Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A

Supporting Information

A novel nitrogen rich porous aromatic framework for hydrogen and carbon dioxide storage

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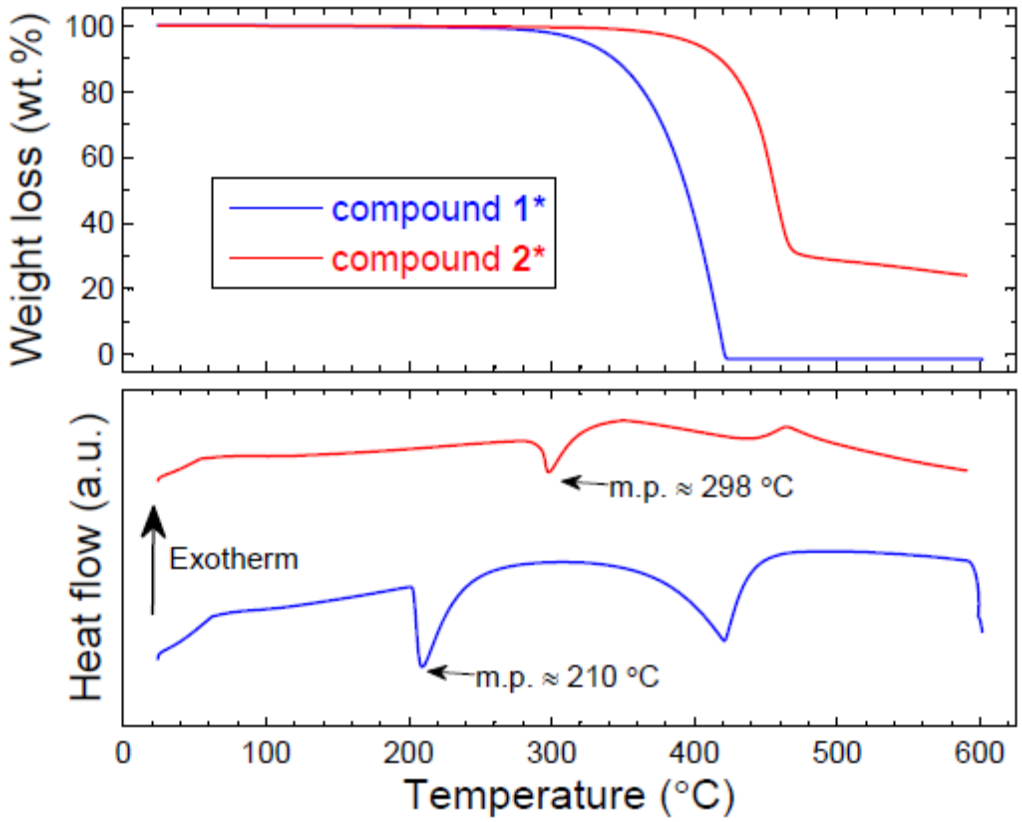

Fig. S1. TGA and DSC of the compounds **1** and **2**. * Refer to Fig. 1 for chemical structure.

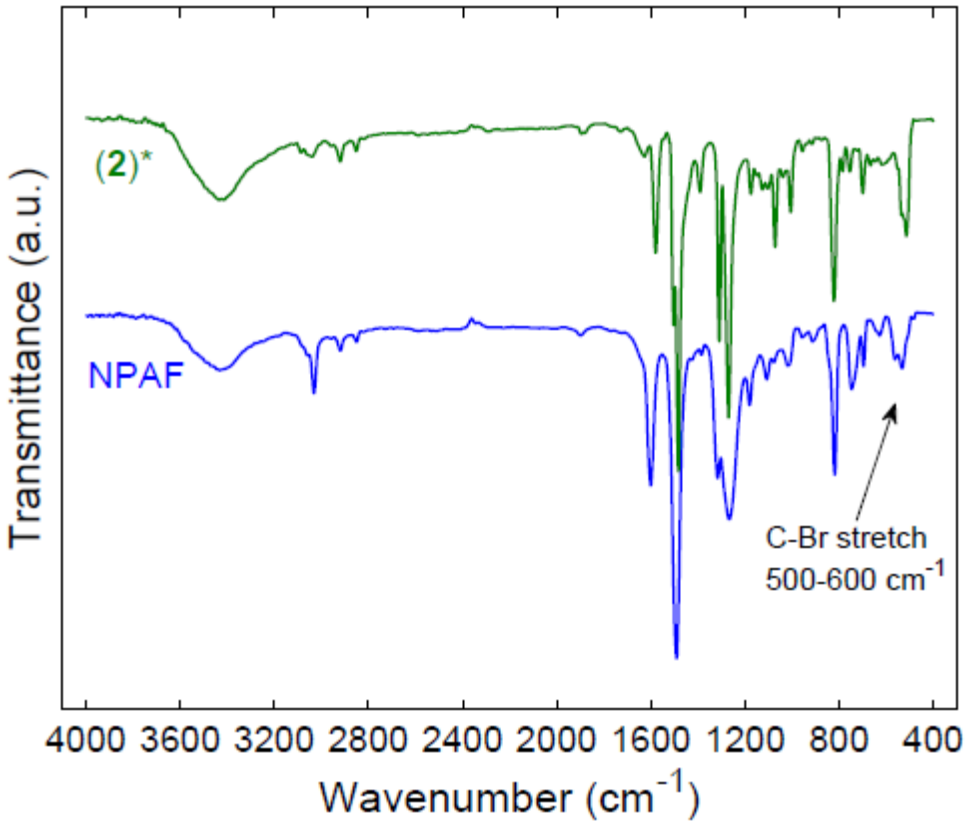

Fig. S2. FTIR of NPAF and compound **2** (building block of the NPAF). * Refer to Scheme 1 for chemical structure.

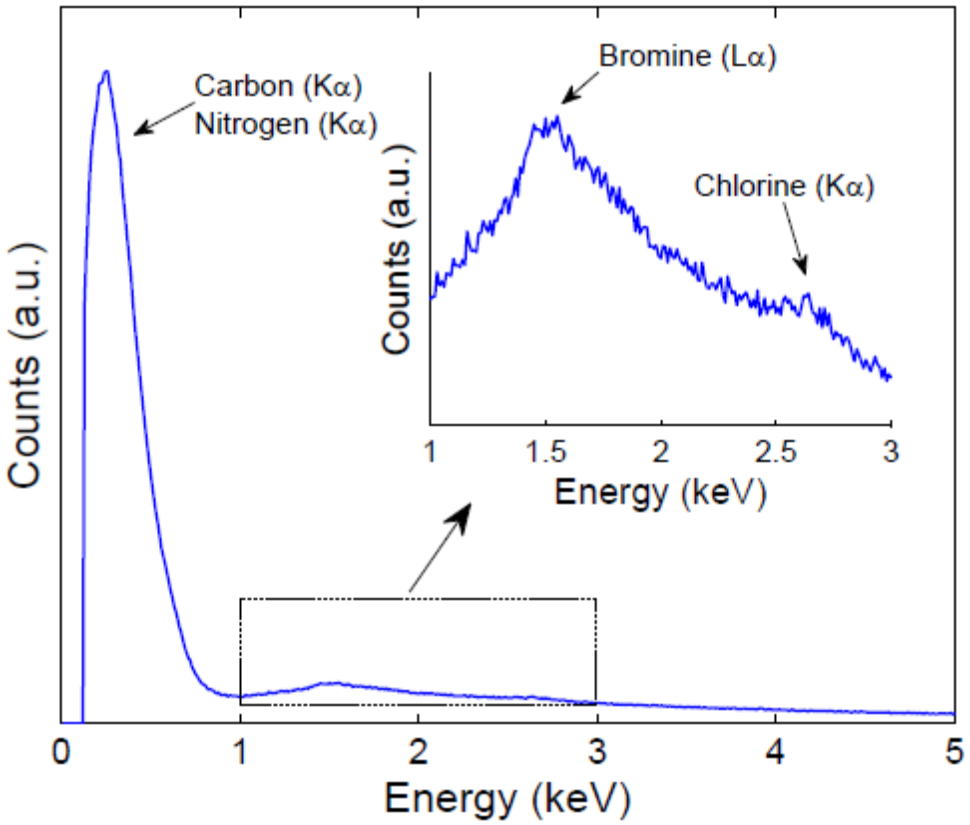

Fig. S3. SEM-EDX analysis of NPAF.

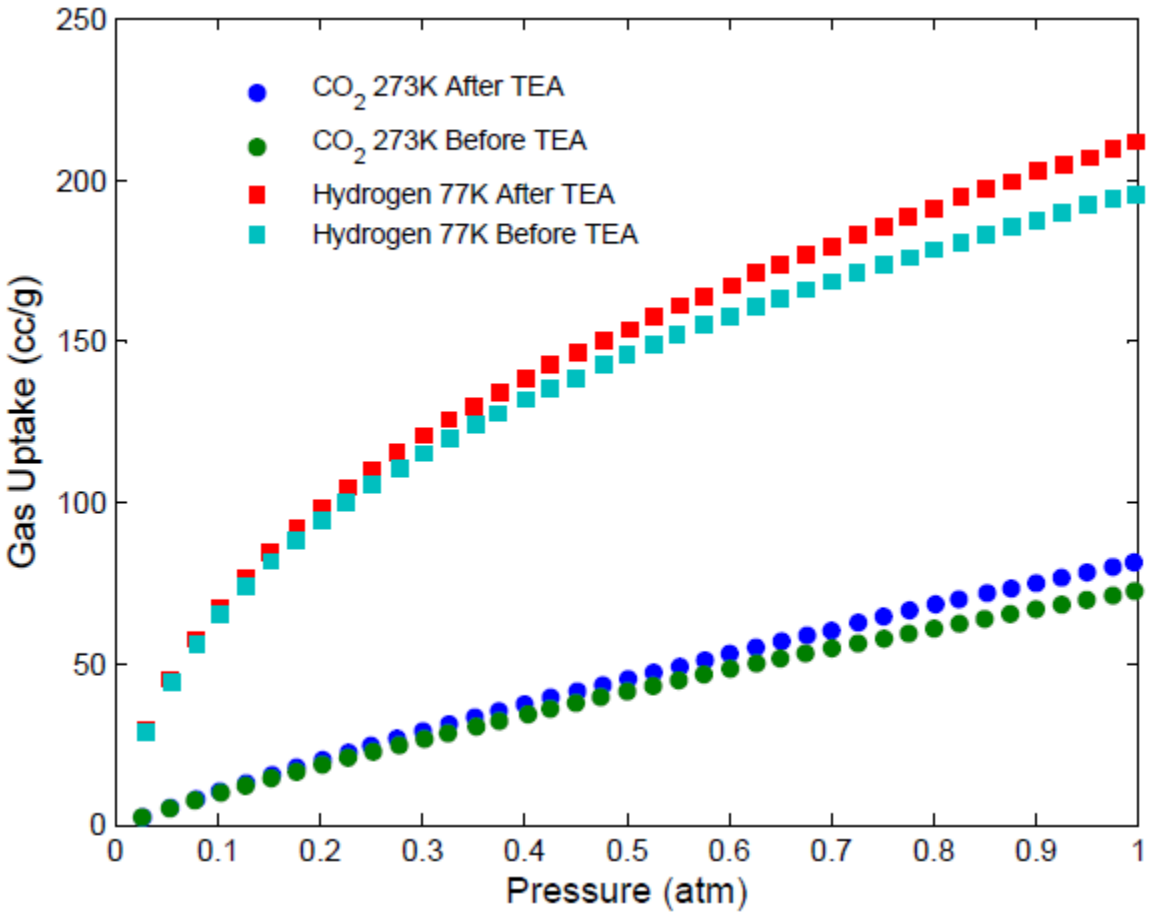

Fig. S4. Effect of triethanolamine (TEA) treatment on hydrogen and CO_2 uptakes of NPAF.

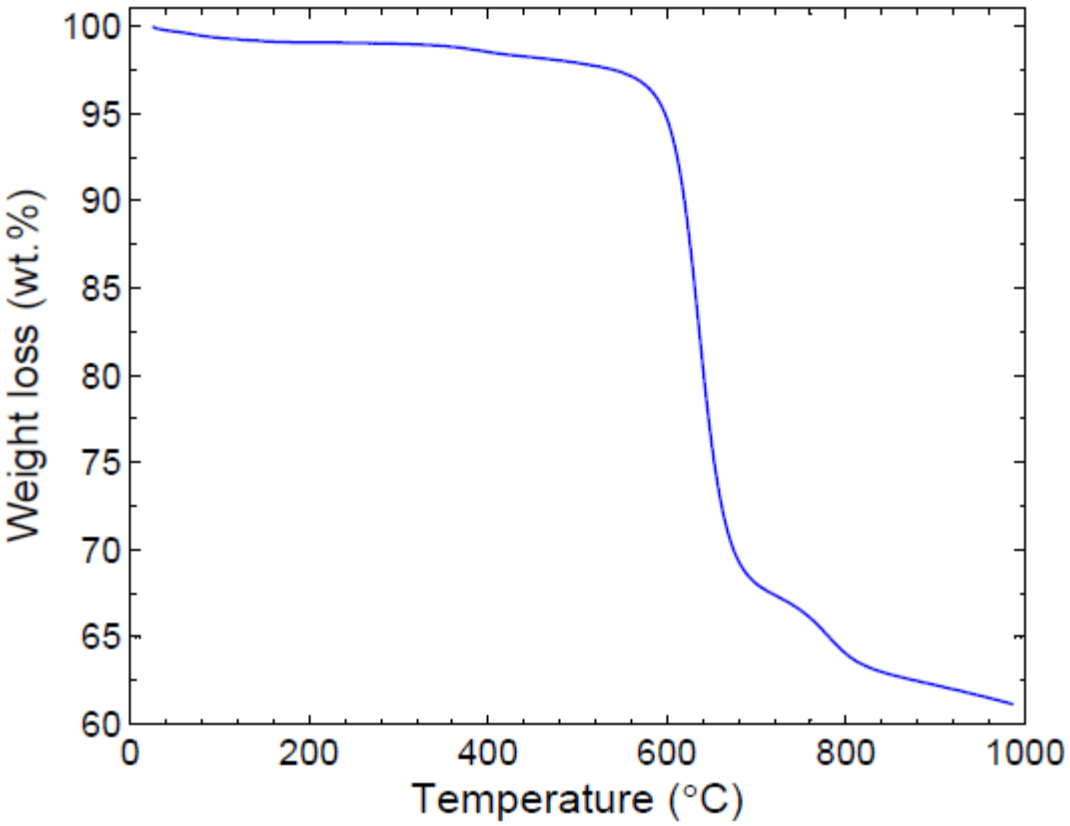

Fig. S5. TGA of NPAF under 100 ml/min nitrogen flow and 20 K/min ramping rate.

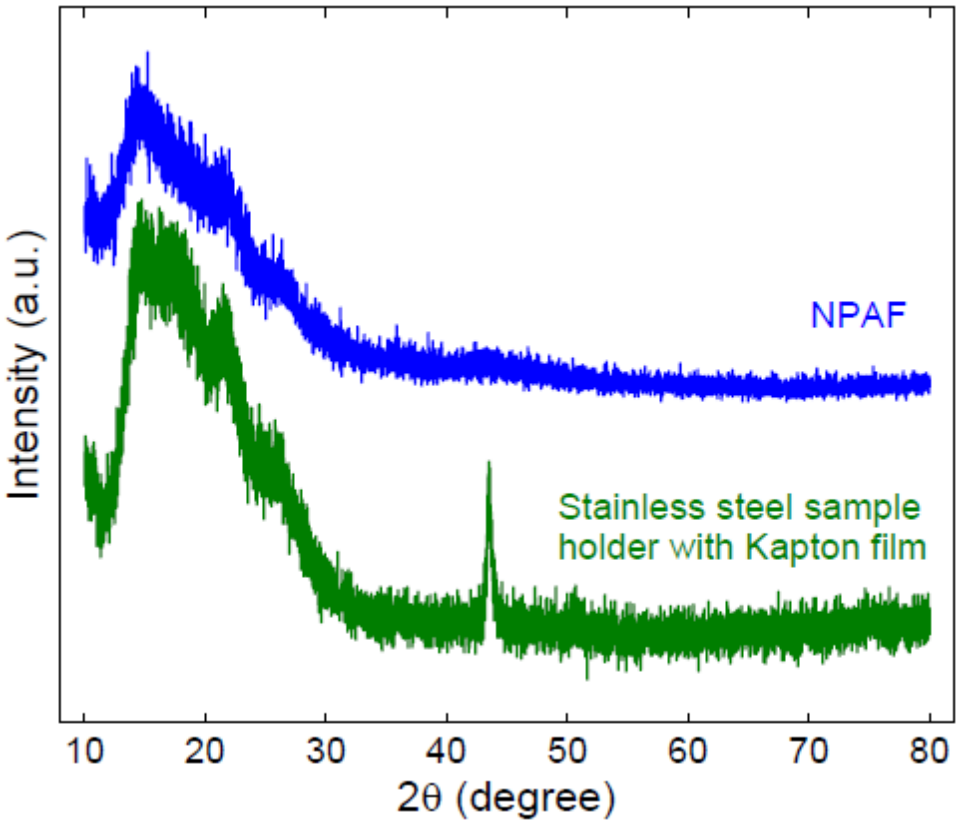

Fig. S6. XRD spectrum of NPAF.

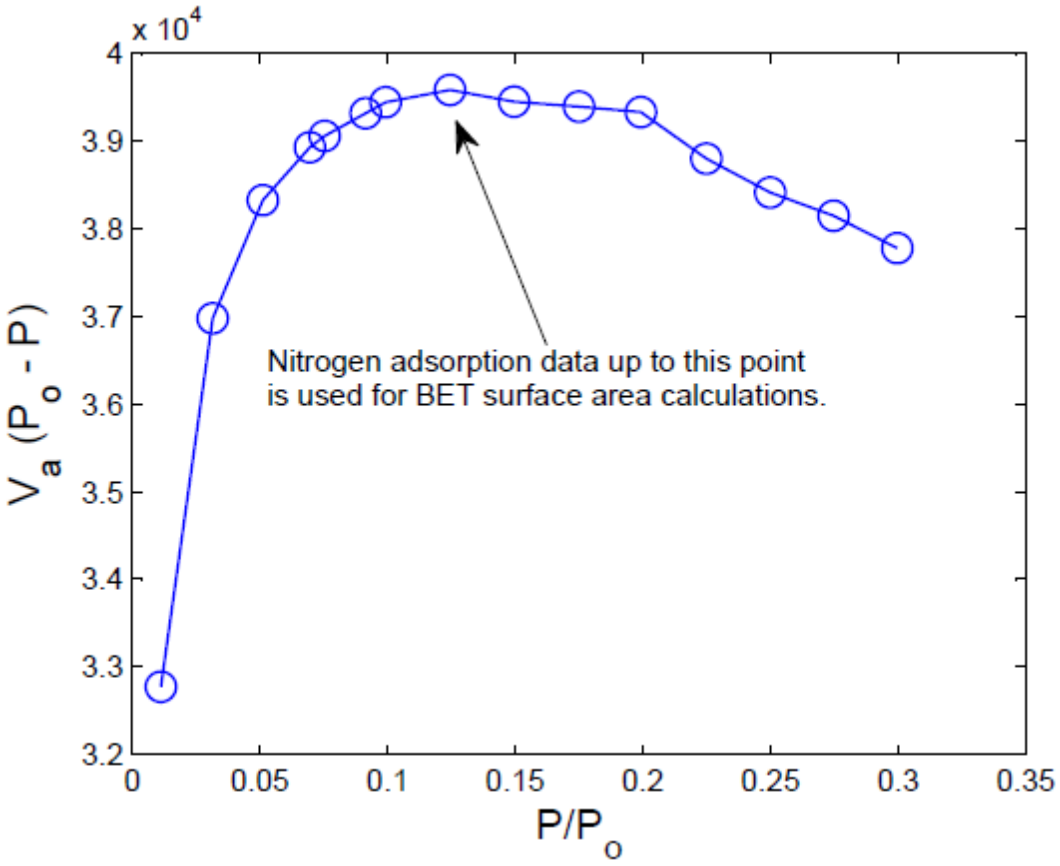

Fig. S7. Plot of the term V_a (P_o - P) vs. P/P_o for BET consistency analysis.

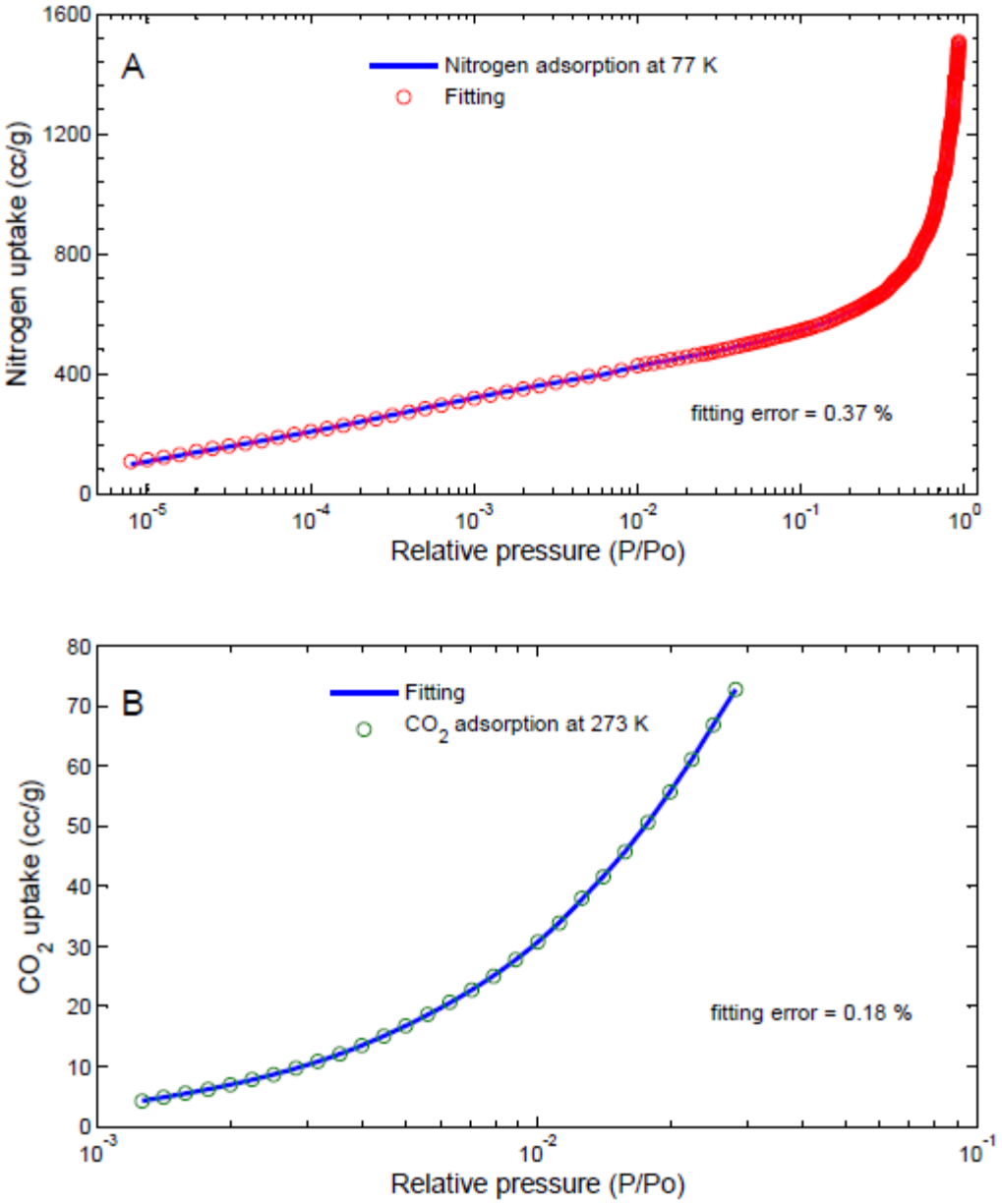

Fig. S8. Nitrogen and CO_2 adsorption isotherms and fittings to experimental data. Nitrogen and CO_2 adsorption isotherms were fitted by using hybrid and slit pore geometry, respectively.

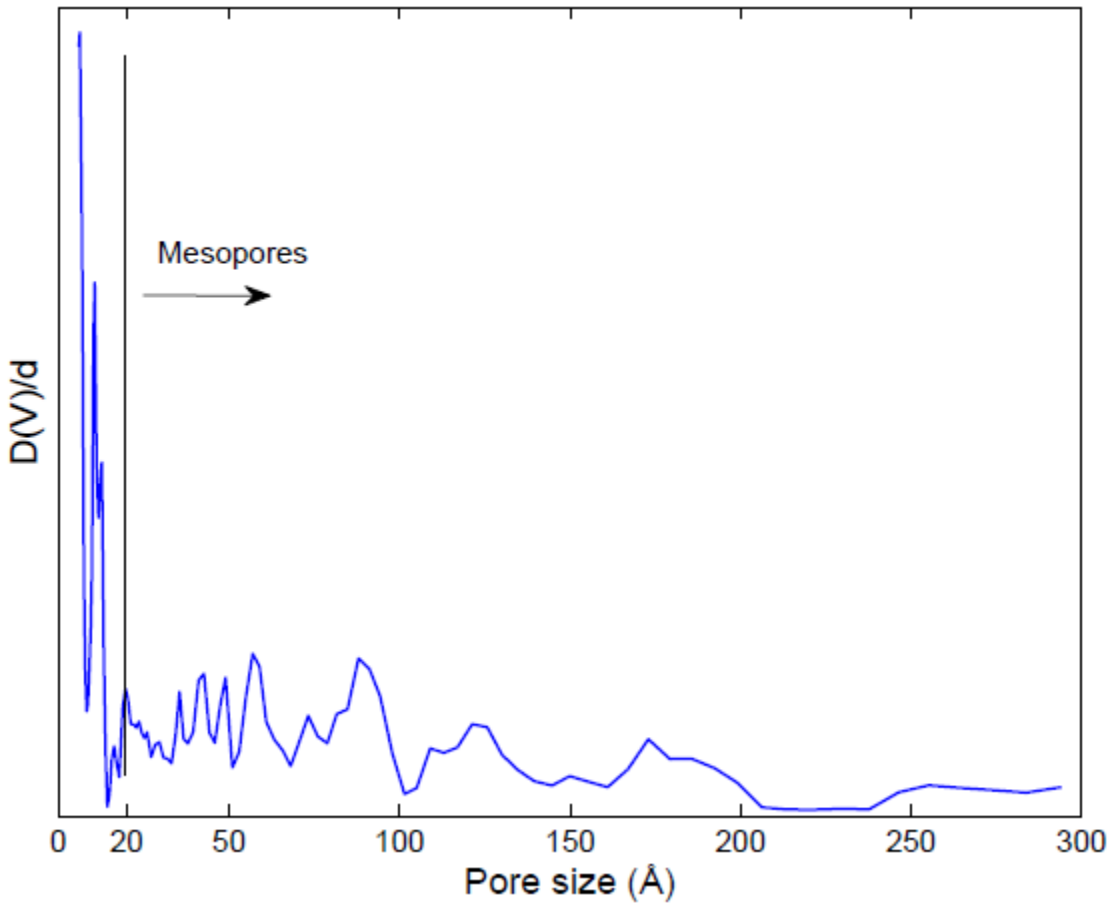

Fig. S9. Micropore and mesopore size distribution of NPAF. Left of the dash line represents the micropores (< 20 Å) and right of the dash line represents mesopores (20 - 500 Å).

Table S1. The CO_2 and hydrogen uptake values of porous polymers reported in the literature.

Materials	S_{BET} (m^2/g)	CO_2 uptake at 1 atm[1] (mmol/g)		H_2 uptake at 77 K / 1 atm[1] (wt. %)	Ref.
		273 K	298 K		
NPAF	1790	3.64 31.1[2]	2.32 28.7[3]	1.87 0.33[4]	This work
POP-diimide	960	4.02[5]	2[6]	–	1
BILP-1	1172	4.27[7]	2.98[5]	1.86[8]	2
BLP-1(H)	1360	1.68	0.94[5]	1.33	3
BLP-12(H)	2244	2.91	1.79[5]	1.93	3
PPN-4	6461	–	38.5[9]	–	4
PPN-6	4023	1.98[10]	1.5[8]	–	5
PPN-6-SO3H	1254	4.98[7]	3.6[8]	–	5
PPN-6-SO3Li	1186	5.08[7]	3.7[11]	–	5
Compound 6[9]	–	–	0.2[12]	–	6
Compound 3[9]	1566	2.1[13]	–	1.1	7
POF1B	917	4.2[14]	2.1[15]	1.25	8
HCP 1	1646	–	1.7[16]	–	9
JUC-Z2	2034	3.2	1.6 13.2[17]	1.62	10 11
BILP-4	1135	5.3[18]	3.6[18]	2.25	12
TFM-1	738	1.73	0.93[18]	–	13
BILP-10	787	4.0	2.5[18] 12.4[19]	1.6	14
4C	1266	–	2.28[18]	–	15
Fe-POP-1	875	4.30	–	–	16
PIM-1	899	2.53[18]	1.41[18]	–	17
Amidoxime-PIM-1	577	2.74[18]	1.65[18]	–	17
BLP-10(Cl)	924	2.7	1.41	1.3	18
BILP-3	1306	5.1[18]	3.3[18]	2.1	19
COP-1	168	–	1.36[18]	–	20
PAF-1	5300	2.06	–	1.6	21
Ni-Por-1	1711	3.13[20]	–	–	22
PAF-18-OH	1121	2.57[18]	1.52[18]	1.35	23
PAF-18-OH-Li	981	3.29[18]	2.02[18]	1.65	23
PAF-1-CH2NH2	1363	4.38	–	–	24
MOP A-B2	614	2.71	1.90[21]	–	25
TPI-1	809	2.45	1.25	–	26

[1] Unless otherwise noted, CO_2 uptake was reported at 1 atm. High pressure data, where available, highlighted in red.
[2] At 34.7 bar
[3] At 57.2 bar
[4] At 298 K and 80 bar

[5] CO_2 uptake at 273 K / 1 atm was not reported explicitly. The value given in the table is calculated by interpolation from the figure.
[6] CO_2 uptake at 298 K / 1 atm was not reported explicitly. The value given in the table is calculated by interpolation from the figure.
[7] Reported values were in mg/g unit. 188 mg/g and 131 mg/g at 273 K and 298 K, respectively.
[8] Reported value was 19 mg/g at 77 K. Converted to wt.% by using the equation [mass hyd / (mass hyd + mass sample)].
[9] At 295 K and 50 bar.
[10] CO_2 uptake at 273 K / 1 atm was not reported explicitly. The value given in the table is calculated by interpolation from the figure.
[11] At 295 K.
[12] At 293 K and 1 bar
[13] At 1 bar
[14] At 1 bar
[15] At 1 bar. The value given in the table is calculated by interpolation from the figure.
[16] At 1 bar
[17] At 18 bar
[18] The value given in the table is calculated by interpolation from the figure.
[19] At 40 bar.
[20] At 1.08 bar
[21] At 293K / 1 atm

Dual site Langmuir Freundlich (DSLF) equation is given in Eq. S1.[27]

$$q = \frac{q_{sat,A} b_A p^{\alpha_A}}{1 + b_A p^{\alpha_A}} + \frac{q_{sat,B} b_B p^{\alpha_B}}{1 + b_B p^{\alpha_B}} \quad \text{(S1)}$$

where 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 dimensionless Langmuir-Freundlich exponent for two adsorption sites A and B.

DSLF fitting parameters were calculated by Igor Pro software using curve fitting toolbar.

Table S2. DSLF fitting parameters for hydrogen, carbon dioxide and nitrogen adsorption isotherms given in Figs. S10, S11 and S12, respectively.

DSLF parameters	**Hydrogen**		**Carbon dioxide**		**Nitrogen**	
	77 K	**87 K**	**273 K**	**298 K**	**273 K**	**298 K**
$q_{sat,A}$	153.54	107.37	15.992	120.9	18.606	2.6122
$q_{sat,B}$	321.88	274.82	160.04	47.811	9.814	3.2054
b_A	4.7669	3.7793	1.7692	0.22016	0.21909	0.95116
b_B	0.41514	0.33141	0.80414	1.7901	1.8447	1.9993
α_A	0.90285	1.0114	4.6664	2.0961	2.9267	2.9875
α_B	1.3682	1.4997	1.074	1.1917	1.2737	1.2322

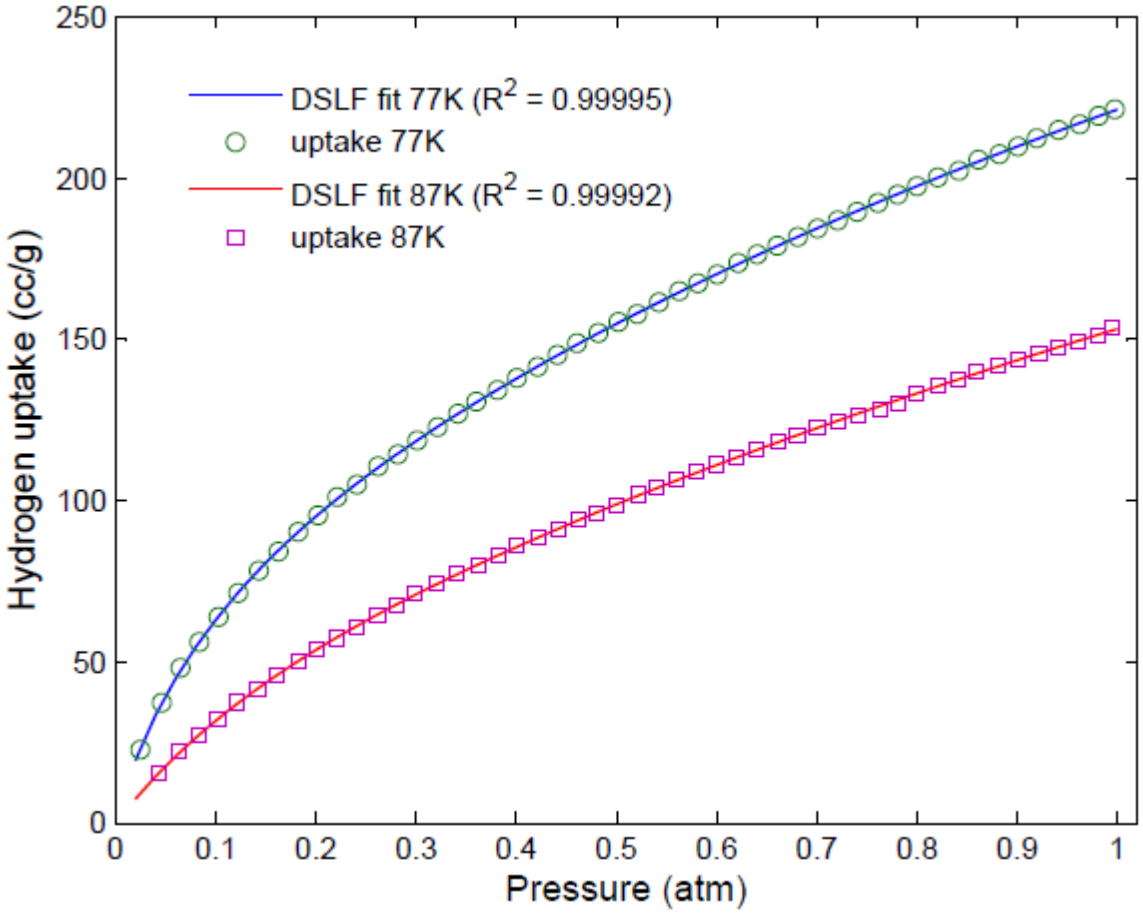

Fig. S10. Dual site Langmuir Freundlich (DSLF) fits to hydrogen uptake at 77 K and 87 K.

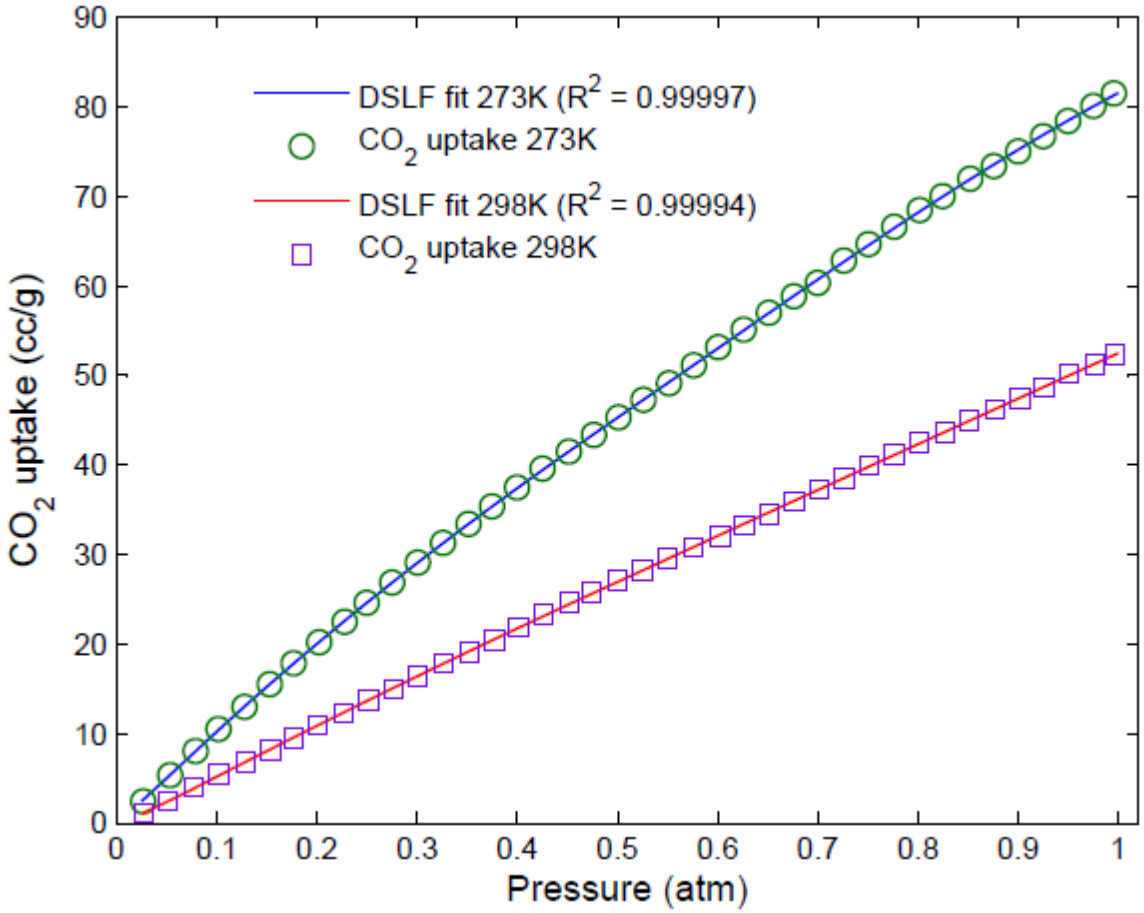

Fig. S11. Dual site Langmuir Freundlich (DSLF) fits to the CO_2 adsorption data at 273 K and 298 K.

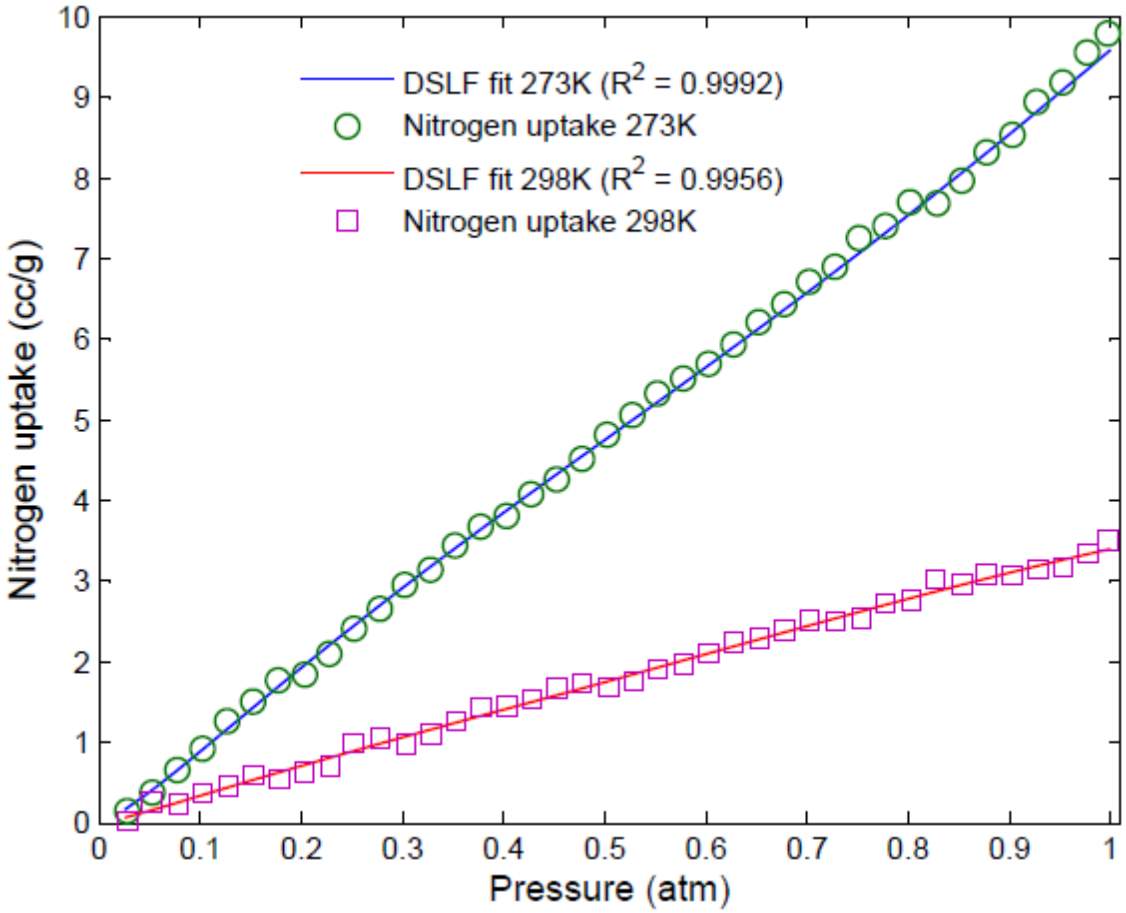

Fig. S12. Dual site Langmuir Freundlich fits to the nitrogen adsorption data at 273 K and 298 K.

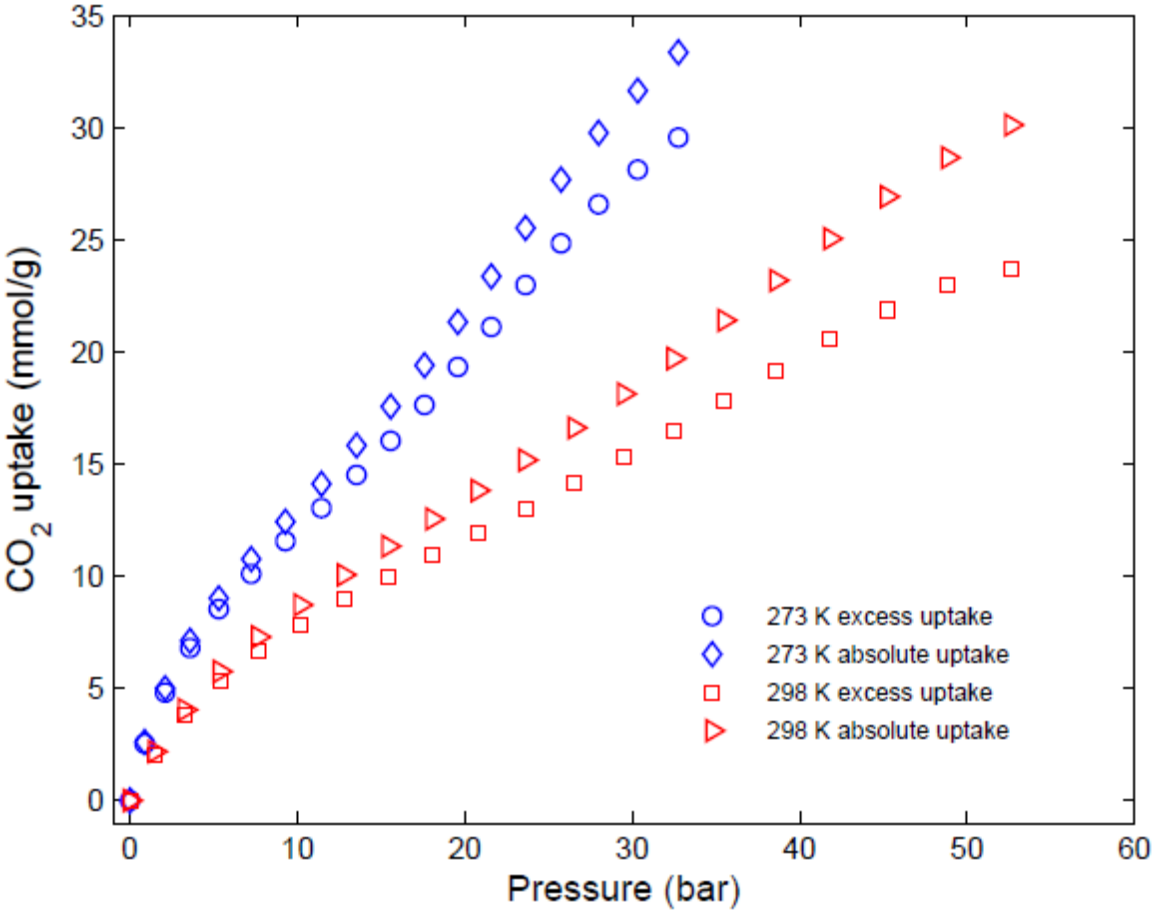

Fig. S13. Absolute and excess CO_2 gravimetric capacities of NPAF at 273 K and 298 K.

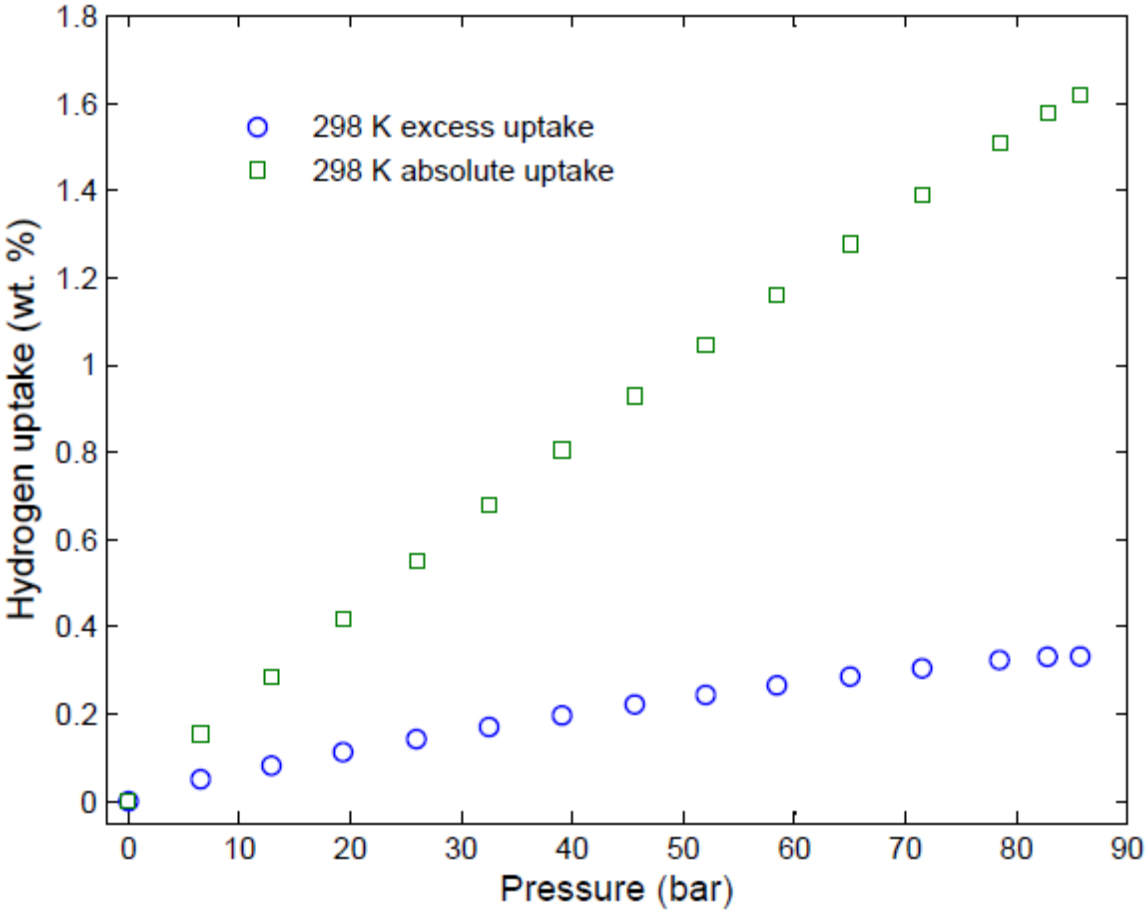

Fig. S14. Absolute and excess hydrogen gravimetric capacities of NPAF at 298 K.

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