Cocrystallization, high pressure/low temperature behaviour and vapochromism in a family of aurophilic copper-gold supramolecular networks

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The synthesis and conception of coordination polymers and supramolecular networks based on gold(I) complexes used as metallo-ligands (especially dicyanoaurate) is an established procedure to obtain materials with exciting properties: phosphorescence, non-linear optical behaviour, vapochromism and non-classical response to temperature and pressure [1-2]. However, the appearance of these solid-state properties is often connected to the manifestation of aurophilic interaction. The Au(I)···Au(I) interaction, an attraction between closed shell d^{10} metal centres, is a relativistic effect that has a strength comparable to that of classical hydrogen bond [3]. Therefore, the study of new functional materials based on gold(I) properties must encourage the formation of these contacts in the crystal environment. We prepared, by a judicious choice of chelating ligands and balance in coordination equilibria [4], a series of 12 new coordination polymers or supramolecular networks based on dicyanoaurate anion and copper complexes presenting aurophilic interactions. The choice of copper as metal centre to connect to $[Au(CN)_2]^-$ makes the synthesis particularly predictable due to the Jahn-Teller effect in the case of Cu(II), and the appearance of Cu(I) compounds due to redox effect of specific ligands will be commented. These compounds have been tested for vapochromism, and their behaviour in presence of ammonia has been interpreted with Raman, Ir and Uv-Vis absorption spectroscopy. On the same time, the response to temperature (T= 100-420 K) and pressure (P= 0.1-1.5 GPa) of $\{Cu(bipy)_2[Au(CN)_2]\}[Au(CN)_2]$ (bipy =2,2'-bipyridine), a prototypical bimetallic aurophilic supramolecular network, has been investigated. Both the dependence of structural and reticular parameters to thermal and compression stimuli has been studied, and a phase transition at 1.2 GPa has been revealed. Moreover, we investigated the possibility to modulate the structural behaviour with the cocrystallization with other d^{10} metal tectons, and we demonstrate the possibility to obtain inclusion compounds with the presence of $Hg(CN)_2$ with a 3D weakly interacting framework still presenting Au···Au contacts.

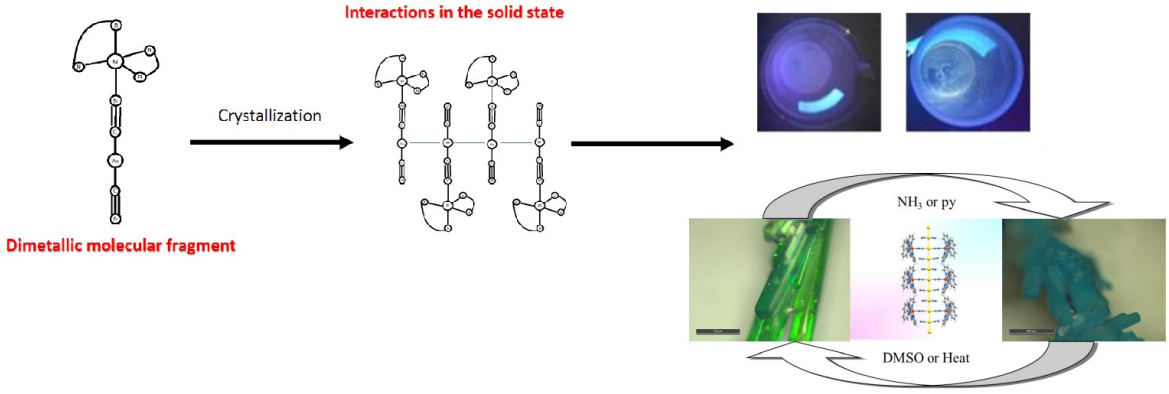

Figure 1. The supramolecular aggregation of dimetallic fragments through aurophilic interaction during the crystallization creates the correct crystal environment for luminescence and vapochromism.

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