

Electronic Supplementary Information (ESI)

**A Unique “Cage-in-Cage” Metal-Organic Framework based on
Nested Cages from Interpenetrated Networks**

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Experimental section

Materials and physical measurements

Tpt was synthesized according to the reported methods,¹ and other solvents and reagents were obtained commercially and used as received. IR spectrum was measured on a TENSOR 27 OPUS (Bruker) FT-IR spectrometer with KBr pellet in the 4000–400 cm^{-1} range. Thermogravimetric analyses (TGA) was carried out on a Rigaku standard TG-DTA analyzer with a heating rate of $10^\circ\text{C min}^{-1}$ from ambient temperature to 800°C , using an empty Al_2O_3 crucible as the reference. The room-temperature X-ray powder diffraction spectra (XRPD) were recorded on a Rigaku D/Max-2500 diffractometer equipped with a Cu-target tube and a graphite monochromator. Simulation of the XRPD patterns based on single-crystal data was carried out by using Mercury (Hg) program that is available free of charge via the Internet at <http://www.iucr.org>.

Synthesis of MOF 1

$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.1 mmol), tpt (0.05 mmol) and H_2bpda (0.05 mmol) were added into a mixture of N, N'-dimethylmethanamide (DMF) and ethanol (10 mL, v:v = 1:1). The mixture was ultrasounded to a suspension and then sealed in a capped vial. The vial was heated at 95°C for 3 days and then cooled to room temperature. Red crystal was obtained with a yield of ca. 30% based on metal salts. FT-IR (KBr pellets, cm^{-1}): 3379 w, 3045 w, 2929 w, 1665 s, 1616 s, 1574 s, 1553 s, 1424 m, 1374 s, 1018 m, 821 m, 769 m, 708 m, 516 w, 454 w.

Single crystal X-ray diffraction analysis

Single crystal X-ray diffraction measurement for **1** was carried out using a Rigaku Saturn724⁺ diffractometer at 113 K. The data collection was performed with Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) and unit cell dimensions were determined with least-squares refinements. The program SAINT² was used for integrating the diffraction profiles. The structure was solved by direct methods using the SHELXS program of the SHELXTL package and refined by full-matrix least-squares methods with SHELXL (semiempirical absorption corrections were applied using SADABS program).³ The final refinement was performed by full-matrix least-squares method with anisotropic thermal parameters for non-hydrogen atoms on F^2 . The location of hydrogen atoms of coordinated water was not able to be assigned. Free solvent molecules in **1** were highly disordered, and attempts to

locate and refine the solvent peaks were unsuccessful. The diffuse electron densities resulting from these residual solvent molecules were removed from the data set using the SQUEEZE routine of PLATON and refined further using the data generated.⁴ The contents of the solvent region are not represented in the unit cell contents in crystal data. Attempts to determine the final formula of such compounds from the SQUEEZE results combined with elemental analysis and TGA data were also unsuccessful because of the volatility and complexity of solvents; therefore, an accurate data set could not be obtained. The contents of the solvent region are not represented in the unit cell contents in crystal data.

Adsorption Measurements

Gas adsorption measurements were performed using an ASAP 2020 M gas adsorption analyzer. UHP-grade gases were used in the measurements. The CO₂ and CH₄ sorption isotherms were collected at 273 and 298 K, respectively. Before the measurements, the sample was soaked in methanol for 3 days to exchange the solvent and then filtered and dried at room temperature. The dried samples were loaded in sample tubes and activated under high vacuum (less than 10⁻⁵ Torr) at 150°C. About 100 mg of degassed sample was used for gas sorption measurements.

Estimation of adsorption enthalpies

Models were used for interpolating isotherm pressure values at specific amount adsorbed from isotherm data. The method uses the following Virial equation:

$$\ln(p) = \ln(n) + (1/T) \sum_{i=0}^m a_i n^i + (1/T) \sum_{j=0}^n b_j n^j$$

where p is pressure, n is amount adsorbed, T is temperature, and a_i and b_j are temperature independent empirical parameters. The isosteric heat of adsorption (Q_{st}) as a function of gas uptake can be obtained over a wide loading range from the following equation:

$$Q_{st} = -R \sum_{i=0}^m a_i n^i$$

Prediction of the Gases Adsorption Selectivity by IAST

IAST (ideal adsorption solution theory)⁵ was used to predict binary mixture adsorption from the experimental pure-gas isotherms. In order to perform the integrations required by IAST, the single

component isotherms should be fitted by a proper model. In practice, several methods to do this are available. We found for this set of data that the dual-site Langmuir-Freundlich equation was successful in fitting the data.

$$q = \frac{q_{m,1}b_1P^{1/n_1}}{1 + b_1P^{1/n_1}} + \frac{q_{m,2}b_2P^{1/n_2}}{1 + b_2P^{1/n_2}}$$

Here, P is the pressure of the bulk gas at equilibrium with the adsorbed phase (kPa), q is the adsorbed amount per mass of adsorbent (mmol/g), $q_{m,1}$ and $q_{m,2}$ are the saturation capacities of sites 1 and 2 (mmol/g), b_1 and b_2 are the affinity coefficients of sites 1 and 2 (1/kPa), and n_1 and n_2 represent the deviations from an ideal homogeneous surface. The fitted parameters were then used to predict multicomponent adsorption with IAST.

The selectivity $S_{A/B}$ in a binary mixture of components A and B is defined as $(x_A/y_A) / (x_B/y_B)$, where x_i and y_i are the mole fractions of component i ($i = A, B$) in the adsorbed and bulk phases, respectively.

References

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3. *SHELXTL NT Version 5.1. Program for Solution and Refinement of Crystal Structures*, University of Gttingen: Germany, G. M. Sheldrick, 1997.
4. A. L. Spek, *J. Appl. Crystallogr.*, 2003, **36**, 7.
5. Myers, A. L. and Prausnitz, J. M. *AIChE J.* **1965**, *11*, 121.

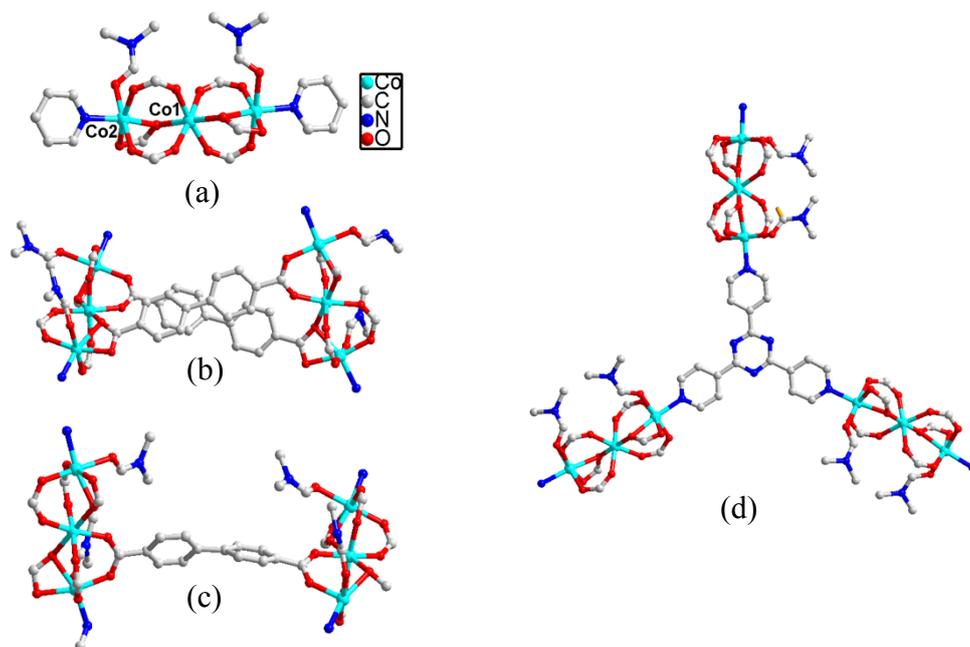


Fig. S1 View of (a) the coordination environment of Co_3 cluster; (b) double-arm linking pattern between two Co_3 cluster; (c) the single arm linking pattern between two Co_3 cluster and (d) the coordination mode of tpt.

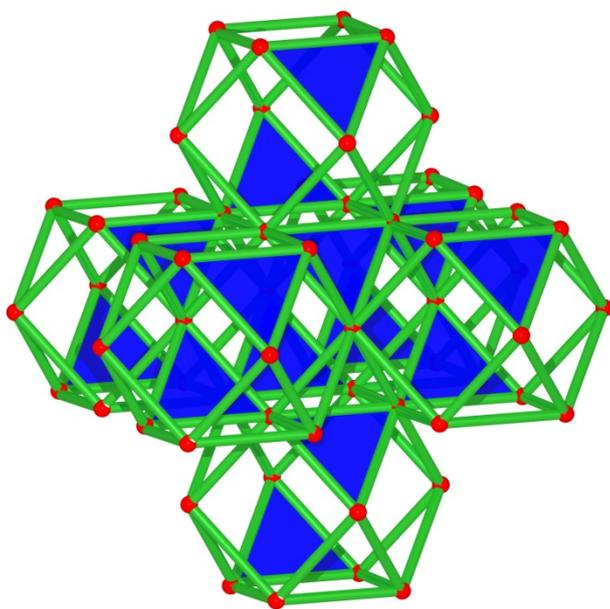


Fig. S2 The packing of cuboctahedral cages in the individual network.

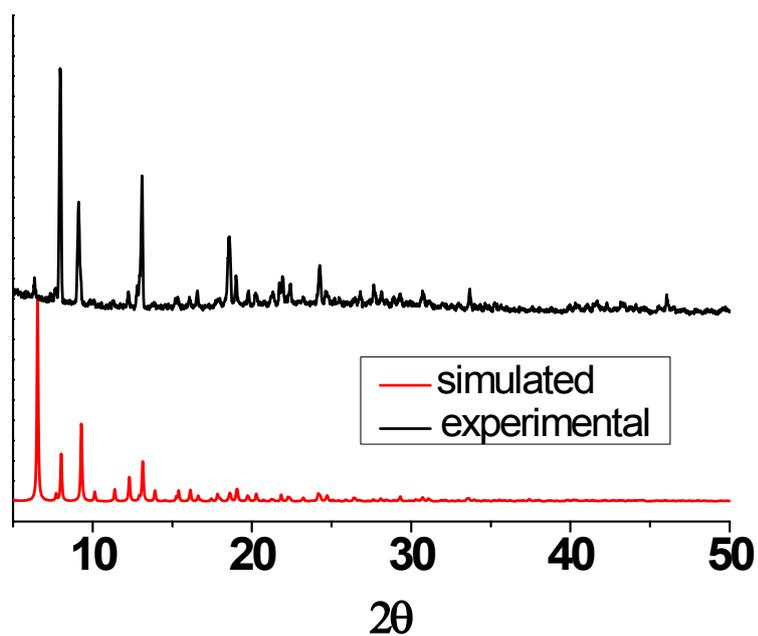


Fig. S3 The experimental and simulated PXR D patterns of 1.

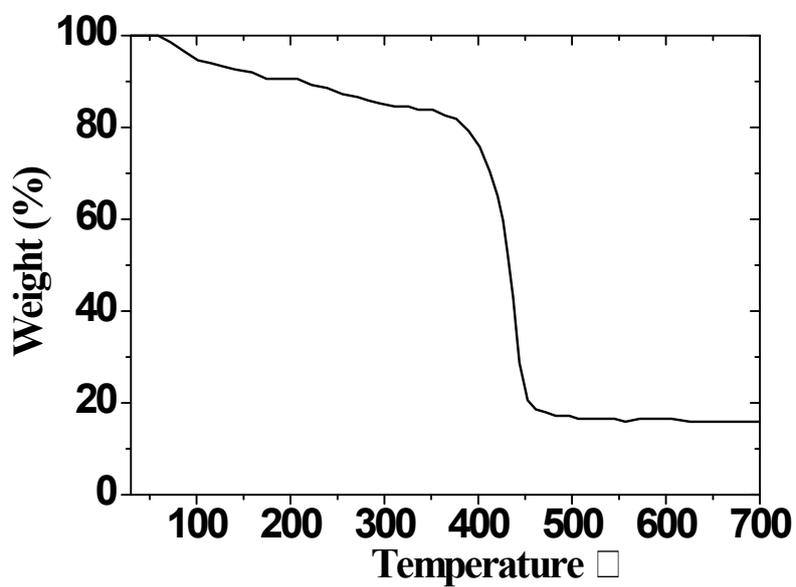


Fig. S4 The TGA profile of 1.

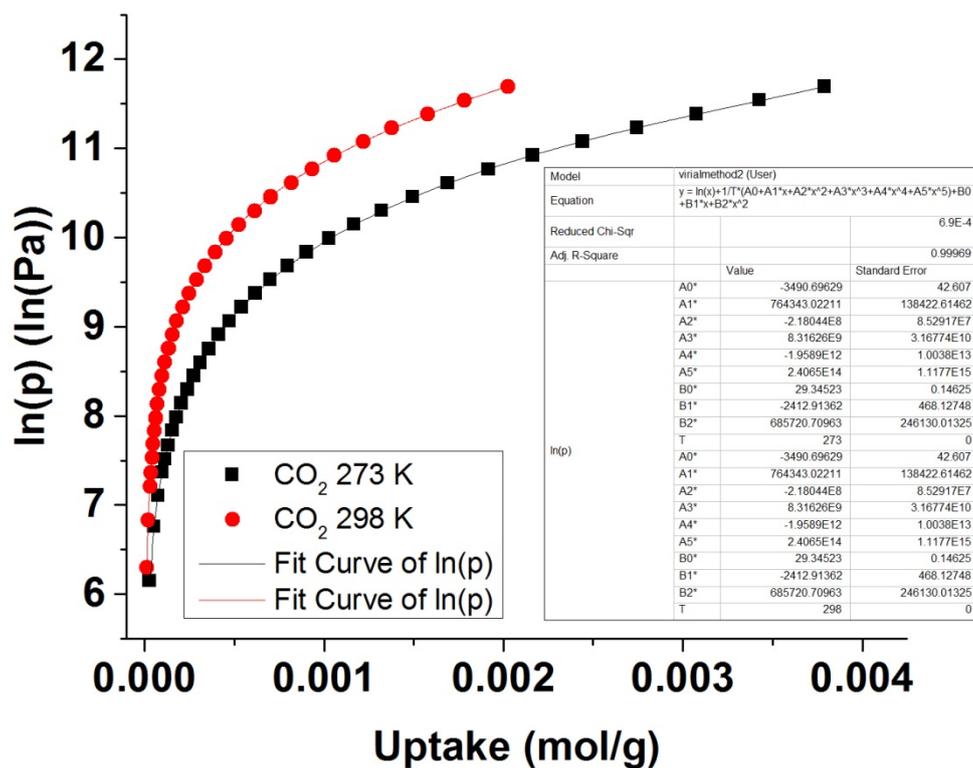


Fig. S5 Virial fitting of CO₂ adsorption isotherms of **1** at 273 K and 298 K.

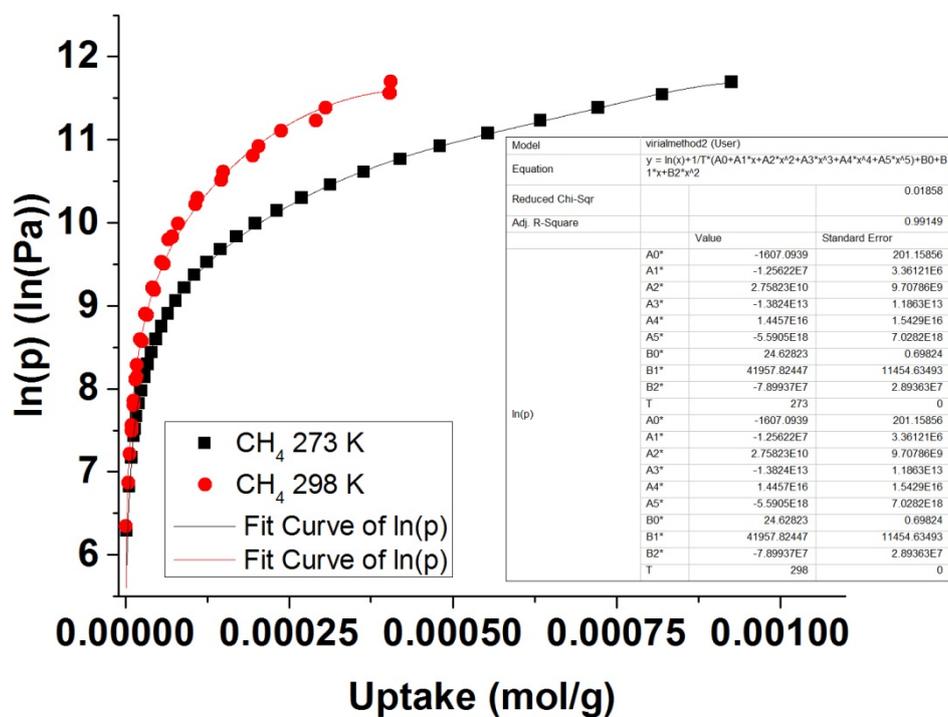


Fig. S6 Virial fitting of CH₄ adsorption isotherms of **1** at 273 K and 298 K.

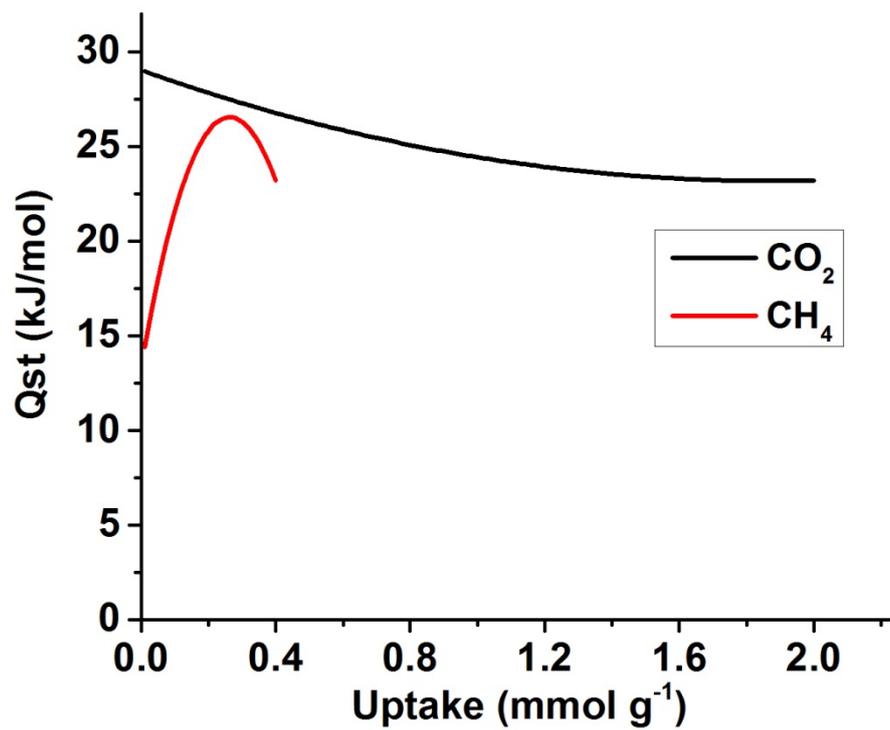


Fig. S7 The CO₂ and CH₄ adsorption enthalpies (Q_{st}) of **1**.