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Additional Information

Wired metal-organic chalcogenides

Self-assembled transition metal organic chalcogenide nanowires pave the way to a new family of electron conducting materials with tuneable properties.

Fernando Rey and José L. Jordá

Organic structure-directing agents (OSDAs) have been widely used in the past for the bottom-up synthesis of various porous materials. These molecules, which template the void volumes and stabilize the assembly of the porous structures while not constituting an integral part of the final inorganic framework¹, have been key to realize microporous zeolites that are nowadays used massively in detergency, catalysis and separation processes, as well as in supercapacitors and chemical sensors². Similarly, organic molecules have been used to direct the synthesis of metal organic frameworks (MOFs), a microporous organic-inorganic counterpart of zeolites formed by neighboring metallic nodes connected by bidentated organic linkers³. Writing in this issue of *Nature Materials*⁴, Hao Yan and colleagues now show that such approach can be extended to the synthesis of non-porous metal organic chalcogenides (MOCs) having a crystalline inorganic core elongating in one direction and having band-like electronic conductivity.

Microporous and ordered mesoporous germanium sulphides resembling zeolitic structures had been previously synthesized using OSDAs that were not covalently bound to the bridging sulphur atoms⁵⁻⁸. In some cases, sulphide-containing organic molecules were used, which provided a dual function of structure-directing agents and sulphur sources^{9,10}. Following a similar rationale, Yan and coworkers chose two types of diamondoid thiols as OSDAs to obtain MOCs with no structural porosity. These diamondoid compounds present relatively bulky and rigid structures, with strong van der Waals interactions between neighbor molecules. These intermolecular attractions enable the face-on addition of precursors to form elongated nanowires. Using adamantane-1-thiol (Fig. 1a, top), they obtained CuS nanowires having a cross section formed by alternating three-atom S and Cu rings (Fig. 1a, bottom), whereas nanoribbon cores formed by alternating eight and four-atom rings of Cu and S atoms (Fig. 1b, bottom) were obtained using diamantane-4-thiol (Fig. 1b, top). In both cases, the cores are surrounded by the organic moieties that are covalently linked to the S atoms and act as an insulating coating that prevents conduction of electric charges in the direction perpendicular to the nanowire axis while direct the elongated growth of the wires.

These particular topologies provide adequate electronic band structures that allow the monodirectional electron transport along the chalcogenide column. The nature of the CuS chains and organic branches controls the band-gap of the resulting materials and, therefore, their charge transport properties. Furthermore, exposure to H₂O₂ solutions leads to the partial oxidation of the Cu species and to the tuning of the nanowires' resistivity over three orders of magnitude. Yan and colleagues also reported preliminary results replacing Cu with other metals such as Cd, Zn and Fe. This extension of chemical compositions could allow obtaining MOC nanowires where the electronic transport is aided by the simultaneous presence of metals with different oxidation states in the inorganic core. This would avoid using H₂O₂ to

trigger the oxidation of Cu and may lead to even higher electron conductivities than those reported in this study.

Strictly speaking, the MOCs described here cannot be fully seen as tridirectional covalent framework as in typical MOFs, since the structural arrangement of the subnanometric Cu-chalcogenide wires is built through the van der Waals interactions between adjacent organic linkers, rather than through coordination metal-organic or covalent organic-organic bonding. As a result, not only the electronic properties but also the thermal, mechanical and chemical characteristics of the reported MOCs are expected to be very different from those found in MOFs. Indeed, the lack of covalent bonding between adjacent CuS-columns may likely lead to a lower stability of the final materials when compared to MOFs, since the van der Waals interactions between organic moieties are much weaker than those found in metal-to-ligand coordination bonds and covalent C-C linkages. The thermal and mechanical stability is of paramount importance for possible applications in catalysis, electronics and sensing, where typically the material is exposed to relatively high temperatures. Then, further investigations regarding the MOCs stability would be required to assess the limits of application of such materials for the target final uses.

Finally, the versatility of the synthesis approach already demonstrated in this work, as well as the future expansion to other transition metals, could allow the realization of novel chalcogenide-organic frameworks tailored for other uses, such as superconductors, thermoelectrics, sensors and catalysis. Particularly, the development of biocompatible and highly photoluminescent solids with high quantum yield could be envisaged, and this may open new possibilities for biological applications. Also, the formation of chiral metal-organic chalcogenide nanowires aided by the use of enantiomerically pure organothiols could be a promising route for affording optical chirality in solid materials.

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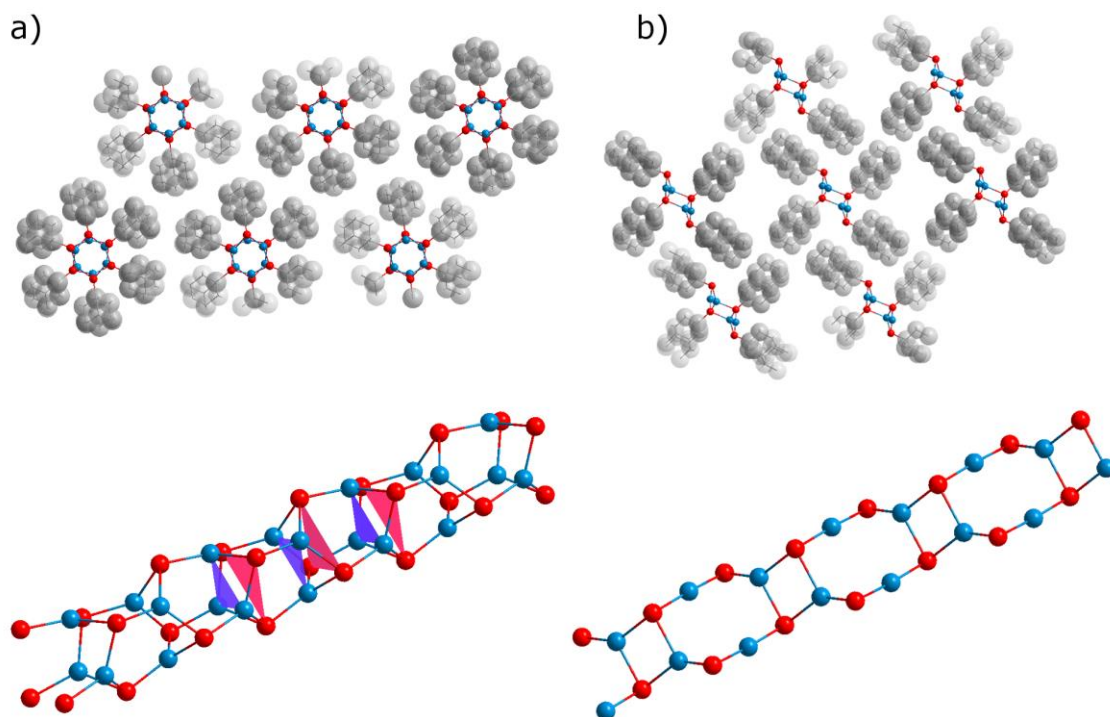


Figure 1 | Metal organic chalcogenides (MOC). a), structure of the adamantane-1-thiol (top) used as OSDA and core of its corresponding CuS MOC nanowire (bottom), with alternating Cu and S rings (blue and red triangles, respectively). b), diamantane-4-thiol (top) and nanoribbon-like core of its corresponding CuS MOC (bottom). Red: S; blue: Cu; grey: C. The carbon atoms surrounding the cores of the MOCs have been removed from the bottom structures for clarity.