

Divergent Electrically Conductive Pathways in Yttrium-Based 2- and 3-Dimensional Metal–Organic Frameworks

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**On the Divergent Electrically Conductive Pathways in
Yttrium-Based 2- and 3-Dimensional Metal-Organic
Frameworks**

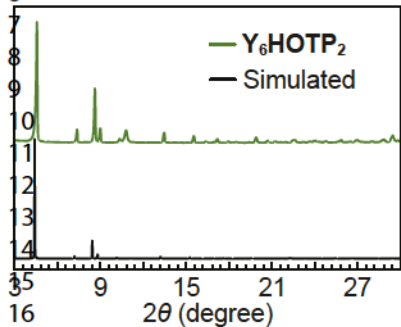
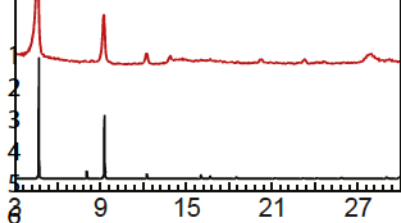
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Manuscripts

a

Page 1 of 10

— YHOTP
— Simulated



b

Electrical conductivity (S cm^{-1})

10^{-1}
 10^{-2}
 10^{-3}
 10^{-4}
 10^{-5}
 10^{-6}

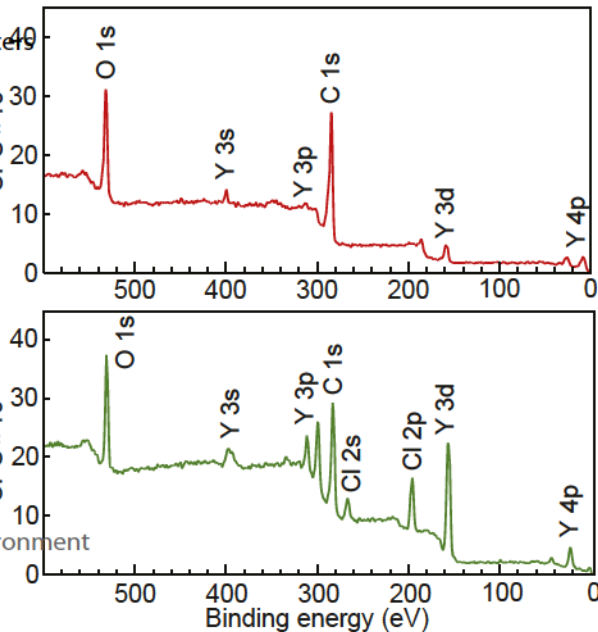
YHOTP

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▲
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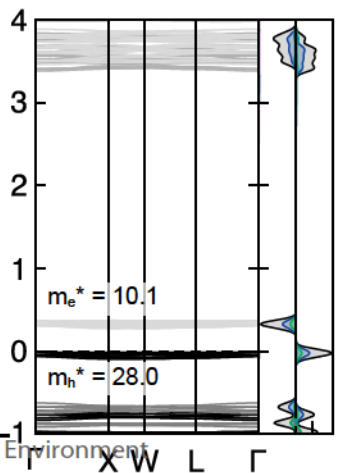
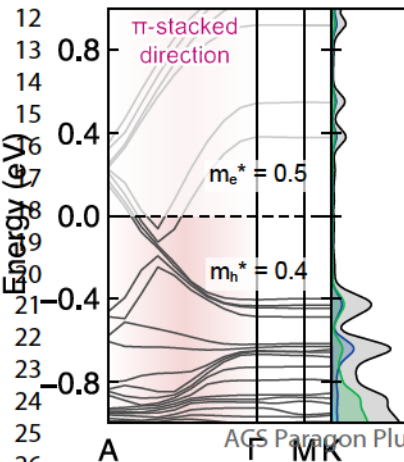
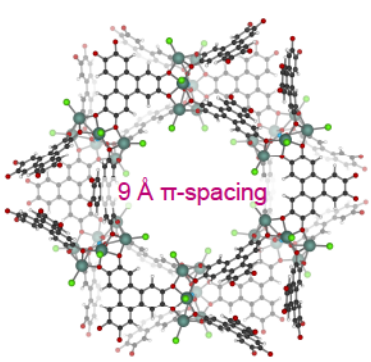
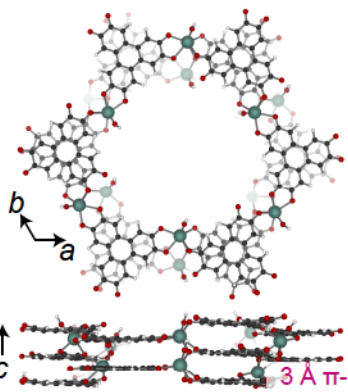
Y₆HOTP₂

ACS Paragon Plus Environment

c

CPS $\times 10^{-3}$ CPS $\times 10^{-3}$ 

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28



– Total DOS – C (p) – O (p) – Y (d)

Hexagonal YHOTP

Cubic Y_6HOTP_2

Page 3 of 10

ACS Materials Letters

HT 2 meV

ET 47 meV

ACS Paragon Plus Environment

HT 308 meV

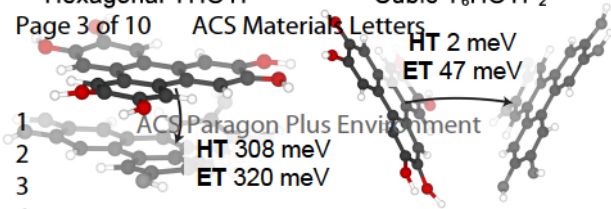
ET 320 meV

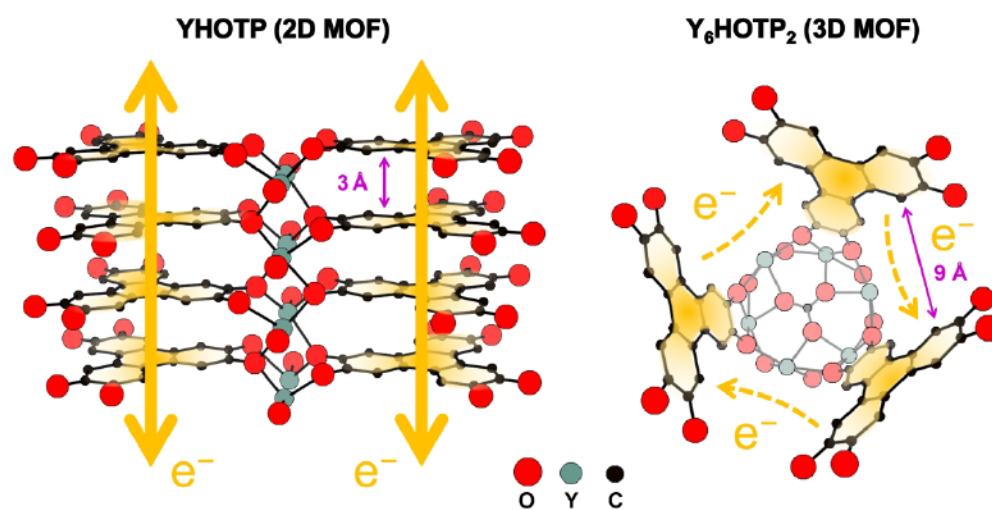
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TOC Image

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On the Divergent Electrically Conductive Pathways in Yttrium-Based 2- and 3-Dimensional Metal–Organic Frameworks

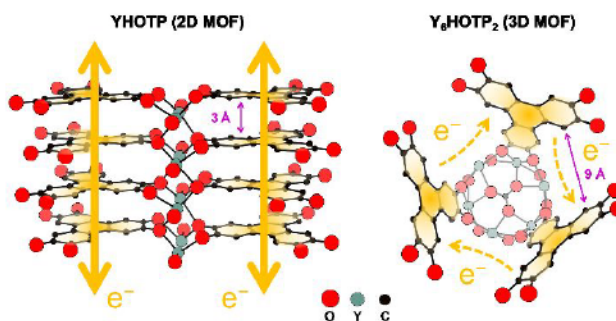
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ABSTRACT: Despite most porous framework solids exhibiting insulating character, some are known to conduct electrical charge. The peak performing conductive metal-organic frameworks are composed of redox-active hexasubstituted triphenylene linkers, but the impact of redox activity on material conductivity remains enigmatic because of limited availability of direct structure-function relationships. Here, we report a hexagonal yttrium-based conductive porous scaffold, comprising hexahydroxytriphenylene connected by Y-chains (YHOTP). In comparison to its known porous cubic counterpart (Y₆HOTP₂), this material features a 1000-fold increase in peak conductivity in polycrystalline samples ($\sim 10^{-1}$ S cm⁻¹). Furthermore, through a comparison of their electronic structures, we rationalize the origin of this difference and highlight the role of charge carrier concentration in dictating bulk electrical conductivity. Together, this work provides a design principle for the development of next-generation conductive porous frameworks..



Most metal-organic frameworks (MOFs) are electrical insulators due to energetic mismatch between the metal clusters and the ligands that support them.^{1–3} MOFs that do conduct electricity feature conductive pathways that permit charge mobility either through space (through π -stacking or other secondary bonding)⁴ or through bond (through dative, ionic, or covalent bonds)⁵, and are potentially useful as active materials in electrocatalysis^{6–8} and in electrochemical energy storage devices.^{9–13} To date, the highest performing conductive MOFs feature conductivity values exceeding 100 S cm⁻¹ and are through-space conductors. Effort has been invested in understanding how the spatial orientation of the MOF components dictates the crystal conductivity, however very few structure-function relationships have been revealed. A comparison of compositionally similar frameworks with dissimilar geometries is required to elucidate basic principles that underpin electrical conduction in molecular materials.

Since electrical conductivity is primarily dictated by the number and mobility of charge carriers, interest has been focused on methods to affect band curvature and the free carrier concentration in the materials. Towards the latter, two strategies have been developed; either through electrochemical doping¹⁴ or through narrowing of the electronic band gap via ligand functionalization.¹⁵ With the exception of mixed-valent Fe-based frameworks, the most conductive MOFs are composed of hexasubstituted triphenylenes (e.g., hexahydroxytriphenylene, HHTP, which is referred to as HOTP once incorporated into the framework)¹⁶ and their synthesis does not afford an obvious route to introduce functionalization beyond the ligating atoms themselves.^{17–19} Instead, those linkers are known to oxidize during self-assembly, introducing charge carriers through redox events. Once assembled, the charge carriers are thought to traverse the closely-spaced π -

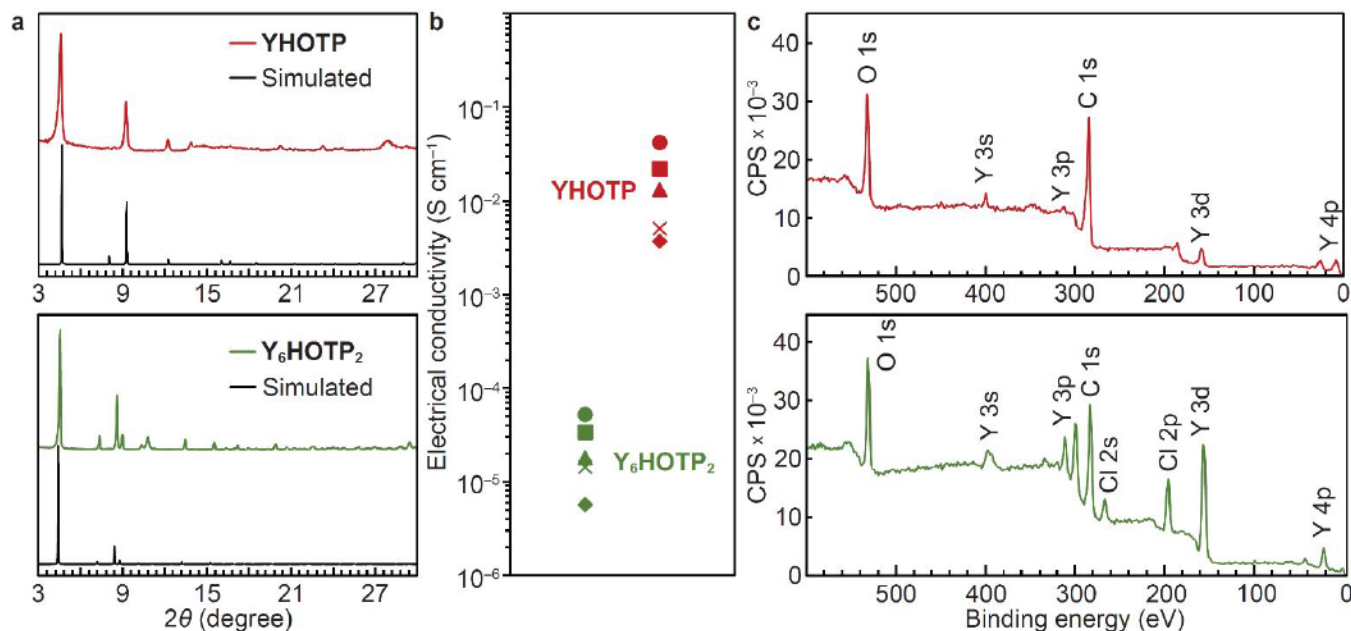


Figure 1. Materials characterization comparison of **YHOTP** and **Y₆HOTP₂**. **(a)** Powder XRD patterns reveals the microcrystalline sample is highly crystalline. **(b)** Pressed pellet conductivities of five different batches of each MOF. **(c)** XPS show the presence of Cl in the **Y₆HOTP₂**, and differences in the C 1s binding energy, attributed to differences in linker oxidation state.

stacked layers, leading to anisotropic through-space conduction.^{20, 21}

When paired with first row transition metals (e.g., Co, Ni, Cu)^{22–24}, the resultant 2D-connected layered materials exhibit among the highest known electrical conductivity of any MOFs to date. Stacking faults may disrupt the π -overlap between layers, and subsequently result in variable and reduced conductivity. Larger metal cations (e.g., La, Ho, Nd, Yb) have been shown to reduce stacking faults and form large crystals.²⁵ In those cases, the metals sit between the organic sheets and, like the other 2D-conductive MOFs, those formed from *f*-block elements are known to be in-plane insulators, and out-of-plane metals. Meanwhile, some of the same metal ions can be used to form a 3D-connected cubic framework, with reported structures made from La, Eu, and Y.²⁶ Thus, the formation of iso-compositional frameworks with dissimilar connectivity, but high degrees of covalency remain key targets in MOF syntheses.

Noting that Y³⁺ supports a larger coordination sphere than its kinosymmetric azimuthal analogue (Sc³⁺), we surmised that Y could be used to form the tightly spaced layered structure of MHOTP. In doing so, Y would be the only *d*-block element capable of reliably forming both the hexagonal and cubic structures, permitting a controlled analysis of the properties that drive electrical conduction in this class of materials. Here, we report the synthesis of YHOTP, and through comparison with its known cubic 3D counterpart, Y₆HOTP₂, we show that the spatial orientation of the linkers dictates the conductive pathways due to divergent linker behavior. The 2D material exhibits strong intermolecular electron and hole charge transfer coupling, while the 3D structure hosts high charge carrier concentrations.

To target the layered hexagonal 2D structure, YHOTP was obtained by mixing Y(NO₃)₃·6H₂O with HHTP in a mole ratio

of 10:1 in a mixture of water, *N,N'*-dimethylimidazolidinone (DMI), and sodium acetate (NaOAc). The reaction mixture was held at 80 °C for 16 h in air, then washed and dried to obtain (YOH)_{1-x}HOTP(H₂O)_x ($x = 0$ to 0.2; referred to as **YHOTP**). Y-vacancies are accounted for with positive values of x . To obtain the cubic 3D structure, YCl₃ was used in a metal:linker mole ratio of 80:1. To promote crystallization and disincentivize oxidation, the mixture was heated to 135 °C for 72 h in a nitrogen-filled glovebox in a similar solvent mixture. The resultant material, Y₆(HOTP)₂(CO₃)Cl₆ (**Y₆HOTP₂**) was obtained. We surmised that the carbonate was formed during self-assembly through solvent decomposition, and trace nitrogen in the elemental analysis likely corresponds to trapped solvent within the pores. Both products' chemical compositions were determined by a combination of single-crystal X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and elemental analysis (Tables S1–S6). Microcrystalline samples of each product were found to have the same crystallographic structure as that of the bulk single crystals of each MOF (Figure 1a).

Following the reported procedure for measuring electrical conductivity on polycrystalline samples, pressed pellet conductivities were determined in pentaplicate, using a two-point probe device detailed in the Experimental Methods. The hexagonal 2D framework, **YHOTP**, consistently exhibited at least 1000× higher conductivity than its cubic 3D counterpart, with a peak conductivity of $\sim 3 \times 10^{-1}$ S cm⁻¹ (Figure 1b). A similar conclusion is predicted through a comparison of the computed electronic band structures (Figure 2). However, despite the cubic material possessing an insulating ground state electronic structure⁸, the material has surprisingly high peak conductivities of $\sim 10^{-4}$ S cm⁻¹, which is as much as 9 orders of magnitude greater than MOFs with comparable band

gaps.⁵ Thus, we surmised that another effect may be dictating the electrical conduction in these frameworks.

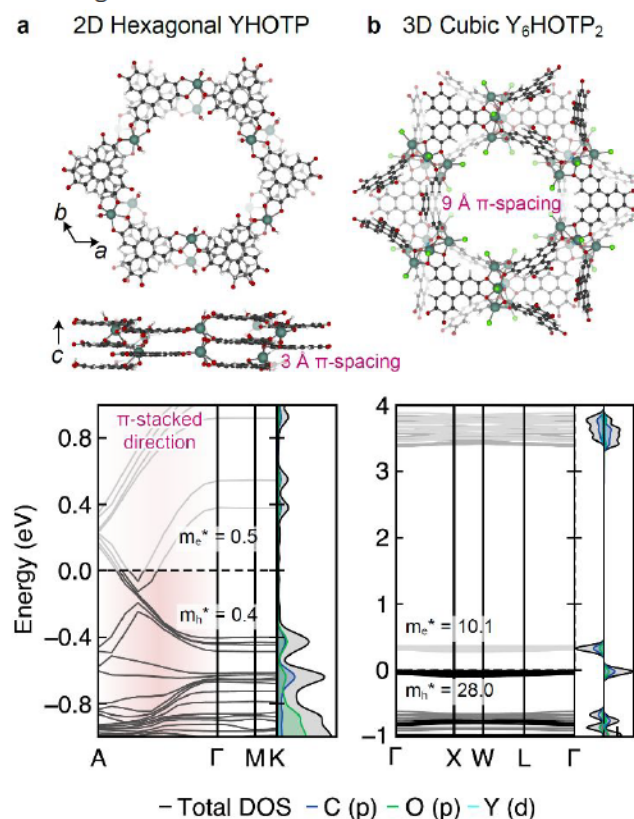


Figure 2. (a) The hexagonal (YHOTP) and (b) cubic (Y₆HOTP₂) crystal structures and corresponding electronic band structures. The former has pathways of through-space π -interactions, while the latter features isolated chemical motifs. The proximity of π -clouds in YHOTP is reflected in its electronic band structure, where it is predicted to be an out-of-plane metal and in-plane narrow gap insulator. Y₆HOTP₂ is predicted to be a narrow gap insulator due to limited spatial overlap throughout the crystal, with band edge densities localized on the ligand. Charge carrier effective masses are labeled. C, O, Cl, H, and Y, are depicted in black, red, green, white, and sage, respectively.

One explanation for this divergence could be a difference in charge carrier concentration. Since we are unable to grow single crystals large enough to perform a Hall measurement, we instead deduce the concentration from theory. By comparing the curvature of the bands in the direction with the lightest holes and electrons (Γ -A for YHOTP, Γ -X for Y₆HOTP₂), the electronic band structure calculations reveal approximately two orders of magnitude difference in effective mass of the charge carriers, with the heavier carrier belonging to Y₆HOTP₂. Since conductivity is proportional to the charge carrier concentration and mobility, and the differences in mobility are of the same order of magnitude as the pressed-pellet conductivity, the corresponding carrier concentration must not vary by more than one order of magnitude.

Considering the composition differences, and that the XPS data presented in Figure 1c indicate that Y exists in the 3+ oxidation state, the differences in conductivity are driven by a combination of dissimilar linker oxidation state and

intermolecular orientation. Since the 2D structure only forms in the presence of air, it is understood that the linker oxidizes during self-assembly. With complementary deprotonation, the hexagonal layered material hosts linkers with nominal 3- charge. This charge should result in a single unpaired electron per linker but solid-state EPR reveals YHOTP has substantially less radical character than the cubic analogue (Figure S1), which has been previously attributed to linker vacancies rather than native ligand-centered unpaired electrons.²⁵ Thus, we surmised that the linkers rather exist as a delocalized 2- and 4- pair, an electronic configuration common in the 2D conductive family of frameworks.²⁰

Conversely, Y₆HOTP₂ forms under a nitrogen atmosphere and, hence, should be less oxidized. In its case, the linkers exhibit a formal 5- charge. In this charge state, the linkers are nominally more aromatic than their oxidized counterparts and should host unpaired electrons. EPR revealed a ligand-centered radical associated with a single unpaired electron per linker (Figure S1). The difference concentration in mobile charge carriers cannot vary by more than one electron per linker, supporting our offering that the difference in charge carrier concentration will never exceed one order of magnitude. This may be the origin of elevated conductivity in Y₆HOTP₂ compared to other similarly flat-banded materials — the linker is likely installing large numbers of charge carriers.

Both YHOTP and Y₆HOTP₂ are through-space conductors but have different ligand geometries. This is generally interesting because intermolecular distances usually increase with increasing porosity, and these frameworks serve as a platform to understand how orientation impacts through-space conduction, and whether having spatially separated ligands can permit charge transfer between them. To do so, we turn to Marcus theory to assess the charge transfer coupling between neighboring ligands. We created two models from the bulk crystals, each featuring a pair of linkers with their geometry remaining fixed, as imposed by the geometry obtained for the crystal.²⁷ The linkers were then protonated to create a charge-neutral system (Figure 3). The electron and hole couplings for each cluster were calculated using CATNIP.²⁸ For comparison, the cluster's molecular orbitals were also computed using the ZINDO method (Figure S4), and the electron and hole couplings were then extracted using the Molecular Orbital Overlap (MOO) method.²⁹ For the cubic system, the hole transfer coupling was found to be 2 meV, while the electron coupling was 47 meV. Both of these values are extremely weak. The hexagonal crystal featured coupling energies of 320 and 308 meV for the electron and hole, respectively. These values are relatively large and are comparable to other organic charge transfer aggregates.^{30, 31} Together we surmise that for the hexagonal system, the mobility of the charge carriers is high reflected in the band structure and also in the hole and electron coupling energies. Conversely, the cubic system features weak couplings, and highly localized electronic bands.

By further computing the reorganization energies for both the electron and hole transfer to the protonated ligand, the rate of charge transfer can also be computed. Since the linkers are the same for both the cubic and hexagonal phase,

the reorganization energies should be roughly the same for both systems: 587 meV for electron reorganization and 491 meV for hole reorganization. Applying Marcus theory, the Arrhenius rates of charge transfer for the hexagonal system are then $7.5 \times 10^{12} \text{ s}^{-1}$ and $1.9 \times 10^{13} \text{ s}^{-1}$ for electron and hole transfer, respectively. The cubic material exhibits rates 2–4 orders of magnitude slower: $1.6 \times 10^{11} \text{ s}^{-1}$ and $6.6 \times 10^8 \text{ s}^{-1}$ for electron and hole transfer, respectively. These calculations suggest that differences in conductivity are further dictated by differences in charge transfer rates, associated with differences in geometry.

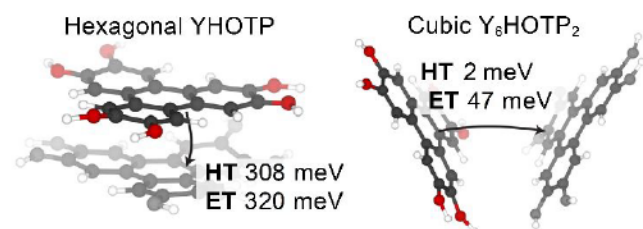


Figure 3. A comparison of the hexagonal (YHOTP) and cubic (Y₆HOTP₂) ligand charge transfer interactions. The electron coupling (ET) is consistently larger than the hole coupling (HT) driven by the propensity for the ligands to rearomatize. C, O, and H are depicted in black, red, and white, respectively.

Thus, through the isolation of a Y-based hexagonal layered conductor, YHOTP, and by comparison to its cubic counterpart, Y₆HOTP₂, we can make several conclusions. Given that the coupling energies in the latter are extremely weak, but its charge carrier effective masses are comparable to other flat-band insulators, the reason for its surprisingly high conductivity ($\sim 10^{-4} \text{ S cm}^{-1}$) is likely due to the differences in linker oxidation state, which we believe is directly influencing the charge carrier concentration in the MOF. Further, given that the linker is more aromatic in the 3D framework — a property that is typically inversely proportional to conductivity³² — this strongly indicates that linker redox is a critical and primary deciding factor dictating electrical charge conduction in MOFs, and highlights that the interplay between linker redox potential and orientation dictates bulk conductivity. Looking forward, these findings help rationalize why the HOTP-based materials are the best conductors in their class and should instruct future efforts to diversify ligand design.

EXPERIMENTAL SECTION

Synthesis of YHOTP and Y₆HOTP₂. Prior to synthesis, HHTP was dissolved in DMI and recrystallized from hot H₂O to remove impurities. For the synthesis of YHOTP, 0.63 mmol of Y(NO₃)₃·6H₂O was dissolved in 3 mL of deionized H₂O in a 20 mL scintillation vial in air. 0.063 mmol of HHTP was dissolved in 0.8 mL of DMI and the two solutions were combined. A solution of 0.189 mmol of NaOAc dissolved in 0.6 mL of deionized H₂O was added to the mixture. The mixture was transferred to a 15 mL pressure tube containing sanded glass slides and heated at 80 °C for 16 h. For the synthesis of Y₆HOTP₂, 4.8 mmol of YCl₃·6H₂O was dissolved in 3 mL of deionized H₂O and added to a solution of 0.06 mmol of HHTP dissolved in 0.8 mL of DMI in a N₂-filled glovebox. 0.18 mmol of NaOAc dissolved in 0.6 mL of

deionized H₂O was added to the mixture and then the solution was filtered into a 15 mL pressure tube containing sanded glass slides using a 0.2 μm PTFE filter. The reaction was heated at 135 °C for 72 h and then brought back into the N₂-filled glovebox. The mother liquor was decanted and the resulting powder was washed 3× with deoxygenated DI water and 3× with deoxygenated methanol. Both samples were activated by drying under vacuum at 90 °C for 1 h.

Electrical conductivity measurements. Two-point probe measurements were made on activated pressed pellets using a custom apparatus previously described.³³ 2–3 mg of powder was loaded into a glass tube and compressed by copper rods that also served as leads. The apparatus was compressed using a hydraulic press while dual linear I-V curves were obtained using a Keithley 2450 source meter. The pellets were further compressed between I-V measurements until the change in resistance was low (Figure S2). The conductivity measurements were made in pentaplicate.

Materials Characterization. Powder XRD measurements were performed using a Bruker D8 Advance diffractometer with Cu Kα_{1,2} radiation ($\lambda = 1.54 \text{ Å}$) in reflection geometry. XPS measurements were performed using a Physical Electronics VersaProbe II photoelectron spectrometer with monochromatized Al Kα radiation ($E = 1486.6 \text{ eV}$). Binding energy was calibrated by shifting the main C1s peak to 284.8 eV. EPR was performed using a Magnetech ESR5000 spectrometer with a microwave power of 20 mW and an amplitude of 0.3 G.

Computational Methods. Density functional theory (DFT) calculations were performed using the Vienna *ab initio* Simulation Package (VASP)³⁴. All structures were optimized using the PBEsol functional with a plane wave energy cutoff of 500 eV, and an ionic convergence criterion of -0.005 eV . Bulk YHOTP was optimized using a $2 \times 2 \times 5$ k-mesh to sample the first Brillouin zone, and all structures involving Y₆HOTP₂ used a Γ -only k-mesh due to the size of the unit cell and the resulting computational cost of the calculation. Y₆HOTP₂ is charge-balanced by disorder guest molecules in the pores. Here, we achieved charge balance by adding one Cl per Y, capping the open metal sites in the metal clusters. The electron count was adjusted by the removal of 4 electrons, achieving charge neutrality. This strategy significantly reduced the net charge of the structure in the calculations, aligned with the experimental number of charges on each linker from EPR, and is justified due to the presence of Cl in the elemental analysis. We also tested an alternate charge balancing method, by removing the chlorides and subtracting 20 electrons (2.5 per linker) from the system. The former strategy yielded a plausible structure that was then used for the electronic band structure calculation. The HSEsol hybrid functional³⁵ was used to compute the band structures. Charge transfer calculations were performed on clusters of HOTP ligands extracted from the geometrically equilibrated crystal structures and protonated to achieve charge neutrality. Initial calculations were performed using the ZINDO method²⁹ (Figure S4), as implemented in Gaussian09³⁶, and yielded similar coupling energies as computed by *ab initio* methods (using CATNIP²⁸ with the B3LYP functional and 6-31G basis set, as shown in Figure 3). Coupling energies were

calculated from the resulting molecular orbitals using the MOO method.²⁹

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Further synthetic and experimental details, supplemental calculations, physical characterization, and supporting tables and figures (PDF).

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Author Contributions

The manuscript was written through contributions of all authors.

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