Cation-Dependent Intrinsic Electrical Conductivity in Isostructural Tetrathiafulvalene-Based Microporous Metal-Organic Frameworks

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Supporting Information Placeholder

ABSTRACT: The isostructural metal-organic frameworks M₄(TTFTB) (M = Mn, Co, Zn, and Cd; H₂TTFTB = tetrathiafulvalene-tetrabenzoate) exhibit a striking correlation between their single crystal conductivities and the shortest S-S interaction defined by neighboring TTF cores, which inversely correlates with the ionic radius of the metal ions. The larger cations cause a pinching of the S-S contact, which is responsible for better orbital overlap between pₓ orbitals on neighboring S and C atoms. DFT calculations show that these orbitals are critically involved in the valence band of these materials, such that modulation of the S-S distance has an important effect on band dispersion and, implicitly, on the conductivity. The Cd analog, with the largest cation and shortest S-S contact shows the largest electrical conductivity, \( \sigma = 2.86 (\pm 0.53) \times 10^{-4} \, \text{S/cm} \), which is also among the highest in microporous MOFs. These results describe the first demonstration of tunable intrinsic electrical conductivity in this class of materials and serve as a blueprint for controlling charge transport in MOFs with \( \pi \)-stacked motifs.

Imbuining metal-organic frameworks (MOFs) with orthogonal properties that complement their porosity will add a new dimension to the range of potential applications for these materials.¹ Chief among these would be those that employ the extended nature of the MOFs' structures to impart emerging properties that are not available in the molecular precursors. Cooperative magnetism, exciton transport, or charge transport phenomena are some examples that are slowly emerging along this line.² Among these, electrical conductivity is particularly difficult to engineer in MOFs³ because these materials generally have flat bands determined by highly localized organic states and weak hybridization with the inorganic secondary building units. Indeed, of the many hundreds of microporous MOFs, only a few exhibit intrinsic conductivity.⁴ Nevertheless, should electrical conductivity be enabled in such materials, their crystalline structures may provide highly ordered and nearly defect-free infinite charge transport pathways,⁵ leading to superior electrical properties relative to typical conductive polymers, which suffer from chain recoiling and disorder that limit their charge mobility.⁶ The challenge, then, sits squarely in the realm of synthetic chemistry: how can one control the supramolecular arrangement of molecular building blocks to enable electrical conductivity in a microporous MOF?

Three charge transport mechanisms can be operative in molecular conductors such as MOFs: one relies on \( \pi \)-stacking (through-space charge transport), another involves charge transport through the covalent bonds, as in molecular wires, and the third is charge hopping.⁷⁸ The first two mechanisms are ideally based on band transport, while the hopping mechanism is governed by Marcus theory.⁹ Recently, it has been shown that all three mechanisms can be exploited to synthesize MOFs with excellent intrinsic charge mobility and conductivity. For instance, tetrathiafulvalene-tetrabenzoic acid (H₂TTFTB) forms a zinc MOF with infinite \( \pi \)-stacked TTF columns that shows a charge mobility of 0.2 cm²/Vs, as determined by time-resolved microwave conductivity.¹⁰ Triazole- and sulfur-ligated MOFs, such as MET (metal-triazolates),¹¹ M₄(DSBDC) (DSBDC = 2,5-disulphhydrilterephthalate) and Cu[ Ni(pdt)₂] (pdt²⁺ = pyrazine-2,3-dithiolate)¹² have also shown promising electrical properties. Recent work from us and others has also highlighted the excellent properties of two-dimensional graphite-like materials,¹³ with Ni₃(HITP)₂ (HITP = hexaiminotriphenylene) reaching the same bulk conductivity as graphite itself.¹⁴

However, one of the more exciting aspects of producing conductive MOFs, in addition to their potential utility in electronic devices, is the ability to tune their electrical properties. This has been shown with Cu₃(BTC) (BTC = 1,3,5-benzenetricarboxylate), for instance, whose conductivity can be tuned by six orders of magnitude when various amounts of tetracyanoquinodimethane (TCNQ) are introduced in the pores.¹⁵ To our knowledge, however, there are no examples where the conductivity of a MOF can be tuned in the absence of intentional doping or other external factors that often
reduce the available surface area by pore blocking. Here, we show that varying the metal cation employed in the synthesis of TTFTB-based MOFs from Zn\(^{2+}\) to Co\(^{2+}\), Mn\(^{2+}\), and Cd\(^{2+}\) changes the shortest S-S distance between neighboring TTF cores in the infinite \(\pi\)-stacked columns. In turn, this causes a modulation of the single crystal conductivity by nearly two orders of magnitude in the absence of any other external variables. The variation correlates very well with the S-S distance and is confirmed by conductivity measurements of over 20 single crystals for each sample.

As previously reported, reaction of H\(_2\)TTFTB with Zn(NO\(_3\))\(_2\) produces Zn\(_2\)(TTFTB), wherein TTF ligands form a chiral \(\pi\)-stack with 6\(_{2}\) symmetry, which are connected to infinite zinc benzoate chains (Figure 1c). Because \(\pi\)-\(\pi\) interactions are weaker than covalent interactions, we surmised that changing the metal cation would maintain the overall structure of the covalent lattice. At the same time, we hypothesized that increasing the ionic radius of the metal cation would lengthen the metal-carboxylate chains, thereby possibly pinching the TTF stack, leading to a shorter intermolecular S-S distance. Decreasing this parameter would increase the dispersity of the band formed by the sulfur 3p orbitals because it would increase the overlap integral for these orbitals. Overall, this should have a positive effect on the electrical properties of isostructural MOFs made with cations of increasing radius.

To verify these hypotheses, we employed density functional theory to calculate the band structure of the reported Zn\(_2\)(TTFTB) material. Several important facts emerge from this calculation, which is shown in Figure 1. First, the valence band has a dispersity of 43 meV. This is much larger than reported for many other MOFs,\(^{45}\) whose bands are so narrow that they may be more prosaically described as discrete energy levels.\(^{46}\) The valence band is also considerably wider than the conduction band, as expected for a hole conductor based on electron-donating TTF units. Finally, the p orbitals of the sulfur and central carbon atoms on TTF define the valence band, suggesting that indeed the likely pathway for charge transport involves these orbitals and that, according to the extended Hückel theory, the band dispersion of a TTF stack would be dramatically varied as the overlap of these p orbitals changes. A qualitatively similar picture is observed for the Cd analog of this material (vide infra and Figure S1).

Reacting H\(_2\)TTFTB with Mn(NO\(_3\))\(_2\)-xH\(_2\)O, Co(NO\(_3\))\(_2\)-6H\(_2\)O, or Cd(NO\(_3\))\(_2\)-4H\(_2\)O under conditions mimicking those used for the synthesis of Zn\(_2\)(TTFTB) produced [Mn\(_2\)(C\(_\text{5}\)H\(_\text{4}\)O\(_\text{6}\))\(_2\)](DMF)\(_{0.5}\)(H\(_2\)O)\(_{0.5}\) (Mn\(_2\)(TTFTB)), [Co\(_2\)(C\(_\text{5}\)H\(_\text{4}\)O\(_\text{6}\))\(_2\)](DMF)\(_{0.5}\)(H\(_2\)O)\(_{0.5}\) (Co\(_2\)(TTFTB)) and [Cd\(_2\)(C\(_\text{5}\)H\(_\text{4}\)O\(_\text{6}\))\(_2\)](DMF)\(_{0.5}\)(H\(_2\)O)\(_{0.5}\) (Cd\(_2\)(TTFTB)) as dark red needles. Powder X-ray diffraction (PXRD) confirmed the homogeneity of the bulk crystalline samples, which are all isostructural with Zn\(_2\)(TTFTB) (Figure S2). Single crystal X-ray diffraction confirmed that all three compounds crystalize in the P\(_6_1\) space group, where the 6\(_{\text{3}}\) screw axis is slightly offset from the central ethylene unit of the TTF core, such that the TTF units are rotated by 60° relative to one another and translated in the c direction (Figure 2a and 2b). The plane containing the TTF core is not perfectly perpendicular to the screw axis, which results in only one relatively close S-S contact between each pair of neighboring TTF units. The secondary building units are helical chains of corner-sharing metal-oxygen polyhedra joined by helical stacks of benzoates pertaining to TTFTB\(^{48}\). Whereas the Zn, Co, and Mn materials exhibit corner-sharing pseudo-octahedra, Cd\(_2\)(TTFTB) exhibits alternating seven- and six-coordinate metal ions.

Figure 1. a) Calculated band structure and projected density of states (PDOS) of Zn\(_2\)(TTFTB). The work function, \(\phi\), and absolute energy scale are aligned relative to vacuum according to Ref. 20. The coordinates of the reciprocal space points are \(\Gamma = (0, 0, 0)\) and \(A = (0, 0, 1/2)\). Corresponding pictorial representation of the valence band orbitals in Zn\(_2\)(TTFTB) (b) and one of the TTF cores (c). Zn atoms and their coordination sphere are represented by black polyhedra. Golden, red, black, and white spheres represent S, O, C, and H atoms, respectively.

Thermogravimetric analysis (TGA) coupled with elemental analysis of samples desolvated at 200 °C and 4 mtorr showed that Mn\(_2\)(TTFTB) and Co\(_2\)(TTFTB) lose both coordinated and guest solvent molecules, while Cd\(_2\)(TTFB) loses the coordinated water molecules only above ~220 °C (Figure S3). All show permanent microporosity evidenced by N\(_2\) adsorption isotherms at 77 K, which revealed uptakes of ~150 cm\(^3\)/g, ~30 cm\(^3\)/g, and ~140 cm\(^3\)/g of N\(_2\) and BET surface areas of 470 m\(^2\)/mmol, 531 m\(^2\)/mmol, and 512 m\(^2\)/mmol, respectively for Mn\(_2\)(TTFTB), Co\(_2\)(TTFTB), and Cd\(_2\)(TTFTB) (Figure S4). These are comparable with the surface area of Zn\(_2\)(TTFTB) (537 m\(^2\)/mmol).

Most importantly, the shortest S-S distance observed in each of the materials follows the predicted pattern and in-
creases from 3.6538(23) Å in Cd$_2$(TTFTB) to 3.6929(6) Å, 3.7568(13) Å, and 3.7732(26) Å in Mn$_2$(TTFTB), Zn$_2$(TTFTB), and Co$_2$(TTFTB), respectively. The respective ionic radii vary inversely from 109 pm for Cd$^{2+}$ to 97 pm, 88 pm, and 88.5 pm for high spin Mn$^{2+}$, Zn$^{2+}$, and Co$^{2+}$. These values are summarized in Table 1. These short intermolecular S–S distances are comparable to those found in charge transfer salts such as TTF-TCNQ ($d_{S-S} = 3.75$ Å), TTF-dicyanoquinonediimine ($d_{S-S} = 3.69$ Å), and TTFCl, ($d_{S-S} = 3.60$ Å).

Figure 2. The helical TTF stack with a depiction of the shortest intermolecular S–S contacts (dashed red line): (a) view along the ab plane, (b) view down the c axis. Yellow and gray spheres represent S and C atoms, respectively. Phenyl rings and metal atoms were omitted for clarity.

Table 1. Closest interatomic S–S distance between neighboring TTF cores.

<table>
<thead>
<tr>
<th>Ionic radius of M$^{II}$ (pm)</th>
<th>S–S (Å)</th>
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<tbody>
<tr>
<td>Co$_2$(TTFTB)</td>
<td>88.5</td>
</tr>
<tr>
<td>Zn$_2$(TTFTB)</td>
<td>88</td>
</tr>
<tr>
<td>Mn$_2$(TTFTB)</td>
<td>97</td>
</tr>
<tr>
<td>Cd$_2$(TTFTB)</td>
<td>109</td>
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</tbody>
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Figure 3. Histograms with the distribution of single crystal electrical conductivities for Cd$_2$(TTFTB), Mn$_2$(TTFTB), Zn$_2$(TTFTB), and Co$_2$(TTFTB).

To assess the influence of the S–S separation on the intrinsic electrical properties of each material, we performed single crystal conductivity measurements, which are less affected by grain boundaries than bulk pellet measurements (see Supporting Information for experimental details). Because conductivity is the product of charge mobility and charge carrier density, and the dispersity of the valence band was expected to influence the mobility, but not the carrier density; we needed to estimate the latter in each case. To this end, it is well known that the length of the C–S and C=C bonds in TTF are sensitive to the level of doping in stacked TTF materials. As shown in Table S4, we found that among the M$_2$(TTFTB) materials these bonds vary by less than 0.0025 Å and 0.009 Å for the C–S and C=C bonds, respectively. Although small variations in charge carrier densities caused by slightly different positions of the Fermi energy level may not be apparent in these distances, and may yet influence conductivity, this analysis suggests that the level of doping is similar in each material.

The single crystal conductivity measurements were performed along the crystallographic c axis of millimeter-sized needle-shaped crystals, using two gold probes attached by carbon paste at each end of a crystal. Current-voltage (I–V) curves were measured by sweeping the voltage from −1 V to 1 V. Ohmic contacts were observed in this potential interval. To eliminate variations stemming from batch/device preparation and microscopic defects, we performed measurements on more than 20 crystals coming from 4–5 independent batches for each M$_2$(TTFTB) variant. A histogram of the results is shown in Figure 3. The average conductivity values obtained under these conditions, plotted against the observed S–S distance in Figure 4, evidences a remarkable vari-
ation among the four isostructural MOFs. Thus, Cd₄(TTFTB), which exhibits the shortest S–S distance, has an average conductivity of 2.86 (±0.53) × 10⁻⁴ S/cm. This is 72 times higher than the average conductivity of Zn₄(TTFTB) (σ = 3.95 (±0.56) × 10⁻⁶ S/cm). Mn₄(TTFTB) and Co₄(TTFTB), which display intermediate S–S distances between those observed in the Zn and Cd analogues, also show intermediate conductivity values of 8.64 (±1.21) × 10⁻⁵ S/cm and 1.49 (±0.29) × 10⁻⁵ S/cm, respectively, both tracking inversely with increasing S–S distance. We note that four-point probe conductivity measurements of single crystals of Cd₄(TTFTB), Mn₄(TTFTB), and Co₄(TTFTB) revealed values of 6.79 × 10⁻⁴ S/cm, 1 × 10⁻⁴ S/cm, and 5 × 10⁻⁵ S/cm, respectively. These evidenced a trend that is in line with that observed by two-probe measurements, suggesting that contact resistances are not responsible for the observed differences among the four analogs. The consistently smaller size of the Zn₄(TTFTB) crystals prevented us from performing a similar experiment on this material. On the other hand, measurement of the single crystal conductivity of Zn₄(TTFTB) in a direction perpendicular to the c axis, performed by attaching two gold leads parallel to the ab plane (see Figure S9), revealed a value of 2.03 × 10⁻⁷ S/cm. Thus, the conductivity of Mn₄(TTFTB) is anisotropic and is largest along the direction of the TTF column. Overall, the conductivity values of all Mn₄(TTFTB) are among the highest for any microporous coordination polymer.

In conclusion, we showed that using increasingly larger cations causes an elongation of the one-dimensional SBUs and a concomitant contraction of the inter-TTF distance in Mn₄(TTFTB), a series of MOFs with π-stacked TTF columns. By decreasing the S–S distance between neighboring TTF cores, we were able to increase the overlap between the sulfur 3p orbitals, which are critically involved in the charge transport pathway, as revealed by DFT calculations. This led to the isolation of a series of new, permanently porous MOFs with high intrinsic conductivity, and an improvement of nearly two orders of magnitude for Cd₄(TTFTB) over the original analogous zinc compound. These results provide a systematic blueprint for designing new electrically conductive MOFs based on the through-space charge transport formalism.

ASSOCIATED CONTENT
Supporting Information
Detailed experimental procedures and computational details; X-ray crystal data (PXRD and single crystal), Nₛ adsorption isotherms, conductivity measurements, and TGAs. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interests.

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REFERENCES


$M_{i} (TTFTB)$

\[ \text{M} = \text{Mn}^{2+}, \text{Co}^{2+}, \text{Zn}^{2+}, \text{Cd}^{2+} \]

S-S distance