

*Electronic Supplementary Information*

**Template-directed construction of conformational supramolecular  
isomers for bilayer porous metal–organic frameworks with  
distinct gas sorption behaviors**

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***Chem. Commun.***

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## **References**

## Section 1. General materials and methods

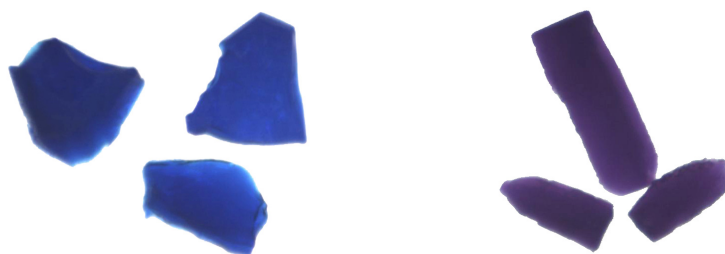
With the exception of the organic ligand 4,4',4''-(benzene-1,3,5-triyl-tris(oxy))tribenzoic acid (H<sub>3</sub>BTTB) that was prepared according to the literature method,<sup>S1</sup> all of the starting reagents and solvents were obtained commercially and used as received. Elemental analysis (C, H, and N) was performed on a Vario EL III Elementar analyzer. IR spectra were measured on a Bruker Tensor 27 OPUS FT-IR spectrometer (with KBr pellet) in 4000–400 cm<sup>-1</sup> range. Powder X-ray diffraction (PXRD) patterns were recorded on a Rigaku model Ultima IV diffractometer with a Rigaku D/teX ultrahigh-speed position sensitive detector and Cu-K $\alpha$  X-ray (40 kV, 40 mA). The powder samples were prepared by crushing the single crystals and the intensity data were taken in the step-scan mode with a scan rate of 2 °/min and a step size of 0.02°. Simulation of the PXRD patterns was performed by diffraction-crystal module of the *Mercury* program with the single-crystal data. Thermogravimetric analysis (TGA) experiments were carried out on a Perkin-Elmer Diamond SII thermal analyzer from room temperature to 800 °C, with a heating rate of 5 °C min<sup>-1</sup> under 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%) N<sub>2</sub>, Ar, O<sub>2</sub>, CO<sub>2</sub>, H<sub>2</sub>, CH<sub>4</sub>, and He gases were applied in all measurements. The experimental temperatures were maintained by liquid nitrogen (77 K), liquid argon (87 K), dry ice-acetone baths (195 K), and temperature-programmed water bath (273 and 293 K).

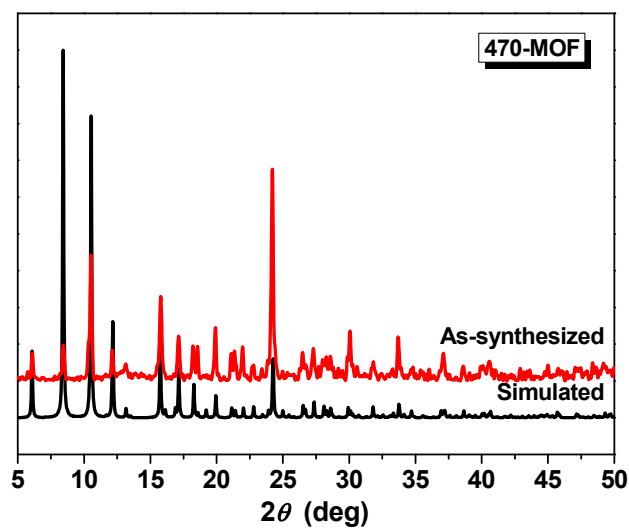
## Section 2. Synthesis and characterization

**Synthesis of 470-MOF.** A mixture of  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  (47.6 mg, 0.2 mmol),  $\text{H}_3\text{BTTB}$  (48.6 mg, 0.1 mmol), and *N,N'*-dimethylformamide (DMF) (3 mL) was sealed into a 23-mL Teflon-lined stainless steel vessel, which was heated at 120 °C for 3 days in an oven. After cooling to room temperature, blue block crystals were collected and washed three times with 5 mL fresh DMF. Yield: 40.3 mg (51% based on  $\text{H}_3\text{BTTB}$ ). IR ( $\text{cm}^{-1}$ ): 3445m (br), 1703s, 1598s, 1556m, 1503m, 1462m, 1393vs, 1225vs, 1158w, 1122m, 1004m, 854w, 782w, 707w, 647w, 423w. Anal. Calcd for  $[\text{Co}_3(\text{BTTB})_2(\text{H}_2\text{O})_2] \cdot (\text{DMF})_{4.5} \cdot (\text{H}_2\text{O})_4$ : C, 51.29; H, 4.69; N, 3.99%. Found: C, 51.16; H, 4.25; N, 4.08%.

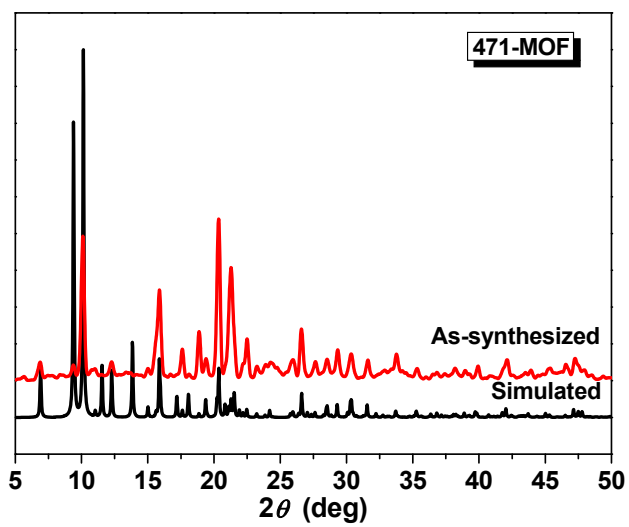
**Synthesis of 471-MOF.** 471-MOF was obtained by the same method used for the preparation of 470-MOF except that the solvent was a mixture of DMF (2 mL) and 1,4-dioxane (2 mL). Purple prism crystals were collected and washed three times with 5 mL fresh DMF, in a yield of 41% (35.0 mg, based on  $\text{H}_3\text{BTTB}$ ). IR ( $\text{cm}^{-1}$ ): 3444m (br), 1594vs, 1557m, 1504m, 1463m, 1391vs, 1223w, 1157m, 1119m, 1006m, 872w, 780w, 707w, 647w, 408w. Anal. Calcd for  $[\text{Co}_3(\text{BTTB})_2(\text{H}_2\text{O})_2] \cdot (\text{DMF})_3 \cdot (\text{H}_2\text{O})_4 \cdot (\text{dioxane})_{2.5}$ : C, 51.84; H, 4.95; N, 2.48%. Found: C, 52.16; H, 4.80; N, 2.42%.



**Fig. S1** Crystal photographs for 470-MOF (left) and 471-MOF (right).

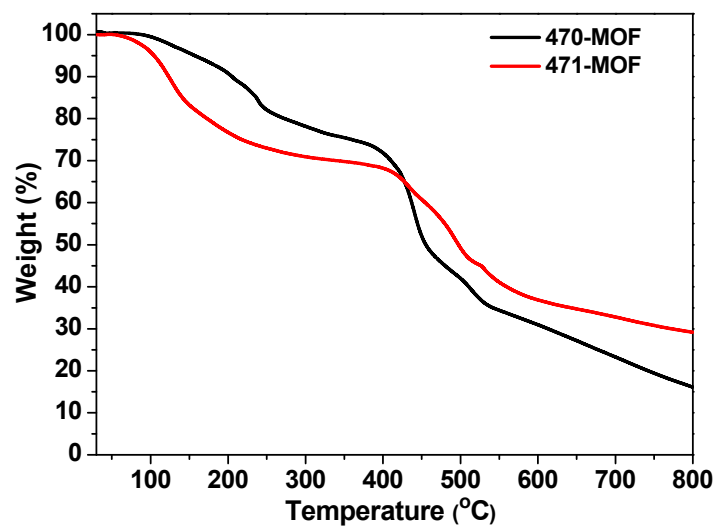


(a)



(b)

**Fig. S2** PXRD patterns for 470-MOF (a) and 471-MOF (b).



**Fig. S3** TGA curves for as-synthesized 470-MOF (black) and 471-MOF (red).

### Section 3. Single-crystal X-ray crystallography

Single-crystal X-ray diffraction data for 470-MOF and 471-MOF were collected on an Oxford Xcalibur Gemini Eos diffractometer with Mo-K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) at different temperatures. Multi-scan absorption corrections were performed with the *CrysAlisPro* program.<sup>S2</sup> Empirical absorption corrections were carried out by using spherical harmonics, implemented in *SCALE3 ABSPACK* scaling algorithm. The structures were solved by direct methods and all non-hydrogen atoms were refined anisotropically by full-matrix least-squares method with the SHELXTL crystallographic software package.<sup>S3</sup> All hydrogen atoms were generated geometrically and refined isotropically as riding. Attempts to locate and model the highly disordered solvent molecules in the pores were unsuccessful. Thus, the SQUEEZE routine, a part of the PLATON software package,<sup>S4</sup> was used to calculate the disorder area and remove the diffraction contribution to afford a set of solvent free diffraction intensity. Crystallographic data and structural refinement details for 470-MOF and 471-MOF at different temperatures were listed in Table S1. A comparison of the selected bond lengths and angles was shown in Table S2.

**Table S1** Crystallography data and structural refinement summary.

Compound reference	470-MOF	471-MOF	470-MOF_120K	470-MOF_195K	471-MOF_120K	471-MOF_195K
Temperature (K)	294(2)	294(2)	120.0(1)	195.0(1)	120.0(1)	195.0(1)
Chemical formula	C <sub>18</sub> H <sub>11.33</sub> O <sub>6.67</sub> Co	C <sub>18</sub> H <sub>11.33</sub> O <sub>6.67</sub> Co	C <sub>18</sub> H <sub>11.33</sub> O <sub>6.67</sub> Co	C <sub>18</sub> H <sub>11.33</sub> O <sub>6.67</sub> Co	C <sub>18</sub> H <sub>11.33</sub> O <sub>6.67</sub> Co	C <sub>18</sub> H <sub>11.33</sub> O <sub>6.67</sub> Co
Formula weight	393.20	393.20	393.20	393.20	393.20	393.20
Crystal system	Trigonal	Trigonal	Trigonal	Trigonal	Trigonal	Trigonal
Space group	<i>P</i> -31 <i>c</i>	<i>R</i> -3 <i>c</i>	<i>P</i> -31 <i>c</i>	<i>P</i> -31 <i>c</i>	<i>R</i> -3 <i>c</i>	<i>R</i> -3 <i>c</i>
<i>a</i> (Å)	16.789(2)	17.4310(11)	16.7639(7)	16.7335(4)	17.2813(4)	17.3321(4)
<i>b</i> (Å)	16.789(2)	17.4310(11)	16.7639(7)	16.7335(4)	17.2813(4)	17.3321(4)
<i>c</i> (Å)	15.144(3)	48.043(5)	14.9592(11)	14.9637(12)	47.354(2)	47.616(2)
Unit cell volume (Å <sup>3</sup> )	3696.5(10)	12641.7(17)	3640.7(3)	3628.6(3)	12247.4(7)	12387.5(7)
No. of formula units per unit cell ( <i>Z</i> )	6	18	6	6	18	18
Absorption coefficient (mm <sup>-1</sup> )	0.721	0.632	0.732	0.734	0.653	0.645
<i>R</i> <sub>int</sub>	0.0229	0.0334	0.0313	0.0255	0.0199	0.0186
Final <i>R</i> <sub>1</sub> <sup><i>a</i></sup> values ( <i>I</i> > 2σ( <i>I</i> ))	0.0565	0.0816	0.0590	0.0571	0.0626	0.0639
Final <i>wR</i> <sup><i>b</i></sup> ( <i>F</i> <sup>2</sup> ) values ( <i>I</i> > 2σ( <i>I</i> ))	0.1710	0.2356	0.1880	0.1731	0.2089	0.2183
Final <i>R</i> <sub>1</sub> <sup><i>a</i></sup> values (all data)	0.0705	0.0971	0.0786	0.0826	0.0696	0.0736
Final <i>wR</i> <sup><i>b</i></sup> ( <i>F</i> <sup>2</sup> ) values (all data)	0.1841	0.2474	0.2049	0.1921	0.2174	0.2299
Goodness of fit on <i>F</i> <sup>2</sup>	1.038	1.049	1.030	1.051	1.107	1.088
CCDC number	1031076	1031077	1031078	1031079	1031080	1031081

<sup>*a*</sup>  $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ . <sup>*b*</sup>  $wR_2 = |\sum w(|F_o|^2 - |F_c|^2)| / \sum w(F_o)^2^{1/2}$ , where  $w = 1 / [\sigma^2(F_o^2) + (aP)^2 + bP]$ .  $P = (F_o^2 + 2F_c^2) / 3$ .

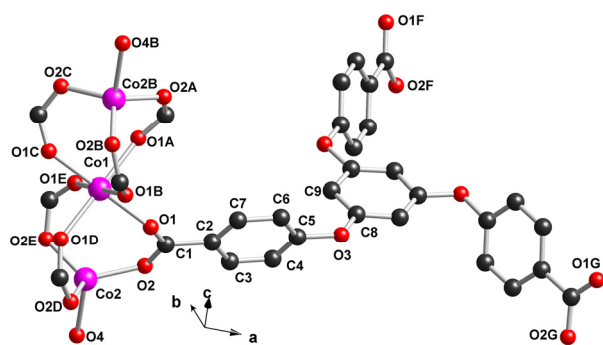


**Table S2** A comparison of the selected bond lengths (Å) and angles (°).<sup>a</sup>

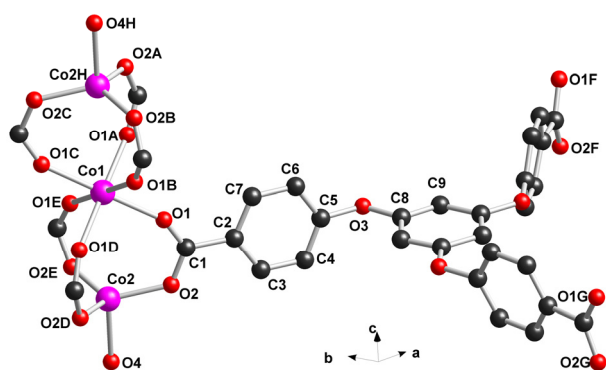
470-MOF			
Co1–O1	2.091(2)	Co2–O2	1.934(2)
Co2–O4	2.203(2)		
O1 <sup>#1</sup> –Co1–O1 <sup>#3</sup>	84.49(12)	O1 <sup>#1</sup> –Co1–O1 <sup>#2</sup>	85.46(14)
O1 <sup>#2</sup> –Co1–O1	95.03(10)	O1 <sup>#1</sup> –Co1–O1	179.35(11)
O2–Co2–O4	102.37(8)	O2 <sup>#3</sup> –Co2–O2	115.54(5)
471-MOF			
Co1–O1	2.088(4)	Co2–O2	1.931(4)
Co2–O4	2.080(8)		
O1 <sup>#1</sup> –Co1–O1 <sup>#3</sup>	83.6(3)	O1 <sup>#3</sup> –Co1–O1 <sup>#2</sup>	179.1(2)
O1 <sup>#3</sup> –Co1–O1	85.0(2)	O1 <sup>#1</sup> –Co1–O1	95.68(18)
O2–Co2–O4	99.29(12)	O2 <sup>#1</sup> –Co2–O2	117.44(6)

<sup>a</sup> Symmetry codes. For 470-MOF: #1 =  $-x + y, y, -z + 3/2$ ; #2 =  $-y + 1, x - y + 1, z$ ; #3 =  $-x + y, -x + 1, z$ . For 471-MOF: #1 =  $-x + y + 1, -x + 1, z$ ; #2 =  $-y + 1, x - y, z$ ; #3 =  $-x + 4/3, -x + y + 2/3, -z + 1/6$ .

## Section 4. Additional structural figures and tables

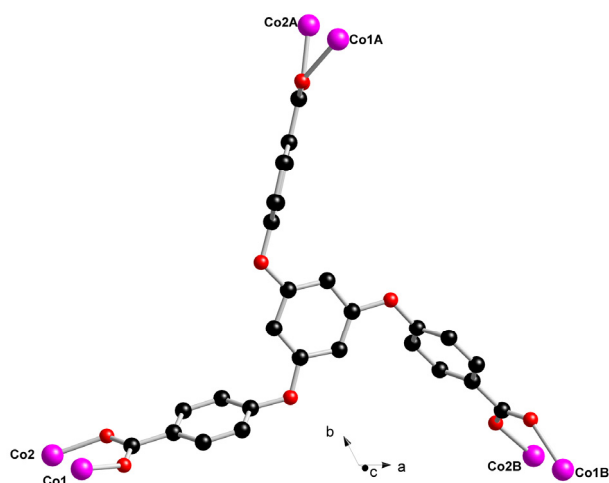


(a)

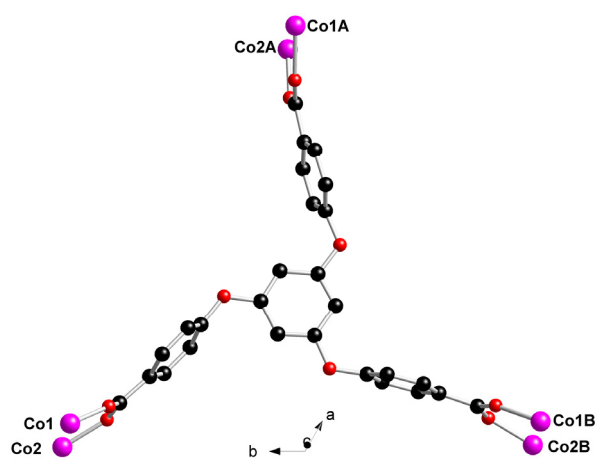


(b)

**Fig. S4** Coordination linkages in 470-MOF (a) and 471-MOF (b). Symmetry codes for (a): A =  $x, 1 + x - y, 3/2 - z$ ; B =  $1 - y, 1 - x, 3/2 - z$ ; C =  $-x + y, y, 3/2 - z$ ; D =  $-x + y, 1 - x, z$ ; E =  $1 - y, 1 + x - y, z$ ; F =  $1 - x + y, 2 - x, z$ ; G =  $2 - y, 1 + x - y, z$  and for (b): A =  $1/3 + x - y, 2/3 - y, 1/6 - z$ ; B =  $4/3 - x, 2/3 - x + y, 1/6 - z$ ; C =  $1/3 + y, -1/3 + x, 1/6 - z$ ; D =  $1 - x + y, 1 - x, z$ ; E =  $1 - y, -1 + x - y, z$ ; F =  $2 - x + y, 1 - x, z$ ; G =  $1 - y, -1 + x - y, z$ ; H =  $1/3 + x - y, 2/3 - y, 1/6 - z$ .

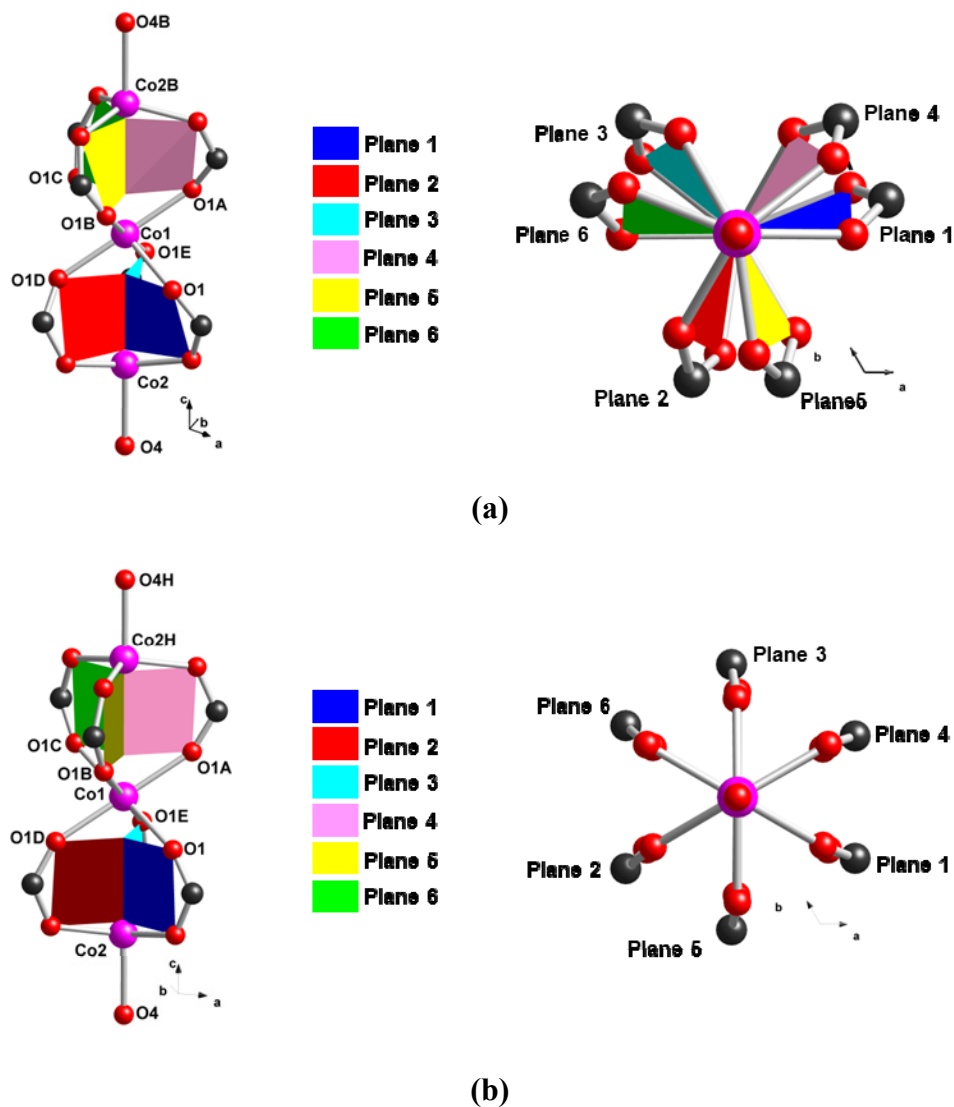


(a)



(b)

**Fig. S5** Coordination modes of the ligands in 470-MOF (a) and 471-MOF (b). Symmetry codes for (a):  $A = 1 + x, 1 + y, z$ ;  $B = 1 - x, y, z$  and for (b):  $A = 1 + x, y, z$ ;  $B = x, -1 + y, z$ .



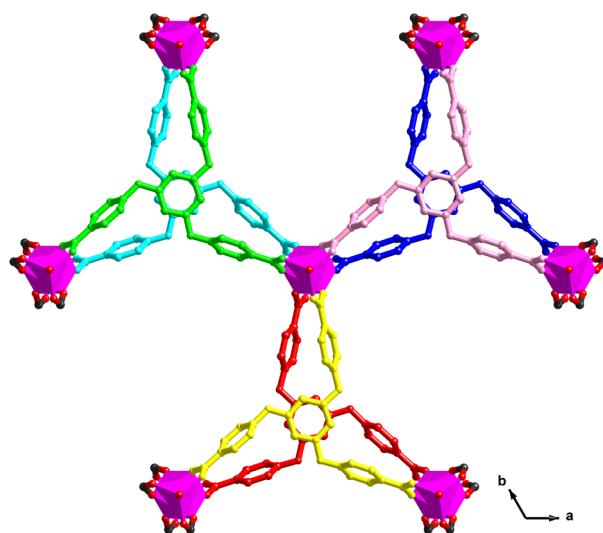
**Fig. S6** Arrangements of the carboxylate groups in  $\text{Co}_3$  SBUs for 470-MOF (a) and 471-MOF (b). Symmetry codes for (a): A =  $x$ ,  $1 + x - y$ ,  $3/2 - z$ ; B =  $1 - y$ ,  $1 - x$ ,  $3/2 - z$ ; C =  $-x + y$ ,  $y$ ,  $3/2 - z$ ; D =  $-x + y$ ,  $1 - x$ ,  $z$ ; E =  $1 - y$ ,  $1 + x - y$ ,  $z$  and for (b): A =  $1/3 + x - y$ ,  $2/3 - y$ ,  $1/6 - z$ ; B =  $4/3 - x$ ,  $2/3 - x + y$ ,  $1/6 - z$ ; C =  $1/3 + y$ ,  $-1/3 + x$ ,  $1/6 - z$ ; D =  $1 - x + y$ ,  $1 - x$ ,  $z$ ; E =  $1 - y$ ,  $-1 + x - y$ ,  $z$ ; H =  $1/3 + x - y$ ,  $2/3 - y$ ,  $1/6 - z$ .

**Table S3** Geometrical parameters of the carboxylate groups in Co<sub>3</sub> SBU for 470-MOF.

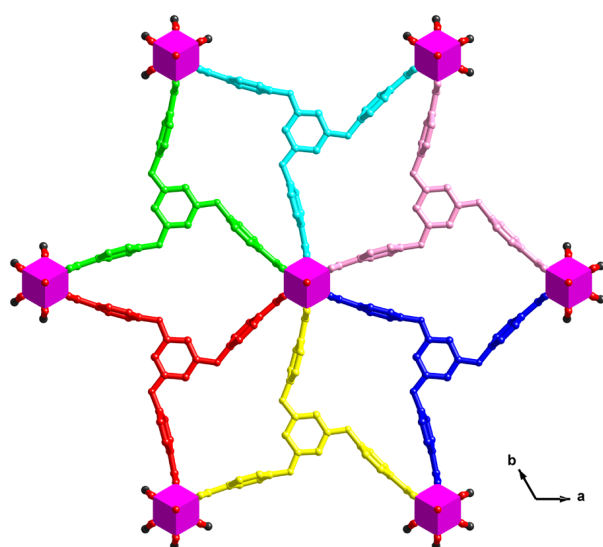
	Plane 1	Plane 2	Plane 3	Plane 4	Plane 5	Plane 6
Plane 1	—	62.2	58.5	38.4	82.3	20.1
Plane 2	62.2	—	59.3	23.9	35.4	82.3
Plane 3	58.5	59.3	—	83.2	23.9	38.4
Plane 4	38.4	23.9	83.2	—	59.3	58.5
Plane 5	82.3	35.4	23.9	59.3	—	62.2
Plane 6	20.1	82.3	38.4	58.5	62.2	—

**Table S4** Geometrical parameters of the carboxylate groups in Co<sub>3</sub> SBU for 471-MOF.

	Plane 1	Plane 2	Plane 3	Plane 4	Plane 5	Plane 6
Plane 1	—	60.0	60.0	59.5	60.5	0.7
Plane 2	60.0	—	60.0	0.7	59.5	60.5
Plane 3	60.0	60.0	—	60.5	0.7	59.5
Plane 4	59.5	0.7	60.5	—	60.0	60.0
Plane 5	60.5	59.5	0.7	60.0	—	60.0
Plane 6	0.7	60.5	59.5	60.0	60.0	—

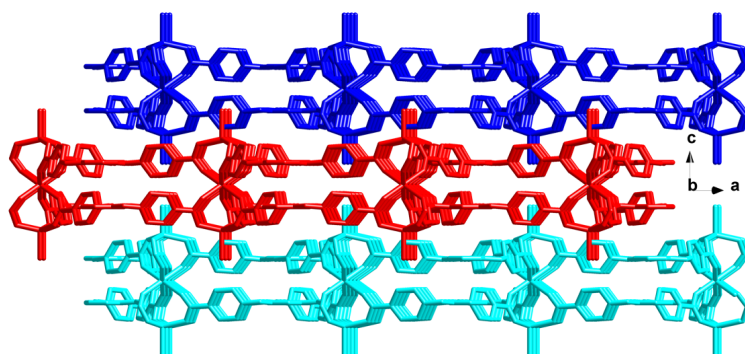


(a)

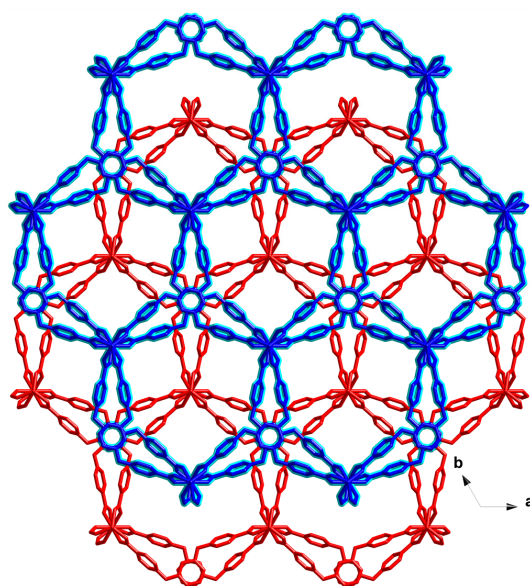


(b)

**Fig. S7** Connectivity of Co<sub>3</sub> SBUs and BTTB ligands in 470-MOF (a) and 471-MOF (b).

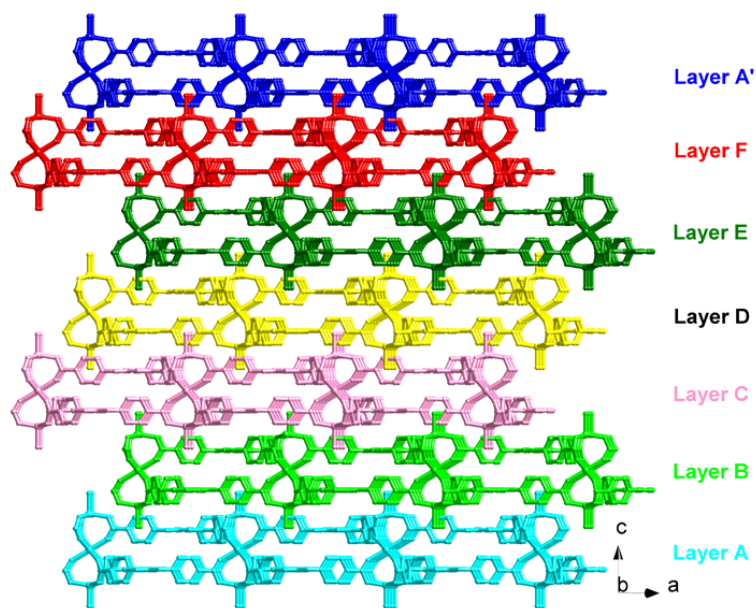


(a)

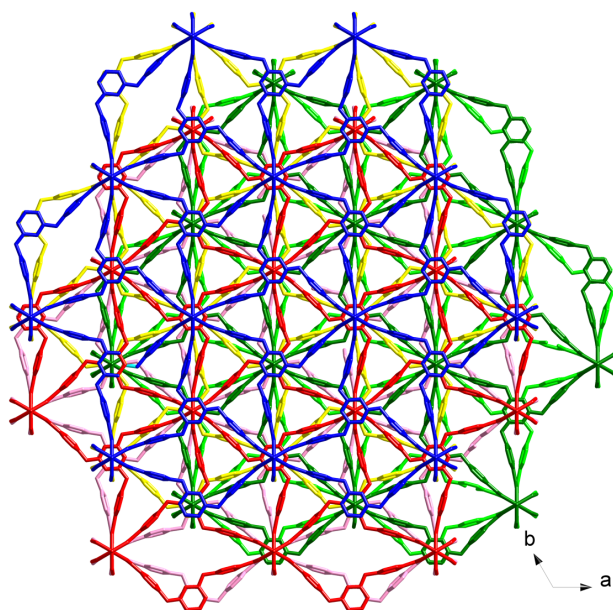


(b)

**Fig. S8** Arrangements of the 2-D bilayers in 470-MOF along *b*-axis (a) and *c*-axis (b).



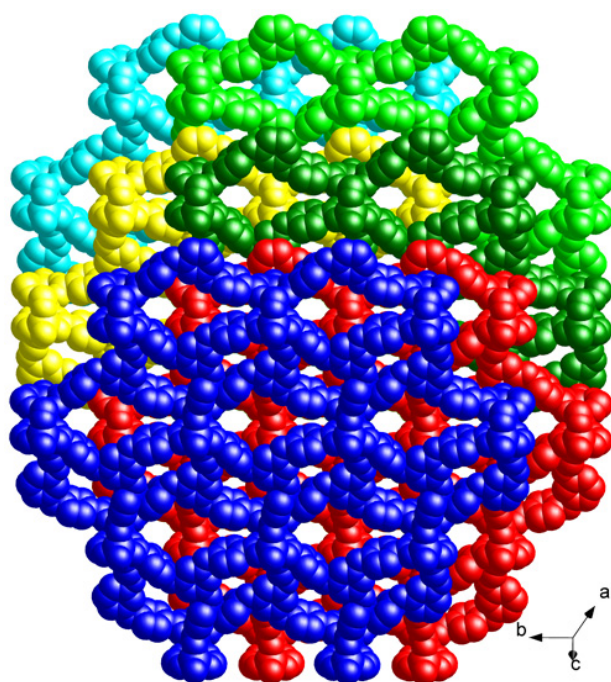
(a)



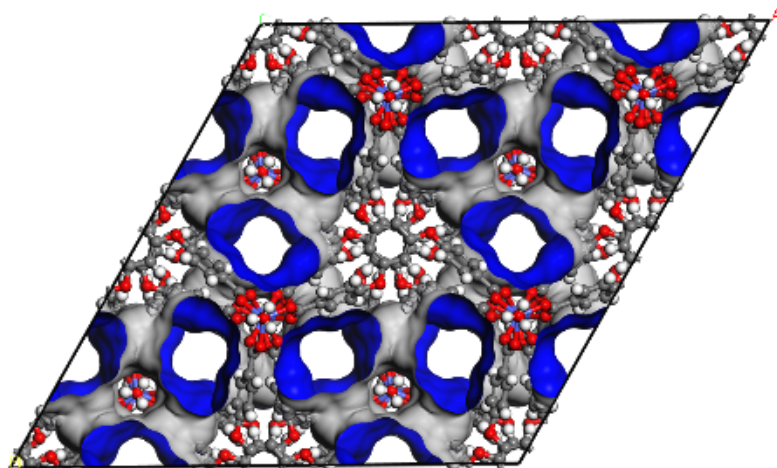
(b)

**Fig. S9** Arrangements of the 2-D bilayers in 471-MOF along *b*-axis (a) and *c*-axis (b).

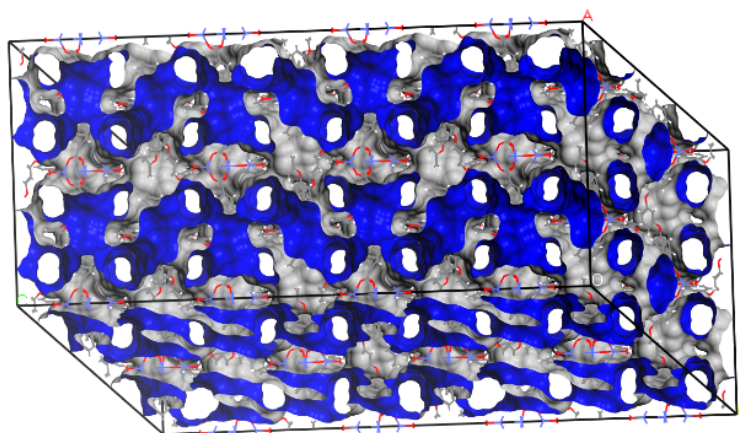




**Fig. S10** Space-filling view of the 3-D porous lattice with 1-D channels in 471-MOF.



(a)

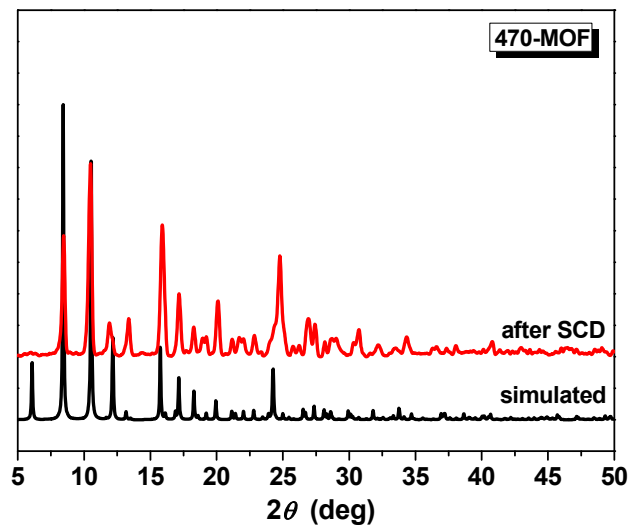


(b)

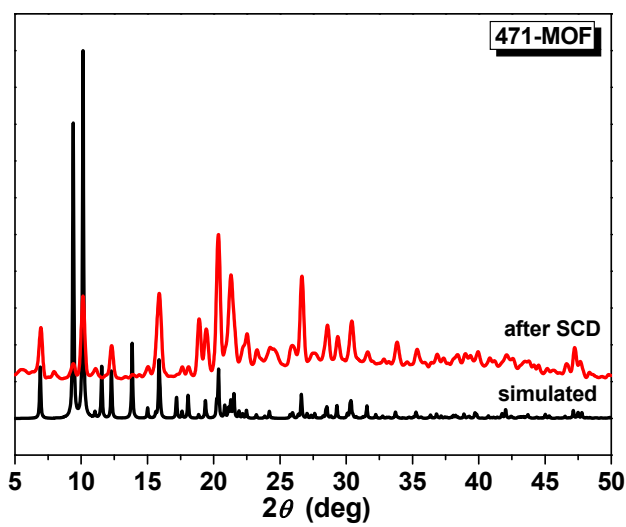
**Fig. S11** Pore surfaces for 470-MOF (a) and 471-MOF (b) in  $2 \times 2 \times 2$  unit cell with the conolly radius of  $1.4 \text{ \AA}$ , showing the 1-D channels along the  $[001]$  and  $[101]$  directions.

## Section 5. Gas adsorption

**Activation of 470-MOF and 471-MOF.** The as-synthesized 470-MOF or 471-MOF crystals were soaked into fresh DMF for one day, during which the solvent was refreshed three times. After that, the sample was evacuated by supercritical carbon dioxide drying (SCD) process in a Tousimis Samdri PVT-3D critical point dryer. The sample was placed into the chamber, and the solvent was exchanged with liquid carbon dioxide. The CO<sub>2</sub> filling was maintained for 2.5 hours and followed by a purge vent for 30 minutes. Such a refilling and purging of liquid CO<sub>2</sub> recycle was repeated three times. Then, the chamber holding the MOF sample and liquid CO<sub>2</sub> was heated to 40 °C and kept under the supercritical condition (typically 1300 psi) for 1 hour. The CO<sub>2</sub> can be slowly vented from the chamber at 40 °C. The resulting activated sample was transferred to a pre-weighed 12-mm sample tube, evacuated ( $< 10^{-3}$  Torr) at room temperature overnight prior to gas sorption.



(a)



(b)

**Fig. S12** PXRD patterns for 470-MOF (a) and 471-MOF (b) after SCD activation.

### Isosteric heat of adsorption

The Clausius-Clapeyron equation<sup>S5</sup> was applied to calculate the enthalpies of CO<sub>2</sub> adsorption. The isosteric heat of adsorption ( $Q_{st}$ ), as defined by eqn (I), in which  $p$  is the pressure,  $q$  is the amount adsorbed,  $T$  is the temperature, and  $R$  is the universal gas constant, can be determined by using the pure-component isotherm fits. The Langmuir-Freundlich equation (II), where  $q$  is amount adsorbed,  $q_{sat}$  is amount adsorbed at saturation,  $p$  is the pressure,  $b$  is the T-dependent parameter, and  $\nu$  is constant, was used to fit CO<sub>2</sub> adsorption isotherms and predict the adsorption capacity of the coordination framework at saturation.

$$Q_{st} = RT^2 \left( \frac{\partial \ln p}{\partial T} \right)_q \quad (\text{I})$$

$$q = q_{sat} \frac{bp^\nu}{1+bp^\nu} \quad (\text{II}) \quad \text{where } b_A = b_0 \exp\left(\frac{E}{RT}\right)$$

### Calculation of adsorption selectivity

The selectivity factors ( $S_{ads}$ ) of component 1 over component 2 in a mixture of 1 and 2, can be formally defined as eqn (III), where  $q$  is the quantity of gas adsorbed and  $p$  is the partial pressure of the gas adsorbed. The calculations assumed a mixed gas composition of 15% component 1 (CO<sub>2</sub>) and 85% component 2 (CH<sub>4</sub>, H<sub>2</sub>, O<sub>2</sub>, Ar or N<sub>2</sub>) based on the Ideal Adsorbed Solution Theory of Myers and Prausnitz.<sup>S6</sup>

$$S_{ads} = \frac{q_1/q_2}{p_1/p_2} \quad (\text{III})$$

## References

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