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Cucurbit[7]uril: an amorphous molecular material for highly selective carbon dioxide uptake†

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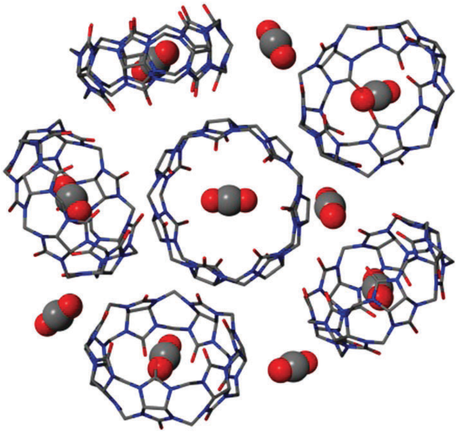
Cucurbit[7]uril (CB[7]), in its amorphous solid state, shows one of the highest CO_2 sorption capacities among known organic porous materials at 298 K and 0.1 and 1 bar. In addition to the highest CO_2 capacity, CB[7] also shows remarkable selectivity of CO_2 over N_2 and CH_4. These properties, along with the existence of readily available precursors, indicate amorphous CB[7] might find applications in recycling CO_2 particularly considering the easy synthesis and potentially low manufacturing costs.

The desire to reduce greenhouse gas emissions has stimulated significant interest in sequestration of carbon dioxide (CO_2) from major emission sources, such as power plants and industrial facilities.[1] In this regard, various alkyl amine solutions have been widely used in industry to selectively capture CO_2 from the flue gas through a chemsorptive process.[2] Although such systems have achieved significant sorption capacities, major drawbacks including degradation of the solvent and the high temperature required to regenerate the adsorbed gas, leading to low energy efficiency and high cost.[3] Therefore, alternative concepts such as physical sorption on porous solids have been proposed.

Recently, metal–organic frameworks (MOFs) or porous coordination polymers (PCPs) have drawn a great deal attention as very promising adsorbents.[4] These hybrid materials generally have exceptional high surface areas, tunable functionalities and significant CO_2 sorption capacity and selectivity.[5] However, the majority of MOFs and PCPs are sensitive to water, a major component in flue gas, thus creating barriers for MOFs and PCPs to be utilized in CO_2 capture and sequestration. On the other hand, low-density porous organic hosts, particularly supramolecular organic frameworks (SOFs) assembled from cheap, robust and readily available organic molecules, may be good alternatives as CO_2 adsorbents.[6,7] One recent example is the organic host cucurbit[6]uril (CB[6]), which assembles into a honeycomb-like structure with isolated 1D nanochannels and shows highly selective CO_2 sorption.[8] Nevertheless, relatively few types of SOF materials show permanent porosity, as most SOFs are not sufficiently robust to retain microporosity upon guest removal. Thus, amorphous molecular solids with intrinsic microporosity as synthesized may be of great importance for large-scale CO_2 capture applications in industry. Herein, we report a well-known molecular cage compound, CB[7], retains significant porosity in its amorphous solid state and shows highly selective adsorption towards CO_2 and SO_2 (Scheme 1).

Organic amorphous molecular solids have been largely neglected in the gas adsorption arena due to two main reasons: (1) organic molecules tend to pack into a dense phase to maximize attractive inter- and intra-molecular interactions in the solid state, which generally precludes the formation of large voids and channels;[9] (2) it is very difficult to characterize the intrinsic structure of amorphous molecular solids due to the loss of crystallinity. Previously, we have reported porous amorphous molecular materials based on "Noria" and its derivatives.[10] These molecules possess large accessible internal cavities in a rigid molecular structure, which was considered a key feature to alter the close-packing in the amorphous solid state. Inspired by this phenomenon, we decided to study



Scheme 1 Schematic diagram of CO_2 molecules stored in the amorphous solid of CB[7].

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organic hosts with similar 'hollowed-out'' structural features, focusing on the readily available CB[7], which has a larger inner cavity (279 Å^3) compared to the molecules of the 'Noria' family.

CB[7] can be readily prepared ($\sim 10^2$ gram scale) in high yield by one-pot synthesis from cheap starting materials, glycoluril and formaldehyde.[11] Like its analogue CB[6], the molecule has an enclosed cavity accessible through two identical carbonyl-laced portals. The diameters of the cavity and the portal are approximately 5.4 Å and 7.3 Å, respectively, large enough to incorporate various gas molecules and small guest molecules.[12] CB[7] was precipitated as an off-white powder during the workup, which was proved to be amorphous by powder X-ray diffraction and selected area electron diffraction (SAED). Thermogravimetric analysis (TGA) of freshly synthesized CB[7] reveals a rapid weight loss of 15% up to 150 °C, corresponding to the liberation of the enclosed solvent and water molecules, followed by a wide plateau region until 370 °C, where the solid starts to decompose. Notably, the solvent-free powder of CB[7] gains weight quickly upon cooling in the air, implying the solid contains porosity and uptakes surrounding gases.

The sorption capacity of bulk CB[7] was measured volumetrically up to 1 bar at 297 K for CO_2, CH_4 and N_2 under isothermal conditions (Fig. 1). CB[7] showed an exceptionally high CO_2 sorption capacity with little hysteresis (50 cm^3 g^{-1}, 10 wt%, 2.3 mmol g^{-1}), which is higher than those of any known organic molecular porous materials. Most remarkably, at 0.1 bar, a typical partial pressure of CO_2 in flue gas, the CO_2 uptake of CB[7] is up to 48 mg g^{-1} (1.1 mmol g^{-1}), which is the highest capacity among any porous organic molecular solids and even superior to that of many MOFs. The BET surface area of the material is calculated to be 293 m^2 g^{-1} from the isotherm of CO_2 at 196 K (see ESI). In contrast, the N_2 sorption capacity of CB[7] is very low with only 5.5 cm^3 g^{-1} (0.25 mmol g^{-1}) at 1 bar and RT. Surprisingly, N_2 gas was not detectably absorbed at 77 K, indicating that N_2 molecules are unable to diffuse into the pores due to the low kinetic energy of N_2 at such a temperature. As for CH_4, CB[7] uptake only 6.0 cm^3 g^{-1} at 1 bar and RT. The high selectivity of CO_2 over CH_4 and N_2 can be ascribed to the high charge density at the oxygen sites of the portal which might facilitate local-dipole/quadrupole interactions with CO_2 that would be absent for CH_4 or N_2. In addition, the electron lone pair on nitrogen may have strong interaction with CO_2 molecules which accounts for high uptake. The absorbed CO_2 in CB[7] can be mostly regenerated by the pressure swing process and the remaining trace CO_2 can be fully liberated by heating at 50 °C under vacuum. The CO_2 storage capacities of amorphous CB[6] solid were also investigated at 297 K to confirm its porosity and compare with those of CB[7]. It was found that at 0.1 and 1 bar pressure, 5 cm^3 g^{-1} and 25.2 cm^3 g^{-1} CO_2 could be stored in CB[6] solid, corresponding to 0.23 mmol g^{-1} and 1.2 mmol g^{-1} respectively. This implies that at low pressure, CB[7] has a higher affinity for CO_2 than CB[6] in the amorphous solid state, which may ascribe to combined factors of pore sizes and numerous adsorption sites.

To investigate the high affinity of CB[7] toward CO_2, the enthalpy of CO_2 adsorption was estimated from the sorption isotherms at 273 K and 297 K using the virial equation. At zero coverage, the enthalpy of CO_2 adsorption is as high as 40.0 kJ mol^{-1}, which is significantly higher than those of porous organic solids and can be comparable to those of MOFs with open metal sites or amine-functionalized pore walls for strong CO_2 binding.[5f,k] The strongly absorbed CO_2 in the solid is further evidenced by the solid state NMR study. The ^{13}C MAS NMR spectrum of the sample containing CO_2 shows, in addition to the broad peaks of matrix carbon atoms, a neat signal at δ = 123.6 ppm which was assigned to the unprotonated carbon of CO_2 (Fig. 2). The remarkable upfield shift of $\Delta\delta_C$ = −1.8 ppm for the stored CO_2 with respect to the gas phase implies the gas carbon atoms are located as closely as possible to the molecular walls, presumably in close proximity to the negative-charged carbonyl oxygen atoms and or electron-donating nitrogen atoms of host molecules.

Even though it is very difficult to determine the exact CO_2 sorption sites in amorphous CB[7] due to the lack of crystallinity, we can still get some insights based on the isotherms and molecular structure. It is evident by the gas adsorption study that in disordered fashion molecules of CB[7] could not pack efficiently in the solid state to rule out voids. The internal cavity (inside cages) of the molecule could not be blocked or shielded by the neighboring host molecules. In addition, the bulkiness and shape of molecule may also attribute to the generation of the interstitials voids. This is manifested by the calculation of host: guest ratios from the

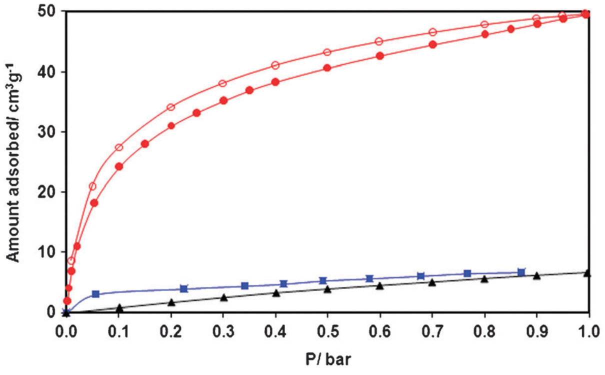

Fig. 1 CO_2 (red circles), CH_4 (blue squares), and N_2 (black triangles) sorption isotherms for CB[7] at 297 K (filled symbols: adsorption; open symbols: desorption).

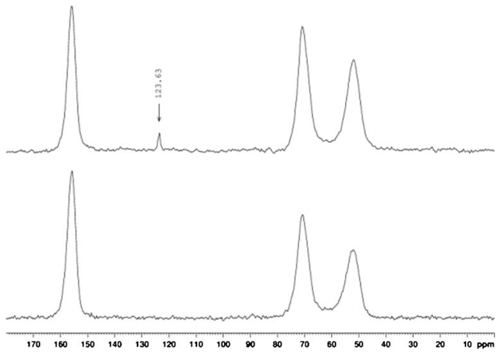

Fig. 2 (a) Solid-state ^{13}C NMR spectrum of CB[7] amorphous solid at room temperature (Bottom). (b) With stored CO_2 which give rise to the signal at δ = 123.6 ppm (Top).

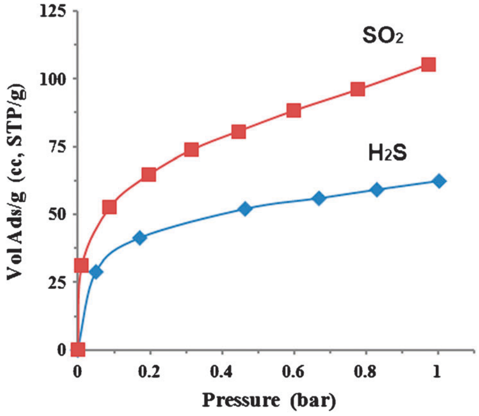

Fig. 3 SO_2 (red squares) and H_2S (blue squares) sorption isotherms for CB[7] at 297 K.

isotherms: the maximum sorption capacity for CO_2 measured at 1 bar and 196 K is 118 cm^3 g^{-1} (5.3 mmol g^{-1}), which corresponds to 6.1 CO_2 molecules per CB[7]. Based on 60% occupancy, the molecular cavity is suitable to accommodate four CO_2 molecules. Thus, the remaining 2.1 CO_2 molecules must be absorbed in the interstitials voids.

The porous solid of CB[7] was also investigated for the storage of other gases of interest, such as SO_2 and H_2S (Fig. 3). It was found that CB[7] showed an exceptionally high affinity toward SO_2. At 1 bar and 297 K, the uptake capacity is measured as 4.7 mmol g^{-1} (105 cm^3 g^{-1}, 30 wt%), corresponding to 5.5 mol of SO_2 per mole of CB[7]. Even at 0.01 bar, a typical partial ratio of SO_2 in flue gas, the uptake is still as high as 1.4 mmol g^{-1} (1.6 mol SO_2 per mol of CB[7]). Such a high affinity may largely be ascribed to the strong dipole–dipole interactions between the polar SO_2 molecules and highly charged portal of CB[7]. CB[7] has also exhibited high affinity for H_2S with a capacity of 2.8 mmol g^{-1} (62.5 cm^3 g^{-1}, 9.5 wt%) at 1 bar. These results imply the CB[7] solid could be very useful for the removal of SO_2 from flue gas and H_2S for natural gas purification.

In summary, we have reported an amorphous molecular porous materials based on CB[7] and revealed that the porosity is intrinsic to the molecular cage structure. CB[7] exhibits high thermal stability, permanent porosity and remarkable sorption properties toward CO_2 and SO_2 at 1 bar and 297 K. Considering the ease and low cost of preparing these materials, they may find suitable application for recycling CO_2 or removing SO_2 from flue gas stream. These results indicate further investigation of porous solids based on covalently assembled cage molecules for gas separation applications is warranted. Future work will be focused on the investigation of CB[7] analogues with larger molecular cavities (CB[*n*], $n = 8$, 10) for improved CO_2 storage capacities and selectivity.

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