## Chemical reduction of a diimide based porous polymer for selective uptake of carbon dioxide *versus* methane<sup>†</sup>

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A diimide based porous organic polymer (POP) post-synthetically reduced with lithium metal demonstrates a drastic increase in selectivity for carbon dioxide over methane.

Elimination of contaminant carbon dioxide from natural gas and landfill gas streams, composed mostly of methane, is an important problem. The presence of CO<sub>2</sub> in natural gas significantly lowers the energy density of the gas stream and can lead to pipeline corrosion over time.<sup>1</sup> Current technologies for separation of CO<sub>2</sub> from CH<sub>4</sub> include cryogenic distillation, membrane separation, chemical absorption, and physical adsorption. The pressure swing adsorption (PSA) method is of particular industrial interest for its outstanding energy efficiency and low operating costs.<sup>2</sup> The fundamental component of any PSA system is a highly selective adsorbent that can accommodate large quantities of gas and is easily regenerated.<sup>3</sup> Separations with porous materials such as zeolites<sup>4</sup> and activated carbons<sup>5</sup> have been widely explored. More recently, new classes of materials such as metal-organic frameworks (MOFs),<sup>6</sup> covalent organic frameworks (COFs),<sup>7</sup> and porous polymers<sup>8</sup> have shown a propensity for selective gas adsorption.9 These microporous solid materials have also shown promise in gas storage<sup>10</sup> and catalytic applications<sup>11</sup> in addition to their gas separation capabilities.

Recently we reported a porous organic polymer (3) constructed from the condensation of a tetrahedral tetraamino building block (1) with a naphthalene dianhydride linker (2) in dimethylformamide (DMF) (Scheme 1).<sup>12</sup> This amorphous material was shown to be permanently porous and robust, maintaining these properties even when exposed to aqueous and acidic conditions. In addition, polymer 3 exhibited good adsorption selectivity for carbon dioxide over methane. It is believed that the high charge density at the oxygen sites of 3 induces a local-dipole–quadrupole interaction with guest  $CO_2$ ; no such interaction is expected with  $CH_4$  guests.<sup>12</sup> We reasoned from the connectivity of the naphthalene diimide

material that chemical reduction using lithium metal would be possible. Moreover, we envisioned that addition of electron density to the linker through chemical reduction would increase the attractive interactions and thus enhance CO<sub>2</sub>/CH<sub>4</sub> adsorption selectivities. In support of this hypothesis is the previous work by Mulfort et al., who showed the chemical reduction of a MOF with a chemically similar naphthalene diimide ligand to be possible with lithium metal.<sup>13</sup> This doubly interpenetrated MOF material demonstrated a dramatic increase in hydrogen gas uptake. The slight framework shift caused by intercalation of lithium ions between the catenated frameworks was used to explain the increased H<sub>2</sub> uptake. Subsequent density functional theory (DFT) calculations showed intercalation of lithium ions between networks to be the most energetically favorable state.<sup>14</sup> In the case of polymer 3. lithium cations would be expected to intercalate between the multiple catenated networks.

As-synthesized polymer **3** was thermally evacuated under vacuum to give **4**. Chemical reduction of polymer **4** (Scheme 1) was effected by reacting **4** with a solution of lithium metal dissolved in DMF under dry argon gas atmosphere. Upon exposure to the DMF solution of Li, polymer **4** undergoes a color change from pale orange color to dark violet (see ESI†—Fig. S1). When dried under vacuum, the resulting powder changed back to pale orange when exposed to air within a few minutes. Radical formation in the reduced polymer was confirmed with electron paramagnetic resonance (EPR) measurements (see ESI†—Fig. S5). Reduced samples of polymer **4** were sealed under inert atmosphere and evacuated under vacuum by heating; care was taken to minimize exposure to oxygen. Two levels of Li doping were explored, 0.35 and 0.55 lithium atoms per naphthalene diimide linker



**Scheme 1** Experimental conditions: (i) DMF, propionic acid, 150 °C; (ii)  $10^{-2}$  mmHg vacuum, 120 °C; (iii) DMF. Structure of **3** is shown as MM2 minimized geometry of repeat unit (carbons are grey, oxygens are red, nitrogens are blue and hydrogens are omitted for clarity).

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(5 and 6, respectively). Doping levels were controlled by the amount of lithium metal dissolved in DMF as well as the time it was allowed to react. ICP-AES was used to quantify the amount of lithium (see ESI<sup>+</sup>). Attempts to generate levels higher than 0.55 Li-diimide resulted in loss of material porosity, as evidenced by gas sorption measurements. Thermogravimetric analysis (TGA) of the as-synthesized 3 indicates permanent porosity and shows stability up to 500 °C. Porosity of the materials was quantitatively determined by low-pressure adsorption of  $CO_2$ . Nitrogen isotherm measurements for 4, 5 and 6 showed no significant uptake of nitrogen for 5 and 6 at 77 K (see ESI<sup>+</sup>—Fig. S2). Surface areas were calculated using non-local density functional theory (NLDFT) methods with  $CO_2$  at 273 K. Overall surface area decreases from 960 m<sup>2</sup> g<sup>-1</sup> for the as-synthesized material to 750 m<sup>2</sup> g<sup>-1</sup> and 560 m<sup>2</sup> g<sup>-1</sup> for 5 and 6, respectively. Partial pore blockage is believed to account for the lower surface areas of the doped materials.

Pure-component isotherms of  $CO_2$  and  $CH_4$  were measured volumetrically on the evacuated samples of **4**, **5** and **6** at 298 K, Fig. 1A.<sup>9b</sup> Adsorbed  $CO_2$  and  $CH_4$  around 17 bar adhere to the trend of the measured surface areas and decrease with increasing levels of Li-doping, since Li partially reduces the void space within the materials pores. The  $CO_2/CH_4$ selectivities under mixture conditions were predicted from the experimental pure component isotherms using the ideal adsorbed solution theory (IAST). The IAST method is a benchmark tool for determining gas mixture selectivities in zeolites and MOFs. The predicted selectivities at various mixture compositions and pressures are presented in Fig. 1B. The selectivity clearly increases with increasing Li-doping. The most striking feature of Fig. 1B is the extremely high  $CO_2/CH_4$ selectivity (~170) of **6** at low pressures.

A typical feed composition for natural gas purification is  $y_{CH_4} = 0.95$ , and a general pressure in the PSA process is around 2 bar (CO<sub>2</sub> partial pressure = 0.1 bar). In the CO2/CH4 separation from landfill gas, general feed composition and pressure are  $y_{CH_4} = 0.5$  and 2 bar, respectively (CO<sub>2</sub> partial pressure = 1 bar). Extremely high CO<sub>2</sub>/CH<sub>4</sub> selectivities are obtained for 5 (17) and 6 (38) in the typical condition of natural gas purification ( $y_{CH_c} = 0.95$  and 2 bar). Also, 5 and 6 represent very high CO<sub>2</sub>/CH<sub>4</sub> selectivities (15 and 30, respectively) in the conditions of landfill gas separation ( $y_{CH_4} = 0.5$  and 2 bar). These are among the highest selectivities reported for any porous material at similar conditions. Despite the fact that CO<sub>2</sub> uptakes at 298 K and 1 bar (5: 9.1 wt%, 6: 6.6 wt%) are smaller than the values reported for Cu-BTC (17.9 wt%)<sup>15</sup> and zeolite-13X (20.2 wt%),<sup>4a</sup> the Li-doped materials (5 and 6) show drastically higher CO<sub>2</sub>/CH<sub>4</sub> selectivity than these materials (Cu-BTC:<sup>16</sup> 6 and zeolite-13X:<sup>4a</sup> 6) at the condition of landfill gas separation. Additionally, at 298 K and 1 bar CO<sub>2</sub> uptakes are comparable with the value reported for MIL-53  $(9.6 \text{ wt})^{17}$  and larger than the values for IRMOF-1 (4.7 wt%),  $^{15}$  ZIF-100 (4.3 wt%) $^{18}$ and MOF-177 (3.5 wt%).<sup>15</sup> These results indicate that 5 and 6 are potential candidates for natural gas purification and landfill gas separation by adsorptive processes.

Fig. 2 compares the normalized  $CO_2$  and  $CH_4$  isotherms for 4, 5 and 6 at low pressures. The normalized isotherm was obtained by dividing the adsorbed amount at each pressure (*N*) by the adsorbed amount at the maximum pressure around 17 bar ( $N_{max}$ ). In the case of  $CO_2$ , stronger adsorption (as indicated by a higher initial adsorption at low pressure) is observed as the Li-doping amount increases. For  $CH_4$ , however, nearly the same relative adsorption is shown



**Fig. 1** (A) Measured  $CO_2$  and  $CH_4$  isotherms at 298 K along with the dual-site Langmuir–Freundlich fits and (B) IAST selectivity of  $CO_2$  versus  $CH_4$  at various pressures and mole fractions of  $CH_4$  ( $v_{CH_4}$ ) for as-synthesized **4** (left), Li<sub>0.35</sub> reduced **5** (center) and Li<sub>0.55</sub> reduced **6** (right).



**Fig. 2** Normalized isotherm data for  $CO_2$  (closed symbols) and  $CH_4$  (open symbols).

independent of the Li-doping amounts. This indicates that Li-doping may induce highly energetic sites within the pores of the material. These could come from chemically reduced ligands or constricted pores. The calculated DFT pore size distributions (CO<sub>2</sub> at 273 K) of **4**, **5** and **6** do not suggest any significant change in pore size upon Li-doping (see ESI—Fig. S4). Hence, the strong CO<sub>2</sub> adsorption in **5** and **6** at low pressures likely does not come from the constriction of pores. These energetic sites may also arise from an increased dipole–quadrupolar interaction between CO<sub>2</sub> and the reduced material, but there is little to no effect on the binding of non-polar CH<sub>4</sub>. It is evident that the chemically reduced nature of the material leads to the drastic increase in selectivity of polar CO<sub>2</sub> over non-polar CH<sub>4</sub>.

In summary, we have chemically reduced a permanently porous polymer material with lithium metal. The reduced material retains porosity and demonstrates highly selective adsorption of  $CO_2$  over  $CH_4$ . Reduction of similarly structured catenated porous materials with alkali metals could be utilized as a method to increase selective adsorption.

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