Electronic Supplementary Information for

A novel low density metal-organic framework with pcu topology by dendritic ligand

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Contents: The preparation and characterization of the ligand and single crystal, TGA, PXRD, IR, NMR and other measurements.
**General Methods:** All the chemical reagents used were bought from commercial supplier without further purification, unless otherwise noted. Powder X-ray diffractions (XRD) were carried out on Scintag X1 diffractometer with Cu-Kα (λ = 1.5418 Å) at 40 kV, 35 mA. The elemental analyses were carried out on a PerkinElmer 240C element analyzer. Fourier-Transform infrared spectra were got with a Nicolet Impact 410 FT-IR spectrometer where KBr disks dispersed with sample powders was used in the 4000–400 cm⁻¹ range. Thermogravimetric analysis (TGA) curve were collected on a Perkin-Elmer TGA 7 thermogravimetric analyzer with a heating rate of 10 °C/min at air. ¹H NMR and ¹³C NMR spectra were collected using a Bruker AV 400 or VARIAN 300 spectrometer at 298 K. Tetramethysilane (TMS) of internal standard in ¹H NMR experiments was used, and deuterated solvents as internal standard in ¹³C NMR experiments (CDCl₃, δ = 77.00 ppm; D₆-DMSO, δ = 39.52 ppm). Nitrogen and hydrogen adsorption experiments were performed with Autosorb-iQ2-MP-AG. High resolution mass spectra (HRMS) were collected using a FT-ICR-MS instrument (model: IonSpec 7.0T).

**Synthesis of the Ligand and JUC-100:**

**Dimethyl 5′-bromo-[1,1′:3′,1′′-terphenyl]-4,4′″-dicarboxylate (1):**

1,3,5-Tribrombenzene (5.0 g, 16 mmol), p-methoxyl-carbonphenylboronic acid (7.2 g, 40 mmol), Na₂CO₃ (8.4 g, 79 mmol), Pd(PPh₃)₄ (1.3 g, 1.1 mmol) were added to a three-necked flask with degassed toluene-methanol-water (80 ml: 40 ml: 40 ml). The solution was stirred under nitrogen atmosphere for 50 h with reflux. The product was extracted using dichloromethane (80 ml×3), washed with brine (80 ml), and dried with anhydrous MgSO₄. The filtered solution was eliminated under reduced pressure. The residue was purified using column chromatography of silica gel (dichloromethane/ petroleum = 1/ 2, v/ v) to obtain compound 1 of 2.5 g (yield: 37%).

¹H NMR (CDCl₃) 8.15 (d, 4 H, J = 8.0 Hz), 7.78 (s, 2 H), 7.75 (s, 1 H), 7.69 (d, 4 H, J = 8.0 Hz), 3.96 (s, 6 H).

**Dimethyl 5′-pinacolatoborontel-[1,1′:3′,1′′-terphenyl]- 4,4′″-dicarboxylate (2):**

Compound 1 (2.3 g, 5.3 mmol), bis(pinacolato)diboron (1.4 g, 5.7 mmol), KOAc (4.0 g, 40 mmol), and Pd(dppf)Cl₂ (0.12 g, 0.16 mmol) were added to a three-necked flask
with degassed 100ml 1,2-dimethoxyethane (DME). The solution was stirred for 3 h with reflux to get the product which was eliminated under reduced pressure. The residue was extracted using dichloromethane (80 ml × 3), washed with brine and dried with anhydrous MgSO4. The filtered solution was eliminated under reduced pressure. The residue was purified using column chromatography of silica gel (dichloromethane/ petroleum = 1/ 1, v/ v) to obtain 2 of 2.0 g (yield: 78%). 1H NMR (CDCl3), 8.13 (d, 4 H, J = 8.2 Hz), 8.09 (d, 2 H, J = 6.0 Hz), 7.94 (t, 1 H, J = 2.0Hz), 7.76 (d, 4 H, J = 8.2 Hz), 3.95 (s, 6 H), 1.39 (s,12 H); 13C NMR (CDCl3) 166.953, 145.225, 140.147, 133.320, 130.066, 129.077, 128.956, 127.253, 84.162, 52.125, 24.877

1,3,5-Tri(3,5-di(4-methoxylcarboxyphenyl-1-yl)phenyl-1-yl)benzene (3):

Compound 2 (2.0 g, 4.2 mmol), 1,3,5-tribromobenzene (0.31 g, 1.0 mmol ), Na2CO3 (0.53 g, 5.0 mmol) and Pd(PPh3)4 (0.090 g, 0.076 mmol) were added to a three necked flask with degassed toluene-methanol-water (30 ml, 15 ml, 15 ml). The solution was stirred under nitrogen atmosphere for 50 h with reflux. The product was extracted using CHCl3 (80 ml × 3), washed with brine (80 ml), and dried with anhydrous MgSO4. The filtered solution was eliminated under reduced pressure. The residue was purified using column chromatography with silica gel (CHCl3/ petroleleum/ CH3OH = 50/ 10/ 1, v/ v/ v) to obtain 3 of 0.70 g (yield: 63%). 1H NMR (CDCl3) 8.162 (d, 12 H, J = 8 Hz), 7.980 (s,3 H), 7.945 (s,6 H), 7.888 (s, 3 H), 7.794 (d, 4 H, J = 12 Hz), 3.953 (s, 18 H) 13C NMR (D6-DMSO) 166.832, 145.012, 142.488, 141.713, 132.298, 130.263, 129.488, 127.329, 126.266, 125.065.

1,3,5-Tri(3,5-di(4-carboxyphenyl-1-yl)phenyl-1-yl)benzene (4, TDCPB) :

Compound 3 (0.70 g, 0.63 mmol) and NaOH (2.0 g, 50 mmol) were added to a flask with THF-methanol-water (40ml:40ml:40ml). The solution was stirred for 24 h with reflux. After the solution was cool down, 1M HCl was added to it to get a solution with pH= 2.0. White precipitation was filtered to obtain 4 of 0.60 g (yield: 92%). 1H NMR (D6-DMSO) 8.3513 (s, 3 H), 8.236 (s, 6 H), 8.107-8.057 (q, 18 H). 13C NMR (D6-DMSO) 167.014, 14.165, 142.202, 141.784, 140.628, 129.892, 127.539, 126.266, 125.065. HRMS (ESI) (m/z) calcd for C66H42O12+Na: 1049.25685, found:
Zn₅O(TDCPB) (JUC-100): 4 (10 mg, 0.0097 mmol) and Zn(NO₃)₂·6H₂O (20 mg, 0.067 mmol) were added to a solvent of DMF (3.0 ml), ethanol (0.20 ml) and then 0.10 ml concentrated HNO₃ was added. After ultrasonic diffusion, the solution was heated at 85 °C for 24 h to obtain the product of 70% (yield based on Zn) with colorless crystal. Anal. Calcd (Found) for Zn₅C₉₆H₁₁₆N₁₀O₂₈: C, 54.41 (54.88); H, 5.47 (5.91); N, 6.61 (6.71) %. According to element analysis and TGA measurements, the crystal formula is Zn₅O(TDCPB)·10DMF·5H₂O.

**Scheme 1:** The synthetic route of TDCPB

**Crystallography data:** Colorless, block-shaped crystal of JUC-100 was picked for X-ray structural analysis on a Bruker SMART CCD diffractometer at 296(2) K. The complex crystallized in the space group R-3c, trigonal, a = 20.4586(8), b = 20.4586(8), c =
80.370(3) Å, $V = 29132(2) \text{ Å}^3$, $\lambda = 0.71073$ Å, $\rho_{\text{calc}} = 0.888$ g/cm$^3$. A total of 51924 reflections were collected, of which 6430 were unique ($R_{\text{int}} = 0.0490$). Final $GooF = 1.061$, $R_1 = 0.0743$, $wR_2 = 0.2258$. 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. The routine SQUEEZE was applied to the structures in order to remove diffuse electron density associated with badly disordered DMF molecules.[2]

**Low-pressure gas and vapor sorption measurements:** The JUC-100 sample after activation is used for N$_2$ adsorption measurement. The as-synthesized sample is soaked in CH$_2$Cl$_2$ for 3 days and then heated at 135 °C and vacuum for 12 h. The N$_2$ and H$_2$ sorption-desorption experiments were performed on an Autosorb-iQ2-MP-AG machine. N$_2$ and H$_2$ used were of 99.999% purity. The sample was treated at 130 °C under vacuum for 12 h before the measurement. The H$_2$ sorption-desorption isotherms were collected at 77 K and 87 K. Surface area was determined by the N$_2$ gas isotherm measured at 77 K.

Reference:


Fig. S1 The optimized configuration of TDCPB: The configuration of TDCPB was optimized by DFT method with the software of Gaussian09. The density functional B3LYP level using the 6-31G(d) basis set was utilized for the geometry optimizations. After the calculation, we got the most optimized configuration as shown above and it just took a distorted octahedral configuration.

Fig. S2 The asymmetric unit of JUC-100
**Fig. S3** View outside (a) and inside (b) of the nanocage

**Fig. S4** 3D space packing of JUC-100 view along (111)
**Fig. S5** C-H⋯π effect between ligands (C atom-black, O atom-red, H atom-green, distance (Å)-blue).

**Fig. S6** Staggered conformation between the ligand TDCPB and SBU Zn₄O
Fig. S7 TGA curves of desolvated (red) and solvated (black) form of JUC-100. The desolvated sample starts to decompose at about 420 °C, and up to 550 °C, the decomposition finishes, and there is 70.44 % weight loss attributed to the destruction of organic part. The solvated sample starts to lose guests at the beginning of heat-up, and there is 41.14 % weight loss attributed to the departure of guests before 200 °C. Furthermore, this sample starts to decompose at about 420 °C, and the decomposition finishes up to 550 °C, and there is 43.66 % weight loss attributed to the loss of organic framework part.

Fig. S8 PXRD patterns of JUC-100 (calculated, black; as-synthesized, red; activated at 130 °C for 12 h, blue; heated at 300 °C for 2 h, green)
**Fig. S9** H₂ uptake data recorded at 77 K (blue) and 87 K (green) in JUC-100, and the corresponding virial curves fitted to the data. Inset: virial coefficients obtained from the fit of the data.

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<tr>
<th>Adj. R-Square</th>
<th>Value</th>
<th>Standard Error</th>
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| a0             | 7.0435974 | 7.42922       |
| a1             | 15.402320 | 4.80852       |
| a2             | 0.079643  | 0.06742       |
| a3             | -0.115155 | 0.06071       |
| a4             | 0.000653  | 0.05933       |
| a5             | -1.33904E-4 | 7.63071E-5    |
| b0             | 11.40933  | 0.00936       |
| b1             | -0.54917  | 0.04914       |
| b2             | 0.000908  | 0.00408       |

**Fig. S10** FT-IR spectra of desolvated (black) and solvated (red) form of JUC-100. The characteristic peak of C=O of DMF at 1664 cm⁻¹ was only found in the red curve, implying that the guest was removed completely.
Fig. S11 FT-IR spectra of compound 2

Fig. S12 FT-IR spectra of compound 3
Fig. S13 FT-IR spectra of compound 4
Fig. S14 $^1$H and $^{13}$C NMR spectra of compound 2 recorded in neat CDCl$_3$. 
Fig. S15 $^1$H and $^{13}$C NMR spectra of compound 3 recorded in neat CDCl$_3$. 
Fig. S16 $^1$H and $^{13}$C NMR spectra of compound 4 recorded in neat D$_6$-DMSO.
Fig. S17 The HRMS spectra of ligand TDCPB (top: measured; bottom: calculated).