

Branching out with Aminals: Microporous Organic Polymers from Difunctional Monomers

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Supplementary Information

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Section 1: Nitrogen gas sorption

Pore size distributions and pore volumes were derived from the adsorption branches of the isotherms using the non-local density functional theory (NL-DFT) pore model for pillared clay with cylindrical pore geometry, as these were found to give the best fit.

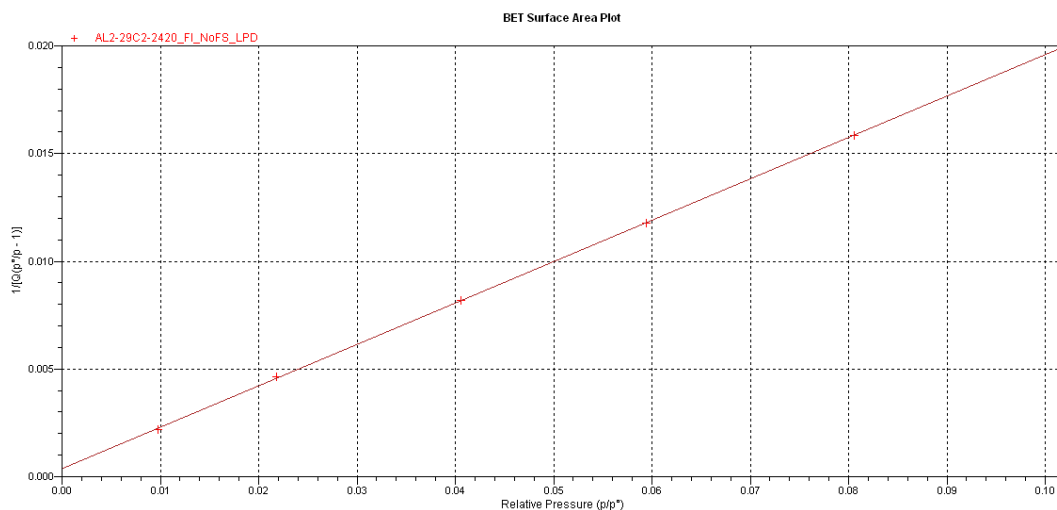


Figure S1-1: PI-1 BET-Plot

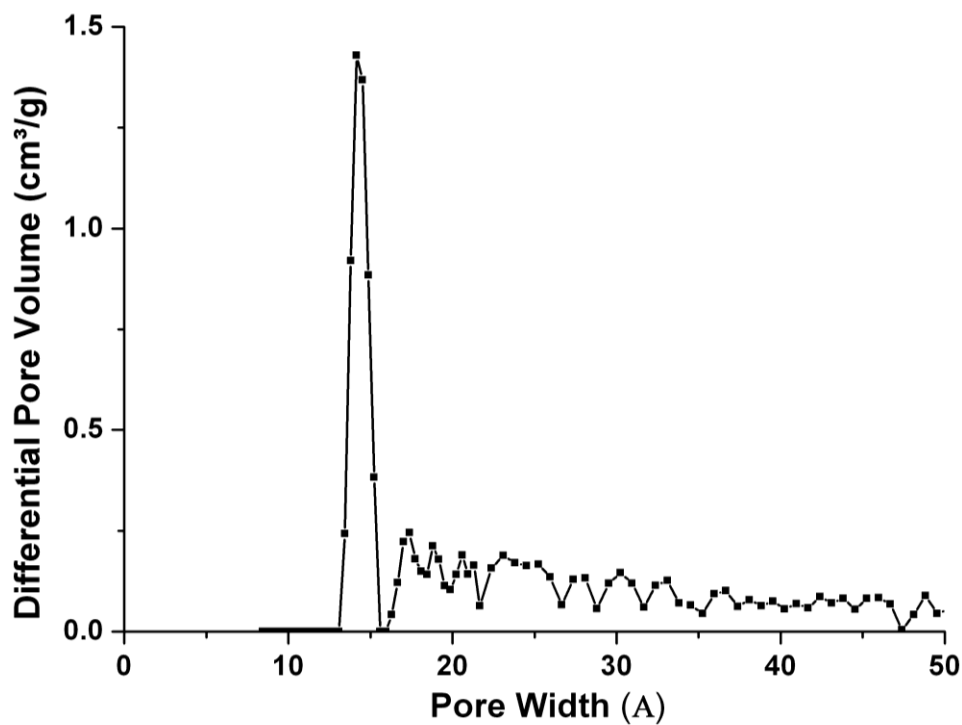


Figure S1-2: PI-1 Pore size distribution curve

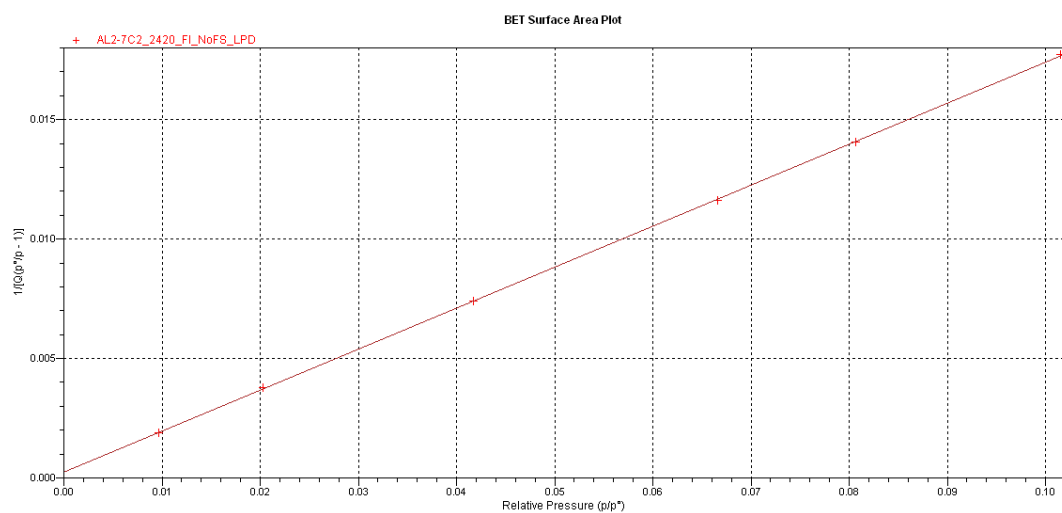


Figure S1-3: PI-2 BET-Plot

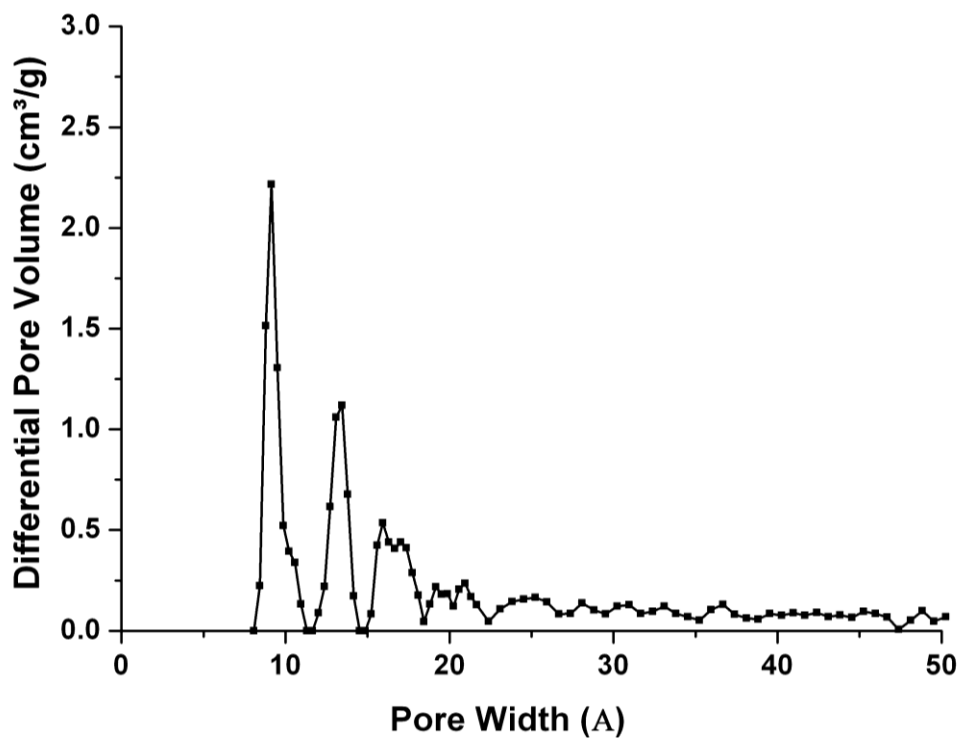


Figure S1-4: PI-2 Pore size distribution plot

Section 2: Scanning Electron Microscopy (SEM) Images

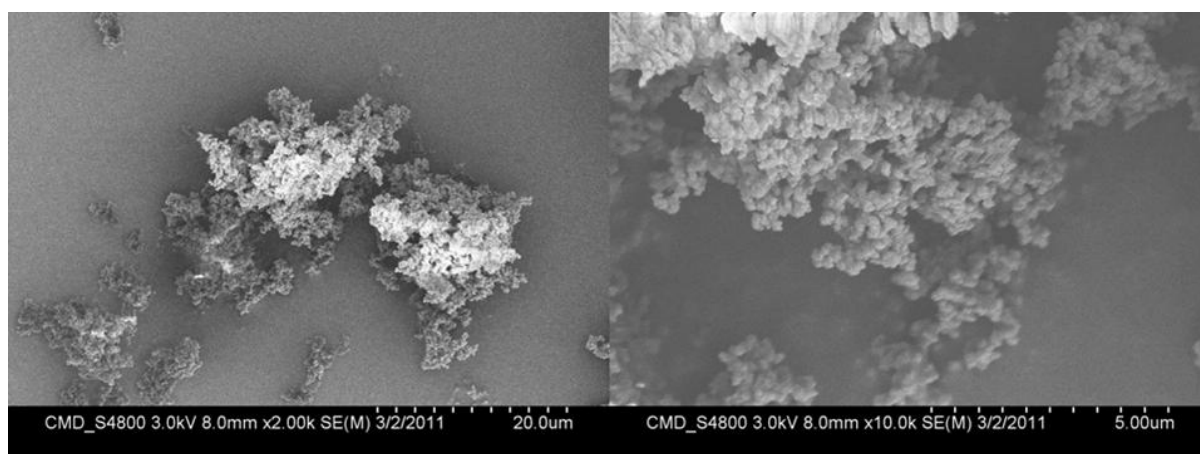


Figure S2-1: SEM image of PI-1 (scale bars inset)

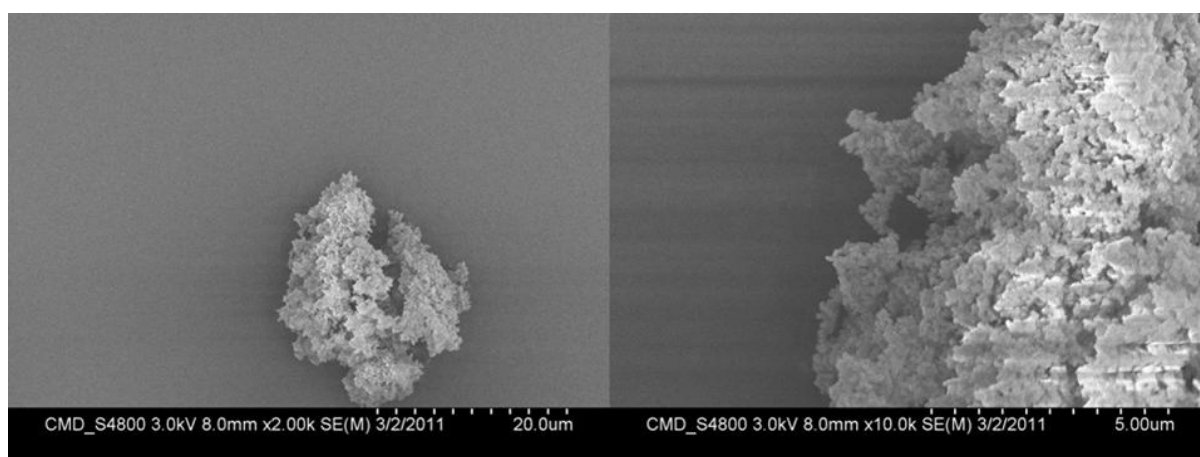


Figure S2-2: SEM image of PI-2 (scale bars inset)

Section 3: Thermogravimetric Analysis (TGA) Curves

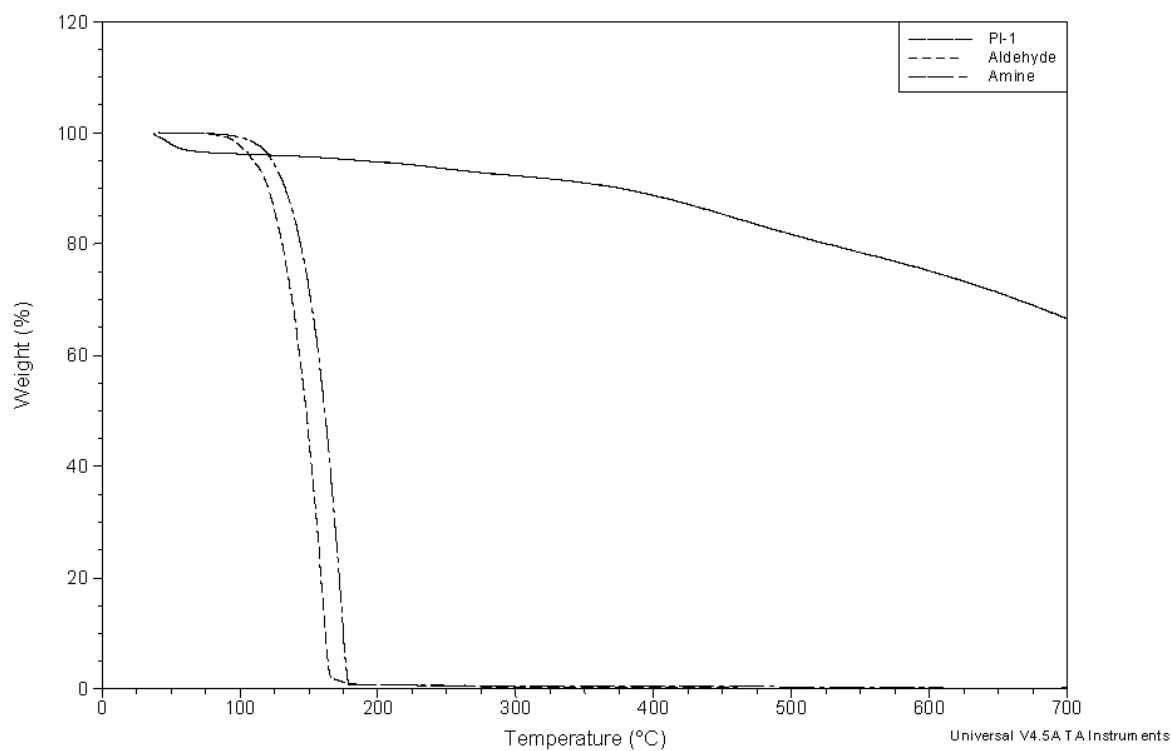


Figure S3-1: TGA curve of PI-1 along with starting monomers

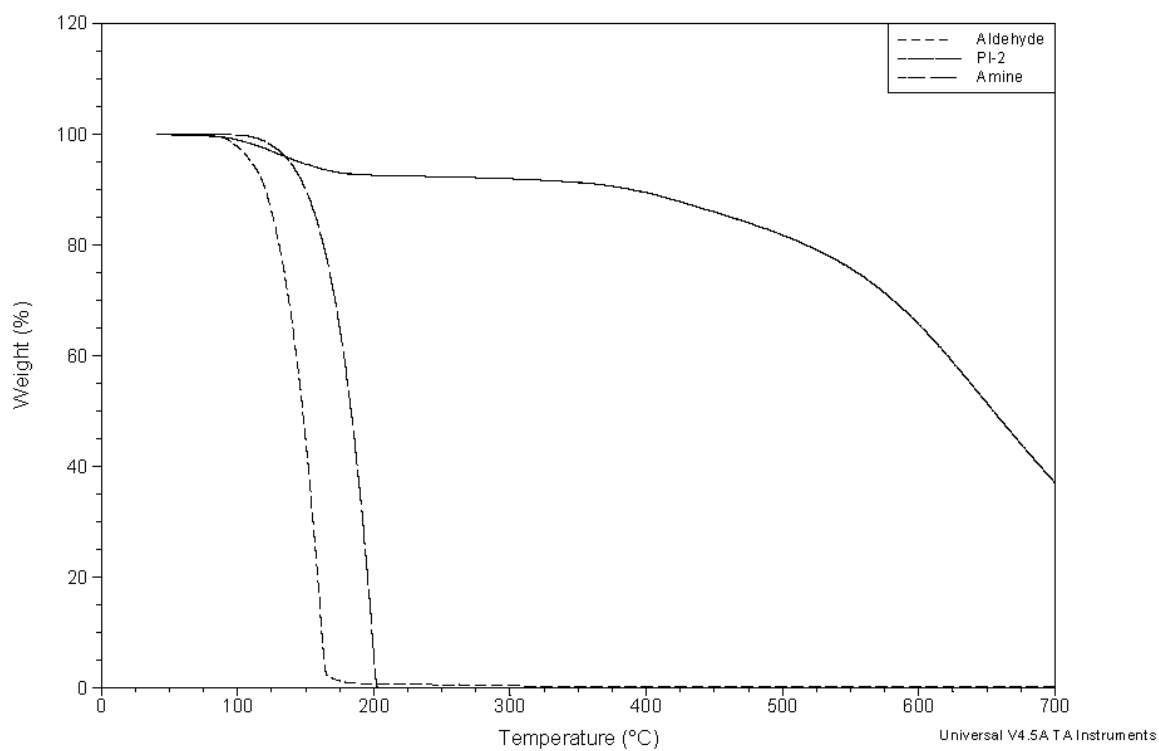
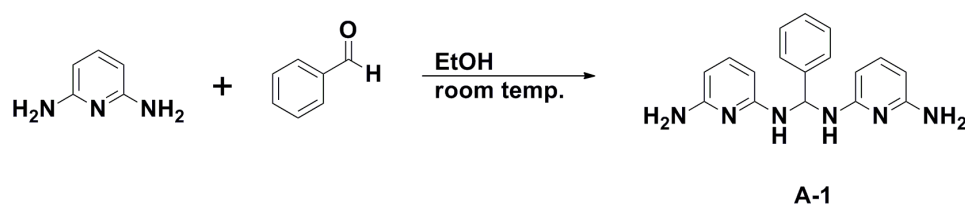


Figure S3-2: TGA curve of PI-2 along with starting monomers

Section 4: Synthesis of Small Molecule Analogue



Scheme S4-1: Reaction used to synthesise small molecule analogue **A-1** of **PI-1**

Method

The small molecule analogue **A-1** (See Scheme S4-1) was synthesised using a similar procedure to that reported previously.¹ To a stirred solution of 2,6-diaminopyridine (109 mg, 1.0 mmol) in ethanol (anhydrous, *ca.* 10 mL) was added dropwise a solution of benzaldehyde (0.20 mL, 2.0 mmol) in ethanol (anhydrous, 13.0 mL). The reaction mixture was heated to 80°C for 3 hours. After this time, the solvent was removed *in vacuo* and the crude product was recrystallised. Compound **A1** was obtained as a dark yellow solid. Yield: 152.8 mg, 49.9%. Dissolution of **A-1** in CDCl₃ led to hydrolytic cleavage of the aminal bond, resulting in peaks corresponding to the amine and aldehyde starting materials in solution NMR. Elemental Analysis: Observed (%):C, 74.67; H, 5.58; N, 15.58. Required C, 66.65; H, 5.92; N, 27.43 (Assuming only aminal formation occurs). Required C, 79.98; H, 5.30; N, 14.73 (Assuming only imine formation occurs). FTIR (KBr discs) cm⁻¹: 3449 (-N-H amine, broad), 3385 (-N-H aminal, broad), 1630 (-C=N- imine, sharp).

Section 5: ^1H - ^{15}N CP/MAS solid-state NMR Spectra

To unambiguously assign the ^{15}N peaks, ^1H - ^{15}N CP/MAS NMR data (at an MAS rate of 5 kHz) were collected for model compounds (structures and chemical shifts are given in **Table S5-1**). The corresponding NMR spectra are shown in **Figure S5-1**.

Table S5-1

Name of Compound	Structure	^{15}N chemical shift (ppm)	Type of nitrogen environment
2,4-diaminotoluene (Aldrich)		57	Primary amine (R-NH ₂)
Reduced Cage 3 (ref 2)		47	Secondary amine (R-NH-R)
Cage 1-beta R3 (ref 2)		336	Imine (R-C=N-R) (split into 3 peaks due to R3 symmetry) ²
A1 (see method in Section 4)		32	Primary amine (R-NH ₂)
		60 to 90	Secondary amine (R-NH-R)
		227	Pyridine heterocyclic nitrogen

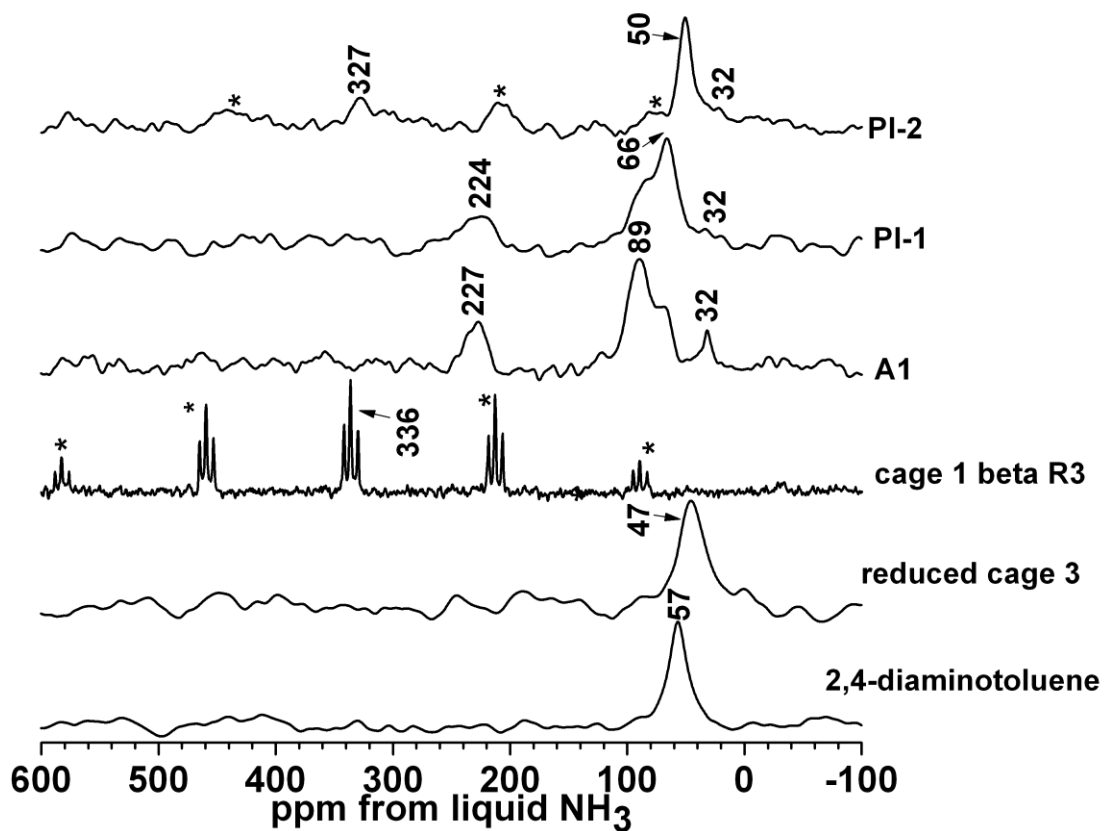


Figure S5-1: ^1H - ^{15}N CP/MAS NMR spectra of MOPs and model compounds. Asterisks denote spinning sidebands. An MAS rate of 5 kHz was used.

Section 6: Carbon dioxide sorption and selectivity

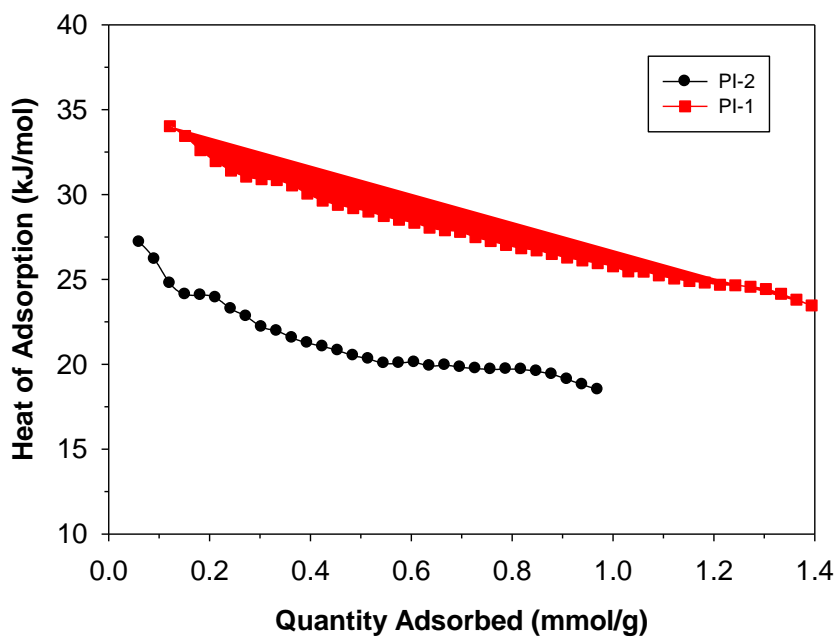


Figure S6-1: Isothermic heats of adsorption

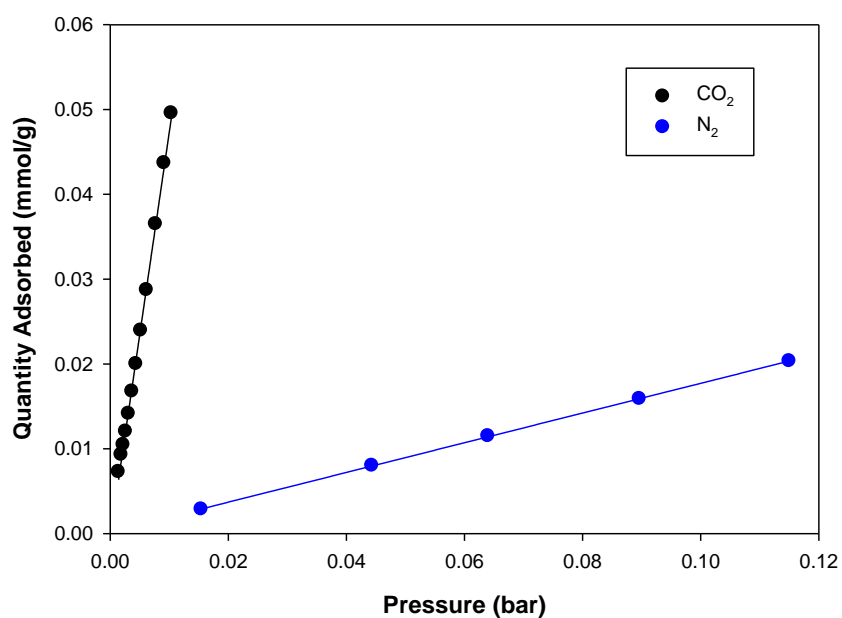


Figure S6-2: CO₂/N₂ gas selectivity at 298 K for PI-1

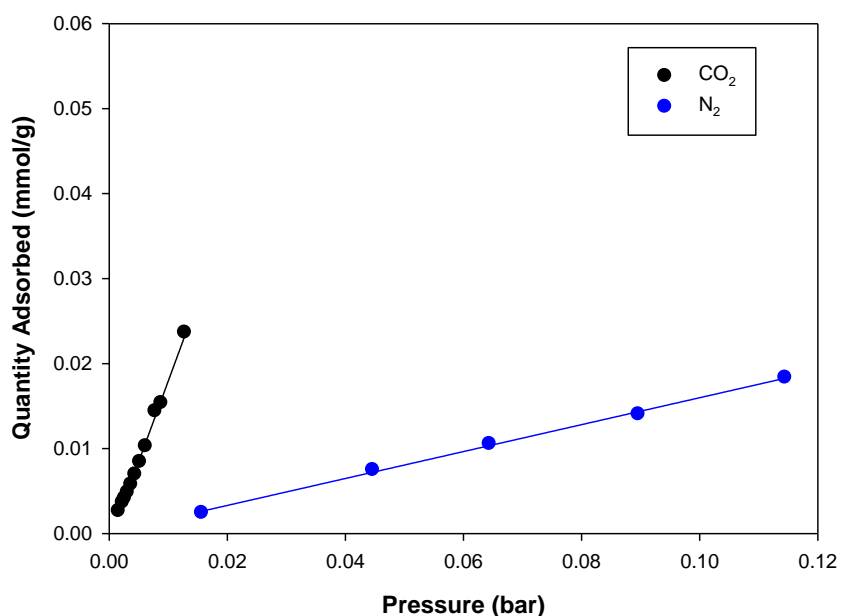


Figure S6-2: CO₂/N₂ gas selectivity at 298 K for PI-1

Table S6-1: Carbon dioxide uptakes and selectivity summary

	CO ₂ uptake at 1 bar (mmol/g)		N ₂ uptake at 298 K and 1 bar (mmol/g)	Heat of adsorption for CO ₂ (kJ/mol)	CO ₂ /N ₂ selectivity	
	273 K	298 K			Ideal selectivity	Henry law constants
PI-1	2.00	1.41	0.15	34	9.5	27:1
PI-2	1.51	1.00	0.15	27	6.7	12:1

References and Acknowledgements

1. Miao, Z.; Fu, Y.; Xu, Z.; Li, G.; Jiang, J., *Mendeleev Commun.*, **2009**, *19*, 270-271.
2. Tozawa, T.; Jones, J. T. A.; Swamy, S.; Jiang, S.; Adams, D. J.; Shakespeare, S.; Clowes, R.; Bradshaw, D.; Hasell, T.; Chong, S. Y.; Tang, C.; Thompson, S.; Parker, J.; Trewin, A.; Bacsa, J.; Slawin, A. M. Z.; Steiner, A.; Cooper, A.I., *Nat. Mat.*, **2009**, *8*, 973-978.