

Electronic Supplementary Information (ESI)

for

Structure Stabilization of a Metal-Organic Framework for Gas Sorption Investigation

Qiang Gao,^{a,c} Xiao-Lin Zhao,^{a,c} Ze Chang,^{a,c,*} Jian Xu,^{a,c} Xian-He Bu^{a,b,c}

^aSchool of Materials Science and Engineering, National Institute for Advanced Materials, TKL of Metal and Molecule-Based Material Chemistry, Nankai University, Tianjin 300350, China.

^bCollege of Chemistry, Nankai University, Tianjin 300071, China.

^cCollaborative Innovation Center of Chemical Science and Engineering (Tianjin), Nankai University, Tianjin, 300071, China.

Corresponding author Email: changze@nankai.edu.cn

Materials and Instruments

All commercial available reagents and organic solvents were used as received without further purification. The organic ligands 4-(4'-carboxyphenyl)-1,2,4-triazole (Hcpt) and tri(4-pyridyl)-1,3,5-triazine (tpt) were synthesized according to the procedure described in the literatures.^{S1} The IR spectrum in KBr pellet was recorded in the range 500-4000 cm⁻¹ with a TENSOR 27 OPUS Fourier transform infrared (FT-IR) spectrometer (Bruker). Thermogravimetric analysis was carried out by using a Rigaku standard TG-DTA analyzer with a heating rate of 10 °C/min from ambient temperature to 700 °C. Powder X-ray diffraction spectra were collected on a Rigaku D/Max-2500 diffractometer at 40 kV and 100 mA with a Cu-target tube and a graphite monochromator. Gas adsorption isotherms were collected using a Micromeritics surface area analyzer ASAP-2020 M. Before the measurements, the sample of **Co-MOF1-tpt** was activated at the “degas” port under the vacuum at 150 °C for 6 hours. The measurement temperatures of 77 K, 273 K, and 298 K were achieved using a liquid nitrogen bath, water-ice bath, and electric heating jacket, respectively.

Synthesis of [Co₃(μ₃-O)(cpt)₃tpt·NO₃]_x S (Co-MOF1-tpt)

A mixture of Hcpt (5.3 mg, 0.0028 mmol), Co(NO₃)₂·6H₂O (220 mg, 0.75 mmol) and 40.0 mg tpt was mixed with 10 mL DMF, 3 mL EtOH and 0.3 mL water. The mixture was placed in a scintillation vial (20 mL) and kept at 90 °C for 24 hours. After the vial was cooled to room temperature, orange-red block crystals were obtained with a yield of ~ 20 % [based on Co(NO₃)₂]. IR (KBr, cm⁻¹): 3423.73 (s), 2360.58 (m), 1656.79 (m), 1607.35 (m), 1519.22 (m), 1384.7 (s), 1257.07 (w), 1102.10 (w), 1060.47 (m), 784.47 (w), 669.26 (w), 518.28 (w).

X-ray crystallography

The crystallographic data of **Co-MOF1-tpt** was collected using a Rigaku Saturn 724+ diffractometer at 113 K with Mo K α monochromated radiation ($\lambda = 0.71073 \text{ \AA}$). The structure was solved by using the direct method and refined through the full matrix least-squares method on F^2 using SHELXL-2014.^{S2} Anisotropic thermal parameters were used to refine all non-hydrogen atoms. The hydrogen atoms were added theoretically riding on the concerned atoms, and refined with fixed thermal factor. The structure has been refined as an inversion twin. The highly disordered guests (solvent and counter ions) in **Co-MOF1-tpt** were removed by the SQUEEZE routine in PLATON and the result was appended in the CIF file.^{S3} The existence of NO₃⁻ could be ascertained by the strong IR peak at 1385 cm⁻¹ (assigned to the asymmetrical stretching vibration of N-O bands in NO₃⁻),^{S4} and the quantity of NO₃⁻ is determined based on the electroneutrality principle. The crystal structure has been deposited at the Cambridge Crystallographic Data Center and allocated the deposition number (CCDC 1443859). The data can be obtained free of charge via http://www.ccdc.cam.ac.uk/data_request/cif.

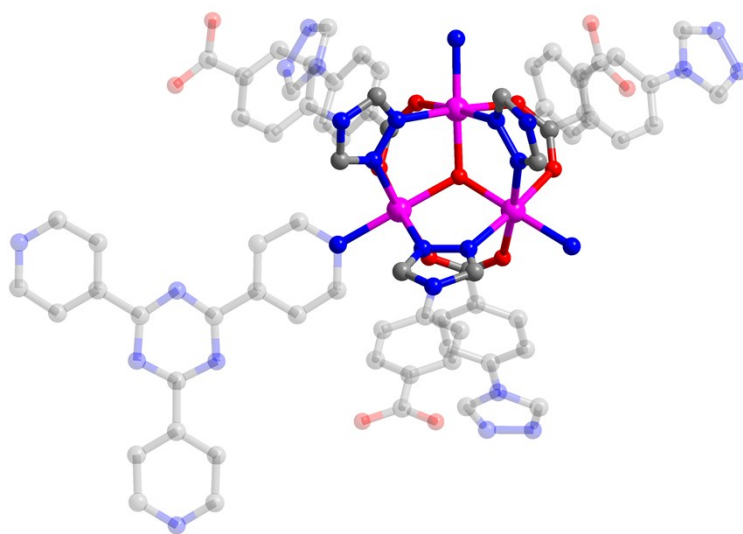


Figure S1. The cobalt trigonal prismatic SBU in **Co-MOF1-tpt**.

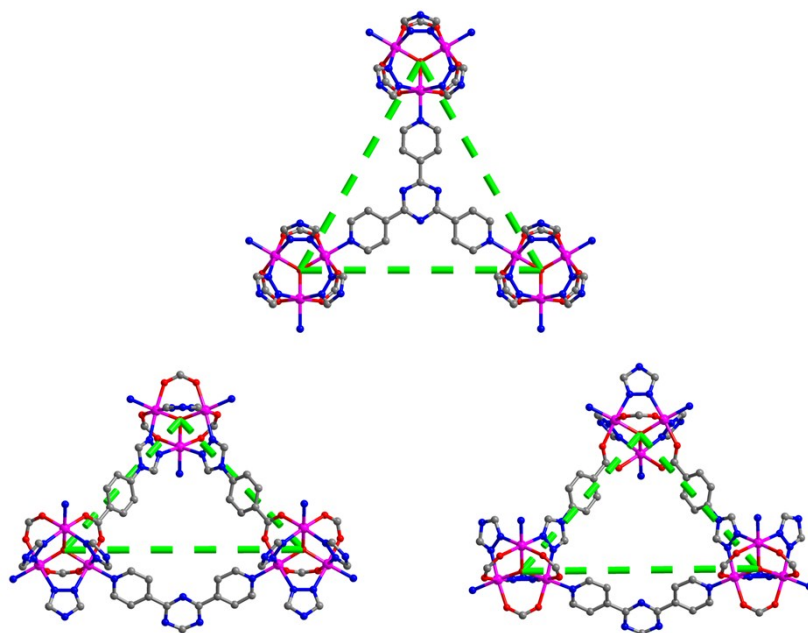


Figure S2. Fundamental triangle motifs in the framework of **Co-MOF1-tpt**.

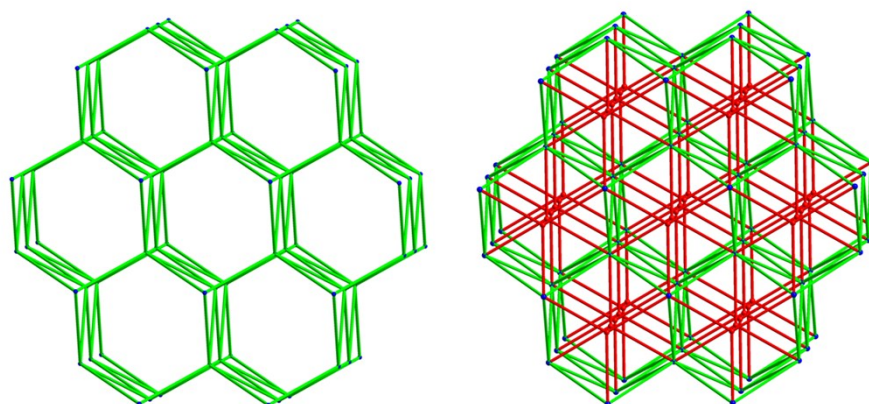


Figure S3. The acs net of **Co-MOF1** (left) and the uncoded binodal 3,9-c net (vertex symbol $\{4^{21}.6^{15}\}\{4^3\}$) of **Co-MOF1-tpt** (right).

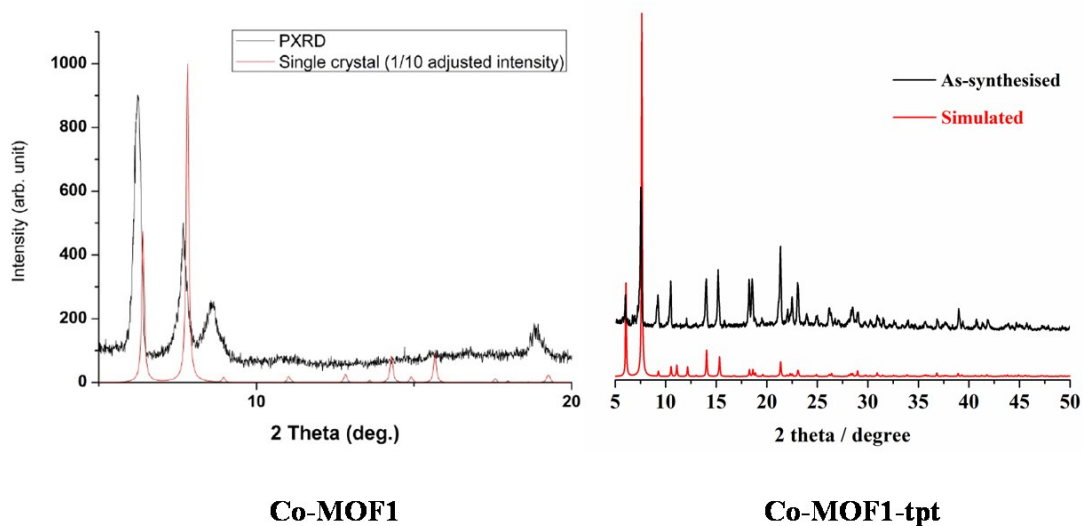


Figure S4. The X-ray powder diffractions patterns of the simulated and as-synthesised **Co-MOF1^{SS}** (left) and **Co-MOF1-tpt** (right).

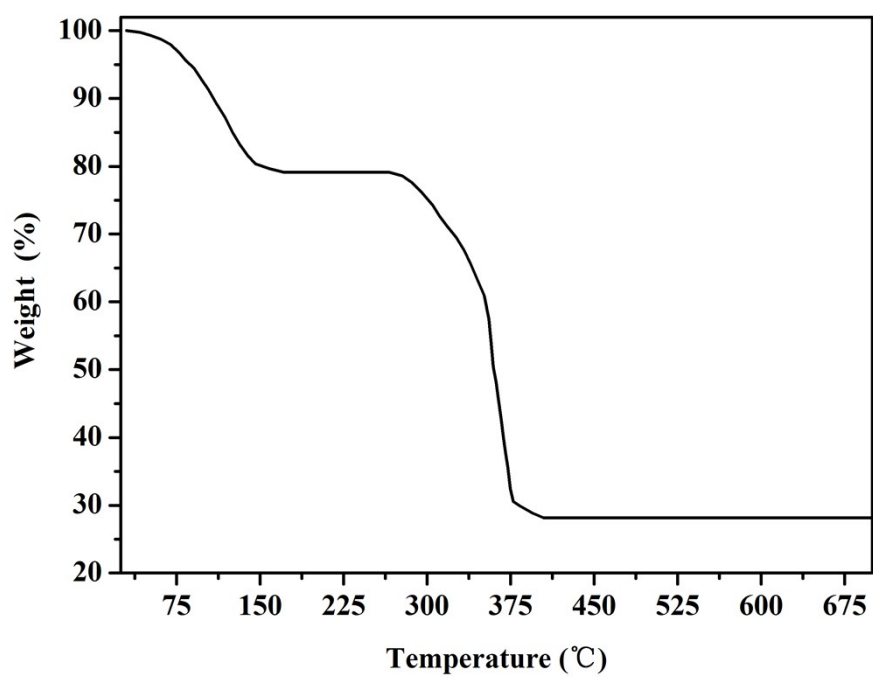


Figure S5. The TGA profile of Co-MOF1-tpt.

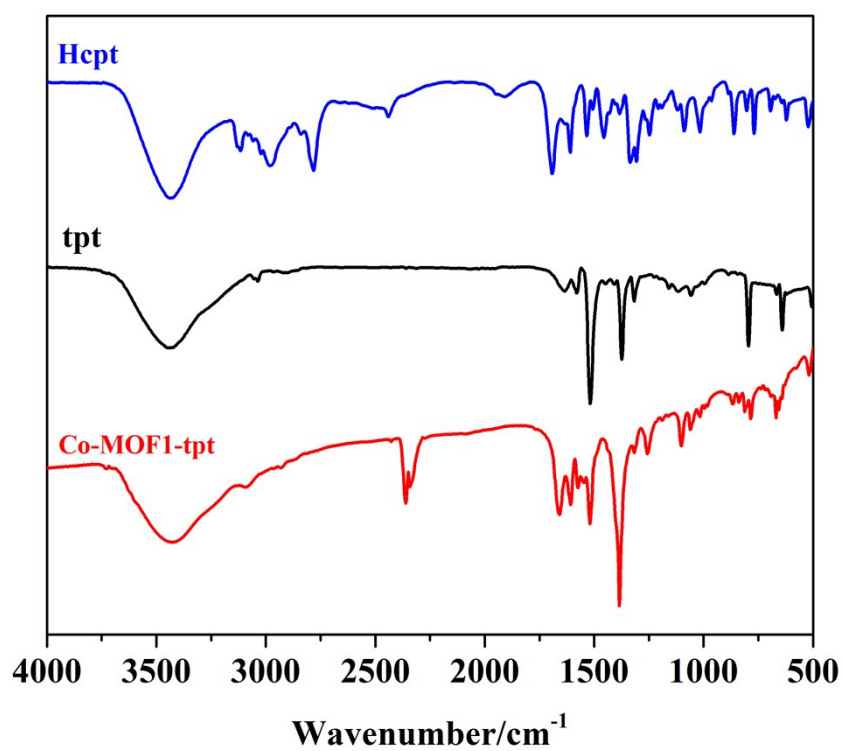


Figure S6. The IR spectrums of Hcpt, tpt and Co-MOF1-tpt .

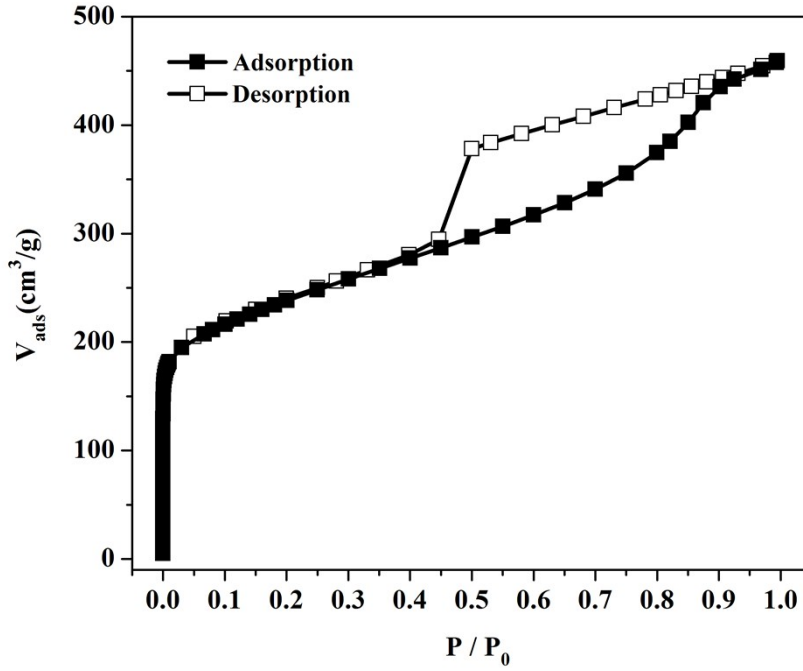


Figure S7. N₂ sorption isotherms of **Co-MOF1-tpt** at 77 K.

Estimation of the Isostatic Heat of Adsorption

The virial-type expression comprising the temperature-independent parameters a_i and b_i was employed to estimate the enthalpies of CO₂ on **Co-MOF1-tpt**.^{S6} The data were fitted by the equation (I):

$$\ln P = \ln N + \frac{1}{T} \sum_{i=0}^m a_i N^i + \sum_{i=0}^n b_i N^i \quad (\text{I})$$

Here, P is the pressure expressed in Pa, N is the amount adsorbed in mol/g, T is the temperature in K, a_i and b_i are virial coefficients, m and n represent the number of coefficients required to adequately describe the isotherms. The values of the virial coefficients a_0 to a_m were used to estimate the isosteric heat of adsorption using the equation (II):

$$Q_{st} = -R \sum_{i=0}^m a_i N^i \quad (\text{II})$$

Where, Q_{st} is the coverage-dependent isosteric heat of adsorption and R is the universal gas constant.

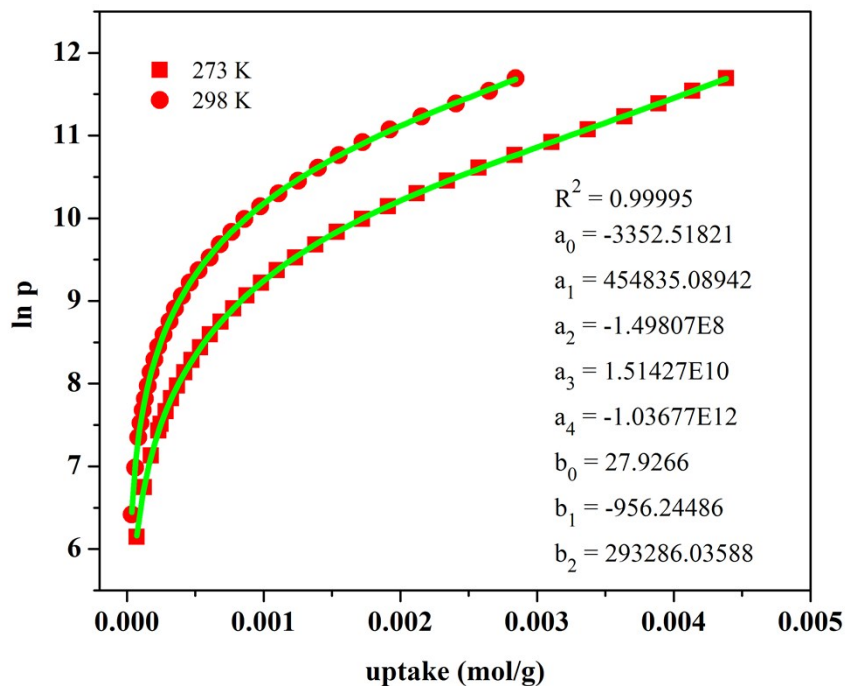


Figure S8. The CO₂ adsorption data at 273 K and 298 K (symbols) and the virial equation fits (green lines) for **Co-MOF1-tpt**.

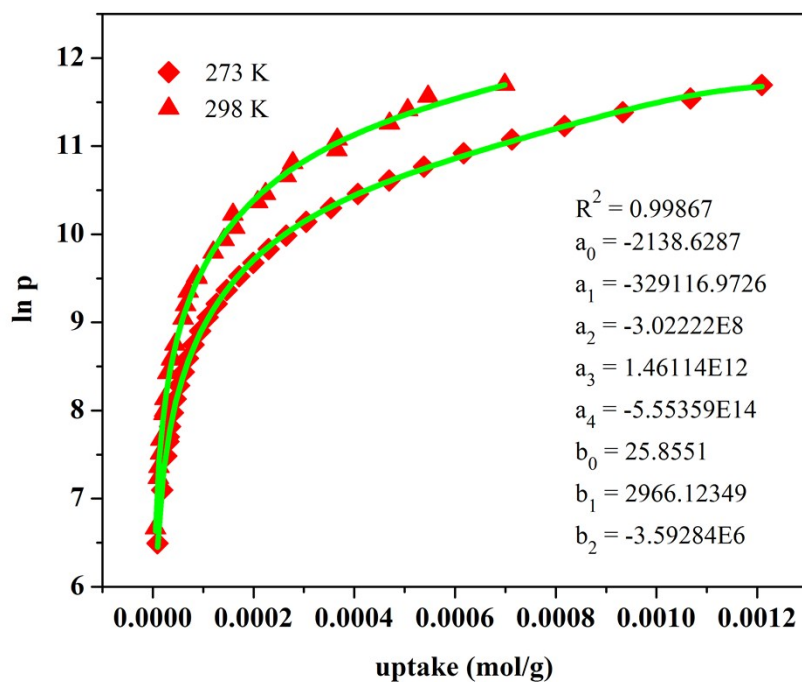


Figure S9. The CH₄ adsorption data at 273 K and 298 K (symbols) and the virial equation fits (green lines) for **Co-MOF1-tpt**.

Prediction of the Gases Adsorption Selectivity by IAST

IAST (ideal adsorption solution theory) was used to predict binary mixture adsorption from the experimental pure-gas isotherms.^{S7} In order to perform the integrations required by IAST, the single-component isotherms were fitted by the dual-site Langmuir-Freundlich equation (III).

$$q = \frac{q_{m,1}b_1P^{1/n_1}}{1 + b_1P^{1/n_1}} + \frac{q_{m,2}b_2P^{1/n_2}}{1 + b_2P^{1/n_2}} \quad (\text{III})$$

where P = the pressure of the bulk gas at equilibrium with the adsorbed phase

q = the adsorbed amount per mass of adsorbent (mmol /g)

$q_{m,1}$ and $q_{m,2}$ = the saturation capacities of sites 1 and 2 (mmol/g)

b_1 and b_2 = the affinity coefficients of sites 1 and 2 (1/kPa)

n_1 and n_2 = the deviations from an ideal homogeneous surface.

The selectivity $S_{A/B}$ in a binary mixture of components A and B is defined as

$(\frac{x_A}{y_A})/(\frac{x_B}{y_B})$, where x_i and y_i are the mole fractions of component i ($i = A, B$)

in the adsorbed and bulk phases, respectively.

Table S1. The parameters for the Dual-site Langmuir-Freundlich equation fit for the pure isotherms of CO₂ and CH₄ in Co-MOF1-tpt.

	273 K		298 K	
	CO ₂	CH ₄	CO ₂	CH ₄
R ²	0.99999	0.99998	0.99994	0.99919
q_{m1}	4.04662	0.76038	4.87557	0.89638
q_{m2}	1.90696	3.42117	0.31838	0.00874
b_1	0.00238	0.01748	0.01148	0.00685
b_2	0.07719	4.03559E-4	4.11938E-11	3.88229E-12
$1/n_1$	1.41637	0.91421	0.95576	1.08513
$1/n_2$	0.91624	1.37418	5.43852	6.51765

Table S2. The comparison about porosity, gas sorption of **Co-MOF1** and **Co-MOF1-tpt**.

	Co-MOF1	Co-MOF1-tpt
BET surface area	15 m ² /g	826 m ² /g
CO ₂ adsorption amount at 273 K and 1 atm	Framework collapsed upon removal of solvent molecules	4.38 mmol/g
CO ₂ /CH ₄ selectivity at 273 K (at low pressure)		11.5

Reference:

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