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Gas Storage and Separation in Water-Stable [Cu$_1$BTT$_3$]$^4^-$ Anion Framework Comprising Giant Multi-prismatic Nanoscale Cage

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A novel water-stable open poly-nuclear Cu(I)-based metal-organic framework, [NC$_3$H$_8$]$_4$Cu$_2$(BTT)$_3$:xG (G=guest of DMA and H$_2$O) (1), featuring with giant multi-prismatic nanoscale cage, and high CO$_2$/N$_2$ and CO$_2$/H$_2$ sorption selectivities, was successfully assembled by using the nitrogen-rich ligand of 1,3,5-tris(2H-tetrazol-5-yl)benzene (H$_3$BTT) to bridge two types of Cu$_3$ and Cu$_2$ clusters.

With CO$_2$ being one of the greatest contributors to global warming (ca. 30 Gt per year of worldwide CO$_2$ emissions), there is increasing interest in removing CO$_2$ from the air to combat the greenhouse gas effect. The development of carbon capture and sequestration (CCS) technologies that efficiently capture CO$_2$ from existing emission sources is of critical importance to the current energy framework, since the transition of the existing infrastructure from carbon-based sources to cleaner alternatives requires considerable modifications to be realized. The key process in CCS is the capture of CO$_2$ from pre-combustion shifted syngas and post-combustion flue gas. Pre-combustion CO$_2$ capture is a process in which fuel is decarbonated prior to combustion. It is especially used for the separation of CO$_2$ from H$_2$ within the mixture, which can then be performed to afford pure H$_2$ suitable for the generation of electricity in fuel cell industry. The principle of post-combustion capture is to remove CO$_2$ from flue gas after combustion at low pressure and low-CO$_2$-content. For a typical post-combustion flue gas for a coal-fired power plant, N$_2$ (73–77%), CO$_2$ (15–16%), H$_2$O (5–7%) and O$_2$ (3–4%) are the main constituents. Chemical absorption of CO$_2$ using monoethanolamine is a leading technology in post-combustion capture which can efficiently remove CO$_2$ from the flue gas. However, large energy penalty is associated with the liberation of captured CO$_2$ from the capture medium. In contrast, physisorption process requires much less energy which could allow conveniently reversible process to capture CO$_2$ gas. Since the low concentration of CO$_2$ and large quantities of N$_2$ originating from the flue gas, the selectivity toward CO$_2$ is crucial for the adsorption-based separation processes. Therefore, high selectivity, moderate affinity of the materials toward CO$_2$, high stability and low cost as well as high adsorption uptake are the most important criteria by which adsorbents for improving CO$_2$/N$_2$ or CO$_2$/H$_2$ separation performance will be judged for the CCS process concerning physical absorption technology.

In the past few decades, extensive research efforts have been mainly focused on porous solids of zeolites and activated carbons. The common shortfalls of these traditional absorbents are either low capacities or difficult regeneration processes. Porous metal-organic frameworks (MOFs), as a promising class of sorbents, have many properties that make them attractive for applications in gas storage, molecular recognition and separation, heterogeneous catalysis, and biomedical area. In regard to CO$_2$/N$_2$ separation relevant to post-combustion CO$_2$ capture, to the best of our knowledge, a record of simulated selectivity (~1.9×10$^4$ for CO$_2$/N$_2$=15/75) was found in rho-ZMOF and a record on the basis of experiment (1700 for CO$_2$/N$_2$=10/90, which was validated by gas mixture gravimetric adsorption experiments at various pressures) was found in SIFSIX-3-Zn by Zaworotko et al. The top CO$_2$/N$_2$ selectivities (CO$_2$/N$_2$=15/75) at 298 K, on the basis of experiments, are ~~165 in the post-synthesis modified mmen-Cu-BTTri, ~1~1~01~1 in the HKUST-1 with coordinatively unsaturated metal sites, ~65 in the bio-MOF-11 with multiple Lewis basic sites afforded by adenine, and ~45 in the zine-paddle wheel MOF with highly polar ligands. A remarkable enhancement of the CO$_2$/N$_2$ selectivity was achieved through axial ligand substitution of Cl$^-$ by TiF$_6$$^{2-}$. Research on MOFs aiming for the separation of CO$_2$ from H$_2$ are still in their infancy although significant promise in this regard is observed by them.$^{15}$ Two frameworks with exposed metal cation sites, H$_2$[Cu$_3$(Cl)$_4$(BTT)$_3$] (CuBTTri) and Mg$_2$(dobdc) display by far the highest selectivities of CO$_2$/H$_2$, probably owing to the greater polarizability of CO$_2$ versus H$_2$.

To develop new MOFs sorbents for CO$_2$ capture, a new route is the design and construction of open MOFs through the incorporation of accessible nitrogen-donor groups, such as pyridine, imidazole, triazole and tetrazole, into the pore walls of porous materials which can dramatically affect the gas uptake capacity and selectivity of the materials. For example, compounds of CuBTTri and NTU-105 incorporated with nitrogen-rich or coordination-free triazole units exhibit high stability and remarkable uptake towards CO$_2$ (14.3 wt% at 298 K and 90 wt% at 195 K for the former; 26.8 wt% at 273K for the latter). For this reason, we are especially interested in ligand containing multiple triazole group (1,3,5-tris(2H-tetrazol-5-yl)benzene or H$_3$BTT in short, see Fig. S1, ESI†), as such ligand can
achieve high connectivity and high percentage of open nitrogen-donor sites.

![Fig. 1](image)

**Fig. 1** (a) View of the 3D open anion framework of 1 embedded with meso-helical chains; (b) View of the L1 and R1 helical chains.

Reaction of CuCl$_2$·2H$_2$O (0.068 g, 0.4 mmol) and H$_2$BTT·2HCl (0.071 g, 0.2 mmol) in DMA (N,N’-Dimethylacetamidamide) solvent at 140 °C for 3 days afforded [NC$_2$H$_4$]$_2$Cu$_2$(BTT)$_2$·xG (G=guest of DMA and H$_2$O) (1) as brown microcrystalline powders. Single-crystal X-ray diffraction analysis reveals that 1 crystallizes in the orthorhombic Pdd2 space group. The asymmetric unit of the solvent-free structure contains four dimethylammonium cations, three crystallographically independent Cu$^+$ centers, two BTT$^-$ ligands (BTT-1 and BTT-2), in which Cu(3) atom and BTT-1 molecule are half-occupied, as shown in Fig. S2, ESI†. The dimethylammonium cations are originating from the decomposition of the DMA molecule. All Cu$^+$ centers are four-coordinated by four nitrogen atoms from four tetrazole rings in different BTT molecules in a distorted tetrahedral geometry. The Cu–N distances are in the range of 1.978(2)–2.097(2) Å. It should be noted that BTT11 and BTT12 exhibit different coordination styles, which serve as µ$_1$-bridgings, respectively, bonding to eight and six Cu$^+$ centers, respectively (Fig. S3, ESI†). Through the connection of BTT-2 and BTT-1, respectively, a Cu$_3$ cluster and a Cu$_2$ cluster are formed, which are further linked to form linear chains along c axis and b axis (Fig. S4, ESI†). The Cu$_3$ and Cu$_2$ clusters in the corresponding 1D chain are further terminally coordinated by BTT-1 and BTT-2 ligands, respectively, leading to a 3D open framework imparting meso-helical chains as viewed along [100] direction (Fig. 1a). The two symmetrically related helices (which are labeled as L1 and R1) coexist and arrange alternatively in the centrosymmetric structure (Fig. 1b), which results in an achirality structure. The pitch for the helice, represented by the Cu$_3$·Cu$_3$ distance, is 14.62 Å.

A prominent structural feature of 1 is the presence of a giant multi-prismatic nanoscale cage built from the upholding of the helices, in which large cavities (23.8 Å × 18.9 Å × 16.2 Å, Fig. 2) are interconnected with four types of small windows (−6.4 Å × 10.4 Å, −6.9 Å × 11.2 Å, −8.8 Å × 10.3 Å and −4.0 Å × 4.3 Å; see Fig. S5, ESI†). Extensive nitrogen-donor sites of 67% are exposed to the four tetrazole rings, which enable compound 1 to serve as promising porous material for gas storage and separation. The solvent-accessible void fraction calculated using PLATON$^{19}$ is ~40.5% of the total crystal volume (31702 Å$^3$).

PXRD patterns for the as-synthesized material and samples after treatment at different conditions are shown in Fig. S6 (ESI†). The diffraction peaks of the as-synthesized MOF match well with the simulated pattern on the basis of the single-crystal structure. Crystalline 1 is stable in air, DMA, methanol, acetone and water, as confirmed from the PXRD test. Thermogravimetric analyses (TGA) indicate that the acetone, as compared with methanol, is a better solvent for exchanging the higher boiling point solvents of DMA and water remained in 1 (Fig. S7, ESI†).

In order to confirm its permanent porosity, N$_2$ sorption isotherm was collected at 77 K. An activated sample 1a was prepared by exchange of the solvent of the as-synthesized 1 with acetone followed by evacuation at 40 °C. The N$_2$ sorption isotherm (Fig. S8, ESI†) of 1a shows typical Type I behaviour, indicating a microporous structure, with a Brunauer–Emmett–Teller (BET) surface area of 701 m$^2$ g$^{-1}$ (Langmuir surface area of 801 m$^2$ g$^{-1}$). The BET surface area was calculated from a line regression plot of 1/(Q(P/P$_0$−1)) versus P$_0$/P, where Q is the total volume absorbed at a particular point P$_0$/P and P$_0$ is 1 atm pressure, within the range 0.005 < P$_0$/P < 0.05 (Fig. S9, ESI†). The single point adsorption total pore volume at P = 0.99 bar from the N$_2$ sorption data is 0.302 cm$^3$ g$^{-1}$, which is a little lower than the value of 0.36 cm$^3$ g$^{-1}$ estimated from the single-crystal structure. The activated 1a also reversibly adsorbs up to 1.03 wt% (116 m$^3$ g$^{-1}$) of hydrogen gas at 77 K and 1 bar (Fig. S8, ESI†), which is much less than those of M–BTT (M=Fe, Mn, Cu) series MOFs with exposed M$^{2+}$ coordination sites (1.7–2.3 wt%, Table S5, ESI†).

Establishment of the permanent porosity of 1a encourages us to examine its potential application of selective gas separation. Interestingly, 1a has higher affinity and capacity for CO$_2$ (82.8 cm$^3$ g$^{-1}$, 3.7 mmol g$^{-1}$ and 14.0 wt% at 273 K and 800 Torr) than that for CH$_4$, N$_2$ or H$_2$ (Fig. 3 and Table S6, ESI†). With 162.8 mg g$^{-1}$ of the CO$_2$ uptake, 1a is also comparable to many MOFs although its specific surface area is much lower (Table S5, ESI†). In general,
nitrogen-rich porous polymers have high CO$_2$ affinity and adsorption capacity due to dipole-quadrupole interactions between CO$_2$ and nitrogen sites. The obtained results demonstrate that the presence of high percentage of open nitrogen-donor sites within the framework is mainly responsible for the high and selective CO$_2$ uptake. The isosteric heat of adsorption ($Q^	ext{st}$) for CO$_2$ was calculated based on the adsorption isotherms at different temperatures (273 and 298 K, Fig. S10, ESI$	extsuperscript{†}$) through virial-equation. The CO$_2$ sorption isotherms are completely reversible, indicating that the interaction between CO$_2$ and 1a is weak enough to allow material regeneration without heating. The $Q^	ext{st}$ at zero coverage was found to be 31.4 kJ mol$^{-1}$, and was followed by the convergence into a pseudo-plateau (~28.2 kJ mol$^{-1}$) with relatively high uptake (Fig. S11a, ESI†). It is within the desirable range for CO$_2$ sorbents according to recent findings by Wilmer et al.$^{26}$ Remarkably, three consecutive cycles of CO$_2$ sorption isotherms at 298 K didn’t show any hysteresis and exhibit very good reversibility even without further evacuation treatment after every cycle test (Fig. S11b, ESI†).

<table>
<thead>
<tr>
<th>MOFs</th>
<th>BET</th>
<th>CO$_2$ uptake at 0.15 bar (wt%, mmol g$^{-1}$)</th>
<th>N$_2$ uptake at 0.75 bar (wt%, mmol g$^{-1}$)</th>
<th>selecivity</th>
<th>Tem (K)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>mmen-Cu-BTTr</td>
<td>870</td>
<td>9.5/2.38</td>
<td>0.2/0.07</td>
<td>165$^a$</td>
<td>298</td>
<td>2a, 11</td>
</tr>
<tr>
<td>HKUST-1</td>
<td>1400</td>
<td>11.6/2.98</td>
<td>0.41/0.15</td>
<td>101</td>
<td>298</td>
<td>2a, 12</td>
</tr>
<tr>
<td>en-Cu-BTTr</td>
<td>345</td>
<td>2.3/0.54</td>
<td>0.17/0.06</td>
<td>44</td>
<td>298</td>
<td>2a, 17</td>
</tr>
<tr>
<td>Mg$_2$(dobdc)</td>
<td>2060</td>
<td>20.6/5.9</td>
<td>1.8/0.67</td>
<td>44</td>
<td>303</td>
<td>2a, 4</td>
</tr>
<tr>
<td>1a</td>
<td>701</td>
<td>2.6/0.63</td>
<td>0.22/0.08</td>
<td>40</td>
<td>298</td>
<td>This work</td>
</tr>
<tr>
<td>Fe-BTTr</td>
<td>2010</td>
<td>5.3/1.27</td>
<td>0.95/0.34</td>
<td>18</td>
<td>298</td>
<td>2a, 23</td>
</tr>
<tr>
<td>Cu-BTTr</td>
<td>1900</td>
<td>2.9/0.69</td>
<td>0.49/0.18</td>
<td>19</td>
<td>298</td>
<td>2a, 17</td>
</tr>
<tr>
<td>MOP-177</td>
<td>5400</td>
<td>0.6/0.14</td>
<td>0.39/0.14</td>
<td>5</td>
<td>298</td>
<td>2a, 4</td>
</tr>
</tbody>
</table>

$^a$ reported by ref. 2a $^b$ reported by ref. 11

Since 1a is stable in liquid water, the effect of water treatment (immersion in liquid water for 1 day) on the BET and CO$_2$ uptake were examined. The BET surface area decreased to about one quarter (from 701 to 179 m$^2$ g$^{-1}$) of the dehydrated form and the CO$_2$ uptake at 273 K decreased to about one third (from 82.8 to 30.4 cm$^3$ g$^{-1}$, see Fig. S12, ESI†) of its original value, which are attributed to the water adsorption in the channels. In combination with the PXRD analysis, the overall framework of 1a remains intact upon exposure to water, indicating that the tetrazole-based linkers afford stronger M–N bond which protect the material from hydrolysis.

The CO$_2$/CH$_4$, CO$_2$/N$_2$, CO$_2$/H$_2$ selectivities at low pressure for 1a were evaluated by using the initial slope ratios estimated from Henry’s law$^{20,21}$ constants for single-component adsorption isotherms collected at 273 and 298 K as summarized in Fig. S13 and Table S7 (ESI†). Generally speaking, gas sorption on MOF’s is most often driven by physisorption which is closely related to the specific surface area. Therefore, a high CO$_2$ uptake is often accompanied by a comparably high N$_2$ uptake as well. Remarkably, the selectivities of CO$_2$/N$_2$ and CO$_2$/H$_2$ at 273 K, which were calculated to be 69.7 and 577.2, respectively, are greatly higher than that of CO$_2$/CH$_4$ (13.3). Moreover, for all the cases, the selectivity decreases as temperature increases. The high adsorption selectivity of 1a towards CO$_2$ over N$_2$ and H$_2$ under the same condition indicates that 1a is highly applicable in the separation of CO$_2$ over N$_2$ and H$_2$.

The selectivity studies described above were also supported by results from the ideal adsorbed solution theory (IAST)$^{22}$ which were predicted based on the experimental single-component isotherms (Fig. S14 and Table S8–S9, ESI†). The CO$_2$/N$_2$ selectivity increases with decreasing total pressure and increasing partial pressure (Fig. S15, ESI†). For the case of $P_{CO_2}/P_{N_2}=0.15:0.75$, which is a typical composition for the flue gas from power plants, the obtained CO$_2$/N$_2$ selectivity of 40 (298 K) for 1a at low pressure ranks among the high end for MOF materials (Table 1). In fact, only few materials show a high CO$_2$/N$_2$ selectivity (>40), including the MOF-74 series, HKUST-1, and post-synthesis modified framework mmcn-Cu-BTTr, bio-MOF-11, etc. The CO$_2$/H$_2$ selectivity increases with increasing partial pressure (Fig. S16, ESI†). As for the CO$_2$ capture and H$_2$ purification under a 0.2:0.8 or a 0.4:0.6 CO$_2$/H$_2$ gas mixture, the selectivities at 298 K are in the range of 267–355 and 237–278, respectively.

Because the low pressure gas sorption studies indicate that 1a is far from saturation at 1 bar, high pressure gas sorption measurements for CO$_2$, H$_2$ and N$_2$ were performed by using a MSB (Magnetic suspension balance) apparatus. The CO$_2$ uptake by 1a shows a sharp increase below 5 bar. At saturation, 1a takes up 253.44 mg g$^{-1}$ of CO$_2$ at 273 K, 30 bar and 233.64 mg g$^{-1}$ of CO$_2$ at 298 K, 45 bar (Fig. 4). As expected, 1a can only adsorb a very small amount of N$_2$ (52.92 mg g$^{-1}$) and H$_2$ (2.84 mg g$^{-1}$) even at 273 K and 65 bar. The CO$_2$ uptake by 1a is comparable to the reported values for UiO-66 (24.3 wt%, at 303 K and 18 bar)$^{24}$ and SNU-9 (29.9 wt%, at 298 K and 30 bar)$^{25}$ with a similar pore volume of 0.35 cm$^3$ g$^{-1}$ for the former and 0.366 cm$^3$ g$^{-1}$ for the latter. And, it is much lower than that of MOF-210 (74.2 wt% at 298 K and 50 bar)$^{26}$ and MOF-177 (56.8 wt% at 298 K and 30 bar)$^{27}$ with a very big pore volume of 3.60 and 1.89 cm$^3$ g$^{-1}$, respectively. These results further prove that CO$_2$ capacities at high pressure are much dependent on surface area and pore volume of the MOFs.

The CO$_2$ capture performance of 1a under more practical condition was evaluated using a thermogravimetric analysis apparatus, with use of a CO$_2$–N$_2$ mixture (15:85 v/v) to simulate the major components of flue gas. About 30 mg sample of 1a was blown repeatedly by CO$_2$–N$_2$ mixture and pure N$_2$ flow at 303 K (Fig. S17–
promising porous material for gas storage and separation. This work demonstrates its ability to withstand cyclic exposure to the mixed gas stream, which may render the material suitable for use as an adsorbent in pressure swing absorption process for CO₂ capture.

Conclusions

In conclusion, through the incorporation of accessible nitrogen-rich tetrazole-based molecule of H₂BT, we successfully isolated a water-stable poly-nuclear Cu(I)-based MOF which incorporates giant multi-prismatic cages interconnected by four types of windows. Extensive nitrogen-donor sites of 67% are exposed to these channels. The gas sorption studies toward CO₂, N₂, H₂ and CH₄ under low-pressure or high-pressure conditions are discussed in detail. These results indicate that the activated 1a has high CO₂/N₂ and CO₂/H₂ sorption selectivities. Significantly, 1a is able to maintain its CO₂ capacity after long-term storage under a more practical condition, which enables compound 1a to serve as promising porous material for gas storage and separation. This work clearly demonstrates the potential of using the nitrogen-donor ligand for preparing porous inorganic materials use for selective capture of CO₂.

This work was financially supported by the NNSF of China (No. 21301152, 21371150), Foundation from the Priority Academic Program Development of Jiangsu Higher Education Institutions.

Notes and references

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† Electronic Supplementary Information (ESI) available: Experimental details, characterization and additional structural data. CCDC 1034129. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c000000x