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A Self-Assembled Metal-Organic Framework for Enhanced UO_2^{2+} Fluorescent Sensing: Integration of Octa-Nuclear Zinc Cluster with Hexakis(4-Carboxyphenoxy)Cyclotriphosphazene

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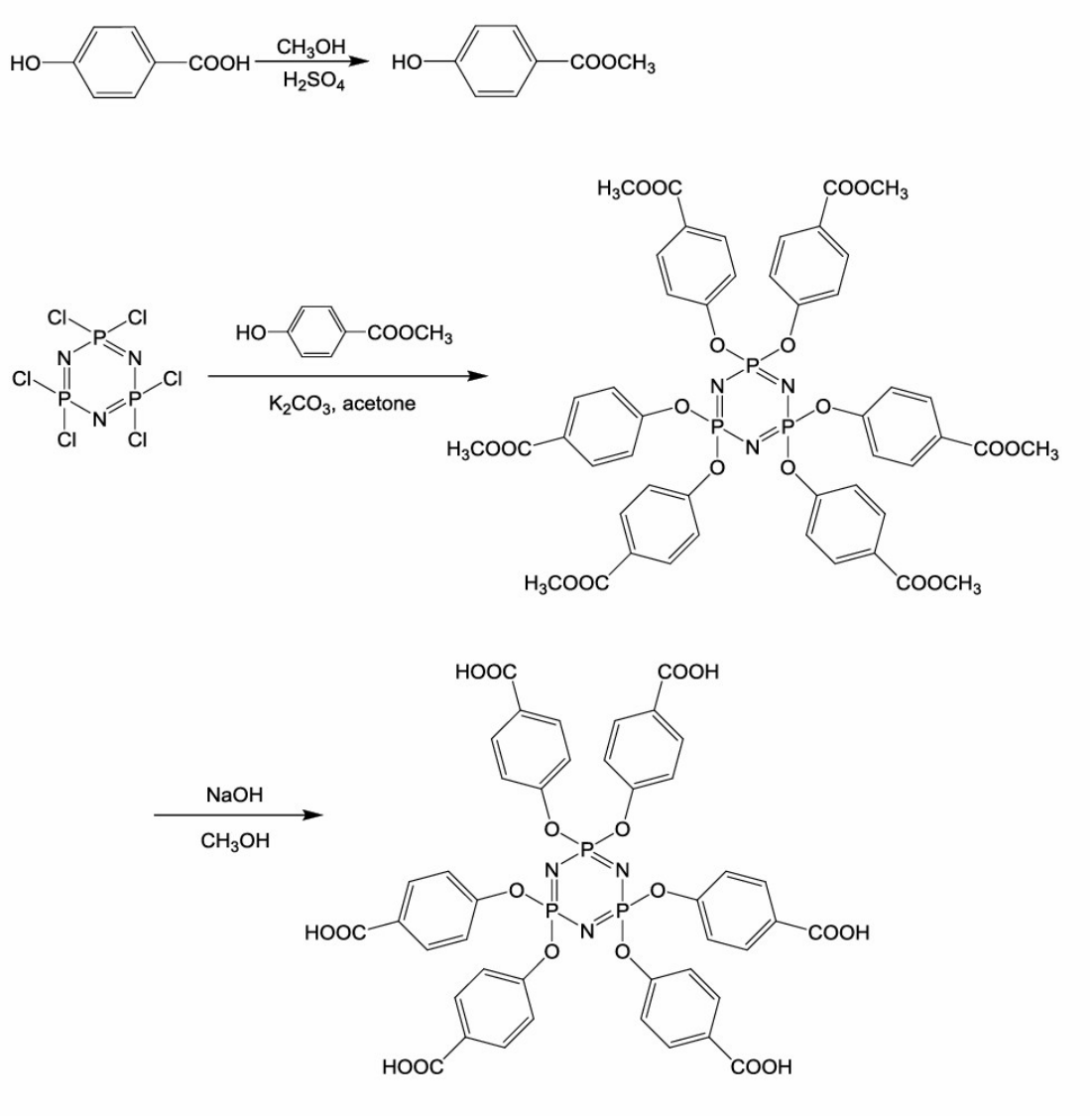
Experimental sections

Materials and General Methods. All reagents were purchased from commercial sources and were used without further purification. Elemental analyses (C, H and N) were performed on a Perkin-Elmer 2400 analyzer. FT-IR spectra were recorded as KBr pellets with an Equinox 55 FT-IR spectrophotometer (4000-400 cm^{-1}). Thermogravimetric analysis (TGA) was performed on a Perkin-Elmer TGA4000 analyzer from room temperature to 800 °C at an rate of 10 °C/min under a N_2 atmosphere. Powder X-ray diffraction (PXRD) patterns for the as-synthesized samples were recorded on a X-ray diffraction meter (D/max 2500 PC, Rigaku) with Cu-Kα radiation (1.5406 Å), PXRD data were collected over the 2θ range 5~50°at room temperature, with a step size of 0.02° in 2θ angle. All fluorescence spectra were measured with an RF-5301PC fluorescence spectrophotometer. Ultraviolet-visible (UV-vis) adsorption spectra were recorded at room temperature on UV-2550 spectrophotometer.

Synthesis of hexakis(4-carboxyphenoxy)cyclotriphosphonitrile (H_6L)

Potassium carbonate (6.00 g, 0.043 mol) was added into a solution of anhydrous acetone (80 mL) containing 4-hydroxy-2-methylbenzoate (8.2 g, 0.054 mmol) and $P_3N_3Cl_6$ (3.13g, 0.009 mol). The mixture was stirred overnight at 70°C. The solvent was removed by evaporation under reduced pressure, and the obtained solid was redissolved in 50 mL dichloromethane. The organic phase was washed with water and then dried over anhydrous Na_2SO_4. The volatiles were removed by evaporation under reduced pressure, and the product was dried as white powder (8.56 g, 91.5% yield).

A quantity of sodium hydroxide (3.0 g) was dissolved in 50 mL methanol, and then $P_3N_3(OC_6H_4COOOCH_3)_6$ (8.32 g) was added. The mixture was stirred overnight at 80°C. The volatiles were removed and the residue was dissolved in water, filtered and acidified to pH~2 using dilute hydrochloric acid. The product as a precipitate was obtained after stirring. The precipitate was collected by filtration, washing with water and drying (8.12 g, 93.6% yield). IR (KBr): ν/cm-1 3097 (s), 2540 (m), 1700 (s), 1601 (m), 1509 (m), 1427 (m), 1288 (s), 1160 (s), 949 (s), 861(m), 771(m) and 732 (m).



Scheme S1 Synthetic route for the ligand H_6L

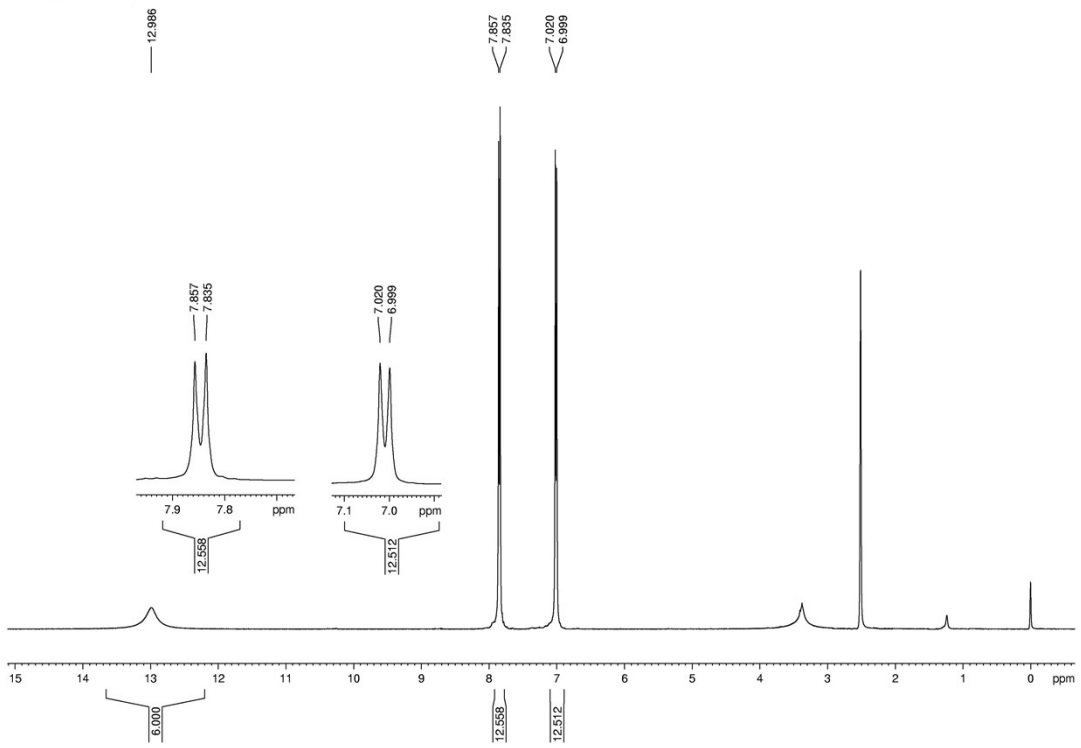


Figure S1 ^{1}HNMR spectra of ligand H_6L

Synthesis of Zn-MOF

A mixture of $Zn(NO_3)_2 \cdot 6H_2O$ (60 mg, 0.2 mmol), H_6L (30 mg, 0.032 mmol) was dissolved in 3 mL of H_2O and 3mL of acetonitrile. The mixture was put into a 25 ml Teflon-lined stainless steel vessel and sonicated for 5 min at room temperature, then the steel was placed in an oven at 160°C for 48 hours, and then cooled to room temperature at the rate of 5 °C/h, then white block crystals were obtained. The crystals were collected by filtration, washing and drying under ambient conditions. Yield of the reaction was ca.62% based on Zn. Anal. Element analysis for fresh sample: H, 2.59%; C, 38.24%; N, 3.18%; IR (KBr, cm^{-1}): 3189 (s), 1601 (s), 1542(s), 1411 (s), 1213 (s), 1157 (s), 959 (s), 861 (m), 788 (s), 689 (m).

X-Ray Structural Determination.

Diffraction data for Zn-MOF (0.1 × 0.05 × 0.05 mm) was collected via Bruker Venture using Mo-Kα (λ =0.71073 Å) radiation at 298 K. The structures of complexes were solved by direct methods, and the non-hydrogen atoms were located from the trial structure and then refined anisotropically with SHELXTL using a full-matrix leastsquares procedure based on F2 values. The hydrogen atom positions were fixed

geometrically at calculated distances and allowed to ride on the parent atoms. Attempts to define the highly disordered solvent molecules were unsuccessful, so the structure was refined with the PLATON "SQUEEZE" procedure. The diffraction intensity of crystal sample was very weak due to the very small size and low density, which must be responsible for the corresponding alert A. CCDC-2349495 for the data under different temperature contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/datarequest/cif.

Table S1 Crystal data and structure refinements for Zn-MOF

Identification code	Zn-MOF
Empirical formula	$C_{42}H_{24}N_3O_{30}P_3Zn_4$
Formula weight	1405.03
Temperature/K	293(2)
Crystal system	triclinic
Space group	P-1
a/Å	7.3860(15)
b/Å	15.868(3)
c/Å	19.198(4)
α/°	103.38(3)
β/°	95.61(3)
γ/°	99.79(3)
Volume/Å^3	2134.9(8)
Z	1
ρ_{calc}g/cm^3	1.093
μ/mm^{-1}	1.227
F(000)	702.0
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	2.692 to 58.484
Reflections collected	10412
Independent reflections	10412 [R_{sigma} =0.0289]
Data/restraints/parameters	10412/24/689
Goodness-of-fit on F^2	1.101
Final R indexes [I>=2σ (I)]	R_1 = 0.0799, wR_2 = 0.2234
Final R indexes [all data]	R_1 = 0.0865, wR_2 = 0.2300
Largest diff. peak/hole / e Å^{-3}	1.65/-2.50

Table S2 Bond Lengths for Zn-MOF

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Zn01	Zn04[1]	3.0988(11)	O19	Zn02[3]	1.927(3)
Zn01	O2	1.897(4)	O10	C22	1.170(6)
Zn01	O24[1]	1.884(4)	O11	Zn01[6]	2.035(4)
Zn01	O4[2]	2.168(3)	O11	C22	1.171(6)
Zn01	O7	1.930(3)	O5	Zn04[4]	1.815(3)
Zn01	O19	1.828(4)	O5	C8	1.178(7)
Zn01	O11[2]	2.035(4)	O17	Zn04[5]	1.797(4)
Zn02	Zn02[3]	2.8607(14)	O17	C36	1.206(6)
Zn02	O1	1.899(3)	O15	C33	1.275(6)
Zn02	O8[3]	1.939(3)	O14	Zn03[4]	1.902(4)
Zn02	O19[3]	1.927(3)	O14	C29	1.153(7)
Zn02	O19	1.919(4)	O16	C36	1.155(7)
Zn02	O21	1.954(3)	O13	C29	1.182(8)
Zn02	O20	2.030(4)	C19	C18	1.285(8)
Zn03	Zn04[4]	2.9591(11)	C19	C20	1.264(8)
Zn03	O24[4]	1.947(4)	C4	C5	1.336(6)
Zn03	O10	1.877(3)	C4	C3	1.328(5)
Zn03	O23	1.874(3)	C1	C2	1.363(6)
Zn03	O14[4]	1.902(4)	C16	C15	1.394(6)
Zn03	O22	1.898(5)	C16	C17	1.290(8)
Zn03	C22	2.586(5)	C16	C21	1.278(8)
Zn04	Zn01[1]	3.0988(11)	C25	C26	1.291(7)
Zn04	Zn03[4]	2.9592(11)	C25	C24	1.290(6)
Zn04	O24	1.804(3)	C18	C17	1.290(7)
Zn04	O5[4]	1.815(4)	C26	C27	1.270(8)
Zn04	O17[5]	1.797(4)	C6	C7	1.334(6)
Zn04	O13	1.801(5)	C6	C5	1.343(6)
Zn04	C8[4]	2.544(5)	C7	C2	1.345(6)
Zn04	C36[5]	2.485(6)	C24	C23	1.264(8)
P005	P006	2.5561(19)	C20	C21	1.305(7)
P005	P007	2.585(2)	C27	C28	1.291(7)
P005	O9	1.457(4)	C39	C40	1.280(8)
P005	O12	1.463(3)	C39	C38	1.285(8)
P005	N00U	1.459(5)	C23	C22	1.400(6)
P005	N00Y	1.459(5)	C23	C28	1.299(7)
P006	P007	2.554(2)	C33	C32	1.261(8)
P006	O18	1.474(4)	C33	C34	1.261(8)
P006	O15	1.464(4)	C10	C11	1.335(5)

Atom	Atom	Length/Å	Atom	Atom	Length/Å
P006	N00S	1.458(5)	C10	C9	1.329(6)
P006	N00U	1.459(5)	C41	C40	1.293(7)
P007	O6	1.466(4)	C41	C42	1.267(9)
P007	O3	1.462(4)	C14	C13	1.338(6)
P007	N00S	1.475(5)	C14	C9	1.339(6)
P007	N00Y	1.466(5)	C3	C2	1.335(6)
O9	C19	1.295(5)	C11	C12	1.330(6)
O12	C26	1.290(5)	C13	C12	1.331(6)
O1	C1	1.171(6)	C8	Zn04[4]	2.544(5)
O6	C12	1.260(6)	C8	C9	1.365(6)
O8	Zn02[3]	1.939(3)	C38	C37	1.291(7)
O8	C15	1.152(6)	C37	C36	1.384(9)
O3	C5	1.258(6)	C37	C42	1.282(8)
O2	C1	1.172(7)	C36	Zn04[5]	2.485(6)
O18	C40	1.284(7)	C30	C29	1.369(8)
O24	Zn01[1]	1.884(4)	C30	C35	1.269(9)
O24	Zn03[4]	1.947(4)	C30	C31	1.271(10)
O4	Zn01[6]	2.168(3)	C32	C31	1.261(10)
O4	C8	1.152(6)	C34	C35	1.288(9)
O7	C15	1.174(6)			

[1]1-X,1-Y, 1-Z; [2]1+X,1+Y, +Z; [3]2-X, 2-Y, 2-Z; [4]-X,-Y,1-Z; [5]-X,1-Y,1-Z; [6]-1+X,-1+Y,+Z

Table S3 Bond Angles for Zn-MOF

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O2	Zn01	Zn04[1]	80.36(11)	O3	P007	P005	127.55(16)
O2	Zn01	O4[2]	93.74(15)	O3	P007	P006	126.50(17)
O2	Zn01	O7	91.36(16)	O3	P007	O6	94.6(2)
O2	Zn01	O11[2]	173.87(15)	O3	P007	N00S	110.7(2)
O24[1]	Zn01	Zn04[1]	32.03(10)	O3	P007	N00Y	112.0(3)
O24[1]	Zn01	O2	86.98(17)	N00S	P007	P005	88.90(19)
O24[1]	Zn01	O4[2]	88.57(14)	N00S	P007	P006	29.26(18)
O24[1]	Zn01	O7	91.00(15)	N00Y	P007	P005	27.9(2)
O24[1]	Zn01	O11[2]	86.91(16)	N00Y	P007	P006	87.5(2)
O4[2]	Zn01	Zn04[1]	58.16(10)	N00Y	P007	O6	110.8(2)
O7	Zn01	Zn04[1]	122.23(11)	N00Y	P007	N00S	116.7(3)
O7	Zn01	O4[2]	174.85(15)	C19	O9	P005	124.3(3)
O7	Zn01	O11[2]	88.17(14)	C26	O12	P005	130.3(3)
O19	Zn01	Zn04[1]	138.43(11)	C1	O1	Zn02	123.8(3)

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O19	Zn01	O2	97.98(17)	C12	O6	P007	118.4(4)
O19	Zn01	O24[1]	168.43(14)	C15	O8	Zn02[3]	129.8(3)
O19	Zn01	O4[2]	80.70(14)	C5	O3	P007	122.4(4)
O19	Zn01	O7	99.29(15)	C1	O2	Zn01	130.5(4)
O19	Zn01	O11[2]	88.13(16)	C40	O18	P006	123.5(3)
O11[2]	Zn01	Zn04[1]	94.73(10)	Zn01[1]	O24	Zn03[4]	115.38(18)
O11[2]	Zn01	O4[2]	86.69(14)	Zn04	O24	Zn01[1]	114.32(19)
O1	Zn02	Zn02[3]	97.74(12)	Zn04	O24	Zn03[4]	104.10(18)
O1	Zn02	O8[3]	172.27(16)	C8	O4	Zn01[6]	142.5(4)
O1	Zn02	O19[3]	92.90(15)	C15	O7	Zn01	122.3(4)
O1	Zn02	O19	98.63(16)	Zn01	O19	Zn02	117.42(18)
O1	Zn02	O21	88.81(15)	Zn01	O19	Zn02[3]	119.42(18)
O1	Zn02	O20	83.73(16)	Zn02	O19	Zn02[3]	96.09(16)
O8[3]	Zn02	Zn02[3]	89.95(12)	C22	O10	Zn03	114.1(3)
O8[3]	Zn02	O21	86.04(15)	C22	O11	Zn01[6]	119.6(3)
O8[3]	Zn02	O20	90.38(16)	C8	O5	Zn04[4]	114.8(3)
O19	Zn02	Zn02[3]	42.06(10)	C36	O17	Zn04[5]	110.1(4)
O19[3]	Zn02	Zn02[3]	41.85(12)	C33	O15	P006	132.8(4)
O19	Zn02	O8[3]	87.59(16)	P006	N00S	P007	121.1(3)
O19[3]	Zn02	O8[3]	92.32(15)	C29	O14	Zn03[4]	118.1(4)
O19	Zn02	O19[3]	83.91(16)	P006	N00U	P005	122.3(3)
O19	Zn02	O21	95.22(16)	C29	O13	Zn04	121.6(4)
O19[3]	Zn02	O21	178.18(15)	P005	N00Y	P007	124.2(3)
O19[3]	Zn02	O20	92.25(16)	C18	C19	O9	117.2(5)
O19	Zn02	O20	175.57(14)	C20	C19	O9	120.4(5)
O21	Zn02	Zn02[3]	137.26(13)	C20	C19	C18	122.3(5)
O21	Zn02	O20	88.56(16)	C5	C4	C3	118.6(5)
O20	Zn02	Zn02[3]	134.05(11)	O1	C1	O2	126.1(5)
O24[4]	Zn03	Zn04[4]	36.24(10)	O1	C1	C2	116.8(5)
O24[4]	Zn03	C22	80.20(16)	O2	C1	C2	117.2(5)
O10	Zn03	Zn04[4]	77.38(13)	C17	C16	C15	118.6(5)
O10	Zn03	O24[4]	91.11(16)	C21	C16	C15	121.7(5)
O10	Zn03	O14[4]	127.46(18)	C21	C16	C17	119.7(5)
O10	Zn03	O22	93.93(18)	C26	C25	C24	118.1(5)
O10	Zn03	C22	24.39(16)	C19	C18	C17	118.7(6)
O23	Zn03	Zn04[4]	127.48(13)	C25	C26	O12	113.5(5)
O23	Zn03	O24[4]	91.50(16)	C27	C26	O12	124.9(5)
O23	Zn03	O10	119.67(16)	C27	C26	C25	121.5(5)
O23	Zn03	O14[4]	112.82(18)	C7	C6	C5	118.3(5)

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O23	Zn03	O22	89.23(18)	C6	C7	C2	119.6(5)
O23	Zn03	C22	97.94(16)	C23	C24	C25	122.0(5)
O14[4]	Zn03	Zn04[4]	72.97(14)	C19	C20	C21	118.5(5)
O14[4]	Zn03	O24[4]	89.67(17)	C26	C27	C28	119.1(5)
O14[4]	Zn03	C22	147.88(17)	C40	C39	C38	117.8(5)
O22	Zn03	Zn04[4]	141.93(13)	O8	C15	O7	125.6(5)
O22	Zn03	O24[4]	173.74(16)	O8	C15	C16	117.0(5)
O22	Zn03	O14[4]	84.31(19)	O7	C15	C16	117.3(5)
O22	Zn03	C22	105.86(18)	C24	C23	C22	120.8(5)
C22	Zn03	Zn04[4]	81.27(12)	C24	C23	C28	118.8(5)
Zn03[4]	Zn04	Zn01[1]	64.58(3)	C28	C23	C22	120.4(5)
O24	Zn04	Zn01[1]	33.65(12)	O10	C22	Zn03	41.5(2)
O24	Zn04	Zn03[4]	39.66(13)	O10	C22	O11	123.1(5)
O24	Zn04	O5[4]	116.44(16)	O10	C22	C23	119.3(5)
O24	Zn04	C8[4]	96.95(16)	O11	C22	Zn03	81.7(3)
O24	Zn04	C36[5]	100.23(17)	O11	C22	C23	117.6(5)
O5[4]	Zn04	Zn01[1]	90.79(12)	C23	C22	Zn03	160.7(4)
O5[4]	Zn04	Zn03[4]	105.71(13)	C16	C17	C18	120.3(6)
O5[4]	Zn04	C8[4]	24.87(16)	C32	C33	O15	115.8(5)
O5[4]	Zn04	C36[5]	130.34(19)	C32	C33	C34	119.2(6)
O17[5]	Zn04	Zn01[1]	107.82(14)	C34	C33	O15	125.0(5)
O17[5]	Zn04	Zn03[4]	150.03(12)	C9	C10	C11	120.0(5)
O17[5]	Zn04	O24	118.13(18)	C42	C41	C40	119.4(6)
O17[5]	Zn04	O5[4]	103.27(18)	C4	C5	O3	116.9(5)
O17[5]	Zn04	O13	115.8(2)	C4	C5	C6	122.4(5)
O17[5]	Zn04	C8[4]	101.98(18)	C6	C5	O3	120.6(5)
O17[5]	Zn04	C36[5]	27.12(18)	C13	C14	C9	118.6(5)
O13	Zn04	Zn01[1]	130.82(17)	C2	C3	C4	120.1(5)
O13	Zn04	Zn03[4]	66.31(16)	C12	C11	C10	117.9(5)
O13	Zn04	O24	102.2(2)	C7	C2	C1	119.0(5)
O13	Zn04	O5[4]	99.94(19)	C3	C2	C1	120.0(5)
O13	Zn04	C8[4]	121.12(19)	C3	C2	C7	120.9(5)
O13	Zn04	C36[5]	103.8(2)	C12	C13	C14	118.9(5)
C8[4]	Zn04	Zn01[1]	67.30(12)	O4	C8	Zn04[4]	84.3(3)
C8[4]	Zn04	Zn03[4]	101.08(12)	O4	C8	O5	124.5(5)
C36[5]	Zn04	Zn01[1]	104.88(13)	O4	C8	C9	120.4(5)
C36[5]	Zn04	Zn03[4]	123.69(14)	O5	C8	Zn04[4]	40.4(2)
C36[5]	Zn04	C8[4]	126.67(19)	O5	C8	C9	115.1(5)
P007	P006	P005	60.77(6)	C37	C36	Zn04[5]	159.0(4)

[1]1-X,1-Y,1-Z; [2]1+X,1+Y, +Z; [3]2-X,2-Y,2-Z; [4]-X, -Y,1-Z; [5]-X,1-Y,1-Z; [6]-1+X, -1+Y, +Z

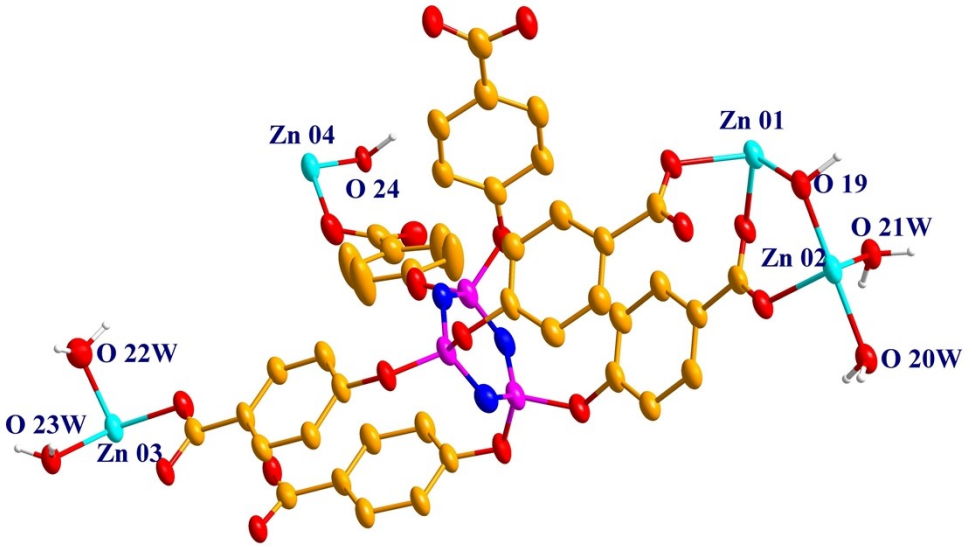


Figure S2 Asymmetric unit of Zn-MOF.

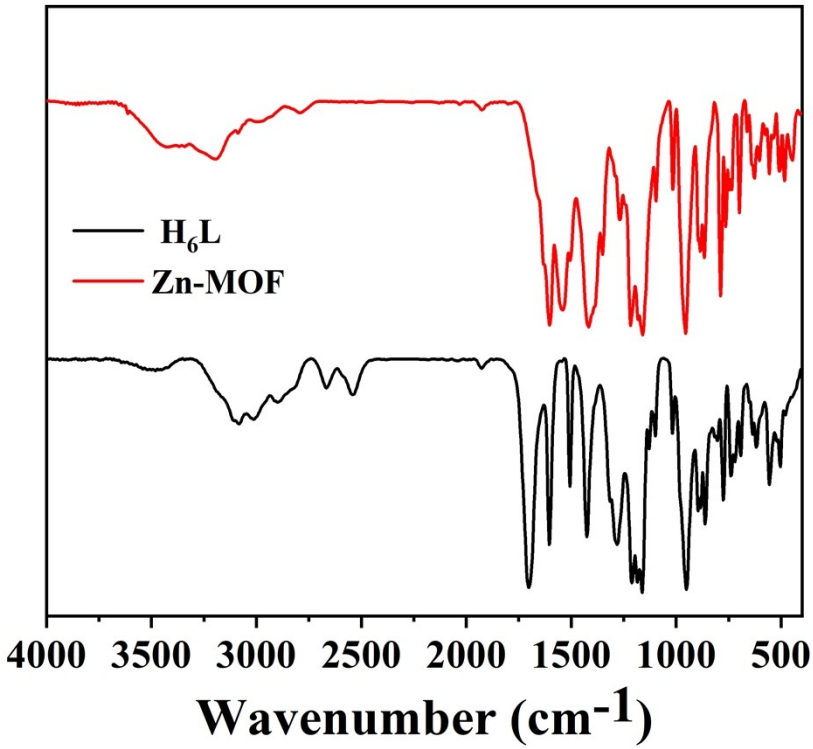


Figure S3 IR spectra of Ligand (black) and Zn-MOF (red)

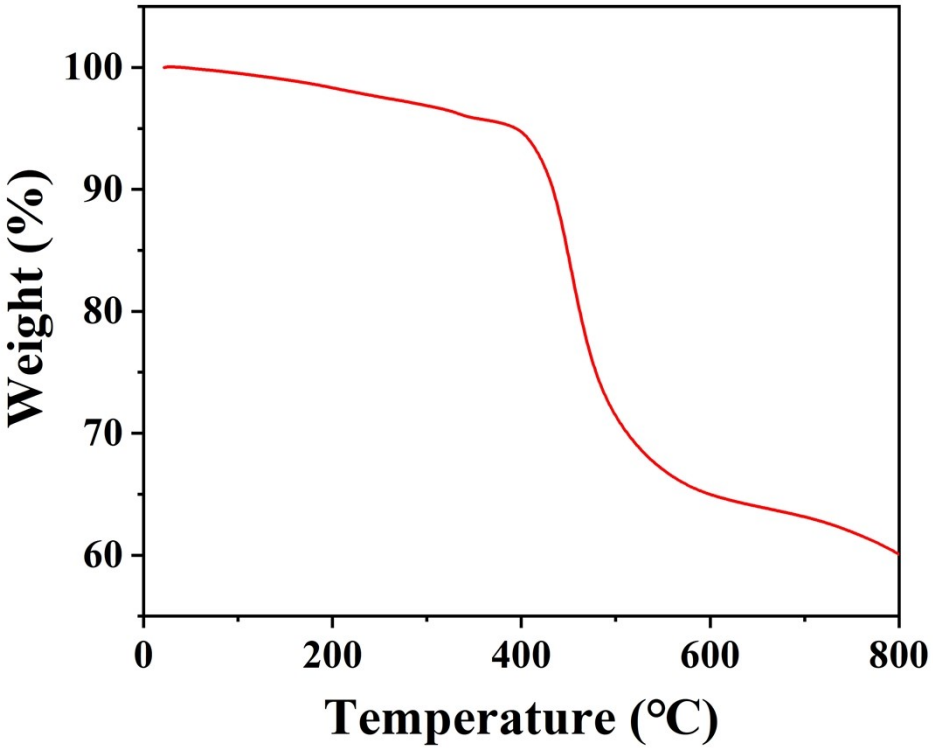


Figure S4 TGA curve of Zn-MOF

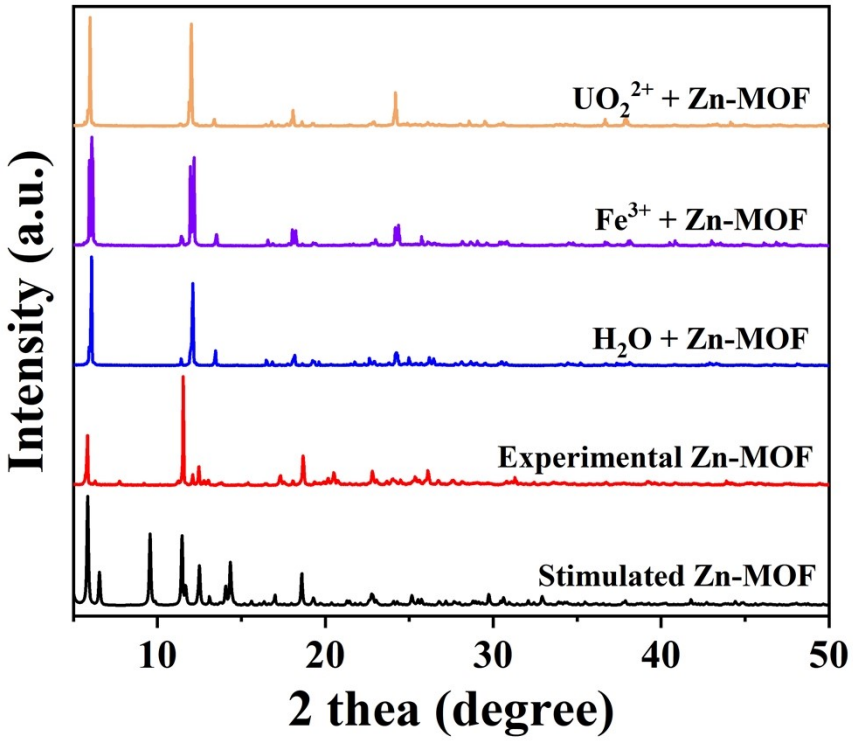


Figure S5 PXRD of Zn-MOF

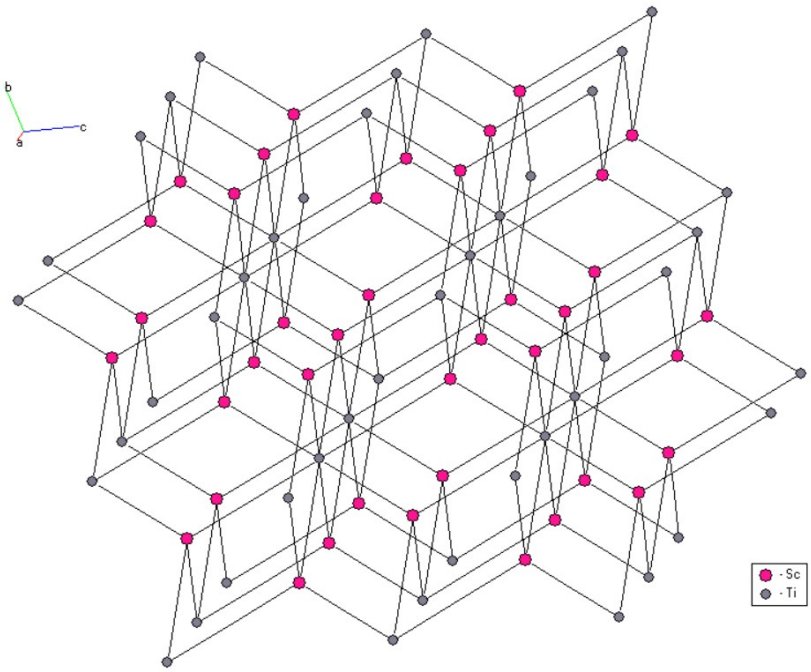


Figure S6. Topological structure of Zn-MOF(Si and Ti represent 4-c ligand and 8-c metal nodes)