MS13 Structural Characterization of Functional Materials

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Structural determination of a photoemissive chiral 3D silver(I)-benzenedithiolate coordination polymer

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Abstract

These last few years, Metal Organic Chalcogenolate (MOC) coordination polymers (CPs) have received increasing interest due to the formation of new materials with interesting electrical transport and photoluminescence properties [1]. 1D and 2D MOCs, showing great photoluminescence properties in the solid state, have been synthesized from numerous functionalized monothiolate ligands [2, 3]. This study has recently been extended to copper and silver networks obtained with a multithiolate ligand, the benzenehexathiolate (BHT). These MOCs exhibit up to now the highest room temperature conductivity among the CPs and Metal-Organic Frameworks (MOFs), with 250 $S.cm^{-1}$ for the 3D $[Ag_5(BHT)]_n$ compound and 1580 $S.cm^{-1}$ for the 2D $[Cu_3(BHT)]_n$ one [4, 5]. In order to control their band gap to either get photoluminescent or conducting materials, there is a tremendous need to understand their structure-properties relationships and therefore to develop new d^{10} coinage MOCs with other thiolate ligands. In this context, the first d^{10} coinage MOC based on silver and a ditopic thiolate linker, the 1,3-benzenedithiolate (1,3-BDT) ligand, $[Ag_2(1,3\text{-BDT})]_n$ has been obtained. Its structure was solved *ab initio* from powder X-ray diffraction (PXRD) collected at the CRISTAL beamline of the SOLEIL synchrotron facility (Gif-Sur-Yvette, France). The final Rietveld plot shows the perfect agreement between the calculated data obtained from the structural model and the observed ones (Fig. 1). $[Ag_2(1,3\text{-BDT})]_n$ crystallizes in the cubic chiral $P2_13$ space group with a = 12.88562(3) Å, V = 2139.52(1) $Å^3$ and Z = 12. The asymmetric unit contains four independent silver atoms with one in general position, and the three others on the threefold axes, as well as one 1,3-BDT ligand ($C_6H_4S_2$) in general position. Each silver atom is coordinated to three sulfur atoms to form a near planar triangular geometry, and each sulfur atom is also coordinated to three silver atoms. The 3D framework can be described from a sulfur network constructed from two independent empty octahedra, Ag_4S_6 and Ag_2S_6 (Fig. 2, in dark and light blue, respectively), centred on the threefold axes and connected through sharing edges to generate eight membered ring channels filled by the organic moiety of the bridging 1,3-BDT ligands. In situ PXRD have shown that $[Ag_2(1,3\text{-BDT})]_n$ is stable up to 400°C under air. Although, this new MOC behaves as an insulator, it exhibits low temperature solid state photoemission and a Second Harmonic Generation (SHG) response.

References

[1] Y. Kamakura & D. Tanaka, Chem. Lett., 2021, 50, 523.
[2] O. Veselska & A. Demessence, Coord. Chem. Rev., 2018, 355, 240.
[3] Q. Wang, S.-L. Dong, D.-D. Tao, Z. Li & Y.-B. Jiang, Coord. Chem. Rev., 2021, 432, 213717.
[4] X. Huang, H. Li, Z. Tu, L. Liu, X. Wu, J. Chen; Y. Liang, Y. Zou, Y. Yi, J. Sun, W. Xu & D. Zhu, J. Am. Chem. Soc., 2018, 140, 15153.
[5] Q. Wang, S.-L. Dong, D.-D. Tao, Z. Li & Y.-B. Jiang, Coord. Chem. Rev., 2021, 432, 213717.

Fig.1: Final Rietveld plot of [Ag2(1,3-BDT)]n

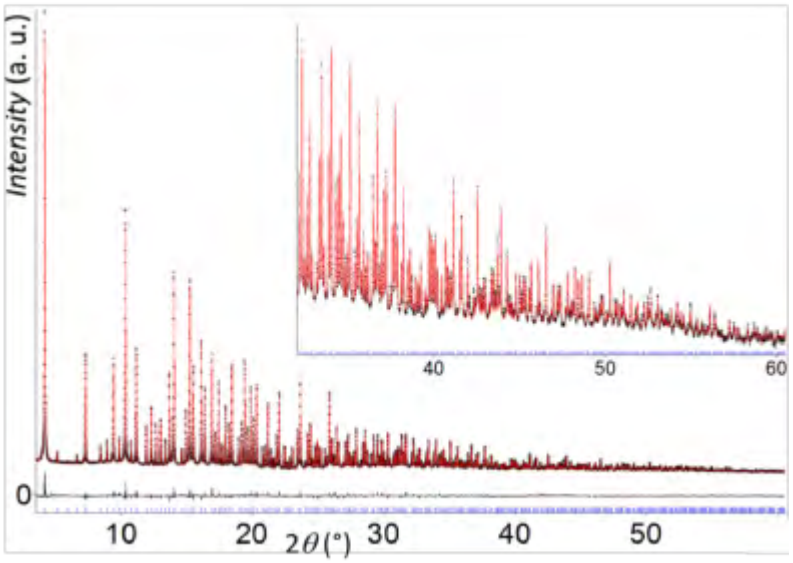

Fig. 2: Structure of [Ag2(1,3-BDT)]n