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The Accessibility of Nitrogen Sites Makes Difference to Selective CO₂ Adsorption in a Family of Isostructural Metal-Organic Frameworks

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By using three rigid diisophthalate organic linkers incorporating different number and orientation of Lewis basic nitrogen atoms in the spacers between two terminal isophthalate moieties, namely, 5,5'-(quinoline-5,8-diyl)-diisophthalate, 5,5'-(isoquinoline-5,8-diyl)-diisophthalate, and 5,5'-(quinoxaline-5,8-diyl)-diisophthalate, a family of isostructural copper-based metal-organic frameworks, **ZJNU-43**, **ZJNU-44** and **ZJNU-45** were successfully solvothermally synthesized and structurally characterized by single-crystal X-ray diffractions. The three MOFs, after activation, exhibited almost the same porosities but distinctly different CO₂ adsorption properties. At room temperature and 1 atm, the adsorption capacities for CO₂ reached 103, 116 and 107 cm³ (STP) g⁻¹ for **ZJNU-43a**, **ZJNU-44a** and **ZJNU-45a**, respectively. Furthermore, Ideal Adsorbed Solution Theory (IAST) and simulated breakthrough analyses indicated that **ZJNU-44a** bearing much more easily accessible nitrogen sites is the best among the three MOFs for the separation of the following two binary gas mixtures at 296 K, ie, 50/50 CO₂/CH₄ and 15/85 CO₂/N₂ gas mixtures, indicating that the accessibility of nitrogen sites plays much more crucial role, which is further confirmed by comprehensive quantum chemical calculations. The work demonstrates that the CO₂ adsorption properties of MOFs depend not only on the number of Lewis basic nitrogen sites but more importantly on their accessibility.

Introduction

Carbon dioxide emitted through human activities is considered the primary greenhouse gas causing the global climate change. In addition, natural gas contains methane as its major component but also contains a certain amount of CO₂. The presence of CO₂ not only reduces the energy content of natural gas but also causes corrosion of pipeline and equipment during down and upstream natural gas processing. Therefore, effective capture and separation of CO₂ is thus becoming increasingly important for the reduction of CO₂ emission and upgradation of natural gas quality. The currently employed carbon capture method involves chemisorption by amine solution systems. However, Amine regeneration

requires cleavage of the N-C covalent bond formed between CO₂ and amine species by heating and thus has a high operational cost. In addition, the volatile solvents might undergo degradation and loss during the operation, resulting in negative environmental impact. In contrast, physisorption based separation is regarded as a very promising technology because of its low energy cost and high efficiency. However, the success of this approach is strongly dependent on the development of suitable porous adsorbents with very high adsorption selectivity and uptake capacity of CO₂. In this context, a new class of crystalline porous materials, metal-organic frameworks (MOFs),¹ also known as porous coordination polymers (PCPs),² assembled by bridging metal ions/clusters through organic linkers into extended networks, have shown promising potentials because of the pore sizes of MOFs can be tuned by the interplay of metal ions/metal containing clusters and organic linkers to enhance their size-selective separations, while the pore surfaces can be functionalized by the immobilization of specific sites to direct the recognition of CO₂ molecule. In fact, much research on MOFs has demonstrated their enormous potential for CO₂ storage and separation.³

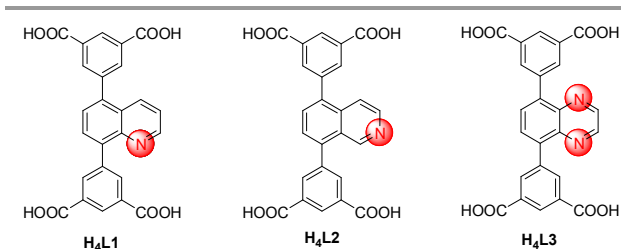
To improve the selective CO₂ adsorption, current efforts are largely devoted to enhancing the CO₂ binding affinity in MOFs. Reported strategies include creation of open metal sites, ligand functionalization, and construction of size/shape-specific pores. Among these methods, ligand functionalization,

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† Electronic Supplementary Information (ESI) available: PXRD patterns (Fig. S1-3), TGA (Fig. S4), gas sorption isotherms (Fig. S5-7), schematic of the breakthrough apparatus (Fig. S8), FTIR spectra (Fig. S9-11), ¹H and ¹³C NMR (Fig. S12), comparison of the textural properties of **ZJNU-43a**, **ZJNU-44a** and **ZJNU-45** (Table S1), single-site Langmuir fit parameters (Tables S3-5), Crystal data and structure refinement (Table S6). CCDC 1052691, 1052692, and 1055566. For ESI and crystallographic data in CIF or other electronic format See DOI: 10.1039/x0xx00000x



Scheme 1 The organic building blocks, H₄L1-H₄L3, used to construct MOFs **ZJNU-43**, **ZJNU-44** and **ZJNU-45**.

namely, adding specific functional groups into the organic linkers comprising MOFs by pre- or post-synthetic modification is widely performed, with its own advantages such as the chemical diversity of the available organic functional groups incorporated into MOFs. So far, various functional groups were explored including OH, NH₂, NO₂, COOH, SO₃H, alkyl, alkoxy, halogen groups, amide, and heterocyclic moieties.^{3g, 3r, 4} For example, Zhao *et al.* reported that hydroxyl and amino-functionalized MOFs exhibited the enhanced CO₂ uptakes compared to the parent MOF.^{4d} Also, Biswas demonstrated the sulphonate-, carboxylate- and iodo-functionalized UiO-66 frameworks displayed higher adsorption selectivity of CO₂ over CH₄ compared to unfunctionalized UiO-66 compound.^{4b} Wang *et al.* synthesized a nitrogen-rich triazole functionalized MOF presenting exceptionally high uptake capacity for CO₂.^{4c} The authors attributed to the enhanced CO₂ adsorption capacity and selectivity to the favourable interactions between CO₂ molecules and the functional sites, namely, electronic effect of functional groups. However, in design and development of MOFs materials for CO₂ adsorption, one should not only consider the electronic effect of the functional groups, but more importantly the accessibility of functional groups should also be taken into account. It was envisaged that if these functional groups are blocked, they will have a limited effect on the improvement of CO₂ uptake capacities and adsorption selectivities. Although intuitive, the study in the aspect is less experimentally performed.

Based on the considerations and with the aim to understand how accessibility of the Lewis basic nitrogen atoms may affect the adsorption properties of a given structure, in this study, we have targeted an isostructural family of MOFs bearing different number and orientation of nitrogen sites. The organic linkers outlined in Scheme 1, H₄L1-H₄L3, bearing different Lewis basic nitrogen number and orientation, were combined with paddlewheel dicopper [Cu₂(COO)₄] secondary building units (SBUs) to construct three-dimensional (3D) NbO-type MOFs which we termed **ZJNU-43**, **ZJNU-44**, and **ZJNU-45**, respectively (“**ZJNU**” represents “Zhejiang Normal University”). The three MOFs are isostructural but differ only in the number and orientation of uncoordinated nitrogen atoms in the bridging ligands. Remarkably, systematic gas sorption studies on these materials show that the activated **ZJNU-44a** (thereafter, the letter “a” indicates activated MOF materials) bearing more exposed nitrogen atoms, albeit the less nitrogen atoms than the one in **ZJNU-45a**, exhibits the better CO₂

adsorption separation properties, indicating the accessibility of nitrogen sites plays a more important role on CO₂ adsorption.

Results and discussions

Synthesis and characterization

The organic ligands, H₄L1 to H₄L3, were synthesized by cross-coupling reaction between dimethyl 5-(pinacolboryl)isophthalate and the corresponding dibromo derivatives followed by hydrolysis and acidification. The detailed synthetic procedures were provided in the Experimental Sections. The chemical structures of all the intermediates and ligands were characterized by NMR spectroscopy.

Solvothermal reactions of Cu(NO₃)₂·3H₂O with H₄L1 in a mixed solvent of *N,N*-dimethyl formamide (DMF)/EtOH/H₂O under acidic conditions at 353 K for 120 h afforded blue rhombic-shaped single crystals of **ZJNU-43** ([Cu₂L1(H₂O)₂]·3DMF·2EtOH·4H₂O). **ZJNU-44** ([Cu₂L2(H₂O)₂]·3DMF·3CH₃CN·3H₂O) was obtained by treating H₄L2 and CuCl₂·2H₂O in a mixed solvent of DMF/CH₃CN/H₂O under acidic condition at 353 K for 72 h, while **ZJNU-45** ([Cu₂L3(H₂O)₂]·3DMF·3MeOH·3H₂O) was synthesized by a solvothermal reaction of H₄L3 and Cu(NO₃)₂·3H₂O in a mixed solvent of DMF/MeOH/H₂O under acidic conditions at 363 K for 48 h. Their structures were determined by single-crystal X-ray diffraction analyses, and the phase purity for the bulk crystalline materials was confirmed by a good match between the experimental and simulated powder X-ray diffraction patterns (Fig. S1-3). The formulae were established based on single-crystal X-ray structure determination, thermogravimetric analyses (TGA, Fig. S4), and microanalysis.

Structural Description

Single-crystal X-ray diffraction analyses showed all the three compounds are isostructural, crystallizing in the trigonal space group *R*-3m. The crystal structure of **ZJNU-43** was representatively described. The two Cu centres are bridged by four carboxylate groups in a bis-monodentate fashion to form 4-connected square-planar [Cu₂(COO)₄] SBUs, which link the 4-connected diisophthalate ligands to form a (4,4)-connected NbO-based 3D network. Alternatively, if the bridging organic linker is considered as having two 3-coordinated (3-c) branch points, then in combination with the 4-coordinated dicopper paddlewheels, the derived net is the one with the RCSR symbol fof.⁵ The net topology is different with the one appearing in MOF **NOTT-109** constructed from paddlewheel dicopper [Cu₂(COO)₄] SBUs and 5,5-(naphthyl-1,4-diyl)-diisophthalate although the used ligands are structurally similar,⁶ indicating the tolerance of the NbO-net to the steric congestion imposed by ligand functionalization. In the framework, there exist two types of polyhedral nanocages which are stacked alternately through shared triangular windows along the crystallographic *c* axis. One cage shown in green sphere consists of 6 SBUs and 12 ligands, and the diameter is *ca.* 11.5 Å taking into account the van der Waals radius of the atoms, while the other one

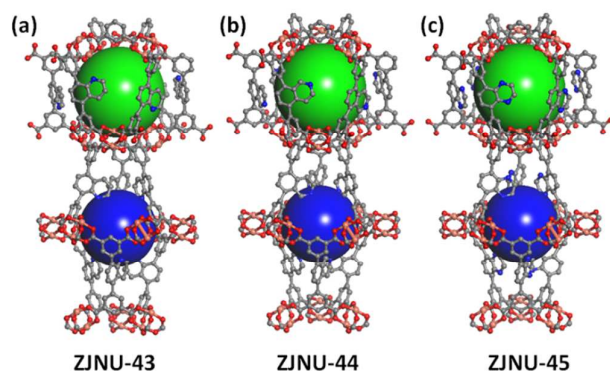


Fig. 1 Two different types of polyhedral nanocages in **ZJNU-43** (a), **ZJNU-44** (b) and **ZJNU-45** (c) decorated with different number and orientation of uncoordinated nitrogen atoms, which are shown in green and blue spheres, respectively. Hydrogen atoms and coordinated water molecules are omitted for clarity.

shown in blue sphere is constructed from 6 ligands and 12 SBUs with the dimension of *ca.* 13×22 Å (Fig. 1a). The central quinolone ring is twisted from the plane defined by the two terminal isophthalates with a dihedral angle of 48.1°. The nitrogen atoms of the bridging ligands do not participate in the binding of Cu²⁺ ions, affording additional binding sites for the electron acceptor gases.

By comparison of the crystal structures of three MOFs (Fig. 1), it can be seen that the nitrogen atoms in **ZJNU-44** protrude into the pore which are much more easily accessible to the gas molecules, while the nitrogen atoms in **ZJNU-43** and **ZJNU-45** might be partially blocked by the neighbouring isophthalate moieties, which might lead to their different gas sorption properties.

Permanent porosities

The permanent porosities of the three compounds were established by nitrogen adsorption at 77 K. Prior to gas adsorption experiments, the samples were activated by solvent exchange with dry acetone followed by evacuation under dynamic vacuum at 373 K. The activated **ZJNU-43a**, **ZJNU-44a** and **ZJNU-45a** adsorbed a significant amount of N₂ gas at 77 K, showing typical type-I sorption isotherms, characteristics of microporous materials (Fig. 2a). Brunauer-Emmett-Teller (BET) surface areas were estimated by applying BET equation, and pore volumes were calculated from the maximum amount of N₂ adsorbed. From the N₂ adsorption isotherms measured at 77 K, BET surface areas (pore volumes) were found to be 2243 m² g⁻¹ (0.8943 cm³ g⁻¹), 2314 m² g⁻¹ (0.9158 cm³ g⁻¹), and 2232 m² g⁻¹ (0.8774 cm³ g⁻¹) for **ZJNU-43a**, **ZJNU-44a** and **ZJNU-45a**, respectively (Table S1). The results indicate that the three compounds have almost the same porosities even after the number of nitrogen atoms is increased or the orientation of nitrogen atom is shifted.

Selective CO₂ adsorption

The successful incorporation of nitrogen heteroatom-containing building blocks into isostructural frameworks opens up a great opportunity toward delineating the relationships

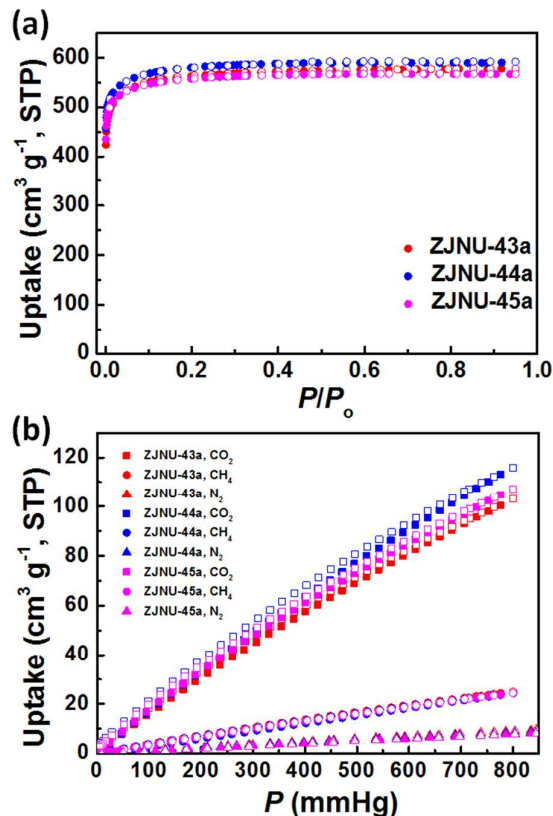


Fig. 2 (a) N₂ adsorption-desorption isotherms of **ZJNU-43a** (red), **ZJNU-44a** (blue) and **ZJNU-45a** (magenta) at 77 K. Solid and open symbols represent adsorption and desorption, respectively. (b) CO₂, CH₄, and N₂ sorption isotherms of **ZJNU-43a** (red), **ZJNU-44a** (blue) and **ZJNU-45a** (magenta) at 296 K. Solid and open symbols represent adsorption and desorption, respectively.

between the accessibility of nitrogen sites and gas adsorption performance. To investigate selective CO₂ adsorption properties of the three MOFs, single-component CO₂, CH₄ and N₂ gas sorption experiments were systematically carried out at 273 K and 296 K up to 1 atm accordingly (Fig. S5-7). As shown in Fig. 2b, the CO₂ isotherms are completely reversible, indicating the fast adsorption and desorption kinetics. At 296 K, **ZJNU-43a** bearing the uncoordinated nitrogen atoms at alpha (α) position in the spacer of the bridging ligands takes up CO₂ of 103 cm³ (STP) g⁻¹ under 1 atm. Interestingly, when nitrogen atom is shifted from α to beta (β) position, the resulting MOF **ZJNU-44a** shows a significant increase in CO₂ uptake capacity reaching 116 cm³ (STP) g⁻¹ at the same conditions. Furthermore, even though the number of the uncoordinated nitrogen atoms at the α position is increased from one to two, the resultant MOF **ZJNU-45a** adsorbs much lower amounts of CO₂ (107 cm³ (STP) g⁻¹) than **ZJNU-44a**. Compared to **ZJNU-43a** and **ZJNU-45a**, the significant increase in CO₂ uptake capacity observed in **ZJNU-44a** is believed to stem from the uncoordinated nitrogen atoms pointing to the pore and thus being more easily accessible toward the incoming CO₂ gas molecules. These results indicate that the less blocked nitrogen site is beneficial for enhancing CO₂ adsorption amount.

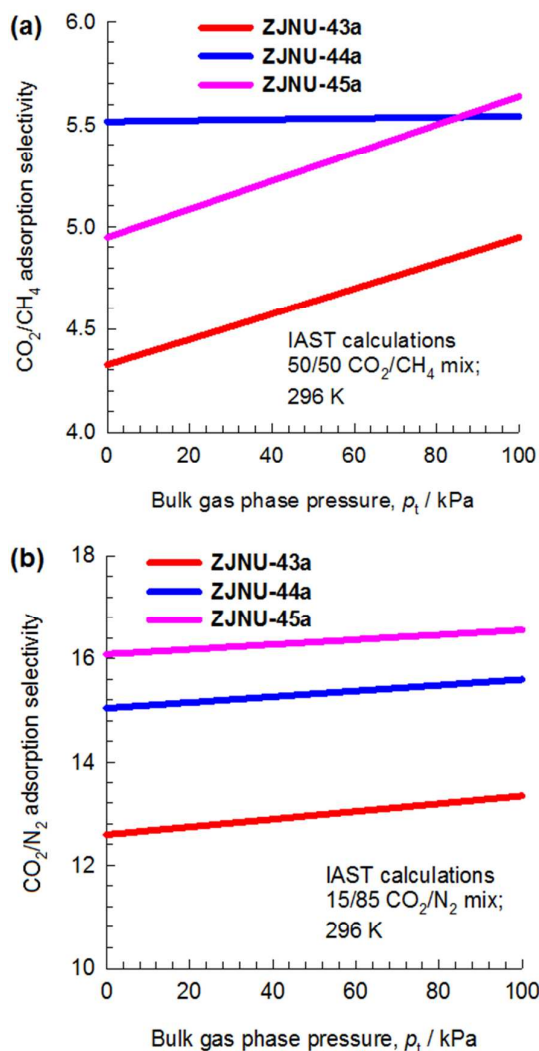


Fig. 3 Calculations using Ideal Adsorbed Solution Theory (IAST) of Myers and Prausnitz⁷ for adsorption selectivities for (a) 50/50 CO₂/CH₄, and (b) 15/85 CO₂/N₂ gas mixtures maintained at isothermal conditions at 296 K in **ZJNU-43a** (red), **ZJNU-44a** (blue) and **ZJNU-45a** (magenta).

Most significantly, the three MOFs adsorbed much more CO₂ gas than CH₄, and N₂ (Fig. 2b), indicating the potential for selective CO₂ capture. Since the Ideal adsorbed Solution Theory (IAST) method⁷ has been shown to predict well mixed gas behaviour in MOFs from single-component isotherms,⁸ we employed it to calculate the adsorption selectivities and CO₂ uptake capacities of the three MOFs for the separation of the following two binary gas mixtures: 50/50 CO₂/CH₄ and 15/85 CO₂/N₂. These mixtures mimic natural gas purification and post-combustion capture applications, respectively. Fig. 3a presents the values of adsorption selectivities as a function of the bulk pressure for 50/50 CO₂/CH₄ gas mixtures maintained under isothermal conditions at 296 K in the three MOFs. It can be seen that **ZJNU-44a** and **ZJNU-45a** have much higher selectivity towards CO₂ than **ZJNU-43a** in the entire pressure range measured. **ZJNU-44a** exhibits higher selectivity towards

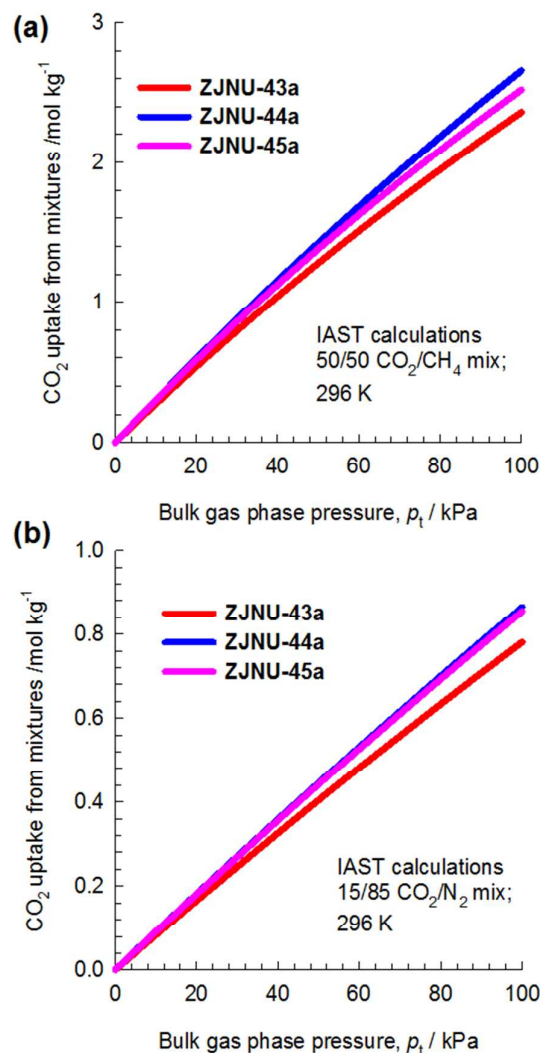


Fig. 4 Calculations using Ideal Adsorbed Solution Theory (IAST) of Myers and Prausnitz⁷ for uptake of CO₂ from (a) 50/50 CO₂/CH₄, and (b) 15/85 CO₂/N₂ gas mixtures maintained at isothermal conditions at 296 K in **ZJNU-43a** (red), **ZJNU-44a** (blue), and **ZJNU-45a** (magenta).

CO₂ than **ZJNU-45a** in the pressure below 80 kPa. The CO₂/CH₄ adsorption selectivities of **ZJNU-44a** are *ca.* 5.5, which is similar to those observed in amine-substituted MOFs IRMOF-1(NH₂)₄ where the selectivity ranges from 5 to 6.⁹ Fig. 3b presents the values of adsorption selectivities as a function of the bulk pressure for 15/85 CO₂/N₂ gas mixtures maintained under isothermal conditions at 296 K in the three MOFs. **ZJNU-45a** exhibits the highest selectivity towards CO₂ for adsorption from 15/85 CO₂/N₂ gas mixtures.

Besides adsorption selectivity, uptake capacity is equally important for a MOF applied as a gas separation material. Fig. 4a, and 4b present IAST calculations for CO₂ uptakes from (a) 50/50 CO₂/CH₄, and (b) 15/85 CO₂/N₂ gas mixtures maintained at isothermal conditions at 296 K in **ZJNU-43a**, **ZJNU-44a**, and **ZJNU-45a**. For both mixtures, the lowest uptake of CO₂ is with **ZJNU-43a**.

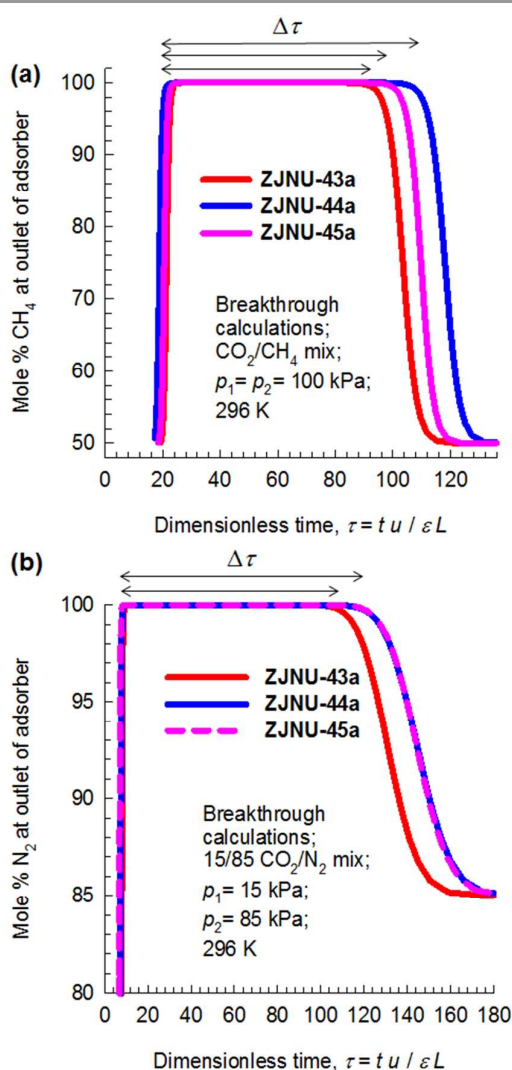


Fig. 5 (a) Comparison of the % CH₄ exiting the adsorber packed with **ZJNU-43a**, **ZJNU-44a**, and **ZJNU-45a** fed with 50/50 CO₂/CH₄ gas mixtures at 200 kPa total pressure and 296 K. (b) Comparison of the % N₂ exiting the adsorber packed with **ZJNU-43a**, **ZJNU-44a**, and **ZJNU-45a** fed with 15/85 CO₂/N₂ gas mixtures at 100 kPa total pressure and 296 K.

The combination of higher adsorption selectivity and higher uptake capacity of CO₂ is most desirable and leads to enhanced separations in fixed beds. On the basis of the IAST calculations presented in Fig. 3 and Fig. 4, we should expect the separation performance of **ZJNU-43a** to be poorer than that of **ZJNU-44a** and **ZJNU-45a**. To confirm this expectation, we performed transient breakthrough simulations using the simulation methodology described in the literature.^{8a, 10} For the breakthrough simulations, the following parameter values were used: length of packed bed, $L = 0.3$ m; voidage of packed bed, $\varepsilon = 0.4$; superficial gas velocity at inlet, $u = 0.04$ m s⁻¹; see schematic in Fig. S8. The transient breakthrough simulation results are presented in terms of a dimensionless time, τ , defined by dividing the actual time, t , by the characteristic time, $L\varepsilon/u$.

In natural gas purification processes, the primary objective is to produce CH₄ with a specified purity level, which is typically 500 ppm CO₂, i.e. 0.05 mole % CO₂. Let us compare the productivities of pure CH₄ that fulfils the specified impurity level for CO₂. Fig. 5a presents a comparison of the mole% CH₄ exiting the adsorber packed with **ZJNU-43a**, **ZJNU-44a**, and **ZJNU-45a** fed with 50/50 CO₂/CH₄ gas mixtures at 200 kPa total pressure and 296 K. During the time intervals, $\Delta\tau$, 99.95%+ pure CH₄ can be produced. From the comparison presented in Fig. 5a, we conclude that the productivity of 99.95%+ pure CH₄ is highest with **ZJNU-44a**, and lowest with **ZJNU-43a**. This fulfils the expectations on the basis of the IAST calculations of adsorption selectivities and uptake capacities in the foregoing section.

Next, we compare separation of 15/85 CO₂/N₂ gas mixtures, which is relevant for CO₂ capture from flue gases. Fig. 5b presents a comparison of the mole% N₂ exiting the adsorber packed with **ZJNU-43a**, **ZJNU-44a**, and **ZJNU-45a** fed with 15/85 CO₂/N₂ gas mixtures at 100 kPa total pressure and 296 K. N₂ with a purity of 99.95% can be produced during the time intervals, $\Delta\tau$, as indicated in Fig. 5b. On the basis of the results, we conclude that the productivities of pure N₂ with a purity of 99.95% with **ZJNU-44a**, and **ZJNU-45a** are comparable, and higher than that with **ZJNU-43a**.

Taken together, IAST and simulated breakthrough analyses indicated that **ZJNU-44a** bearing much more easily accessible nitrogen sites outperform the other two MOFs for the separation of 50/50 CO₂/CH₄ and 15/85 CO₂/N₂ gas mixtures, indicating that the accessibility of nitrogen sites play much more crucial role.

Quantum Chemical Calculations

As discussed above, experimental data indicate that the MOF material **ZJNU-44a** has higher adsorption loading for CO₂ than **ZJNU-43a** and **ZJNU-45a**. However, the adsorption mechanism still remains unclear. The vdW corrected DFT-D2 method have been proved to be an effective tool to probe the occupation sites and orientations of CO₂ molecule at various sites inside the framework, allowing us to better understand the adsorption mechanism. Therefore, we performed calculations to obtain binding energies of CO₂ starting from various configurations, and several typical occupation sites are obtained and listed in Fig. 6. The binding energy is calculated as:

$$E_b = E_{\text{gas/MOF}} - E_{\text{gas}} - E_{\text{MOF}}$$

where $E_{\text{gas/MOF}}$, E_{gas} , and E_{MOF} represent the energies for CO₂ adsorbed **ZJNU-43** (**44**, **45**), isolated CO₂ molecule, and pure **ZJNU-43** (**44**, **45**) material, respectively. Three typical adsorption sites (triangular window site A, open metal site B, and N adsorption site C) are shown in Fig. 6, as well as their binding energies. Not surprisingly, the triangular window site (site A) for each material has a very strong adsorption affinity for CO₂ molecule. The calculated E_b values for **ZJNU-43**, **44**, and **45** are almost the same, i.e., -25.1, -26.1, and -26.1 kJ mol⁻¹, respectively, which is due to their very similar chemical environment at the triangular window sites. The distances

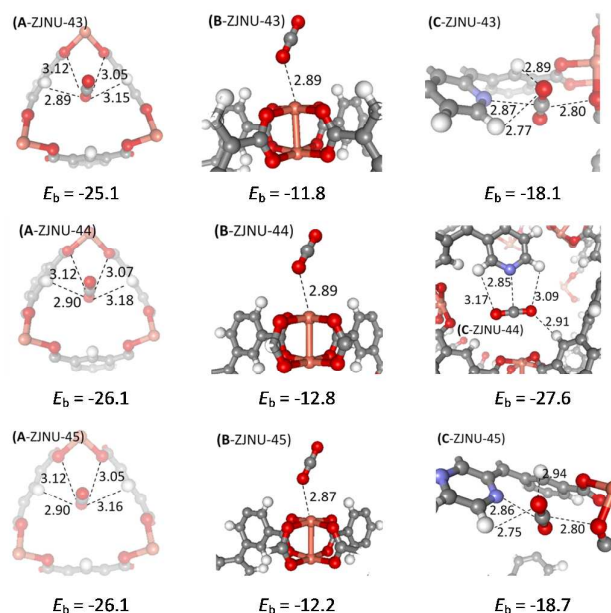


Fig. 6 Three optimized structures representing the typical adsorption sites for CO₂ in ZJNU-43, ZJNU-44, and ZJNU-45 are shown, as well as several hydrogen bond lengths and DFT-D2 computed binding energy for each configuration. The units for bond distance and binding energy are Å and kJ mol⁻¹, respectively. A, B, and C represent window site, open metal site, and N adsorption site, respectively. The O, H, C, Cu, N atoms are represented with red, white, grey, brown, and blue balls, respectively.

between CO₂ and the atoms on the framework (e.g., O and H atoms, see Fig. 6) surrounding the window have been listed in Fig. 6, and we conclude that the CO₂ orientation at site A in the three MOF materials are almost the same. For each material, the open metal site (site B) has a much lower binding energy compared to the site A. For example, the E_b of CO₂ at site B in ZJNU-43 (structure B-ZJNU-43 in Fig. 6) is -11.8 kJ mol⁻¹, much smaller than the value of -25.1 kJ mol⁻¹ for structure A-ZJNU-43. Our calculations show that the binding energies of CO₂ at the same open metal site in ZJNU-44 and ZJNU-45 are -12.8 and -12.2 kJ mol⁻¹, respectively, very close to -11.8 kJ mol⁻¹ in ZJNU-43. It is reasonable that three MOF materials have almost the same binding energies for CO₂ adsorption at the sites A and B since the environment of the adsorption sites are the same. Therefore, we speculate that the CO₂ binding energies at the open N sites are different.

The open N sites in the three MOF materials have different environment, especially for ZJNU-44, where the open N is more accessible for gas molecule occupation, while the other two materials, ZJNU-43 and ZJNU-45 have the same N orientations. As shown in Fig. 6, the CO₂ molecule is trapped in a very narrow window in structures C-ZJNU-43 and C-ZJNU-45, forming many hydrogen bonding between CO₂ and the open N, H and O atoms on the framework. In structure C-ZJNU-43, there are several weak bonding such as N^{δ-}C (CO₂) distance of 2.87 Å, C (CO₂)-O distance of 2.80 Å, and several hydrogen bonding O (CO₂)...H bonding of 2.77 and 2.89 Å. The calculated binding energy at this site is about -18.2 kJ mol⁻¹, much stronger than that at open metal site, suggesting this is also an important adsorption site for CO₂ molecule. In contrast, in

ZJNU-44a framework, the N site points to the pore and thus is completely available for occupation. The optimized structure C-ZJNU-44 shows that the CO₂ molecule parallelly bridges to the organic ligand, forming three weak bonding, C (CO₂)-N, C (CO₂)-H, and C (CO₂-H) with distances of 2.85, 3.09 and 3.17 Å, respectively. Also, the O (CO₂) atom forms a hydrogen bonding with H atom surrounding the pore with a distance of 2.91 Å. Surprisingly, the calculated E_b is -27.6 kJ mol⁻¹, even larger than the E_b value of -26.1 kJ mol⁻¹ at the triangular window site, and also much larger than those of -18.1 and -18.7 kJ mol⁻¹ in C-ZJNU-43 and C-ZJNU-45, respectively. Comparing to the N at α site, the N at more open β site prevails on CO₂ adsorption, and thus well explains the relatively larger adsorption loading in ZJNU-44. Furthermore, the double N sites in ZJNU-45 leads to more available sites for CO₂ adsorption than ZJNU-43, which is in well accordance with the relatively larger CO₂ loading for ZJNU-45. Our calculations confirm that rational design of the open N sites in the framework could effectively enhance CO₂ adsorption.

Conclusions

In summary, we have designed and developed three nitrogen-containing diisophthalate organic ligands, and used them to construct three isostructural MOFs featuring different number and orientation of nitrogen sites. Gas adsorption studies showed that ZJNU-44a exhibited higher CO₂ adsorption capacities than ZJNU-43a and ZJNU-45a despite their similar porosities. Furthermore, IAST and simulated breakthrough calculations showed that ZJNU-44a performed better than the other two MOF materials for selective CO₂/CH₄ and CO₂/N₂ separations. Comprehensive DFT calculations indicated that the higher CO₂ adsorption capacities and better separation performance of ZJNU-44a is attributed to much more easily accessible nitrogen atoms in ZJNU-44a, indicating that the accessibility of nitrogen atoms play much more crucial role. This work demonstrates that rationally design of open nitrogen sites will effectively enhance CO₂ adsorption, and thus provides useful information toward future design and synthesis of new MOF materials with improving CO₂ gas adsorption and separation capacity.

Experimental sections

Materials and Methods

All chemicals were purchased from commercial sources and used as received unless otherwise noted. MeOH (purity \geq 99.5%), EtOH (purity \geq 99.7%), CH₃CN (purity \geq 99.0%), toluene (purity \geq 99.5%), dioxane (purity \geq 99.5%) and DMF (purity \geq 98%) were obtained from Chinasun Specialty Products Co., Ltd. Pd(PPh₃)₄ (Pd, 9.2%) and DEF (purity \geq 99%) were obtained from Beijing HWRK Chem Co.,Ltd. Cs₂CO₃ (purity \geq 99%) were obtained from Shanghai Shaoyuan Co. Ltd. Cu(NO₃)₂·3H₂O (99.0~102.0%) and CuCl₂·2H₂O (\geq 99.0%) were obtained from Sinopharm Chemical Reagent Co., Ltd. 5,8-dibromoquinoline,¹¹ 5,8-dibromoisoquinoline,¹² 5,8-dibromoquinoxaline¹³ and

dimethyl 5-(pinacolboryl)isophthalate¹⁴ were synthesized according to the reported methods. Column chromatography was carried out on silica gel (100-200 mesh, Qingdao Haiyang Chemical Co., Ltd). Thin-Layer Chromatography (TLC) analyses were carried out using aluminium sheets pre-coated with silica gel 60 F254 purchased from Merck. The elemental analysis of C, H and N was performed on a Vario EL III CHNOS elemental analyser. Fourier Transform infrared spectroscopy (FTIR) spectra were recorded on a Nicolet 5DX FT-IR spectrometer with samples in KBr pellets. Thermogravimetric analysis (TGA) was performed on Netzsch STA 449C thermal analyzer with a heating rate of 5 °C min⁻¹ in a flowing nitrogen atmosphere (10 mL min⁻¹). ¹H NMR and ¹³C NMR spectra of the compounds were measured using a Bruke AVANCE 400 or 600 NMR spectrometer by dissolving the samples in DMSO-*d*₆ or CDCl₃. The chemical shifts were reported as parts per million (ppm) with use of residual solvent as an internal standard for ¹H (δCDCl₃ = 7.26 ppm, δDMSO-*d*₆ = 2.50 ppm) and ¹³C spectra (δCDCl₃ = 77.16 ppm, δDMSO-*d*₆ = 39.52 ppm). Coupling constants are reported in Hz. Resonance patterns were reported with the notations of s (singlet), d (doublet), t (triplet) and m (multiplet). Powder X-ray diffraction (PXRD) patterns were recorded on a Philips PW3040/60 automated powder diffractometer, using Cu-K_α radiation (λ = 1.542 Å) with a 2θ range of 5–40°. An ASAP 2020 surface area analyser was used to measure the adsorption behaviours of N₂, CH₄, and CO₂. Before gas adsorption measurement, the sample was activated by solvent exchange with dry acetone, followed by evacuation at 373 K until the degas rate reached 5 μmHg min⁻¹.

Single-crystal X-ray Crystallography

The X-ray diffraction data were collected on a Agilent supernova dual diffractometer with Cu-K_α radiation (λ = 1.54178 Å). Absorption corrections were performed using a multi-scan method. The structure was solved by direct methods with SHELXS-97¹⁵ and refined with a full-matrix least-squares technique within the SHELXL program package. The unit cell includes a large region of disordered solvent molecules, which could not be modelled as discrete atomic sites. We employed PLATON/SQUEEZE¹⁶ to calculate the diffraction contribution of the solvent molecules and, thereby, to produce a set of solvent-free diffraction intensities; structures were then refined again using the data generated. Hydrogen atoms of the ligand were calculated in ideal positions with isotropic displacement parameters, while H atoms of water molecules were not included in the final refinement. The crystal data and structure refinement results are listed in Table S6 in the Supporting Information. The CCDC reference numbers are 1052691, 1052692, and 1055566 for **ZJNU-43**, **ZJNU-44** and **ZJNU-45**, respectively. The supplementary crystallographic data for these compounds can be obtained free of charge from the Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.

Synthesis and Characterization of the Organic Linkers

5,5'-(quinolone-5,8-diyl)-diisophthalate (H₄L1): To a mixture of 5,8-dibromoquinoline (1.00 g, 3.48 mmol), dimethyl 5-(pinacolboryl)isophthalate (2.45 g, 7.67 mmol), Cs₂CO₃ (3.41 g, 10.45 mmol) and Pd(PPh₃)₄ (0.20 g, 0.18 mmol) were added dry dioxane (80 mL). The resulting mixture was stirred under reflux under a nitrogen atmosphere for 72 h. After removal of the solvents, CH₂Cl₂ (100 mL) and H₂O (100 mL) were added. The mixture was filtered. The organic phase was separated and the aqueous phase was extracted with CH₂Cl₂. The combined organic phase was washed with brine, dried over anhydrous MgSO₄ and filtered. Volatiles were removed by rato-evaporation under reduced pressure and the residue was recrystallized with toluene to afford the tetramethyl intermediate. Yield: 1.44 g, 2.80 mmol, 81%. ¹H NMR (CDCl₃, 400.1 MHz) δ (ppm): 9.002 (dd, *J* = 1.6 Hz, 4.0 Hz, 1H), 8.831 (t, *J* = 1.6 Hz, 1H), 8.787 (t, *J* = 1.6 Hz, 1H), 8.639 (d, *J* = 1.6 Hz, 2H), 8.408 (d, *J* = 1.6 Hz, 2H), 8.193 (dd, *J* = 1.6, 8.8 Hz, 1H), 7.873 (d, *J* = 7.6 Hz, 1H), 7.646 (d, *J* = 7.2 Hz, 1H), 7.464 (dd, *J* = 4.0 Hz, 8.8 Hz, 1H), 4.016 (s, 6H), 4.003 (s, 6H).

To a suspension of the tetramethyl intermediate (1.44 g, 2.80 mmol) in THF (20 mL) and MeOH (20 mL) was added 6 M NaOH (20 mL, 120 mM). The resulting mixture was refluxed overnight. After removal of the solvents, the residue was dissolved in water, and acidified with conc. HCl under ice-water bath. The resulting precipitation was collected by filtration, and dried in vacuum at 70 °C, affording the target compound in a quantitative yield. ¹H NMR (DMSO-*d*₆, 600.1 MHz) δ (ppm): 8.989 (dd, *J* = 4.2, 1.2 Hz, 1H), 8.596 (t, *J* = 1.8 Hz, 1H), 8.548 (t, *J* = 1.8 Hz, 1H), 8.486 (d, *J* = 1.2 Hz, 2H), 8.273 (d, *J* = 1.8 Hz, 2H), 8.252 (dd, *J* = 1.2 Hz, 8.4 Hz, 1H), 7.970 (d, *J* = 7.8 Hz, 1H), 7.755 (d, *J* = 7.2 Hz, 1H), 7.619 (dd, *J* = 4.2 Hz, 8.4 Hz, 1H); ¹³C NMR (DMSO-*d*₆, 150.9 MHz) δ (ppm): 167.154, 166.854, 151.098, 145.580, 140.253, 139.763, 138.849, 138.531, 135.866, 134.859, 134.220, 132.346, 131.405, 130.401, 129.827, 129.285, 128.019, 126.564, 122.699.

5,5'-(isoquinoline-5,8-diyl)-diisophthalate (H₄L2): To a mixture of 5,8-dibromoisoquinoline (0.50 g, 1.74 mmol), dimethyl 5-(pinacolboryl)isophthalate (1.23 g, 3.83 mmol), Cs₂CO₃ (1.70 g, 5.23 mmol) and Pd(PPh₃)₄ (0.10 g, 0.09 mmol) were added dry dioxane (60 mL). The resulting mixture was stirred under reflux under a nitrogen atmosphere for 72 h. After removal of the solvents, CH₂Cl₂ (100 mL) and H₂O (100 mL) were added. The mixture was filtered. The organic phase was separated and the water phase was extracted with CH₂Cl₂. The combined organic phase was washed with brine, dried over anhydrous MgSO₄ and filtered. Volatiles were removed by rato-evaporation under reduced pressure and the residue was purified using silica gel column chromatography with petroleum ether/CH₂Cl₂/ethyl acetate (2/2/1, v/v/v) as eluent, affording the tetramethyl intermediate. Yield: 0.67 g, 1.30 mmol, 75.0%; ¹H NMR (CDCl₃, 400.1 MHz) δ (ppm): 9.279 (s, 1H), 8.858 (t, *J* = 1.6 Hz, 1H), 8.839 (t, *J* = 1.6 Hz, 1H), 8.598 (t, *J* = 6.0 Hz, 1H), 8.454 (d, *J* = 1.6 Hz, 2H), 8.419 (d, *J* = 1.6 Hz, 2H), 7.773 (d, *J* = 7.2 Hz, 1H), 7.663 (t, *J* = 7.2 Hz, 2H), 4.020 (s, 6H), 4.016 (s, 6H).

To a suspension of the tetramethyl intermediate (0.67 g, 1.30 mmol) in THF (20 mL) and MeOH (20 mL) was added 6 M NaOH (20 mL, 120 mM). The resulting mixture was refluxed

overnight. After removal of the solvents, the residue was dissolved in water, and acidified with conc. HCl under ice-water bath. The precipitation was collected by filtration, and dried in vacuum at 70 °C to afford the target compound in a quantitative yield. ¹H NMR (DMSO-*d*₆, 600.1 MHz) δ (ppm): 9.195 (s, 1H), 8.603 (t, *J* = 1.8 Hz, 1H), 8.589 (t, *J* = 1.8 Hz, 1H), 8.577 (d, *J* = 6.0 Hz, 1H), 8.327 (d, *J* = 1.8 Hz, 2H), 8.280 (d, *J* = 1.2 Hz, 2H), 7.907 (d, *J* = 7.2 Hz, 1H), 7.777 (d, *J* = 7.2 Hz, 1H), 7.716 (d, *J* = 6.0 Hz, 1H); ¹³C NMR (DMSO-*d*₆, 150.1 MHz) δ (ppm): 166.815, 150.529, 144.112, 139.416, 139.111, 138.842, 137.187, 134.934, 134.788, 134.063, 132.398, 132.350, 131.705, 130.043, 129.906, 129.019, 126.360, 118.320.

5,5'-(quinoxaline-5,8-diyl)-diisophthalate (H₄L3): To a mixture of 5,8-dibromoquinoxaline (0.29 g, 0.99 mmol), dimethyl 5-(pinacolboronyl)isophthalate (0.70 g, 2.18 mmol), Cs₂CO₃ (0.97 g, 2.98 mmol) and Pd(PPh₃)₄ (0.06 g, 0.05 mmol) were added dry dioxane (40 mL). The resulting mixture was stirred under reflux under a nitrogen atmosphere for 72 h. After removal of the solvents, CH₂Cl₂ (40 mL) and H₂O (40 mL) were added. The mixture was filtered. The organic phase was separated and the water phase was extracted with CH₂Cl₂. The combined organic phase was washed with brine, dried over anhydrous MgSO₄ and filtered. Volatiles were removed by evaporation under reduced pressure and the residue was recrystallized with toluene to afford the tetramethyl intermediate. Yield: 0.39 g, 0.076 mmol, 77%. ¹H NMR (CDCl₃, 600.1 MHz) δ (ppm): 8.957 (s, 2H), 8.817 (t, *J* = 1.8 Hz, 2H), 8.620 (d, *J* = 1.8 Hz, 4H), 7.992 (s, 2H), 4.019 (s, 12H).

To a suspension of the tetramethyl intermediate (0.39 g, 0.076 mmol) in THF (20 mL) and MeOH (20 mL) was added 6 M NaOH (20 mL, 120 mM). The resulting mixture was refluxed overnight. After removal of the solvents, the residue was dissolved in water, and acidified with conc. HCl under ice-water bath. The precipitation was collected by filtration, and dried in vacuum at 70 °C to afford the target compound in a quantitative yield. ¹H NMR (DMSO-*d*₆, 400.1 MHz) δ (ppm): 9.035 (s, 2H), 8.555 (t, *J* = 1.6 Hz, 2H), 8.479 (d, *J* = 1.6 Hz, 4H), 8.088 (s, 2H); ¹³C NMR (DMSO-*d*₆, 100.6 MHz) δ (ppm): 167.034, 145.967, 140.408, 138.960, 138.853, 135.809, 131.614, 130.941, 129.596.

Synthesis and Characterization of the MOFs

ZJNU-43: A mixture of the organic linker H₄L1 (5.0 mg, 10.93 μmol) and Cu(NO₃)₂·3H₂O (15.0 mg, 62.10 μmol) was dissolved into a mixed solvent of DMF, ethanol and H₂O (1.5 mL / 0.5 mL / 0.08 mL) in a screw-capped vial (20 mL). After 80 μL of 6 M HCl were then added, the vial was capped and heated at 353 K for 120 h. Blue rhombic crystals were obtained in 63% yield.

ZJNU-43 can be best formulated as [Cu₂L1(H₂O)₂]₂·3DMF·2C₂H₅OH·4H₂O on the basis of single-crystal X-ray diffraction structure determination, TGA and microanalysis. Selected FTIR (KBr, cm⁻¹): 1655, 1637, 1630, 1502, 1439, 1387, 1369, 1302, 1254, 1097, 1049, 918, 862, 777, 756, 731, 661, 494; anal. for C₃₈H₅₆Cu₂N₄O₁₉, calcd: C, 45.64%, H, 5.64%, N, 5.60%; found: C, 45.59%, H, 5.57%, N, 5.55%.

ZJNU-44: A mixture of the organic linker H₄L2 (5.0 mg, 10.93 μmol) and CuCl₂·2H₂O (10.0 mg, 58.66 μmol) was dissolved into a mixed solvent of DMF, acetonitrile and H₂O (1.5 mL / 0.5 mL / 0.08 mL) in a screw-capped vial (20 mL). After 50 μL of 6 M HCl were then added, the vial was capped and heated at 353 K for 72 h. Blue rhombic crystals were obtained in 53% yield. **ZJNU-44** can be best formulated as [Cu₂L2(H₂O)₂]₂·3DMF·3CH₃CN·3H₂O on the basis of single-crystal X-ray diffraction structure determination, TGA and microanalysis. Selected FTIR (KBr, cm⁻¹): 1655, 1570, 1439, 1413, 1373, 1306, 1254, 1099, 1053, 777, 756, 731, 694, 661, 492; anal. for C₄₀H₅₁Cu₂N₇O₁₆, calcd: C, 47.43%, H, 5.07%, N, 9.68%; found: C, 47.39%, H, 5.15%, N, 9.54%.

ZJNU-45: A mixture of the organic linker H₄L3 (5.0 mg, 10.91 μmol) and Cu(NO₃)₂·3H₂O (15.0 mg, 62.10 μmol) was dissolved into a mixed solvent of DMF, methanol and H₂O (1.5 mL / 0.5 mL / 0.08 mL) in a screw-capped vial (20 mL). 50 μL of 6 M HCl were then added. The vial was capped and heated at 363 K for 48 h. Blue rhombic crystals were obtained in 60% yield. **ZJNU-45** can be best formulated as [Cu₂L3(H₂O)₂]₂·3DMF·3MeOH·3H₂O on the basis of single-crystal X-ray diffraction structure determination, TGA and microanalysis. Selected FTIR (KBr, cm⁻¹): 1655, 1578, 1439, 1419, 1383, 1362, 1298, 1254, 1101, 1049, 777, 756, 729, 488; anal. for C₃₆H₅₃Cu₂N₅O₁₉, calcd: C, 43.81%, H, 5.41%, N, 7.10%; found: C, 43.79%, H, 5.49%, N, 6.91%.

Fitting of Pure Component Isotherms

The measured experimental data on excess loadings, *q*_{excess}, of the pure components CO₂, CH₄, and N₂ in **ZJNU-43a**, **ZJNU-44a**, and **ZJNU-45a**, were first converted to absolute loadings, *q*, using

$$q = q^{\text{excess}} + \frac{pV_{\text{pore}}}{ZRT} \quad (1)$$

where *Z* is the compressibility factor. The Peng-Robinson equation of state was used to estimate *Z*. The accessible pore volumes are provided in Table S1.

The absolute component loadings were fitted with the Langmuir model

$$q = q_{\text{sat}} \frac{bp}{1 + bp} \quad (2)$$

with *T*-dependent parameter *b*

$$b = b_0 \exp\left(\frac{E}{RT}\right) \quad (3)$$

where *q* (mol kg⁻¹) is the adsorbed amount, *p* (Pa) is the equilibrium pressure, *q*_{sat} (mol kg⁻¹) is the monolayer adsorption capacity, and *b* (Pa⁻¹) is the Langmuir adsorption equilibrium constant. The Langmuir parameters for adsorption of CO₂ are provided in Table S2, Table S3, and Table S4 for **ZJNU-43a**, **ZJNU-44a** and **ZJNU-45a**, respectively.

Isosteric Heat of Adsorption

The isosteric heat of adsorption, *Q*_{st}, was determined using the pure-component isotherm fits using the Clausius-Clapeyron equation, defined as

$$Q_{st} = RT^2 \left(\frac{\partial \ln p}{\partial T} \right) \quad (4)$$

where p (Pa) is the pressure, T (K) is the temperature, R is the gas constant, and q (mol kg⁻¹) is the adsorption amount.

IAST Calculations of Adsorption Selectivities and Uptake Capacities

The selectivity of preferential adsorption of component 1 over component 2 in a mixture containing 1 and 2, perhaps in the presence of other components too, can be formally defined as

$$S_{ads} = \frac{q_1/q_2}{p_1/p_2} \quad (5)$$

In equation (5), q_1 and q_2 are the absolute component loadings of the adsorbed phase in the mixture. These component loadings are also termed the uptake capacities. We calculate the values of q_1 and q_2 using the Ideal Adsorbed Solution Theory (IAST) of Myers and Prausnitz.⁷

Quantum Chemical Calculations

All of the periodic density functional theory (DFT) calculations were performed in Vienna ab initio simulation package with version of vasp.5.3.3.¹⁷ The van der Waals (vdW) corrected DFT method, DFT-D2,¹⁸ was employed to capture the weak vdW forces between CO₂ and the three materials. The Brillouin zone was sampled with gamma point only, which is sufficient for the calculations of CO₂ binding energies since the values are almost unchanged by increasing Monkhorst-Pack grids¹⁹ in our test calculations. In all of our calculations a planewave energy cutoff of 500 eV was employed. The experimental unit cells of **ZJNU-43**, **ZJNU-44**, and **ZJNU-45** are reduced to primitive cells (**ZJNU-43**: $a = b = c = 16.79 \text{ \AA}$, $\alpha = \beta = \gamma = 67.27^\circ$; **ZJNU-44**: $a = b = c = 16.77 \text{ \AA}$, $\alpha = \beta = \gamma = 67.57^\circ$; **ZJNU-45**: $a = b = c = 16.75 \text{ \AA}$, $\alpha = \beta = \gamma = 67.28^\circ$) for the sake of computational efficiency. The lattice constants are fixed while all of the atoms were allowed to relax using DFT-D2 method. Note that it is reasonable to fix the lattice constants in our calculations since the relaxation of the lattice constants only slightly changes the values, which should have negligible effect on the CO₂ binding energies. For the optimizations of adsorbates/**ZJNU-43** (**44**, **45**), all of the atoms were relaxed until the force on each ion was less than 0.01 eV Å⁻¹.

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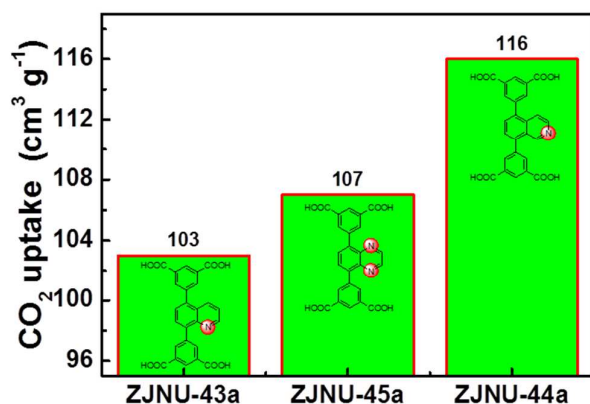
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TOC



Three isostructural metal-organic frameworks exhibit different CO₂ adsorption depending on the number and orientation of nitrogen sites in the frameworks, and the accessibility of nitrogen sites plays much more crucial role in enhancing CO₂ adsorption.