The continuously increasing level of atmospheric CO₂, which is emitted from the combustion of fossil fuels, is leading to a severe climate change and environmental issues. Therefore, the removal of CO₂ from flue gas is pressing and of particular importance in preserving environmental health.\(^1\) 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 much more prevalent than CO₂. To enhance the enthalpy and improve the performance of CO₂ capture 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 CO₂ capture performance and heat of CO₂ adsorption, and exceptionally high CO₂/N₂ selectivity under ambient conditions.

The MIL-101 framework, Cr₃X(H₂O)₂O(BDC)₃·nH₂O (BDC = benzene-1,4-dicarboxylate, X = F or OH, n = 25)\(^{[12]}\) 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; DTA, 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.\(^{[13]}\) This MOF also possesses unsaturated metal centers in MOFs, and their CO₂ capture properties have been demonstrated to be effective for CO₂ adsorption. So far, the CO₂ 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\(^{-1}\) of CO₂ mainly due to the unsaturated Mg²⁺ centers in the structure.\(^{[9]}\) In addition, the polarizability and quadrupole moment of the CO₂ 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 CO₂-philic moieties have been grafted onto MOF pore surfaces to enhance the enthalpy and improve the performance of CO₂ capture.\(^{[8c, 10, 11]}\) Among all organic groups, alkylamine, which not only polarizes the framework surfaces but also affords the chemisorption of CO₂, has been recognized as the strongest interaction with CO₂ molecules. Bearing in mind the importance of physicochemical stability for practical applications, 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.\(^{[12]}\) 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.\(^{[12]}\) More importantly, as shown in Figure 1, the exposed Cr³⁺ 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.\(^{[13]}\) 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 CO₂ 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 m² g\(^{-1}\) 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 alkylamine modification.
Significantly, the introduction of alkylamine into the pore walls of MIL-101 resulted in materials with excellent CO$_2$ adsorption performances at 296 K and low pressures (Figure 3). The trend of enhancement in CO$_2$ uptake in terms of tethered alkylamine is DETA $>$ ED/C$_2$5 DADPA $>$ AEP whereas the pristine MIL-101 has the lowest CO$_2$ uptake at 1 bar. Clearly, MIL-101-DETA has the highest CO$_2$ adsorption capacity (up to 3.56 mmol g$^{-1}$ 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$_2$ 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$_2$ adsorption. The assumption is supported by the most recently reported CO$_2$ uptake of PEI-mediated amine-MIL-101(Cr), in which the sample loaded with 75 wt% PEI gives the best CO$_2$ uptake of 3.6 mmol g$^{-1}$ at 25°C and 1 bar, whereas higher or lower PEI loadings impair CO$_2$ adsorption capability.$^{15c-e}$

Post-combustion flue gas contains around 15% CO$_2$ at a total pressure of 1 bar; thus, the simplest evaluation for capacity of porous materials is the quantity of CO$_2$ adsorbed at about 0.15 bar. At 296 K and 0.15 bar, pristine MIL-101 only adsorbs 0.5 mmol g$^{-1}$ CO$_2$ and MIL-101-ED, MIL-101-DADPA, and MIL-101-AEP adsorb 1.48, 1.01, and 0.73 mmol g$^{-1}$ CO$_2$ respectively. In sharp contrast, under the same conditions, MIL-101-DETA takes up 1.95 mmol g$^{-1}$ CO$_2$, an uptake only lower than MOF-74,$^{9}$ Cu-UTSA-16,$^{8a}$ SIFSIX-2-Cu-i,$^{8c}$ mmen-CuBTri,$^{14}$ 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$_2$ capture.

It has been reported that water vapor in flue gas deteriorates CO$_2$ uptake for many MOFs or other sorbents as a result of their affinities for H$_2$O, pore space occupation by H$_2$O, as well as water sensitivity of the MOF.$^{15a-c}$ However, the CO$_2$ 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$_2$ and the coordinated water molecules.$^{15c-e}$ A recent study has shown that trace flue gas contaminants (H$_2$O, NO, SO$_2$) have minimal impact on the CO$_2$ adsorption capacity and regeneration of MIL-101(Cr).$^{15f}$ Therefore, it can be expected that CO$_2$ 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$_2$ at 296 K. Therefore, they could be promising candidates for selective CO$_2$/N$_2$ separation. Given the very low N$_2$ uptake at 296 K, the CO$_2$/N$_2$ 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$_2$ and 85% N$_2$. The selectivity factor ($S$) can be defined as the ratio of the CO$_2$ uptake at 0.15 bar to the adsorbed amount of N$_2$ at 0.85 bar, and the value is then normalized for the given pressures. The whole calculation can be expressed as Equation (1):$^{14}$

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

(1)
The CO₂/N₂ selectivity factor for MIL-101-DETA is as high as 346 (the Supporting Information, Section 2),¹⁶ which is very high compared to that for all MOF-based solid sorbents.⁸c,₁⁴ 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 CO₂/N₂ because the method takes the higher affinity of the framework towards CO₂ into account (the Supporting Information, Section 2). To better understand the adsorption properties, the isosteric heat of CO₂ adsorption ($Q_{st}$) of 98 kJ mol⁻¹ was calculated at zero coverage and 273 K for MIL-101-DETA using a triple-site Langmuir adsorption model (Figure 4, the Supporting Information, Section 3), which usually gives higher values at zero coverage than the virial method that is commonly employed for MOFs.¹⁴,¹⁷ The value is among the largest for CO₂ adsorption in MOFs reported thus far and compared to that for other alkylamine modified MOFs or PPNs.¹⁴,¹⁸ The considerable surface area of DETA-tethered MIL-101 indicates sufficient pore space for CO₂ movement inside the pores and a great number of amines available to bind guest CO₂ molecules, improving CO₂ adsorption. Taking all these factors together, MIL-101-DETA could be an excellent candidate for post-combustion carbon capture and CO₂/N₂ separation applications. Based on this exceptional high selectivity, the isosteric heat of adsorption ($Q_{st}$) is calculated to be approximately 20 kJ mol⁻¹. Hence, the average enthalpy of adsorption for CO₂ in CO₂ capture applications would be significantly lower than the value at zero coverage (98 kJ mol⁻¹), which has important implications for good regeneration and recyclability performance of MIL-101-DETA.¹⁴

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 Cr³⁺ centers offers new binding sites and strong interaction with CO₂ molecules and endows MIL-101 with dramatically enhanced CO₂ uptake capacity and significantly lowered N₂ uptake capacity at low pressures. Given the exceptional stability, high CO₂ uptake capacity, ultrahigh selectivity for CO₂/N₂, 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 CO₂ capture and CO₂/N₂ separation.

Experimental Section
Preparation of MIL-101: MIL-101 was synthesized according to the previous report with modifications.¹² Typical, a mixture of terephthalic acid (332 mg, 2.0 mmol) with Cr(NO₃)₃·9H₂O (800 mg, 2.0 mmol) in the presence of aqueous HF (0.4 mL, 2.0 mmol) and

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**Figure 4.** CO₂ isosteric heat of adsorption ($Q_{st}$) at different temperatures for MIL-101-DETA.

**Figure 5.** Fifteen cycles of CO₂ 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.
de-ionized water (9.5 mL) was reacted at 200 °C for 8 h. The reactor produced microcrystalline green powder of MIL-101 with formula Cr₃X(H₂O)₂O[(O₂C)C₆H₄(CO₂)]₃ (X=F or OH, n ≤ 25). To eliminate the unreacted terephthalic acid trapped in the giant pores, the as-synthesized MIL-101 product was refluxed in water, ethanol, and NH₄F 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 ethylenediamine (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-ethylenediamine (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 diethyleneetriamine (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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