Electronic Supplementary Information

Two porous metal-organic frameworks containing zinc-calcium clusters or calcium cluster chains

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Syntheses of Materials

Chemicals used in this work: $Zn(NO_3)_2 \cdot 6H_2O$, $Ca(OH)_2$, and tetrahydrofuran (THF) were purchased from Daejung Chemicals & Metals Co., Ltd. All starting materials were used without further purifications. 1,3,5-Tris(4′-carboxyphenyl)benzene (H_3BTB) was prepared according to a literature method.[S1]

General Methods. Single-crystal X-ray diffraction data for ZnCaBTB and CaBTB were collected at 100 K using synchrotron radiation at a beamline 2D-SMC, Pohang Accelerator Laboratory (PAL) in Korea. Powder X-ray diffraction (PXRD) data were measured on a Rigaku MiniFlex diffractometer with CuKα radiation. Thermogravimetric analyses (TGA) were carried out using a Scinco TGA-S1000 thermal analysis system. Fourier-transform infrared (FT-IR) spectra of samples prepared as KBr pellets were recorded using a JASCO FT/IR-4000 spectrophotometer. ^{1}H-NMR spectra were obtained on a Bruker 400 MHz NMR spectrometer. Elemental analyses were performed with a Perkin-Elmer 2400 Series II CHN analyzer.

Synthesis of $[Zn_2Ca(BTB)_2(H_2O)_2]\cdot 3(THF)_{3.81}\cdot(H_2O)_{1.32}$ (ZnCaBTB). $Zn(NO_3)_2 \cdot 6H_2O$ (0.0446 g, 0.15 mmol) and H_3BTB (0.0658 g, 0.15 mmol) were completely dissolved in the mixture of THF (19.2 mL) and H_2O (1.8 mL). After adding $Ca(OH)_2$ (0.0111 g, 0.15 mmol), the reaction mixture was placed in a 30 mL vial and treated by sonication for 10 min. The vial was tightly capped and then heated at 75 °C for 4 d to produce colourless hexagonal plate crystals. The crystals were washed with THF for 4-5 times and stored in fresh THF. When exposed to air, the crystals lose transparency. ZnCaBTB is unstable in water. However, it is stable in common organic solvents such as DMF, acetone, and MC, and under vacuum. Elemental Analysis: Calcd. (%), C 60.43, H 4.92, N 0.00; Found, C 59.54, H 4.30, N 0.00. The found values are matched with 2 THF and 2 H_2O guest molecules: calcd. (%), C 59.20, H 4.33, and N 0.00. Thus, it is presumed that the volatile THF molecules inside the pore were partially evaporated during the elemental analysis.

Synthesis of $[Ca_5(BTB)_2(HBTB)_2(H_2O)_6]\cdot(THF)_{12}(H_2O)_2$ (CaBTB). In a 20 mL vial, H_3BTB (0.154 g, 0.35 mmol) was dissolved in the mixture of THF (14.7 mL) and H_2O (2.8 mL). Into the solution, $Ca(OH)_2$ (0.026 g, 0.35 mmol) was added and mixed. The vial was tightly capped and then heated at 85 °C for 7 d. Rectangular plate crystals formed when the solution was standing at room temperature for 1 d. It is noticeable that the yield and quality of the crystals are best when the reaction mixture is heated for 7 d. The separated crystals were washed with THF for 4-5 times and stored in fresh THF. When exposed to air, the crystals became opaque and shattered, but they are stable under vacuum. Yield: 0.100 g, 69.6%. Elemental Analysis: Calcd. (%), C 63.44, H 5.94, N 0.00; Found, C 63.03, H 5.60, N 0.00.

S1. S. B. Choi, M. J. Seo, M. Cho, Y. Kim, M. K. Jin, D.-Y. Jung, J.-S. Choi, W.-S. Ahn, J. L. C. Rowsell and J. Kim, *Cryst. Growth Des.*, **2007**, *7*, 2290.

Single Crystal X-ray Diffraction Analyses

A. ZnCaBTB

The crystals of ZnCaBTB were grown with thin hexagonal plate morphology, and stacked among themselves. An isolated single crystal was selected and used for the collection of X-ray data using a synchrotron light source (Table S2). The non-H atoms in the asymmetric unit were found by a direct method using SHELXS, and refined with anisotropic thermal parameters using SHELXL.[S2] The H atoms were generated with ideal geometry and refined with a riding model. As there was a possibility of unexpected distributions of the metal ions over two sites, the possible cases were considered by conducting structure refinement as listed in Table S1. The refinement results did not allow any situations except for the case E, requiring that Zn1 and Ca1 must be located on a 3-fold axis and at a site with 32-symmetry, respectively.

During the refinement of the framework unit, disordered solvent molecules could be modelled and incorporated into the subsequent refinement processes. There were two independent THF molecules and one water molecule in the pore. Their site occupancy factors were independently refined to give 0.30976, 0.32555, and 0.22031 respectively for THF-1, THF-2, and H_2O, which corresponded to the formula, $[Zn_2Ca(BTB)_2(H_2O)_2](3.8118\ THF)(1.3219\ H_2O)$. All non-H atoms were refined with anisotropic temperature factors. However, the refinement process did not converge and became unstable. Thus, the final stage of the refinement was carried out with a 'DAMP 0 0' instruction. The crystal and refinement data are listed in Table S2, and the asymmetric unit is represented in Figure S1.

The structure was also refined without the disordered guest molecules by applying the PLATON SQUEEZE method.[S3] The results are also listed in Table S2. There are two asymmetric units in the unit cell, and the total numbers of THF and H_2O molecules are respectively 7.6237 and 2.6437 per unit cell. As the number of electrons of THF and H_2O are respectively 40, and 8, the total number of electrons per unit cell is calculated to $7.6237 \times 40 + 2.6437 \times 8 = 326.1$ (e- per unit cell). This value is well-matched with the 326 electrons that are calculated for the contribution from the removed entity by the SQUEEZE process.

S2. G. M. Sheldrick, *Acta Cryst*. **2008**, *A64*, 112-122.

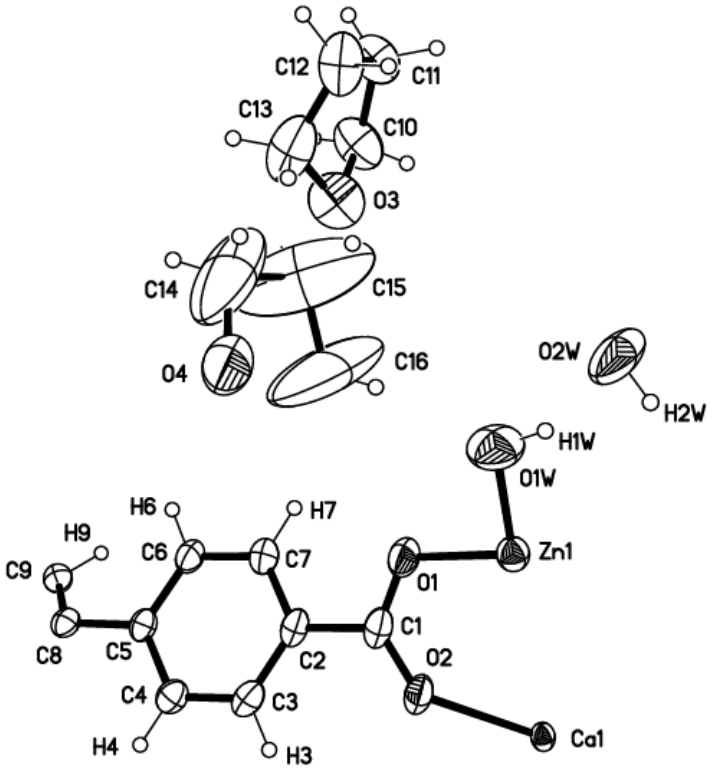
S3. A. L. Spek, *Acta Cryst*. **2009**, *D65*, 148-155.

Table S1. Selected refinement results are summarized for ZnCaBTB which has two metal ions at the Wyckoff positions **4f** (1/3, 2/3, *z*) or on a 3-fold axis, and **2d** (1/3, 2/3, 3/4) or at a site with 32-symmetry, respectively for the space group, *P*-31*c* (No. 163). All non-H and H atoms are included in the structural model of the ZnCaBTB framework without the occluded solvent molecules, and their thermal parameters are refined isotropically to prevent unfavourable correlations between the thermal parameters and occupancy factors. The positional disorders at each position are considered with varying the site occupancy factors (s.o.f.); that is, various Zn/Ca ratios were tested by structure refinement processes. The models with the mixed metal ions at the Wyckoff position 4f or 2d give rise to unreasonable or unstable refinement results. The best model (***E***) has been chosen such that Zn ion and Ca ions are located respectively at the 4f and 2d positions. The quite abnormal results are highlighted in red.

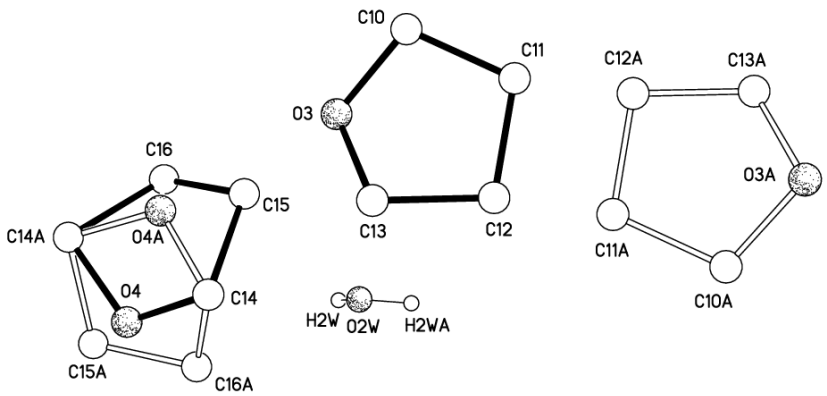
Model	**Sites**	**Metal ion**	***z***	**s.o.f.**	U_{eq} (Å^2)	R_1	**Comment**
A	**4f**	Zn1	0.500230	1/3	0.02481	0.1636	without Ca ions
	2d	Zn2	0.750000	1/6	0.04235		
B	**4f**	Zn1	0.500862	1/3	0.05208	0.5805	Zn/Ca disorder at **2d** negative occupancy for Zn2
	2d	Zn2 Ca1	0.750000 0.750000	-0.0125 (1/6)+0.0125	1.99837 0.01669		
C	**4f**	Zn1 Ca2	0.500179 0.500179	0.3192 0.0141	0.00382 0.02937	N/A	Zn/Ca disorder at **4f** refinement unstable
	2d	Ca1	0.750000	1/6	0.31962		
D	**4f**	Ca2	0.500241	1/3	0.02088	0.1839	without Zn ions
	2d	Ca1	0.750000	1/6	0.03661		
E	**4f**	Zn1	0.500297	1/3	0.02937	0.1386	Zn : Ca = 2 : 1 The best model
	2d	Ca1	0.750000	1/6	0.02004		

Table S2. Crystal data and structure refinement for ZnCaBTB.

	With Guest	**Without Guest**
Framework formula	$Zn_2Ca(BTB)_2(H_2O)_2$	$Zn_2Ca(BTB)_2(H_2O)_2$
Guests included for refinement	(3.8118 THF)(1.3219 H_2O)	None (**SQUEEZE)**
Empirical formula	C69.25 H65.28 O19.14 Ca Zn2	C54 H34 O14 Ca Zn2
Formula weight	1374.41	1077.63
Temperature	100(2) K	
Wavelength	0.63000 Å	
Crystal system	Trigonal	
Space group	*P* -3 1 *c* (No. 163)	
Unit cell dimensions	*a* = 16.550(2) Å	α = 90°
	b = 16.550(2) Å	β = 90°
	c = 14.748(3) Å	γ = 120°
Volume	3498.3(10) $Å^3$	
Z	2	
Density (calculated)	1.305 Mg/m^3	1.023 Mg/m^3
Absorption coefficient	0.597 mm^{-1}	0.807 mm^{-1}
F(000)	1428	1100
Crystal size	0.30 × 0.30 × 0.05 mm^3	
Theta range for data collection	1.76 to 24.83°	
Index ranges	-21 <= *h* <= 21, -22 <= *k* <= 22, -19 <= *l* <= 19	
Reflections collected	31148	
Independent reflections	2894 [*R*(int) = 0.0340]	2894 [*R*(int) = 0.0349]
Completeness to theta = 24.83°	99.6%	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2894 / 8 / 193	2894 / 2 / 113
Goodness-of-fit on F^2	1.187	1.092
Final *R* indices [*I*>2sigma(*I*)]	R_1 = 0.0701, wR_2 = 0.2006	R_1 = 0.0613, wR_2 = 0.1846
R indices (all data)	R_1 = 0.0707, wR_2 = 0.2010	R_1 = 0.0630, wR_2 = 0.1867
Extinction coefficient	0.052(5)	0.032(4)
Largest diff. peak and hole	0.840 and -0.766 e.$Å^{-3}$	0.801 and -1.141 e.$Å^{-3}$



(a)



(b)

Fig. S1 (a) Asymmetric unit of ZnCaBTB: ORTEP drawing (50% level) with atomic labels. (b) The guest molecules in the pore with ball-and-stick models. Two independent THF molecules disordered over two sites are displayed with filled and open stick bonds.

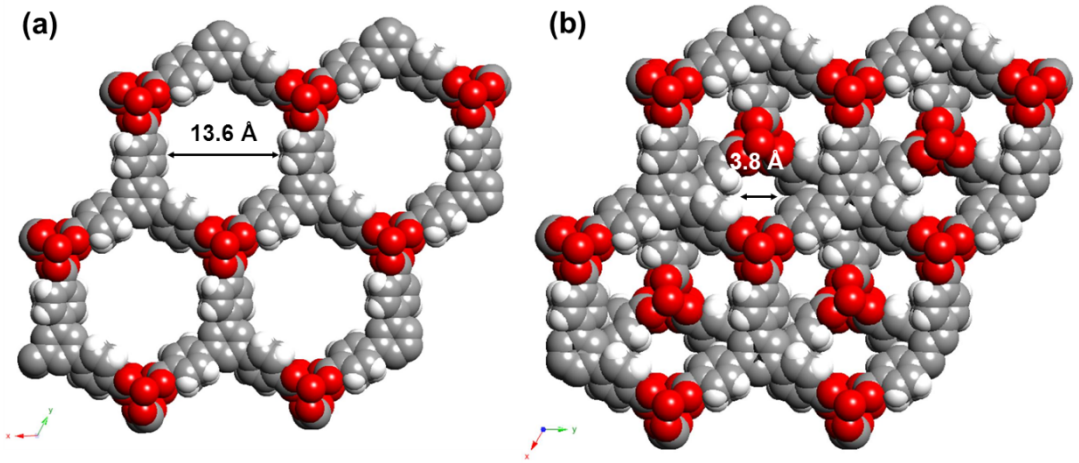


Fig. S2 Fragment structures of ZnCaBTB displayed with space-filling models: (a) pores in one layer with the effective size of 13.6 Å, and (b) channels of the effective size of 3.8 Å generated by layer stacking.

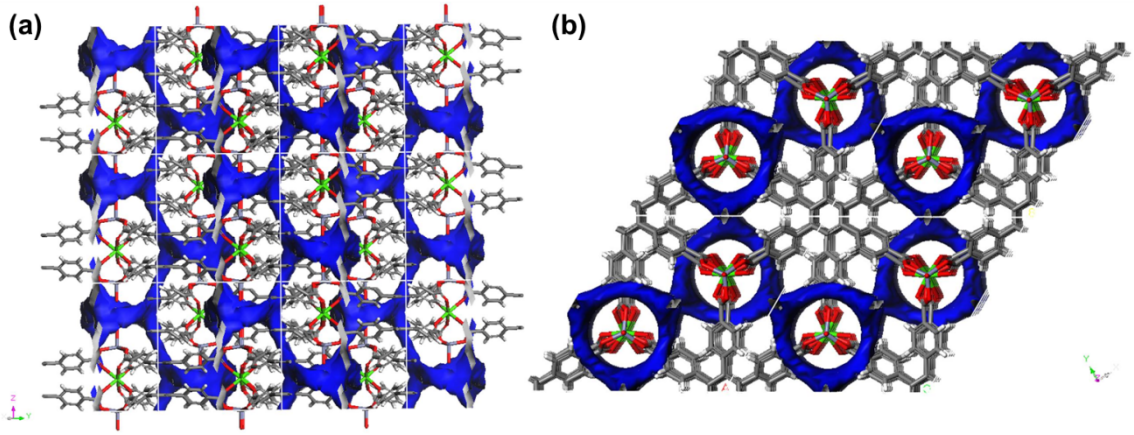


Fig. S3 The solvent accessible areas (blue) of ZnCaBTB viewed along the crystallographic (a) *a*- and (b) *c*-axis, respectively.

Table S3. Crystal data and structure refinement for CaBTB

Formula	$[Ca_5(BTB)_2(HBTB)_2(H_2O)_6]\cdot(THF)_{12}(H_2O)_2$	
Empirical formula	C156 H174 O44 Ca5	
Formula weight	2953.35	
Temperature	100(2) K	
Wavelength	0.80000 Å	
Crystal system	Monoclinic	
Space group	$P\ 2_1/c$ (No. 14)	
Unit cell dimensions	a = 16.135(3) Å	$\alpha = 90°$.
	b = 26.792(5) Å	$\beta = 110.57(3)°$.
	c = 18.630(4) Å	$\gamma = 90°$.
Volume	7540(3) $Å^3$	
Z	2	
Density (calculated)	1.301 Mg/m^3	
Absorption coefficient	0.358 mm^{-1}	
$F(000)$	3124	
Crystal size	0.35 x 0.30 x 0.30 mm^3	
Theta range for data collection	1.57 to 28.07°.	
Index ranges	$-18 <= h <= 18$, $-28 <= k <= 28$, $-21 <= l <= 21$	
Reflections collected	23192	
Independent reflections	11946 [R(int) = 0.0360]	
Completeness to theta = 28.07°	93.0%	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	11946 / 182 / 998	
Goodness-of-fit on F^2	1.196	
Final R indices [I>2sigma(I)]	R_1 = 0.0864, wR_2 = 0.2614	
R indices (all data)	R_1 = 0.1006, wR_2 = 0.2786	
Extinction coefficient	0.0074(10)	
Largest diff. peak and hole	1.047 and -0.851 e.$Å^{-3}$	

Table S4. Possible hydrogen bonds for CaBTB [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(1W)-H(1WA)...O(10)#	0.84(3)	2.39(4)	2.692(4)	102(3)
O(1W)-H(1WB)...O(6')	0.84(3)	2.01(2)	2.723(9)	142(3)
O(1W)-H(1WB)...O(6T)	0.84(3))	2.118(12)	2.819(11)	140.7(9)
O(2W)-H(2WA)...O(9)#2	0.84(3)	1.888(16)	2.672(4)	155(4)
O(2W)-H(2WB)...O(2T)	0.84(3)	1.965(10)	2.769(8)	159.8(19)
O(3W)-H(3WA)...O(5)#3	0.84(3)	1.999(7)	2.745(3)	147.5(11)
O(3W)-H(3WB)...O(4W)	0.84(3)	1.837(5)	2.667(4)	169.4(13)
O(4W)-H(4WA)...O(1T)	0.84(3)	1.953(14)	2.772(6)	165(4)
O(4W)-H(4WB)...O(8)#3	0.84(3)	2.001(14)	2.815(4)	163(5)
O(4)-H(4O)...O(1)#4	0.84(3)	1.72(2)	2.540(4)	175(4)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,y+1/2,-z+1/2 #2 -x,-y,-z #3 x+1,-y+1/2,z+1/2

#4 x-1,y,z

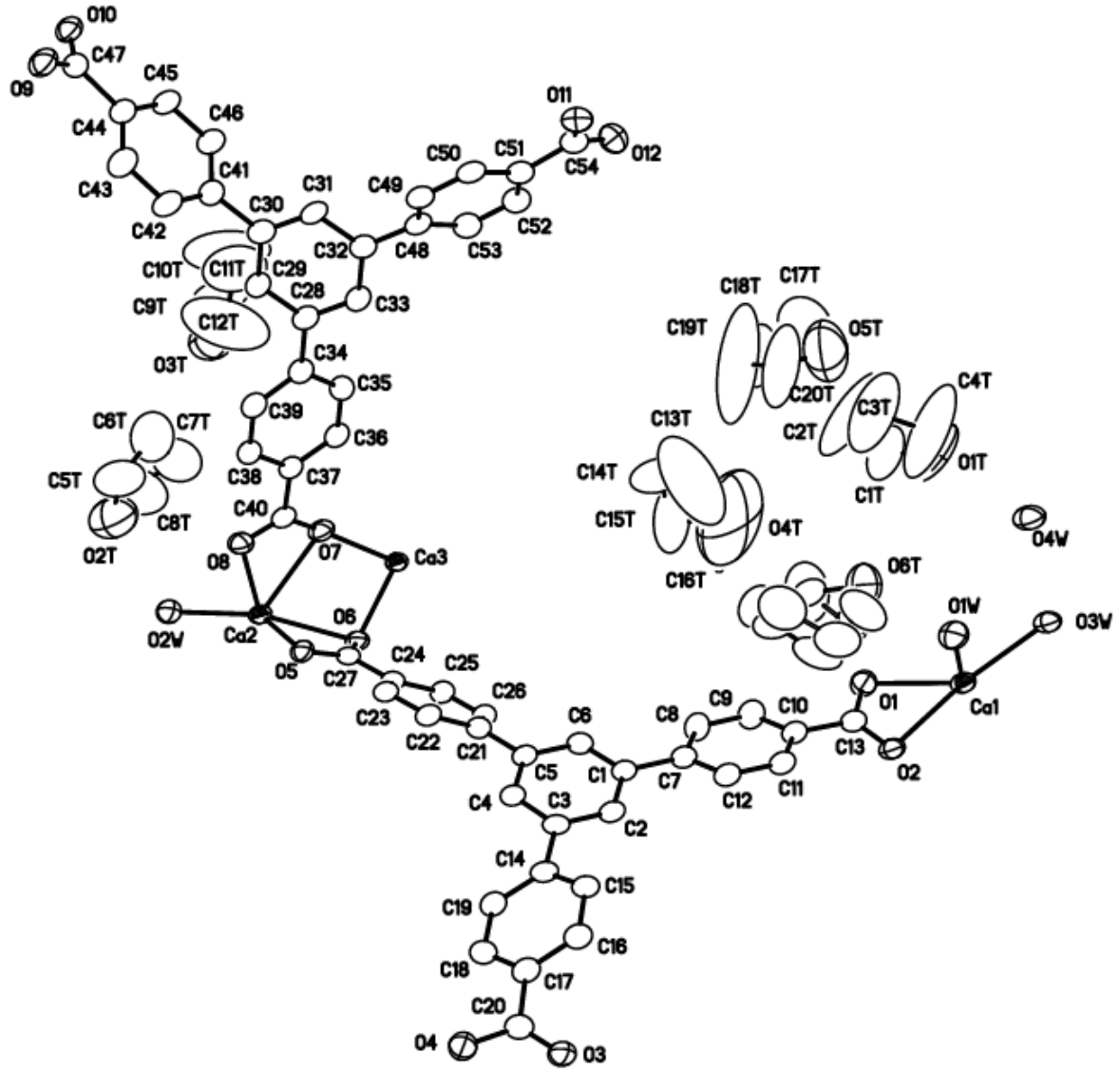


Fig. S4 Asymmetric unit of CaBTB, $[Ca_5(BTB)_2(HBTB)_2(H_2O)_6]\cdot(THF)_{12}(H_2O)_2$: ORTEP drawing (50% level) with atomic labels. H atoms are omitted for simplicity.

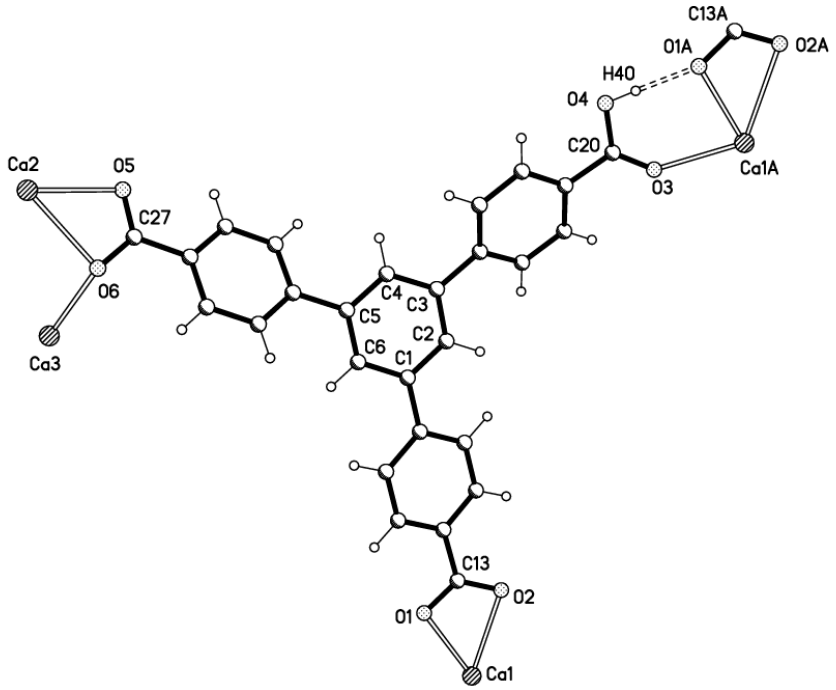


Fig. S5 The $HBTB^{2-}$ ligand in CaBTB formulated as $[Ca_5(BTB)_2(HBTB)_2(H_2O)_6]\cdot(THF)_{12}(H_2O)_2$ is displayed with a ball-and-stick model. One of the three –COOH groups in H_3BTB has not been deprotonated, which is identified by the bond distance differences between C and O atoms (Å): O3–C20 1.220(5); O4–C20 1.320(5); O1–C13 1.262(5); O2–C13 1.241(5); O5–C27 1.260(4); O6–C27 1.286(4). The O4-H4O donor is engaged in the H-bond with the O1A acceptor (See details in Table S4.). The Ca3 atom lies on an inversion centre.

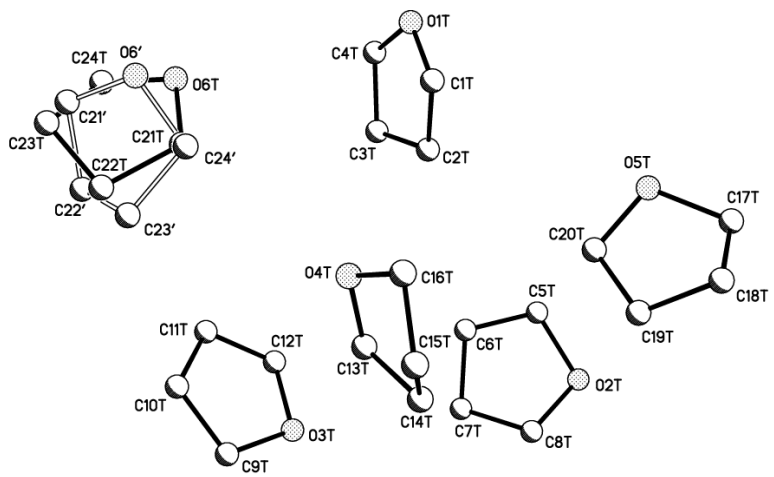


Fig. S6 The occluded THF molecules in the channel of CaBTB are displayed with ball-and-stick models. A THF molecule is disordered over two sites.

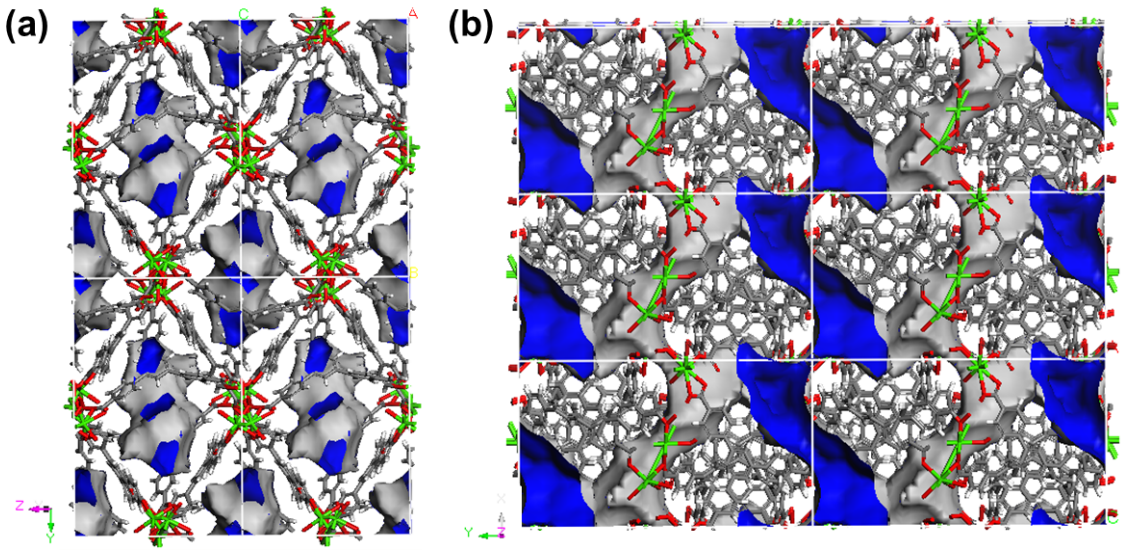


Fig. S7 The solvent accessible areas (blue) of CaBTB viewed along the crystallographic (a) *a*- and (b) *c*-axis, respectively.

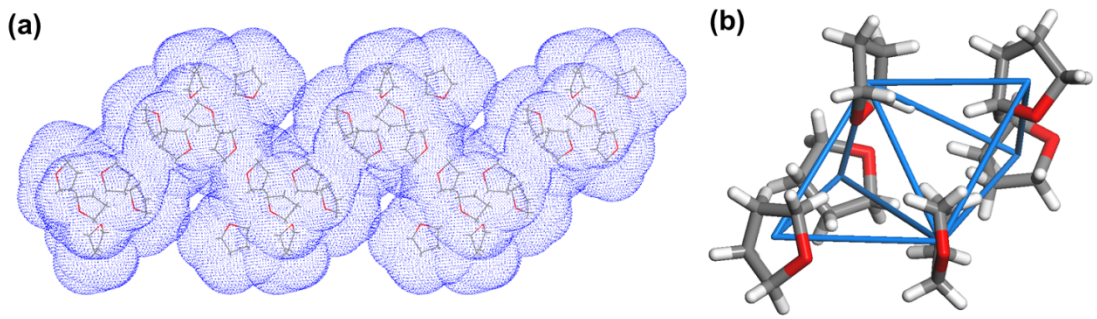


Fig. S8 (a) The position of guest THF molecules along the curved channels and (b) the tetrahedral arrangement of the THF molecules.

Powder X-Ray Diffraction Analyses

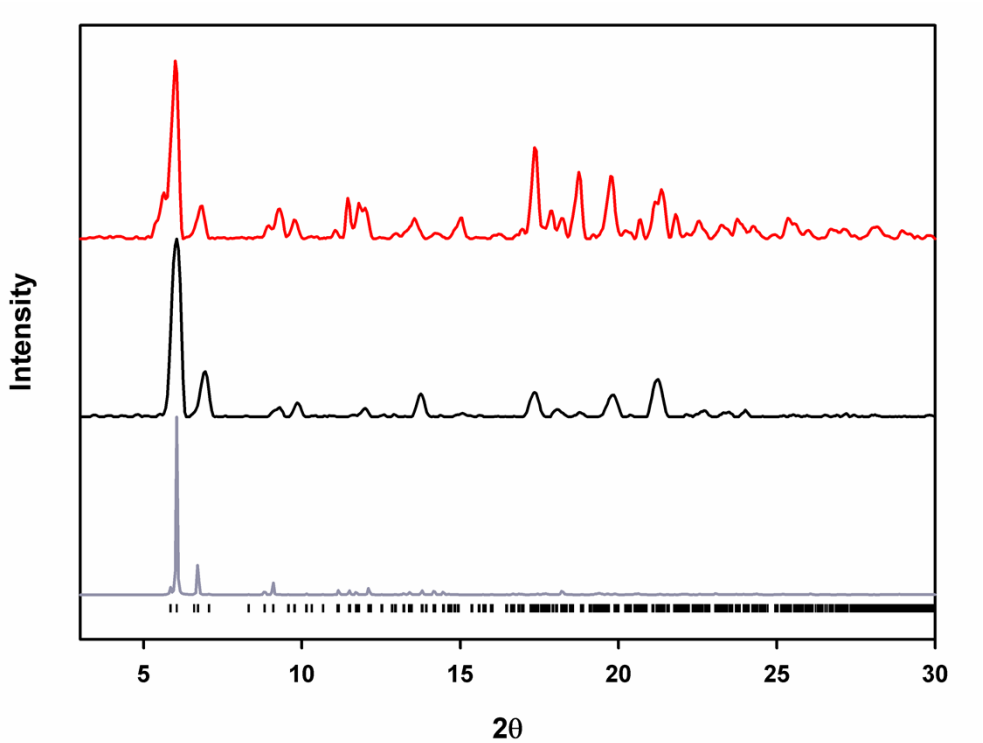


Fig. S9 PXRD patterns of CaBTB; a simulated pattern (grey) derived from the single-crystal X-ray data, an as-prepared sample (black), and an activated sample (red), respectively.

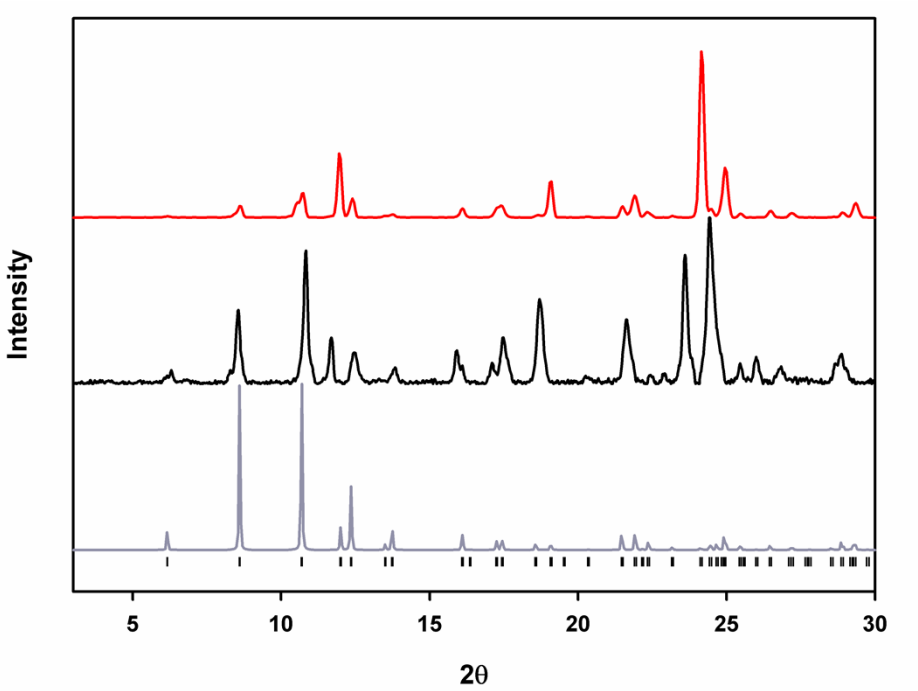


Fig. S10 PXRD patterns of ZnCaBTB; a simulated pattern (grey) derived from the single-crystal X-ray data, an as-prepared sample (black), and an activated sample (red), respectively.

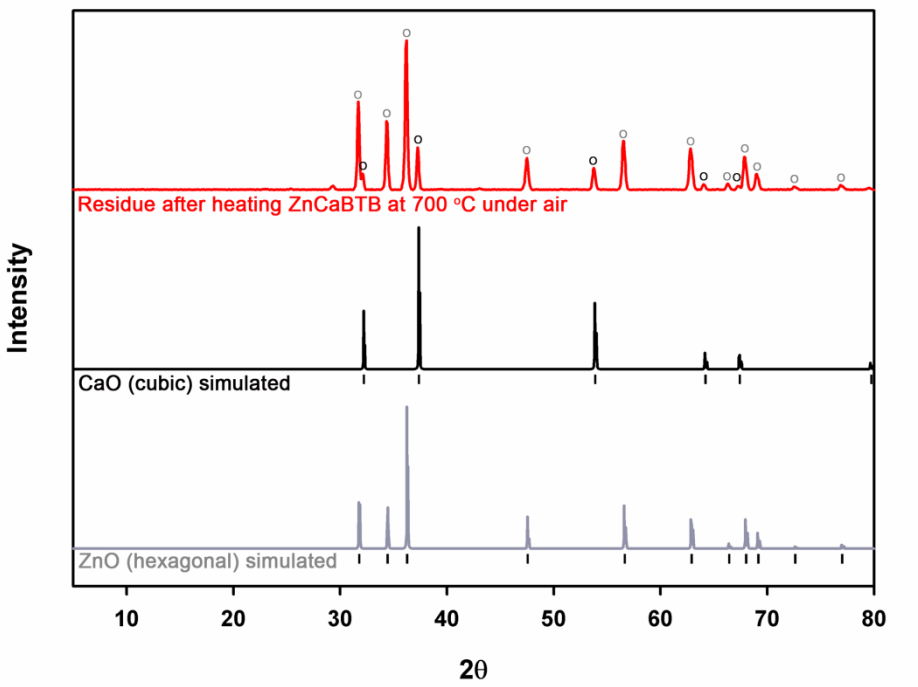


Fig. S11 Comparison of the PXRD pattern for the residue collected after heating ZnCaBTB at 700 °C under air on a TGA apparatus with those of ZnO and CaO, respectively.

Thermogravimetric Analyses

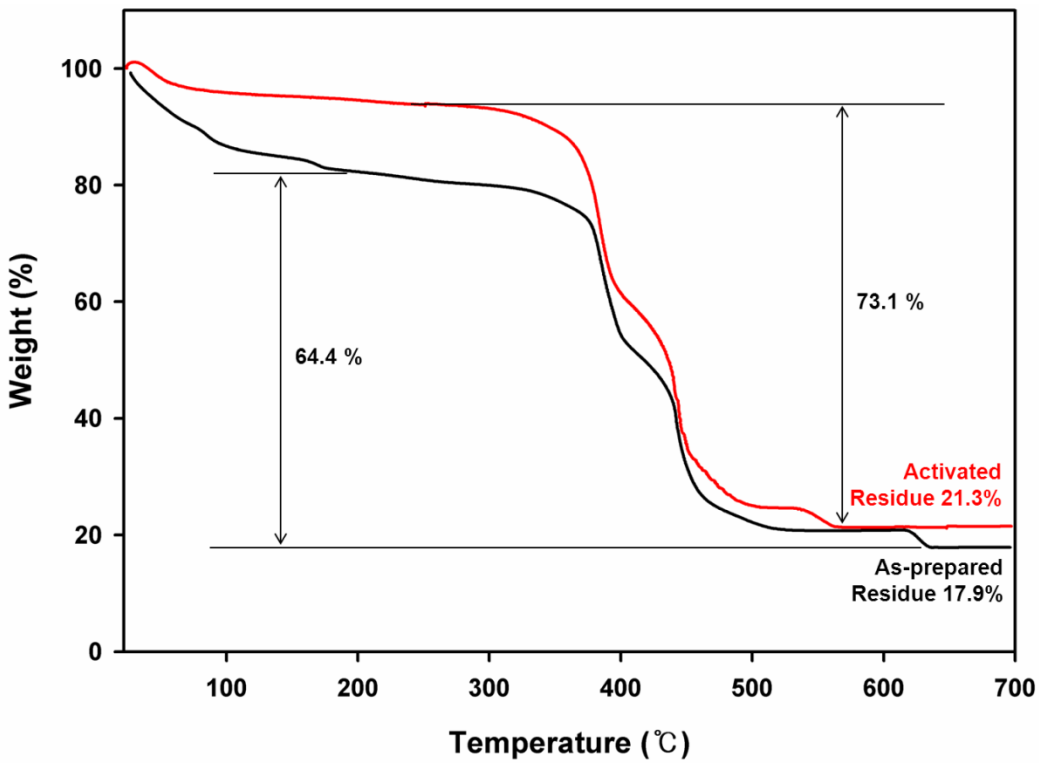


Fig. S12 TGA traces of ZnCaBTB for an as-prepared (black) and an activated sample (red) respectively obtained by heating each sample up to 700 °C at a heating rate of 5 °C/min under ambient atmosphere. The small bump at the start of the sample heating of the activated samples is ascribed to the adsorbed water molecules from the ambient atmosphere, which is sometimes found in the activated samples that have favourable water-binding sites such as open-metal sites or coordinated water molecules.

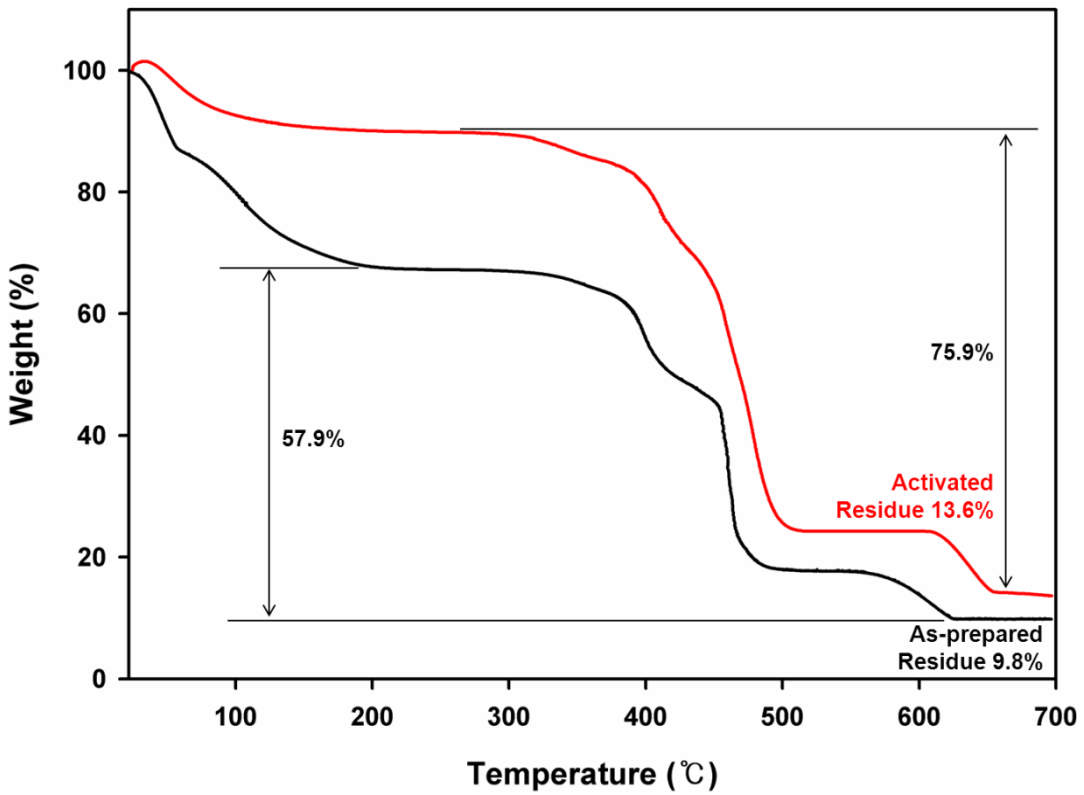


Fig. S13 TGA traces of CaBTB for an as-prepared (black) and an activated sample (red) respectively obtained by heating each sample up to 700 °C at a heating rate of 5 °C/min under ambient atmosphere. The possible origin for the small bump at the low temperature in the trace for the activated sample is explained in the 5 caption of Fig. S12.

Gas Adsorption Analyses

Adsorption isotherms of N_2, H_2, and CO_2 gases at pressures up to 1 bar were conducted by standard volumetric procedures on BELSORP-mini (BEL-Japan, INC.) Ultrahigh-purity-grade N_2, H_2, CO_2, and CH_4 gases were used in all adsorption measurements. The N_2 and H_2 (77 K) gas isotherms were measured using a liquid nitrogen bath and CO_2 (253, 273, and 298 K) gas isotherms were measured using a circulator (253, 273, and 298 K).

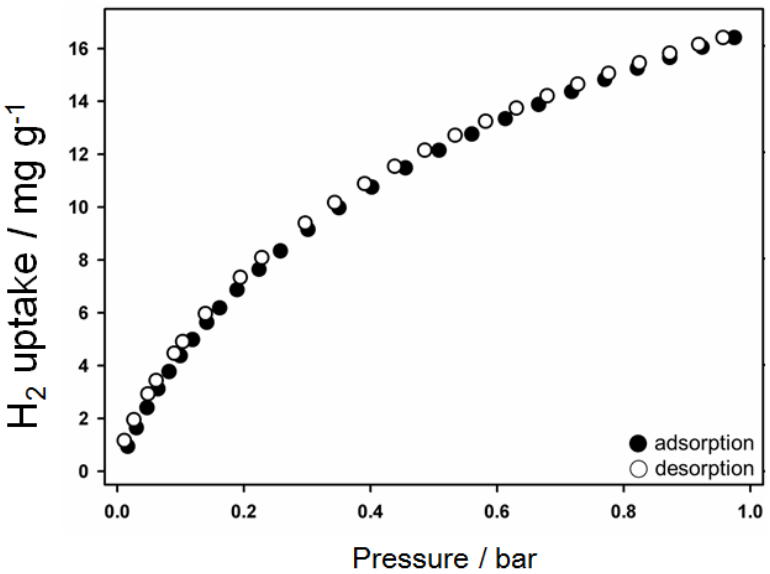


Fig. S14 The H_2 gas sorption isotherm of ZnCaBTB at 77 K.

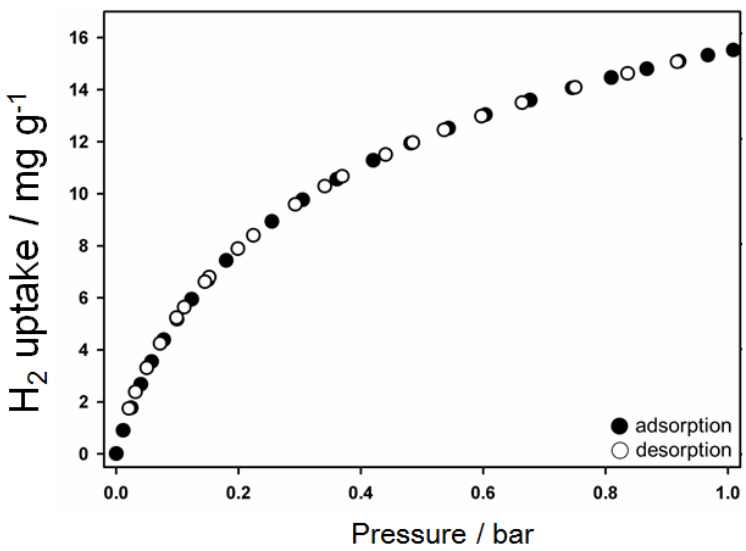


Fig. S15 The H_2 gas sorption isotherm of CaBTB at 77 K.

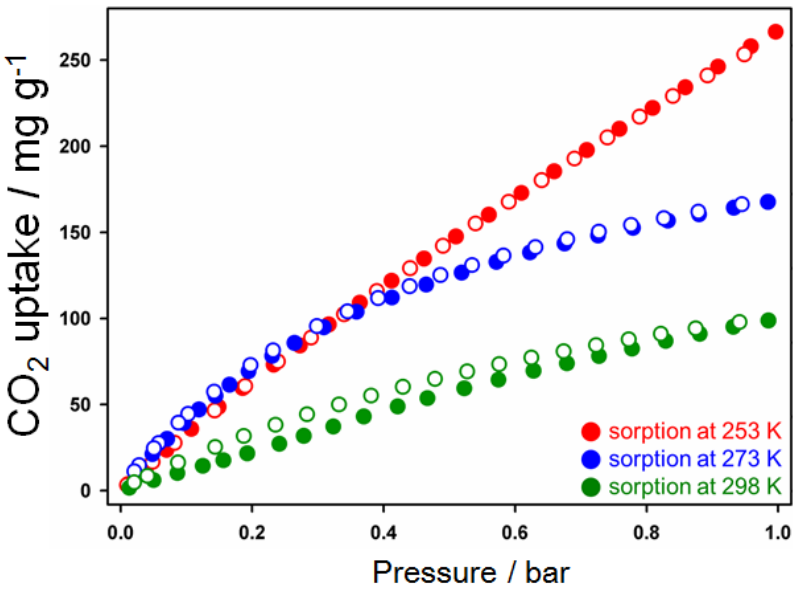


Fig. S16 The CO_2 gas sorption isotherm of ZnCaBTB at 253, 273, and 298 K.

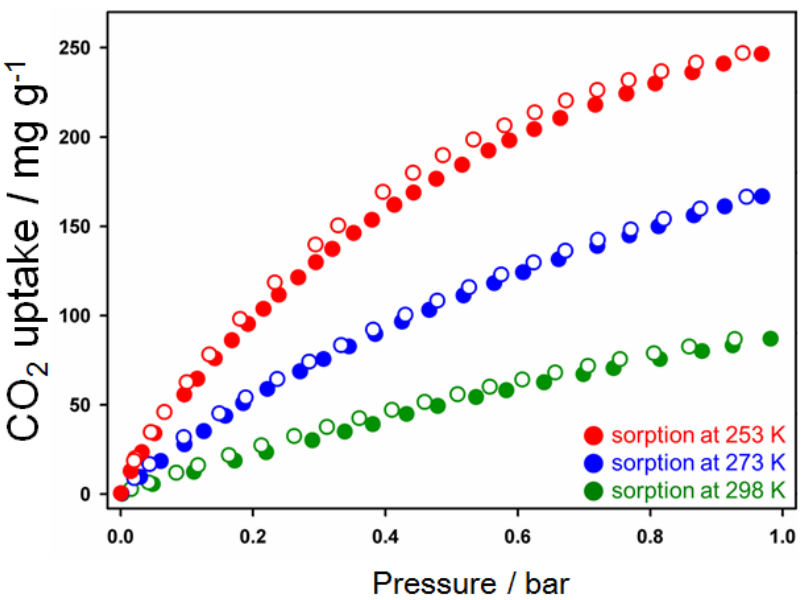


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Fig. S17 The CO_2 gas sorption isotherms of CaBTB at 253, 273, and 298 K.

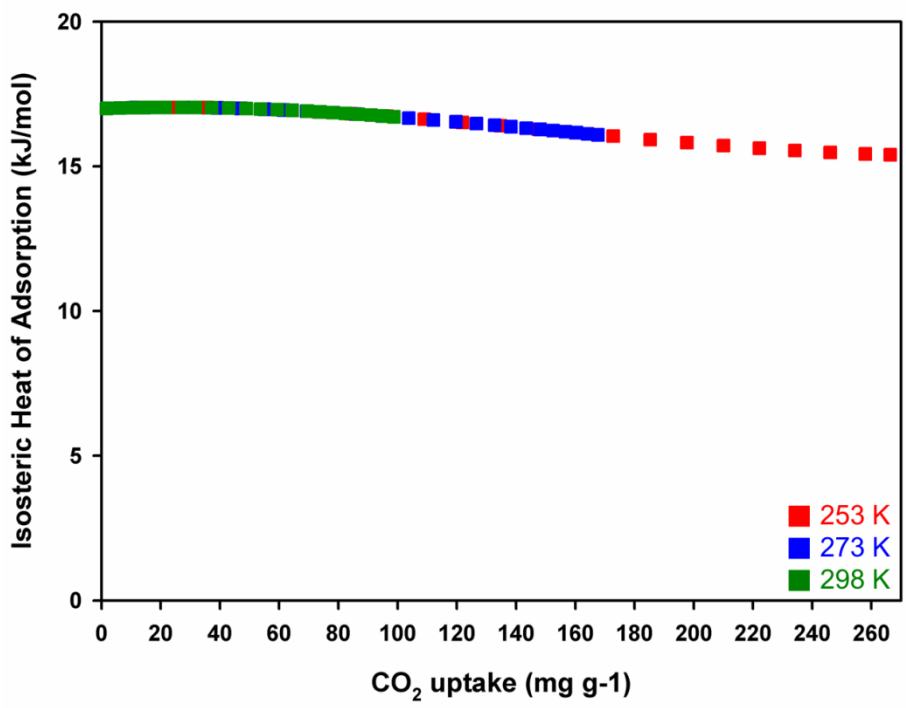
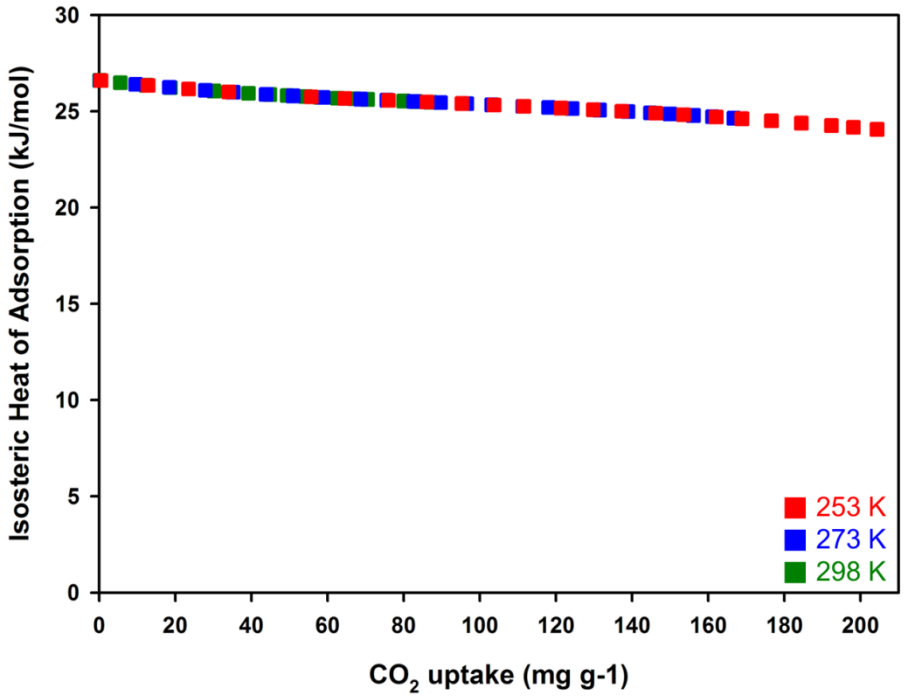


Fig. S18 The isosteric heat of CO_2 adsorption in ZnCaBTB.



5 **Fig. S19** The isosteric heat of CO_2 adsorption in CaBTB.