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# Surface modification induced enhanced CO<sub>2</sub> sorption in cucurbit[6]uril, an organic porous material†

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The CO<sub>2</sub> adsorption properties of an organic macrocycle, cucurbit[6]uril (CB[6]), have been evaluated through experimental and theoretical studies. Quantum mechanical calculations show that CB[6] is capable of adsorbing the CO<sub>2</sub> molecule selectively within its cavity relative to nitrogen. Adsorption experiments at 298 K and at 1 bar pressure gave a CO<sub>2</sub> adsorption value of 1.23 mmol g<sup>-1</sup> for the unmodified material. Significant enhancements in the CO<sub>2</sub> adsorption capacity of the material were experimentally demonstrated through surface modification using physical and chemical methods. Ethanolamine (EA) modified CB[6] provided an excellent sorption selectivity value of 121.4 for CO<sub>2</sub>/N<sub>2</sub> at 323 K and is unique with respect to its discrimination potential between CO<sub>2</sub> and N<sub>2</sub>. The chemical nature of the interaction between CO<sub>2</sub> and amine is shown to be the primary mechanism for the enhanced CO<sub>2</sub> absorption performance.

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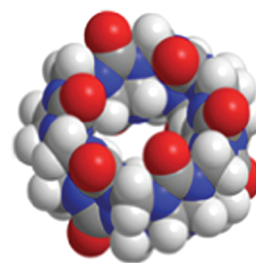
## 1. Introduction

The ever-increasing concentration of CO<sub>2</sub> in the Earth's atmosphere through gaseous waste emissions from the cement, iron and steel industries, as well as from thermal power plants, has necessitated substantial discussions on CO<sub>2</sub> separation, sequestration and reuse.<sup>1–3</sup> The selective adsorption of CO<sub>2</sub> from industrial gaseous wastes and flue gases, followed by its recycling/removal, is therefore a research topic of prime importance.<sup>4–10</sup> The inherent ability of amine solutions to capture CO<sub>2</sub> selectively from flue gas through the absorption between amine and CO<sub>2</sub> molecules is well established in the literature.<sup>11–14</sup> However, the handling and corrosion issues associated with the use of liquid amines and the loss of liquid amine at working temperatures remain the main drawbacks of these kinds of materials.<sup>15–18</sup> In addition, desorption of CO<sub>2</sub> from these materials is energy consuming and thus reinforces the high energy penalty for the CO<sub>2</sub> separation process.<sup>19–21</sup> Therefore, alternative approaches, such as physical and chemical adsorption

on porous solids, have attracted attention as potential alternative solutions.

Recently, porous macrocyclic systems of both organic and inorganic origin have drawn a great deal of interest as promising candidates for molecular gas adsorption.<sup>22–30</sup> Cucurbit[x]uril, (CB), is an interesting organic macrocyclic system typically belonging to the class of porous organic materials, with exceptional properties suitable for potential applications in gas adsorption, host–guest chemistry and supramolecular complexation. The cavity of cucurbit[6]uril has nanoscale dimensions that position CB[6] as the most probable candidate among the CB[x] family for CO<sub>2</sub> adsorption.<sup>31–37</sup> The structure of CB[6] and its approximate cavity dimensions are shown in Fig. 1.

Owing to these favourable structural properties, the material has recently been explored as a prospective candidate for CO<sub>2</sub>



Cavity Dimensions	Size (Å)
Height	9.1
Outer Diameter	5.8
Inner Diameter	3.9

Fig. 1 Structure of Cucurbit[6]uril, C<sub>36</sub>H<sub>36</sub>N<sub>24</sub>O<sub>12</sub> (carbon, nitrogen, oxygen and hydrogen are coloured dark grey, blue, red and light grey, respectively).

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adsorption. For example, Kim and co-workers recently reported that CB[6] recrystallized from HCl showed high selective adsorption capacity towards CO<sub>2</sub> over CO at 298 K and 1 bar pressure.<sup>38</sup> It can therefore be anticipated that the modification of CB[6], either by chemical or physical means, provides an alternate option for the enhancement of the adsorption ability.<sup>39,40</sup> The high quadrupolar moment of CO<sub>2</sub> can be efficiently used for sequestration by logically employing a polar functional group with a high affinity towards CO<sub>2</sub> for modifying the pores of CB[6]. Such modifications will enhance the adsorption capacity as well as the selectivity for CO<sub>2</sub>. However, Vaidhyanathan *et al.* demonstrated that a high degree of flexibility could lead to excessive clustering of amine groups thereby decreasing the adsorption capacity.<sup>41</sup> In this context, the proper incorporation of amine containing molecules on solid sorbents, such as CB[6] or its surface, would be a reasonable strategy to achieve a high performance CO<sub>2</sub> separation system with higher adsorption capacity.<sup>42–47</sup> Here, we have tried to understand the CO<sub>2</sub> adsorption properties of CB[6] through experimental and theoretical studies.<sup>48,49</sup> Later, we have attempted to improve the adsorption properties by modifying the material using physical and chemical means, ultimately realising modified materials with superior CO<sub>2</sub> absorption performance.

## 2. Experimental section

### 2.1 Materials

Cucurbit[6]uril (CB[6]) was purchased from Sigma Aldrich and used as received without any further purification (sample code CB[6]). H<sub>2</sub>O<sub>2</sub> purchased from Merck India Pvt. Ltd, and ethanolamine (EA) purchased from SD Fine Chemicals Ltd were also used without further purification.

### 2.2 Synthesis of physically modified CB[6]

The physical modification of CB[6] was first explored by treating with H<sub>2</sub>O<sub>2</sub>. For this, 0.1 mmol of CB[6] was added to 10 mL of 30% H<sub>2</sub>O<sub>2</sub> followed by sonication for a few minutes. The samples were filtered, dried and characterized using various spectroscopic techniques (sample code CB[6]-H<sub>2</sub>O<sub>2</sub>). Physical modification was also achieved by cryogenic grinding of the samples under liquid N<sub>2</sub> in an agate mortar (sample code CB[6]-liq. N<sub>2</sub>). The modified samples were stored in air-tight sealed containers in all cases.

### 2.3 Synthesis of chemically modified CB[6]

The chemical modification of CB[6] particles was attempted by treating them with molecules having amine groups. We selected EA as the candidate for incorporating amine groups into the hydrophobic CB[6] cavity based on recent literature reports.<sup>50–53</sup> The solvo-thermal process of amine incorporation was carried out at 353 K for 8 h by taking 0.1 mmol of CB[6] and 5 mL of ethanolamine. The sample was further dried and characterized using various analytical and spectral techniques (sample code CB[6]-EA).

### 2.4 Characterization techniques

We evaluated the inherent CO<sub>2</sub> selective adsorption behaviour of CB[6] and modified CB[6] experimentally. Various microscopic and spectroscopic studies were conducted for the characterization. Scanning Electron Microscopy (SEM) analysis was performed using a JEOL JSM-5600LV Scanning Electron Microscope (tungsten source) with an accelerating voltage of 20 kV. Transmission Electron Micrographs (TEMs) of samples were recorded on a JEOL 3000EX TEM. Powder X-ray Diffraction (PXRD) analysis was performed on a XEUS 2D SAXS/WAXS X-Ray diffractometer system operated at 50 kV and 0.6 mA. The source was Cu K<sub>α</sub> radiation ( $\lambda = 1.54 \text{ \AA}$ ). IR spectroscopic studies were carried out using an ALPHA-T BRUKER FT-IR spectrophotometer with a spectral resolution of  $\pm 4 \text{ cm}^{-1}$ . Volumetric CO<sub>2</sub> and N<sub>2</sub> adsorption experiments were performed using a BEL automatic gas sorption analyser (Belsorp max, BEL Japan INC). CO<sub>2</sub> and N<sub>2</sub> gas sorption was also measured gravimetrically at 323 K under flowing gas. A Perkin Elmer STA 6000 Thermo-gravimetric Analyser (TGA) was used to perform this measurement. For the measurement, about 10 mg of sample was initially loaded in the TGA sample pan. These samples were heated to 423 K under a He or N<sub>2</sub> gas flow of 30 mL min<sup>-1</sup> to clean them of any adsorbed impurities. The temperature of the TGA was then decreased to 323 K and then the sweep gas was changed to the adsorbate gas of CO<sub>2</sub> or N<sub>2</sub>. The increase in weight of the sample with time was measured and the amount adsorbed was calculated from it.

We also performed quantum mechanical energy minimizations to investigate the adsorption strength of CO<sub>2</sub> in CB[6] cavities. All such calculations were performed within the framework of Kohn–Sham density functional theory as implemented in the Quickstep module of CP2K.<sup>54</sup> Here, the nuclei and core electrons are described using the pseudo potentials of Goedecker, Teter and Hutter while the valence orbitals were expanded in a triple-zeta, doubly polarized (TZ2P) basis set.<sup>55</sup> An auxiliary plane wave basis set was used for calculating the density with a 400 Ry cut-off. The reason that pseudopotentials were used even for light elements is because the algorithm employed is the Gaussian Plane Wave technique that underpins CP2K. In this approach, the electron density is expanded in an auxiliary basis set of plane waves for the solution of Poisson's equation and therefore to reduce the cutoff of this basis, it is more efficient to replace the 1s core electrons (or smooth them as in the case of hydrogen). This is a standard feature of the method in CP2K, as well as other codes such as SIESTA that use an auxiliary grid for the electron density. The exchange–correlation functional of Perdew, Burke and Ernzerhof (PBE) was used along with dispersion corrections using the D3 approach of Grimme *et al.*<sup>56,57</sup> While there are more elaborate functionals that could be chosen than PBE, the dominant contribution to binding in this physisorption system is the van der Waals term and therefore this choice of exchange–correlation functional should be adequate. For the weaker physisorption prevailing in this system, the bonds in the adsorbate and adsorbent are hardly perturbed and therefore zero point energy changes are not a significant contribution and yet are disproportionately expensive to compute since they



require finite differencing of the forces over the entire system. This could also make the computations more susceptible to numerical noise and therefore they were not considered in our study. All binding energies in the calculations were corrected for basis set superposition error using a counterpoise correction.

### 3. Results and discussion

Firstly, SEM and TEM analyses were performed to understand the morphological properties of CB[6] before modification. The SEM images revealed that the particles possess a rod-like morphology with a length in the range of 2–5  $\mu\text{m}$  and width in the range of 100–300 nm (Fig. 2A). The rod-like morphology of the unmodified CB[6] is further evidenced by TEM analysis (Fig. 2B).

The unmodified CB[6] sample was further characterized using FTIR and XRD analyses (Fig. 3A and B). The X-ray diffraction analysis indicated that CB[6] has an analogous characteristic structural pattern in the solid state as reported in the literature.<sup>58</sup> FTIR analysis indicated peaks corresponding to 1722 and 3518  $\text{cm}^{-1}$ , which clearly confirmed the presence of carbonyl stretching and CO–N vibrations, respectively.

To have a better understanding of the pore structure, we examined the gas adsorption behaviour of the unmodified CB[6] powder samples. The temperature for cleaning pre-treatment (de-gassing) before the gas adsorption was selected based on the weight loss profile of the sample during heating as shown in the TGA analysis (Fig. S1, ESI†). The TGA profile clearly showed four different weight loss patterns in the temperature regimes of RT–120  $^{\circ}\text{C}$  (3.6% loss), 120–330  $^{\circ}\text{C}$  (2.23%),

330–490  $^{\circ}\text{C}$  (54.27%) and finally 490  $^{\circ}\text{C}$  to the measured maximum temperature of 600  $^{\circ}\text{C}$  (11.98%). Based on the TGA results, samples were de-gassed at 150  $^{\circ}\text{C}$  for 2 h prior to  $\text{N}_2$  adsorption measurements at 77 K.

$\text{N}_2$  adsorption isotherms of the unmodified sample at 77 K (Fig. S2, ESI†) showed a Type III isotherm, representative of gas adsorption on the surface, indicating a very restricted entry of  $\text{N}_2$  molecules into CB[6] pores under measurement conditions. As a result, the available porosity of the sample was very limited (0.032  $\text{cc g}^{-1}$ ), which is further reflected in the low surface area value of 9.3  $\text{m}^2 \text{g}^{-1}$  calculated from the adsorption data of the sample.

$\text{N}_2$  adsorption measurements at 323 K also showed a similar type of isotherm, revealing an adsorption capacity of 1.63  $\text{cc g}^{-1}$  (0.073  $\text{mmol g}^{-1}$ ) for  $\text{N}_2$  at 100 kPa pressure (Fig. 4). However, the  $\text{CO}_2$  adsorption isotherms clearly indicated adsorption typical of porous materials with maximum adsorption values of 27.5  $\text{cc g}^{-1}$  (1.23  $\text{mmol g}^{-1}$ ) at 298 K and 9.36  $\text{cc g}^{-1}$  (0.42  $\text{mmol g}^{-1}$ ) at 323 K (Fig. 4).  $\text{CO}_2/\text{N}_2$  adsorption selectivity at 323 K can be calculated as 5.75 from this adsorption data.

Further, gravimetric adsorption capacity measurements were carried out in a TGA as explained earlier. Samples were heated to 423 K under a gas flow of 30  $\text{mL min}^{-1}$  to clean them of any adsorbed impurities. The TGA profile of the sample

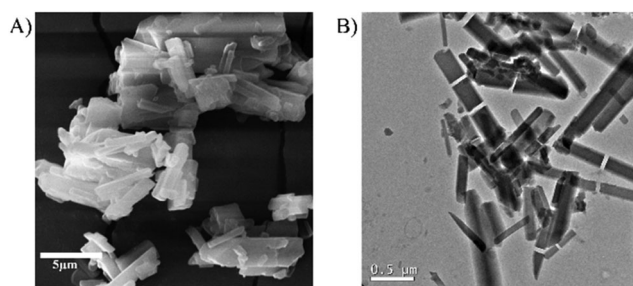


Fig. 2 (A) SEM and (B) TEM images of unmodified CB[6].

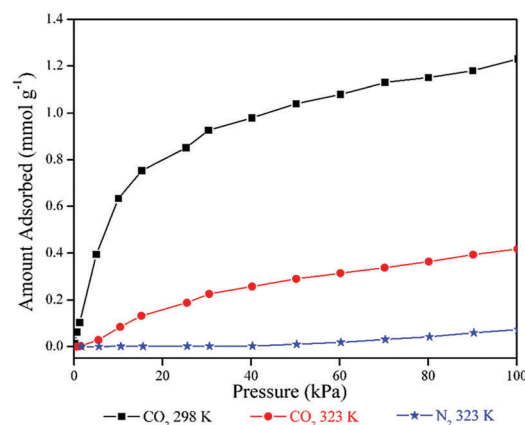


Fig. 4  $\text{CO}_2$  adsorption isotherm of unmodified CB[6] at 298 K and 323 K,  $\text{N}_2$  adsorption isotherm at 323 K.

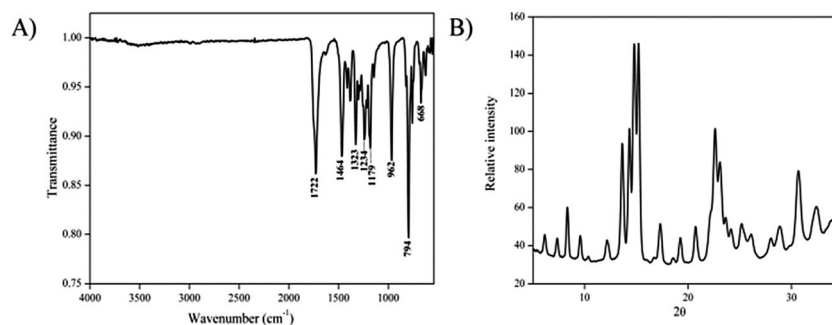


Fig. 3 (A) FT-IR and (B) XRD of unmodified CB[6].



(Fig. S3, ESI†) evidenced a  $\sim 5\%$  weight reduction during the cleaning step. However, the sample weight remained stable after the initial reduction indicating that all of the physically adsorbed impurities were successfully removed before the adsorption step.  $\text{CO}_2$  and  $\text{N}_2$  adsorption capacity values at 323 K after 60 minutes of adsorption were measured as  $0.54 \text{ mmol g}^{-1}$  and  $0.06 \text{ mmol g}^{-1}$  using the gravimetric measurement.  $\text{CO}_2/\text{N}_2$  adsorption selectivity at 323 K can be calculated as 9 from this adsorption data, which reasonably agrees with the adsorption selectivity value calculated using the volumetric adsorption method.

We used quantum mechanical calculations to investigate the strength of adsorption (and selective adsorption) of  $\text{CO}_2$  in the CB[6] cavities. In particular, we considered the binding of  $\text{CO}_2$ ,  $\text{H}_2\text{O}$  and  $\text{N}_2$  on and in CB[6]. Starting with  $\text{CO}_2$ , we considered 9 distinct initial starting geometries as the basis for energy minimization in order to probe different binding modes (final optimized configurations are provided in the ESI†). Three binding configurations were found where  $\text{CO}_2$  was on the outer surface of CB[6] with binding energies spanning  $6.7$  to  $11.1 \text{ kJ mol}^{-1}$ . These geometries involved the oxygen atoms of carbon dioxide being directed towards hydrogen atoms of both CH and  $\text{CH}_2$  groups at distances of  $2.5$ – $2.8 \text{ \AA}$ . In the most favourable state ( $11.1 \text{ kJ mol}^{-1}$ ), the  $\text{CO}_2$  molecule bridges hydrogen of both CH and  $\text{CH}_2$  groups such that there is also a comparable distance of  $2.6 \text{ \AA}$  from a further CH group to the carbon of the adsorbate.

A local minimum was also identified when the carbon of  $\text{CO}_2$  lies approximately in the plane of the oxygen atoms of the

carbonyl groups around the pore opening to CB[6] with the molecular axis tilted at approximately  $30^\circ$  to the principal axis of the host molecule. This leads to stronger binding than in the hydrocarbon regions of the external surface with a value of  $31 \text{ kJ mol}^{-1}$ . However, the strongest adsorption sites are reserved for configurations within the centre of pore, in line with the force field results. The most stable configuration, shown in Fig. 5, is close to the centre of symmetry with  $\text{CO}_2$  oriented such that its molecular axis lies in the plane of the pore. While the strongest binding energy is  $40.0 \text{ kJ mol}^{-1}$ , there appears to be several shallow minima within ambient thermal energy in the centre of the cavity, suggesting that carbon dioxide will be relatively mobile as it explores these states. Rotating  $\text{CO}_2$  to a configuration where the molecular axis is close to parallel to the pore axis lowers the binding energy to  $24 \text{ kJ mol}^{-1}$ .

Turning now to consider the adsorption of water on CB[6], a range of binding sites were identified through the quantum mechanical calculations. The first configuration examined had water bridging two carbonyl oxygen atoms at the rim of the pore, with  $\text{H} \cdots \text{O}$  distances of  $2.03$  and  $2.16 \text{ \AA}$ , which had a binding energy of  $33.2 \text{ kJ mol}^{-1}$ . Starting from this minimum and rotating the water by  $90^\circ$  led to the most stable binding site identified with an exothermic binding energy of  $42.7 \text{ kJ mol}^{-1}$ . Interestingly, this configuration has longer distances between one of the hydrogen atoms of water and the same two carbonyl oxygen atoms of  $\sim 2.9 \text{ \AA}$ , while the remaining hydrogen of water is directed across the pore diameter (Fig. 6). Despite the seemingly longer binding contacts, this configuration appears to be preferred, presumably due to the change in alignment of the water dipole moment.

Several configurations were also explored for water in the cavity of CB[6], either close to the centre or with hydrogen of water directed towards nitrogen as the most electronegative element within this region. All energy minima were found to be isoenergetic within  $1 \text{ kJ mol}^{-1}$ , with a binding energy close to  $32 \text{ kJ mol}^{-1}$ .

Considering the results for  $\text{CO}_2$  and  $\text{H}_2\text{O}$  together, it appears that the former has the stronger preference for binding in the cavity of CB[6], while water is more stable when coordinated around the pore opening. To examine the interaction between mixed adsorbates, we optimised two arrangements where water

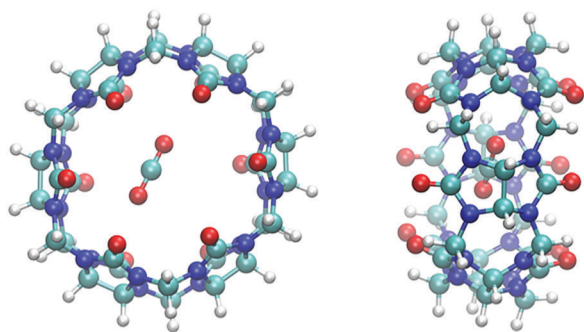


Fig. 5 Lowest internal energy configuration found for  $\text{CO}_2$  binding in CB[6] at the PBE-D3 level of theory (front and side views).

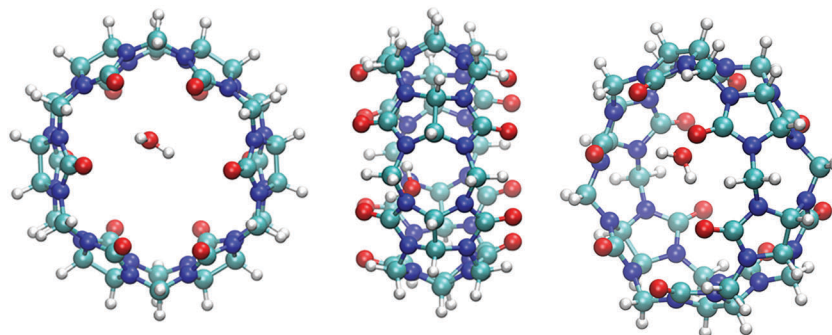


Fig. 6 Most stable binding geometry identified for water in CB[6] at the PBE-D3 level of theory (front, side and tilted views).





is in one of its favoured sites at the pore rim while carbon dioxide occupies the cavity. In both cases, the combined binding energies of CO<sub>2</sub> and H<sub>2</sub>O at their equivalent sites alone were only reduced by an amount that is comparable to ambient thermal energy and the basis set superposition correction between the adsorbates. This indicates that there is neither a penalty nor cooperative enhancement of the binding strength of water and carbon dioxide when low loadings of both are present.

Lastly, for the computational part of this study we investigated the adsorption of N<sub>2</sub> in order to consider the competition for binding sites with CO<sub>2</sub>. As would be expected, nitrogen only exhibits weak van der Waals adsorption on the outer surface of CB[6] with minima varying in binding energy from 5.5 to 10.8 kJ mol<sup>-1</sup>. The less favourable binding strengths occur when N<sub>2</sub> is positioned over the hydrocarbon regions, while adsorption is slightly more favourable closer to the carbonyl groups. Within the centre of the cavity, nitrogen has a binding energy of 26 kJ mol<sup>-1</sup> if the molecular axis lies diametrically across the pore, but is reduced to 17.8 kJ mol<sup>-1</sup> if rotated to be at right angles to this. Based on the relative binding energies of carbon dioxide and nitrogen within CB[6], there is a clear preference for the former with a selectivity ratio of 182 for the first molecule at 323 K, a temperature near which these adsorbents are to be employed for practical CO<sub>2</sub> separation applications. However, the calculations suggest that the binding energy, and also therefore the selectivity, would rapidly decrease with increased loading since only a single molecule of CO<sub>2</sub> can adsorb strongly within the cavity at any given time. Furthermore, if binding in the cavity were to be partially hindered such that both CO<sub>2</sub> and N<sub>2</sub> were to be rotated parallel to the pore axis, then the selectivity for carbon dioxide over nitrogen would be reduced to 11.

As discussed previously, adsorption experiments at 298 K showed that the amount of CO<sub>2</sub> adsorbed at 100 kPa pressure is around 1.23 mmol g<sup>-1</sup> or about 1.2 molecules of CO<sub>2</sub>/molecule of CB[6] (molecular weight of CB[6] being 996.82). This value is reasonable when compared to other reported literature values of CB[6].<sup>59</sup> However, any further improvement in CO<sub>2</sub> adsorption capacity and selectivity to other molecules would be appreciated in view of the large flow rates of CO<sub>2</sub> in industrial flue gas streams. Hence, we tried to improve the adsorption properties of CB[6] by physical and chemical surface modifications. As explained in the Experimental section, the physically modified CB[6] samples were prepared by cryogenically grinding CB[6] powder in one case and treating with H<sub>2</sub>O<sub>2</sub> in another instance. It should be noted that the treatment with H<sub>2</sub>O<sub>2</sub> is considered as a physical modification here because we did not note any chemical changes in the modified material as will be discussed in the later part of this paper. It is possible that under much stronger reaction conditions, chemical changes may occur in CB[6] when treated with H<sub>2</sub>O<sub>2</sub> or similar reagents. For the chemical modifications, we used EA molecules as explained in the experimental part. The selection of EA was based on the simplicity of the molecule for an easy understanding of the mechanism of adsorption. More importantly, we were concerned

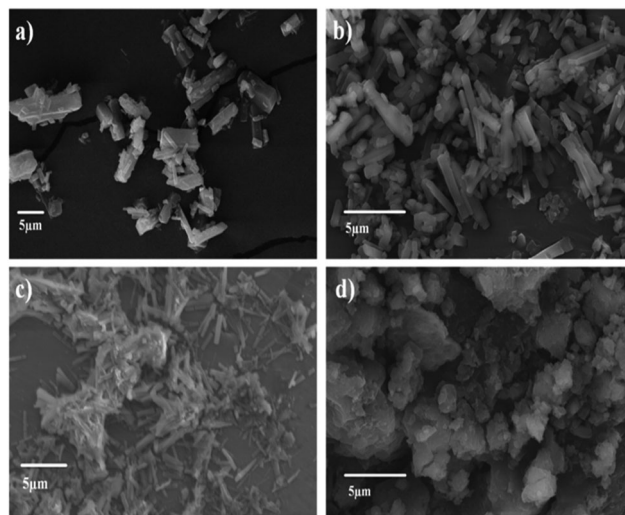


Fig. 7 SEM images of (a) CB[6], (b) CB[6]-H<sub>2</sub>O<sub>2</sub>, (c) CB[6]-liq.N<sub>2</sub> and (d) CB[6]-EA.

that the use of larger molecules such as ethylene diamine may cause steric issues within the limited space of CB[6] cavities and could lead to conflicting results even with minor changes in the conditions of study.<sup>60,61</sup> The characteristics of the modified materials are discussed in the following sections. We also performed gravimetric adsorption experiments at 323 K using CO<sub>2</sub> and N<sub>2</sub> molecules to evaluate the potential of the modified materials for practical CO<sub>2</sub> separation applications.

Firstly, in order to understand the morphological changes in CB[6] by the physical and chemical treatments, we carried out the SEM analysis of the samples. SEM images of both the unmodified (Fig. 7a) and treated samples are shown in Fig. 7b–d. The modification of CB[6] with H<sub>2</sub>O<sub>2</sub> (Fig. 7b) obviously led to some degree of agglomeration of the powder particles. Cryogenic grinding of the samples (Fig. 7c) transformed the rigid rod shaped morphology of CB[6] to much smaller fragments. Fig. 7d shows the SEM microstructure of the samples that underwent incorporation of ethanolamine into the cavity of CB[6]. A significant change in the microstructure is visible in these samples.

All the samples were also characterized using FTIR and XRD techniques (Fig. 8 and 9). XRD analysis in Fig. 8B clearly indicated that no structural modifications were induced in the CB[6] samples before and after treatment with H<sub>2</sub>O<sub>2</sub>. Auxiliary confirmation obtained from the FTIR analysis (Fig. 8A) showed a typical CB[6] spectrum devoid of any chemical modification, at least to a level that could be detected by FTIR. The cryogenically ground samples also revealed no chemical or crystal structural changes.

However, the FTIR results of the ethanolamine incorporated samples showed the presence of amine peaks at 3299 cm<sup>-1</sup>, indicating that the ethanolamine molecules were adsorbed inside the CB[6] cavity (Fig. 9A). From the XRD analysis it is clear that there has been a structural modification from the parent CB[6]. New peaks have appeared due to the presence of amines that are incorporated inside the cavity (Fig. 9B).



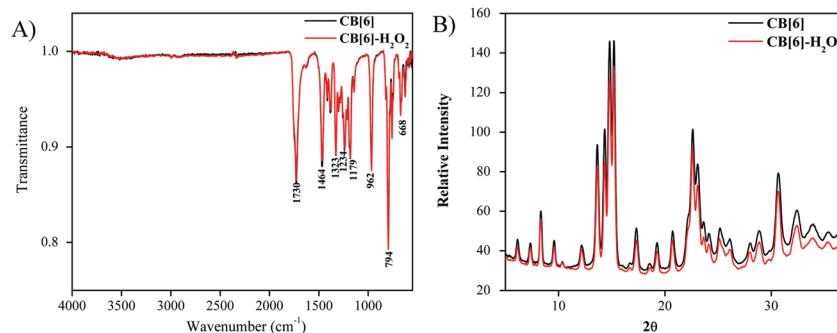


Fig. 8 (A) FT-IR and (B) XRD patterns of H<sub>2</sub>O<sub>2</sub> treated CB[6] in comparison to unmodified CB[6].

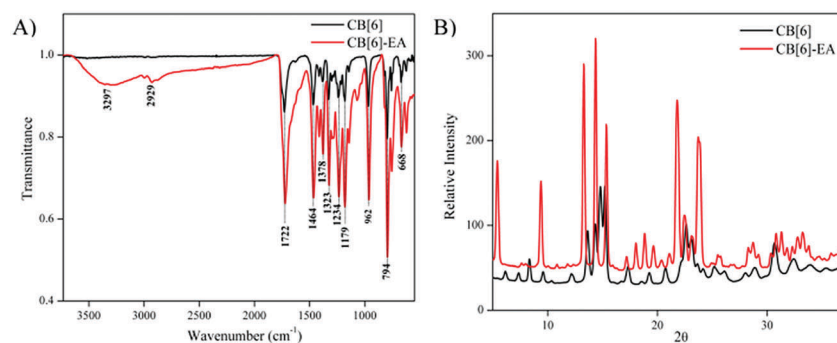


Fig. 9 (A) FTIR and (B) XRD of CB[6]-EA in comparison to unmodified CB[6].

FTIR, XRD and SEM analysis of the sample showed significant changes in CB[6] characteristics that clearly indicated that the incorporation of the amine molecule on CB[6] caused significant chemical and structural changes in the particles.

The gas adsorption behaviour of the CB[6] samples before and after surface modifications was therefore probed using N<sub>2</sub> and CO<sub>2</sub> sorption at 323 K. For the adsorption measurements, all the materials were heated to 423 K for 30 min to fully remove any adsorbed gas molecules in the sample before the gas sorption analysis as explained previously. The modified CB[6] samples were stable under these conditions, with no apparent loss of crystallinity. The adsorption was carried out at 323 K by flowing gas at the rate of 31 mL min<sup>-1</sup> over the sample. The weight gain of the sample due to gas adsorption was tracked against time to obtain plots as shown in Fig. 10.

As shown, the adsorption plots of the samples were very different and signified the chemical and structural changes that took place during the modifications. The unmodified samples attained an adsorption saturation value of 0.54 mmol g<sup>-1</sup> in ~30 min. Samples modified with H<sub>2</sub>O<sub>2</sub> followed a much slower adsorption rate, but reached a larger adsorption value of 0.78 mmol g<sup>-1</sup> within 60 min of adsorption measurement, as seen in Fig. 10. The adsorption saturation value in this case was calculated as 1.06 mmol g<sup>-1</sup>. In the samples modified by H<sub>2</sub>O<sub>2</sub>, no significant chemical changes were observed compared to the unmodified sample in the FTIR or XRD analysis. Yet, the slow kinetics of adsorption here should be an indication of the changes in the surface structure of the CB[6] particles. As shown in the SEM images (Fig. 7b), H<sub>2</sub>O<sub>2</sub> treatment did not

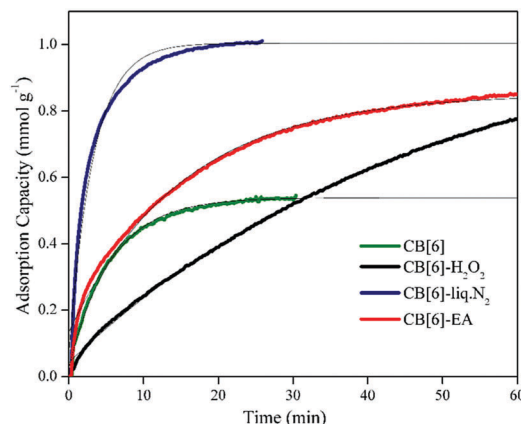


Fig. 10 Adsorption capacity of CO<sub>2</sub> in CB[6] before and after modifications. Adsorption temperature was 323 K and measurement method was gravimetric. 100% CO<sub>2</sub> gas was used. Experimental data, as well as fitted lines, are shown.

alter the morphology of the particles significantly, as in the case of amine or cryogenic grinding treatment. Some amount of surface roughening of the CB[6] particles due to dissolution, leading to increased adsorption volume but slower adsorption rate, could be expected upon treatment with H<sub>2</sub>O<sub>2</sub>.

The cryogenically ground samples exhibited a completely different adsorption pattern. A much larger adsorption value of 1.04 mmol g<sup>-1</sup> was achieved within the first 20 min of adsorption itself. It could be expected that the fragmentation of the particles during liq. N<sub>2</sub> assisted crushing helped to



expose many more cavities directly for CO<sub>2</sub> adsorption, which were possibly not available in the unmodified sample owing to the macro-particle nature of the commercial CB[6] material. Although CB[6] cavities are intrinsic and should be available for adsorption in all cases, the size of the particle could reduce adsorption due to diffusion limitations. Powdering and fragmentation can therefore help in achieving better adsorption performance for practical purposes, as is well supported by the SEM images (Fig. 7), which showed the smaller particle size for the cryogenically ground samples.

The sample treated with ethanolamine reached an adsorption capacity value of 0.85 mmol g<sup>-1</sup> after 60 min of exposure to CO<sub>2</sub> at 323 K. The adsorption saturation value in this case was calculated as 0.93 mmol g<sup>-1</sup> and the rate of adsorption was similar to that of the unmodified sample. However, the adsorption proceeded to attain much higher capacities than the unmodified sample. Compared to the physical modification approach, the maximum adsorption capacity of the EA modified sample was slightly lower.

N<sub>2</sub> adsorption measurement was extremely difficult and the quality of gravimetric isotherms was poor due to the very low adsorption capacity values and therefore only the adsorption value after 60 min of adsorption was extracted from the measurement. These adsorption capacity values of N<sub>2</sub> on CB[6] and the modified CB[6] samples measured at 323 K and 1 bar gas pressure are shown in Table 1. As a rough measure of selectivity, the ratio of adsorption capacity values of CO<sub>2</sub>/N<sub>2</sub> is also listed in Table 1. From the results listed in Table 1, it is clear that the unmodified sample and the physically modified samples only provided limited selectivity for CO<sub>2</sub> against nitrogen. However, the ethanolamine modified samples provided an excellent sorption selectivity value of 121.4 for CO<sub>2</sub>/N<sub>2</sub> at 323 K. The chemical nature of the interaction between CO<sub>2</sub> and amine is hence clear from the results.

We further confirmed the mechanism of adsorption of CO<sub>2</sub> in CB[6] and the modified CB[6] samples using FTIR analysis. The FTIR spectra of all the samples were taken before exposure to CO<sub>2</sub> gas (original material), after the exposure to CO<sub>2</sub> gas and after heating the sample to 423 K for the complete desorption of CO<sub>2</sub> (Fig. 11). After CO<sub>2</sub> adsorption, the FTIR of CB[6] and the modified CB[6] samples showed the characteristic CO<sub>2</sub> vibration peak around 2336 cm<sup>-1</sup> thereby confirming that adsorption had occurred. After heating at 423 K, the FTIR patterns of the samples showed the disappearance of the peak at 2336 cm<sup>-1</sup>, clearly confirming the CO<sub>2</sub> desorption. In the case of CB[6], CB[6]-H<sub>2</sub>O<sub>2</sub> and CB[6]-liq.N<sub>2</sub>, FTIR analysis evidenced only physical adsorption of the CO<sub>2</sub> molecule. However, in the case of

the CB[6]-EA sample, the reaction of CO<sub>2</sub> with the amine occurs through a Zwitterion mechanism to form carbamates, a reaction that has been extensively studied.<sup>62</sup> The ammonium carbamate formation and the interaction of amine molecules with CO<sub>2</sub> are well demonstrated by FTIR observations.

The FTIR spectrum of the CB[6]-EA sample, as shown in Fig. 11D, showed a broad peak for the incorporated amine molecules at 3299 cm<sup>-1</sup>. However, no chemical interaction between CB[6] and the amine could be evidenced from the results. It is expected that the amine molecules were placed in the CB[6] cavities by ethanolamine modification. CO<sub>2</sub> would have adsorbed to the amine end of ethanolamine as well as in the remaining CB[6] cavities. The FTIR results of the CO<sub>2</sub> adsorbed samples indeed support this. On CO<sub>2</sub> gas exposure, broadening of the peak at 3299 cm<sup>-1</sup> was visible, which indicated ammonium carbamate formation. The peak at 1557 cm<sup>-1</sup> clearly supported the formation of ammonium carbamate in CB[6]-EA, which is not present in the other samples. Moreover, the absorption band at 1458 cm<sup>-1</sup> (C-N stretching) showed a slight shift to the lower wavelength region confirming CO<sub>2</sub> adsorption to the amine moiety. As mentioned earlier, the peak at 2336 cm<sup>-1</sup> clearly confirmed the presence of physical adsorption in the sample. Thus, in the case of the CB[6]-EA sample, CO<sub>2</sub> molecules were not only trapped in the cavities (physical adsorption) of CB[6], but also chemically bonded to amine molecules forming weak chemical bonds. However, the presence of amine molecules in the cavities should have reduced the available free cavity space for CO<sub>2</sub> adsorption and therefore no significant increase in adsorption capacity could be realised by this modification. Fig. 12 shows the CO<sub>2</sub> adsorption isotherms at 313 K, 323 K and 353 K for the CB[6]-EA samples as measured using the volumetric method. As in the case of the unmodified CB[6] samples, the measured adsorption value at 323 K is slightly smaller than the values measured using the gravimetric method, which could be due to the differences in conditions between the measurements. Comparison of data in Fig. 4 and 12 reveals that the effect of temperature on the amount of CO<sub>2</sub> adsorbed is less drastic in the amine modified sample compared to the unmodified sample. Our previous studies on CO<sub>2</sub> adsorption in amine functionalized microporous silica materials have shown a similar trend wherein the incorporation of amines helped to realize a less drastic drop in CO<sub>2</sub> adsorption with increases in adsorption temperatures.<sup>44</sup> However, the heat of adsorption values of the amine modified material and comparison to values reported in the literature gave a clearer picture of the possible mechanism of CO<sub>2</sub> adsorption. Calculated heat of adsorption for the CB[6]-EA sample was -37 kJ mol<sup>-1</sup> (at 0.15 mmol g<sup>-1</sup> CO<sub>2</sub> loading), which is smaller than the value of -48 to -90 kJ mol<sup>-1</sup> reported in the literature for adsorption of CO<sub>2</sub> in amine-functionalized adsorbents.<sup>63</sup> This value, however, is higher than the heat of adsorption values of -30 to -33 kJ mol<sup>-1</sup> reported for adsorption of CO<sub>2</sub> in CB[6] micropores.<sup>38</sup> These results point to an adsorption mechanism wherein part of the CO<sub>2</sub> gas molecules are adsorbed physically in the CB[6] pores and the remaining CO<sub>2</sub> molecules are attached to the amine end of EA molecules

**Table 1** Adsorption capacity of CO<sub>2</sub> and N<sub>2</sub> (60 min at 323 K) as well as CO<sub>2</sub>/N<sub>2</sub> ratio measured on CB[6] and modified CB[6] samples

Samples	Adsorption capacity (mmol g <sup>-1</sup> )		CO <sub>2</sub> :N <sub>2</sub> ratio
	CO <sub>2</sub>	N <sub>2</sub>	
CB[6]	0.54	0.06	9.0
CB[6]-H <sub>2</sub> O <sub>2</sub>	0.78	0.15	5.2
CB[6]-liq.N <sub>2</sub>	1.04	0.28	3.7
CB[6]-EA	0.85	0.007	121.4



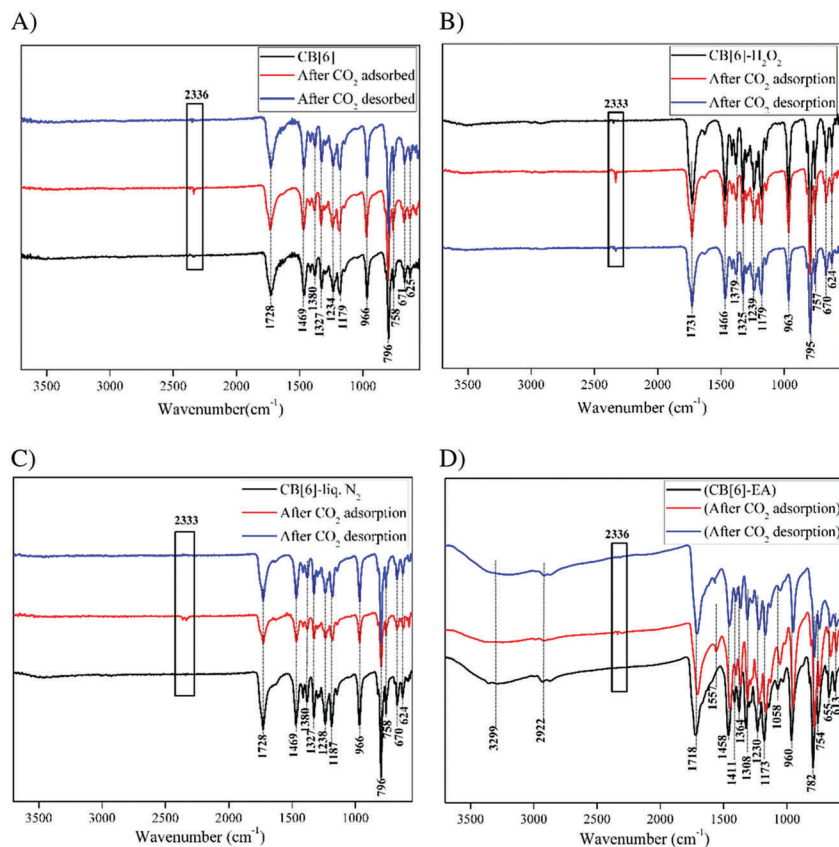


Fig. 11 (A) FTIR spectra of (—) CB[6], (—) after CO<sub>2</sub> adsorption and (—) after CO<sub>2</sub> desorption. (B) FTIR spectra of (—) CB[6]-H<sub>2</sub>O<sub>2</sub>, (—) after CO<sub>2</sub> adsorption and (—) after CO<sub>2</sub> desorption. (C) FTIR spectra of (—) CB[6]-liq. N<sub>2</sub>, (—) after CO<sub>2</sub> adsorption and (—) after CO<sub>2</sub> desorption. (D) FTIR spectra of (—) CB[6]-EA, (—) after CO<sub>2</sub> adsorption and (—) after CO<sub>2</sub> desorption.

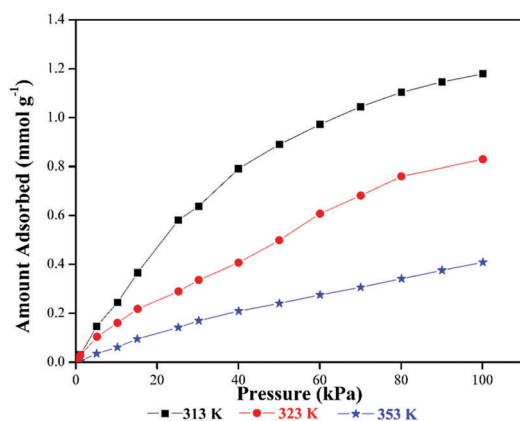


Fig. 12 CO<sub>2</sub> adsorption isotherm of CB[6]-EA at 313 K, 323 K and 353 K.

in the modified material as mentioned before. The reduction in the amount of N<sub>2</sub> adsorbed in the sample should be due to the fact that EA selectively occupied most of the available sites in the surface cavities, edges and pore-mouths of the material where CO<sub>2</sub> molecules tend to adsorb less selectively compared to N<sub>2</sub>, thereby selectively reducing the amount of N<sub>2</sub> adsorbed in the modified material. Hence, the large CO<sub>2</sub>/N<sub>2</sub> adsorption selectivity value measured for the CB[6]-EA sample, as shown in Table 1, can be well justified.

Even though it is very difficult to determine the exact nature of CO<sub>2</sub> sorption sites and mechanism of adsorption in the modified materials, we have obtained some insights based on the preliminary adsorption studies presented in this paper. Characterisation studies, especially FTIR, of the adsorbed and desorbed samples helped us to understand the mechanism of CO<sub>2</sub> adsorption and desorption in these materials to some extent. NMR studies would have contributed more, however the low solubility of CB[6] in generally employed solvents has impeded such studies. Based on the present experimental and theoretical results, it can be concluded that the higher adsorption capacity of the surface treated CB[6] samples could be attributed to the availability of a larger amount of cavity when compared to the unmodified one. In the case of the amine incorporated samples, CO<sub>2</sub>-amine interactions and poor N<sub>2</sub> adsorption in the amine rich sample as evidenced by the FTIR and CO<sub>2</sub>/N<sub>2</sub> adsorption analysis should have contributed well to the resulting adsorption selectivity.

## 4. Conclusions

The mechanism of CO<sub>2</sub> adsorption in the organic macrocycle CB[6] has been studied and modifications based on physical and chemical treatments have been attempted. Quantum mechanical





calculations have shown that the binding energy for the adsorption of CO<sub>2</sub> in CB[6] is greater than that of N<sub>2</sub> and the estimated upper bound to selectivity within the cavity is consistent with the experimentally measured data. In addition, it was found that carbon dioxide will preferentially bind in the cavity of CB[6] relative to water, though H<sub>2</sub>O can bind with a slightly more exothermic strength than CO<sub>2</sub> when it is situated in its preferred site close to the pore opening. While the loading of CO<sub>2</sub> in the cavity of CB[6] appears to be limited to a single molecule, at least close to the maximum binding energy, the co-adsorption of carbon dioxide and water appears to be possible with only a minimal effect on the individual thermodynamics due to the preference for different binding sites.

Experimental studies have shown that the material is capable of adsorbing 1.23 mmol g<sup>-1</sup> of CO<sub>2</sub> at 298 K/100 kPa CO<sub>2</sub> pressure. Physical and chemical modifications achieved by various methods including H<sub>2</sub>O<sub>2</sub> treatment, cryogenic grinding as well as incorporation of amine into the CB[6] cavity effectively helped to enhance the selective sequestration potential of the material. The increased adsorption values for the surface modified samples were mainly due to the availability of most of the CB[6] cavities for CO<sub>2</sub> adsorption compared to the unmodified sample. The increase in CO<sub>2</sub>/N<sub>2</sub> selectivity value of 121.4 measured with the chemically (with ethanolamine) modified sample was found to be due to the chemical nature of the interaction between CO<sub>2</sub> and the amine group and the poor adsorption of N<sub>2</sub> in the amine rich modified material. The modified CB[6] material with its exceptional selectivity coupled with its inherent thermal stability and pore sizes compatible with gas molecular dimensions may find useful applications in various separation processes. The mechanism of the gas adsorption selectivity of modified CB[6] and methods to enhance it to the level of commercial adsorbents need further detailed investigations.

## Abbreviations

CB[6]	Cucurbit[6]uril
CO <sub>2</sub>	Carbon dioxide
EA	Ethanolamine
TZ2P	Triple-zeta doubly polarized

## Conflicts of interest

There are no conflicts to declare.

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