Conductivity in Porous 2D Materials Made Crystal Clear

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Single crystal metal–organic framework devices reveal intrinsic conductive properties that are unseen in their polycrystalline forms.

Two-dimensional (2D) metal–organic framework (MOF) materials are often composed of many crystallites of varying size and orientation. Such structural heterogeneity can make it difficult to draw meaningful conclusions about the intrinsic conductivity of these materials, since charge transport in polycrystalline materials is often dominated by extrinsic effects such as grain boundaries between crystals or anisotropy in crystallite orientation. Now, Dinca and co-workers have isolated micron-long single rods of a Ni-based MOF, Ni₃(HITP)₂, and have shown that these materials demonstrate metallic conductivity—a feature that was obfuscated in previous studies of polycrystalline films.

2D MOFs share the same in-plane metal–organic bond layers as the more conventional 3D MOFs but differ in that their out-of-plane interactions are held together by intermolecular forces such as hydrogen bonding or van der Waals interactions rather than metal–ligand bonds. Notably, layered 2D MOFs demonstrate much higher conductivities than conventional MOF structures due to their rigid lateral structure and strong intralayer π–d orbital mixing. 2D MOFs have become major players in the 2D electronic materials field that includes perovskites, graphitic structures, transition metal dichalcogenides, MXenes, among others. What distinguishes 2D MOFs from these other classes of layered materials, however, is that 2D MOFs are both crystalline and intrinsically porous. Conductive 2D MOFs are particularly attractive for applications that harness the high conductivity of the material for electronically manipulating or responding to guest molecules captured in the MOF pores. Notable applications for 2D MOFs that operate on this principle include electrocatalytic chemical transformations, chemiresistive analyte and environment sensing, and supercapacitive energy storage.

Conductive 2D MOFs are constructed from two modular building blocks: π-conjugated organic linkers and metal nodes. Tremendous molecular tunability exists for each building block, as virtually any polycyclic aromatic hydrocarbon with appropriately positioned metal-linking heteroatoms can serve as a linker, and any tetracoordinate metal can serve as a node. There is great interest in understanding how the molecular structure of the 2D MOF dictates its electronic properties. In the ideal scenario, by controlling structure through molecular design, it would be possible to finely tune the MOF material’s band structure, optical absorption, charge transport, electrocatalytic activity, and capacitance.

Of course, obtaining such precise control over structure and thereby electronics in any material is much easier said than done, and 2D framework materials are no exception. Experimental measurements are often misaligned with the expected properties of conductive MOFs predicted by theoretical calculations for idealized structures. Indeed, this was the case for Dinca and co-workers, who previously found that polycrystalline bulk Ni₃(HITP)₂ behaves as a semiconductor, despite subsequent computational studies predicting metallic conductivity in Ni₃(HITP)₂.

Dinca and co-workers have settled this discrepancy in the ACS Central Science article. In a beautiful example of collaborative and interdisciplinary science, the authors combined their expertise in crystal engineering, device physics, theory, and electron microscopy to show that single Ni₃(HITP)₂ rods are indeed metallic in nature when measured in single crystal devices. In order to study charge transport in such devices, MOF crystal lengths must be on the order of microns. Growing 2D MOF crystals of this size is not trivial;
it requires careful control of MOF nucleation rates and crystal growth kinetics. The authors were able to obtain single rods with the length of up to 2 μm by judicious selection of chemical precursors, and titrating in the right amount of oxygen into the solvent.

With these micron-long crystals in hand, the authors compared the temperature-dependent conductivities of single crystals and polycrystalline 2D MOFs in electronic devices (Figure 1A). Metallic conductors exhibit small changes in conductance as temperature decreases, and a nonzero conductance extrapolated at 0 K, whereas semiconductors demonstrate large decreases in conductance as temperature decreases, and no conductance extrapolated at 0 K. The authors found that single rod Ni₃(HITP)₂ devices demonstrate a small 2-fold decrease in conductance when temperature decreases from 295 to 1.4 K (Figure 1B), whereas conductance in the polycrystalline Ni₃(HITP)₂ devices drops many orders of magnitude over a shorter temperature range (Figure 1C). To confirm metallicity, the authors constructed Zabrodskii plots and found that single rod Ni₃(HITP)₂ devices yield a positive slope whereas polycrystalline devices yield a negative slope, indicating metallic and semiconducting transport, respectively.

The metallic nature of the single Ni₃(HITP)₂ rods is particularly fascinating in light of the fact that the orientation of measurement occurs along the pore axis rather than along the lateral layer axis. That is, through-space out-of-plane transport is dominant in these orientations rather than through-bond in-plane transport. To further investigate the differences in interlayer versus intralayer transport, the authors compared conductivity in Cu₃(HHTP)₂ rods, where out-of-plane transport dominates, against Cu₃(HHTP)₂ exfoliated flakes, where in-plane transport dominates. The conductivities of these two topologies were measured to be 1.5 and 0.5 S/cm, respectively, suggesting that out-of-plane and in-plane conductivities operate within the same order of magnitude.

Beyond clarifying intrinsic transport properties from extrinsic factors, the 2D MOF single crystals provide new structural insights, showing that Ni₃(HITP)₂ is not isostructural with Cu₃(HHTP)₂, as was previously thought. Structural characterization in 2D MOFs via diffraction is often limited to powder X-ray diffraction (XRD) due to the material’s polycrystallinity. Bulk polycrystalline Ni₃(HITP)₂ and Cu₃(HHTP)₂ share the same powder XRD pattern, which has led researchers to assume that these two materials have the same intrinsic structure. The large crystalline domains of the materials studied here enabled characterization via high resolution transmission electron microscopy (HRTEM), yielding selected area diffraction patterns of the two MOF materials. Their results suggest that Ni₃(HITP)₂ has an eclipsed structure, with the Ni atoms aligned along the interplane z axis, while Cu₃(HHTP)₂ has angled pores where the Cu atoms are slipped in orientation. These results highlight the notion that 2D MOFs that are thought to be isostructural based on powder XRD assignments may demonstrate quite different structures at the molecular level when interrogated by HRTEM.

By isolating and studying large single crystals, Dinca and co-workers unveiled the intrinsic conductive properties of Ni₃(HITP)₂ and Cu₃(HHTP)₂. Their findings presage a future area of emphasis for 2D MOF conductors based on crystal engineering to obtain larger, more crystalline domains, following a tried-and-true structure-conductivity roadmap that has guided silicon semiconductors, organic electronics, and hybrid perovskites toward reaching their full potential. The implications of their study also point toward exploiting out-of-plane transport as a future frontier in revolutionizing conductive 2D MOF materials. Finally, the marked charge transport difference between the Ni₃(HITP)₂ single crystals and polycrystalline films inspires us to consider whether there are other “diamonds in the rough” in the existing library of polycrystalline 2D MOF.
structures that might demonstrate entirely different electronic profiles as single crystals.

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