

Electronic Supplementary Information

## Single-crystal 3D Zn-tetrathiolate Connected Metal-organic Framework

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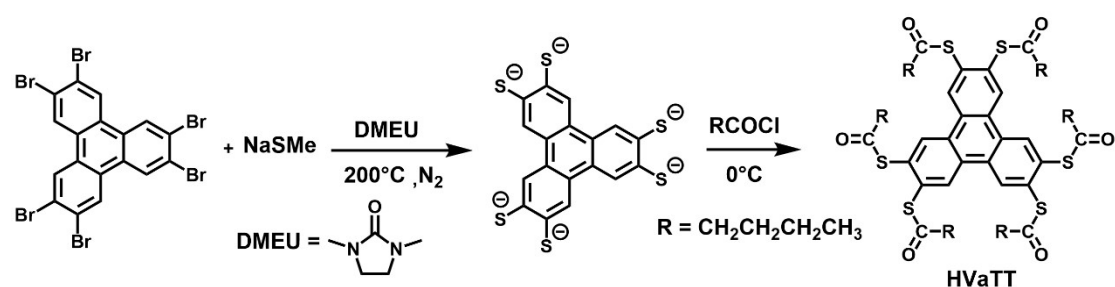
## General procedure.

All the starting materials, reagents, and solvents were purchased from commercial sources (J&K, Zhengzhou Alfa and Acros) and used without additional purification. Powder X-ray diffraction (PXRD) patterns were collected on a Rigaku Smart lab diffractometer with Cu K $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ) at room temperature. The X-ray tube operated at a voltage of 40 kV and a current of 15 mA. Fourier-transform infrared (FT-IR) spectra in the 400–4000  $\text{cm}^{-1}$  range were recorded on a Nicolet Avatar 360 FT-IR spectrophotometer. Solution  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded on a 400 MHz Bruker superconducting magnet high-field NMR spectrometer at room temperature, with tetramethylsilane (TMS) as the internal standard. Chemical shifts ( $\delta$ ) are expressed in ppm relative to the residual solvent (*e.g.*, chloroform  $^1\text{H}$ : 7.26 ppm,  $^{13}\text{C}$ : 77.0 ppm) reference. Coupling constants are expressed in hertz (Hz). Thermogravimetric analysis (TGA) was performed in a PerkinElmer thermal analysis equipment. Elemental analysis (EA) was obtained with a Vario Micro CUBE CHN elemental analyser. The porosity and surface area analysis were performed using a Quantachrome Autosorb iQ gas sorption analyser. The sample was outgassed at 0.03 torr with a 5  $^\circ\text{C}/\text{min}$  ramp to 110  $^\circ\text{C}$  and held at 110  $^\circ\text{C}$  for 12 h. X-ray photoelectron spectroscopy (XPS) was carried out by a Scanning Auger/X-ray Photoelectron Spectroscopy System (PHI 5802). The morphology of the samples was investigated using scanning electron microscopy (SEM, SIGMA 500, ZEISS, Germany). UV-vis absorption spectra were recorded by SHIMADZU model UV-3600 Plus instruments using  $\text{BaSO}_4$  as a reference.

## Single crystal X-ray crystallography.

The X-ray diffraction data of **HTT-Zn** crystals were determined using the Bruker APEX-II CCD diffractometer using Ga K $\alpha$  radiation ( $\lambda = 1.34138 \text{ \AA}$ ) at 150 K. Reflections were indexed and reduced by using SAINT V8.40A and the files were corrected for absorption using SADABS-2016/2. Reflections were merged by SHELXL according to the crystal class for the calculation of statistics and refinement. The space group was assigned, and the structure was solved by direct methods using ShelXS<sup>1</sup> and refined by full-matrix least-squares against  $F^2$  with all reflections using ShelXL<sup>2</sup> of Olex2<sup>3</sup> software packages. All non-hydrogen atoms were refined with anisotropic thermal parameters, and all hydrogen atoms were included in calculated positions and refined with isotropic thermal parameters riding on those of the parent atoms. The structure was deposited at Cambridge Crystallographic Data Centre as CCDC 2407349. Detailed parameters are shown in Table S1.

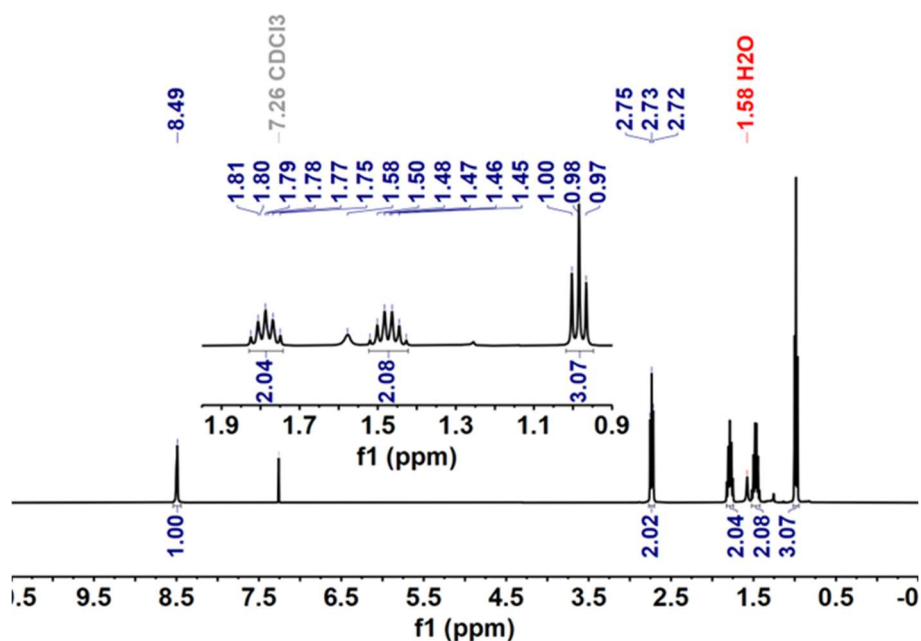
## Preparation of HVaTT.



**Scheme. S1** The synthetic route of HVaTT.

The synthesis of HVaTT was based on a modified procedure of our previous work<sup>4</sup>. 2,3,6,7,10,11-hexabromotriphenylene (2.68 g, 0.004 mmol) and CH<sub>3</sub>SNa (8.2 g, 0.1 mmol) were loaded into a 200-mL Schlenk flask. Then, the flask was evacuated and backfilled with N<sub>2</sub> three times on a Schlenk line. *N,N'*-dimethylethyleneurea, DMEU,

(anhydrous, bubbled with N<sub>2</sub>, 124 mL) was transferred into the flask *via* cannula. The reaction mixture was then stirred at 200 °C for 72 h. After the mixture was cooled to 0 °C (first naturally to 25 °C, then by an ice bath), pentanoyl chloride (18.5 mL) was injected under N<sub>2</sub>. After stirring at 25 °C for 2 h, the mixture was poured into ice water (100 mL) and extracted with ethyl acetate (3 × 100 mL). The combined organic layer was then washed with water (10 × 100 mL), dried over MgSO<sub>4</sub>, and volatiles were removed in vacuo. The crude product (black solid) was purified by column chromatography on silica gel (eluent: petroleum ether (PE)/ethyl acetate (EA) = 4:1, v/v) to afford the pure product as pale yellow solid (2.00 g, yield 56.6%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.49 (s, 1H), 2.73 (t, *J* = 7.5 Hz, 2H), 1.79 (p, *J* = 7.5 Hz, 2H), 1.47 (h, *J* = 7.4 Hz, 2H), 0.98 (t, *J* = 7.4 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 196.66, 132.86, 132.47, 130.16, 43.69, 27.78, 22.39, 13.95.



**Fig. S1** Solution <sup>1</sup>H NMR spectrum of HVaTT (CDCl<sub>3</sub>, 400 MHz).

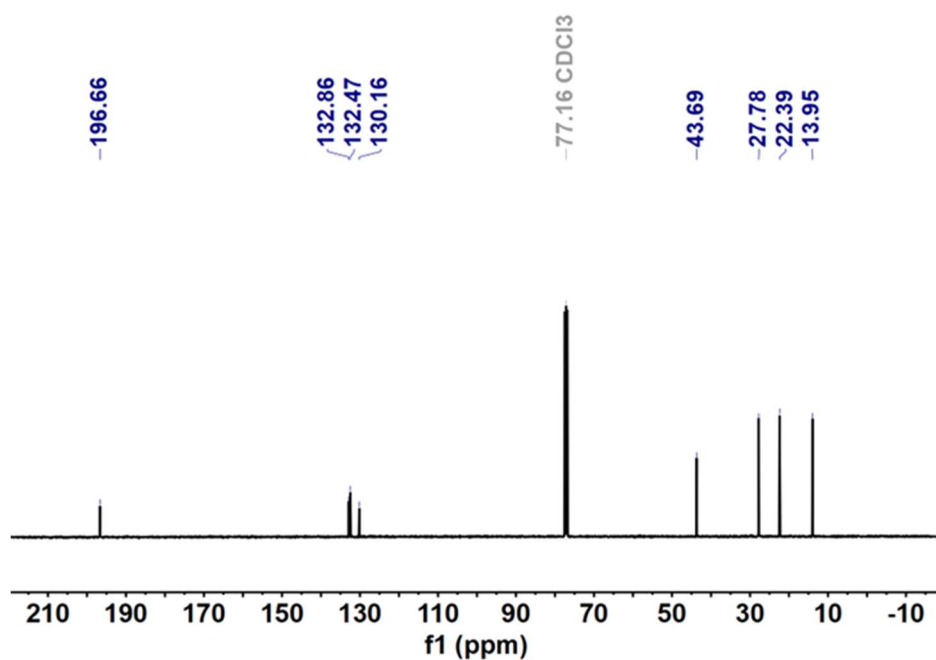
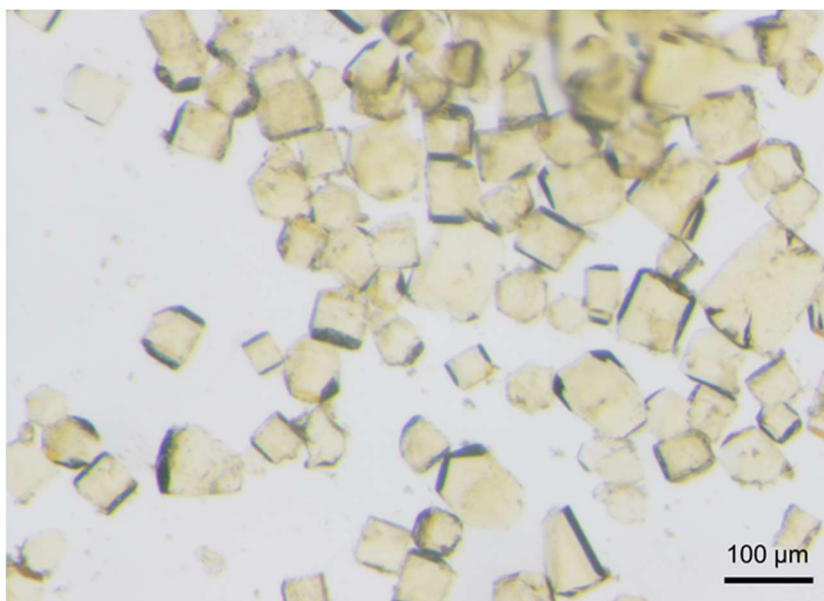


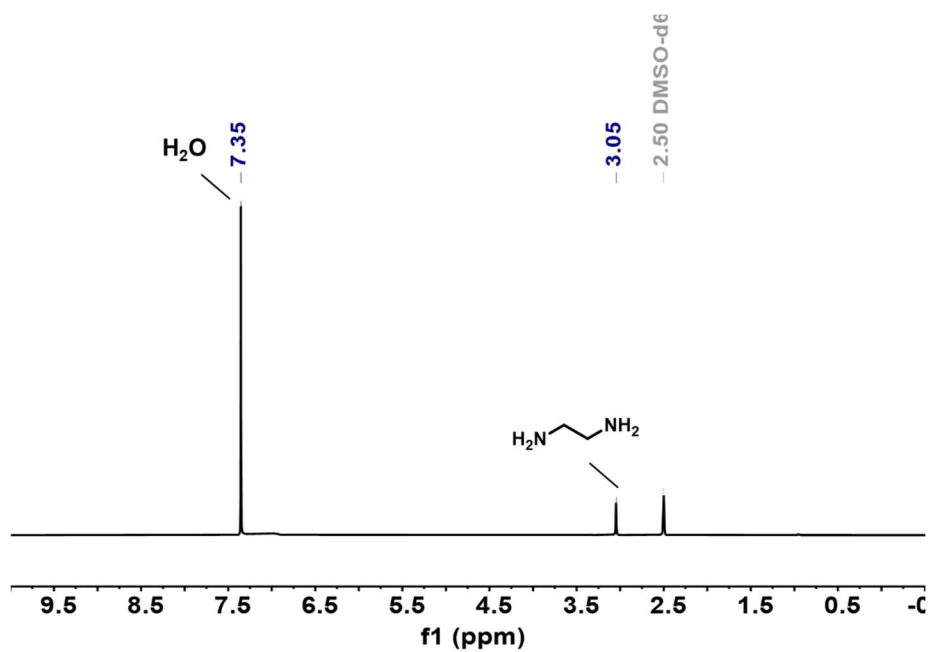
Fig. S2 Solution  $^{13}\text{C}$  NMR spectrum of HVaTT ( $\text{CDCl}_3$ , 101 MHz).

### Preparation of HTT-Zn.

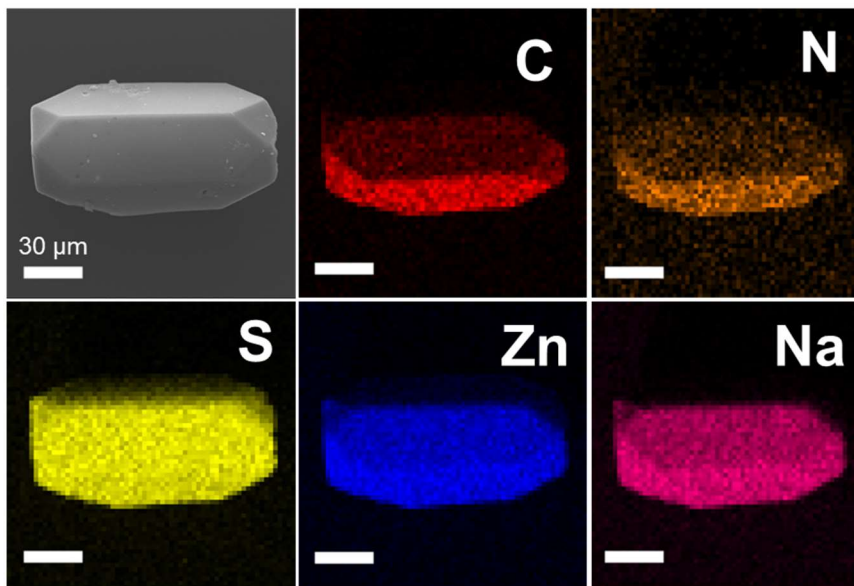
A 25-mL Schlenk tube was loaded with HVaTT (30.0 mg, 0.03 mmol) and then evacuated and backfilled with  $\text{N}_2$  three times on a Schlenk line. Dry MeOH solution of NaOH (7 mL, 278 mmol  $\text{L}^{-1}$ ) was bubbled with  $\text{N}_2$  for 5 min and injected into the flask. Then, the mixture was sonicated until HVaTT was completely dissolved. A solution of  $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$  (20.0 mg, 0.09 mmol) in ethylenediamine (7.0 mL) was bubbled with  $\text{N}_2$  for 5 min and then added to the mixture. The obtained mixture was heated at 120 °C in an oven for 48 h, followed by natural cooling until room temperature. Yellow-block crystals were thus collected, washed with MeOH ( $3 \times 5$  mL), and evacuated at room temperature to give **HTT-Zn** (yield: 13.1 mg, 56.8% based on HVaTT). Elemental analysis found C (33.63%), H (3.42%), and N (6.54%), thus fitting the formula of  $\text{Zn}_3(\text{C}_{18}\text{H}_6\text{S}_6)_2(\text{Na})_6(\text{C}_2\text{H}_8\text{N}_2)_{3.6}(\text{H}_2\text{O})_9$  ( $M_w$  1541.79); calculated: C (33.65%), H (3.84%), and N (6.54%).



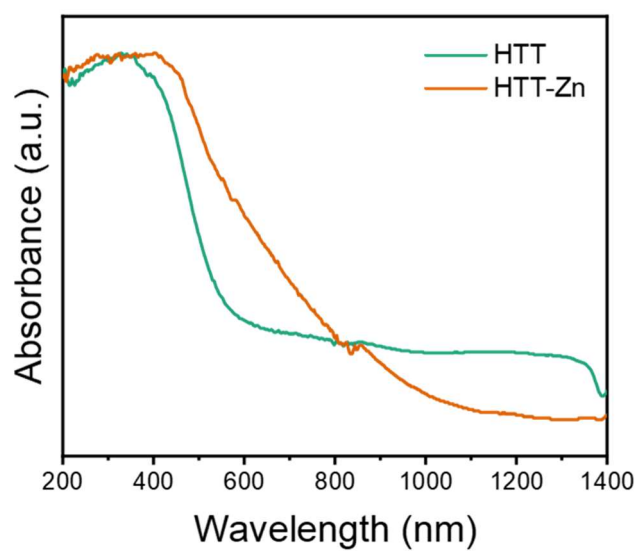
**Fig. S3** The optical photograph of **HTT-Zn** under a microscope.



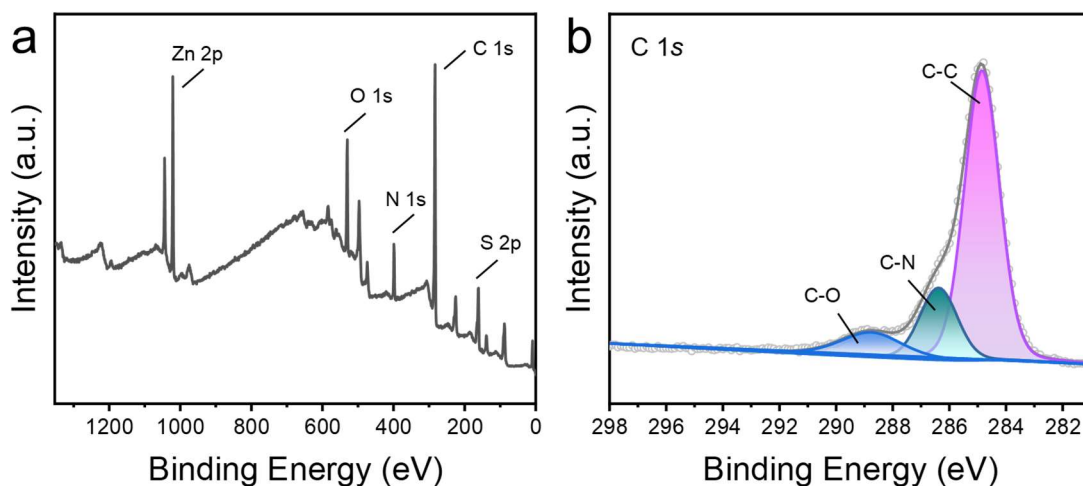
**Fig. S4** Solution  $^1\text{H}$  NMR spectrum ( $\text{DMSO-}d_6$ , 400 MHz) for **HTT-Zn** digested with ultrasonication in a solvent mixture of  $\text{DCl}$  (3 drops)/ $\text{DMSO-}d_6$  (0.55 mL).



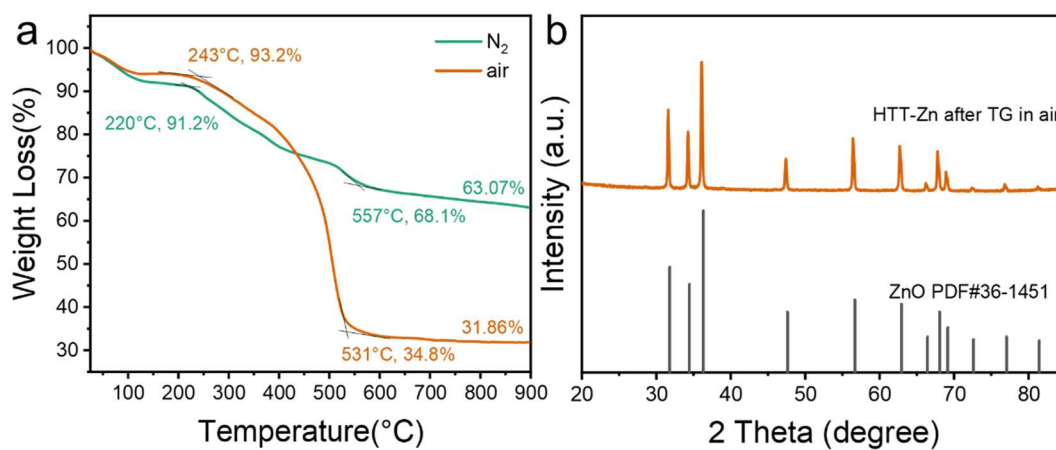
**Fig. S5** SEM and EDS images of **HTT-Zn**, showing the presence and uniform distribution of C, N, S, Zn and Na (scale bar 30  $\mu\text{m}$ ).



**Fig. S6** UV-vis absorption spectra of **HTT** and **HTT-Zn**.

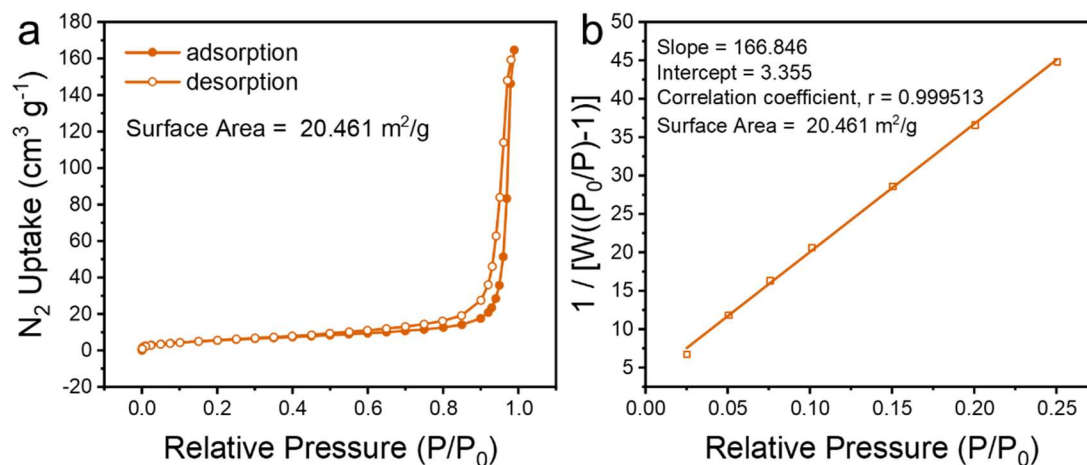


**Fig. S7** XPS survey spectrum (a) and high-resolution C 1s (b) spectrum of **HTT-Zn**.

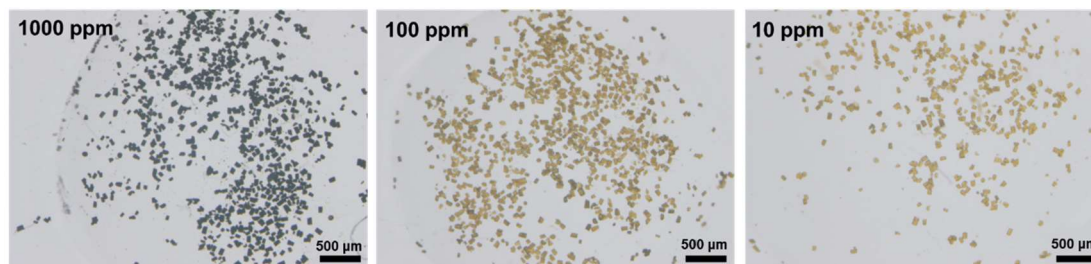


**Fig. S8** (a) The TG plots of **HTT-Zn** under N<sub>2</sub> and air atmosphere. (b) PXRD pattern of remaining samples after thermal analysis in air and model PXRD pattern of ZnO.

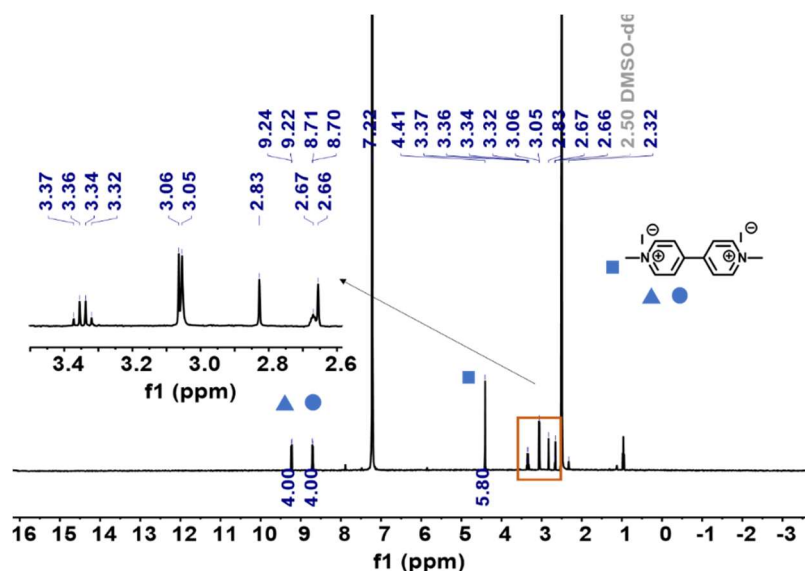




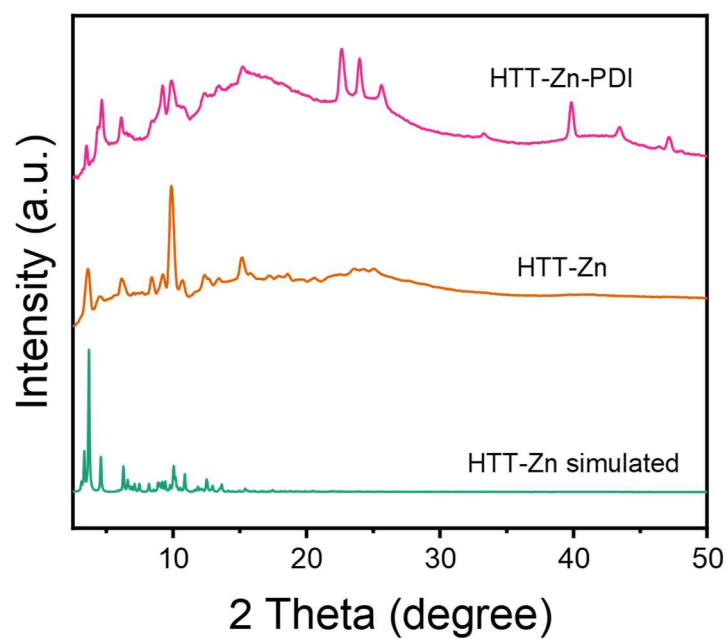
**Fig. S9** (a)  $N_2$  sorption isotherms at 77 K and (b) Multi-Point BET plot of **HTT-Zn**, surface area calculated by Brunauer-Emmett-Teller (BET) equation.



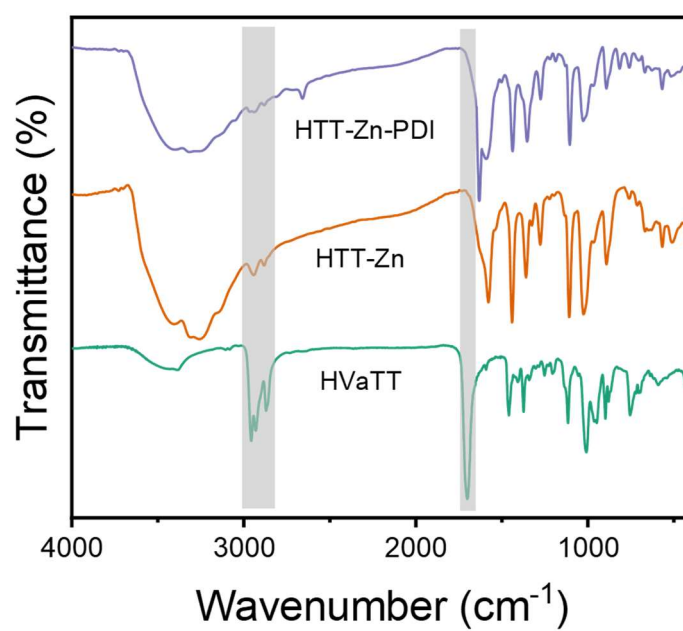
**Fig. S10** Optical photographs of **HTT-Zn** after PDI treatment ( $[PDI] = 1000, 100, 10$  ppm; left, middle, right).



**Fig. S11** Solution  $^1H$  NMR spectrum ( $DMSO-d_6$ , 400 MHz) for PDI-treated **HTT-Zn** digested with ultrasonication in a solvent mixture of DCl (3 drops)/ $DMSO-d_6$  (0.55 mL).



**Fig. S12** XRD patterns of **HTT-Zn** before and after PDI treatment.



**Fig. S13** FT-IR spectra of **HTT-Zn** before and after PDI treatment.

**Table S1** Crystallographic refinement parameters and results of **HTT-Zn**.

Compound	HTT-Zn
CCDC number	2407349
Chemical formula	C <sub>90</sub> H <sub>30</sub> S <sub>30</sub> Zn <sub>7.5</sub>
Formula weight	2563.240
Temperature	150 K
Crystal system	hexagonal
Space group	<i>P6<sub>3</sub>/m</i>
<i>a</i> /Å	30.4115(14)
<i>b</i> /Å	30.4115(14)
<i>c</i> /Å	56.222(5)
$\alpha$ /°	90
$\beta$ /°	90
$\gamma$ /°	120
<i>V</i> /Å <sup>3</sup>	45031.1(5)
<i>Z</i>	4
$\rho_{\text{calc}}$ /g cm <sup>-3</sup>	0.378
$\mu$ /mm <sup>-1</sup>	1.163
<i>F</i> (000)	5100.0
GOF on <i>F</i> <sup>2</sup>	1.179
<i>R</i> <sub>1</sub> <sup>a</sup> [ <i>I</i> > 2σ( <i>I</i> )]	0.1155
<i>wR</i> <sub>2</sub> <sup>b</sup> (all data)	0.3453

<sup>a</sup>  $R_1 = \sum(|F_o| - |F_c|) / \sum|F_o|$ ; <sup>b</sup>  $wR_2 = (\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2)^{1/2}$

## Reference.

- [1] G. M. Sheldrick, *Acta Cryst.* 2008, **A64**, 112–122.
- [2] G. M. Sheldrick, *Acta Cryst.* 2015, **C71**, 3–8.
- [3] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Cryst.* 2009, **42**, 339–341.
- [4] J. Huang, Y. He, M.-S. Yao, J. He, G. Xu, M. Zeller and Z. Xu, *J. Mater. Chem. A*, 2017, **5**, 16139–16143.