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Selective CO₂ adsorption in a metal–organic framework constructed from an organic ligand with flexible joints†

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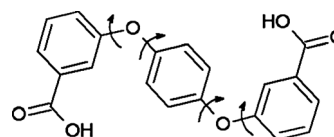
A metal–organic framework (SNU-110) constructed from an organic ligand with flexible joints exhibits selective CO₂ adsorption over N₂, O₂, H₂ and CH₄ gases.

Metal–organic frameworks (MOFs) have great potential to be applied in gas storage,^{1–9} gas separation,^{10–26} and fabrication of metal nanoparticles.^{3,27,28} In particular, they can be applied as capture materials for CO₂ from the industry flue gas that is implicated in the global warming.^{2,10,13} The industry flue gas contains not only CO₂ but also other gases such as N₂, H₂, H₂O, and O₂ depending on the combustion methods. Therefore, selective adsorption properties of MOFs for CO₂–N₂ and CO₂–H₂ are important for post-combustion and pre-combustion CO₂ capture, respectively. In addition, the MOFs with selective adsorption property for CO₂–CH₄ can be applied in purification of low quality natural gas.^{24–26}

To be a CO₂ capture material, the MOFs should have high CO₂ adsorption capacity at ambient temperature,^{8,9} high adsorption selectivity of CO₂ over other gases,^{10–12} and high thermal stability. To increase the CO₂ capture ability of MOFs, various strategies have been employed such as making the network inherently flexible,¹⁰ functionalizing the pore-surface with amines,^{11,12} creating accessible metal sites,¹³ attaching flexible arms,^{14,15} exposing Lewis base sites,¹⁸ and exchanging counter ions included in the charged framework.¹⁹ It has been reported that MOFs constructed from flexible organic components, even if they do not adsorb N₂ and H₂ gases due to the smaller pores of the activated samples than the kinetic diameters of these gases, often selectively adsorb CO₂ since they open the gates for CO₂ that has much higher polarizability (2.51 Å³) and quadrupole moment (1.4 × 10^{−39} C m²) than other gases.^{10,15–17,20} However, some of those MOFs still adsorb considerable amounts of CH₄ at 195 K because they are flexible enough to open the gates for CH₄ having high polarizability (2.45 Å³), and cannot be applied in purification of natural gas.

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† Electronic supplementary information (ESI) available: Detailed experimental procedures, ORTEP drawings, ¹H-NMR spectra, TGA/DSC traces, PXRD patterns, table of X-ray data for SNU-110, tables of gas adsorption data for SNU-110'. CCDC 885397. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2cc34482c



Scheme 1 Design of an organic ligand with flexible joints: 3,3'-(1,4-phenylenebis(oxy))dibenzoic acid (H₂*mpm*-PBODB).

Here we report on {[Zn₂(*mpm*-PBODB)₂bpy]·3DMF}_n (SNU-110) synthesized from the organic linker having flexible joints (Scheme 1). The MOF shows a selective CO₂ adsorption property over CH₄ as well as N₂ and H₂ gases at 195 K.

SNU-110 was synthesized from solvothermal reaction of 3,3'-(1,4-phenylenebis(oxy))dibenzoic acid (H₂*mpm*-PBODB) with Zn(NO₃)₂·6H₂O and 4,4'-bipyridine (bpy) in DMF. It is thermally stable up to 370 °C (see ESI†). In the X-ray crystal structure of SNU-110, two Zn^{II} ions form a paddle wheel cluster unit, each of which is connected by four *mpm*-PBODB ligands to construct a corrugated 2D layer extending along the (10 $\bar{2}$) plane (Fig. 1a). The 2D layers are further connected by bpy ligands along the [101] direction, since the axial sites of the paddle wheel units are coordinated with bpy ligands, which gives rise to a 3D framework generating 1D channels (Fig. 1b and c). The angle made between the corrugated 2D planes and the bpy pillar is 29.4°.

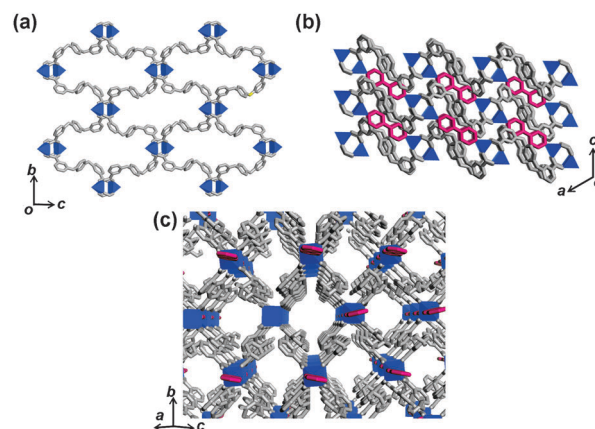


Fig. 1 The X-ray structure of SNU-110. (a) A corrugated 2D layer formed of [Zn₂(*mpm*-PBODB)₂]₂, running on the (10 $\bar{2}$) plane. (b) A view seen on the (010) plane showing corrugated 2D layers connected by bpy pillars. (c) A view seen along the [101] direction showing 1D channels. Color scheme: Zinc, blue; *mpm*-PBODB, gray; 4,4'-bpy, red. Hydrogen atoms are omitted for clarity.

although nearly right angle has been commonly made between the connecting pillar and the 2D layer constructed by the paddle-wheel type Zn_2 cluster units.²⁹ The 1D channels extending along the [101] direction have the rectangular cavities of effective size $4.4 \times 3.7 \text{ \AA}^2$, and they are filled with guest DMF molecules as characterized by IR, EA, and TGA data. The solvent accessible volume estimated by PLATON is 30% of the structure ($0.248 \text{ cm}^3 \text{ g}^{-1}$).³⁰

The desolvated sample, $[\text{Zn}_2(\text{mpm-PBODB})_2\text{bpy}]_n$ (SNU-110'), was prepared by the treatment of SNU-110 with supercritical CO_2 fluid. Since the single crystallinity was not maintained during this activation process, the desolvated phase was analysed by powder X-ray diffraction (PXRD) data of SNU-110'. The PXRD patterns indicate that SNU-110' is different from the structure of the as-synthesized sample (Fig. 2). The PXRD pattern of SNU-110' was indexed by an *ab initio* method, using Dicvol04 program,³¹ and refined by the Pawley method ($R_p = 5.24\%$, $R_{wp} = 8.05\%$, see ESI†), which suggested a triclinic unit cell ($P1$). Appearance of a peak at $2\theta = 4.56^\circ$ ($hkl = 010$), which is systemically absent in the original compound having the $P2_1/c$ space group, also supports the triclinic cell that the screw axis along the b axis does not exist. According to the refined unit cell, the total unit cell volume ($2438.59 \text{ \AA}^3$) of SNU-110' is reduced by *ca.* 8.8% compared with that ($2673.0 \text{ \AA}^3$) of SNU-110, suggesting that the desolvated sample has a shrunken structure. The pore volume of SNU-110' is $0.16 \text{ cm}^3 \text{ g}^{-1}$ as calculated by subtracting the volume of the skeleton ($1909.74 \text{ \AA}^3$; calculated by PLATON³⁰) from its unit cell volume. It is much smaller than that ($0.248 \text{ cm}^3 \text{ g}^{-1}$) of SNU-110. Rietveld refinement was also tried, but the reasonable solution or refined structure could not be obtained from the PXRD data due to low resolution of the diffraction data as well as the low symmetry of the unit cell. When SNU-110' was immersed in DMF for 10 min, the original structure of SNU-110 was restored as evidenced by PXRD patterns (Fig. 2d).

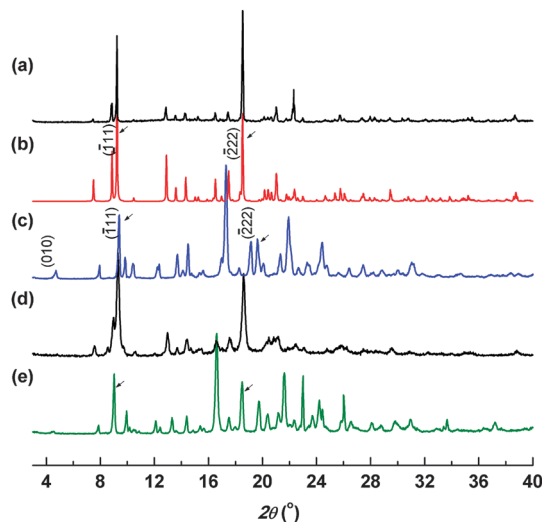


Fig. 2 Powder X-ray diffraction patterns of SNU-110. (a) As synthesized, (b) simulated from X-ray crystal diffraction data, (c) activated sample, SNU-110'; Bragg positions are marked based on cyclically permuted cell parameters for comparison ($abc \rightarrow cab$), (d) resolvated sample obtained by immersion of SNU-110' in DMF for 10 min, and (e) SNU-110' under CO_2 stream at 248 K.

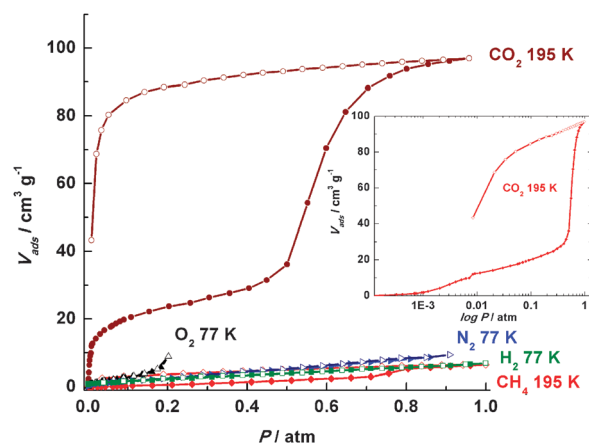


Fig. 3 Gas adsorption isotherms of SNU-110'. Inset diagram represents CO_2 adsorption at 195 K versus $\log P$. Filled shapes: adsorption, open shapes: desorption.

The gas adsorption isotherms of SNU-110' were measured for N_2 , H_2 , O_2 , CH_4 , and CO_2 gases (Fig. 3 and Table 1). As seen in Fig. 3, SNU-110' hardly adsorbs N_2 , O_2 , and H_2 gases at 77 K as well as CH_4 gas at 195 K, but it adsorbs a significant amount of CO_2 at 195 K. Considering the kinetic diameters of CH_4 , O_2 , N_2 , and H_2 , which are 3.8, 3.46, 3.64, and 2.89 $\text{\AA}$, respectively, the window size of SNU-110' must be smaller than 2.89 $\text{\AA}$. However, the fact that CO_2 with a kinetic diameter of 3.3 $\text{\AA}$ is adsorbed in SNU-110' suggests that CO_2 interacts with the flexible MOF and opens up the gate due to its large polarizability and quadrupole moment.¹⁰ The facilitated diffusion of CO_2 at 195 K versus H_2 at 77 K must be also a factor in this phenomenon. The adsorption selectivities of SNU-110' at 195 K and 1 bar for $\text{CO}_2\text{-N}_2$ and $\text{CO}_2\text{-H}_2$ are 35 : 1 (v/v) and 61 : 1 (v/v), respectively, and that for $\text{CO}_2\text{-CH}_4$ is 15 : 1 (v/v).

The CO_2 adsorption isotherm at 195 K shows a two-step adsorption curve with a big desorption-hysteresis. The first step shows a type-I isotherm and the adsorption saturation occurs at 0.40 atm where the uptake amount reaches 1.3 mmol g^{-1} . The second adsorption step starts at 0.48 atm and the uptake amount reaches 4.3 mmol g^{-1} , *i.e.* 3 times greater than that of the first step. The step-wise adsorption of CO_2 at 195 K indicates that the framework structure containing the flexible

Table 1 Gas adsorption data of SNU-110'

Compound	Gas	T/K	P/atm	Adsorption capacity ($\text{cm}^3 \text{ g}^{-1}$)	Ref.
SNU-110'	CO ₂	195	1.0	97.0	This work
		231	1.0	37.0	
		273	1.0	23.6	
		298	1.0	12.9	
	CH ₄	195	1.0	6.49	
		298	1.0	0.91	
	N ₂	77	0.9	9.39	
		195	1.0	2.79	
		298	1.0	0.22	
	H ₂	77	1.0	6.88	
		195	1.0	1.60	
	SNU-31'	O ₂	77	0.2	
CO ₂		298	1.0	13.3	
N ₂		298	1.0	0.56	
PCN-123	CO ₂	295	1.0	10.5–26.4	32
	N ₂	77	0.9	Negligible	

organic linker is altered depending on the CO₂ pressure.^{15–17} The contracted phase of SNU-110' transforms to the open phase when CO₂ pressure exceeds 0.48 atm at 195 K, and then completely opens at 1 atm to get saturated with CO₂. The desorption curve shows a hysteresis with type I isotherm. As the pressure of CO₂ is reduced from 1 atm, the framework maintains the open phase till 3×10^{-2} atm, and then suddenly returns to the contracted phase again. This hysteresis can be reproduced for several cycles in the repeated experiments. The calculated surface areas of SNU-110', as estimated from the first step adsorption curve by applying the Dubinin Radushkevich (DR), Brunauer–Emmett–Teller (BET), and Langmuir methods, are 409 m² g⁻¹, 101 m² g⁻¹, and 111 m² g⁻¹, respectively. When calculated by using the desorption curve, they are 658 m² g⁻¹, 411 m² g⁻¹, and 486 m² g⁻¹, respectively. The pore volume (0.154 cm³ g⁻¹) estimated from the first step adsorption curve by using the DR equation is similar to the value (0.16 cm³ g⁻¹) calculated by the unit cell volume of SNU-110' minus the skeletal volume, while that (0.247 cm³ g⁻¹) obtained from the desorption curve is similar to the free volume (0.248 cm³ g⁻¹) of SNU-110 estimated by using PLATON.³⁰

When temperature was elevated to 231, 273, and 298 K, the P/P_0 value for the phase transition of the MOF decreased to 0.021, 0.0044, 0.0036, respectively (see ESI†). This trend can be explained by the increase of thermal energies for both the framework and the CO₂ molecules as the temperature increases.¹⁶

The PXRD pattern of SNU-110' measured under CO₂ pressure (*ca.* 1 atm) at 248 K indicates that many peaks are shifted to the lower angle regions compared with those of SNU-110', suggesting the expansion of the framework on CO₂ adsorption as well (Fig. 2e). The average isosteric heat (Q_{st}) of the CO₂ adsorption in SNU-110' is 26.2 kJ mol⁻¹, as calculated from the adsorption data at 195, 231, 273, and 298 K by using the Clausius–Clapeyron equation (see ESI†). It is comparable to those (25–35 kJ mol⁻¹) of common MOFs.²

Interestingly, SNU-110' in this work hardly adsorbs CH₄ at 195 K. In general, at 195 K, MOFs show higher uptake capacity for CO₂ than for CH₄ since CO₂ ($T_c = 304.19$ K) is subcritical and thus more condensable than CH₄ ($T_c = 190.09$ K) that is supercritical.^{24–26} Despite this, the flexible MOFs selectively adsorbing CO₂ over N₂ and H₂ often cannot efficiently exclude CH₄ that has high polarizability (2.45 Å³). For example, SNU-M10 adsorbs 123.5 cm³ g⁻¹ of CO₂ and 27.5 cm³ g⁻¹ of CH₄ at 195 K, and SNU-21S adsorbs 257 cm³ g⁻¹ of CO₂ and 124 cm³ g⁻¹ of CH₄ at 195 K.^{10,20} Therefore, it is obvious that the flexibility of the present MOF is so well tuned that only CO₂ can open the gate to be adsorbed in the pores.

In conclusion, we have synthesized a porous metal–organic framework, SNU-110, by using an organic linker having flexible joints. The sample desolvated by using the supercritical CO₂ fluid, SNU-110', has shrunken structure as evidenced by PXRD data. It exhibits a two-step CO₂ adsorption isotherm at 195 K, which is attributed to the structural transformations depending on the amount of CO₂ adsorption. It shows high adsorption selectivity for CO₂ over H₂, N₂, and CH₄ gases at 195 K.

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