

Conjugated Metal–Organic Macrocycles: Synthesis, Characterization, and Electrical Conductivity

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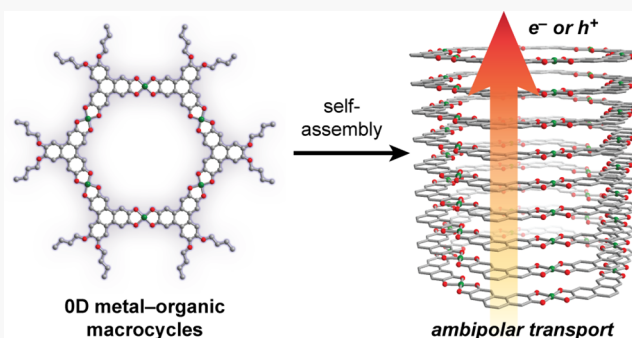
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Supporting Information

ABSTRACT: The dimensional reduction of solids into smaller fragments provides a route to achieve new physical properties and gain deeper insight into the extended parent structures. Here, we report the synthesis of CuTOTP-OR (TOTP^{n−} = 2,3,6,7-tetraoxidotriphenylene), a family of copper-based macrocycles that resemble truncated fragments of the conductive two-dimensional (2D) metal–organic framework Cu₃(HHTP)₂ (HHTP = 2,3,6,7,10,11-hexahydroxytriphenylene). The planar metal–organic macrocycles self-assemble into ordered nanotubes with internal diameters of ~2 nm and short interlayer distances of ~3.20 Å. Strong π – π stacking interactions between macrocycles facilitate out-of-plane charge transport, and pressed pellet conductivities as high as $2(1) \times 10^{-3} \text{ S cm}^{-1}$ are observed.

Peripheral alkyl functionalization enhances solution processability and enables the fabrication of thin-film field-effect transistor devices. Ambipolar charge transport is observed, suggesting that similar behavior may be operative in Cu₃(HHTP)₂. By coupling the attractive features of metal–organic frameworks with greater processability, these macrocycles enable facile device integration and a more nuanced understanding of out-of-plane charge transport in 2D conductive metal–organic frameworks.



INTRODUCTION

By facilitating rapid electronic, ionic, and molecular transport, nanoporous conductors enable key technologies, including electrochemical energy storage and conversion,^{1–3} chemical sensing,^{4,5} and electrochemically driven molecular separations.^{6,7} Electrically conductive metal–organic frameworks (MOFs) are a rapidly emerging class of nanoporous conductors with excellent chemical tunability, high surface areas, and exciting charge transport behavior.⁸ However, metal–organic frameworks are typically isolated as brittle and poorly dispersible microcrystalline powders, presenting significant challenges to thin film fabrication and device integration.⁵ This stands in contrast to established organic semiconductors, which are compatible with scalable and low-cost solution-based processing methods.^{9,10} Beyond these practical considerations, existing conductive MOFs also lack the emerging multifunctional materials properties of semiconducting polymers, including stretchability^{11–13} and the ability to self-heal.^{14,15}

Coupling the attractive porosity, molecular tunability, and electrical conductivity of metal–organic frameworks with the advantageous physical properties of soft matter would open the door to diverse new applications and processing methods.¹⁶ Toward this goal, we are pursuing the dimensional reduction of electrically conductive, triphenylene-based two-dimensional

(2D) metal–organic frameworks into discrete, hexagonal macrocycles. The planar macrocyclic core should favor the formation of π -stacked structures that preserve out-of-plane charge transport and large interior channels, while the richly tunable exterior can be modified to enhance solubility and alter surface properties.

The self-assembly of rigid, shape-persistent organic macrocycles into tubular structures with nanoscale pores is well-studied, and such materials have been investigated for organic electronics, molecular recognition, and ion transport applications.^{17–22} A rich diversity of organic reactions have been successfully applied to macrocycle synthesis, including C–C cross-coupling, olefin and alkyne metathesis, and amide, imine, and boronate ester formation.^{20,23,24} In contrast, the use of coordination chemistry, rather than organic chemistry, to construct rigidly planar, fully conjugated metal–organic macrocycles has been less explored. Many Pd- and Pt-based macrocycles have been reported,^{25–28} and interesting phase

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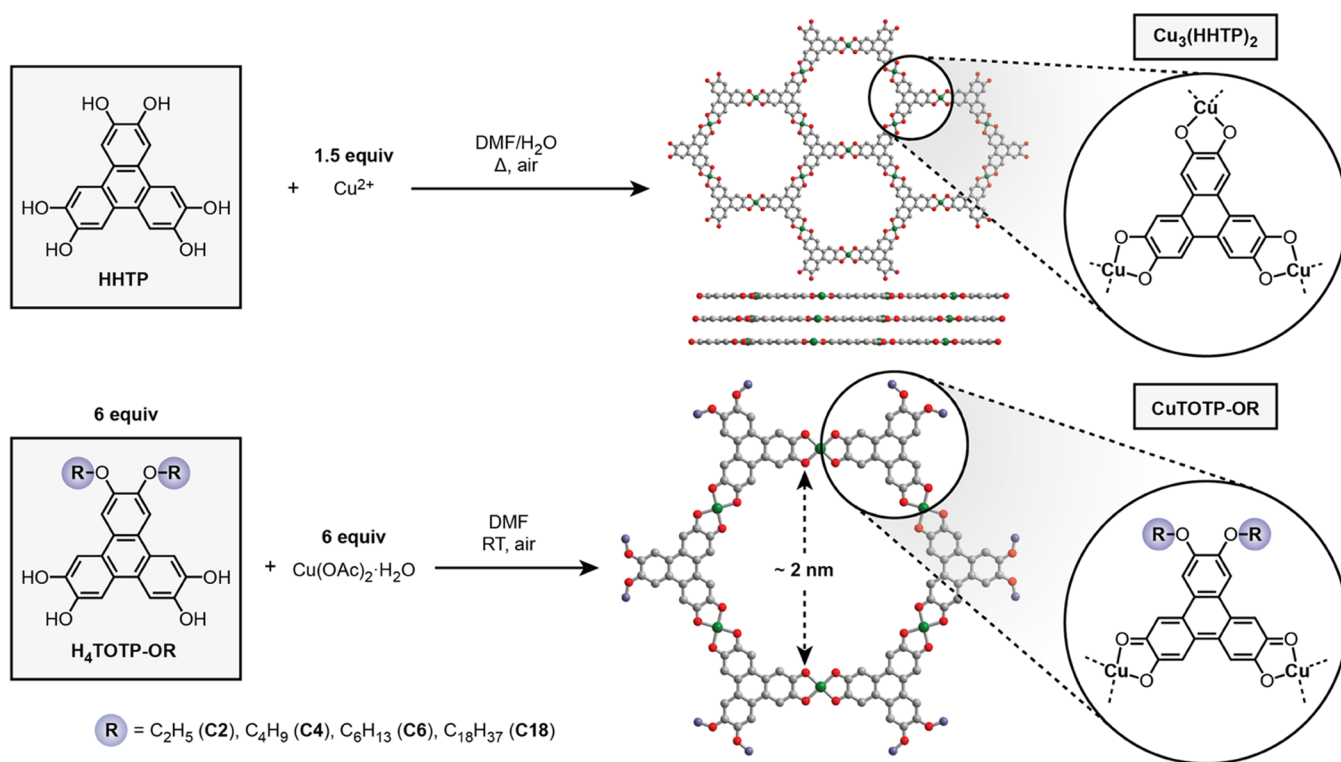


Figure 1. Top: Synthesis and structure of the 2D conductive metal–organic framework $\text{Cu}_3(\text{HHTP})_2$. The material adopts a 2D honeycomb structure with a slipped π - π stacking arrangement between layers (ref 43). Bottom: Overview of our synthetic strategy to truncate $\text{Cu}_3(\text{HHTP})_2$ into discrete copper-based macrocycles CuTOTP-OR (R = C2, C4, C6, C18).

behavior,^{29,30} photophysical properties,³¹ and biological activity³² have been observed. However, the exploration of non-noble metal scaffolds remains relatively rare.

Here, we report the synthesis and characterization of CuTOTP-OR (TOTP^{4-} = 2,3,6,7-tetraoxoditriphenylene, R = linear C2, C4, C6, and C18 alkyl chains), a family of conjugated, copper-based metal–organic macrocycles. The planar structures self-assemble to form ordered, electrically conductive nanochannels. Average pellet conductivities of $2(1) \times 10^{-3} \text{ S cm}^{-1}$ are observed in CuTOTP-OC2 , the shortest alkyl chain variant. Longer alkyl chain variants such as CuTOTP-OC18 readily disperse in organic solvents, facilitating the fabrication of thin-film field-effect transistor (FET) devices. Ambipolar charge transport is observed, with electron and hole mobilities on the order of $\sim 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. Together, these findings show that a simple macrocyclic core can replicate key physical properties of metal–organic frameworks while affording greater processability.

RESULTS AND DISCUSSION

Synthesis and Structure. Our overall synthetic strategy toward fully conjugated, planar metal–organic macrocycles is outlined in Figure 1. To preserve extended π -d conjugation, each Cu^{2+} metal center is bridged by planar triphenylene-based ligands that closely resemble HHTP (HHTP = 2,3,6,7,10,11-hexahydroxytriphenylene), a tritopic linker commonly used to construct conductive 2D MOFs like $\text{Cu}_3(\text{HHTP})_2$.³³ However, because one of the three catechol units is intentionally capped with alkyl groups, the formation of an extended network is instead truncated into 0D, planar macrocycles. This approach was inspired by recent work from Dichtel, Northrop, and co-workers, who used a similar strategy to achieve boronate ester-

based macrocycles that are structurally reminiscent of 2D covalent organic frameworks.^{24,34}

Combining the tetrahydroxytriphenylene ligands shown in Figure 1, which we have abbreviated $\text{H}_4\text{TOTP-OR}$ (TOTP^{4-} = 2,3,6,7-tetraoxoditriphenylene, R = alkyl group), with $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ in dimethylformamide (DMF) under air readily produces the desired copper-based macrocycles CuTOTP-OR in excellent yields (67–88% yield). To probe the influence of peripheral functionalization on macrocycle structure, packing, and solution processability, we further synthesized a family of four macrocycles that differ only in the length of the capping linear alkyl chain (R = C2, C4, C6, and C18).

Powder X-ray diffraction (PXRD) patterns of the resulting dark blue-black solids show three prominent low-angle peaks with a $1:1/\sqrt{3}:1/2$ ratio in d -spacing, consistent with hexagonal packing (Figure 2a). A broader feature at higher angles, which we have assigned as the (001) reflection, reveals a short interlayer distance of $\sim 3.20 \text{ \AA}$. This value is nearly identical to what has been observed in structurally related copper-based 2D metal–organic frameworks ($3.19 \text{ \AA}$) and is indicative of strong π - π stacking interactions between the planar macrocycles.³⁵ The broadness of the (001) peak suggests poor long-range ordering in the π -stacking c direction. In addition to a perfectly eclipsed arrangement between stacked macrocycles, numerous translational and rotational displacements are also possible. Further work and more crystalline materials are needed to accurately determine the preferred π - π stacking pattern in these materials.

Pawley refinements were performed to obtain more precise unit cell dimensions of DMF-solvated CuTOTP-OR (Figures S1–S4). As expected, the in-plane lattice parameter system-

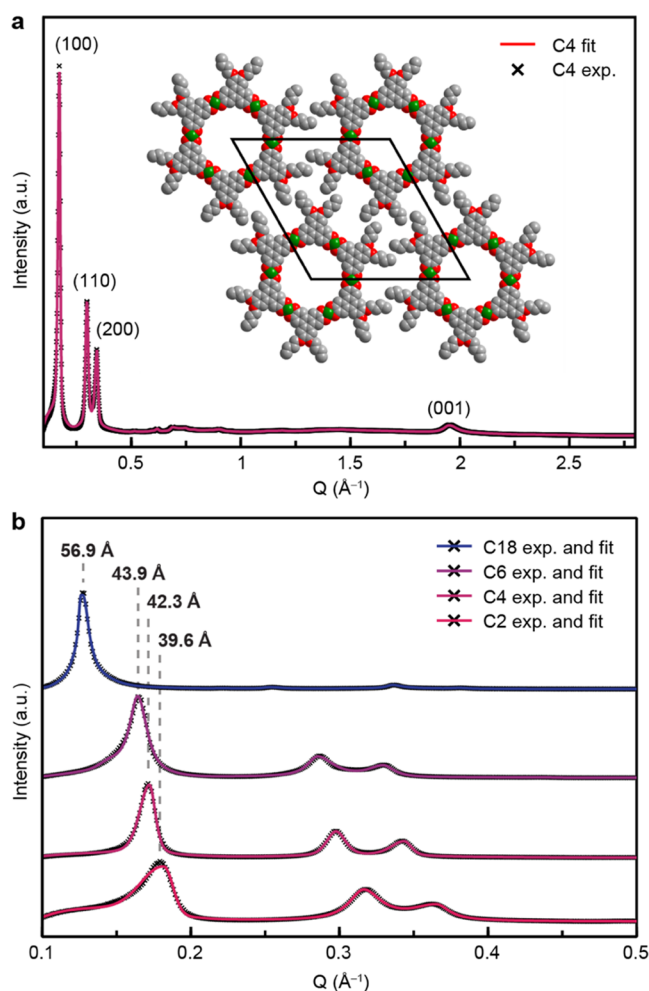


Figure 2. (a) PXRD pattern of DMF-solvated CuTOTP-OC4 and optimized structural model. (b) PXRD patterns and peak positions for DMF-solvated CuTOTP-OR ($R = C2, C4, C6, C18$).

atically increases as the peripheral alkyl chains lengthen ($a = b = 40\text{--}57\text{ Å}$), while the interlayer distance remains relatively constant ($c = 3.20\text{--}3.24\text{ Å}$) (Figure 2b). Geometry optimized structural models afford similar unit cell dimensions (Figures S5 and S6). Transmission electron microscopy (TEM) images of CuTOTP-OC4 drop-cast from dilute solutions reveal average diameters of $1.9(4)\text{ nm}$, consistent with the expected size of the planar macrocyclic core (Figure S7). Atomic force microscopy (AFM) images of more concentrated CuTOTP-OC4 solutions (1 mg mL^{-1}) clearly show the formation of nanotubular structures, with an average length of $23(6)\text{ nm}$ (Figure S9). No porosity was observed via traditional 77 K N_2 adsorption experiments, likely due to partial pore blockage by neighboring alkyl chains. However, similar measurements at 195 K using CO_2 , a smaller probe molecule, led to a surface area of $226(3)\text{ m}^2/\text{g}$ for CuTOTP-OC2. Altogether, the data obtained from PXRD, TEM, AFM, and gas sorption measurements are fully consistent with the columnar stacking of hexagonal macrocycles to form large nanochannels of approximately 2 nm in diameter.

Compared to extended 2D MOFs, the long-range structure of CuTOTP-OR is considerably more dynamic. In particular, the weak noncovalent interactions between neighboring alkyl chains are readily perturbed by the solvent. While the interlayer distance stays relatively constant, reversible ex-

pansions and contractions in the ab plane are observed upon altering the macrocycle solvation state (Table 1). For example, the in-plane lattice parameter of fully dried CuTOTP-OC4 increases by $>5\%$ upon DMF solvation, suggesting partial solvent infiltration between the columnar stacks.

We hypothesized that by tuning both the solvent identity and macrocycle peripheral functionalization, we should be able to fully separate the individual columnar stacks and achieve stable colloidal dispersions. With sonication, average particle sizes of around $90, 200,$ and 300 nm were observed by dynamic light scattering (DLS) for THF-dispersed CuTOTP-OC2, C4, and C6, respectively. However, these dispersions were not stable, and further aggregation was observed over time. In contrast, dispersions of CuTOTP-OC18 in THF appear indefinitely stable across all concentrations tested (up to 10 mg/mL). Furthermore, DLS measurements revealed an average hydrodynamic diameter of $5(1)\text{ nm}$, consistent with short, isolated columnar stacks of macrocycles. Similar diameters ($4\text{--}5\text{ nm}$) were also observed in other organic solvents, such as CHCl_3 and toluene (Table S1). The ease by which CuTOTP-OR forms high concentration inks may afford future processability advantages relative to traditional metal–organic frameworks.

Spectroscopic Characterization. Depending on the synthesis conditions, significant Cu(II)/Cu(I) mixed valency has been observed in the copper-based 2D frameworks $\text{Cu}_3(\text{HHTP})_2$ and $\text{Cu}_3(\text{HITP})_2$ ($\text{HITP} = 2,3,6,7,10,11\text{-hexaminotriphenylene}$).³⁶ To determine whether similar mixed valency is observed in CuTOTP-OR, we probed the metal oxidation state using Cu K-edge X-ray absorption near-edge spectroscopy (XANES) (Figure 3). The edge energy (as defined by the first peak of the first derivative spectra) is typically around 8981 eV for Cu(I) and 8985 eV for Cu(II) compounds.³⁷ The XANES spectra of all four CuTOTP-OR materials ($R = C2, C4, C6, C18$) were nearly identical, with edge energies between 8985 and 8986 eV (Figures 3 and S11). Overall, the observed XANES spectral features, the simple first-neighbor only extended X-ray absorption fine structure (EXAFS) oscillations, and the average Cu–O bond lengths obtained from EXAFS fitting ($d_{\text{Cu–O}} = 1.94(1)\text{ Å}$, see Table S2) are very similar to $\text{Cu}(\text{acac})_2$ ($\text{acac}^{1-} = \text{acetylacetonate}$) and other reference compounds containing square planar Cu(II) centers (Figures S10–S13).³⁸

High-resolution X-ray photoelectron spectroscopy (XPS) measurements of the Cu $2p$ region were carried out to further corroborate our Cu(II) assignment (Figure S15). The Cu $2p_{3/2}$ peak of Cu(II) compounds is characterized by multiplet broadening and strong satellite features at higher binding energies.^{39,40} In contrast, the Cu $2p_{3/2}$ peak of Cu(I) compounds is narrower and displays a very weak shake-up satellite. By comparing the relative areas of the main $2p_{3/2}$ peak and the shake-up satellite, we estimate that $\geq 90\%$ of the copper centers in CuTOTP-OR are in the $+2$ oxidation state.

Table 1. Lattice Parameters of CuTOTP-OR Macrocycle

CuTOTP-OR	dry		DMF-solvated	
	$a = b$ (Å)	c (Å)	$a = b$ (Å)	c (Å)
$R = C2$	38.46(3)	3.19(1)	39.56(2)	3.22(1)
$R = C4$	40.16(2)	3.17(1)	42.30(2)	3.23(1)
$R = C6$	42.93(2)	3.17(1)	43.89(2)	3.20(1)
$R = C18$	55.86(6)	3.21(1)	56.91(2)	3.24(1)

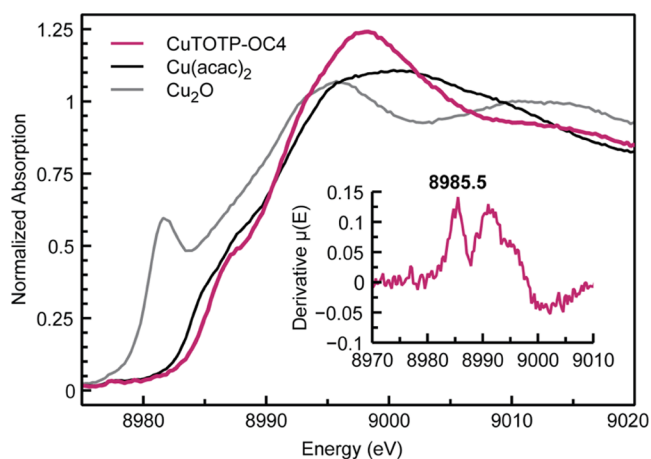


Figure 3. XANES spectra of CuTOTP-OC4 (purple) compared to reference Cu₂O (gray) and Cu(acac)₂ (black) compounds. Inset: Derivative spectra of CuTOTP-OC4, showing a first peak at 8985.5 eV.

(see Table S6 and the Supporting Information for more analysis details). We note that the complexity of Cu 2p XPS spectra can introduce large errors ($\pm 15\%$) in curve-fitting and quantification.⁴⁰ Nevertheless, taken together, our XANES and XPS data provide strong support for a predominantly Cu(II) oxidation state assignment.

After establishing the metal oxidation state in CuTOTP-OR, we next turned to the ligand. The two redox-active dioxolene units present in H₄TOTP-OR can each adopt three distinct redox states: the dianionic catecholate (cat²⁻), monoanionic semiquinone (sq¹⁻), and neutral quinone (q⁰) (Figure 4a). These three states are readily distinguished by infrared spectroscopy. As the dioxolene unit is sequentially oxidized, its C–O stretching frequency ($\nu_{\text{C-O}}$) systematically increases. In general, metal–catecholate, semiquinone, and quinone

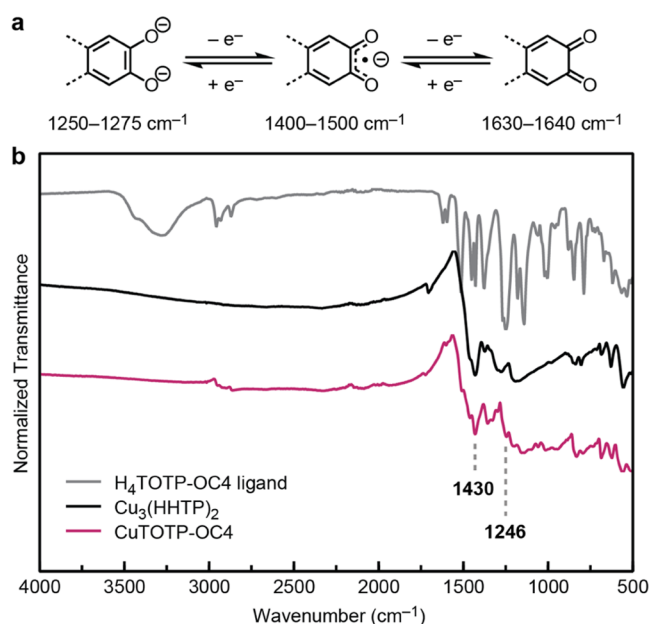


Figure 4. (a) Characteristic $\nu_{\text{C-O}}$ bands for metal–catecholate, semiquinone, and quinone complexes. (b) Infrared spectra of the H₄TOTP-OC4 ligand, Cu₃(HHTP)₂ framework, and CuTOTP-OC4 macrocycle shown in gray, black, and purple, respectively.

complexes display $\nu_{\text{C-O}}$ bands between 1250–1275, 1400–1500, and 1630–1640 cm^{−1}, respectively.⁴¹ The infrared spectrum of CuTOTP-OC4 displays a strong feature at 1430 cm^{−1}, consistent with a metal–semiquinone C–O stretch (Figure 4b). A band at 1246 cm^{−1} is also observed, which we have assigned as the $\nu_{\text{C-O}}$ of the alkyl-capped catechol unit. Similar features are also observed in the other alkyl variants of CuTOTP-OR (Figure S16). Based on the infrared spectra, we propose the ligand is aerobically oxidized during synthesis to the dianionic TOTP-OR²⁻ form, where the bridging dioxolene units are in the [sq, sq]²⁻ state.

UV–vis electronic absorption spectra are also consistent with a semiquinone assignment. Metal–semiquinone complexes typically show an intense band at ~ 300 nm, assigned as an intraligand transition, as well as a broader band between 600 and 700 nm, assigned as a metal-to-ligand charge transfer (MLCT).⁴¹ Indeed, the UV–vis spectra of CuTOTP-OC4 display strong absorbances at both 317 and 598 nm (Figure S18). Similar features are observed in the structurally related Cu₃(HHTP)₂ metal–organic framework (356 and 622 nm).⁴²

Both the macrocycle CuTOTP-OR and the metal–organic framework Cu₃(HHTP)₂ display a broad absorption >1600 cm^{−1} that is not observed in the parent H₄TOTP-OR or HHTP ligands (Figures 4b and S16). In Cu₃(HHTP)₂, this feature has been attributed to a low-energy electronic transition, though its exact nature remains unclear.³⁶ Previously proposed assignments have included low-lying transitions of charge carriers as well as intervalence charge transfer,³⁶ though the latter explanation is less likely for CuTOTP-OR, as no ligand or metal-based mixed valency appears to be present in these macrocycles. The broad electronic absorbance suggests a low activation energy for charge transport, motivating further study into the electrical conductivity of these materials.

Charge Transport Measurements. Two-point conductivity measurements were performed at room temperature on pressed pellets of CuTOTP-OR using a custom screw cell equipped with brass electrodes. Surprisingly, despite the truncated structure, pressed pellets of CuTOTP-OC2 (10^{-3} S cm^{−1}) are nearly as conductive as Cu₃(HHTP)₂ powders (10^{-3} – 10^{-2} S cm^{−1}) (Tables 2, S7, and Figure S19).^{8,43} Similar conductivity values of $\sim 10^{-4}$ S cm^{−1} were obtained for the R = C4 and C6 variants. While the pellet conductivity of CuTOTP-OC18 is only 10^{-7} S cm^{−1} due to the presence of long, insulating alkyl chains, higher values should be possible in thin films with controlled alignment and morphology.^{44,45}

Table 2. Room Temperature (298 K) Conductivity Values of CuTOTP-OR Pressed Pellets and Cu₃(HHTP)₂

sample	conductivity (S cm ^{−1})
CuTOTP-OC2 ^a	$2(1) \times 10^{-3}$
CuTOTP-OC4 ^a	$6(2) \times 10^{-4}$
CuTOTP-OC6 ^a	$4(1) \times 10^{-4}$
CuTOTP-OC18 ^a	$1(1) \times 10^{-7}$
Cu ₃ (HHTP) ₂ (pellet) ^b	10^{-3} – 10^{-2}
Cu ₃ (HHTP) ₂ (single crystal, out-of-plane) ^c	1.5

^aAverage of three measurements. ^bAverage conductivity obtained in this work is $6(2) \times 10^{-3}$ S cm^{−1}; previously reported values tabulated in ref 8 range between 10^{-3} and 10^{-2} S cm^{−1}. ^cValue obtained from ref 43.

Due to similarities in their structural, spectroscopic, and bulk conductivity properties, the CuTOTP-OR macrocycles provide a rare window into the out-of-plane charge transport properties of $\text{Cu}_3(\text{HHTP})_2$ and related 2D conductive frameworks. As described in a recent review by Dincă and co-workers, many uncertainties still remain concerning the charge carrier type, carrier concentration, and carrier mobility in conductive MOFs.⁸ For example, the nature of the charge carriers (electrons or holes) in $\text{Cu}_3(\text{HHTP})_2$ is still under active investigation. Recent reports suggest that the majority charge carrier type in $\text{Cu}_3(\text{HHTP})_2$ depends strongly on the synthesis and processing conditions, as well as the presence of adsorbed species.^{42,46,47} Our macrocyclic system provides an opportunity to study this ambipolar behavior in more detail.

Solution-processable metal–organic macrocycles are amenable to characterization techniques routinely employed by the organic semiconductor community but challenging to access with traditional porous solids. To probe the charge carrier identity and mobility, thin-film field-effect transistors were fabricated using the CuTOTP-OC18 macrocycles as the transport layer. The detailed results of FET characterization are shown in the Supporting Information, and sample transfer curves are shown in Figure S20. All measurements were performed under an N_2 atmosphere. Interestingly, the FETs displayed ambipolar behavior, producing comparable hole and electron mobilities. The average saturation hole mobility ($\mu_{\text{h,sat}}$) was $(6.17 \pm 0.51) \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, and the average saturation electron mobility ($\mu_{\text{e,sat}}$) was $(2.16 \pm 0.61) \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. The voltage thresholds were -50 and 30 V , respectively, and the on/off drain current ratio was on the order of 10^4 . We note that the CuTOTP-OC18 devices were not exhaustively optimized, and it is likely that higher mobilities could be achieved by tuning various parameters, such as the casting solution concentration, deposition spin rate, and device layer interface.

Given the strong structural resemblance between CuTOTP-OR and $\text{Cu}_3(\text{HHTP})_2$, these results suggest that $\text{Cu}_3(\text{HHTP})_2$ may display similar ambipolar conduction in the out-of-plane direction.^{8,48} Together, these studies show how discrete, solution-processable macrocycles can provide deeper insight into the charge transport properties of 2D conductive frameworks.

Electrochemical Characterization. The concentration of charge carriers and the overall conductivity of semiconducting polymers and metal–organic frameworks can be tuned across many orders of magnitude through simple oxidative (p-type) and reductive (n-type) doping.^{49–54} Motivated by these previous studies, we were interested in understanding whether our macrocycles, which contain redox-active ligands (Figure 4a), are stable to further chemical reduction or oxidation. We hypothesized that the large interior channels present in CuTOTP-OR should be able to accommodate the insertion of charge-balancing ions without perturbing the π – π stacking pathways critical for charge transport.

To probe the redox properties of our macrocycles, solid-state cyclic voltammograms (CVs) of CuTOTP-OC2 were collected in 0.05 M NaClO_4 in acetonitrile. Working electrodes were prepared by drop-casting CuTOTP-OC2 dispersed in THF on glassy carbon electrodes. A representative CV of CuTOTP-OC2 is shown in Figure 5. The compound displays quasi-reversible reduction events at $E_{1/2} = -0.20$ and -0.66 V vs Fc^+/Fc . In contrast to the relative reductive stability, scanning to more positive potentials than $\sim 0 \text{ V}$ vs Fc^+/Fc led

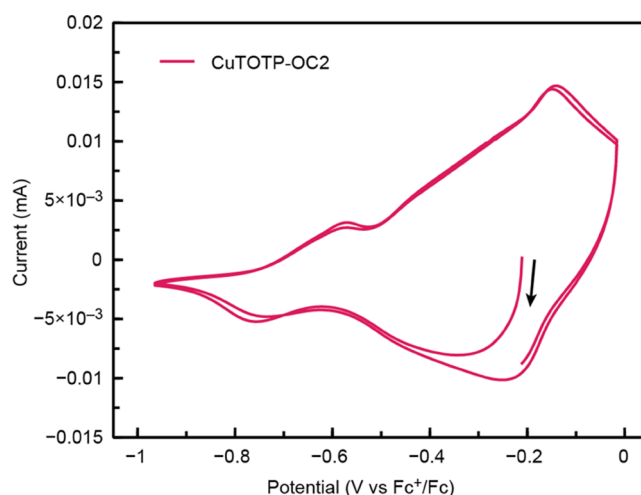


Figure 5. Solid-state cyclic voltammogram (2 cycles) of CuTOTP-OC2 collected at 10 mV s^{-1} in 0.05 M NaClO_4 in acetonitrile. The arrow indicates the direction of the forward scan.

to irreversible oxidative features indicative of either macrocycle decomposition or loss of electrical contact with the electrode. While a comprehensive study is outside the scope of this work, these preliminary CV experiments suggest that reductive doping may be a promising avenue to tune the charge transport properties of CuTOTP-OR.

CONCLUSIONS

The planar metal–organic macrocycles described here, which readily π -stack to form 1D columns, occupy a rare space in between molecules and materials. Going forward, CuTOTP-OR represents an important model system for understanding how magnetic and electronic interactions evolve as individual MOF layers self-assemble into π -stacked materials. More broadly, conjugated metal–organic macrocycles can serve as a bridge between “hard” inorganic porous materials and “soft” organic polymers. Future work will focus on how structural modifications across length scales influence electronic and ionic transport in this new class of soft nanoporous semiconductors.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/jacs.1c12596>.

Additional experimental details, synthetic procedures, and characterization data (PXRD, XAS, XPS, EPR, UV–Vis, and NMR) (PDF)

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Author Contributions

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Notes

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