Electronic Supplementary Material (ESI) for Dalton Transactions

Supporting Information for

A porous metal-organic framework (MOF) with unusual 2D→3D polycatenation based on honeycomb layers

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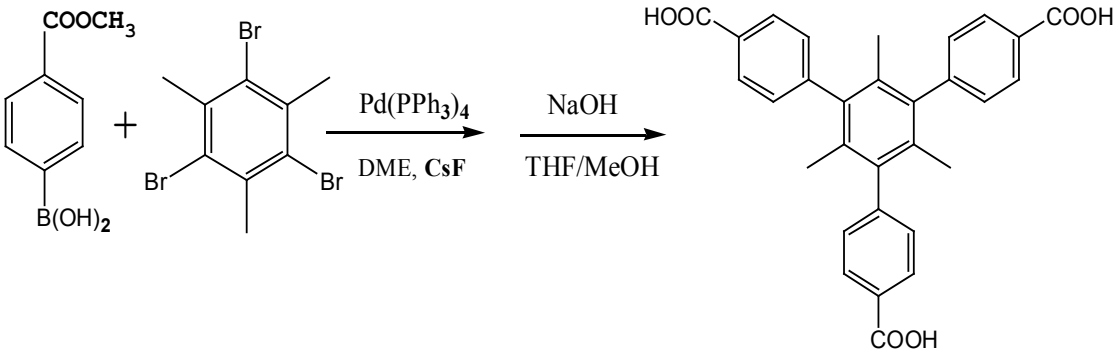
I. General Information

Unless otherwise noted, all reagents were obtained from commercial suppliers and used without further purification. ^{1}H NMR spectra was measured on a Bruker AVANCE-400 NMR Spectrometer. Elemental analyses (C, H, N) were obtained on a PerkinElmer 240 elemental analyzer. The thermogravimetric analysis (TGA) for complex **1** was carried out between room temperature and 700 °C in a static N_2 with a heating rate of 10°C/min. The N_2 adsorption was measured on Coulter 100cx at 77K.

II. Preparation of H_3TMTA and 1

Preparation of H_3TMTA To a 500 mL Schlenk flask, 5.5 g 4-Methoxycarbonylphenylboronic acid, 4.0 g 1,3,5,-trimethyl-2,4,6-tribromobenzene, 9 g CsF and 0.5 g $Pd(PPh_3)_4$ was added. The flask was connected to Schlenk line. About 200 mL 1,2-dimethoxyethane was degassed and added through a canula. The flask was equipped with a water condenser and refluxed under nitrogen for 48 hours. The solution was dried on rotary evaporator. A 100 mL H_2O was added and then extract with $CHCl_3$. The organic phase was eluted with chloroform through a short silica gel column and then dried again to yield a light yellow powder, yield 42.3%. ^{1}H NMR (200 MHz, CD_3Cl) δ 1.67 (s, 9 H), 3.94 (s, 9 H), 7.30 (d, 6 H), 8.12 (d, 6 H).

About 2.2 g of the light yellow powder was suspended in 100 mL THF/MeOH (v:v = 1:1). A 2 mL concentrated NaOH solution was added. The mixture was disturbed overnight. The pH value was adjusted to about 2 using HCl. White solid was filtered out, washed with water and dried under vacuum, yield 90.9%. ^{1}H NMR (200 MHz, d_6-DMSO) δ 1.62 (s, 9 H), 7.36 (d, 6 H), 8.03 (d, 6 H), 12.98 (s, 3 H).



Scheme 1. Synthesis of H_3TMTA

Preparation of 1 H_3TMTA (8 mg, 0.018 mmol), $Zn(NO_3)_2 \cdot 6H_2O$ (13.2 mg, 0.045 mmol) and ′ 4,4 -bipyridyl (1.9 mg, 0.01 mmol) were dissolved in DMF/1,4-dioxane/H_2O (5/2/1, v/v, 1 ml). Upon addition of a drop of HBF_4 a colorless solution formed. The solution was sealed in a glass tube and slowly heated to 90°C from room temperature in 5 h, kept at 90°C for 16.5 h, and then slowly cooled to 40°C in 10 h. The colorless crystals were obtained (Yield: 45%). Elemental analysis (%) for **1**: Calcd: C 49.10, H 4.53, N 4.89; Founf: C 49.27, H 4.51, N 5.26.

III. Crystal structure determination of 1

Crystal structure determination of 1 Single-crystal X-ray diffraction was performed using a Bruker Apex II CCD diffractometer equipped with a fine-focus sealed-tube X-ray source ($Mo_{K\alpha}$ radiation, graphite monochromated). Structures were solved by direct methods using SHELXTL and were refined by full-matrix least-squares on F^2 using SHELX-97. Non-hydrogen atoms were refined with anisotropic displacement parameters during the final cycles. Hydrogen atoms were placed in calculated positions with isotropic displacement parameters set to $1.2 \times U_{eq}$ of the attached atom. Contributions to scattering from all solvent molecules were removed using the

SQUEEZE routine of PLATON; structures were then refined again using the data generated.

Crystal data for **1**: $C_{35}H_{13.75}NO_7Zn_2$, M = 690.96, monoclinic, space group $C2/c$, a = 27.854(6), b = 17.042(4), c = 20.656(4) Å, β = 116.017(4)º, U = 8812(3) Å^3, Z = 8, Dc = 1.042 Mg m^{-3}, μ(Mo Kα) = 1.124 mm^{-1}, T = 273 K, 14611 reflections collected. Refinement of 4621 reflections (406 parameters) with I >1.5σ(I) converged at final R_1 = 0.0763, wR_2 = 0.2064, gof = 0.883. CCDC 831821.

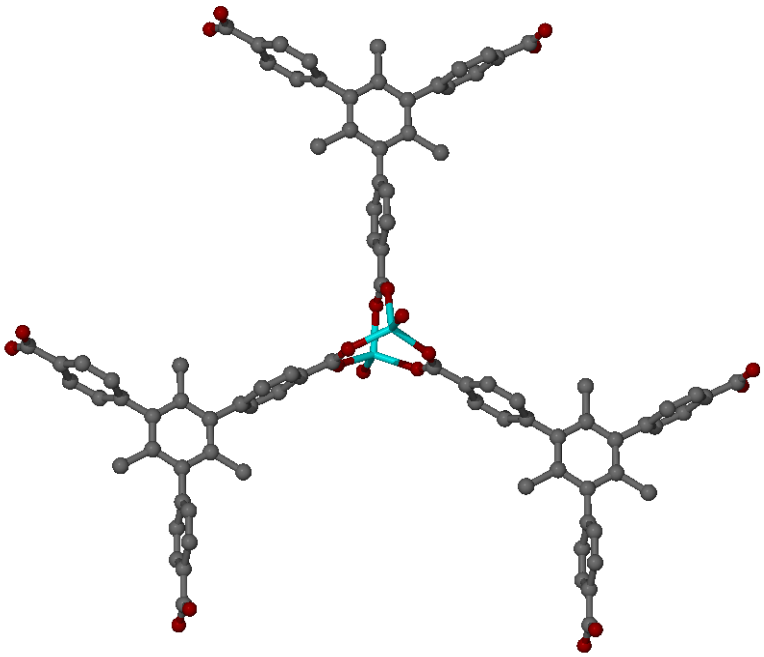


Figure S1. The coordination environment of zinc ion in $Zn_2(TMTA)(H_2O)_2 \cdot NO_3 \cdot 6H_2O \cdot DEF$ showing the binuclear zinc SBU.

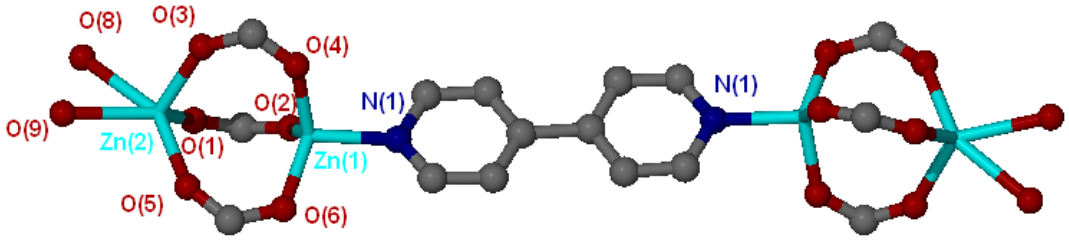


Figure S2. The coordination environment of zinc ion in **1**, showing the binuclear zinc SBU.

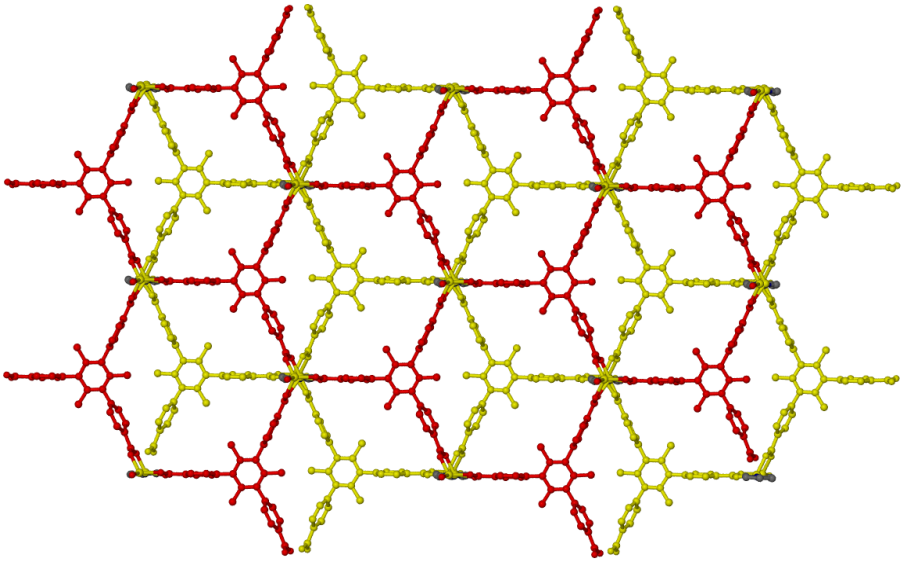


Figure S3. The bilayer structure of **1** along *c* axis.

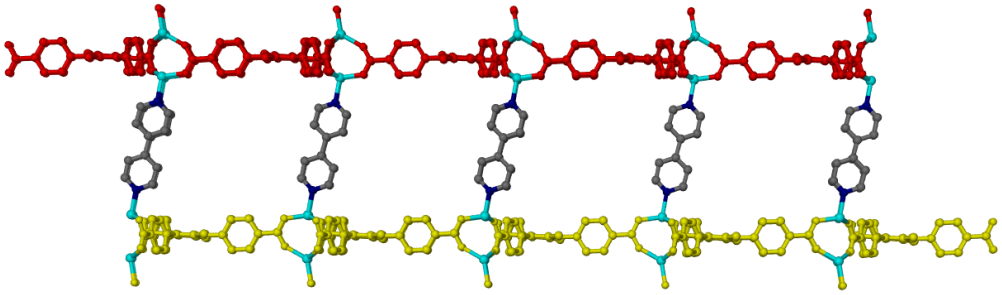


Figure S4. The bilayer structure of **1** along *b* axis.

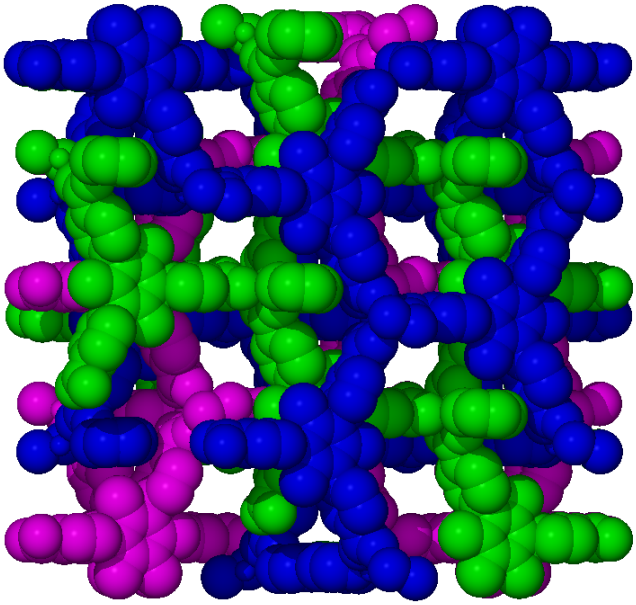


Figure S5. The 3D packing of **1**, viewed through [0 0 1] direction

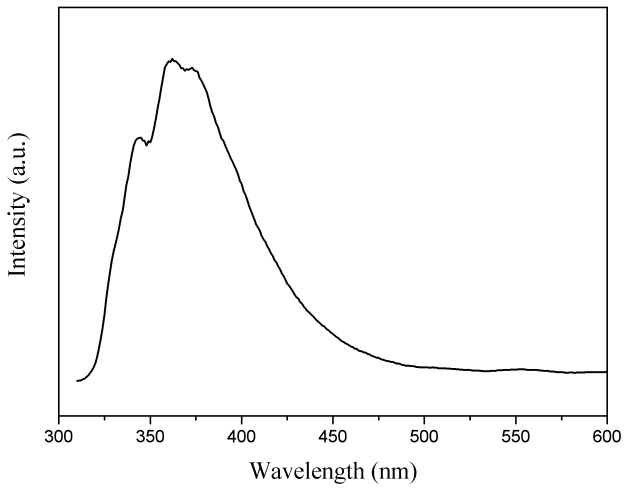


Figure S6. Solid-state fluorescence spectrum of H_3TMTA at room temperature.

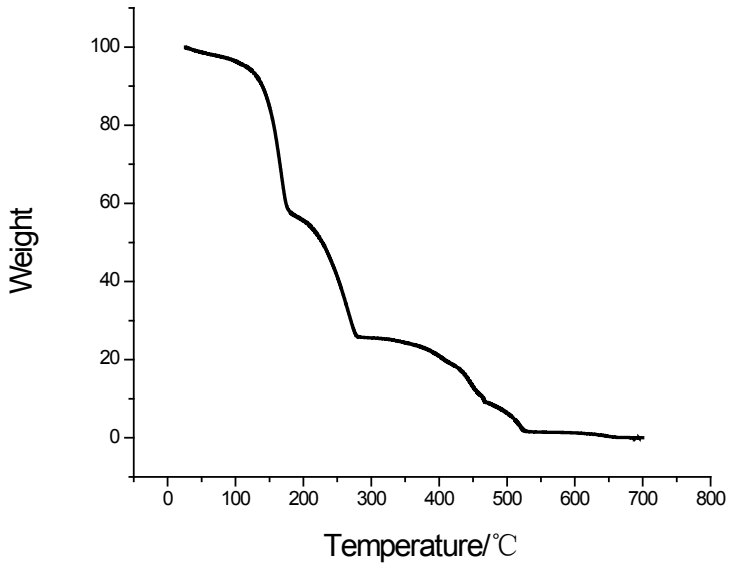


Figure S7. TGA of **1**.

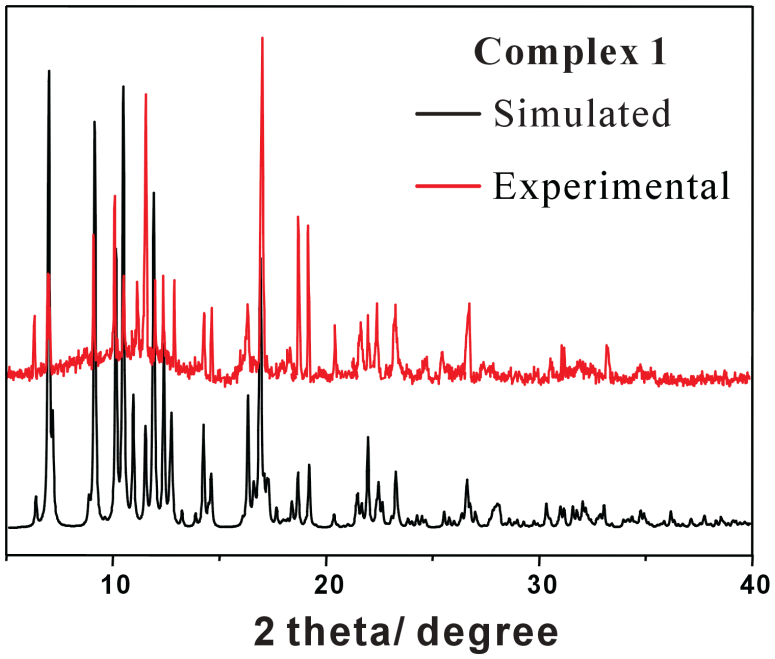


Figure S8. The powder XRD pattern and the simulated one from the single-crystal diffraction data for **1**. (Full phase-purity could not be achieved and the X-ray powder diffractogramm of as-synthesized sample was obtained by manually picking suitable crystals one by one)