Electronic Supplementary Material (ESI) for Polymer Chemistry

Supporting Information

Robust Tri(4-ethynylphenyl)amine-based porous aromatic frameworks for carbon dioxide capture

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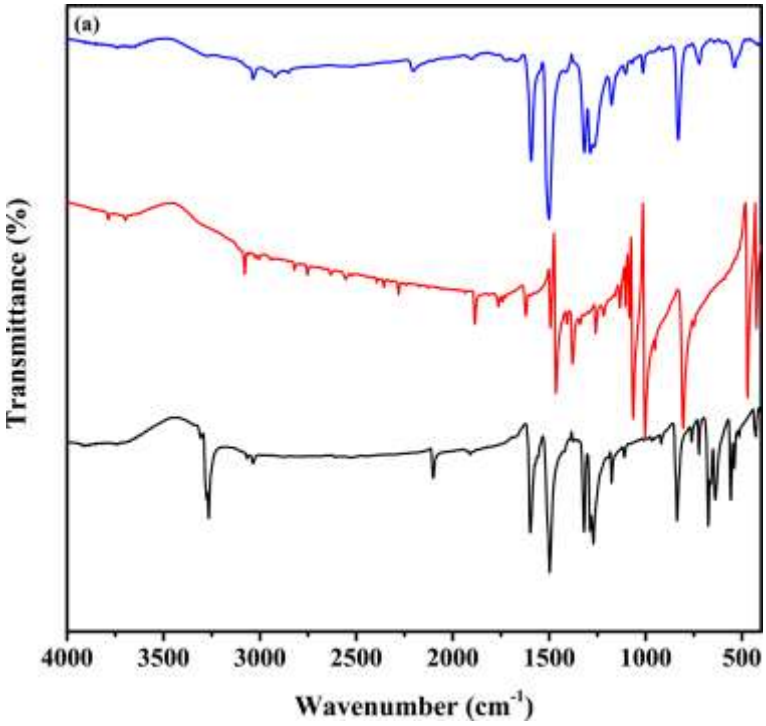

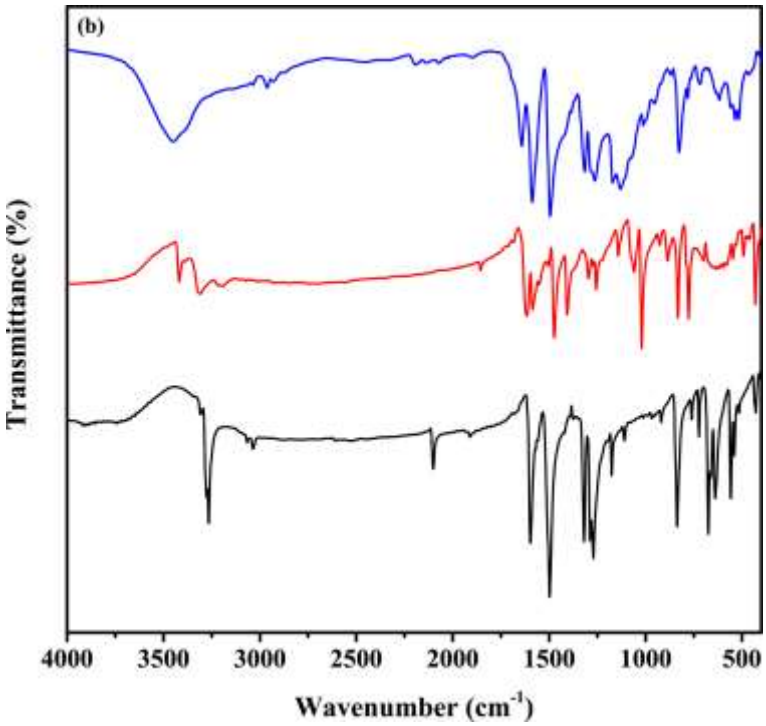

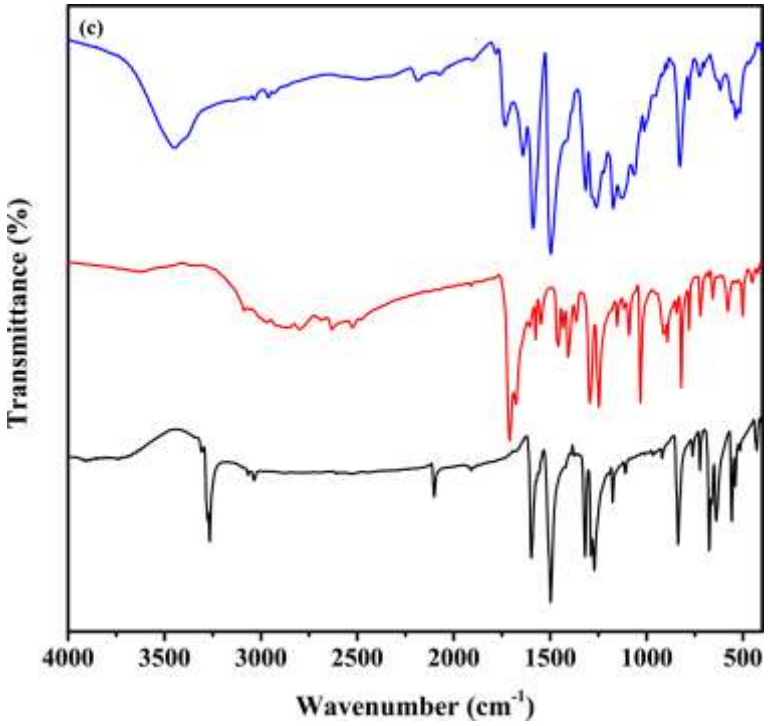

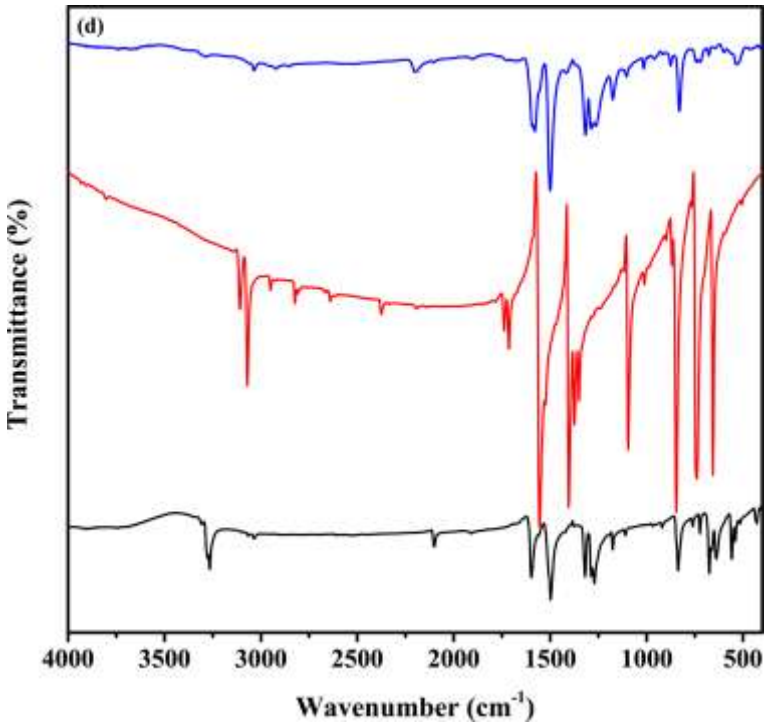

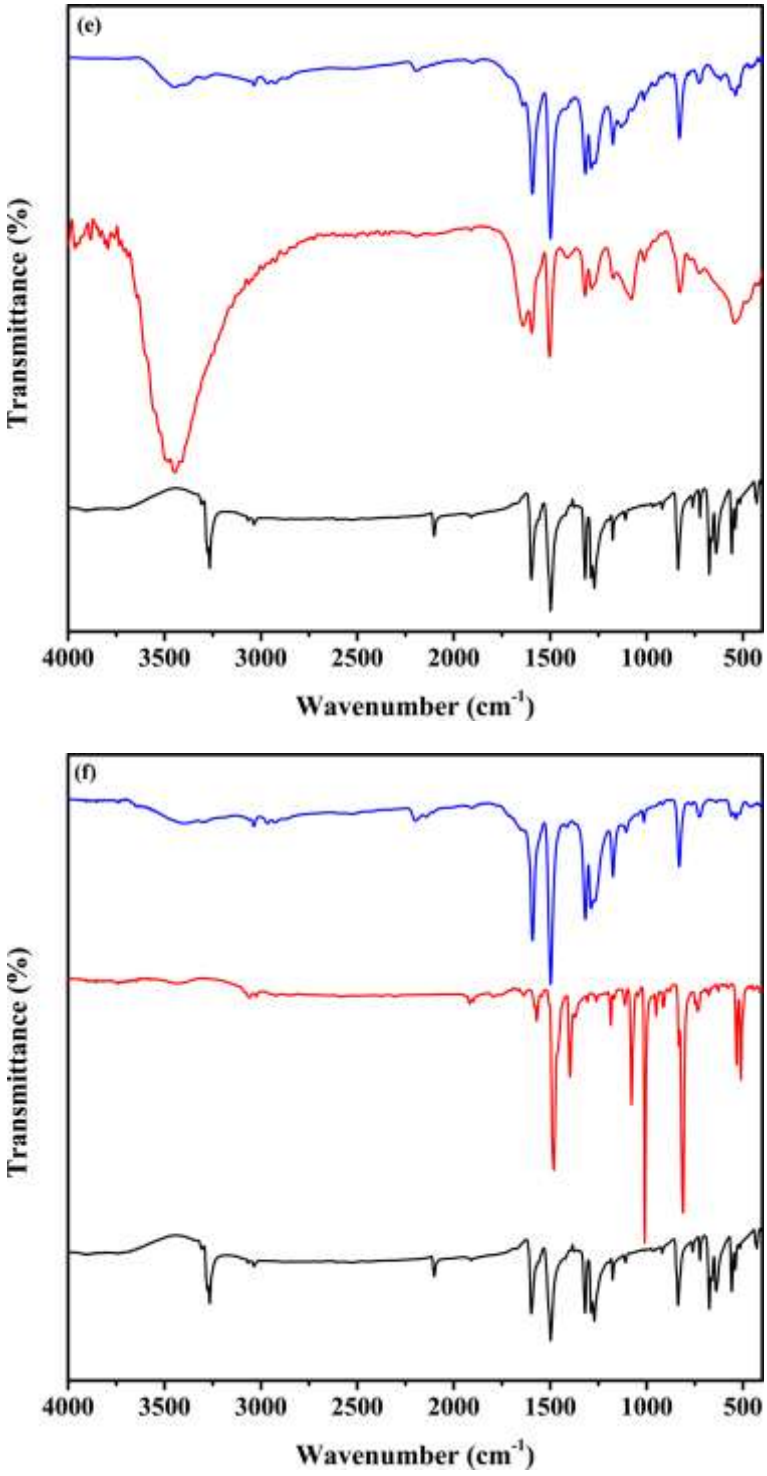

Fig. S1. FT-IR spectra of PAFs, PAF-33 (a), PAF-33-NH_2 (b), PAF-33-COOH (c), PAF-34 (d), PAF-34-OH (e) and PAF-35 (f). [PAFs (blue), Tri(4-ethynylphenyl)amine (black), aryl halides (red)].

Table S1. Characteristic peaks of functional groups in FI-IR spectra of PAFs.

PAFs	Characteristic peaks of the functional groups		
PAF-33	~2200 cm^{-1}, –C≡C– bonds vibration		
PAF-33-NH_2	~2200 cm^{-1}, –C≡C– bonds vibration	3490~3400 cm^{-1}, N-H bond vibration	1340~1250 cm^{-1}, C-N bond vibration
PAF-33-COOH	~2200 cm^{-1}, –C≡C– bonds vibration	3500~3000 cm^{-1}, COOH bond vibration	1750~1680 cm^{-1}, C-O double bond vibration
PAF-34	~2200 cm^{-1}, –C≡C– bonds vibration		
PAF-34-OH	~2200 cm^{-1}, –C≡C– bonds vibration	3500~3200 cm^{-1}, O-H bond vibration	1300~1200 cm^{-1}, C-O bond vibration
PAF-35	~2200 cm^{-1}, –C≡C– bonds vibration		

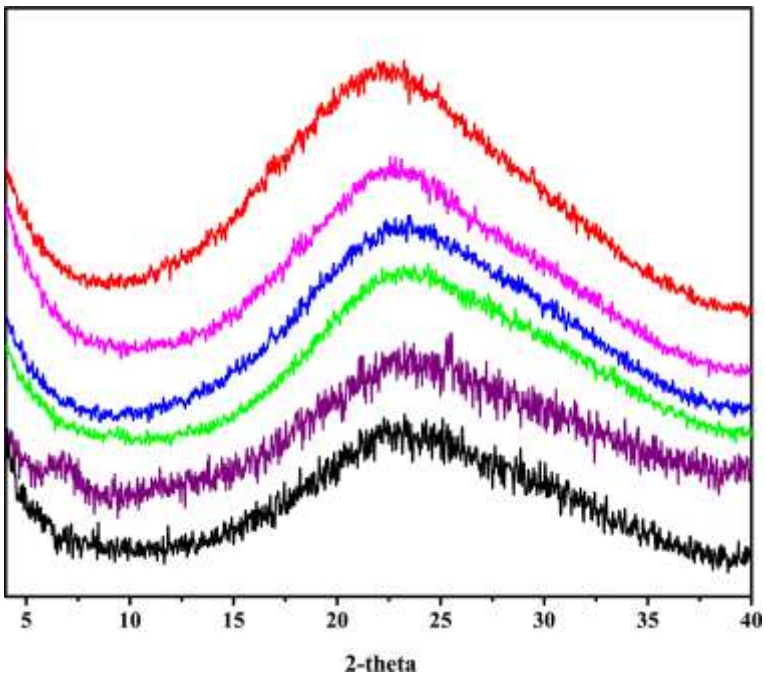

Fig. S2. PXRD patterns of PAFs, PAF-33 (black), PAF-33-NH_2 (purple), PAF-33-COOH (green), PAF-34 (blue), PAF-34-OH (magenta) and PAF-35 (red).

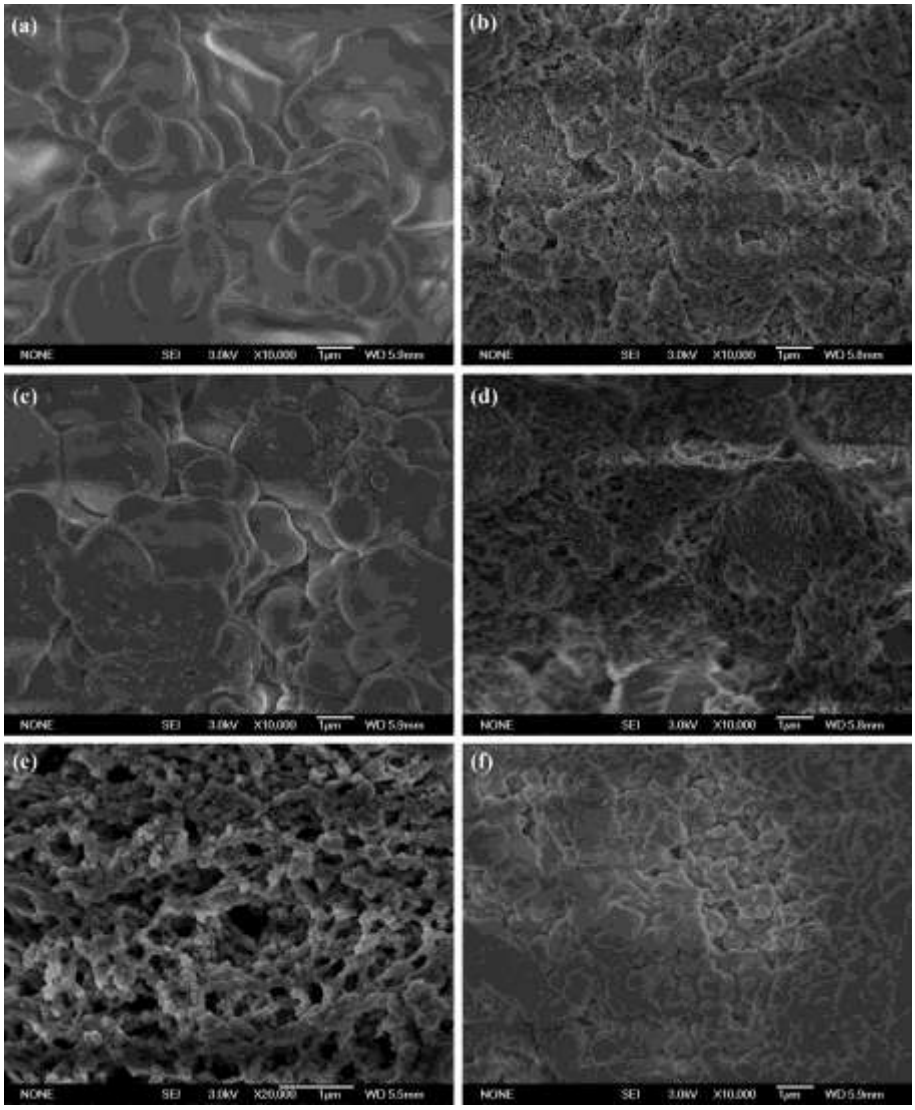

Fig. S3. SEM images of PAFs, PAF-33 (a), PAF-33-NH_2 (b), PAF-33-COOH (c), PAF-34 (d), PAF-34-OH (e) and PAF-35 (f).

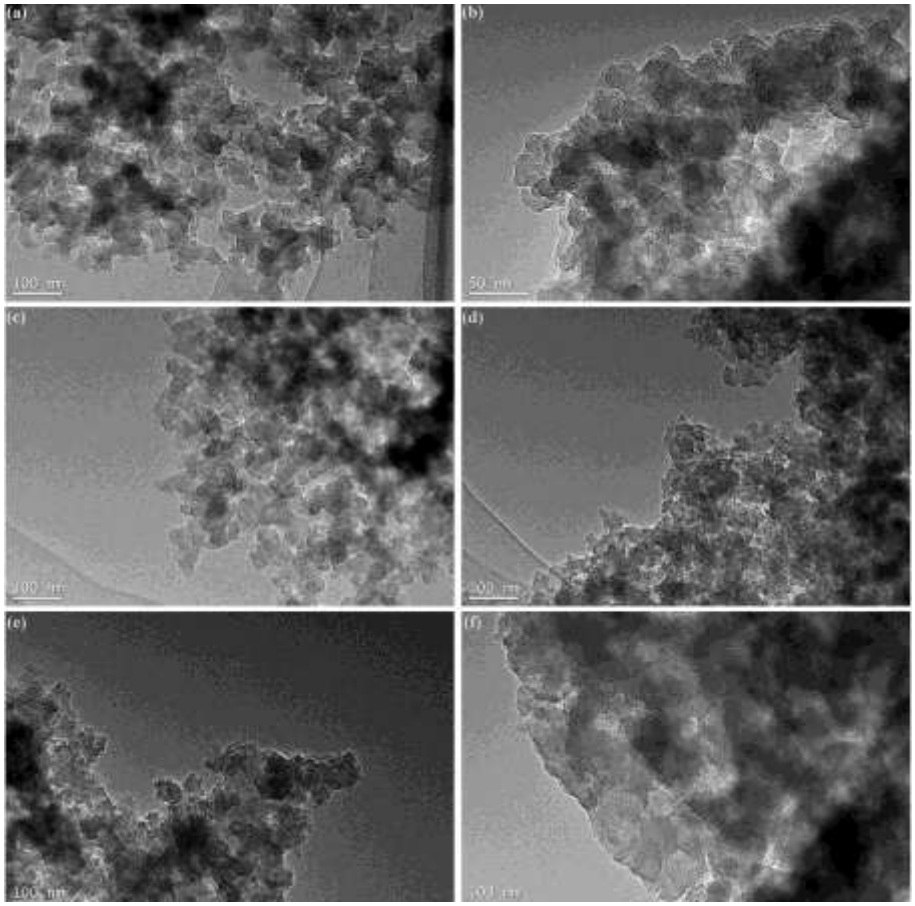

Fig. S4. TEM images of PAFs, PAF-33 (a), PAF-33-NH_2 (b), PAF-33-COOH (c), PAF-34 (d), PAF-34-OH (e) and PAF-35 (f).

Table S2. Thermal stability of PAFs

PAFs	T of loss 5% weight [^{o}C]	T of disintegrate end [^{o}C]
PAF-33	396	573
PAF-33-NH_2	289	627
PAF-33-COOH	365	576
PAF-34	390	572
PAF-34-OH	361	580
PAF-35	330	517

Table S3. ICP analysis for PAFs.

PAFs	Pd content (Wt%)	Cu content (Wt%)
PAF-33	0.0023	0.0020
PAF-33-NH_2	0	0.0089
PAF-33-COOH	0.0047	0.00025
PAF-34	0.0020	0.00023
PAF-34-OH	0.0043	0.00024
PAF-35	0.0027	0.00031

Before analysis, 10~15 mg of sample was digested in 3:1 HCl-HNO_3 (5 mL) and transferred to a 50 mL volumetric flask with distilled water.

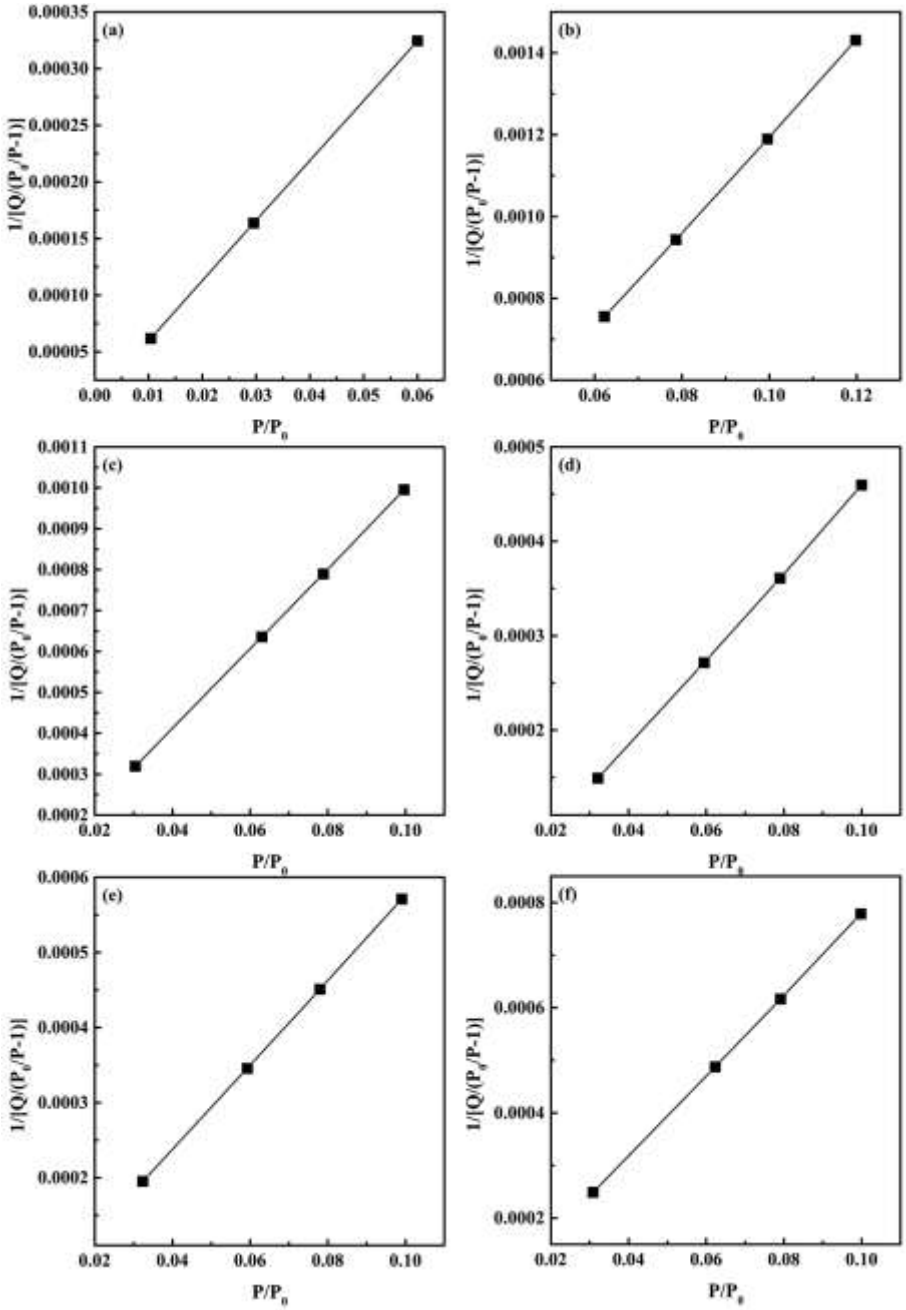

Fig. S5. BET surface area plots of PAFs, PAF-33 (a), PAF-33-NH_2 (b), PAF-33-COOH (c), PAF-34 (d), PAF-34-OH (e) and PAF-35 (f).

Table S4. BET Surface Area Report of PAFs

PAF	Sample weight [mg]	BET [m^2/g]	Slope [g/mmol]	Y-Intercept [g/mmol]	C	Qm [mmol/g]	Correlation Coefficient
PAF-33	95.6	820.75 ± 1.7328	0.119 ±0.00025	0.00015 ± 0.00001	777.99	8.41	0.9999978
PAF-33-NH_2	99.3	369.88 ± 2.3019	0.263 ±0.00163	0.00049 ± 0.00015	535.50	3.79	0.9999615
PAF-33-COOH	73.3	445.01 ± 1.7476	0.219 ±0.00086	0.00048 ± 0.0001	453.960	4.56	0.9999846
PAF-34	97.4	952.56 ± 8.2187	0.102 ±0.00088	0.00003 ± 0.00006	3560.19	9.76	0.9999259
PAF-34-OH	93.3	770.99 ± 2.4626	0.1262 ±0.00040	0.00028 ± 0.00003	457.45	7.90	0.9999898
PAF-35	89.5	566.63 ± 3.1325	0.172 ±0.00095	0.00025 ±0.00007	689.46	5.81	0.9999695

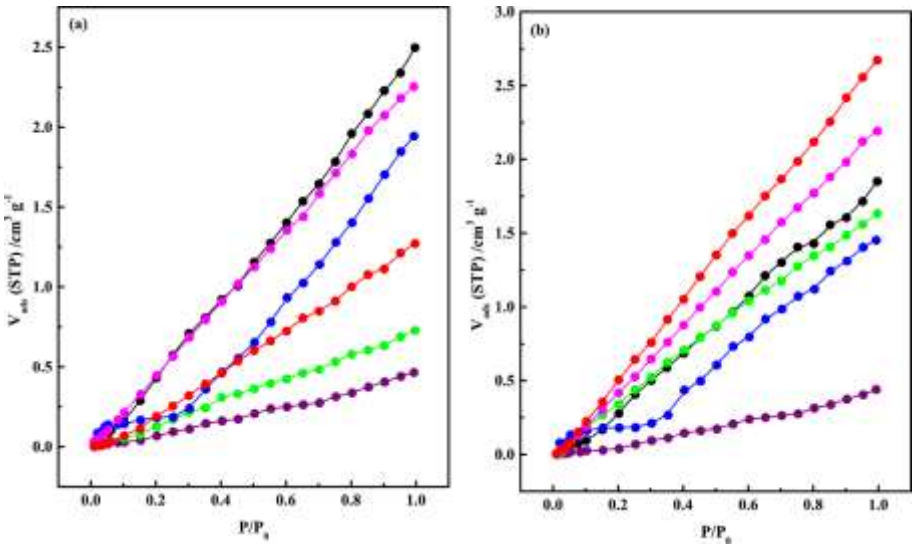

Fig. S6. Nitrogen adsorption isotherms measured at 273 K (a) and 298 K (b) of PAFs, PAF-33 (black), PAF-33-NH_2 (purple), PAF-33-COOH (green), PAF-34 (blue), PAF-34-OH (magenta) and PAF-35 (red).

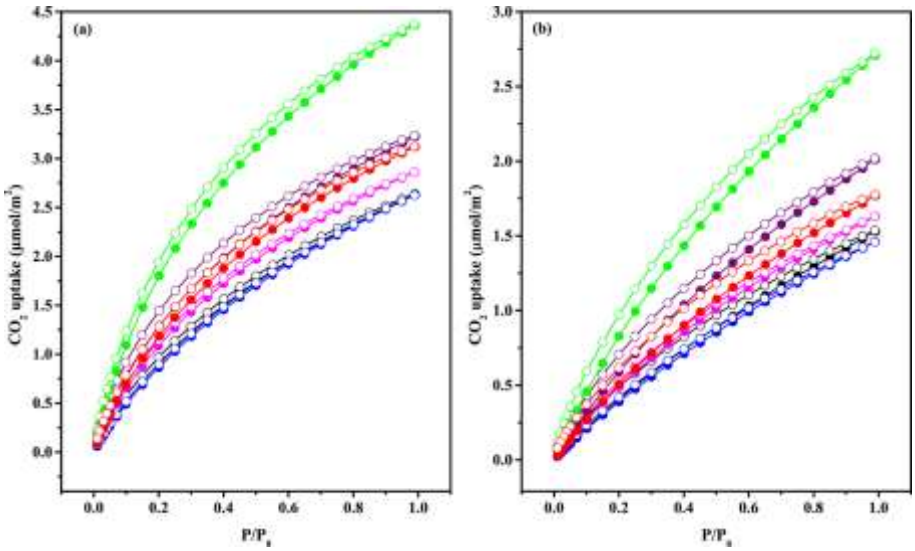

Fig. S7. CO_2 adsorption capacity per unit area of PAF materials, up to 1 bar, 273 K (a) and 298 K (b), respectively. PAF-33 (black), PAF-33-NH_2 (purple), PAF-33-COOH (green), PAF-34 (blue), PAF-34-OH (magenta) and PAF-35 (red).

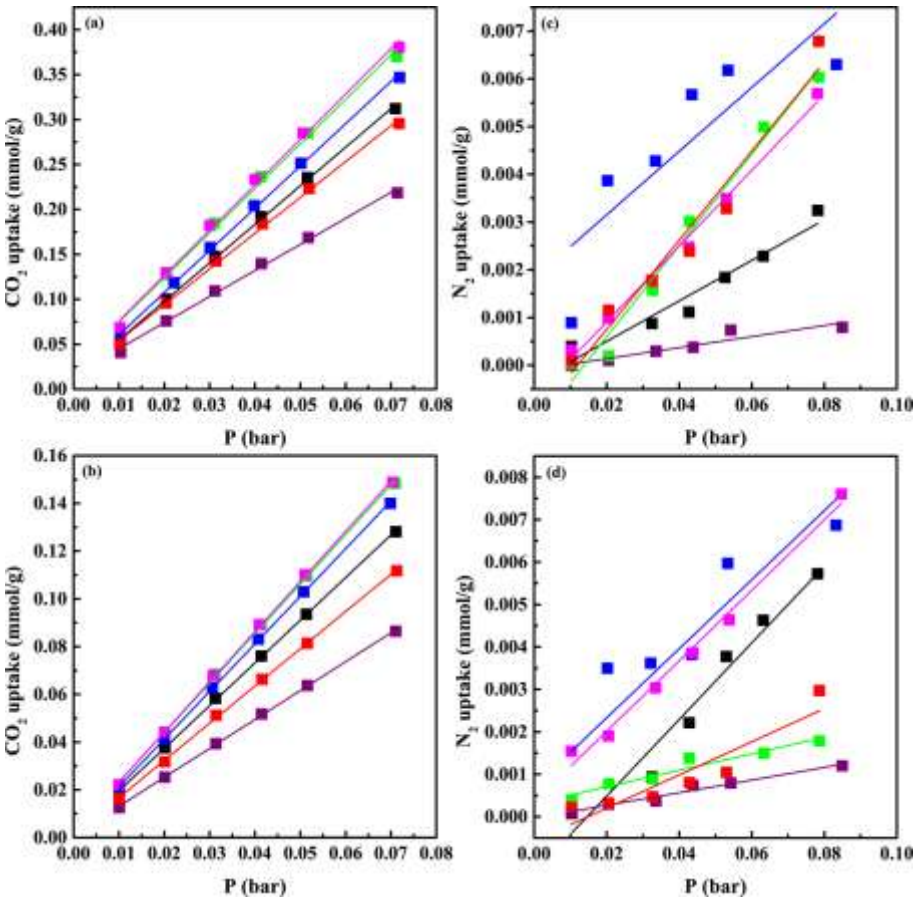

Fig. S8. CO_2/N_2 selectivities for PAF materials calculated using the Henry's Law constants in the linear low pressure (< 0.1 bar) range. PAF-33 (black), PAF-33-NH_2 (purple), PAF-33-COOH (green), PAF-34 (blue), PAF-34-OH (magenta) and PAF-35 (red).

Table S5. Summary of CO_2 uptakes, CO_2 /N_2 selectivities and heats of adsorption in porous materials

Network	BET [m²/g]	CO_2 uptak [mmol g^{-1}]	T [K]	P [bar]	Selectivity CO_2/N_2		Qst [kJ mol^{-1}]	Ref
					IAST	Herry's law		
PAF-1	5600	1.09	298	1 atm			15.6	S1
		2.05	273	1 atm				
PAF-3	2932	1.81	298	1 atm			19.2	S1
		3.48	273	1 atm				
PAF-4	2246	1.16	298	1 atm			16.2	S1
		2.41	273	1 atm				
CMP-1	837	1.18	298	1			26.8	S3
		2.05	273	1				
CMP-1-$(OH)_2$	1043	1.07	298	1			27.6	S2
		1.80	273	1				
CMP-1-$(CH_3)_2$	899	0.94	298	1			26.9	S2
		1.64	273	1				
CMP-1-NH_2	710	0.95	298	1			29.5	S2
		1.64	273	1				
CMP-1-COOH	522	0.95	298	1			32.6	S2
		1.60	273	1				
A	4077	1.45	298	1		8.7		S3
PAF-1		2.65	273	1				
B	1847	1.63	298	1		19.5		S3
COF-300		3.29	273	1				
C	1237	2.20	298	1		14.2		S3
(Click network)		3.86	273	1				
D	1213	1.33	298	1		12.2		S3
(Tetrahedral-CMP)		2.42	273	1				
E	1470	1.77	298	1		9.2		S3
(TPM-HCP)		2.95	273	1				
F	653	1.08	298	1		12.2		S3
(CMP-NH_2CH_3)		1.80	273	1				
G	1056	1.25	298	1		15.1		S4
(CMP-Carbozole)		2.15	273	1				
BILP-2	708	2.36	298	1		71	28.6	S5
		3.39	273	1		113		
BLP-5	599	1.98	298	1		36	28.8	S5
		2.91	273	1		95		
PECONF-1	499	1.34	298	1		51	29	S6
		1.86	273	1		109		
PECONF-2	637	1.98	298	1		44	31	S6
		2.85	273	1		74		

PECONF-4		1.96	298	1		51	34	S6
		2.95	273	1		83		
MgMOF-74	1640	6.2	296	1	182.1			S7
ZnMOF-74	1176	1.67	296	1	87.7			S7
UTSA-16	628	2.37	296	1	314.7		34.6	S7
Cu-TDPAT	1938	1.82	296	1	57.8		42.2	S7
MOF-177		0.16	296	1	3.6			S7
PAF-33	821	1.25	298	1		19.4	27.4	This
		2.16	273	1		99.2		work
PAF-33-NH_2	370	0.75	298	1		79.8	32.9	This
		1.19	273	1		250.5		work
PAF-33-COOH	445	1.21	298	1		104.3	30.0	This
		1.94	273	1		51.8		work
PAF-34	953	1.39	298	1		26.3	27.2	This
		2.50	273	1		72.0		work
PAF-34-OH	771	1.21	298	1		39.1	30.7	This
		2.21	273	1		63.9		work
PAF-35	567	1.01	298	1		29.9	30.3	This
		1.77	273	1		42.7		work

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