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High CO\textsubscript{2}/N\textsubscript{2}/O\textsubscript{2}/CO separation in a chemically robust porous coordination polymer with low binding energy†

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Porous coordination polymers (PCPs), constructed from organic linkers and metal ions, can provide special pore environments for selective CO\textsubscript{2} capture. Although many PCPs have been reported, a rational design for identifying PCPs that adsorb CO\textsubscript{2} molecules with a low binding energy, high separation ability and high chemical stability remains a great challenge. Here, we propose and validate, experimentally and computationally, a new PCP, [La(BTN)DMF]-guest (PCP-1-guest), that has a large aromatic organic surface and a low binding energy for high CO\textsubscript{2} separation from four-gas mixtures (CO\textsubscript{2}–N\textsubscript{2}–O\textsubscript{2}–CO) at ambient temperature. In addition, it shows good water and chemical stability; in particular, it is stable from pH = 2 to 12 at 100 °C, which is unprecedented for carboxylate-based PCPs.

Introduction

CO\textsubscript{2} levels are now 45% higher than in 1990, a reference year for efforts to cut emissions. Flue gases from coal-fired power and steel plants are the main contributors to this increase. Usually, the flue gas contains mostly N\textsubscript{2}, CO\textsubscript{2} and H\textsubscript{2}O vapor as well as excess O\textsubscript{2} at ca. 1 bar. Some flue gases also contain small percentages of pollutants, such as CO, NO\textsubscript{x}, and SO\textsubscript{x}. The development of efficient processes for capturing CO\textsubscript{2} is central to the reduction of the greenhouse gas emissions implicated in global warming.

Highly porous sorbent materials have been considered as plausible solutions for this problem, and this has driven a great deal of effort to design and construct these new adsorbent materials. Porous coordination polymers (PCPs) and metal organic frameworks (MOFs) have high surface areas, periodic but tunable pore sizes and types and functionalizable pore walls are excellent rivals to other porous materials, such as zeolites and activated carbon, for gas storage and separation.

To improve the capability of selective CO\textsubscript{2} capture by PCP materials, immobilizing strong recognition sites into the framework, such as dense open metal sites, alkylamine functionalities, and amine-based organic building blocks, was considered a rational design, and indeed some PCPs show excellent separation behavior. However, the net energy cost of the regeneration process will be increased in frameworks with high binding energies (50–90 kJ mol\textsuperscript{−1}); furthermore, the modified frameworks are very sensitive to moisture which will greatly restrict their application in CO\textsubscript{2} capture, especially in industrial flue gas systems.

Thus, for finding the optimal choice among PCPs, simply increasing the binding energy of CO\textsubscript{2} is not enough; the candidate should meet four prerequisites: first, it should take up enough CO\textsubscript{2} in both static and dynamic environments at ambient temperature; second, the selectivity for CO\textsubscript{2} vs. other gases should be high; third, the degassed framework should maintain its structure in humid or aqueous environments; and finally and most importantly, the binding energy of the framework to CO\textsubscript{2} should permit a completely reversible adsorption and desorption process with a low energy penalty. Many PCPs can meet one or two of these prerequisites, but very few can satisfy all.

A recent computational study found that, as a way to provide suitable physisorption energy (neither too high nor too low) of CO\textsubscript{2} in PCPs, the functionalization of organic linkers would be a good choice. Currently, the organic linkers of most PCPs have backbones such as benzene rings, carbon–carbon triple bonds...
and nitrogen–nitrogen double bonds, only a few of them involve larger aromatic rings such as naphthalene rings.11

Recently, we developed a strategy for using an organic wall to prepare [(La(BTB)H2O)·solvent]12 structures that possess a high surface area, high CH4 separation capability at 273 K, and also show high resistance to water, and alkaline in particular; at pH = 14 and 100 °C. In that work, well-packed organic walls provided a hydrophobic channel environment that is appropriate for the pressure swing adsorption (PSA) process and provided water stability, even under harsh conditions. However, the CO2 adsorption heat was too low (16–20 kJ mol⁻¹) to achieve good performance in CO2 separation using PSA. Herein, in continuing our previous work, a linker (Scheme 1, H3BTN) with larger aromatic rings was synthesized and employed in constructing the candidate PCP. Single crystal X-ray diffraction studies, pure gas adsorption experiments, ideal adsorbed solution theory predictions, packed bed absorber breakthrough simulations, and dynamic adsorption experiments revealed that the [La(BTN)DMF]·solvent (PCP-1·guest) could offer suitable uptake capacity as well as low binding energy to CO2. Importantly, for the first time, good CO2 separation abilities over N2, O2 and CO at 273 K were well characterized, even though the mixture includes four components. In addition, the material also shows good water and chemical stability; in particular, it is stable from pH 2 to 12 at 100 °C, which is unprecedented for carboxylate-based PCPs. Thus, PCP-1 is a good potential candidate for CO2 separation in the context of flue gas streams from coal-fired power and steel plants (CO2–N2, CO2–O2 and CO2–CO), and other cases with four-gas mixtures (CO2–N2–O2–CO) at ambient temperatures.

**Experimental section**

General procedures of the experiment and simulation can be found in the ESL†

**Synthesis of the organic building block**

1,3,5-Tri(6-hydroxycarbonylnaphthalen-2-yl)benzene (H3BTN) was synthesized according to the previous work.12

**Synthesis of [La(BTN)DMF]·solvent (PCP-1·guest)**

La(NO)3·6H2O (18 mg, 0.042 mmol), 1,3,5-tri(6-hydroxycarbonylnaphthalen-2-yl)benzene (H3BTN, 6 mg, 0.01 mmol) and benzoic acid (75 mg, 0.614 mmol) were mixed with 1.25 mL DMF in a glass container, tightly capped with a Teflon vial and heated at 120 °C for 48 h. After cooling to room temperature, brown crystals were obtained. Yield: 62% (based on the ligand).

**Results and discussion**

**Synthesis and structure characterization**

The solvothermal reaction of H3BTN and La(NO)3·6H2O in DMF (N,N'-dimethylformamide) containing benzoic acid leads to polyhedron-shaped brown crystals of [La(BTN)DMF]·solvent (PCP-1·guest). The structure was determined by single-crystal X-ray diffraction analysis, and was confirmed by the powder synchrotron X-ray diffraction pattern, measured at SPring-8 BL02B2 beamline (Fig. 1).† TGA shows that PCP-1 is thermally stable up to 500 °C under an N2 atmosphere; this was further verified using varied temperature PXRD from 50 to 350 °C. After exchanging the guest solvents with methanol, we obtained the completely activated framework, degassed under a high vacuum at 120 °C for 20 hours, as indicated by the IR and TGA results of the evacuated PCP-1 (see the ESIF†).

X-ray crystallography shows that PCP-1 crystallizes in the rare chiral space group of P63 with a = 34.2658(14) Å and c = 21.8681(14) Å. Three carboxylate groups of the BTN ligand have two coordination modes: bridging ([μ₂-η¹·η¹]), and chelating-bridging ([μ₂-η²·η¹]), connecting to six La₃⁺ ions. Each La₃⁺ ion is coordinated by eight oxygen atoms from six carboxylate groups and one coordinated DMF molecule. The adjacent La₃⁺ ions are bridged by three carboxylate groups, leading to edge-shared polyhedrons and an inorganic helical chain with a 21.85 Å screw pitch along the c axis. Each inorganic helical chain was linked to six neighboring chains by BTN ligands to form the 3D framework (Fig. 2). Compared with our previous La-BTB framework, the space between adjacent ligands has enlarged from ~3.8 Å to ~6.2 Å, which should provide a suitable space for CO2 diffusion with low binding energy. Moreover, structural stability can also be expected because of the large coordination numbers of La₃⁺, the inorganic metal oxygen chain and the rigid ligand.

**Scheme 1** Molecular structures of the ligands H3BTB and H2BTN.

**Fig. 1** The results of Le Bail analysis for the PXRD of PCP-1. The wavelength of an incident X-ray is 1.0 Å. Refined parameters and reliability factors are as follows: a = 34.5184(7) Å, c = 22.2682(10) Å, V = 22 978.2(12) Å³. R_p = 0.0424 and R_w = 0.0762.
Gas adsorption and IAST studies

To characterize the permanent porosity of PCP-1, a N₂ adsorption experiment was performed at 77 K. Since only micropores are present in PCP-1, a reversible type-I isotherm was observed. Furthermore, the distribution of the pore size, calculated from the N₂ adsorption profile, was around 0.55 nm, which agrees well with the pore-size parameter derived from the single crystal data.

To elucidate the gas uptake ability of PCP-1, single component gas-adsorption isotherms of CO₂, N₂, O₂ and CO were checked at 195 K and 273 K (Fig. 3a and c). The saturation adsorption amount of PCP-1 is 3.904 mmol g⁻¹, corresponding to about 2.8 molecules of CO₂ per BTN ligand. In addition, volumetric storage capacities, as one of the important standards of adsorbent materials in feasible applications, should also be considered. Because the framework was constructed from the heavy La³⁺ metal chain and densely packed BTN ligands, PCP-1 has a high density (0.975 g cm⁻³), but it also has a high uptake capacity of 167.1 g L⁻¹ at 195 K. Importantly, even at 273 K and 1 bar, the uptake capacity of this PCP can reach 56.5 g L⁻¹, which is higher than that of some important porous materials, (La-BTB: 54.8 g L⁻¹;²¹ MOF-5: 39.9 g L⁻¹;¹⁵ and MOF-177: 50.7 g L⁻¹ (at 298 K, 3.1 bar)²⁰) and lower than that of some frameworks with functional amide groups (NTU-105: 227.0 g L⁻¹;¹⁷ Cu-TPBTM: 279.2 g L⁻¹;²⁰ and Cu-TDPAT, 344.8 g L⁻¹). Meanwhile, the gas uptakes for N₂ and O₂ in these frameworks are also high, revealing the lower efficiency of selective capture of CO₂. In contrast, the uptakes of N₂, O₂ and CO in PCP-1 increase very slowly with the pressure. This may be because of the weaker interactions of these gases with the framework compared with that of CO₂. More importantly, the big gaps in uptake amounts around 10 kPa (CO₂: 2.93 mmol g⁻¹; N₂: 0.186 mmol g⁻¹; O₂: 0.199 mmol g⁻¹; CO: 0.302 mmol g⁻¹) indicate that PCP-1 is a good candidate for the selective capture of CO₂ from four-gas mixtures similar to flue gases.

The ideal adsorbed solution theory (IAST) of Myers and Prausnitz¹⁹ is a well established method for describing gas mixture adsorption in many zeolites and PCP materials. We employed it to predict multi-component adsorption behaviors from the experimental single-component gas isotherms. As shown in Fig. 3b and d, PCP-1 exhibits high selective CO₂ capture in the following trend: CO₂/N₂ > CO₂/O₂ > CO₂/CO at 195 K. At 273 K, the predicted selectivities (CO₂/N₂: ~93–38; CO₂/O₂: ~78–20 and CO₂/CO: ~68–18) are high enough [larger than 8] for the potential feasibility of the practical procedure.¹⁸

Adsorption heat and NH₃-TPD studies

To understand such high separation ability better, the adsorption enthalpies of a series of PCPs were calculated using the Clausius–Clapeyron equation (Fig. 4). We note that the value of the isosteric heats of adsorption for PCP-1 is 28.5 kJ mol⁻¹ (26 kJ mol⁻¹ by the virial method), which is lower than that of other materials with a high separation ability. This implies that the energy required for regeneration of the adsorbed CO₂ in fixed bed absorbers will be lower for PCP-1 than for MgMOF-74, NiMOF-74, Cu-TDPAT, CuBTC, or NaX zeolite. Usually, the Lewis acidity of the open metal site contributes greatly to the adsorption enthalpies. Here, the single crystal data indicate one coordinated DMF around the La³⁺ ions, but the IR and TGA results indicate the complete activation of evacuated PCP-1. Therefore, if the open metal site was generated in the activation process, the isosteric heats should be high. To find out why, temperature-programmed desorption (TPD) of NH₃ was used to examine whether or not the open metal site existed in PCP-1. As shown in the NH₃-TPD profiles (ESI†), there is only one signal for PCP-1 at temperatures ranging from 50 to 140 °C, which can be explained as the physical NH₃ adsorption on the channel surface of the materials (ESI†). In contrast, two signals can be found in MIL-101(Cr) which has a strong open metal site. The first peak, around 200 to 300 °C, indicates the chemisorptions of NH₃ on the exposed chromium metal. The second peak (>300 °C) can be assigned to the partial decomposition of the structures, because the TGA results revealed that MIL-101(Cr) collapsed at high temperatures. Thus, here we can conclude that, after removing the coordinated DMF molecules, the coordination sphere of La³⁺ ions was slightly reorganized, and the exposed La³⁺ sites were recovered again by the other eight oxygen atoms. Thus, only the large aromatics site of PCP-1 affords the binding energy to guest molecules.

Breakthrough simulations

To evaluate the gas separation ability of adsorbents under kinetic flowing gas conditions, breakthrough simulations were performed using a precise methodology established by Krishna and Long, which are strongly pertinent to the pressure swing adsorption (PSA) process, an energetically efficient method for industrial scale capture. The breakthroughs of an equimolar four-component mixture including CO₂, N₂, O₂, and CO were...
explored at 195 K and 273 K. The partial pressures of these four gases were set as 25 kPa, and the relative concentrations of outflowing gas are shown in Fig. 5. The results indicate that at both temperatures, the sequence of breakthroughs is N₂, O₂, CO, and CO₂. The adsorption strengths of N₂, O₂ and CO are very similar, and their breakthroughs are also close together in time. CO₂, the component with the strongest adsorption strengths breaks through last.

Fig. S18† presents the breakthrough characteristics for CO₂–CO–O₂–N₂ (15/1/4/80) with a typical flue gas composition, operating at 195 K, and 273 K, respectively. Compared to the corresponding performance for equimolar mixtures, we note that the breakthrough of CO₂ occurs at significantly later times. This is because of the lower CO₂ content in the realistic flue gas mixtures, 15%. Longer breakthrough times imply a higher productivity in the fixed bed adsorber.

In addition, the composition of flue gas changes frequently. It is therefore important to find out whether or not the gas composition can influence the breakthrough point. Fig. S15† presents breakthrough characteristics for binary 25/75 mixtures of CO₂–CO, CO₂–O₂, and CO₂–N₂ at 100 kPa, and 273 K. The breakthrough of CO₂ for all three binary mixtures occurs at approximately the same dimensionless time, τ = 70, as for the quaternary mixture in Fig. 5, indicating that the separation capability of PCP-1 is not influenced by the gas composition. The significant time interval between the breakthroughs of CO₂, O₂, N₂ and CO₂ demonstrates that very good separation is possible in practice at ambient temperatures.

Fig. 3 Gas adsorption isotherms (circle points) and the dual-site Langmuir–Freundlich fit lines (lines) of CO₂, CO, O₂ and N₂ in PCP-1 at 195 K (a) and 273 K (100 kPa) (c). Calculations using the ideal adsorbed solution theory of Myers and Prausnitz for CO₂/CO, CO₂/O₂, and CO₂/N₂ selectivity for an equimolar quaternary CO₂–CO–O₂–N₂ gas mixture maintained at isothermal conditions at 195 K (b), and 273 K (d).

Fig. 4 Comparison of the isosteric heats of adsorption, Qₜᵢₛ, of CO₂ in PCP-1, MgMOF-74, NiMOF-74, Cu-TDPAT, CuBTC, and NaX zeolite.
Dynamic adsorption studies

Dynamic adsorption uptake is an important factor in the PSA process. Thus, we measured the temperature-dependent gravimetric adsorption cycling performance of PCP-1 with CO₂ using TGA (Fig. 6). After heating the evacuated samples at 150 °C for 40 min, the sample was cooled to 5 °C, and the temperature maintained for 20 min. Three cycles with mass change around 5 wt% were observed, and this value was almost equal to the pure CO₂ uptake. After the first cycle, the sample was exposed to air for 24 h, and a second cycle was performed. The gas uptake of PCP-1 does not change, indicating a good capture of CO₂ under kinetic flowing gas conditions. In addition, the desolvated sample of PCP-1 is a rigid framework during CO₂ adsorption, as verified by powder synchrotron X-ray diffraction (Fig. S22f).

Thermal and chemical stability

With the good separation ability of CO₂ over CO, O₂ and N₂, we now explore the physical properties of PCP-1, especially its thermal and chemical stability, which can strongly affect the feasibility of practical applications.

X-ray thermodiffraction of the as-synthesized PCP-1 was performed under a N₂ atmosphere from room temperature to 350 °C. As shown in Fig. 7, below 100 °C, some small peaks (2θ: from 20 to 30°) can be found in the PXRD results. Following the thermal treatment, these small peaks disappeared gradually, and the (0 3 1) and (1 1 3) peaks shifted very little to the low angle area. However, importantly, the position and the intensity of the (−1 1 1) peak did not change. Thus, it is reasonable to attribute such slight changes of the structure to the thermodiffraction experiment and gas adsorption profiles, the removal of guest water and the following slight reorganization of the inherently flexible coordination sphere of La³⁺. Similar phenomena have been reported in the complex of [La₂(HL)₂(H₂O)₂(CO₃)](H₂O)₇. With the TGA data, we can conclude that the evacuated PCP-1 can maintain porosity to at least 350 °C.

Water and chemical stability are other important physical properties for the PCP sorbent. Almost twenty thousand PCP/MOF structures have been reported to date; however, few of them can maintain their porosity after moisture, water and chemical treatment (La-BTB, MIL-100 and UiO-66), as this is a key challenge for PCP/MOF chemistry. Hence, the evacuated PCP-1 was exposed to a moist 80% RH environment at various temperatures. The resulting PXRD patterns are the same as those of the original phase (Fig. 8). Encouraged by this good...
result, the water and chemical stability of PCP-1 was examined by soaking the as-synthesized samples in harsh conditions: hot (100 °C) aqueous HCl (pH = 2), aqueous NaOH (pH = 12) and water solutions for one day. After cooling, the wet samples were checked by PXRD, which indicated the crystalline nature of the framework. To further demonstrate the integrity of the material, we performed CO₂ adsorption experiments at 195 K with PCP-1 which was treated in boiling water at different pH values for 24 h. The gas uptake of the treated PCP-1 (pH = 2 and 12) decreased a little, however, importantly, both the uptakes and shape of PCP-1 (pH = 7) are nearly identical with that of the fresh sample, exhibiting its high water and chemical stability (Fig. S21 and 22†). In addition, it is necessary to know the stability of degassed PCP-1 under moist environments at different temperatures, as it is difficult to avoid moisture in the industrial separation process, even though there is a much smaller amount. Compared with the isotherm of the fresh PCP-1, we found that the gas uptakes of the moisture treated PCP-1 decreased a little, however, importantly, after the second treatment, the gas uptakes are almost the same as their previous performance, despite the very harsh conditions (80 °C and RH% 80). Moreover, the gas uptakes of the treated PCP-1 are also almost the same at different temperatures, indicating high moisture stability of degassed PCP-1 (Fig. S23†). Taking the crystal structure into consideration, the high aqueous and chemical stability of PCP-1 could be assigned to the combination of the high coordination number of La³⁺, the triangular ligand units and the coordination type. To our knowledge, because of the relatively weak metal–oxygen coordination, only a few carboxylate-bridged PCPs show structural stability in water for as long as a few hours at room temperature, while none have been shown to be stable in acid (pH = 2) or base (pH = 12) solutions at 100 °C for one day; however, this stability has been observed for zeolitic imidazole frameworks such as ZIF-8.24e

Conclusions

In summary, by moving the focus from the traditional open metal site and amide species for selective CO₂ capture, we have demonstrated a new robust porous coordination polymer, PCP-

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Notes and references


