

Supporting Information

Synthesis of an Exceptional Water Stable Two-fold Interpenetrated Zn(II)-Paddlewheel Metal-Organic Framework via Facile Conversion of Its Non-interpenetrated Isomer

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Materials and general methods

Reagents were obtained from commercial sources and used without further purification, and the ligand TCS, was prepared according to the literature.¹ Infrared spectra (FTIR) were recorded in the range 400–4000 cm⁻¹ on a Bruker Vector 22 infrared spectrometer. Elemental analyses for C, H and N were performed on Vario EL III elemental analyzer of Nanjing Normal University. TG-DTA was carried out using the SDT 2980 thermal analyzer under the N₂ flow of 15 mL/min over the temperature range from 25 °C to 600 °C at a heating rate of 5°C min⁻¹. Powder X-ray diffraction (PXRD) patterns were performed on a Bruker D8 Advance instrument using Cu K α radiation ($\lambda = 1.54056 \text{ \AA}$) with a scan speed of 0.1 s per degree at room temperature. Surface area and pore characteristics measurements were measured by Micromeritics ASAP 2020. Extended Pressure Adsorption Analyzer using N₂. And H₂ adsorption isotherms at 77 K up to 1 bar were also measured on the ASAP 2020 instrument. Before analysis, the solvent-exchanged MOF samples were degassed at 150 °C under vacuum for 12 h (36.4-47.7 mg). UV-Vis diffuse reflectance spectral measurements were carried out using Varian Cary 5000 UV-Vis-NIR. The fluorescence spectra were recorded by a FM-4P-TCSPC Transient State Fluorescence Spectrometer.

Synthesis of 1-3

Synthesis of the interpenetrated Zn₂TCS(4,4'-bipy) (1·H₂O) in water

A mixture of TCS (6.40 mg, 0.0125 mmol), 4,4'-bipy (3.90 mg, 0.0250 mmol) and Zn(NO₃)₂·6H₂O (12.8 mg, 0.0400 mmol) in 4 mL H₂O was put into a 30 mL Teflon-lined stainless steel vessel in a oven. The temperature of the oven was then raised to 170°C by a rate of 2°C/min and kept at 170 °C for 3 d. The temperature of the oven was then cooled down to room temperature by a rate of 0.5°C/min. The sample was then dried in a 40 °C oven for 6-7 h. The Yield: 4.5 mg, 45.4% (based on TCS). Elemental analysis for C₃₈H₂₆O₉N₂Zn₂Si (1·H₂O), calcd (%): C, 56.30; N, 3.400; H, 3.200. Found: C, 56.33; N, 3.355; H, 3.332. FTIR (ν_{max} /cm⁻¹): 3425 (m), 3167 (m), 3070 (m), 2651 (w), 2506 (w), 1957 (w), 1828 (w), 1699 (s), 1642 (s), 1530 (m), 1489 (m), 1401 (s), 1255 (m), 1094 (s), 1013 (m), 852 (m), 828 (m), 763 (m), 723 (s), 553 (m), 481 (m), 425 (m).

Synthesis of non-penetrated Zn₂TCS(4,4'-bipy) (2)

A mixture of TCS (6.40 mg, 0.0125 mmol), 4,4'-bipy (3.90 mg, 0.0250 mmol) and Zn(NO₃)₂·6H₂O (14.8 mg, 0.0500 mmol) in 1 mL NMP and 1 mL DMA was heated to 170°C in a 20 mL Teflon-lined stainless steel vessel for 3 days. The mixture was allowed to cool down to room temperature and resulted in colorless cuboid-shaped crystals of **2** which were collected by filtration and washed with DMA for three times, the product is denoted as the as-synthesized sample. The sample was then dried in a 40 °C oven for 12 h. The Yield: 4.5mg, 45.4% (based on TCS). The sample was activated at 200 °C for 12 h during which time it converted to **1** before doing elemental analysis. Elemental analysis for C₃₈H₂₄O₈N₂Zn₂Si, calcd (%): C, 57.37; N, 3.521; H, 3.041. Found: C, 57.30; N, 3.500; H, 3.020. Elemental analysis (%) calcd for

$C_{38}H_{24}O_8N_2Zn_2Si$, FTIR (ν_{max}/cm^{-1}): 3424 (m), 3055(w), 3020 (w), 2927 (w), 1942 (w), 1846 (w), 1640 (s), 1615 (m), 1537 (m), 1493 (m), 1405 (s), 1211 (m), 1095 (m), 1017 (m), 849 (w), 813 (m), 777 (m), 725 (m), 637 (w), 549 (w), 487 (m), 417 (m).

As-synthesized **2** (40 mg) was immersed in CH_3OH (15 mL) for 3 d, and then put into CH_2Cl_2 (15 mL) for 3 d, during which each solvent was decanted and replaced with fresh portion every 12 h. Such obtained sample was denoted as the solvent exchanged sample and was used to obtain gas absorption/desorption data. However, during the activation process (150 °C for 12 h), it converted to **1**. Such the sorption isotherms are the properties of **1** instead of **2**.

Synthesis of $Cu_2TCS(4,4'-bipy) \cdot (3 \cdot H_2O)$

A mixture of TCS (6.40 mg, 0.0125 mmol), 4,4'-bipy (3.90 mg, 0.0250 mmol), $Cu(NO_3)_2 \cdot 6H_2O$ (14.8 mg, 0.0500 mmol) and HCl aqueous solution (2 mol/L, 100 μ L) in 4 mL H_2O was put into a 30mL Teflon-lined stainless steel vessel and then into an oven. The temperature of the oven was then raised to 170°C by a rate of 1°C/min and kept at 170 °C for 2 d. The temperature of the oven was then cooled down to room temperature by a rate of 1°C/min. Blue cubic crystal was separated from the colourless needle crystals by subjecting it to ultrasonic waves, breaking the needle crystals which can be removed by decanting. The obtained sample was heated at 40 °C for 6-7 h. The Yield: 8.8 mg, 87% based on TCS. Elemental analysis for $C_{38}H_{26}O_9N_2Cu_2Si \cdot (3 \cdot H_2O)$, calcd (%):C, 56.3; H, 3.2; N, 3.4. Found: C, 55.9; H, 2.9; N, 3.6. FTIR (ν_{max}/cm^{-1}): 3423 (m), 3066 (w), 1622 (s), 1533 (s), 1407 (s), 1217 (m), 1055 (s), 1016 (m), 770 (m), 500 (w).

X-ray crystallography

Suitable crystals of **2** were selected for single crystal X-ray diffraction. The data were collected at 100(1) K on a Bruker Smart CCD diffractometer with graphite-monochromatic $K\alpha$ radiation ($\lambda=0.71073 \text{ \AA}$) from an enhanced optic X-ray tube. Raw data for the structure were obtained using SAINT, and absorption correction was applied using SADABS programs. The structure was solved by the direct method and refined by full-matrix least-squares on F^2 , using the SHELXS-97 and SHELXL-97 program. The crystallographic data for **2** is given in Table 1. Selected bond lengths (\AA) and angles (deg) is given in Table S1 (SI). Further details on the crystal structure investigations of **2** can be obtained from the Cambridge Crystallographic Data Centre, on quoting the CCDC depository number 1034674.

Single crystals of **3**·H₂O were selected for single crystal X-ray diffraction. The data were collected at 291(2) K. Raw data for the structure were obtained using SAINT, and absorption correction was applied using SADABS programs. The structure was solved by the direct method and refined by full-matrix least-squares on F^2 , using the SHELXS-97 and SHELXL-97 program. Further details on the crystal structure investigations of **3** can be obtained from the Cambridge Crystallographic Data Centre, on quoting the CCDC depository number 1056672.

Single-crystal X-ray diffraction analysis

Details of the crystal parameters, data collection and refinement results of **2** and **3**·H₂O are summarized in Table S1. Selected bond lengths and angles are shown in Table S2.

Table S1 The crystal data for **2** and **3**·H₂O

Compound	2	3 ·H ₂ O
Empirical formula	C ₃₈ H ₂₄ O ₈ N ₂ Zn ₂ Si	C ₃₈ H ₂₆ O ₉ N ₂ Zn ₂ Si
Formula weight	795.42	809.8
Crystal system	Tetragonal	Tetragonal
Space group	<i>P4₂/mmc</i>	<i>P4₂/mcm</i>
<i>a</i> /Å	13.9160(12)	9.7078(3)
<i>c</i> /Å	21.142(4)	21.7592(15)
<i>V</i> /Å ³	4094.2(9)	2050.62(17)
<i>T</i> /K	100(1)	291(2)
<i>Z</i>	2	2
<i>D</i> _{calcd} (g cm ⁻³)	0.645	1.311
μ (mm ⁻¹)	0.624	1.117
θ range (°)	1.46-26.11	1.87-25.98
Reflns collected/unique	29346/2287	11587/1127
Data/parameters	2287/109	1127/117
<i>F</i> (000)	808	824
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0628 <i>wR</i> ₂ = 0.1899	<i>R</i> ₁ = 0.0471 <i>wR</i> ₂ = 0.1401
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0695 <i>wR</i> ₂ = 0.1944	<i>R</i> ₁ = 0.0640 <i>wR</i> ₂ = 0.1503
Gof	1.054	1.055

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

Table S2 Selected bond lengths (Å) and angles (deg) for **2**

2			
Zn(1)-N(1)	1.986(2)	Zn(1)-O(1)#1	2.0170(1)
Zn(1)-O(1)#2	2.0170(1)	Zn(1)-O(1)#3	2.0170(1)
Zn(1)-O(1)	2.0170(1)	Zn(1)-Zn(1)#4	2.8762(6)
N(1)-Zn(1)-O(1)#1	99.55(3)	N(1)-Zn(1)-O(1)#2	99.55(3)
O(1)#1-Zn(1)-O(1)#2	160.89(6)	N(1)-Zn(1)-O(1)#3	99.55(3)
O(1)#1-Zn(1)-O(1)#3	87.00(8)	O(1)#2-Zn(1)-O(1)#3	89.84(8)
N(1)-Zn(1)-O(1)	99.55(3)	O(1)#1-Zn(1)-O(1)	89.84(8)
O(1)#2-Zn(1)-O(1)	87.00(8)	O(1)#3-Zn(1)-O(1)	160.89(6)
N(1)-Zn(1)-Zn(1)#4	180.0	O(1)#1-Zn(1)-Zn(1)#4	80.45(3)
O(1)#2-Zn(1)-Zn(1)#4	80.45(3)	O(1)#3-Zn(1)-Zn(1)#4	80.45(3)
O(1)-Zn(1)-Zn(1)#4	80.45(3)	C(6)#3-N(1)-Zn(1)	120.68(1)
C(6)-N(1)-Zn(1)	120.68(1)	C(6)#1-N(1)-Zn(1)	121.11(2)
C(6)#3-N(1)-Zn(1)	121.11(2)	C(6)#2-N(1)-Zn(1)	121.11(2)
C(6)-N(1)-Zn(1)	121.11(2)	C(1)-O(1)-Zn(1)	126.59(1)

Symmetry codes: (#1) -x+1,y,z (#2) x,y,-z (#3) -x+1,y,-z
(#4) -x+1,-y,-z (#5) -x,-y,z (#6) -y,x,-z+1/2
(#7) y,-x,-z+1/2 (#8) x,-y,z (#9) -x+1,-y+1,-z

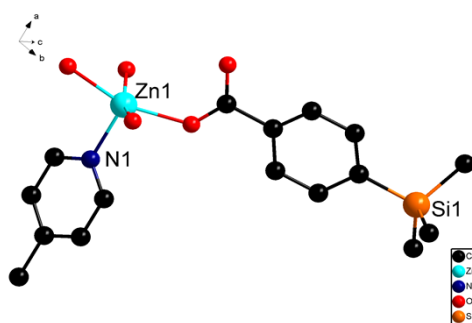


Fig.S1 An ORTEP drawing of the asymmetric unit of **2**. (the H atoms and guest molecules are omitted for clarity)

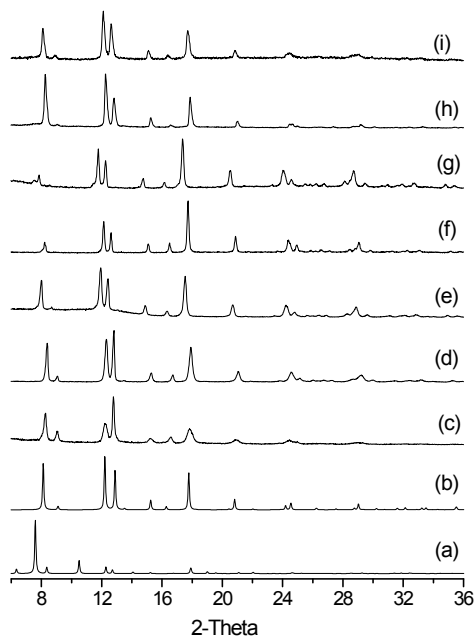


Fig. S2 PXR D patterns. (a) Simulated **2**; (b) simulated **3·H₂O**; (c) as-synthesized **2** washed with CH₂Cl₂ three times, then exposed to air at room temperature for 3 d and converted to **1**; (d) as-synthesized **2** dried at 40 °C for 12 h and exposed to air for 15 d, (e) as-synthesized **2** dried at 40 °C for 12 h and exposed to air for 30 d; (f) as-synthesized **2** dried at 40 °C for 12 h and immersed in water for 15 d; (g) as-synthesized **2** dried at 40 °C for 12 h and immersed in water for 30 d. (h) **2** was exchanged with CH₃OH and CH₂Cl₂ solvent as described above and went through adsorption/desorption experiments during which the samples was activated at 150 °C under vacuum for 12 h and converted to **1**. (i) Sample (h) was put into a 1:1 ratio of NMP and NMA for 3 d, during which solvent was decanted and replaced with fresh portion every 12 h, then dried at 40 °C.

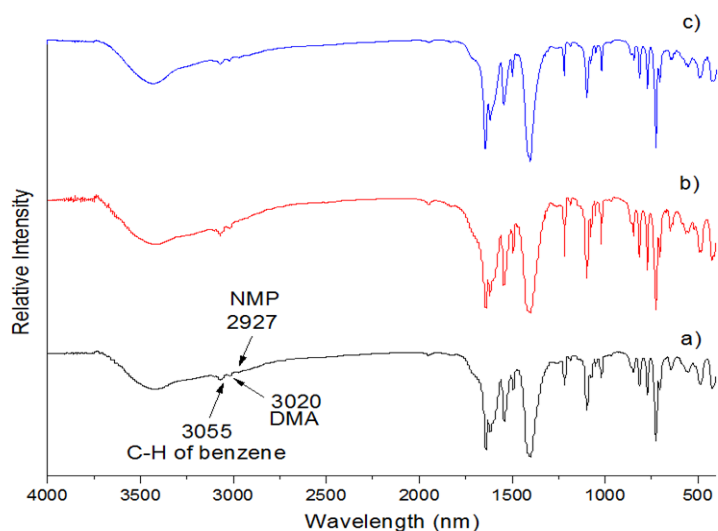


Fig. S3 The IR spectra of the as-synthesized **2** after heating at 40 °C for 12 h which has converted to **1** (a), the as-synthesized **2** after heating at 200 °C for 12 h which has converted to **1** (b), and the solvent-exchanged **2** after evacuating at 150 °C for 12 h which has converted to **1** (c).

The broad peak at around 3400 is due to the adsorbed water. Fig. S3(a) indicates that most physisorbed solvent (NMP and DMA) can be removed after heating the sample at 40 °C for 12 h. It shows that DMA remains in the structure but NMP is removed when activated at 200 °C. Elemental analysis results fit the formula of **1**, indicating that DMA is only in trace amounts.

Fluorescence property

The fluorescence emission of TCS ligand is at 435 nm ($\lambda = 260$ nm) (Fig. 5). The excitation of **1** at 260 nm also gives an emission peak at 435 nm but with much lower intensities. The same peak position and the similar shape of the spectrum of **1** to that of the ligand indicating the emission is ligand based. The weak intensities of the peaks are probably due to the solvent effect since **1** absorbs water from air as indicated by the IR spectra shown in Fig. S3.

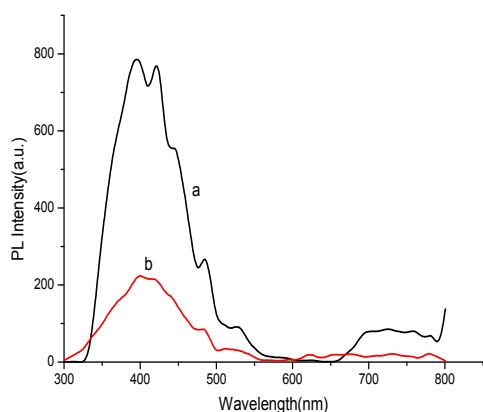


Fig. S4 Solid state photoluminescent spectra of **TCS** (a) and **1** (b). The excitation wavelength is 260 nm.

UV-Vis diffuse reflectance spectrum and band gap of **1**

Fig. S5 shows the UV-vis diffuse reflectance spectra of **1** and TCS, and the characteristic absorption peaks of **1** was 283 nm which was close to 289 nm of TCPS. These absorptions were attributed to the $\pi \rightarrow \pi^*$ transitions of the aromatic rings. The band gap of **1** and TCS were determined based on the spectra. The band gap E_g was defined as the intersection point between the energy axis and the line extrapolated from the linear portion of the adsorption edge in a plot of the Kubelka–Munk function F versus energy E (the inset of Fig. S5). The Kubelka–Munk function, $F = (1-R)^2/2R$, was extracted from the recorded diffuse reflectance data, where R is the reflectance of an infinitely thick layer at any given wavelength.² The band gap (E_g) of **1** was found to be 3.87 eV, which is very similar to that of the ligand. Thus, **1** is a wide gap semiconductor. Similar to UiO-66, in which the organic linker causes a decrease of the band gap of ZrO_2 band gap (from 5.19 to 4.07), the organic linker reduces the band gap of ZnO (5.0 eV) to 3.87 eV; while for MOF-5, the organic linkers lead to an increase of E_g of the band gap of ZnO (from 3.4 eV to 5.0 eV).³

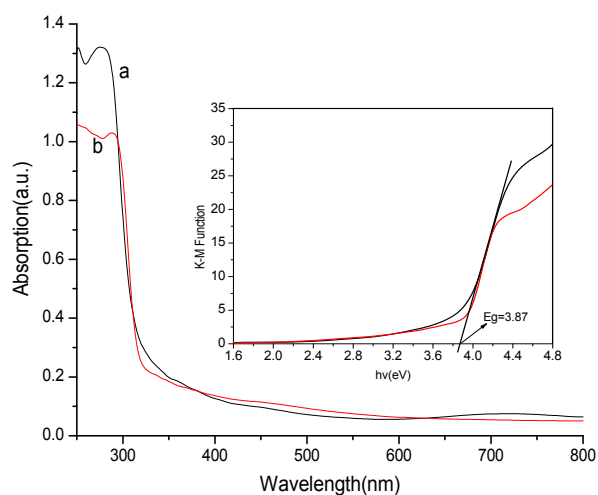


Fig. S5 Diffuse reflectance UV-vis spectra of **1** (a) and the ligand **TCS** (b). Inset: K-M function vs. energy (eV) of **1** and **TCS**.

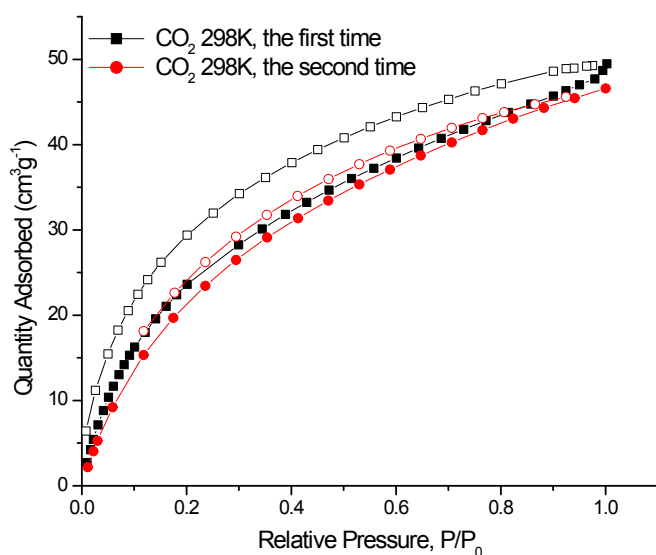


Fig. S6 The CO₂ sorption isotherms for **1** measured at 298 K (Filled and empty symbols represent adsorption and desorption data respectively).

We repeated the CO₂ adsorption/desorption measurement by heating the sample at 150 °C for 12 h under vacuum (red lines). This reduced the hysteresis of the isotherms compared with the previous experiment where the sample was evacuated only at room temperature for less than 2 h (the black lines).

References

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