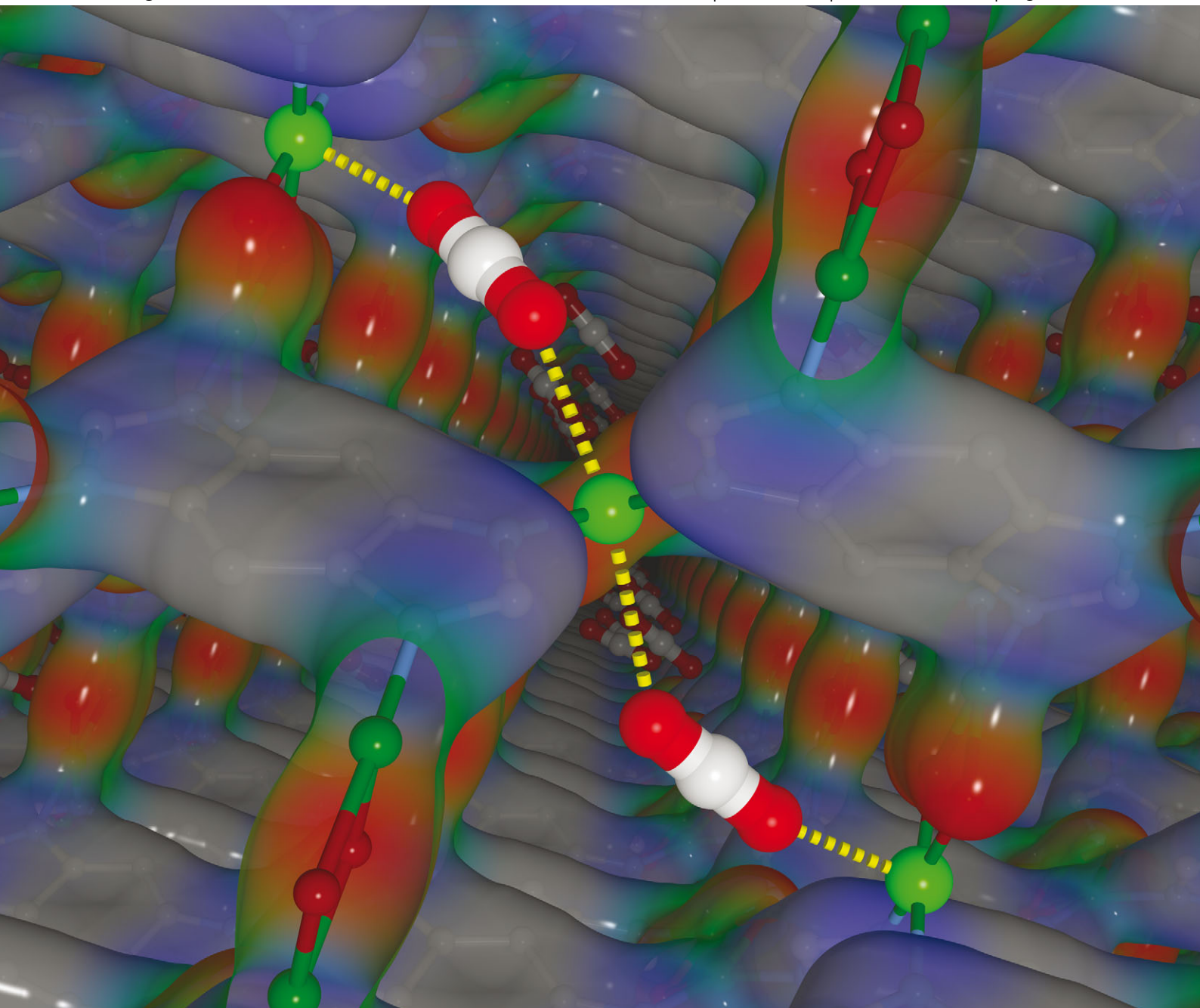


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A flexible porous Cu(II) bis-imidazolate framework with ultrahigh concentration of active sites for efficient and recyclable CO₂ capture†

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By virtue of planar Cu₂(μ-OH)₂²⁺ cluster units, a flexible porous metal azolate framework not only adsorbs large amounts of CO₂ (19.6 wt% or 266 g L⁻¹ at 298 K and 1 atm) with a high zero-coverage adsorption enthalpy (−47 kJ mol⁻¹), but also desorbs quickly at very low temperatures.

The CO₂ capture and separation are of great significance in industrial and environmental aspects.¹ Traditionally, CO₂ is chemically absorbed by aqueous alkanolamine, which is very powerful but costs much energy during the regeneration processes and causes corrosion problems in equipment. Physical adsorption by porous materials is expected to be an alternative strategy, although their CO₂ affinities are much weaker than the chemical absorbents.² Nevertheless, some porous materials have achieved very high CO₂ uptakes under ambient conditions. It should be noted that the volumetric uptakes should be more important than the gravimetric uptakes for evaluation of the CO₂ capture performances of adsorbents, since the fixed-bed equipment for CO₂ capture and separation need not be moved during operation.²

Porous coordination polymers (PCPs) are extensively studied for CO₂ capture due to their advantages such as high porosity, modifiable framework and pore surface, and flexible structures.³ Various types of active sites⁴ can be introduced onto the pore surface to improve the CO₂ affinities. For example, PCPs functionalized by alkylamine active sites can achieve strong CO₂ binding comparable to that of aqueous alkanolamine.⁵ Many types of open metal sites (OMSs)⁶ can also greatly improve the CO₂ capture ability, although very strong active sites are concerned for causing desorption difficulty and high energy cost. On the other hand, the CO₂ adsorption capacity under ambient conditions is usually limited by the relatively

low concentration of these strongly active sites (OMS < 5 mol L⁻¹; Lewis basic site < 10 mol L⁻¹).⁷

To fabricate active sites with suitable CO₂ affinity and higher concentration, a Cu(II) ion should be a good candidate, because it shows moderate activity (much weaker than alkylamines and common metal ions, and comparable to arylamines and azolates) and generally (square-planar coordination geometry) offers two potential coordination sites for guest molecules. Here, we report a novel flexible PCP with ultrahigh concentration of open Cu(II) sites, which shows not only high adsorption affinity and uptake, but also easy desorption for CO₂ capture.

Room-temperature diffusion reaction between benzodiiimidazole (H₂bdim) and [Cu(NH₃)₂]OH with benzene as a buffering layer gave dark-green crystals of a porous metal azolate framework [Cu₂(μ-OH)₂(bdim)]·5.4H₂O (**1**, MAF-35) in low yield (ca. 20%) after 4 months. A few dark-green single crystals of [Cu₂(μ-OCH₃)₂(bdim)]·C₆H₆ (**2**) were also isolated as byproducts. Apparently, Cu(I) was oxidized slowly during the diffusion reaction to give these Cu(II) complexes. When [Cu(NH₃)₄](OH)₂ was used to conduct the diffusion experiment, we always got dark-blue powders with unknown structure (Fig. S1, ESI†). Fortunately, the bulk microcrystalline powder of **1** can be synthesized in high yield (85%) by heterogeneous reaction of H₂bdim and Cu(OH)₂ at room temperature for 5 days.

1 and **2** have very similar network structures (Fig. S2, ESI†). The former crystallizes in the monoclinic space group *P*2₁/*m* while the latter has a higher symmetry (*C*₂/*m*) and slightly expanded unit-cell volume (5%). Their host frameworks can be simplified as 3-dimensional (3D) uninodal 4-connected **lt** networks consisting of four-coordinated bdim^{2−} ligands and planar, four-coordinated [Cu₂(μ-OR)₂]²⁺ (R = H, CH₃) dinuclear clusters (Fig. 1a). To the best of our knowledge, this type of cluster has been only found in one PCP.⁸ The Cu(II) ions in **1** form weak coordination with the guest H₂O molecules [Cu⋯O 2.48(2)–2.97(3) Å] (Fig. 1b). If all water and benzene molecules were removed, **1** and **2** could possess solvent accessible volumes of 48.7% and 33.8%, respectively. Compared with **1**, the void volume of **2** is obviously smaller because of its larger

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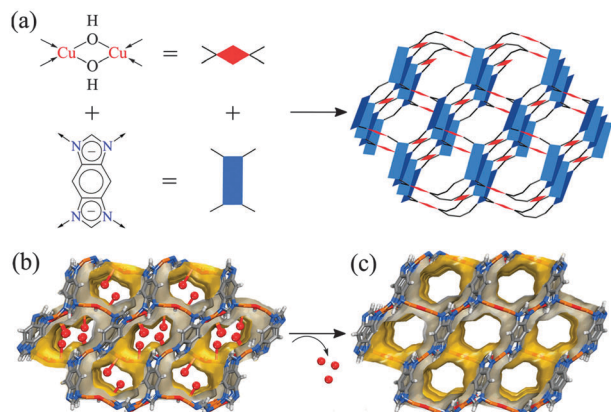


Fig. 1 (a) Linking the planar $[\text{Cu}_2(\mu\text{-OH})_2]^{2+}$ cluster and the bdim^{2-} ligand to construct the 1vt coordination network of **1**. (b) The host and pore surface structures of **1** (weakly coordinated guest H_2O molecules are shown as red spheres). (c) The host and pore surface structures of **1'**.

OCH_3 group. If OCH_3 in **2** could be replaced by OH without changing any other part of the framework, the void volume of **2** would increase to 51.0%.

It is worth noting that **1** has a very high concentration of $\text{Cu}(\text{II})$ ions (8.6 mol L^{-1} or 6.3 mol kg^{-1}). Moreover, since the square planar $\text{Cu}(\text{II})$ ions expose two potential coordination sites on the pore surface, the concentration of OMSs in **1** (17.2 mol L^{-1} or 12.6 mol kg^{-1}) is significantly higher than those of literature-reported PCPs (Table S2, ESI†).⁷ In most PCPs, $\text{Cu}(\text{II})$ ions can only expose one of the two potential coordination sides. For instance, porous $\text{Cu}(\text{II})$ carboxylate frameworks are generally composed of paddlewheel-like $\text{Cu}_2(\text{RCOO})_4$ clusters, in which two square-planar $\text{Cu}(\text{II})$ ions form face-to-face stacking, leading to the blocking of a potential coordination site per metal ion. Pyridyl and azolate ligands tend to form mononuclear Cu building units,⁹ but counter anions or steric hindrance from the ligands usually hinder the exposure of OMSs. Therefore, the planar $[\text{Cu}_2(\mu\text{-OH})_2]^{2+}$ cluster is the key to increase the concentration of the open $\text{Cu}(\text{II})$ sites.

Thermogravimetric analysis of **1** showed a weight loss of 23.5% below 70°C corresponding to 5.4 water molecules per formula unit (calcd 23.4%), and then a plateau from 70 to 180°C until decomposition (Fig. S3, ESI†). The powder X-ray diffraction (PXRD) pattern of the guest-free sample was similar to that of **2** rather than **1**. When **1** was soaked in H_2O or exposed in saturated H_2O vapour, the resulting sample also showed a PXRD pattern similar to that of **2**, but it easily lost partial guest molecules in air to transform back to **1** (Fig. S4, ESI†). These observations demonstrated that the framework structure of $[\text{Cu}_2(\mu\text{-OH})_2(\text{bdim})]$ expanded to a structure similar to that of **2** (hereafter denoted as **1'**) when it was guest-free or saturated by guest molecules, but adopted the narrow pore phase **1** with partial guest loading. A similar phenomenon has been observed in a few PCPs, such as MIL-53.¹⁰ Indeed, the unit-cell parameters of **1'** derived from its PXRD pattern are very similar to those of **2** (Fig. S5, ESI†).

The N_2 sorption isotherm of **1'** measured at 77 K exhibits type-I character with a saturated adsorption capacity of about $240 \text{ cm}^3 (\text{STP}) \text{ g}^{-1}$, corresponding to a pore volume of

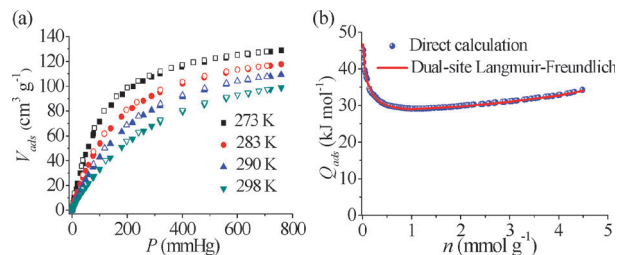


Fig. 2 (a) CO_2 adsorption (solid) and desorption (open) isotherms measured at different temperatures and (b) coverage-dependent CO_2 adsorption enthalpy profiles (calculated by two methods) of **1'**.

$0.375 \text{ cm}^3 \text{ g}^{-1}$ (Fig. S6, ESI†). For comparison, the empirical pore volumes calculated for the crystal structures of **1** and **1'** are $0.359 \text{ cm}^3 \text{ g}^{-1}$ and $0.373 \text{ cm}^3 \text{ g}^{-1}$, respectively. The Brunauer–Emmett–Teller and Langmuir surface areas were calculated to be 974 and $1043 \text{ m}^2 \text{ g}^{-1}$, respectively. The H_2 sorption isotherm (Fig. S7, ESI†) of **1'** measured at 77 K demonstrated an uptake of 1.97 wt\% at 1 atm , which is higher than those of most PCPs with similar/lower surface areas,¹¹ indicating relatively strong H_2 binding affinity of **1'**.

To examine the CO_2 capture performance of **1'**, CO_2 sorption isotherms were measured at 273 , 283 , 290 and 298 K . The CO_2 uptakes at 1 atm reach $129 \text{ cm}^3 \text{ g}^{-1}$ (5.76 mmol g^{-1} , 25.3 wt\% , 0.91 CO_2 per Cu) at 273 K and $100 \text{ cm}^3 \text{ g}^{-1}$ (4.46 mmol g^{-1} , 19.6 wt\% , 0.71 CO_2 per Cu) at 298 K (Fig. 2a). While the gravimetric CO_2 uptakes of **1'** are relatively high among known adsorbents, its volumetric uptakes (343 g L^{-1} and 266 g L^{-1} at 273 K and 298 K , respectively, at 1 atm) are more remarkable (Table S2, ESI†).

For comparison, N_2 sorption isotherms were also measured at 273 and 298 K , which showed uptakes of 16.0 and $9.9 \text{ cm}^3 \text{ g}^{-1}$ at 1 atm , respectively (Fig. S8a, ESI†). The Henry's law CO_2 – N_2 selectivities¹² were calculated (Fig. S8b and Table S3, ESI†) to be 77 and 43 at 273 and 298 K , respectively. Using the ideal absorbed solution theory (IAST),¹³ the CO_2 – N_2 selectivities for the $15/85 \text{ CO}_2$ – N_2 mixture at 1 atm were calculated to be 72 and 37 at 273 K and 298 K , respectively. The highly selective adsorption of CO_2 over N_2 suggests that **1'** may be useful for CO_2 capture.¹⁴

The coverage-dependent CO_2 adsorption enthalpy (Q_{st}) of **1'** was calculated by the Clausius–Clapeyron equation using isotherms measured at 273 , 283 , 290 and 298 K (Fig. 2a), which could be well described by the dual-site Langmuir–Freundlich model¹⁵ (Fig. 2b; Table S4 and Fig. S9, ESI†). The Q_{st} value was $46.7 \pm 1.6 \text{ kJ mol}^{-1}$ at zero-coverage, and then decreased rapidly to $29.0 \pm 0.4 \text{ kJ mol}^{-1}$ at 1 mmol g^{-1} (0.16 CO_2 per Cu), after that it increased slowly to $34.1 \pm 0.5 \text{ kJ mol}^{-1}$ at 4.5 mmol g^{-1} (0.71 CO_2 per Cu). *In situ* PXRD measurement at different CO_2 pressures (CO_2 – N_2 mixed gas flow, 298 K) demonstrated that the transformation from **1'** to **1** started at 4 kPa and completed above 9 kPa (Fig. S10 and S11, ESI†). According to the sorption isotherm at 298 K , the CO_2 uptake at 9 kPa is about 1 mmol g^{-1} , being coincident with the lowest Q_{st} value. These results demonstrated that the transformation from **1'** to **1** could be induced by low-pressure CO_2 , which consumed partial host–guest interaction energy to give relatively low apparent Q_{st} . Above 9 kPa or 1 mmol g^{-1} , the increase of Q_{st} can be ascribed to the increasing contribution of guest–guest interaction at high CO_2 loading.

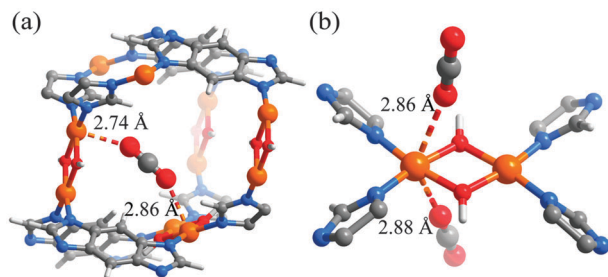


Fig. 3 GCMC derived (a) primary adsorption site at zero coverage and (b) host-guest interactions at the high coverage for the CO₂ adsorption in **1**.

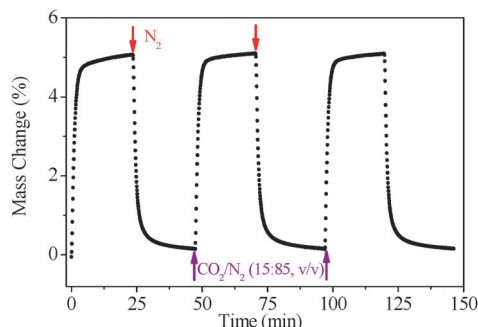


Fig. 4 Repeated adsorption-desorption kinetics for **1'** under a mixed CO₂-N₂ (15 : 85, v/v) flow and a pure N₂ flow at a constant temperature of 30 °C.

Furthermore, grand canonical Monte Carlo (GCMC) simulation was used to evaluate the host-guest interactions between **1'** and CO₂ at 298 K. At zero coverage, a CO₂ molecule is chelated by two Cu(II) ions (Cu...O 2.74 and 2.86 Å) (Fig. 3a) with a high interaction energy of 48.0 kJ mol⁻¹ being similar to the measured value (46.7 ± 1.6 kJ mol⁻¹). At high coverages, each Cu(II) ion can bind two CO₂ molecules by its two exposed sides (Fig. 3b), and guest-guest interactions can also be observed (Fig. S12, ESI†). At 1 atm, the simulated CO₂ uptake and binding energy reached 95 cm³ g⁻¹ and 37.2 kJ mol⁻¹, respectively, which were close to the measured values.

The CO₂ capture performance of **1'** under more practical conditions was evaluated by thermogravimetric analysis, during which the partial pressure of CO₂ and/or temperature were varied to simulate the common adsorption-desorption conditions. Firstly, **1'** was blown repeatedly using a CO₂-N₂ (15 : 85, v/v) mixture and a pure N₂ flow at 30 °C (Fig. 4). A 5.1 wt% weight change was observed over repeated cycles, which was much higher than those of the reported PCPs (under the same conditions), such as en-CuBTTr (0.75 wt%)^{5a} and SNU-21 (0.72 wt%).¹⁶ Significantly, the adsorption and desorption amounts can reach 90% of the total capacity after only 3 and 5 minutes, respectively, and no apparent change in capacity could be observed over repeated cycles, which demonstrated very fast sorption kinetics and good reversibility. When the temperatures of adsorption and desorption changed to 25 °C and 50 °C, respectively (Fig. S13, ESI†), the mass change could increase to 6.5 wt% over each cycle.^{5b} Meanwhile, the adsorption and desorption kinetics were still very fast (4 and 6 min for 90% adsorption and desorption of the total capacity, respectively). So **1** may be suitable for use as an

adsorbent in a pressure swing adsorption type process for CO₂ capture.^{5a}

In summary, a flexible porous MAF with unique planar dinuclear Cu₂(OH)₂²⁺ clusters has been synthesized, which demonstrated that combination of high concentration of active sites and framework flexibility could be a viable strategy for efficient and low-energy CO₂ capture and separation.

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