ChemComm

Cite this: *Chem. Commun.*, 2012, **48**, 1141–1143

www.rsc.org/chemcomm

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High CO_2 uptake and selectivity by triptycene-derived benzimidazole-linked polymers†

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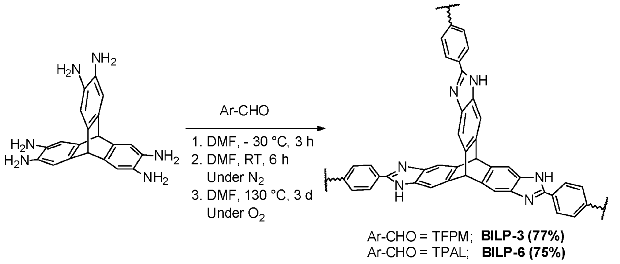
Received 10th November 2011, Accepted 29th November 2011
DOI: 10.1039/c2cc16986j

Successful incorporation of triptycene into benzimidazole-linked polymers leads to the highest CO_2 uptake (5.12 mmol g^{-1}, 273 K and 1 bar) by porous organic polymers and results in high CO_2/N_2 (63) and CO_2/CH_4 (8.4) selectivities.

The continuous and increasing release of carbon dioxide to the atmosphere, especially from coal-fired plants, has initiated considerable interest in the development of new materials and technologies for CO_2 capture and separation due to its drastic impact on the environment.[1] Of similar concern is the removal of CO_2 from natural gas for efficient storage and transportation of the latter.[2] Among the emerging methods for addressing these environmental and economical challenges is the use of porous materials such as metal organic frameworks (MOFs)[3] and nanoporous organic polymer networks[4] as CO_2 adsorbents in which the precise control over the material's chemical composition and textural properties can lead to a significant enhancement in gas storage and separation. In contrast to the current technology used in post-combustion CO_2 capture which employs amine solutions (*i.e.* MEA)[5] that require energy input in the form of heating for their regeneration, porous architectures bind CO_2 less strongly, and therefore materials regeneration can be accomplished more rapidly under ambient conditions. In order to attain higher CO_2 uptake in porous materials, pore functionalization has been instrumental. For example, introducing amine functionality, accessible nitrogen, or open metal sites into the pore wall of metal organic frameworks (MOFs),[6] zeolitic imidazolate frameworks (ZIFs),[7] or microporous organic polymers[8,9] can considerably impact their gas uptake and selectivity. In particular, the selective uptake of CO_2 over CH_4 or N_2 is believed to arise from enhanced CO_2-framework interactions through hydrogen bonding and/or dipole–quadrupole interactions.[10]

We have recently reported the synthesis of BILP-1 and showed that it stores 4.3 mmol g^{-1} of CO_2 at 273 K/1 bar and exhibits high CO_2/N_2 (70) and CO_2/CH_4 (10) selectivity as a result of integrating metal-free imidazole rings into the backbone of this polymer. In addition to pore functionalization, beneficial adsorptive properties can also be attained through the use of rigid organic linkers as in the case of triptycene which allows for a high degree of internal molecular free volume (IMFV).[11,12] Thus, triptycene-based porous materials possess enhanced adsorptive gas uptake capacities as demonstrated for triptycene-based polymers of intrinsic microporosity (PIMs),[13] shape-persistent case molecules,[14] metal salphens,[15] and MOFs.[16]

In this study we report on the synthesis of triptycene-derived BILPs and their performance in small gas (H_2, CO_2, CH_4) uptake and selectivity. The synthesis of 2,3,6,7,14,15-hexaaminotriptycene (HATT) was accomplished by adopting a similar route reported earlier for the 2,3,6,7,10,11-hexaaminotriphenylene analog (Scheme S2, ESI†).[17] The preparation of triptycene-derived BILPs (Scheme 1) was conducted by using the condensation method we reported for BILP-1.[9] A homogeneous solution of HATT (HCl salt) in DMF was treated with tetrakis(4-formylphenyl)methane (TFPM) or terephthalaldehyde (TPAL) dissolved in DMF to afford BILP-3 (77%) and BILP-6 (75%), respectively, as insoluble yellow powders (ESI†). The slow addition of aldehydes at low temperature under nitrogen is essential for enhanced pore formation and the overall porosity[18] whereas higher temperature and exposure to molecular oxygen is needed to facilitate imidazole ring formation.[19] BILPs are insoluble in common organic solvents and they remain intact upon washing with a 2 M solution of HCl or NaOH which reflects their high chemical stability. Thermogravimetric analysis (TGA) showed initial weight loss up to around 100 °C that corresponds to water removal followed by decomposition at ~400 °C (Fig. S1, ESI†) in a similar fashion of porous polybenzimidazole polymers.[9,20] Scanning electron microscopy



Scheme 1 Synthesis of BILP-3 and BILP-6.

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† Electronic supplementary information (ESI) available: Experimental procedures, characterization methods, and gas sorption studies. See DOI: 10.1039/c2cc16986j

(SEM) established phase purity of the polymer and revealed aggregated particles ~0.10–0.20 μm for BILP-3 and ~0.6–0.8 μm for BILP-6 (Fig. S2, ESI†). The material is amorphous as evidenced by powder X-ray diffraction analysis (Fig. S3, ESI†). The chemical connectivity and the formation of the imidazole ring were confirmed by FT-IR and ^{13}C solid-state NMR spectroscopy. The FT-IR spectrum of BILPs (Fig. S4 and 5, ESI†) showed N–H stretching at around 3415 cm^{-1} (free N–H) and 3210 cm^{-1} (hydrogen bonded N–H), while intense new bands appeared at 1610 cm^{-1} (C=N), and 1437 and 1492 cm^{-1} which can be assigned to skeleton vibration of the benzimidazole ring.[9,21] ^{13}C CP-MAS NMR spectra for BILP-3 and BILP-6 (Fig. S6, ESI†) exhibit signals around 152 and 151 ppm, respectively, that correspond to N***C***(Ph)N in benzimidazole units.[22] These are consistent with the value observed for BILP-1 (151 ppm)[9] while additional signals in the aromatic range arise from triptycene and tetraphenylmethane/phenyl units.

The permanent porosity of BILPs was investigated by argon uptake measurements. The fully reversible isotherms depicted in Fig. 1A show a rapid uptake at low pressure (0–0.1 bar) indicating a permanent microporous nature. The gradual increase in argon uptake and the minor hysteresis may be due to the flexible nature of organic polymers. Applying the Brunauer-Emmett-Teller (BET) model within the pressure range of P/P_o = 0.05–0.15 resulted in SA$_{BET}$ = 1306 m^2 g^{-1} (BILP-3) and 1261 m^2 g^{-1} (BILP-6). These values are comparable to those of BILP-1 (1172 m^2 g^{-1}),[9] triptycene-based PIMs (618–1760 m^2 g^{-1})[13] and cage compound (1375 m^2 g^{-1}),[14] and other amorphous nanoporous organic polymer networks.[4,8] Pore size distribution was estimated from argon isotherms by nonlocal density functional theory (NLDFT) and found to be centered around 7.2 Å (BILP-3) and 6.8 Å (BILP-6), (Fig. S11, ESI†) while pore volume was calculated from single point measurements (P/P_o = 0.95) and found to be 0.65 cc/g (BILP-3) and 0.66 cc/g (BILP-6).

To investigate the impact of microporosity and the amphoteric pore walls of BILPs on the uptake of small gases and selectively, we collected CO$_2$, CH$_4$, and H$_2$ isotherms and calculated their respective isosteric enthalpies of adsorption (Q_{st}) as summarized in Table 1. The CO$_2$ isotherms are fully reversible and exhibit a steep rise at low pressures then reach 225 and 145 mg g^{-1} at 273 and 298 K, respectively, for BILP-3 at 1 bar (Fig. 1B). A slightly lower uptake by BILP-6 (211 and 121 mg g^{-1}) was observed under similar conditions. Interestingly, the uptake by BILP-3 (5.12 mmol g^{-1}) which is about ~19% higher than that of BILP-1 at 273 K and 1 bar is the highest for porous organic polymer networks;[8] including PPN,[23] COFs,[24] functionalized CMPs,[25] functionalized POFs,[26] and triptycene-based cage compound.[14] Moreover, BILP-3 outperforms most of MOFs[3,6] and ZIFs.[7] However, its CO$_2$ uptake is still lower than those of the best performing MOFs (Mg-, Co-, Ni-MOF-74) which can store up to 8.0 mmol g^{-1} at 296 K/1 atm.[6d] We also calculated the Q_{st} for CO$_2$ using the virial method (Fig. S15, ESI†).[27] At zero coverage, the Q_{st} values 28.6 kJ mol^{-1} (BILP-3) and 28.4 kJ mol^{-1} (BILP-6) are higher than the values reported for organic polymers, and comparable to CO$_2$ selective MOFs[6] or ZIFs[7] which generally feature –NH$_2$ or –OH functionalized pores. The high CO$_2$ uptake and binding may arise from enhanced interactions of the polarizable CO$_2$ molecules through hydrogen bonding and/or dipole–quadrupole interactions that utilize the protonated and proton-free nitrogen sites of imidazole rings, respectively.[6,10] The readily reversible sorption/desorption behavior and moderate Q_{st} indicate that CO$_2$ interactions with pore walls are weak enough to allow for material regeneration without applying heat.

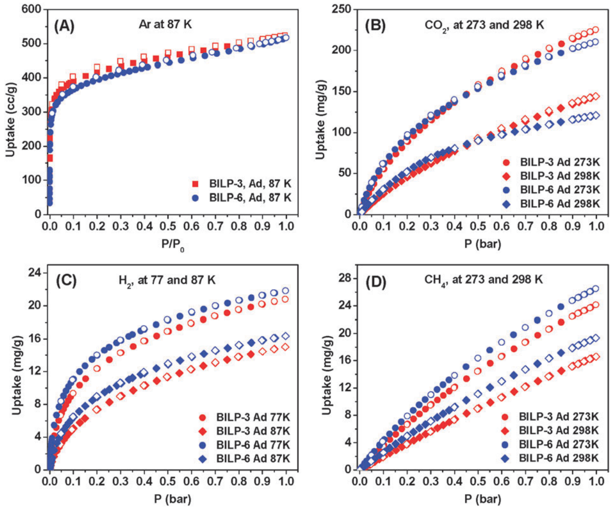

Fig. 1 Gas sorption measurements for BILPs; Ar (A), CO$_2$ (B), H$_2$ (C), CH$_4$ (D). Adsorption (filled) and desorption (empty).

We have also considered BILPs in hydrogen and methane storage studies because both gases are highly attractive candidates for use in automotive applications as a result of their abundance and clean aspect. The hydrogen uptakes for BILPs (2.1–2.2 wt%) at 77 K and 1 bar (Fig. 1C) are higher than any reported microporous organic polymers.[4,13,28] The Q_{st} for H$_2$ was calculated from adsorption data collected at 77 and 87 K. At zero-coverage, the Q_{st} is 8.0 kJ mol^{-1} for BILP-3 and 8.2 kJ mol^{-1} for BILP-6 (Fig. S16, ESI†). In general, the Q_{st} values are higher than the values reported for porous organic polymer networks[4] and similar to those of functionalized POFs (8.3 kJ mol^{-1}).[26] Additionally, the H$_2$ uptakes and Q_{st} compete with the best known MOFs for hydrogen storage under similar conditions.[29] Similarly, we recorded CH$_4$ uptakes at 273 and 298 K up to 1 bar (Fig. 1D). Again, both isotherms are completely reversible and exhibit maximum uptake of 24 and 17 mg g^{-1} at 273 and 298 K, respectively, for BILP-3 and 27 and 19 mg g^{-1} at 273 and 298 K, respectively, for BILP-6. The Q_{st} for CH$_4$ was calculated from adsorption data collected at 273 and 298 K and found to be 16.6 kJ mol^{-1} (BILP-3) and 13.2 kJ mol^{-1} (BILP-6) at zero coverage (Fig. S17, ESI†). The overall observation from porosity measurements and gas uptake studies indicates that changing the aldehyde building units from a linear (terephthalaldehyde) to a tetrahedral (tetrakis(4-formylphenyl)methane) geometry does not appear to have a significant impact on the surface area or gas sorption properties of BILP-3 and BILP-6. One possible reason is the formation of interpenetrated networks as in the case of COF-300 which increases materials density, lowers the expected surface area, and leads to the formation of ultrafine pores.[30]

We have also considered CO$_2$/N$_2$ and CO$_2$/CH$_4$ selectivity studies to evaluate the potential of BILPs in gas separation

Table 1 Gas uptake and selectivity for BILP-3 and BILP-6

		H_2 at 1 bar[b]			CO_2 at 1 bar[b]			CH_4 at 1 bar[b]			N_2 at 1 bar[b]		Selectivity[c]	
Polymer	SA_{BET}/SA_{Lang}[a]	77 K	87 K	Q_{st}	273 K	298 K	Q_{st}	273 K	298 K	Q_{st}	273 K	298 K	CO_2/N_2	CO_2/CH_4
BILP-3	1306/1715	21	15	8.0	225	145	28.6	24	17	16.6	3.3	2.4	59 (31)	8.1 (5.4)
BILP-6	1261/1654	22	16	8.2	211	121	28.4	27	19	13.2	6.8	6.7	63 (39)	8.4 (5.3)

[a] Surface area ($m^2 g^{-1}$) was calculated from Ar isotherm. [b] Gas uptake in mg g^{-1} and the isosteric enthalpies of adsorption (Q_{st}) in kJ mol^{-1}. [c] Selectivity (mol/mol) was calculated from initial slope calculations at 273 K and (298 K).

applications. The selectivity of BILPs toward CO_2 over N_2 and CH_4 was investigated by collecting gas uptake isotherms at 273 and 298 K (Fig. S18, ESI†).

The initial steep rise in CO_2 compared to N_2 and CH_4 as illustrated in Fig. S19, ESI† is most likely due to the high affinity of CO_2 to the accessible nitrogen sites of imidazole moieties. At 273 K and 0.1 bar, which is a typical partial pressure of CO_2 in flue gases, the CO_2 uptake is 1.26 mmol g^{-1} whereas that of N_2 is only 0.031 mmol g^{-1} for BILP-3 (Fig. S19, ESI†); the corresponding values are 1.39 mmol g^{-1} and 0.038 mmol g^{-1} for BILP-6. Thus, based on initial slope calculations in the pressure range of 0 to 0.1 bar, the estimated adsorption selectivity for CO_2 over N_2 is 59 (BILP-3) and 63 (BILP-6), Fig. S19, ESI†. This selectivity surpasses BPL carbon and ZIFs,[7] and are comparable to Bio-MOF-11 (81),[6a] noncovalent porous materials (NPMs) (74)[31] and BILP-1 (70).[9] Recently, organic cage molecules featuring N–H functionality have been reported to have CO_2/N_2 selectivity in the range of 36 to 138.[32] However, such high selectivity is associated with very modest gas uptakes that are very low compared to those of BILPs. The CO_2 selectivity over CH_4 was calculated using initial slope calculations and found to be very similar for both polymers; 8.1–8.4 (273 K) and 5.4–5.3 (298 K), as listed in Table 1. Again, these values exceed reported values for BPL carbon and ZIFs.[7]

In conclusion, we have demonstrated that triptycene-derived BILPs exhibit high CO_2 uptake and selectivity in addition to their chemical and thermal stability which make them very attractive in post-combustion CO_2 capture studies.

We are grateful to the U. S. Department of Energy, Office of Basic Energy Sciences (DE-SC0002576) for generous support of this project.

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