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Communication

New Insights into carbon dioxide interactions with benzimidazole-linked polymers

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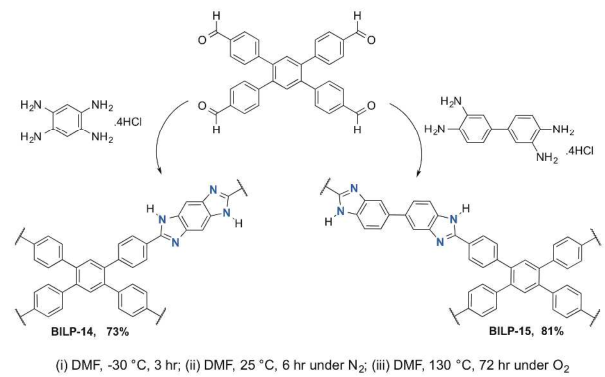
A synergistic experimental and theoretical study (DFT) highlights the impact of material design at the molecular and electronic levels on the binding affinity and interaction sites of CO_2 with benzimidazole-linked polymers (BILPs); CO_2 is stabilized by benzimidazole units through Lewis acid-base (N···CO_2) and aryl C-H···O=C=O interactions.

It is well established now that the release of CO_2 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 CO_2 annually to the atmosphere.[2] The released CO_2 from coal-fired plants accounts for about 33–40% of global CO_2 emissions,[3] hence efficient CO_2 capture from flue gas (~15%) remains at the heart of many academic and industrial research enterprises. Porous adsorbents[4,5] received considerable attention over the past decade because they can be tailored to have high CO_2 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 CO_2 with moderate binding energies which facilitate regeneration processes.[5] In contrast to the well-established metal-organic frameworks (MOFs), the interaction between POPs and CO_2, 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 CO_2 interaction with host POPs, which can aid in the design of enhanced CO_2 adsorbents.

In this study, we report the synthesis of two new BILPs containing benzo-bis(imidazole) and 3,3'-bibenzimidazole moieties and determine their CO_2 uptake and selectivity over CH_4 and N_2. Moreover, we highlight the impact of the electronic nature of imidazole-containing units on the binding site and affinity of CO_2 using density functional theory (DFT). BILP-14 and BILP-15 were synthesized by condensation reactions between 1,2,4,5-tetrakis(4-formylphenyl)benzene, 1,2,4,5-benzenetetramine tetrahydrochloride and 3,3'-diaminobenzidine tetrahydrochloride



Scheme 1. Schematic representation of BILPs synthesis

hydrate, respectively, as depicted in Scheme 1. The resulting polymers were isolated and purified in good yields and their structural aspect and chemical composition were established using spectral and analytical methods (ESI). BILP-14 and BILP-15 form agglomerated particles according to SEM ca. 0.5-0.3 µm in size (Fig. S5, ESI), are thermally stable up to 400 °C under N_2 according to TGA studies (Fig. S6, ESI) and remained intact upon treatment with aqueous HCl and NaOH (4M). The formation of the imidazole ring was confirmed by FT-IR and ^{13}CP-MAS. The FT-IR spectrum (Fig. S7, ESI) contain broad bands at 3425 cm^{-1} (N-H stretching), 3220 cm^{-1} (hydrogen bonded N-H), and new bands at 1620 cm^{-1} (C=N). The ^{13}CP-MAS spectra (Fig. S8, ESI) revealed characteristic peaks of the imidazole ring (N*C*(Ph)N) at ~151 ppm along with other peaks that correspond to the aryl units of BILPs.[7] Both polymers are amorphous according to PXRD (Fig. S9, ESI).

The porosity of the new BILPs was evaluated by argon uptake measurements (Fig. 1A). Ar isotherms are fully reversible with a minor hysteresis consistent with the powdery and the flexible nature of BILPs. The Brunauer-Emmett-Teller (BET) surface area was found to be 1005 m^2 g^{-1} (BILP-14) and 448 m^2 g^{-1} (BILP-15). Pore size distribution (PSD) curves derived from the nonlocal density functional theory (NLDFT) was found to be centered about 7.0 Å (BILP-14) and 5.6 Å (BILP-15). Pore volume was calculated from single point measurements (P/P_o = 0.95) and found to be 0.55 cc g^{-1} (BILP-14) and 0.27 cc g^{-1} (BILP-15). The notably lower surface area and narrower PSD of BILP-15 may arise from network interpenetration facilitated by the longer and flexible nature of the bibenzimidazole linker.

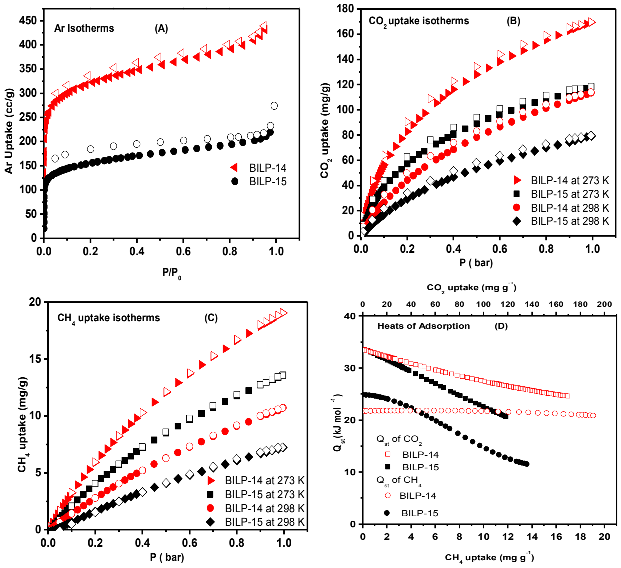


Fig. 1 Gas sorption measurements for BILBs; Ar (A), CO_2 (B), CH_4 (C), and heats of adsorption (D). Adsorption (filled) and desorption (empty).

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}).[7] The CO_2 binding affinity (Q_{st}) 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_{st} 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_{st} 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.[5]

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)[8] and the hybrid meta exchange-correlation functional M06[9] 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[10] 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]

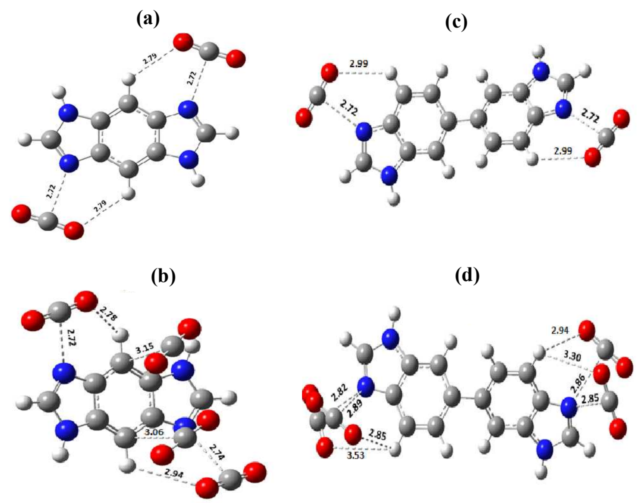


Fig. 2 Fully optimized geometries of BILPs-CO_2 interactions calculated at M06/6-311+G* level of theory. The bond lengths are in Å. The blue, grey, white and red colours stand for N, C, H and O atoms, respectively.

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 *et al* for imidazole-bonded CO_2.[14] 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 (2.72-2.74Å) and the other two bind to the C-atom of the central phenyl ring (3.06-3.15Å). 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^-)···C(δ^+)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 -0.15e, 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 +0.44e and -0.21e whereas in BILP-14@4CO_2, NBO charges on C-atom of CO_2 and the N-atom of BILP-14 are +0.43e and -0.14e and between the C-atom of CO_2 and the C-atom of central phenyl ring are +0.3e and -0.8e, 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_{st} 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*

Cluster	Binding Energy E_b	
	LDA/6-311+G*	M06/6-311+G*
BILP-15@2CO_2	-33.22 kJ/mol	-19.28 kJ/mol
BILP-15@4CO_2	-30.26 kJ/mol	-18.29 kJ/mol
BILP-14@2CO_2	-35.26 kJ/mol	-20.32 kJ/mol
BILP-14@4CO_2	-32.39 kJ/mol	-20.30 kJ/mol

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 adsorpted (Q_{st} = 22.3-26 kJ mol^{-1}, Fig. 1D) than N_2 because of the higher polarizability of CH_4 (26 × 10^{-25} cm^3) vs. N_2 (17.6 × 10^{-25} 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.

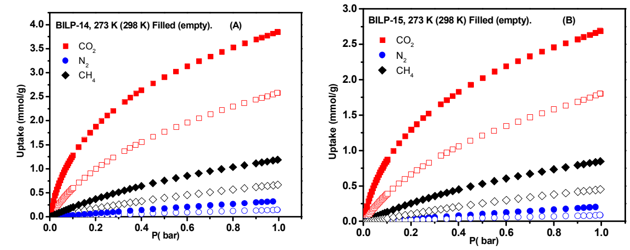


Fig 3. Selective gas uptake by BILPs at 273 K (filled) and 298 K (empty) at low pressure settings.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Experimental procedures, characterization methods, and gas sorption and selectivity studies.

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Table of Content

New insights into carbon dioxide interactions with benzimidazole-linked polymers

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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.