Metal–organic frameworks (MOFs) that display intrinsic electrical conductivity are still rare, but conductivity is emerging as an attractive complement to the inherent porosity of these materials. If high surface area is combined with electrical conductivity or high charge mobility, MOFs could find uses in fields outside traditional areas such as gas storage and separation, and make strides into batteries, supercapacitors, electrocatalysis, and sensing, among others. Although recent reports of conductive MOFs have crystallized several potential avenues toward improved electrical properties, including in-plane π-conjugation, through-space charge transport, through-bond charge transport, and doping, these design strategies require significant refinement.

In this context, we recently reported Mn₄(DSBDC), a MOF-74 analogue that contains (-Mn-S-)∞ chains, and discussed the positive effect of replacing phenoxo by thiophenoxo groups on charge mobility. While this was inspired by the rich literature of inorganic conductors, where heavier chalcogens generally lead to better electrical properties, the equally compelling literature of inorganic semiconductors shows, for instance, that iron chalcogenides are better intrinsic conductors than manganese chalcogenides, highlighting that the metal ions may be as important as the chalcogens. Taking a cue from inorganic chalcogenides, we wanted to test the relative importance of the metal ion for MOFs with infinite chains as their secondary building units. To do so, we set out to compare the Mn²⁺ and Fe²⁺ analogues of the family of materials known as MOF-74, surmising that replacement of Mn²⁺ by Fe²⁺ would lead to superior electrical conductivity, as seen for the inorganic chalcogenides. Here, we show that within isostructural materials, replacing Mn²⁺ with Fe²⁺ leads to a million-fold enhancement in electrical conductivity, a considerably more pronounced effect than substituting bridging O atoms with less electronegative S atoms.

[Fe₂(DSBDC)(DMF)₂]ₓ(DMF) was isolated as dark red-purple crystals after heating a degassed and dry solution of H₂DSBDC and anhydrous FeCl₂ in N,N-dimethylformamide (DMF) at 140 °C under an N₂ atmosphere for 24 h, and washing with additional DMF. Single-crystal X-ray diffraction analysis of Fe₂(DSBDC)(DMF)ₓ(DMF) revealed an asymmetric unit containing one Fe atom coordinated by three carboxylate groups, two thiophenoxide groups, and one DMF molecule. The sulfur atoms are coordinated in trans fashion to the Fe²⁺ atom, with Fe–S bond lengths of 2.444(2) and 2.446(2) Å. This indicates that both S atoms interact with the same d orbital of Fe²⁺, an important orbital symmetry requirement for efficient charge transport. Although Fe₂(DSBDC) is isostructural with Fe₂(DOBDC) and Mn₂(DSBDC), its structure is only topologically related to that of Mn₂(DSBDC). As shown in Figure 1a, whereas Fe₂(DSBDC) has a single metal atom in the asymmetric unit, Mn₂(DSBDC) has two: one that is octahedrally coordinated by donors on DSBDC⁴⁻ ligands, and another that is bound by two DMF molecules. Relevantly, the two distinct metal ions in Mn₂(DSBDC) reduce the symmetry of the (-Mn-S-)∞ chains, which may negatively affect their charge transport properties. As in other MOF-74 analogues, the (-Fe-S-)∞ chains in Fe₂(DSBDC) are bridged by thiophenoxide and carboxylate groups to form a three-dimensional framework with one-dimensional hexagonal pores with a van der Waals diameter of ~16 Å (Figures 1b and S1).

When Mn₄(DSBDC)(DMF)₂ₓ(DMF) are soaked in dichloromethane and then evacuated under vacuum (100 °C, 2 h), they yield Mn₄(DSBDC)(DMF)₂, a series of materials that are guest-free and where DMF completes the coordination sphere of all metal sites. Infrared spectroscopy and microelemental analysis confirmed that all guest molecules were removed under these conditions (Figure S4). Surprisingly, powder X-ray diffraction (PXRD) revealed that Fe₂(DSBDC)(DMF)ₓ(DMF) is distorted in comparison to Fe₂(DSBDC)(DMF)ₓ(DMF), a distortion that was not observed in the other three analogues (Figures S3 and S5). Mathematical simulation and DFT optimization of completely solvent-free Fe₂(DSBDC) gave a structure whose simulated pattern agreed well with the observed PXRD pattern of Fe₂(DSBDC)(DMF)ₓ(DMF) (see Figure 1c and the Supporting Information).

ABSTRACT: Reaction of FeCl₂ and H₄DSBDC (2,5-disulphhydrylbenzene-1,4-dicarboxylic acid) leads to the formation of Fe₂(DSBDC), an analogue of Mn₂(DOBDC) (MOF-74, DOBDC⁻⁴ = 2,5-dihydroxybenzene-1,4-dicarboxylate). The bulk electrical conductivity values of both Fe₂(DSBDC) and Fe₂(DOBDC) are ~6 orders of magnitude higher than those of the Mn₂ analogues, Mn₂(DEBDC) (E = O, S). Because the metals are of the same formal oxidation state, the increase in conductivity is attributed to the loosely bound Fe²⁺/β-spin electron. These results provide important insight for the rational design of conductive metal–organic frameworks, highlighting in particular the advantages of iron for synthesizing such materials.
Supporting Information). This distortion is reversible: soaking Fe₂(DSBDC)(DMF)₂ in fresh DMF produced a crystalline phase with a PXRD pattern identical to that of Fe₂(DSBDC)(DMF)₂·x(DMF) (Figure S6). To our knowledge, although breathing behavior has been observed for several classes of MOFs,₁₆ it has never been associated with MOF-74 analogues.

N₂ sorption analysis revealed Brunauer−Emmet−Teller (BET) surface areas of 232, 241, and 287 m²/g for Mn₂-(DEBDC)(DMF)₂, Fe₂-(DEBDC)(DMF)₂, and Mn₂-(DOBDC)(DMF)₂, respectively, confirming their guest-free nature and permanent porosity (Figure S8). These values are lower than those expected for completely activated MOF-74 analogues because coordinated DMF molecules occupy a significant portion of the pore volume in M₂(DEBDC)(DMF)₂. Fe₂-(DSBDC)(DMF)₂ exhibited a lower BET surface area of 54 m²/g, likely because the distorted pores in this case are almost entirely occupied by coordinated DMF molecules (Figure S9).

Owing to the small crystallite size of all of these materials, single-crystal measurements of their electrical properties proved unfeasible. Accordingly, we prepared pellets of both M₂-(DEBDC)(DMF)₂·x(DMF) and M₂(DEBDC)(DMF)₂ materials, for a total of eight samples, all of which were analyzed by two-probe current−voltage techniques. Plots of measured current density versus electric field strength, shown for the as-synthesized samples in Figure 2a and for the guest-free samples in Figure S10, revealed striking differences in electrical conductivity between the Fe and Mn analogues, regardless of their solvation level. Indeed, both Fe₂-(DSBDC)(DMF)₂·x(DMF) (σ = 3.9 × 10⁻⁶ S/cm) and Fe₂-(DOBDC)(DMF)₂·x(DMF) (σ = 3.2 × 10⁻⁷ S/cm) were ~6 orders of magnitude more conductive than Mn₂-(DSBDC)(DMF)₂·x(DMF) and Mn₂-(DOBDC)(DMF)₂·x(DMF), which exhibited conductivities of 2.5 × 10⁻¹² and 3.9 × 10⁻¹³ S/cm, respectively (Table 1).₁₇ Although the guest-free materials showed slightly lower conductivities overall, possibly due to additional defects and grain boundaries caused by the solvent exchange and guest removal process, they reflected the same remarkable 6 orders of

Figure 1. (a) Parts of the infinite secondary building units in M₂(DEBDC)(DMF)₂·x(DMF) (M = Fe, Mn; E = S, O). The (-M-E-)ₙ chains are represented in purple. (b,c) Partial structures of Fe₂-(DSBDC)(DMF)₂·x(DMF) and Fe₂-(DSBDC)(DMF)₂ as determined by single-crystal X-ray diffraction and DFT structure optimization, respectively. H atoms and solvent molecules are omitted for clarity.

Figure 2. Electrical properties of M₂(DEBDC) (M = Fe, Mn; E = S, O) pressed pellets. (a) Plots of current density versus electric field strength (J−E curves) for M₂(DEBDC)(DMF)₂·x(DMF) at 297 K. (b) Conductance−temperature relationship for M₂(DEBDC)(DMF)₂.
To probe the cause of the large difference between the Fe and Mn analogues, we determined the activation energy in M2(DEBDC)(DMF)2 by measuring their pellet conductance under variable temperature between 200 and 420 K. Working with guest-free rather than as-synthesized materials was necessary because our variable-temperature, air-free electrical microprobe setup requires that samples be passed through an evacuation chamber. However, it is reasonable to assume that because neutral guest solvent molecules are unlikely to occur during our experiments.

Density functional calculations were used to further probe the differences in electronic structure of M2(DEBDC)(DMF)2, and the significance of the additional d electron associated with the Fe2+ ions. The electronic density of states and ionization potentials of the guest-free system are presented in Figure 3, and detailed in the Supporting Information. Because Fe2(ODBC) and Mn2(ODBC) are structurally analogous, while Fe2(DSBDC) and Mn2(DSBDC) differ in the number of metal ions in their asymmetric units, the comparison between Fe2(ODBC) and Mn2(DSBDC) illustrates best the difference between Mn2+ and Fe2+. Most importantly, the valence band maximum of Mn2(DSBDC) is composed of C-p, O-p, and Mn-d states, while in Fe2(ODBC) the Fe-d states dominate the valence band, with negligible contribution from ligand orbitals. This difference is attributed to the low binding energy of the filled β-spin d band of Fe2+, which is empty for the d6 high-spin Mn2+ ions. Furthermore, because the lower conduction band in both MOFs is dominated by ligand-based orbitals, the band gaps are narrowed owing to a decreased work function. As a result, the calculated work functions and band gaps of Fe2(ODBC) are 0.91 and 1.01 eV smaller than those of Mn2(ODBC), respectively.

To assess the relative importance of the chalcogen atom on the charge transport, we also compared the structurally analogous Fe2(DSBDC) and Fe2(ODBC) materials. First, the valence and conduction bands of these frameworks are flat in reciprocal space (dispersion of <100 meV in all cases). This behavior is indicative of localized orbitals rather than delocalized bands, and

Fe2+, these experiments demonstrated that oxidation to Fe3+ did not occur during our experiments.

Differences in electronic structures are reflected in density of states (DOS) of M2(DEBDC)(DMF)2 (M = Fe, Mn; E = S, O). The work function, Φ, and the absolute energy scale are aligned to vacuum according to ref 19. Gray curves represent total DOS. Blue, teal, yellow, red, and black curves represent projected DOS of Fe, Mn, S, O, and C, respectively.

To the Arrenius law (eq 1) revealed notables differences in activation

\[ G = G_0 \exp \left( \frac{-E_a}{kT} \right) \]  

energies, \( E_a \), shown in Table 1. Thus, both Fe2(DSBDC)(DMF)2 (\( E_a = 0.27 \) eV) and Fe2(ODBC)(DMF)2 (\( E_a = 0.41 \) eV) had considerably lower activation energies than Mn2(DSBDC)(DMF)2 (\( E_a = 0.81 \) eV) and Mn2(ODBC)(DMF)2 (\( E_a = 0.55 \) eV), suggesting that the Fe-based MOFs have smaller band gaps and hence higher charge density than the Mn-based MOFs.

Table 1. Electrical Properties of M2(DEBDC) (M = Fe, Mn; E = S, O)

<table>
<thead>
<tr>
<th></th>
<th>Fe2 (DSBDC)</th>
<th>Mn2 (DSBDC)</th>
<th>Fe2 (DOBC)</th>
<th>Mn2 (DOBC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \sigma_{\text{as-synthesized}} ) (S/cm)</td>
<td>3.9 \times 10^{-4}</td>
<td>2.5 \times 10^{-12}</td>
<td>3.2 \times 10^{-7}</td>
<td>3.9 \times 10^{-13}</td>
</tr>
<tr>
<td>( \sigma_{\text{vacuum}} ) (S/cm)</td>
<td>5.8 \times 10^{-7}</td>
<td>1.2 \times 10^{-12}</td>
<td>4.8 \times 10^{-8}</td>
<td>3.0 \times 10^{-13}</td>
</tr>
<tr>
<td>( E_a ) (eV)</td>
<td>0.27</td>
<td>0.81</td>
<td>0.41</td>
<td>0.55</td>
</tr>
<tr>
<td>( E_a ) (eV)</td>
<td>1.92</td>
<td>2.60</td>
<td>1.47</td>
<td>2.48</td>
</tr>
<tr>
<td>( \Phi ) (eV)</td>
<td>3.71</td>
<td>3.81</td>
<td>2.81</td>
<td>3.72</td>
</tr>
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</table>

\( a \)Electrical conductivity of M2(DEBDC)(DMF)2 at 297 K. 
\( b \)Electrical conductivity of M2(DEBDC)(DMF)2 at 297 K. 
\( c \)Activation energy of M2(DEBDC)(DMF)2. 
\( d \)Calculated bandgap of M2(DEBDC)(DMF)2. 
\( e \)Calculated work function of M2(DEBDC)(DMF)2.
is typical of many MOFs.21 Thus, we anticipate that the primary mode of conduction is through charge hopping. Moreover, because the Fe$^{3+}$ d orbitals dominate the valence band (83% of the orbital contribution), intervalence transitions between Fe atoms will proceed with little contribution from O. In contrast, due to the enhanced orbital overlap in Fe$_2$(DDBDC), where Fe and S orbitals contribute 53% and 14% to the valence band, transport will occur through both Fe and S in the (Fe-S)$_\infty$ chains. This mechanism lowers the charge hopping barrier and is also associated with the larger work function of Fe$_2$(DDBDC) compared with that of Fe$_2$(DOBDC). Finally, the increased contribution of C-p states to the valence band in Fe$_2$(DDBDC) compared to Fe$_2$(DOBDC) may also indicate a more efficient interchain transport, which further increases the conductivity of materials in this class.

**ASSOCIATED CONTENT**

**Supporting Information**
Experimental details, table of X-ray refinement details, PXRD patterns, IR spectra, I−V curves, Mössbauer spectra, isotherms, computational details, and crystallographic data (CIF). The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b02897.

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**Notes**

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

This work was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under award no. DE-SC0006937. Part of the characterization was performed at the Shared Experimental Facilities, supported by the NSF under the MRSEC Program (DMR-08-19762). M.D. thanks the Sloan Foundation, the Research Corporation for Science Advancement, and 3M for non-tenured faculty awards. Work in the UK benefited from access to ARCHER through fellowship (Grant No. 277758). We thank Prof. S. J. Lippard for use of the Mössbauer spectrometer and Prof. J. R. Long for valuable discussions.

**REFERENCES**

19. (s) Bhide, V. G.; Dani, R. H. Physica 27, 21, 821.