Electronic Supplementary Information

Dynamic Behaviours of a Rationally Prepared Flexible MOF by Postsynthetic Modification of Ligand Struts

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S1. Materials and Instrumentation.

General: All chemicals were of reagent grade from commercial sources and used without further purification. Powder X-ray diffraction (PXRD) patterns were collected in a sealed glass capillary on a Rigaku DMAX 2500 power diffractometer with ultra 18 KW Cu radiation. Thermogravimetric analysis (TGA) was performed using a Shimadzu TGA-60 equipped with a alumina pan and heated at a rate of 5 °C/min under nitrogen atmosphere. ¹H and ³¹P NMR data were collected using Bruker AVANCE III 600 spectrometers. Solid-state NMR spectra were recorded on a Bruker ANANCE III 400 M spectrometer. IR spectra were recorded from KBr pellets on a Brucker EQUINOX 55 FT-spectrometer. UV-Vis absorption spectra were obtained using a Shimadzu UV-2550 PC UV-Vis recording Spectrophotometer. The contents of Zn, Mn, Fe, Co, Mg and Zr were determined by a Varian 710-ES Inductively Coupled Plasma-Atomic Emission Spectrometer (ICP-AES). N₂ and vapor sorption studies were carried out using a Micromeritics ASAP 2020 surface area analyzer and a Hiden IGA100B intelligent gravimetric sorption analyser, respectively. Raman spectra were collected on a LabRAM HR system using a Ventus 532 laser system.

4,4'-Stilbenedicarboxylic acid (H₂SDC), benzoic acid was purchased from Energy Chemical. N,N-dimethylformamide (DMF), zirconium(IV) chloride were purchased from Alfa Aesar. Trifluoroacetic acid, Trimethylphosphine (1 M solution in THF), tetraphenylporphyrin (TPP), magnesium(II) meso-tetraphenylporphine (MgTPP) were purchased from J&K Chemical. (S)-CPA-1, (S)-CPA-2, (S)-BINAP were purchased from Daicel Chiral Technologies (China). Cobalt phthalocyanine (CoPc) were purchased from Sigma-Aldrich. Zinc Phthalocyanine (ZnPc) and Iron phthalocyanine (FePc) were purchased from TCI. Trichloromethane (CHCl₃), ethanol (C₂H₅OH), tetrahydrofuran (THF) and acetone were purchased from Beijing Chemical Reagent Company.

Drying of solvents: commercial DMF was stirred in calcium hydride for 24 hours, and subsequent stored over 4Å molecular sieves. A 1-L sample of commercial ethanol distilled from Mg/I₂. Commercial THF, CHCl₃ and acetone were stored over 4A molecular sieves.

Synthesis

Crystals of 1. ZrCl₄ (0.024 g, 0.102 mmol), benzoic acid (0.377 g, 3.086 mmol) were added into 5ml DMF and was sonicated for several minutes until a clear solution

formed. 4,4'-stilbenedicarboxylic acid (0.027 g, 0.102 mmol) and CF₃COOH (0.03 ml) was added and further sonicated for 10 minutes, and then the reaction mixture was added to a 25 ml Teflon-lined stainless steel Parr bomb and placed in the oven at 130°C for 3 days. The reaction vessel was removed from the oven and allowed to cool to room temperature. The obtained crystals were exchanged with fresh dehydrated DMF at 120°C for 1 day and then with dehydrated C₂H₅OH at 70°C for 1 day, which repeated for 3 times.

Crystals of 2. 2 was obtained from 1 by post-synthetic bromination: The guest-exchanged crystals 1 (100 mg) were immersed in CHCl₃ (5 mL) and liquid Br_2 (10 drops) was added and being placed in the oven at 40°C. After 3 days, unreacted Br_2 and CHCl₃ were decanted off and the crystals were washed several times with fresh CHCl₃, then stored in CHCl₃.

Crystals of 1'. Crystals of **2** were debrominated back to alkene by heating in DMF at 120°C after 2 days, and the obtained crystals **1'** were characterized by powder XRD, ¹H-NMR, Raman, IR, BET, confirming a successful re-formation of the parent **1**.

S2. Structural Analysis by Powder X–ray Diffraction

The flexible behaviours of 2 were analyzed by Powder XRD patterns. The solvated samples were obtained by immersion in DMF for 20 min; and the desolvated samples were afforded after immersion in CHCl₃ for one day and subsequent desolvation under vacuum for four hours.



Figure S1. Powder XRD of 2 in the crystal deformation/recovery process.



Figure S2. Powder XRD of sample 2 after adsorption: Co-Pc⊂2 (a), Fe-Pc⊂2 (b), Zn-Pc⊂2 (c), TPP⊂2 (d), MgTPP⊂2 (e), (R)-BINAP⊂2 (f), (S)-BINAP⊂2 (g), (S)-CPA-1⊂2 (h) and (S)-CPA-2⊂



Figure S3. Powder XRD of Co-Pc⊂1 (a), (S)-BINAPO⊂1 (b), (S)-CPA-1⊂1 (c) and (S)-CPA-2⊂1 (d).

S3. Infrared Spectroscopy Analysis

The IR spectra of 2 demonstrate that quantitative bromination has occurred due to the complete disappearance of the stretch at ca. 960 cm⁻¹, which is typical of alkene units conjugated with aromatic rings. The appearance of a peak at 545 cm⁻¹ in 2 corresponds to the stretching of the newly formed dibromoalkane moiety. Along with the debromination process, 1' was obtained by heating of 2 in DMF, resulting the resurgence of the stretch at 960 cm⁻¹ and complete disappearance of the peak at 545 cm⁻¹.



Figure S4. IR spectra performed at room temperature in the 4000-400 cm⁻¹ region of **1**, **2** and **1**'. In turn, corresponds to the Line 1, 2, 3.

S4. Thermogravimetric Analysis (TGA)

TGA was carried out in flowing nitrogen atmosphere (20 mL/min). The approximate sample weight was 5 mg in all experiments and the heating rate was 10 °C/min. It can be seen that 1 exhibits typical thermal behavior for rigid porous MOFs, with the large mass loss around 450 °C attributed to loss of the ligand (see Figure S5). However, the TG curve of 2 is completely different with 1. Because of the flexibility of ligand, the whole framework is severely distorted and the windows of the pores in the framework are blocked, which leads to different release stages of dissociated ligand and solvent (see Figure S6). The re-obtained 1' exhibits a similar thermal behavior with 1 (see Figure S7).



Figure S6. TGA curve of 2.



Figure S7. TGA curve of 1'.

S5. Raman Spectroscopy Analysis.



Figure S8. Raman spectra of 1 (a), 2 (b) and 1' (c). Spectroscopic evidence of the transformation between 1 and 2 is found in the loss and appearance of an alkene stretch at 1640 cm^{-1} .

S6. ¹H NMR Spectra in Solution

¹H NMR of digested MOFs: In a typical procedure, approximately 5 mg activated MOF samples were digested with sonication in the mixture of 0.55 mL DMSO-d₆, 30 μ L 30% DCl and 5 mg CsF for ¹H NMR study. In this case, a broad peak was observed around 5 ppm.



Figure S9. ¹H NMR spectra of 1 (a), 2 (b) and 1' (c).

S7. Gas Adsorption Analysis

Approximately 100 mg of activated sample was used for all measurements. Prior to the measurements, the samples were degassed for 10 h at 150 °C. Ultra-high purity N₂ was used for all measurements. Oil-free vacuum pumps and oil-free pressure regulators were used for all measurements to prevent contamination of the samples during the isotherm measurement. Total pore volumes were calculated from the uptake at a relative pressure (P/P₀) of 0.95. The BET surface areas calculated from the isotherms show a typical BET behavior for Zr-MOFs with 2867 m²g⁻¹ for **1** and 2640 m²g⁻¹ for **1**'. The BET surface areas were determined by multi-point BET method using the adsorption data in the relative pressure (P/P₀) range of 0.05 to 0.30. The isotherm points chosen to calculate the BET surface area were subject to the three consistency criteria detailed by Walton and Snurr.



Figure S10. N₂ adsorption isotherms of 1 collected at 77 K.



Figure S11. N₂ adsorption isotherms of 1' collected at 77 K.



Figure S12. Pore size distribution of **1** and **1**', calculated from nitrogen adsorption data using the HK method. The major peak centered at 13.6 Å agrees well with the pore size from the structural model.

S8. Vapor Adsorption Analysis



Figure S13. Vapor adsorption isotherms of 1 at room temperature.

S9. X-ray energy dispersive spectrum

Freely choosing two positions in the material surface for testing, the results show the presence of bromine element, corresponding to ¹H NMR, Raman and IR spectra.



Element	Wt %	At %
СК	44.64	71.90
ОК	15.60	18.86
BrL	27.06	06.55
ZrL	12.70	02.69

Element	Wt %	At %
СК	36.37	65.16
ОК	16.92	22.75
BrL	32.09	08.64
ZrL	14.62	03.45

Figure S14. Scanning electron microscopy-X-ray energy dispersive spectrum (SEM-EDS) of 2.

S10. Soild-State ¹³C NMR Analysis



Figure S15. Solid-state ¹³C NMR spectra of **1** (a), solvated **2** (b), **2-cp** (c) and resolvated **2**. The asterisks mark the signal of solvent DMF. It is noteworthy that there are two sets of resonances of DMF at 166, 38, 33 ppm and 163, 36, 31 ppm, respectively, which demonstrates that DMF molecules locate two different sites of the interior cavity in crystalline **2**.

The chemical shifts of ¹³C are ca. 170 (C₁), 140 (C₅) and 129-135 ppm (C₂-C₄, C₆) for 4,4'stilbenedicarboxylic in **1**, ca. 170 (C₁), 145 (C₅), 127-134 (C₂-C₄) and 54 ppm (C₆) for meso-4,4'-(1,2-dibromoethane-1,2-diyl)dibenzoate in solvated **2**, ca. 171 (C₁), 144 (C₅), 130 (C₂-C₄) and 53 ppm (C₆) for meso-4,4'-(1,2-dibromoethane-1,2-diyl)dibenzoate in **2-cp**.

S11. Photos of Crystals after Adsorption



Figure S16. Optical photos of a) 2, b) TPP⊂2, c) MgTPP⊂2, d) CoPc⊂2, e) ZnPc⊂2 and f) FePc⊂2.



Figure S17. Photos of crystals immersed in ethanol after adsorption. From left to right: (1) TPP⊂2,
(2) MgTPP⊂2, (3) CoPc⊂2, (4) ZnPc⊂2 and (5) FePc⊂2.

S12. UV-Vis Absorption Analysis



Figure S18. (left) The UV-vis spectra of TPP with different concentrations; (right) The UV-vis absorption calibration curves of TPP solutions at 416 nm. 1 after immersion in TPP solution did not show perceptible absorption. The results demonstrate From the concentration of digested TPP **<2** sample, the guest loading ratio per octahedral cage was estimated as 24%.



Figure S19. (left) The UV-vis spectra of Mg-TPP with different concentrations; (right) The UV-vis absorption calibration curves of Mg-TPP solutions at 418 nm. 1 after immersion in Mg-TPP solution did not show perceptible absorption. From the concentration of digested Mg-TPP<2 sample, the guest loading ratio per octahedral cage was estimated as 40%, which is in agreement with the result of ICP-AES data (molar ratio of Zr/Mg = 14.2).



Figure S20. (left) The UV-vis spectra of Co-Pc with different concentrations; (right) The UV-vis absorption calibration curves of Co-Pc solutions at 664 nm. 1 after immersion in Co-Pc solution

did not show perceptible absorption. From the concentration of digested Co-Pc $\subset 2$ and Co-Pc $\subset 1$ samples, the guest loading ratios per octahedral cage were estimated as 71% and 12%, respectively, which are in agreement with the result of ICP-AES data (molar ratio of Zr/Co = 8.5 and 49.4, respectively).



Figure S21. (left) The UV-vis spectra of Fe-Pc with different concentrations; (right) The UV-vis absorption calibration curves of Fe-Pc solutions at 667 nm. 1 after immersion in Fe-Pc solution did not show perceptible absorption. From the concentration of digested Fe-Pc \simeq 2 sample, the guest loading ratio per octahedral cage was estimated as 19%, which is in agreement with the result of ICP-AES data (molar ratio of Zr/Fe = 30.5).



Figure S22. (left) The UV-vis spectra of Zn-Pc with different concentrations; (right) The UV-vis absorption calibration curves of Zn-Pc solutions at 670 nm. 1 after immersion in Zn-Pc solution did not show perceptible absorption. From the concentration of digested Zn-Pc \subset 2 sample, the guest loading ratio per octahedral cage was estimated as 23%, which is in agreement with the result of ICP-AES data (molar ratio of Zr/Zn = 25.7).



Figure S23. Release ratio of TPP⊂2 in CHCl₃, which was monitored by UV-vis spectra of TPP. After 170 hours TPP**⊂2** only released about 3.2% TPP guest.

S13. Theoretical Calculation



Figure S24. The host-guest structures of TPP⊂2 that were optimized using the PM6 semiempirical method.

TPP

S14. ¹H NMR Spectra after Adsorption of Guests



(S)-CPA-1





Figure S25. The ¹H NMR spectra of digested materials after adsorption of (S)-CPA-1. a) (S)-CPA-1 \subset 2; b) (S)-CPA-1 \subset 1 formed during debromination; c) 1 after immersion in (S)-CPA-1 solution. The results demonstrate that 2 and the formed 1 after debromination both accommodate one guest per octahedral cage, while 1 cannot adsorb (S)-CPA-1.



Figure S26. The ¹H NMR spectra of digested materials after adsorption of (S)-CPA-2. a) (S)-CPA-2 \subset 1 formed during debromination; b) 1 after immersion in (S)-CPA-2 solution. The results demonstrate that during the debromination process, the formed 1 originated from 2 can immobilize about 0.5 guest per octahedral cage, while 1 cannot adsorb (S)-CPA-2.





Figure S27. The ¹H NMR spectra of digested materials after adsorption of (S)-BINAP. a) 1 formed during debromination; b) 1 after immersion in (S)-BINAP solution. c) The ³¹P NMR spectrum of digested materials after adsorption of (S)-BINAP, which demonstrates that during the debromination process, BINAP has been completely oxidized into BINAPO. The formed 1 originated from 2 can immobilize about one guest BINAPO per octahedral cage, while 1 did not show any adsorption for guest molecule.



Figure S28. The ¹H NMR spectra of digested materials after adsorption of Au_3 . a) $Au_3 \subset 2$; b) 1 after immersion in Au_3 solution. The results demonstrate that 2 can adsorb ca. 0.42 guest per octahedral cage while 1 cannot adsorb Au_3 .





Figure S29. Circular dichroism spectra of pure (S)-CPA-1 solution (black), digested (S)-CPA-1⊂2 (red) and digested (S)-CPA-1⊂1 (blue).