Electronic Supplementary Information

Impact of post-synthesis modification of nanoporous organic frameworks on small gas uptake and selective CO_2 capture

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Section S1: NMR Spectral Characterization of Starting Building Unit

Figure S1: ^{1}H NMR spectrum for 1,3,5,7-tetrakis(4-acetylphenyl)adamantane in $CDCl_3$.

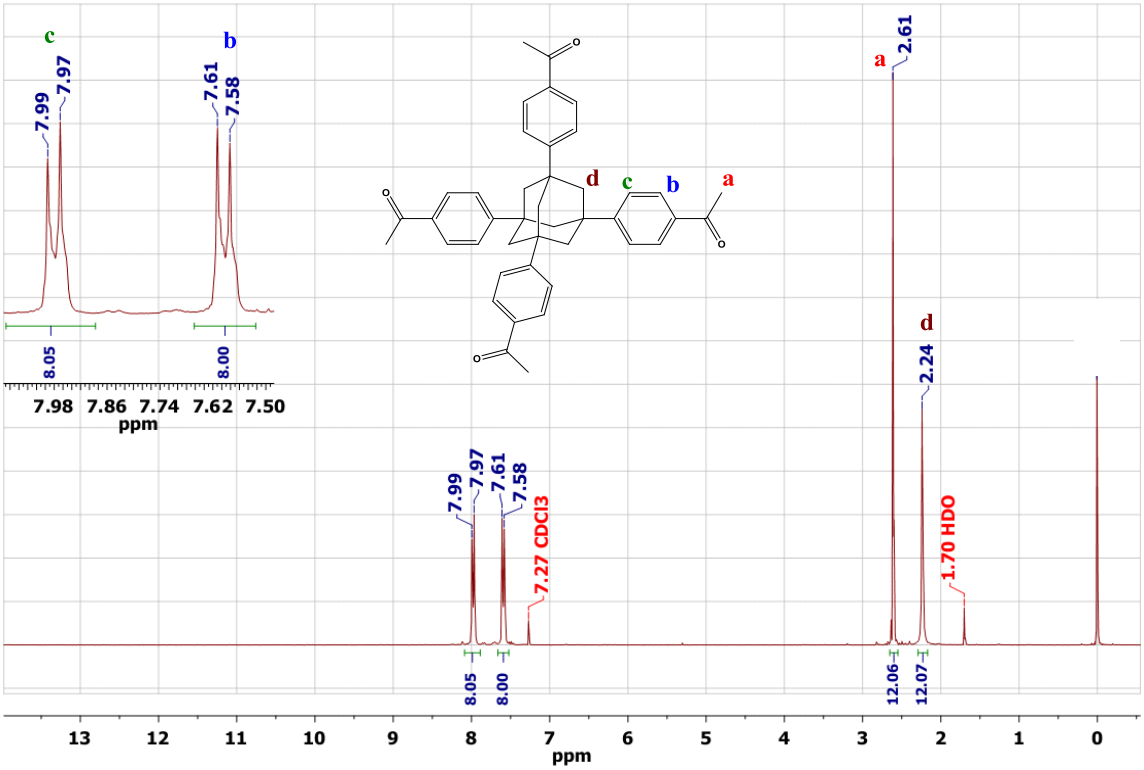
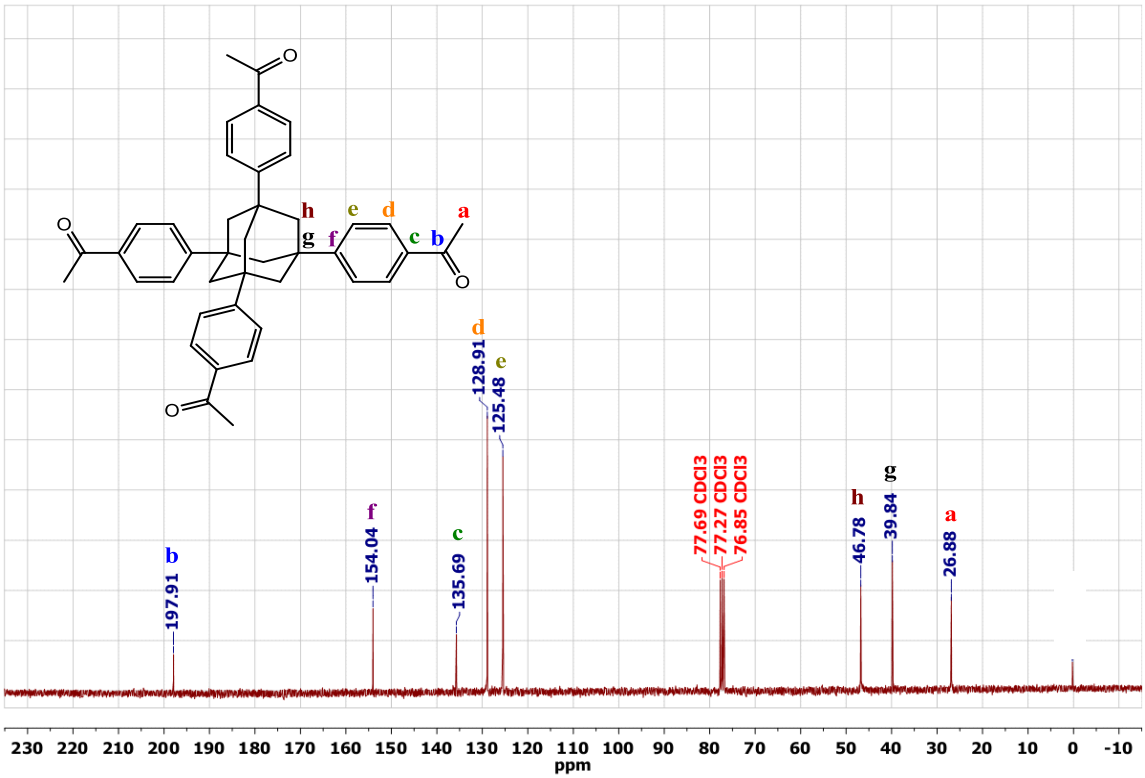


Figure S2: ^{13}C NMR spectrum for 1,3,5,7-tetrakis(4-acetylphenyl)adamantane in $CDCl_3$.



Section S2: Synthesis and Characterization of Polymers

Scheme S1: Synthetic scheme for TAPA, NPOF-4, NPOF-4-NO_2 and NPOF-4-NH_2.

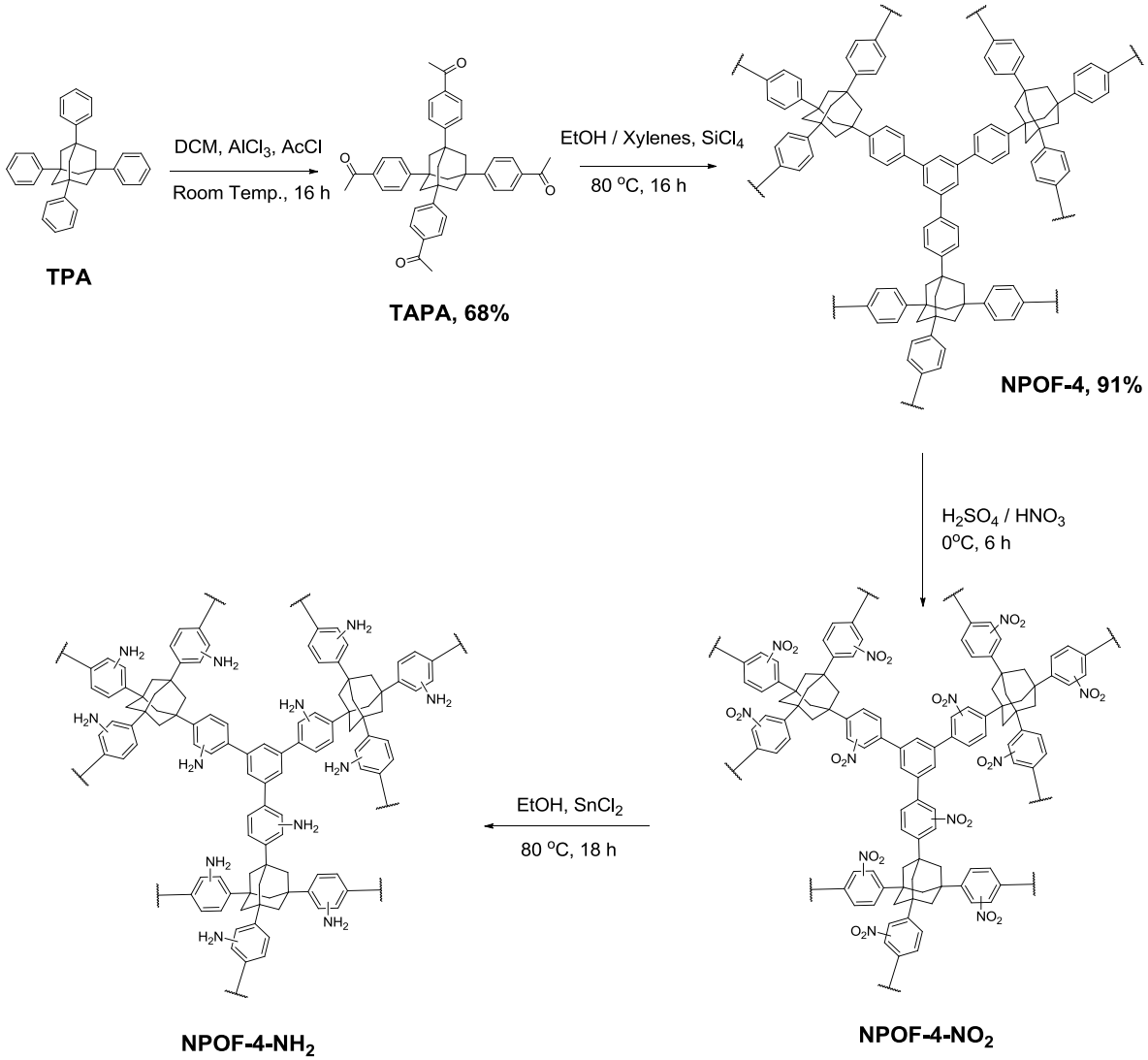


Figure S3: TGA traces of NPOF-4, NPOF-4-NO_2 and NPOF-4-NH_2.

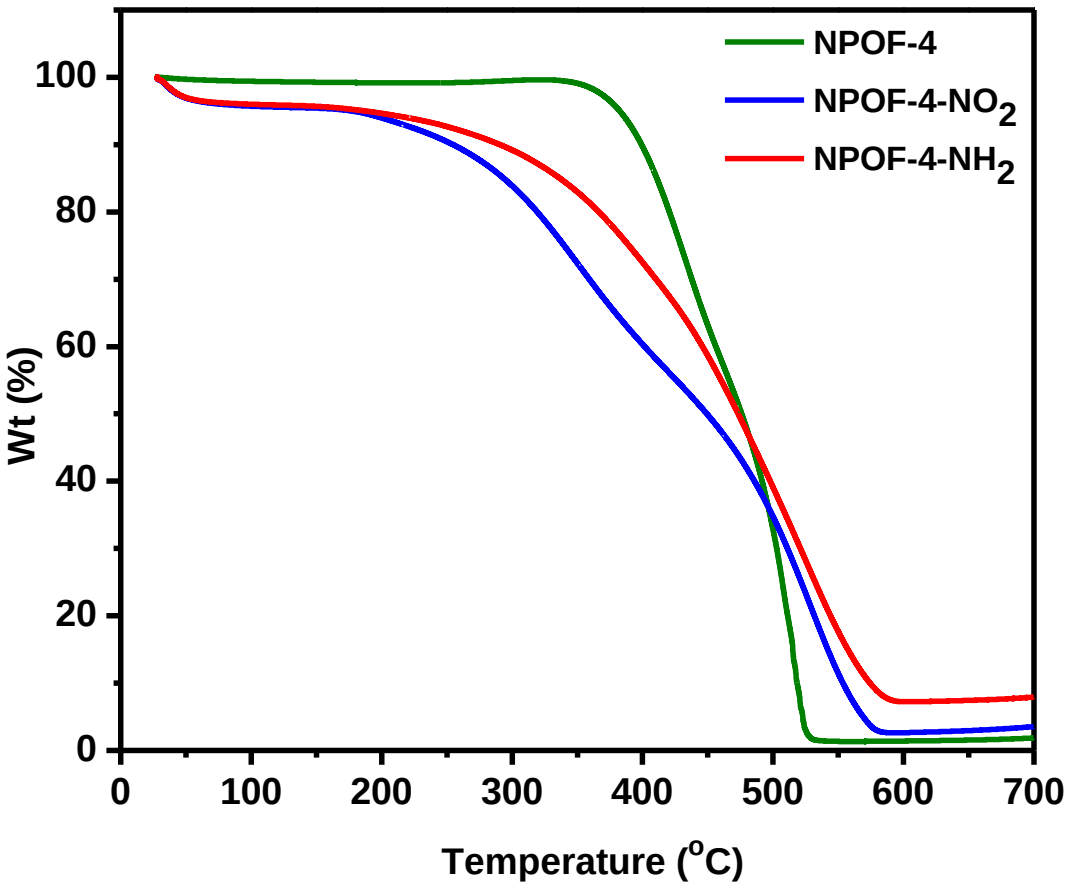
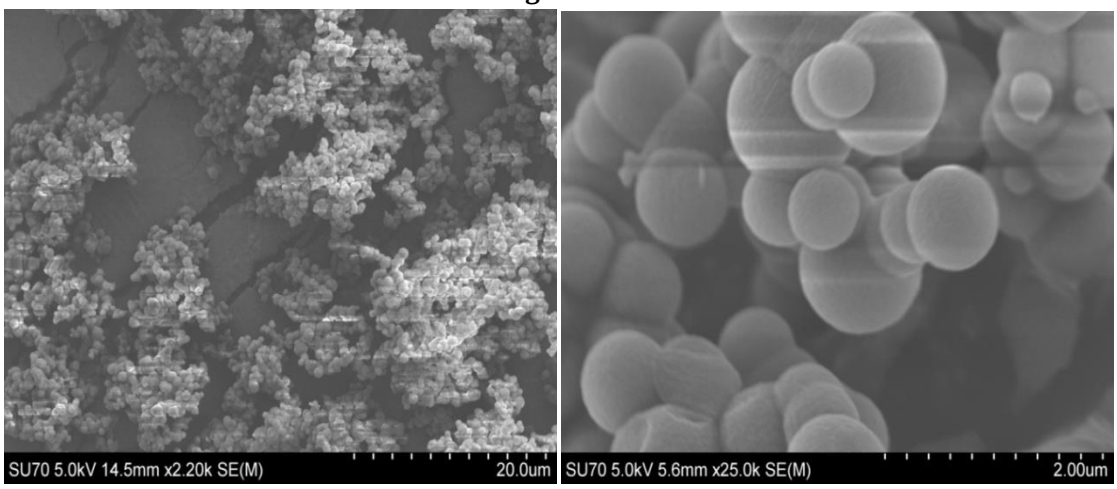
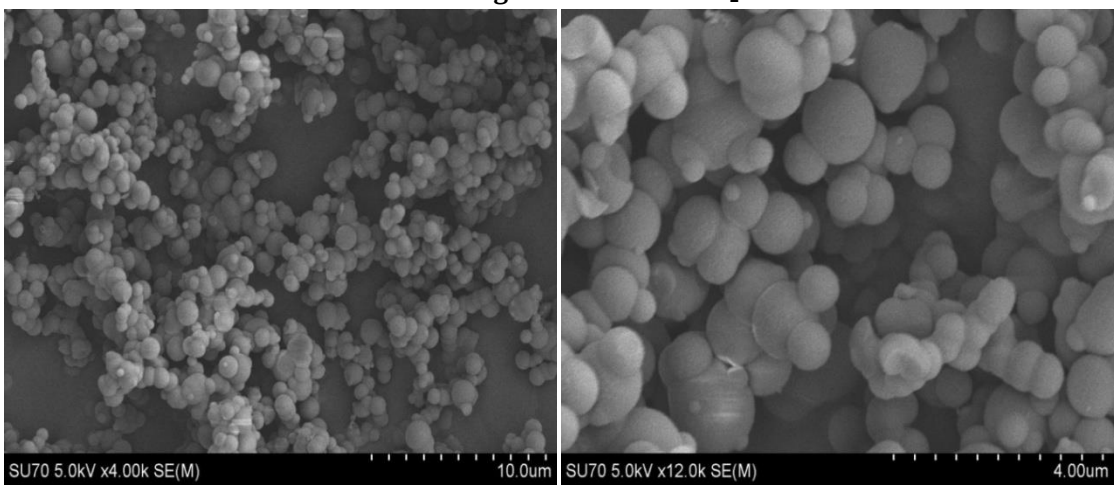


Figure S4: SEM images of NPOF-4, NPOF-4-NO_2 and NPOF-4-NH_2.

SEM images of NPOF-4



SEM images of NPOF-4-NO_2



SEM images of NPOF-4-NH_2

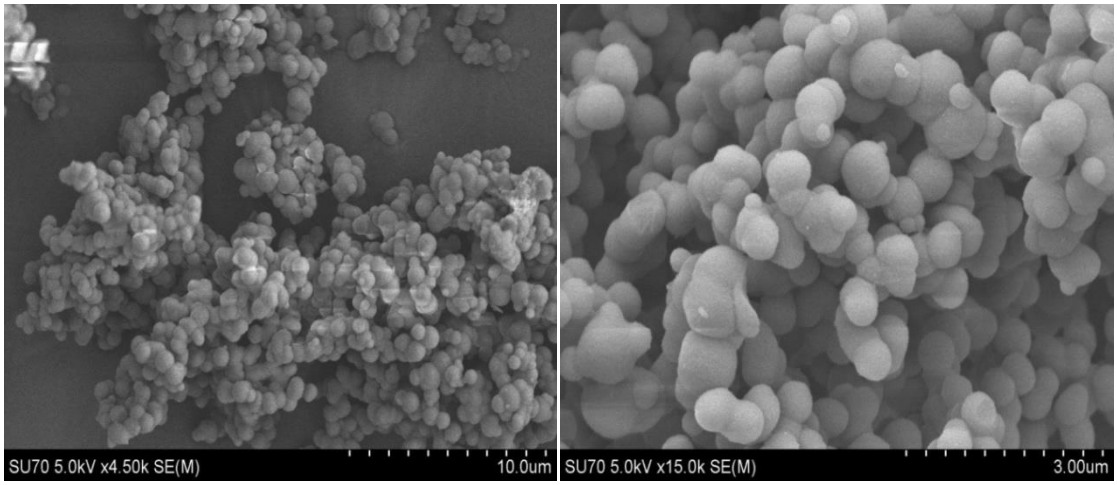


Figure S5: PXRD-patterns for NPOF-4, NPOF-4-NO_2, and NPOF-4-NH_2.

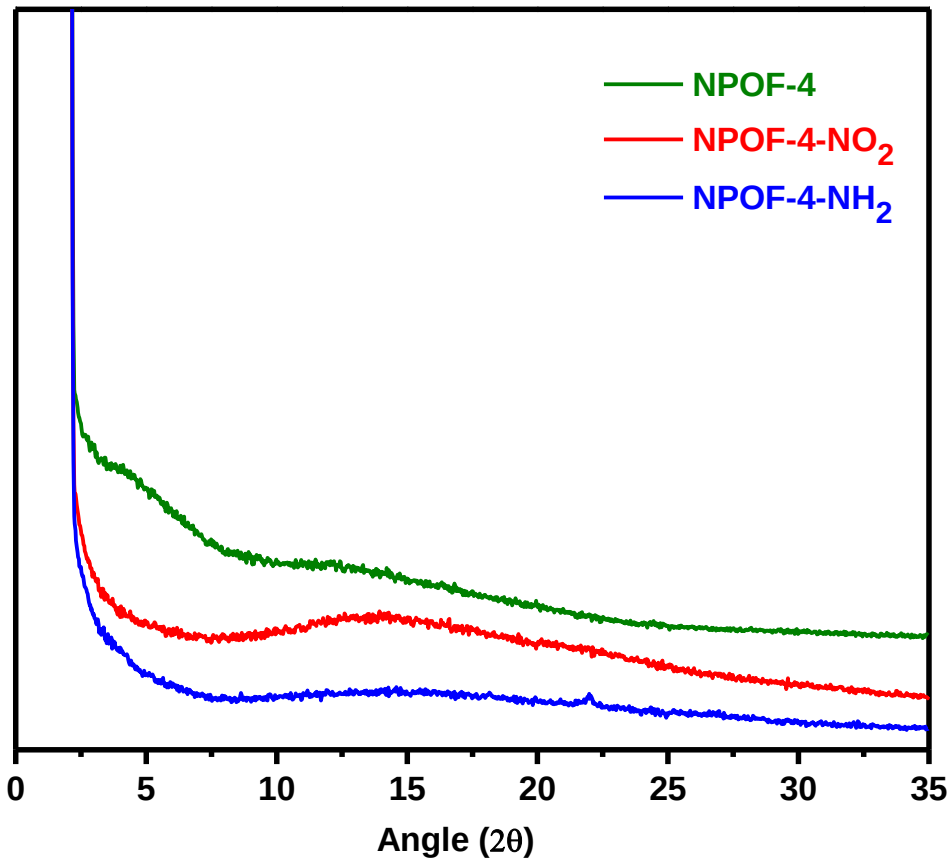


Figure S6: FT-IR spectra of TAPA, NPOF-4, NPOF-4-NO_2 and NPOF-4-NH_2.

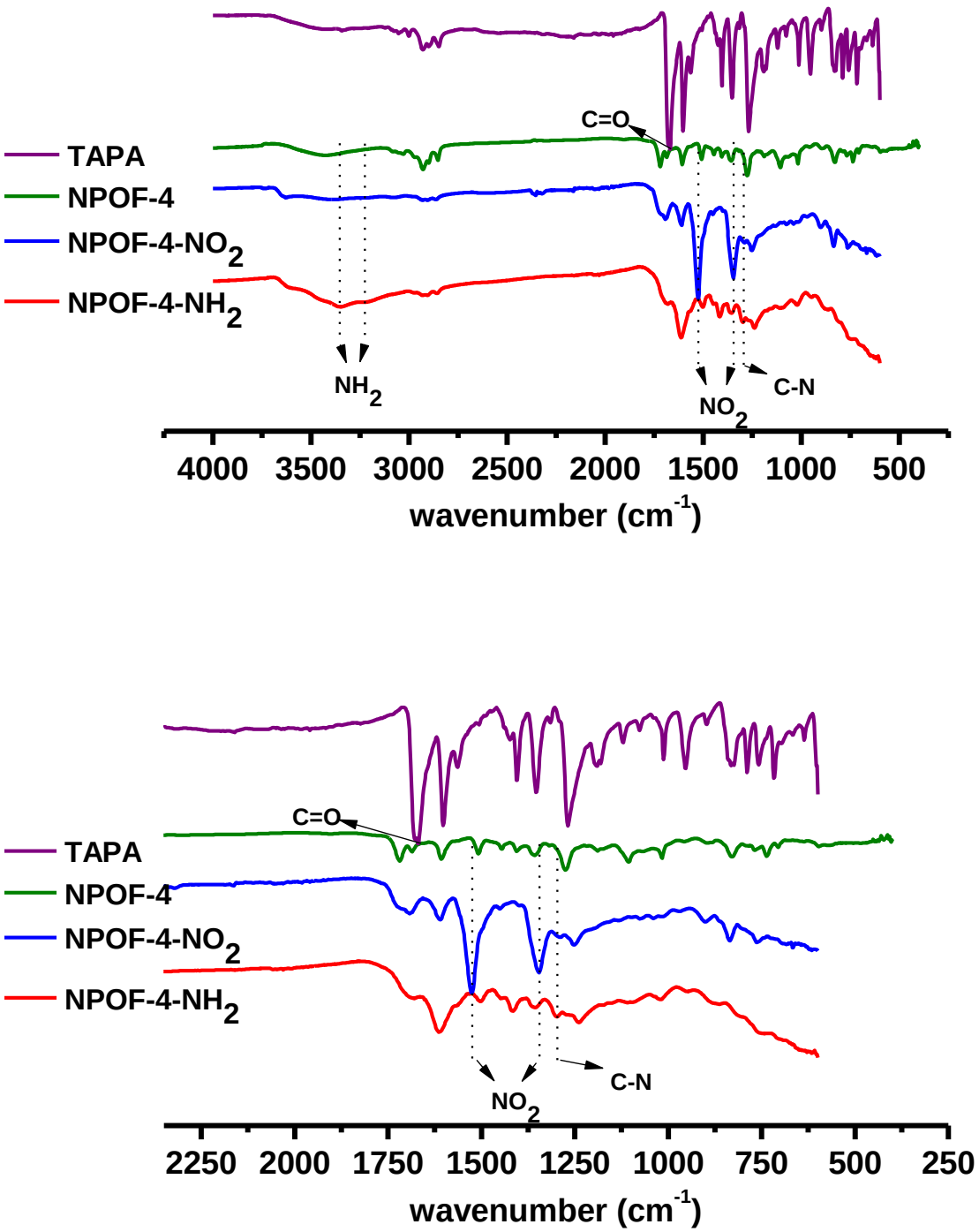
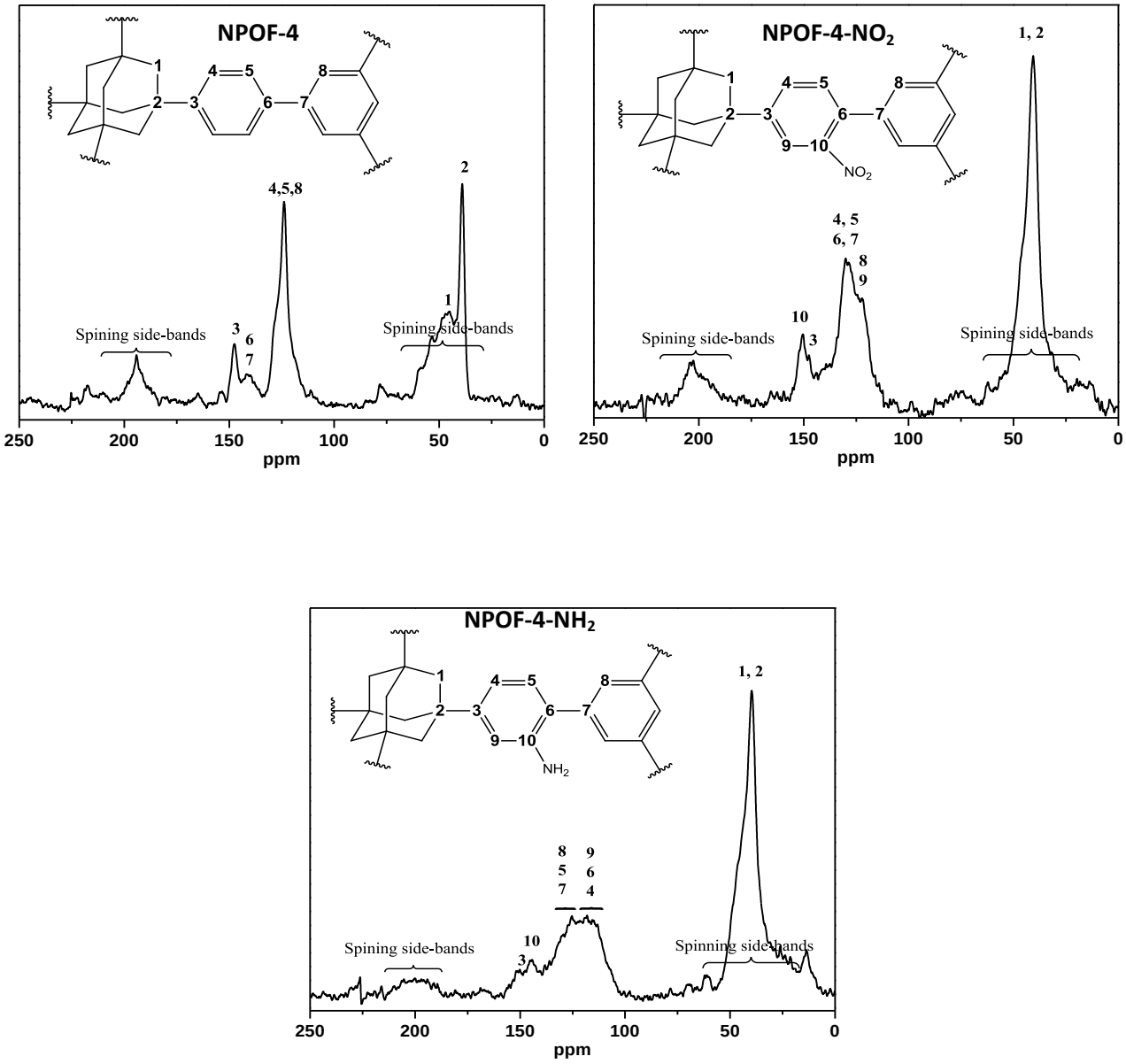


Figure S7: Solid-state ^{13}C CP-MAS NMR spectra of NPOF-4, NPOF-4-NO_2 and NPOF-4-NH_2.



Section 3: Low-Pressure (0 – 1.0 bar) Gas Adsorption Measurements.

Activation of polymers for gas adsorption measurements: A sample was loaded into a 9 mm large bulb cell (Quantachrome) of known weight and then was degassed at 120 °C / 1 x 10^{-5} bar for 12 hours. The degassed sample was weighed precisely and then transferred back to the analyzer. The temperature for adsorption measurements was controlled by using refrigerated bath of liquid nitrogen (77 K) or liquid argon (87 K), and temperature controlled water bath (273 K and 298 K). Adsorption measurements were performed on an Autosorb-1 C (Quantachrome) volumetric analyzer using gas adsorbates of UHP grade.

Figure S8: Ar adsorption isotherms for NPOF-4, NPOF-4-NO_2 and NPOF-4-NH_2 measured at 87 K. The filled markers are adsorption points and the empty markers are desorption points.

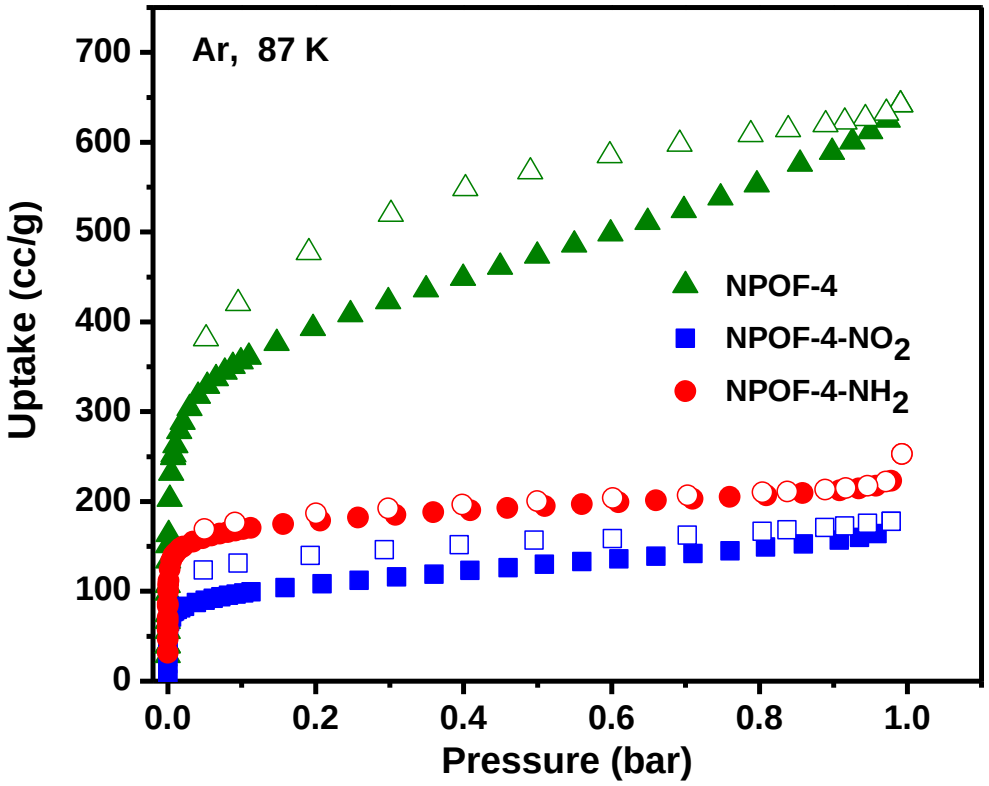


Figure S9: Multipoint BET plots for NPOF-4, NPOF-4-NO_2 and NPOF-4-NH_2 calculated from the argon adsorption in the range of P/P_o = 0.04-0.16.

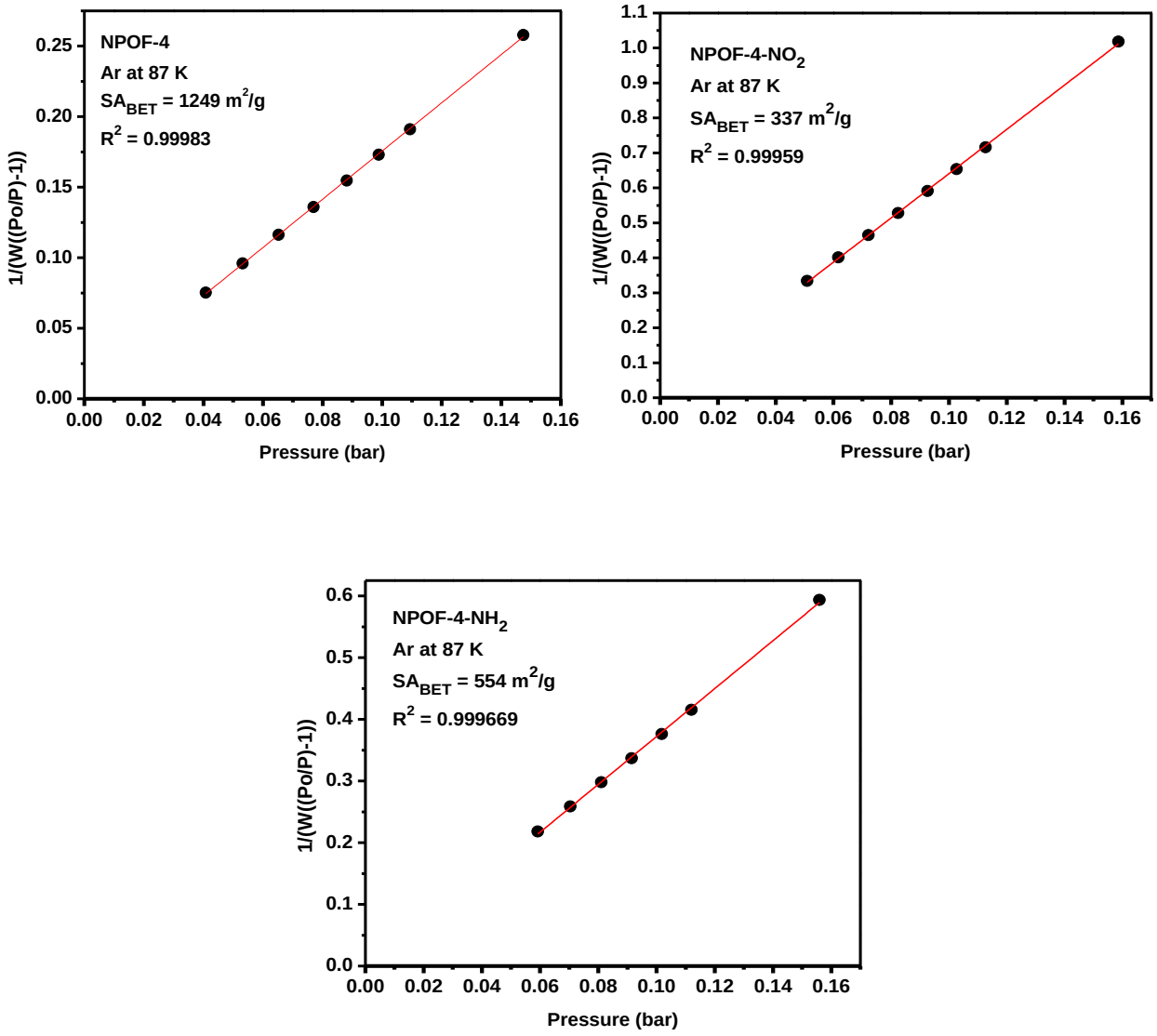


Figure S10: Experimental argon adsorption isotherms (filled circles) for NPOF-4, NPOF-4-NO_2 and NPOF-4-NH_2 measured at 87 K. The calculated NLDFT isotherm is overlaid as open circle.

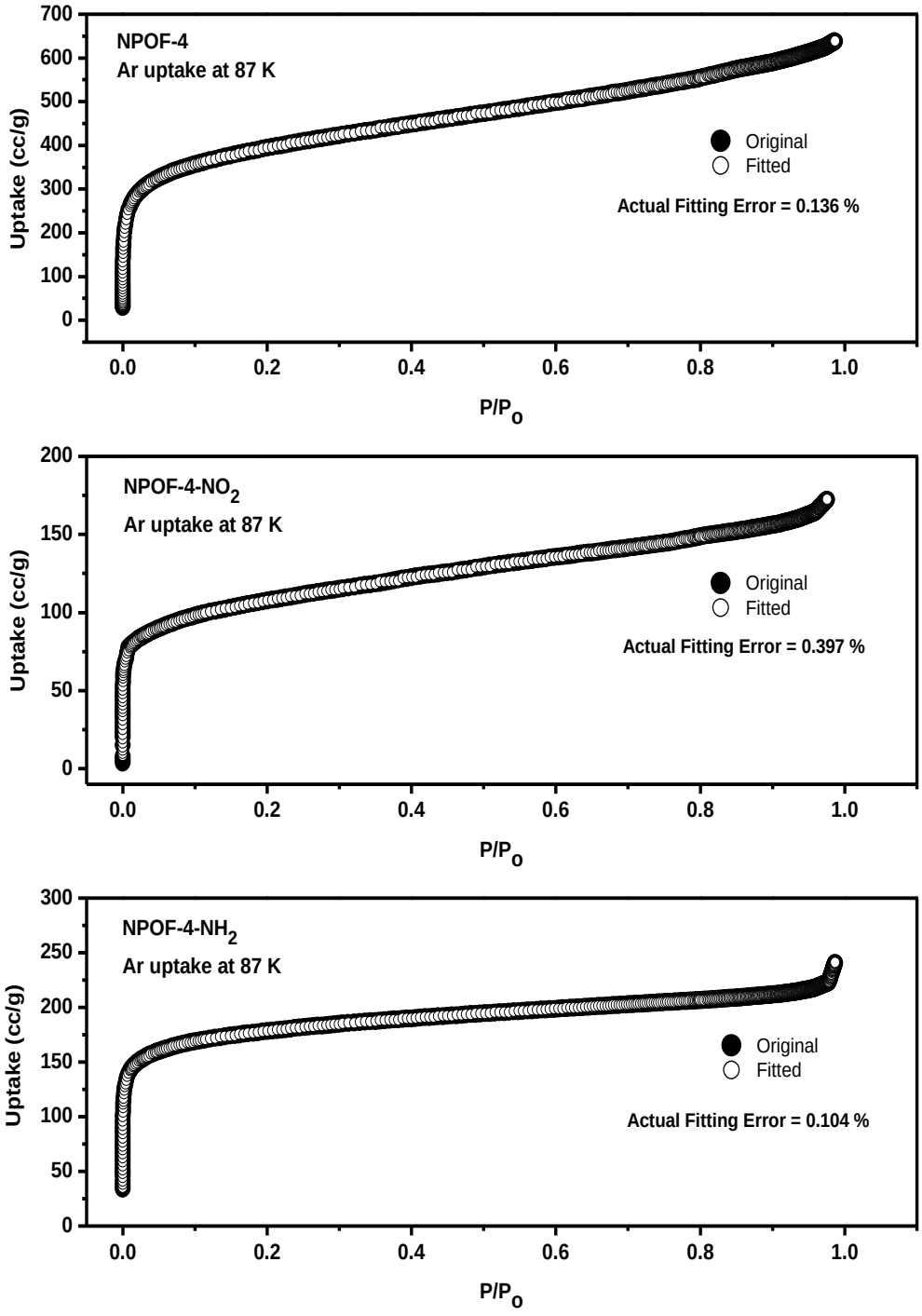


Figure S11: Gas uptake isotherms for NPOF-4 (green triangles), NPOF-4-NO_2 (blue squares) and NPOF-4-NH_2 (red circles).

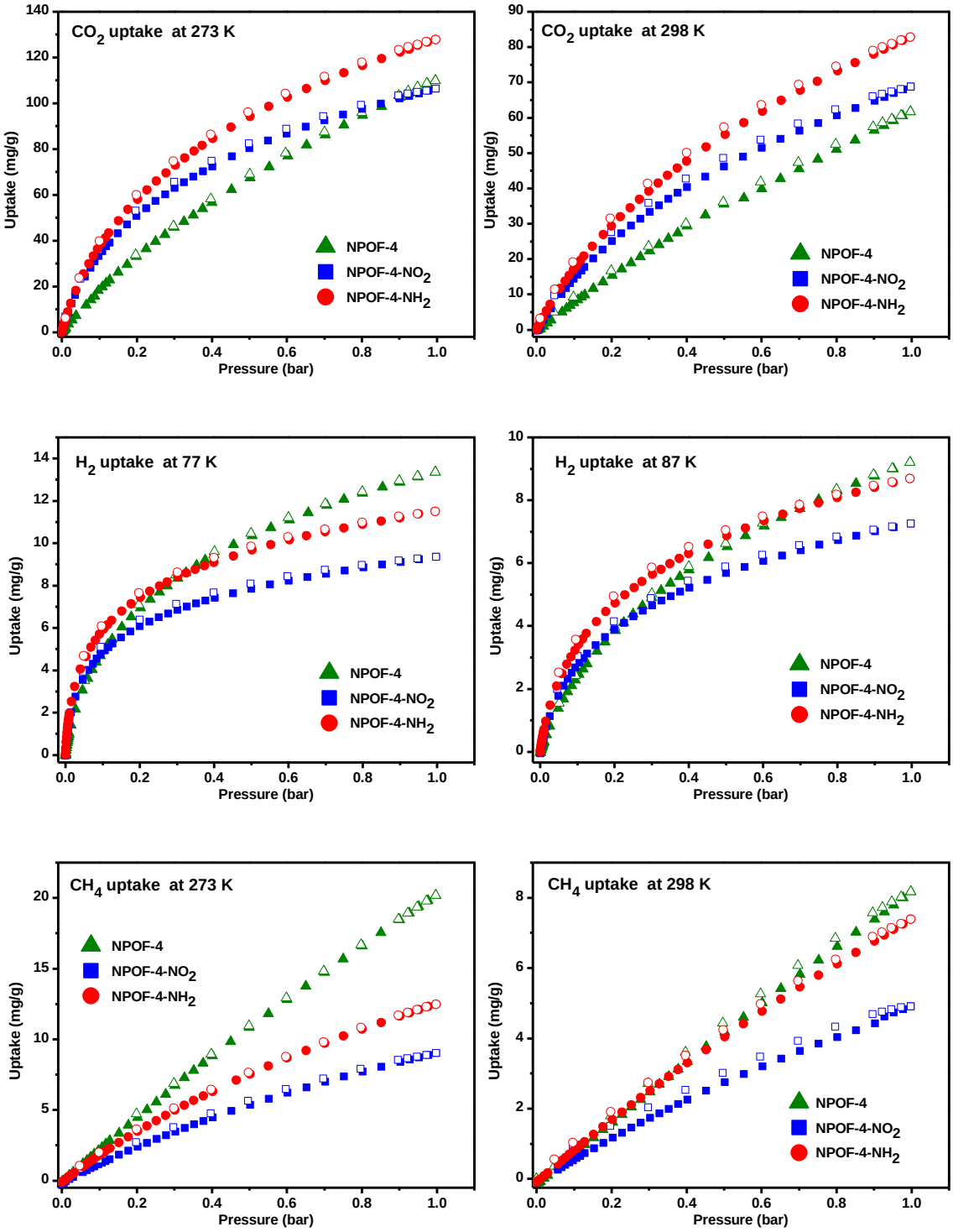


Figure S12: Virial analysis[1] of CO_2 adsorption data for NPOF-4, NPOF-4-NO_2 and NPOF-4-NH_2 (blue circles: 273 K, olive squares: 298 K) used for isosteric heat of adsorption (Q_{st}) calculations.

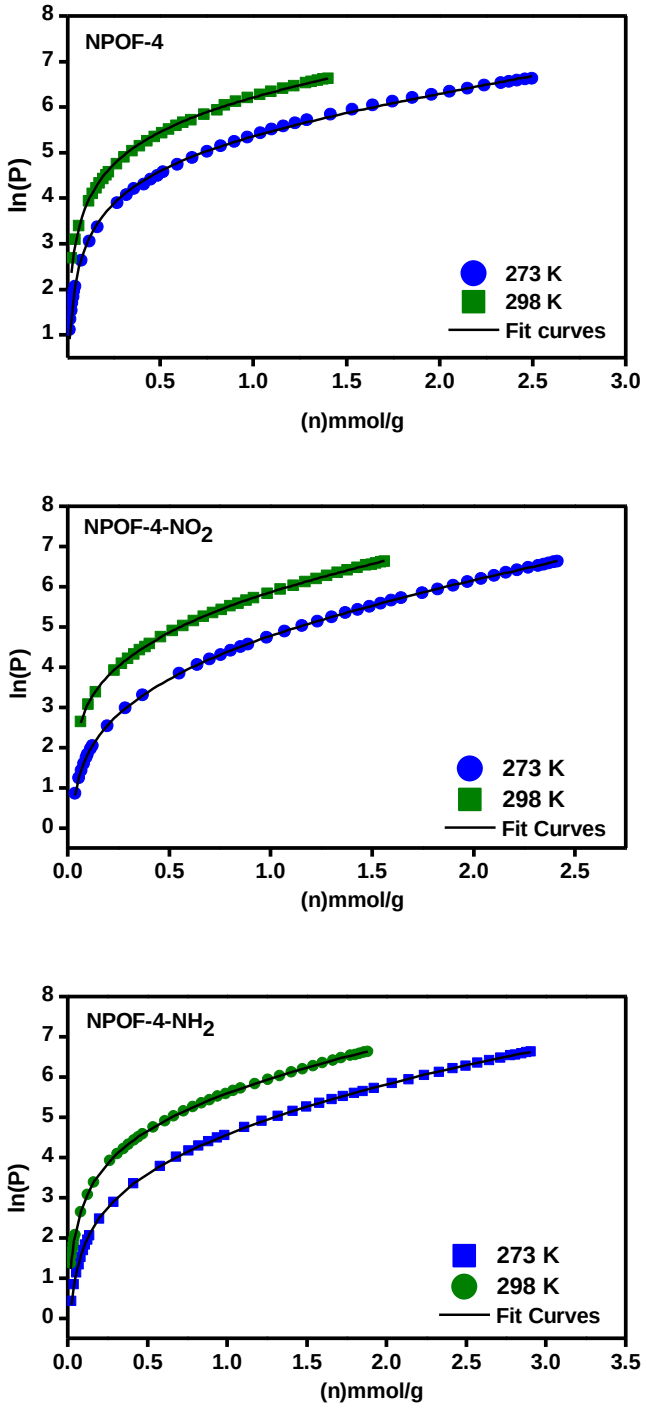


Figure S13: Virial analysis[1] of CH_4 adsorption data for NPOF-4, NPOF-4-NO_2 and NPOF-4-NH_2 (blue circles: 273 K, olive squares: 298 K) used for isosteric heat of adsorption (Q_{st}) calculations.

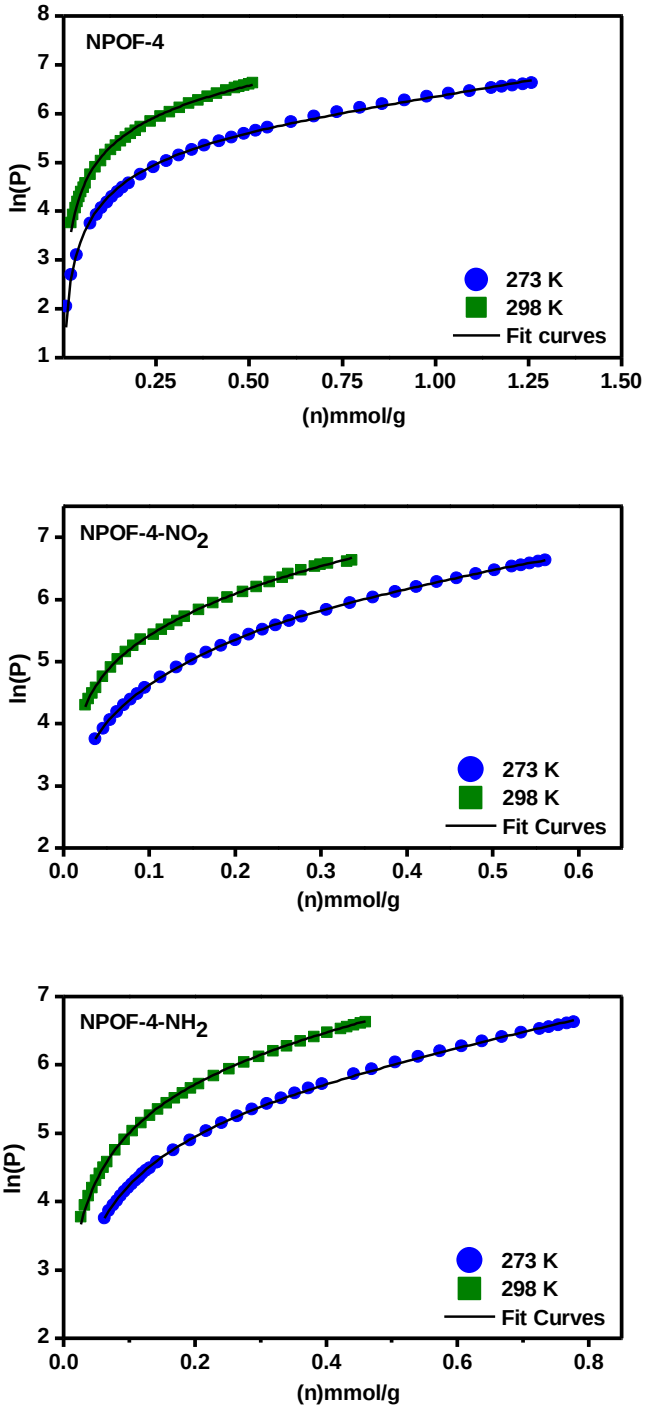


Figure S14: Virial analysis[1] of H_2 adsorption data for NPOF-4, NPOF-4-NO_2 and NPOF-4-NH_2 (blue circles: 77 K and olive squares: 87 K) used for isosteric heat of adsorption (Q_{st}) calculations.

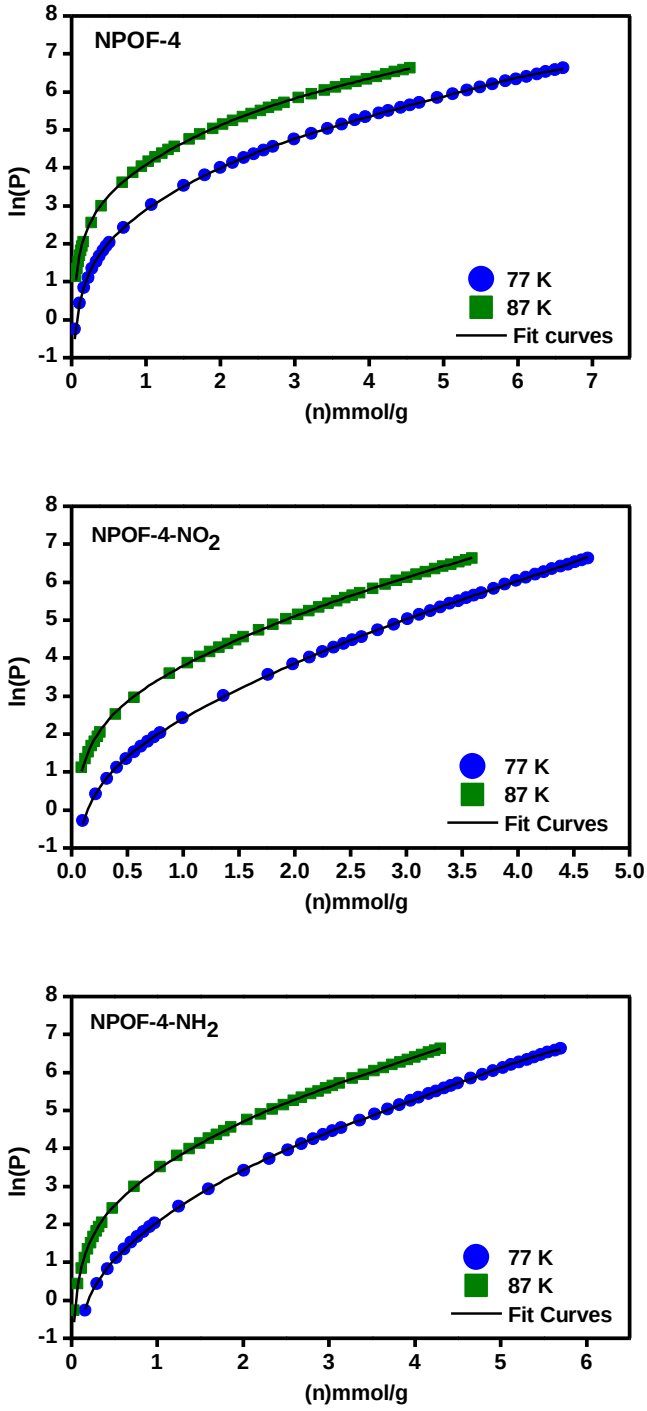


Figure S15: Initial slope selectivity studies for NPOF-4, NPOF-4-NO_2 and NPOF-4-NH_2 at 273 K and 298 K (CO_2 over CH_4 and N_2).[2]

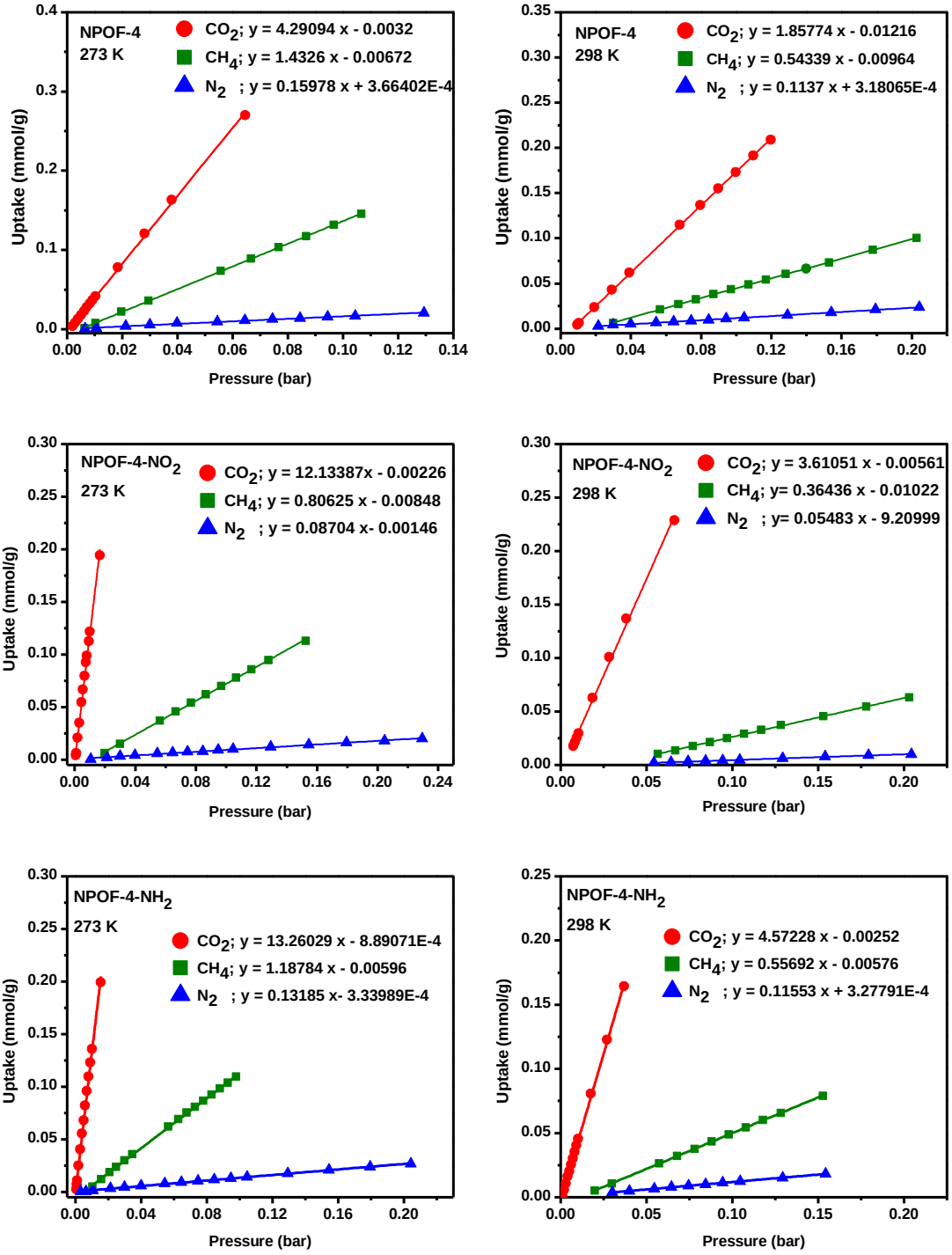


Table S1: Hydrogen uptakes and binding affinities for NPOF-4, NPOF-4-NO_2 and NPOF-4-NH_2.

Network	SA_{BET} $m^2\ g^{-1}$	H_2 uptakes at 1 bar $mg\ g^{-1}$		Q_{st} $kJ\ mol^{-1}$
		77 K	87 K	
NPOF-4	1249	13.3	9.2	7.2
NPOF-4-NO_2	337	9.3	7.2	8.3
NPOF-4-NH_2	554	11.5	8.7	8.1

Table S2: CO_2 and N_2 uptakes for selectivitiy studies of CO_2/N_2 at 273 K and 298 K by using S = $[q_1/q_2]/[p_1/p_2]$.[3]

	273 K				**298 K**			
	CO_2		**N_2**		**CO_2**		**N_2**	
Material	Pressure (bar)	Uptake (mmol)	Pressure (bar)	Uptake (mmol)	Pressure (bar)	Uptake (mmol)	Pressure (bar)	Uptake (mmol)
NPOF-4	0.15	0.5932	0.75	0.0604	0.15	0.2604	0.75	0.0956
NPOF-4-NO_2	0.15	0.9677	0.75	0.0365	0.15	0.4475	0.75	0.0361
NPOF-4-NH_2	0.15	1.0888	0.75	0.0676	0.15	0.5310	0.75	0.0929

Table S3: CO_2 and CH_4 uptakes for selectivitiy studies of CO_2/CH_4 at 273 K and 298 K by using S = $[q_1/q_2]/[p_1/p_2]$.[3]

	273 K				**298 K**			
	CO_2		**CH_4**		**CO_2**		**CH_4**	
Material	Pressure (bar)	Uptake (mmol)	Pressure (bar)	Uptake (mmol)	Pressure (bar)	Uptake (mmol)	Pressure (bar)	Uptake (mmol)
NPOF-4	0.05	0.2133	0.95	1.2038	0.05	0.0885	0.95	0.4841
NPOF-4-NO_2	0.05	0.4653	0.95	0.5410	0.05	0.1796	0.95	0.3108
NPOF-4-NH_2	0.05	0.5116	0.95	0.7507	0.05	0.2175	0.95	0.4403

Dual-site Langmuir Fruendlich (DSLF) equation

$$\boldsymbol{q} = q_A + q_B = \frac{q_{sat,A} * b_A * \boldsymbol{p}^{\alpha_A}}{\mathbf{1} + b_A * \boldsymbol{p}^{\alpha_A}} + \frac{q_{sat,B} * b_B * \boldsymbol{p}^{\alpha_B}}{\mathbf{1} + b_B * \boldsymbol{p}^{\alpha_B}} \qquad \text{Equation S1}$$

In this equation, $\boldsymbol{q}$ is the amount of gas adsorbed (mmol/g), p is the pressure (bar), q_{sat} is the saturation capacity (mmol/g), b is the Langmuir−Freundlich parameter ($bar^{-\alpha}$) and α is the Langmuir−Freundlich exponent (dimensionless) for the site A and B. For CO_2 isotherms dual-site Langmuir-Freundlich ($q = q_A + q_B$) was employed to get a reasonable fitting. For CH_4 and N_2 isotherms single-site Langmuir-Freundlich ($q = q_A$) was able to describe the isotherms sufficiently since there were no discernible isotherm inflections for these isotherms. The parameters obtained from fittings were used for ideal adsorption solution theory (IAST) selectivity calculations which were performed according to revious reports.[4,5]

Figure S16: Experimental pure component isotherms for CO_2 (red circle), CH_4 (olive square) and N_2 (blue triangle) at 298 K, and their corresponding isotherm fits (solid black lines) dual-site Langmuir-Freundlich (DSLF) fits for CO_2 and single-site Langmuir-Freundlich (SSLF) for CH_4 and N_2.

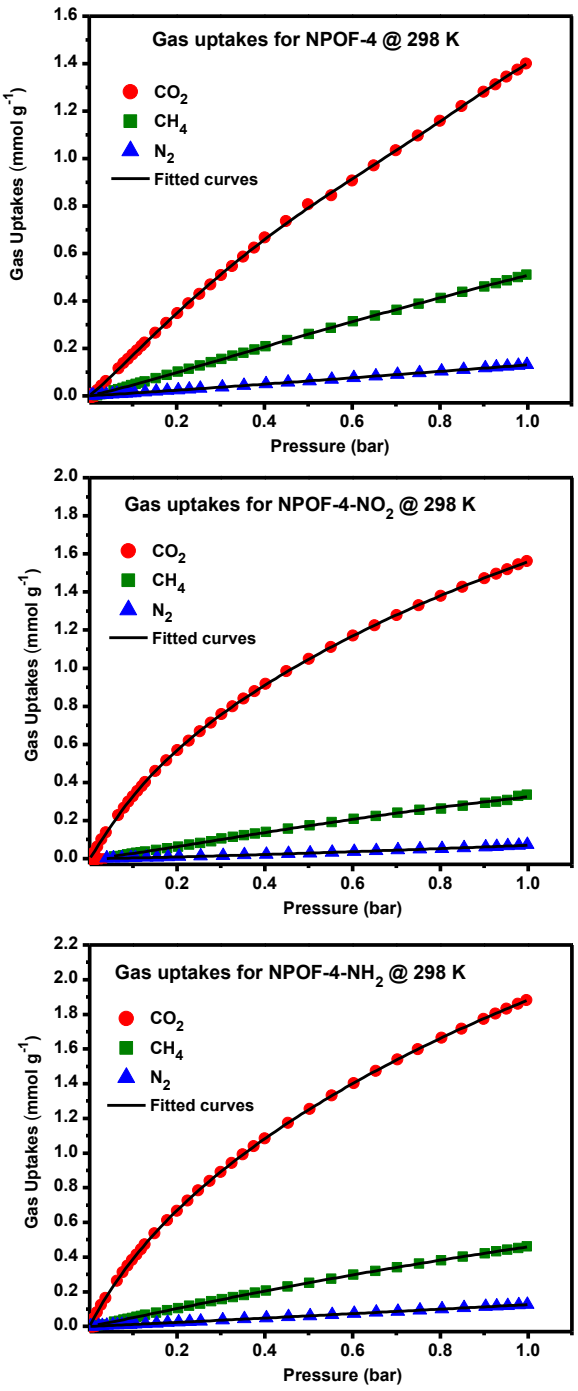
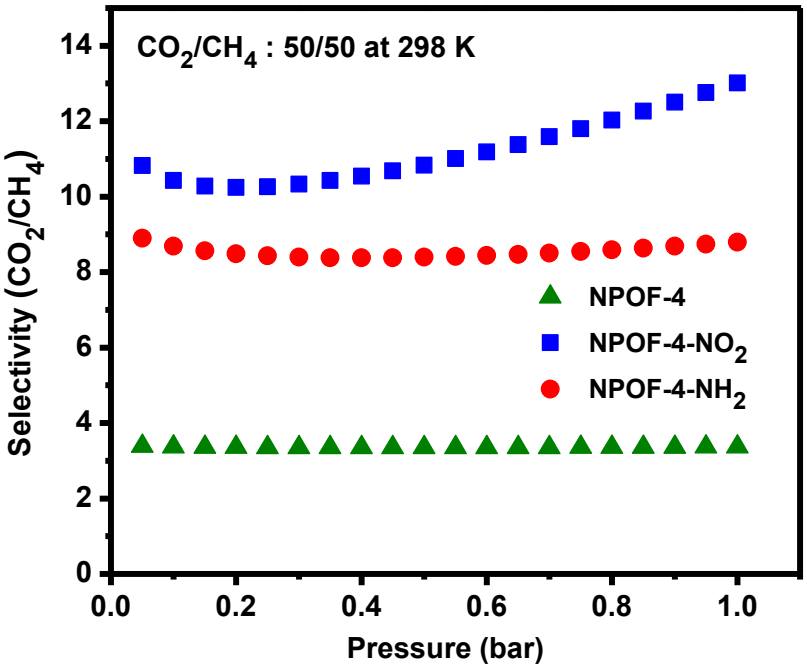


Figure S17: IAST selectivities of CO_2 over CH_4 for 50/50 binary mixture at 298 K for NPOF-4, NPOF-4-NO_2 and NPOF-4-NH_2.



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3. K. Sumida, D. L. Rogow, J. A. Mason, T. M. McDonald, E. D. Bloch, Z. R. Herm, T.-H. Bae and J. R. Long, *Chem. Rev.*, 2012, **112**, 724.

4. A. L. Myers and J. M. Prausnitz, *AIChE J.*, 1965, **11**, 121.

5. Z. R. Herm, J. A. Swisher, B. Smit, R. Krishna and J. R. Long, *J. Am. Chem. Soc.*, 2011, **133**, 5664.