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

SUBJECT AREAS:
CARBON NANOTUBES
AND FULLERENES
POLLUTION REMEDIATION

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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.

Curbing CO₂ emissions with effective sequestration is among one of the major contemporary environmental and technological challenges^{1,2}. Organic amines in solution or tethered to high-surface area supports are commonly used for the absorption of CO₂³⁻⁵. 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 CO₂ absorption capacity (g CO₂/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 (CO₂ 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 CO₂ absorption since it has one amine group every two carbon atoms. However, high molecular weight branched PEIs absorb CO₂ extremely slowly because of their high viscosity. PEIs have been applied in combination with various supports⁶⁻¹⁰, and in particular very high PEI loadings were attained using silica foam and mesoporous capsules as supports^{8,9}. Alternatively higher PEI loadings (CO₂ absorption capacities) could be obtained by cross-linking PEI. The mass of cross-linker used to convert the PEI to an effective CO₂ 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^{11,12}. However, there is no known work in the cross-linking of PEI for enhanced CO₂ capture. Herein, we show how the loading and CO₂ absorption performance of PEI can be maximized using C₆₀ as PEI cross-linker. In particular, the resulting composite material, PEI-C₆₀, has excellent CO₂ absorption capacity at high temperature and very high selectivity both in the presence of N₂ and CH₄.

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 (M_w =



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 bar¹³, 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)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 hydrophilic PEI segregates from the hydrophobic surface of the SWNT¹⁴, 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/g¹⁵, 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^{16,17}. Importantly, the performance of PEI- C_{60} at low pressure and high temperature is better than that of Mg-MOF-74, $Mg_2(1,4$ -dioxido-2,5-benzenedicarboxylate), which has exceptionally high CO_2 capacity at very low CO_2 pressure^{18,19}. 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

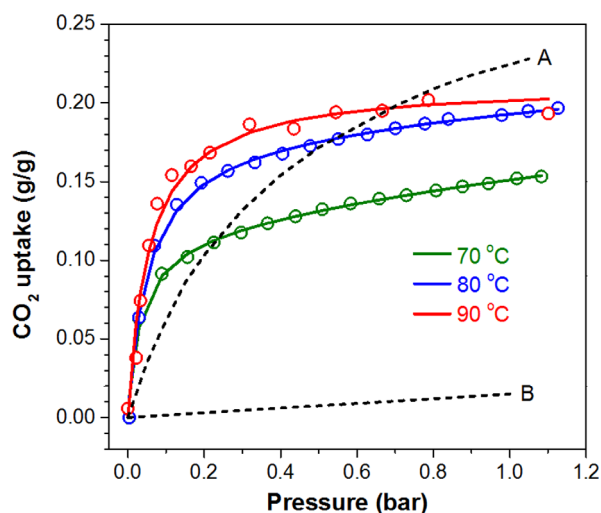


Figure 1 | CO_2 uptake of PEI- C_{60} . Comparison of the CO_2 uptake of PEI- C_{60} , Mg-MOF-74, and MOF-177 in the low pressure range. The CO_2 uptake of PEI- C_{60} was measured at 70, 80 and 90°C. The dashed curves are for the absorption of CO_2 on (A) Mg-MOF-74 and (B) MOF-177 both at 90°C. PEI- 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 ^{16,19,20}. As a comparison, without such binding sites the performance of MOF-177²⁰, $Zn_4O(1,3,5$ -benzenetricarboxylate)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 gases²¹.

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 gas²¹, 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 (dobpcd), mmen = N,N' -dimethylethylenediamine and $dobpcd^{4-} = 4,4'$ -dioxido-3,3'-biphenyldicarboxylate, an amine-functionalized expanded MOF-74 structure²². 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^{23,24}. Of particular interest is CO_2 removal at the wellhead where the gas is typically at $>50^\circ C$. 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

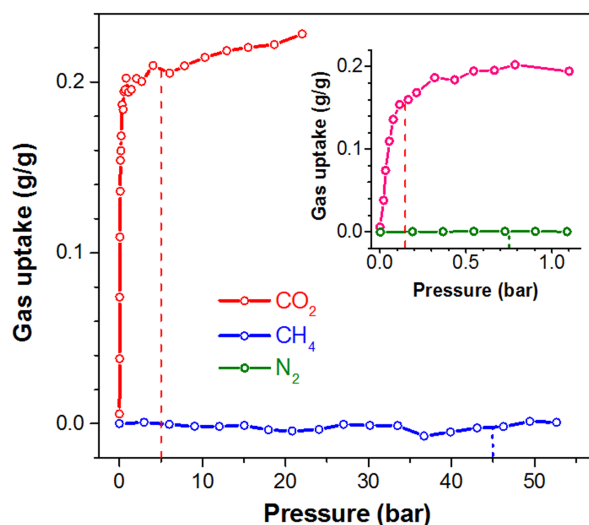


Figure 2 | Selectivity of CO_2 uptake of PEI- C_{60} . Single component CO_2 , CH_4 and N_2 uptakes of PEI- C_{60} at 90°C in the high pressure range. The dashed lines indicate the corresponding uptakes at the typical pressures of natural gas (5 bar CO_2 and 45 bar CH_4) and flue gas (0.15 bar CO_2 and 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.

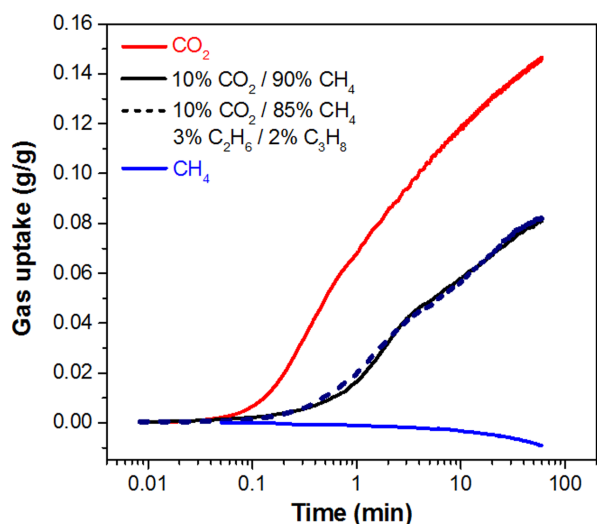


Figure 3 | CO₂ uptake from simulated natural gas mixtures. CO₂ uptake of PEI-C₆₀ from single- and multi-component mixtures of CO₂, CH₄, C₂H₆, and C₃H₈ at 1 atm and 90°C. The decrease of mass in CH₄ is likely due to a progressive drying of the absorbent. The superposition of the absorption curves in 10% CO₂/90% CH₄ and 10% CO₂/90% CH₄/3% C₂H₆/2% C₃H₈ further indicates the lack of interaction of PEI-C₆₀ with hydrocarbons.

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 step²⁵.

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^{14,26}. 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^{27,28}. 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

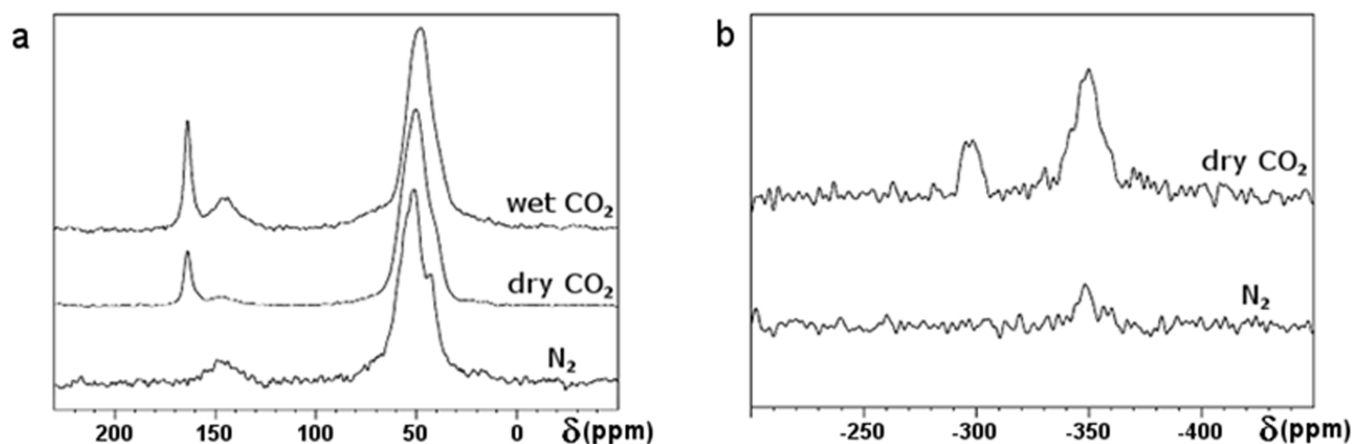


Figure 4 | Solid state NMR of PEI-C₆₀. Solid state (a) ¹H-¹³C and (b) ¹H-¹⁵N CP-MAS NMR characterization of PEI-C₆₀ after conditioning in wet CO₂, dry CO₂ or N₂.



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, M_w = 25,000 Da) and chloroform (≥99.8%) from Sigma Aldrich, toluene (99.98%) from OmniSolv EMD, and triethylamine (99%) from Acros. Ar, 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 NEt₃) 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 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 CO₂ was used either in dry or wet form. Dry CO₂ was prepared using a stainless still bubbler filled with 3 Å molecular sieves (vacuum dried at 250 °C overnight) through which the CO₂ was passed at room temperature and 50 psig. Wet CO₂ was prepared using a stainless still bubbler filled with deionized water (bubbled with high-flow CO₂ at atmospheric pressure and slow-flow CO₂ at 50 psig for 1 h each) through which the CO₂ was bubbled at room temperature and 2 psig. This last procedure was also used to prepare wet N₂. 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 CO₂ (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 (R² > 0.999). The solid state ¹H-¹³C and ¹H-¹⁵N CP-MAS NMR spectra were obtained at room temperature using a Bruker AVANCE-III spectrometer (50.3 MHz ¹³C, 20.3 MHz ¹⁵N, 200.1 MHz ¹H). Chemical shifts are reported relative to glycine defined as 176.46 ppm for the carbonyl carbon²⁹ and -347.58 ppm for the nitrogen³⁰. All of the ¹³C 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-C₆₀ conditioned in wet CO₂ and 16,800 each in the case of N₂ and dry CO₂. All of the ¹⁵N 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 CO₂, 82,000 for N₂, 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_α 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 (~10⁻⁹ 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-C₆₀ composites were collected using a FEI Quanta 400 ESEM at an accelerating voltage of 10–20 kV and high vacuum (< 5 × 10⁻⁹ Torr). The surface morphology and area of the PEI-C₆₀ composites were characterized using a Veeco Nanoscope IIIA Atomic Force Microscope and a Quantachrome Autosorb-3B Surface Analyzer, respectively.

- Metz, B., de Coninck, H., Loos, M. & Meyer, L., Eds., *Carbon Dioxide Capture and Storage* (Intergovernmental Panel on Climate Change, Cambridge University Press, 2005).
- Jacobson, M. Z. Review of solutions to global warming, air pollution, and energy security. *Energy Environ. Sci.* **2**, 148–173 (2009).
- Rochelle, G. T. Amine scrubbing for CO₂ capture. *Science* **325**, 1652–1654 (2009).

- D'Alessandro, D. M., Smit, B. & Long, J. R. Carbon dioxide capture: prospects for new materials. *Angew. Chem. Int. Ed.* **49**, 6058–6082 (2010).
- Choi, S., Drese, J. H. & Jones, C. W. Adsorbent materials for carbon dioxide capture from large anthropogenic point sources. *ChemSusChem* **2**, 796–854 (2009).
- Kuwahara, Y. *et al.* Dramatic enhancement of CO₂ uptake by poly(ethyleneimine) using zirconosilicate supports. *J. Am. Chem. Soc.* **134**, 10757–10760 (2012).
- Goepfert, A. *et al.* Carbon dioxide capture from the air using a polyamine based regenerable solid adsorbent. *J. Am. Chem. Soc.* **133**, 20164–20167 (2011).
- Qi, G. G., Fu, L. L., Choi, B. H. & Giannelis, E. P. Efficient CO₂ sorbents based on silica foam with ultra-large mesopores. *Energy Environ. Sci.* **5**, 7368–7375 (2012).
- Qi, G. G. *et al.* High efficiency nanocomposite sorbents for CO₂ capture based on amine-functionalized mesoporous capsules. *Energy Environ. Sci.* **4**, 444–452 (2011).
- Lin, Y. C., Yan, Q. J., Kong, C. L. & Chen, L. Polyethyleneimine incorporated metal-organic frameworks adsorbent for highly selective CO₂ capture. *Sci. Rep.* **3**, 1859; DOI:10.1038/srep01859 (2013).
- Jäger, M., Schubert, S., Ochrimenko, S., Fischer, D. & Schubert, U. S. Branched and linear poly(ethylene imine)-based conjugates: synthetic modification, characterization, and application. *Chem. Soc. Rev.* **41**, 4755–4767 (2012).
- Thomas, M. G., Ge, Q., Lu, J. J., Chen, J. Z. & Klivanov, A. M. Cross-linked small polyethylenimines: while still nontoxic, deliver DNA efficiently to mammalian cells in vitro and in vivo. *Pharm. Res.* **22**, 373–380 (2005).
- Nagano, Y., Kiyobayashi, T. & Nitta, T. CO₂ absorption in C-60 solid. *Chem. Phys. Lett.* **217**, 186–190 (1994).
- Dillon, E. P., Crouse, C. A. & Barron, A. R. Synthesis, characterization, and carbon dioxide adsorption of covalently attached polyethyleneimine-functionalized single-wall carbon nanotubes. *ACS Nano* **2**, 156–164 (2008).
- Yang, S. *et al.* Graphene-based porous silica sheets impregnated with polyethyleneimine for superior CO₂ capture. *Adv. Mat.* **25**, 2130–2134 (2013).
- Zhang, Z., Yao, Z.-Z., Xiang, S. & Chen, B. Perspective of microporous metal-organic frameworks for CO₂ capture and separation. *Energy Environ. Sci.* **7**, 2868–2899 (2014).
- Liu, J., Thallapally, P. K., McGrail, B. P., Brown, D. R. & Liu, J. Progress in adsorption-based CO₂ capture by metal-organic frameworks. *Chem. Soc. Rev.* **41**, 2308–2322 (2012).
- Remy, T. *et al.* Selective dynamic CO₂ separations on Mg-MOF-74 at low pressures: a detailed comparison with 13X. *J. Phys. Chem. C* **117**, 9301–9310 (2013).
- Sumida, K. *et al.* Carbon dioxide capture in metal-organic frameworks. *Chem. Rev.* **112**, 724–781 (2012).
- Mason, J. A., Sumida, K., Herm, Z. R., Krishna, R. & Long, J. R. Evaluating metal-organic frameworks for post-combustion carbon dioxide capture via temperature swing adsorption. *Energy Environ. Sci.* **4**, 3030–3040 (2011).
- Aaron, D. & Tsouris, C. Separation of CO₂ from flue gas: a review. *Sep. Sci. Technol.* **40**, 321–348 (2005).
- McDonald, T. M. *et al.* Capture of carbon dioxide from air and flue gas in the alkylamine-appended metal-organic framework mmen-Mg-2(dobpdc). *J. Am. Chem. Soc.* **134**, 7056–7065 (2012).
- Rufford, T. E. *et al.* The removal of CO₂ and N₂ from natural gas: a review of conventional and emerging process technologies. *J. Petrol. Sci. Eng.* **94–95**, 123–154 (2012).
- Yeo, Z. Y., Chew, T. L., Zhu, P. W., Mohamed, A. R. & Chai, S. P. Conventional processes and membrane technology for carbon dioxide removal from natural gas: a review. *J. Nat. Gas Chem.* **21**, 282–298 (2012).
- Dietzel, P. D. C., Besikiotis, V. & Blom, R. Application of metal-organic frameworks with coordinatively unsaturated metal sites in storage and separation of methane and carbon dioxide. *J. Mat. Chem.* **19**, 7362–7370 (2009).
- Dillon, E. P., Andreoli, E., Cullum, L. & Barron, A. R. Polyethyleneimine functionalized nanocarbons for the efficient adsorption of carbon dioxide with a low temperature of regeneration. *J. Exp. Nanosci.* DOI:10.1080/17458080.2014.894256 (2014).
- Yang, J., Alemany, L. B., Driver, J., Hartgerink, J. D. & Barron, A. R. Fullerene-derivatized amino acids: synthesis, characterization, antioxidant properties, and solid phase peptide synthesis. *Chem. Eur. J.* **13**, 2530–2545 (2007).
- Zeng, L. L., Alemany, L. B., Edwards, C. L. & Barron, A. R. Demonstration of covalent sidewall functionalization of single wall carbon nanotubes by NMR spectroscopy: side chain length dependence on the observation of the sidewall sp(3) carbons. *Nano Res.* **1**, 72–88 (2008).
- Hayashi, S. & Hayamizu, K. Chemical-shift standards in high-resolution solid-state NMR (1) C-13, Si-29 and H-1 nuclei. *Bull. Chem. Soc. Jpn.* **64**, 685–687 (1991).
- Hayashi, S. & Hayamizu, K. Chemical-shift standards in high-resolution solid-state NMR (2) N-15 nuclei. *Bull. Chem. Soc. Jpn.* **64**, 688–690 (1991).

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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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