

# High Charge Mobility in a Tetrathiafulvalene-Based Microporous Metal-Organic Framework

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**Materials.** Tetraethyl tetrathiafulvalene tetrabenzoate (Et<sub>4</sub>TTFTB) was prepared according to a literature procedure.<sup>1</sup> Zinc nitrate hexahydrate (99%, Alfa Aesar), tetrabutylammonium hexafluorophosphate (≥99%, Fluka), ethanol (Macron Chemical), and *N,N*-dimethylformamide (DMF, Macron Chemical) were obtained from commercial sources and used as received unless otherwise indicated. Dry, deaerated DMF was obtained by degassing with a vigorous flow of argon for 30 min and then passing the solvent through two alumina columns in a Glass Contour Solvent System. CDCl<sub>3</sub> and DMSO-*d*<sub>6</sub> were purchased from Cambridge Isotope Laboratories and used as received.

**Physical characterization.** NMR spectra were recorded on a Varian 300 Mercury NMR spectrometer and a Bruker Avance-400 NMR spectrometer. <sup>1</sup>H NMR data are reported as follows: chemical shift (multiplicity (br s = broad singlet, dt = doublet of triplets), integration, coupling constants, and peak assignments). <sup>1</sup>H and <sup>13</sup>C chemical shifts are reported in ppm from TMS with the residual solvent resonances as internal standards. Elemental analyses were performed by Midwest Microlab. Thermogravimetric analysis (TGA) was performed on a TA Instruments Q500 Thermogravimetric Analyzer at a heating rate of 0.5°C/min under a nitrogen gas flow of 90 mL/min on a platinum pan.

**X-ray diffraction studies.** A diffraction-quality single crystal was mounted on a Kapton loop using motor oil. Low temperature (100 K) diffraction data ( $\phi$ - and  $\omega$ -scans) were collected on a Bruker-AXS X8 Kappa Duo diffractometer coupled to a Smart APEX II CCD detector with MoK $\alpha$  radiation ( $\lambda = 0.71073$  Å) from a *I* $\mu$ S-micro source. Absorption and other corrections were applied using SADABS. The structure was solved by direct methods using SHELXS and refined against  $F^2$  on all data by full-matrix least squares as implemented in SHELXL-97. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the model at geometrically calculated positions using a riding model.

Powder X-ray diffraction (PXRD) patterns were recorded with a Bruker D8 Advance diffractometer equipped with a  $\theta/2\theta$  Bragg-Brentano geometry and nickel-filtered Cu K $\alpha$  radiation ( $K\alpha_1 = 1.5406$  Å,  $K\alpha_2 = 1.5444$  Å,  $K\alpha_1/K\alpha_2 = 0.5$ ). The tube voltage and current were 40 kV and 40 mA, respectively. Samples for PXRD were prepared by placing a thin layer of **1** on a zero-background silicon (510) crystal plate.

**Gas sorption studies.** A Micromeritics ASAP 2020 Surface Area and Porosity Analyzer was used to measure the nitrogen adsorption isotherm. An oven-dried sample tube equipped with a TranSeal™ (Micromeritics) was evacuated and tared. The sample was transferred to the sample tube, which was then capped by a TranSeal™. The sample was heated to 200°C under a vacuum of 2 mtorr for 12 hours, at which point the outgas rate was less than 2 mtorr/minute. The evacuated sample tube was weighed again and the sample mass was determined by subtracting the mass of the previously tared tube. The N<sub>2</sub> isotherm was measured using a liquid nitrogen bath (77 K). Ultra high purity grade (99.999% purity) N<sub>2</sub> and He, oil-free valves and gas regulators were used for the free space correction and measurement.

**Flash photolysis-time-resolved microwave conductivity (FP-TRMC) measurements.**

FP-TRMC measurements were conducted at 25 °C under ambient conditions, using MOF/poly(methylmethacrylate) films (40/ 60 in wt%). The microwave power and frequency were set at 3mW and ~ 9.1 GHz, respectively. The charge carriers were generated in the films by direct excitation of MOFs using a third harmonic generation ( $\lambda = 355$  nm) light pulses from a Nd: YAG laser (spectra Physics, INDY-HG). The excitation density was tuned at  $6.4 \times 10^{15}$  cm<sup>-2</sup> photons per pulse. The TRMC signal from a diode was recorded on a digital oscilloscope (Tektronix, TDS 3032B). Details of the experimental setup are described elsewhere.<sup>ii</sup>

To determine the values of charge carrier generation quantum yield  $\phi$ , we integrated the time-of-flight (TOF) transient at fixed bias voltage. The values of charge carrier generation quantum yield  $\phi$  were estimated by time-of-flight (TOF) transient current integration with 10 k $\Omega$  terminate resistance to be  $1.6 \times 10^{-4}$  and  $4.3 \times 10^{-3}$  for **1** and H<sub>4</sub>TTFTB, respectively, upon irradiation with a 355 nm pulse laser at a power of  $8.3 \times 10^{15}$  photons cm<sup>-2</sup>. TOF transient current integration measurements performed on 5-7  $\mu$ m thick (**1**) and 9-12  $\mu$ m thick (H<sub>4</sub>TTFTB) /poly(methyl methacrylate) blend films (40/60 in wt%) between Al (70 nm) and Au (30 nm) electrodes on silicon wafer substrates.

**Flash photolysis transient absorption measurements.**

Transient spectroscopy were conducted at 25 °C under ambient conditions, using H<sub>4</sub>TTFTB /poly(methylmethacrylate) films (40/ 60 in wt%) deposited onto quartz substrate at ~ 500 nm thick. Transmittance of excitation light pulses at 355 nm for the dispersed film was measured by PE25 power meter of Ophir Optorionics Ltd. Time-dependent absorption spectral changes were monitored by Hamamatsu C7700 streak camera via a Hamamatsu C5094 spectrometer upon direct excitation of H<sub>4</sub>TTFTB using a third harmonic generation ( $\lambda = 355$  nm) light pulses from a Nd: YAG laser (spectra Physics, INDY-HG). The excitation density was tuned at  $6.1 \times 10^{15}$  cm<sup>-2</sup> photons per pulse. To correct a 2-dimensional time-wavelength correlation data of the transient absorption, the streak scope images were averaged over 1600 images.

**Tetrathiafulvalene tetrabenzoic acid · 1.5 CH<sub>3</sub>OH (H<sub>4</sub>TTFTB).** This procedure was adapted from a literature procedure.<sup>iii</sup> Methanol, THF, and distilled water were degassed under a vigorous flow of nitrogen for 30 minutes. A 50 mL flask was charged with Et<sub>4</sub>TTFTB (734 mg, 0.921 mmol) and subjected to three cycles of evacuation and refilling with N<sub>2</sub>. Degassed methanol (7 mL) and THF (7 mL) were added to generate a suspension. In a separate flask, sodium hydroxide (466 mg, 11.6 mmol) was dissolved in degassed water (5 mL). The sodium hydroxide solution was added to Et<sub>4</sub>TTFTB under N<sub>2</sub> and the reaction was heated to reflux for 12 hours. The

reaction was then cooled to room temperature and the volatiles were removed *in vacuo*. A 1M solution of HCl (30 mL) was added to afford a maroon precipitate, which was collected by filtration and washed with water (50 mL). The product was collected and dried under high vacuum for 12 hours to afford **H<sub>4</sub>TTFTB** as a maroon solid (556.5 mg, 0.813 mmol, 88% yield). <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>): δ = 13.14 (br s, 4H, CO<sub>2</sub>H), 7.87 (dt, 8H, *J* = 8.3 Hz, 1.8 Hz, CHCCO<sub>2</sub>H), 7.35 (dt, 8H, *J* = 8.4 Hz, 1.8 Hz, SCCCH). <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>): δ = 166.5, 135.5, 131.2, 129.9, 129.2, 129.1, 107.7. Anal. Calcd. for C<sub>35.5</sub>H<sub>26</sub>O<sub>9.5</sub>S<sub>4</sub>: C, 58.18; H, 3.57. Found: C, 57.99; H, 3.60.

**Zn<sub>2</sub>TTFTB(H<sub>2</sub>O)<sub>3</sub>(DMF)<sub>2</sub> (1).** *X-ray quality single crystals:* A solution of zinc nitrate hexahydrate in 1:1 water/ethanol (66.5 mM, 0.7 mL) was added to a solution of **H<sub>4</sub>TTFTB** in 3:1 DMF/ethanol (17.9 mM, 0.7 mL). The reaction was heated to 65°C for 72 hours to afford dark red needles. Anal. Calcd. for C<sub>40</sub>H<sub>36</sub>N<sub>2</sub>O<sub>13</sub>S<sub>4</sub>Zn<sub>2</sub>: C, 47.48; H, 3.59; N, 2.77. Found: C, 47.51; H, 3.60; N, 2.70.

*Bulk synthesis:* Zinc nitrate hexahydrate (319 mg, 1.07 mmol) was dissolved in 1:1 water/ethanol (32 mL). **H<sub>4</sub>TTFTB** (200 mg, 0.292 mmol) was dissolved in DMF (24 mL). To this was added ethanol (8 mL). The zinc nitrate solution was slowly added to **H<sub>4</sub>TTFTB**, making sure that no precipitate formed upon addition. The reaction was heated at 75°C for 72 hours to afford a precipitate. The product was collected by filtration and washed with DMF (40 mL) and ethanol (40 mL) to afford a dark maroon powder (221 mg, 0.218 mmol, 75%). PXRD of the bulk material confirmed phase purity. The powder was evacuated at 200°C for 12 hours at 4 mtorr. Anal. Calcd. for C<sub>34</sub>H<sub>16</sub>O<sub>8</sub>S<sub>4</sub>Zn<sub>2</sub>: C, 50.32; H, 1.99. Found: C, 49.80; H, 1.64.

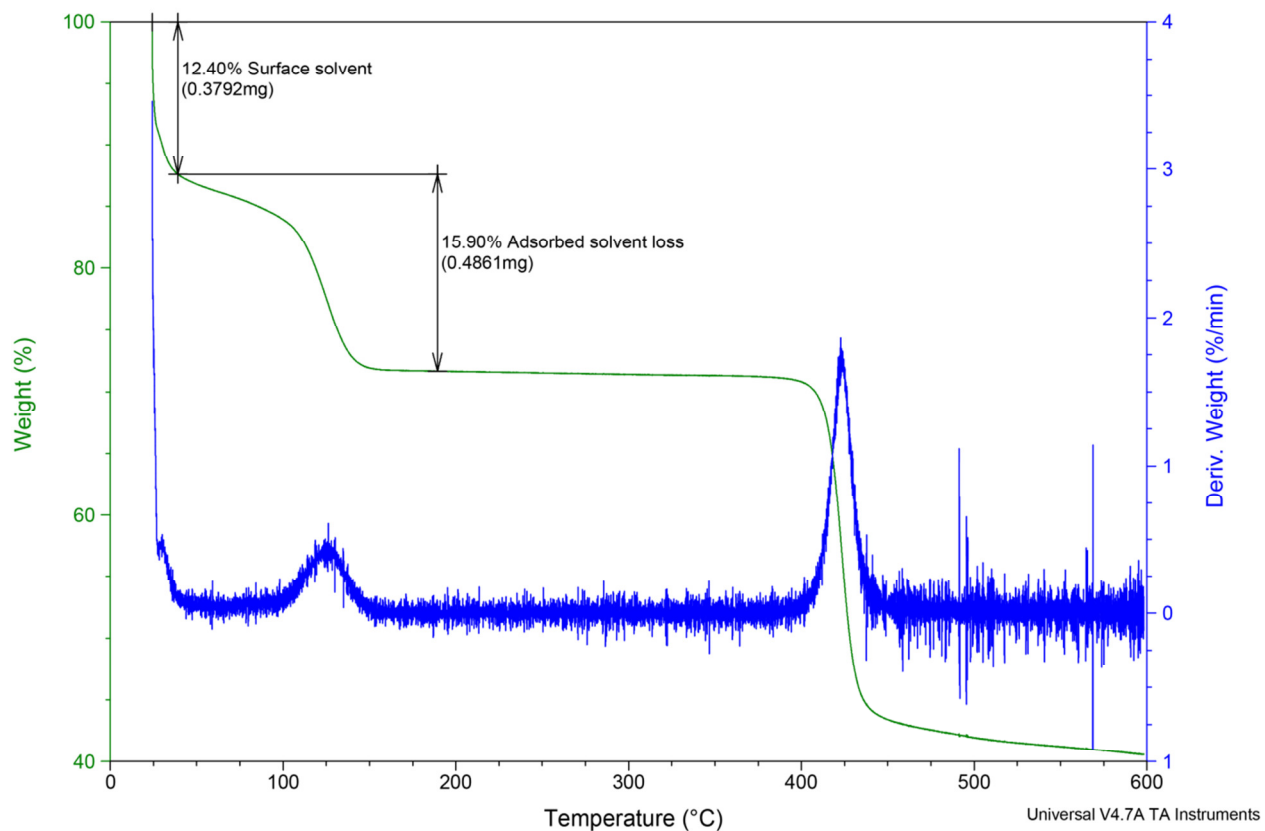
**Table S1.** Crystal data and structure refinement parameters for **1**.

empirical formula	C <sub>41.59</sub> H <sub>38.99</sub> N <sub>1.90</sub> O <sub>12.85</sub> S <sub>4</sub> Zn <sub>2</sub>
formula weight	1029.96
Temperature/K	100(2)
$\lambda/\text{\AA}$	0.71073
crystal dimensions/mm <sup>3</sup>	0.20 x 0.05 x 0.05
crystal system	Hexagonal
space group	P6 <sub>5</sub>
a/ $\text{\AA}$	19.293(3)
b/ $\text{\AA}$	19.293(3)
c/ $\text{\AA}$	20.838(3)
$\alpha/^\circ$	90
$\beta/^\circ$	90
$\gamma/^\circ$	120
V/ $\text{\AA}^3$	6717.4(17)
Z	6
$\rho$ calcd/mg·m <sup>-3</sup>	1.528
$\mu/\text{mm}^{-1}$	1.322
F(000)	3172
$\theta$ range collected	2.33 to 24.34°
limiting indices	-22 ≤ h ≤ 22
	-22 ≤ k ≤ 22
	-24 ≤ l ≤ 24
Completeness to $\theta$	99.8%
Reflections collected/unique	105711/7532
min and max transmission	0.9368 and 0.7779
data/restraints/parameters	7352/5/589
R(int)	0.0665
goodness-of-fit on F <sup>2</sup>	1.062
Final R indices [I>2 $\sigma$ (I)]	R <sub>1</sub> = 0.0216
	wR <sub>2</sub> = 0.0498
R indices (all data)	R <sub>1</sub> = 0.0227
	wR <sub>2</sub> = 0.0504
largest diff. peak and hole	0.430 and -0.193 e <sup>-</sup> / $\text{\AA}^3$

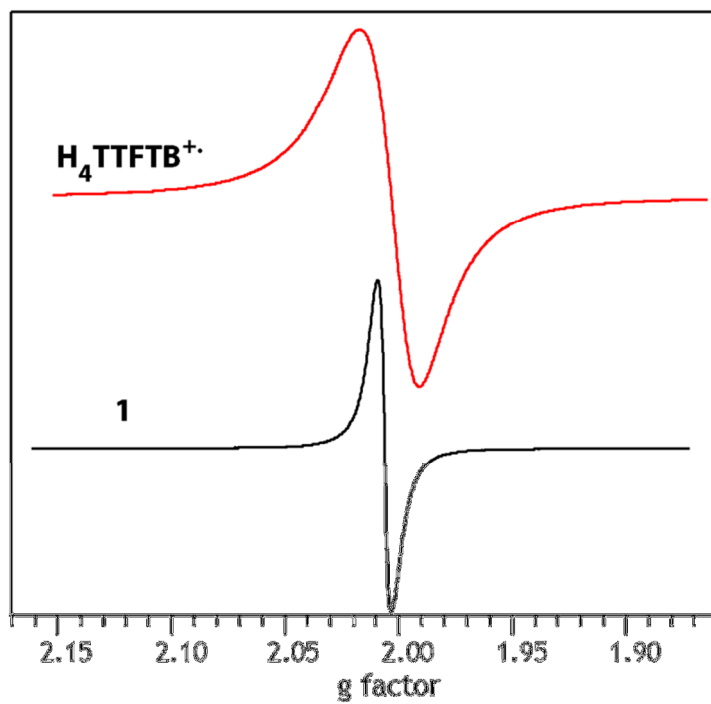
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Size: 3.0570 mg  
Method: Ramp

TGA

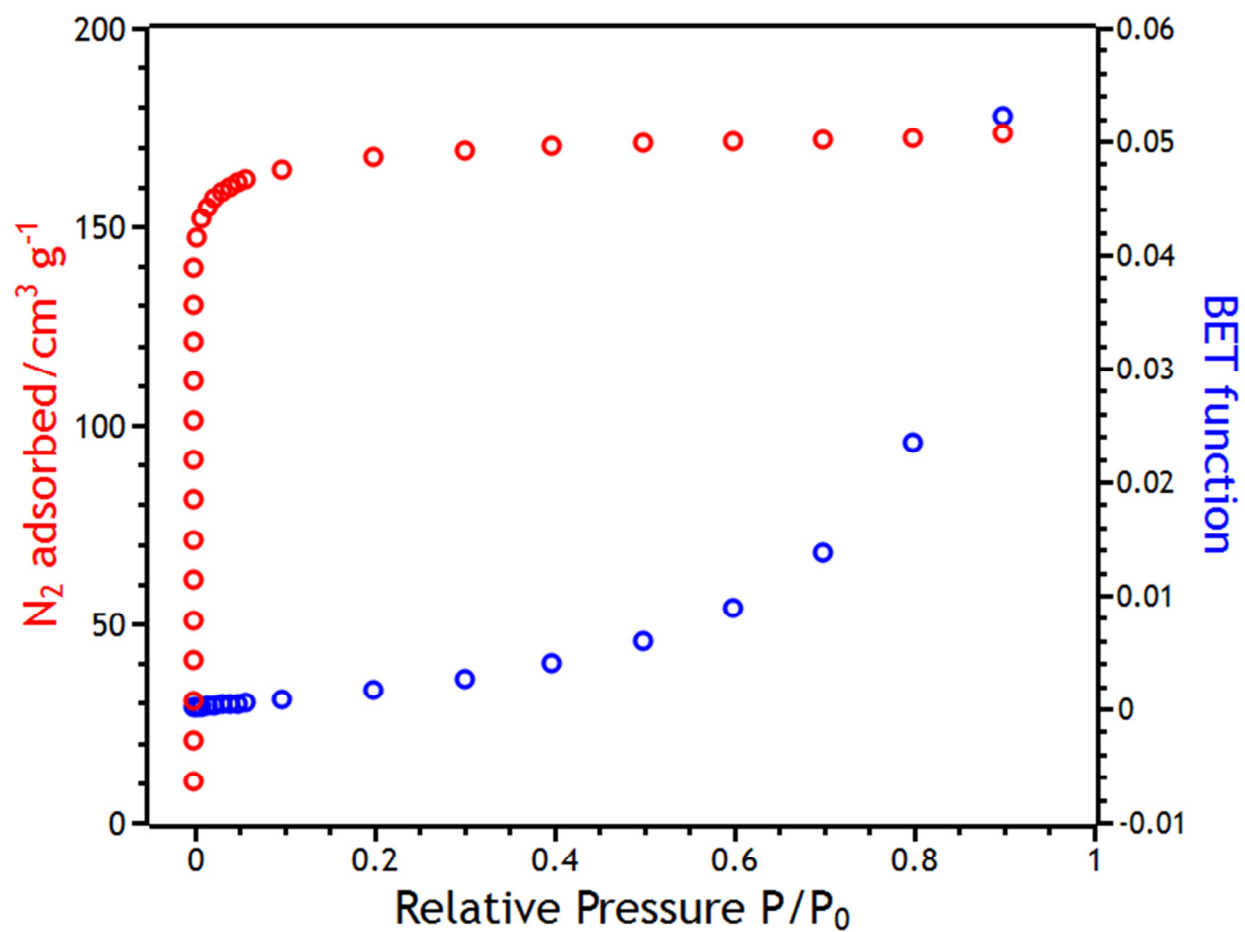
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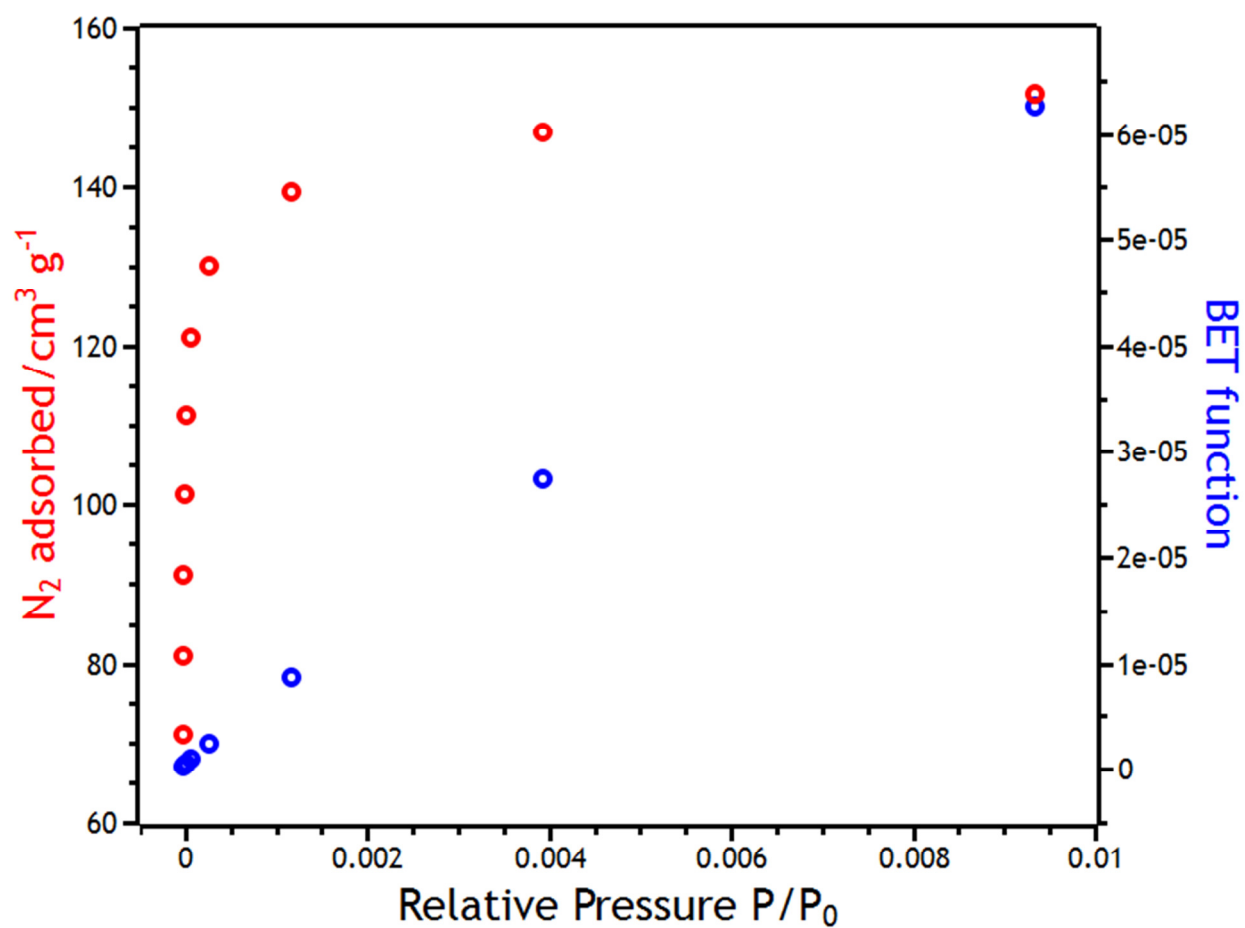
**Figure S1.** TGA profile of **1** obtained at a heating rate of 1°C/min under a constant stream of N<sub>2</sub>.



**Figure S2.** EPR spectra of **1** and  $H_4TTFTB$ .

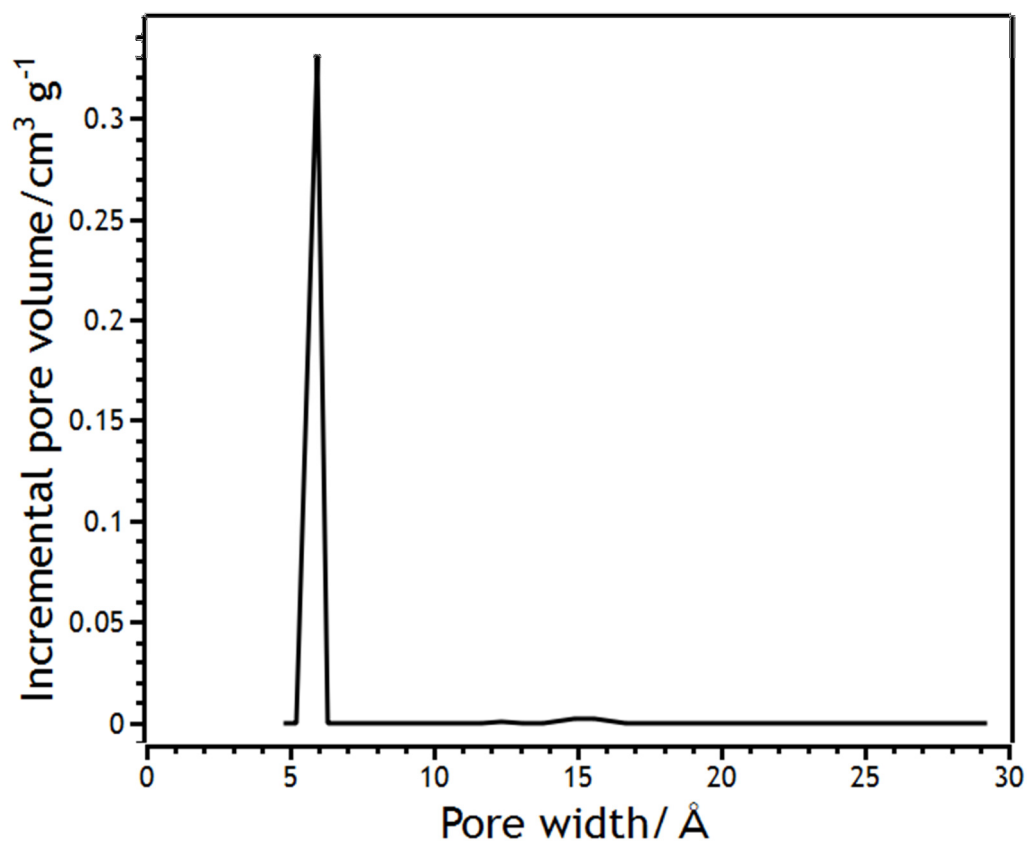


**Figure S3.**  $N_2$  adsorption isotherm (red) and BET function (blue) for **1** at 77K. The MOF was activated at 200°C and 4 mtorr.

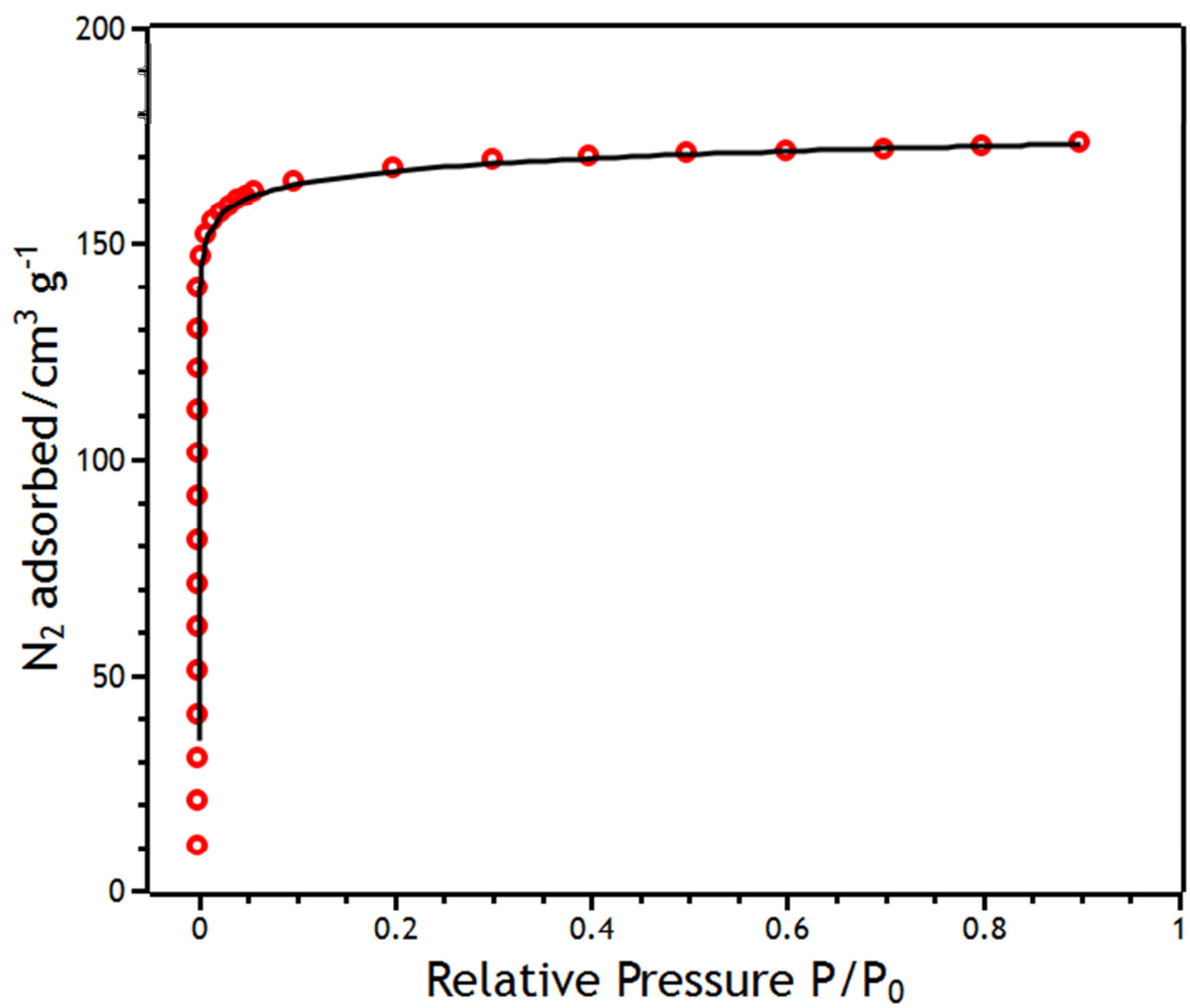


**Figure S4.** The portion of the  $N_2$  adsorption isotherm (red) giving a linear BET function (blue) that was used to find the BET surface area of **1**. The resulting fit gave  $C = -8189$  and a surface area of  $662(2) \text{ m}^2/\text{g}$  with a correlation coefficient of 0.9999730.





**Figure S5.** The pore size distribution of **1** calculated from the N<sub>2</sub> adsorption isotherm using the Tarazona non-local density functional theory method implemented in the ASAP 2020 software provided by Micromeritics.



**Figure S6.** Fit calculated from the Tarazona non-local density functional theory pore size fit of the  $N_2$  adsorption isotherm of **1**.

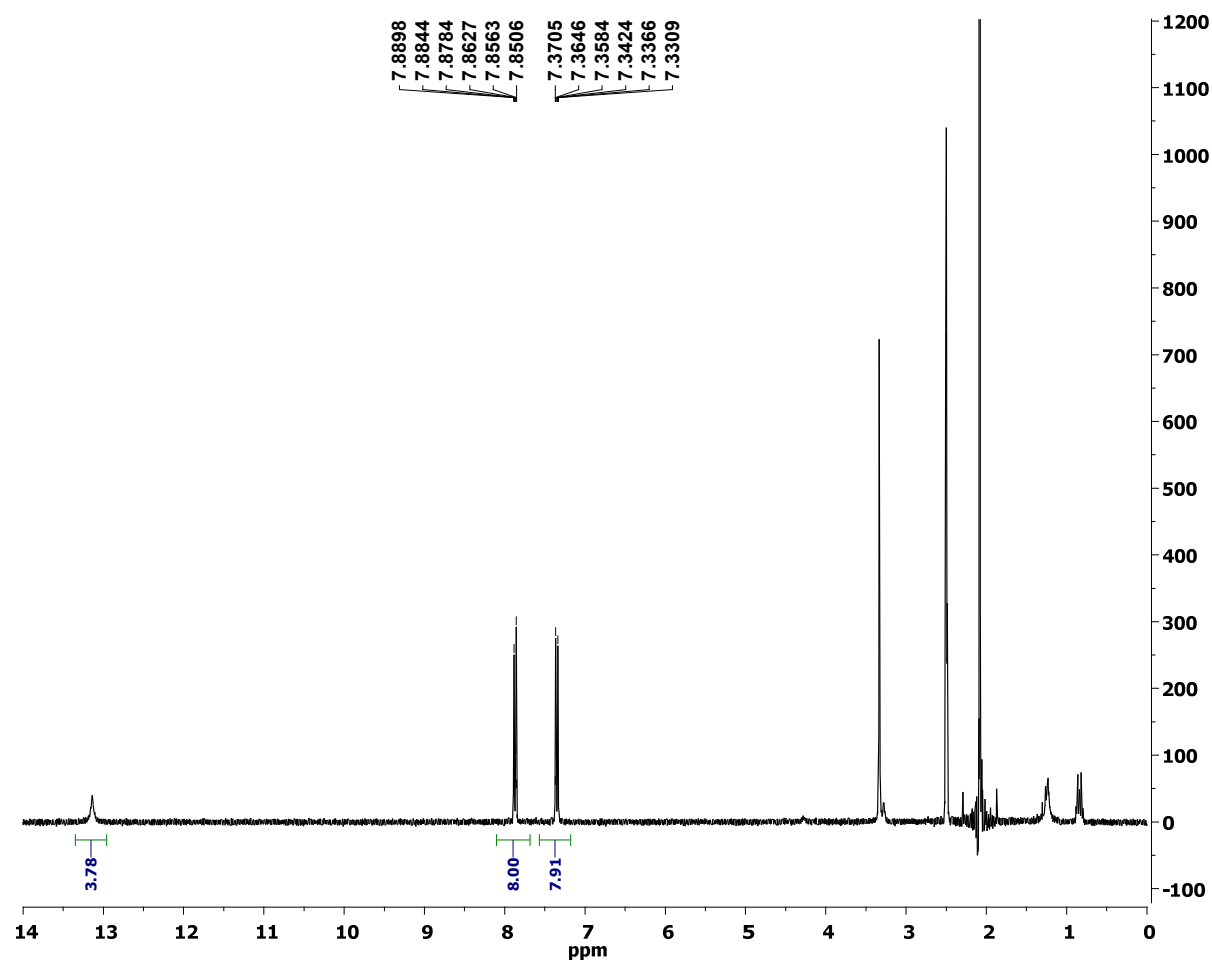
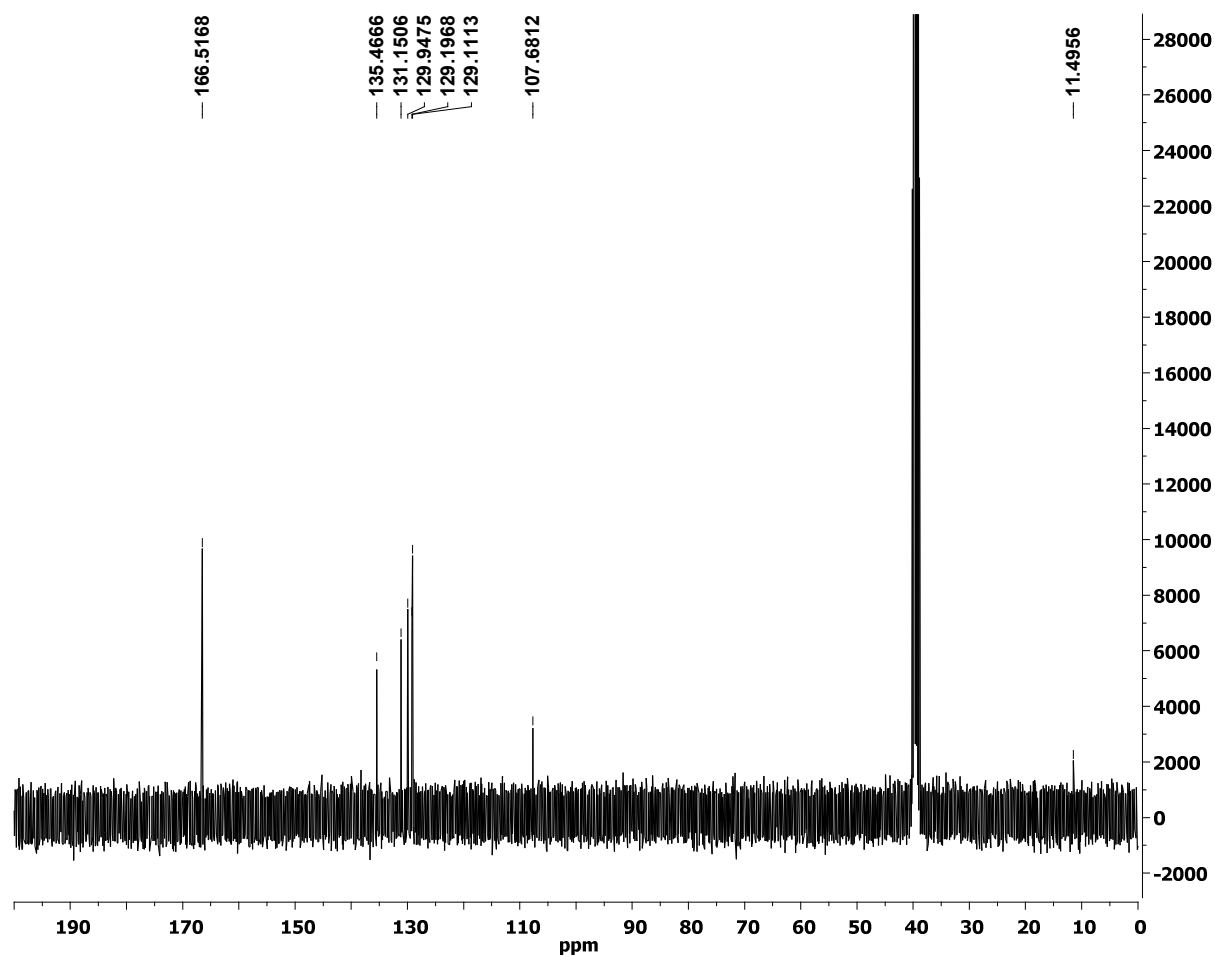
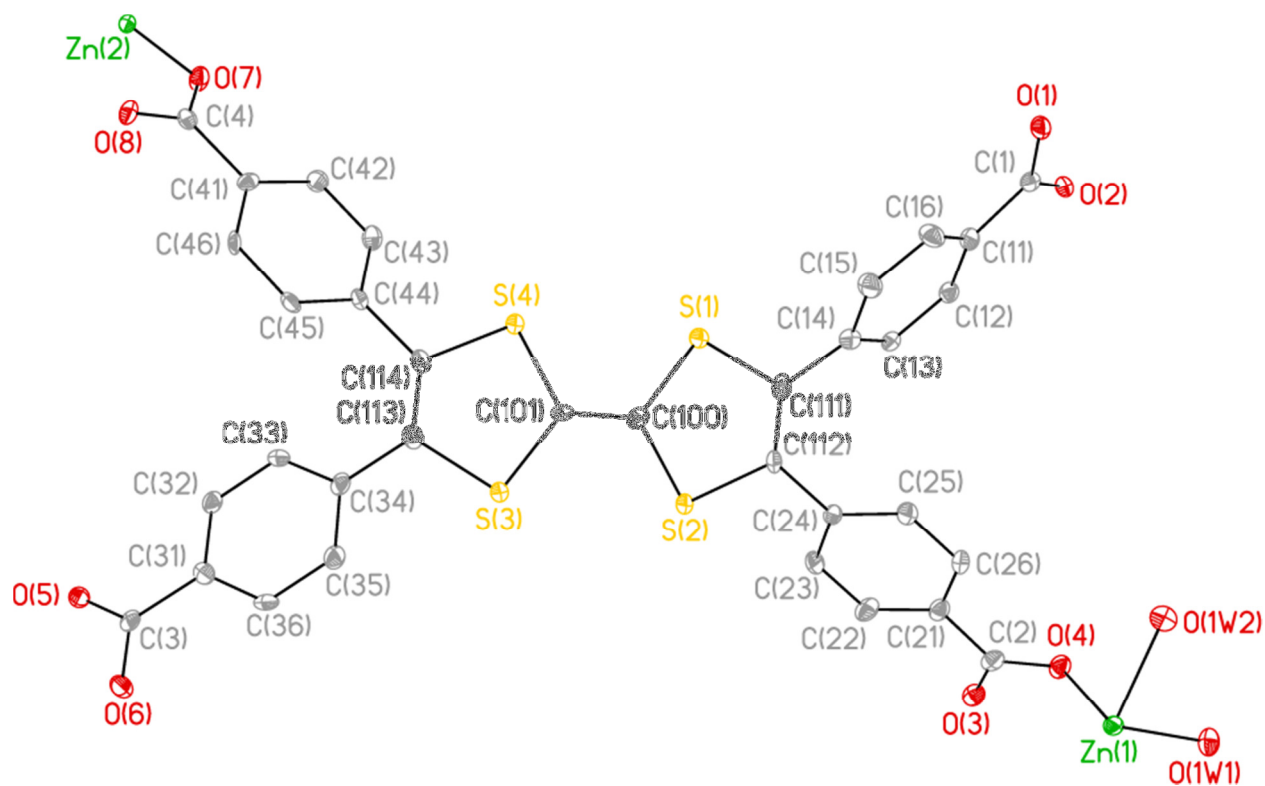


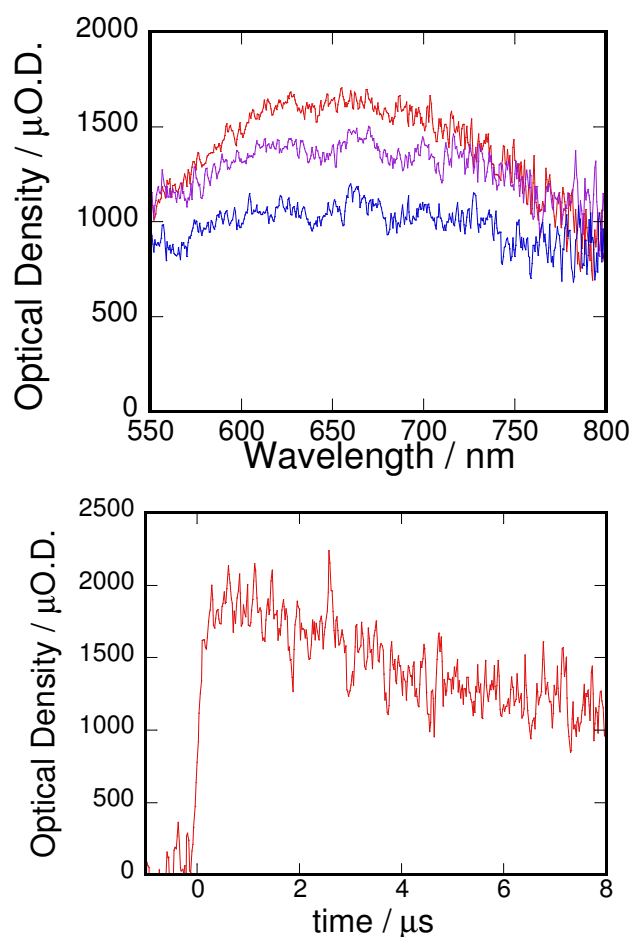
Figure S7.  $^1\text{H}$  NMR spectrum of  $\text{H}_4\text{TTFTB}$ .



**Figure S8.**  $^{13}\text{C}$  NMR spectrum of  $\text{H}_4\text{TTFTB}$ .



**Figure S9.** An ORTEP representation of the asymmetric unit of **ZnTTFTB** with ellipsoids drawn at the 50% probability level. Solvent molecules and hydrogen atoms have been removed for clarity.



**Figure S10.** *Top:* transient absorption spectra of H<sub>4</sub>TTFTB film dispersed into PMMA. Red, violet, and blue lines are recorded at 0.5 (averaged in the range of 0.45~0.55), 1 (0.95~1.05), and 8 (7.95~8.05)  $\mu$ s after pulse exposure, respectively. *Bottom:* kinetic trace of the transient absorption at 650 nm.

<sup>i</sup> Mitamura, Y.; Yorimitsu, H.; Oshima, K.; Osuka, A. *Chem. Sci.* **2011**, 2, 2017.

<sup>ii</sup> (a) Seki, S.; Yoshida, Y.; Tagawa, S.; Asai, K.; Ishigure, K.; Furukawa, K.; Fujiki, M.; Matsumoto, N. *Philos. Mag. B* 1999, 79, 1631-1645. (b) Grozema, F. C.; Siebbeles, L. D. A.; Warman, J. M.; Seki, S.; Tagawa, S.; Scherf, U. *Adv. Mater.* 2002, 14, 228-231. (c) Saeki, A.; Seki, S.; Sunagawa, T.; Usida, K.; Tagawa, S. *Philos. Mag. B* 2006, 86, 1261-1276.

<sup>iii</sup> Li, J.-R.; Zhou, H.-C. *Angew. Chem. Int. Ed.* **2009**, 48, 8465.