Amide and N-oxide functionalization of T-shaped ligands for isoreticular MOFs with giant enhancements in CO2 separation†

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By stepwise functionalization of a T-shaped ligand with amide and N-oxide groups, we obtained a MOF with drastically strengthened CO2–framework interactions, induced by a “open donor sites” (ODSs) effect, resulting in a high heat of adsorption and high CO2/CH4, CO2/CO2 and CO2/N2 separation selectivities at room temperature.

The CO2 capture and separation (CCS) process has caught public attention and is under urgent investigation in laboratories all over the world due to industrial demand.1 Nowadays, industrial scale CCS processes mostly use amine solvents as CO2 capture adsorbents,2 which suffer from high cost of regeneration, excessive corrosion and toxicity issues.3 In the past decade, newly emerged porous materials4 such as metal–organic frameworks (MOFs) have attracted great attention owing to their tailorable porosity, moderate CO2 affinity and suitable adsorption kinetics, and great efforts have been devoted to their potential applications in gas storage and separation,5 as well as in catalysis.6

In order to develop MOFs for efficient CO2 separation, some effective strategies have been applied. For example, modification of the pore surface by introducing functional groups, such as –CH3, –NO2, –NH2, –OH, –COOH,7 or exposed N sites,8 has been proven to allow for tuning of the polarity and acidity of the porous environment, thus offering higher affinity towards CO2 to boom adsorption amount and selectivity. Another successful approach to promote CCS by MOFs is to create so-called “open metal sites” (OMS, or coordinatively unsaturated sites, CUS), usually produced by removal of weakly coordinating solvents.9 However, removal of coordinating solvents in many instances would result in decomposition of the whole framework, or, the metal site might transform its coordination geometry to a thermodynamically more stable form instead of keeping the metal site open.10 Other effective methods include the use of flexible MOFs as well as MOFs with specific narrow pores.

Herein, we propose an alternative way to combine contributions from both bridging ligands and coordination sites. As shown in Fig. 1, we first prepare a T-shaped functional ligand11,12 to incorporate an amide (H2INIA). Furthermore, we introduce an N-oxide group as a charge variable coordination site (H2INOIA). The pyridyl N-oxide has been used to generate MOFs13 with magnetic14 and fluorescence properties.15 However, the adsorption properties endowed by this group have not been well studied,16 and its effect towards CO2 uptake has not been understood. Compared to the common pyridine-N donor, the N-oxide donor can bring charge-separated character and metal-binding variation to the coordination site. As seen from Fig. 1 and Fig. S1 (ESI†), the resulting O donor has two lone pairs of electrons, which can bind one metal in a bent fashion with a ∠M–O–N angle of ca. 120° and leave another lone pair of electrons to interact with the electrophilic atom of a guest molecule. Such unique charge-separated character, plus the electron-rich bent coordination of the N-oxide donor, may provide an enhanced affinity towards CO2 to match the distinct
electrophilicity of its C and O atoms (Fig. S1, ESI†). Therefore, the N-oxide donor might offer an alternative type of coordination site to capture CO$_2$, denoted here as “open donor sites” (ODSs), in comparison to the well-known OMS or CUS.

The structural model of MOFs based on T-shaped ligands and paddlewheel units has been previously reported by us and others and fully rationalized by Eddaoudi et al.\textsuperscript{11} as an effective MOF pillaring strategy. Through a ligand-to-axial approach,\textsuperscript{11c} 3D MOFs of rtl or ScD$_{0.33}$ topologies could be generated based on pillaring of the 2D edge transitive nets, sql and kmg, respectively. As expected, solvothermal reactions of Cu$^{2+}$ with H$_2$INIA and H$_2$INIOA afforded two isoreticular MOFs, LIFM-10 and LIFM-11 (LIFM: Lehn Institute of Functional Materials), respectively. Single crystal analyses verified their isostructures, with their asymmetric units containing one Cu$^{2+}$ and one ligand (Fig. 1, Fig. S1 and S2 and Tables S1 and S2, ESI†). Typically, every two Cu$^{2+}$ ions are chelated by four carboxylate groups from four different ligands to form a square paddlewheel Cu$_2$(O$_2$C)$_4$ cluster. The axial positions of the cluster are occupied by two pyridine-N (LIFM-10) or N-oxide O (LIFM-11) donors from another two ligands. Therefore, the whole coordination skeleton can be regarded as a 3D framework based on 2D kgm sheets comprised of 4-connected Cu$_2$(O$_2$C)$_4$ clusters, with pillars provided by ligand bridges. The T-shaped ligands serve as 3-connected nodes and the paddlewheel clusters as 6-connected nodes, thus generating a (3,6)-connected framework of ScD$_{0.33}$ topology, as calculated by Topos 4.0.\textsuperscript{17}

One unique structural feature in these two isoreticular MOFs is that the axial coordination of Cu$^{2+}$ by either the pyridine-N donor or the N-oxide donor is in a bent fashion (Fig. 1a). In LIFM-10 the pyridyl plane shows a strained bent angle of 152.5$^\circ$ with respect to the N–Cu bond, while in LIFM-11 the angle of 119.1$^\circ$ is natural due to metal–ligand bonding via one lone pair of electrons from the sp$^2$ O donor, which is important for interaction with CO$_2$ (vide infra). Furthermore, two types of cavities are formed: one is a 6-nuclear Cu-cage and the other a 12-nuclear Cu-cage (Fig. 1, diameters: 8 and 12 Å in LIFM-10; 9 and 12 Å in LIFM-11). These cages are aligned alternately in parallel to constitute 1D hourglass-shaped channels (Fig. 2a, ESI†), which afford considerable void spaces (59% in LIFM-10 and 60% in LIFM-11, as calculated by PLATON\textsuperscript{18}) for gas uptake.

The thermal stabilities tested by TG analyses revealed that a large amount of solvent could be removed by heating, and that the frameworks started to decompose at about 270 °C (Fig. S4 and S5, ESI†). The permanent porosity of the framework was confirmed by variable temperature powder X-ray diffraction (VT-PXRD) up to 260 °C (Fig. S6 and S7, ESI†). Activation of the samples was simply carried out by heating under vacuum at 150 °C (Fig. S8 and S9, ESI†), giving broadened PXRD peaks which indicate degradation of crystallinity but persistence of framework porosity. The crystals are stable in air, however, slight framework changes can be observed when monitoring the samples by XRD when immersed in water (Fig. S28 and S29, ESI†).

The N$_2$ sorption measurements for LIFM-10 and LIFM-11 at 77 K both show typical type-I adsorption isotherms (Fig. S10, ESI†), indicative of microporous gas uptake behaviors. Table 1 lists the experimental and simulated pore textural properties of two MOFs. It is noted that the experimental BET surface areas of both MOFs are slightly lower than the simulated ones, suggesting a little collapsing/blocking of pores during activation, especially for LIFM-11, which is in accordance with observations from PXRD (Fig. S9, ESI†). However, the final total pore volumes reach comparable values after N$_2$ uptake.

The CO$_2$ adsorption isotherms of two MOFs (Fig. S11 and S12, ESI†) reveal that they exhibit almost the same high CO$_2$ uptake capacity at 1 atm and 273 K: 129.5 mL g$^{-1}$ (20.3 wt%) for LIFM-10 and 129.6 mL g$^{-1}$ (20.3 wt%) for LIFM-11. However, as the temperature rises, the CO$_2$ storage capacity of LIFM-11 surpasses that of LIFM-10 (65.9 mL g$^{-1}$ vs. 78.0 mL g$^{-1}$ at 298 K). After carefully examining their CO$_2$ adsorption behaviors, we found that LIFM-11 performs better because of a more abrupt rise in the amount of CO$_2$ adsorbed at relatively low pressures (~0.1 atm, Fig. 2a inset). This obvious enhancement could be mainly attributed to the optimized interactions between CO$_2$ and the pore surface, which hints at the existence of high affinity adsorption sites contributed by N-oxide groups in LIFM-11 (vide infra).\textsuperscript{19}

On the basis of CO$_2$, CH$_4$, CO and N$_2$ isotherms measured at 298 K (Fig. 2a), the separation selectivities of CO$_2$ versus CH$_4$, N$_2$ and CO were calculated up to 1 atm using the ideal adsorption solution theory (IAST) based method (Fig. 3, Table 1, see ESI†).\textsuperscript{20,21}

![Image](https://via.placeholder.com/150)

**Fig. 2** (a) Gas adsorption isotherms at 298 K. Red: LIFM-11; blue: LIFM-10. Inset: enlarged CO$_2$ adsorption isotherms of LIFM-10 and LIFM-11 below 0.1 bar. (b) Comparison of CO$_2$/CH$_4$, CO$_2$/CO and CO$_2$/N$_2$ IAST selectivities of LIFM-10 and LIFM-11 with other MOFs under similar conditions.\textsuperscript{24}

### Table 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>Experimental $S_{BET}$ (m$^2$ g$^{-1}$)</th>
<th>$V_{t}$ (cc g$^{-1}$)</th>
<th>$D_f$ (Å)</th>
<th>Simulation $S_{BET}$ (m$^2$ g$^{-1}$)</th>
<th>$V_t$ (cc g$^{-1}$)</th>
<th>Initial enthalpy $Q_0$ (kJ mol$^{-1}$)</th>
<th>IAST selectivity</th>
<th>Virial selectivity</th>
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<tr>
<td>LIFM-10(Cu)</td>
<td>1550</td>
<td>0.64</td>
<td>6 × 6</td>
<td>1791</td>
<td>0.66</td>
<td>29</td>
<td>4.7–4.3</td>
<td>6.2–10.0</td>
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<tr>
<td>LIFM-11(Cu)</td>
<td>1176</td>
<td>0.68</td>
<td>5 × 5</td>
<td>1695</td>
<td>0.66</td>
<td>53</td>
<td>17.2–9.4</td>
<td>6.4–22.8</td>
</tr>
</tbody>
</table>

$^a$ Data at 298 K. $^b$ BET surface area. $^c$ Total pore volume. $^d$ Effective pore size. $^e$ CO$_2$/CH$_4$ = 50 : 50; CO$_2$/CO = 50 : 50; CO$_2$/N$_2$ = 15 : 85, 0–1 bar.
which predicts separation performances for 15/85: CO2/N2, 50/50: CO2/CH4 and 50/50: CO2/CO binary mixtures, mimicking those in natural gas upgrading, post-combustion capture and biogas purification processes. In general, the IAST selectivities for CO2/CH4 and CO2/N2 decrease slightly as the pressure increases. Surprisingly, the CO2/CO selectivity shows a rapid increase from the starting point at low pressure (up to ~0.1 atm). This means that CO may have abnormal uptake behavior at very low pressures. If only considering the starting values calculated by the IAST method, all IAST selectivities are closely comparable with those obtained by the Virial method (Tables 1, S4 and S5, Fig. S13–S22, ESI†), which are usually calculated for the zero coverage evaluations. Fig. 2b illustrates a comparison of the CO2 separation performances of LIFM-10 and LIFM-11 with some other MOFs evaluated by the IAST method under similar conditions.21 It is immediately clear that LIFM-11 shows outstanding selectivities for CO2/CH4 and CO2/N2 when compared with MOF-5, HKUST-1 and PCN-11 at room temperature and 1 atm. Meanwhile, it is noteworthy that the separation selectivities of LIFM-11 are significantly Improved in contrast to those of LIFM-10, e.g. more than 2-fold for CO2/CH4 and CO2/CO, and 5-fold for CO2/N2. This means that functionalization of the T-shaped ligand with a N-oxide group can remarkably enhance CO2 affinity towards the pore surface. A similar enhancement of CO2 selectivities over CH4 and N2 has been observed in porous MPM-1 by replacing Cl− with TiF6− anions.22 However, it should be noted that even exceptional CO2/CH4 and CO2/N2 selectivities have been achieved by strictly limiting the pore shape and size, or by introducing anionic interactions or chemisorbent-like behaviors,21,22 e.g. 231 for CO2/CH4 and 1818 for CO2/N2 in SIFSIX-Zn, 590 for CO2/N2 in [Cu(bcpm)H2O], and 182 for CO2/N2 in MgMOF-74. If using the Virial selectivity for comparison, LIFM-11 also surpasses known MOFs like MOF-5 (15.5 for CO2/CH4; 17.5 for CO2/N2),22c ZIF-78 (10.6 for CO2/CH4; 50.1 for CO2/N2),22b en-Cu-BTTri (44 for CO2/N2),22c and widely used industrial BPL activated carbon (3.8 for CO2/CH4; 20 for CO2/N2)24 under the same conditions, but could not reach the high values of a few MOFs which possess OMS, exposed N sites or chemisorbed groups.21,22,25 Finally, LIFM-11 displays excellent CO2/CO IAST selectivity (22.8) at 1 atm, which is very crucial in the oxy-combustion process19 but is rarely studied.

To explore why LIFM-11 exhibits higher CO2 separation selectivities than LIFM-10, their isosteric heats of adsorption (Qst) were calculated from the sorption data at 273, 298 and 308 K by the Virial fitting method (Fig. S13 and S14, ESI†).26 A significant increase (183%) in the CO2 Qst value was observed for LIFM-11 in comparison to LIFM-10, giving enthalpies at zero coverage of 53 and 29 kJ mol−1, respectively (Fig. 4a, Table 1 and Table S3, ESI†). In the case of LIFM-11, the Qst values decrease steadily upon CO2 loading, reaching a plateau at around 28 kJ mol−1 after 1 mmol g−1 uptake of CO2. This curve shape is characteristic for MOFs that possess specific CO2 adsorption sites embedded in their pore walls,25a,27 suggesting that strong CO2-framework interactions have been introduced by N-oxide functionalization in LIFM-11. On the contrary, the curve of LIFM-10 shows a rather gentle decrease in Qst values during the adsorption process, indicative of more homogenous binding sites in LIFM-10. To our knowledge, the CO2 Qst of LIFM-11 at zero loading is the highest value among MOFs containing saturated metal centers, comparable to those of top-performing MOFs which possess OMS and exposed N sites, but lower than those containing functional amine groups (Table S3, ESI†).

The experimental data were treated with and interpreted by simulated annealing techniques48,56 and periodic DFT calculations (see ESI†) to understand the mechanism of CO2 adsorption and the nature of the CO2-framework interactions. Charge analyses of the two MOFs revealed a significant charge variation (Fig. S23, ESI†) after oxidation of the pyridine-N. In LIFM-10, the pyridine-N carries a negative charge of −1.118e. While in LIFM-11, the O and N atoms of the N-oxide group carry opposite charges of −0.889e and 0.623e, respectively. Such a charge-separated nature, together with the bent coordination and electron-rich nature of the N-oxide donor, provide preferential CO2 adsorption sites on the pore surface of LIFM-11 in contrast to LIFM-10 (Fig. 1 and Fig. S24–27, ESI†). The CO2 molecules adsorbed in the pores of LIFM-10 are broadly distributed around the carboxylate groups and benzene rings. In contrast, CO2 molecules in the pores of LIFM-11 are predominantly located right next to the N-oxide groups. As seen in Fig. 4b, CO2 molecules in LIFM-11 mainly interact with three surrounding N-oxide groups (dC–O = 3.2–3.5 Å; dN–O = 3.6–4.0 Å), lying alongside the N-oxide groups with the electron deficient C atom of CO2 forming short contacts with the negatively charged O atom of N-oxide, and the electron rich O atom of CO2 forming short contacts with the positively charged N atom of N-oxide. This result elucidates the exact nature of N-oxide as a CO2 binding ODS and the mechanism of enhanced CO2-framework affinity in LIFM-11 which leads to a higher Qst value and separation selectivity.
In summary, through successive functionalization of T-shaped pyridine-dicarboxylate ligands with an amide group and both an amide and a N-oxide groups, we have synthesized two isoreticular MOFs. The clever modification of the pyridine-N into the N-oxide donor endowed charge variation and bent-binding, offering “open donor sites” for preferential CO$_2$ interactions and thus remarkably enhancing the CO$_2$ adsorption enthalpy and separation selectivities over CH$_4$, CO, and N$_2$ at room temperature. The mechanism of CO$_2$ adsorption and the preferred binding sites have been studied and elucidated by theoretical simulations, which reveal that N-oxidation of N-donor ligands may be considered as a new potential way to functionalize porous MOFs for CO$_2$ sequestration, comparable to the approaches of introducing OMS or exposed N sites. Further studies are underway to generate more MOFs with N-oxide ligands, and separation behaviors will be evaluated in more practical conditions with regards to water stability and moisture influence.

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Notes and references