

Drastic enhancement of carbon dioxide adsorption in fluoroalkyl-modified poly(allylamine)

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SEM-EDX

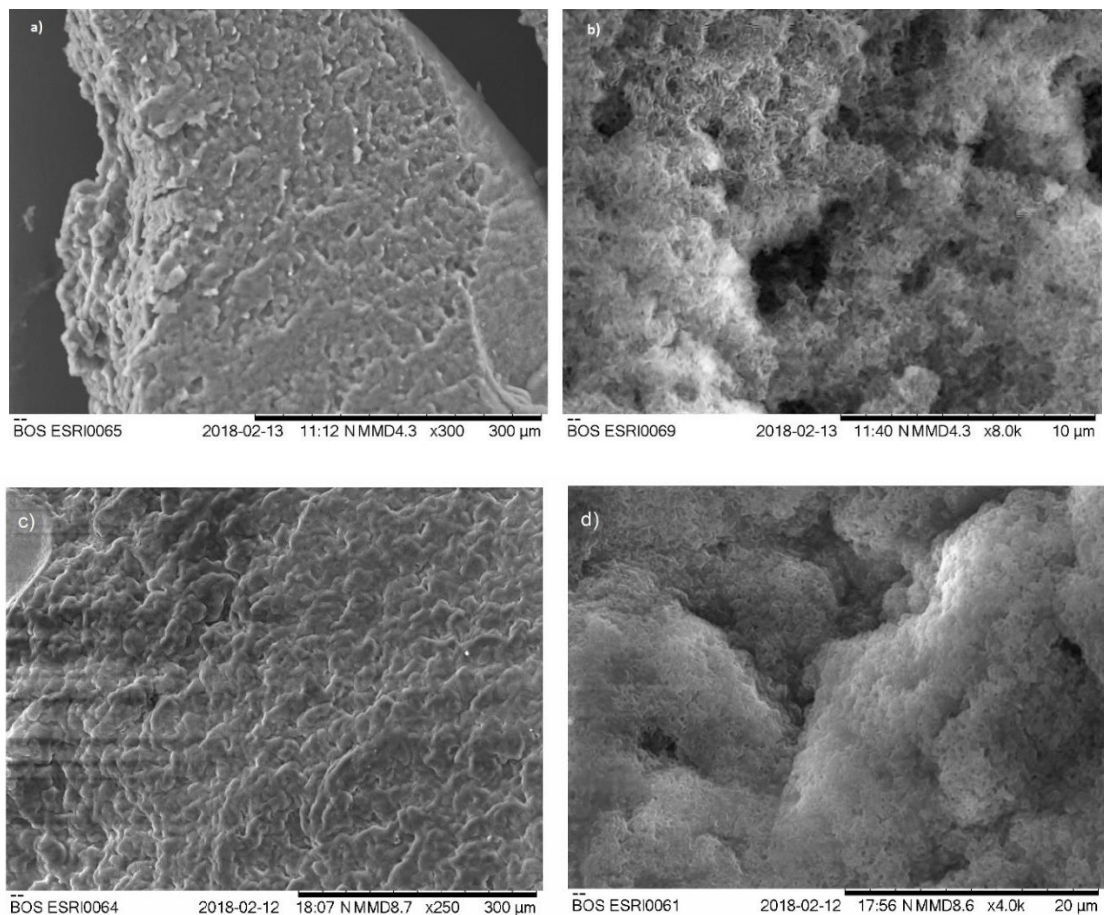


Figure S1. SEM micrographs of PAA-C₆₀ (a and b) and F2-PAA-C₆₀ (c and d). Scale bar is a) 300 μm b) 10 μm c) 300 μm and d) 20 μm.

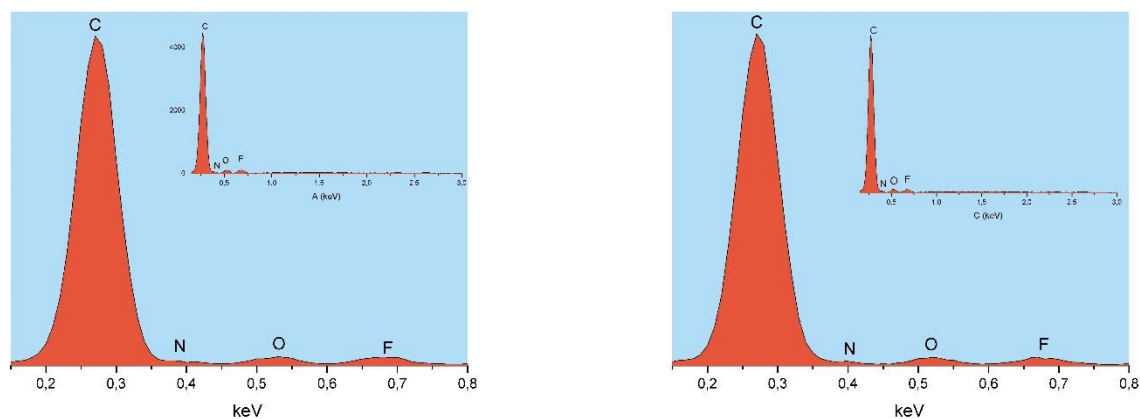


Figure S2. Energy dispersive X-ray spectra of F1-PAA-C₆₀ at two different points. Inset image shows broader range of the same spectrum

FTIR

The IR spectra of the vacuum conditioned PAA-C₆₀ and F1-PAA-C₆₀ differ only in the peak present at 1165 cm⁻¹ in the F1-PAA-C₆₀ spectrum assigned to the C-O stretching of alcohols. In Figure S3, the spectral features of the vacuum evacuated PAA-C₆₀ are assigned to their respective vibrational modes. Starting from the left: the broad absorption peak above 3000 cm⁻¹ is associated to the amine N-H stretching,¹ the two sharper peaks coming right after at 3000-2500 cm⁻¹ are due to the methylene bridge C-H stretching,^{2,3} the doublet centred at 1600 cm⁻¹ to N-H deformation,^{1,4} the single peak at 1450 cm⁻¹ to the C-H scissoring,¹ and the last three doublets to C-H wagging, C-N stretching, and N-H bending at 1300, 1100, and 900 cm⁻¹, respectively.¹⁻³

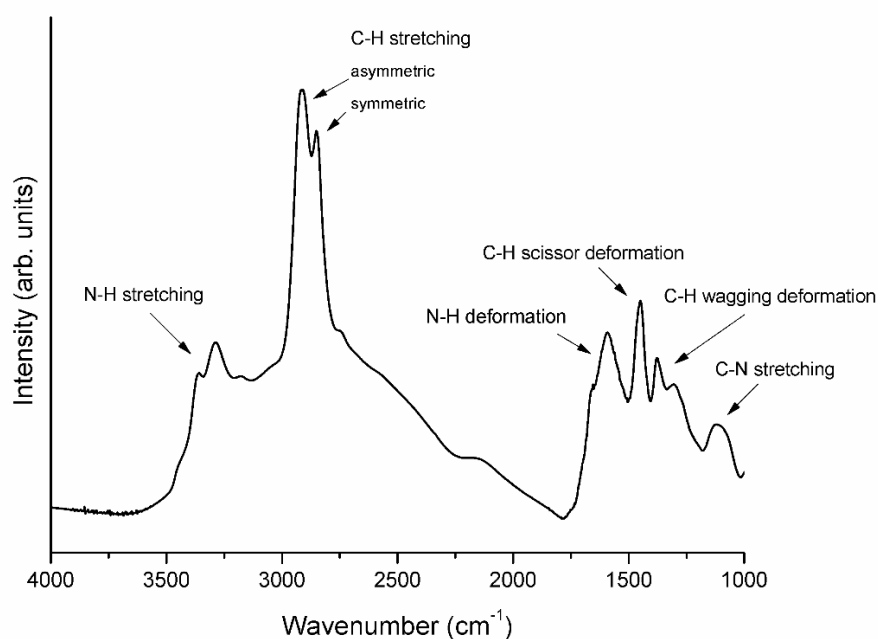


Figure S3. Peak assignments of the FTIR spectrum of PAA-C₆₀

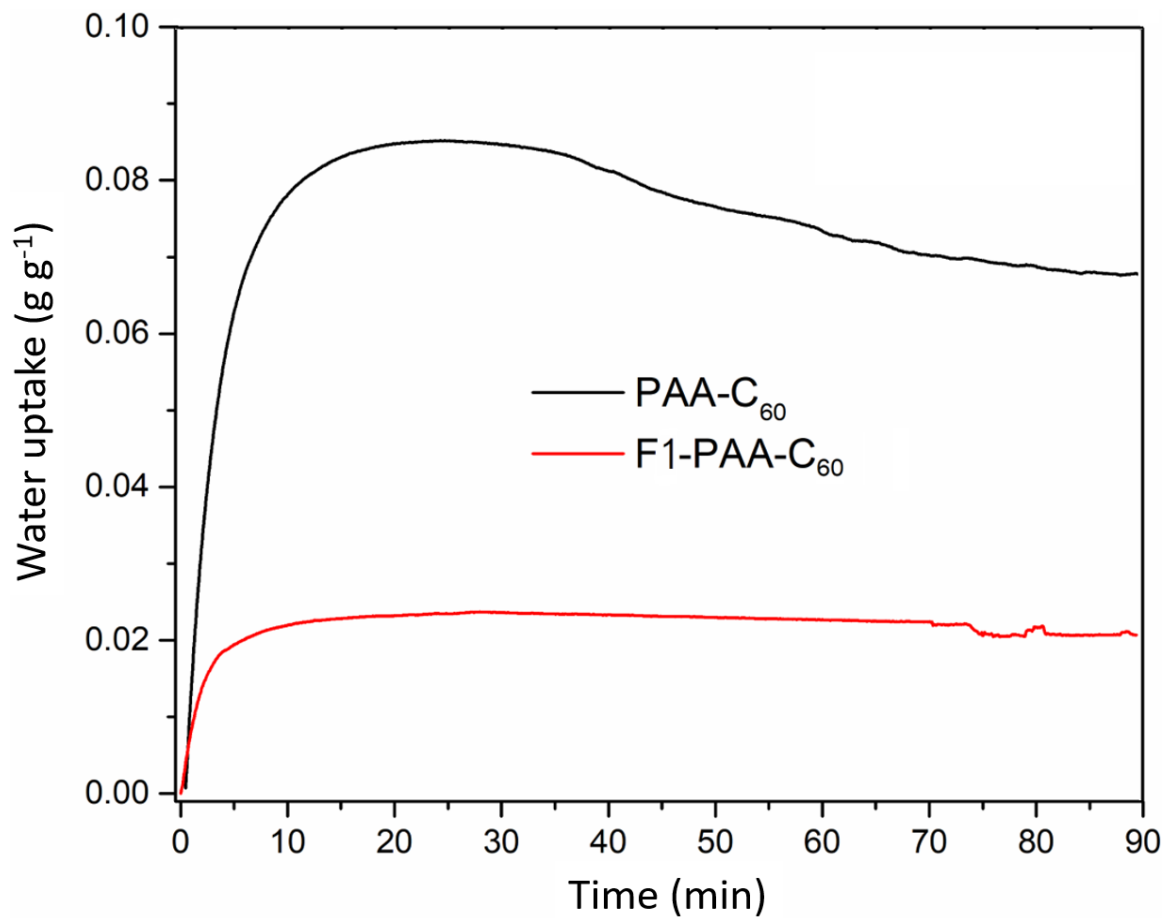


Figure S4. Gravimetric water uptake of PAA-C₆₀ and F1-PAA-C₆₀

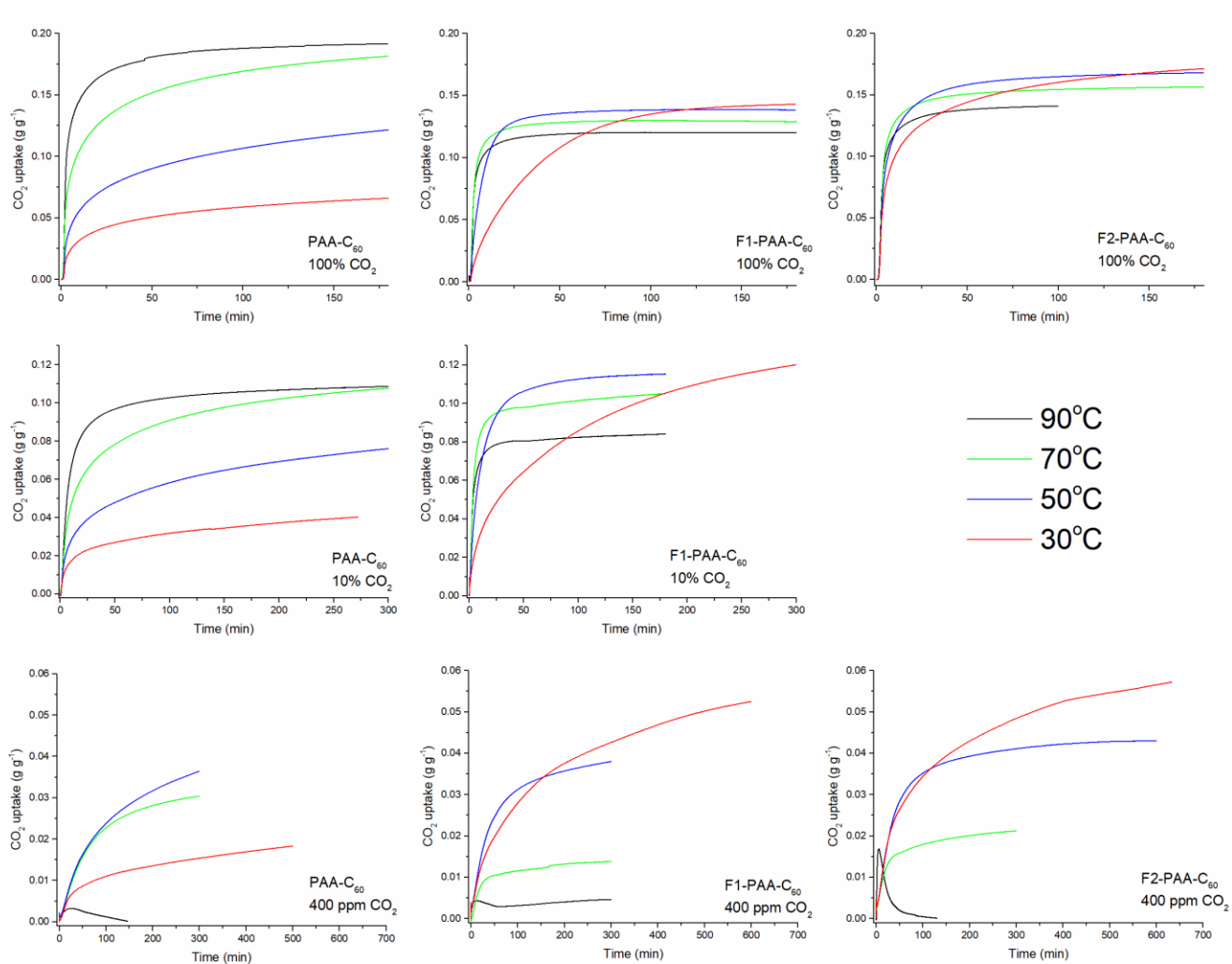
CO₂ gravimetric uptakes

Figure S5. Gravimetric CO₂ uptake curves for PAA-C₆₀, F1-PAA-C₆₀, and F2-PAA-C₆₀ in pure CO₂, 10% CO₂, and 400 ppm CO₂ at 30, 50, 70 and 90 °C, except for F2-PAA-C₆₀ at 10% CO₂ which was not tested.

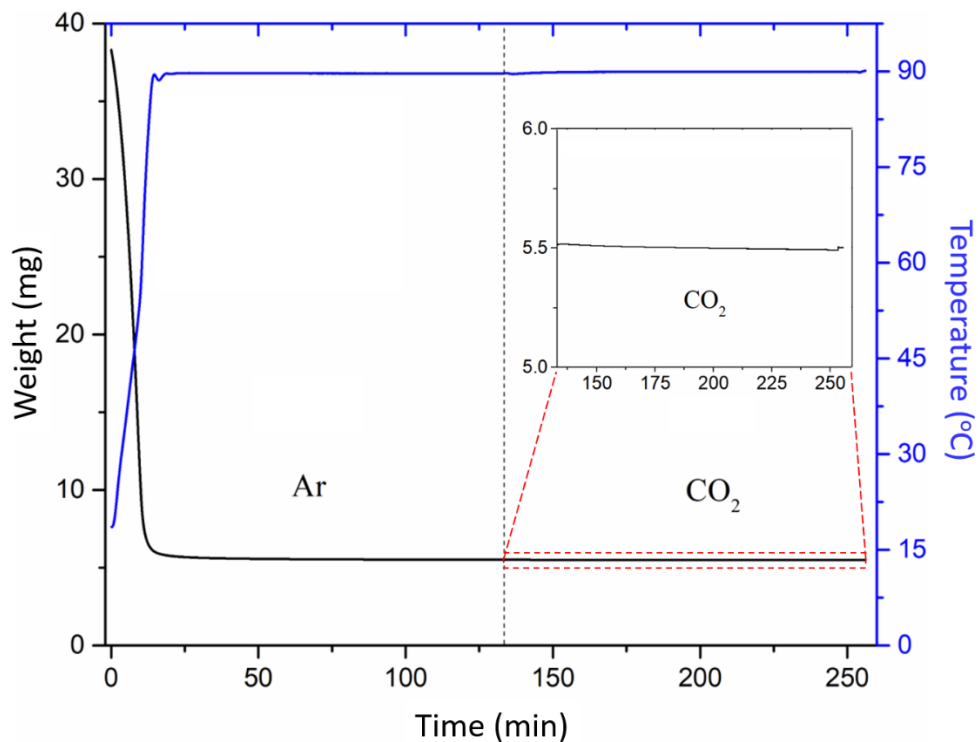


Figure S6. CO₂ uptake of plain PAA. A methanolic solution of PAA was initially conditioned at 90 °C under Ar atmosphere until constant weight to achieve the complete evaporation of methanol solvent. The resulting PAA sample was subsequently exposed to CO₂ to study its CO₂ uptake gravimetrically (inset).

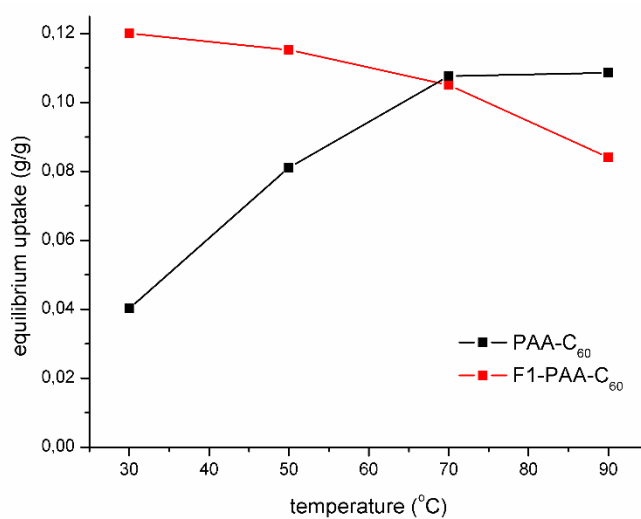
Equilibrium CO₂ uptakes under simulated flue gas conditions

Figure S7. CO₂ uptake vs temperature for PAA-C₆₀ (black), F1-PAA-C₆₀ (red) under 10% CO₂ (the gravimetric curves corresponding to each data point are provided in Figure S4).

Adsorption-desorption cycles

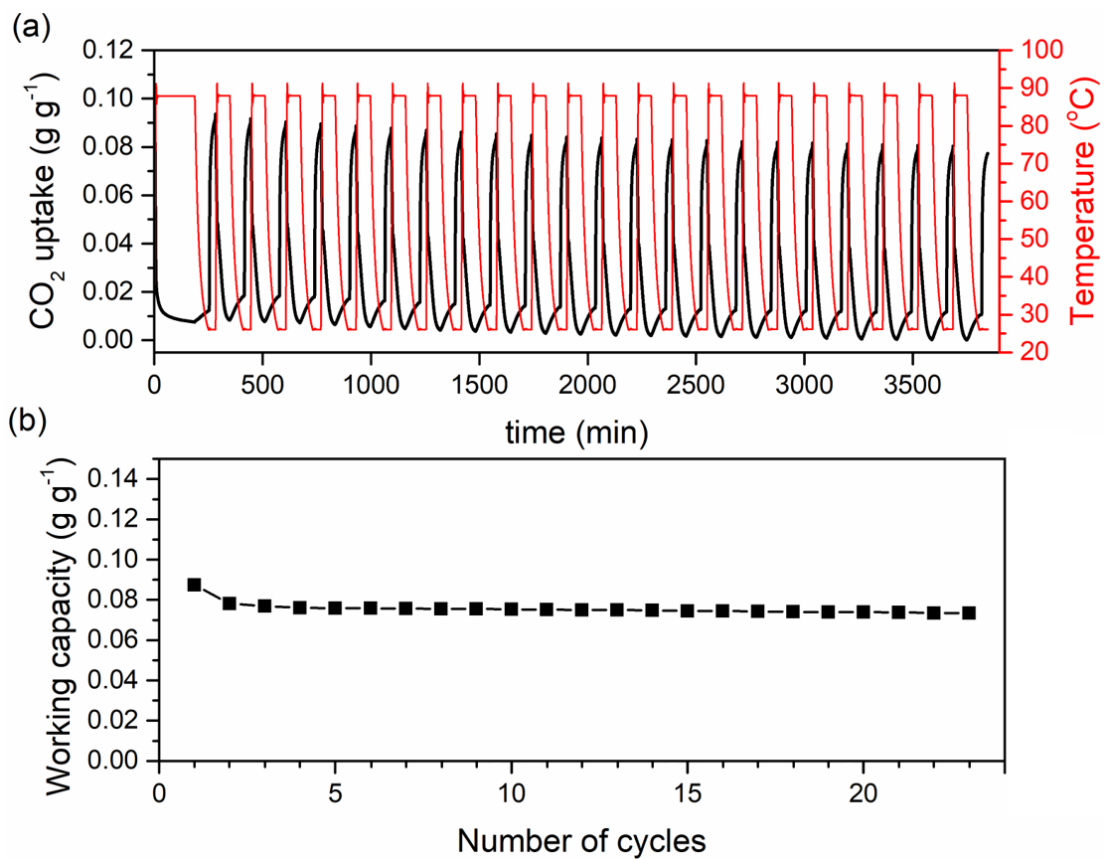


Figure S8. a) CO₂ adsorption–desorption profiles of F-PAA-C₆₀ (adsorption: 100% CO₂ at 25 °C; desorption 100% Ar at 90 °C). b) CO₂ working capacities of the sorbent plotted over the number of adsorption-desorption cycles.

In-situ FTIR

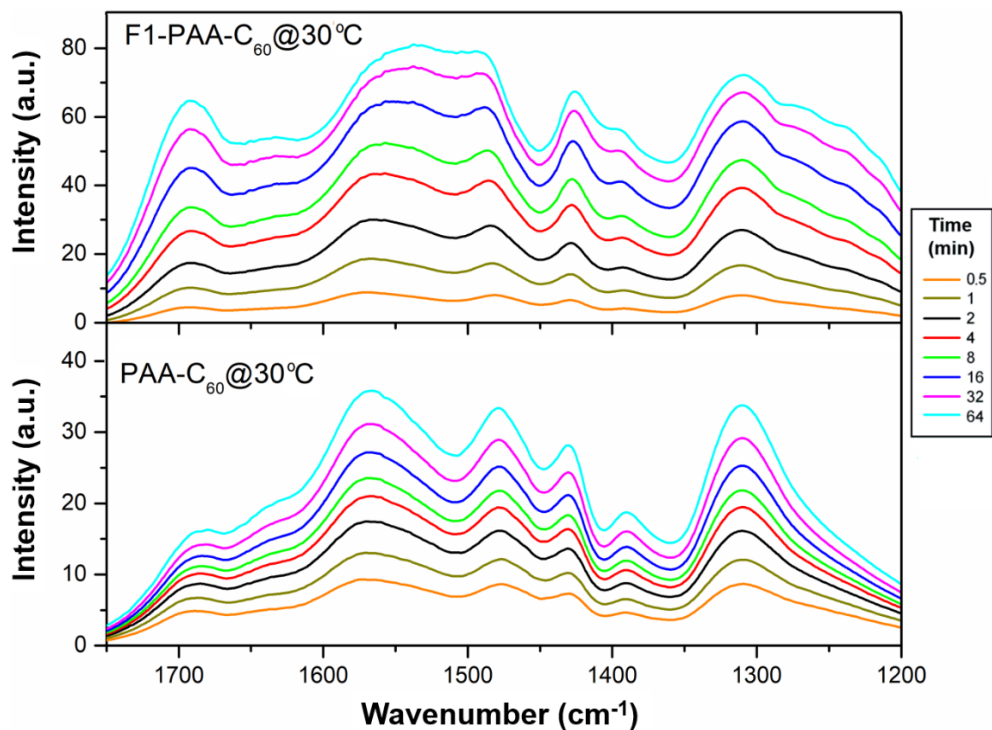


Figure S9. FTIR spectra for CO₂ sorption by PAA-C₆₀ and F₁PAA-C₆₀ at 30 °C over 1h.

CHN elemental analyses

Table S1. Results from the elemental analysis of PAA-C₆₀, F₁-PAA-C₆₀ and F₂-PAA-C₆₀ conditioned at 110 °C under vacuum.

Sample	N (wt%)	N (mol)	C (wt%)	C (mol)	H (wt%)	H (mol)
PAA-C ₆₀	17.70	1.26	62.78	5.23	9.74	9.66
F ₁ -PAA-C ₆₀	13.52	0.96	55.29	3.95	8.55	8.48
F ₂ -PAA-C ₆₀	13.62	0.97	57.74	4.81	7.96	7.90

The weights obtained from elemental analysis are converted into moles from which the molar ratios were calculated as follows (MW = molecular weight; AW = atomic weight)

PAA-C₆₀

PAA = (allylamine)_x = (AA)_x = (C₃H₇N)_x

PAA-C₆₀ = (C₃H₇N)_X (C₆₀)_Y (H₂O)_Z, even after conditioning the sample at 110 °C under vacuum, there is some moisture in the materials as they are extremely hydrophilic and they exposed to the environment for some time before being inserted in the CHN analyzer.

$$C_{5.23} H_{9.66} N_{1.26} = (C_3H_7N)_X (C_{60})_Y (H_2O)_Z = C_{3X+60Y} H_{7X+2Z} N_X$$

$$3X+60Y = 5.23; 7X+2Z = 9.66; X = 1.26 \rightarrow Y = 0.024, Z = 0.42$$

$$MW(C_3H_7N) = 57.09 \text{ g/mol} \rightarrow PAA = MW(C_3H_7N) * 1.23 = 71.93 \text{ g}$$

$$MW(C_{60}) = 720.66 \text{ g/mol} \rightarrow C_{60} = MW(C_{60}) * 0.024 = 17.30 \text{ g}$$

$$MW(H_2O) = 18.02 \text{ g/mol} \rightarrow H_2O = MW(H_2O) * 0.42 = 7.57 \text{ g}$$

PAA:C₆₀ dry weight ratio 80.6/19.4

$$PAA-C_{60} \text{ dry} = (AA)_{1.26} (C_{60})_{0.024} = (AA)_1 (C_{60})_{0.019}$$

F-PAA-C₆₀

$$PAA = (\text{allylamine})_x = (C_3H_7N)_X$$

$$\text{Glycidyl 2,2,3,3,4,4,5,5-octafluoropentyl ether (GOF)} = C_8H_8F_8O_2$$

$$F2-PAA-C_{60} = (C_3H_7N)_X (C_{60})_Y (C_8H_8F_8O_2)_Z (H_2O)_E = C_{3X+60Y+8Z} H_{7X+8Z+2E} N_X O_{2Z+E} F_{8Z}$$

$$3X+60Y+8Z = 4.81 ; X = 0.97 ; 7X+8Z+2E = 7.90$$

We also use the mass balance for the sample: C+H+N+F+O = 100 → F+O = 100-C-H-N = 100-57.74-13.62-7.96 = 20.68 → (2Z+E)*AW(O)+8Z*AW(F) = (2Z+E)*15.999+8Z*18.998 = 20.68 → 183.982Z + 15.999E = 20.68 (eq.1)

Replacing X = 0.97 in the hydrogen balance, 7X+8Z+2E = 7.90, we get 8Z+2E=1.11 (eq. 2). Based on equations 1 and 2, we calculate Z=0.098 and E=0.16.

Using the mass balance of carbon, 3X+60Y+8Z = 4.81, we calculate Y= 0.019.

So F2-PAA-C₆₀=(C₃H₇N)_{0.97} (C₆₀)_{0.019} (C₈H₈F₈O₂)_{0.098} (H₂O)_{0.16} or for the dry material:

$$F2-PAA-C_{60} \text{ dry} = (AA)_1 (C_{60})_{0.020} (F)_{0.101}$$

Similarly, we calculate the composition of F1-PAA-C₆₀ = (C₃H₇N)_{0.97} (C₆₀)_{0.019} (C₈H₈F₈O₂)_{0.073} (H₂O)_{0.57} or for the dry material:

$$F1-PAA-C_{60} \text{ dry} = (AA)_1 (C_{60})_{0.020} (F)_{0.075}$$

Literature on DAC sorbents performance

Table S2. Polyamine-based direct air capture CO₂ adsorbents (from 2011 – 2020). PEI: Poly(ethylenimine) ; PAA: Poly(allylamine) ; PPG: poly(propylene guanidine) ; TEPA: Tetraethylenepentamine ; TPTA: Tripropylene-tetramine ; TREN: Tris (2-amino ethyl)amine ; PEHA: Pentaethylenehexamine ; APTES: 3-(aminopropyl)triethoxysilane ; AEAPDMS-NFC: N-(2-aminoethyl)-3-aminopropylmethyldimethoxysilane nanofibrilated cellulose.

Adsorbent	Amine	amine wt% [mmol N g⁻¹]	Temp .[°C]	CO₂ conc. [% RH]	Pressure	CO₂ capacity [mmol g⁻¹]	Amine Eff. [mol CO₂ permol of amine]	Ref.
PAA-C ₆₀	PAA (M _w 120 – 180 K)	80.5 wt% (14.10)	30	400 ppm	1 atm	0.43	0.03	This paper
F1-PAA-C ₆₀	PAA (M _w 120 – 180 K)	61.3 wt% (10.74)	30	400 ppm	1 atm	1.20	0.11	This paper
F2-PAA-C ₆₀	PAA (M _w 120 – 180 K)	57.0 wt% (9.98)	30	400 ppm	1 atm	1.30	0.13	This paper
48% PEI/SBA-15	PEI (M _w 1800)	48 wt% (11.14)	30	400 ppm	1 atm	1.10	0.10	Silica supported poly(propylene guanidine) as a CO ₂ Sorbent in simulated flue gas and direct air

Electronic Supplementary Information

								capture Sang Jae Park, Adsorption, 2020
50% PPG/SBA-15	PPG	50 wt%	30	400 ppm	1 atm	0.63	0.04	As above
EtSNTs-50 PEI encapsulated in nanotubes	PEI (M _w 600)	(11.2)	30	400 ppm	1 atm	1.05	0.09	Aminopolymer Confined in Ethane-Silica Nanotubes for CO ₂ Capture from Ambient Air, Lina Liu, ChemNanoMat, 2020
PEI_H-SiO ₂	PEI (M _w 800)	2.62 g PEI/g sorbent (16.72)	30	400 ppm (19% RH)	1 atm	3.36	0.20	Aminopolymer-Impregnated Hierarchical Silica Structures: Unexpected Equivalent CO ₂ Uptake under Simulated Air Capture and Flue Gas Capture Conditions Hyuk Taek Kwon et al, ChemMater 2019
PEI_H-SiO ₂	PEI (M _w 800)	2.62 g PEI/g sorbent (16.72)	30	400 ppm	1 atm	2.34	0.14	As above
PEHA-PO-1-2/50S	PEHA	59.5 wt% organic (10.24 mmolN/g)	25	400 ppm	1 atm	1.25	0.12	Oxidation-Resistant Cost-Effective Epoxide-Modified Polyamine Adsorbents for CO ₂ Capture from Various Sources Including Air 2019
TEPA-PO-1-2/50S	TEPA	61.0 wt% organic	25	400 ppm	1 atm	1.34	0.13	As above

Electronic Supplementary Information

		(9.99)						
PEI-CA-SiO ₂	PEI (M _w 800 Da)	0.7 g PEI/gSiO ₂ (9.52)	35	380 ppm	1 atm	0.36	0.04	Direct CO ₂ Capture from Air using Poly(ethylenimine)-Loaded Polymer/Silica Fiber Sorbents 2019
40% TPTA/SBA-15	TPTA	41 wt% organic (8.71)	35	400 ppm	1 atm	1.86	0.21	Design of Aminopolymer Structure to Enhance Performance and Stability of CO ₂ Sorbents: Poly(propylenimine) vs Poly(ethylenimine) Simon H. Pang, JACS, 2017
SBA-15/PEI/PEG200	PEI (M _w 800)	(8.38)	30	400 ppm	1 atm	1.64	0.20	Role of Additives in Composite PEI/Oxide CO ₂ Adsorbents: Enhancement in the Amine Efficiency of Supported PEI by PEG in CO ₂ Capture from Simulated Ambient Air Miles A. Sakwa-Novak, ACS Appl. Mater. Interfaces, 2015
Templated Alumina/PEI/PEG200	PEI (M _w 800)	(5.98)	30	400 ppm	1 atm	1.29	0.22	As above

Electronic Supplementary Information

PEI/PIM-1 composite	PEI (M_w 800)	21 wt % (4.88)	35	100%	0.0004 bar	0.23	0.05	PIM-1 as a Solution-Processable “Molecular Basket” for CO ₂ Capture from Dilute Sources Simon H. Pang, ACS Macro Letters, 2015
HP20/PEI-50	PEI	50 wt % (11.61 mmol/g)	25	400 ppm	1 atm	2.26	0.19	Polyethylenimine-Impregnated Resin for High CO ₂ Adsorption: An Efficient Adsorbent for CO ₂ Capture from Simulated Flue Gas and Ambient Air Zhenhe Chen,† Applied Materials and Interfaces, 2013
FS-PEI-50	PEI (M_w 25,000)	50 wt % (11.61)	25	410 – 420 ppm	10.3 bar	1.65 – 1.71	0.15	Carbon Dioxide Capture from the Air Using a Polyamine Based Regenerable Solid Adsorbent Alain Goeppert, JACS 2011
FS-PEI-50	PEI (M_w 25,000)	50 wt % (11.61)	25	410 – 420 ppm (RH 67%)	10.3 bar	1.41	0.12	As above
FS-PEI-33	PEI (M_w 25,000)	33 wt % (7.66)	25	410 – 420 ppm (RH 67%)	10.3 bar	1.74	0.23	As above

Electronic Supplementary Information

AEAPDMS-NFC-FD	AEAPDMS-NFC	(4.9)	25	506 ppm (40% RH)	1 atm	1.39	0.28	Amine-Based Nanofibrillated Cellulose As Adsorbent for CO ₂ Capture from Air. Gebald, C. Environ. Sci. Technol. 2011
SynA50	PEI (M _w 800)	(11.20)	25	400 ppm	1 atm	1.74	0.16	Mesoporous Alumina-Supported Amines as Potential Steam-Stable Adsorbents for Capturing CO ₂ from Simulated Flue Gas and Ambient Air. Watcharop Chaikittisilp, Energy and Fuels 2011
SynA40	PEI (M _w 800)	(8.66)	25	400 ppm	1 atm	1.33	0.15	As above
MS40	PEI (M _w 800)	(9.23)	25	400 ppm	1 atm	1.05	0.11	As above
PEI/Silica	PEI (M _w 800)	(10.5)	25	400 ppm	1 atm	2.36	0.22	Amine-Tethered Solid Adsorbents Coupling High Adsorption Capacity and Regenerability for CO ₂ Capture From Ambient Air, Choi et al. 2011
A-PEI/Silica	PEI (M _w 800), APTES	(10.7)	25	400 ppm	1 atm	2.26	0.21	As above

Electronic Supplementary Information

T-PEI/Silica	PEI (M_w 800), tetrapropyl orthotitanate	(10.5)	25	400 ppm	1 atm	2.19	0.21	As above
PAA_MCM_4 1	PAA (M_n 1130 Da)	(7.24)	25	400 ppm	1 atm	0.86	0.12	Poly(allylamine)Mesoporous Silica Composite Materials for CO ₂ Capture from Simulated Flue Gas or Ambient Air Watcharop Chaikittisilp 2011

PALS

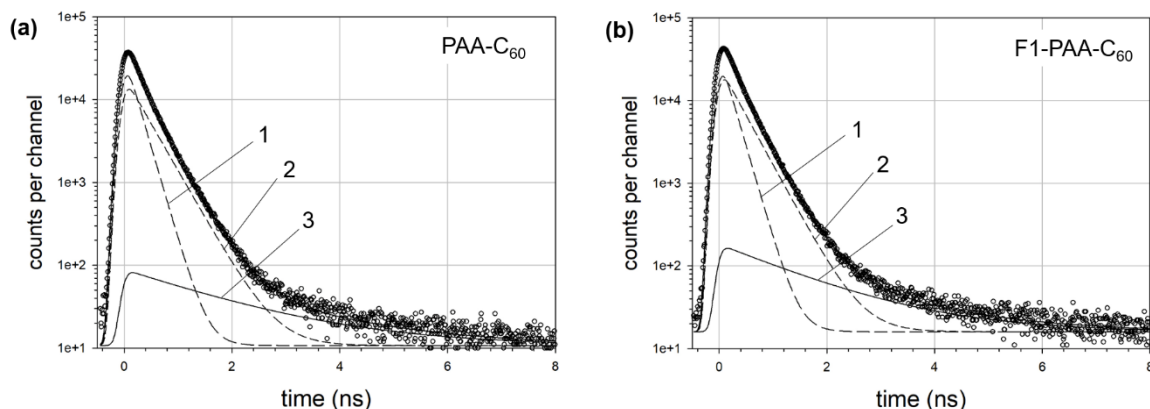


Figure S10. Positron lifetime spectra of (a) PAA-C₆₀ and (b) F1-PAA-C₆₀ with fitting lines corresponding to components 1) indium reference, 2) localised molecular defects, and 3) free volume present in the materials. Fitting lines of source contributions have not been included for ease of representation.

Table S3. The values of the three lifetime components and their respective intensities for PAA-C₆₀ and F1-PAA-C₆₀. The shortest lifetime was fixed at 194 ps at a lifetime for Indium,⁵ which was used a reference material in our experimental geometry. The source correction was assumed at 15%, with contributions from 372 ps at 98% in NaCl salt and at 2000 ps (2 ns) with 2 % from epoxy sealing of the source.

Sample	τ_1 [ps]	I_1 [%]	τ_2 [ps]	I_2 [%]	τ_3 [ps]	I_3 [%]
PAA-C ₆₀	194 fixed	49.57(0.61)	389.9(2.0)	47.9(0.26)	1710(36)	5.02(0.30)
F1-PAA-C ₆₀	194 fixed	50.1(0.5)	386.3(2.8)	49.04(0.49)	2100(170)	1.76(1.2)

In a PALS experiment, a positron is injected into the material to thermalize within a few picoseconds. The positron diffuses into the material where it either self-annihilates or forms a metastable bound state with an electron called positronium (Ps) with a dimension of about 1.06 Å.⁶ There are two states of Ps derived from different combinations of positron and electron: the para-Ps (p-Ps) with anti-parallel spin ($\uparrow\downarrow$) with the probability 1/4, and the ortho-Ps (o-Ps) with parallel spin combination ($\uparrow\uparrow$), with the probability 3/4.⁷ Due to the spin rules, the intrinsic p-Ps lifetime is over a thousand times shorter than the o-Ps lifetime. The intrinsic lifetime of p-Ps is 125 ps. o-Ps annihilates intrinsically with a lifetime of 142 ns, in a vacuum in the absence of electrons. If a positron is injected in a physical material, it interacts with electrons and the environment, behaving as a quantum particle with characteristic de-Broglie wavelength. In areas of free volume with low electron density, a positron is preferentially

trapped creating an o-Ps that subsequently annihilates with an electron of opposite spin present in the surrounding material. This phenomenon is called “pick-off annihilation” and while it reduces the annihilation lifetime of o-Ps,⁸ it gives information about the size of free volume and its frequency via its pick-off lifetime and intensity. It is thus anticipated that o-Ps lifetime reveals information on the size of the free volume elements where it is confined. The larger the free volume holes, the longer are the positron lifetimes, and vice versa. Due to its substantially smaller size in comparison with physical molecules, like nitrogen (3.64 Å), typically employed in physisorption studies, Ps are used to probe “closed pores” that molecular and atomic size gas molecules cannot access. In the present study, N₂ porosimetry was inadequate to provide information on the free volume present in the materials. Plain and alkylfluorinated cross-linked PAA sorbents contain really small “nano-spaces”, which could not be assessed by N₂ molecules. As a result, we did not observe measurable N₂ adsorption in these materials.

References

1. S. S. York, S. E. Boesch, R. A. Wheeler and R. Frech, *Macromolecules*, 2003, 36, 7348-7351.
2. S. Lakard, G. Herlem, B. Lakard and B. Fahys, *Journal of Molecular Structure: THEOCHEM*, 2004, 685, 83-87.
3. G. Socrates, *Infrared and Raman Characteristic Group Frequencies: Tables and Charts*, Wiley, 2004.
4. J. M. El Khoury, D. Caruntu, C. J. O’ Connor, K.-U. Jeong, S. Z. D. Cheng and J. Hu, *J. Nanopart. Res.*, 2007, 9, 959-964.
5. J. del Río, F. Plazaola, N. de Diego and P. Moser, *Solid State Commun.*, 1994, 89, 913-915.
6. P. Hautojärvi and A. Vehanen, in *Positrons in Solids*, ed. P. Hautojärvi, Springer Berlin Heidelberg, Berlin, Heidelberg, 1979, DOI: 10.1007/978-3-642-81316-0_1, pp. 1-23.
7. Y. C. Jean, P. E. Mallon and D. M. Schrader, *Principles and Applications of Positron and Positronium Chemistry*, 2003.
8. D. M. Schrader and Y. C. Jean, *Positron and positronium chemistry*, Elsevier, Amsterdam [The Netherlands]; New York, 1988.