Electronic Supplementary Information

Cost-Effective Synthesis of Furan- and Thienyl-Based Microporous Polyaminals for Adsorptions of Gases and Organic Vapors

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Experimental Section

Table S1 Porosity parameters of PAN-F and PAN-T obtained by N_2 adsorption at 77 K.

Sample	S_{BET} ($m^2\ g^{-1}$)	$S_{Langmuir}$ ($m^2\ g^{-1}$)	S_{micro} ($m^2\ g^{-1}$)	V_{micro} ($m^3\ g^{-1}$)	V_{total} ($cm^3\ g^{-1}$)	Pore size (nm)
PAN-F	702	1095	147	0.07	0.89	0.68
PAN-T	795	1167	365	0.17	0.73	0.59

Table S2 Uptakes of H_2, CO_2, and CO_2/N_2 selectivity for PAN-F and PAN-T.

	H_2 uptake (wt%)[a]		CO_2 uptake (wt%)[b]		CO_2/N_2 selectivity[c]	
Sample	77 K	87 K	273 K	298 K	Henry law	IAST
PAN-F	0.85	0.69	10.0	7.5	36.0	42.8
PAN-T	1.27	0.82	14.8	11.5	45.8	68.4

[a)] Uptakes for H_2 determined at 1 bar. [b)] Uptakes for CO_2 determined at 1 bar. [c)] Henry law selectivity of CO_2/N_2 was calculated from the ratio of initial slope of CO_2 to N_2 in the pure-component adsorption isotherms at 273 K, whereas IAST selectivity of CO_2/N_2 was calculated from 0.15/0.85 gas mixture for CO_2/N_2 at 273 K and 1 bar.

Table S3 K_H, A_o, A_1 and Q_o values of CO_2 adsorption in PAN-F and PAN-T.

Samples	T K	K_H mol g^{-1} Pa^{-1}	A_o ln(mol g^{-1} Pa^{-1})	A_1 g mol^{-1}	Q_o kJ mol^{-1}
PAN-F	273	1.749×10^{-7}	-15.559	-1291.684	31.7
	298	5.418×10^{-8}	-16.731	-986.977	
PAN-T	273	3.692×10^{-7}	-14.812	-1130.751	36.3
	298	9.618×10^{-8}	-16.157	-781.632	

Table S4 K_H, A_o, A_1 and Q_o values of H_2 adsorption in PAN-F and PAN-T.

Samples	T K	K_H mol g^{-1} Pa^{-1}	A_o ln(mol g^{-1} Pa^{-1})	A_1 g mol^{-1}	Q_o kJ mol^{-1}
PAN-F	77	2.521×10^{-6}	-12.891	-1178.218	6.79
	87	7.434×10^{-7}	-14.112	-1361.510	
PAN-T	77	4.082×10^{-6}	-12.409	-942.402	7.41
	87	1.081×10^{-6}	-13.737	-1039.750	

Table S5 Uptakes of organic vapors for PAN-F and PAN-T.

Sample	Vapor uptake (wt%, 298 K)[a]		
	C_6H_6	*c*-C_6H_{12}	H_2O
PAN-F	54.4	43.3	12.8
PAN-T	57.0	51.8	16.2

[a] Uptakes for C_6H_6 (benzene vapor), *c*-C_6H_{12} (cyclohexane vapor) and H_2O (water vapor) were determined at $P/P_0 = 0.9$.

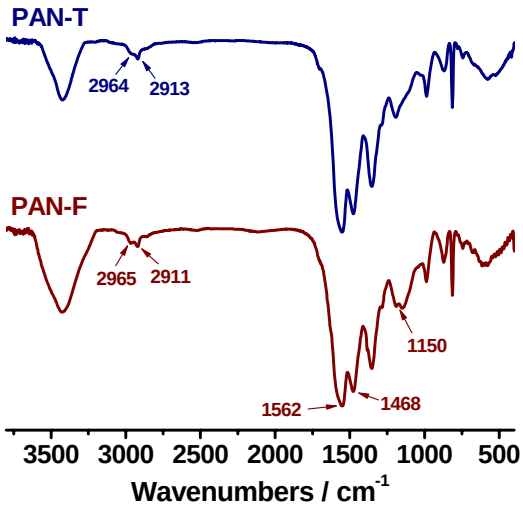

Fig. S1 FTIR spectra of PAN-F and PAN-T.

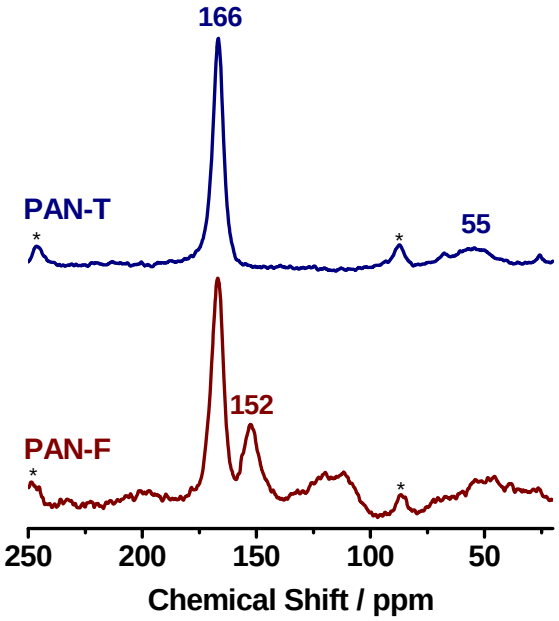

Fig. S2 Solid-state ^{13}C CP/MAS NMR spectra for PAN-F and PAN-T. Asterisks (*) indicate peaks arising from spinning side bands.

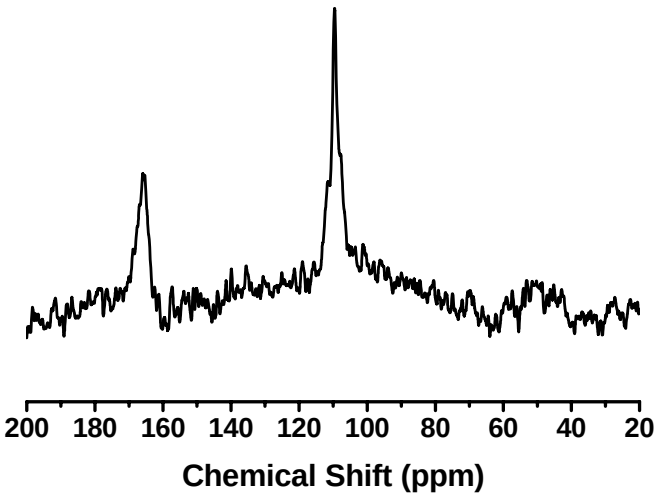

Fig. S3 Solid-state ^{13}C MAS NMR spectrum for PAN-T.

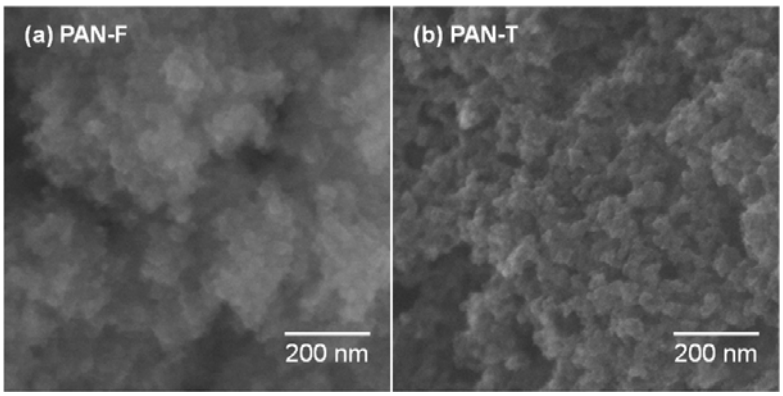

Fig. S4 Field-emission SEM images of PAN-F and PAN-T.

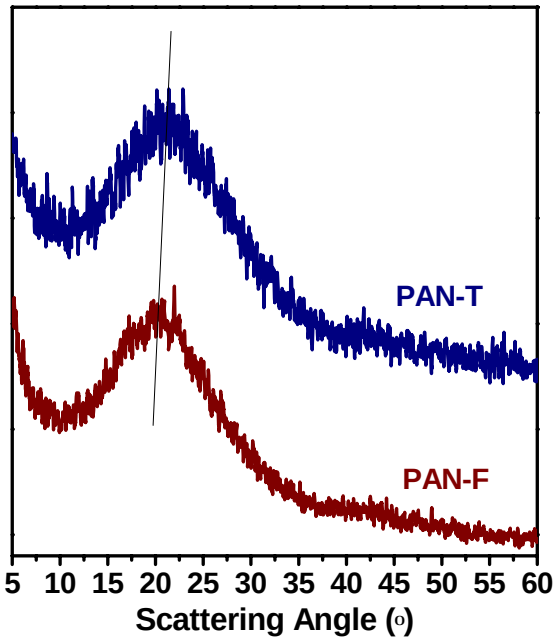

Fig. S5 Wide angle X-ray diffractions of PAN-F and PAN-T.

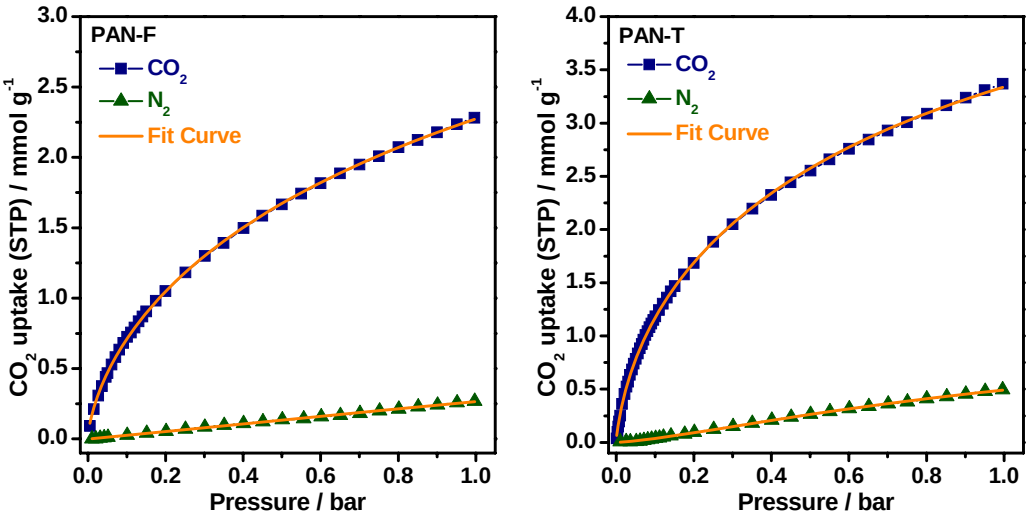

Fig. S6 Experimental pure component adsorption isotherms for CO_2 and N_2 at 273 K, and the corresponding single-site Langmuir-Freundlich fitting curves for PAN-F and PAN-T.

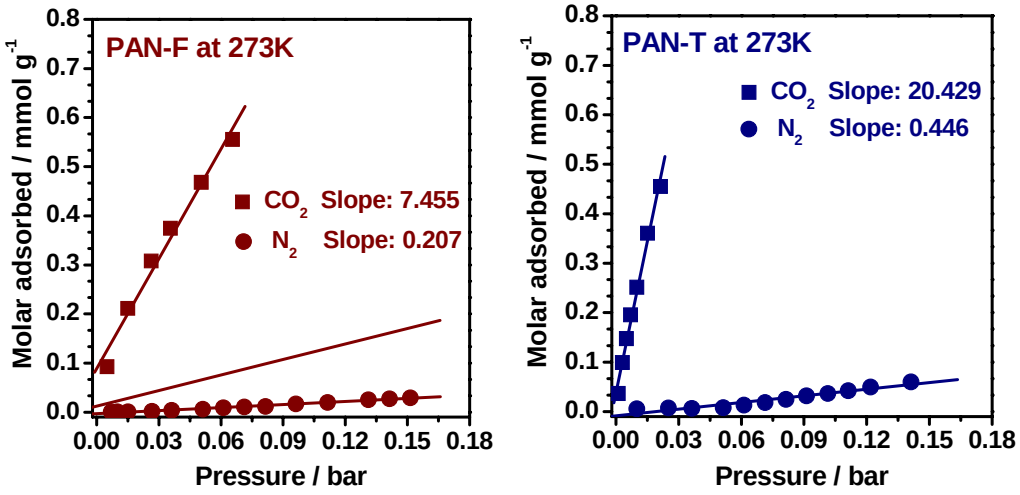

Fig. S7 Adsorption selectivity of CO_2 over N_2 for PAN-F and PAN-T from initial slope calculations of CO_2 and N_2 isotherms at 273 K.

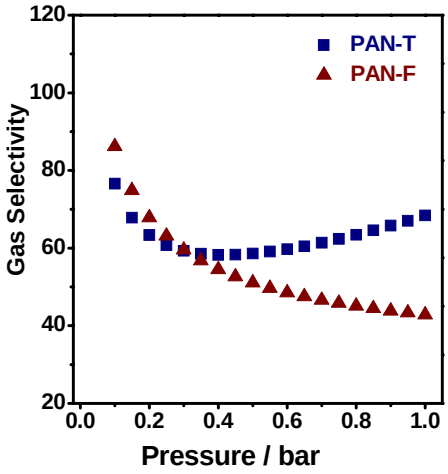

Fig. S8 IAST selectivity for 0.15/0.85 CO_2/N_2 mixture as a function of pressure for PAN-F and PAN-T.

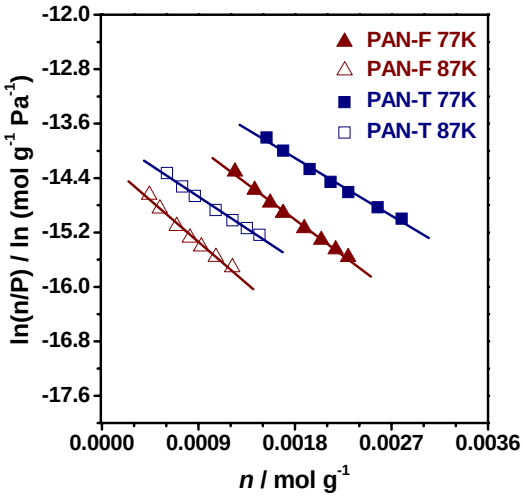

Fig. S9 Virial plots of H_2 adsorption in PAN-F and PAN-T at 77 and 87 K.

Experimental Section

Materials. Melamine, 2-furanaldehyde and 2-thenaldehyde were purchased from J&K Chemical Co., Ltd. Dimethyl sulfoxide (DMSO), tetrahydrofuran (THF), *N,N*-dimethylformamide (DMF) and other reagents were purchased from Shanghai Chemical Reagent Co. DMSO was purified by distillation under reduced pressure and dehydrated with 4Å molecular sieves, and other reagents were of reagent grade and used as received.

Instrumentation. Fourier transform infrared spectra (FTIR) of synthesized products were recorded using a Nicolet 20XB FT-IR spectrophotometer in 400−4000 cm^{-1}. Samples were prepared by dispersing the complexes in KBr to form disks. Solid-state ^{13}C CP/MAS (cross-polarization with magic angle spinning) spectra were measured on a Varian Infinity-Plus 400 spectrometer at 100.61 MHz at an MAS rate of 10.0 kHz using zirconia rotors 4 mm in diameter using a contact time of 4.0 ms and a relaxation delay of 2.0 s. Wide-angle X-ray diffractions (WAXD) from 5° to 60° were performed on Rigku D/max-2400 X-ray diffractometer (40 kV, 200 mA) with a copper target at a scanning rate of 2°/min. Field-emission scanning electron microscopy (FE-SEM) experiments were carried on a Nova NanoSEM 450. Adsorption and desorption measurements for all the gases and vapors were conducted on an Autosorb iQ (Quantachrome) analyzer. Prior to measurements, the samples were degassed at 120 °C under high vacuum overnight.

Preparation of microporous polyaminal networks (PAN-F and PAN-T). The polymerizations of PAN-F and PAN-T were carried out in a similar procedure. Only the

polymerization of PAN-T is described here as an example. A dry Schlenk flask equipped with a stirrer and a condenser was degassed using two evacuation-argon-backfill cycles. Under argon flow, melamine (0.50 g, 3.96 mmol), 2-thenaldehyde (0.80 g, 7.16 mmol) and 25 mL DMSO were added and heated at 180 °C for 72 h. Finally, the system was cooled down and the solid was isolated, washed successively with DMF, methanol and THF. The resultant product was extracted with THF in a Soxhlet apparatus for 24 h, and dried at 120 °C under vacuum to constant weight with a quantitative yield.

The enthalpy of adsorption at zero coverage (Q_0) can be investigated from the CO_2 isotherms at different temperatures using virial equation:

$$\ln\left(n/P\right) = A_0 + A_1 \cdot n + A_2 \cdot n^2 + \cdots \quad (1)$$

where n is the adsorbed amount at pressure P, and A_0, A_1, etc. are virial coefficients. At low surface coverage, A_2 and higher terms can be neglected, thus, the Henry's law constant (K_H) can be calculated by equation of $K_H = \exp(A_0)$. Based on the K_H values at different temperature, the Q_0 value is derived from the slope of the plot of $\ln K_H$ versus 1/T.

Ideal adsorbed solution theory (IAST) was performed to evaluate the adsorption selectivities of CO_2/CH_4 and CO_2/N_2 gas mixtures.[1] According to Myers and Prausnitz, the method of IAST can be reduced to the mathematical integration:

$$\int_{t=0}^{\frac{Py_1}{x_1}} F_1(t)d\ln t = \int_{t=0}^{\frac{Py_2}{x_2}} F_2(t)d\ln t \quad (2)$$

where P is the total pressure, x_i is the adsorbed phase molar ratio of gas i, y_i is the bulk phase

molar ratio of gas i and the function F_i (t) is a fitting function for the pure component i based on the single-site or dual-site Langmuir-Freundlich model:

$$n = \frac{a \cdot b \cdot p^{1/c}}{1 + b \cdot p^{1/c}} \tag{3}$$

Where n is amount of gas adsorbed (mmol g^{-1}), p is the pressure (bar) of the bulk gas at equilibrium with the adsorbed phase, a is the saturation capacity (mmol g^{-1}), b is the single-site affinity coefficient (1/bar), c is the deviation from an ideal homogeneous surface. These isothermal parameters (a, b, c) are the fitting parameters according to the experimental pure-component isotherms of N_2, CO_2 and CH_4.

Since $x_1 + x_2 = 1$ and $y_1 + y_2 = 1$, the adsorption selectivity ($\alpha_{A/B}$) of gas A over gas B is defined as:

$$\alpha_{A/B} = \frac{x_A / y_A}{x_B / y_B} \tag{4}$$