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New Insights into carbon dioxide interactions with benzimidazole-linked polymers

Suha Altarawneh¹, S. Behera², Puru Jena² and Hani M. El-Kaderi¹*

A synergistic experimental and theoretical study (DFT) highlights the impact of material design at the molecular and electronic levels on the binding affinity and interaction sites of CO₂ with benzimidazole-linked polymers (BILPs); CO₂ is stabilized by benzimidazole units through Lewis acid-base (N⁺CO₂) and ary1 C-H–O=C–O interactions.

It is well established now that the release of CO₂ from anthropogenic activities such as fossil fuel burning is among the leading causes for global warming.¹ Therefore, considerable efforts have been directed towards the development of viable technologies for carbon dioxide capture and sequestration (CCS). Currently fossil fuels provide ca. 87% of the world’s energy which release significant amount of CO₂ annually to the atmosphere.² The released CO₂ from coal-fired plants accounts for about 33–40% of global CO₂ emissions,³ hence efficient CO₂ capture from flue gas (~15%) remains at the heart of many academic and industrial research enterprises. Porous adsorbents⁴,⁵ received considerable attention over the past decade because they can be tailored to have high CO₂ capture capacity and selectivity and most importantly, can be regenerated with modest energy input when compared to amine solutions which are corrosive, toxic, and subject to decomposition and evaporation.⁶ Among the promising adsorbents are covalent porous organic polymers (POPs) having basic sites that can bind considerable amounts of CO₂ with moderate binding energies which facilitate regeneration processes.⁵ In contrast to the well-established metal-organic frameworks (MOFs), the interaction between POPs and CO₂, to a large extent, has been limited to routine physisorption studies because of the amorphous nature of POPs, which precludes theoretical studies and investigation by powder X-ray diffraction or inelastic neutron scattering techniques. Overcoming such limitations would be essential to pinpoint factors that govern CO₂ interaction with host POPs, which can aid in the design of enhanced CO₂ adsorbents.

In this study, we report the synthesis of two new BILPs containing benzo-bis(imidazole) and 3,3′-bibenzimidazole moieties and determine their CO₂ uptake and selectivity over CH₄ and N₂. Moreover, we highlight the impact of the electronic nature of imidazole-containing units on the binding site and affinity of CO₂ using density functional theory (DFT). BILP-14 and BILP-15 were synthesized by condensation reactions between 1,2,4,5-tetraiodo-4-formylphenyl)benzene, 1,2,4,5-benzenetetramine tetrahydrochloride and 3,3′-diaminobenzidine tetrahydrochloride.

Scheme 1. Schematic representation of BILPs synthesis.
Low-pressure CO$_2$ uptake measurements were collected at 273 K and 298 K to estimate the binding affinity of the polymers for CO$_2$ and to determine their storage capacity. The CO$_2$ isotherms (Fig. 1B) are fully reversible and exhibit a steep rise at low pressures and significant uptake at 1.0 bar; 170 mg g$^{-1}$ (BILP-14) and 118 mg g$^{-1}$ (BILP-15) at 273 K. The lower CO$_2$ uptake of BILP-15 could be explained by its modest surface area and pore volume. On the other hand, the uptake by BILP-14 is similar to the best performing BILPs derived from 2D building units (e.g. BILP-10: 177 mg g$^{-1}$, BILP-2: 149 mg g$^{-1}$, BILP-5: 128 mg g$^{-1}$). The CO$_2$ binding affinity ($Q_a$) was first calculated by using the virial method (Fig. S13, ESI) then estimated using DFT calculations that can also assist in determining the interaction site(s) of CO$_2$ with the polymers. The $Q_a$ values are highest at zero coverage then drop with higher loading; the initial high binding affinities are driven by favourable interactions between CO$_2$ and the nitrogen sites which become less accessible as loading increases. The $Q_a$ values of 33.5 kJ mol$^{-1}$ (BILP-14) and 33.0 kJ mol$^{-1}$ (BILP-15) are within the range of reported values for BILPs and other nitrogen functionalized organic polymers.$^{2}$

To gain insight into the impact of the electronic nature of the benzimidazole-containing units on CO$_2$ binding affinity and interaction sites we carried out DFT calculations with two different forms for exchange-correlation potential. These include the local density approximation (LDA) functional consisting of the Slater exchange and Volk-Wilk-Nusair correlation functional (SVWN)$^9$ and the hybrid meta exchange-correlation functional M06$^7$ formulated by Zhao and Truhlar. The M06 functional includes corrections for long-range dispersive forces. We note that since the interaction of CO$_2$ molecules with these units is expected to be weak (physisorption), it is necessary to go beyond the generalized gradient functionals that do not include van der Waal’s terms and hence underestimate binding affinities. LDA, on the other hand, overestimates binding$^{18}$ and in cases of weak interactions it yields binding energies closer to experiment. It must be stated that LDA does not include dispersive forces and the agreement between theory and experiment in weakly bound systems is due to fortunate cancellation of errors. We have used Gaussian 09 package$^{11}$ and 6-311+G*$^{12}$ basis sets for all our computations. The convergence in the total energy and force were set at 1×10$^{-6}$ eV and 1×10$^{-2}$ eV/Å, respectively. Several initial geometries were taken where the CO$_2$ molecules were allowed to approach different binding sites of the benzimidazole-containing units (Fig. 2). The geometries were first optimized without symmetry constraint at the LDA level of theory, which were then used as input and re-optimized using M06 functional. All optimizations are followed by frequency calculations to confirm that the structures represent genuine minima in the potential energy surface (PES). The atomic charges have been evaluated by applying the Natural Bonding Orbital method (NBO).$^{13}$

In case of BILP-15@2CO$_2$ and BILP-14@2CO$_2$, where two CO$_2$ molecules were allowed to interact with different binding sites of BILP-15 and BILP-14, the minimum energy structures were obtained when CO$_2$ binds to the N-sites of BILP-15 and BILP-14 at a bond length of 2.73 and 2.72 Å respectively, on opposite sides of the aromatic system (Fig. 2a,c). The bond lengths between the C and O atoms of the CO$_2$ molecule interacting with these monomeric systems remain the same (i.e 1.16 Å) as that of the neutral CO$_2$, whereas its bond angle reduces to 176°. A similar angle deformation value (3.1°) was reported by Vogiatzis$^{14}$ et al for imidazole-bonded CO$_2$. On the other hand, in BILP-15@4CO$_2$ and BILP-14@4CO$_2$, the interacting sites for CO$_2$ are different for both systems. In BILP-15@4CO$_2$ (Fig. 2d), all CO$_2$ molecules preferably bind to the N-sites of BILP-15 (2.82-2.89 Å), whereas in BILP-14@4CO$_2$ (Fig. 2b), two CO$_2$ molecules bind to the N-sites of BILP-14 (2.72-2.74 Å) and the other two bind to the C-atom of the central phenyl ring (3.06-3.15 Å). This can be explained by the fact that the imidazole ring attached to these systems are highly polar and carry a net dipole moment. The CO$_2$ molecule, on the other hand, is highly symmetric and has a permanent electrical quadrupole moment that can be described as two electrical dipoles sitting back-to-back and pointing in opposite directions. The electrostatic force of interaction between the CO$_2$ molecules and these polymeric systems can be attributed to the dipole-quadrupole interaction. The DFT study also reveals that these interactions are further stabilized by complementary interactions involving aryl C-H and CO$_2$ (C=H–O=C=O) with variable bond distances in the range of 2.79-2.94 Å (Fig 2). Moreover, side-on intermolecular
interactions between CO$_2$ molecules in BILPs@4CO$_2$ systems lead to O=C–O(δ$^-$)–Cðδ$^+$)O$_2$ interactions (2.90 to 3.33 Å; Fig. S1-2, ESI). Noteworthy, similar interactions have been authenticated by both experimental and theoretical studies for CO$_2$ loaded NOT–300; a MOF that has channel window diameter of ~6.5 Å similar to the PSDs of BILP–14 (7.0 Å) and for BILP–15 (5.6 Å).$^{15}$

The bonding preference can be explained by examining the NBO charges. In BILP–15@2CO$_2$, the NBO charge on the C-atom of CO$_2$ and the N-atom of BILP–15 are +0.44e and ~0.14e, respectively, whereas in BILP–15@4CO$_2$, NBO charges on C-atoms are +0.38e and the N-atom of BILP–15 are ~0.20e respectively. Similarly, in BILP–14@2CO$_2$, NBO charges on the C-atom of CO$_2$ and the N-atom of BILP–14 are +0.41e and ~0.22e whereas in BILP–14@4CO$_2$, NBO charges on C-atom of CO$_2$ and the N-atom of BILP–14 are +0.38e and ~0.20e respectively. The theoretically calculated binding affinities (E$_B$) using different methods for BILP–15@nCO$_2$ and BILP–14@nCO$_2$ where n = 2, 4 are given in Table 1; it was found that the experimental $Q_m$ values at zero coverage agree well with those predicted by the LDA/6-311+G* method.

Table 1. CO$_2$ Binding energies calculated at the LDA/6-311+G* and M06/6-311+G*.

<table>
<thead>
<tr>
<th>Cluster</th>
<th>Binding Energy E$_B$ (kJ/mol)</th>
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<tbody>
<tr>
<td></td>
<td>LDA/6-311+G*</td>
</tr>
<tr>
<td>BILP–15@2CO$_2$</td>
<td>-33.22</td>
</tr>
<tr>
<td>BILP–15@4CO$_2$</td>
<td>-30.26</td>
</tr>
<tr>
<td>BILP–14@2CO$_2$</td>
<td>-35.26</td>
</tr>
<tr>
<td>BILP–14@4CO$_2$</td>
<td>-32.39</td>
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The selectivity of BILPs toward CO$_2$/N$_2$ and CO$_2$/CH$_4$ was calculated because CO$_2$ removal from flue gas or methane-rich gases (natural gas and landfill gas) is needed to mitigate climate change and to enhance the quality and energy density of methane-rich fuels. Selectivity studies were performed by using the initial slopes of pure gas isotherms collected at 273 K and 298 K (Fig. 3) and (Fig. S14, ESI). The CO$_2$/N$_2$ selectivity at 273 K/298 K is higher for BILP–15 (83/63) when compared to that of BILP–14 (56/49), most likely because of the narrower pores of BILP–15 (5.6 Å). These values are among the highest for purely organic polymers that show considerable CO$_2$ uptake at low pressure.$^{5}$ In contrast, the selectivity for CO$_2$/CH$_4$ was much lower and falls in a narrower range (8-9) that does not seem to change significantly upon temperature change. This low selectivity level is typical of porous organic polymers and originates from the fact that methane is more strongly adsorbed ($Q_m$ = 22.3-26 kJ mol$^{-1}$, Fig. 1D) than N$_2$ because of the higher polarizability of CH$_4$ (26 × 10$^{-23}$ cm$^3$) vs. N$_2$ (17.6 × 10$^{-23}$ cm$^3$),$^{16}$ which makes CO$_2$ removal from natural gas by porous adsorbents very challenging. The selectivity levels at 298 K were also validated by the Ideal Adsorbed Solution Theory (IAST), which predicts the adsorption selectivity for gas mixtures based on pure component gas isotherms.$^{17}$ The results from the IAST calculations (Table S1 and Fig. S15, ESI) are consistent with the selectivity levels reported above.

Overall, our studies reveal that BILPs offer multiple interaction sites for CO$_2$ and these sites, along with their binding affinities, can be effectively and conveniently predicted using DFT calculations.

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Notes and references

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Computational studies reveal that the excellent performance of benzimidazole-linked polymers in selective carbon dioxide capture over methane and nitrogen is facilitated by several electrostatic interactions involving the Lewis basic sites and the aryl C-H of the benzimidazole units with CO$_2$.

![Graph showing uptake of CO$_2$, N$_2$, and CH$_4$ vs. pressure](image)