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Electronic Supplementary Information for

Trigonal prism or octahedron: the conformation changing of a dendritic six-node ligand in MOFs

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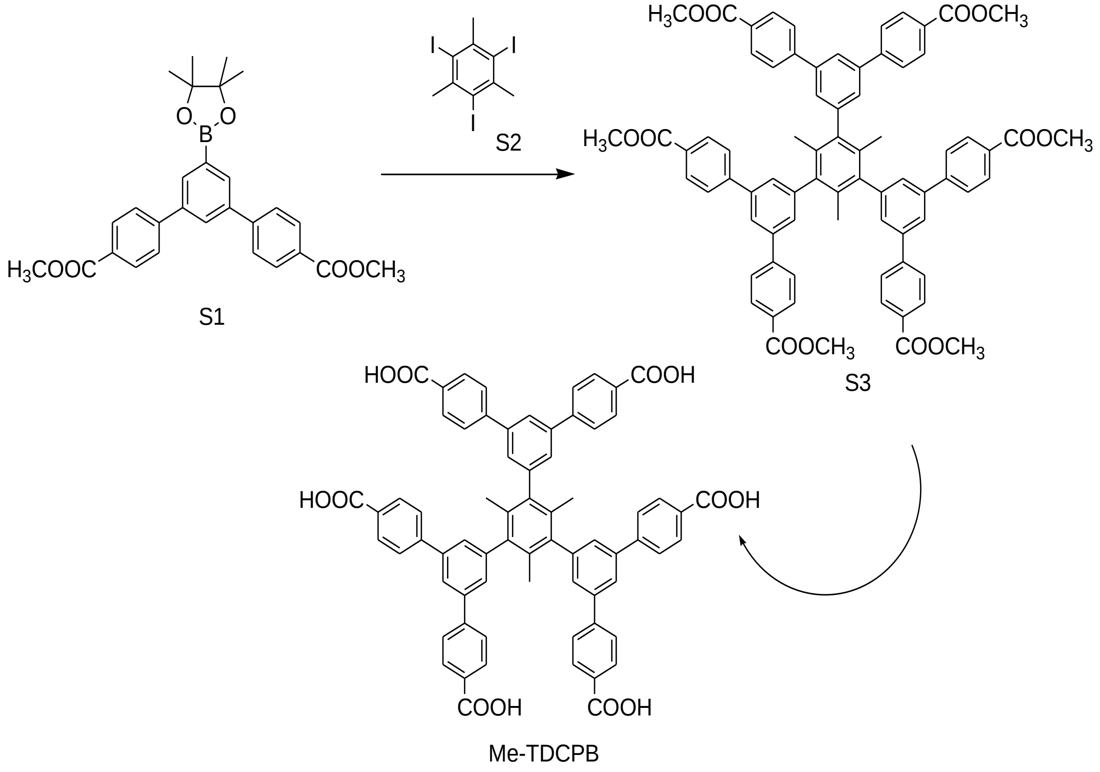
1. General Methods

All the chemical reagents used were purchased from commercial source, unless otherwise noted. Powder X-ray diffractions (PXRD) were collected on a Scintag X1 diffractometer with Cu-Kα (λ = 1.5418 Å) at 50 kV, 200 mA. The elemental analyses data were collected using a PerkinElmer 240C element analyzer. Thermogravimetric analysis (TGA) measurements were performed at a Perkin-Elmer TGA 7 thermogravimetric analyzer with a heating rate of 10 ºC/min at air. ^{1}H NMR and ^{13}C NMR spectra were collected using a Bruker AV 400 or VARIAN 300 spectrometer at 298 K. Tetramethylsilane (TMS) of internal standard in ^{1}H NMR experiments was used, and deuterated solvents as internal standard in ^{13}C NMR experiments ($CDCl_3$, $\delta = 77.00$ ppm; D_6-DMSO, $\delta = 39.52$ ppm). N_2 and H_2 adsorption tests were performed with equipment of Autosorb-iQ2-MP-AG.

2. Synthesis:



Scheme S1 Synthetic route of Me-TMCPB ligand

Synthsis of 1,3,5-Tri-methyl-2,4,6-tri(3,5-di(4-methoxylcarboxyphenyl-1-yl)phenyl-1-yl)benzene (S3). Compound S1 (2.0 g, 4.2 mmol), S2 (0.49 g, 1.00 mmol), Na_2CO_3 (0.53 g, 5.0 mmol) and $Pd(PPh_3)_4$ (0.090 g, 0.076 mmol) were added to a three necked flask with degassed toluene (30 ml), ethanol (15 ml) and water (15 ml). The solution was stirred under nitrogen atmosphere for 30 h at 110 ^{o}C, and subsequently extracted using trichloromethane (80 ml × 3), washed with brine (80 ml), and dried with anhydrous $MgSO_4$. The filtrate was eliminated under reduced pressure. The residue was purified using column chromatography with silica gel (trichloromethane/petroleum ether/methanol = 50/30/1, v/v/v) to obtain S3 of 0.71 g (yield: 62 %). ^{1}H NMR (400 MHz, d6-DMSO), δ (ppm): 8.152 (d, 12H, J = 8.4 Hz), 7.879 (t, 3H, J =1.5 Hz), 7.777 (d, 12H, J = 8.4 Hz), 7.590 (d, 6H, J = 1.5Hz), 3.955 (s, 18H), 1.950 (s, 9H). ^{13}C NMR (100 MHz, d6-DMSO), δ (ppm): 166.873, 145.021, 143.254, 141.255, 139.540, 133.598, 130.204, 129.317, 127.940, 127.152, 124.658, 52.181, 19.924.

Synthsis of 1,3,5-Tri-methyl-2,4,6-(3,5-di(4-carboxyphenyl-1-yl)phenyl-1-yl)benzene (Me-TDCPB). Compound S3 (0.71 g, 0.62 mmol) and NaOH (2.0 g, 50 mmol) were added to a flask with THF (40 ml), ethanol (40 ml) and water(40 ml). The solution was stirred for 24 h under reflux. At room temperature , the pH value of the solution is adjusted to ~1.0 by concentrated HCl. The resultant white precipitate was filtered to obtain 2 of 0.61 g (yield: 90%). ^{1}H NMR (400 MHz, d6-DMSO), δ (ppm): 7.992-8.085 (m, 24H), 7.693 (d, 9H, J = 1.5Hz), 1.909 (s, 9H). ^{13}C NMR (100 MHz, d6-DMSO), δ (ppm): 166.929, 143.707, 142.913, 140.219, 138.824, 132.706, 129.864, 129.788, 127.517, 127.130, 124.040, 19.525.

Synthsis of JUC-103, ((Zn_4O)·(H2O)·(Me-TDCPB)·(xGuests)). Me-TDCPB (10 mg, 0.0093 mmol) and $Zn(NO_3)_2·6H_2O$ (20 mg, 0.067 mmol) were added to a mixed solvent of DMF (3.0 ml) and H_2O (0.60 ml), and then 0.050 ml concentrated HNO_3 was added. After ultrasonic diffusion, the solution was heated at 85 ^{o}C for 72 h to obtain the product of 65% yield (based on ligand) as colorless crystal.

Synthsis of JUC-104, (($Pb_6·4H_2O$)·(Me-TDCPB) ·(xGuests)). Me-TDCPB (10 mg, 0.0093 mmol) and $Pb(NO_3)_2$ (30 mg, 0.090 mmol) were added to a mixed solvent of DMF (3.0 ml) and H_2O (0.010 ml). After ultrasonic diffusion, the solution was heated at 85 ^{o}C for 72 h to obtain the product of 55% yield (based on ligand) as colorless crystal.

Because the guest molecules cannot be resolved in the crystal structure, the exact molecular formula of the two MOFs with guest molecules cannot be calculated and we do not characterize the element components in the MOFs.

3. Crystallographic data determination

Block crystals of JUC-103 and JUC-104 were picked for X-ray structural analysis on a Bruker SMART CCD diffractometer with a Mo-Kα radiation source (λ = 0.71073 Å) at 293 K. The structure was solved and refined by full matrix least-squares on F^2 values (SHELXL-97).[1] Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were fixed at calculated positions and refined using a riding mode. It is unable to locate the H atoms of the water molecule. The large volume fractions of disordered solvents in the lattice pores could not be modelled in terms of atomic sites. SQUEEZE routine in PLATON was used to remove the contribution of the electron density by the remaining guest molecules. In JUC-103, Ueq value of O6 is high compared to the neighbors and a high peak hole exists. This is due to the poor data of JUC-103. In JUC-104, the bond length of Pb2-O6 is too short and unreasonable. This is due to two reasons: 1) There exists high pore volume and the diffraction data of JUC-104 is very poor; 2) The high ghost peak of Pb2 leads to high residual electron density so that the O6 position is biased. If we restrict the bond length of Pb2-O6, the ligand structure will become more biased. However, from chemical structure we can exactly make sure that the position is an O atom.

Table S1 Crystal data and structure refinement for JUC-103 and JUC-104 single crystals.

Complex	JUC-103	JUC-104
Empirical formula	$C_{69}H_{42}O_{14}Zn_4$	$C_{69}H_{42}O_{14}Pb_3$
Formula weight	1356.51	1716.60
Temperature (K)	293(2)	293(2)
Crystal system, Space group	Rhombohedral, *R*-3	Monoclinic, *C*2/*c*
Unit cell dimensions	$a = b =$ 19.8906(7) Å $c =$ 83.351(6) Å $\alpha = \beta = 90°$ $\gamma = 120°$	$a =$ 26.4685(12) Å $b =$ 22.6646(11) Å $c =$ 40.1626(18) Å $\alpha = \beta = 90°$ $\gamma =$ 100.1710(10) °
Volume (Å^3)	28559(2)	23714.8(19)
Z, Calculated density (g/cm^3)	12, 0.946	8, 0.962
Absorption coefficient (mm^{-1})	1.038	4.283
F(000)	8256	6512
Crystal size (mm)	0.4 × 0.3 × 0.3	0.4 × 0.4 × 0.4
θ range for data collection (°)	1.28 to 28.27	1.19 to 25.25
Limiting indices	$-21 \le h \le 26$ $-25 \le k \le 25$ $-107 \le l \le 110$	$-31 \le h \le 31$ $-19 \le k \le 27$ $-48 \le l \le 42$
Reflections collected / unique	57010 / 7856 $R_{int} = 0.0452$	60662 / 21458 $R_{\mathrm{int}} = 0.0589$
Completeness to θ	28.27, 99.6 %	25.25, 100.0 %
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	0.7458 and 0.6815	0.2791 and 0.2791
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	7856 / 6 / 262	21458 / 53 / 775
Goodness-of-fit on F^2	1.055	0.961
Final *R* indices [$I > 2\mathrm{sigma}(I)$]	$R_1 = 0.0773$ $wR_2 = 0.2536$	$R_1 = 0.0723$ $wR_2 = 0.2130$
R indices (all data)	$R_1 = 0.1015$ $wR_2 = 0.2763$	$R_1 = 0.1188$ $wR_2 = 0.2316$
Largest diff. peak and hole (e.Å^{-3})	1.461 and -3.265	2.716 and -1.842
CCDC	896050	896049

4. Conformation optimization

To obtain the most optimized conformation of Me-TDCPB, the forcite module of Material Studio software is used. Geometry optimization work with fine quality is selected.

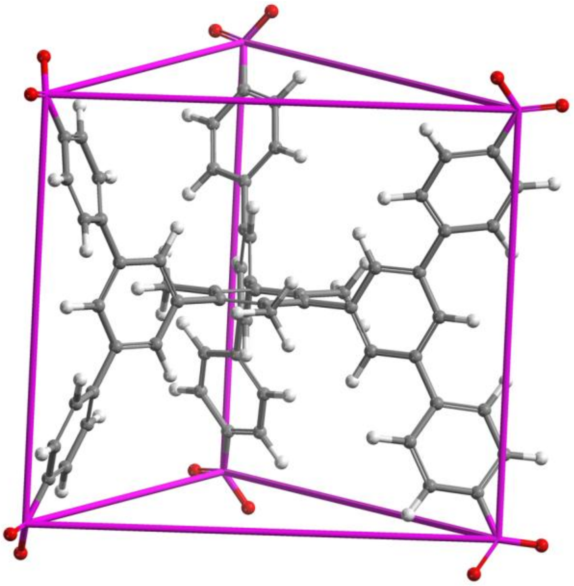


Fig. S1, Calculated conformation of Me-TDCPB

5. Asymmetrical unit of JUC-103

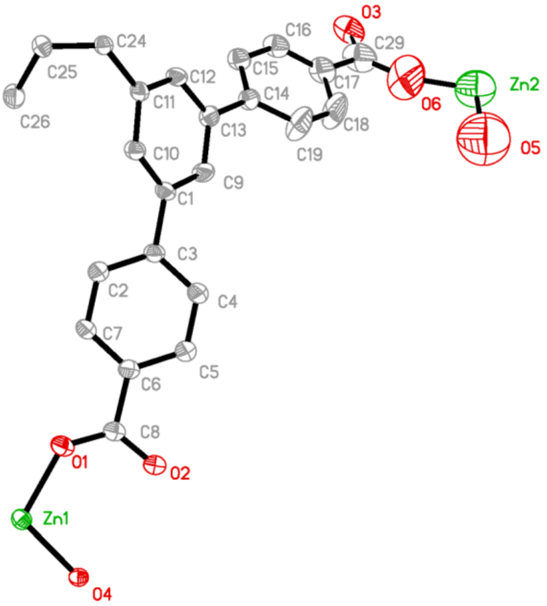


Fig. S2 Asymmetrical unit of JUC-103

6. XRD patterns of JUC-103

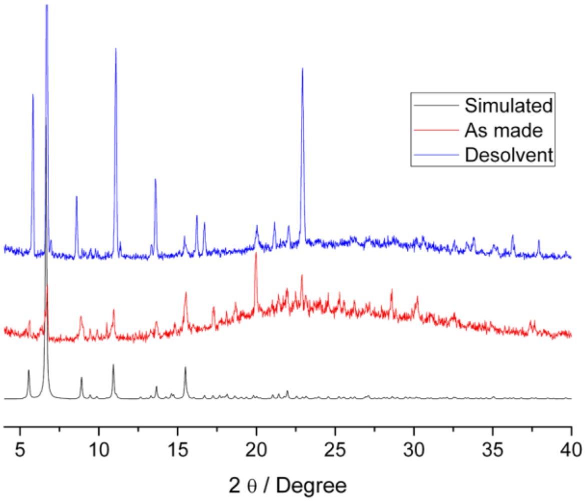


Fig. S3 XRD patterns of JUC-103

7. The cage structure in JUC-103

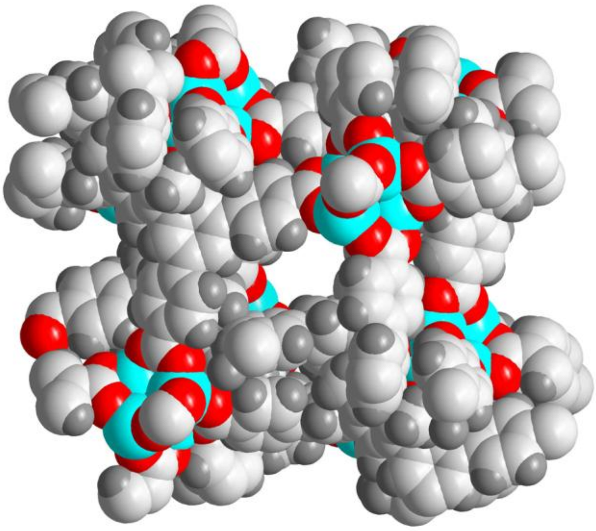


Fig. S4 The cage structure in JUC-103

8. The torsion of Me-TDCPB in JUC-103

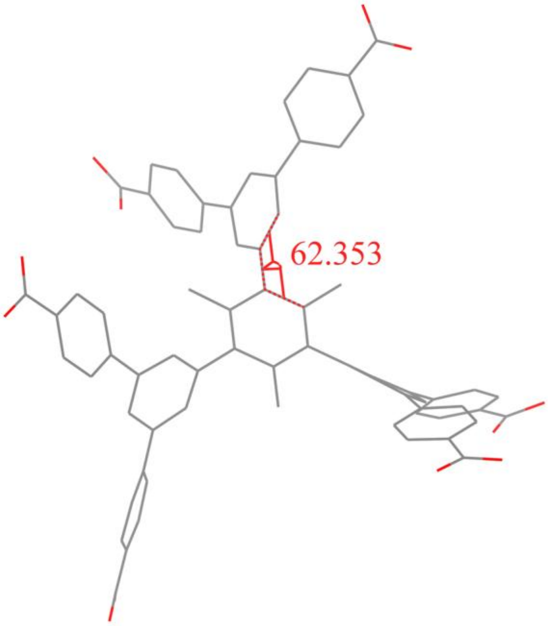


Fig. S5 The torsion of Me-TDCPB in JUC-103

9. The distances between two interpenetrated structures

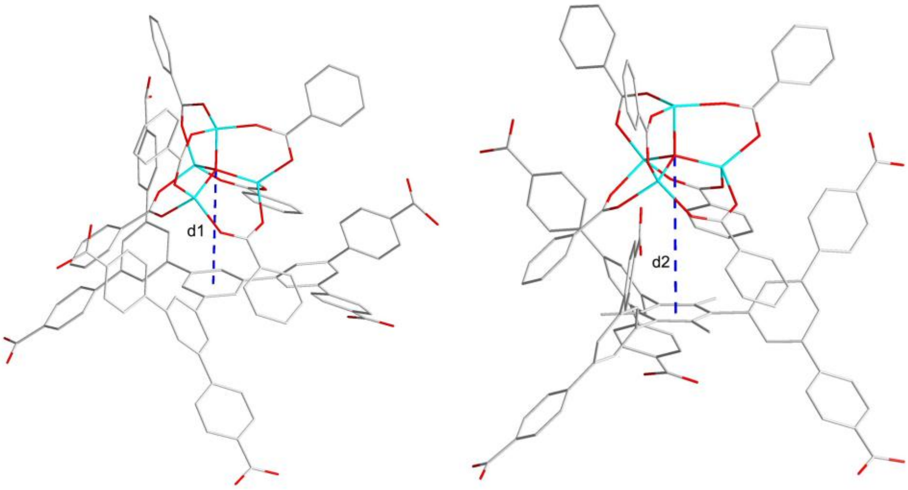


Fig. S6 The distances of two interpenetrated structures in JUC-100 (left) and JUC-103 (right), d1=5.609 Å and d2=6.418 Å.

10. TG curve of JUC-103

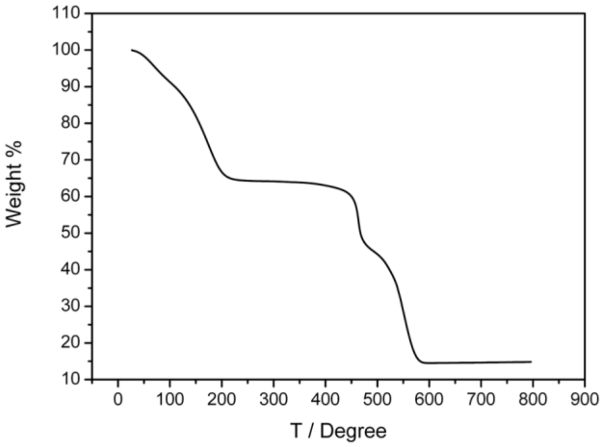


Fig. S7 TG curve of JUC-103

11. Asymmetrical unit of JUC-104

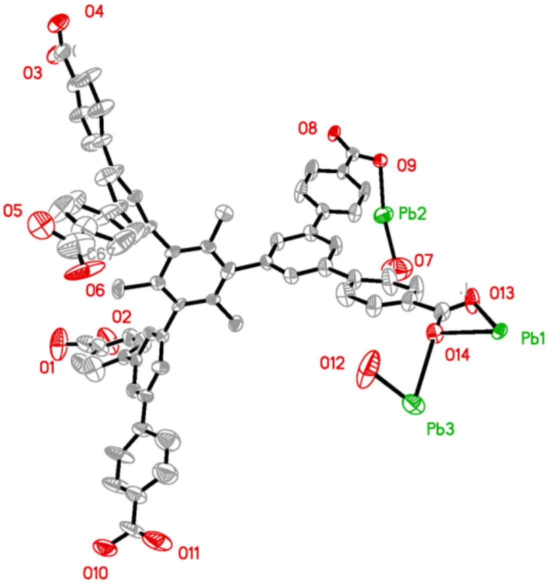


Fig. S8 Asymmetrical unit of JUC-104

12. TG curve of JUC-104

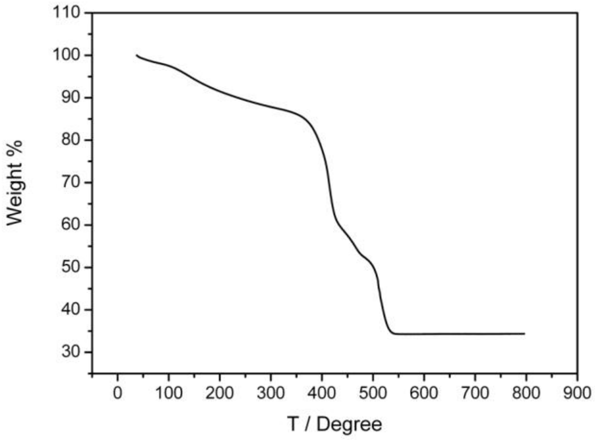


Fig. S9 TG curve of JUC-104

13. XRD patterns of JUC-104

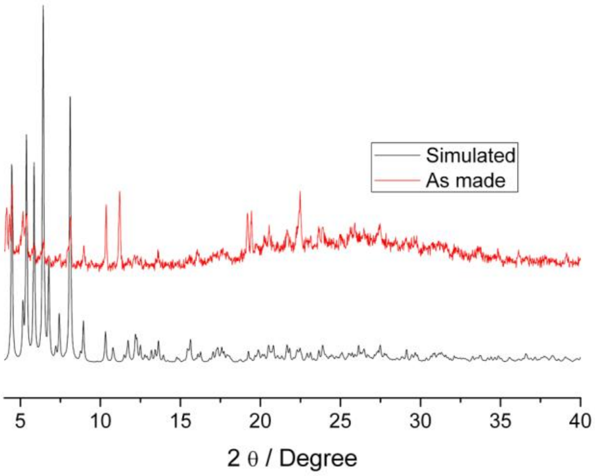


Fig. S10 XRD patterns of JUC-104

14. The torsion of Me-TDCPB in JUC-104

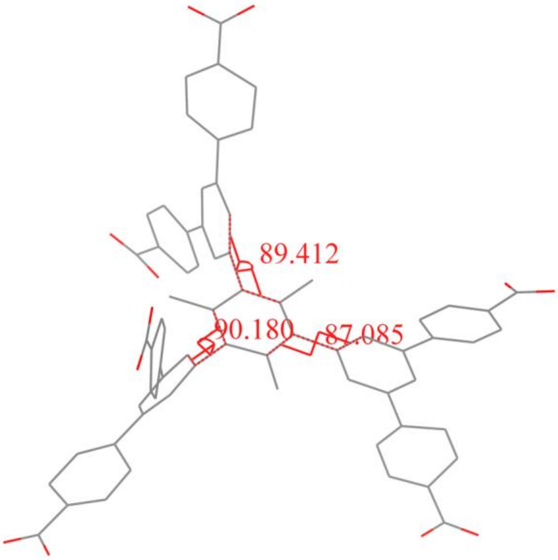


Fig. S11 The torsion of Me-TDCPB in JUC-104

15. Ideal Adsorption Solution Theory (IAST) calculations:

The IAST adsorption selectivity, S, for binary mixtures of **1**(C_2H_6, C_2H_4)/**2**(CH_4, N_2), is defined as follows:

$S=(q_1/q_2)/(p_1/p_2)$

where q_i and p_i (i=1,2) are the mole fractions of component **1** and **2** in the adsorbed and bulk phases, respectively. The IAST calculations were carried out for binary mixture containing 50% **1** and 50% **2**, which is typical composition of flue gases.