Supplementary Information

Coordination-Bond-Directed Synthesis of Hydrogen-bonded Organic Frameworks from Metal–Organic Frameworks as Templates

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Experimental Procedures

Synthesis of H_4TTFTB . H_4TTFTB were prepared adopting the previously reported procedure.¹

Synthesis of Cu¹-TTFTB, [Cu(H₂TTFTB)(NH₂Me₂)]·2DMF·4H₂O. It follows the dissolution of H₄TTFTB (0.010 g, 0.015 mmol) in 6 mL DMF before addition of a solution of Cu(NO₃)₂·2.5H₂O (0.025 g, ~ 0.107 mmol) in 1 mL DMF and 1 mL CH₃CN, followed by the addition of 0.08 mL CF₃COOH. The mixture was heated to 85 °C for 72 h, then allowed to cool to room temperature. The crystalline products were filtered and washed with CH₃COCH₃ three times. red needle-like crystals (0.007 g; Yield 46% based on H₄TTFTB). Calcd for C₄₂H₄₈N₃O₁₄S₄Cu (Mr = 1010.65 g/mol): C, 49.91; H, 4.79; N, 4.16 %; O, 22.16; S, 12.69 %. Found: C, 50.06; H, 4.84; N, 4.02 %. FT-IR (KBr, cm⁻¹): 3001 ww, 2472 w, 1943 w, 1705 s, 1603 m, 1576 m, 1536 m, 1385 vs, 1360 s, 1309 w, 1248 s, 1220 s, 1177 m, 1100 w, 1016 m, 864 m, 773 s, 755 m, 703 m, 528 m, 487 w, 431 w.

Synthesis of Cu^{II}-TTFTB, [Cu(H₂O)(H₂TTFTB)(NH₂Me₂)_{0.5}]·2C₆H₁₂. Crystals of Cu^I-TTFTB was immerged in water/cyclohexane solution (1 vol%) for about one month at room temperature. The color of the crystals gradually deepens and turn to a black-red color. FT-IR (KBr, cm⁻¹): 2921 vs, 2848 s, 1919 w, 1688 m, 1602 m, 1541 m, 1448 w, 1378 vs, 1310 w, 1255 m, 1177 w, 1101 w, 1016 m, 902 m, 861 s, 773 s, 703 m, 521 w, 431 w.

Synthesis of TTFTB-HOF, $[(H_4TTFTB)] \cdot [Cu(OH)_2(H_2O)_4)] \cdot 2CH_3COCH_3$. Crystals of Cu¹-TTFTB was immerged in acetone for about two weeks at room temperature. The color of the crystals gradually deepens and turn to a black-red color. Calcd for C₄₀H₄₂O₁₆S₄Cu (Mr = 970.56 g/mol): C, 49.50; H, 4.36 %; O, 26.38; S, 13.22 %. Found: C, 50.60; H, 4.17 %. Selected FT-IR (KBr, cm⁻¹): 2919 w, 1712 w, 1599 s, 1576 m, 1526 s, 1397 vs, 1283 w, 1179 w, 1018 m, 861 m, 843 w, 781 m, 764 s, 700 m, 507 w, 445 w.

Characterization. All the reagents and solvents were commercially available and used as received. Elemental analyses for C, H, and N were performed on a Perkin-Elmer 240C analyzer. FT-IR data were recorded on a Vector27 Bruker Spectrophotometer with KBr pellets in the $4000 - 400 \text{ cm}^{-1}$ region. The PXRD data were collected with a scan speed of 5 s·deg⁻¹ on a Bruker Advance D8 (40 kV, 40 mA) diffractometer with Cu radiation (λ = 1.54056 Å) at room temperature. Calculated PXRD patterns were generated using Mercury 3.0. The SEM images were recorded on Hitachi S-3400N II and with EX-250 energy-dispersive X-ray micro analyzer. X-ray photoelectron spectroscopy (XPS) was recorded on a PHI 5000 Versa Probe X-ray

photoelectron spectrometer using standard and monochromatic Al K_a radiation. The binding energies from the spectra were calibrated against the C 1s peak located at 284.6 eV. Solid state cyclic voltammetry measurements were performed in LiBF₄/CH₃CN as electrolyte using a CORREST 4-channel electrochemical workstation and a three-electrode system. The CVs were recorded using a glassy carbon working electrode (3.0 mm diameter), a platinum wire auxiliary electrode and an Ag/AgCl reference electrode. The sample was mounted on the glassy carbon working electrode by dipping the electrode into a paste made of the powder sample in ethanol. Ferrocene was measured as a standard. All potentials are reported in milli-Volts (mV) versus the Fc/Fc⁺ couple.

Pawley Refinement. Pawley refinement of the Cu^I-TTFTB, and TTFTB-HOF PXRD pattern $(2\theta \text{ range: } 4.80-45.0^\circ)$ was conducted with the cell parameters and space group (C2/c) by the Reflex module in the software Material Studio (ver. 2018).² Peak profiles, zero shift, background, asymmetry, and unit cell parameters were refined together. All of the peaks in profiles were refined with the pseudo-Voigt model which contains asymmetric correction parameters. The background was refined with a 20th-order polynomial.

Single Crystal Structure Studies. Data of Cu^I-TTFTB, Cu^{II}-TTFTB and TTFTB-HOF were collected on a Bruker D8 Venture diffractometer outfitted with a PHOTON-100 CMOS detector using monochromatic microfocus Mo- K_{α} radiation ($\lambda = 0.71073$ Å) that was operated at 50 kV and 40 mA at 173 K by a chilled nitrogen flow controlled by a KRYOFLEX II low temperature attachment. The raw data collection and reduction were done using APEX3 software.3 Adsorption corrections were applied using the SADABS routine. The structures were solved by direct methods and refined by full-matrix least-squares on F^2 using the SHELXTL software package.⁴ Non-hydrogen atoms were refined with anisotropic displacement parameters during the final cycles. Hydrogen atoms of TTFTB⁴⁻ were calculated in ideal positions with isotropic displacement parameters. The free solvent molecules of DMF, acetone, and cyclohexane for compounds CuI-TTFTB, CuII-TTFTB and TTFTB-HOF were highly disordered and were not successfully located or refined. The diffuse electron densities resulting from these residual solvent molecules were removed from the data set using the SQUEEZE routine of PLATON and refined further using the data generated.⁵ The contents of the solvent region are not represented in the unit cell contents in crystal data. Attempts to precisely refine the solvent molecules were unsuccessful due to the disorder of solvent molecules. The X-ray crystallographic coordinates for structures reported in this article have been deposited at the Cambridge Crystallographic Data Centre (CCDC), under deposition numbers CCDC 2082445, 2082446, and 2082447 for compounds Cu^I-TTFTB, Cu^{II}-TTFTB and TTFTB-HOF,

respectively. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. All relevant data supporting the findings of this study are available from the corresponding authors on request.

	Cu ^I -TTFTB	Cu ^{II} -TTFTB	TTFTB-HOF
Empirical	$C_{42}H_{48}N_3O_{14}S_4Cu$	$C_{47}H_{48}N_{0.5}O_9S_4Cu$	$CuC_{40}H_{42}O_{16}S_4$
formula			
Formula weight	1010.65	955.69	970.56
Temperature	173	173	173
(K)			
Crystal system	monoclinic	monoclinic	monoclinic
Wavelength (Å)	0.71073	0.71073	0.71073
Space group	<i>C</i> 2/ <i>c</i> (No. 15)	<i>C</i> 2/ <i>c</i> (No. 15)	<i>C</i> 2/ <i>c</i> (No. 15)
Unit cell			
dimensions			
(Å,°)			
a	19.1651(9)	18.757 (4)	20.495(10)
b	34.7043(16)	35.559 (7)	34.798(16)
c	8.8821(4)	8.899 (2)	8.801(5)
β	97.583(1)	101.17 (3)	102.997(13)
Volume (Å ³)	5855.9(5)	5823 (2)	6116(5)
Z	4	4	4
Calculated	0.949	0.872	0.744
density (gcm^{-3})			
F(000)	1788	1556	1408
Absorption	0.551	0.55	0.183
coefficient,			
μ/mm^{-1}			
No. of	25669	15760	21673
reflections			
measured			
No. of	6751	5307	6285
independent			
reflections			
θ (°)	2.4-27.6	2.0-25.4	2.0-26.5
Rint	0.031	0.120	0.0726
R_1 , $wR_2[I > 2\sigma]$	0.0643/ 0.2094	0.1094 / 0.3075	0.0726/ 0.2148
(D)			
R_1 , wR_2 [all	0.0780/ 0.2253	0.1228 / 0.3475	0.1339/ 0.2422
datal	, co. c. 	0.12207 0.0 170	5.12257 012 122
GOF	1.062	1.02	0.988
Largest diff	1.273 / -0.631	1.00 /-1.18	0.43 /-0.32
peak and	1.2,0, 0.001	1.007 1.10	0.107 0.02
hole($e^{A^{-3}}$)			

Table S1 Crystal data and structure refinement parameters for Cu^I-TTFTB, Cu^{II}-TTFTB and TTFTB-HOF.

	Cu ^I -TTFTB	TTFTB-HOF
Crystal system	monoclinic	monoclinic
Space group	<i>C</i> 2/ <i>c</i> (No. 15)	<i>C</i> 2/ <i>c</i> (No. 15)
Unit cell		
dimensions		
(Å,°)		
a	19.1769(26)	20.523(13)
b	34.5920(26)	35.152(20)
с	8.8878(12)	8.815(6)
β	97.583	102.997
R_p	6.77%	8.26%
R_{wp}	10.52%	13.29%

Table S2 Unit cell parameters determined through Pawley Refinements of PXRD Data for Cu^I-TTFTB, and TTFTB-HOF.

Table S3 The shape parameters of Cu^{I} -TTFTB, Cu^{II} -TTFTB and TTFTB-HOF used for the calculating of electrical conductivity.

	Length (cm)	Width (cm)	Thickness (cm)	Cross- sectional area (cm ²)	Electrical conductance (G)	Electrical conductivity (S/m)
Cu ^I - TTFTB	0.130	0.180	0.0689	1.240e-2	1.067e-8	1.119e-5
Cu ^{II} - TTFTB	0.128	0.206	0.0452	9.311e-3	8.527e-9	1.172e-5
TTFTB- HOF	0.172	0.200	0.0457	9.140e-3	1.539e-8	2.896e-5

$$\sigma = G \frac{L}{A}$$

Electrical conductivity, σ , measures a material's ability to conduct electrical current. Measuring σ typically requires incorporating the material of interest into an electronic device, typically a resistor, and measuring the electrical conductance (G), length (L), and cross-sectional area (A) of the conduction channel.



Figure S1. The asymmetric units of Cu^I-TTFTB. Displacement ellipsoids are drawn at the 50% probability level.



Figure S2. The three-dimensional framework of Cu^{I} -TTFTB viewed in the *c* direction.



Figure S3. The location of Cu^I in the two layers of hydrogen nets viewed in the **[110]** direction, the coordination bonds are omitted for clarity.



Figure S4. The photograph of Cu^I-TTFTB exposed in air for different times.



Figure S5. The photograph of Cu^I-TTFTB, Cu^{II}-TTFTB, and TTFTB-HOF.



Figure S6. Crystal photographs in the transformation of Cu^I-TTFTB to TTFTB-HOF.



Figure S7. IR spectra for compounds Cu^I-H₂TTFTB, Cu^{II}-TTFTB, and TTFTB-HOF.



Figure S8. X-ray photoelectron spectra of N 1s for compounds Cu^{I} -H₂TTFTB, Cu^{II} -TTFTB, and TTFTB-HOF.



Figure S9. Plot of the Pawley refinement of Cu^I-TTFTB.



Figure S10. Plot of the Pawley refinement of TTFTB-HOF. A little difference may be owing to few collapsed materials.



Figure S11. X-ray photoelectron spectra for compounds $Cu^{I}-H_2TTFTB$, $Cu^{II}-TTFTB$, and TTFTB-HOF.



Figure S12. X-ray photoelectron spectra of Cu 2p for Cu^I-H₂TTFTB, Cu^{II}-TTFTB, and TTFTB-HOF.



Figure S13. Element mapping of Cu^{I} -H₂TTFTB (a), Cu^{II} -TTFTB (b), and TTFTB-HOF (c) under SEM/EDX.



Figure S14. The powder X-ray diffraction patterns for TTFTB-HOF in different conditions.



Figure S15. The TGA plots of Cu^{I} -TTFTB and TTFTB-HOF at N_{2} atmosphere.



Figure S16. Tauc plots of Cu^I-TTFTB, Cu^{II}-TTFTB and TTFTB-HOF.

References

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