

Fine-Tuning Pore Size by Shifting Coordination Sites of Ligands and Surface Polarization of Metal–Organic Frameworks To Sharply Enhance the Selectivity for CO₂

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S Supporting Information

ABSTRACT: Based upon the (3,6)-connected metal–organic framework {Cu(L1)·2H₂O·1.5DMF}_∞ (L1 = 5-(pyridin-4-yl)isophthalic acid) (SYSU, for Sun Yat-Sen University), iso-reticular {Cu(L2)·DMF}_∞ (L2 = 5-(pyridin-3-yl)isophthalic acid) (NJU-Bai7; NJU-Bai for Nanjing University Bai group) and {Cu(L3)·DMF·H₂O}_∞ (L3 = 5-(pyrimidin-5-yl)isophthalic acid) (NJU-Bai8) were designed by shifting the coordination sites of ligands to fine-tune pore size and polarizing the inner surface with uncoordinated nitrogen atoms, respectively, with almost no changes in surface area or porosity. Compared with those of the prototype SYSU, both the adsorption enthalpy and selectivity of CO₂ for NJU-Bai7 and NJU-Bai8 have been greatly enhanced, which makes NJU-Bai7 and NJU-Bai8 good candidates for postcombustion CO₂ capture. Notably, the CO₂ adsorption enthalpy of NJU-Bai7 is the highest reported so far among the MOFs without any polarizing functional groups or open metal sites. Meanwhile, NJU-Bai8 exhibits high uptake of CO₂ and good CO₂/CH₄ selectivity at high pressure, which are quite valuable characteristics in the purification of natural gases.

The past two decades have witnessed the rapid development of metal–organic frameworks (MOFs) due to their fantastic structures and various potential applications, such as in strategic storage and separation of gases, catalysis, and chemical sensing.¹ Most interestingly, compared with traditional porous materials (zeolite, active carbon, etc.), many MOFs can be used as platforms, such as MOF-5, ZIFs, HKUST-1, etc., and their structures can be further modified systematically toward higher performance.²

Selective capture of CO₂ is of paramount importance for the purification of natural gases and the reduction of CO₂ emission. A proper material that offers high selectivity for and uptake of CO₂, especially at relatively low pressures (~0.15 bar, the partial pressure of CO₂ in postcombustion flue gases)^{3a} and at pressures from 0 to 17 bar (the partial pressure in natural gas streams),^{4a} and requires minimal energetic input to liberate the captured CO₂, is essential to make the process practical. MOFs are of great interest as new materials in this respect.³ Several strategies have been introduced to improve the selective adsorption of CO₂: (1) rational decorations in the pore with nitrogen bases or some other polarizing groups;⁵ (2) pore size

narrowing by interpenetration;⁶ and (3) altering the size of the ligands in those MOFs with iso-reticular structures.⁷ However, these strategies generally lead to a decline in surface area and CO₂ uptake capacity. Very recently, we directly inserted acylamide functional groups into several MOFs and realized a balance between large storage capacity and high selectivity for CO₂.⁸

Herein, we expand our work by using a (3,6)-connected structure {Cu(L1)·2H₂O·1.5DMF}_∞ (L1 = 5-(pyridin-4-yl)isophthalic acid) (SYSU, for Sun Yat-Sen University) as a new platform that contains no open metal sites and offers low energy cost in potential industrial applications.^{7a} Based on this structure, we synthesized iso-reticular {Cu(L2)·DMF}_∞ (L2 = 5-(pyridin-3-yl)isophthalic acid) (NJU-Bai7; NJU-Bai for Nanjing University Bai group) and {Cu(L3)·DMF·H₂O}_∞ (L3 = 5-(pyrimidin-5-yl)isophthalic acid) (NJU-Bai8) by a new strategy: shifting the coordination sites of the ligands and polarizing the inner environment with uncoordinated nitrogen atoms, respectively. Compared with prototype SYSU, NJU-Bai7 and NJU-Bai8 showed sharply improved CO₂ adsorption enthalpy and selectivity for CO₂ over N₂ and CH₄ at about 0.15 bar (enthalpy of 28.2 kJ/mol compared to 40.5 and 37.7 kJ/mol and selectivity of 5.1/4.7 compared to 97.1/14.1 and 111.3/40.8 at 273 K and low pressure), without changes in topology, inner surface area, or porosity. Remarkably, the CO₂ adsorption enthalpy of NJU-Bai7 is the highest reported so far among MOFs with no polarizing functional groups or open metal sites. Meanwhile, NJU-Bai8 maintains the balance between high selectivity for CO₂ and large capacity for CO₂ storage, with the value of 220 v/v at 298 K and 20 bar.

SYSU was first reported by Su's group,^{9a} as shown in Figure 1a. The whole structure is topologically a (3,6)-connected net, with point (Schläfli) symbol of (4-6₂)₂(4₂-6₁₀-8₃). There exist wide channels of 6.3 × 6.3 Å² along the *a* axis (defined by the diameters of the inserted interior contact atoms). All Cu-paddlewheel unsaturated metal sites are occupied by pyridyls from the ligands, resulting in no specific active sites for the adsorption of CO₂ in the channels. This MOF offers an opportunity to tune the pore size through the rotation of pyridine rings along the C4–C7 bonds. Thus, we substituted pyridin-4-yl with pyridin-3-yl and obtained NJU-Bai7 with the same topology as SYSU. As shown in Figure 1f, shifting the

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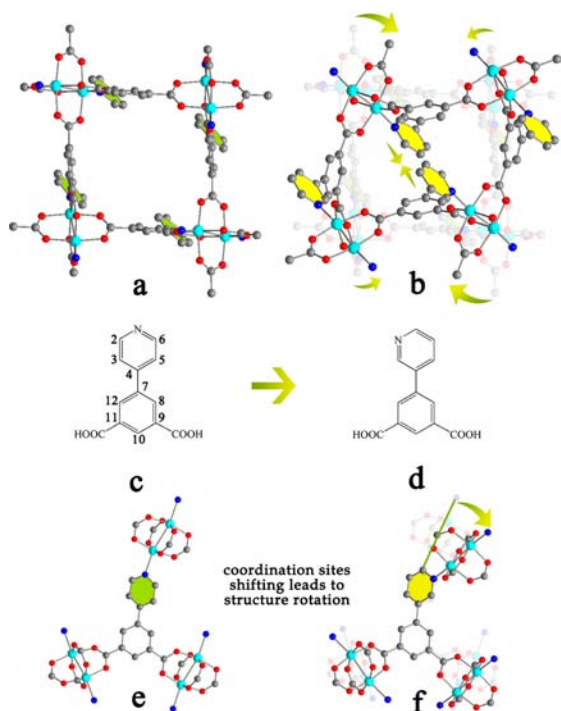


Figure 1. (a) A channel of SYSU viewed along the *a* axis. (b) Separated channels of NJU-Bai7 viewed along the *a* axis. (c,d) Ligands for SYSU and NJU-Bai7. (e,f) Coordination modes of SYSU and NJU-Bai7, respectively.

coordination sites leads to structure distortion. In planes perpendicular to the *a* axis (Figure 1b), neighboring Cu-paddlewheels rotate in opposite directions, such that all pyridine rings stretch into the channel aligned along the *a* direction, dividing the channel into two equal parts. The size of the resulting channel is about $3.4 \times 3.4 \text{ \AA}^2$, which is quite close to the kinetic diameter of carbon dioxide (3.3 Å). To further polarize the inner surface, uncoordinated nitrogen atoms were introduced, to give NJU-Bai8 (Figure 2). The pyrimidine rings make that section of the channel look like a dumbbell, with the size of the bell heads about $4 \times 3.3 \text{ \AA}^2$. The structure of NJU-Bai8 is a little different from that of NJU-Bai7, but after being soaked in acetone for a few hours, its PXRD pattern became almost the same as that of NJU-Bai7 (see Supporting Information, Figure S7d).

The permanent porosity of SYSU, NJU-Bai7, and NJU-Bai8 is confirmed by N_2 sorption isotherms at 77 K (Figure S6). The type-I isotherms indicate that they are microporous materials. The Brunauer–Emmett–Teller (BET) surface area and Langmuir surface area of SYSU are calculated to be 1100 and 1216 m^2/g , while those of NJU-Bai7 are about 1155 and 1238 m^2/g , and those of NJU-Bai8 are 1103 and 1196 m^2/g . The total pore volumes of SYSU, NJU-Bai7, and NJU-Bai8 are estimated to be 0.436, 0.439, and 0.431 cm^3/g , respectively. These values demonstrate that the surface area and porosity of NJU-Bai7 and NJU-Bai8 are almost unchanged after the channels are narrowed and polarized.

To systematically evaluate the effect of narrowing channels and the inner environment on adsorption of gases, the ability of SYSU, NJU-Bai7, and NJU-Bai8 to adsorb CO_2 , CH_4 , and N_2 was investigated at 273 and 298 K. At 298 K, as shown in Figure 3a, NJU-Bai7 and NJU-Bai8 perform much better than SYSU (8.0 wt% for NJU-Bai7 and 5.4 wt% for NJU-Bai8 vs 3.6

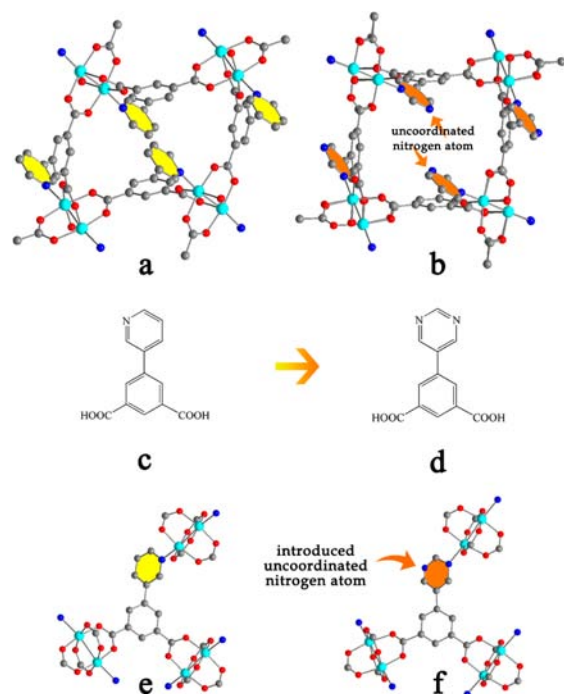


Figure 2. (a) Separated channels of NJU-Bai7 viewed along the *a* axis. (b) A dumbbell-like channel of NJU-Bai8 viewed along the *a* axis. (c,d) Ligands for NJU-Bai7 and NJU-Bai8. (e,f) Coordination modes of NJU-Bai7 and NJU-Bai8, respectively.

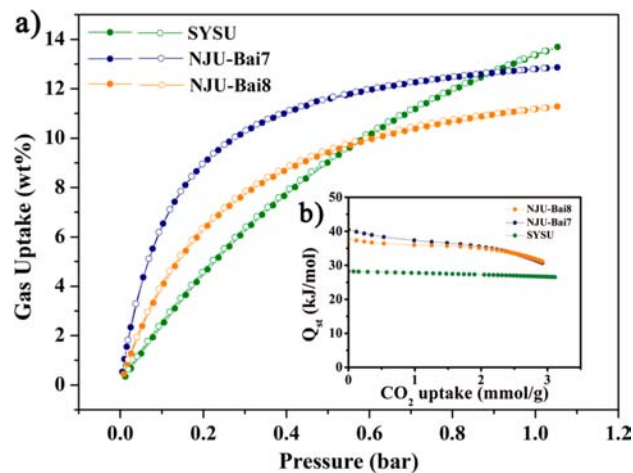


Figure 3. (a) CO_2 adsorption isotherms for SYSU, NJU-Bai7, and NJU-Bai8 at 298 K. (b) CO_2 adsorption enthalpy of SYSU, NJU-Bai7, and NJU-Bai8.

wt% for SYSU) at a relatively low pressure (~ 0.15 bar). The CO_2 uptake for NJU-Bai7 at 298 K and 0.15 bar is larger than those of many well-known MOFs with open metal sites or functional groups, such as bio-MOF-11^{9b} (5.4 wt%), ZIF-78^{5c} (3.3 wt%), MIL-53(Al)^{9e} (3.1 wt%), en-Cu-BTTri^{5a} (2.3 wt%), and MOF-177^{10b} (0.6 wt%). The obvious enhancement from SYSU to NJU-Bai7 and NJU-Bai8 at low pressure could be mainly attributed to the narrow channels created in NJU-Bai7 and NJU-Bai8, which facilitate the interaction between CO_2 and the channel walls.^{9b} This interaction is further confirmed by the adsorption enthalpies of CO_2 for these three MOFs (Figure 3b). The zero-coverage adsorption enthalpies of CO_2 in SYSU, NJU-Bai7, and NJU-Bai8 are 28.2, 40.5, and 37.7 kJ/

mol, respectively. Notably, the CO₂ adsorption enthalpy of NJU-Bai7 is the highest reported so far among the MOFs with no polarizing functional groups or open metal sites,^{10c} and is quite comparable to those of famous compounds with open metal sites such as Mg/DOBDC^{3c} and MIL-101^{9d} (47 and 44 kJ/mol, respectively).

The separation ratios of CO₂ versus CH₄ and N₂ were calculated from the ratio of the initial slopes based on the isotherms,^{3d,5c,9b} as listed in Table 1. Compared with SYSU, the

Table 1. Porosities, CO₂ Enthalpies, and CO₂/N₂ and CO₂/CH₄ Selectivities of SYSU, NJU-Bai7, and NJU-Bai8 at 273 K

MOF	BET (m ² g ⁻¹)	pore volume (cm ³ g ⁻¹)	-Q _{st,H=0} (kJ mol ⁻¹)	CO ₂ /N ₂	CO ₂ /CH ₄
SYSU	1100	0.436	28.2	25.5	4.7
NJU-Bai7	1155	0.439	40.5	97.1	14.1
NJU-Bai8	1103	0.431	37.7	111.3	40.8

separation ratios of CO₂/N₂ and CO₂/CH₄ for NJU-Bai7 are significantly improved from 25.5 to 97.1 and from 4.7 to 14.1 (almost quadruple). The separated channels in NJU-Bai7 show a pore size effect preference for CO₂ over N₂ and CH₄, as CO₂ possesses a smaller kinetic diameter (3.3 Å, <3.64 Å for N₂, <3.8 Å for CH₄). To the best of our knowledge, this is the first example of enhancing the selectivity for CO₂ to such a significant extent by shifting coordination sites without changing the inner surface areas or porosities. Combining this selectivity with the high CO₂ uptake at relatively low pressure, NJU-Bai7 may be a good candidate for carbon capture from industrial postcombustion flue gases. Furthermore, NJU-Bai8 shows an even higher selectivity for CO₂, with separation ratios of 111.3 for CO₂/N₂ and 40.8 for CO₂/CH₄. These values are larger than those of CAU-1^{3d} (CO₂/N₂, 101; CO₂/CH₄, 28) and bio-MOF-11^{9b} (CO₂/N₂, 81) under similar conditions. Meanwhile, the separation ratios of CO₂/N₂ and CO₂/CH₄ for NJU-Bai8 at 298 K are 58.3 and 15.9 (see Supporting Information, Table S3), which are higher than those for some well-known MOFs, such as ZIF-78^{5c} (CO₂/N₂, 50.1; CO₂/CH₄, 10.6), Mg-MOF-74^{3c,9c} (CO₂/N₂, 49), and en-Cu-BTTri^{5a,10c} (CO₂/N₂, 44). Making it even more attractive, NJU-Bai8 shows a high saturated CO₂ uptake amount of 220 v/v at 20 bar and 298 K, which is quite comparable to those of some leading MOFs for CO₂ storage (Figure S15 and Table S2). Obviously, from the type-IV-like CO₂ isotherms with hysteresis at 273 and 298 K, a gate-opening process^{10d} exists in both NJU-Bai7 and NJU-Bai8, and the gate-opening pressure for NJU-Bai8 (4 bar at 273 K and 7 bar at 298 K) is much lower than that for NJU-Bai7 (10 bar at 273 K and no gate opening observed at 298 K), which indicates a greater mutability of NJU-Bai8. In contrast to NJU-Bai7, with NJU-Bai8 the saturated CO₂ uptake amount increases while the CH₄ amount decreases at both 273 and 298 K. Thus, by qualitative evaluation, the selectivity of NJU-Bai8 for CO₂/CH₄ in the high pressure range is also much higher than that of NJU-Bai7. The high selectivity of CO₂ and large capacity for CO₂ storage may make NJU-Bai8 a versatile material in methane purification and carbon capture.

The discrepancies in CO₂ adsorption behavior mentioned above between NJU-Bai7 and NJU-Bai8 could mainly be attributed to their structural differences. Uncoordinated nitrogen atoms in NJU-Bai8 make the whole structure more flexible, which can be confirmed by the VT-PXRD patterns in

Figure S12. After activation, both NJU-Bai7 and NJU-Bai8 contract, but to a larger extent for NJU-Bai8 (Figure S7d). As a result, the uncoordinated nitrogen atoms in NJU-Bai8 are blocked. Thus, the CO₂ uptake amount at low pressure and zero-coverage adsorption enthalpy of CO₂ for NJU-Bai8 are a bit lower than those for NJU-Bai7. As the pressure increases, the channels in NJU-Bai8 extend to reveal uncoordinated nitrogen atoms that can easily capture CO₂ molecules, causing a steeper increase in isotherms than for NJU-Bai7. Although theoretical studies have predicted that uncoordinated nitrogen atoms in five- or six-membered heteroarene rings could strengthen the adsorption of CO₂,¹¹ and some research results have shown this effect in five-membered heteroarene rings,^{4b,11c,d} to our best knowledge, this is the first experimental substantiation of the theoretical conclusions on six-membered heteroarene rings. Besides, varying the inner environment caused a repulsive effect that resulted in highly unfavorable conditions for nonpolar CH₄ molecules.¹² As a synergistic result, NJU-Bai8 exhibits good CO₂/CH₄ selectivity and large CO₂ uptake capacity.

In summary, based on a platform of (3,6)-connected MOF SYSU, we successfully synthesized iso-reticular NJU-Bai7 and NJU-Bai8 by a new strategy: shifting the coordination sites of ligands and polarizing the inner environment with uncoordinated nitrogen atoms, respectively. Compared with the prototype structure, both NJU-Bai7 and NJU-Bai8 exhibit much higher adsorption enthalpies, uptake amounts, and selectivities for CO₂ at low pressure, which make them excellent candidates for postcombustion carbon capture. Additionally, NJU-Bai8 may be a good material for purification of natural gases because of its high uptake of CO₂ and good selectivity for CO₂ over CH₄ at high pressure. Our work presents a new strategy for fine-tuning pore size, and this strategy may provide a new way to finely tune the size and properties of MOFs, thus facilitating further exploration of more amazing MOFs with high CO₂ selectivity and uptake capacity.

■ ASSOCIATED CONTENT

📄 Supporting Information

Synthetic procedures, crystallographic tables, PXRD data, additional gas adsorption isotherms, and details of the isosteric adsorption enthalpy. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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