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# Cross-Linking Amine-Rich Compounds into High Performing Selective CO<sub>2</sub> Absorbents

SUBJECT AREAS:  
CARBON NANOTUBES  
AND FULLERENES  
POLLUTION REMEDIATION

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Amine-based absorbents play a central role in CO<sub>2</sub> sequestration and utilization. Amines react selectively with CO<sub>2</sub>, 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 CO<sub>2</sub> capacity, but limited selectivity to N<sub>2</sub> and CH<sub>4</sub>, 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 CO<sub>2</sub> absorbent using buckminsterfullerene (C<sub>60</sub>) as a cross-linker. PEI-C<sub>60</sub> (CO<sub>2</sub> 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 CH<sub>4</sub> at 50 bar. Thus, PEI-C<sub>60</sub> can perform better than MOFs in the sweetening of natural gas.

Curbing CO<sub>2</sub> emissions with effective sequestration is among one of the major contemporary environmental and technological challenges<sup>1,2</sup>. Organic amines in solution or tethered to high-surface area supports are commonly used for the absorption of CO<sub>2</sub><sup>3-5</sup>. Although the amines impart intrinsic selectivity to these systems, a major drawback is that the solvent and support add unproductive weight to the absorbent. The CO<sub>2</sub> absorption capacity (g CO<sub>2</sub>/g absorbent) is maximized when the amount of solvent and support is minimized. Furthermore, removing anything that is not amine (especially solvent) would reduce the energy demand for regeneration (CO<sub>2</sub> desorption). It would be ideal to exploit the intrinsic selectivity of amine-bearing materials by using the lowest amount of support to maximize uptake, and avoid the energy demand of solvent heating. Polyethyleneimine (PEI) has a high potential for CO<sub>2</sub> absorption since it has one amine group every two carbon atoms. However, high molecular weight branched PEIs absorb CO<sub>2</sub> extremely slowly because of their high viscosity. PEIs have been applied in combination with various supports<sup>6-10</sup>, and in particular very high PEI loadings were attained using silica foam and mesoporous capsules as supports<sup>8,9</sup>. Alternatively higher PEI loadings (CO<sub>2</sub> absorption capacities) could be obtained by cross-linking PEI. The mass of cross-linker used to convert the PEI to an effective CO<sub>2</sub> absorbent could be lower than that of an actual support. The cross-linking of PEI with bi-functional reagents is employed in gene transfection using biodegradable bridges to improve transfection efficacy and reduce cytotoxicity<sup>11,12</sup>. However, there is no known work in the cross-linking of PEI for enhanced CO<sub>2</sub> capture. Herein, we show how the loading and CO<sub>2</sub> absorption performance of PEI can be maximized using C<sub>60</sub> as PEI cross-linker. In particular, the resulting composite material, PEI-C<sub>60</sub>, has excellent CO<sub>2</sub> absorption capacity at high temperature and very high selectivity both in the presence of N<sub>2</sub> and CH<sub>4</sub>.

## Results and discussion

Initially, PEI-C<sub>60</sub> was synthesized with different molecular weights (600, 1,800, 10,000 and 25,000 Da), showing that the CO<sub>2</sub> 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-C<sub>60</sub> is readily scalable. A brown precipitate of PEI-C<sub>60</sub> is formed upon mixing solutions of PEI and C<sub>60</sub> dissolved in chloroform and toluene, respectively, in the presence of NEt<sub>3</sub>. PEI-C<sub>60</sub> is insoluble in water, ethanol and chloroform. The PEI/C<sub>60</sub> 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 C<sub>60</sub> per molecule of PEI (M<sub>w</sub> =

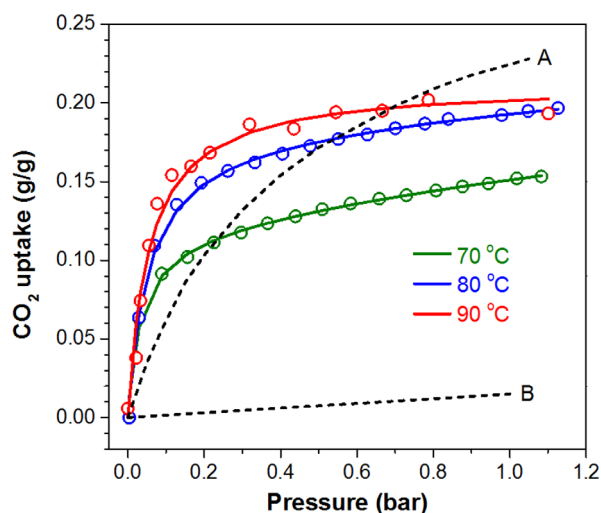


25,000 Da). Covalent functionalization of  $C_{60}$  (rather than physical wrapping) is confirmed by NMR spectroscopy, *vide infra*. Since branched PEI has many primary amines, it is likely that PEI would react with several nanocarbon molecules resulting in a highly interconnected network. The surface 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  $CO_2$  on solid  $C_{60}$ , 0.002 g/g (g  $CO_2$ /g absorbent) at 1 bar<sup>13</sup>, 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  $CO_2$  than PEI-SWNTs (single walled carbon nanotubes) (0.09 g/g)<sup>14</sup> 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 hydrophilic PEI segregates from the hydrophobic surface of the SWNT<sup>14</sup>, 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  $CO_2$  more effective. PEI/G-silica (PEI-impregnated graphene-porous silica sheets) also exhibited high absorption capacity, 0.19 g/g<sup>15</sup>, due, as we speculate, to a comparable hydrophobic-hydrophilic enhancing effect.

The performance of PEI- $C_{60}$  equates or outperforms those of metal organic frameworks (MOFs) particularly at higher temperatures<sup>16,17</sup>. Importantly, the performance of PEI- $C_{60}$  at low pressure and high temperature is better than that of Mg-MOF-74,  $Mg_2(1,4\text{-dioxido-2,5-benzenedicarboxylate})$ , which has exceptionally high  $CO_2$  capacity at very low  $CO_2$  pressure<sup>18,19</sup>. The absorption capacity of PEI- $C_{60}$  is more than twice that of Mg-MOF-74 in single-component  $CO_2$ . Moreover, PEI- $C_{60}$  is extremely selective.

The  $CO_2$  absorption performance of PEI- $C_{60}$  in the low pressure range (Fig. 1) shows uptake increasing with temperature with a  $CO_2$

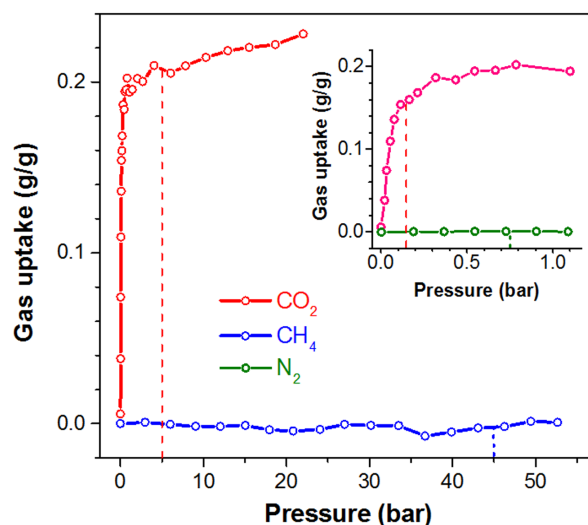


**Figure 1** |  $CO_2$  uptake of PEI- $C_{60}$ . Comparison of the  $CO_2$  uptake of PEI- $C_{60}$ , Mg-MOF-74, and MOF-177 in the low pressure range. The  $CO_2$  uptake of PEI- $C_{60}$  was measured at 70, 80 and 90°C. The dashed curves are for the absorption of  $CO_2$  on (A) Mg-MOF-74 and (B) MOF-177 both at 90°C. PEI- $C_{60}$  outperforms Mg-MOF-74 in the capture of  $CO_2$  at low pressure: the uptake of PEI- $C_{60}$  is twice as much as that of Mg-MOF-74 at 0.1 bar and 90°C. Furthermore, the  $CO_2$  absorption capacity of PEI- $C_{60}$  increases with increasing temperature in striking contrast with MOFs which capacity decreases with increasing temperature.

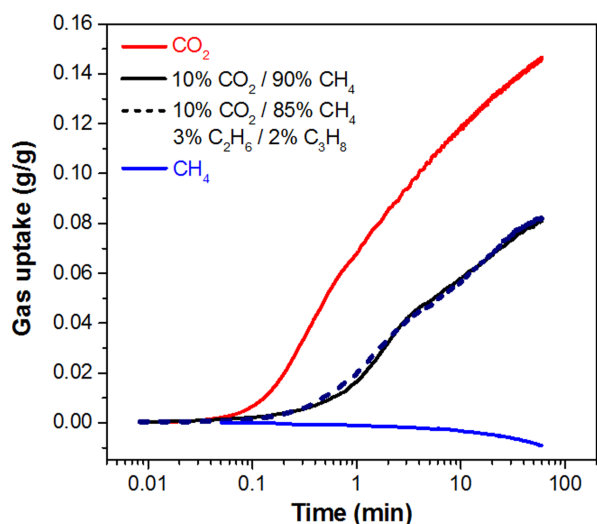
absorption capacity (at 1 bar) going from 0.15 to 0.20 g/g at 70 and 90°C, respectively. This is in dramatic contrast with MOFs whose uptake decreases above room temperature. More significant is the uptake at lower pressures. The  $CO_2$  uptake of PEI- $C_{60}$  surpasses that of Mg-MOF-74 (Fig. 1, dashed curve A) for pressures below 0.7 bar at 90°C. Mg-MOF-74 is one of the best MOFs for the adsorption of  $CO_2$  at low pressure and high temperature due to the presence of unsaturated Mg sites that have strong affinity to  $CO_2$ <sup>16,19,20</sup>. As a comparison, without such binding sites the performance of MOF-177<sup>20</sup>,  $Zn_4O(1,3,5\text{-benzenetribenzoate})_2$ , 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  $CO_2$  making PEI- $C_{60}$  an excellent material for the capture of  $CO_2$  at very low pressures (already significant at 0.05 bar) and relatively high temperatures (70–90°C) both ideal properties for the absorption of  $CO_2$  from flue gases<sup>21</sup>.

The absorption performance of PEI- $C_{60}$  in  $CO_2$ ,  $CH_4$  and  $N_2$  at various pressures is compared in Fig. 2. PEI- $C_{60}$  does not absorb any measurable amount of  $CH_4$  at pressures up to 50 bar. Practically no  $N_2$  is absorbed in the range from 0 to 1 bar. Whereas, PEI- $C_{60}$  reaches almost its full  $CO_2$  absorption capacity, 0.2 g/g, at 1 bar. This very high selectivity has two practical implications. One is related to the capture of  $CO_2$  from flue gas<sup>21</sup>, assuming that the partial pressures of  $CO_2$  and  $N_2$  in the flue gas are 0.15 and 0.75 bar, respectively, PEI- $C_{60}$  would absorb about 0.15 g/g of  $CO_2$  and 0.0005 g/g  $N_2$  at 90°C (inset of Fig. 2). This compares to 0.14 g/g of  $CO_2$  and 0.002 g/g of  $N_2$  at 25°C for mmen- $Mg_2(\text{dobpcd})$ , mmen =  $N,N'$ -dimethylethylenediamine and  $\text{dobpcd}^{4-} = 4,4'$ -dioxido-3,3'-biphenyldicarboxylate, an amine-functionalized expanded MOF-74 structure<sup>22</sup>. Thus, PEI- $C_{60}$  has promise for capturing  $CO_2$  from  $N_2$ -rich hot flue gases.

A second major implication is important for natural gas sweetening<sup>23,24</sup>. Of particular interest is  $CO_2$  removal at the wellhead where the gas is typically at  $>50^\circ\text{C}$ . 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  $CO_2$ . Selectivity is essential for natural gas sweetening because if the absorbent captures both  $CO_2$  and  $CH_4$  an extra step must be added in order to recover that part of final product



**Figure 2** | Selectivity of  $CO_2$  uptake of PEI- $C_{60}$ . Single component  $CO_2$ ,  $CH_4$  and  $N_2$  uptakes of PEI- $C_{60}$  at 90°C in the high pressure range. The dashed lines indicate the corresponding uptakes at the typical pressures of natural gas (5 bar  $CO_2$  and 45 bar  $CH_4$ ) and flue gas (0.15 bar  $CO_2$  and 0.75  $N_2$ ) in the inset. The outstanding selectivity of PEI- $C_{60}$  is particularly evident for natural gas where PEI- $C_{60}$  reaches full  $CO_2$  capacity at 5 bar with no significant amount of absorbed  $CH_4$  at 45 bar.



**Figure 3** | CO<sub>2</sub> uptake from simulated natural gas mixtures. CO<sub>2</sub> uptake of PEI-C<sub>60</sub> from single- and multi-component mixtures of CO<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, and C<sub>3</sub>H<sub>8</sub> at 1 atm and 90°C. The decrease of mass in CH<sub>4</sub> is likely due to a progressive drying of the absorbent. The superposition of the absorption curves in 10% CO<sub>2</sub>/90% CH<sub>4</sub> and 10% CO<sub>2</sub>/90% CH<sub>4</sub>/3% C<sub>2</sub>H<sub>6</sub>/2% C<sub>3</sub>H<sub>8</sub> further indicates the lack of interaction of PEI-C<sub>60</sub> with hydrocarbons.

captured in the absorbent. This is not necessary with PEI-C<sub>60</sub>, the removal of CO<sub>2</sub> from natural gas at 50 bar, roughly made of 5 bar CO<sub>2</sub> and 45 bar CH<sub>4</sub>, would give maximum absorption capacity for CO<sub>2</sub> of 0.2 g/g at 5 bar and no measurable absorption for CH<sub>4</sub> at 45 bar (Fig. 2). This compares to 0.35 g/g for CO<sub>2</sub> and 0.1 g/g for CH<sub>4</sub> at the same pressures and 70°C for Mg-MOF-74, which would require the recovery of large amounts of CH<sub>4</sub> captured by the absorbent following the CO<sub>2</sub> removal step<sup>25</sup>.

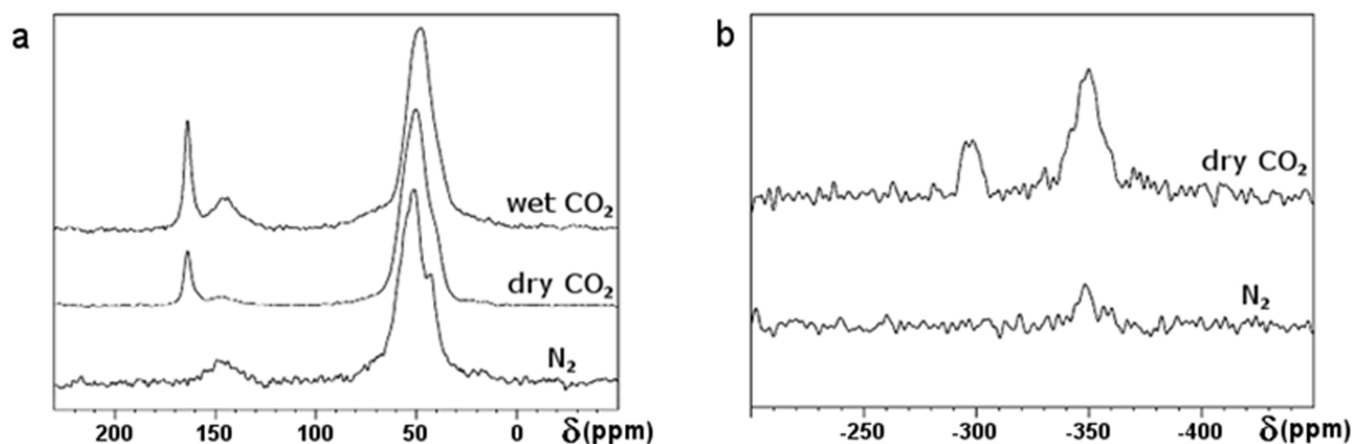
The absorption of CO<sub>2</sub> by PEI-C<sub>60</sub> from mixtures with CH<sub>4</sub> and simulated natural gas at atmospheric pressure (Fig. 3) is about 0.15 g/g (after 60 min.), while CH<sub>4</sub> is not absorbed. In the case of the two 10% CO<sub>2</sub> mixtures, balanced with CH<sub>4</sub> alone or CH<sub>4</sub>, ethane and propane, the two absorption curves are almost identical. The amount of CO<sub>2</sub> captured in this case is about 0.08 g/g after 60 min. exposure, more than 50% of what is absorbed in single-component CO<sub>2</sub>, 0.15 g/g. This is a further evidence of the high affinity of PEI-C<sub>60</sub> toward CO<sub>2</sub>, in fact the capture performance of PEI-C<sub>60</sub> 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 CO<sub>2</sub>.

The performance of PEI-C<sub>60</sub> was also analysed at atmospheric pressure with thermogravimetric analysis using dry and wet CO<sub>2</sub>. A total uptake of about 0.21 g/g CO<sub>2</sub> was measured and confirmed with elemental analysis showing that moisture in the feeding gas does not affect the CO<sub>2</sub> capture performance. Moreover, PEI-C<sub>60</sub> 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<sup>14,26</sup>. PEI-C<sub>60</sub> 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 CO<sub>2</sub> in PEI-C<sub>60</sub> were analysed using nuclear magnetic resonance (NMR). The <sup>13</sup>C 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 <sup>13</sup>C CP-MAS NMR spectra: one with a peak maximum at 50 ppm (sp<sup>3</sup> carbons of PEI) and a weaker band with a peak maximum at about 150 ppm (sp<sup>2</sup> carbons of functionalized C<sub>60</sub>). The former band has a shoulder at about 75 ppm consistent with the presence of sp<sup>3</sup> nitrogen-substituted carbon atoms on C<sub>60</sub>, as seen for the sidewall functionalization of SWNTs<sup>27,28</sup>. A third sharper signal (164 ppm) is also evident in the spectra of samples exposed to wet or dry CO<sub>2</sub> (but not in the spectrum for wet N<sub>2</sub>). 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-C<sub>60</sub> conditioned in CO<sub>2</sub>. Fortunately, <sup>15</sup>N CP-MAS NMR presents a much more secure way to determine the presence of carbamate in the presence of bicarbonate. The <sup>15</sup>N CP-MAS NMR spectra of the PEI-C<sub>60</sub> conditioned in N<sub>2</sub> and dry CO<sub>2</sub> are given in Fig. 4(b). In the <sup>15</sup>N spectrum recorded after conditioning in dry CO<sub>2</sub>, 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<sup>-</sup> carbamate species. In the sample conditioned in N<sub>2</sub>, the only appreciable signal, after more than 80,000 scans, was that of the PEI amine nitrogens. The XPS characterization of PEI-C<sub>60</sub> conditioned in wet CO<sub>2</sub> also supports the formation of bicarbonate and/or carbamate species (Supplementary Information).

With PEI-C<sub>60</sub>, we introduce a new class of materials where specifically selected cross-linkers are used to convert amine-rich compounds into effective CO<sub>2</sub> absorbents. The C<sub>60</sub> 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 C<sub>60</sub> anchoring points. In



**Figure 4** | Solid state NMR of PEI-C<sub>60</sub>. Solid state (a) <sup>1</sup>H-<sup>13</sup>C and (b) <sup>1</sup>H-<sup>15</sup>N CP-MAS NMR characterization of PEI-C<sub>60</sub> after conditioning in wet CO<sub>2</sub>, dry CO<sub>2</sub> or N<sub>2</sub>.



this way, the amount of support is minimized in order to maximize the amine content and the CO<sub>2</sub> absorption capacity. This simple approach redefines the way we think about preparing CO<sub>2</sub> 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 C<sub>60</sub> 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 CO<sub>2</sub> capture performance with associated reduction in the cost of materials. These new composites could allow for a more efficient capture of CO<sub>2</sub> and, when integrated in sequestration and utilization technologies, for the containment of the adverse effects of CO<sub>2</sub> on the environment.

## Methods

**Materials.** All materials were used as received. Fullerene C<sub>60</sub> (99.5%) was purchased from Alpha Aesar, polyethyleneimine branched (PEI, M<sub>w</sub> = 25,000 Da) and chloroform (≥99.8%) from Sigma Aldrich, toluene (99.98%) from OmniSolv EMD, and triethylamine (99%) from Acros. Ar, N<sub>2</sub> and CO<sub>2</sub> high purity gases were all purchased from Matheson TRIGAS. Certified multi-component CO<sub>2</sub> mixtures were obtained from Applied Gas, Inc.

**Synthesis.** PEI-C<sub>60</sub> was prepared by adding a PEI/chloroform solution (1.00–1.20 g PEI in 35 mL CHCl<sub>3</sub>) to a C<sub>60</sub>/toluene solution (0.12 g C<sub>60</sub> in 150 ml toluene with 6 mL NEt<sub>3</sub>) while rapidly stirring. A dark-brown PEI-C<sub>60</sub> precipitate was formed and filtered on a 0.45 μm pore PTFE filter. The precipitate was washed with excess CHCl<sub>3</sub> and transferred to a clean flask where 50 ml CHCl<sub>3</sub> was added. The precipitate was bath sonicated for 10 min and again filtered and washed as before. The PEI-C<sub>60</sub> 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 PCTPro volumetric apparatus using at least 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, the CO<sub>2</sub> was used either in dry or wet form. Dry CO<sub>2</sub> was prepared using a stainless still bubbler filled with 3 Å molecular sieves (vacuum dried at 250 °C overnight) through which the CO<sub>2</sub> was passed at room temperature and 50 psig. Wet CO<sub>2</sub> was prepared using a stainless still bubbler filled with deionized water (bubbled with high-flow CO<sub>2</sub> at atmospheric pressure and slow-flow CO<sub>2</sub> at 50 psig for 1 h each) through which the CO<sub>2</sub> was bubbled at room temperature and 2 psig. This last procedure was also used to prepare wet N<sub>2</sub>. All gases were at ambient pressure when in contact with the absorbent. All uptake values are given in the unit of g/g, i.e., in weight of CO<sub>2</sub> (in g) per unit weight of absorbent (in g). A Cosctech ECS 4010 Nitrogen/Protein Analyzer was used for CHNO elemental analysis. Linear calibrations obtained with acetanilide standard were used for all elements (R<sup>2</sup> > 0.999). The solid state <sup>1</sup>H-<sup>13</sup>C and <sup>1</sup>H-<sup>15</sup>N CP-MAS NMR spectra were obtained at room temperature using a Bruker AVANCE-III spectrometer (50.3 MHz <sup>13</sup>C, 20.3 MHz <sup>15</sup>N, 200.1 MHz <sup>1</sup>H). Chemical shifts are reported relative to glycine defined as 176.46 ppm for the carbonyl carbon<sup>29</sup> and -347.58 ppm for the nitrogen<sup>30</sup>. All of the <sup>13</sup>C spectra were obtained with a 1 ms contact time, 32.8 ms FID with spin64 decoupling, 5 s relaxation delay, and with 50 Hz (1 ppm) of line broadening applied to the FID. The number of scans varied: 20,512 with PEI-C<sub>60</sub> conditioned in wet CO<sub>2</sub> and 16,800 each in the case of N<sub>2</sub> and dry CO<sub>2</sub>. All of the <sup>15</sup>N spectra were obtained with a 3 ms contact time, 20.5 ms FID with spin64 decoupling, 5 s relaxation delay, and with 20 Hz (1 ppm) of line broadening applied to the FID. The number of scans varied: 65,000 for dry CO<sub>2</sub>, 82,000 for N<sub>2</sub>, and 1648 for ammonium carbamate (ammonium signal at -358.1 ppm, carbamate signal at -300.9 ppm). The rotors were packed in a glove bag filled with the same gas used for the conditioning of the absorbent. The XPS spectra were acquired using a Physical Electronics PHI Quantera SXM equipped with an Al X-ray monochromatic source (K<sub>α</sub> 1486.6 eV at 50.3 W) set at a 200 μm beam diameter and a 45° incident angle. The spectra were collected in ultra-high vacuum conditions (~10<sup>-9</sup> Torr). The high-resolution spectra were deconvoluted into overlapping peaks using mixed Gaussian-Lorentzian curves after subtraction of a Shirley-type background. The SEM images of the PEI-C<sub>60</sub> composites were collected using a FEI Quanta 400 ESEM at an accelerating voltage of 10–20 kV and high vacuum (< 5 × 10<sup>-9</sup> Torr). The surface morphology and area of the PEI-C<sub>60</sub> composites were characterized using a Veeco Nanoscope IIIA Atomic Force Microscope and a Quantachrome Autosorb-3B Surface Analyzer, respectively.

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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.

### Additional information

**Supplementary information** accompanies this paper at <http://www.nature.com/scientificreports>

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