

Electronic Supporting Information for

Microporous metal-organic open framework containing uncoordinated carbonyl groups as postsynthetic modification sites for cation exchange and Tb³⁺ sensor

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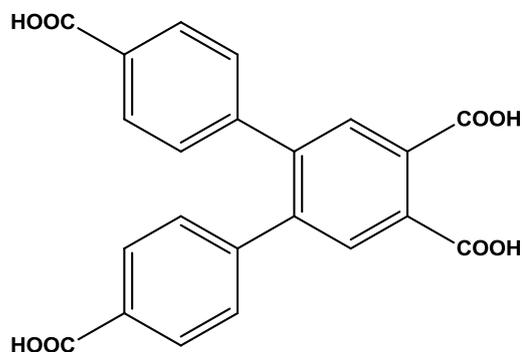
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Experimental Section

Materials and Physical Measurements:

All reagents and solvents were used as received from commercial supplies without further purification. Fourier transform infrared (FTIR) spectra (KBr disk) were measured with a Vertex 70 FTIR on a spectrophotometer (4000–400 cm^{-1}). Elemental analyses for C, H and N were obtained from a Perkin-Elmer 2400 elemental analyzer. The TG curves were recorded on a STA409PC Thermal analyzer in the N_2 atmosphere and at a heating rate of $10^\circ\text{C}/\text{min}$ in the temperature range of 20~800 $^\circ\text{C}$. Powder X-ray diffraction pattern (PXRD) was carried out on a EMPYREAN PANALYTICAL apparatus. The luminescence spectra for the powdered solid samples were measured at room temperature on a FLS920 fluorescence spectrophotometer. The excitation slit and the emission slit were 0.5 nm.

Structure of H_4ttca Ligand



[1,1':2',1'']-terphenyl]-4,4',4'',5'-tetracarboxylic acid(H_4ttca)

Preparation of MOF-COOH:

To synthesize the title compound, a mixture of $\text{Zn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (223 mg, 0.6 mmol), H_4ttca (120 mg, 0.3 mmol), 4,4'-bpy (94 mg, 0.6 mmol) in molar ratio 2 : 1 : 2 was dissolved in water (12 mL), then the solution was adjusted to pH 5.0 with 1 M NaOH solution, finally, it was placed in a 25 mL stainless steel reactor with a Teflon liner and heated to 160 $^\circ\text{C}$. The temperature was held for 120 h, then the reaction system was gradually cooled to room temperature at a rate of 5 $^\circ\text{C}/\text{h}$.

White block crystals of MOF-COOH were obtained with a yield of 61% (based on $\text{Zn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$). Anal. Calcd. (found) for $\text{Zn}_3\text{C}_{54}\text{H}_{34}\text{O}_{18}\text{N}_2$ ($M_w = 1194.94$): C, 54.27 (54.21); H, 2.87 (2.60); N, 2.34 (2.32) %. IR (KBr, cm^{-1}) = 3475(m), 3418(s), 3120(vs), 1720(s), 1597(s), 1543(s), 1463(s), 1398(s), 1281(m), 1226(s), 1074(w), 1009(w), 812(m), 712(m), 631(m), 469(w).

Crystallography:

Crystallographic data of MOF-COOH were collected on a SuperNova single crystal diffractometer equipped with graphite-monochromatic Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$). The data integration and empirical absorption correction were carried out by SAINT program. The crystal was kept at 153(2) K during data collection. Using Olex2,^{S1} the structure was solved with the XS^{S2} structure solution program using Direct Methods and refined with the XL^{S3} refinement package using Least Squares minimization. All hydrogen atoms in these coordination polymers were generated geometrically and refined isotropically using the riding model. Crystallographic data and structure refinement parameters for MOF-COOH are listed in Table S1. Selected Distances and Bond Angles for MOF-COOH are listed in Table S2.

Reference:

- S1. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, OLEX2: a complete structure solution, refinement and analysis program. *J. Appl. Cryst.* 2009. **42**, 339-341.
- S2. *SHELXS-97*. (Sheldrick, 1990)
- S3. XL, G.M. Sheldrick, *Acta Cryst.* (2008). **A64**, 112-122

Table S1. Crystal Data and Structure Refinement for MOF-COOH

Identification code	MOF-COOH
Empirical formula	C ₅₄ H ₃₄ N ₂ O ₁₈ Zn ₃
Formula weight	1194.94
Temperature/K	153(2)
Crystal system	triclinic
Space group	P $\bar{1}$
a/Å	10.2304(13)
b/Å	10.5293(13)
c/Å	13.0853(14)
α /°	100.836(10)
β /°	90.736(9)
γ /°	113.420(12)
Volume/Å ³	1264.3(3)
Z	1
ρ_{calc} /mg/mm ³	1.564
m/mm ⁻¹	1.490
F(000)	602.0
2 θ range for data collection	5.14 to 50°
Index ranges	-12 ≤ h ≤ 6, -12 ≤ k ≤ 12, -15 ≤ l ≤ 15
Reflections collected	7884
Independent reflections	4462[R(int) = 0.1044]
Data/restraints/parameters	4462/371/350
Goodness-of-fit on F ²	0.992
Final R indexes [I ≥ 2σ(I)]	R ₁ = 0.0847, wR ₂ = 0.1659
Final R indexes [all data]	R ₁ = 0.1550, wR ₂ = 0.2137
Largest diff. peak/hole / e Å ⁻³	1.35/-0.92

Table S2. Selected Distances and Bond Angles for MOF-COOH

MOF-COOH			
Distances [Å]			
Zn1- O6 ^B	2.070(6)	Zn2- O3	2.105(6)
Zn1- O8 ^C	2.055(5)	Zn2- O5 ^A	2.139(6)
Zn1- O9	2.211(6)	Zn2 ^C - O7	1.948(6)
Zn2- N1	2.062(8)	Zn2- O9	2.057(6)
Angles [°]			
O6 ^B -Zn1-O9	86.4(2)	O7 ^C -Zn2-N1	119.1(3)
O6 ^A -Zn1-O9	93.6(2)	O7 ^C -Zn2-O3	87.8(2)
O8 ^C -Zn1-O6 ^A	91.8(2)	O7 ^C -Zn2-O5 ^A	97.0(2)
O8 ^C -Zn1-O6 ^B	88.2(2)	O7 ^C -Zn2-O9	122.3(2)
O8 ^C -Zn1-O9	89.0(2)	O9-Zn2-N1	118.5(3)
O8 ^E -Zn1-O9	91.0(2)	O9-Zn2-O3	88.1(2)
N1-Zn2-O3	91.6(3)	O9-Zn2-O5 ^A	85.9(2)
N1-Zn2-O5 ^A	89.5(3)		

Symmetry code: A $-1+x, -1+y, -1+z$; B $2-x, 1-y, 2-z$; C $1-x, -y, 2-z$; D $x, y, -1+z$; E $1-x, -y, 1-z$.

Preparation of Na⁺@MOF-COO⁻ and Ln³⁺@MOF-COO⁻ (Ln = Sm³⁺, Eu³⁺, Dy³⁺ or Tb³⁺)

One solution of MeONa in MeOH (0.05 M) and the other of Ln³⁺ nitrate in MeOH (0.1 M) both were prepared in advance. Ln³⁺ cation exchange process is carried out in the following manner: a) the MOF-COOH (0.2 mmol, 0.3g) was soaked with MeONa solution (20 ml), held for 120 h, then washed with MeOH five times and removed solution; b) the material was soaked in the Ln³⁺ nitrate solution (6 ml), held for 24 h, then refreshed the Ln³⁺ nitrate solution, repeated the procedure in total of 15 times; c) After cation exchange was completed, the materials were thoroughly washed with MeOH for five times, then soaked in MeOH for 24 h, and the solution was removed in the end. After completion of this procedure, XRD patterns were collected for each cation-exchanged material (Fig 3).

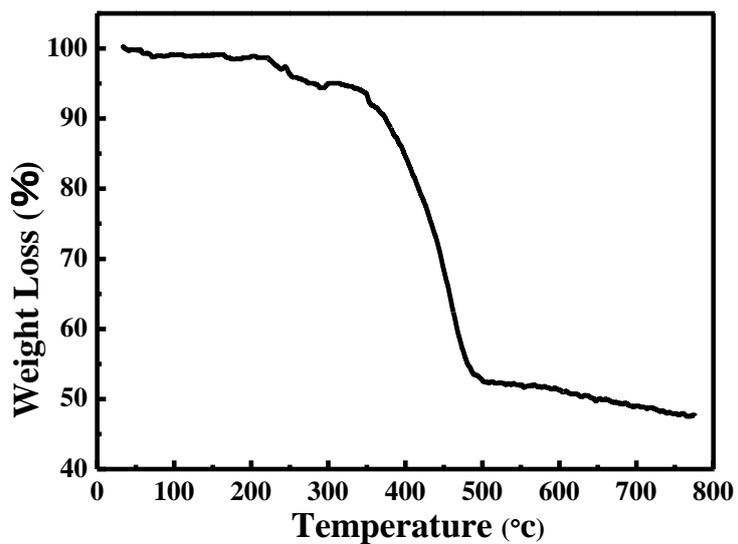


Fig S1. Thermogravimetric analyses of MOF-COOH.

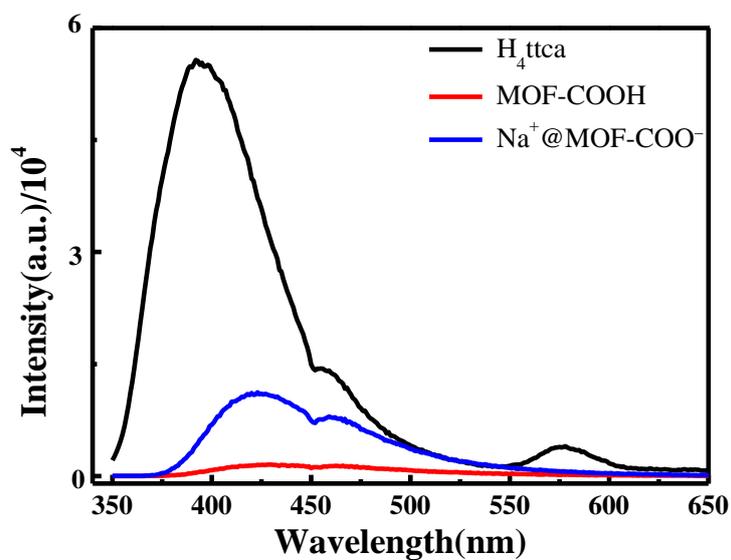


Fig S2. Photoluminescences of H₄ttca ligand , MOF-COOH and Na⁺@MOF-COO⁻.

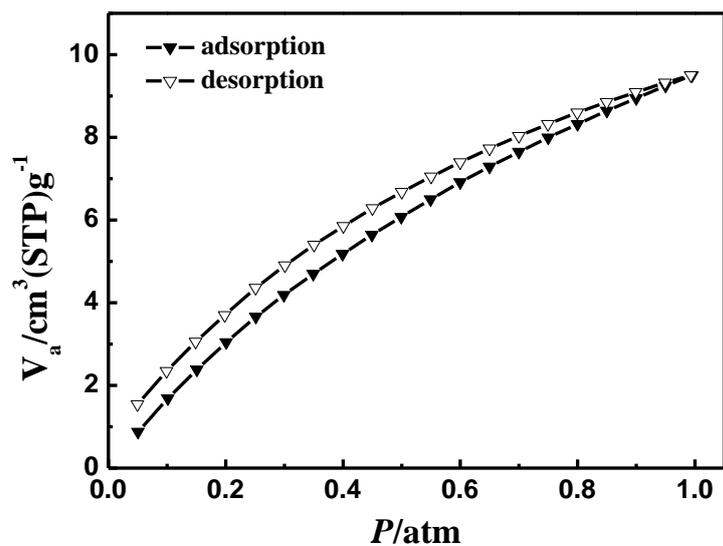


Fig S3. CO₂ (298K) sorption isotherms for MOF-COOH.

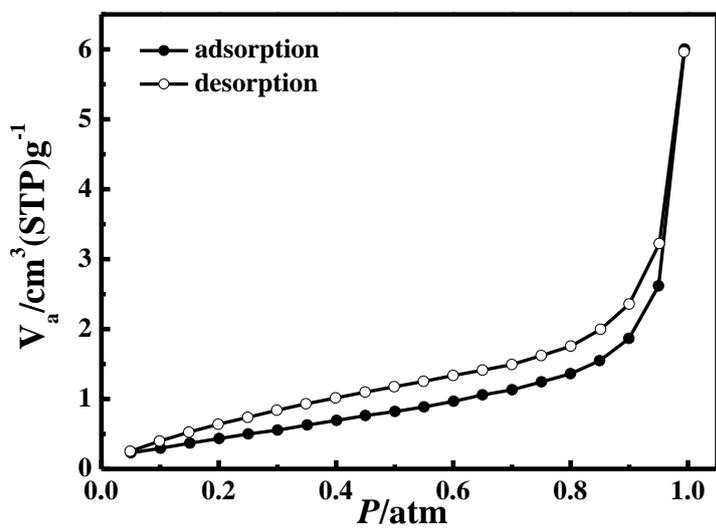


Fig S4. N₂ (77K) sorption isotherms for MOF-COOH.

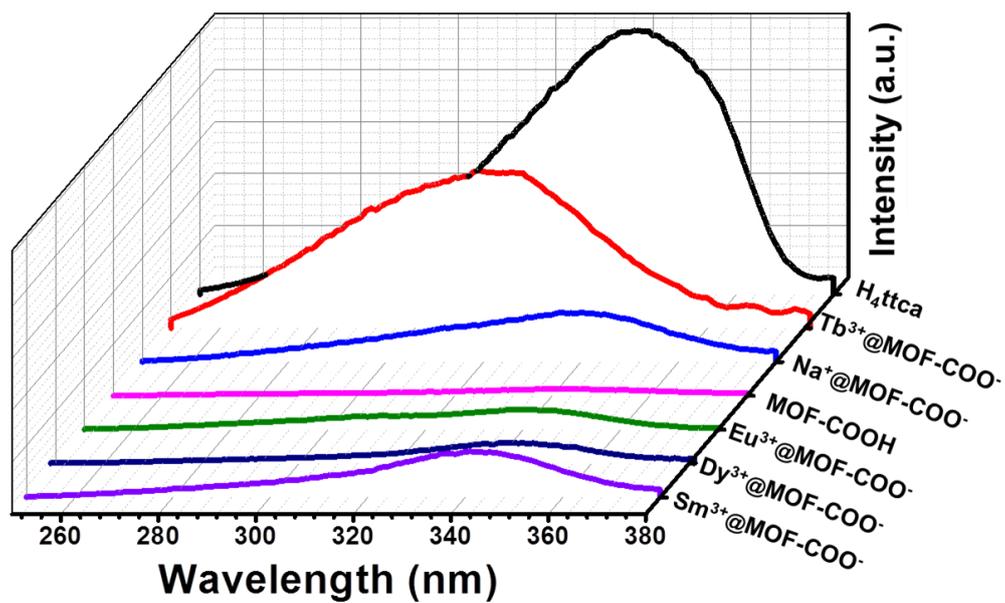


Fig S5. The excitation spectrum of H₄ttca ligand, MOF-COOH, Na⁺@MOF-COO⁻ and Ln³⁺@MOF-COO⁻.

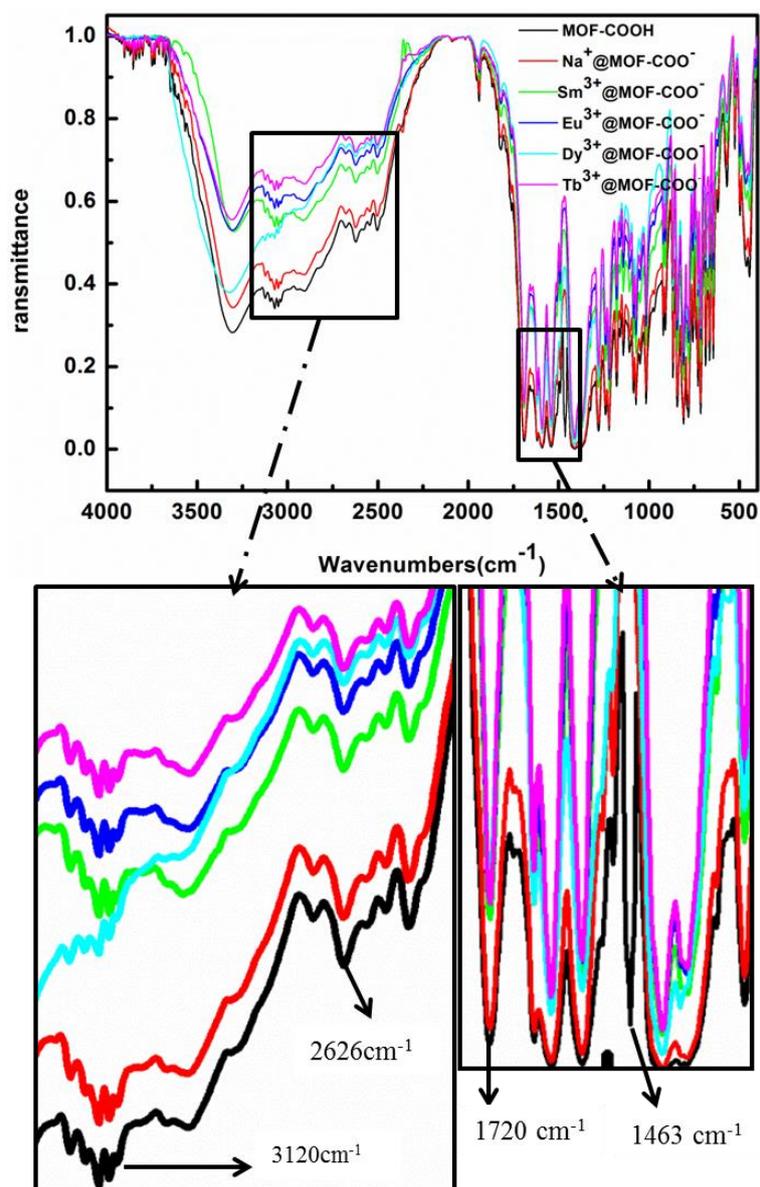


Fig. S6. IR spectra of MOF-COOH, Na⁺@MOF-COO⁻ and Ln³⁺@MOF-COO⁻ (Ln = Sm³⁺, Dy³⁺, Eu³⁺ or Tb³⁺).

IR spectra of MOF-COOH and Ln³⁺@MOF-COO⁻ indicate that lanthanide cations incorporated into the pores of MOF. For MOF-COOH, characteristic absorption peaks at 1463cm⁻¹ and ~3000 cm⁻¹ attributing to the free carbonyl O-H groups appears. While, for the cations exchanged MOFs (Ln³⁺@MOF-COO⁻ or Na⁺@MOF-COO⁻), these characteristic absorption peaks become much weaker. In addition, the strong absorption at 1720 cm⁻¹ belongs to stretching vibrations of carbonyl C=O group changed weaker due to the coordination effect between Ln³⁺ and the carbonyl groups