Linker Redox Mediated Control of Morphology and Properties in Semiconducting Iron-Semiquinoid Coordination Polymers

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ABSTRACT: The emergence of conductive 2D, and less commonly 3D, coordination polymers (CPs) and metal–organic frameworks (MOFs) promises novel applications in chemical sensing, energy storage, optoelectronics, thermoelectrics, and spintronics. While classic CPs and MOFs now have relatively sophisticated synthetic parameters to control morphology, crystallinity, and phase purity, similar parameters are not thoroughly understood for electronically more complex materials. In particular, many linkers used in conducting CPs have multiple accessible redox states and the relationship between starting linker oxidation state and final material structure and properties is not well understood. Here we report a new 3D semiconducting coordination polymer, Fe5(C6O6)3, which is composed of hexagonal Fe5(C6O6)3 layers which are bridged by additional Fe ions. This material, which is a fusion of 2D Fe-semiquinoid materials and recently reported 3D cubic Fe5(C6O6)3, materials, is obtained by using a different initial redox-state of the C6O6 linker. The material displays high electrical conductivity (0.02 S cm–1), broad electronic transitions in the visible to middle-infrared region, promising thermoelectric behavior (S2σ = 4.2×10–9 W m–1 K–2), and strong antiferromagnetic interactions even at room temperature. The unique structure and properties of this material illustrates that controlling the oxidation states of redox-active components in conducting CPs can be a “pre-synthetic” strategy to carefully tune material topologies, properties, and functionalities in contrast to more commonly encountered post-synthetic modifications.

Introduction

Introducing novel bulk electronic properties such as charge mobility or electrical conductivity into coordination polymers (CPs) and metal–organic frameworks (MOFs) has been an area of very active research in recent years.1 These features, while interesting in their own right, are even more appealing when combined with the tunable topologies and structures that are hallmarks of CPs and MOFs.2 Thus, this emerging class of multifunctional materials has found many novel applications in chemical sensing,3 electrochemical energy storage,4 optoelectronics,5 thermoelectrics,6 magnetism and spintronics.7 While the exploration of promising functionalities and applications in these materials has been a major focus, for instance in using sophisticated physical characterization methods8 and theoretical calculations9 to study carrier transport mechanisms, the exploration of the synthetic space10,11 of these new electronic materials is still nascent. This is particularly true when contrasted to the rich morphological, structural, defect, and phase space of more traditional MOF candidates which can largely be controlled by choice of synthetic conditions, additives, or linker morphology.12

When considering synthetic variables for electronically complex CPs and MOFs, the redox-states of the metal and linker components are a critical factor.12 For example, Sun et al. measured the electrical conductivity and activation energy for twenty different MOFs in four distinct structural families. They found that Fe-based MOFs displayed significantly higher conductivities and smaller charge activation energies due to in-situ oxidation to form Fe(II/III) mixed valency in contrast to the other metals which maintain divalent oxidation states.13 Similar examples can be seen for linkers. Quinone-based linkers are prototypical redox-active motifs and numerous examples of new conducting or magnetic CPs/MOFs have been reported using linkers of the form (C6O6X2) (X =H, F, Cl, Br, I, NO2, CN).14 Despite the importance of the final linker redox-state for materials structure and properties, leveraging different linker-redox states as a synthetic strategy, such as using different quinone redox-isomers in syntheses, has not been thoroughly investigated.

Taken to the limit of monocyclic quinones, hexahydroxybenzene (HHB) or tetrahydroxy-1,4-quinone (THQ), has the most accessible redox-isomers and several possible radical based intermediates (Figure 1).10c,15 As such, this linker is an extremely attractive target for incorporation into new materials, but also offers unique challenges in predicting or controlling the redox-state of resulting MOFs. The first 2D semiconducting MOF featuring this motif, Cu-HHB

Figure 1. Multiple accessible oxidation states (top) and possible intermediates (in dashed box) of C6O6.
[[Cu2(C6O6)2]] was synthesized in 2018 by reacting Cu(II) with either HHB or THQ.10e This material displays good performance in lithium-ion battery and photoconductivity applications as illustrated by later reports,4e,8c but an interesting observation is that the same structure is formed regardless of the linker precursor oxidation state. Switching from Cu(II) to a more easily oxidized Fe(II) ion results in two novel 3D conducting MOFs, namely Fe12(C6O6)6 and Fe8(C6O6)6.16 Although these two materials have generally cubic unit cells, the connections between metals and linkers as well as the final oxidation states of the linkers are different (Figure 2A top), likely due to the subtle differences in reaction conditions. Both of these examples provide concrete illustrations of how different materials can result from common or closely related precursors due to different synthetic protocols. This is particularly true in metal-semiquinoid based materials as spontaneous redox chemistry likely plays an important role upon material formation and growth.

We were intrigued by the multiple accessible precursor redox-states of C6O6 linkers in this family of materials, particularly in the context of varying material structure and properties through different initial linker redox states. Herein, we present the synthesis of a new 3D semiconducting CP, Fe5(C6O6)3, which is generated by reacting Fe(II) with the most reduced linker precursor HHB instead of THQ. In contrast to the Cu systems mentioned above, the use of a different redox-state of the linker results in a dramatically different structure. Like most other quinone-based coordination polymers of this type, Fe5(C6O6)3 consists of hexagonal layers but with a staggered AB stacking. Moreover, these layers are further bridged by axial Fe centers through Fe–O bonds to generate a 3D material (Figure 2A bottom). This novel topology is reminiscent of retrofitting modifications used in carboxylate-based MOFs to affect material properties,17 as well as proposed approaches to promote delocalization of charge by extending into three dimensions.18 The optical absorption, conductivity, Seebeck coefficient, and magnetic susceptibility of Fe5(C6O6)3 have been explored, revealing redox-state and structurally dependent trends. The isolation of this new material in the Fe5(C6O6)3 family demonstrates the rich morphological, structural, and phase space available to these electronically interesting CPs. Furthermore, our studies demonstrate that, in contrast to post-synthetic modifications, pre-synthetically controlling the redox-states of components in conductive or magnetic coordination polymers is an important parameter for encoding properties and functionalities.

Results and Discussion

Synthesis and structure

Fe5(C6O6)3 was prepared by reacting anhydrous FeCl2 with HHB in dimethylformamide (DMF) at 100 °C for three days under an inert atmosphere. These synthetic conditions are similar to those reported for Fe12(C6O6)6 and Fe8(C6O6)6 but with slight modifications to maintain the integrity of the HHB linker. Reaction condition screening

Figure 2. (A) Schematic illustration of the previously reported 3D materials Fe12(C6O6)6, Fe8(C6O6)6 and the Fe5(C6O6)3 material reported here. (B) Orientation of neighboring layers in Fe5(C6O6)3. Orange: Fe, red: O, grey: C; coordinated solvent molecules are omitted for clarity. (C) Comparison of the synchrotron X-ray powder diffraction data (295 K, λ = 0.458093 Å) and calculated (LeBail and Rietveld) patterns in P63. (D) SEM image of Fe5(C6O6)3 powder.
shows that adding base (triethylamine, dimethylamine) or other polar solvents (water, methanol, diethylene glycol) decreases the crystallinity of the resulting material. X-ray powder diffraction (XRPD) data of the product indicated formation of a crystalline material (Figure 2C, Figure S2), and the pattern can be indexed in a primitive hexagonal unit cell \( a = b = 24.63 \ \text{Å}, c = 14.93 \ \text{Å}, \alpha = \beta = 90^\circ, \gamma = 120^\circ \). The Le Bail fit shows that essentially all of the observed Bragg peaks can be accounted for by this unit cell and the \( P6_3 \) space group (Figure S4-S5, see experimental section for a description of the structure solution).

The structure was solved by scripting the algebraic computations of the molecular fragments and the resulting framework layers with a python programming language that followed simulated annealing global optimizations. The final structure of \( \text{Fe}_5(\text{C}_6\text{O}_6)_3 \), as depicted in Figure 2A, shows that 40% of the Fe atoms are octahedrally coordinated with \( \text{C}_6\text{O}_6 \) units to form extended hexagonal layers. These hexagonal layers are reminiscent of similar layers in quinone-based materials and are significantly different from the pseudocubic structures observed for the \( \text{Fe}_{12}(\text{C}_6\text{O}_6)_6 / \text{Fe}_8(\text{C}_6\text{O}_6)_6 \) materials previously reported. However, in \( \text{Fe}_5(\text{C}_6\text{O}_6)_3 \), the layers are packed in a staggered ABAB pattern and neighboring layers have a mirror-like orientation (Figure 2B). These 2D layers are further bridged by extra Fe atoms (60%) which link them into a 3D structure similar to that found in layered lanthanide metal–organic frameworks. The coordination environment of these bridging Fe atoms is completed by solvent molecules, however, the positions of these solvents are unsurprisingly highly disordered, thus precluding a precise determination of their positions. The Rietveld refinement of the model lacking exact positions of solvent molecules shows a satisfactory agreement with the experimental pattern (a final \( R_b \) value is 12.2%, Figure 2C, Table S3).

Combustion and thermogravimetric analysis are consistent with this structural assignment with a formula of \( \text{Fe}_5(\text{C}_6\text{O}_6)_3(\text{H}_2\text{O})_3(\text{C}_3\text{H}_7\text{NO})_3 \) (Table S1 and Figure S11). Scanning electron microscopy (SEM) images show a hexagonal rod- or needle-like morphology which is also consistent with the structural assignment (Figure 2D). The size of the particles ranges from 200 nm to 1 \( \mu \)m due to substantial interparticle growth. Furthermore, \( N_2 \) uptake experiments suggest a type II isotherm and a measured BET surface area of 41.7 m\(^2\)/g (Figure S12). Both results indicate a lack of porosity of the material as expected from the staggered AB packing and the existence of interlayer bridging Fe with coordinated solvent molecules.

This unusual structure is distinct from both 2D semiquinoid MOFs as well as the 3D materials derived from THQ. \( \text{Fe}_5(\text{C}_6\text{O}_6)_3 \) has two distinct coordination environments for Fe: octahedral intralayer and pseudotetrahedral interlayer. In \( \text{Fe}_{12}(\text{C}_6\text{O}_6)_6 \), the O atoms from each \( \text{C}_6\text{O}_6 \) linker all coordinate in an \( \eta^2 \)-bridging manner such that each Fe atom is either connected with six O atoms from three perpendicular \( \text{C}_6\text{O}_6 \) linkers (66%) or ligated by a combination of two O atoms from \( \text{C}_6\text{O}_6 \) linkers and four O atoms from solvent (33%). In \( \text{Fe}_5(\text{C}_6\text{O}_6)_3 \), all the Fe atoms are symmetrically coordinated to three perpendicular \( \text{C}_6\text{O}_6 \) units but the O can either be \( \eta^1 \) or solely coordinated to a single Fe center. In contrast, all of the O atoms in \( \text{Fe}_8(\text{C}_6\text{O}_6)_6 \) coordinate to only one Fe atom. The unusual structure of \( \text{Fe}_5(\text{C}_6\text{O}_6)_3 \) suggests that it should also have unusual electronic and physical properties.

**Oxidation states of the components**

X-ray photoelectron spectroscopy (XPS) was initially used to probe the oxidation state of the Fe ions in \( \text{Fe}_5(\text{C}_6\text{O}_6)_3 \) (Figure S14). A broad Fe 2p\(3/2 \) peak is observed which is centered around 710.5 eV. The position of this peak suggests a mixed valent material as compared with values in iron oxides (FeO \( \approx 709.5 \) eV, Fe\(_2\)O\(_3 \) \( \approx 711 \) eV). Further corroboration of mixed valency is obtained from \(^{57}\text{Fe} \) Mössbauer spectroscopy where three sets of signals are observed in the spectrum (Figure 3A and Figure S15). One of the Fe sites (~24%) has an isomer shift (\( \delta \)) of 0.665(1) mm/s and a quadrupole splitting (\( \Delta E_Q \)) of 0.933(7) mm/s while another (~49%) has a \( \delta \) of 0.683(2) mm/s and a \( \Delta E_Q \) of 1.308(14) mm/s. Both of these sets of parameters are consistent with an assignment of high-spin Fe(III) centers although the observed \( \delta \)’s are slightly larger than those assigned to high spin Fe(III) centers in iron-semiquinoid complexes and CPs. For instance, the \( \delta \) is 0.574(2) mm/s.
for the 3D \((\text{NBu}_4)_2\text{Fe}_2(\text{dhbq})_3\) material.\(^{14b}\) The larger isomer shift may be due to a decrease in electron density on the Fe(III) centers in our material.\(^{14c}\) The third feature (~27\%) has a \(\delta\) of 1.269(3) mm/s and a \(\Delta E_p\) of 3.105(4) mm/s which distinctly assigns this site as a high-spin Fe(II) species.\(^{21}\) Digestion experiments show no evidence for the presence of \(\text{Me}_2\text{NH}_2^+\) in the material for charge balance (Figure S13). Given the overall oxidation states of the Fe centers obtained from Mössbauer spectroscopy and the molecular formula, the oxidation state of the organic linkers is estimated to be ~4.5 per \(\text{C}_6\text{O}_6\) unit.

Corroborating evidence of the oxidation state of the linkers was obtained from Fourier-transform infrared (FTIR) spectroscopy. As shown in Figure 3B, after coordination a stretching band around 1000 cm\(^{-1}\) in \(\text{Fe}(\text{C}_6\text{O}_6)_3\), tentatively assigned to a C-O vibration, shifts to a higher frequency compared to the free ligand HHB. This shift suggests a more oxidized linker in \(\text{Fe}(\text{C}_6\text{O}_6)_3\) than in the starting ligand. A similar shift is also observed between THQ and \(\text{Fe}(\text{C}_6\text{O}_6)_6\). In addition, comparison of the two Fe materials reveals a slightly lower C-O stretching frequency in \(\text{Fe}(\text{C}_6\text{O}_6)_3\) than in \(\text{Fe}(\text{C}_6\text{O}_6)_6\). This supports a more reduced linker oxidation state in the former material, as would be consistent with the formal oxidation state of roughly ~4.5 which would arise from mixed valency between \(L^5^-/L^6^+\) for the HHB linkers as indicated by Mössbauer analysis. In comparison, the calculated average charge from Mössbauer analysis is ~5.4 and ~3.6 per \(\text{C}_6\text{O}_6\) unit in the related cubic materials \(\text{Fe}_{12}(\text{C}_6\text{O}_6)_6\) and \(\text{Fe}_8(\text{C}_6\text{O}_6)_6\), potentially suggesting a mixed valency of \(L^6^-/L^5^+\) in and \(L^4^-/L^3^-\) respectively. The significantly different formal linker oxidation states in these materials, in addition to their distinct structures, illustrates the rich composition space that is available for these conductive MOFs and also shows how using linker redox states can be a valuable tool to explore new phases of these materials.

**Electronic properties**

The electronic properties of \(\text{Fe}_5(\text{C}_6\text{O}_6)_3\) were then explored with a variety of techniques. UV-vis-NIR diffuse reflectance spectroscopy shows four major absorption signals (Figure 4A, S16). The sharp peak centered at around 300 nm, which is also seen in the free ligand, is assigned to a \(\pi \rightarrow \pi^*\) transition in the organic linkers.\(^{22}\) The shoulder-like peak, which is more obvious in the solution spectra of a suspension (Figure S16), at around 370 nm is tentatively assigned to an internal transition from the radical linkers (\(L^5^-\)) although this transition occurs at around 470 nm in the chloranilate based radical (CA\(^3^-\)) and the 2,5-dihydroxy-1,4-benzoquinone based radical (DHBO\(^3^-\)).\(^{21}\) The peak at around 560 nm in \(\text{Fe}_5(\text{C}_6\text{O}_6)_3\) is reasonably assigned as a ligand-to-metal charge transfer band, which is similarly observed in a semiquinone-catecholate based mononuclear iron complex and iron semiquinoid-based MOFs.\(^{14c,22}\)

Most notably, \(\text{Fe}_5(\text{C}_6\text{O}_6)_3\) displays a strong and broad absorption starting from 650 nm and tailing to 2700 nm. This broad absorption is indicative of an intercalation charge transfer (IVCT) and can be classified as Class II/III according to the Robin-Day formalism.\(^{12b}\) It is worthwhile to note that the first observation of Class II/III ligand-based mixed-valency in a MOF was in \((\text{NBu}_4)_2\text{Fe}_2(\text{dhbq})_3\) with an IVCT transition band centered at around 1428 nm (\(\lambda_{\text{max}} = 7000\) cm\(^{-1}\)).\(^{14b}\) Later, several metal-semiquinoid frameworks have displayed Robin–Day Class II/III mixed-valency with broad absorbances in the mid-IR region extending to the near-IR region.\(^{14e}\) Even among this group, our material features a notably broad adsorption ranging from the visible to mid-IR region. The breadth of this feature may be attributed to dual mixed valency from both metal centers and organic linkers. An estimated band gap \((E_g)\) of 0.75 eV is obtained from a Tauc plot with a direct band gap fitting (Figure 4A inset) and is very similar to that observed in the two 3D \(\text{Fe}_{12}(\text{C}_6\text{O}_6)_6/\text{Fe}_8(\text{C}_6\text{O}_6)_6\) materials supporting that all of these compounds feature mixed-valency.

The electrical conductivity of \(\text{Fe}_5(\text{C}_6\text{O}_6)_3\) was measured as an average of 0.02 ± 0.004 Scm\(^{-1}\) on pressed pellets at room temperature using a two-probe method (Figure S17). This value is similar to other 3D conducting MOFs and slightly higher than \(\text{Fe}_5(\text{C}_6\text{O}_6)_3\) and \(\text{Fe}_{12}(\text{C}_6\text{O}_6)_6\) despite the more anisotropic layered structure in \(\text{Fe}_5(\text{C}_6\text{O}_6)_3\).\(^{14d,24}\)

![Figure 4](image)

(A) UV-vis-NIR diffuse reflectance spectrum (four absorption features are marked; inflection around 800 nm is due to lamp change, F(R) is the Kubelka–Munk conversion of the raw diffuse reflectance ). Inset is the Tauc plot with a direct band gap fitting (dashed line) for the near-IR feature. (B) Arrhenius fitting (red line) of the variable-temperature conductance (G) data (black dots) by the equation of \(G = G_0\exp(E_a/kT)\).
Variable-temperature conductivity measurements over 140–295 K show that the conductance of the material increases with temperature, indicative of semiconducting behavior (Figure S18). Arrhenius fitting to the nearest-neighbor hopping (NNH) model\textsuperscript{14e,24} suggests a small activation energy (E\(_a\)) of 0.26 eV (Figure 4B). This value is similar to that reported for the Fe\(_8\)(C\(_6\)O\(_6\))\(_3\) and Fe\(_{12}\)(C\(_6\)O\(_6\))\(_6\), which again can be ascribed to dual mixed-valency that facilitates redox-hopping between neighboring ligands or metal centers.\textsuperscript{16}

The thermoelectric properties of Fe\(_8\)(C\(_6\)O\(_6\))\(_3\) were also explored and the Seebeck coefficient was measured as +45.7 μV K\(^{-1}\) at room temperature, suggesting a p-type thermoelective behavior (Figure S19).\textsuperscript{\textperiodcentered} Combined with its comparatively high conductivity, Fe\(_8\)(C\(_6\)O\(_6\))\(_3\) is a promising candidate for thermoelectric conversion with further optimization. Interestingly, Fe\(_{12}\)(C\(_6\)O\(_6\))\(_6\) exhibits n-type thermoelectric behavior (−130 μVK\(^{-1}\)) with a lower conductivity (2.7×10\(^{-4}\) S cm\(^{-1}\)) at room temperature. The calculated power factor (\(\sigma_S\sigma\)) is 4.2×10\(^{-8}\) W m\(^{-1}\) K\(^{-2}\) for Fe\(_8\)(C\(_6\)O\(_6\))\(_3\) and 4.6×10\(^{-8}\) W m\(^{-1}\) K\(^{-2}\) for Fe\(_{12}\)(C\(_6\)O\(_6\))\(_6\). These values are lower than those reported for 2D conductive MOFs. For instance, a high \(\sigma_S\sigma\) value of 8.3×10\(^{-7}\) W m\(^{-1}\) K\(^{-2}\) has been reported for the hexaiminotriphenylene based MOF Ni\(_5\)(HTPP); and a record of 2.0×10\(^{-6}\) W m\(^{-1}\) K\(^{-2}\) was reported for the perthiolated coronene based MOF Ni-PTC.\textsuperscript{20,21} The lower power factor of 3D materials is mostly ascribed to their lower electrical conductivity compared to the 2D conductive MOFs mentioned above, although both a high \(\sigma\) and \(S\) is desirable to achieve a high power factor. A critical disadvantage in these 3D materials is that redox hopping is the major contributor to conductivity while high metal-ligand covalency and strong in-plane π-d conjugation are more efficient for carrier transport in the 2D MOFs.\textsuperscript{14d,24,18} As the primary challenge for developing high performance thermoelectric CPs/MOFs is improving charge carrier mobility, both "pre-synthetic" strategies (i.e. π-d conjugation enhancement) and post-synthetic modifications (i.e., doping) are promising approaches for further optimization.\textsuperscript{6a,25}

**Magnetic properties**

Fe\(_8\)(C\(_6\)O\(_6\))\(_3\) also displays interesting magnetic properties. DC magnetic susceptibility measurements were performed and the experimental \(\chi_M T\) per formula unit decreases almost linearly from 300 K to around 80 K (Figure 5A). This behavior suggests the existence of a dominant antiferromagnetic exchange coupling. Moreover, the observed \(\chi_M T\) value at 300 K is 9.53 cm\(^3\) K mol\(^{-1}\) for each Fe\(_8\)(C\(_6\)O\(_6\))\(_3\) unit. This value is much smaller than the estimated magnetically uncoupled spin-only value for the number of Fe and linker spin centers implied from Mössbauer analysis (\(\chi_M T \approx 20\) cm\(^3\) K mol\(^{-1}\)) which is also consistent with antiferromagnetic exchange.\textsuperscript{16a} The presence of odd-electron linkers as well as mixed-valency between Fe centers suggests that superexchange, double exchange, and direct exchange pathways may all be present in Fe\(_8\)(C\(_6\)O\(_6\))\(_3).\textsuperscript{26,27} Variable field magnetization data were also collected at 10 K, 5 K and 2 K, respectively. Each temperature indicates the presence of magnetic hysteresis, with corresponding coercive fields of \(H_c = 148\) Oe, 415 Oe, and 880 Oe respectively (Figure 5B, S23).

In addition to the general antiferromagnetic trend in the susceptibility data, there is also a clear inflection at ~30 K which displays some field dependence (Figure S20). Variable-temperature zero-field-cooled and field-cooled DC magnetization data (Figure S21) shows a divergence at 30 K, likely suggesting some long-range interactions.\textsuperscript{26} We have attempted to interrogate this behavior with variable-temperature AC susceptibility measurements, however only weak signals were observed. The data shows a broad cusplike peak for the in-phase susceptibility (\(\chi_M\)), and a noticeable rising anomaly for the out-of-phase susceptibility (\(\chi_M''\)) at around 10 K at low frequencies (Figure S22). While weak, these features may also be consistent with long-range magnetic interactions at low temperature.\textsuperscript{26,27} Variable field magnetization data were also collected at 10 K, 5 K and 2 K, respectively. Each temperature indicates the presence of magnetic hysteresis, with corresponding coercive fields of \(H_c = 148\) Oe, 415 Oe, and 880 Oe respectively (Figure 5B, S23).

The complicated geometric pattern, multiple possible exchange interactions in the system, and the small AC signals...
make interpreting the magnetic behavior of this material challenging. A potential explanation for the data is a coexistence of antiferromagnetic and spin-glass states at low temperature, which could arise from strong coupling within the 2D planes with a relatively weak antiferromagnetic exchange between the layers giving rise to spin-canting due to the mirrored interlayer orientation. Indeed, strong intralayer and weak interlayer coupling in related hexagonal chloranilate frameworks have been observed and are dependent on the interlayer spacing. Nevertheless, this proposal is speculative in our system and further studies, such as exchange of the interlayer metals with diamagnetic ions, will be required to thoroughly understand the magnetic behavior.

Conclusions

In summary, here we report a new 3D semiconducting material Fe$_5$(C$_6$O$_6$)$_3$ generated from Fe(II) and the most reduced version of HHB. This material is composed of AB stacked hexagonal planes further bridged by Fe–O bonds to generate a 3D structure that features intrinsic dual mixed valency. The use of HHB as a linker precursor, instead of the more oxidized congener THQ, generates a material which is distinct from two previously reported Fe$_{12}$(C$_6$O$_6$)$_6$ materials in terms of topology, connectivity, and the final oxidation states of the linkers. Fe$_5$(C$_6$O$_6$)$_3$ displays relatively high electrical conductivity, broad absorptions across the visible and near-IR region, interesting thermoelectric behavior, and strong antiferromagnetic interactions. Together these properties suggest that this material has promising applications in photosensitization, efficient thermoelectric conversion, and magnetic studies. These results highlight that redox-active components with multiple accessible oxidation states can be an important synthetic parameter in exploring the phase-space of conductive CPs/MOFs via “bottom-up” synthetic strategies. This approach illustrates an avenue which is orthogonal to post-synthetic modifications to enrich the library of multifunctional conductive inorganic-organic hybrid materials.

Experimental Section

General consideration: All manipulations were performed under an inert atmosphere of dry N$_2$ using a Schlenk line or MBraun UNILab glovebox unless otherwise noted. Dimethylformamide (DMF), tetrahydrofuran (THF), diethyl ether (Et$_2$O) and acetonitrile (MeCN) used in preparing the materials were initially dried and purified with N$_2$ on a solvent purification system from Pure Process Technology. All manipulations were performed in a dry lab using N$_2$ gas as an inert atmosphere. All solutions were stirred at room temperature and was then placed in an ice bath to induce precipitation. White needles were then collected by filtration on a Schlenk frit under N$_2$ and washed with 10 mL of degassed cold EtOH/HCl (1:1). The crude product was redissolved in 36 mL of 2 M HCl (degassed by sparging with N$_2$) and heated near to boiling. 100 mg of decolorizing charcoal was then added and continued stirring for 10 mins under boiling. The solution was then filtered quickly through a Schlenk frit. The filtrate was cooled in an ice bath to form white needles under N$_2$. Pure product was then collected and dried under vacuum to afford 813 mg white solid (yield 64%). $^{13}$C NMR (DMSO-d$_6$): 128 ppm.

Synthesis of material Fe$_5$(C$_6$O$_6$)$_3$(DMF)(H$_2$O)$_n$. Anhydrous FeCl$_3$ (1.2 mmol, 150 mg) and hexahydroxybenzene (0.60 mmol, 105 mg) were combined in 15 mL of DMF in a vial. The reaction mixture was heated at 100 °C for 3 days in the N$_2$ filled glovebox. After cooling to room temperature, the mother liquor was decanted. The remaining solid was washed with fresh DMF, further separated by centrifugation and washed sequentially 3x each with DMF then CH$_3$CN. The resulting black powder was dried under vacuum overnight at room temperature (108 mg, 40% yield). Different batches were combined for other characterizations. Solid used for N$_2$ adsorption measurement was further solvent exchanged with DMF (3 x 20 mL, 50 °C), THF (3 x 20 mL, 50 °C) and Et$_2$O (3 x 20 mL) for 2 days of each. The solid was recycled after N$_2$ adsorption and used for elemental analysis, thermogravimetric analysis, and FT-IR. FT-IR (KBr, cm$^{-1}$): 3420(s, br); 1648(s); 1501(m); 1403(s, br); 1111(w); 1050(s); 687(w).

X-Ray Powder Diffraction. Laboratory XRPD data were acquired on a Rigaku MiniFlex benchtop X-ray diffractometer equipped with CuKα radiation in Bragg-Brentano reflection geometry (samples were exposed to air for 3 minutes during measurement; longer exposure to air will decrease the crystallinity dramatically, Figure S1). Synchrotron X-ray powder diffraction data collections were carried out at 295 K at beamline 11-BM of the Advanced Photon Source at Argonne National Laboratory using a calibrated wavelength of $\lambda$ = 0.458095 Å from 0.5 to 50° 2θ. The data were then further rebinned with a constant step size of 0.001° to produce an equiostated pattern using Pre Dict. The data outside of the 1.5° - 13.5° 2θ range (corresponding to a 2 Å spatial resolution) presented very little structural information and were excluded from the data analysis. The powder was sealed in boron-rich thin-walled capillary tubes to avoid air exposure.

Structure Determination: The search for a suitable unit cell using PREDICT/DICVOL14 consistently reveals the same triclinic/hexagonal cell $a$ = 24.6 Å, $c$ = 14.9 Å, VOL = 7843 Å$^3$, with 5, 8 and 9 used indexing peaks, consistent with Z = 6 (Figure S3, Table S2). The indexing results were then confirmed by an excellent LeBail fit in P6$_3$ obtained from both diffractograms using the GSAS software (Figure...
S4). Only a single very weak Bragg peak at about 2θ = 4.16° remained unaccounted for (Figure S5). It should be noted that space group searches were generally inconclusive and several space groups such as P6_3cm, P6, P6_3, P6_3cm, P6_4 and P6_5 were subsequently tried with simulated annealing in order to select the most appropriate one, if any. The building block of [Fe(C6O6)3] (a.k.a. tripod) similar to a previous report\textsuperscript{14c,23b} was modeled with a Python programming language, assuming C=O = 1.28 Å and aromatic C–C = 1.38 Å. The length of a tripod leg should be 1/3 of the lattice parameter a thus resulting in a Fe-Fe and Fe-O distance of about 8.2 Å and 2.24 Å, respectively. These tripods were then used for Simulated Annealing Global Optimization in FOX.\textsuperscript{33} The P6_3 space group provided a chemically sensible molecular framework. Importantly, this space group suggests that the framework should have a ABAB staggered layered structure (Figure S8). It can be noted here that the high symmetry P6_3cm space group provided a potentially sensible layered framework, but the derived calculated XRPD pattern did not reproduce the two most intense 110 and 111 Bragg peaks and featured a huge 200 unobserved reflection at ca. 2.5° (Figure S6). This model would also represent a not-staggered framework having large accessible solvent pores that is inconsistent with N\textsubscript{2} uptake experiments.
All other attempts failed to produce any sensible models (Figure S7). After choosing the P6_3 space group and consequently the staggered framework model, the remaining Fe atoms (bridging two adjacent layers of tripods with 4-coordinated Fe atoms) were added to the main framework according to the molecular formula of [Fe(C6O6)3][Fe(H2O)(C6H5NO)]. The 4-coordinated Fe (41, 44, 47) are placed into a framework in such a way that they have similar interatomic distances (7.362 Å) within the same horizontal plane (perpendicular to the c-axis, Figure S8). Once the 4-coordinated Fe atoms were placed, the remaining two O-atoms were attached assuming regular tetrahedra. Presumably, one oxygen atom is coming from a water solvent molecule, whereas the other belongs to a DMF molecule based on combustion analysis (Figure S9). The orientation of the FeO₄ tetrahedra was chosen in such a way that all tetrahedral - tetrahedral neighboring distances were identical, resulting in a Fe-Fe distance of 7.362 Å. It can be noted that this partial crystallographic model reveals that the two extraneous O-atoms attached to the tetrahedral Fe-atoms represent two distinct groups of O-atoms: 043, 045, 048 (located at 3.8 Å from each other) and 042, 046, 049 (located at 4.9 Å from each other). While it was not possible to elucidate the precise solvent spatial positions in the framework voids, such a distribution may suggest that the first group pertains to the water molecules and the second to the DMF molecules. Despite the missing DMF molecules, a Rietveld refinement revealed an acceptable fit for the experimental data. The GSAS-borne least-squares refinement utilized a mild preferred orientation modeled by spherical harmonics up to the order of 6 associated with a moderate texture index of 1.7 (Table S3, Figure S10).

**Thermogravimetric Analysis (TGA).** TGA was performed using a TA Instruments Discovery analyzer. Approximately 2 mg of sample was loaded into a pre-tared Pt pan and measured from ambient to 600 °C using a linear temperature ramp of 3 °C/min under N\textsubscript{2}.

**Nitrogen Adsorption Measurements.** Crystalline solid was transferred to a pre-weighed analysis tube in the glovebox and capped with a Transseal. The sample tube was then transferred to a Micrometrics ASAP 2020 Plus gas adsorption analyzer and degassed at a rate of 1.0 °C/min from room temperature to a final temperature of 70 °C. The sample was further activated at 70 °C for one week until an out-gas rate of less than 1 mTorr/min was observed. The N\textsubscript{2} adsorption isotherm at 77 K was measured in liquid nitrogen. After the experiment, the PXRD pattern of the sample was checked, and the crystallinity was maintained (Figure S1). A separate previous trial showed the sample was totally amorphous if degassed at 120 °C.

**Scanning Electron Microscopy.** Scanning electron microscope (SEM) images were taken on the Carl Zeiss Merlin using the In-Lens detector in the Materials Research Science and Engineering Center (MRSEC) at the University of Chicago. The accelerating voltage is 5.00 kV.

**X-ray Photoelectron Spectroscopy.** X-ray photoelectron spectra (XPS) were collected with the AXIS Nova spectrometer (Kratos Analytical) equipped with a monochromatic Al K\textalpha\ x-ray source. The instrument work function was calibrated to give an Au 4f/2 metallic gold binding energy of 83.95 eV. For calibration purposes, the binding energies were referenced to C 1s peak at 284.8 eV. Survey spectra were collected with a step size of 1 and 160 eV pass energy. The high-resolution spectra were collected with a pass energy of 40 and 0.1 eV step size. Pressed pellets of samples were affixed to conductive carbon tape in N\textsubscript{2} filled glovebox before loading into the spectrometer.

**Mössbauer Spectroscopy.** Zero-field iron-57 Mössbauer spectrum were obtained at 77 K with a constant acceleration spectrometer and a cobalt-57 rhodium source. Prior to measurements, the spectrometer was calibrated at 295 K with α-iron foil. The sample was encased in Paratone-N oil and placed in a polyethylene sample cup inside a N\textsubscript{2} filled glovebox. The spectra were analyzed using the WMoss Mössbauer Spectral Analysis Software (www.wmoss.org).

**FT-IR Spectroscopy.** Powder samples for FT-IR were pressed into pellets in a potassium bromide matrix. Spectra were acquired in transmission mode on a Bruker Tensor II spectrometer with MCT detector operated at 77 K. Data was processed with background subtractions.

**UV–Vis–NIR Spectroscopy.** Solution UV–Vis spectra were collected on Thermo Scientific Evolution 300 spectrometer. Solid UV-vis-NIR diffuse reflectance spectra were collected on a Thermo Scientific Evolution 300 spectrometer and a CARY 5000 spectrophotometer with powder samples loaded in a Praying Mantis air-free diffuse reflectance cell with KBr powder as the non-adsorbing matrix. The Kubelka-Munk conversion of the raw diffuse reflectance spectrum was obtained by applying the formula F(R) = (1–R)²/2R.

**Conductivity Measurements.** Room temperature electrical conductivity measurements were performed in a two-contact geometry using a BASi Epsilon potentiostation/Galvanostation fitted to an N\textsubscript{2} glovebox. Samples were prepared as pressed pellets clamped between two brass electrodes (4.8 mm diam, 0.178 cm² area.) in a glass sleeve using a hand press. Sample pellet thicknesses were measured.
with a caliper and were typically in the range of 200 to 500 μm. Linear sweep voltammetry was conducted with the reference and counter electrode terminals connected to one electrode and the working electrode terminal to the other. The resulting data were fit to a straight line to obtain the sample resistance. Variable-temperature electrical conductivity measurements were performed under vacuum through a custom design using NIPCI-6221 DAQ, Stanford Research Systems SR570 current preamplifier and Montana Instruments $50 cryostation. Sample pellets were prepared in the glovebox using a hand press and fitted to a customized cell (4 mm*2mm*1mm) made of ceramic (Figure S18a). The cell has copper wire contacting points at each corner and can be sealed with a fitted lid through screws. Ohmic I-V profiles were observed for all temperatures from 140K to 295K with a 20 K interval, and a linear fit of the I-V curve was used to get the conductance (G) of the sample.

**Seebeck Coefficient Measurement.** The Seebeck coefficient measurement was performed using a custom-designed probe station in an argon glovebox. Around 20 mg sample powder was pressed into a pellet with a diameter of 8 mm using a TMAX Laboratory Manual Hydraulic Press under a pressure of 3 ton. Gold electrical contacts (~75 nm thick) were deposited onto the pressed pellet (~160 μm thick) of bulk sample powder via thermal evaporation (Figure S19a). Two thermocouples were used to collect the hot and cold side temperatures, and another two probes were used to measure the corresponding voltage value. A delay of 200 s was adopted for voltage measurements to allow a steady-state temperature gradient and voltage. The Seebeck coefficient was calculated from the slope of a linear fit for the AV vs ΔT plot.

**Magnetic Measurements.** Magnetic measurements were performed on a Quantum Design MPMS3 SQUID magnetometer. The bulk powder of the sample (29.0 mg) was suspended in an eicosane matrix in a polycarbonate capsule to prevent movement and protect the sample from incidental air exposure. Diamagnetic corrections for the capsule and eicosane were made by measuring temperature vs moment in triplicate for each to determine a moment per gram correction. Diamagnetic corrections for the sample itself was applied using Pascal’s constants of each atom based on the formula of Fe$_2$(C$_6$O$_6$)$_3$(H$_2$O)$_3$(C$_3$H$_7$NO)$_3$.

**ASSOCIATED CONTENT**

**Supporting Information**

Additional experimental details and characterization data are included in supporting information. The Supporting Information is available free of charge on the ACS Publications website.

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**REFERENCES**


