Electronic Supplementary Information

A New Microporous Carbon Material Synthesized via Thermolysis of Porous Aromatic Framework Embedded with Extra Carbon Source for Low-Pressure CO_2 Uptake

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Experimental Details

All reagents were purchased from Sigma-Aldrich or Alfa and used as received unless otherwise indicated. PAF-1[1] and PAF-1-SO_3H[2] were synthesized according to procedures reported in the literatures.

Synthesis of PAF-1-SO_3H

To an ice-cooled mixture of PAF-1 (100 mg) in dichloromethane (15 mL), chlorosulfonic acid (1.0 mL) was added drop wise. The resulting mixture was stirred at room temperature for three days. Then, the mixture was poured into ice, and the solid was collected, washed with water substantially, and dried to produce PAF-1-SO3H as blue powder.

Synthesis of PAF-1/C-900

Prior to carbon precursor loading, PAF-1-SO_3H was evacuated at 120 ºC for 10 h. Liquid FA was then introduced into the pretreated PAF-1-SO_3H at room temperature, and it was observed that the polymerization FA almost finished within 5 min. The mixture then remained stirred in an evacuated environment for 2 days to maximize the introduction and polymerization of FA within the interior pores of PAF-1-SO_3H. After filtration and washing with ethanol to remove FA adsorbed on the exterior surface, the composite powder was heated in a horizontal quartz reactor under an N_2 flowing atmosphere, at 80 ºC for 24 h and then at 150 ºC for 6 h, and was finally carbonized at 900 ºC for 8 h to afford the carbon material designated as PAF-1/C-900.

Synthesis of PAF-1-900 and Poly(FA)-900

For comparison studies, PAF-1-900 and Poly(FA)-900 samples were also prepared using the same aforementioned thermolysis procedures.

Characterizations

PXRD data were collected on a Bruker D8 Advance X-ray diffractometer. Gas sorption experiments were carried out on the surface area analyzer ASAP-2020. N_2 gas sorption isotherms were collected at 77 K using a liquid N_2 bath. CO_2 sorption isotherms were measured at 273 K using a water-ice bath and at 295 K with a water bath. Prior to the measurements, the samples were degassed for 10 h at 200 °C.

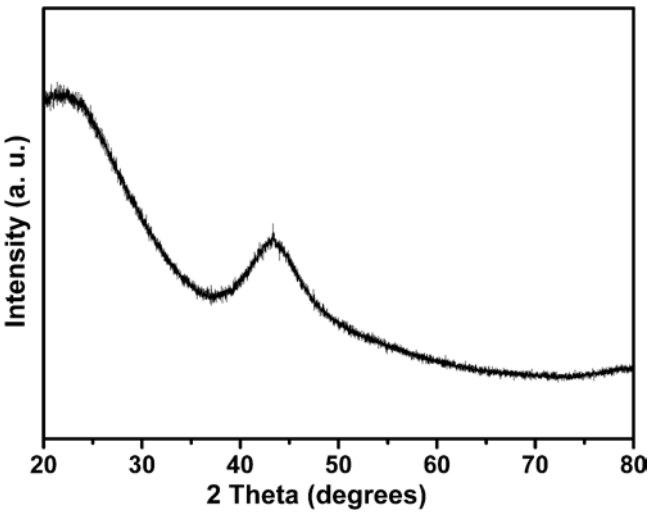


Fig. S1. PXRD patterns of PAF-1/C-900.

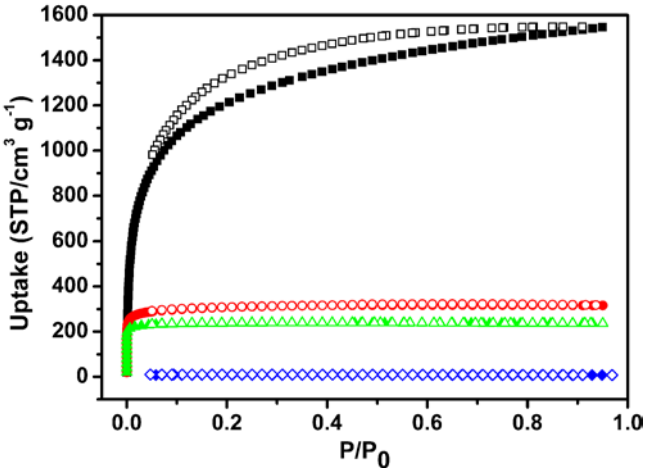


Fig. S2. N_2 sorption isotherms for PAF-1 and carbonized samples. (adsorption: filled; desorption: open; PAF-1: black squares; PAF-1/C-900: red circles; PAF-1-900: green triangles; Poly(FA)-900: blue diamonds).

Table S1 Texture properties of PAF-1 and carbonized samples

Sample	S_{BET}[a] (m^2 g^{-1})	Pore size[b] (Å)
PAF-1	4246	14.5
PAF-1/C-900	1174	5.4
PAF-1-900	923	9.4
Poly(FA)-900	28	21.6

[a] S_{BET} was calculated in the partial pressure (P/P_0) range of 0.01 to 0.1 which gives the best linear fitting.

[b] Maxima of the pore size distribution calculated using the Horvath-Kawazoe (HK) model.

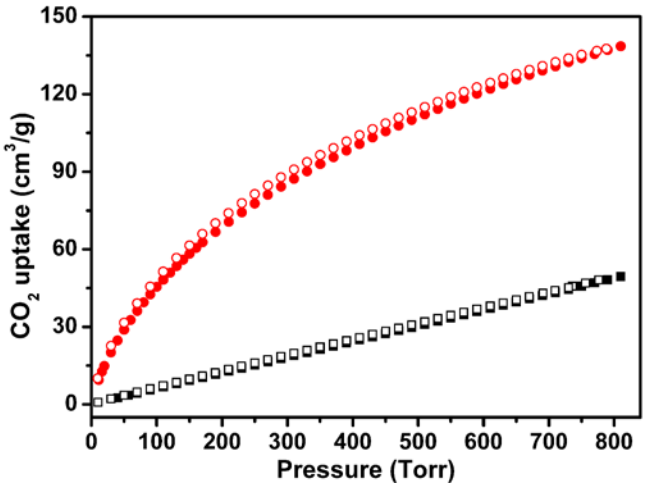


Fig. S3. CO_2 adsorption isotherms of PAF-1/C-900 and PAF-1 at 273K. (adsorption: filled; desorption: open; PAF-1/C-900: red circles; PAF-1: black squares).

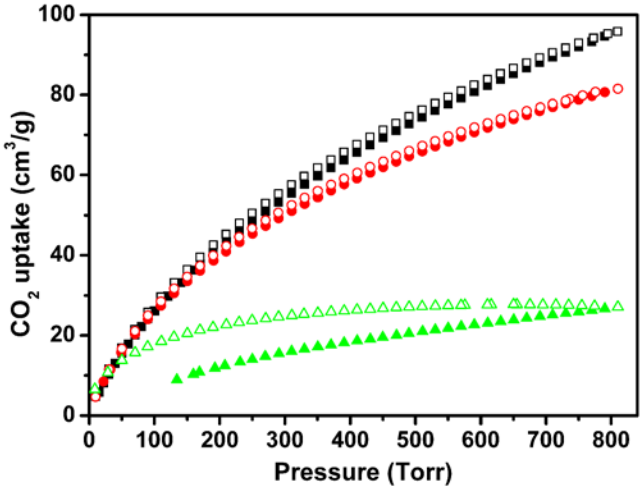


Fig. S4. CO_2 adsorption isotherms of PAF-1/C-900, PAF-1-900 and Poly(FA)-900 at 295K. (adsorption: filled; desorption: open; PAF-1/C-900: black squares; PAF-1-900: red circles; Poly(FA)-900: green triangles).

Heats of Adsorption (Q_{st}) Calculation.

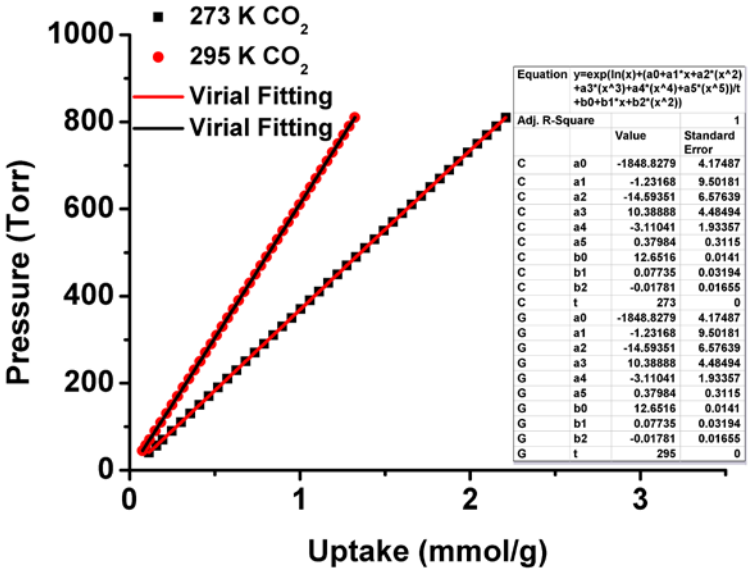
The virial equation of the form given in Equation (1) was employed to calculate the enthalpies of adsorption for CO_2 on PAF-1 and PAF-1/C-900.

$$\ln P = \ln N + 1/T \sum_{i=0}^{m} a_i N^i + \sum_{i=0}^{n} b_i N^i \qquad (1)$$

where P is the pressure expressed in Torr, N is the amount adsorbed in mmol/g, T is the temperature in K, a_i and b_i are virial coefficients, and m and n represent the number of coefficients required to adequately describe the isotherms. The equation was fitted by using the the least-squares method; m and n were gradually increased until the contribution of a and b

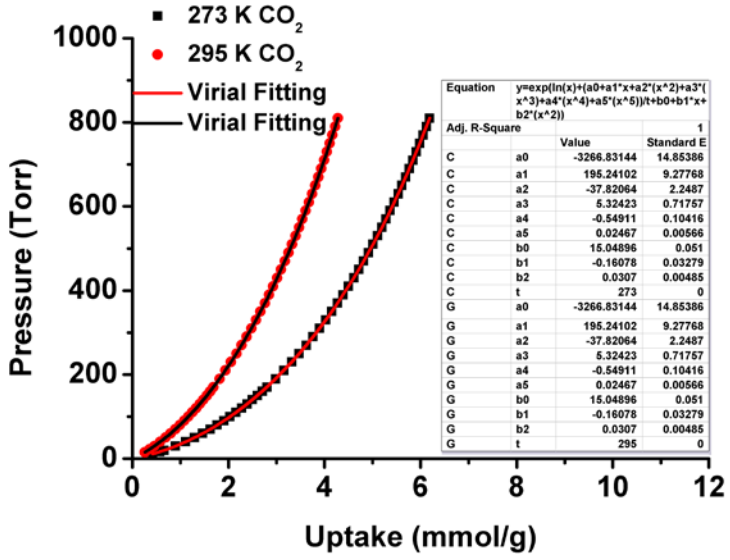
coefficients toward the overall fitting is statistically trivial, as determined by the t-test. The values of the virial coefficients $a_0 \ldots a_m$ were then used to calculate the isosteric heat of adsorption by the following expression:

$$Q_{st} = -R \sum_{i=0}^{m} a_i N^i \quad (2)$$



Equation	y=exp(ln(x)+(a0+a1*x+a2*(x^2)+a3*(x^3)+a4*(x^4)+a5*(x^5))/t+b0+b1*x+b2*(x^2))		
Adj. R-Square			1
		Value	Standard Error
C	a0	-1848.8279	4.17487
C	a1	-1.23168	9.50181
C	a2	-14.59351	6.57639
C	a3	10.38888	4.48494
C	a4	-3.11041	1.93357
C	a5	0.37984	0.3115
C	b0	12.6516	0.0141
C	b1	0.07735	0.03194
C	b2	-0.01781	0.01655
C	t	273	0
G	a0	-1848.8279	4.17487
G	a1	-1.23168	9.50181
G	a2	-14.59351	6.57639
G	a3	10.38888	4.48494
G	a4	-3.11041	1.93357
G	a5	0.37984	0.3115
G	b0	12.6516	0.0141
G	b1	0.07735	0.03194
G	b2	-0.01781	0.01655
G	t	295	0

Fig. S5 The plots of virial equation of PAF-1.



Equation	y=exp(ln(x)+(a0+a1*x+a2*(x^2)+a3*(x^3)+a4*(x^4)+a5*(x^5))/t+b0+b1*x+b2*(x^2))		
Adj. R-Square			1
		Value	Standard E
C	a0	-3266.83144	14.85386
C	a1	195.24102	9.27768
C	a2	-37.82064	2.2487
C	a3	5.32423	0.71757
C	a4	-0.54911	0.10416
C	a5	0.02467	0.00566
C	b0	15.04896	0.051
C	b1	-0.16078	0.03279
C	b2	0.0307	0.00485
C	t	273	0
G	a0	-3266.83144	14.85386
G	a1	195.24102	9.27768
G	a2	-37.82064	2.2487
G	a3	5.32423	0.71757
G	a4	-0.54911	0.10416
G	a5	0.02467	0.00566
G	b0	15.04896	0.051
G	b1	-0.16078	0.03279
G	b2	0.0307	0.00485
G	t	295	0

Fig. S6 The plots of virial equation of PAF-1/C-900.

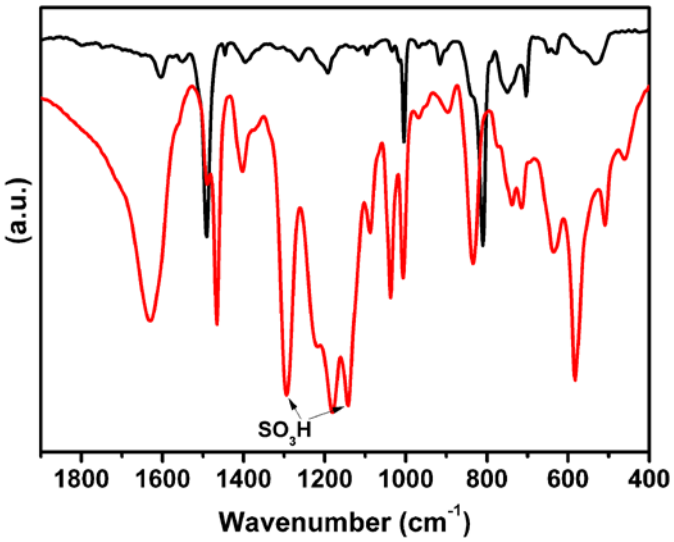


Fig. S7 FT-IR spectra of PAF-1 (black) and PAF-1-SO_3H (red).

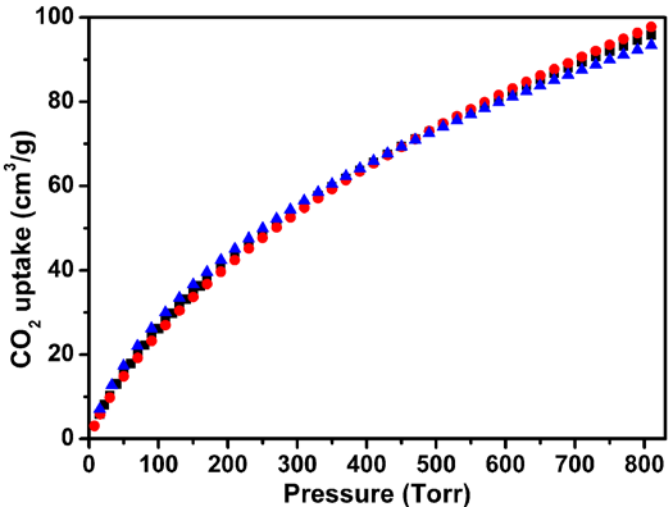


Fig. S8 CO_2 adsorption isotherms at 295 K for PAF-1/C-900 prepared from three different batches.

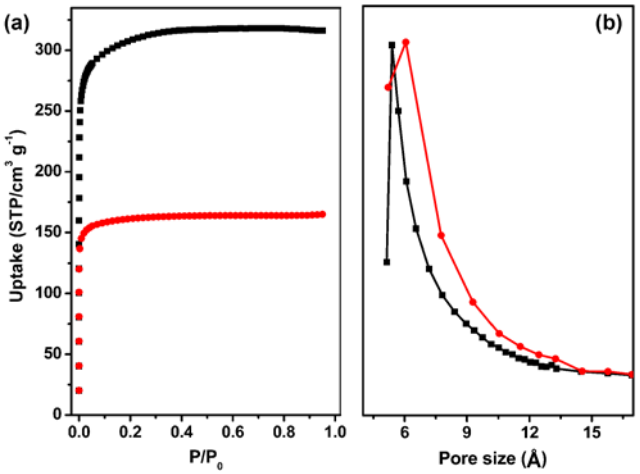


Fig. S9 (a) N_2 adsorption isotherms at 77 K and (b) pore size distributions for PAF-1/C-900 obtained by PAF-1-SO_3H with different SO_3H amounts (black, S/C: 0.053; red, S/C: 0.027).

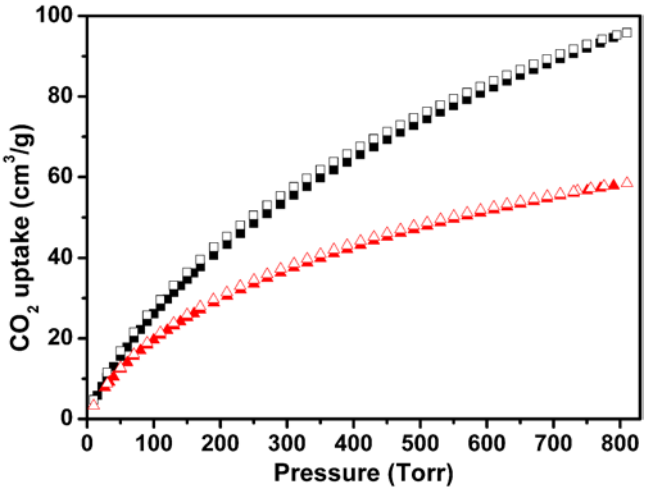


Fig. S10 The CO_2 adsorption isotherms of PAF-1/C-900 obtained by PAF-1-SO_3H with different SO_3H amounts (S/C ratio: black, 0.053; red, 0.027).

Reference

1 T. Ben, H. Ren, S. Ma, D. Cao, J. Lan, X. Jing, W. Wang, J. Xu, F. Deng, J. M. Simmons, S. Qiu, and G. Zhu, *Angew. Chem. Int. Ed.*, 2009, **48**, 9457.

2 W. Lu, D. Yuan, J. Sculley, D. Zhao, R. Krishna, and H.-C. Zhou, *J. Am. Chem. Soc.*, 2011, **133**, 18126.