Tunable Mixed-Valence Doping toward Record Electrical Conductivity in a Three-Dimensional Metal–Organic Framework

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Supporting Information

ABSTRACT: Partial oxidation of an iron–tetrazolate metal–organic framework (MOF) upon exposure to ambient atmosphere yields a mixed-valence material with single-crystal conductivities tunable over 5 orders of magnitude and exceeding 1 S/cm, the highest for a three-dimensionally connected MOF. Variable-temperature conductivity measurements reveal a small activation energy of 160 meV. Electronic spectroscopy indicates the population of midgap states upon air exposure and corroborates intervalence charge transfer between Fe$^{2+}$ and Fe$^{3+}$ centers. These findings are consistent with low-lying Fe$^{3+}$ defect states predicted by electronic band structure calculations and demonstrate that inducing metal-based mixed valency is a powerful strategy toward realizing high and systematically tunable electrical conductivity in MOFs.

Electrical conductive metal–organic frameworks (MOFs) are emerging as a class of porous materials of interest for diverse applications as well as for fundamental studies of charge transport in molecular materials. Several strategies for enhancing conductivities in MOFs have been demonstrated—for example, utilizing non-innocent ligands to introduce charge carriers, minimizing energy differences between metal and ligand frontier orbital energies, and employing redox-active guest molecules in post-synthetic modification. Although mixed valency is a feature that has been observed in many conductive MOFs to varying degrees, studies that actively and systematically introduce mixed-valence motifs and correlate their effect on conductivity in this class of materials are lacking.

We reported previously that frameworks based on Fe$^{5+}$ exhibit higher conductivities and lower activation energies compared to many other divalent transition metals across different structural families, likely due to hole doping with small amounts of Fe$^{3+}$ in these frameworks. However, previous materials did not allow for systematic variation of the doping level, and thus the influence of Fe$^{3+}$ sites was inferred indirectly. As such, we sought to develop additional Fe$^{5+}$-based frameworks in order to ascertain the influence of metal-based mixed valency on transport properties and expand the range of conductivities accessible via this approach. In particular, we targeted frameworks with structural motifs such as infinite one-dimensional secondary building units (SBUs) and relatively electropositive ligands that would reduce the activation barrier for charge transfer, thereby engendering low-energy charge transport pathways.

With this motivation, we studied the electronic properties of the Fe$_2$(H$_{0.67}$BDT)$_3$·17(H$_2$O)·0.5(PrOH) (H$_2$BDT = 5,5′-(1,4-phenylene)bis(1H-tetrazole)) (Fe$_2$(BDT)$_3$)$_{17}$ and found that the single-crystal conductivity of this material is tunable over 5 orders of magnitude by varying the extent of Fe$^{2+/3+}$ mixed valency. The results herein illustrate how inducing metal-based mixed valency in a MOF with continuous through-bond charge transport pathways results in electrical conductivity that is rationally tunable to values exceeding those of any other three-dimensional MOFs.

Single crystals of Fe$_2$(BDT)$_3$ were isolated from a solvothermal reaction between H$_2$BDT, FeSO$_4$·7H$_2$O, and NaSCN in water and isopropyl alcohol (PrOH) under oxygen-free conditions. Powder X-ray diffraction (PXRD) analysis confirmed that the product was phase-pure and had the desired structure, containing one-dimensional (Fe–N–N–N) chains extending in the [001] direction (Figure 1). Experimental indexing of a single crystal indicated that the long axis of the crystal corresponds to the crystallographic a axis (Figure S1). Orange-red crystals of as-synthesized Fe$_2$(BDT)$_3$, gradually darken upon exposure to air over the course of several days, and progress to deep red and then black (Figure S2), with otherwise no structural distortion or degradation indicated by PXRD (Figure 1c). In comparison, crystals kept under oxygen-free conditions retain their original color over time. Further confirmation of structural integrity came through gas sorption studies: A nitrogen adsorption isotherm of air-exposed black Fe$_2$(BDT)$_3$ upon activation under dynamic vacuum at 120 ºC yielded an apparent Brunauer–Emmett–Teller (BET) surface area of 614(1) m$^2$/g (Figure S3), similar to the reported value for the Co analogue.

Very dark colors or even black are commonly associated with mixed-valence compounds, as might be expected with Fe$_2$(BDT)$_3$ from the oxidation of some Fe$^{2+}$ sites to Fe$^{3+}$. To ascertain whether these color changes and the presumed mixed

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valency led to improved charge transport, 11 two-probe
devices20 were fabricated by contacting single crystals of
Fe$_2$(BDT)$_3$ from six separate batches (∼300−900 μm in
length) along the crystallographic a axis. The average electrical
conductivity of the as-synthesized red crystals was 6(2) × 10$^{-5}$
S/cm at room temperature (296 K). Upon exposure to air, the
conductivity invariably increased, exhibiting a remarkable
correlation with the duration of exposure. Average conductivity
values reached 0.3(2) S/cm after 7 days and 1.2(4) S/cm after
30 days, with a champion conductivity of 1.8 S/cm (Figure 2).

To the best of our knowledge, the conductivity of Fe$_2$(BDT)$_3$
after 30 days in ambient atmosphere is the highest value
reported to date for the single-crystal conductivity of any MOF
material$^{1,3,21,22}$ as well as for a three-dimensionally connected
MOF.6,8,11 Conductivity values remained constant thereafter,
with no degradation observed in devices stored under ambient
conditions for durations up to 7 months.

A variable-temperature (VT) conductivity measurement on a
two-probe single-crystal device of Fe$_2$(BDT)$_3$ that had been
exposed to air for 30 days revealed semiconducting behavior (Figure 3). Fitting the data between 225 and 350 K to the

$$\sigma = \sigma_0 \exp(-E_a/k_B T)$$

Arrhenius equation, yielding an average value for $E_a$ of 160
meV.

Changes in the color of Fe$_2$(BDT)$_3$ crystals along with the
increasing conductivity with air exposure can be quantitatively
probed optically. Fresh single crystals of Fe$_2$(BDT)$_3$ were
diluted with BaSO$_4$ and diffuse reflectance UV−vis−near-
infrared (NIR) spectra were taken at different time points over
the course of 48 h as the sample was exposed to the atmosphere
(Figure 4). The bands at 300, 380, and 520 nm observed in

Figure 1. (a) Structure of Fe$_2$(BDT)$_3$. (b) (Fe−N−N)$_\infty$ chains,
which serve as the presumed charge transport pathways in this
material. (c) Powder X-ray diffraction patterns of air-exposed, as-
synthesized, and simulated Fe$_2$(BDT)$_3$.

Figure 2. Conductivities of single-crystal devices of Fe$_2$(BDT)$_3$
exposed to ambient atmosphere for different lengths of time measured
under ambient conditions.

Figure 3. Variable-temperature conductivity measurement on a single-
crystal device of Fe$_2$(BDT)$_3$. Inset: black line indicates fitting of the
data to the Arrhenius equation, yielding an average value for $E_a$ of 160
meV.

Figure 4. Diffuse reflectance UV−vis−NIR spectra of Fe$_2$(BDT)$_3$
exposed to ambient atmosphere for different lengths of time. Inset: Tauc plot of the data.
every spectrum are characteristic of low-spin (LS) Fe²⁺ centers octahedrally coordinated by tetrazole ligands. The transition at 300 nm corresponds to a ligand-to-metal charge transfer (LMCT), while the features at 380 and 520 nm can be assigned to d→d transitions of LS Fe²⁺ (¹A₁→¹T₂ and ¹A₁→¹T₂, respectively).

The evolution of the Fe₂(BDT)₃ spectra as the material is exposed to atmosphere correlates with increasing Fe³⁺ concentrations. In particular, we assign the peak centered at 690 nm, which grows in with longer air exposure times, to intervalence charge transfer (IVCT) between Fe²⁺ and Fe³⁺ centers. This feature is very similar to an IVCT band observed in Prussian blue, a canonical Class II mixed-valence compound in the Robin–Day classification. Furthermore, the broad feature observed in the NIR region after 21 and 48 h in air is tentatively assigned to polaron transitions, which we attribute to increasing concentrations of charge carriers. The intensities of analogous features in conductive polymers correlate directly with doping levels.

A Tauc plot of the Kubelka–Munk-transformed spectra reveals an optical bandgap of 2.0 eV in as-synthesized Fe₂(BDT)₃, as indicated from a linear fit to the onset of absorption (Figure 4 inset). In samples kept in air for 21 and 48 h, the energy of the absorption onset decreases to 1.4 eV. The shift observed with increasing air exposure time indicates that midgap states are being populated in these samples and is consistent with the higher conductivity of crystals of Fe₂⁺(BDT)₃, left in air for longer periods.

On the basis of transport and spectroscopic studies, Fe₂(BDT)₃ can be described as a Class II material, defined by the coexistence of distinguishable localized valences along with measurable electronic coupling. Here, the d→d transition bands in the optical data are characteristic of localized Fe²⁺ centers, while the IVCT features and transport properties indicate the presence of electronic coupling between mixed-valent Fe²⁺ and Fe³⁺ centers.

To further probe the oxidation and spin states of the iron centers in air-exposed Fe₂(BDT)₃, we turned to ⁵⁷Fe Mössbauer spectroscopy. At 80 K, a sample of Fe₂(BDT)₃ exposed to ambient atmosphere for 12 days exhibited a broad signal that could be fitted with an isomer shift δ = 0.378(3) mm/s and quadrupole splitting ΔE_Q = 0.280(6) mm/s (Figure S6). This result is consistent with expected parameters for LS Fe²⁺ in an O₆ environment and in line with experimental results for LS Fe²⁺ centers in similar ligand environments.

As the Mössbauer signal from high-spin (HS) Fe³⁺ may overlap with that of LS Fe²⁺, these data neither rule out nor confirm the presence of a small proportion of HS Fe³⁺ centers. However, the data do indicate the absence of other iron spin states in the material, and also suggest at least partially localized Fe³⁺. The LS Fe²⁺ (or HS Fe³⁺) assignment also agrees with the Fe–N bond lengths of 1.948(3) and 1.961(3) Å from the published crystal structure.

The importance of even a small concentration of Fe³⁺ centers is apparent from density functional theory (DFT) calculations, which revealed the intrinsic electronic band structure of Fe₂(BDT)₃ (Figure S5). Importantly, the computed bandgap of the native LS Fe²⁺ framework is 2.0 eV, in agreement with the optical bandgap obtained from electronic spectroscopy. The valence band (VB) dispersion width, about 380 meV, is also relatively large for a semiconducting MOF material. In addition, the density of states (DOS) indicates that the VB predominantly comprises Fe- and N-centered orbitals, confirming that the (Fe–N–N–)₅ chains function as the primary charge transport pathways in Fe₂(BDT)₃.

Air-exposed Fe₂(BDT)₃ was modeled as a partially oxidized hypothetical material with a doubled unit cell wherein 1/8 of the Fe²⁺ sites were replaced with HS Fe³⁺. The Fe³⁺ defect unoccupied orbitals appear as midgap states, where the lowest energy state is separated from the VB maximum by only ~60 meV. The location of these states is consistent with the higher conductivity and lower energy of the optical absorption onset experimentally observed upon air exposure. In particular, the proximity of the lowest energy Fe³⁺ state to the VB corroborates the small E_v obtained from VT conductivity measurements.

In conclusion, we have shown that the single-crystal conductivity of the MOF Fe₂(BDT)₃ can be tuned over 5 orders of magnitude by varying the length of air exposure time, reaching the highest values yet for any three-dimensionally connected MOF. The partial oxidation of the material, resulting in Fe³⁺ defect states, is responsible for the high conductivity of the resulting mixed-valence MOF. The wide range of conductivities accessible on purpose in this material and the direct correlation between hole-doping, metal-based mixed valency, and conductivity demonstrated here serve as a blueprint for designing new conductive frameworks across diverse structures and compositions.

**ASSOCIATED CONTENT**

◆ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.8b03604.

Experimental and computational methods, and Figures S1–S7, showing crystal indexing results, images of devices, nitrogen adsorption isotherm, I–V curves, Mössbauer spectrum, and cyclic voltammogram (PDF)

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