*Electronic Supplementary Information*

# A bracket approach to improve the stability and gas sorption performance of metal–organic framework via *in situ* incorporating the size-matching molecular building blocks

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## Experimental section

**Materials and methods.** All the chemicals purchased were of reagent grade and used without further purification. Analyses for C, H, and N were carried out on a Perkin-Elmer 240 CHN elemental analyzer. IR spectra were recorded in 400−4000 $cm^{-1}$ on a Bruker TENOR 27 spectrophotometer using KBr pellets. Powder X-ray diffraction measurements were performed on a Rigaku D/Max-2500 X-ray diffractometer using Cu Kα radiation. TGA curves were taken on a Labsys NETZSCH TG 209 Setaram apparatus with a heating rate of 10 °C/min in nitrogen atmosphere. The gas sorption isotherms were collected on a Micromeritics 3Flex surface area and pore size analyzer under ultrahigh vacuum in a clean system, with a diaphragm and turbo pumping system. Ultrahigh-purity-grade (> 99.999%) He, $N_2$, $C_2H_2$, $CO_2$, $H_2$, and $CH_4$ gases were applied in all the measurements. The experimental temperatures were maintained by liquid nitrogen (77 K), dry ice-acetone baths (195 K), and temperature-programmed water bath (273 and 298 K).

**Synthesis of $\{(NH_2Me_2)[Co_3(\mu_3\text{-}OH)(H_2O)_3(TZB)_3](H_2O)_{10}(DMA)_3\}_n$ (1).** A mixture of $H_2TZB$ (9.5 mg, 0.05 mmol) and $CoCl_2\cdot 6H_2O$ (24 mg, 0.1 mmol) was dissolved in DMA (2 mL) and $H_2O$ (0.3 mL) in a screw-capped vial. After addition of six drops of $HBF_4$ (40%, aq), the vial was heated at 120 °C for 48 h under autogenous pressure. The crystals were collected by filtration and washed with DMA. Yield: 35% (based on $H_2TZB$). IR (selected bands, $cm^{-1}$): 3397w, 1677s, 1554s, 1384s, 1261m, 1016m, 779m. Elemental analysis (%) found (calcd) for $C_{38}H_{74}Co_3N_{16}O_{23}$: C, 35.19 (35.11); H, 5.99 (5.74); N, 17.95 (17.24).

**Synthesis of {[$Co_5(\mu_3\text{-}OH)(INT)_3(H_2O)_2(TZB)_3](DMA)_8\}_n$ (2)**. A mixture of $H_2TZB$ (9.5 mg, 0.05 mmol), $CoCl_2 \cdot 6H_2O$ (24 mg, 0.1 mmol) and HINT (12.3 mg, 0.1 mmol) was dissolved in the solvent of DMA (2 mL) in a screw-capped vial. After addition of six drops of $HBF_4$ (40%, aq), the vial was heated at 120 °C for 36 h under autogenous pressure. The crystals were collected by filtration and washed with DMA. Yield: 50% (based on $H_2TZB$). IR (selected bands, $cm^{-1}$): 3397w, 1677s, 1554s, 1384s, 1261m, 1016m, 779m. Elemental analysis (%) found (calcd) for $C_{74}H_{101}Co_5N_{23}O_{23}$: C, 44.58 (44.99); H, 4.96 (5.15); N, 16.55 (16.31).

**X-ray single crystal analysis.** Single-crystal X-ray diffraction data were collected on an Agilent Technologies SuperNova Diffractometer equipped with graphite-monochromatic Mo Kα or Cu Kα radiation (λ = 0.71073 Å or 1.54184 Å). The structures were solved by SHELXS (direct methods) and refined by SHELXL (full matrix least-squares techniques) in the Olex2 package.[1] The TZB ligand is disordered over two positions (occupancy: 0.5:0.5), in which the tetrazole and carboxylate of the ligand show similar coordination modes and thus can substitute each other at the given site. All non-H atoms were refined with anisotropic displacement parameters. H-atoms attached to carbon were placed in geometrically idealized positions and refined using a riding model. For the highly disordered nature of the solvents, they could not be finely made out in the refinement. Thus, the SQUEEZE routine of PLATON was applied to remove the diffraction contributed from the highly disordered guest molecules.[2] The chemical formulas were determined by the combination of single crystal data, TGA results and elemental analysis. Crystal data for **1**: hexagonal, space group $P6_3/mmc$ (no. 194), $a = 16.8676(7)$ Å, $c = 18.8186(6)$ Å, $V = 4636.9(4)$ Å$^3$, $Z = 2$, $T = 131.9(2)$ K, $\mu$ (Mo Kα) = 0.556 $mm^{-1}$, $D_{calc}$

= 0.588 g/cm$^3$, 9132 reflections measured ($5.984° \le 2 \quad \le 49.994°$), 1563 unique reflections ($R_{\mathrm{int}}$ = 0.0562, $R_{\mathrm{sigma}}$ = 0.0425) which were used in all calculations. The final $R_1$ was 0.0407 (I > 2σ(I)) and $wR_2$ was 0.1502 (all data). Crystal data for **2**: hexagonal, space group $P6_3$/mmc (no. 194), $a$ = 18.8605(4) Å, $c$ = 16.6183(4) Å, $V$ = 5119.5(3) Å$^3$, $Z$ = 2, $T$ = 293(2) K, $\mu$ (Cu Kα) = 6.561 mm$^{-1}$, $D_{\mathrm{calc}}$ = 0.826 g/cm$^3$, 11139 reflections measured ($7.59° \le 2\Theta \le 129.88°$), 1665 unique reflections ($R_{\mathrm{int}}$ = 0.0577, $R_{\mathrm{sigma}}$ = 0.0277) which were used in all calculations. The final $R_1$ was 0.0968 (I > 2σ(I)) and $wR_2$ was 0.2881 (all data).

**GCMC simulation methodology.** Grand canonical Monte Carlo (GCMC) simulations were performed for the adsorption of $C_2H_2$ and $CO_2$ in **2** by the sorption module of Material Studio according to the reference.[3] The host framework and gas molecules were considered to be rigid. The partial charges for gas molecules were derived from ESP charges via DMOL3 module. The partial charges for atoms were derived from QEq method and QEq_neutral1.0 parameter. 2*2*2 unit cells were used during the simulations. All the parameters for gas molecules and atoms of **2** were modeled with the universal force field (UFF) embedded in the MS modeling package. The distribution of gas molecules and adsorption potential were derived from the Fix Pressure task.

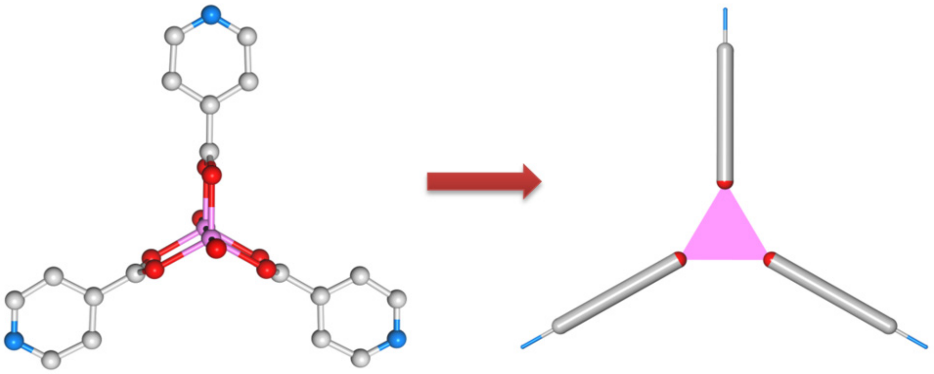


**Fig. S1** Schematic representation of a MBB inserted in **2** and its simplified style.

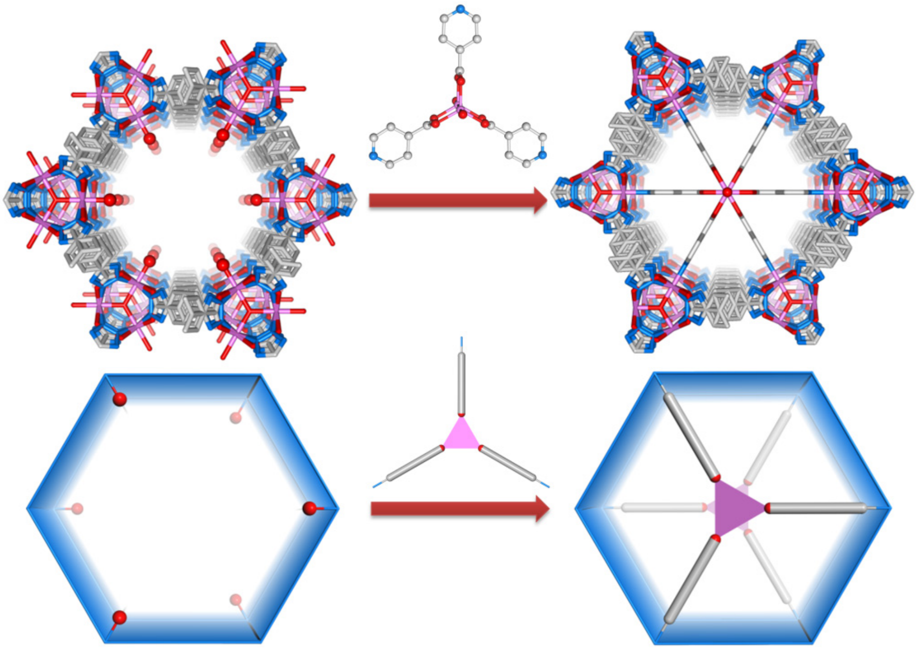
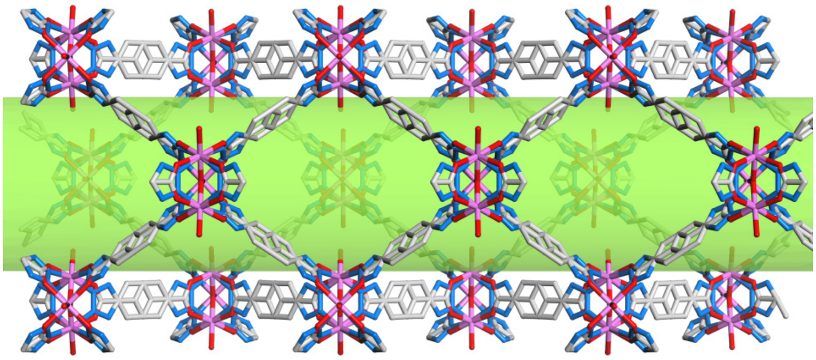
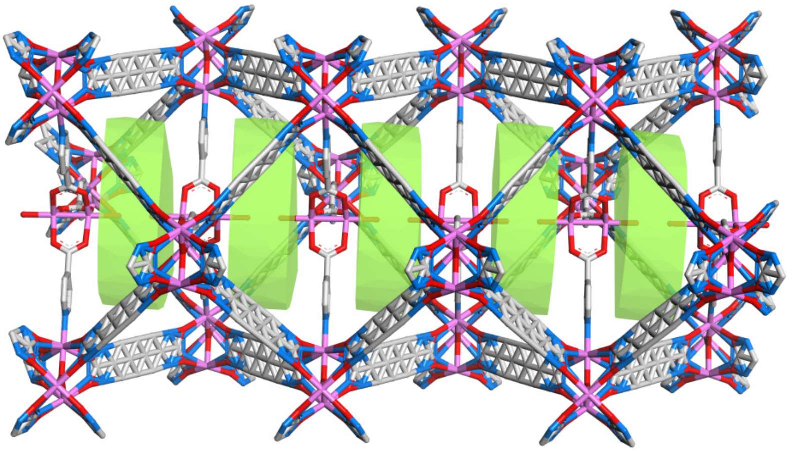


**Fig. S2** Schematic representation of the 1D channels along *c* axis in **1** and **2**.

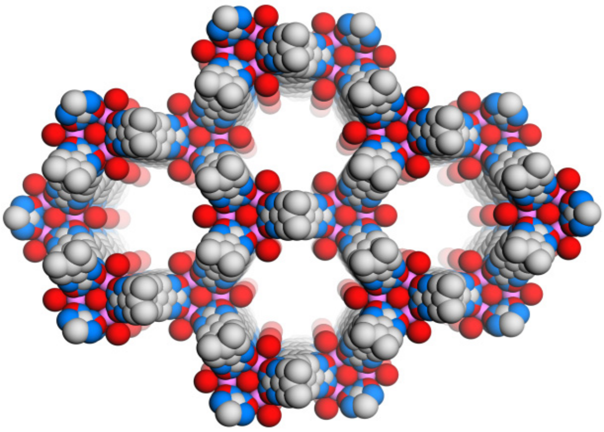


**(a)**

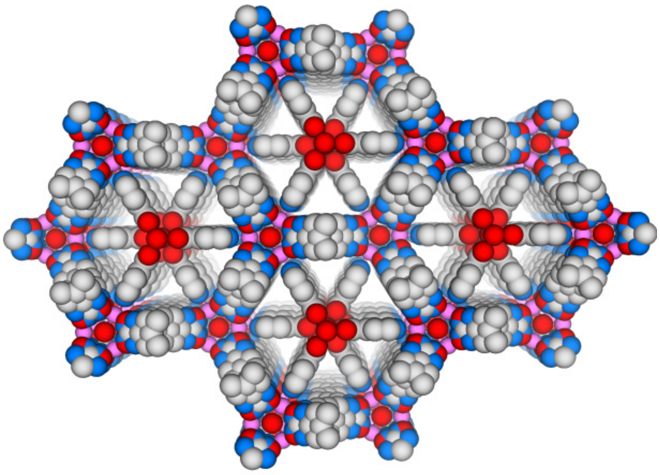


**(b)**

**Fig. S3** The infinite and finite 1D channels in **1** (a) and **2** (b)



**(a)**



**(b)**

**Fig. S4** The space-filling diagrams for the porous framework of **1** (a) and **2** (b).

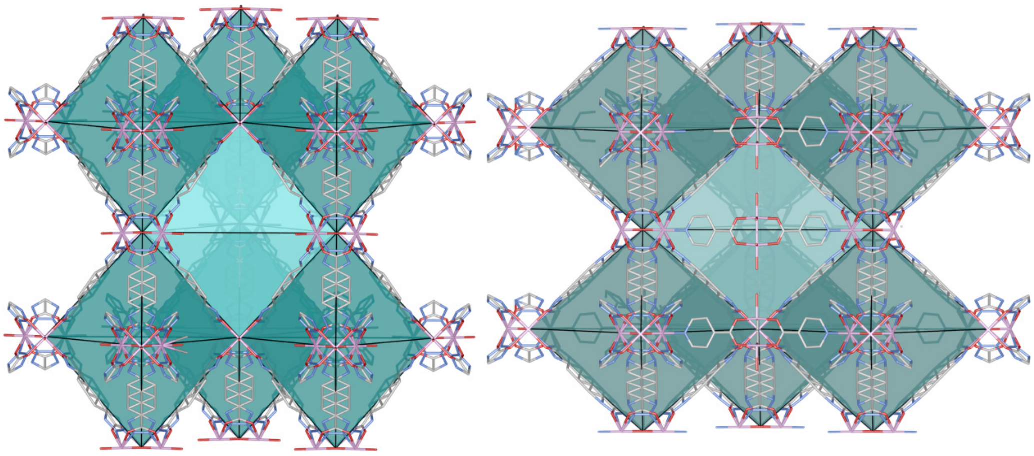


**Fig. S5** View of the cages in **1** (left) and **2** (right).

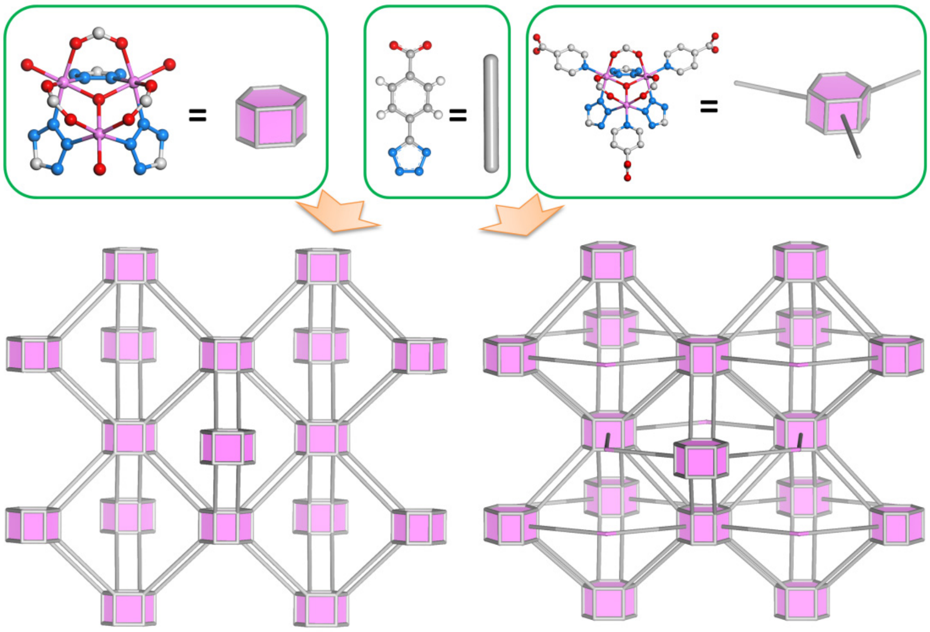


**Fig. S6** Schematic representation of the 6- and 9-connected nets of **1** (left) and **2** (right).

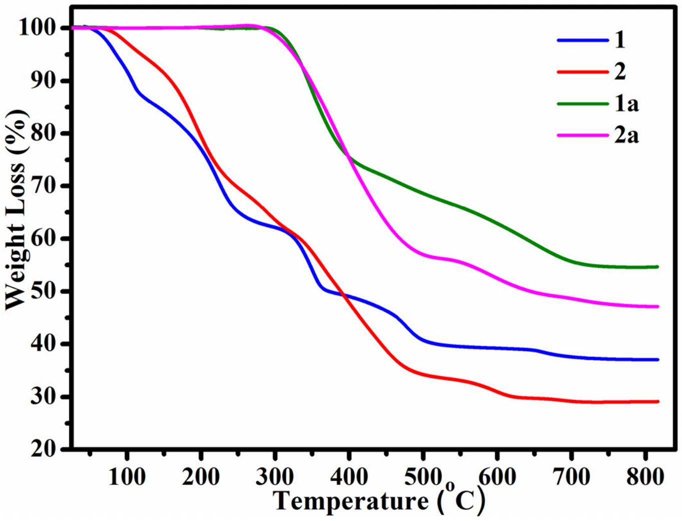


**Fig. S7** Thermogravimetric analysis (TGA) curves of **1** and **2** and their activated samples.

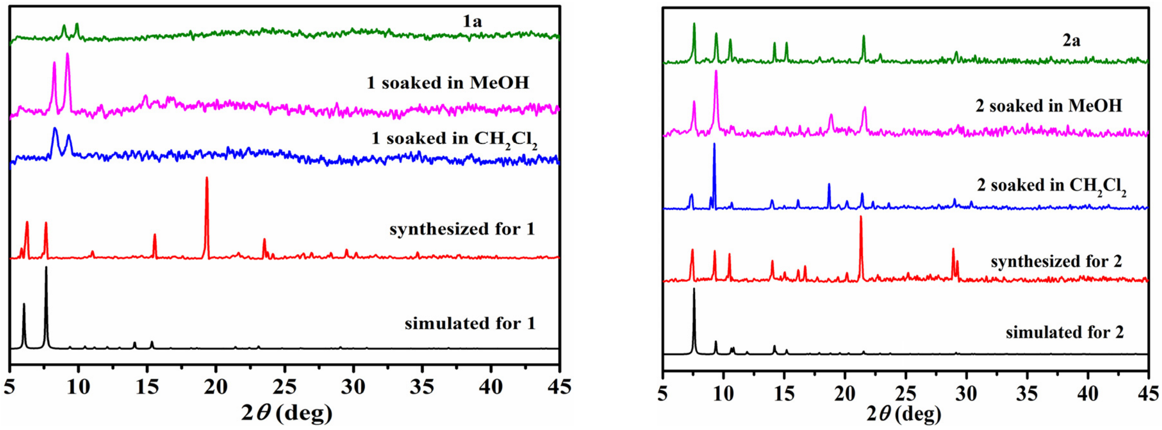


**Fig. S8** Powder X-ray diffraction (PXRD) patterns for **1** (left) and **2** (right).

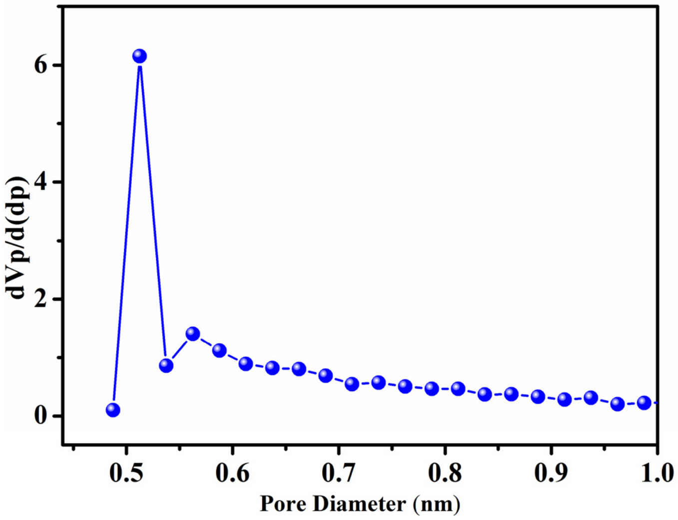


**Fig. S9** The pore size distribution calculated using the Horvath-Kawazoe method.

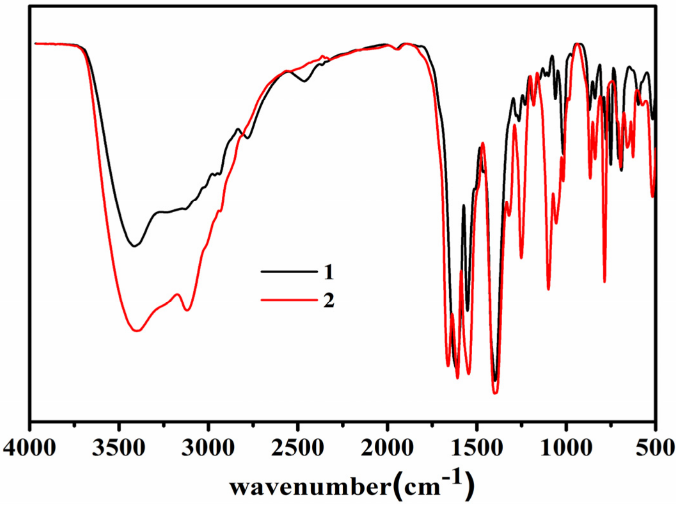


**Fig. S10** IR spectra for **1** (black) and **2** (red).

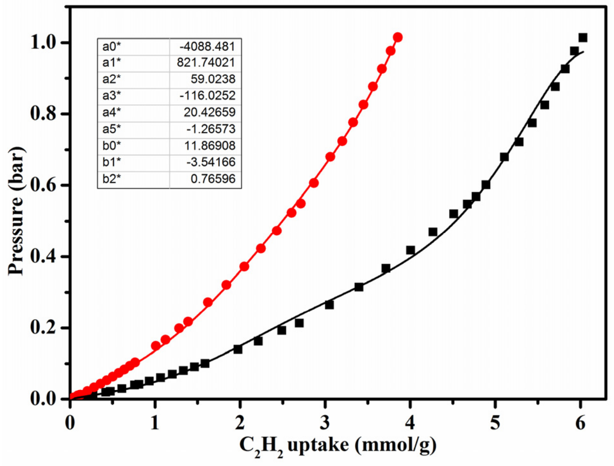
**Calculation of the isosteric heats of gas adsorption (Qst).** A Virial-type 2 expression comprising the temperature-independent parameters *ai* and $b_j$ was used to calculate the adsorption enthalpies for $C_2H_2$ and $CO_2$ (at 273 and 298 K). The data were fitted using the equation:

$$ln^P = ln^N + {}^1/_T\sum_{i-0}^{m} a_i N^i + \sum_{j-0}^{n} b_j N^j$$

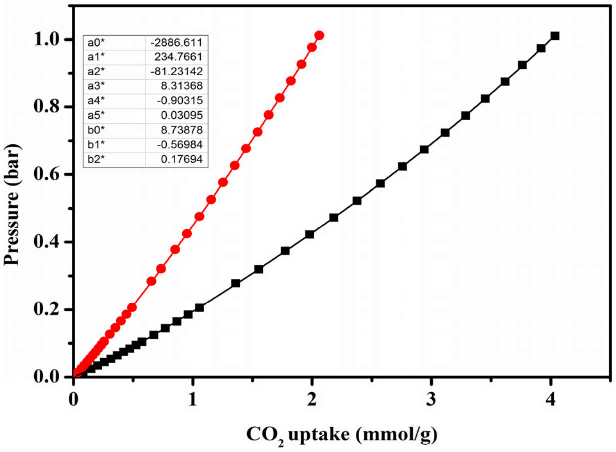
Herein, *P* is the pressure expressed in bar, *N* is the amount adsorbed in mmol/g, *T* is the temperature in K, *ai* and *bj* are Virial coefficients, and *m* or *n* represents the number of coefficient required to adequately describe the isotherms (*m* and *n* gradually increase till the contribution of extra added *a* and *b* coefficients are statistically insignificant towards the overall fit as well as the average value of the squared deviations from the experimental data is minimized). The values of the Virial coefficients $a_0$ through $a_m$ were then used to calculate the isosteric heat of adsorption using the following expression:

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

$Q_{st}$ is the coverage-dependent isosteric heat of adsorption and *R* is the universal gas constant. The heat of gas sorption for **2a** in this work was determined by using the sorption data measured in the pressure range of 0~1 bar (273 and 298 K for gas), as fitted by the Virial-equation very well.



**(a)**



**(b)**

**Fig. S11** Virial fitting of the $C_2H_2$ (a) and $CO_2$ (b) adsorption isotherms for **2a**.

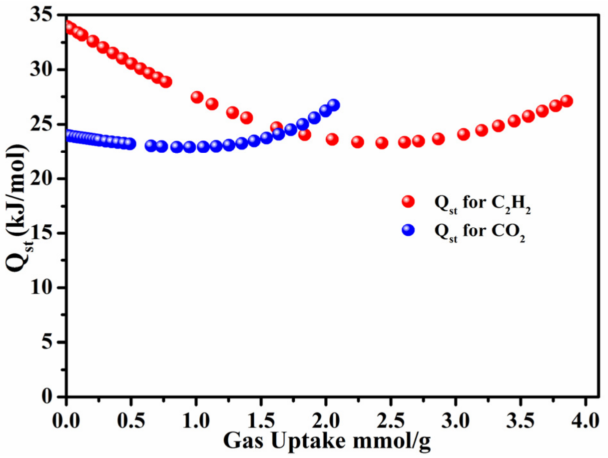
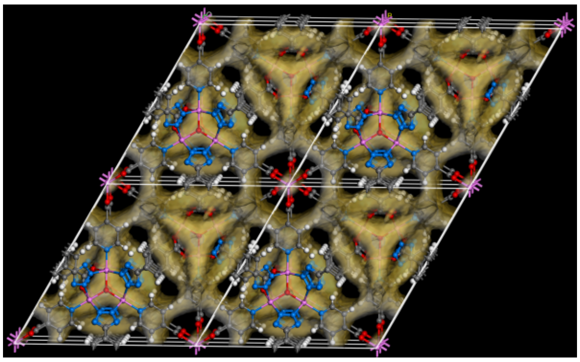
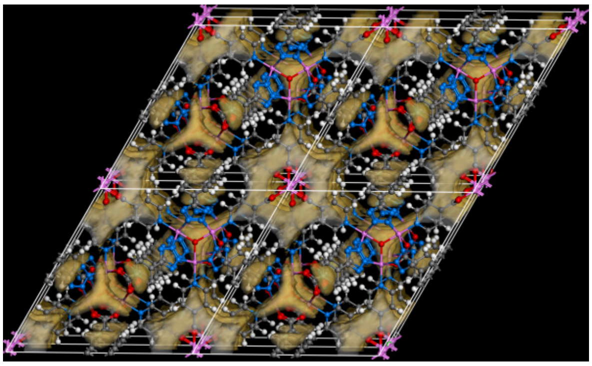


**Fig. S12** The calculated $C_2H_2$ and $CO_2$ enthalpies of adsorption for **2a**.



**(a)**



**(b)**

**Fig. S13** Distribution probability of mass center for $C_2H_2$ (a) and $CO_2$ (b) in **2a**.

**Bond valence sum (BVS).** The valence of a bond between two atoms, i and j, is given by $S_{ij}$ and the sum of $S_{ij}$ is the valence of i atom. The calculated results (Table S1) are closed to that reported in the literatures.

**Table S1** BVS for the $\mu_3$-oxygen atom in the trimetallic SBU.

| **Element 1** | **Element 2** | R0 value | B value | Length | Valence |
|---|---|---|---|---|---|
| O | Co | 1.692 | 0.370 | 2.000 | 0.435 |
| O | Co | 1.692 | 0.370 | 2.000 | 0.435 |
| O | Co | 1.692 | 0.370 | 2.000 | 0.435 |

VO = sum of selected values (1.305)

## References

1 O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Cryst.*, 2009, **42**, 339.

2 A. L. Spek, *J. Appl. Crystallogr.*, 2003, **36**, 7.

3 J. Pang, F. Jiang, M. Wu, C. Liu, K. Su, W. Lu, D. Yuan and M. Hong, *Nat. Commun.*, 2015, **6**, 7575.