

Stepwise and hysteretic sorption of N₂, O₂, CO₂, and H₂ gases in a porous metal–organic framework [Zn₂(BPnDC)₂(bpy)][†]

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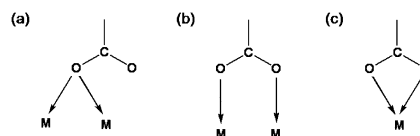
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A doubly interpenetrated 3D porous metal–organic framework (SNU-9) exhibits high gas uptake capacities for N₂, O₂, CO₂, and H₂ gases, with uncommon stepwise adsorption and hysteretic desorption behaviors, while not adsorbing CH₄ gas.

Porous metal–organic frameworks (MOFs) have attracted great attention because of their potential applications in selective adsorption and separation of organic molecules,¹ gas separation² and storage,³ ion exchange,⁴ and fabrication of metal nanoparticles.⁵ Some MOFs exhibit unusual stepwise gas adsorption and hysteretic desorption behavior due to the changes in the framework structures during the gas adsorption,⁶ the multilayer adsorption on energetically homogeneous surface, multiple adsorbent–adsorbate interactions that differ in energy, or sorbate–sorbate interactions in the large pores.⁷ The hysteretic gas desorption behavior helps to store the gas in the material even after the gas pressure is decreased. The materials that change their structures in response to external stimuli such as gas pressure can be applied in switching, sensing, and information storage.⁸

Here we report a porous MOF, {[Zn₂(BPnDC)₂(bpy)]·2DEF·2MeOH}_n (**1**) (BPnDC = benzophenone 4,4'-dicarboxylic acid, bpy = 4,4'-bipyridine, DEF = *N,N*-diethylformamide). The X-ray structure of **1** reveals a doubly interpenetrated 3D network generating curved 3D channels. The gas adsorption isotherms of desolvated solid [Zn₂(BPnDC)₂(bpy)]_n (SNU-9) show three-step adsorption for N₂ and O₂ gases, and two-step adsorption for CO₂ and H₂ gases with large hysteresis on desorption, while it does not uptake CH₄ gas. Although two-step gas adsorption isotherms have been previously reported,^{6–8} the isotherms with more than three well-resolved steps are extremely rare.^{6c,7a} SNU-9 has Langmuir surface area of 1030 m² g^{−1}, pore volume of 0.366 cm³ g^{−1}, and high gas uptake capacities for O₂, CO₂, and H₂ gases.

Colorless crystals of **1** were prepared by heating the DEF/MeOH solution of Zn(NO₃)₂·6H₂O, H₂BPnDC, and 4,4'-bpy at 80 °C for 24 h. In the X-ray crystal structure of **1**, there are two independent BPnDC^{2−} units, BPnDC1 and BPnDC2, both of which act as a tetradentate ligand. In BPnDC1, each carboxylate group adopts a bidentate mode



Scheme 1 Coordination modes of carboxylate groups in **1**.

to coordinate two Zn^{II} ions (*a* and *b* modes, Scheme 1). In BPnDC2, one carboxylate group coordinates two Zn^{II} ions in *b* mode, while the other carboxylate group coordinates one Zn^{II} ion in *c* mode. The dihedral angles between the two phenyl rings of BPnDC1 and BPnDC2 are 57.90(14) and 52.21(19)°, respectively.

In general, 2D layers are assembled from paddle wheel Zn₂ cluster units and dicarboxylate linkers, and 3D MOFs are constructed by linking the 2D layers with diamine pillars.⁹ In **1**, however, every binuclear Zn₂ unit is bridged by BPnDC1 and 4,4'-bpy to form a distorted square grid 2D network that runs parallel to the *ab* plane (Fig. 1). Interestingly, BPnDC2 acts as a pillar linking the layers along the *c* axis, which gives rise to the 3D framework that can be described as a primitive cubic (α -Po) net. Actually, the cubic net is distorted to the parallelepiped because of the bent dicarboxylate ligand, BPnDC^{2−}. Interestingly, 4,4'-bpy is significantly twisted with the dihedral angle of 24.47(20)° between the two pyridyl rings. In addition, two 3D frameworks are mutually interpenetrated to generate 3D curved channels.

The solvent accessible volume estimated by PLATON¹⁰ is 37.5%. The guest molecules inside the pores could not be refined owing to the severe thermal disorder, and they were characterized by the IR, elemental analysis, and TGA data. The final structural model was refined without the guest molecules by using the *SQUEEZE* option of PLATON.¹⁰ The thermogravimetric analysis (TGA) performed under N₂ atmosphere indicates 13.2% weight loss at 25–90 °C, followed by additional weight loss of 12.4% at 90–220 °C, each of which corresponds to the loss of one DEF and one MeOH guests per formula unit (calcd 12.2%). Temperature dependent powder

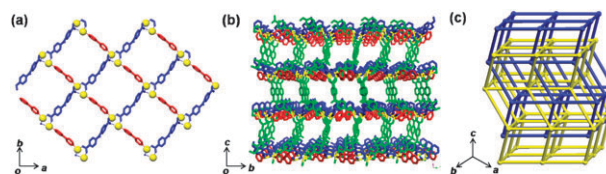


Fig. 1 The X-ray crystal structures of **1**. (a) A distorted 2D square grid formed of [Zn₂(BPnDC)(bpy)]²⁺, running on the *ab* plane. (b) A 3D network. Color scheme: Zn, yellow; 4,4'-bpy, red; BPnDC1, blue; BPnDC2, green. (c) Schematic description of the doubly interpenetrated (α -Po) nets.

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[†] Electronic supplementary information (ESI) available: Detailed experimental procedures, ORTEP drawings, X-ray structures, TGA/DSC traces, PXRD patterns, tables of X-ray data for **1** and **1m**, tables of gas adsorption data for SNU-9. CCDC 726043, 726044. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b913067e

X-ray diffraction (PXRD) patterns as well as TGA data suggest that the framework structure of **1** changes upon guest removal at 250 °C but the framework is thermally stable up to 300 °C (see ESI†).

Previously, we reported porous MOF having a Kagome-type structure, $\{[\text{Cu}_2(\text{BPnDC})_2(\text{bpy})]\cdot 8\text{DMF}\cdot 6\text{H}_2\text{O}\}_n$, which was synthesized from the same organic building blocks as in **1**, but with a Cu^{II} metal ion.¹¹ Despite the same organic building block, the framework structure of the present compound (**1**) is completely different from that previously reported, indicating that the change of metal ion greatly affects the framework structure.

When a single crystal of **1** was immersed for 24 h in MeOH where **1** was completely insoluble, the guest exchanged single crystal, $\{[\text{Zn}_2(\text{BPnDC})_2(\text{bpy})]\cdot 6\text{MeOH}\}_n$ (**1m**), resulted. The X-ray crystal parameters, as well as framework structure of **1m**, are very similar to those of **1** (see ESI†). When **1m** was heated at 60 °C under vacuum for 1.5 h, the desolvated solid (SNU-9) resulted with the loss of transparency and single crystallinity. The comparison of synchrotron PXRD patterns of **1**, **1m**, and SNU-9 indicates that framework structure changes significantly upon removal of guest solvent molecules although it is not altered upon guest exchange (see ESI†). However, the PXRD pattern of SNU-9 was restored to that of **1m** when it was exposed to MeOH vapor. These suggest that the framework is flexible and changes its structure reversibly on guest removal and reintroduction.

To confirm the porosity of SNU-9, the gas sorption isotherms were measured for N_2 , O_2 , H_2 , CO_2 , and CH_4 gases. Interestingly, the N_2 gas sorption isotherm at 77 K measured up to 1 atm exhibits three distinct steps (Fig. 2a). The first step at $P = 0.00096\text{--}0.0010$ atm provides the surface area of $259\text{ m}^2\text{ g}^{-1}$ as estimated by the Langmuir and Brunauer–Emmett–Teller (BET) methods, and the pore volume of $0.106\text{ cm}^3\text{ g}^{-1}$ as estimated by the Dubinin–Radushkevich (DR) equation. In the second step at $P = 0.001\text{--}0.019$ atm, the isotherm shows a sharp increase to reach the plateau, displaying a type I isotherm. The second step provides Langmuir and BET surface areas of 684 and $669\text{ m}^2\text{ g}^{-1}$, respectively, and pore volume of $0.261\text{ cm}^3\text{ g}^{-1}$. At $P > 0.019$ atm, the isotherm exhibits another sharp increase and then finally attains a saturation with the adsorbed N_2 amount of $262\text{ cm}^3\text{ g}^{-1}$ (32.7 wt%, 362 g L^{-1}) at 0.91 atm. The Langmuir and BET surface area estimated by the third step ($P = 0.029\text{--}0.31$ atm) are 1034 and $824\text{ m}^2\text{ g}^{-1}$, respectively, and the pore volume is $0.366\text{ cm}^3\text{ g}^{-1}$, which is in good agreement with the void volume of **1** estimated from the crystal structure ($0.334\text{ cm}^3\text{ g}^{-1}$). The N_2 adsorption isotherm at 87 K also

exhibits distinct three step curves that are shifted to higher pressures compared to that at 77 K, with each step adsorbing similar quantity of N_2 . The N_2 isotherms both at 77 K and 87 K reveal a large hysteresis loop between the adsorption and desorption curves, and the hysteresis is more pronounced at 87 K, particularly at very low pressures. The adsorbed N_2 gas is only partially desorbed (the desorbed amount is $70\text{ cm}^3\text{ g}^{-1}$) even when pressure is reduced to $P = 10^{-3}$ atm, revealing the trapping effect of the gas in the pores.¹²

The O_2 sorption isotherms of SNU-9 at 77 K and 87 K look similar to N_2 sorption isotherms (Fig. 2b). They also exhibit distinct three steps with marked hysteresis on desorption. In an initial step at 77 K and 0.00045 atm, SNU-9 adsorbs 17.2 wt% O_2 (5.37 mmol g^{-1} , $120\text{ cm}^3\text{ g}^{-1}$ at STP), and in the second step at 77 K and 0.014 atm, it adsorbs 24.0 wt% O_2 (7.51 mmol g^{-1} , $168\text{ cm}^3\text{ g}^{-1}$ at STP). After passing a point at 0.014 atm, the O_2 adsorption abruptly increases and the total amount of adsorbed O_2 reaches 51.4 wt% (16.1 mmol g^{-1} , $360\text{ cm}^3\text{ g}^{-1}$ at STP, 569 g L^{-1}) at 0.20 atm. This capacity is comparable to that (48 wt%, 592 g L^{-1}) of FMOF-1 measured under the same condition.¹³ At 87 K, the distinct three steps are shifted to higher pressures and SNU-9 adsorbs 39.2 wt% (12.3 mmol g^{-1} , $275\text{ cm}^3\text{ g}^{-1}$ at STP) at 0.61 atm. The O_2 isotherms at both temperatures show a hysteretic loop, indicating the presence of trapping effect for the O_2 gas in the pores even at very low pressures.

Contrary to the three-step adsorption isotherms for N_2 and O_2 gases, the CO_2 adsorption isotherm at 195 K measured up to 1 atm exhibits a two-step curve with two abrupt jumps at 0.026 and 0.16 atm as well as a hysteretic desorption curve (Fig. 2c). In the initial step, SNU-9 adsorbs 11.8 wt% CO_2 (2.69 mmol g^{-1} , $60.1\text{ cm}^3\text{ g}^{-1}$ at STP), and in the second step it stores up to 43.0 wt% CO_2 (9.78 mmol g^{-1} , $219\text{ cm}^3\text{ g}^{-1}$ at STP) at 1 atm. Interestingly, the desorption isotherm does not retrace the adsorption isotherm and shows an abrupt drop at 0.039 atm. This hysteresis profile was reproducible for several cycles. At 273 K up to 1 atm, SNU-9 adsorbs almost no CO_2 (5.49 wt%, $28\text{ cm}^3\text{ g}^{-1}$ at STP). At 298 K and high pressures (Fig. 2d), SNU-9 again exhibits double-step CO_2 adsorption with the large hysteresis on desorption. The second adsorption jump begins at ca. 8 bar and reaches an excess storage capacity of 29.9 wt% at 30 bar and the desorption curve shows sudden decrease at 3.5 bar. The CO_2 storage capacities of SNU-9 is lower than 114 wt% in SNU-6¹¹ and 149 wt% in MOF-5^{7b} at 195 K and 1 atm, but comparable to that (ca. 39.6 wt% at 303 K and 20 bar) of MIL-53.¹⁴

SNU-9 adsorbs almost no CH_4 (2.13 wt%, $30\text{ cm}^3\text{ g}^{-1}$ at STP) at 195 K under pressure up to 1 atm, contrary to CO_2 .

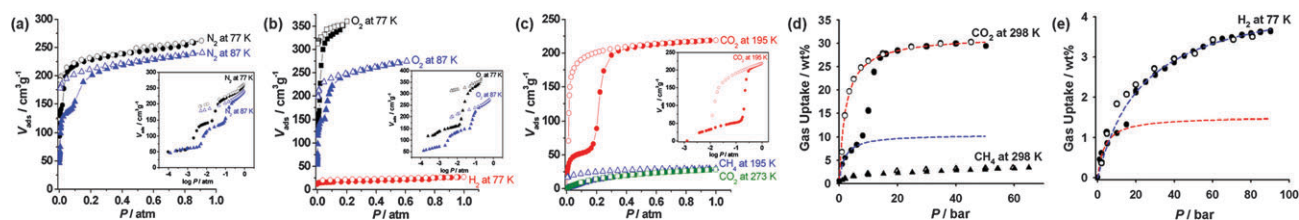


Fig. 2 Gas sorption isotherms of SNU-9. (a) N_2 at 77 K (black) and 87 K (blue). (b) O_2 at 77 K (black) and 87 K (blue), and H_2 at 77 K (red). (c) CO_2 and CH_4 at 195 K and 273 K. (d) CO_2 (black circle) and CH_4 (black triangle) at 298 K. (e) H_2 at 77 K. The Langmuir fits for two-step adsorption are indicated by red and blue dashed lines. Filled shapes: adsorption. Open shapes: desorption.

However, at 298 K and 65 bar, it uptakes 3.40 wt% CH₄ (37.6 g L⁻¹ and 52.6 v(STP)/v), which is much lower than the CO₂ storage capacity. The big difference between CO₂ and CH₄ adsorption capacities in SNU-9 must be attributed to the quadrupole moment (1.43×10^{-39} C m²) of CO₂,¹⁵ which can be applied in the separation processes of these gases at 195 K.

The H₂ gas adsorption isotherm of SNU-9 at 77 K measured up to 1 atm (Fig. 2b) shows very low H₂ uptake capacity (0.24 wt%, 27 cm³ g⁻¹ at STP). However, at 77 K and high pressures, SNU-9 adsorbs up to 3.63 wt% H₂ (Fig. 2e). The H₂ adsorption isotherm shows a double-step curve together with the hysteretic desorption. In the initial step, SNU-9 adsorbs 1.32 wt% of H₂ at 15 bar. In the second step, H₂ adsorption increases sharply at ca. 20 bar and then reaches a plateau around 90 bar, providing an excess storage capacity of 3.63 wt% (volumetric capacity = 40.2 g L⁻¹) at 90 bar with the total storage capacity of 6.23 wt% as estimated by using the densities of the framework skeleton and the crystal. This capacity is comparable to those (3.1 wt% at 77 K and 30 bar) of Co(BDP).^{7a}

To explain the stepwise and hysteretic gas sorption isotherms of the present material, gas-pressure dependent structural characterizations at 77 K for N₂ and O₂ gases as well as at 195 K for CO₂ should be done. However, due to the lack of the facility to control the gas pressures at the low temperature during the PXRD measurement, we only measured the synchrotron PXRD patterns for the guest removed and reintroduced samples. As shown in Fig. S7, the PXRD patterns change on guest removal/reintroduction, suggesting that the framework SNU-9 is highly flexible. Therefore, the present uncommon stepwise gas sorption isotherms must be attributed to the guest-induced structural phase transitions on gas adsorption and desorption.^{6,8,15} The fact that pore volume of SNU-9 estimated from the N₂ gas isotherm at 77 K is similar to that of **1** indicates that fully open structure is formed by the N₂ gas adsorption at 1 atm. The gas sorption isotherms of SNU-9 for H₂ and CO₂ gases at high pressures show two distinct steps that are satisfactorily fit to Langmuir isotherms (Fig. 2 and ESI†). These are very similar to recent reports that were explained by the structural transitions between two distinct states of the framework structures during the gas adsorption.^{13,16,17} The present results showing three-step transitions for N₂ and O₂ adsorptions versus two-step transitions for CO₂ and H₂ adsorptions, suggest that the structural phase transitions of a MOF is extremely sensitive to the type of adsorbates.

In conclusion, we have prepared a doubly interpenetrated 3D porous metal-organic framework with a primitive cubic (α -Po) topology. The desolvated solid (SNU-9) exhibits high surface area and high gas uptake capacities for N₂, O₂, CO₂, and H₂ gases, while it does not adsorb CH₄ gas. In particular, the material shows uncommon multistep gas adsorptions with hysteretic desorption, which are sensitive to adsorbate. The present material can be applied in the development of sensors as well as H₂ storage, CO₂ capture, and CO₂/CH₄ gas separation material.

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