)]_n$ , where M is a coinage metal - gold, silver or copper - in oxidation degree +I and (SR) is a thiolated ligand, have been known for a long time for their applications in pharmaceuticals, for their structural analogy to metalloproteins and as crucial intermediates in the synthesis of functionalized nanoparticles [1].

Recently these materials have attracted attention of broader scientific community due to their interesting photophysical [2] and conductivity [3] properties and as emerging anisotropic nanomaterials, as nanowires and nanosheets, holding great promises in diverse applications related to nanotechnology [4].

However, despite all their potential, a little is known about these materials, and in particular about their crystalline structure [1]. This lack of knowledge is due to the challenges encountered while crystallization, preventing a deep understanding of the structure-properties link.

The first in-depth study was performed by our team and concerned series of 2D coordination polymers of the following formula  $[M(p\text{-}SPhCO_2R)]_n$  ( $M = Au(I), Ag(I), Cu(I); R = H, Me$ ). Depending on the metal and the presence/absence of hydrogen bonds, different Metal-Sulfur connectivities were observed giving rise to different processes involved in their photophysical properties [2-7] (Fig. 1). For example the compound  $[Cu(p\text{-}SPhCO_2Me)]_n$  exhibits intrinsic triple emission bands associated with luminescence thermochromism, a great potential a self-referenced optical thermometer (Fig. 1). Recently, we analyzed the influence of the position of the substituent on the benzyl ring ( $[M(x\text{-}SPhCO_2H)]_n$ ,  $x = p\text{-}, m\text{-}, o\text{-}$ ) and were able to design new 1D coordination polymers.

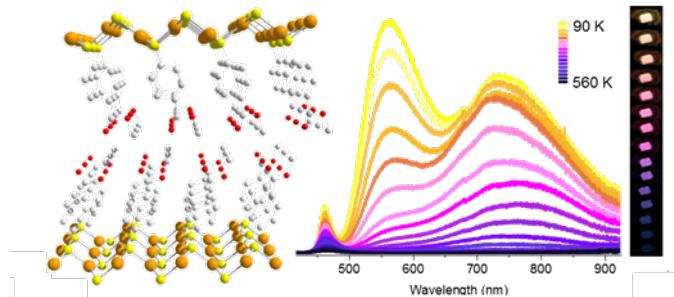


Fig. 1. Structure and photophysical properties of  $[Cu(p\text{-}SPhCO_2Me)]_n$ .

During this internship project, it is proposed to work with series of compounds ( $[M(x\text{-}SPhCO_2R)]_n$ ,  $x = p\text{-}, m\text{-}, o\text{-}$ ;  $R = Me, Et, iPr$ ) with various esterified ligands in order to elucidate the influence of both the position of the substituent and its bulkiness on the structure and the physical properties. The study involves the optimization of the synthetic procedures (combinatorial and large scale synthesis), the in-depth characterizations of the obtained products, the structural studies and their photophysical properties investigation. The conductivity studies will be analyzed. Particular attention will be paid to the stability, the reproducibility studies and the shaping of the materials which are tremendous steps 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.

1. O. Veselska, A. Demessence,  $d^{10}$  coinage metal organic chalcogenolates: From oligomers to coordination polymers, *Coord. Chem. Rev.*, **2018**, 355, 240.
2. (a) C. Lavenn, N. Guillou, M. Monge, D. Podbevšek, G. Ledoux, A. Fateeva, A. Demessence, Shedding light on an ultra-bright photoluminescent lamellar gold thiolate coordination polymer  $[Au(p\text{-}SPhCO_2Me)]_n$ . *Chem. Commun.*, **2016**, 52, 9063.  
 (b) O. Veselska, L. Okhrimenko, N. Guillou, D. Podbevšek, G. Ledoux, C. Dujardin, D. Chevrier, R. Yang, P. Zhang, A. Fateeva, A. Demessence, Intrinsic Dual-Emitting Gold Thiolate Coordination Polymer,  $[Au(+I)p\text{-}SPhCO_2H)]_n$ , for Ratiometric Temperature Sensing. *J. Mater. Chem. C*, **2017**, 5, 9843.  
 (c) O. Veselska, L. Cai, D. Podbevšek, G. Ledoux, N. Guillou, G. Pilet, A. Fateeva, A. Demessence, Structural Diversity of Coordination Polymers Based on a Heterotopic Ligand: Cu(II)-Carboxylate vs Cu(I)-Thiolate, *Inorg. Chem.*, **2018**, 57, 2736.  
 (d) O. Veselska, D. Podbevšek, G. Ledoux, A. Fateeva, A. Demessence, Intrinsic triple-emitting 2D copper thiolate coordination polymer as a ratiometric thermometer working over 400 K range, *Chem. Commun.*, **2017**, 53, 12225.  
 (e) O. Veselska, C. Dossal, S. Melizi, N. Guillou, D. Podbevšek, G. Ledoux, E. Elkaim, A. Fateeva, A. Demessence, New Lamellar Silver Thiolate Coordination Polymers with Tunable Photoluminescence Energies by Metal Substitution, *submitted to Inorg. Chem.*
3. (a) Y. Zhang, T. Xia, K. M. Yu, F. Zhang, H. Yang, B. Liu, Y. An, Y. Yin, X. Chen. Facile Synthesis of  $[Cu(SCH_3)]$  Nanowires

with High Charge Mobility. *ChemPlusChem*. **2014**, 79, 559.

(b) C.-M. Che, C.-H. Li, S.S.-Y. Chui, V.A.L. Roy, K.-H. Low. Homoleptic Copper(I) Arylthiolates as a New Class of p-Type Charge Carriers: Structures and Charge Mobility Studies. *Chem. Eur. J.* **2008**, 14, 2965.

(c) K.-H. Low, V.A.L. Roy, S.S.-Y. Chui, S.L.-F. Chan, C.-M. Che. Highly conducting two-dimensional copper(I) 4-hydroxythiophenolate network. *Chem. Commun.* **2010**, 46, 7328.

4. (a) L. L.G. Al-Mahamad, O. El-Zubir, D. G. Smith, B. R. Horrocks, A. Houlton A coordination polymer for the site-specific integration of semiconducting sequences into DNA-based materials. *Nature Communications*. **2017**, 8, 720.

(b) H. Yan, J.N. Hohman, F.H. Li, C. Jia, D. Solis-Ibarra, B. Wu, J.E.P. Dahl, R.M.K. Carlson, B.A. Tkachenko, A.A. Fokin, P.R. Schreiner, A. Vailionis, T.R. Kim, T.P. Devreux, Z.-X. Shen, N.A. Melosh, Hybrid metal-organic chalcogenide nanowires with electrically conductive inorganic core through diamondoid-directed assembly. *Nat. Mater.* **2017**, 16, 349.

(c) Q. Xiao, J. A. Burg, Y. Zhou, H. Yan, C. Wang, Y. Ding, E. Reed, R. D. Miller, R. H. Dauskardt. Electrically Conductive Copper Core-Shell Nanowires through Benzenethiol-Directed Assembly. *Nano Lett.* **2018**, 18, 4900.

(d) D. V. P. Massote, M. S. C. Mazzoni. Two-dimensional semiconductors: The case of silver thiolates, *Applied Physics Letters*. **2016**, 109, 133104.

#### Techniques utilisées

Among the characterization methods available are: single crystal and powder X-Ray diffraction; IR, Raman, UV-vis and XPS spectroscopies; N<sub>2</sub> adsorption, SEM and TEM, TGA-DTA and DSC. Internship will take place in collaboration with Dr Gilles Ledoux (emission, excitation and lifetime measurements), and Dr Stéphane Pailhes (conductivity measurements, shaping techniques) in ILM on the Doua campus.

#### Compétences souhaitées

The candidate is required to have 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.

#### Coordonnées du Correspondant : Aude Demessence – [aude.demessence@ircelyon.univ-lyon1.fr](mailto:aude.demessence@ircelyon.univ-lyon1.fr)

Institut de Recherches sur l'Environnement et la Catalyse de Lyon (IRCELYON), CNRS – Université Lyon 1 - 2, avenue Albert Einstein - 69626 Villeurbanne.

To apply, send your CV, motivational letter and grades from the first year of your master studies to Aude Demessence ([aude.demessence@ircelyon.univ-lyon1.fr](mailto:aude.demessence@ircelyon.univ-lyon1.fr)).

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