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Design of Calix-Based Cages for CO₂ Capture

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ABSTRACT: Cage compounds offer a unique opportunity to capture CO₂, but a perfect design has been elusive. Herein, we computationally designed cage compounds by using linkers to connect two calix[4]pyrrole units together into a cage for capturing CO₂. Quantum mechanical calculations based on dispersion-corrected density functional theory show that the $-(\text{CH}_2)_n-$ linker has an optimal length at $n=5$ where the N-H groups from the pyrrole molecules form four H---O interactions with the two terminal O atoms of CO₂. The cationic and zwitterionic cages can also achieve high CO₂ affinity and CO₂/N₂ selectivity in the cage cavity compared with previously synthesized cages. Based on the computed potential energy curves of gas entering the cage, we conclude that all the cages are easily accessible by CO₂. This work shows that the calix-based cages have great potential for selective CO₂ capture.

KEYWORDS: gas separation, CO₂ capture, calix-based cages, binding energy, dispersion-corrected DFT

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1. Introduction

Carbon capture and sequestration is necessary to mitigate CO₂ emissions from burning fossil fuels that eventually lead to global warming and climate change. Various materials have been utilized for separation of CO₂ from other gases, including amines,¹ ionic liquids,²⁻⁶ polymers,⁷⁻¹⁴ metal-organic frameworks(MOFs),¹⁵⁻¹⁹ covalent organic frameworks (COFs),²⁰⁻²² amorphous porous materials,^{23,24} among others.

There has been significant recent interest in porous organic cages that are capable of selective guest binding, in particular with respect to CO₂/N₂ separations.²⁵⁻³¹ For example, Zhang *et al.* synthesized an organic cage molecule which showed high ideal CO₂/N₂ adsorption selectivity at 20 °C and 1 bar.^{30,31} Cooper *et al.* synthesized several acid- and base-stable porous organic cages which have high shape persistence and pH stability.²⁹ These cages also showed relatively high CO₂/N₂ adsorption selectivity (CO₂/N₂ = 57) at 298K and 1 bar, though the capacity of CO₂ adsorbed is still not competitive with other porous materials.^{6,12,19} One reason for the low capacity could be that the interaction strength between the cage and CO₂ is not strong enough to provide a very high thermodynamic driving force. Given the large quadrupole moment of CO₂, our design idea is to introduce more polar functionalities around the cage that can have multiple sites of binding. This idea leads us to consider the calix ligands, especially those with nitrogen-containing groups, such as calix[4]pyrroles, as it has been shown previously that nitrogen-containing groups are versatile in binding with CO₂.^{15,32}

Calix[4]pyrroles and their congeners, the so-called ditopic receptors, have cation- and anion- recognition sites within a single framework.³³⁻³⁷ These multifunctional receptors are of inherent interest due to their potential ability to achieve higher levels of ion-

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3 recognition selectivity in a neutral complex that minimizes the effects of ion solvation.
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5 For example, Sessler *et al.* introduced calix[4]pyrroles to extract CsCl from solution: the
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7 halide anion is bound via pyrrole-NH hydrogen-bonding interactions and the Cs⁺ counter
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9 cation is accommodated within the electron rich cavity.³⁷ Recently, they used a lithium-
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11 coordinating subunit to strap a calix[4]pyrrole anion-recognizing core so that they were
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13 able to bind neutral lithium salts in its cavity with high preference relative to NaCl, KCl
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15 and RbCl.³⁶ Most recently, Holman *et al.* showed that CO₂ gas molecule can be taken up
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17 by single crystals of calix[4]resorcinarene-based cavitand, though fraction of occupancy
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19 is still low even at 25 bar of CO₂.³³
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25 These breakthroughs in calix-based host-guest complexes led us to investigate the
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27 possibility of utilizing the bowl-like structure of a calix ligand to create new cages for gas
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29 separation. To test our design, we use quantum mechanical calculations to investigate the
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31 binding energy of CO₂ and N₂, as explained next.
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35 2. Methods

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38 To demonstrate the ability of the designed cages for CO₂ adsorption and CO₂/N₂ separation, we
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40 employed density functional theory (DFT) with the B-LYP functional^{38,39} and the empirical
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42 dispersion correction (DFT-D3) correction⁴⁰ as implemented in Turbomole V6.5 package,⁴¹ to
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44 compute binding energy (BE) between the cage and gas molecule (CO₂ and N₂) using a non-
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46 periodic, isolated-molecule model. Def2-TZVP orbital and auxiliary basis sets were utilized.⁴²
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48 We tested other methods such as PBE0-D3 and MP2 and other basis sets such as def2-SVP and
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50 def2-TZVPP; we estimated the uncertainty in our computed BE to be about 10 kJ/mol. Geometry
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52 optimization was performed with a force convergence criterion of 0.025 eV/Å. The local minima
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3 were confirmed with frequency analysis to have no imaginary frequencies. The potential energy
4 curves of a single CO₂ molecule moving from outside to inside of a cage via the side window
5 between two linkers were also obtained from Turbomole at the same level of theory, by fixing
6 the geometries of both the cage and the gas and evaluating only the single-point energy along the
7 entering path. This potential energy curves are likely to overestimate the actual barriers of entry
8 and therefore can be viewed as an upper bound.
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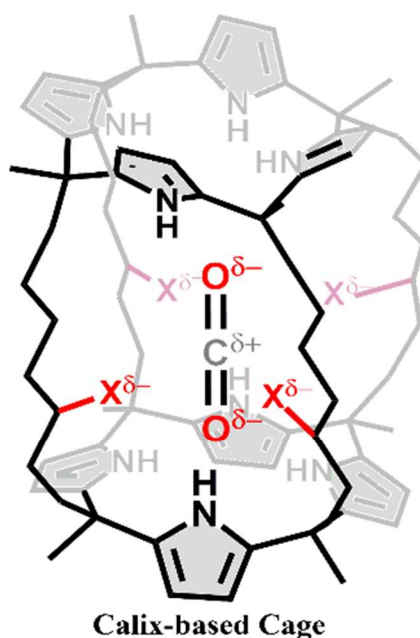


Figure 1. Connecting two calix[4]pyrrole units to make a cage for enclosing CO₂.

3. Results and discussion

3.1. Design concept. Figure 1 shows our design idea of cage compounds based on calix[4]pyrrole: two calix groups are jointed together with several types of linkers. This cage can enclose CO₂ through multiple interactions. We know that a positive partial charge locates on the carbon of CO₂ and the negative charges are on the oxygen atoms. The acidic H atom from

pyrrole can form strong hydrogen bond with oxygen atoms of CO₂. Then we can add some negatively charged groups on the side linkers for interacting with C. We expect that this cage design can increase both CO₂ affinity and CO₂/N₂ selectivity. Based on the cage design in Figure 1, we explored three types of calix[4]pyrrole cages (Figure 2): (a) varying the $-(CH_2)_n-$ linker length, denoted as CC1-Cn cages, where n is the repeating units of $-CH_2-$; (b) using a cation on the linker, denoted as CC2; (c) using a zwitterion on the linker, denoted as CC3. Below we explore how CO₂ and N₂ interact with these designed cages.

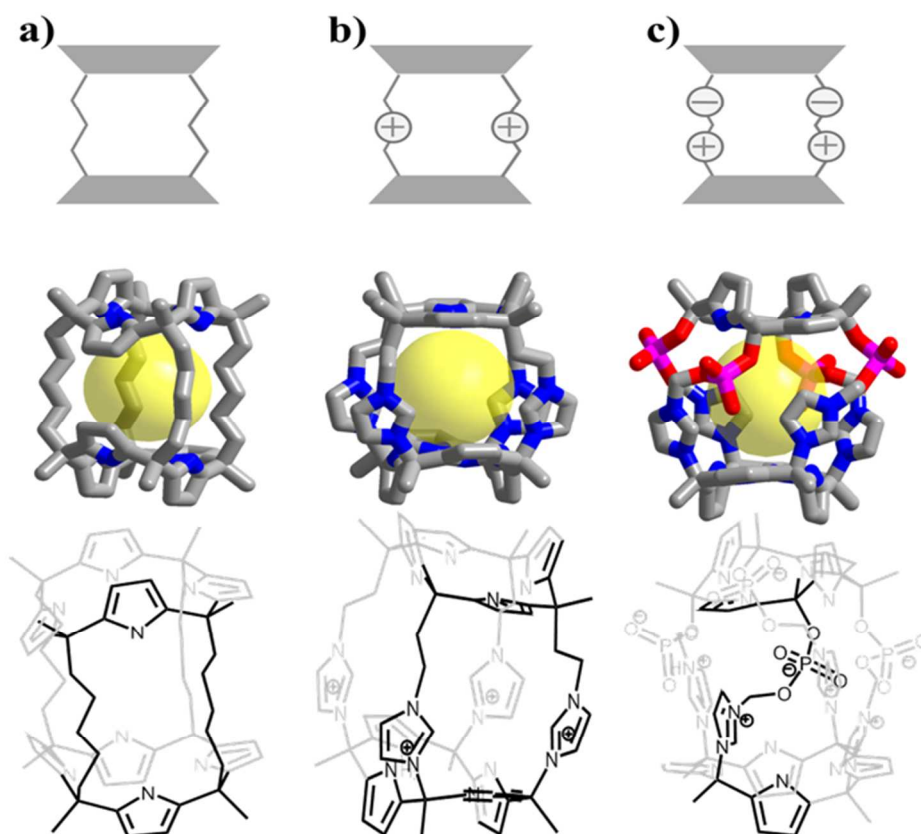
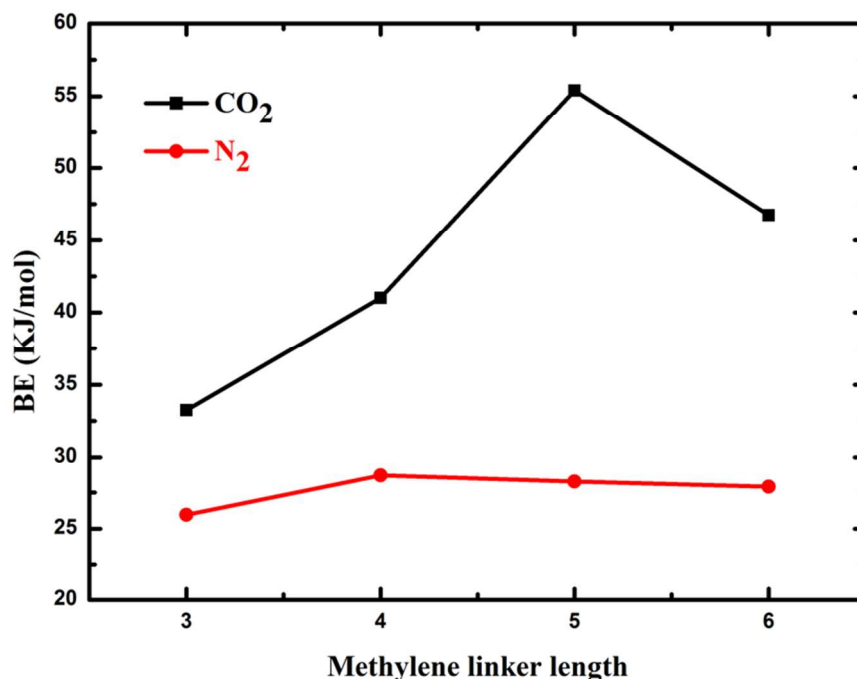


Figure 2. The molecular structure of designed calix-based cages: (a) CC1-Cn cages, where n is the repeating units of $-CH_2-$ in the linker; (b) CC2 cage, with cations on the linkers; (c) CC3 cage, with zwitterions on the linkers. Hydrogen atoms are omitted for clarity. Color code: C, gray; N, blue; O, red; P, Pink.

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7 **3.2. Binding energy of CO₂ and N₂ in the CC1-C_n cages.** For the CC1-C_n cages, we found
8 that the binding energy (BE) of CO₂ shows a volcano shape and reaches a maximum at 55
9 kJ/mol at n=5, that is, -(CH₂)₅- as the linker (Figure 3). On the other hand, the BE of N₂ shows a
10 much less variation between 25 and 30 kJ/mol. This optimal linker length of n=5 for caging CO₂
11 is very interesting. We found that at this linker length, CO₂ is snugly held inside the cage by four
12 N-H---OCO interactions, two at each end (Figure 4a) with H-O distances of 2.37 to 2.45 Å. In
13 contrast, the closest contact to N₂ is at least 3.16 Å (Figure 4b). In other words, n=5 is perfect for
14 this kind of H—O interactions; n=4 would be a little short while n=6 would be too long. N₂
15 interaction is, on the other hand, insensitive to this linker length. This difference between CO₂
16 and N₂ provides a nice handle to tune the selectivity.



55 **Figure 3.** Binding energy (BE) of CO₂ and N₂ as a function of the methylene linker length for the type-a
56 cage (CC1-C_n) in Figure 2. The binding energy is for the most stable binding site.
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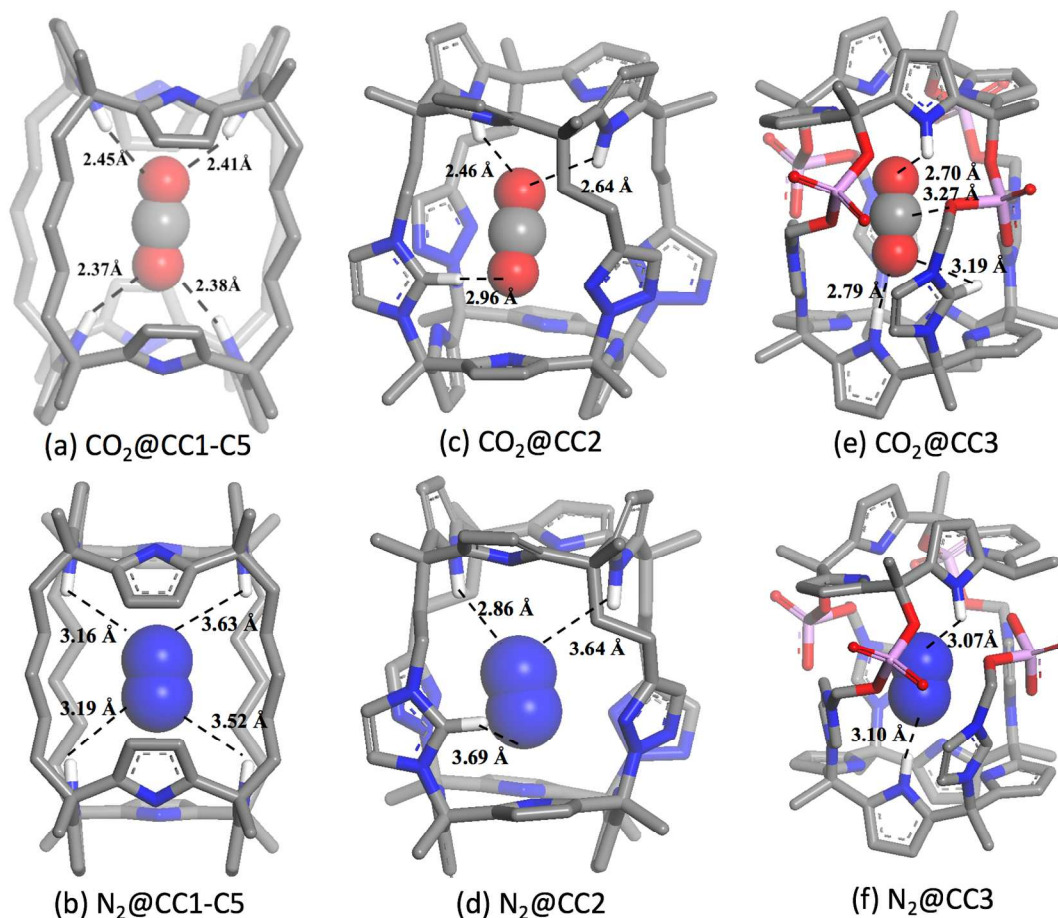


Figure 4. Structures of CO₂ and N₂ inside the CC1-C5, CC2, and CC3 cages.

3.3. Binding energy of CO₂ and N₂ in the CC2 and CC3 cages. We also examined the binding energies of CO₂ and N₂ in the other two types of cages (CC2 and CC3 in Figure 2) and compared them with the CC1-C_n cages. Figure 5 shows the difference in BE for CO₂ and N₂ (Δ BE, an indicator of CO₂/N₂ selectivity) vs the CO₂ BE (BE_wCO₂) for all the cages examined. One can see that CC2 cage (Figure 2b) is as good as CC1-C5 (Figure 4) for selective CO₂ capture, while the CC3 cage can offer even greater CO₂ BE at 72 kJ/mol. For comparison, we also computed Δ BE and BE_wCO₂ for three previously synthesized porous organic cages (POC1-3).²⁷⁻²⁹ We found that the best of the three, POC3, has a BE_wCO₂ at 32 kJ/mol, much weaker than those of

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CC1-C4, CC1-C5, CC1-C6, and CC2 and CC3. Figure 5 shows that the cage with zwitterions on the linkers (CC3) has much higher CO₂ binding energy than the cages with either the cationic linkers (CC2) or the neutral ones (CC1). This is due to the stronger interaction between the much larger dipole of the zwitterion and the quadrupole of CO₂. Comparison of the optimized structures of CO₂ and N₂ inside CC2 and CC3 cages (Figure 4c-f) shows that there are multiple short contacts from both the negative and positive parts of the zwitterion linkers to CO₂ (Figure 4e).

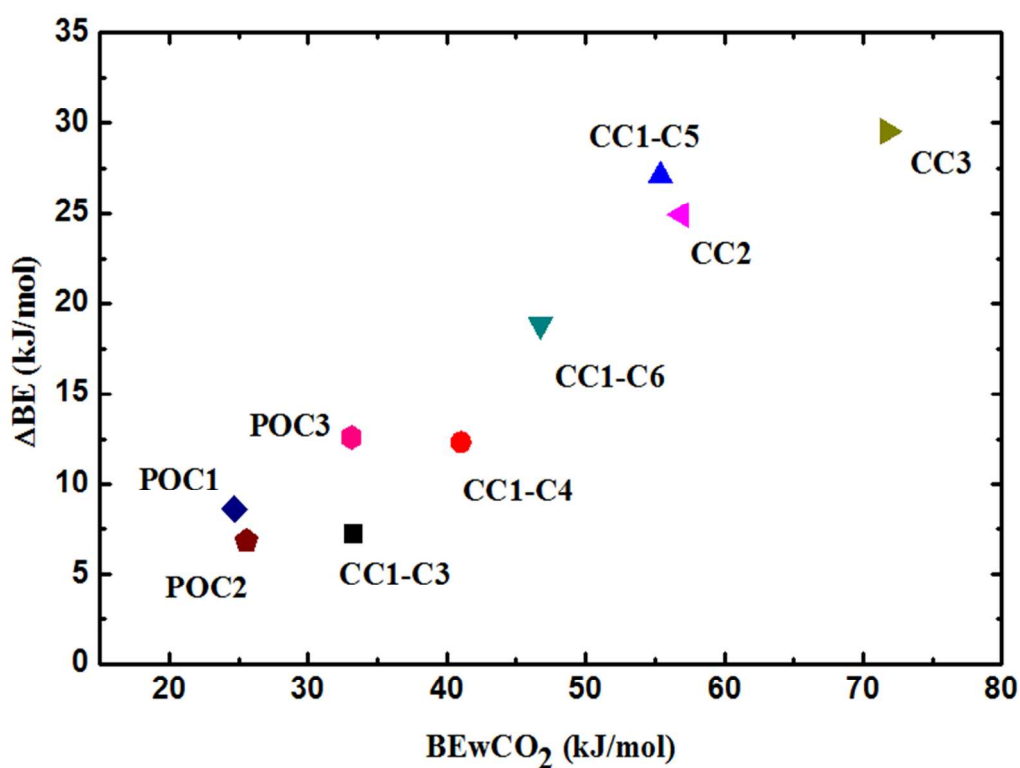


Figure 5. The binding energy with carbon dioxide (BEwCO₂) and the difference in binding energy between CO₂ and N₂ (ΔBE) for all cage compounds examined. CC cages are from Figure 2, while porous-organic cages (POC) from literature are shown for comparison. The binding energy is for the most stable binding site.

Based on the computed ΔBE , we estimated CO_2/N_2 selectivity at 300 K by using the Boltzmann factor. As listed in Table 1, one can see that CC1-C5, CC1-C6, CC2 and CC3 cages have CO_2/N_2 selectivity over 1000, while CC1-C4 and POC3 have similar CO_2/N_2 selectivity around 150. To find out if these promising thermodynamic selectivity is obtainable, we next examined the kinetics of gases entering the cages, especially for the most selective ones.

Table 1. Estimated CO_2/N_2 selectivity at 300 K for selected cage compounds based on their difference in BE for CO_2 and N_2 and the Boltzmann factor.

Cage	CO_2/N_2 selectivity	Cage	CO_2/N_2 selectivity
CC1-C4	144	CC2	2.4×10^4
CC1-C5	5.7×10^4	CC3	1.5×10^5
CC1-C6	2.0×10^3	POC3	160

3.4. Potential energy of CO_2 and N_2 entering the cages. Figure 5 shows that CC1-C5, C2, and C3 cages are among the best performing ones for selective CO_2/N_2 capture from our design. To examine whether or not the cage center is easily accessible for the gases from outside, we examined the potential-energy surface for gas entry into the three cages (Figure 6). One can see that there is no energy barrier for CO_2 entering either the CC1-C5 or CC2 cage (Figure 6a). For CC3 (calix-based cage3; Figure 6b), the potential energy curves show that the energy barrier entering the cage is about 38 kJ/mol for CO_2 and 56 kJ/mol for N_2 . By a simple estimate from the Arrhenius equation, one can conclude that these barriers are easily surmountable at room temperature. In addition, the barrier difference can further contribute to the CO_2/N_2 selectivity.

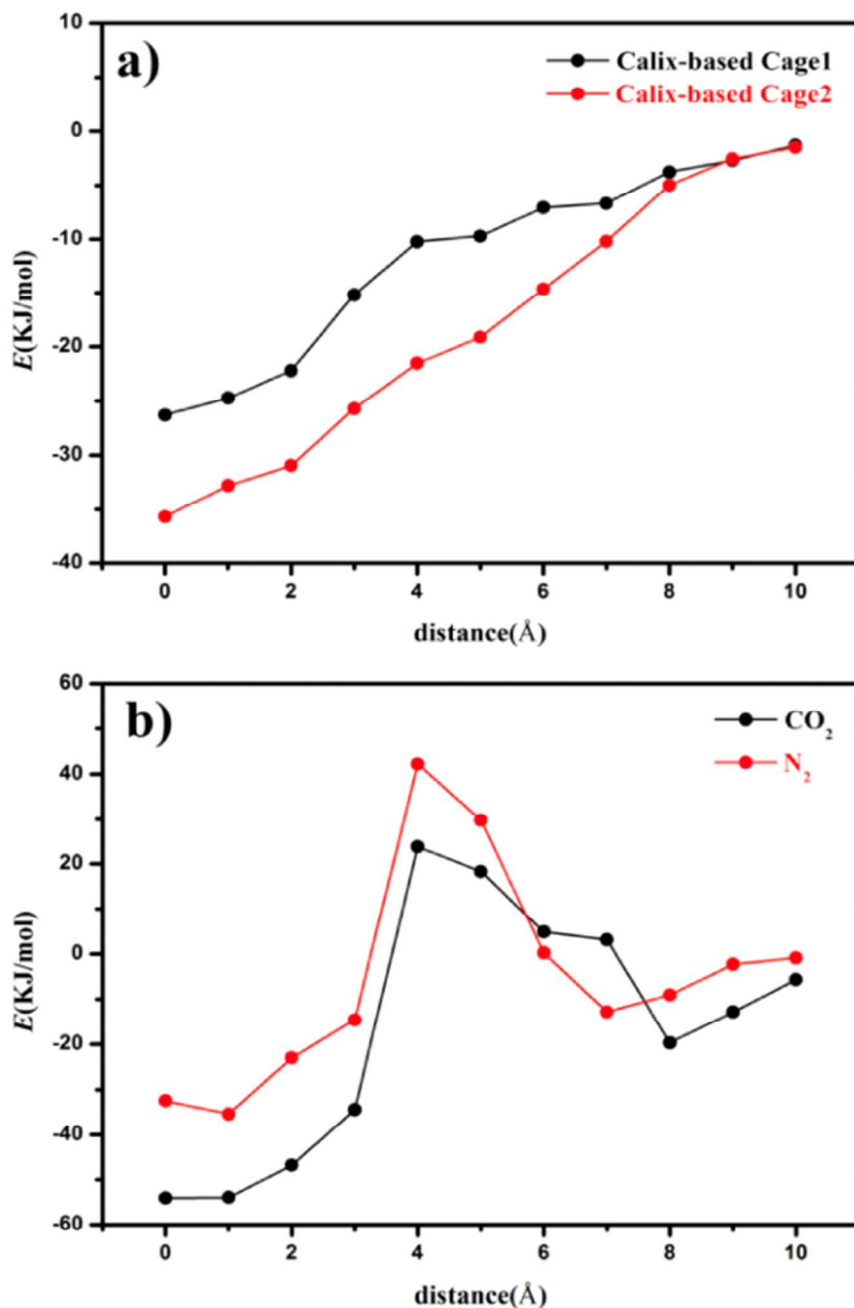


Figure 6. Potential energy curves of the gas-cage interaction as a function of the distance between the gas and the center of the cage: a) CO_2 into the calix-based type-1 cage (CC1-C5) and calix-based type-2 cage (CC2); b) CO_2 and N_2 into the calix-based type-3 cage (CC3).

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3 **3.5. Comparison with other sorbent materials.** A recent review suggested that 40-80 kJ/mol is
4 optimal for CO₂ binding,⁴³ and our CC1-C4, CC1-C5, CC1-C6, CC2, and CC3 cages fall into
5 this range. Here we compare the promising CO₂ binding energies in our designed cages with
6 other reported CO₂ sorbents. Metal-organic frameworks (MOFs), zeolites, covalent organic
7 frameworks (COFs), porous organics polymers (POPs), and porous carbonaceous materials are
8 most common sorbents for CO₂. Previous studies have shown that calculated CO₂ binding energy
9 is comparable to the experimental isosteric heat of adsorption (Q_{st}).^{44,45} MOF-74-Mg had the
10 highest CO₂ uptake (8.0 mmol/g) at 298 K and 1 bar, with a Q_{st} of 42 kJ/mol.⁴⁶ This value is
11 comparable to our CC1-C6 cage. Similar to MOFs, Q_{st} of zeolite is usually large, due to the
12 strong dipole-quadrupole interaction; for example, the Ca-A zeolite has CO₂ uptake of 4.9
13 mmol/g at 298 K and 1 bar with Q_{st} of 58 KJ/mol.⁴⁷ Most COFs and POPs have lower CO₂
14 uptake and Q_{st} than MOFs; for example, HAT-CTF-450/600, one of the best POPs for CO₂
15 uptake, has a Q_{st} of 27.1 KJ/mol.⁴⁸ A typical carbonaceous sorbent has a Q_{st} of about 30 kJ/mol.⁴⁹
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34 **4. Conclusions**

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38 In summary, we have used calix[4]pyrrole to design three types of calix-based cages, by using
39 linkers to connect two calix[4]pyrrole units together into a cage. The -(CH₂)_n- linker shows an
40 optimal length at n=5 where the N-H groups from the pyrrole molecule form four H---O
41 interactions with the two O atoms of CO₂. The cationic and zwitterionic cages can also achieve
42 high CO₂ affinity and CO₂/N₂ selectivity in the cage cavity compared with previously
43 synthesized cages. Based on the potential energy curves of gas entering the cage, we conclude
44 that all the cages are easily accessible by CO₂. Therefore this work shows that the calix-based
45 cages have great potential for selective CO₂ capture.
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TOC Graphic

