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Supporting Information

Construction and adsorption properties of Porous Aromatic Frameworks via $AlCl_3$-triggered Coupling Polymerization

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Synthetic procedures

Synthesis of PAF-41: Anhydrous aluminium chloride (500 mg, 3.75 mmol) was added to a 100 mL round-bottomed flask. Then, after pumped to vacuum, the system was inflated with inert gas N_2 for 3 times. Next, dried chloroform (40 mL) was injected through a syringe and the mixture was heated to 60 ^oC for 3 h. Then triphenylamine (1.5 mmol, 367 mg) in 20 mL $CHCl_3$ was added into the system and the mixture kept stirring at 60 ^oC for 24 h. After cooling down to room temperature, the crude product was obtained by filtration and washed with 1 M hydrochloric acid solution, methanol, and acetone to remove unreacted monomers and catalyst residues. Further purification of product was carried out by Soxhlet extraction with ethanol, THF, and $CHCl_3$ for 48 h. The product was dried in vacuum for 8 h at 80 ^oC to give PAF-42 (364 mg, 98.6% yield).

Synthesis of PAF-42: Anhydrous aluminium chloride (500 mg, 3.75 mmol) was added to a 100 mL round-bottomed flask. Then, after pumped to vacuum, the system was inflated with inert gas N_2 for 3 times. Next, dried chloroform (40 mL) was injected through a syringe and the mixture was heated to 60 ^oC for 3 h. Then tetraphenylmethane (1.5 mmol, 480 mg) in 20 mL $CHCl_3$ was added into the system and the mixture kept stirring at 60 ^oC for 24 h. After cooling down to room temperature, the crude product was obtained by filtration and washed with 1 M hydrochloric acid solution, methanol, and acetone to remove unreacted monomers and catalyst residues. Further purification of product was carried out by Soxhlet extraction with ethanol, THF, and $CHCl_3$ for 48 h. The product was dried in vacuum for 8 h at 80 ^oC to give PAF-42 (469 mg, 96.1% yield).

Synthesis of PAF-43: Anhydrous aluminium chloride (500 mg, 3.75 mmol) was added to a 100 mL round-bottomed flask. Then, after pumped to vacuum, the system was inflated with inert gas N_2 for 3 times. Next, dried chloroform (40 mL) was injected through a syringe and the mixture was heated to 60 ^oC for 3 h. Then tetraphenylsilane (1.5 mmol, 504 mg) in 20 mL $CHCl_3$ was added into the system and the mixture kept stirring at 60 °C for 24 h. After cooling down to room temperature, the crude product was obtained by filtration and washed with 1 M hydrochloric acid solution, methanol, and acetone to remove unreacted monomers and catalyst residues. Further purification of product was carried out by Soxhlet extraction with ethanol, THF, and $CHCl_3$ for 48 h. The product was dried in vacuum for 8 h at 80 °C to give PAF-42 (469 mg, 96.0% yield).

Synthesis of PAF-44: Anhydrous aluminium chloride (500 mg, 3.75 mmol) was added to a 100 mL round-bottomed flask. Then, after pumped to vacuum, the system was inflated with inert gas N_2 for 3 times. Next, dried chloroform (40 mL) was injected through a syringe and the mixture was heated to 60 °C for 3 h. Then tetraphenylgermane (1.5 mmol, 570 mg) in 20 mL $CHCl_3$ was added into the system and the mixture kept stirring at 60 °C for 24 h. After cooling down to room temperature, the crude product was obtained by filtration and washed with 1 M hydrochloric acid solution, methanol, and acetone to remove unreacted monomers and catalyst residues. Further purification of product was carried out by Soxhlet extraction with ethanol, THF, and $CHCl_3$ for 48 h. The product was dried in vacuum for 8 h at 80 °C to give PAF-42 (535.8 mg, 93.8% yield).

Table S1. Raw material input and yield of PAF-41, PAF-42, PAF-43, and PAF-44.

PAFs	Monomers	$AlCl_3$	Yield (%)
PAF-41	367 mg, 1.5 mmol	375 mg, 2.81 mmol	96.1%
PAF-42	480 mg, 1.5 mmol	500 mg, 3.75 mmol	98.6%
PAF-43	504 mg, 1.5 mmol	500 mg, 3.75 mmol	96.0%
PAF-44	570 mg, 1.5 mmol	500 mg, 3.75 mmol	93.8%

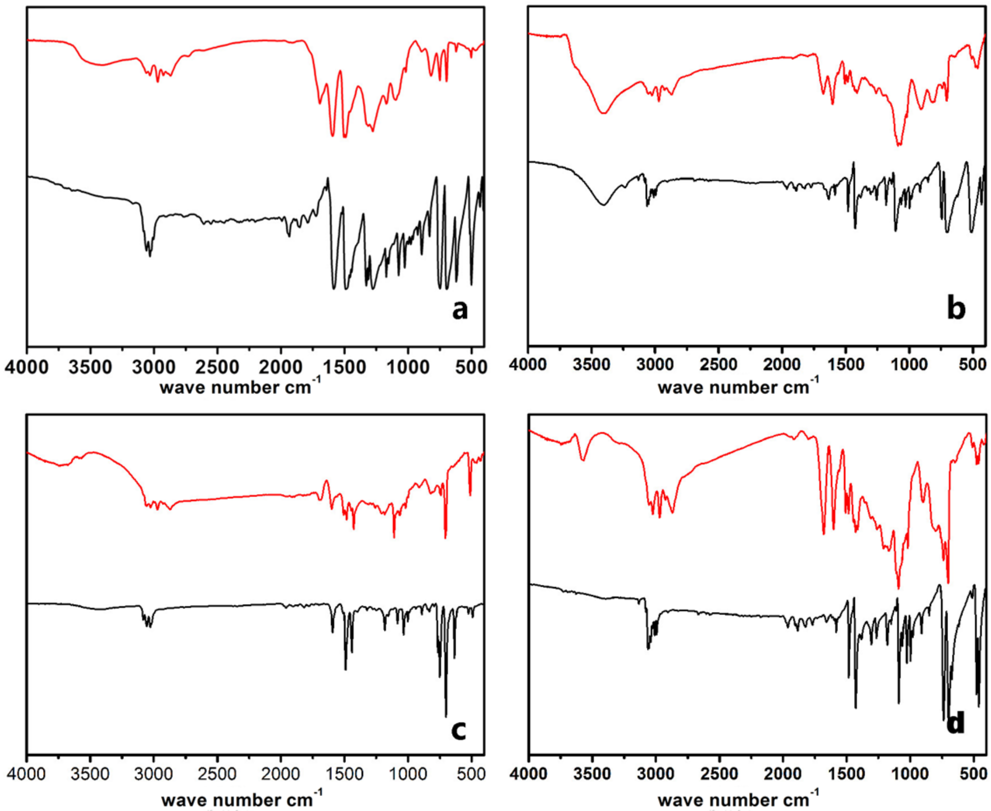

Fig. S1. FTIR spectra of monomers (black) and corresponding polymerization products (red), PAF-41 (a), PAF-42 (b), PAF-43 (c) and PAF-44 (d), respectively.

Table S2. Characteristic peaks in FIIR spectra of benzene ring

Category	PAFs	monomers (Monosubstituted Benzene, cm^{-1})	Product (Disubstituted Benzene, cm^{-1})
C-C stretching vibration	PAF-41 PAF-42 PAF-43 PAF-44	1586 1594 1586 1582	1596 1602 1603 1602
C-C stretching vibration	PAF-41 PAF-42 PAF-43 PAF-44	1491 1491 1481 1483	1504 1507 & 1483 1507 &1481 1507
Ring deformation vibration 710- 695 cm^{-1}	PAF-41 PAF-42 PAF-43 PAF-44	normal normal normal normal	weakened weakened weakened weakened
C-H deformation vibration of ring hydrogens: ring CH wagging, 770-730 cm^{-1} (5 adjacent hydrogens)	PAF-41 PAF-42 PAF-43 PAF-44	normal normal normal normal	weakened weakened weakened weakened
C-H deformation vibration of ring hydrogens: 1,4-disubstituted, CH wagging, 860- 800 cm^{-1} (2 adjacent hydrogens)	PAF-41 PAF-42 PAF-43 PAF-44	normal normal normal normal	enhanced enhanced enhanced enhanced

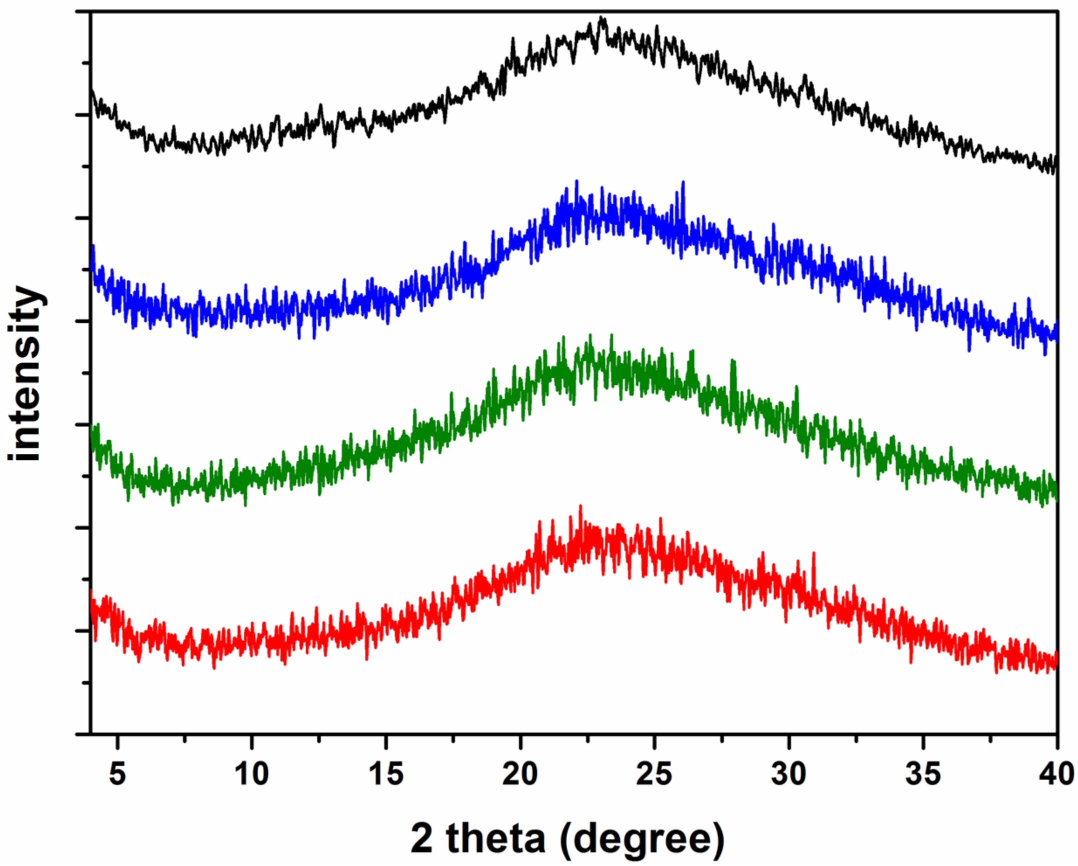

Fig. S2. PXRD patterns of the PAFs, PAF-41 (black), PAF-42 (blue), PAF-43 (olive), and PAF-44 (red).

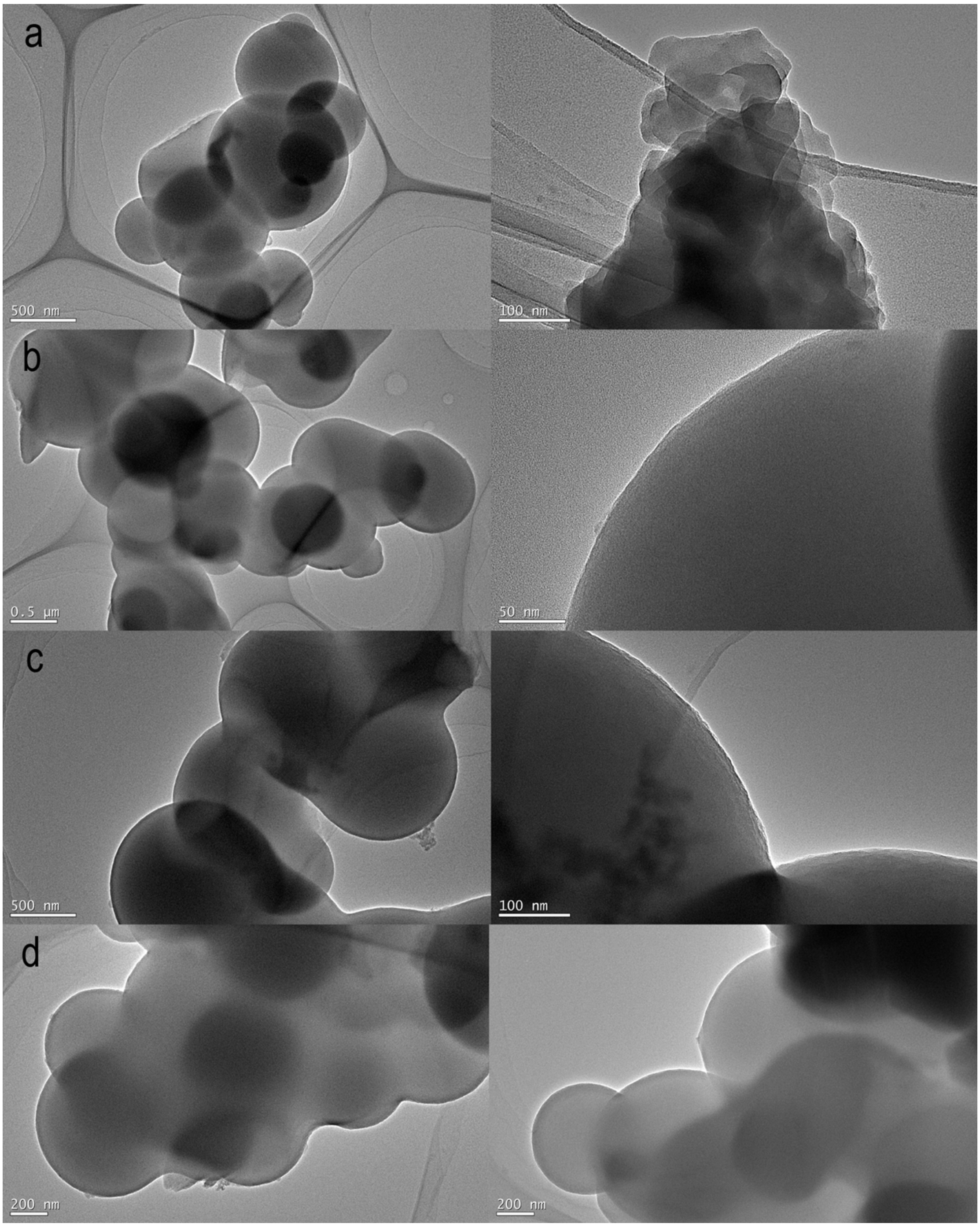

Fig. S3. TEM images of PAF-41 (a), PAF-42 (b), PAF-43 (c) and PAF-44 (d).

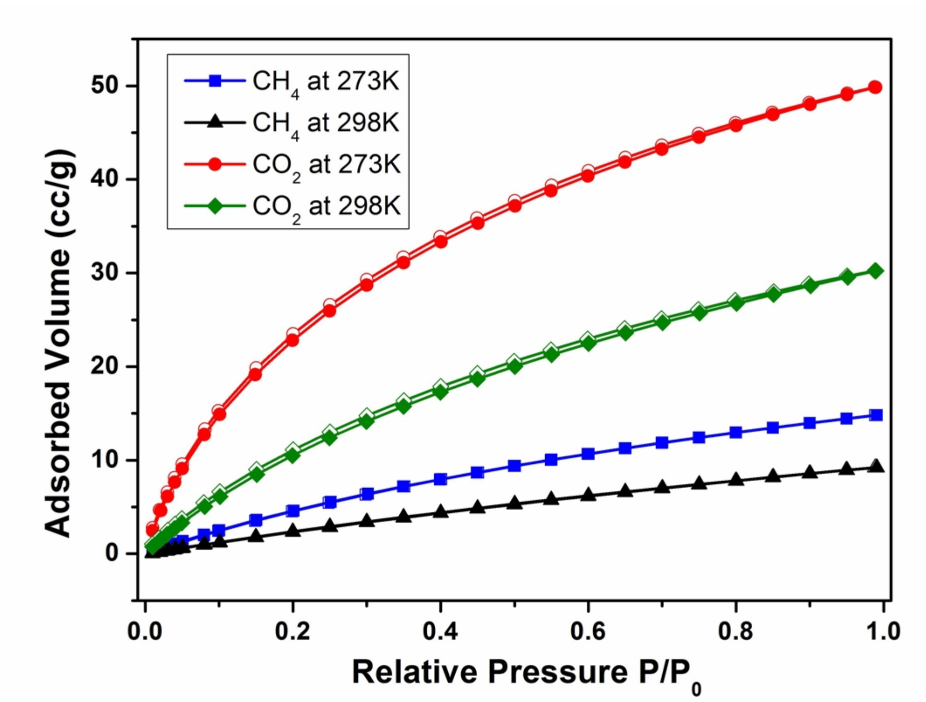

Fig. S4. CO_2 and CH_4 adsorption (solid circles) and desorption (open circles) isotherms of PAF-41.

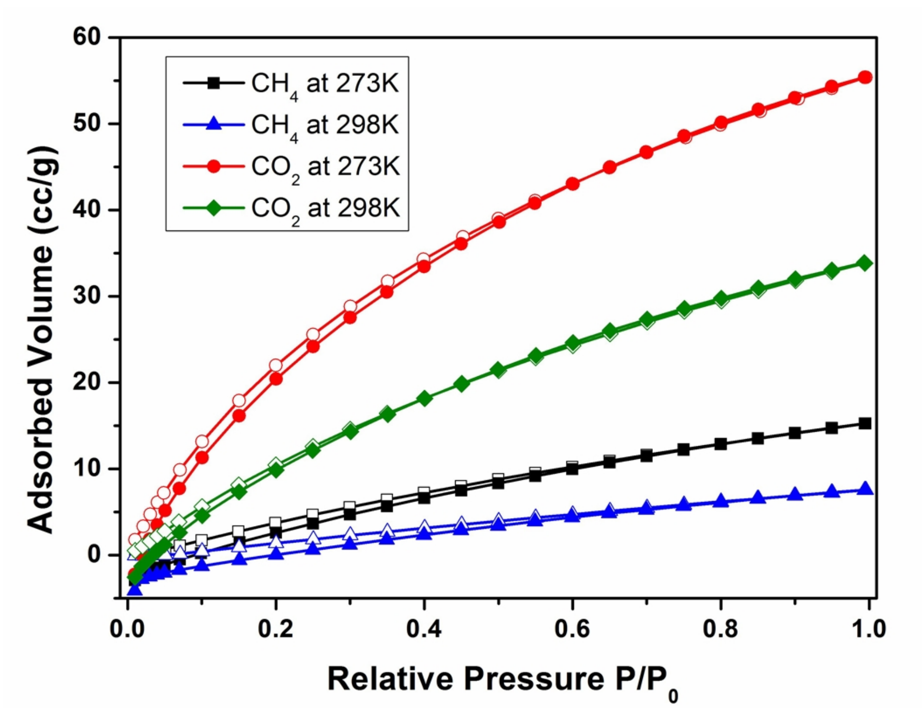

Fig. S5. CO_2 and CH_4 adsorption (solid circles) and desorption (open circles) isotherms of PAF-42.

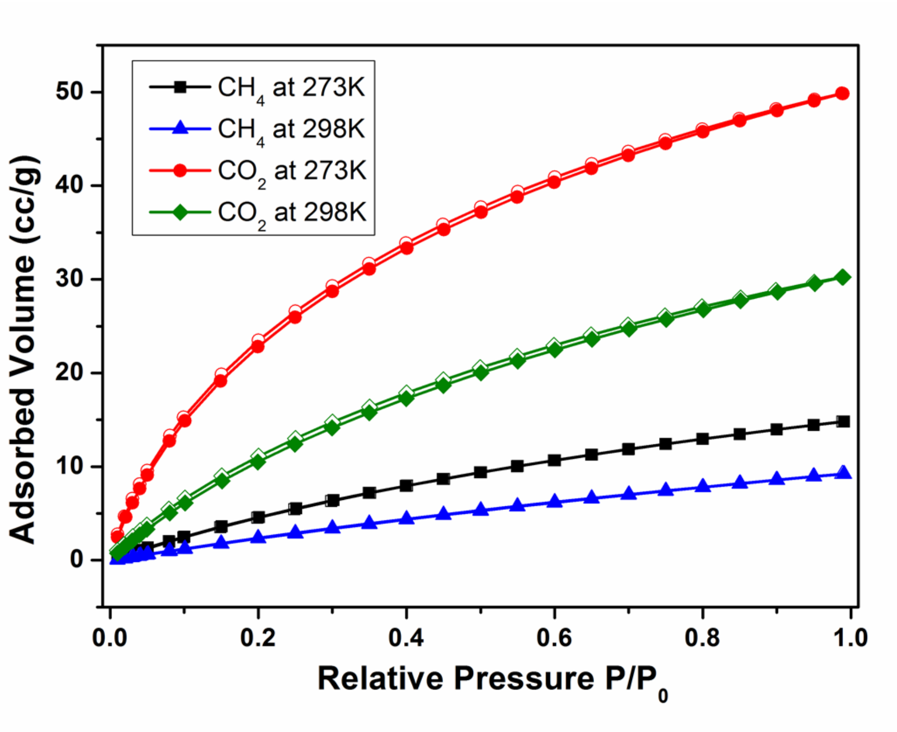

Fig. S6. CO_2 and CH_4 adsorption (solid circles) and desorption (open circles) isotherms of PAF-43.

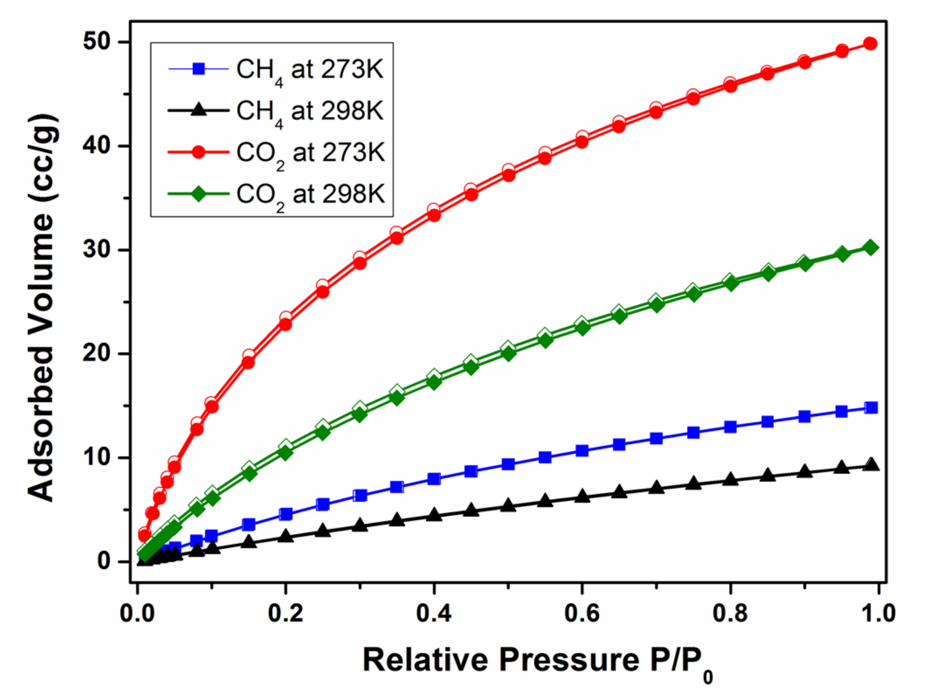

Fig. S7. CO_2 and CH_4 adsorption (solid circles) and desorption (open circles) isotherms of PAF-44.

Table S3. Porosity data of PAFs synthesized at different temperature.

Product	BET surface area (45 ^{o}C)	BET surface area (60 ^{o}C)
PAF-41	564 $m^2 g^{-1}$	1119 $m^2 g^{-1}$
PAF-42	553 $m^2 g^{-1}$	640 $m^2 g^{-1}$
PAF-43	500 $m^2 g^{-1}$	515 $m^2 g^{-1}$
PAF-44	495 $m^2 g^{-1}$	532 $m^2 g^{-1}$

Table S4. Comparison of CO_2 uptakes and isosteric heat of adsorption in POFs

material	S_{BET}/ $m^2\ g^{-1}$	CO_2 uptake mmol g^{-1}	T (K)	Q_{stCO2} KJ mol^{-1}	Ref
PAF-1	5600	2.05	273	15.6	1
		1.09	298		
PAF-3	2932	3.48	273	19.2	1
		1.81	298		
PAF-4	2246	2.41	273	16.2	1
		1.16	298		
COF-1	750	2.32	273		2
COF-5	1670	1.34	273		2
COF-6	750	3.84	273		2
COF-8	1350	1.43	273		2
COF-10	1760	1.21	273		2
COF-102	3620	1.56	273		2
COF-103	3530	1.70	273		2
MOP-A	4077	2.65	273	23.7	3
		1.45	298		
MOP-B	1847	3.29	273	21.8	3
		1.63	298		
MOP-C	1237	3.86	273	33.7	3
		2.20	298		
MOP-D	1213	2.42	273	26.5	3
		1.33	298		
MOP-E	1470	2.95	273	25.4	3
		1.77	298		
MOP-F	653	1.80	273	26.7	3
		1.08	298		
MOP-G	1056	2.15	273	26.6	3
		1.25	298		
CMP-1	837	2.05	273	26.8	4
		1.18	298		
CMP-1-$(OH)_2$	1043	1.80	273	27.6	4
		1.07	298		
CMP-1-$(CH_3)_2$	899	1.64	273	26.9	4
		0.94	298		
CMP-1-NH_2	710	1.64	273	29.5	4
		0.95	298		
CMP-1-COOH	522	1.60	273	32.6	4
		0.95	298		
PPF-1	1740	6.07	273	25.6	5
PPF-2	1470	5.55	273	29.2	5
PPF-3	419	2.09	273	21.8	5

PPF-4	726	2.59	273	25.1	5
BILP-2	708	3.39	273	28.6	6
		2.36	298		
BILP-5	599	2.91	273	28.8	6
		1.98	298		
PAF-18-OH	1121	2.50	273	28.0	7
PAF-18-OH	981	3.27	273	29.5	7
PAF-41	1119	3.48	273	28.1	this work
		2.26	298		
PAF-42	640	2.65	273	31.8	this work
		1.51	298		
PAF-43	515	2.16	273	34.8	this work
		1.24	298		
PAF-44	532	2.23	273	34.2	this work
		1.35	298		

Table S5. Comparison of CH_4 uptakes and isosteric heat of adsorption in POFs

material	S_{BET}/ $m^2\ g^{-1}$	CH_4 uptake mmol g^{-1}	T (K)	Q_{stCH4} KJ mol^{-1}	Ref
PAF-1	5600	0.80	273	14.0	1
PAF-3	2932	1.21	273	15.0	1
PAF-4	2246	0.80	273	23.0	1
PPF-1	1740	1.52	273	15.1	5
PPF-2	1470	1.44	273	15.9	5
PPF-3	419	0.63	273	19.4	5
PPF-4	726	0.83	273	13.9	5
BILP-2	708	0.88	273	18.4	6
		0.56	298		
BILP-4	1135	1.63	273	13.0	6
		1.13	298		
BILP-5	599	0.94	273	14.6	6
		0.63	298		
BILP-7	1122	1.63	273	14.7	6
		1.13	298		
BILP-3	1306	1.50	273	16.6	8
		1.06	298		
BILP-6	1261	1.69	273	13.2	8
		1.19	298		
PAF-41	1119	1.04	273	17.0	this work
		0.68	298		
PAF-42	640	0.68	273	25.6	this work
			298		
PAF-43	515	0.60	273	29.8	this work
		0.28	298		
PAF-44	532	0.66	273	22.9	this work
		0.41	298		

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