

# Charge Transport Mechanisms in Electrically Conductive Metal Organic Frameworks

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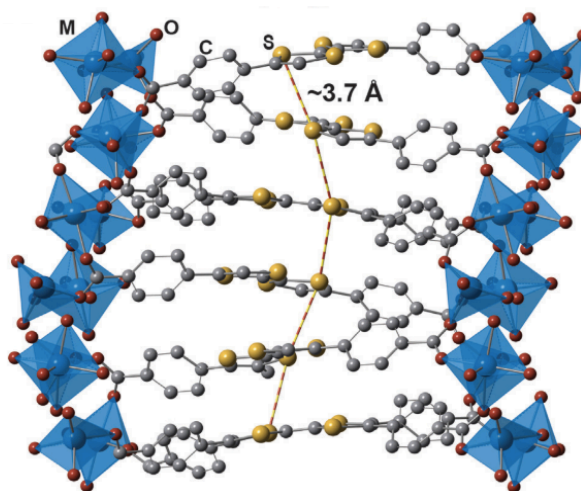
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Two decades ago, a new class of porous materials known as metal-organic frameworks (MOFs) left an indelible mark on the field of chemistry. In 1999, researchers were astonished to observe surface areas of  $2900 \text{ m}^2\text{g}^{-1}$ , which far surpassed those of the highest surface area zeolites, for MOF-5.<sup>1</sup> Since then, MOFs were deemed to have enormous potential for gas storage and separation applications, causing research efforts in this field to increase exponentially. This led to successes in increasing MOF surface areas to as high as  $7140 \text{ m}^2\text{g}^{-1}$ , improvements to their chemical stability, and advancements in their selectivity and degree of adsorption of specific gases.<sup>2,3</sup> MOFs have found applications as heterogeneous catalysts and electrocatalysts as well.<sup>4</sup> Applicability in the latter of the two fields has been limited thus far by their high intrinsic resistivity. Hence, imparting conductivity into these materials would expand their range of applications and allow them to be implemented into technologies such as fuel cells, capacitors, thermoelectrics, and resistive sensing.<sup>5-7</sup>

Fortunately, a number of recent publications report the synthesis and characterization of electrically conductive MOFs.<sup>6,7,9-11</sup> Unlike typical MOFs, this new subclass of MOFs employs multiple design principles, such as incorporating redox-active organic linkers or metal ions with low electron binding energies into the MOF structure, to achieve a desirable semi-conductive behavior. Characterization of electrically conductive MOFs has led to the discovery of three primary mechanisms of charge transport. These are through-space charge transport, whereby charges travel through overlapped orbitals, through-bond charge transport, in which charges are free to travel along delocalized orbitals, and charge hopping, whereby charges tunnel between localized states. A clear understanding of these modes of transport is critical for achieving rational design of electrically conductive MOFs.

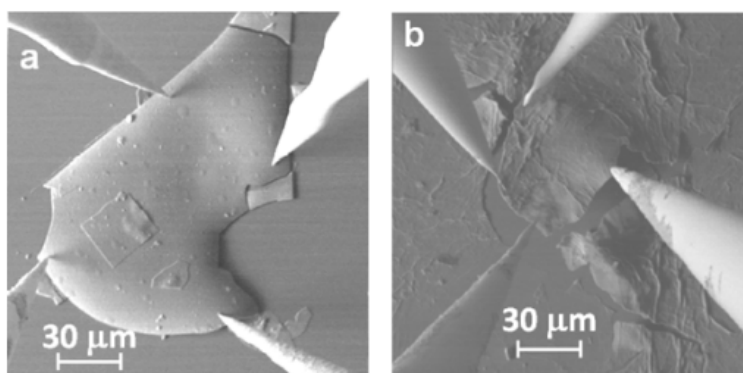
In 2012, Narayan et al. set out to obtain an electrically conductive MOF by integrating  $\pi$ -bond stacking into its structure, which facilitates through-space charge transport.<sup>6</sup> This work builds on a previous report that displays the high conductivity, which stems from charge transport through stacked  $\pi$  bonds, of tetrathiafulvene (TTF)-tetracyanoquinodimethane, an electron-donor-acceptor complex.<sup>8</sup> More recently, the same group unambiguously revealed  $\pi$ -bond orbital overlap to be the source of that charge transport by modulating the  $\text{S}\cdots\text{S}$  distance between neighboring TTF cores and



**Figure 1.** Side view of helical TTF-based MOF, showing average inter-TTF core  $\text{S}\cdots\text{S}$  distances

observing changes to the MOF's electrical conductivity.<sup>9</sup> Helically structured TTF-based MOFs (Fig. 1) were obtained by simply heating TTF derivatives with zinc, manganese, cobalt, or cadmium nitrates in solution. Single crystal XRD determination of their crystal structures shows an inversely proportional relationship between the ionic radii of the transition metal and interatomic S···S distance between neighboring TTF cores. Shifts to S···S distance were induced by the degree of pinching of the TTF stack, which was caused by differences in bulkiness among the metal cations. Two-point and four-point probe conductivity measurements reveal an inversely proportional relationship between these S···S distances and electrical conductivity. Conductivity measurements performed along different planes of a TTF-based MOF show an order of magnitude higher conductivity in the direction parallel to the  $\pi$ -bond stack relative to that observed along the perpendicular plane, which serves to further confirm that this material exhibits through-space charge transport. Moreover, with DFT calculations a band gap energy of 1.75 eV, which is typical of semi-conductors, was found, and an increased overlap between the sulfur 3p<sub>z</sub> orbitals with increased cation size was observed.

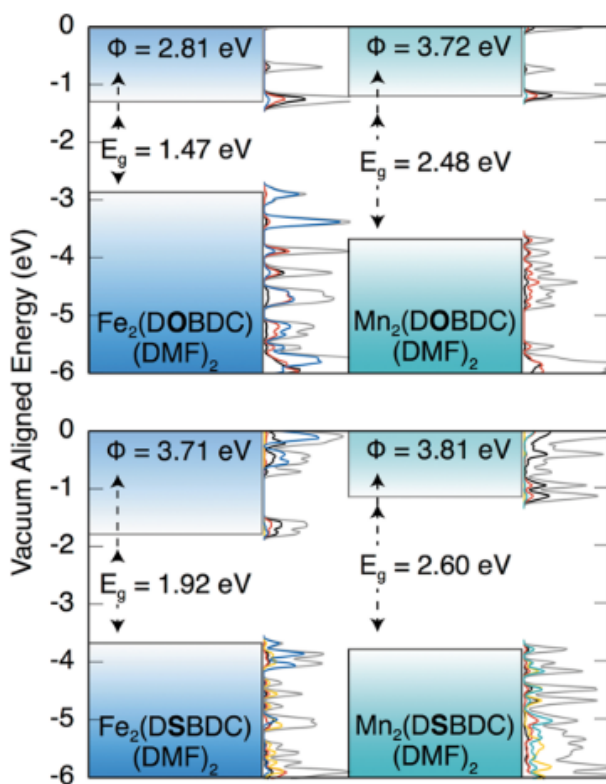
In 2013, Kambe et al. synthesized an electrically conductive MOF that exhibits remarkably high conductivities, which were modulated by altering the oxidation state of the material.<sup>10</sup> The MOF was obtained by liquid-liquid interface reaction of nickel acetate with benzenehexathiol. This MOF's 2D  $\pi$ -conjugated structure, which facilitates through-bond charge transport, was verified via PXRD,



**Figure 2.** SEM images of van der Pauw measurements of oxidized (a) and as-prepared (b) nickel bis(dithiolene)

selected area diffraction, and IR spectroscopy. Subsequent studies observed an increase in conductivity from 2.8 S cm<sup>-1</sup> to 160 S cm<sup>-1</sup> upon chemical oxidation of the as-prepared 2D MOF.<sup>11</sup> The oxidation states were determined via XPS and the conductivity was obtained with four-probe van der Pauw measurements on micro-flakes of the nickel dithiolene 2D MOF (Fig. 2). Owing to the delocalization of orbitals through an extended  $\pi$ -conjugated framework, it is not surprising that this material exhibits one of the highest conductivities among electrically conductive MOFs.

Sun and coworkers recently reported an electrically conductive MOF that exhibits charge-hopping as its primary mode of charge transport.<sup>7</sup> Similar to the aforementioned study, their experiments consisted of exchanging the cation to control the conductivity. Their work focused on the MOF-74 family, which had been previously discovered by Rosi et al., but for which no conductivity had been reported.<sup>12</sup> Briefly, four MOF-74 analogues were synthesized by heating 2,5-disulfhydrylbenzene-1,4-dicarboxylic acid (DSBDC) or 2,5-dihydroxybenzene-1,4-dicarboxylic acid (DOBDC) with iron or manganese chlorides in solution for several days. Two-point probe conductivity measurements of pelletized samples of these MOFs show a million-fold increase to the electrical conductivity upon replacing the Mn<sup>2+</sup> with Fe<sup>2+</sup> for either DSBDC or



**Figure 3.** Density of states (DOS) of Mn and Fe MOF-74 analogues. Gray curves represent total DOS. Blue, teal, and yellow curves represent contribution to DOS from Fe, Mn, and S, respectively.

spawn a host of exciting technologies in the future. Although substantial characterization efforts and clever experimental designs have been employed to understand charge transport mechanisms in these materials, more work must be conducted to better rationalize the supposed modes of transport. For example, experimental determination of their electronic band structure through UV photoelectron spectroscopy could be used to complement first principles calculations. A robust understanding of the charge transport mechanisms in electrically conductive MOFs will only serve to discover better design principles and allow more effective control of their chemical and physical properties.

DOBDC-based MOFs. This dramatic increase in conductivity was attributed to an increased valence band energy arising from the pairing of electrons in  $d^6$   $\text{Fe}^{2+}$  as compared to  $d^5$   $\text{Mn}^{2+}$ . Whereas Mossbauer spectroscopy corroborated the presence of high spin  $\text{Fe}^{2+}$  in MOF-74-Fe analogues, DFT calculations showed that the decreased binding energy of d-band electrons in  $\text{Fe}^{2+}$  relative to  $\text{Mn}^{2+}$  leads to a relative increase in contribution of the cation's d states to the electronic band structure (Fig 3). The authors relate this to a decrease in band gap energy upon exchange of  $\text{Mn}^{2+}$  for  $\text{Fe}^{2+}$ , which is followed by an increase to the electrical conductivity. Further investigation of MOF-74-Fe band structure through DFT, revealed a localization of orbitals, which suggests that the primary mode of conduction is through charge hopping. However, this conclusion is marred by a lack of experimental evidence.

Electrically conductive MOFs are a novel subclass of MOFs that are likely to

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