

Supporting Information

An enhanced extended hook method to realize tetranuclear metal clusters embedded in energetic metal–organic framework channels

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1. Experimental section

1.1 Materials and Instruments

All the chemicals were purchased commercially and used without further purification. The elemental analyses of C, H and N were performed on an Elementar Vario EL III microanalyzer. The FT-IR spectra were obtained on a VERTEX70 spectrophotometer using KBr disks in the range 4000–400 cm⁻¹. ¹H NMR (400 MHz) and ¹³C NMR (101 MHz) spectra were recorded on a Bruker AVANCE 400 NMR spectrometer with Me₄Si as the internal standard in deuterated solvent DMSO-d₆. ESI mass spectra were recorded on a DECAX-30000 LCQ Deca XP mass spectrometer. Powdered X-ray diffraction (PXRD) patterns were performed on a Rigaku Miniflex II diffractometer using Cu-K α radiation ($\lambda = 1.540598 \text{ \AA}$) at 40 kV and 40 mA in the range of $5 \leq 2\theta \leq 60^\circ$. Thermogravimetric analysis (TGA/DSC) experiments were done on a TGA/DSC 1 merriker toledo thermogravimetric analyzer in N₂ with the sample heated in an Al₂O₃ crucible at a heating rate of 10 K min⁻¹. Simulated PXRD patterns were derived from the Mercury Version 1.4 software (<http://www.ccdc.cam.ac.uk/products/mercury/>). The photoluminescence (PL) and lifetime determination were conducted on a single-grating Edinburgh FL920 fluorescence

spectrometer equipped with a 450 W Xe lamp, an nF900 lamp, and a PMT detector. The CIE coordinates, was calculated using the CIE calculator-version 3 software. The impact and friction sensitivities were performed on a BAM fall hammer BFH-12 and a BAM friction apparatus FSKM-10, respectively. The combustion heats were measured by oxygen bomb calorimetry (5E-AC8018, Changsha Kaiyuan Instruments Co., LTD, China).

1.2 Synthesis

Synthesis of 1-(2-cyanoethyl) piperidine-4-carboxylic acid (HCPC). A mixture of piperidine-4-carboxylic acid (0.025 mol, 3.23g), NaOH (0.025 mol, 1.00g) and acrylonitrile (1.33 g, 0.025 mol) in 20mL H₂O was stirred for 10min, and then standing for one day at room temperature. After that, 0.025 mol HCl (m%=37.5) was poured into the reaction mixture and then heat to 70 °C to evaporate the solution. Finally, pale yellow precipitates were obtained and the yield is about 63% (based on the piperidine-4-carboxylic acid). ESI-MS: m/z [M - H]⁻, 181.2 (calcd for C₉H₁₄N₂O₂, 182.2). NMR analysis for HCPC, ¹H NMR (400 MHz, DMSO): ¹H NMR (400 MHz, DMSO): δ 2.78 (d, *J* = 11.3 Hz, 2H), 2.63 (t, *J* = 6.6 Hz, 2H), 1.99 (dd, *J* = 26.9, 15.6 Hz, 2H), 1.74 (d, *J* = 10.7 Hz, 1H), 1.50 (dd, *J* = 20.9, 11.3 Hz, 2H). ¹³C NMR (101 MHz, DMSO): δ 178.21 (s), 120.52 (s), 53.50 (s), 52.68 (s), 41.92 (s), 28.86 (s), 15.44 (s). Anal. Calcd for C₉H₁₄N₂O₂: C, 59.75; H, 8.11; N, 15.58 %. Found: C, 59.32; H, 7.74; N, 15.37%. Selected IR (KBr pellet, cm⁻¹): 3436 b, 2950 w, 2254 w, 1644 m, 1571 s, 1456w, 1408 s, 1126 w, 934 w, 787 w (Fig. S1).

Synthesis of [Zn₄(N₃)_{0.8}(OH)_{1.2}(BTEC)(HTZPC)₂(H₂O)₂] 3.25H₂O A mixture of ZnCl₂ (0.73mmol, 100 mg), HCPC (0.55mmol, 100 mg), H₄BTEC (0.20mmol, 50 mg), NaN₃ (1.54mmol, 100 mg) and H₂O (8 mL) was sealed in a poly(tetrafluoroethylene)-lined stainless steel container under autogenous pressure and then heated to 90 °C for 3 days, and cooled to

room temperature at a rate of 2.5 °C/h. Orange block crystals suitable for X-ray analysis were obtained. Yield: 90%. For **1**: Anal. calcd for C₂₈H_{41.7}N_{12.4}O_{18.45}Zn₄: Zn, 23.59; C, 30.32; H, 3.79; N, 15.66%. Found: Zn, 21.46; C, 30.47; H, 3.80; N, 15.67%. Selected IR (KBr pellet, cm⁻¹): 3437 b, 3024 w, 2749 w, 1578 vs, 1497 s 1434 s, 1376s, 1209 m, 1130 m, 1030 m, 941 m, 877 m, 822 m, 563 s.

1.3 X-ray Crystallography

Single-crystal X-ray diffraction measurements was performed on a Rigaku Saturn724 CCD, which was equipped with Mo K_α radiation ($\lambda = 0.71073 \text{ \AA}$), using the ω -scan technique for collection of the intensity data sets. The Primitive structures were solved by the direct methods reduced by CrystalClear software¹. Subsequent successive difference Fourier syntheses yielded the other non-hydrogen atoms. The hydroxyl O and terminal azido N atoms locate at the same position, labelled as X atom, in which the $\mu_2\text{-OH}^-/\mu_{1,1}\text{-N}_3^-$ occupancy rate is 6:4. The coordinated water O2W has a certain degree of disorder, and the site occupancy ratio for O2WA/O2WB is 8:2. Hydrogen atoms attached to C atoms of HTZPC ligands were added geometrically and refined using the riding model. Hydrogen atoms attached to N15 atoms of HTZPC ligand are revealed according to the difference-Fourier map. In this heavy-atom structure as it was not possible to see clear electron-density peaks in difference maps which would correspond with acceptable locations for the various H atoms bonded to water oxygen atoms, the refinement was completed with no allowance for these water H atoms in the model. Final structures were refined using a full-matrix least-squares refinement on F^2 . All of the calculations were performed by the Siemens SHELXTL version 5 package of crystallographic software². Pertinent crystal data and structural refinement results and selected bond distances and angles for **1** are listed in [Tables S1](#) and [S2](#), respectively.

Notes and references

1. CrystalClear, version 1.35; Software User's Guide for the Rigaku R-Axis, and Mercury and Jupiter CCD Automated X-ray Imaging System; Rigaku Molecular Structure Corporation: Utah, **2002**.
2. SHELXTL Reference Manual, version 5; Siemens Energy & Automation Inc.: Madison, WI, **1994**.

2. Table section

Table S1 Crystal data and structure refinement for compound **1**

Compound	1
Empirical formula	C ₂₈ H _{41.70} N _{12.40} O _{18.45} Zn ₄
M_r (g mol ⁻¹)	1108.72
Crystal system	tetragonal
Space group	<i>P</i> -4
a (Å)	14.952(2)
b (Å)	14.952(2)
c (Å)	9.0826(18)
α (°)	90
β (°)	90
γ (°)	90
V (Å ³)	2030.5(7)
Z	2
D_c / g cm ⁻³	1.813
μ / mm ⁻¹	2.426
$F(000)$	1128.0
Reflections collected	21606
Unique Reflections	4655
GOF	1.007
R_1^a [$I > 2\sigma(I)$]	0.0393
wR_2^b (all data)	0.1033
CCDC No.	1471950

$$^a R_1 = \sum(F_o - F_c)/\sum F_o; \quad ^b wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$$

Table S2 Selected bond lengths (Å) and angles (°) for compound **1**

1			
Zn(1)–O(22)	2.030(6)	Zn(2)–X	2.00(4)
Zn(1)–O(23)#1	2.027(6)	Zn(2)–O(11)	2.023(9)
Zn(1)–N(11)#2	2.047(7)	Zn(2)–O(12)#3	2.039(8)
Zn(1)–N(14)	2.076(7)	Zn(2)–O(2W)	2.100(11)
		Zn(2)–X#3	2.06(4)
O(22)–Zn(1)–O(23)#1	138.0(2)	X#3–Zn(2)–O(11)	88.8(8)
O(22)–Zn(1)–N(11)#2	102.9(3)	X–Zn(2)–O(12)#3	101.7(8)
O(23)#1–Zn(1)–N(11)#2	107.1(3)	O(12)#3–Zn(2)–X#3	90.1(7)
O(22)–Zn(1)–N(14)	101.7(3)	O(12)#3–Zn(2)–O(11)	161.1(4)
O(23)#1–Zn(1)–N(14)	103.6(3)	X–Zn(2)–O(2W)	98.8(11)
N(11)#2–Zn(1)–N(14)	95.9(3)	X#3–Zn(2)–O(2W)	143.3(10)
X–Zn(2)–X#3	118.0(18)	O(11)–Zn(2)–O(2W)	87.9(5)
X–Zn(2)–O(11)	95.5(7)	O(12)#3–Zn(2)–O(2W)	81.7(4)

Symmetry transformations used to generate equivalent atoms: for **1**: (#1) $x, y, z + 1$; (#2) $y, -x, -z + 2$; (#3) $-y + 1, x, -z$.

3. Figure section

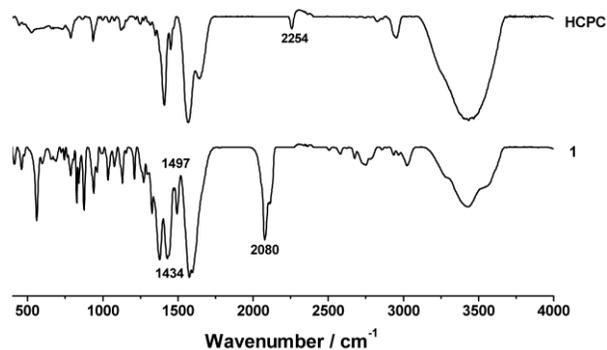


Fig. S1 IR spectra of HCPC ligand and compound **1**.

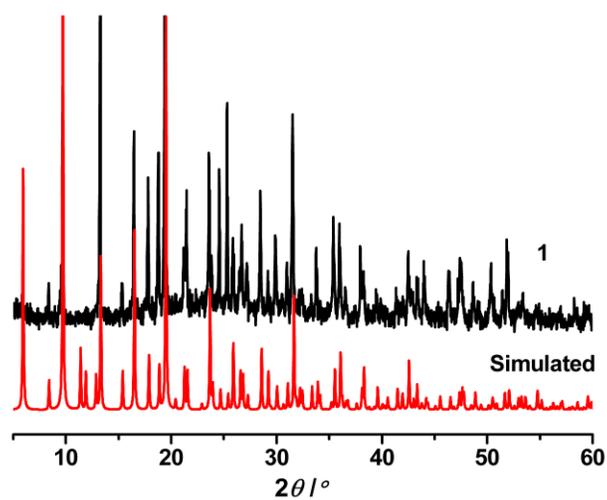


Fig. S2 Comparison between PXRD patterns for the as-synthesized **1** and the simulated one from single-crystal X-ray data.

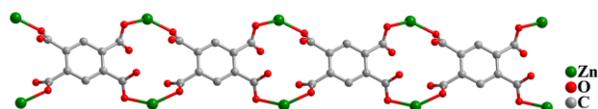


Fig. S3 The 1D chain constructed by the Zn1 atom and BTEC⁴⁻ ligand.

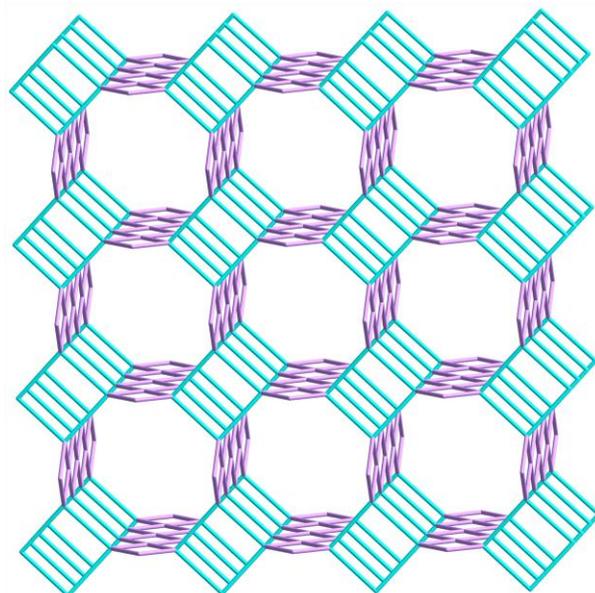


Fig. S4 3D mot-e type net (the BTEC⁴⁻ ligand and Zn1 atoms are regarded as square and tetrahedral 4-c vertices, respectively and the tetrazolate group as a linker bridging two Zn atoms)

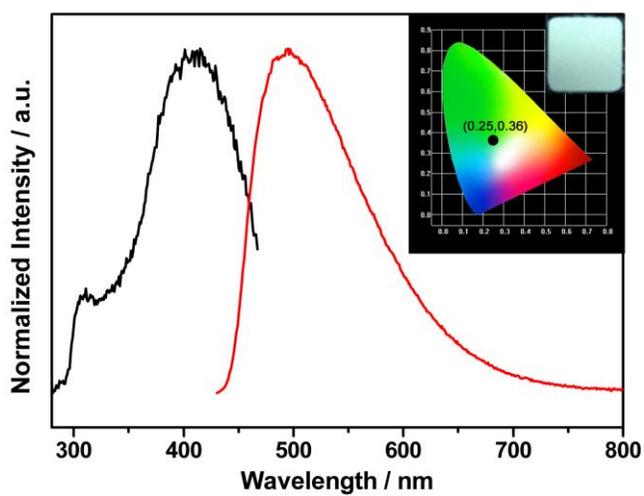


Fig. S5 The excitation (black line) and emission (red line) spectra of **1**. Insert: the 1931 CIE chromaticity diagram and optical image of the emission in the powdered sample.

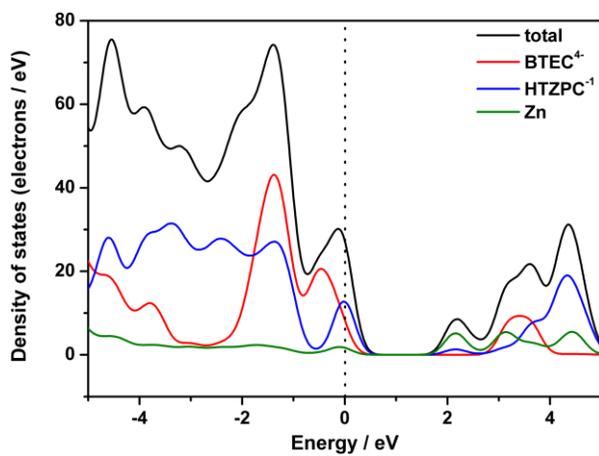


Fig. S6 The total and partial DOS of compound **1**. The position of the Fermi level is set at 0 eV.

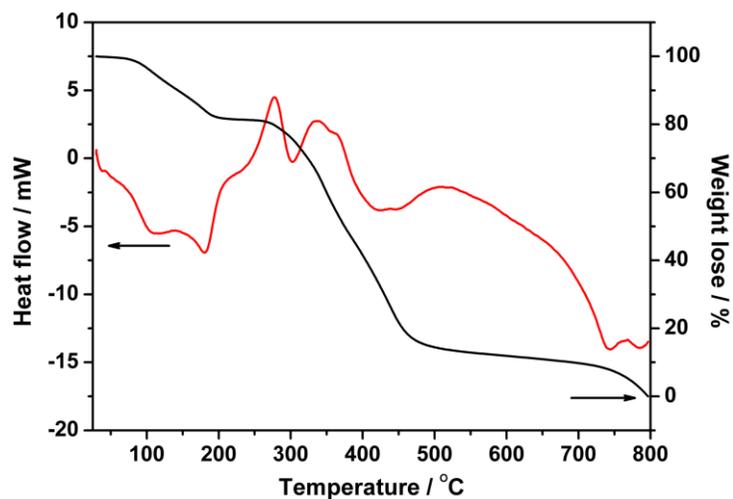


Fig. S7 DSC and TGA curves of compound **1**.