# Enhancement of $CO_2/N_2$ selectivity in a metal-organic framework by cavity modification

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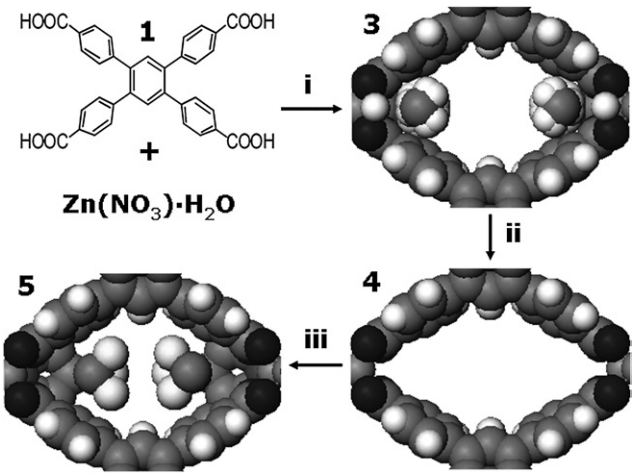
**Post-synthesis modification of a MOF by replacing coordinated solvent molecules with highly polar ligands leads to considerable enhancement of $CO_2/N_2$ selectivity.**

Concerns about greenhouse gas concentrations in the atmosphere are a strong motivation to reduce $CO_2$ emissions from industrial processes. Burning of fossil fuel to generate electricity is a major source of $CO_2$ in the atmosphere, but the capture and sequestration of $CO_2$ from flue gas emissions of power plants is a daunting challenge.[1] Flue gases consist of nitrogen (typically more than two-thirds), $CO_2$, water vapor, oxygen, and minor components such as carbon monoxide, nitrogen oxides, and sulfur oxides. Several technologies have been considered for $CO_2$ separation from nitrogen-rich streams, including absorption, membranes, and adsorption separations.[2] Adsorption-based separations such as pressure-swing adsorption (PSA) are attractive due to their low energy requirements. However, an adsorbent with high $CO_2$ selectivity and capacity is essential in PSA processes for $CO_2$ separations.[3]

Recently, metal-organic frameworks (MOFs) have attracted great interest as adsorbents due to their extremely high surface areas, low densities, and uniform, tailorable pore structures. These properties make them promising candidates for adsorption separations, as well as gas storage, catalysis, and sensing.[4] Efforts to tune the pore size and provide desired surface chemistries in MOFs can be divided into two main strategies: (1) direct assembly of new MOFs from particular metal nodes and organic linkers and (2) post-synthesis modification of pre-constructed robust *precursor* MOFs. In the direct-assembly strategies, certain desirable functional groups may be hard to incorporate into MOFs, either because of thermal instability under MOF synthesis conditions or due to competitive reaction with intended framework components.[5] Additionally, it is known that both the connectivity and the degree of catenation can be very sensitive to small changes in the organic ligands for the synthesis of MOFs through direct assembly.[6] Because of these complexities, post-synthesis modification strategies are emerging as an alternative method for tailoring MOFs toward specific applications. Several reports on this strategy have appeared recently.[7]

Recently, Farha *et al.* proposed a new MOF strut (4,4′,4″,4‴-benzene-1,2,4,5-tetrayltetrabenzoic acid, **1**, Scheme 1) and used it to synthesize a 3D non-catenated Zn-paddlewheel MOF




**Scheme 1** Preparation methods of **3**, **4**, and **5**. i) DMF/80 °C/24 h, followed by evacuation while heating at 100 °C; ii) evacuation while heating at 150 °C; iii) soak in a solution of $CHCl_3$/4-(trifluoromethyl)pyridine, followed by evacuation while heating at 100 °C.

$[Zn_2(\mathbf{1})(DMF)_2]_n(DMF)_m$ (**2**) [DMF = dimethylformamide].[5] The single-crystal X-ray structure of **2** indicates that two DMF molecules are coordinated to the axial sites of the $Zn(II)_2$ units. Farha *et al.* showed that by heating **2** at 100 °C under vacuum for 24 h, free non-coordinated DMF molecules (designated $(DMF)_m$) were removed and a partially evacuated MOF, **3**, was prepared. In **3**, the coordinated DMF molecules remain in the pores. A DMF-free version, **4**, was obtained by heating **2** at 150 °C under vacuum for 24 h. In this case, all free and coordinated DMF molecules were removed and open metal sites were formed. By immersing **4** in $CHCl_3$ solutions of each of several pyridine derivatives (py-R), a collection of py-R-modified MOFs was obtained. $^1$H NMR and TGA results showed the formation of highly porous cavity-modified MOFs, $[Zn_2(\mathbf{1})(py\text{-}R)_2]_n$, as well as the coordinative binding of the py-R ligands.[5]

In this work, we compare adsorption in MOFs **3**, **4**, and **5**, where **5** is the py-$CF_3$ modified version of **4**, *i.e.* $[Zn_2(\mathbf{1})(py\text{-}CF_3)_2]_n$. Single-component adsorption isotherms for $CO_2$, $N_2$, and $CH_4$ were measured experimentally in all three MOFs. Then from the pure-component isotherms, the selectivities for $CO_2/N_2$ and $CO_2/CH_4$ mixtures were calculated using ideal adsorbed solution theory (IAST).[8] Many studies have shown that IAST can be used to successfully predict gas mixture adsorption in zeolites,[9–11] and recently the theory has been tested in MOFs using molecular simulations.[9,12,13]

MOFs **3**, **4**, and **5** form an interesting series for elucidating the effects of different framework features on adsorption capacity and selectivity. MOF **4** has open-metal sites, which are expected to enhance adsorption, especially for $CO_2$ and $N_2$, which are

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quadrupolar molecules. Similarly, the highly polar -$CF_3$ functional group was introduced into **5** with the intention of increasing $CO_2$ sorption. Finally, the pore sizes and surface areas of the three MOFs are different due to the cavity modification. These factors may also have a strong effect on adsorption and selectivity of $CO_2$, $N_2$, and $CH_4$. By comparing adsorption in the three MOFs, we can obtain information on the relative importance of open-metal sites, polar surface groups, pore size, and surface area.

The parent MOF material (**2**) was synthesized from a solvothermal reaction of **1** and $Zn(NO_3)_2 \cdot 6H_2O$ in DMF solution at 80 °C for 24 h. Then, **3** and **4** were obtained by heating this material at 100 °C and 150 °C, respectively. The py-$CF_3$ modified MOF (**5**) was prepared by immersing **4** in a $CHCl_3$ solution of the py-$CF_3$ ligand for 24 h (Scheme 1). The details are described elsewhere.[5] Surface areas were obtained from $CO_2$ isotherms measured at 273 K using the BET theory (Fig. 1 and Table 1). We also calculated the surface areas of **3**, **4**, and **5** geometrically[14] assuming that they all have the same framework structure as **2**. The excellent agreement between the BET and geometric surface areas provides indirect evidence that all three MOFs have essentially the same structure as **2**, with the main difference being the presence or absence of DMF or py-$CF_3$ at the open-metal sites.

Fig. 2 shows the adsorption isotherms of $CO_2$, $N_2$, and $CH_4$ at 298 K up to 18 bar, measured volumetrically on evacuated samples of **3**, **4**, and **5**. The detailed procedure can be found elsewhere.[13] In each sample, $CO_2$ is the most strongly adsorbed molecule due to its large quadrupolar moment. Also, $CH_4$ shows stronger adsorption than $N_2$ as already reported in all known sorbents. This is attributed to the higher polarizability of $CH_4$ ($26 \times 10^{-25}$ cm$^3$) vs. $N_2$ ($17.6 \times 10^{-25}$ cm$^3$).[3] Interestingly, it was impossible to measure $N_2$ isotherms for any of the three MOFs at 77 K, but the materials do take up $N_2$ at 298 K. This suggests that the pores of **3**, **4**, and **5** may be close to the kinetic diameter of $N_2$ (3.64 Å).[15] For such tightly constricted pores, a likely explanation is that $N_2$ molecules cannot enter the pores at 77 K due to large diffusional resistances, but at 298 K the additional thermal energy allows the molecules to overcome these resistances. Similar behavior has been reported in other studies.[16]

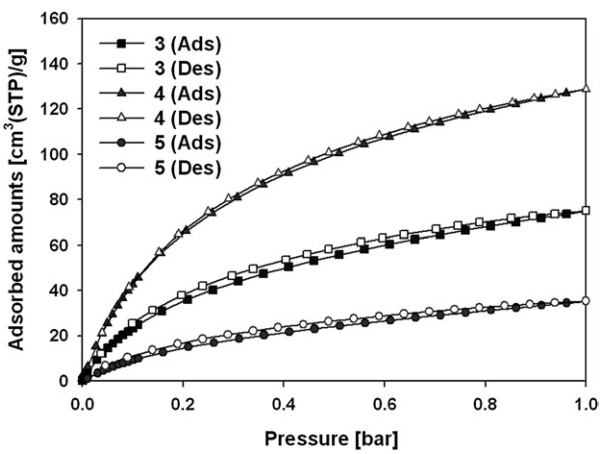


**Fig. 1** Adsorption and desorption isotherms of $CO_2$ in **3**, **4**, and **5** at 273 K.

**Table 1** Comparisons between the experimental surface areas and the calculated surface areas of **3**, **4**, and **5** (all units are m$^2$/g)

| | Experimental surface area | Calculated surface area |
|---|---|---|
| **3** | 800 | 769 |
| **4** | 1370 | 1805 |
| **5** | 390 | 454 |

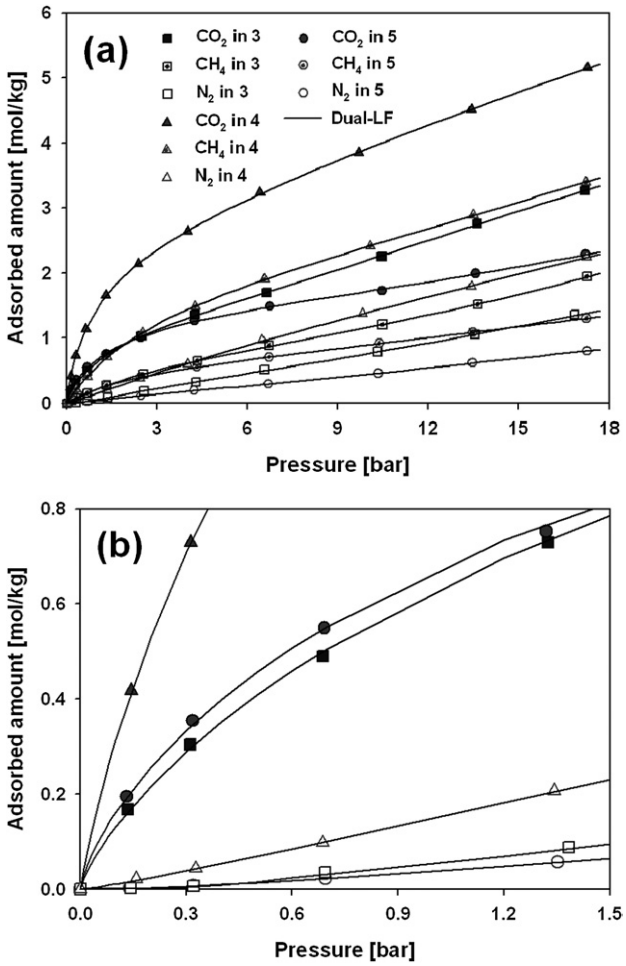


**Fig. 2** Adsorption isotherms of $CO_2$, $N_2$, and $CH_4$ in **3**, **4**, **5** at 298 K: (a) full pressure range, (b) low pressure range ($CH_4$ isotherms are omitted for clarity). Lines are fits to a dual-site Langmuir–Freundlich (Dual-LF) equation.[13]

None of the isotherms in Fig. 2 show saturation at 18 bar. For all gases, the order of the adsorbed amounts around 18 bar is as follows: **4** > **3** > **5** (Fig. 2a). This coincides with the order of the surface areas, in agreement with the notion that at intermediate loadings the amount adsorbed should correlate with the surface area.[17] At low pressures, adsorption is not expected to correlate with the surface area. Instead, adsorption should correlate with the strength of binding.[17] Here, we again find that **4** shows the highest adsorption of the three MOFs for all three gases (Fig. 2b), but this is presumably due to strong adsorption on the open-metal sites rather than the larger surface area of **4**. At low loading, the py-$CF_3$-modified MOF **5** adsorbs more $CO_2$ than **3** at 298 K, but less $N_2$ and $CH_4$. This selectivity difference is discussed below.

The selectivities of $CO_2/N_2$ and $CO_2/CH_4$ binary mixtures were predicted from the experimental single-component isotherms using IAST. Fig. 3a and b present the predicted selectivities for equimolar

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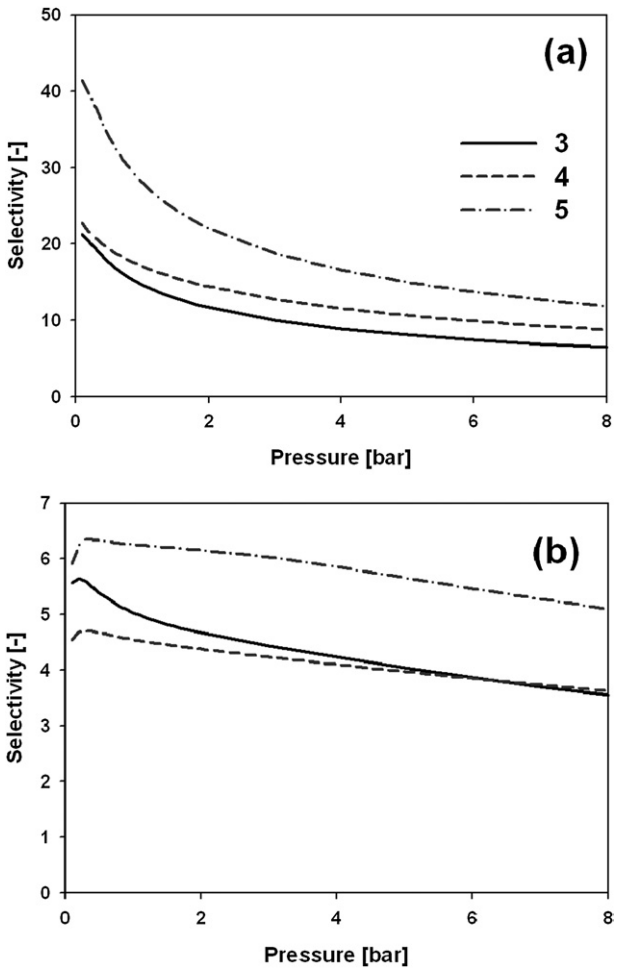


**Fig. 3** IAST selectivities of (a) $CO_2$ over $N_2$, and (b) $CO_2$ over $CH_4$ for equimolar binary mixtures in **3**, **4**, **5** at 298 K.

$CO_2/N_2$ and $CO_2/CH_4$ mixtures in **3**, **4**, and **5** as a function of total bulk pressure. The most remarkable point of Fig. 3 is the high $CO_2/N_2$ selectivity (~42) of **5** at low pressure. Throughout the entire pressure range, **5** exhibits larger $CO_2/N_2$ and $CO_2/CH_4$ selectivities than **3** and **4**. This can be explained by the following factors. First, the highly polar -$CF_3$ groups in **5** should be more attractive to $CO_2$ (large quadrupole moment, 13.4 C $m^2$) than $N_2$ (smaller quadrupole moment, 4.7 C $m^2$) or $CH_4$ (nonpolar).[18] Second, the more constricted pores of **5** should enhance the selectivity of the more strongly adsorbed $CO_2$ over $N_2$ and $CH_4$ due to the increased potential.[19]

Fig. 4 shows the $CO_2/N_2$ selectivities in **5** at different pressures and different mixture compositions predicted by IAST. The selectivity increases with decreasing pressure. Also, the selectivity increases as $y_{N2}$ approaches unity, but at zero coverage it does not depend on the gas composition. For the case of $y_{N2} = 0.85$, which is a typical composition for flue gas from power plants,[2] the selectivity is in the range of 25–45. In addition, the selectivity is high (30–37) at or slightly above atmospheric pressure, which is the pressure regime of interest for removing $CO_2$ from flue gas. For these conditions, the selectivity of **5** is higher than that of Cu-BTC (20–22 as predicted by molecular simulation), to our knowledge the largest previously reported for MOFs.[20] Even for equimolar mixtures of $N_2$ and $CO_2$, the selectivity

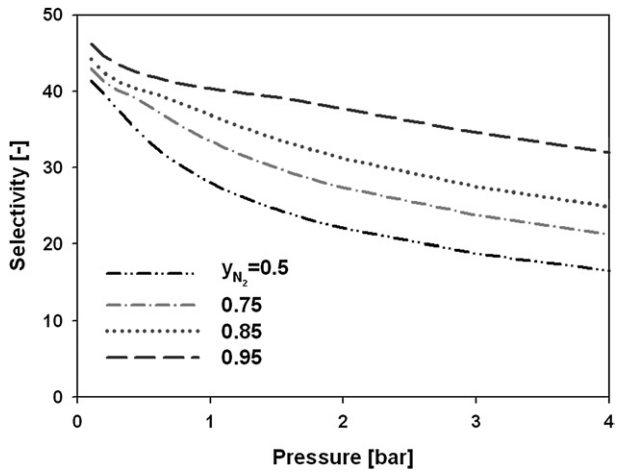


**Fig. 4** IAST selectivities of $CO_2$ over $N_2$ in **5** at different pressures and mixture compositions.

is fairly high (17–41) compared to reports for other MOFs: Cu-BTC (20–25)[20] and MOF-508b (4–6).[21] Moreover, these selectivities are considerably higher than the experimental $CO_2/N_2$ selectivities reported for zeolite and carbon adsorbents under similar conditions: zeolite 4A (19),[22] zeolite 13X (18),[22] activated carbon (15).[23] While the selectivity of **5** is high, the adsorption capacity for $CO_2$ is not as high as some other MOFs such as Cu-BTC, MOF-508b, MIL-101 and MIL-53.[20,21,24,25]

For PSA processes, the kinetics and reversibility of adsorption are also important. Adsorption of $CO_2$ was found to be completely reversible in **5** (Fig. 1), and a graph of the time evolution for $CO_2$ and $N_2$ adsorption in **5** at the first point of the isotherms (0.2 atm and 298 K) shows that the adsorption rate of $CO_2$ is much faster than that of $N_2$ (Fig. 5). This means that the selectivity of $CO_2$ over $N_2$ would increase even more if we considered the adsorption kinetics in addition to the adsorption equilibria. The fast and reversible adsorption of $CO_2$ in **5**, along with the high selectivity, indicate that this material is an attractive candidate for the adsorptive separation of $CO_2$ from $N_2$.

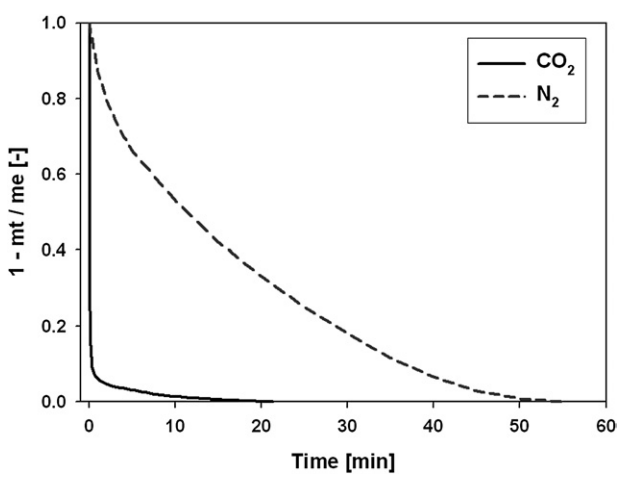


**Fig. 5** Adsorption rates of $CO_2$ and $N_2$ in **5** at 298 K (at the 1st adsorption points). *mt* is the amount adsorbed at time *t*, and *me* is the equilibrium amount adsorbed.

In summary, experimental isotherms and IAST calculations have shown that **5** is a promising material for $CO_2/N_2$ separations. In addition, they provide preliminary insight into the factors of most importance for adsorption selectivity of $CO_2$, $N_2$, and $CH_4$ mixtures in MOFs. Post-synthesis modification of MOFs by replacing coordinated solvent molecules with highly polar ligands or ligands featuring other chemical functionalities may be a powerful method for generating new sorbents for other difficult separations.

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