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# Alkylamine-Tethered Stable Metal–Organic Framework for CO<sub>2</sub> Capture from Flue Gas

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Different alkylamine molecules were post-synthetically tethered to the unsaturated Cr<sup>III</sup> centers in the metal–organic framework MIL-101. The resultant metal–organic frameworks show almost no N<sub>2</sub> adsorption with significantly enhanced CO<sub>2</sub> capture under ambient conditions as a result of the interaction between amine groups and CO<sub>2</sub> molecules. Given the extraordinary stability, high CO<sub>2</sub> uptake, ultrahigh CO<sub>2</sub>/N<sub>2</sub> selectivity, and mild regeneration energy, MIL-101-diethylenetriamine holds exceptional promise for post-combustion CO<sub>2</sub> capture and CO<sub>2</sub>/N<sub>2</sub> separation.

The continuously increasing level of atmospheric CO<sub>2</sub>, which is mostly emitted from the combustion of fossil fuels, is leading to a severe climate change and environmental issues. Therefore, the removal of CO<sub>2</sub> from flue gas is pressing and of particular importance in preserving environmental health.<sup>[1]</sup> Generally, a flue gas mixture consists of nitrogen, carbon dioxide, water vapor, oxygen, and minor components such as carbon monoxide, nitrogen oxides, and sulfur oxides, in which nitrogen is more than 66.6% and carbon dioxide is around 10–15%. The selective removal of low-concentration CO<sub>2</sub> from N<sub>2</sub>-rich streams remains a challenging task. Different technologies have been explored for such CO<sub>2</sub> separation; one major route is chemical adsorption of CO<sub>2</sub> from industrial streams by aqueous amine solutions (for example, monoethanolamine, MEA). Such a “wet scrubbing” approach allows a high capacity and selectivity for CO<sub>2</sub> removal, but suffers from high regeneration cost, equipment corrosion, as well as solvent boil off.<sup>[2]</sup> To develop an alternative and effective solution, porous adsorbents that preferentially adsorb CO<sub>2</sub> over N<sub>2</sub> based on a physisorption mechanism have attracted a great deal of attention. Adsorption-based CO<sub>2</sub> capture and separation such as pressure-swing adsorption (PSA) are very attractive due to their low energy requirements.

As a relatively new type of porous solids, metal–organic frameworks (MOFs) with very high surface area and chemical tailorability and tunability exhibit multifunctional applications

in catalysis, sensors, drug delivery, gas storage, and, in particular, selective CO<sub>2</sub> capture and separation.<sup>[3–8]</sup> The coordinatively unsaturated metal centers in MOFs have been demonstrated to be effective for CO<sub>2</sub> adsorption. So far, the CO<sub>2</sub> capture record holder in MOFs at typical conditions (0.15 bar, 25 °C) is Mg-MOF-74, which captures as high as 6.1 mmol g<sup>-1</sup> of CO<sub>2</sub>, mainly due to the unsaturated Mg<sup>II</sup> centers in the structure.<sup>[9]</sup> In addition, the polarizability and quadrupole moment of acidic oxide CO<sub>2</sub> molecule mean that it interacts with polarizing and alkaline functional groups, which can be rationally introduced into the pore walls of MOFs. In this regard, different CO<sub>2</sub>-philic moieties have been grafted onto MOF pore surfaces to enhance the enthalpy and improve the performance of CO<sub>2</sub> capture.<sup>[8c,10,11]</sup> Among all organic groups, alkylamine, which not only polarizes the framework surfaces but also affords the chemisorption of CO<sub>2</sub>, has been recognized to have the strongest interaction with CO<sub>2</sub> molecules. Bearing in mind the importance of physicochemical stability for practical applications, in this work, an ultrastable MOF possessing a very high surface area and large pore sizes, has been employed for the introduction of different alkylamines. The resultant alkylamine-tethered MOFs exhibit remarkable increases in CO<sub>2</sub> capture performance and heat of CO<sub>2</sub> adsorption, and exceptionally high CO<sub>2</sub>/N<sub>2</sub> selectivity under ambient conditions.

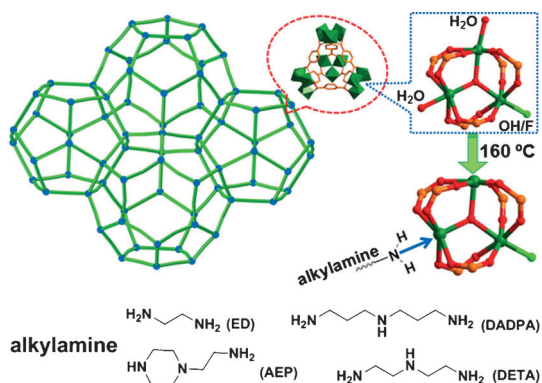
The MIL-101 framework, Cr<sub>3</sub>X(H<sub>2</sub>O)<sub>2</sub>O(BDC)<sub>3</sub>·nH<sub>2</sub>O (BDC = benzene-1,4-dicarboxylate, X = F or OH, n ≈ 25),<sup>[12]</sup> was subjected to activation for further alkylamine tethering to afford MIL-101-amine (amine = ED, ethylenediamine; DADPA, 3,3'-diaminodipropylamine; AEP, 1-(2-aminoethyl)piperazine; DETA, diethylenetriamine). We have chosen classical MIL-101 because it has a three-dimensional (3D) network featuring two types of giant cages with diameters of 2.9 and 3.4 nm, high physicochemical stability, as well as a large surface area [Brunauer–Emmett–Teller (BET), over 3000 m<sup>2</sup> g<sup>-1</sup>]. More importantly, as shown in Figure 1, the exposed Cr<sup>III</sup> centers in activated MIL-101 have been shown in the previous reports to serve as Lewis acid sites to facilitate the anchoring of amine groups;<sup>[13]</sup> thus, they are desirable for binding small alkylamine molecules to the internal pore surfaces. As a result of the large cage sizes in MIL-101, enough free space would remain even after alkylamine modification, and it is well suited for CO<sub>2</sub> movement inside the cages.

Nitrogen gas adsorption/desorption isotherms were collected at 77 K (Figure 2). The calculated BET surface areas were 3185, 2040, and 1644 m<sup>2</sup> g<sup>-1</sup> for MIL-101, MIL-101-ED, and MIL-101-DETA, respectively. The significant decrease of surface area reveals the successful tethering of alkylamine inside the cages. Moreover, both powder X-ray diffraction (PXRD) and IR spectra indicate that the MIL-101 framework is preserved upon alkyla-

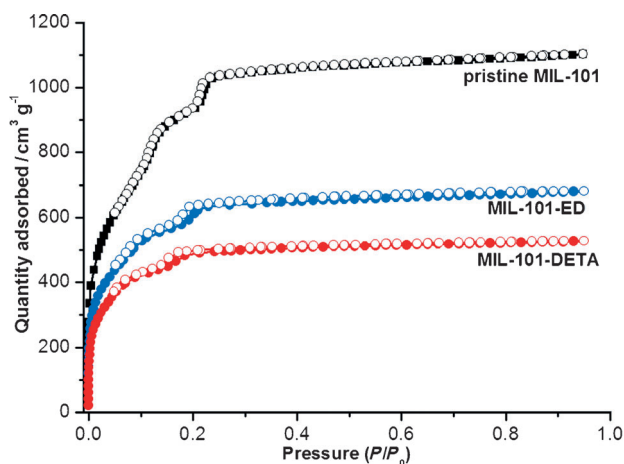
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**Figure 1.** Schematic illustration for the formation of alkylamine-tethered MIL-101.

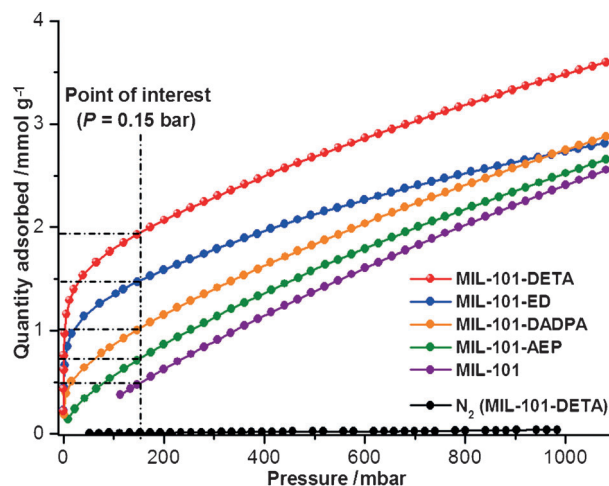


**Figure 2.** N<sub>2</sub> adsorption (●) and desorption (○) isotherms for pristine MIL-101, MIL-101-ED, and MIL-101-DETA at 77 K.

mine functionalization (the Supporting Information, Figure S1 and S2).

Significantly, the introduction of alkylamine into the pore walls of MIL-101 resulted in materials with excellent CO<sub>2</sub> adsorption performances at 296 K and low pressures (Figure 3). The trend of enhancement in CO<sub>2</sub> uptake in terms of tethered alkylamine is DETA > ED ≈ DADPA > AEP whereas the pristine MIL-101 has the lowest CO<sub>2</sub> uptake at 1 bar. Clearly, MIL-101-DETA has the highest CO<sub>2</sub> adsorption capacity (up to 3.56 mmol g<sup>-1</sup> of CO<sub>2</sub> at 296 K and 1 bar) among all the alkylamine-tethered MIL-101 samples, although its surface area is lowest, revealing the importance of alkylamine groups for CO<sub>2</sub> capture. It is assumed that the weight of alkylamine, the free space in MOF pores (accessibility of alkylamine), and the number and type of amine group synergistically affect the final performance of CO<sub>2</sub> adsorption. The assumption is supported by the most recently reported CO<sub>2</sub> uptake of PEI-mediated amine-MIL-101(Cr), in which the sample loaded with 75 wt% PEI gives the best CO<sub>2</sub> uptake of 3.6 mmol g<sup>-1</sup> at 25 °C and 1 bar, whereas higher or lower PEI loadings impair CO<sub>2</sub> adsorption capability.<sup>[10c]</sup>

Post-combustion flue gas contains around 15% CO<sub>2</sub> at a total pressure of 1 bar; thus, the simplest evaluation for ca-



**Figure 3.** CO<sub>2</sub> adsorption isotherms for MIL-101 and various alkylamine-tethered MIL-101 and N<sub>2</sub> adsorption isotherm for MIL-101-DETA at 296 K.

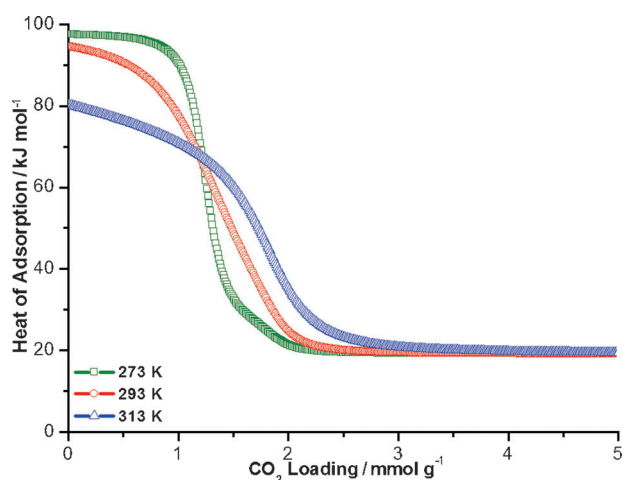
capacity of porous materials is the quantity of CO<sub>2</sub> adsorbed at about 0.15 bar. At 296 K and 0.15 bar, pristine MIL-101 only adsorbs 0.5 mmol g<sup>-1</sup> CO<sub>2</sub>, and MIL-101-ED, MIL-101-DADPA, and MIL-101-AEP adsorb 1.48, 1.01, and 0.73 mmol g<sup>-1</sup> CO<sub>2</sub>, respectively. In sharp contrast, under the same conditions, MIL-101-DETA takes up 1.95 mmol g<sup>-1</sup> CO<sub>2</sub>, an uptake only lower than MOF-74,<sup>[9]</sup> Cu-UTSA-16,<sup>[8a]</sup> SIFSIX-2-Cu-i,<sup>[8c]</sup> mmen-CuBTtri,<sup>[14]</sup> among all top-performing MOFs. However, compared to these MOFs, the exceptional stability of MIL-101 means that MIL-101-DETA may be more easily applicable for realistic CO<sub>2</sub> capture.

It has been reported that water vapor in flue gas deteriorates CO<sub>2</sub> uptake for many MOFs or other sorbents as a result of their affinities for H<sub>2</sub>O, pore space occupation by H<sub>2</sub>O, as well as water sensitivity of the MOF.<sup>[15a-c]</sup> However, the CO<sub>2</sub> uptake of HKUST-1 and MIL-101 was reported to be enhanced in the presence of a small amount of water due to interactions between CO<sub>2</sub> and the coordinated water molecules.<sup>[15c-e]</sup> A recent study has shown that trace flue gas contaminants (H<sub>2</sub>O, NO, SO<sub>2</sub>) have minimal impact on the CO<sub>2</sub> adsorption capacity and regeneration of MIL-101(Cr).<sup>[15f]</sup> Therefore, it can be expected that CO<sub>2</sub> adsorption of the water-stable MIL-101 grafted with alkylamine remains even under humid conditions.

Remarkably, all alkylamine-tethered MIL-101 take up very little N<sub>2</sub> at 296 K. Therefore, they could be promising candidates for selective CO<sub>2</sub>/N<sub>2</sub> separation. Given the very low N<sub>2</sub> uptake at 296 K, the CO<sub>2</sub>/N<sub>2</sub> selectivity has been roughly evaluated by the single-component isotherm data. At a total pressure of 1 bar, the rough composition of flue gas is assumed to be 15% CO<sub>2</sub> and 85% N<sub>2</sub>. The selectivity factor (*S*) can be defined as the ratio of the CO<sub>2</sub> uptake at 0.15 bar to the adsorbed amount of N<sub>2</sub> at 0.85 bar, and the value is then normalized for the given pressures. The whole calculation can be expressed as Equation (1):<sup>[14]</sup>

$$S = \frac{q(\text{CO}_2)/p(\text{CO}_2)}{q(\text{N}_2)/p(\text{N}_2)} \quad (1)$$

The CO<sub>2</sub>/N<sub>2</sub> selectivity factor for MIL-101-DETA is as high as 346 (the Supporting Information, Section 2),<sup>[16]</sup> which is very high compared to that for all MOF-based solid sorbents.<sup>[8c,14]</sup> The selectivity factor calculated from this method does not consider the competition of gas molecules for the adsorption sites on the pore surface; therefore, the ideal adsorbed solution theory (IAST) model affords an even higher selectivity of CO<sub>2</sub>/N<sub>2</sub> because the method takes the higher affinity of the framework towards CO<sub>2</sub> into account (the Supporting Information, Section 2). To better understand the adsorption properties, the isosteric heat of CO<sub>2</sub> adsorption ( $Q_{st}$ ) of 98 kJ mol<sup>-1</sup> was calculated at zero coverage and 273 K for MIL-101-DETA using a triple-site Langmuir adsorption model (Figure 4, the

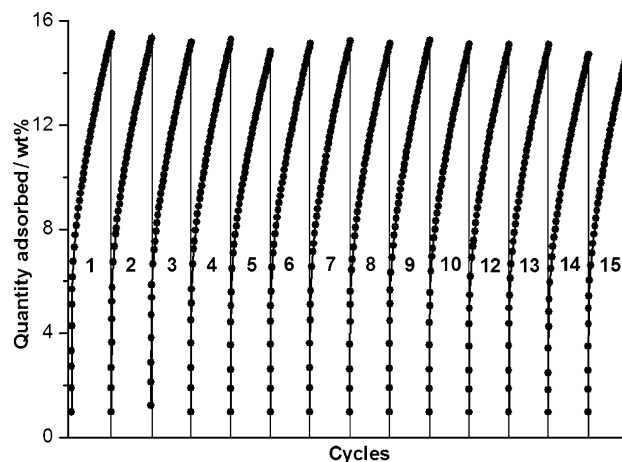


**Figure 4.** CO<sub>2</sub> isosteric heat of adsorption ( $Q_{st}$ ) at different temperatures for MIL-101-DETA.

Supporting Information, Section 3), which usually gives higher values at zero coverage than the virial method that is commonly employed for MOFs.<sup>[14,17]</sup> The value is among the largest for CO<sub>2</sub> adsorption in MOFs reported thus far and compared to that for other alkylamine modified MOFs or PPNs.<sup>[14,18]</sup> The considerable surface area of DETA-tethered MIL-101 indicates sufficient pore space for CO<sub>2</sub> movement inside the pores and a great number of amines available to bind guest CO<sub>2</sub> molecules, improving CO<sub>2</sub> adsorption. Taking all these factors together, MIL-101-DETA could be an excellent candidate for post-combustion carbon capture and CO<sub>2</sub>/N<sub>2</sub> separation applications. Based on this exceptional high selectivity, the dependence of working capacity on desorption/recovery temperature was calculated, neglecting the influence of N<sub>2</sub> in the mixed gas stream. We assumed a temperature swing process with loading conditions of 40 °C, 1 bar, and 15% CO<sub>2</sub>. At a recovery temperature of 120 °C, the captured CO<sub>2</sub> amount per temperature swing cycle is around 1 mmol g<sup>-1</sup> CO<sub>2</sub> (the Supporting Information, Section 4).

There always remain concerns about the regenerability of solid adsorbents for industrial use. To examine the recyclability of MIL-101-DETA, we simulated temperature and vacuum

swings by using an ASAP2020 analyzer and saturating with CO<sub>2</sub> up to around 1.1 bar at 296 K and then a high vacuum for 60 min at 90 °C.<sup>[17]</sup> As displayed in Figure 5, there is almost no



**Figure 5.** Fifteen cycles of CO<sub>2</sub> uptake at 296 K at 1 bar. After each cycle, the sample was regenerated with a temperature swing to 90 °C and then placed under vacuum for 60 min. Data was collected with an ASAP2020 analyzer.

apparent drop in CO<sub>2</sub> adsorption capacity during 15 cycles, which indicates that CO<sub>2</sub> molecules can be completely desorbed during the thermal treatment process and the MIL-101-DETA can be well recycled. At a loading of 1.95 mmol g<sup>-1</sup>, the approximate capacity of MIL-101-DETA for CO<sub>2</sub> at 0.15 bar, the  $Q_{st}$  is calculated to be approximately 20 kJ mol<sup>-1</sup>. Hence, the average enthalpy of adsorption for CO<sub>2</sub> in CO<sub>2</sub> capture applications would be significantly lower than the value at zero coverage (98 kJ mol<sup>-1</sup>), which has important implications for good regeneration and recyclability performance of MIL-101-DETA.<sup>[14]</sup> Based on the thermogravimetric analysis (TGA) data, the alkylamine-tethered MIL-101 is thermally stable up to over 200 °C and thus should remain intact during the regeneration process.

In conclusion, a facile post-synthetic modification of MIL-101 with different alkylamine groups has been established in this work. Grafting alkylamine onto exposed Cr<sup>III</sup> centers offers new binding sites and strong interaction with CO<sub>2</sub> molecules and endows MIL-101 with dramatically enhanced CO<sub>2</sub> uptake capacity and significantly lowered N<sub>2</sub> uptake capacity at low pressures. Given the exceptional stability, high CO<sub>2</sub> uptake capacity, ultrahigh selectivity for CO<sub>2</sub>/N<sub>2</sub>, recyclability, mild regeneration energy/cost, large surface area and free pore space, the optimized MIL-101-DETA holds great potential for practical applications in post-combustion CO<sub>2</sub> capture and CO<sub>2</sub>/N<sub>2</sub> separation.

## Experimental Section

**Preparation of MIL-101:** MIL-101 was synthesized according to the previous report with modifications.<sup>[12]</sup> Typically, a mixture of terephthalic acid (332 mg, 2.0 mmol) with Cr(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (800 mg, 2.0 mmol) in the presence of aqueous HF (0.4 mL, 2.0 mmol) and

de-ionized water (9.5 mL) was reacted at 200 °C for 8 h. The reaction produced microcrystalline green powder of MIL-101 with formula  $\text{Cr}_3\text{X}(\text{H}_2\text{O})_2\text{O}[(\text{O}_2\text{C})_6\text{H}_4(\text{CO}_2)]_3 \cdot n\text{H}_2\text{O}$  ( $\text{X}=\text{F}$  or  $\text{OH}$ ,  $n \leq 25$ ). To eliminate the unreacted terephthalic acid trapped in the giant pores, the as-synthesized MIL-101 product was refluxed in water, ethanol, and  $\text{NH}_4\text{F}$  solution, each for over 12 h, then washed with hot water. The resultant product was finally dried overnight at 160 °C under vacuum.

**Preparation of MIL-101-EDF:** Activated MIL-101 (250 mg, 0.33 mmol) was immersed and stirred in 10 mL dichloromethane solution of ethylene diamine (ED, 0.17 mL, 2.24 mmol) at room temperature for one day, followed by filtration, washing with dichloromethane three times, and drying at 60 °C.

**Preparation of MIL-101-DADPA:** Activated MIL-101 (100 mg, 0.139 mmol) was immersed and stirred in 10 mL dichloromethane solution of 3,3'-diaminodipropylamine (DADPA, 0.146 mL, 1.042 mmol) at room temperature for one day, followed by filtration, washing with dichloromethane three times, and drying at 60 °C.

**Preparation of MIL-101-AEP:** Activated MIL-101 (100 mg, 0.139 mmol) was immersed and stirred in 9 mL dichloromethane solution of 1-(2-aminoethyl)piperazine (AEP, 0.137 mL, 1.042 mmol) at room temperature for one day, followed by filtration, washing with dichloromethane three times, and drying at 60 °C.

**Preparation of MIL-101-DETA:** Activated MIL-101 (100 mg, 0.139 mmol) was immersed and stirred in 8 mL dichloromethane solution of diethylenetriamine (DETA, 0.12 mL, 1.042 mmol) at room temperature for one day, followed by filtration, washing with dichloromethane three times, and drying at 60 °C.

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