Electronic Supplementary Information

From 3-Fold to 6-Fold: Tuning Interpenetration of Zn-triphenylenehexathiolate MOF through Precursor Hydration

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General procedure.

Starting materials, reagents, and solvents were purchased from commercial sources (*e.g.*, J&K, Zhengzhou Alfa and Macklin) and used without additional purification. The ligand **HVaTT** was synthesised according to the previously reported literature.[1, 2] Powder X-ray diffraction (PXRD) patterns were collected on a Rigaku Smart lab diffractometer with Cu Kα radiation (λ = 1.5418 Å) 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 cm^{-1} range were recorded on a Nicolet Avatar 360 FT-IR spectrophotometer. Solution ^1H 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 (δ) are expressed in ppm relative to the residual solvent (*e.g.,* dimethyl sulfoxide ^1H: 2.50 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 amounts of the metal ions were collected by Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES, Agilent 5800(OES)). 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-NIR absorption spectra were recorded by SHIMADZU model UV-3600 Plus instrument using $BaSO_4$ as a reference.

Single-crystal X-ray crystallography.

The X-ray diffraction data of crystals **Zn-HTT-6F** were determined using the Bruker APEX-II CCD diffractometer using Ga Kα radiation (λ = 1.34138 Å) at 80 K. Reflections were indexed and reduced by using SAINT V8.40A. The files were corrected for absorption using SADABS-2016/2. Reflections were merged by SHELXL according to the crystal class for statistics calculation and refinement. The space group was assigned, and the structure was solved by direct methods using ShelXS[3] and refined by full-matrix least-squares against F^2 with all reflections using ShelXL[4] in the Olex2[5] software package. 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 2478650. Detailed parameters are shown in Table S1.

Preparation of Zn-HTT-6F.

A 25-mL Schlenk tube was charged with **HVaTT** (30.0 mg, 0.03 mmol), then evacuated and backfilled with N_2 thrice using a Schlenk line. A dry MeOH solution of NaOH (7 mL, 278 mmol L^{-1}) was bubbled with N_2 for 5 min and added to the tube. The mixture was sonicated until **HVaTT** completely dissolved. Next, anhydrous $Zn(OAc)_2$ (30.0 mg, 0.16 mmol) in ethylenediamine (7.0 mL) was bubbled with N_2 for 5 min before addition. The mixture was heated at 120 °C in an oven for 48 h, then allowed to cool naturally to room temperature. Yellow crystals were collected, washed with MeOH (3 × 5 mL), and dried under vacuum at room temperature to obtain **Zn-HTT-6F** (yield: 12.6 mg, 36.8% based on **HVaTT**). Elemental analysis found C (32.32%), H (5.48%), and N (12.09%); ICP-OES analysis found: Na (0.4054 wt%) and Zn (24.3430 wt%), thus fitting the formula of $Zn_9(C_{18}H_6S_6)_6(C_6H_{24}N_6Zn)_{8.5}Na(C_2H_8N_2)_4(H_2O)_{40}$ (M_w 5968.03); calculated: C (32.40%), H (5.54%), N (12.44%), Na (0.39 wt%) and Zn (19.17 wt%).

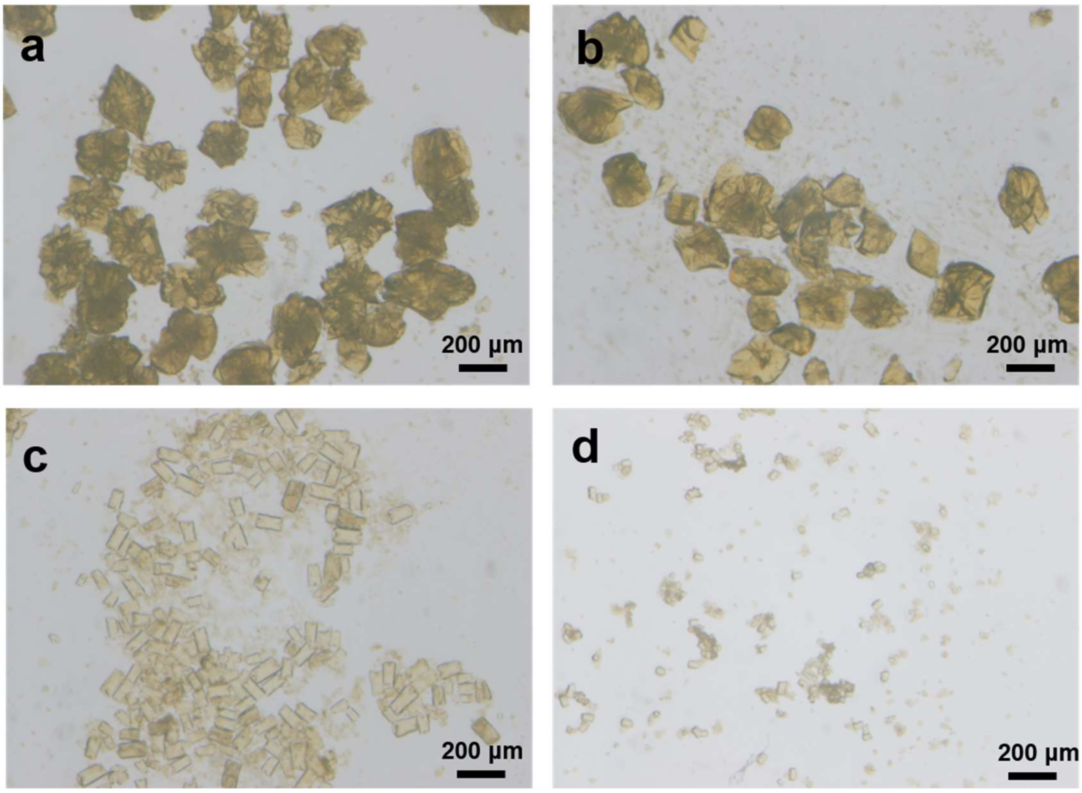

Fig. S1 Optical microscopy images showing the water-content-dependent assembly. (a, b) **Zn-HTT-6F** platelet crystals obtained with the addition of 2 μL and 5 μL of H_2O, respectively. (c, d) **Zn-HTT-3F** blocky crystals obtained with the addition of 10 μL and 20 μL of H_2O, respectively.

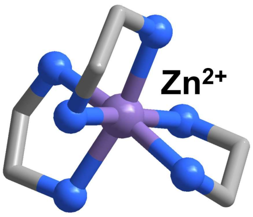

Fig. S2 Structure of $[Zn(EDA)_3]^{2+}$ ion free in the pore channel. Purple spheres, Zn; gray, C; blue, N. H atoms are omitted for clarity.

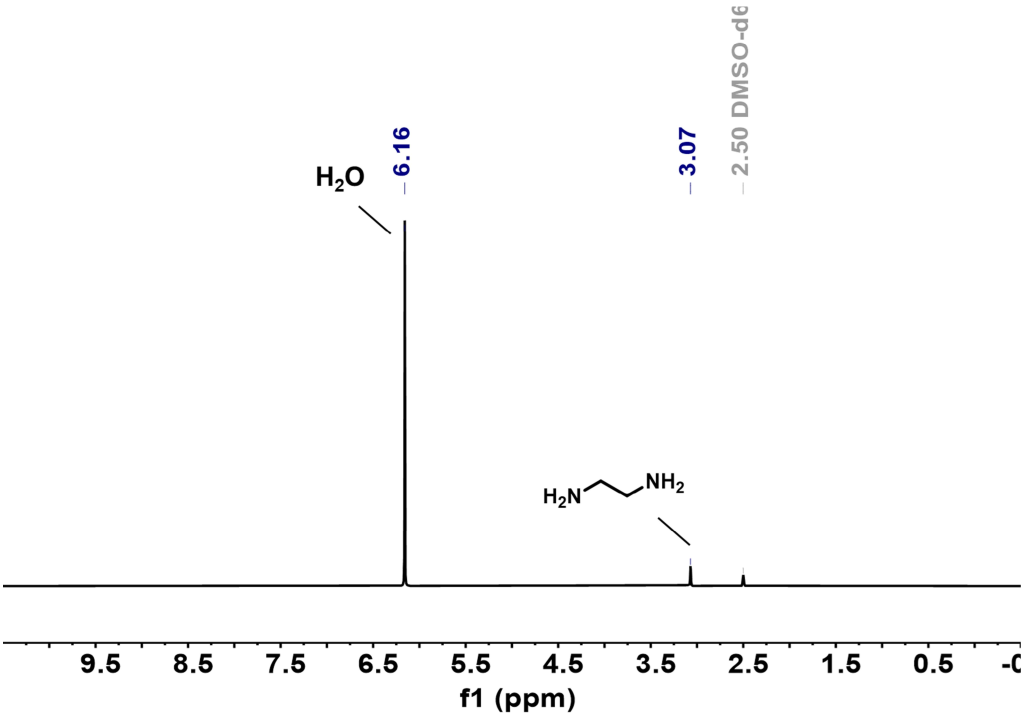

Fig. S3 Solution ^{1}H NMR spectrum (DMSO-*d*$_6$, 400 MHz) for **Zn-HTT-6F** digested with ultrasonication in a solvent mixture of DCl (3 drops)/DMSO-*d*$_6$ (0.55 mL).

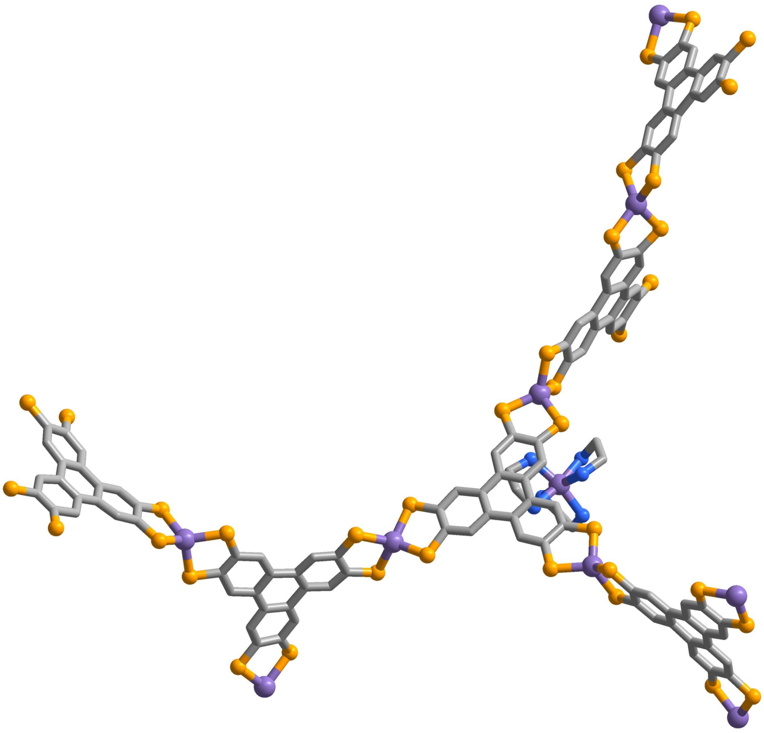

Fig. S4 Partial view of **Zn-HTT-6F** network. H atoms are omitted for clarity.

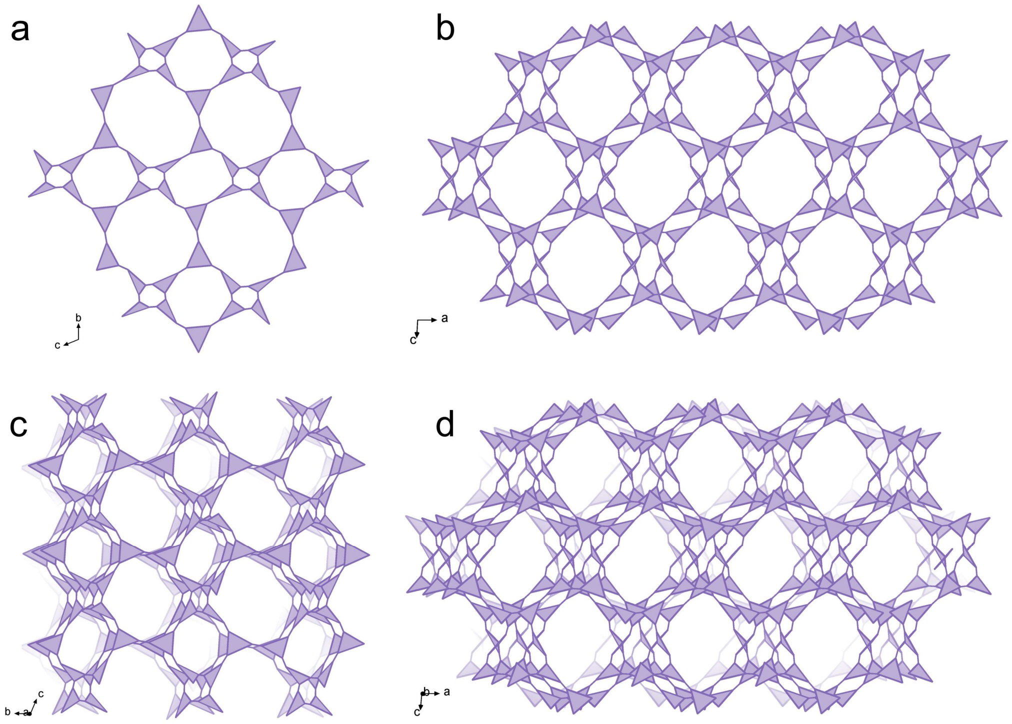

Fig. S5 Topological representations showing (a) partial view of network, (b) 2-fold interpenetration along the *b*-axis direction, (c) 4-fold interpenetration along the *a*-axis direction and (d) 6-fold interpenetration along the *b*-axis direction of **Zn-HTT-6F**.

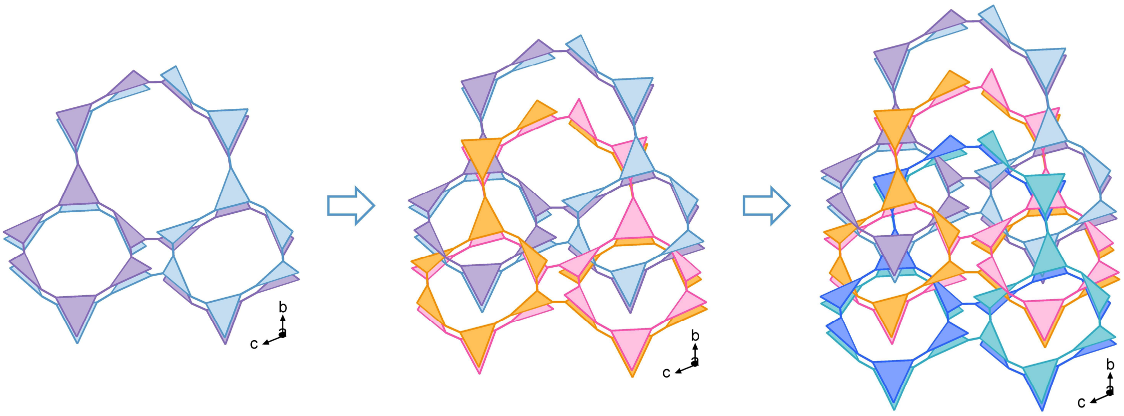

Fig. S6 Topological representation along the *a*-axis direction of the transition from symmetrical 2-fold twine to 4-fold twine and finally the 6-fold interpenetration in **Zn-HTT-6F**.

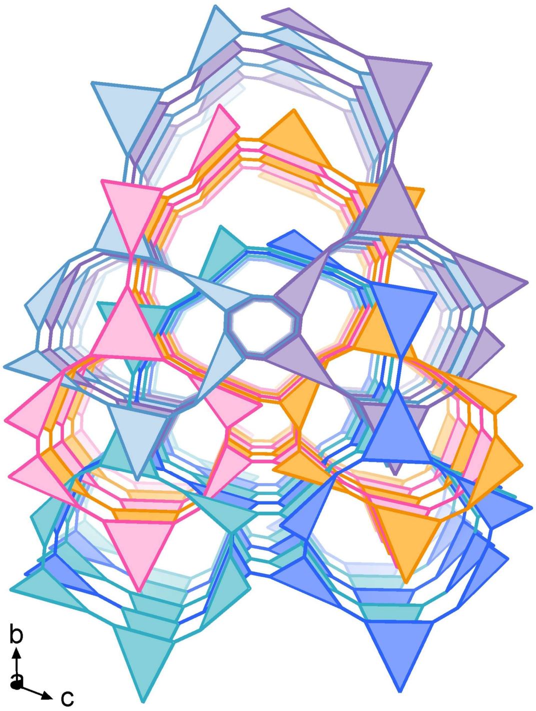

Fig. S7 Topological representation of the 6-fold interpenetration structure of **Zn-HTT-6F** along the *a*-axis direction.

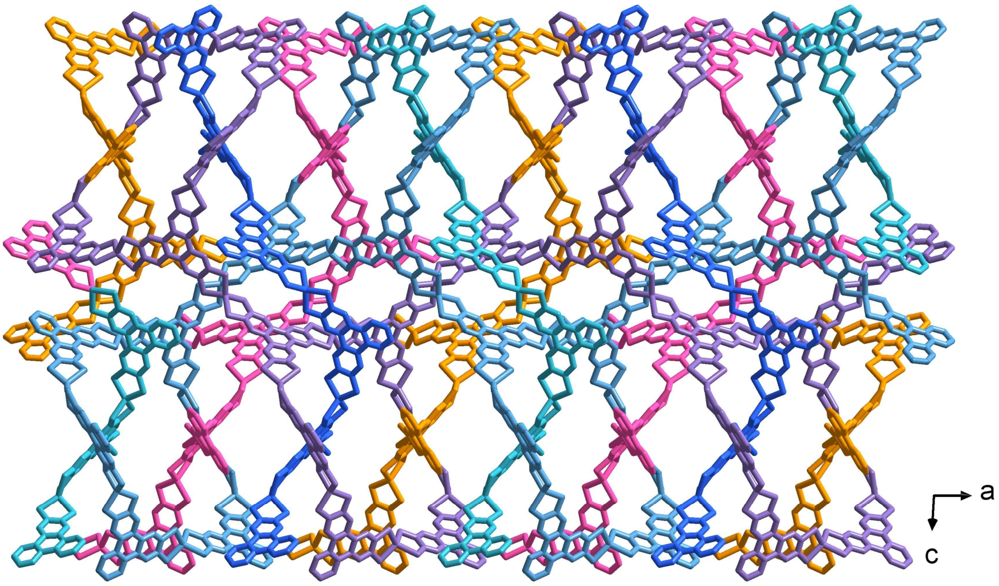

Fig. S8 6-fold interpenetration viewed along the *b*-axis direction of **Zn-HTT-6F**.

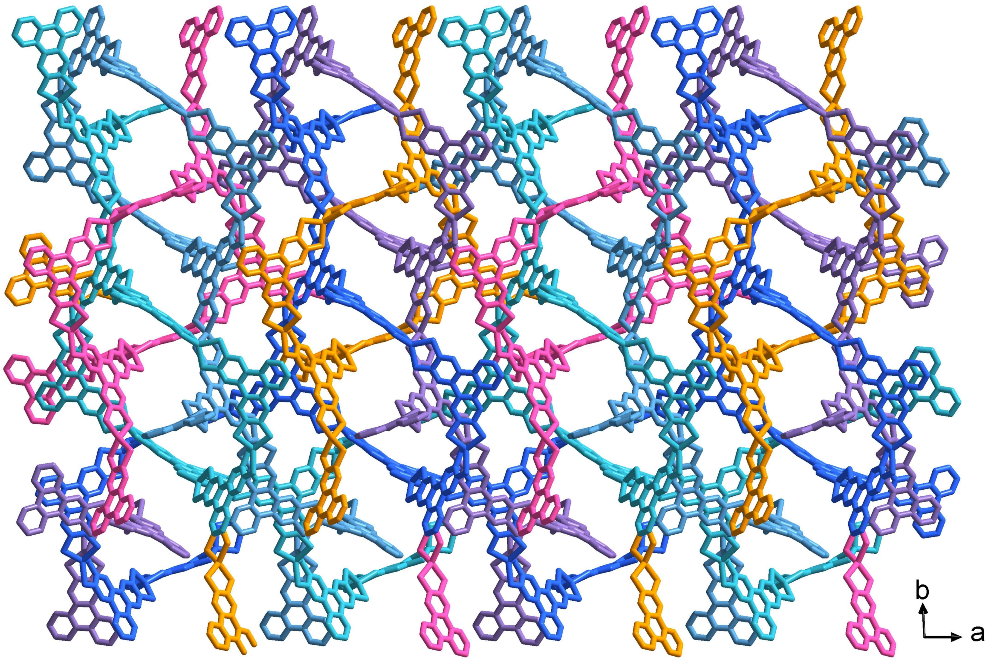

Fig. S9 6-fold interpenetration viewed along the *c*-axis direction of **Zn-HTT-6F**.

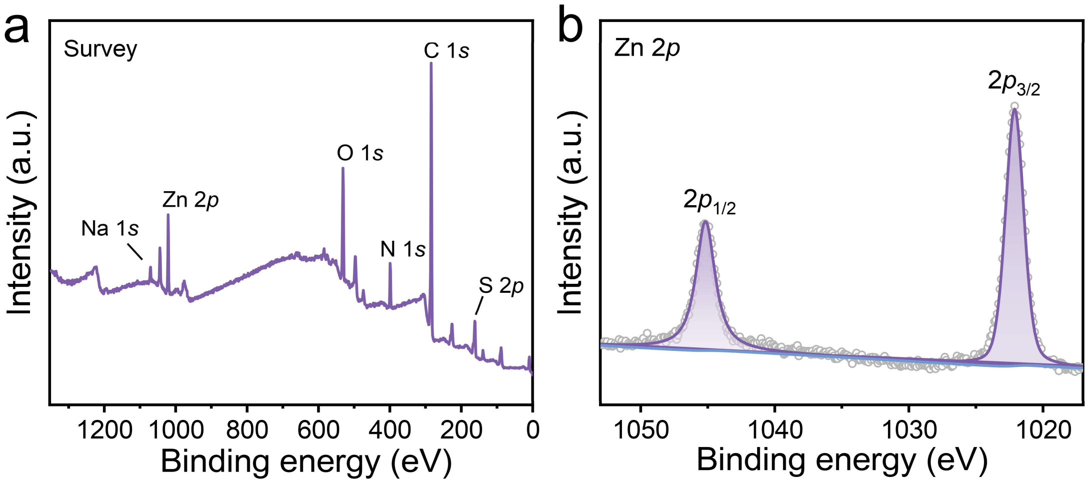

Fig. S10 High-resolution XPS (a) survey and (b) Zn 2*p* spectra of **Zn-HTT-6F**.

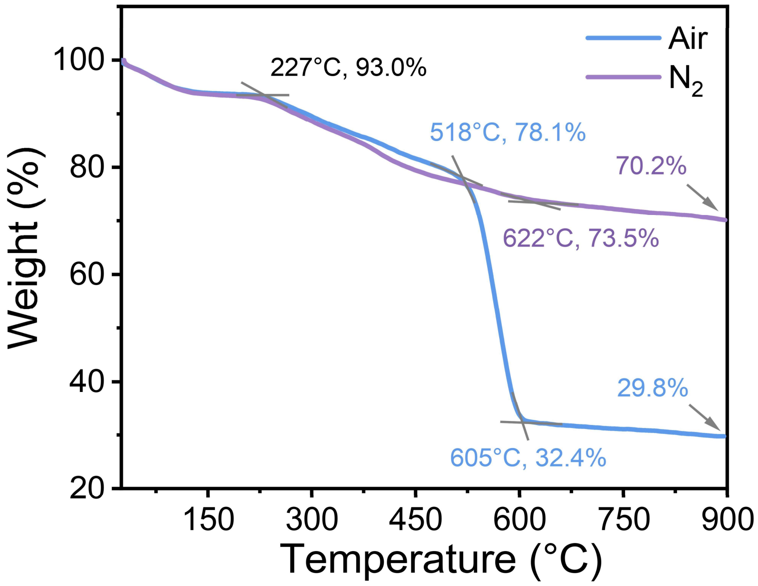

Fig. S11 The TGA curves of **Zn-HTT-6F** under air and N_2 atmosphere, respectively.

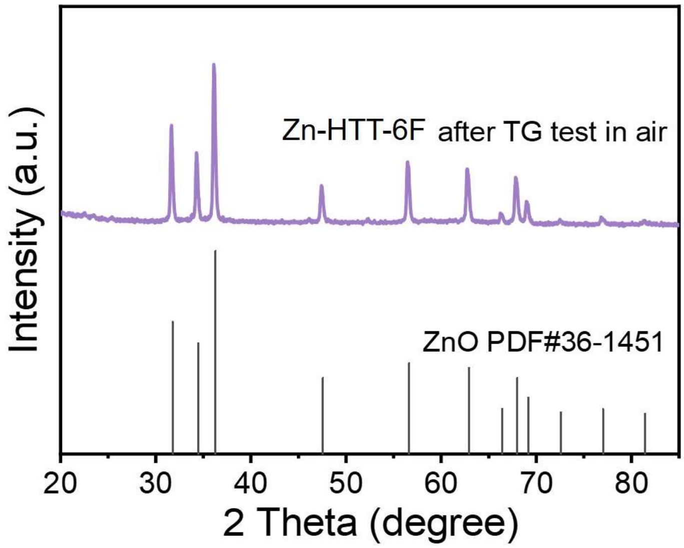

Fig. S12 PXRD pattern of remaining samples after thermal analysis test in air and model PXRD pattern of ZnO.

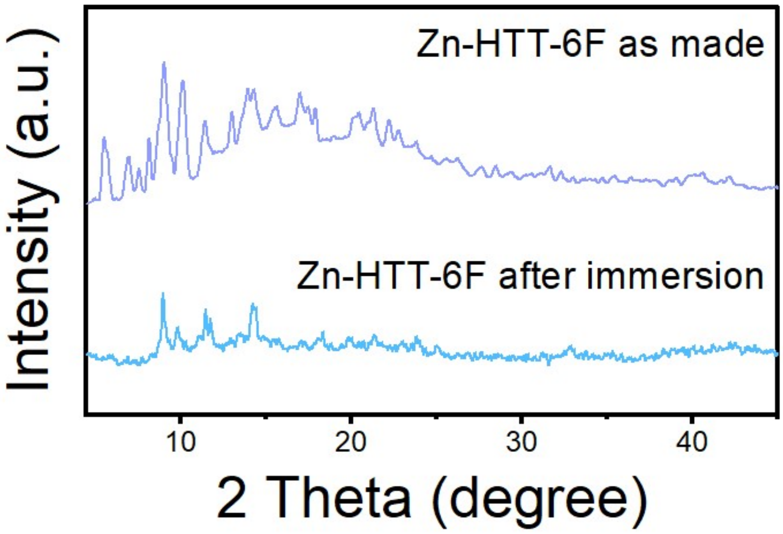

Fig. S13 PXRD patterns of **Zn-HTT-6F** before and after immersion in water.

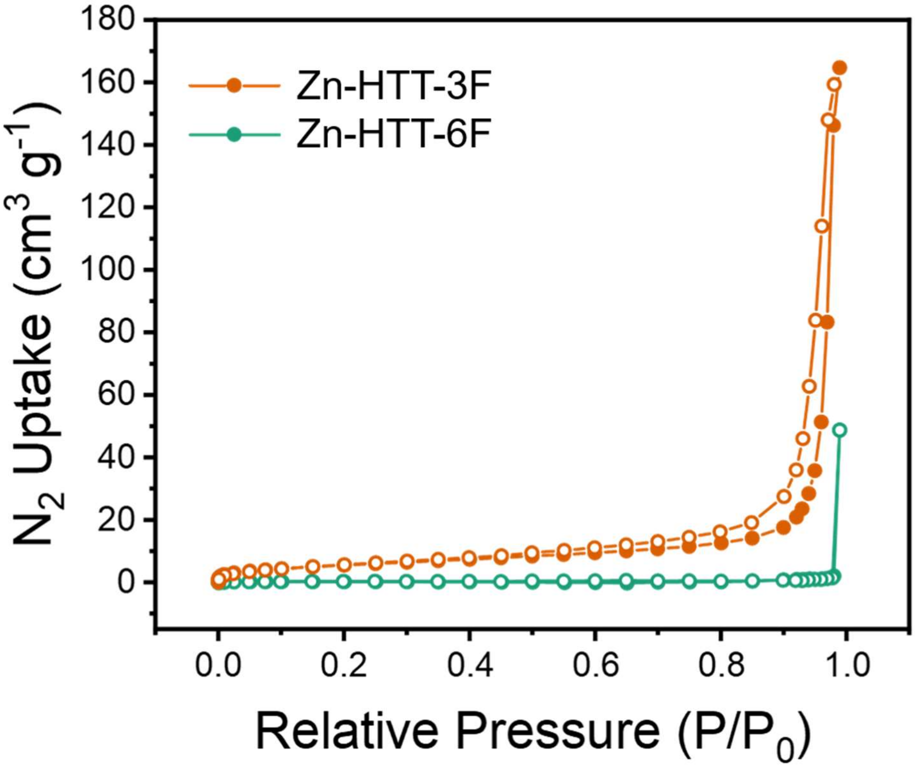

Fig. S14 N_2 adsorption-desorption isotherms at 77K for **Zn-HTT-6F** and **Zn-HTT-3F**.

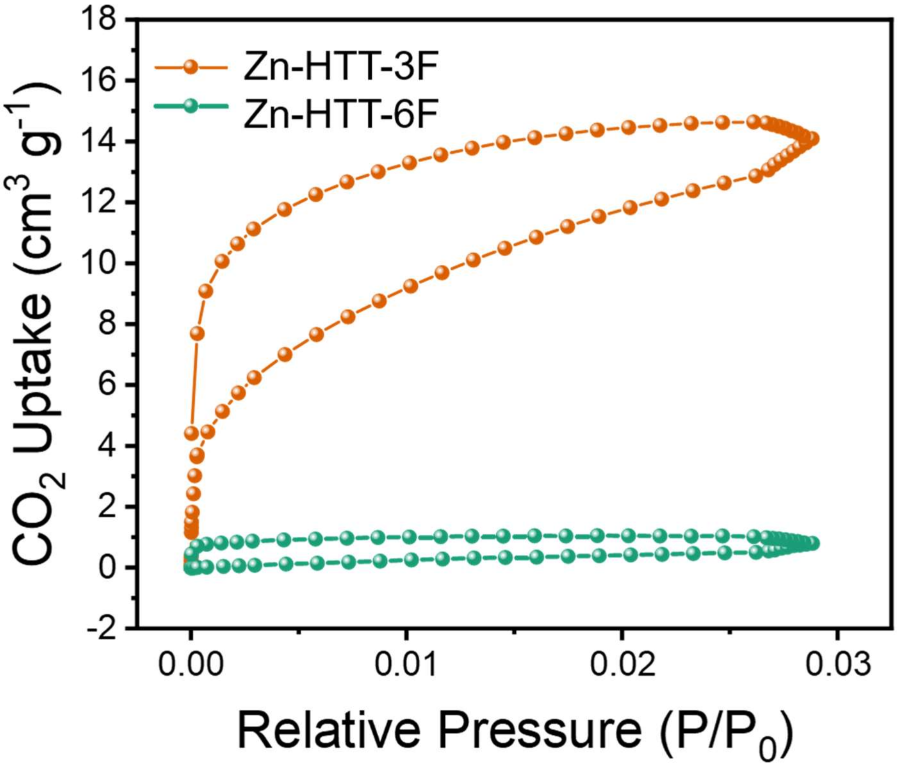

Fig. S15 CO₂ adsorption-desorption isotherms at 273K for **Zn-HTT-6F** and **Zn-HTT-3F**.

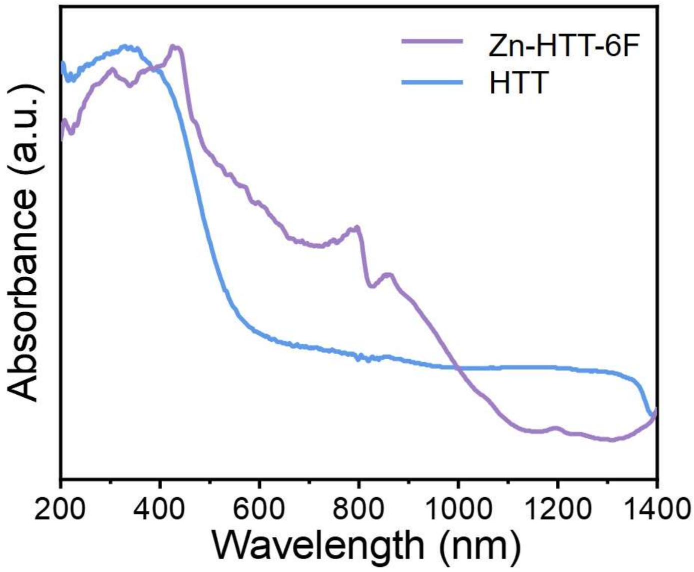

Fig. S16 UV-vis absorption spectra of HTT and **Zn-HTT-6F**.

Table S1 Crystallographic refinement parameters and results of **Zn-HTT-6F**.

Compound	**Zn-HTT-6F**
CCDC number	2478650
Chemical formula	$C_{114}H_{60}N_6S_{36}Zn_{10}$
Formula weight	3321.54
Temperature	80.00 K
Crystal system	triclinic
Space group	P-1
a/Å	20.8124(10)
b/Å	24.2224(11)
c/Å	31.0731(11)
α/°	112.136(2)
β/°	92.155(2)
γ/°	91.899(2)
V/Å^3	14480.9(11)
Z	2
ρ_{calc}/g cm^{-3}	0.762
μ/mm^{-1}	2.237
F (000)	3324.0
GOF on F^2	1.065
$R_1{}^a$[I > 2σ(I)]	0.1199
$wR_2{}^b$ (all data)	0.2534

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

Reference.

1. J.-R. Li, J. Hu, L. Jiang, Y. He, W.-M. Liao, X. Yang, L.-H. Chung and J. He, *Chem. Commun.*, 2025, **61**, 3852.
2. J. Hu, J.-Z. Xiao, W.-M. Liao, S. Liu, J. Li, Y. He, L. Yu, Q. Li, G. Xu and J. He, *J. Mater. Chem. A*, 2023, **11**, 11463.
3. G. Sheldrick, *Acta Cryst.*, 2008, **64**, 112.
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