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Electronic Supplementary Information

Novel lithium-laded porous aromatic framework for efficient CO_2 and H_2 uptake

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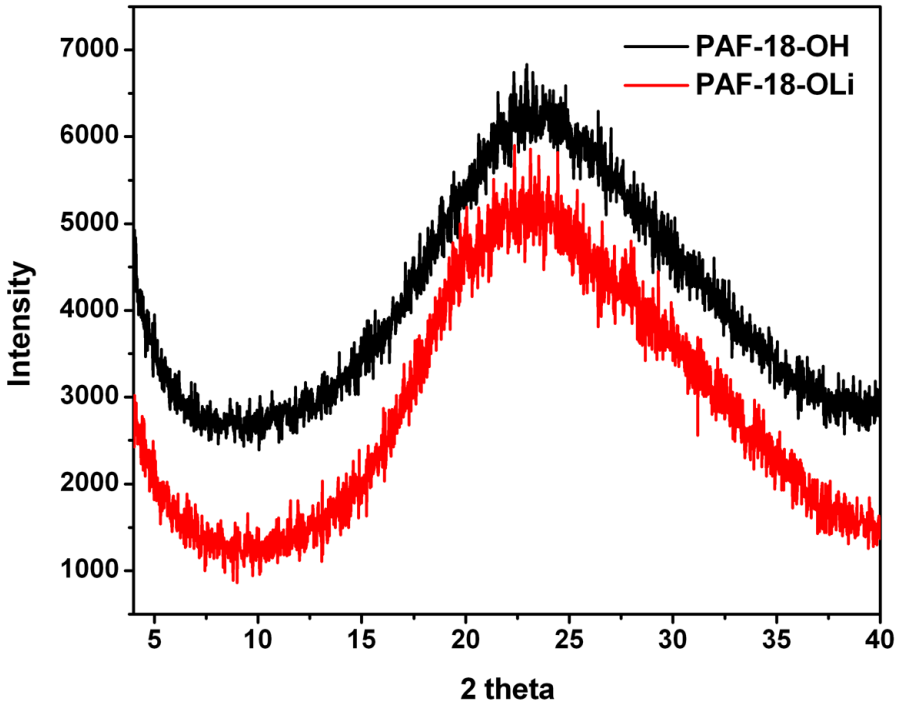

Fig. S1 PXRD patterns of PAF-18-OH and PAF-18-OLi samples.

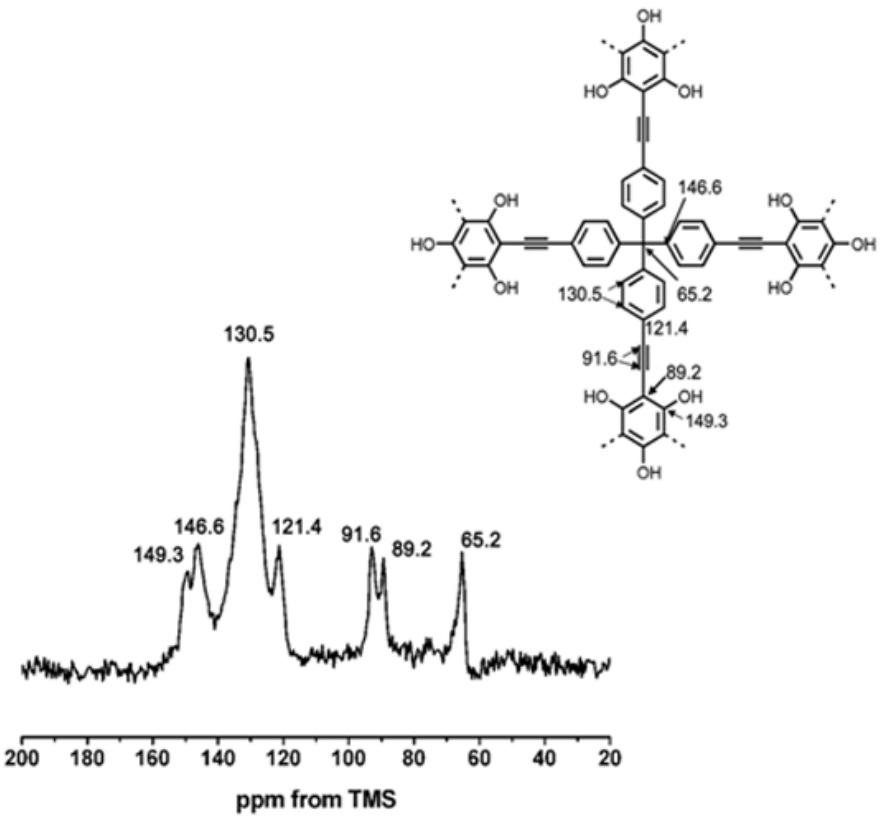

Fig. S2 ^{13}C CP/MAS NMR spectrum of PAF-18-OH.

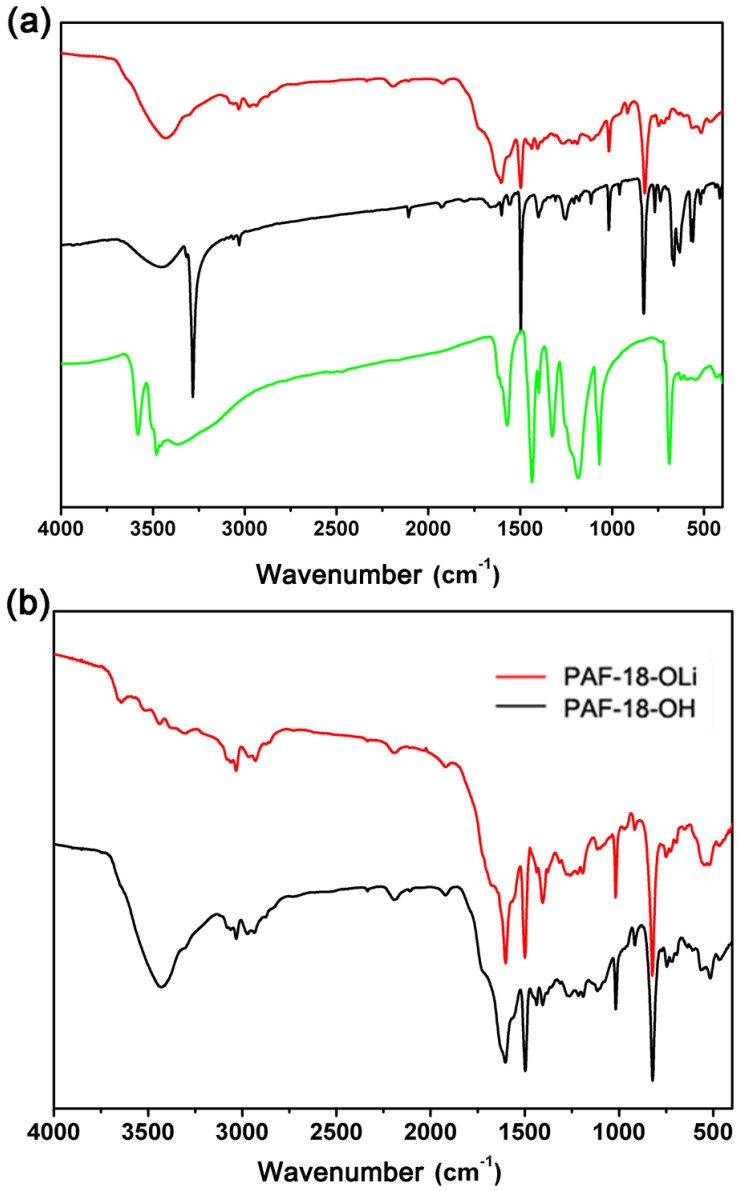

Fig. S3 (a) FTIR spectra of tetrakis(4-ethynylphenyl)methane (black), 2,4,6-tribromo-benzene-1,3,5-triol (green) and PAF-18-OH (red), (b) FT-IR spectra of PAF-18-OH and PAF-18-OLi products.

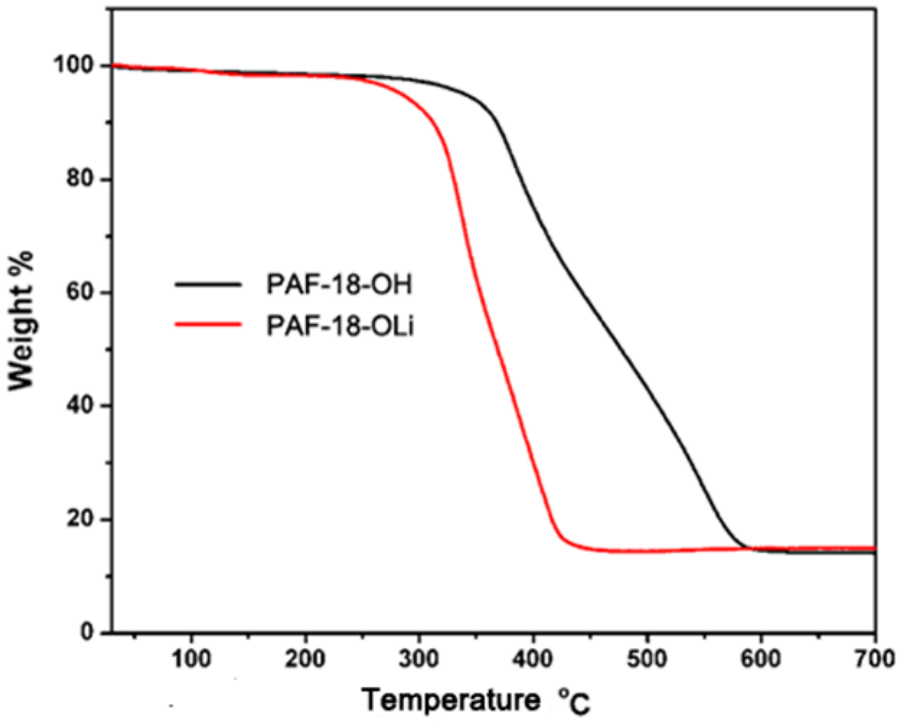

Fig. S4 TG curves of PAF-18-OH and PAF-18-OLi samples.

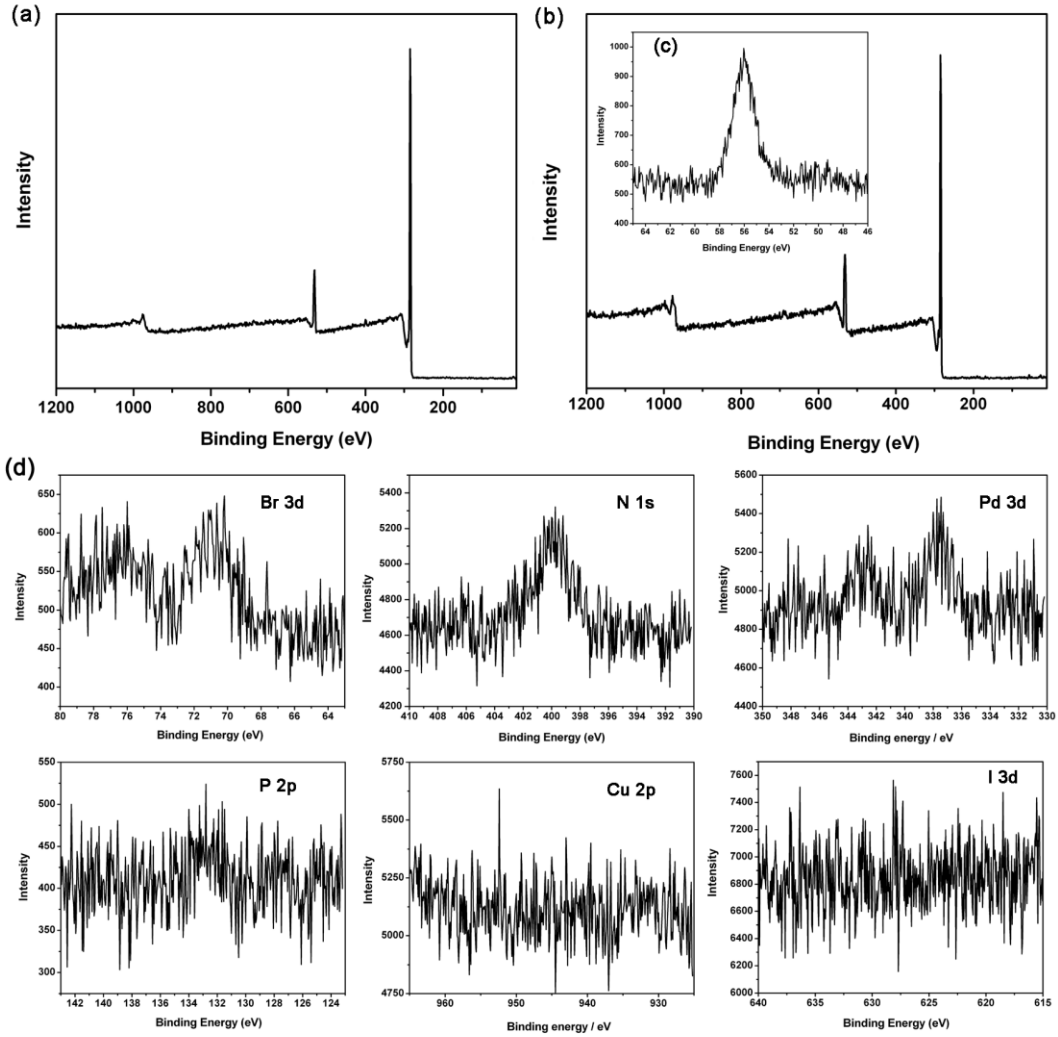

Fig. S5 XPS spectra of PAF-18-OH (a), PAF-18-OLi (b), Li 1s spectrum of PAF-18-OLi (c), and enlarged views of XPS spectra of Br 3d, N 1s, Pd 3d, P 2p, Cu 2p and I 3d (d) in the PAF-18-OH sample.

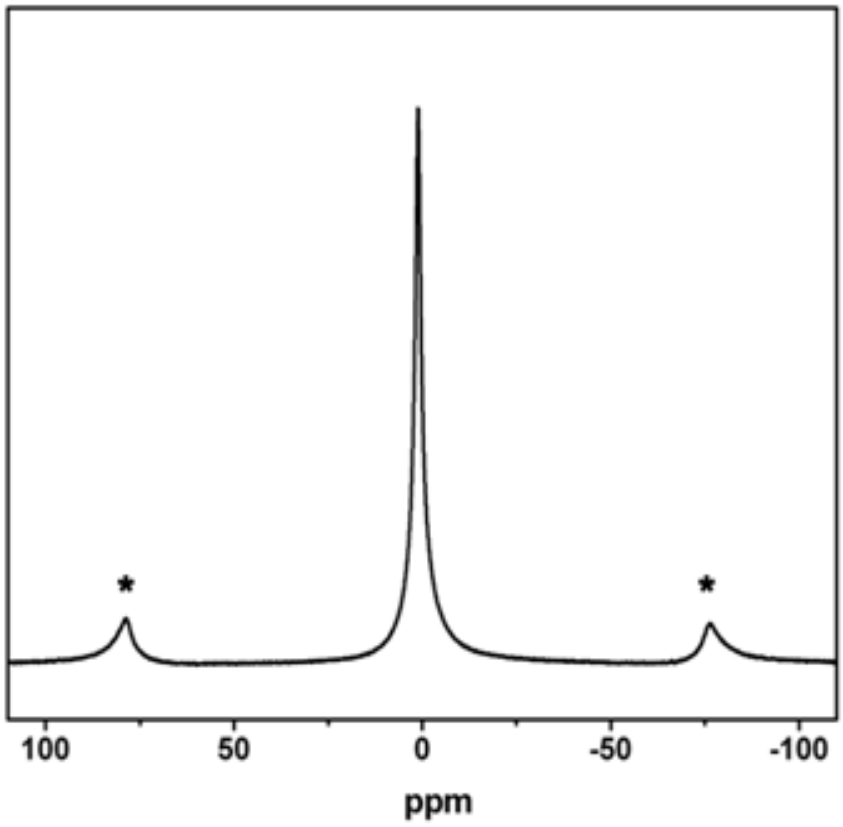

Fig. S6 ^{7}Li MAS NMR spectrum of PAF-18-OLi exhibiting a single resonance at δ = 0.80 ppm.

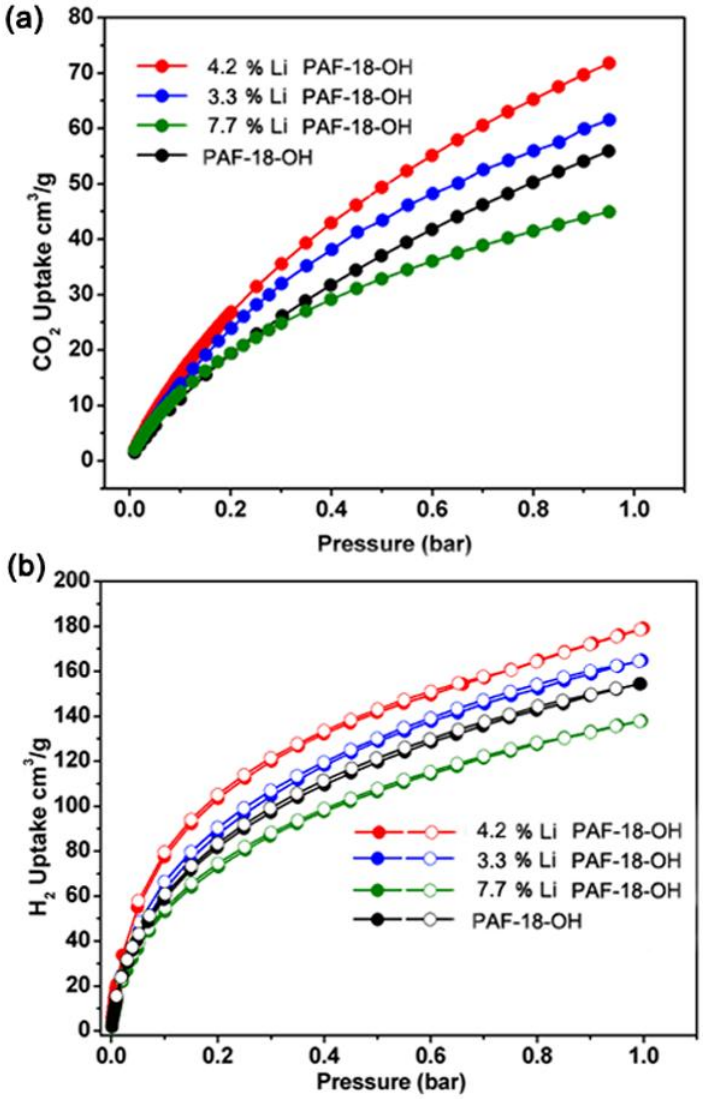

Fig. S7 Plots of CO_2 (a) and H_2 (b) adsorption isotherms on PAF-18-OH and PAF-18-OLi with different Li contents.

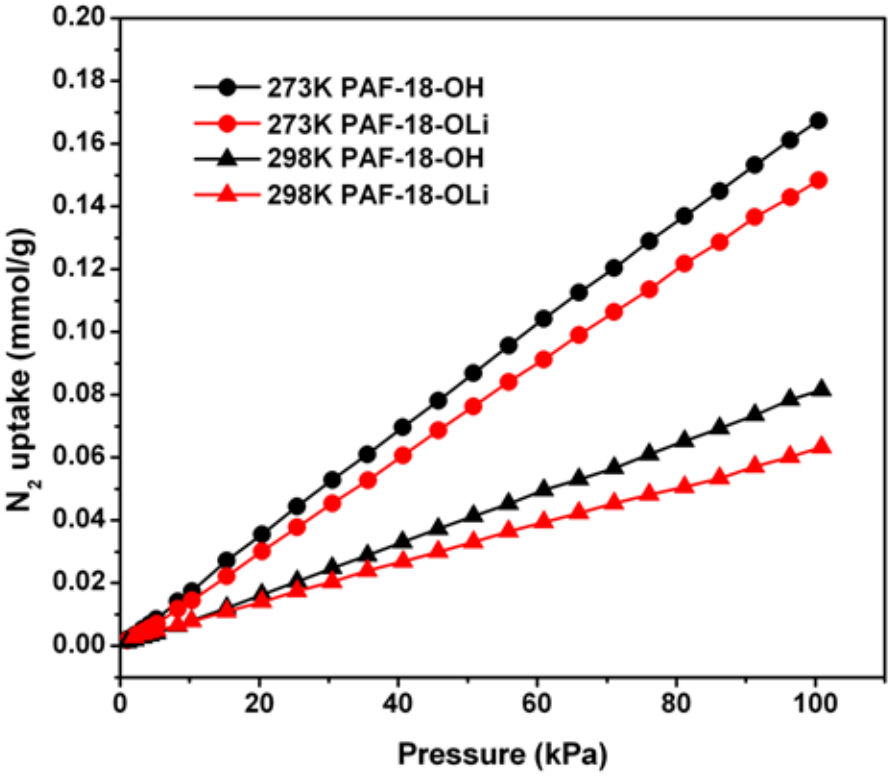

Fig. S8 N_2 adsorption isotherms of PAF-18-OH and PAF-18-OLi at 273 K and 298 K.

Table S1 The summary of the BET surface areas and gas uptakes of PAF-18-OH and PAF-18-OLi with different Li contents.

Samples	Li content (wt %)	S_{BET} (m^2 g^{-1})	H_2 uptake (wt %)	CO_2 uptake (wt %)
1	0	1121	1.4	11
2	3.3	1046	1.5	12.2
3	4.2	981	1.7	14.4
4	7.7	948	1.2	8.8

Calculation of Q_{st}:

The Q_{st} of CO_2 was calculated as a function of the CO_2 uptake based on the adsorption isotherms at 273 K and 298 K (the isotherms and fitting parameters are shown in Fig. S9-S10). The Q_{st} of H_2 was calculated as a function of the H_2 uptake based on the adsorption isotherms at 77 K and 87 K (the isotherms and fitting parameters are shown in Fig. S11-S12). The data were modelled with a virial-type expression composed of parameters a_i and b_i according to Eq 1. The isosteric heat of adsorption was calculated by fitting the parameters according to Eq 2. In these two equations, p is the pressure, N is the amount adsorbed, T is the temperature, and R is the universal gas constant. m and n determine the number of terms required to adequately describe the isotherm. a_i and b_i are virial coefficients.

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

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

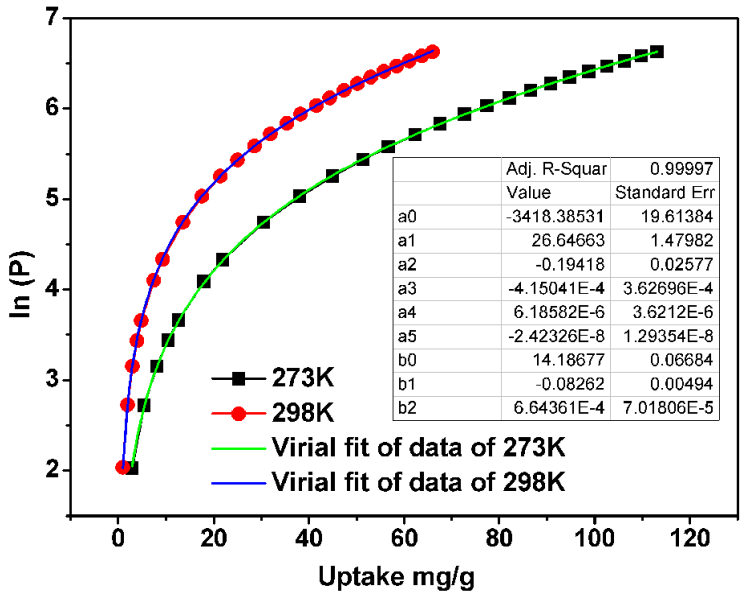

Fig. S9 CO_2 adsorption isotherms of PAF-18-OH at 273K and 298K and the corresponding fittings based on the virial equation.

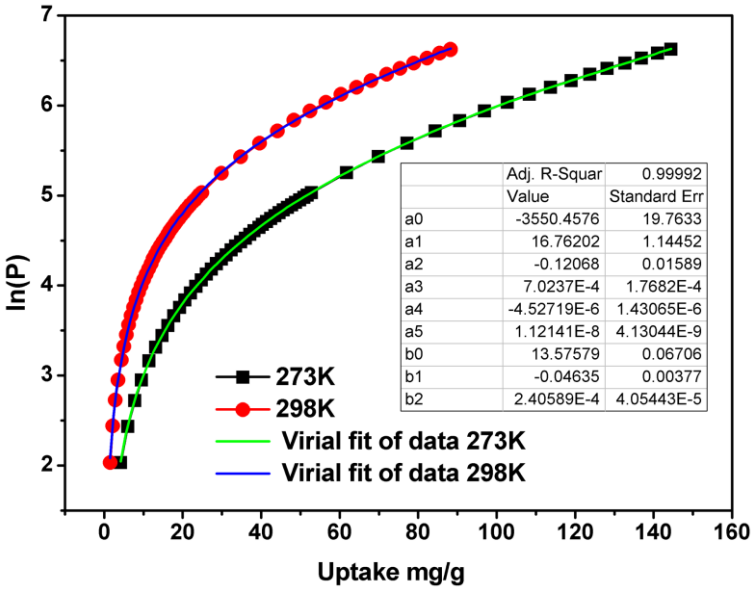

Fig. S10 CO_2 adsorption isotherms of PAF-18-OLi at 273K and 298K and the corresponding fittings based on the virial equation.

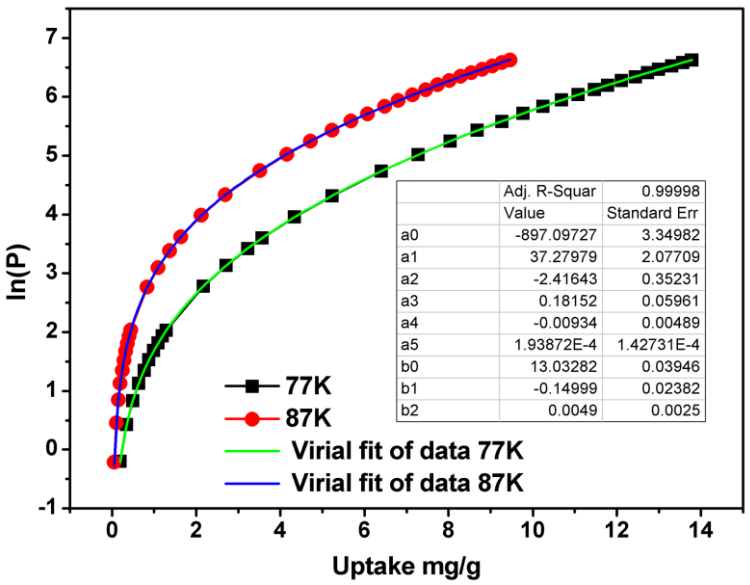

Fig. S11 H_2 adsorption isotherms of PAF-18-OH at 77 K and 87 K and the corresponding fittings based on the virial equation.

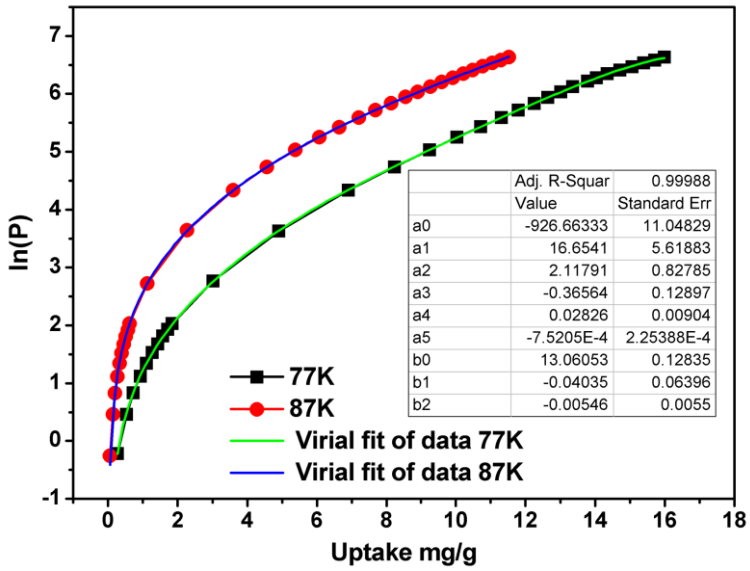

Fig. S12 Hydrogen adsorption isotherms of PAF-18-OLi at 77 K and 87 K and the corresponding fittings based on the virial equation.

Ideal Adsorption Solution Theory calculations:

The ideal adsorption solution theory (IAST) was used to predict the binary mixture adsorption of CO_2 and N_2 from the experimental pure-gas isotherms. Previous studies have shown that the IAST can predict mixture gas adsorption in many nanoporous materials, including porous-organic frameworks. The single-component isotherms were fitted using a dual-site Langmuir-Freundlich equation:

$$q = q_{m1} \cdot \frac{b_1 \cdot p^{1/n_1}}{1 + b_1 \cdot p^{1/n_1}} + q_{m2} \cdot \frac{b_2 \cdot p^{1/n_2}}{1 + b_2 \cdot p^{1/n_2}}$$

Here, p is the pressure of the bulk gas at equilibrium with the adsorbed phase (kPa), q is the adsorbed amount per mass of adsorbent (mmol/g), q_{m1} and q_{m2} are the saturation capacities of sites 1 and 2 (mmol/g), b_1 and b_2 are the affinity coefficients of sites 1 and 2 (1/kPa), and n_1 and n_2 represent the deviations from an ideal homogeneous surface.

The IAST adsorption selectivity, S, for binary mixtures of CO_2 (1)/N_2 (2), is defined as follows:

$$S = \frac{q_1 / q_2}{p_1 / p_2}$$

where q_i and p_i (i=1,2) are the mole fractions of component 1 and 2 in the adsorbed and bulk phases, respectively. The IAST calculations were carried out for binary mixture containing 15% CO_2 and 85% N_2, which is typical composition of flue gases.

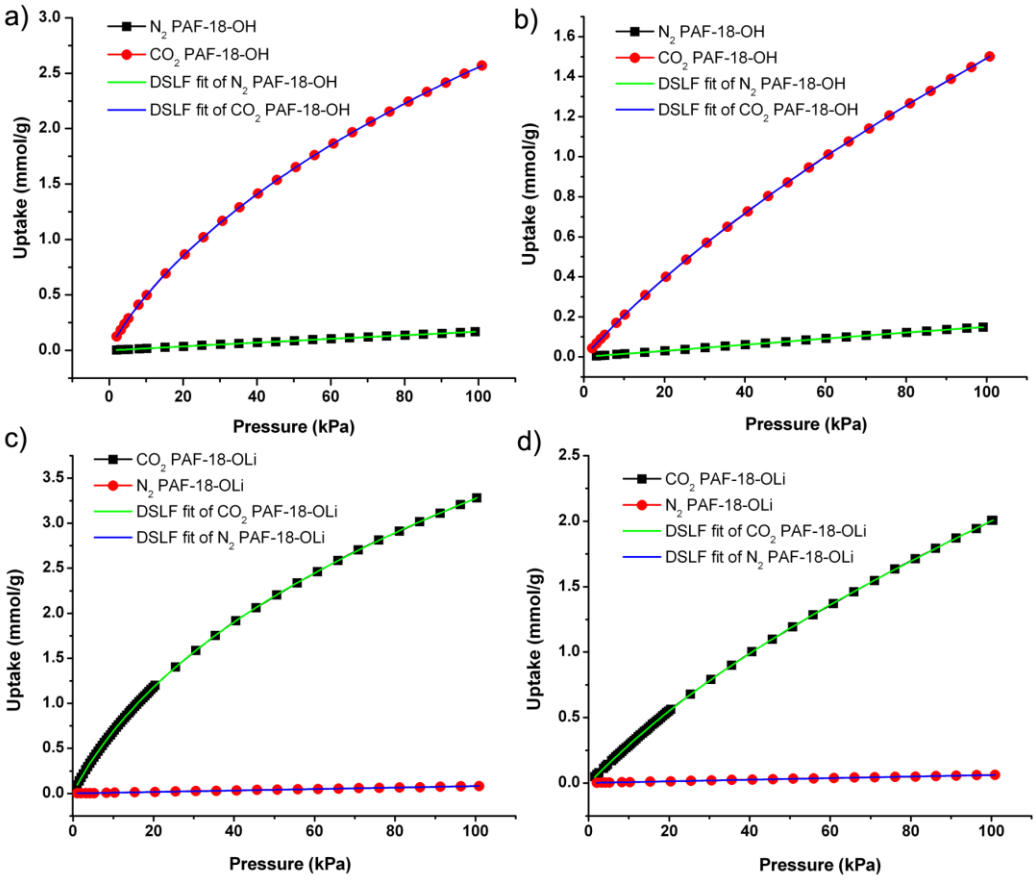

Fig. S13 The adsorption isotherms of pure component CO_2 and N_2 for PAF-18-OH at 273K (a) and 298K (b), and for PAF-18-OLi at 273K (c) and 298K (d). Isotherms are fitted using the dual-site Langmuir-Freundlich equation.