In-depth study of the solid-state crystallization of a luminescent gold-thiolate coordination polymer

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Gold(I) thiolate coordination polymers are an important class of materials [1]. Indeed gold thiolate, $(Au\text{-}SR)_n$, have been commercialized in diverse areas as pharmaceuticals or as gilding inks for a long time and today they are essential in nanotechnology for Self-Assembled Monolayers fabrication for electronics or as a key step in nanoparticles synthesis that find application as sensors, biomaterials or in catalysis [2]. Gold(I) atoms are also known to form aurophilic interactions that can induced luminescence. However, despite the importance of $(Au\text{-}SR)_n$ coordination polymers in these different areas, their structure and the relationship with their luminescent properties are not very well-known.
Here we present first, the direct solvothermal synthesis and the structure resolution of a new $(Au\text{-}SPh)_n$ coordination polymer with thiophenolate. The structure is made of two interpenetrated helices made of infinite –Au-S-Au-S- chains (Figure 1). This gold thiophenolate hybrid material is luminescent at room temperature due to the aurophilic interactions. A two-step synthesis can also be used to obtain this crystalline $(Au\text{-}SPh)_n$ compound, which consists on the heating of a preformed amorphous and non-luminescent $(Au\text{-}SPh)_n$ at solid-state (Figure 1).

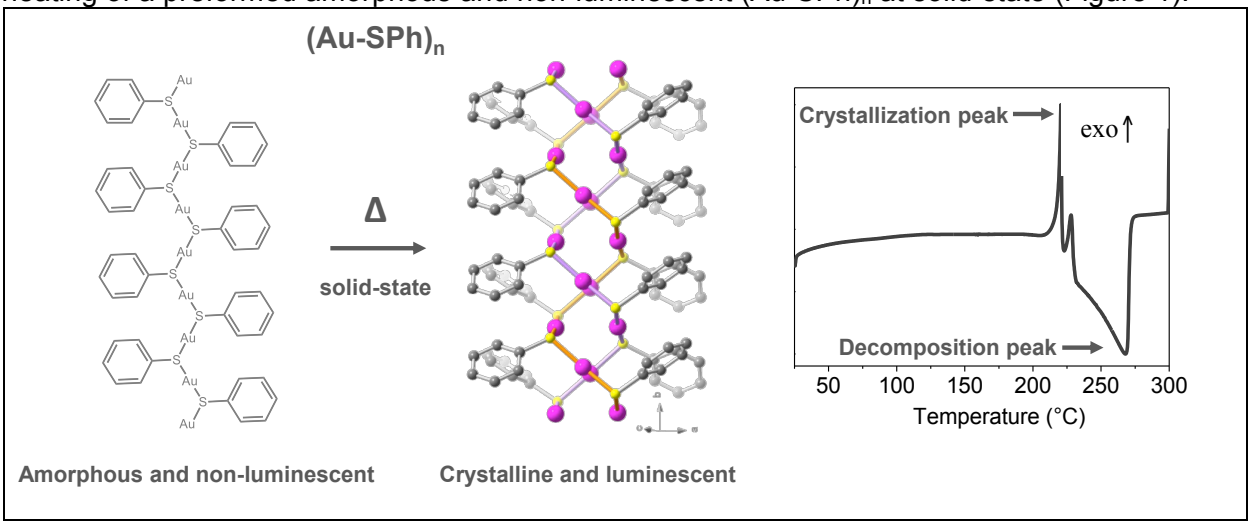

Figure 1. On the left, scheme of the thermal induced amorphous-to-crystalline isomerization of $(Au\text{-}SPh)_n$ at solid-state along with the apparition of luminescent properties. On the right, DSC experiment carried out on the amorphous $(Au\text{-}SPh)_n$ to characterize the crystallization process.

This amorphous-to-crystalline isomerization is fully characterized by powder X-ray diffraction, thermogravimetric analysis, differential scanning calorimetry (Figure 1), scanning electron microscopy and the apparition of the luminescence with the temperature is followed by emission experiments. Different conditions to observe this crystallization, namely heating rate, targeted temperature and isotherms are also discussed.
This gold thiophenolate material is the second structure reported for $(Au\text{-}SR)_n$ coordination polymer and the first example of a thermal induced amorphous-to-crystalline isomerization along with the apparition of light emission.

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[2] C. Lavenn, F. Albrieux, A. Tuel, A. Demessence, *J. Colloid Interface Sci.* **418** (2014) 234.