

Tuning the 1D-2D dimensionality upon ligand exchange in silver thiolate coordination polymers with photoemission switch

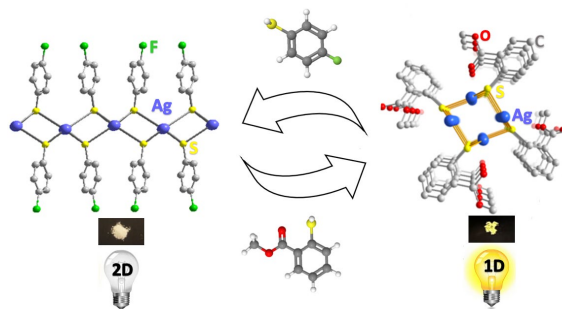
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Hybrid materials with thiolate-based ligands and d^{10} coinage metals ($M(I) = Cu, Ag$ and Au) are known for a long time mainly in the domains of biology and pharmaceutics.^[1] Indeed, in our daily life, silver nanoparticles are widely used as biocides, for their microbial activity, in textiles, food packaging, drink water and medical devices such as pads.^[2] The biocidal activity is due to the high toxicity of $Ag(I)$ ions that are released from silver nanoparticles. Thus, during their life cycle, silver nanoparticles, and more particularly $Ag(I)$ soluble species, are dispersed in the environment where they are subjected to various reactions throughout the cells in bacteria, plants or animals with different toxic potentials. While $Ag(I)$ is an unphysiological ion, it shows, as the physiological $Cu(I)$ ion, which are both soft acids, high binding affinity for thiolate ligands, which are soft bases. Thiol-based molecules present in cells are mainly glutathione and metallothionein, which are important proteins involved in cellular copper homeostasis. Consequently, it has been proposed that the toxicity of $Ag(I)$ ions in cells is due to their ability to easily bond to thiol biomolecules and replace $Cu(I)$ in their native binding sites. In this study we focused on the chemical stability of $Ag(I)$ -thiolate and more importantly their ability to thiolate ligand exchange, which may be a way of $Ag(I)$ to enter in a cell in a biota. Here the synthesis and structure of two new 2D silver thiolate coordination polymers (CP) are presented $[Ag(p\text{-SPhF})]_n$ and $[Ag(p\text{-SPhCl})]_n$ and the studies of their stability in basic and acidic media are presented. More importantly, we showed that in presence of a thiol excess, the ester $o\text{-HSPHCO}_2\text{Me}$, this 2D CP is dissolved and recrystallized in a 1D network that exhibits an intense photoemission. This study confirms that $Ag(I)$ has strong affinity with thiol molecules and while silver-thiolate compounds are highly stable, they can undergo thiol-ligand exchange, that could be a mechanism to enter onto a cell.

[1] Veselska, O. & Demessence, A. (2018), *Coord. Chem. Rev* 355, 240.

[2] K. Chaloupka, Y. Malam & A. M. Seifalian (2010), *Trends in Biotechnology* 28, 580-588.