Supporting Information

Synthesis, characterization, and luminescence modulation of a barium-tetracarboxylate framework with I^2O^1 connectivity

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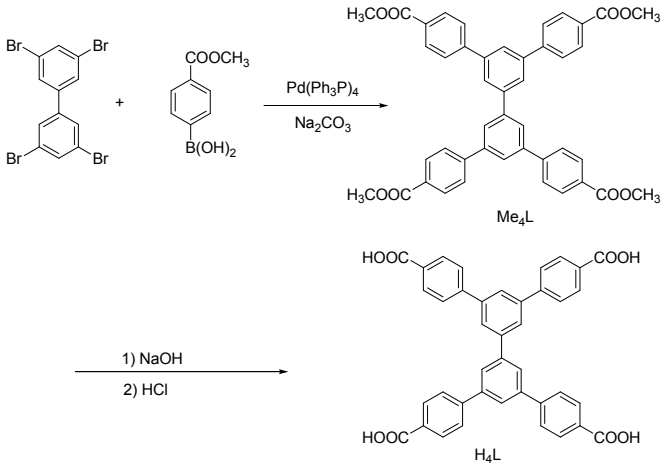
1. General remark

All reagents and solvents were used as received from commercial suppliers without further purification. The elemental analyses of C and H were performed on a Perkin-Elmer 2400 II elemental analyzer. NMR spectra were recorded on a Bruker AV400 MHz spectrometer. IR spectrum was measured in KBr pellets on a Nicolet 5DX FT-IR spectrometer. The thermogravimetric measurement was performed on preweighed samples in an oxygen stream using a Netzsch STA449C apparatus with a heating rate of 10 °C/min. Powder X-ray diffraction data were obtained using a Philips PW3040/60 automated powder diffractometer, using Cu-Kα radiation (λ = 1.542 Å) with a 2θ range of 5–30°. The varied temperature PXRD patterns were recorded using Bruke D8 ADVANCE.The excitation and luminescence spectra were performed on a HITACHIF-2500 fluorescence spectrometer in solid state at room temperature. The diffraction data was collected on a Bruker APEX II diffractometer equipped with a graphite-monochromatized Mo-Kα radiation (λ = 0.71073 Å) at 296(2) K. Data intensity was corrected by Lorentz-polarization factors and empirical absorption. The structures were solved by direct methods and expanded with difference Fourier techniques. All calculations were performed using SHELXS-97 and SHELXL-97 program packages.

2. Synthesis and characterization of the organic building block (H_4L)

The ligand biphenyl-3,3’,5,5’-tetra-(phenyl-4-carboxylic acid) was synthesized using a Suzuki coupling reaction. biphenyl-3,3’,5,5’-tetrabromide (1.00g, 2.13mmol), 4-(methoxycarbonyl)phenylboronic acid (2.32g, 29.01mmol) and Na_2CO_3(3.61g, 34.05mmol) were mixed in 75 mL of 2:2:1 $PhCH_3$/ MeOH/H_2O, and the mixture was de-aerated under Ar for 20 min.

[$Pd(PPh_3)_4$] (0.5g, 0. 22mmol) was added to the reaction mixture with stirring and the mixture heated to 90 ºC for three days under N_2. The product Me_4L was isolated by conventional extraction procedures. The final product H_4L was obtained by hydrolysis of the crude product Me_4L with 6M aqueous NaOH, followed by acidification with concentrated HCl. Yield: 0.85g, 85%. Elemental analyses (percentage calculated/found) for H_4L (C 75.7/75.3, H 4.13/4.17). Mass (ESI) m/z ($M-H^+$): 633.16. ^1H NMR (DMSO-d_6, 300 MHz): δ = 13.03 (s, 4H), 8.25 (d, 4H, J = 0.8 Hz), 8.09 (m, 18H); ^{13}C NMR (DMSO-d_6, 100 MHz): 167.65, 144.50, 142.07, 141.14, 130.42, 130.34, 127.98, 126.41, 125.69; Selected infrared (KBr，cm^{-1}): 3671, 2974, 2467, 1943, 1657, 1592, 1544, 1394, 1198, 1055, 1019, 858, 787, 733, 692, 668, 554.



Scheme S1 The synthetic route to the organic linker H_4L.

3. Synthesis and characterization of the compound

The organic linker H_4L (10.0 mg, 15.7 μmol) and $Ba(NO_3)_2$ (30.0 mg, 44.5 μmol) were dissolved in 4 mL of 1:1 DMF/H_2O in a disposable scintillation vial (20 mL). The vial was capped tightly and placed at an oven at 140 ºC for 48 h. The colourless block-shaped crystals were collected by filtration and washed with DMF in 26.1% yield. The compound can be characterized by the single-crystal X-ray structure determination, TGA, PXRD and microanalysis. Elemental analysis (percentage calculated/found): for $[Ba_5(L)_3(H_2O)_6]\cdot 25H_2O\cdot 10DMF\cdot 2Me_2NH_2^+$ (C 46.7/47.1, H 5.40/5.44, N 4.24/4.30). Selected infrared (KBr，cm^{-1}): 3392, 2971, 1751, 1652, 1646, 1586, 1540, 1395, 1184, 1091, 1045, 854, 788, 723, 670, 459.

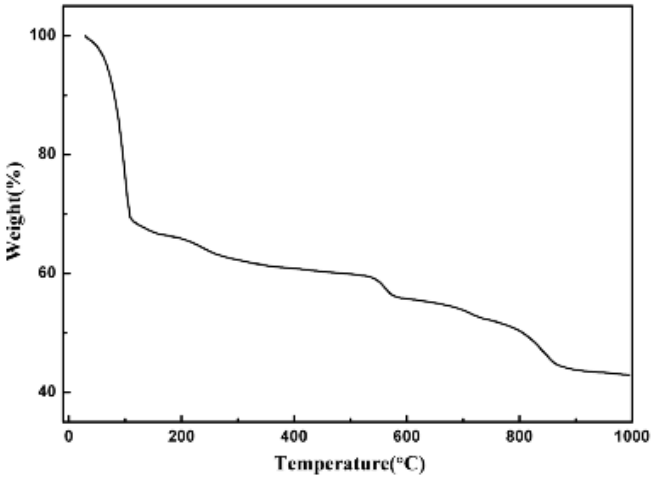


Fig. S1 TGA curves of the compound.

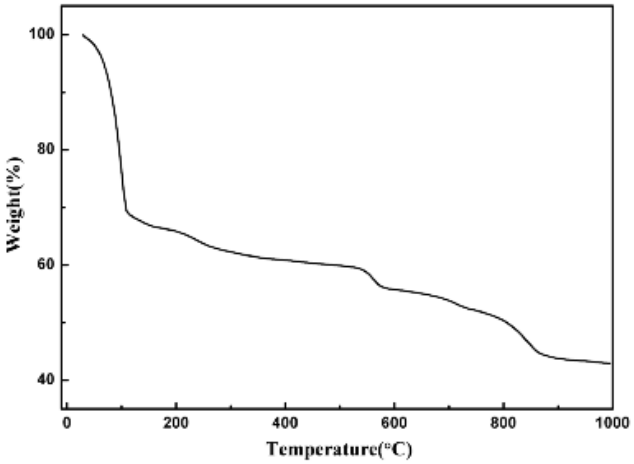


Fig. S2 PXRD patterns of the compound, along with the simulated XRD patterns (black) from their single-crystal X-ray structures and experimental patterns (red).

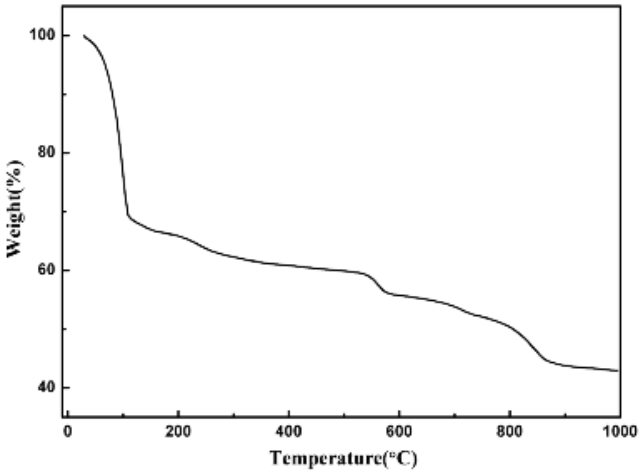


Fig. S3 PXRD patterns of the simulated from single X-ray crystal structure (black) and thermally activated the MOF at different temperatures.

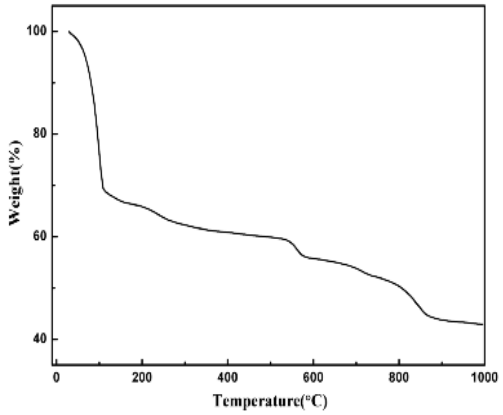


Fig. S4 Photoluminescent spectra of H_4L and the compound in solid state at room temperature.

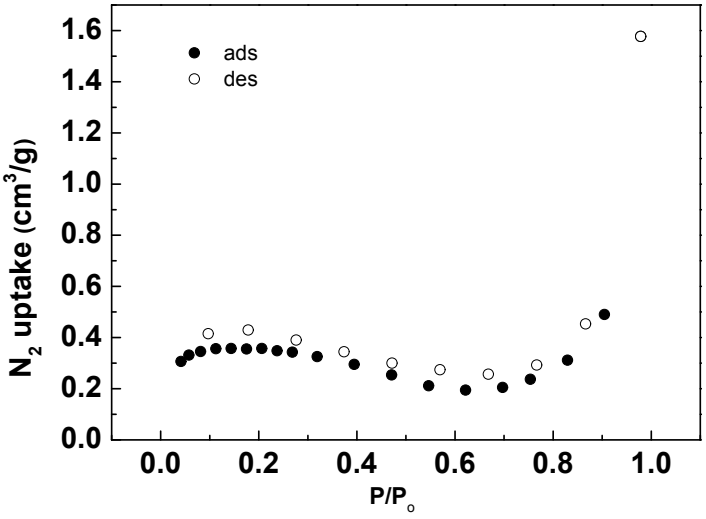


Fig. S5 The N_2 adsorption-desorption isotherms at 77 K. The sample was guest exchanged with dry acetone and evacuated under high vacuum at 60 °C to obtain the activated sample.

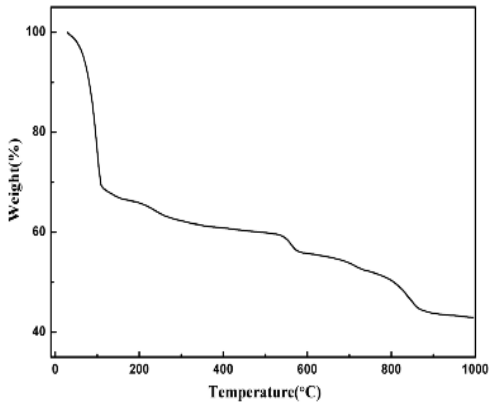


Fig. S6 FTIR spectra of the compound (red), H_4L (black).

Table S1 Crystal data and structure refinement for the compound

Empirical formula	$C_{154}\ H_{214}\ Ba_5\ N_{12}\ O_{65}$
Formula weight	3960.07
Temperature (K)	296(2) K
Wavelength (Å)	0.71073 Å
Crystal system, Space group	Hexagonal, *P* 6/m
Unit cell dimensions	*a* = 15.0263(3) Å
	b = 15.0263(3) Å
	c = 17.6363(6) Å
	α = 90.00 º
	β = 90.00 º
	γ = 120.00 º
Volume ($Å^3$)	3448.59(15)
Z, Calculated density ($g\ cm^{-3}$)	1, 1.907
Absorption coefficient (mm^{-1})	1.522
F (000)	2022
Crystal color	colourless

θ range for data collection (º)	1.94 to 27.48
Limiting indices	-19≤ h ≤16, -19≤ k ≤19, -22≤ l ≤22
Reflections collected / unique / observed reflections	25665 /2685 (R_{int} = 0.0779) / 1973 [$I > 2\sigma(I)$]
Completeness to theta = 27.48	98.0 %
Absorption correction	Empirical
Refinement method	Full-matrix least-squares on F^2
parameters	124
Goodness-of-fit (on F^2)	1.000
Final R indices [$I>2\sigma(I)$]	R = 0.0504, wR = 0.1651
R indices (all data)	R = 0.0772, wR = 0.1785
Largest diff. peak / hole (e Å^{-3})	1.405 / -1.243
CCDC	1001306

Table S2 Selected bond lengths and bond angles for the compound

Bond	Dist(Å)	Bond	Dist(Å)
Ba(1)-O(2)#1	2.812(5)	Ba(1)-C(13)	3.214(6)
Ba(1)-O(2)#2	2.812(5)	Ba(2)-O(1)#4	2.771(4)
Ba(1)-O(2)#3	2.812(5)	Ba(2)-O(1)#5	2.771(4)
Ba(1)-O(2)	2.812(5)	Ba(2)-O(1)#2	2.771(4)
Ba(1)-O(1W)	2.840(8)	Ba(2)-O(1)	2.771(4)
Ba(1)-O(1W)#3	2.840(8)	Ba(2)-O(1)#6	2.771(4)
Ba(1)-O(1)#3	2.896(4)	Ba(2)-O(1)#7	2.771(4)
Ba(1)-O(1)	2.896(4)	Ba(2)-O(1W)	2.945(8)
Ba(1)-O(1)#1	2.896(4)	Ba(2)-O(1W)#4	2.945(8)
Ba(1)-O(1)#2	2.896(4)	Ba(2)-O(1W)#7	2.945(8)
Angle	(°)	Angle	(°)
O(2)#1-Ba(1)-O(2)#2	180.0(3)	O(1W)#3-Ba(1)-O(1)#2	112.45(17)
O(2)#1-Ba(1)-O(2)#3	102.6(3)	O(1)#3-Ba(1)-O(1)#2	111.79(18)
O(2)#2-Ba(1)-O(2)#3	77.4(3)	O(1)-Ba(1)-O(1)#2	68.21(18)
O(2)#1-Ba(1)-O(2)	77.4(3)	O(1)#1-Ba(1)-O(1)#2	180.00(19)
O(2)#2-Ba(1)-O(2)	102.6(3)	O(1)#4-Ba(2)-O(1)#5	71.75(19)
O(2)#3-Ba(1)-O(2)	180.0(2)	O(1)#4-Ba(2)-O(1)#2	132.20(6)
O(2)#1-Ba(1)-O(1W)	70.47(14)	O(1)#5-Ba(2)-O(1)#2	89.13(14)
O(2)#2-Ba(1)-O(1W)	109.53(14)	O(1)#4-Ba(2)-O(1)	89.13(14)
O(2)#3-Ba(1)-O(1W)	70.47(14)	O(1)#5-Ba(2)-O(1)	132.20(6)
O(2)-Ba(1)-O(1W)	109.53(14)	O(1)#2-Ba(2)-O(1)	71.75(19)
O(2)#1-Ba(1)-O(1W)#3	109.53(14)	O(1)#4-Ba(2)-O(1)#6	89.13(14)

O(2)#2-Ba(1)-O(1W)#3	70.47(14)	O(1)#5-Ba(2)-O(1)#6	132.20(6)
O(2)#3-Ba(1)-O(1W)#3	109.53(14)	O(1)#2-Ba(2)-O(1)#6	132.20(6)
O(2)-Ba(1)-O(1W)#3	70.47(14)	O(1)-Ba(2)-O(1)#6	89.13(14)
O(1W)-Ba(1)-O(1W)#3	180.0(5)	O(1)#4-Ba(2)-O(1)#7	132.20(6)
O(2)#1-Ba(1)-O(1)#3	100.21(17)	O(1)#5-Ba(2)-O(1)#7	89.13(14)
O(2)#2-Ba(1)-O(1)#3	79.79(17)	O(1)#2-Ba(2)-O(1)#7	89.13(14)
O(2)#3-Ba(1)-O(1)#3	45.73(14)	O(1)-Ba(2)-O(1)#7	132.20(6)
O(2)-Ba(1)-O(1)#3	134.27(14)	O(1)#6-Ba(2)-O(1)#7	71.75(19)
O(1W)-Ba(1)-O(1)#3	112.45(17)	O(1)#4-Ba(2)-O(1W)	64.45(17)
O(1W)#3-Ba(1)-O(1)#3	67.55(17)	O(1)#5-Ba(2)-O(1W)	64.45(17)
O(2)#1-Ba(1)-O(1)	79.79(17)	O(1)#2-Ba(2)-O(1W)	67.76(16)
O(2)#2-Ba(1)-O(1)	100.21(17)	O(1)-Ba(2)-O(1W)	67.76(16)
O(2)#3-Ba(1)-O(1)	134.27(14)	O(1)#6-Ba(2)-O(1W)	144.07(9)
O(2)-Ba(1)-O(1)	45.73(14)	O(1)#7-Ba(2)-O(1W)	144.07(9)
O(1W)-Ba(1)-O(1)	67.55(17)	O(1)#4-Ba(2)-O(1W)#4	67.76(16)
O(1W)#3-Ba(1)-O(1)	112.45(17)	O(1)#5-Ba(2)-O(1W)#4	67.76(16)
O(1)#3-Ba(1)-O(1)	180.0(2)	O(1)#2-Ba(2)-O(1W)#4	144.07(9)
O(2)#1-Ba(1)-O(1)#1	45.73(14)	O(1)-Ba(2)-O(1W)#4	144.07(9)
O(2)#2-Ba(1)-O(1)#1	134.27(14)	O(1)#6-Ba(2)-O(1W)#4	64.45(17)
O(2)#3-Ba(1)-O(1)#1	100.21(17)	O(1)#7-Ba(2)-O(1W)#4	64.45(17)
O(2)-Ba(1)-O(1)#1	79.79(17)	O(1W)-Ba(2)-O(1W)#4	120
O(1W)-Ba(1)-O(1)#1	112.45(17)	O(1)#4-Ba(2)-O(1W)#7	144.07(9)
O(1W)#3-Ba(1)-O(1)#1	67.55(17)	O(1)#5-Ba(2)-O(1W)#7	144.07(9)
O(1)#3-Ba(1)-O(1)#1	68.21(18)	O(1)#2-Ba(2)-O(1W)#7	64.45(17)
O(1)-Ba(1)-O(1)#1	111.79(18)	O(1)-Ba(2)-O(1W)#7	64.45(17)
O(2)#1-Ba(1)-O(1)#2	134.27(14)	O(1)#6-Ba(2)-O(1W)#7	67.76(16)
O(2)#2-Ba(1)-O(1)#2	45.73(14)	O(1)#7-Ba(2)-O(1W)#7	67.76(16)
O(2)#3-Ba(1)-O(1)#2	79.79(17)	O(1W)-Ba(2)-O(1W)#7	120
O(2)-Ba(1)-O(1)#2	100.21(17)	O(1W)#4-Ba(2)-O(1W)#7	120
O(1W)-Ba(1)-O(1)#2	67.55(17)		

Symmetry transformations used to generate equivalent atoms: #1 -x+1,-y,-z #2 -x+1,-y,-z+1 #3 x,y,z-1 #4 x-y,x-1,-z #5 -x+y+1,-x+1,z #6 -y+1,x-y,z-1 #7 -x+y+1,-x+1,z-1 #9 x,y,-z+1 #10 -x+1,-y+1,-z+1 #11 1-x,-y,1-z, #12 x-y,-1+x,-z #13 1-y,x-y,-1+z #14 1-x+y,1-x,-1+z