

Supplementary Information

Target Synthesis of a Novel Porous Aromatic Framework and Its High Selective Separation of CO₂/CH₄

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1. Instruments

Fourier transform infrared spectroscopy

Fourier transform infrared spectroscopy (FTIR) was carried out on a Nicolet Impact 410 Fourier transform infrared spectrometer. Samples were pestle and packed firmly to get transparent films.

Powder X-ray diffraction measurement

Powder X-ray diffraction (PXRD) patterns were recorded with a Rigaku XDS 2000 diffractometer using nickel-filtered Cu KR radiation ($\lambda=1.5418 \text{ \AA}$) over a range of $4^\circ < 2\theta < 40^\circ$ in 0.1° steps with a 1 s counting time per step.

Thermogravimetric analyses

Thermogravimetric analysis (TGA) was performed on a Mettler-Toledo TGA/SDTA851e. Samples (3-5 mg) in alumina pans were heated from 25 to 700 °C, at a heating rate of 10 °C /min under air atmosphere.

SEM analysis

SEM imaging was performed on JEOL-JSM-6300 under an accelerating voltage of 20-30 kV. The samples were sputtered with a thin film of Pt prior to imaging.

Low-pressure gas adsorption measurement

Gas adsorption/desorption isotherms were recorded on an Autosorb-Q1 Surface Area and Pore Size Analyzer. The samples were degassed at 393 K for 12 h (3×10^{-3} torr) prior to adsorption measurements. UHP grade (99.999%) N₂, Ar, H₂, CO₂, and CH₄ were used for all measurements. The temperatures were maintained at 77 K in liquid nitrogen bath, 87 K in liquid argon bath, 195 K in acetone - dry ice bath, 273 K in ice - water bath, and 298 K in water bath, respectively. The specific surface areas of the samples were calculated by the BET method.

Gas Chromatographic Separation

For the column preparation, PAF-30 powders were sieved before packing. A 2 mm id stainless steel tube was precut to 20 cm. The tube was positioned vertically against the floor. The lower end of the tube was filled with glass wool during the column packing. Around 0.20 g of PAF-30 powders were packed into the column; occasional shaking was applied during packing to ensure no void left in the tube. GC separation of selected light gases using a column packed with PAF-30 was performed with a SP-2100A GC system equipped with a thermal conductivity detector. H₂ was used as the carrier gas and was driven at the inlet pressure of 40 psi. A fresh column of PAF-30 was conditioned at 373 K for 5 h before injection of gas mixture. For a typical run, 1.0 mL of equimolar mixtures of CO₂/CH₄ or CO₂/N₂ was injected through an automatic gas sampling valve.

2. Materials and Synthesis

All starting materials were purchased from commercial suppliers and used without further purification unless otherwise noted. Cyanuric chloride was purchased from Alfa Aesar.

Tetra-(4-anilyl)-methane was obtained according to the procedure reported by Hegedus and co-workers.

Tetra-(4-anilyl)-methane (152 mg, 0.3 mmol), dimethylacetamide (DMAc) (10 mL) and N, N-diisopropylethylamine (DIPEA) (0.2 mL) were mixed well under nitrogen. After the resulting mixture was cooled down to 0 °C, 2 mL of cyanuric chloride solution in DMAc (73.8 mg, 0.4 mmol) were added dropwise into the mixture within 30 min under vigorously stirring. Then the reaction solution was warmed up and heated at 50 °C for 12h and then at 95 °C for 24 h. After removal of most of the solvent under reduced pressure, the product was extracted with THF in a Soxhlet apparatus least 48 h.

3. FTIR study of PAF-30

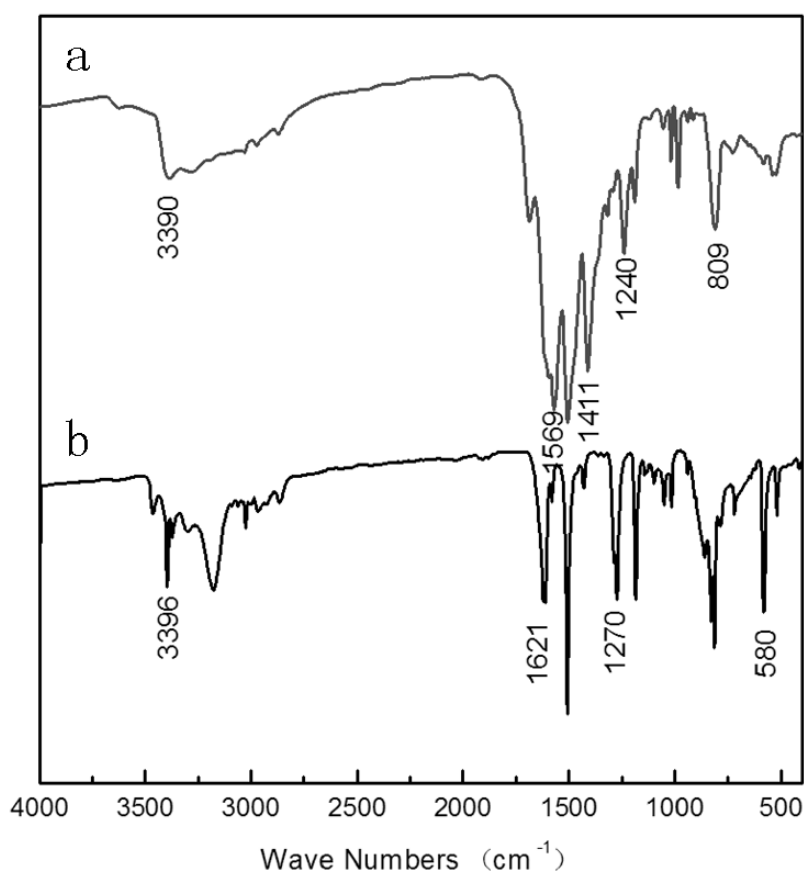


Fig. S1. FTIR spectra of PAF-30 (a) and Tetra-(4-anilyl)-methane (b)

4. Solid-state ^{13}C NMR

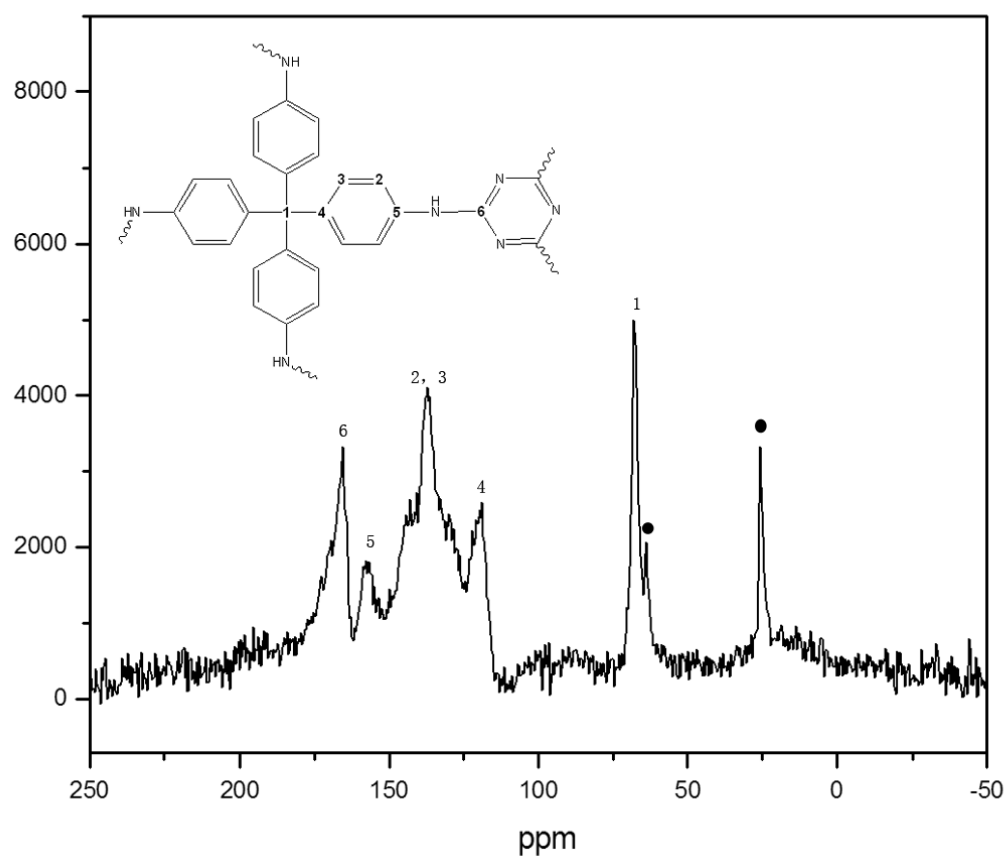


Fig. s2 Solid-state ^{13}C CP/MAS NMR spectrum of PAF-30.

5. Simulated structure of PAF-30

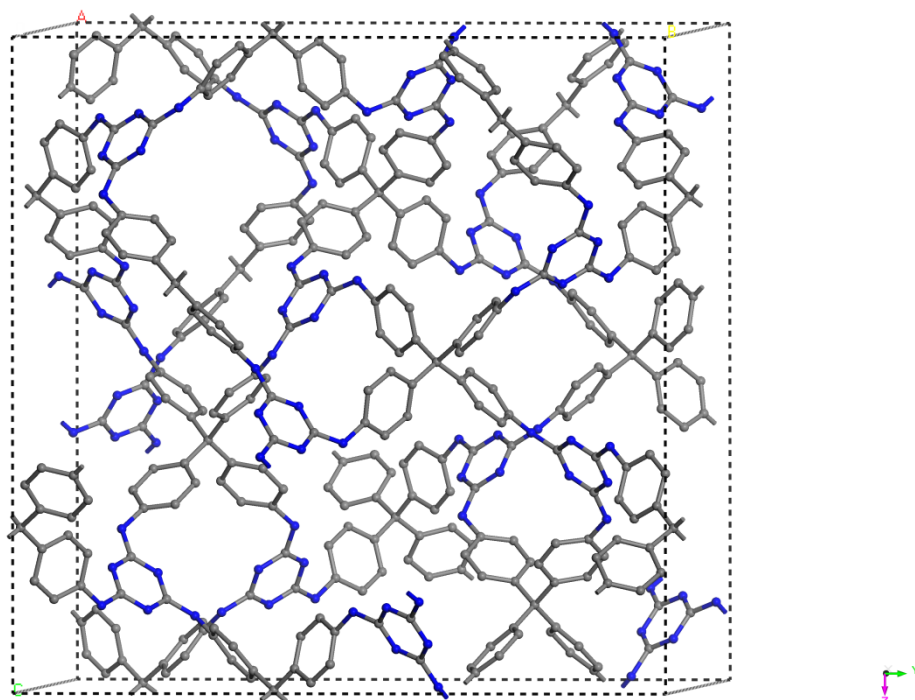


Fig. s3 Simulated structure of PAF-30, obtained based on field-force calculation and crystal lattice parameters. N atoms are highlighted by blue and H atoms are omitted for clarity.

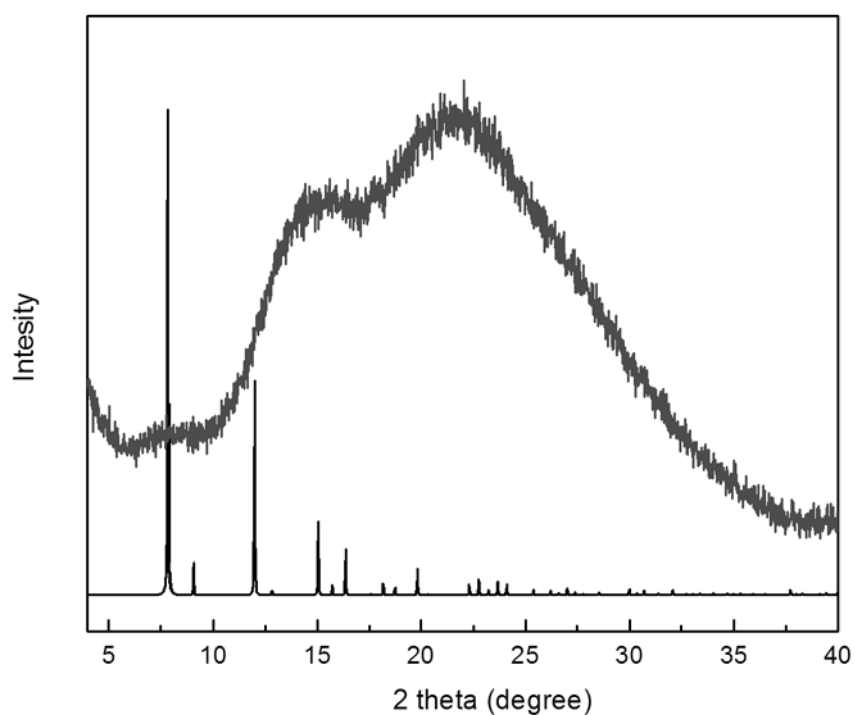


Fig. s4 Experimental PXRD patterns (upper) and calculated PXRD patterns (down) from the simulated structure.

6. TGA study of PAF-30

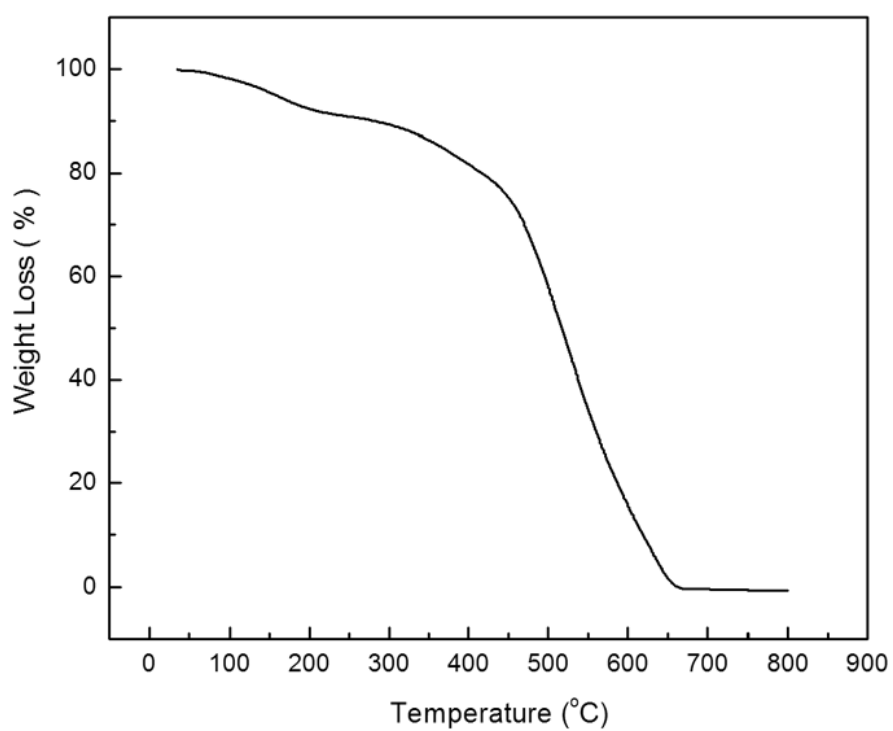


Fig. s5. TGA thermogram of PAF-30 under air.

7. SEM

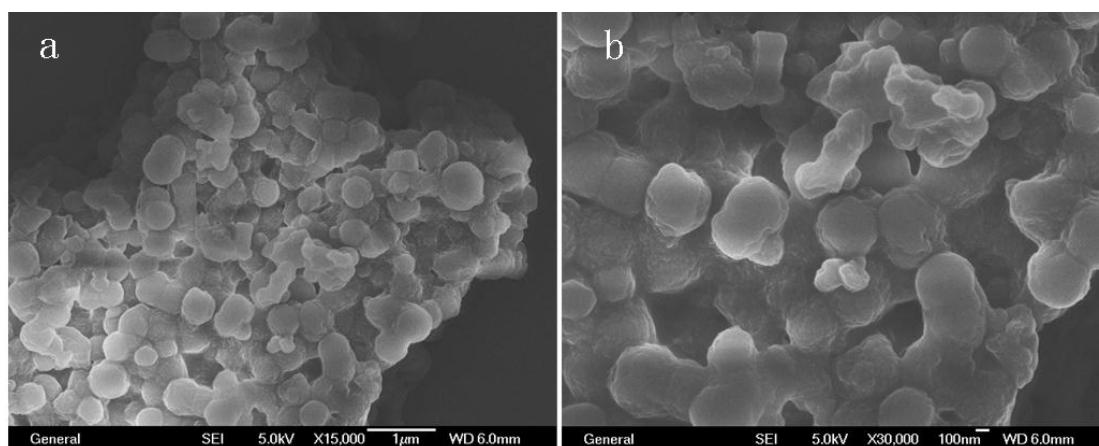


Fig. s6. Low (a) and high (b) magnification SEM images of PAF-30.

8. Selective adsorption behavior of PAF-30 at low temperature

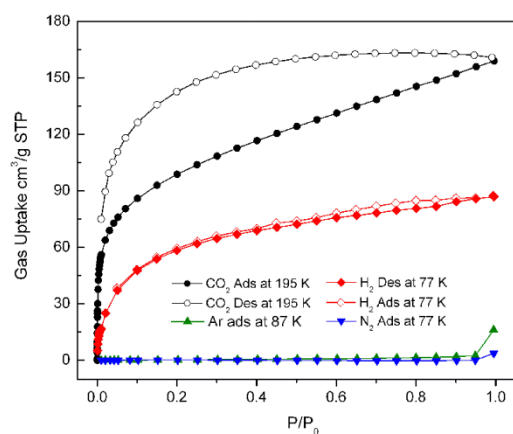


Fig.s7. Gas sorption isotherms of PAF-30 at low temperature

9. Isostatic heat of adsorption of carbon dioxide and hydrogen

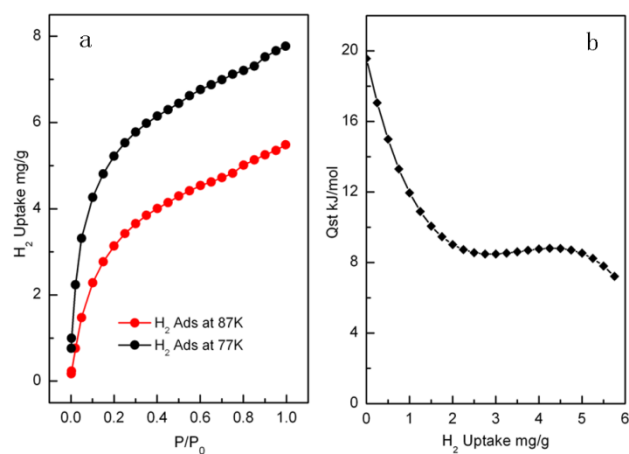


Fig.S8 H₂ adsorption isotherms of PAF-30 at 273 K and 298 K (a) and Plot of the isosteric heat of adsorption of H₂ versus the uptake amount of H₂ (b)

10. Assessment of adsorption of binary gas mixtures by IAST theory

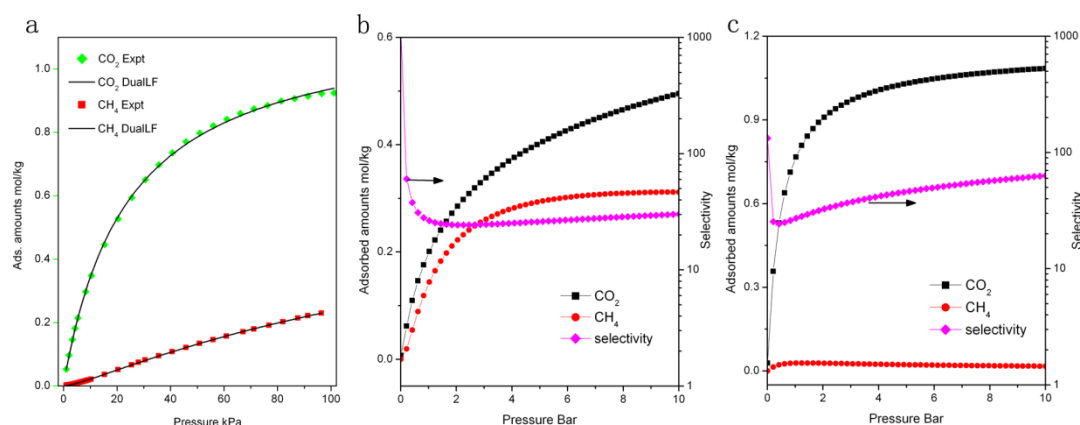


Fig.s9 a) Experimentally measured CO₂ and CH₄ adsorption isotherms of PDF-36 at 298 K. The isotherms are fitted with dual-site Langmuir–Freundlich adsorption model-based IAST theory. (b and c) Experimentally measured isotherms of adsorption of the mixtures of CH₄ and CO₂ in PAF-30 at 298 K. The CH₄ to CO₂ volume ratio is 50:50 (b) and 95:5 (c) The isotherms are fitted with dual-site Langmuir–Freundlich adsorption model-based IAST theory to reveal the CO₂ adsorption selectivity

The adsorption isotherms for pure CO₂ and CH₄, measured at 298 K, were first converted to absolute loadings according to Peng-Robinson Equation. In order to perform the IAST calculation, the single-component gas absorption isotherms was fitted by the dual-site Langmuir-Freundlich (DSLFF) adsorption model, which was adopted to correlate the pure-component equilibrium data and further to evaluate the adsorption of binary gas mixtures. The DSLF model is described as

$$N^0(f) = \frac{N_1 k_1 f}{1 + k_1 f} + \frac{N_2 k_2 f}{1 + k_2 f} \quad (1)$$

where f is the fugacity of bulk gas at equilibrium with adsorbed phase, N_i is the model parameter of the maximum adsorption amount at the site i ($i = 1$ or 2) and k_i is the affinity constant.

Based on the above model parameters of pure gas adsorption, we used the IAST model, which was proposed by Myer and Prausnitz in 1965 to predict the multi-component adsorption. Analogous to Raoult's law for vapor-liquid equilibrium, the IAST assumes that the adsorbed solution is ideal and all activity coefficients in the adsorbed phase are unity. Thus, the adsorption equilibrium between adsorbed and gas phases will lead to the following equation.

$$Py_i \varphi_i = x_i f_i^0(\pi)$$

where f_i^0 is the fugacity of the equilibrium gas phase corresponding to the spreading pressure π for the adsorption of pure gas i , φ_i is the gas fugacity coefficient of component i calculated

by Peng Robinson equation of state, and x_i and y_i are the molar fraction of component i at the adsorbed and bulk phases, respectively. The binary gas mixing process is carried out at constant spreading pressure π and indicated by

$$\int_0^{f_1^0} N_1^o(f_1) d\ln f_1 = \int_0^{f_2^0} N_2^o(f_2) d\ln f_2$$

where the single-component adsorption amount and selectivity are further obtained from the above equation by numerical integration and root exploration.

To investigate the separation of binary mixtures, the adsorption selectivity is defined by

$$S_{i/j} = \frac{x_i/x_j}{y_i/y_j}$$

where the selectivity refers to the first component over the second one, and the x_i , x_j and y_i , y_j denote the molar fractions of species i , j in the adsorbed and bulk phases, respectively.

Table s1. Parameters used for fitting adsorption of pure CO₂ and CH₄ based on Dual-site Langmuir-Freundlich equation.

T	adsorbate	N ₁	k ₁	N ₂	k ₂
298	CO ₂	0.00476	9.78597e12	1.15772	0.04135
	CH ₄	-0.04086	0.07742	0.79372	0.00522

11. Optical photo of the interior of the Column Compartment of GC



Fig. s10. Optical photo of the interior of the Column Compartment of the GC used in the present work.