Supplementary Information for

From 0D to 2D: Microwave-assisted Synthesis of Electrically Conductive Metal-Organic Frameworks with Controlled Morphologies

Xiaoyu Fang,[a] Ji Yong Choi,[a] Chenwei Lu,[a] Elizabeth Reichert,[b] Hoai T. B. Pham,[a] and Jihye Park[a,*]

[a] Department of Chemistry, University of Colorado Boulder, Boulder, Colorado 80309, United States

[b] Chemical and Biological Engineering, University of Colorado Boulder, Boulder, Colorado 80303, United States

* Corresponding Author Email: jihye.park@colorado.edu

Table of Contents

Experimental methods

Materials and characterizations. Chemicals were purchased from Sigma-Aldrich and TCI America, and used without purification, except for 2, 3, 6, 7, 10, 11-hexahydroxytriphenylene (HHTP) which was prepared according to literature procedures with minor modifications.[1] Powder X-ray diffraction (PXRD) was taken using a Rigaku SmartLab Automated Multipurpose X-ray Diffractometer with a Copper beam source (λ = 1.5418 Å) at 45 kV and 200 mA. Scanning electron microscopy (SEM) was carried out on Hitachi SU3500. Solution-phase UV-Vis NIR absorption spectra were measured on CARY 5000 spectrophotometer. To prepare the UV-vis-NIR sample, MOFs were dispersed in isopropanol (IPA). N_2 sorption isotherms were measured by a Micromeritics ASAP 2020 PLUS porosimeter. Electrical conductivity was measured with a Keithley SCS-4200 parameter analyzer using the four-point probe method. Pressed pellets were prepared with approximately 5 mg of material in a 5 mm diameter circular dye under 1.5 Tons of pressure.

Microwave Settings. Microwave reactions were carried out in a CEM Discover microwave reactor. The procedure involves three typical stages. In the first stage, the temperature rapidly increases from room temperature to the set value, with microwave power automatically adjusted by the instrument, usually ranging between 100 and 200 W. In the second stage, the set temperature is maintained, during which the microwave power typically remains between 0 and 10 W. Once the temperature is cooled to 55 °C, the microwave reaction tube is ejected.

Electrochemical Measurements. All the electrochemical measurements were carried out on a Biologic VSP-300 potentiostat in a three-electrode cell system. Pt wire is used as a counter electrode and Ag/AgCl in 1 M KCl aqueous solution and 0.01 M $Ag/AgNO_3$ in 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) - acetonitrile solution were used for aqueous and nonaqueous reference electrodes, respectively.

For cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) measurements, an electrolyte solution of 0.1 M tetraethylammonium tetrafluoroborate ($TEBF_4$) was prepared by dissolving 4.34 g of $TEBF_4$ in 200 mL of acetonitrile. The 0.1 M $TEBF_4$ electrolyte was degassed for 10 minutes with nitrogen prior to electrochemical measurements. Then, an ink composed of 80 wt% of MOF powders and 20 wt% of PTFE binder solution (60 wt% in H_2O, Aldrich) was prepared and drop-casted on a glassy carbon electrode as the working electrode.

For transient photocurrent response measurement, an electrolyte solution of 0.5 M Na_2SO_4 was prepared by dissolving 7.10 g of Na_2SO_4 in 100 mL of degassed water. Then, 0.05 g of MOF powders were ground with 5 uL of Nafion (5 wt%, Aldrich) and mixed with 2 mL of IPA under sonication for 30 min to obtain a slurry. Then, the slurry was coated onto a 1 cm × 2 cm ITO glass electrode by the drop-casting. Light source was a 300 W Xe lamp (Merry Change MC PF300C). The working electrode was back-illuminated through the ITO glass in order to minimize absorption by the dark and thick catalyst layer.

Synthesis of Cu-HHTP

1D Cu-HHTP: HHTP ligand (0.0259 g, 0.08 mmol), $Cu(NO_3)_2 \cdot 2.5H_2O$ (0.0355 g, 0.15 mmol) were added to a tube. *N,N*-Dimethylformamide (DMF) (10 mL) was added to the tube. Then, sonicate the tube to dissolve the reactants completely. Place the tube in a microwave synthesizer and set the reaction time to 15 minutes at 100 °C. Black precipitate was isolated by centrifugation, washed with acetone (35 mL), H_2O (2 × 15 mL), DMF (2 × 15 mL), and ethanol (2 × 15 mL), and dried in a 70 °C oven under reduced pressure for further characterization. Yield after solvent removal was 0.0062 g (19% yield).

2D Cu-HHTP: HHTP ligand (0.0259 g, 0.08 mmol) was dissolved in DMF (4 mL) and H_2O (2 mL) and $Cu(NO_3)_2 \cdot 2.5H_2O$ (0.0355 g, 0.15 mmol) was dissolved in H_2O (4 mL) and NH_4OH (0.6 mL). Next, sonicate the tube to dissolve the reactants completely and two solutions were added to a tube. Place the tube in a microwave synthesizer and set the reaction time to 15 minutes at 100 °C. Black precipitate was isolated by centrifugation, washed with H_2O (2 × 15 mL), DMF (2 × 15 mL), and ethanol (2 × 10 mL), and dried in a 70 °C oven under reduced pressure for further characterization. Yield after solvent removal was 0.0245 g (74% yield).

0D Cu-HHTP: HHTP ligand (0.0259 g, 0.08 mmol), $Cu(NO_3)_2 \cdot 2.5H_2O$ (0.0355 g, 0.15 mmol) were added to a tube. DMF (10 mL) was added to the tube. Sonicate the tube to dissolve the reactants completely. Place the tube in a sonicator for 1 hour until the solution color changed from light brown to dark brown with ice added into the bath to keep the temperature low (0 °C). Then, place the tube in a microwave synthesizer and set the reaction time to 15 minutes at 100 °C. Black precipitate was isolated by centrifugation, washed with acetone (35 mL), H_2O (2 × 15 mL), DMF (2 × 15 mL), and ethanol (2 × 15 mL), and dried in a 70 °C oven under reduced pressure for further characterization. Yield after solvent removal was 0.0055 g (16% yield).

Optimization of 0D Cu-HHTP

General procedure in optimization. 0D Cu-HHTP was synthesized based on the standard procedure with reaction time, reaction temperature, and solvent (x% DMF and (100-x)% H_2O) as the scanned variables.

As the temperature increased to 120 °C, the crystallinity further decreased, and a new diffraction peak attributed to copper oxide appeared at *ca.* 37.5°.

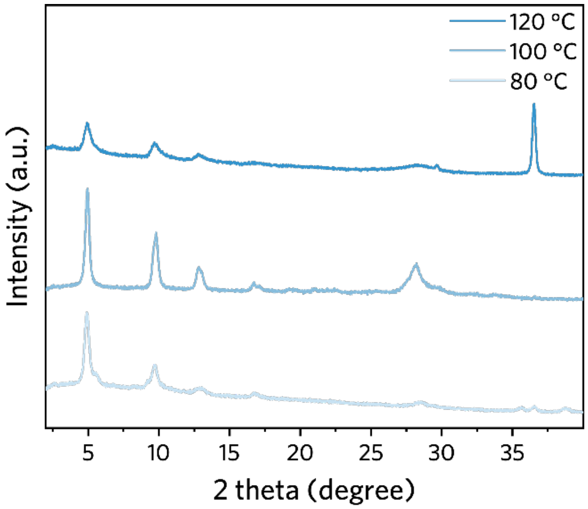

Fig. S1 PXRD of 0D Cu-HHTP synthesized with different temperature.

As the reaction time increased from 5 minutes to 15 minutes, the intensity of the diffraction peaks corresponding to Cu-HHTP continuously increased, indicating an enhancement in crystallinity. However, when the reaction time reached 20 minutes, the diffraction peaks decreased, and a new diffraction peak at *ca.* 37.5° corresponding to copper oxide emerged.

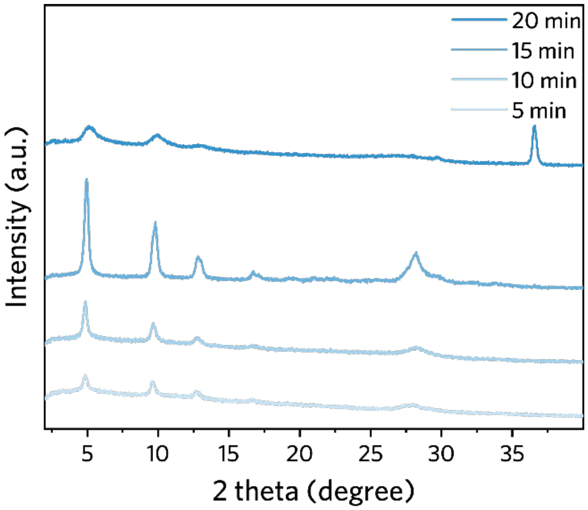

Fig. S2 PXRD of 0D Cu-HHTP synthesized with different reaction time.

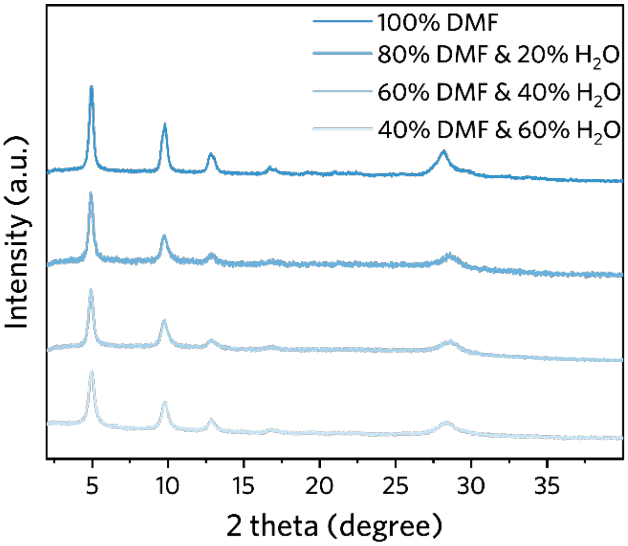

Fig. S3 PXRD of 0D Cu-HHTP synthesized with different solvent (x% DMF and (100-x)% H_2O).

SEM analysis

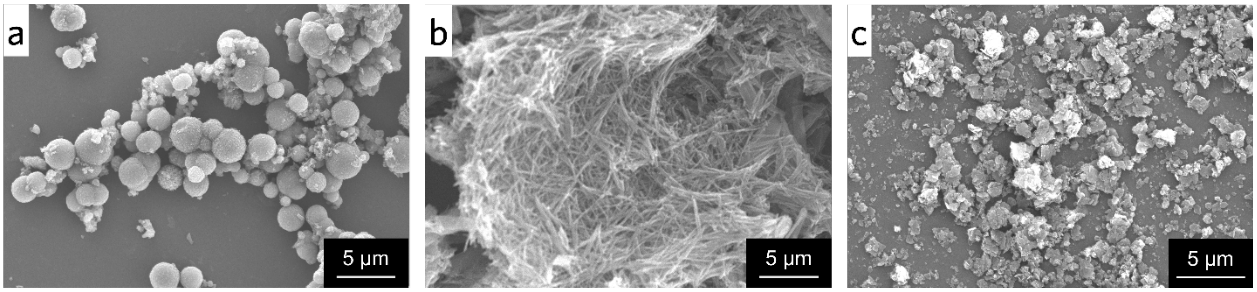

Fig. S4 SEM image of (a) 0D, (b)1D, and (c) 2D Cu-HHTP at a lower magnification.

Structural characterizations

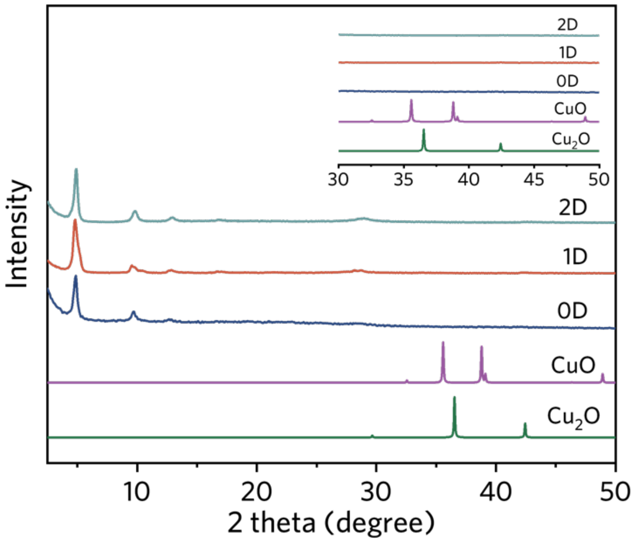

Fig. S5 PXRD patterns of 0D, 1D, and 2D Cu-HHTP and possible impurities (Cu_2O and CuO). Inset: A zoomed-in view in the range of 30° - 50°.

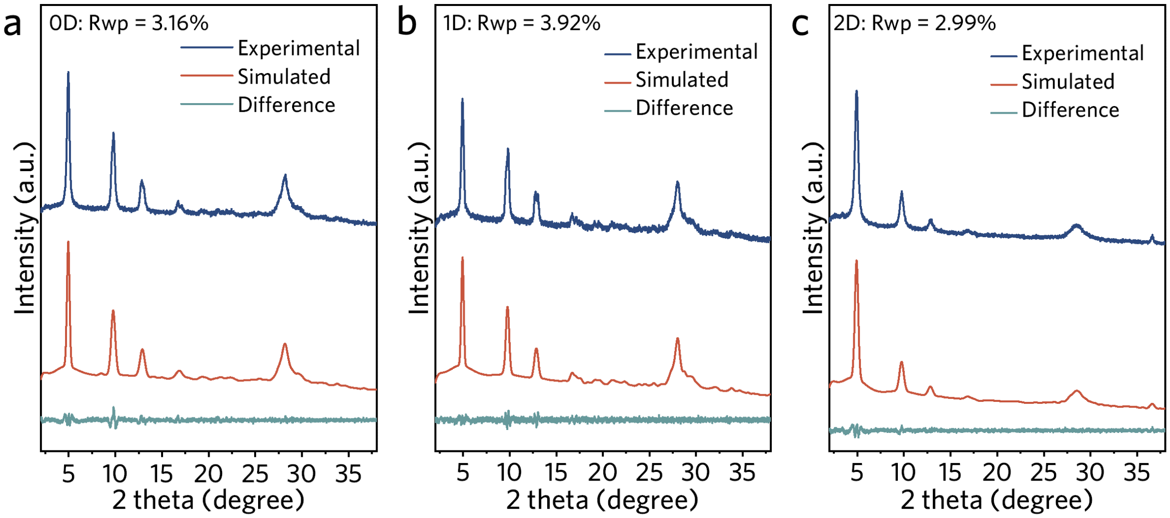

Fig. S6 Experimental PXRD patterns of (a) 0D, (b) 1D, and (c) 2D Cu-HHTPs against the simulated eclipsed Cu-HHTP.

Name	Cu-HHTP	1D	2D	0D
Crystal system	Hexagonal	Hexagonal	Hexagonal	Hexagonal
Space group	P6/mmm	P6/mmm	P6/mmm	P6/mmm
a / Å	21.50	20.89	20.98	21.11
b / Å	21.50	20.89	20.98	21.11
c / Å	3.35	3.35	3.30	3.35
α / °	90	90	90	90
β / °	90	90	90	90
γ / °	120	120	120	120

Table S1. Ideal eclipsed and refined crystallographic data of the Cu-HHTP structures.

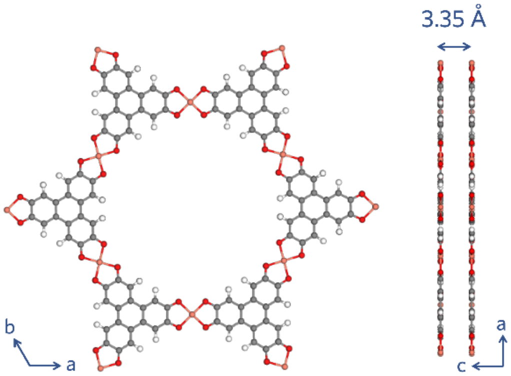

Fig. S7 Structural models of Cu-HHTP viewed along c-axis (left) and b-axis (right).

Additional characterizations

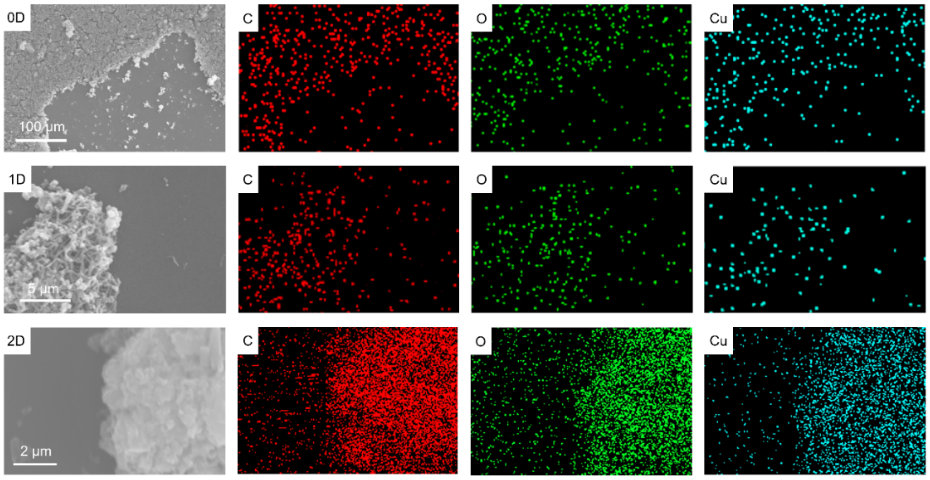

Fig. S8 SEM-EDS elemental mapping images of 0D, 1D, and 2D Cu-HHTP.

Element	Predicted At%	0D At%	1D At%	2D At%
Cu	5.88	5.24	6.51	5.90
C	70.59	77.23	63.95	65.10
O	23.53	17.53	29.54	29.00

Table S2. Predicted & experimental elemental analysis results from EDS.

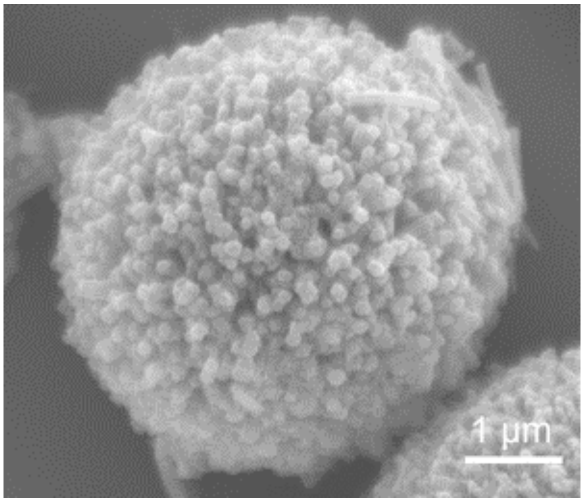

Fig. S9 SEM image of 0D sphere Cu-HHTP, showing 0D crystals composed of smaller 1D rods.

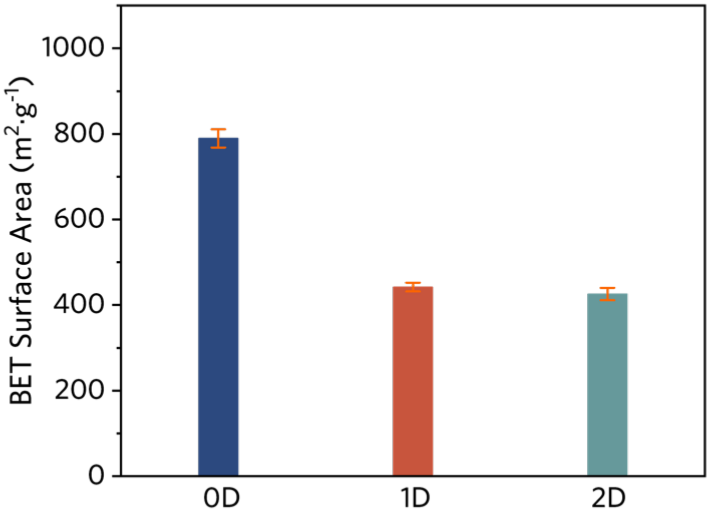

Fig. S10 BET surface area of 0D, 1D, and 2D Cu-HHTP.

Morphology	FWHM
0D	0.38629 ± 0.00831
1D	0.38248 ± 0.01028
2D	0.58857 ± 0.00846

Table S3. Summary of the full-width at half-maximum (FWHM) for Cu-HHTP at 4.93°.

From the PXRD patterns, we selected the diffraction peak at *ca.* 4.93° and calculated the corresponding FWHM.

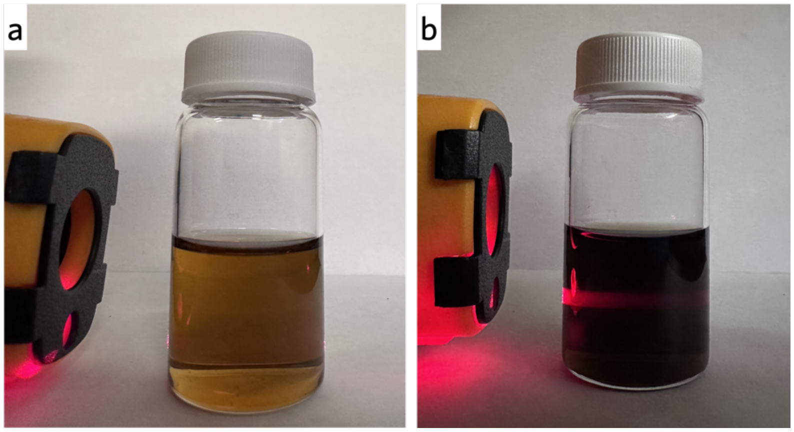

Fig. S11 Tyndall effect in solution (a) before and (b) after temperature-controlled ultrasonication.

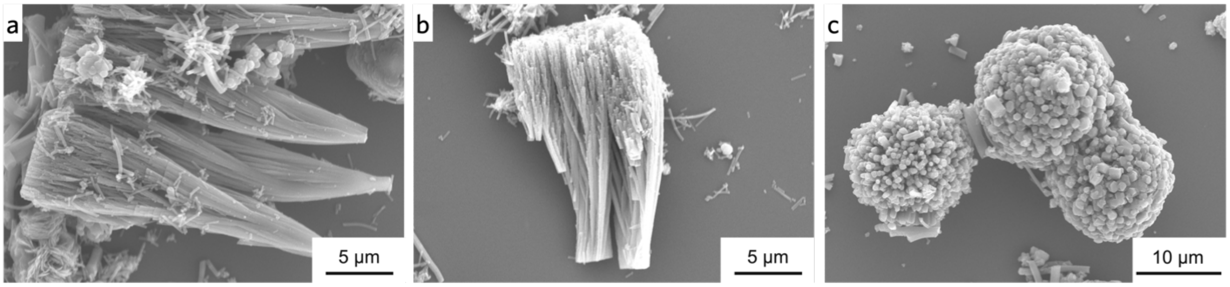

Fig. S12 SEM images for the fragments of the 0D by microwave method with temperature-controlled ultrasonication.

Electronic/electrochemical characterizations

Electrical conductivity measurement

Ref.	Morphology	State	Electrical Conductivity
This work	0D	powder	7.34×10^{-1} S cm^{-1}
	1D	powder	3.00×10^{-2} S cm^{-1}
	2D	powder	2.70×10^{-2} S cm^{-1}
S1	1D	single crystal	1.5 S cm^{-1}
	2D	single crystal	5.00×10^{-1} S cm^{-1}
	1D	powder	1.00×10^{-2} S cm^{-1}
	2D	powder	1.00×10^{-1} S cm^{-1}
S2	1D	powder	2.66×10^{-3} S cm^{-1}
	2D	powder	3.00×10^{-3} S cm^{-1}
	blocks	powder	9.00×10^{-3} S cm^{-1}
S3	1D	powder	2.22×10^{-3} S cm^{-1}
	2D	powder	1.74×10^{-3} S cm^{-1}
	agglomerates	powder	2.04×10^{-3} S cm^{-1}

Table S4. Summary of the electronic conductivity for Cu-HHTP.

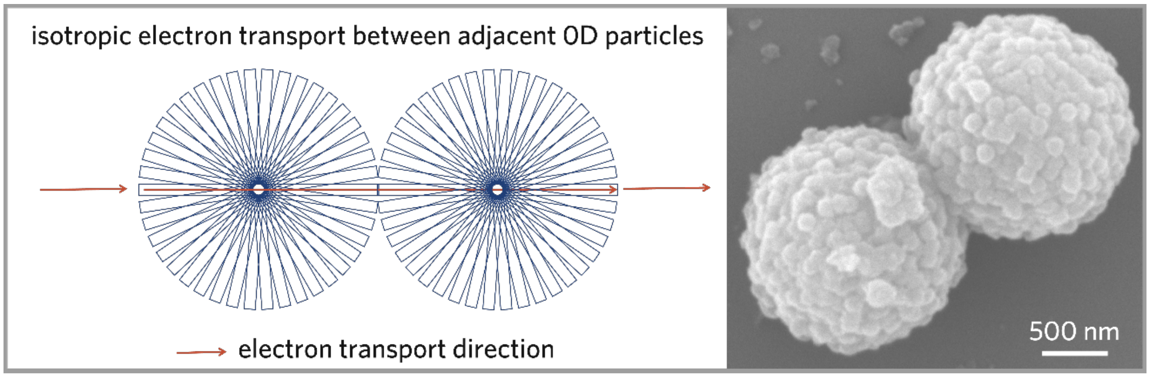

Fig. S13 Schematic of hypothetical isotropic electron transport between adjacent 0D Cu-HHTP particles and the respective SEM image.

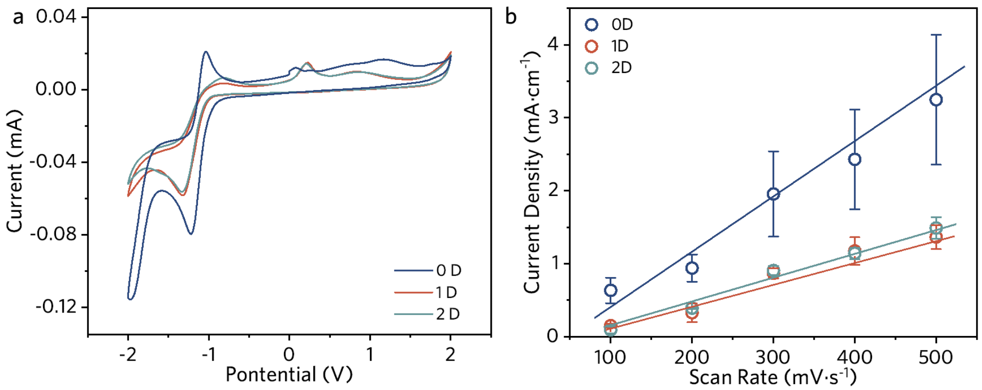

Fig. S14 (a) Cyclic voltammetry curves of 0D, 1D, and 2D Cu-HHTP. (b) Plots of changing current density as a function of scan rate for 0D, 1D, and 2D Cu-HHTP.

ECSA analysis

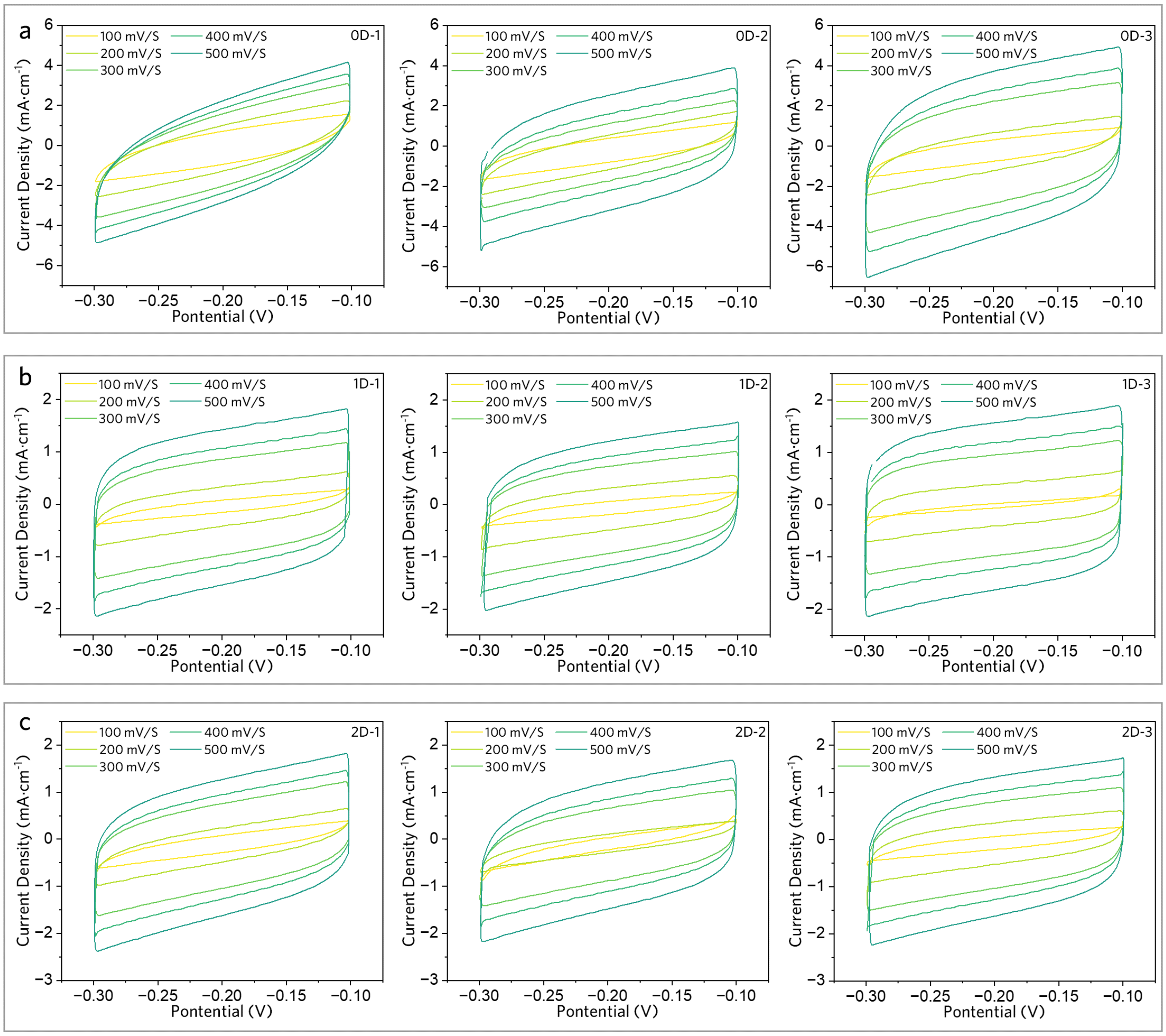

Fig. S15 ECSA analysis of (a) 0D, (b) 1D, and (c) 2D Cu-HHTP based on double layer capacitance with scan rates ranging from 100 to 500 mV s^{-1}, showing triplicate experiments for each sample.

UV-Vis spectroscopy

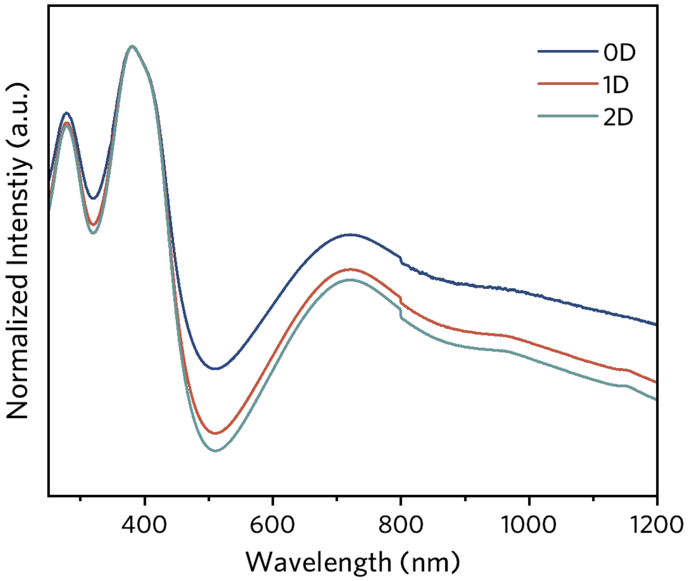

Fig. S16 UV–vis-NIR absorption spectra of 1D, 2D, and 0D Cu-HHTP.

References

S1 R. W. Day, D. K. Bediako, M. Rezaee, L. R. Parent, G. Skorupskii, M. Q. Arguilla, C. H. Hendon, I. Stassen, N. C. Gianneschi, P. Kim and M. Dincă, *ACS Cent. Sci.*, 2019, **5**, 1959–1964.

S2 K. M. Snook, L. B. Zasada, D. Chehada and D. J. Xiao, *Chem. Sci.*, 2022, **13**, 10472–10478.

S3 J. W. Gittins, C. J. Balhatchet, S. M. Fairclough and A. C. Forse, *Chem. Sci.*, 2022, **13**, 9210–9219.