Cross-Linking Amine-Rich Compounds into High Performing Selective CO2 Absorbents

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Amine-based absorbents play a central role in CO2 sequestration and utilization. Amines react selectively with CO2, but a drawback is the unproductive weight of solvent or support in the absorbent. Efforts have focused on metal organic frameworks (MOFs) reaching extremely high CO2 capacity, but limited selectivity to N2 and CH4, and decreased uptake at higher temperatures. A desirable system would have selectivity (cf. amine) and high capacity (cf. MOF), but also increased adsorption at higher temperatures. Here, we demonstrate a proof-of-concept where polyethyleneimine (PEI) is converted to a high capacity and highly selective CO2 absorbent using buckminsterfullerene (C60) as a cross-linker. PEI-C60 (CO2 absorption of 0.14 g/g at 0.1 bar/90°C) is compared to one of the best MOFs, Mg-MOF-74 (0.06 g/g at 0.1 bar/90°C), and does not absorb any measurable amount of CH4 at 50 bar. Thus, PEI-C60 can perform better than MOFs in the sweetening of natural gas.

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Results and discussion
Initially, PEI-C60 was synthesized with different molecular weights (600, 1,800, 10,000 and 25,000 Da), showing that the CO2 capture performance improved with increasing molecular weight (Supplementary Information). Thus all results presented herein are related to branched PEI 25,000 Da. The preparation of PEI-C60 is readily scalable. A brown precipitate of PEI-C60 is formed upon mixing solutions of PEI and C60 dissolved in chloroform and toluene, respectively, in the presence of NEt3. PEI-C60 is insoluble in water, ethanol and chloroform. The PEI/C60 weight ratio was measured as 73/27 using thermogravimetric analysis, corresponding to a C/N weight ratio of ca. 74/26. This value is comparable to the results from X-ray photoelectron spectroscopy (XPS), 70/30, and elemental analysis, 72/28, which corresponds to about 10 molecules of C60 per molecule of PEI (Mw =

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25,000 Da). Covalent functionalization of C_{60} (rather than physical wrapping) is confirmed by NMR spectroscopy, vide infra. Since branched PEI has many primary amines, it is likely that PEI would react with several nanocarbon molecules resulting in a highly interconnected network. The surface area of PEI-C_{60} was measured in the order of about 2.7-2.9 m^{2}/g (Supplementary Information).

It should be noted that PEI-C_{60} behaves completely differently to a physical mixture or its components. PEI is a viscous material, while PEI-C_{60} is a non-sticky porous composite capable of absorption. The absorption of CO\textsubscript{2} on solid C_{60}, 0.002 g/g (g CO\textsubscript{2}/g absorbent) at 1 bar\textsuperscript{13}, is dramatically lower than that of PEI-C_{60} (0.2 g/g at the same pressure). PEI-C_{60} also shows a greater absorption of CO\textsubscript{2} than PEI-SWNTs (single walled carbon nanotubes) (0.09 g/g)\textsuperscript{14} in agreement with a higher loading of PEI on C_{60} (75% w/w) compared to SWNTs (50% w/w). Additionally, the PEI:C molar ratio of PEI-C_{60} (1:695) is larger than that of PEI-SWNTs (1:2065) showing that C_{60} can accommodate more PEI molecules than SWNTs despite its much smaller aspect ratio. The hydrophobic surface of the SWNT\textsuperscript{14}, in contrast C_{60} appears fully internalized in the PEI matrix as inter- and/or intra-molecular cross-linker. The incorporation of hydrophobic centres in the PEI media would possibly force the hydrophilic amine moieties to point toward the surface of the material making the reactions with CO\textsubscript{2} more effective. PEI/G-silica (PEI-impregnated graphene-porous silica sheets) also exhibited high absorption capacity, 0.19 g/g, due, as we speculate, to a comparable hydrophilic-hydrophobic enhancing effect.

The performance of PEI-C_{60} equates or outperforms those of metal organic frameworks (MOFs) particularly at higher temperatures and high temperature is better than that of Mg-MOF-74, Mg_{2}(1,4-dioxido-2,5-benzenedicarboxylate), which has exceptionally high CO\textsubscript{2} capacity at very low CO\textsubscript{2} pressure and high temperature due to the presence of unsaturated Mg sites that have strong affinity to CO\textsubscript{2}\textsuperscript{16,19,20}. As a comparison, without such binding sites the performance of MOF-177\textsuperscript{20}, Zn_{2}O(1,3,5-benzenetribenzoate)\textsubscript{2}, is poorer (Fig. 1, dashed curve B). In the case of PEI-C_{60} the amine groups appear to have a higher affinity (reactivity) toward CO\textsubscript{2} making PEI-C_{60} an excellent material for the capture of CO\textsubscript{2} at very low pressures (already significant at 0.05 bar) and relatively high temperatures (70–90°C) both ideal properties for the absorption of CO\textsubscript{2} from flue gases\textsuperscript{21}.

The absorption performance of PEI-C_{60} in CO\textsubscript{2}, CH\textsubscript{4} and N\textsubscript{2} at various pressures is compared in Fig. 2. PEI-C_{60} does not absorb any measurable amount of CH\textsubscript{4} at pressures up to 50 bar. Practically no N\textsubscript{2} is absorbed in the range from 0 to 1 bar. Whereas, PEI-C_{60} reaches almost its full CO\textsubscript{2} absorption capacity, 0.2 g/g, at 1 bar. This very high selectivity has two practical implications. One is related to the capture of CO\textsubscript{2} from flue gas\textsuperscript{21}, assuming that the partial pressures of CO\textsubscript{2} and N\textsubscript{2} in the flue gas are 0.15 and 0.75 bar, respectively, PEI-C_{60} would absorb about 0.15 g/g of CO\textsubscript{2} and 0.0005 g/g of N\textsubscript{2} at 90°C (inset of Fig. 2). This compares to 0.14 g/g of CO\textsubscript{2} and 0.002 g/g of N\textsubscript{2} at 25°C for mmen-Mg\textsubscript{2}(dopbc), mmen = N,N’-dimethylmethylenediamine and dopbc\textsuperscript{4-} = 4,4’-dioxido-3,3’-biphenyldicarboxylate, an amine-functionalized expanded MOF-74 structure\textsuperscript{22}. Thus, PEI-C_{60} has promise for capturing CO\textsubscript{2} from N\textsubscript{2}-rich hot flue gases.

A second major implication is important for natural gas sweetening\textsuperscript{23,24}. Of particular interest is CO\textsubscript{2} removal at the wellhead where the gas is typically at ˃50°C. To date physical adsorbent like activated carbons, zeolites and MOFs have not been able to replace in large-scale amine scrubbing solutions because of their lack of selectivity toward the capture of CO\textsubscript{2}. Selectivity is essential for natural gas sweetening because if the absorbent captures both CO\textsubscript{2} and CH\textsubscript{4} an extra step must be added in order to recover that part of final product.

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**Figure 1** | CO\textsubscript{2} uptake of PEI-C\textsubscript{60}. Comparison of the CO\textsubscript{2} uptake of PEI-C\textsubscript{60}, Mg-MOF-74, and MOF-177 in the low pressure range. The CO\textsubscript{2} uptake of PEI-C\textsubscript{60} was measured at 70, 80 and 90°C. The dashed curves are for the absorption of CO\textsubscript{2} on (A) Mg-MOF-74 and (B) MOF-177 both at 90°C. PEI-C\textsubscript{60} outperforms Mg-MOF-74 in the capture of CO\textsubscript{2} at low pressure: the uptake of PEI-C\textsubscript{60} is twice as much as that of Mg-MOF-74 at 0.1 bar and 90°C. Furthermore, the CO\textsubscript{2} absorption capacity of PEI-C\textsubscript{60} increases with increasing temperature in striking contrast with MOFs which capacity decreases with increasing temperature.

**Figure 2** | Selectivity of CO\textsubscript{2} uptake of PEI-C\textsubscript{60}. Single component CO\textsubscript{2}, CH\textsubscript{4}, and N\textsubscript{2} uptakes of PEI-C\textsubscript{60} at 90°C in the high pressure range. The dashed lines indicate the corresponding uptakes at the typical pressures of natural gas (5 bar CO\textsubscript{2} and 45 bar CH\textsubscript{4}) and flue gas (0.15 bar CO\textsubscript{2} and 0.75 bar N\textsubscript{2}) in the inset. The outstanding selectivity of PEI-C\textsubscript{60} is particularly evident for natural gas where PEI-C\textsubscript{60} reaches full CO\textsubscript{2} capacity at 5 bar with no significant amount of absorbed CH\textsubscript{4} at 45 bar.
captured in the absorbent. This is not necessary with PEI-C60, the removal of CO2 from natural gas at 50 bar, roughly made of 5 bar CO2 and 45 bar CH4, would give maximum absorption capacity for CO2 of 0.2 g/g at 5 bar and no measurable absorption for CH4 at 45 bar (Fig. 2). This compares to 0.35 g/g for CO2 and 0.1 g/g for CH4 at the same pressures and 70°C for Mg-MOF-74, which would require the recovery of large amounts of CH4 captured by the absorbent following the CO2 removal step.

The absorption of CO2 by PEI-C60 from mixtures with CH4 and simulated natural gas at atmospheric pressure (Fig. 3) is about 0.15 g/g (after 60 min.), while CH4 is not absorbed. In the case of the two 10% CO2 mixtures, balanced with CH4 alone or CH4, ethane and propane, the two absorption curves are almost identical. The amount of CO2 captured in this case is about 0.08 g/g after 60 min. exposure, more than 50% of what is absorbed in single-component CO2, 0.15 g/g. This is a further evidence of the high affinity of PEI-C60 toward CO2, in fact the capture performance of PEI-C60 is five times better than that expected from a simple proportionality between absorption and dilution factor, i.e., 50% of the maximum capacity from a 10% diluted CO2.

The performance of PEI-C60 was also analysed at atmospheric pressure with thermogravimetric analysis using dry and wet CO2. A total uptake of about 0.21 g/g CO2 was measured and confirmed with elemental analysis showing that moisture in the feeding gas does not affect the CO2 capture performance. Moreover, PEI-C60 has a relatively low temperature of regeneration (<90°C) when compared to the amine scrubbing processes (120–130°C), in agreement with what we previously observed with other PEI-modified nanocarbons. PEI-C60 is relatively stable upon cycling maintaining more than 60% of its starting absorption capacity after 100 absorption/desorption cycles at 90°C (Supplementary Information).

The chemical species formed upon absorption of CO2 in PEI-C60 were analysed using nuclear magnetic resonance (NMR). The 13C NMR spectra (Fig. 4a) do not allow a definitive differentiation of the carbamate carbonyl signal from the bicarbonate carbonyl signal that may be present. Two bands are present in all 13C CP-MAS NMR spectra: one with a peak maximum at 50 ppm (sp3 carbons of PEI) and a weaker band with a peak maximum at about 150 ppm (sp2 carbons of functionalized C60). The former band has a shoulder at about 75 ppm consistent with the presence of sp3 nitrogen-substituted carbon atoms on C60, as seen for the sidewall functionalization of SWNTs. A third sharper signal (164 ppm) is also evident in the spectra of samples exposed to wet or dry CO2 (but not in the spectrum for wet N2). Since this signal can be attributed to carbonate and/or carbamate species, we cannot readily determine the relative contributions of these two species in PEI-C60 conditioned in CO2. Fortunately, 15N CP-MAS NMR presents a much more secure way to determine the presence of carbamate in the presence of bicarbonate. The 15N CP-MAS NMR spectra of the PEI-C60 conditioned in N2 and dry CO2 are given in Fig. 4(b). In the 15N spectrum recorded after conditioning in dry CO2, the band at about -347 ppm can reasonably be assigned to PEI amine nitrogen environments, while the signal at about -297 ppm can reasonably be assigned to PEI-NH-COO- carbamate species. In the sample conditioned in N2, the only appreciable signal, after more than 80,000 scans, was that of the PEI amine nitrogens. The XPS characterization of PEI-C60 conditioned in wet CO2 also supports the formation of bicarbonate and/or carbamate species (Supplementary Information).

With PEI-C60, we introduce a new class of materials where specifically selected cross-linkers are used to convert amine-rich compounds into effective CO2 absorbents. The C60 cross-linker can be depicted as the final result of a progressive shrinkage of a carbon support where PEI increasingly loses contact with the scaffold, as this shrinks, to end suspended between single C60 anchoring points. In
this way, the amount of support is minimized in order to maximize the amine content and the CO₂ absorption capacity. This simple approach redefines the way we think about preparing CO₂ absorbents from anchoring amine compounds to a support to making the amine materials self-supporting with the aid of cross-linkers. We propose that the hydrophobic nature of C₆₀ is responsible for the externalization of the hydrophilic amine groups of PEI boosting the absorption performance of the polymer. Accordingly, other cross-linkers could improve this or other critical properties of the resulting composites to achieve further enhanced CO₂ capture performance with associated reduction in the cost of materials. These new composites could allow for a more efficient capture of CO₂ and, when integrated in sequestration and utilization technologies, for the containment of the adverse effects of CO₂ on the environment.

Methods

Materials. All materials were used as received. Fullerene C₆₀ (99.5%) was purchased from Alpha Aesar, polyethyleneimine branched (PEI, M₆₉ = 25,000 Da) and chloroform (>99.8%) from Sigma Aldrich, toluene (99.9%) from Omnisolv EMD, and triethylamine (99%) from Acros. Ac. N₂ and CO₂ high purity gases were all purchased from Matheson TRIGAS. Certified multi-component CO₂ mixtures were obtained from Applied Gas, Inc.

Synthesis. PEI-C₆₀ was prepared by adding a PEI/chloroform solution (1.00-1.20 g PEI in 35 mL CHCl₃) to a C₆₀/toluene solution (0.12 g C₆₀ in 150 ml toluene with 6 mL N₂) while rapidly stirring. A dark-brown PEI-C₆₀ precipitate was formed and filtered on a 0.45 µm pore PTFE filter. The precipitate was washed with excess CHCl₃ and transferred to a clean flask where 50 ml CHCl₃ was added. The precipitate was bath sonicated for 10 min and again filtered and washed as before. The PEI-C₆₀ precipitate was left drying in air overnight and collected as a clustery/rubbery brown solid.

Equipment. All low and high-pressure gas absorption isotherms were collected with a Setaram 920 volumetric apparatus at 100 mg of sample. The absorption isotherms at atmospheric pressure were collected with a TA Instrument SDT Q600 thermogravimetric apparatus using at least 5 mg of sample. In this case, absorption isotherms at atmospheric pressure were collected with a TA Instrument Setaram PCTPro volumetric apparatus using at least 100 mg of sample. The precipitate was left drying in air overnight and collected as a clustery/rubbery brown solid.

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Author contributions
E.A., E.P.D. and L.C. performed the experiments and analysed the data. L.B.A. performed NMR analysis. E.A. created the Figures. E.A. and A.R.B. wrote the manuscript. A.R.B. supervised the project.

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