## Supporting Information for

# Oxidative control over the morphology of Cu<sub>3</sub>(HHTP)<sub>2</sub>, a 2D conductive metal–organic framework

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#### 1. General Materials and Methods:

Reactions were performed using standard Schlenk or glovebox procedures under a nitrogen atmosphere unless otherwise specified. Reagents and solvents were purchased from commercial vendors and used without further purification unless otherwise noted. 2,3,6,7,10,11hexahydoxytriphenylene was purchased from TCI America (95% purity) and Acros Organics (95% purity). Copper sulfate pentahydrate (Fine Crystals/Certified ACS grade, 100.1% purity), 1,4-benzoquinone (98% purity), and barium sulfate (USP grade) were purchased from Fisher Scientific. Dimethylformamide (HPLC grade, 99% purity) was purchased from VWR. 2-methyl-1,4-benzoquinone (98% purity), 2,6-dimethyl-1,4-benzoquinone (98% purity), and 2,6-dichloro-1,4-benzoquinone (98% purity) were purchased from TCI America. 2,5-dichloro-1,4benzoquinone (98% purity) and copper acetate monohydrate (99% purity) were purchased from Millipore Sigma. The purity of all quinones were confirmed via quantitative <sup>1</sup>H NMR and, if necessary, were recrystallized before use. 2,5-dichloro-1,4-benzoquinone was recrystallized twice from ethanol; 2,6-dichloro-1,4-benzoquinone was recrystallized once from ethanol; 1,4benzoquinone was recrystallized from diethyl ether. Deuterated solvents (DMSO-d<sub>6</sub>, D<sub>2</sub>O) were purchased from Cambridge Isotope Laboratories. NMR spectra were acquired using Bruker DRX499 or AV500 spectrometers. All <sup>1</sup>H NMR spectra were referenced to residual deuterated solvent peaks.

Scanning electron microscopy (SEM) images were collected on a Thermo Fisher Scientific Apreo-S with LoVac scanning electron microscope with an operating voltage of 2kV at the University of Washington Molecular Analysis Facility. All samples were prepared *via* dropcasting from ethanol suspensions onto silicon wafers.

Powder X-ray diffraction (PXRD) data were collected on a Bruker D2 PHASER benchtop diffractometer. All samples were dropcast from acetone suspensions onto silicon wafers and allowed to slowly evaporate. Significant peak broadening was observed when samples were rapidly filtered rather than air dried.

Dynamic light scattering (DLS) data were collected on a Malvern Zetasizer Nano ZS.

UV-Vis spectra were collected on a Cary 5000 spectrophotometer (Agilent).

Infrared spectra were recorded on a Perkin-Elmer Frontier Fourier transform infrared spectrometer.

Thermogravimetric analysis (TGA) data were collected on a TA Instruments TGA Q5000.

#### 2. Ligand purification

A 200 mL Schlenk flask was charged with 2,3,6,7,10,11-hexahydroxytriphenylene (HHTP, 1.19 g, 3.66 mmol, 1.00 equiv), degassed ethyl acetate (75.0 mL), and methanol (75.0 mL). A solution of sodium dithionite in water (1.00 M, 22.0 mL, 6.00 equiv) was added dropwise under purging nitrogen with stirring. At this point, the dark, purple-black solution became a light, beige suspension. The suspension was allowed to stir at room temperature for 18 hours. The organic solvents were then removed *in vacuo* and the resulting beige powder was filtered under a nitrogen pillow and washed with H<sub>2</sub>O (3 x 75 mL). Drying under vacuum at 100 °C for several hours afforded reduced HHTP (0.980 g, 3.02 mmol, 82.6% yield, purity of 93.3 wt%). The sample was further purified by dissolving 388 mg of the compound in methanol and stirring with activated charcoal for 5 minutes, at which point the solution was filtered and dried *in vacuo* at 220 °C to afford pure HHTP (326 mg, 1.01 mmol, 84.1% yield, purity of 101 wt%). Purity of the compound was assessed *via* quantitative <sup>1</sup>H NMR. <sup>1</sup>H NMR (500 MHz, (CD<sub>3</sub>)<sub>2</sub>SO):  $\delta$  9.27 (s, 6OH), 7.60 (s, 6H).

## 3. Cu<sub>3</sub>(HHTP)<sub>2</sub> synthesis

Cu<sub>3</sub>(HHTP)<sub>2</sub> was synthesized in air following known literature preps for producing rod and blocklike particle morphologies.<sup>1</sup> Unless otherwise noted, these literature preps were completed using as-received hexahydroxytriphenylene from TCI. See the control syntheses below for exact experimental details for these literature syntheses.

All Cu<sub>3</sub>(HHTP)<sub>2</sub> made with chemical oxidants were prepared inside an inert-atmosphere glovebox using purified HHTP ligand. To obtain an accurate mass for sublimation, quinones were diluted with BaSO<sub>4</sub> and finely ground with a mortar and pestle before use. After synthesis, the vials were removed from the box and washed and analyzed in air. PXRD data was collected after the H<sub>2</sub>O and acetone washes; SEM imaging was conducted after the ethanol washes. For both techniques, samples were prepared *via* dropcasting onto silicon wafers. Regardless of oxidant used, significant peak broadening was observed in all samples *via* PXRD if the sample was dried quickly *via* vacuum filtration or nitrogen flow, likely due to slippage in the Cu<sub>3</sub>(HHTP)<sub>2</sub> sheets.

### Synthesis of Rod, Block, and Flake Morphologies:

**Synthesis of Cu<sub>3</sub>(HHTP)<sub>2</sub> rods:** A 20 mL scintillation vial was charged with a ground 2,6dimethyl-1,4-benzoquinone/BaSO<sub>4</sub> mixture (10.0 wt% quinone, 31.5 mg, 23.1 µmol, 3.00 equiv). A 4 mL vial was placed inside of the 20 mL scintillation vial. The 4 mL vial was charged while stirring at ~700 rpm with purified hexahydroxytriphenylene solution (0.125 mL of a 20.0 mg/mL solution in DMF, 7.70 µmol, 1.00 equiv), followed by DMF (0.175 mL) and H<sub>2</sub>O (2.60 mL). The 4 mL vial was then stirred at ~700 rpm for an additional 5 minutes, followed by rapid addition of CuSO<sub>4</sub>·5H<sub>2</sub>O (0.096 mL of a 30.0 mg/mL solution in H<sub>2</sub>O, 11.6 µmol, 1.50 equiv). The outer teflon-taped 20 mL scintillation vial was then sealed and heated at 80 °C for 24 hours without stirring. Cu<sub>3</sub>(HHTP)<sub>2</sub> was obtained as a blue-black powder *via* centrifugation and washed with H<sub>2</sub>O (2x), acetone (3x), ethanol (2x), and acetone (4x). The powder was then filtered and stored inside an inert-atmosphere box. On a 17 vial scale-up, 51.3 mg of Cu<sub>3</sub>(HHTP)<sub>2</sub> rods were obtained prior to solvent removal; the adjusted yield post-solvent removal was 35.6 mg (65.7% yield). *Note:* Sometimes, a secondary phase is observed in the powder X-ray diffraction pattern if insufficient oxidant is used during synthesis. This phase impurity can be removed without altering the morphology by post-synthetic oxidative treatment (heating in air at 80 °C in 1:9 DMF:H<sub>2</sub>O).

Synthesis of Cu<sub>3</sub>(HHTP)<sub>2</sub> blocks: A 20 mL scintillation vial was charged with a ground 2,6dimethyl-1,4-benzoquinone/BaSO<sub>4</sub> mixture (10.0 wt% quinone, 31.5 mg, 23.1 µmol, 3.00 equiv). A 4 mL vial was placed inside of the 20 mL scintillation vial. The 4 mL vial was charged while stirring at ~700 rpm with purified hexahydroxytriphenylene solution (0.125 mL of a 20.0 mg/mL solution in DMF, 7.70 µmol, 1.00 equiv), followed by DMF (0.073 mL) and H<sub>2</sub>O (2.60 mL), and then by rapid addition of 2,5-dichloro-1,4-benzoquinone (0.102 mL of a 4.00 mg/mL solution in DMF, 23.1 µmol, 0.300 equiv). The 4 mL vial was then stirred at ~700 rpm for an additional 5 minutes, followed by rapid addition of CuSO<sub>4</sub>·5H<sub>2</sub>O (0.096 mL of a 30.0 mg/mL solution in H<sub>2</sub>O, 11.6 µmol, 1.50 equiv). The outer teflon-taped 20 mL scintillation vial was then sealed and heated at 80 °C for 24 hours without stirring. Cu<sub>3</sub>(HHTP)<sub>2</sub> was obtained as a blue-black powder *via* centrifugation and washed with H<sub>2</sub>O (2x), acetone (3x), ethanol (2x), and acetone (4x). The powder was then filtered and stored inside an inert-atmosphere box. On a 23 vial scale-up, 52.4 mg of Cu<sub>3</sub>(HHTP)<sub>2</sub> blocks were obtained prior to solvent removal; the adjusted yield post-solvent removal was 41.6 mg (56.8% yield).

Synthesis of Cu<sub>3</sub>(HHTP)<sub>2</sub> flakes: A 20 mL scintillation vial was charged with a ground 2,6dimethyl-1,4-benzoquinone/BaSO<sub>4</sub> mixture (10.0 wt% quinone, 31.5 mg, 23.1 µmol, 3.00 equiv). A 4 mL vial was placed inside of the 20 mL scintillation vial. The 4 mL vial was charged while stirring at ~700 rpm with purified hexahydroxytriphenylene solution (0.125 mL of a 20.0 mg/mL solution in DMF, 7.70 µmol, 1.00 equiv), followed by DMF (0.090 mL) and H<sub>2</sub>O (2.60 mL), and then by rapid addition of 2,5-dichloro-1,4-benzoquinone (0.085 mL of a 8.00 mg/mL solution in DMF, 38.5 µmol, 0.500 equiv). The 4 mL vial was then stirred at ~700 rpm for an additional 5 minutes, followed by rapid addition of CuSO<sub>4</sub>·5H<sub>2</sub>O (0.096 mL of a 30.0 mg/mL solution in H<sub>2</sub>O, 11.6 µmol, 1.50 equiv). The outer teflon-taped 20 mL scintillation vial was then sealed and heated at 80 °C for 24 hours without stirring. Cu<sub>3</sub>(HHTP)<sub>2</sub> was obtained as a blue-black powder *via* centrifugation and washed with H<sub>2</sub>O (2x), acetone (3x), ethanol (2x), and acetone (4x). The powder was then filtered and stored inside an inert-atmosphere box. On a 36 vial scale-up, 57.8 mg of Cu<sub>3</sub>(HHTP)<sub>2</sub> flakes were obtained prior to solvent removal; the adjusted yield post-solvent removal was 48.9 mg (42.6% yield).

## **Control Syntheses:**

Literature synthesis of Cu<sub>3</sub>(HHTP)<sub>2</sub> rods in air<sup>1</sup>: A 20 mL scintillation vial was charged with Cu<sub>2</sub>(OAc)<sub>4</sub>·H<sub>2</sub>O (0.52 mL of a 15.0 mg/mL solution in H<sub>2</sub>O, 39.1 µmol, 1.81 equiv), H<sub>2</sub>O (0.98 mL), and hexahydroxytriphenylene (7.0 mg, 22 µmol, 1.0 equiv). The teflon-taped 20 mL vial was sonicated at room temperature for 5 minutes, and then heated at 80 °C for 6 hours without stirring. Cu<sub>3</sub>(HHTP)<sub>2</sub> was obtained as a blue-black powder *via* centrifugation and washed with H<sub>2</sub>O (2x), ethanol (2x), and acetone (4x). The powder was then filtered and stored inside an inert-atmosphere box. On an 8 vial scale-up (56.0 mg ligand scale), a typical yield was 84.3 mg prior to solvent removal; the adjusted yield post-solvent removal was 56.7 mg (79% yield).

Literature synthesis of Cu<sub>3</sub>(HHTP)<sub>2</sub> particles in air<sup>1</sup>: A 20 mL scintillation vial was charged with hexahydroxytriphenylene (51.0 mg, 157  $\mu$ mol, 1.00 equiv), DMF (0.60 mL), and H<sub>2</sub>O (4.80 mL). A separate 20 mL scintillation vial was charged with CuSO<sub>4</sub>·5H<sub>2</sub>O (89.8 mg, 360  $\mu$ mol, 2.29 equiv). The two vials were heated separately at 80 °C for 5 minutes without stirring. The two solutions were combined and heated in a teflon-taped 20 mL scintillation vial at 80 °C for 12 hours without stirring. Cu<sub>3</sub>(HHTP)<sub>2</sub> was obtained as a blue-black powder *via* centrifugation and washed with H<sub>2</sub>O (2x), ethanol (2x), and acetone (4x). The powder was then filtered and stored inside an inert-atmosphere box. A typical yield for this synthesis was 58.8 mg Cu<sub>3</sub>(HHTP)<sub>2</sub> prior to solvent removal; the adjusted yield post-solvent removal was 41.6 mg (63.9% yield).

General procedure using varying equiv of quinone pre-oxidant: A 20 mL scintillation vial was charged with ground quinone/BaSO<sub>4</sub> mixture (5.00-10.0 wt% quinone,  $23.1 \mu$ mol, 3.00 equiv). A 4 mL vial was placed inside of the 20 mL scintillation vial. The 4 mL vial was charged while stirring at ~700 rpm with purified hexahydroxytriphenylene solution (0.125 mL of a 20.0 mg/mL solution in DMF, 7.70  $\mu$ mol, 1.00 equiv), followed by DMF\* and H<sub>2</sub>O (2.60 mL), and then by rapid addition of quinone pre-oxidant (~4–8 mg/mL DMF, varying equiv). The 4 mL vial was then stirred at ~700 rpm for an additional 5 minutes, followed by rapid addition of CuSO<sub>4</sub>·5H<sub>2</sub>O (0.096

mL of a 30.0 mg/mL solution in H<sub>2</sub>O, 11.6  $\mu$ mol, 1.50 equiv). The outer teflon-taped 20 mL scintillation vial was then sealed and heated at 80 °C for 24 hours without stirring. Cu<sub>3</sub>(HHTP)<sub>2</sub> was obtained as a blue-black powder *via* centrifugation and washed with H<sub>2</sub>O (2x), acetone (3x), and ethanol (2x).

\*The amount of DMF used should total 0.175 mL for each synthesis.

**0.3 equiv 2,5-dichloro-1,4-benzoquinone pre-oxidant synthesis in air:** A 4 mL vial was placed inside of the 20 mL scintillation vial. The 4 mL vial was charged while stirring at ~700 rpm with purified hexahydroxytriphenylene solution (0.125 mL of a 20.0 mg/mL solution in DMF, 7.70  $\mu$ mol, 1.00 equiv), followed by DMF (0.073 mL) and H<sub>2</sub>O (2.60 mL), and then by rapid addition of 2,5-dichloro-1,4-benzoquinone (0.102 mL of a 4.00 mg/mL solution in DMF, 23.1  $\mu$ mol, 0.300 equiv). The 4 mL vial was then stirred at ~700 rpm for an additional 5 minutes and removed from the inert-atmosphere box. After 5 min exposure to air, CuSO<sub>4</sub>·5H<sub>2</sub>O (0.096 mL of a 30.0 mg/mL solution in H<sub>2</sub>O, 11.6  $\mu$ mol, 1.50 equiv) was added rapidly to the 4 mL vial. The outer teflon-taped 20 mL scintillation vial was then sealed and heated at 80 °C for 24 hours without stirring. Cu<sub>3</sub>(HHTP)<sub>2</sub> was obtained as a blue-black powder *via* centrifugation and washed with H<sub>2</sub>O (2x), acetone (3x), and ethanol (2x).

Air-free synthesis without chemical oxidation: A 4 mL vial was placed inside of the 20 mL scintillation vial. The 4 mL vial was charged while stirring at ~700 rpm with purified hexahydroxytriphenylene solution (0.125 mL of a 20.0 mg/mL solution in DMF, 7.70  $\mu$ mol, 1.00 equiv), followed by DMF (0.175 mL) and H<sub>2</sub>O (2.60 mL). The 4 mL vial was then stirred at ~700 rpm for an additional 5 minutes, followed by addition of CuSO<sub>4</sub>·5H<sub>2</sub>O (0.096 mL of a 30.0 mg/mL solution in H<sub>2</sub>O, 11.6  $\mu$ mol, 1.50 equiv). The outer teflon-taped 20 mL scintillation vial was then sealed and heated at 80 °C for 24 hours without stirring. A mixed-phase framework and Cu<sub>2</sub>O (see Fig. S7) were obtained as a black powder *via* centrifugation and washed with H<sub>2</sub>O (2x), acetone (3x), and ethanol (2x).

#### 4. Electron paramagnetic resonance spectroscopy

X-band EPR data were collected at 200 K on a Bruker EMXnano spectrometer (microwave (mw) frequency, 9.64 GHz) equipped with a liquid nitrogen cooling system. A mw power of 0.03 mW, modulation amplitude of 8 G and a modulation frequency of 100 kHz were used. Samples were prepared inside an inert atmosphere box by serial dilutions in a 1:1 mixture of DMSO- $d_6$ , to D<sub>2</sub>O. Tubes were capped and sealed with electrical tape before obtaining spectra. 10, 100, and 1000  $\mu$ M samples of 2,2-diphenyl-1-picrylhydrazyl (DPPH) radical were used as quantitative standards. Ligand-based samples were diluted to a hexahydroxytriphenylene concentration of 80–90 mM.

The area of ligand-based radical signals was compared to the DPPH radical calibration curve to determine the sample's radical concentration (see **Fig. S1**).<sup>2</sup> For all samples, the following parameters were used: center field 3445 G, sweep width 100 G, sweep time 5.24 s, receiver gain 35 dB, modulation amplitude 8, 20 scans, and attenuation 40 dB.

#### 5. X-ray photoelectron spectroscopy

X-ray photoelectron spectra (XPS) were collected on a Kratos Axis Ultra DLD X-ray photoelectron spectrometer using a monochromatic Al K $\alpha$  x-ray source. Samples were prepared by pressing the powder onto a piece of double-sided Scotch tape. A low energy electron flood gun was used for charge neutralization of the sample. High-resolution spectra were obtained using an analysis area of ~ 700 × 300 µm and a 20 eV pass energy. Survey spectra were collected at a pass energy of 80 eV. Cu high resolution scans were collected first to minimize x-ray damage, and the Cu 2p peak was used for the following analysis. Data analysis and curve-fitting was carried out using CasaXPS.<sup>3</sup> A standard Shirley background was used for all samples, and Gaussian (30%)-Lorentzian (70%) (GL(70)) profiles were used for each component. Spectra are referenced to the C 1s hydrocarbon peak calibrated to 285.0 eV.

The %Cu(II) was quantified according to a previously reported procedure that uses the relative areas of the Cu  $2p_{3/2}$  main peak and shake-up satellite peaks to estimate the Cu(II) and Cu(I) + Cu(0) content.<sup>4</sup> Specifically, the equation shown below was used, where A = the area of the main peak in the sample of interest, B = the area of the shake-up satellite peak in the sample of interest, and A1<sub>s</sub>/B<sub>s</sub> = the ratio of the main peak/shake-up peak in a 100% pure, reference Cu(II) compound:

$$\%Cu(II) = \frac{B(1 + \frac{A1_s}{B_s})}{A + B} * 100$$

We note that the constant  $A1_s/B_s$  can vary widely across reference Cu(II) compounds (e.g., Cu(OH)<sub>2</sub> 1.57, CuO 1.89, CuBr<sub>2</sub> 2.45).3 We have chosen Cu(acac)<sub>2</sub> and Cu(OAc)<sub>2</sub>·H<sub>2</sub>O as our reference compounds, because they mimic the ligand environment of Cu<sub>3</sub>(HHTP)<sub>2</sub>. Previous data from our group indicates close  $A1_s/B_s$  values of 0.9 for Cu(acac)<sub>2</sub> and 1.1 for Cu(OAc)<sub>2</sub>·H<sub>2</sub>O; the average value of 1.0 was used for our data analysis.<sup>5</sup> We note that, due to poor signal-to-noise, errors in curve-fitting, and uncertainties in  $A1_s/B_s$ , our XPS data can only provide a rough estimate of the %Cu(II).

#### 6. Electrochemical characterization

All cyclic voltammetry and conductivity measurements were carried out using a BioLogic SP-200 Potentiostat. Conductivity measurements were run on packed pellets using a 2-electrode screw cell. A polyetheretherketone (PEEK) spacer with a 2.8 mm smooth internal diameter was prepared with threading for two brass screws to compress powders from either side.<sup>6</sup> The tips of the screws were polished to a flat surface 2.75 mm in diameter. Cells were prepared by screwing one screw into the PEEK spacer, then adding 7–10 mg of powder, and screwing the second screw in fingertight, and then tightening to 0.56 Nm with a controlled torque screwdriver on both screws. Sample thicknesses were measured with calipers and were typically in the range of 300–800  $\mu$ m. Cells were allowed to settle for 4 hr, before re-tightening to 0.56 Nm and settling for an additional 18 hr at which point I-V curves measured using current scan (CS).

### 7. Gas sorption

**Sample activation:** Cu<sub>3</sub>(HHTP)<sub>2</sub> samples were transferred into a pre-weighed glass tube, sealed with a Transeal, and dried under dynamic vacuum at 80 °C for 20 hours on a Micromeritics Smart VacPrep instrument. Activation at lower temperatures resulted in a decrease in the measured surface area. The glass tube and Transeal were subsequently weighed to determine the final mass of the activated sample.

 $N_2$  adsorption measurements: For all gas adsorption measurements, ~40 mg of sample was transferred to a preweighed glass sample tube. Low-pressure  $N_2$  adsorption experiments (up to 1 bar) were performed using a Micromimetics 3Flex Surface Characterization Analyzer. Ultrahigh purity  $N_2$  (5.0 grade, 99.999%) was used in all adsorption experiments.  $N_2$  adsorption measurements were performed using a liquid  $N_2$  bath (77 K).

BET surface areas were calculated using data points between 0.02 and 0.09  $P/P_{\theta}$ . In all cases, the following BET consistency criteria were followed: 1) the pressure range has values of  $v(P_{\theta}-P)$  increasing with  $P/P_{\theta}$ , and 2) positive y intercept.<sup>7</sup> All correlation coefficients were  $\geq$  0.999.

#### 8. Supplementary Tables

Sample	HHTP <sup>a</sup> (wt%)	H <sub>2</sub> O <sup>b</sup> (wt%)	Unaccounted (wt%)	
Acros HHTP, Batch 1	59.0	2.5	38.5	
Acros HHTP, Batch 2	68.0	2.5	29.5	
TCI HHTP, Batch 1	87.0	6.7	6.3	
TCI HHTP, Batch 2	81.0	6.0	13.0	
<b>Purified HHTP</b>	100.7	N/A	N/A	
Purified HHTP + 0.3 equiv chemical oxidant	67.4	6.0	26.6	

**Table S1** | Summary of hexahydroxytriphenylene purity determined via quantitative nuclearmagnetic resonance spectroscopy and thermogravimetric analysis.

a = determined by quantitative NMR; b = determined by thermogravimetric analysis.

**Table S2** | Summary of dynamic light scattering (DLS) measurement results for number particle size distribution (PSD). All measurements were done in a 1:1 mixture of DMSO and H<sub>2</sub>O. Samples were sonicated for  $\geq$  30 min prior to analysis to prevent particle aggregation. The number size distribution is the number of particles of discrete sizes, normalized across the total number of particles present.

Sample	Diameter (nm)	Number (%)
Acros HHTP	$\begin{array}{c} 160\pm40\\ 790\pm270\end{array}$	84 16
ТСІ ННТР	$380\pm50$	100
HHTP + 0.3 equiv 2,5- dichloro-1,4-benzoquinone	$\begin{array}{c} 80\pm10\\ 530\pm130\end{array}$	98 2
1:1 DMSO:H <sub>2</sub> O	$0.6\pm0.1$	100

Quinone	1 e <sup>-</sup> E <sup>0, a</sup> (V vs Fc <sup>0/+</sup> )	Sublimation Rate <sup>b</sup> (10 <sup>-4</sup> mmol/min)
1,4-benzoquinone	-0.882	$9.7 \pm 3.9$
2-methyl-1,4-benzoquinone	-0.963	$7.3 \pm 2.5$
2,6-dimethyl-1,4- benzoquinone	-1.035	$1.6 \pm 0.2$
2,5-dichloro-1,4-benzoquinone	-0.561	not observed

Table S3 | Summary of one electron reduction potentials and sublimation rates of selected substituted quinones.

a = obtained from literature report<sup>8</sup>; b = obtained from UV-Vis spectroscopy aided sublimation studies (see **Fig. S6**). The uncertainty is approximated using line-of-best-fit analysis of the average values for each time point.

**Table S4** | Summary of Cu  $2p_{3/2}$  XPS curve-fitting parameters for Cu<sub>3</sub>(HHTP)<sub>2</sub> made with chemical oxidant for the rods, blocks, and flakes morphology types.

	Rods	Blocks	Flakes
	ito ub	Diotity	1 141105
GL(x) value	70	70	70
Peak 1 (eV)	944.12	944.41	943.86
%	21.63	13.55	17.39
FWHM	3.80	2.58	3.22
Peak 2 (eV)	939.74	940.56	939.76
%	25.53	30.72	25.74
FWHM	5.00	5.00	5.00
Peak 3 (eV)	935.10	934.99	934.89
%	45.53	45.97	43.69
FWHM	2.13	2.29	2.18
Peak 4 (eV)	933.21	932.93	932.89
%	7.31	9.76	13.18
FWHM	1.05	1.16	1.32

	Air Synthesis, Rods	Air Synthesis Particles
GL(x) value	70	70
Peak 1 (eV)	944.35	944.28
%	14.59	15.64
FWHM	2.60	3.04
Peak 2 (eV)	940.51	940.03
%	29.69	27.55
FWHM	5.00	5.00
Peak 3 (eV)	935.06	935.12
%	46.91	44.93
FWHM	2.16	2.07
Peak 4 (eV)	932.97	933.08
%	8.81	11.88
FWHM	1.28	1.36

 $\label{eq:solution} \begin{array}{l} \textbf{Table S5} \mid Summary \ of \ Cu \ 2p_{3/2} \ XPS \ curve-fitting \ parameters \ for \ Cu_3(HHTP)_2 \ made \ without \ chemical \ oxidant \ in \ air \ following \ a \ literature \ procedure.^1 \end{array}$ 

**Table S6** | Summary of XPS main peak (A1) and shake-up satellite peak (B) areas for  $Cu_3(HHTP)_2$  materials prepared with and without chemical oxidant. The % Cu was calculated using the following equation.<sup>4</sup> Based on previous results in our laboratory, an A1<sub>s</sub>/B<sub>s</sub> ratio of 1 was used.<sup>5</sup>

Sample	Main peak area (A) (%)Shake-up peak area (B) (%)		% Cu(II)	
Cu <sub>3</sub> (HHTP) <sub>2</sub> Rods	52.8	47.2	94.3	
Cu <sub>3</sub> (HHTP) <sub>2</sub> Blocks	55.7	44.3	88.5	
Cu <sub>3</sub> (HHTP) <sub>2</sub> Flakes	56.9	43.1	86.3	
Cu3(HHTP)2 Air Synthesis, Rods	55.7	44.3	88.5	
Cu <sub>3</sub> (HHTP) <sub>2</sub> Air Synthesis, Particles	56.8	43.2	86.4	

$0/C_{\rm ex}(H) =$	$B(1 + \frac{AI_s}{B_s})$
%Cu(II) -	A+B * 100

Sample	Conductivity (S/cm)
Cu <sub>3</sub> (HHTP) <sub>2</sub> Rods	4 x 10 <sup>-3</sup> 1 x 10 <sup>-3</sup> 3 x 10 <sup>-3</sup>
Cu <sub>3</sub> (HHTP) <sub>2</sub> Blocks	1 x 10 <sup>-2</sup> 1 x 10 <sup>-2</sup> 7 x 10 <sup>-3</sup>
Cu <sub>3</sub> (HHTP) <sub>2</sub> Flakes	1 x 10 <sup>-3</sup> 4 x 10 <sup>-3</sup> 4 x 10 <sup>-3</sup>
Cu <sub>3</sub> (HHTP) <sub>2</sub> Air Synthesis, Rods	9 x 10 <sup>-3</sup> 8 x 10 <sup>-3</sup> 2 x 10 <sup>-2</sup>
Cu <sub>3</sub> (HHTP) <sub>2</sub> Air Synthesis, Particles	2 x 10 <sup>-2</sup> 3 x 10 <sup>-2</sup> 9 x 10 <sup>-3</sup>

**Table S7** | Pellet conductivities for  $Cu_3(HHTP)_2$  materials collected with a 2-electrode screw cell.Three separate  $Cu_3(HHTP)_2$  pellets were made and measured for each material type.

**Table S8** | Summary of Brunauer–Emmett–Teller (BET) surface areas of  $Cu_3(HHTP)_2$  materials.The reported errors are associated with the goodness of fit.

Sample	BET SA (m²/g)	Slope (g/mmol)	BET y intercept (g/mmol)	<b>BET Correlation</b> <b>Coefficient (R<sup>2</sup>)</b>
Cu3(HHTP)2 Rods	$560.8445 \pm \\ 2.6198$	$\begin{array}{c} 0.17388 \pm \\ 0.00081 \end{array}$	$\begin{array}{c} 0.00007 \pm \\ 0.00003 \end{array}$	0.9999673
Cu <sub>3</sub> (HHTP) <sub>2</sub> Blocks	$536.1005 \pm \\ 2.3787$	$\begin{array}{c} 0.18194 \pm \\ 0.00081 \end{array}$	$\begin{array}{c} 0.00004 \pm \\ 0.00003 \end{array}$	0.9999705
Cu3(HHTP)2 Flakes	$385.0867 \pm \\ 1.2960$	$\begin{array}{c} 0.25323 \pm \\ 0.00085 \end{array}$	$\begin{array}{c} 0.00011 \pm \\ 0.00004 \end{array}$	0.9999830
Cu3(HHTP)2 Air Synthesis, Rods	$517.3851 \pm 1.9405$	$\begin{array}{c} 0.18847 \pm \\ 0.00071 \end{array}$	$\begin{array}{c} 0.00009 \pm \\ 0.00004 \end{array}$	0.9999649
Cu3(HHTP)2 Air Synthesis, Particles	$563.9355 \pm \\ 2.2252$	$\begin{array}{c} 0.17295 \pm \\ 0.00068 \end{array}$	$\begin{array}{c} 0.00005 \pm \\ 0.00003 \end{array}$	0.9999845

## 9. Supplementary Figures



**Fig. S1** | Quantitative electron paramagnetic resonance calibration curve based on 2,2-diphenyl-1picrylhydrazyl standards. The line of best fit was used to determine the radical concentration of ligand-based samples (see section 4 of the Supporting Information, and **Figs. S2** and **S12**).<sup>2</sup>



**Fig. S2** | Quantitative electron paramagnetic resonance spectrum of 90.1 mM as-received Acros hexahydroxytriphenylene ligand in 1:1  $d_6$ -DMSO:D<sub>2</sub>O. The HHTP concentration accounts for 2.5 wt% water. The radical species is 86.0  $\mu$ M or less than 0.1 mol% of the original ligand concentration.



**Fig. S3** | The quantitative <sup>1</sup>H NMR spectra in  $d_6$ -DMSO of purified hexahydroxytriphenylene, with reference compound 1,3,5-trimethoxybenzene. The NMR solution was prepared by diluting a solution of 15.0 mg of hexahydroxytriphenylene and 17.7 mg 1,3,5-trimethoxybenzene. The relative ratio of 6.00:6.79 observed between hexahydroxytriphenylene's aromatic singlet at 7.60 ppm and 1,3,5-trimethoxybenzene's aromatic singlet at 6.09 ppm indicates 15.1 mg NMR active hexahydroxytriphenylene. An overestimate of HHTP by ~0.1 mg is within the error of the analytical balance and this experimental technique.



**Fig. S4** | Scanning electron microscopy images of  $Cu_3(HHTP)_2$  prepared *via* literature preps<sup>1</sup> in air designed to yield particle (a,b,c) and rod (d,e,f) morphologies with varying qualities of HHTP ligand: purified (a,d), as-received from Acros (b,e), and as-received from TCI (c,f).



**Fig. S5** | Particle thickness distributions for  $Cu_3(HHTP)_2$  prepared *via* a literature prep designed to yield a rod-like morphology with varying qualities of HHTP ligand: purified, as-received from Acros, and as-received from TCI.<sup>1</sup>



**Fig. S6** | Sublimation rates of substituted quinones measured *via* UV-Vis spectroscopy. Overall, the rate of quinone sublimation appears to be inversely proportional to molecular weight. In a typical experiment, a 20 mL scintillation vial was charged with ~25 mg of quinone (1,4-benzoquinone, 2-methyl-1,4-benzoquinone, and 2,6-dimethyl-1,4-benzoquinone). A 4 mL vial containing 3 mL of dimethylformamide was then placed inside the 20 mL vial. The 20 mL vial was teflon taped and sealed, and heated inside an inert atmosphere box at 80 °C for varying time points, allowing the quinones to sublime. Then, the resulting solvent-quinone mixture was measured by UV-Vis spectroscopy, and a calibration curve was used to determine the amount of quinone that had sublimed. Sublimation could not be detected for 2,5-dichlorobenzoquinone, as the absorbance values were below the detection limits of the instrument. The analysis is summarized in **Table S3**.



**Fig. S7** | Powder X-ray diffraction pattern of  $Cu_3(HHTP)_2$  prepared without any oxidant inside an inert-atmosphere box. A predicted pattern for  $Cu_2O$  is plotted for comparison.<sup>9</sup> Without any oxidant, an unidentified secondary phase (labeled with \*) and  $Cu_2O$  are formed in addition to  $Cu_3(HHTP)_2$ . The produced morphology is shown in **Fig. S8**.



**Fig. S8** | Scanning electron microscopy image of Cu<sub>3</sub>(HHTP)<sub>2</sub> prepared without any oxidant inside an inert-atmosphere box. As determined by powder X-ray diffraction (see **Fig. S7**), a mixture of phases (Cu<sub>3</sub>(HHTP)<sub>2</sub>, Cu<sub>2</sub>O, and an unidentified secondary phase) are the predominant products.



**Fig. S9** | Powder X-ray diffraction patterns of  $Cu_3(HHTP)_2$  prepared according to a literature procedure designed to yield a particle morphology.<sup>1</sup> When HHTP ligand provided by TCI is used, the expected powder pattern for this framework forms; when purified ligand is used, there is framework formation, as well as an additional phase impurity. We hypothesize this phase impurity is due to insufficient oxidation of the ligand during framework formation.



**Fig. S10** | Scanning electron microscopy images of  $Cu_3(HHTP)_2$  prepared in an inert atmosphere box with 3.0 equiv sublimed 2,6-dimethylbenzoquinone and HHTP ligand as-received from a) Acros and b) TCI. The Acros ligand was determined to have 29.5% impurity, and the TCI ligand 13% impurity (see **Table S1**). The Acros morphology strongly resembles  $Cu_3(HHTP)_2$  made with 0.3 equiv pre-oxidant (see the main text). The TCI morphology somewhat resembles the  $Cu_3(HHTP)_2$  made with 0.1 equiv pre-oxidant (see **Fig. S14**).



**Fig. S11** | The quantitative <sup>1</sup>H NMR spectra in 1:1 *d*<sub>6</sub>-DMSO:D<sub>2</sub>O of purified hexahydroxytriphenylene combined with 0.3 equiv 2,5-dichlorobenzoquinone, with reference compound dimethyl sulfone. with reference compound 1,3,5-trimethoxybenzene. The NMR solution was prepared by combining 125  $\mu$ L of 55.67 mg/mL HHTP in (CD<sub>3</sub>)<sub>2</sub>SO, 78.4  $\mu$ L of 25.24 mg/mL dimethyl sulfone in (CD<sub>3</sub>)<sub>2</sub>SO, 67.3  $\mu$ L (CD<sub>3</sub>)<sub>2</sub>SO, 349  $\mu$ L D<sub>2</sub>O, and lastly 75.3  $\mu$ L of 15.18 mg/mL 2,5-dichlorobenzoquinone in (CD<sub>3</sub>)<sub>2</sub>SO. At this point, the solution was stirred for 5 minutes and then immediately removed from the inert-atmosphere box for NMR analysis. The relative ratio of 6.00:8.72 observed between HHTP's aromatic singlet at 7.68 ppm and dimethyl sulfone's aliphatic singlet at 2.95 ppm accounts for 64.7 wt% of the HHTP sample; water accounts for an additional 6 wt%. 26.6 wt% of the HHTP is then NMR silent, likely existing as an oxidized polymeric species. The quinone signal at 6.91 ppm corresponds to 2,5-dichlorohydroquinone; no other quinone signals are detected. Furthermore, this signal integrates to 103 wt% of the expected quinone species.



**Fig. S12** | Quantitative electron paramagnetic resonance spectrum of 82.9 mM purified hexahydroxytriphenylene ligand combined with 0.3 equiv 2,5-dichlorobenzoquinone in 1:1  $d_6$ -DMSO:D<sub>2</sub>O. The HHTP concentration accounts for 6.0 wt% water. The radical species is 17.3  $\mu$ M or less than 0.1 mol% of the original ligand concentration.



**Fig. S13** | Scanning electron microscopy image of  $Cu_3(HHTP)_2$  prepared in an inert atmosphere box with 0.3 equiv 2,6-dichlorobenzoquinone pre-oxidant and 3 equiv sublimed 2,6dimethylbenzoquinone. Compared to the 0.3 equiv pre-oxidant synthesis using 2,5dichlorobenzoquinone, there is no significant change in the produced  $Cu_3(HHTP)_2$  morphology, suggesting this strategy may be generalizable to other stronger quinone oxidants.



**Fig. S14** | Scanning electron microscopy image of  $Cu_3(HHTP)_2$  prepared in an inert atmosphere box with 0.1 equiv 2,5-dichlorobenzoquinone pre-oxidant and 3 equiv sublimed 2,6dimethylbenzoquinone. Compared to the no pre-oxidant syntheses, the produced rods are thicker and shorter, representing a transition to the hexagonal particles observed with 0.3 equiv preoxidant.



**Fig. S15** | Scanning electron microscopy images of  $Cu_3(HHTP)_2$  prepared with 0.3 equiv 2,5dichlorobenzoquinone as pre-oxidant, in a) air or in an inert atmosphere box with varying sublimed oxidants: b) *p*-benzoquinone, and c) 2,6-dimethylbenzoquinone. The rate and strength of oxidation has a strong impact on the resulting morphology; a slow, weak oxidant produces hexagonal blocks with more well-defined edges.



**Fig. S16** | Diameter distributions of  $Cu_3(HHTP)_2$  morphologies produced with chemical oxidant. Three separate batches were analyzed for each morphology type. In all cases as the amount of chemical pre-oxidant used increases, the diameter of the produced  $Cu_3(HHTP)_2$  increases.



Fig. S17 | Length distributions of  $Cu_3(HHTP)_2$  morphologies produced with chemical oxidant. Three separate batches were analyzed for each morphology type. In all cases as the amount of chemical pre-oxidant used increases, the length of the produced  $Cu_3(HHTP)_2$  decreases.



**Fig.** S18 | Infrared spectra of the  $Cu_3(HHTP)_2$  materials made with chemical oxidants (rods, blocks, and flakes) and in air following literature procedures (particles and rods).<sup>1</sup> The infrared spectra of the purified hexahydroxytriphenylene ligand is included for comparison.



**Fig. S19** | Cu  $2p_{3/2}$  X-ray photoelectron spectra of Cu<sub>3</sub>(HHTP)<sub>2</sub> materials made with chemical oxidants (rods, blocks, and flakes) and following literature syntheses in air (particles and rods).<sup>1</sup> The experimental data is depicted in grey and the overall fit in black. The Cu(II) to Cu(I) ratio was estimated by using the ratio of the shake-up satellite area (blue curves) to the main  $2p_{3/2}$  peak (red curves). The curve-fitting results and analysis are summarized in **Tables S4–6**, as well as in section **5** of the Supporting Information.



**Fig. S20** | Representative I-V curves of the CuHHTP materials made with chemical oxidants (rods, blocks, and flakes) and in air following literature procedures (particles and rods).<sup>1</sup>



**Fig. S21** |  $N_2$  gas sorption isotherms for Cu<sub>3</sub>(HHTP)<sub>2</sub> materials prepared *via* literature synthesis.<sup>1</sup> The BET surface area for the particles prep is 560 m<sup>2</sup>/g, whereas for the rods prep, it is 520 m<sup>2</sup>/g.



**Fig. S22** | N<sub>2</sub> gas sorption isotherms for Cu<sub>3</sub>(HHTP)<sub>2</sub> blocks prepared with chemical oxidant and Cu<sub>3</sub>(HHTP)<sub>2</sub> rods prepared *via* literature synthesis.<sup>1</sup> Desorption points are indicated with hollow circles, and adsorption points are indicated with filled circles. The measured BET surface areas were 680 and 590 m<sup>2</sup>/g for the blocks and rods, respectively.

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