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Electronic Supplementary Information

Synthesis and Evaluation of Porous Azo-Linked Polymers for Carbon Dioxide Capture and Separation

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Contents

Table S1. The effect of amount of catalyst on surface area of ALP-7.[a]

Entry	CuBr (mg)	Pyridine (mg)	Surface area (m^2 g^{-1})[b]
1	20	80	60
2	40	160	400
3	80	320	100
4	80	160	390
5	60	160	380
6	60	120	240
7	40	120	370
8	30	80	230

[a]Reaction conditions: monomer (100 mg), THF (11 ml), toluene (11 ml), stirred at 25 °C for 24 h, at 60 °C for 12 h, and at 80 °C for 12 h. [b]BET surface areas were calculated from N_2 adsorption isotherms collected by NOVA (*Quantachrome*).

Fig. S1 FT-IR spectra of ALP-5 and its corresponding monomer (TASBF).

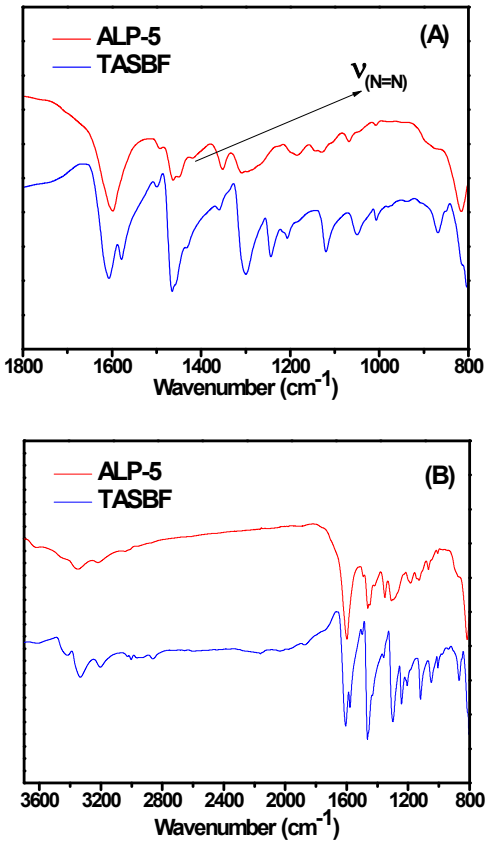

Fig. S2 FT-IR spectra of ALP-6 and its corresponding monomer (TAPPA).

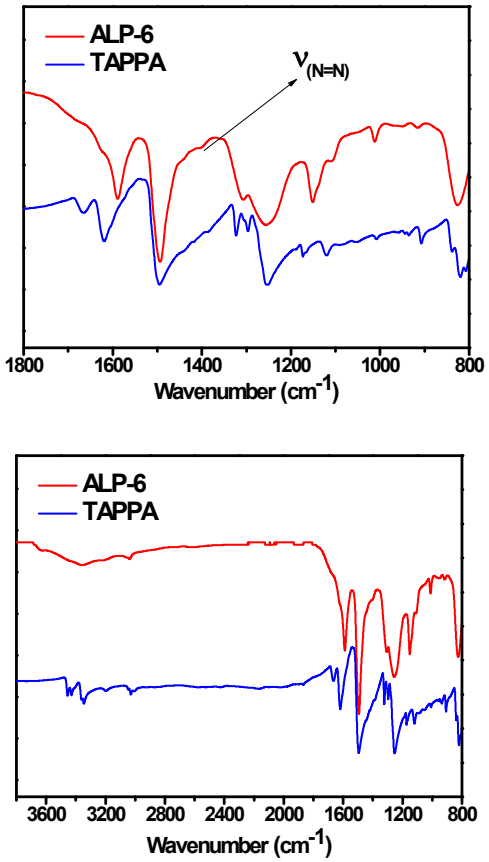

Fig. S3 FT-IR spectra of ALP-7 and its corresponding monomer (TAPA).

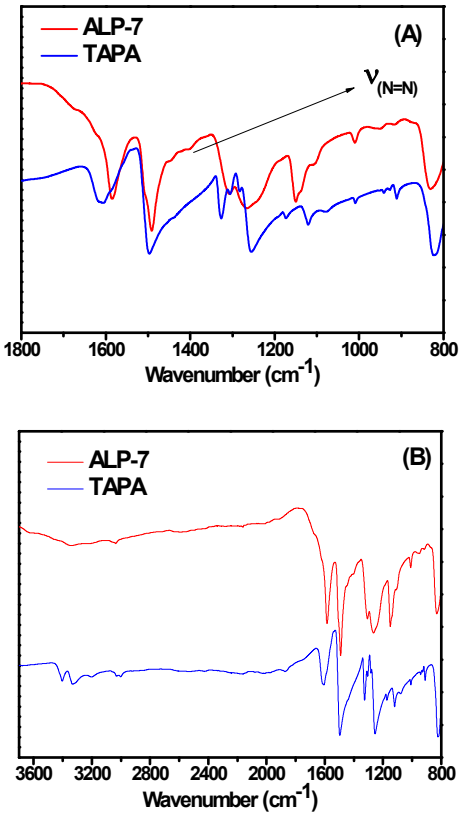

Fig. S4 FT-IR spectra of ALP-8 and its corresponding monomer (TAPE).

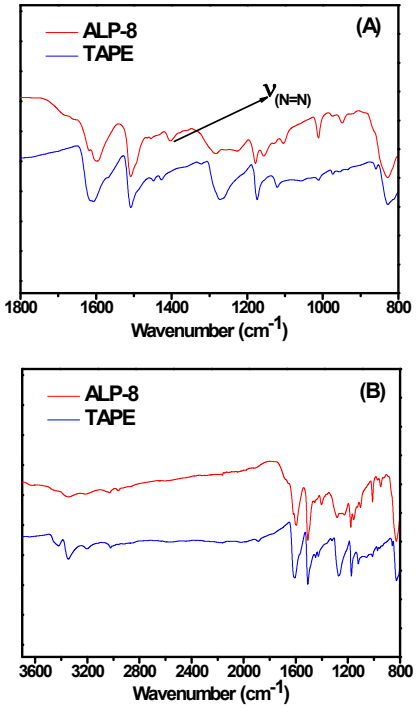

Fig. S5 Solid state ^{13}C CP-MAS NMR spectrum of ALP-5. Asterisks denote spinning side-bands.

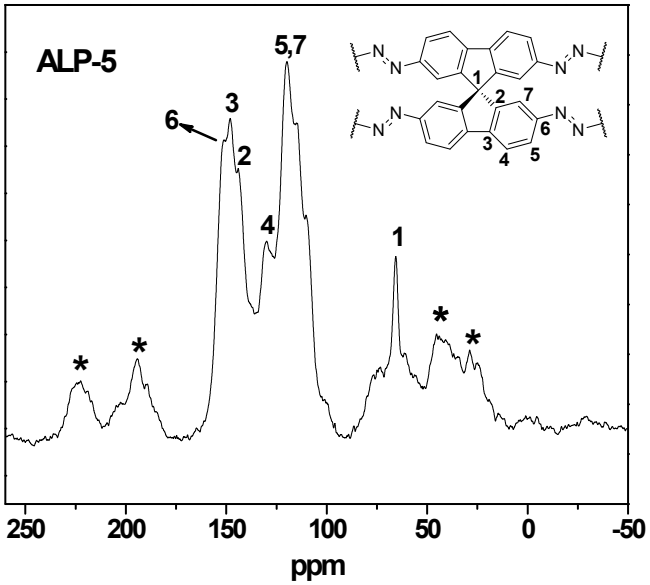

Fig. S6 Solid state ^{13}C CP-MAS NMR spectrum of ALP-6. Asterisks denote spinning side-bands.

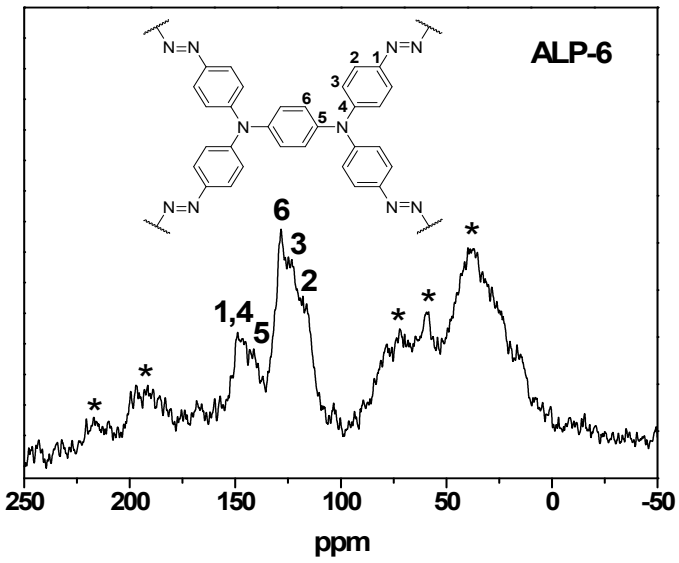

Fig. S7 Solid state ^{13}C CP-MAS NMR spectrum of ALP-7. Asterisks denote spinning side-bands.

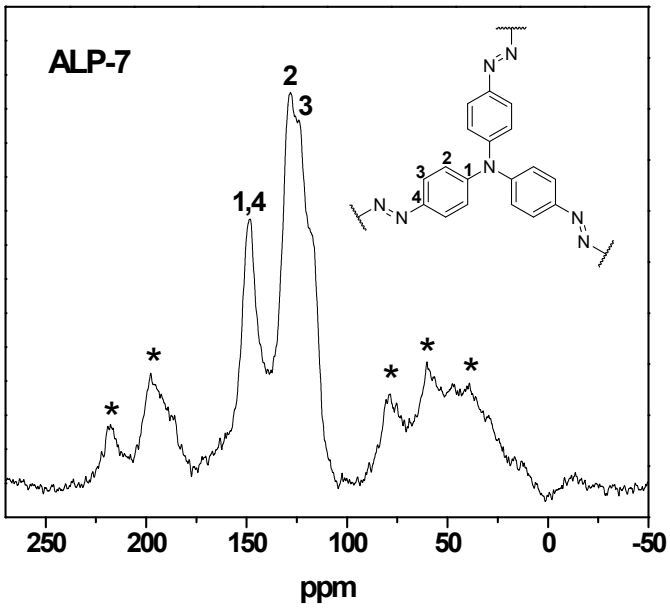

Fig. S8 Solid state ^{13}C CP-MAS NMR spectrum of ALP-8. Asterisks denote spinning side-bands.

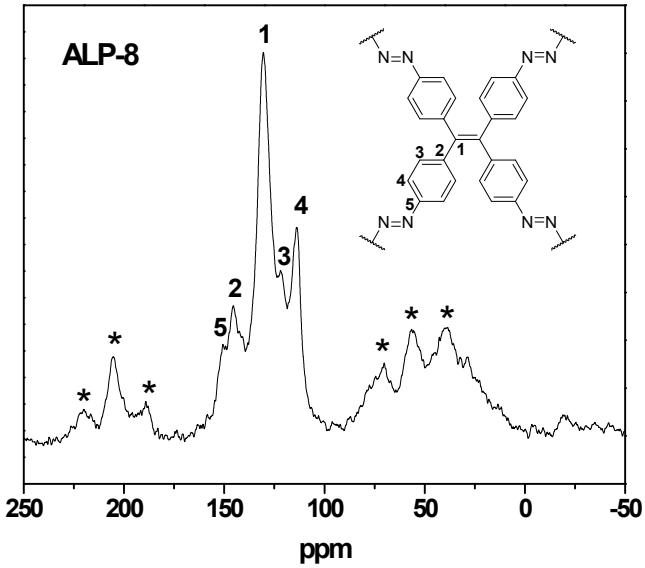

Fig. S9 SEM image of ALP-5.

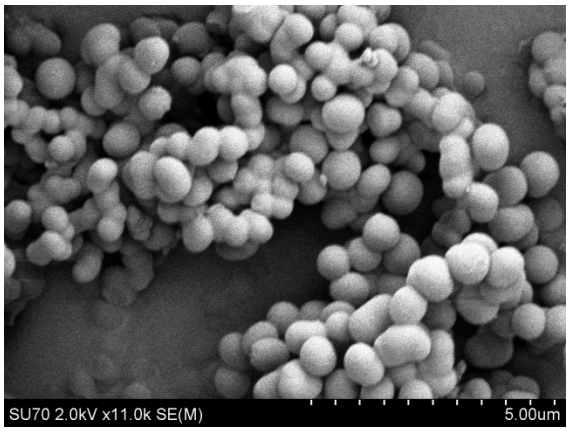

Fig. S10 SEM image of ALP-6.

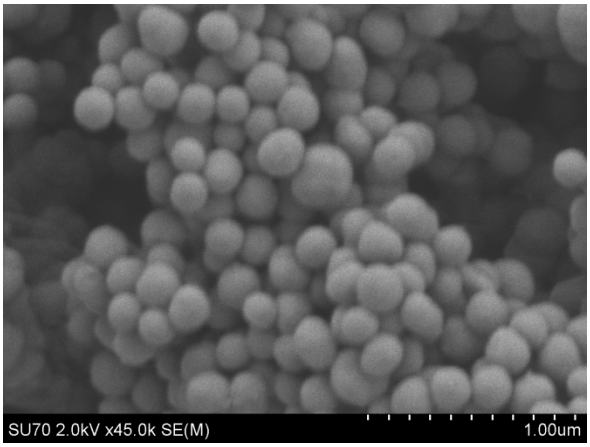

Fig. S11 SEM image of ALP-7.

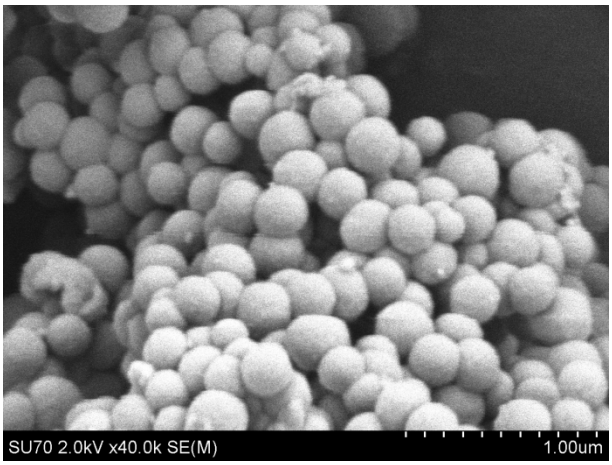

Fig. S12 SEM image of ALP-8.

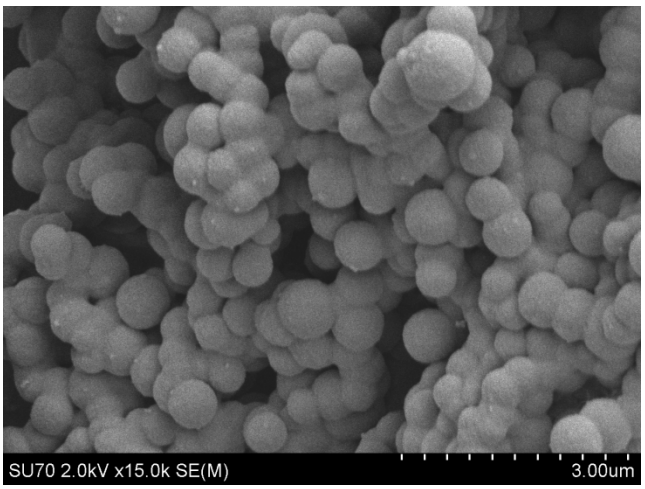

Fig. S13 PXRD pattern of ALPs.

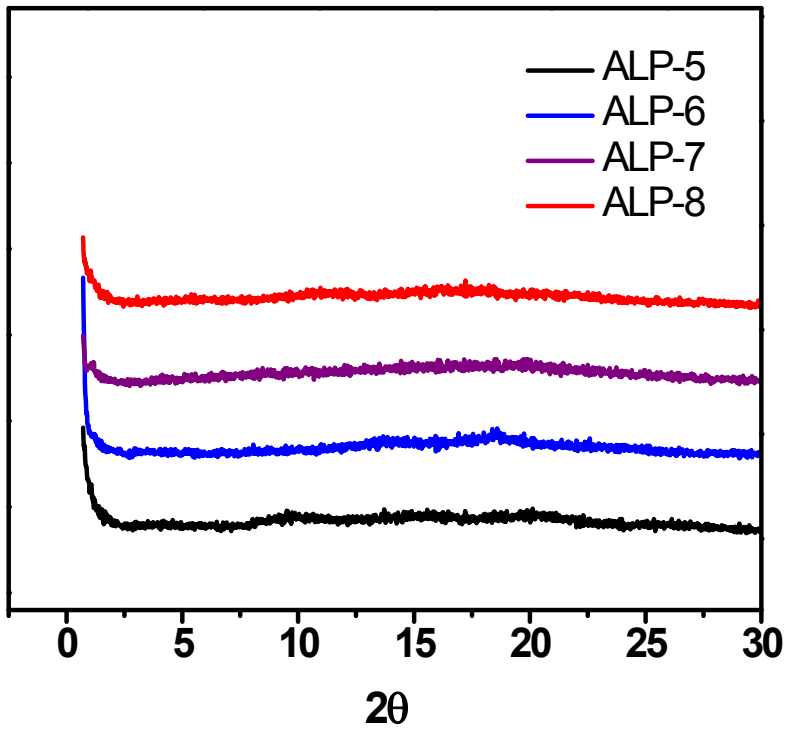

Fig. S14 TGA traces of ALPs.

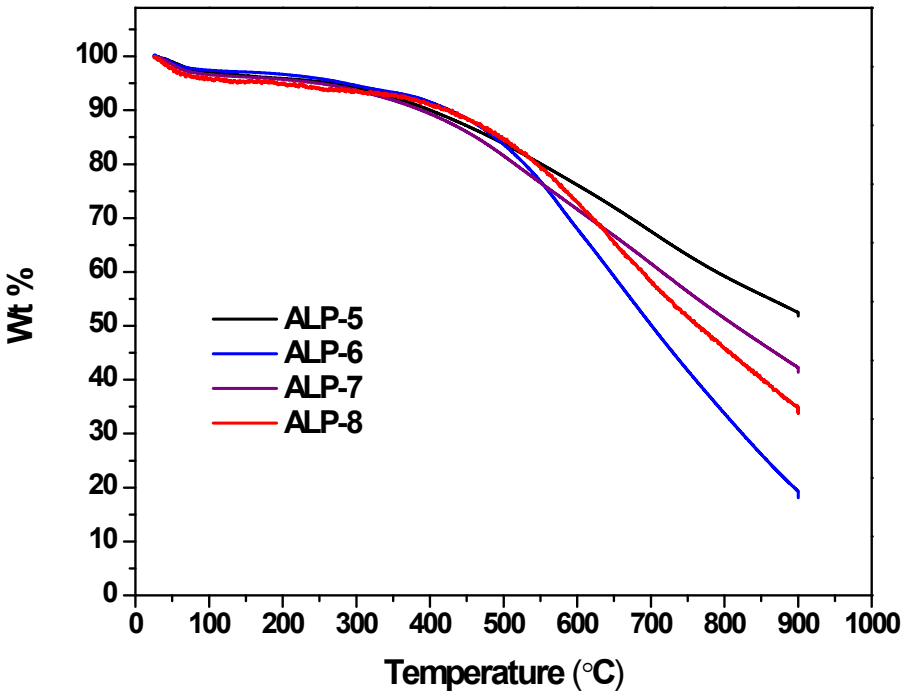

Fig. S15 BET plots for ALPs.

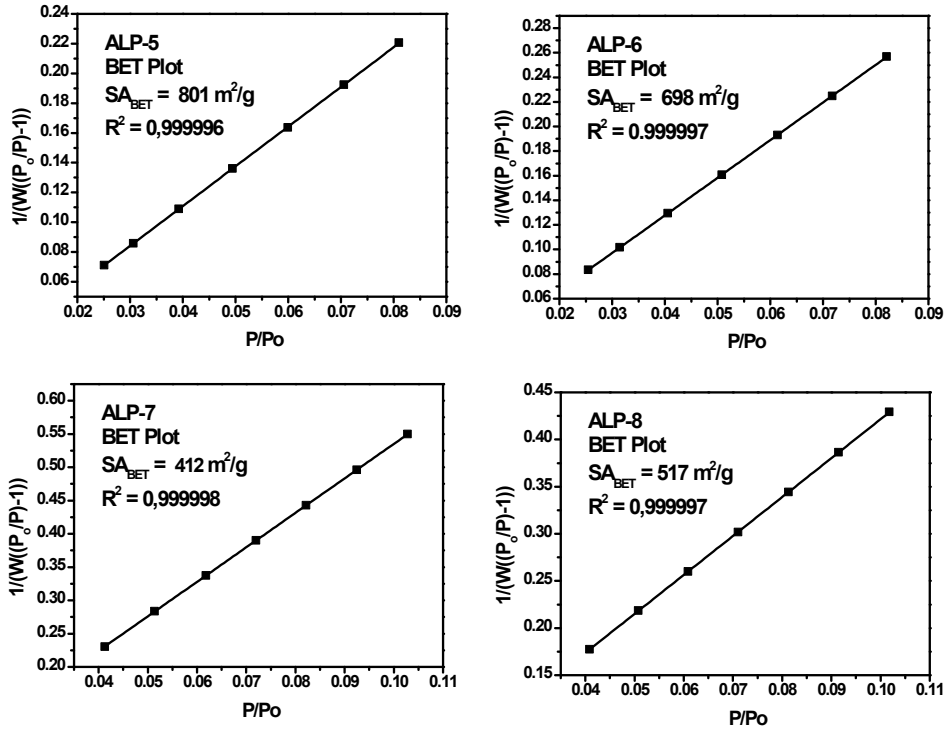

Fig. S16 Langmuir plots for ALPs.

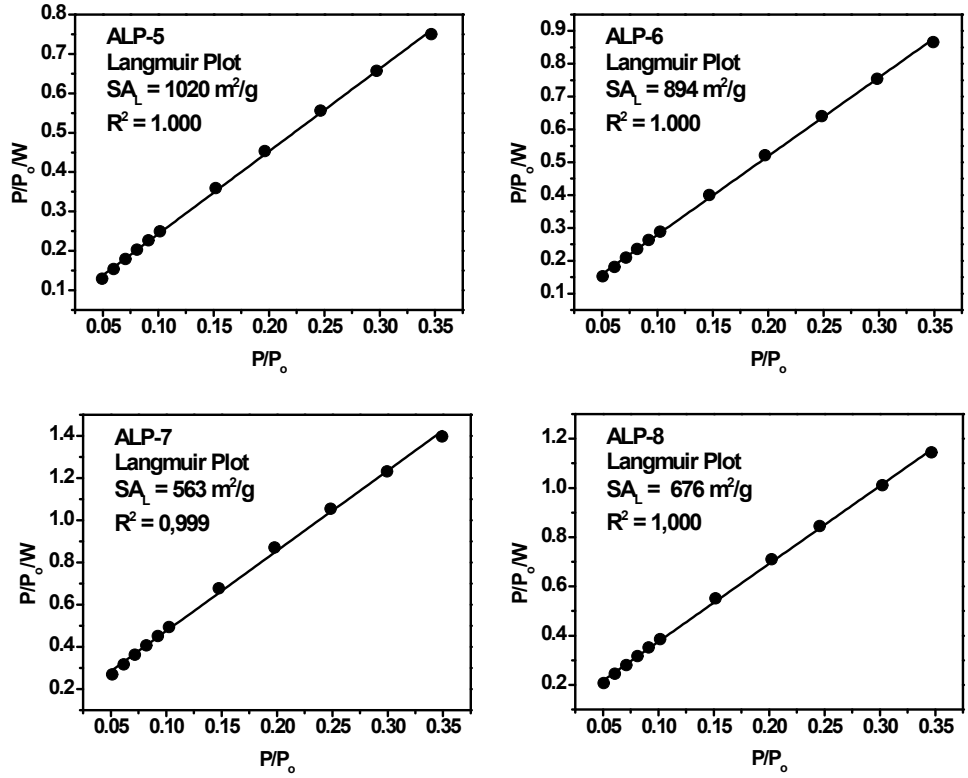

Fig. S17 Pore size distribution of ALPs calculated from Ar adsorption branch using NLDFT (spherical/cylindrical model).

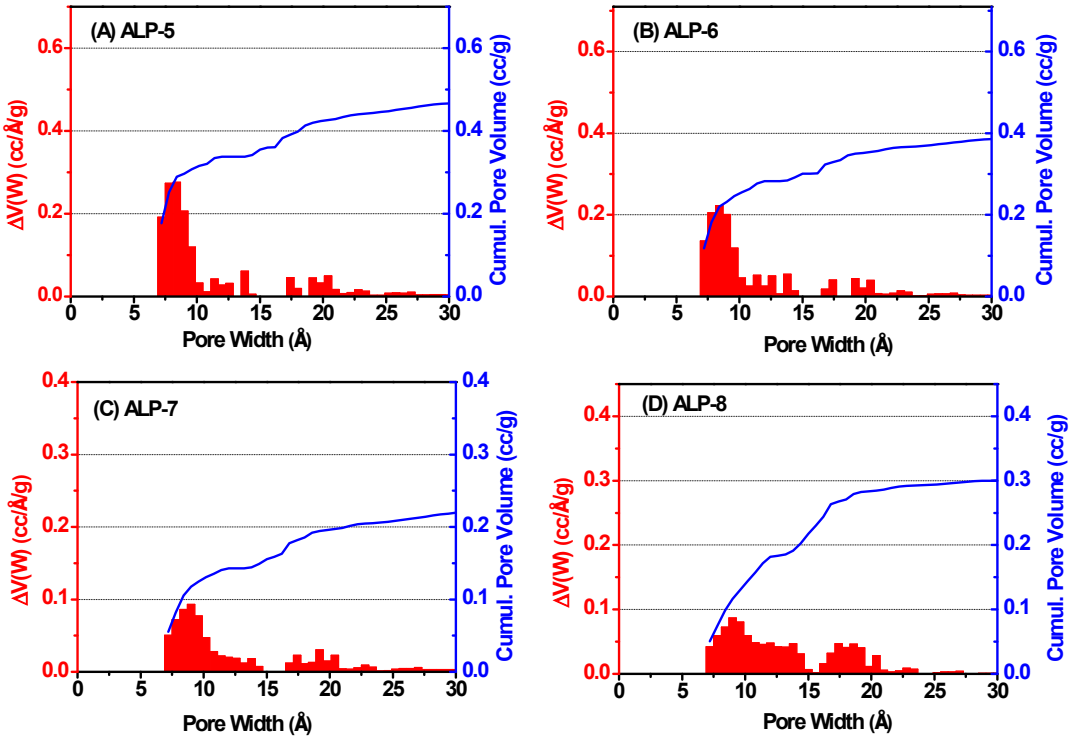

Fig. S18 CO_2, CH_4, and N_2 adsorption isotherms of ALPs at 298 K.

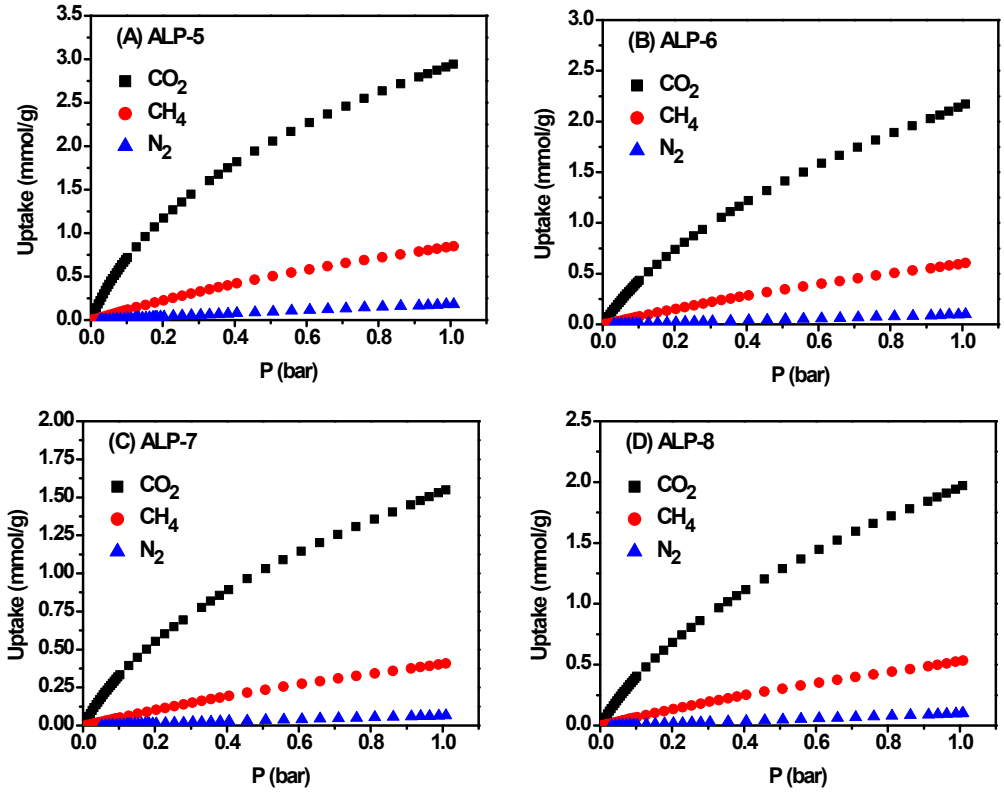

Table S2. Porosity parameters for ALPs.

Polymer	SA_{BET} [a]	Dominant pore size (nm)[b]	Total Pore Volume [c]	Ref.
ALP-1	1235	1.0	0.66	[1]
ALP-2	1065	1.1	0.57	[1]
ALP-3	975	1.3	0.63	[1]
ALP-4	862	1.1	0.50	[1]
ALP-5	801	0.80	0.39	This Work
ALP-6	698	0.85	0.36	This Work
ALP-7	412	0.90	0.27	This Work
ALP-8	517	0.92	0.25	This Work

[a]Surface area ($m^2\ g^{-1}$) calculated from the Ar adsorption branch according to the BET model. [b]Pore size distributions (PSDs) were estimated from the adsorption branch of the Ar isotherms by NLDFT. [c]The total pore volume ($cm^3\ g^{-1}$) calculated from single point Ar uptake at P/Po= 0.90.

Table S3. CO_2, CH_4, and N_2 uptakes, and isosteric heats of adsorption (Q_{st}) for ALPs.

Polymer	CO_2 Uptake at 1 bar[a]			CH_4 Uptake at 1 bar[a]			N_2 Uptake at 1 bar[a]		Ref.
	273 K	298 K	Q_{st}[b]	273 K	298 K	Q_{st}[b]	273 K	298 K	
ALP-1	5.4	3.3	29.2	1.6	0.94	20.8	0.41	0.21	[1]
ALP-2	4.8	2.4	27.9	1.1	0.67	18.5	0.31	0.14	[1]
ALP-3	3.8	2.3	29.6	1.1	0.60	21.0	0.25	0.12	[1]
ALP-4	3.5	1.8	28.2	0.89	0.52	21.2	0.24	0.12	[1]
ALP-5	4.5	2.9	32.5	1.4	0.85	22.4	0.40	0.18	This Work
ALP-6	3.4	2.2	28.6	1.0	0.60	19.0	0.25	0.10	This Work
ALP-7	2.5	1.5	30.7	0.73	0.40	22.2	0.19	0.06	This Work
ALP-8	3.0	2.0	29.4	0.90	0.53	20.0	0.21	0.10	This Work

[a]Uptake in mmol g^{-1}.[b]Isosteric enthalpies of adsorption (Q_{st}) in kJ mol^{-1}at zero coverage.

Table S4. Surface area, CO_2 uptake, and isosteric heat of adsorption of porous azo-linked polymers.

Polymer	Surface area[a]	CO_2 uptakeat 1 bar[b]		Q_{st} for CO_2[c]	Reference
		273 K	298 K		
ALP-1	1235	5.4	3.3	29.2	[1]
ALP-2	1065	4.8	2.4	27.9	[1]
ALP-3	975	3.8	2.3	29.6	[1]
ALP-4	862	3.5	1.8	28.2	[1]
ALP-5	801	4.5	2.9	32.5	This Work
ALP-6	698	3.4	2.2	28.6	This Work
ALP-7	412	2.5	1.5	30.7	This Work
ALP-8	517	3.0	2.0	29.4	This Work
azo-COP-1	635	2.4	1.5	29.3	[2]
azo-COP-2	729	2.6	1.5	24.8	[2]
azo-COP-3	493	1.9	1.2	32.1	[2]
azo-POF-1	712	3.0	1.9	27.5	[3]
azo-POF-2	439	1.9	1.3	26.6	[3]

[a]Surface area ($m^2\ g^{-1}$) calculated based on the BET model. [b]CO_2 uptake in mmol g^{-1}. [c]Isosteric heat of adsorption (Q_{st}) at zero coverage in kJ mol^{-1}.

Fig. S19 Virial fitting for CO_2 isotherms of ALPs.

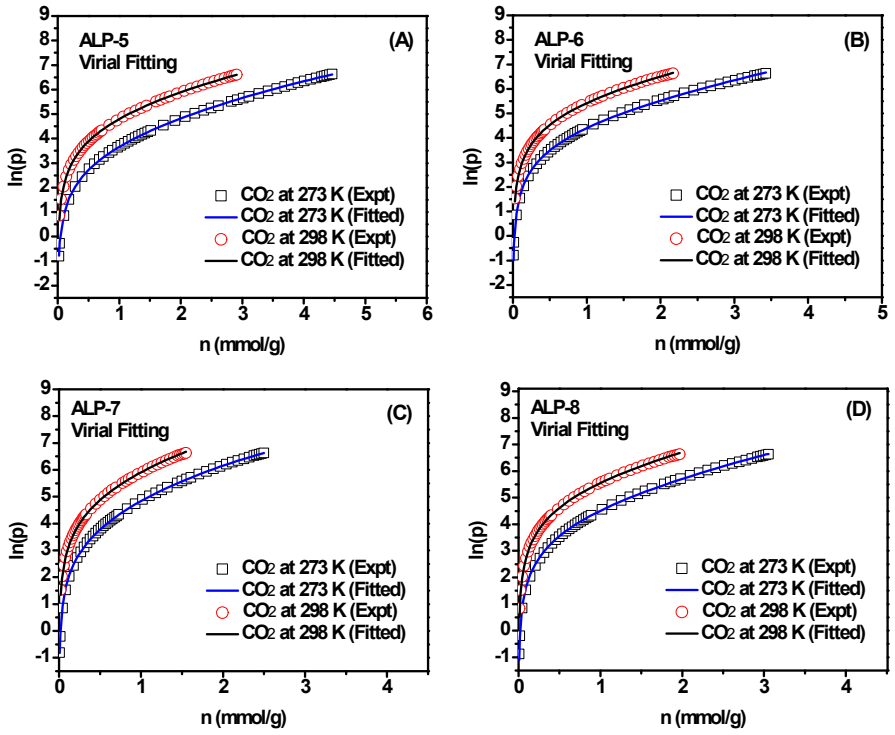

Fig. S20 Virial fitting for CH_4 isotherms of ALPs.

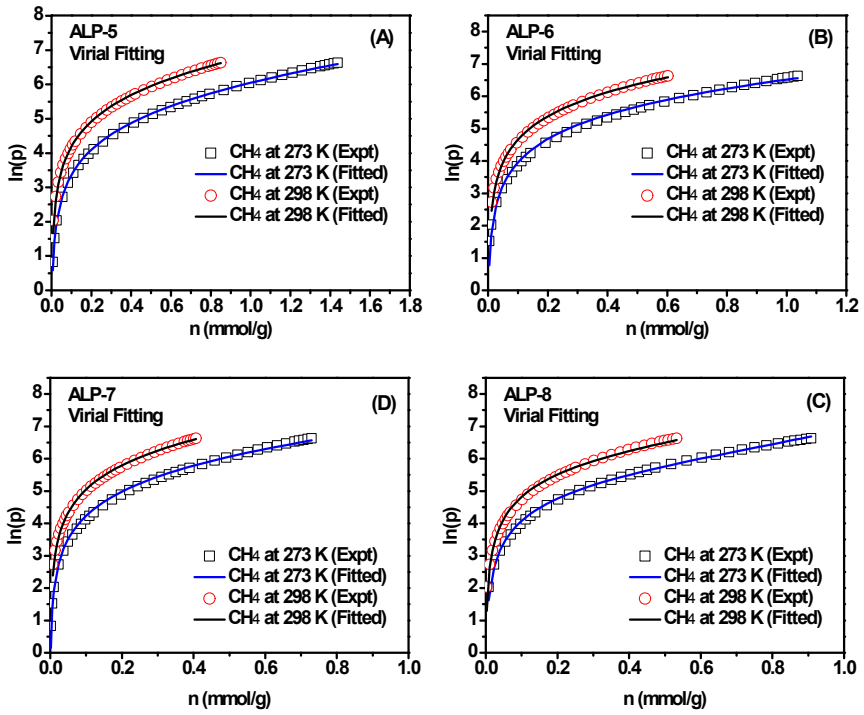

Fig. S21 Experimental data and corresponding fittings of gas isotherms for ALP-5. (Dual site Langmuir-Freundlich for CO_2, and single site Langmuir-Freundlich for CH_4 and N_2 with temperature dependent parameter at 273 and 298 K).

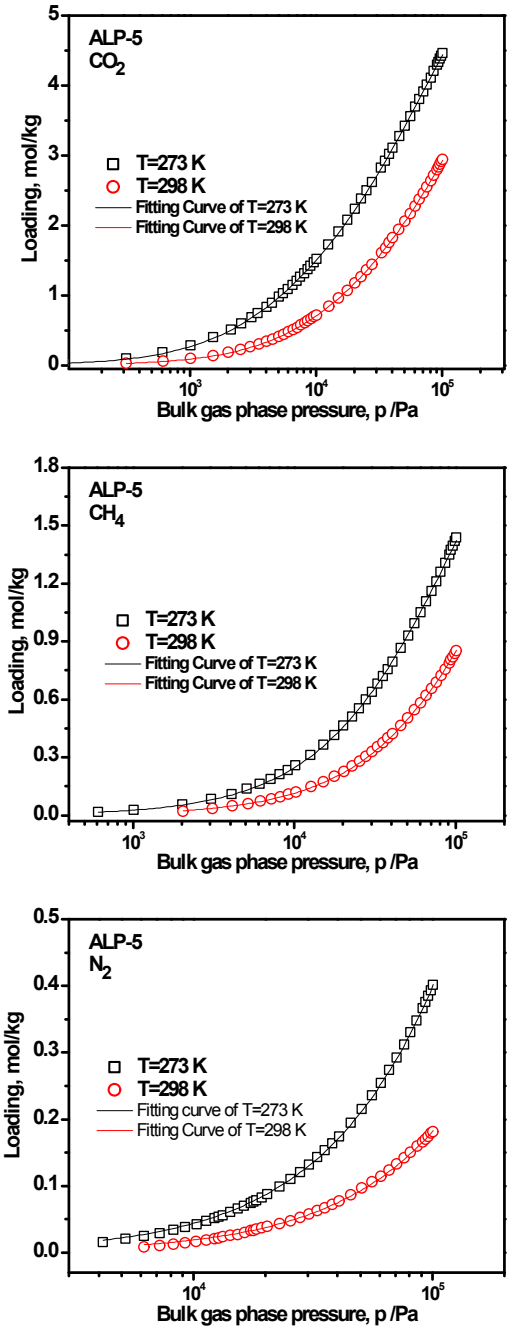

Fig. S22 Experimental data and corresponding fittings of gas isotherms for ALP-6. (Dual site Langmuir-Freundlich for CO_2, and single site Langmuir-Freundlich for CH_4 and N_2 with temperature dependent parameter at 273 and 298 K).

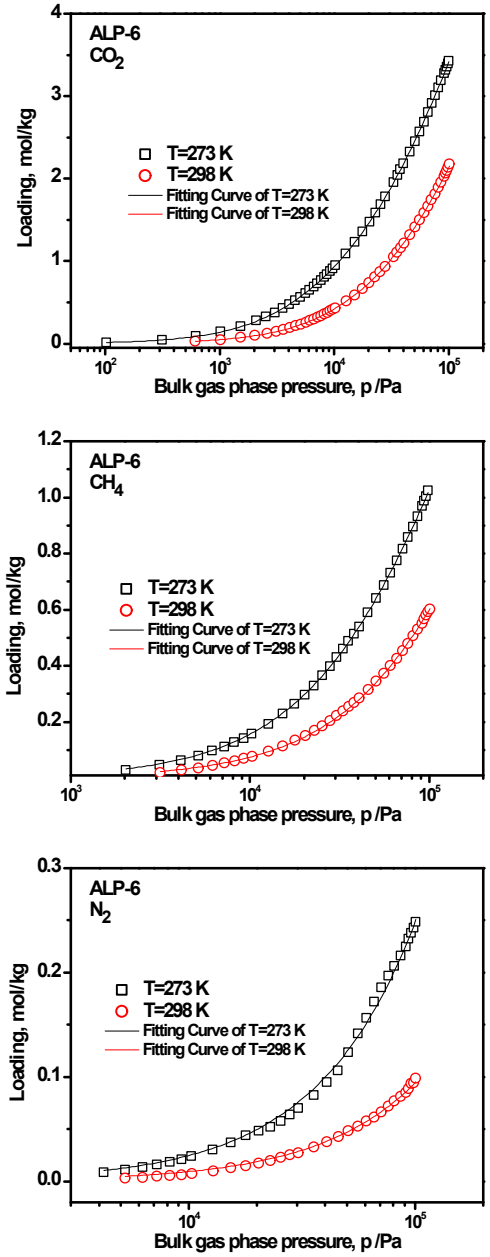

Fig. S23 Experimental data and corresponding fittings of gas isotherms for ALP-7. (Dual site Langmuir-Freundlich for CO_2, and single site Langmuir-Freundlich for CH_4 and N_2 with temperature dependent parameter at 273 and 298 K).

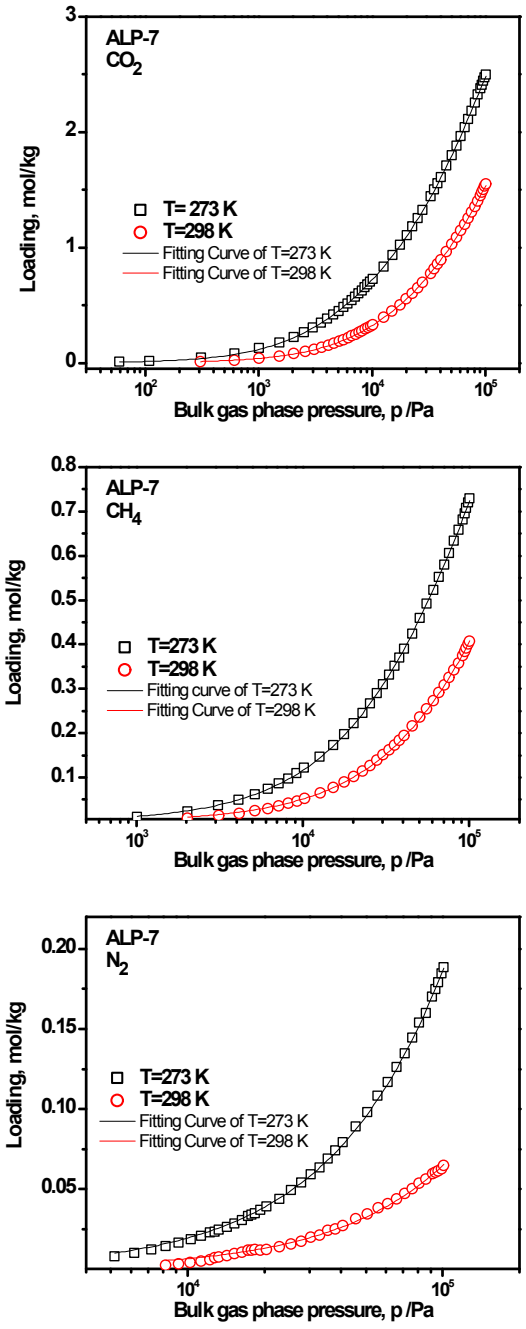

Fig. S24 Experimental data and corresponding fittings of gas isotherms for ALP-8. (Dual site Langmuir-Freundlich for CO_2, and single site Langmuir-Freundlich for CH_4 and N_2 with temperature dependent parameter at 273 and 298 K).

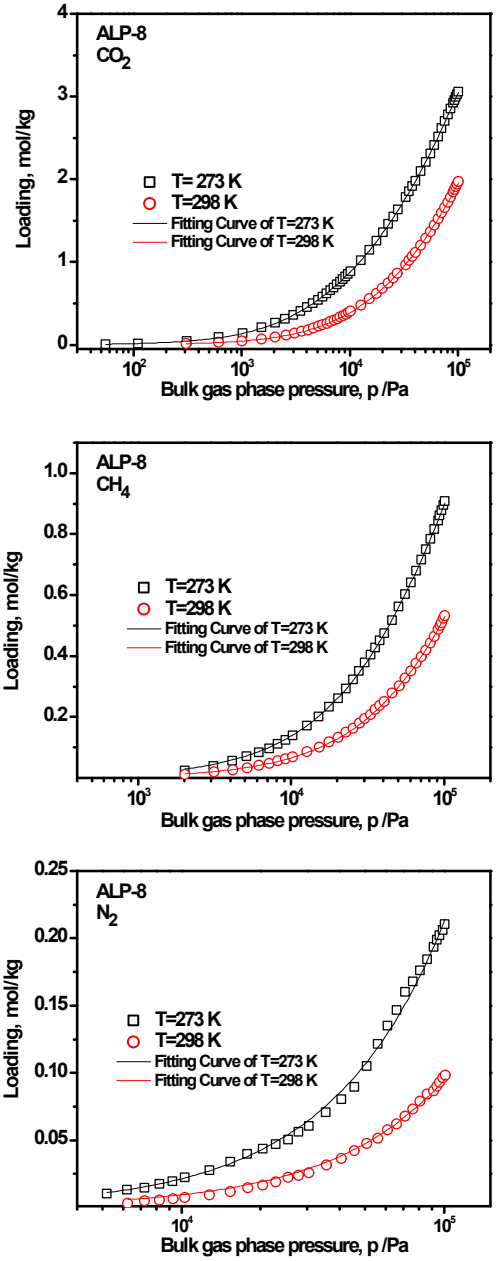

Fig. S25 High-pressure total (absolute) CO_2 uptake of ALP-1 and ALP-5 at 298 K.

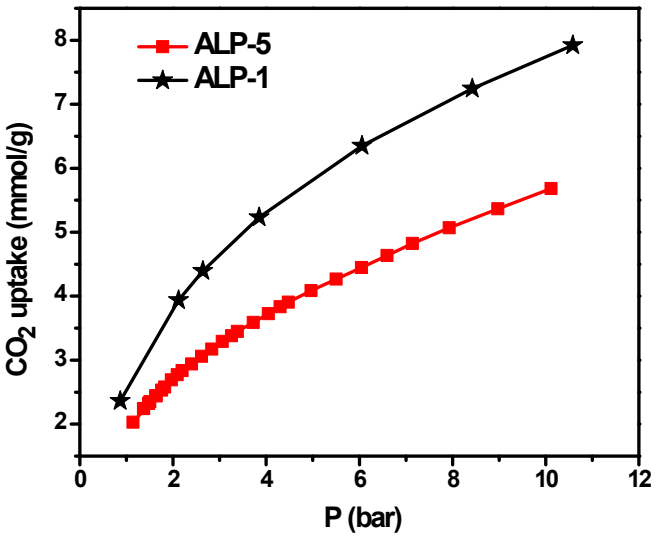

Fig. S26 High pressure total (absolute) CH_4 uptake of ALP-1 and ALP-5 at 298 K.

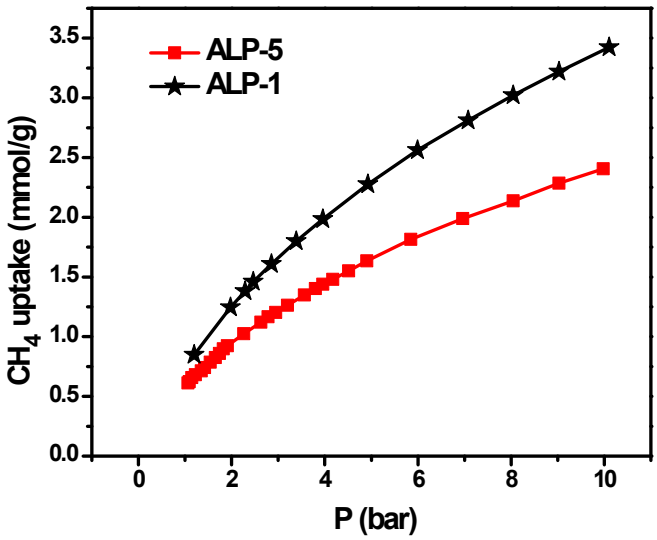

Table S5. IAST selectivity of different classes of azo-linked porous polymers.

Polymer	CO_2/N_2 selectivity at 1 bar		Reference
	273 K	298 K	
ALP-1[a]	40	28	[1]
ALP-2[a]	34	26	[1]
ALP-3[a]	44	35	[1]
ALP-4[a]	35	26	[1]
ALP-5[b]	60	47	This Work
ALP-6[b]	45	48	This Work
ALP-7[b]	52	56	This Work
ALP-8[b]	51	44	This Work
azo-COP-1[a]	64	97	[2]
azo-COP-2[a]	110	131	[2]
azo-COP-3[a]	79	96	[2]
azo-POF-1[a]	52	37	[3]
azo-POF-2[a]	55	42	[3]

[a]For CO_2:N_2 mole ratio of 15:85. [b]For CO_2:N_2 mole ratio of 10:90.

Fig. S27 Gas uptakes and initial slope selectivity studies of ALP-5.

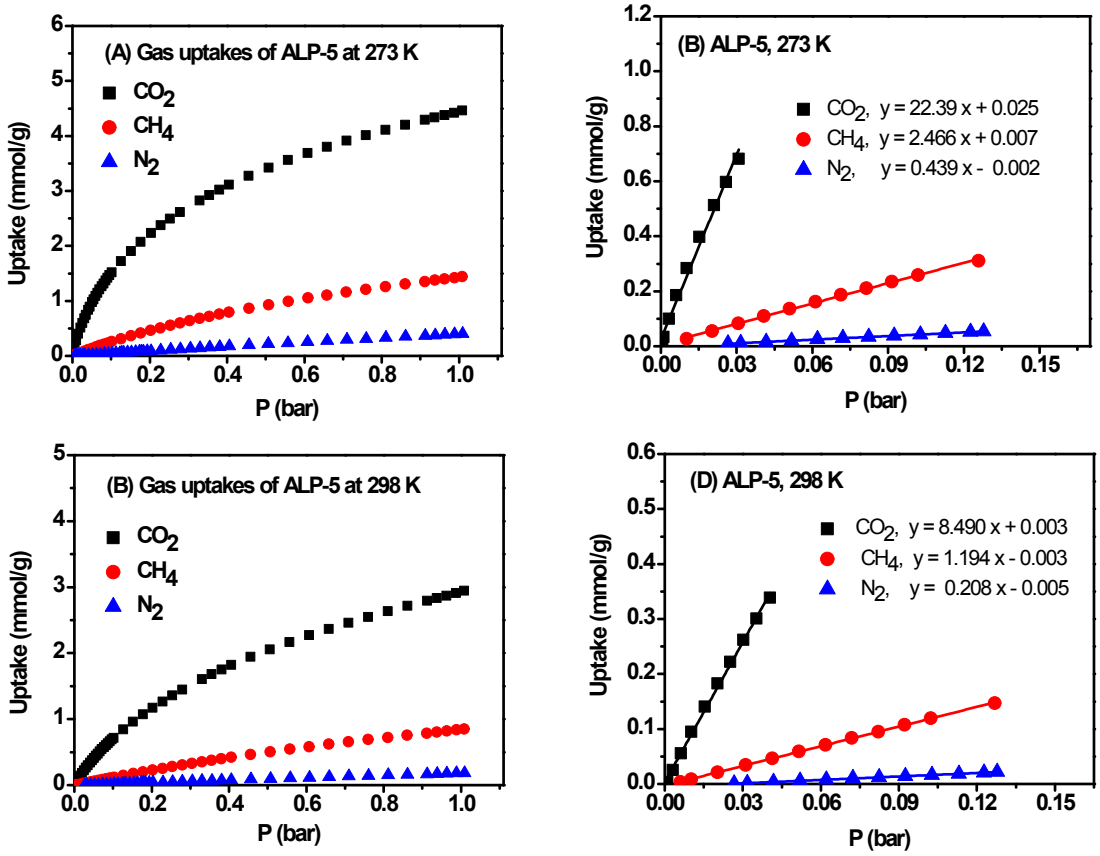

Fig. S28 Gas uptakes and initial slope selectivity studies of ALP-6.

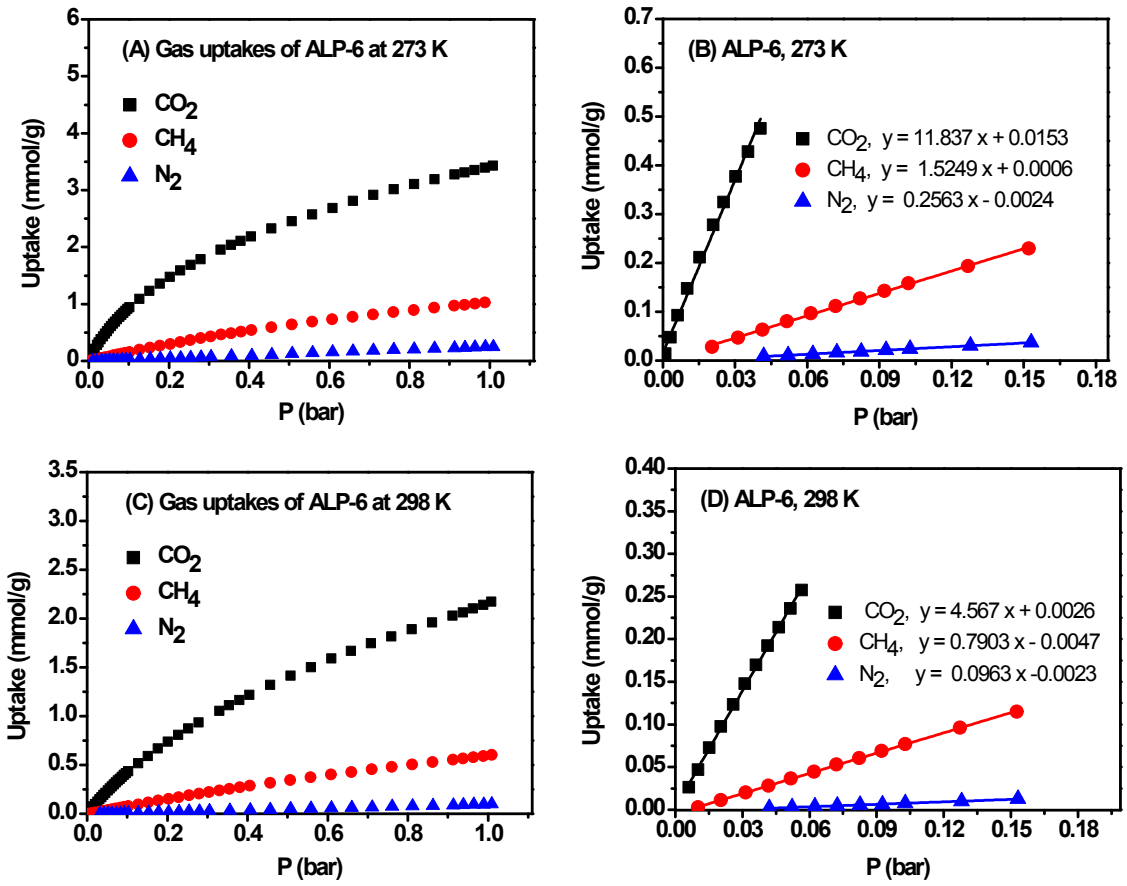

Fig. S29 Gas uptakes and initial slope selectivity studies of ALP-7.

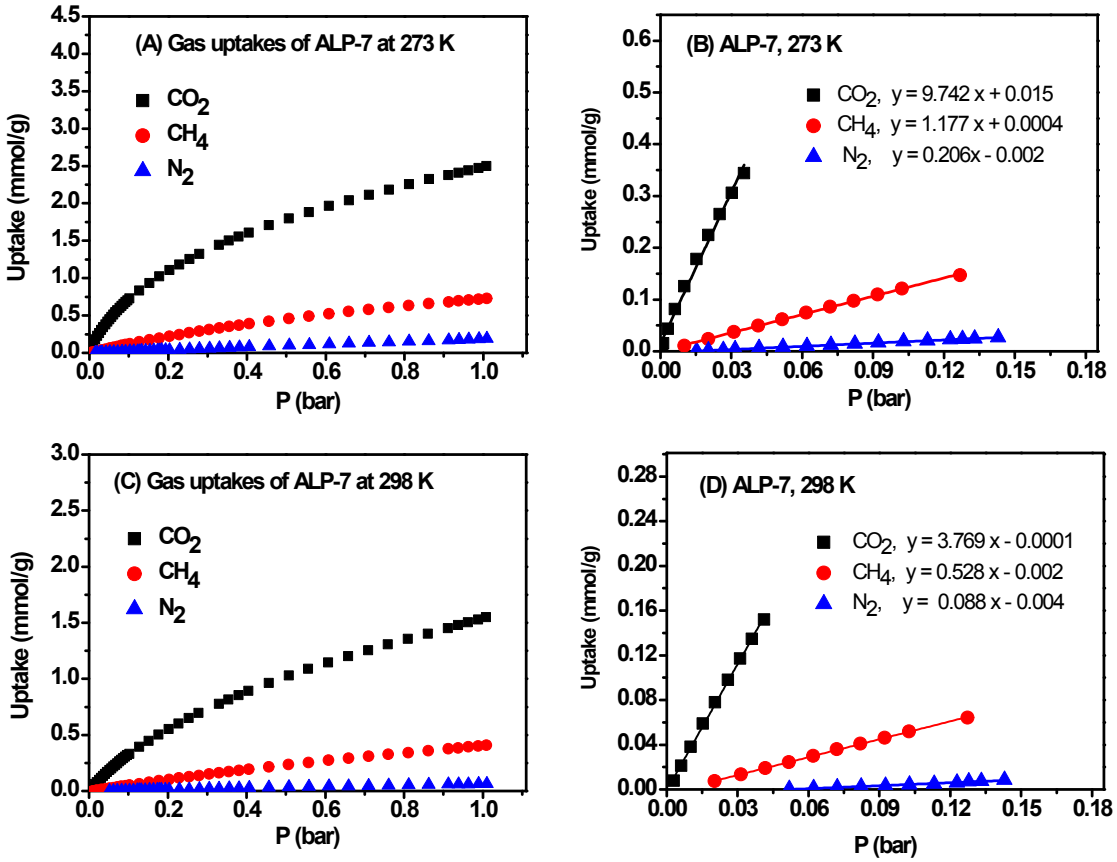

Fig. S30 Gas uptakes and initial slope selectivity studies of ALP-8.

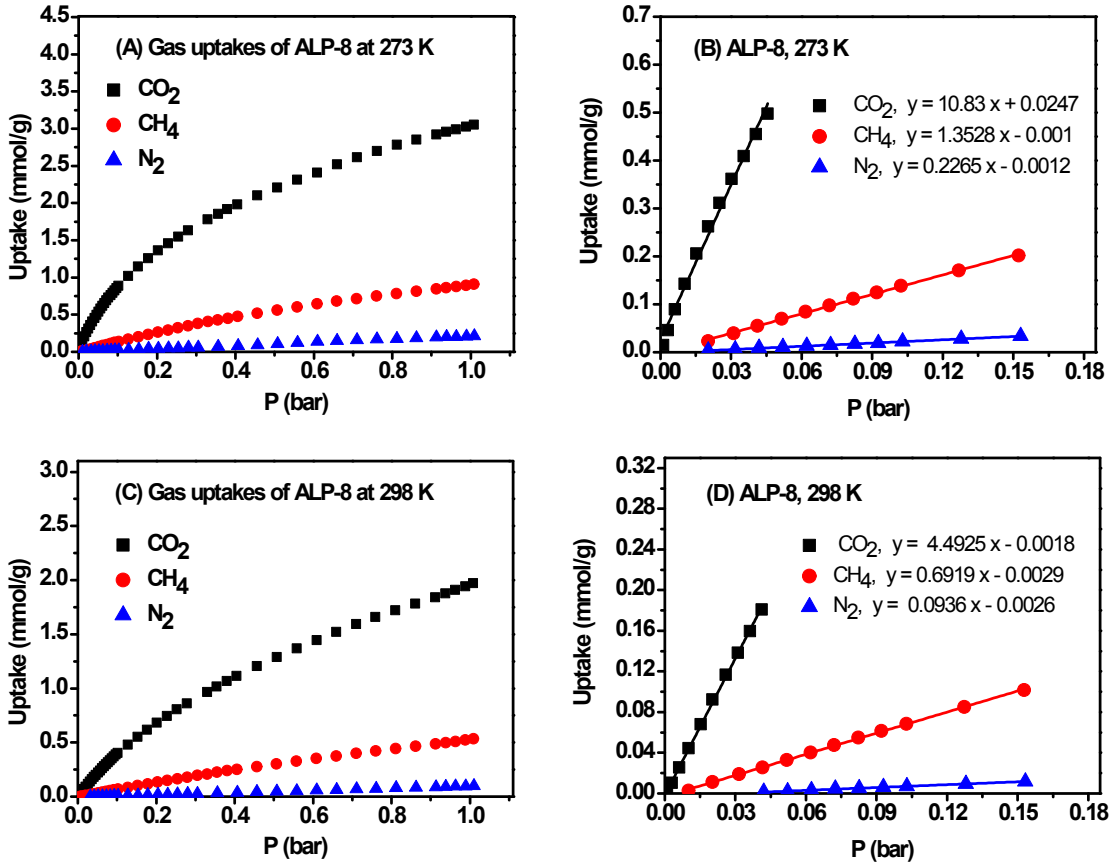

Table S6. Initial slope selectivity of ALPs.

Polymer	CO_2/N_2 Selectivity[a]		CO_2/CH_4 Selectivity[a]		Reference
	273 K	298 K	273 K	298 K	
ALP-1	35	27	6	5	[1]
ALP-5	51	41	9	**7**	This Work
ALP-6	46	47	8	6	This Work
ALP-7	47	43	8	7	This Work
ALP-8	48	48	8	6	This Work

[a](mol mol^{-1}).

References

1. P. Arab, M. G. Rabbani, A. K. Sekizkardes, T. İslamoğlu and H. M. El-Kaderi, *Chem. Mater.*, 2014, **26**, 1385-1392.
2. H. A. Patel, S. H. Je, J. Park, D. P. Chen, Y. Jung, C. T. Yavuz and A. Coskun, *Nat. Commun.*, 2013, **4**, 1357.
3. J. Lu and J. Zhang, *J. Mater. Chem. A.*, 2014, **2**, 13831-13834.