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Strong CO_2 Binding in a Water-Stable, Triazolate-Bridged Metal−Organic Framework Functionalized with Ethylenediamine

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The development of more efficient processes for capturing CO_2 from power plant flue streams is critical for the reduction of greenhouse gas emissions implicated in global warming. A typical flue gas has an overall pressure of ca. 1 bar and contains mainly N_2, H_2O, and CO_2 in a ca. 6.5:1:1 ratio by weight.[1] Conventional CO_2 capture processes involving the chemisorption of CO_2 by alkylamine-containing liquids present several disadvantages, including the considerable heat required to regenerate the liquid and the necessary use of inhibitors for corrosion control. Attempts to address these limitations have focused on the adsorption of CO_2 in porous solids such as zeolites[2] and amine-modified silicas.[3] In the latter, surface modification facilitates the selective adsorption of CO_2 (typically at 40−60 °C) via the formation of carbamate or bicarbonate species and permits the stripping of CO_2 at temperatures of 100−120 °C. Owing to their exceptionally high surface areas and chemical tunability, much recent attention has turned toward the use of metal−organic frameworks as CO_2 capture materials.[4] In terms of capacity, it has been shown that certain frameworks are capable of storing more than 150 wt % CO_2 at 298 K and 40 bar.[4a,h] Most of the compounds studied, however, show little uptake in the low pressure regime of 0.1−0.2 bar relevant to capture from flue streams. In addition, the viability of the materials under realistic flue stream conditions requires air and water stability, corrosion resistance, high thermal stability, and high selectivity for CO_2 over other components in flue gas.

The incorporation of pendant alkylamine functionalities within the pores of metal−organic frameworks offers a significant opportunity to produce highly efficient capture materials by virtue of the affinity of alkylamines for CO_2. Two major strategies are envisaged to achieve this goal: (i) the direct use of an amine-based bridging ligand to generate a three-dimensional network[5] and (ii) postsynthetic approaches that covalently modify a bridging ligand[4h,6] or graft an alkylamine functionality onto a coordinatively unsaturated metal center.[7] Herein, we utilize the latter strategy in a new air- and water-stable metal−organic framework, $H_3[(Cu_4Cl)_3(BTTri)_8]$ (**1**; H_3BTTri = 1,3,5-tris(1*H*-1,2,3-triazol-5-yl)benzene), featuring open Cu^{II} coordination sites.

Triazolate-bridged frameworks were sought as analogues of known tetrazolate-bridged structures[8] with enhanced chemical and thermal stability as a result of the increased metal−ligand bond strength. Reaction of $CuCl_2\cdot 2H_2O$ with H_3BTTri in a mixture of DMF and aqueous HCl at 100 °C afforded $H_3[(Cu_4Cl)_3(BTTri)_8(DMF)_{12}]\cdot 7DMF\cdot 76H_2O$ (**1-DMF**) as a purple powder. Powder X-ray diffraction data show the compound to be isotypic with the cubic sodalite-type structure of $H[Cu(DMF)_6][(Cu_4Cl)_3(BTT)_8(H_2O)_{12}]\cdot 3.5HCl\cdot 12H_2O\cdot 16CH_3OH$ (Cu-BTT),[8c] displaying a similar unit cell parameter of $a = 18.647(6)$ Å. Here, the framework structure consists of chloride-centered $[Cu_4Cl]^{7+}$ squares linked via triangular $BTTri^{3-}$ ligands (see Figure 1), and each Cu^{II} center has a terminal DMF ligand directed toward the interior of the larger pores. The anionic charge of the framework is balanced solely by protons, which are presumably bound to either the N3 atoms of the triazolate rings or guest water molecules.

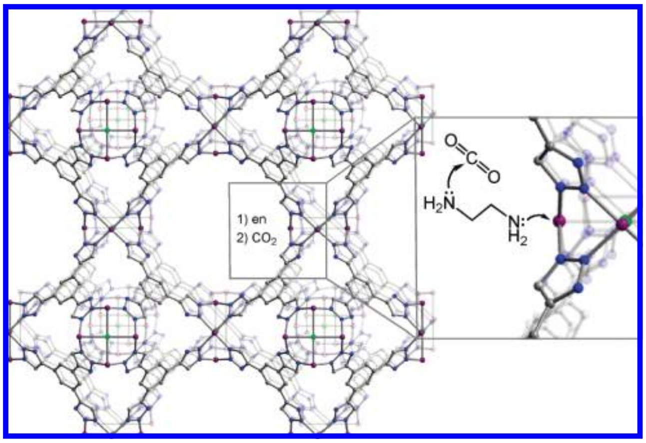

Figure 1. A portion of the structure of the sodalite-type framework of Cu-BTTri (**1**) showing surface functionalization of a coordinatively unsaturated Cu^{II} site with ethylenediamine, followed by attack of an amino group on CO_2. Purple, green, gray, and blue spheres represent Cu, Cl, C, and N atoms, respectively; framework H atoms are omitted for clarity.

The chemical stability of **1-DMF** was tested in water and acidic media. After soaking the solid for 3 days in boiling water or 1 day in a solution of HCl (0.001 M pH = 3), the powder X-ray diffraction pattern of the compound remained unchanged. Thermogravimetric analysis (TGA) and X-ray diffraction experiments further demonstrated the remarkable thermal stability of the framework, with no loss of framework composition or structure occurring up to at least 270 °C. Soaking **1-DMF** in boiling water or methanol leads to exchange of the guest solvent and coordinated DMF molecules to give **1-H_2O** and **1-MeOH**, respectively. The abrupt weight-loss step in the TGA traces for **1-H_2O** and **1-MeOH** in the range 25−40 °C correspond to the release of guest solvent, with the former indicating that the hydrophilic pores can take up 33 wt % water.

Prior to gas adsorption measurements, **1-MeOH** was activated by heating at 180 °C under a reduced pressure to obtain the fully desolvated framework **1**. A color change from purple to red occurred upon removal of the coordinated solvent molecules to yield unsaturated Cu^{II} centers. Diffuse reflectance UV−vis spectra revealed a shift in the d−d transitions of Cu^{II} from 18 020 cm^{-1} in **1-MeOH** to 19 070 cm^{-1} in **1**. The sensitivity of these metal-based transitions to the geometry change, which occurs upon conversion of the Cu^{II} centers from six- to five-coordination, is reminiscent of the color variations observed for other frameworks in which open Cu^{II} sites can be generated.[9]

The N_2 and H_2 adsorption isotherms for **1** at 77 K are depicted in Figure 2, together with the CO_2 isotherm at 195 K. The data for N_2 correspond to a type I isotherm characteristic of a microporous material, with BET and Langmuir fits affording surface areas of 1770 and 1900

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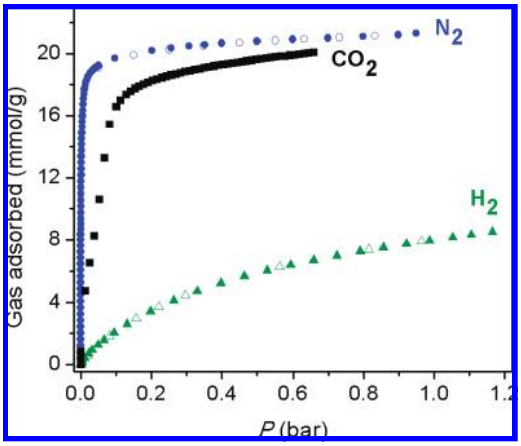

Figure 2. Adsorption isotherms in **1** for the uptake of N_2 (blue circles) and H_2 (green triangles) at 77 K and for CO_2 (black squares) at 195 K. Filled and open symbols represent adsorption and desorption, respectively.

m²/g, respectively. The H_2 adsorption data indicate fully reversible uptake of 1.7 wt % at 1.2 bar, which is considerably less than the 2.4 wt % uptake observed for Cu-BTT under the same conditions.[8c] This result is consistent with a reduced affinity of the Cu^{II} centers for H_2 as a consequence of the greater basicity of the triazolate ligands. Indeed, the H_2 adsorption isotherms for **1** at 77 and 87 K indicate an isosteric heat of adsorption at zero coverage of just 6.1 kJ/mol, considerably less than the 9.5 kJ/mol observed for Cu-BTT.[8c] The CO_2 adsorption isotherm for **1** at 195 K reveals a maximum uptake of 90 wt % at 1 bar, placing it among the highest capacity CO_2 adsorbents under such conditions.[4j,k] The S-shape character of the isotherm in the low pressure region (0−0.1 bar) has been observed previously for inflexible frameworks and can be attributed to the attractive electrostatic interactions between CO_2 molecules.[10]

Alkylamine functionalization of the coordinatively unsaturated Cu^{II} sites was accomplished using a procedure analogous to that reported recently for MIL-101.[7] An excess amount (2.3 equiv per Cu) of ethylenediamine (en) was added to a suspension of **1** in toluene, prompting an immediate color change from red to blue. The suspension was heated at reflux for 12 h to optimize the extent of grafting, and the resulting solid was washed copiously with hexane to ensure complete removal of nonappended en. The diffuse reflectance UV−vis spectrum of the product (**1-en**) displays a shift and broadening in the Cu^{II} d−d bands compared with **1**. Aside from minor changes in the peak intensities, the powder X-ray diffraction pattern is unchanged from that of **1**, indicating preservation of the framework structure. The infrared spectrum of **1-en** provides further support for en grafting through (i) observation of en-based ν_{NH} and ν_{CH} stretching vibrations and (ii) a shift in the ν_{CH} bands to higher energies in **1-en** (2887 and 2947 cm^{-1}) compared with free en (2848 and 2924 cm^{-1}),[7] as expected when en binds a Lewis acid.

Thermogravimetric analysis of **1-en** showed a 12% weight loss at 160 °C, which, coupled with the elemental analysis data, is consistent with incorporation of 1.25 en molecules per $[Cu_4Cl]^{7+}$ unit. The incomplete grafting of significantly less than one en molecule per Cu^{II} center is likely due to steric hindrance within the pores. Indeed, N_2 adsorption data collected at 77 K on a sample of **1-en** that had been activated at 100 °C reveal a much reduced gas uptake capacity, with BET and Langmuir fits affording surface areas of just 345 and 376 m²/g, respectively.

The CO_2 and N_2 adsorption isotherms for **1** and **1-en** at 298 K are compared in Figure 3. At low pressures (up to 0.06 bar), **1-en** takes up a greater amount of CO_2: 0.366 mmol/g (1.6 wt %) versus 0.277 mmol/g (0.92 wt %) in **1**. At pressures above 0.1 bar, however, the CO_2 uptake for **1-en** is less than that for **1**, leading to a significant difference in their capacities at 1 bar: 1.27 mmol/g (5.5 wt %) for **1-en** versus 3.24 mmol/g (14.3 wt %) for **1**. This behavior can be explained by the greater attraction of CO_2 to the more basic amine sites at low pressures, followed by a filling of the available pore volume at higher pressures. While the CO_2 desorption isotherms for **1** and **1-en** indicate reversible sorption processes, both exhibit a slight hysteresis which is more pronounced in **1-en**, reflecting its greater affinity for CO_2. Note that the binding of one CO_2 molecule per en ligand in **1-en** would lead to an uptake of 6.8 wt %. Thus, while en grafting does lead to a steeper rise in the CO_2 adsorption isotherm at low pressures, the original pore size of **1** appears to be too small to permit complete exposure of the resulting terminal alkylamines.

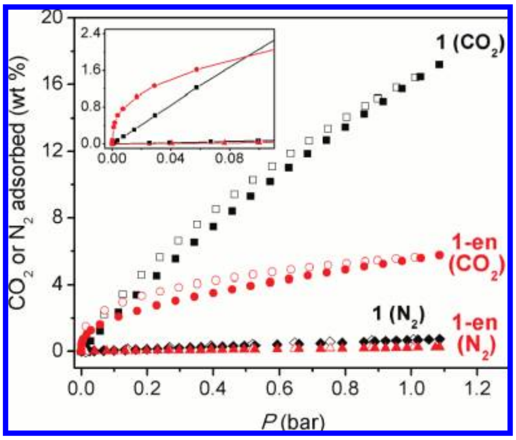

Figure 3. Adsorption isotherms for the uptake of CO_2 at 298 K in **1** (black squares) and **1-en** (red circles) and for the uptake of N_2 in **1** (black diamonds) and **1-en** (red triangles). Filled and open symbols represent adsorption and desorption, respectively. The inset shows the higher uptake of CO_2 for **1-en** compared with **1** at low pressures.

The selectivity for adsorption of CO_2 over N_2 is a prerequisite for the application of a framework as a capture material. At 298 K, the CO_2/N_2 selectivity for **1** is 10:1 at 0.09 bar and 21:1 at 1 bar. Owing to a reduction in the N_2 uptake, these ratios improve slightly for **1-en** to 13:1 at 0.1 bar and 25:1 at 1 bar. Importantly, despite the reduction in CO_2 capacity upon en grafting, the alkylamine functionalities endow the material with a higher CO_2/N_2 selectivity over the entire pressure range measured.

The isosteric heat of CO_2 adsorption, Q_{st}, for **1** and **1-en** were calculated from the Clausius−Clapeyron equation using adsorption data collected at 303, 308, and 313 K (see Figure 4). The corresponding adsorption curves for N_2 over the same temperature range are provided in the Supporting Information. For **1**, Q_{st} remains constant within error at a mean value of 21 kJ/mol as the degree of CO_2 loading is varied. Note that this is only slightly higher than the enthalpy of liquefaction of CO_2 (17 kJ/mol), indicating that the metal−organic framework surface provides only a minor improvement over the affinity of the gas for itself. Indeed, the Q_{st} value is significantly lower than has been observed for other frameworks featuring exposed Cu^{II} centers, such as the 35 kJ/mol in $Cu_3(BTC)_2$ (BTC^{3-} = 1,3,5-benzenetricarboxylate).[4h] It is well established, however, that the enthalpies of adsorption for gases in frameworks of this type are dependent on both the metal ion and the nature of the ligand donor atoms that contribute to its electronic structure.[4j] Here, the strong bonds between Cu^{II} and the triazolate ligands reduce the Lewis acidity of the exposed metal sites relative to those within carboxylate-based frameworks.

Significant increases in Q_{st} are apparent for the adsorption of CO_2 in **1-en**, particularly at very low loadings. At zero coverage,

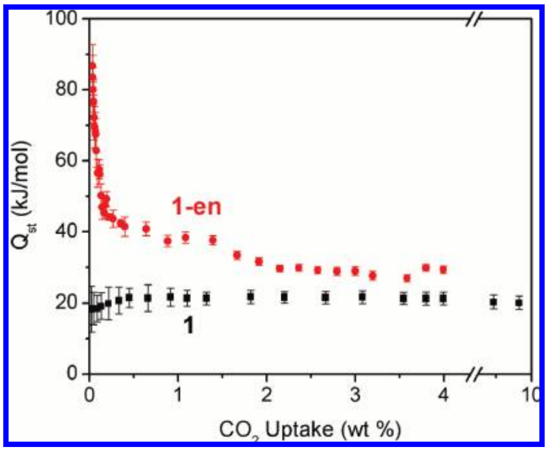

Figure 4. Isosteric heat of adsorption for CO_2 in **1** (black) and **1-en** (red).

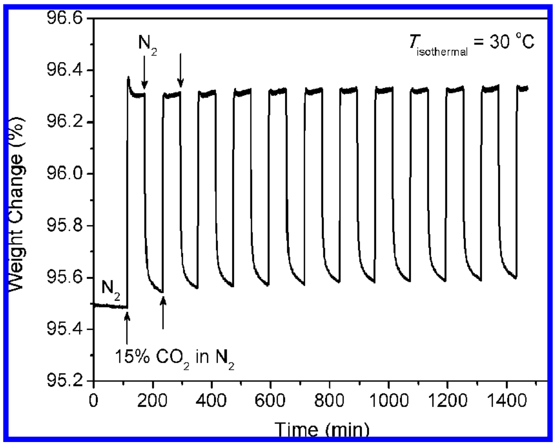

Figure 5. Gas cycling experiment for **1-en** at 30 °C, employing a flow of 15% CO_2 in N_2 followed by a flow of pure N_2.

a maximum value of 90 kJ/mol occurs, indicating a strong and selective interaction of CO_2 with the alkylamine functionalities. This value compares well with previously reported data obtained for alkylamine-functionalized silicas (100 kJ/mol).[10a] To our knowledge, this is the highest binding energy reported to date for CO_2 adsorption in a metal−organic framework, surpassing the previous record of 63 kJ/mol in MIL-100[4h] and the values for amine-functionalized frameworks in which the NH_2 groups are directly bound to aromatic ligands (50 kJ/mol).[6] The high binding energy for CO_2 in **1-en** at low coverage is indicative of a chemisorption interaction, akin to the chemisorption mechanisms that are operative for CO_2 separation in industry using alkylamine solvents. As the available alkylamine groups bind CO_2 with increasing pressure, Q_{st} decreases, approaching the values observed for **1** as CO_2 is adsorbed onto less reactive surface sites.

The reversibility of the CO_2 adsorption process in **1-en** during gas cycling at 30 °C was measured using a thermogravimetric analysis apparatus, with use of a 15% CO_2 in N_2 mixture to simulate the major components of flue gas (see Figure 5). A 0.75 wt % weight change was observed over repeated cycles, indicating that the material is able to withstand cyclic exposure to the mixed gas stream. Significantly, the CO_2 adsorption ability of **1-en** is maintained over repeated cycling, and the material can be regenerated by switching the gas stream to N_2. This may render the material suitable for use as an adsorbent in a pressure swing absorption type process for CO_2 capture.

The foregoing results demonstrate the use of $BTTri^{3-}$ in generating an air- and water-stable analogue of Cu-BTT, as well as the ability of Cu-BTTri (**1**) to incorporate en molecules that afford a highly selective affinity for CO_2 binding. Significantly, the en-functionalized framework **1-en** exhibits a higher uptake of CO_2 at very low pressures compared with the nongrafted material and displays a record isosteric heat of adsorption of 90 kJ/mol. Future efforts will attempt to increase the CO_2 capture capacity by extending this approach to frameworks containing larger pores and to adjust the heat of adsorption by varying the amine substituents[11] and investigating the effects of the presence of water.[12]

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Supporting Information Available: Complete experimental details, including characterization data and sorption analysis data. This material is available free of charge via the Internet at http://pubs.acs.org.

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