

Supporting Information

Novel Nanoporous Ferrocenyl Framework for Clean Energy Application

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Section S1: Materials, methods and full synthetic procedures of FNOPs-1.

1. Materials

All chemicals were purchased from commercial suppliers (Aladdin, Sigma-Aldrich) and used without further purification, unless otherwise noted. Tetra-(4-anilyl)-methane was synthesized with slight modification according to our recent report.^[1] The synthesis of 1,1'-ferrocenedicarboxaldehyde was used published procedures.^[2] All reactions were performed at ambient laboratory conditions without excluding oxygen or atmospheric moisture, unless otherwise specified. Pyrex glass tube charged with reagents and flash frozen with liquid N₂ were evacuated by the Schlenk line.

2. Synthesis of 1,1'-ferrocenedicarboxaldehyde.

The reaction was carried out in the Schlenk-type apparatus under nitrogen. Ferrocene (10 g, 54

mmol) in 100 mL of hexane (previously dried over CaH) was treated with 75 mL of 1.6 M n-butyllithium (120 mmol) in hexane, and subsequent tetramethylethylenediamine (TMEDA) (17 mL, 56 mmol). The reaction mixture was stirred for 20 h before 13 mL of DMF (previously dried over CaH, and distilled) was added dropwise at -78 °C. After 4 h stirring, the mixture was hydrolysed with 40 mL hydrochloric acid (4.0 M, 0.2 mol). The organic phase was extracted with dichloromethane, and dried over MgSO₄. After the solvent was removed, the crude residue was two crystallisations in the cyclohexane to get the shiny red crystals (3.38 g, 52% yield). ¹H NMR in (300 MHz, CDCl₃,) δ: 4.68 (s, 4H, C₅H₅); 4.89 (s, 4H, C₅H₅); 9.95 (s, 2H, -CHO).

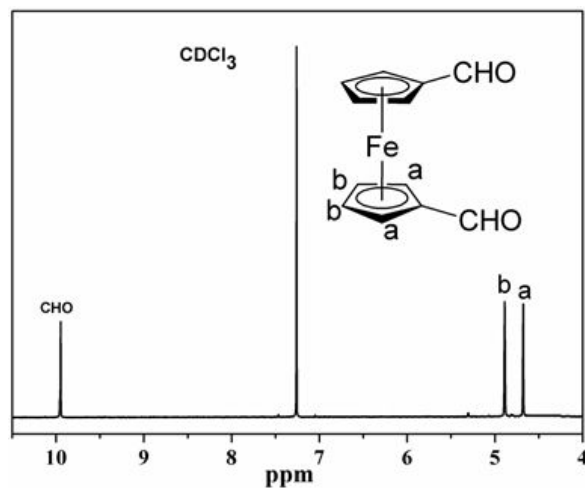
3. Synthesis of FNOPs-1

In a Pyrex tube, Melamine (8.75 mg, 0.069mmol) and 1,1'-ferrocenedicarboxaldehyde (21.54 mg, 0.089 mmol) were suspended in mixed solution of anhydrous 1,4-dioxane (1.0 mL) and aqueous acetic acid (0.2 mL, 3.0 M). The tube was then degassed by freeze-pump-thaw technique twice in the liquid nitrogen bath. Finally the tube was evacuated to an internal pressure of 150 mtorr and flame sealed. The reaction was heated at 120 °C for 3 days to yield a reddish brown solid, which was filtered and washed with anhydrous dioxane and anhydrous THF. The resulting powder was immersed in a THF/chloroform mixture (1:1) for 1 day and dried 10⁻² mtorr for 12 h and 100 °C to afford a reddish brown powder (17 mg, 58.7 % or 21mg, 66.5 % based on 1,1'-ferrocenedicarboxaldehyde). FTIR (KBr): $\tilde{\nu}$ = 3410, 3027, 2920, 2860, 1700, 1621 (C=N), 1602, 1558, 1491, 1460, 1409, 1305, 1194, 1173, 1105, 1005, 980, 880, 838, 814 cm⁻¹;

Section S2: Characterization

1. Structure characterization of 1,1'-ferrocenedicarboxaldehyde

Figure S1 ^1H NMR spectra of 1,1'-ferrocenedicarboxaldehyde



2. FT-IR Spectroscopy of Synthesized FNOPs-1.

Figure S2 Stack plot of the FT-IR spectrum of ferrocenyl network (red line, top), 1,1'-ferrocenedicarboxaldehyde (blue line), and melamine (black line, bottom)

FT-IR spectra ($500\text{-}3600\text{ cm}^{-1}$) of starting materials and ferrocenyl network: Intense N-H stretching peaks for melamine at around $3300\text{-}3500\text{ cm}^{-1}$ and the intense C=O stretching peaks for 1,1'-ferrocenedicarboxaldehyde were disappeared in the network. The presence of a new band at around 1552 cm^{-1} in the FNOPs-1 confirmed the formation of imine linked C=N.

Figure S3 Cross-polarization (CP) ^{13}C MAS natural abundance NMR spectrum of FNOPs-1.

Figure S4 PXRD pattern of starting materials Melamine (black line, top) and synthesized FNOPs-1 (red line, down)

3. Low-Pressure (0–1 bar) Gas Adsorption Measurements for FNOPs-1

Low-pressure gas sorption experiments were carried out by N_2 , H_2 , CO_2 and CH_4 . Firstly, the N_2 adsorption isotherms at 76 K was perform to evaluate the surface properties, including surface

areas, pore volume and pore size distributions. Gas storage and selective adsorption properties were evaluated with the adsorption isotherms of CO₂ (273 K and 298 K) and CH₄ (273 K and 298 K). The isosteric heats of adsorption was evaluated the binding affinity by single-component adsorption isotherms based on virial equation and Clausius-Clapeyron equation.^[3, 4]

Virial Equation

A virial-type expression in the following form can be used to fit the experimental isotherm data for a given material at different temperatures.

$$\ln(P) = \ln(N) + \frac{1}{T} \sum_{i=0}^m a_i N^i + \sum_{i=0}^n b_i N^i \quad (\text{I})$$

Where N is the amount adsorbed at a pressure P and a temperature T , and m and n determine the number of terms which are required to adequately describe the isotherm, both a_i and b_i are temperature independent empirical parameters. And then, the isosteric heats of adsorption as a function of uptake was calculate by the resulting virial coefficients from a_0 to a_m :

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

Where R is the universal gas constant (8.314 J K⁻¹ mol⁻¹)

Isosteric heats of adsorption was then calculated from the Clausius-Clapeyron equation.

$$Q_{st} = RT^2 \left[\frac{\partial \ln p}{\partial T} \right]_N \quad (\text{IV})$$

Where R is the universal gas constant, T is the temperature and P is the pressure for given quantity of gas adsorbed (N). Meanwhile, The temperature dependent experimental data should be fit to model isotherms to obtain P for given N .

$$(\ln P)_N = -(Q_{st}/R)(1/T) + C \quad (\text{V})$$

Equation (IV) can be rearranged to the equation (V).

Q_{st} can be get from the slope of $\ln(P)$ vs. $1/T$ plot in the equation.

Nitrogen Sorption Analysis. Special surface areas and pore size distributions in polymers were measured by nitrogen adsorption and desorption at 77.3 K using either a Micromeritics ASAP 2020 volumetric adsorption analyzer. The surface areas were calculated in the relative pressure (P/P_0) range from 0.01 to 0.10. Pore size distributions and pore volumes were derived from the adsorption branches of the isotherms based on the DFT model using the nonlocal density functional theory (NL-DFT). Samples were degassed at 120 °C for 20 h under vacuum (10^{-5} bar) before analysis.

Figure S5 BJH pore size distribution of the ferrocenyl network

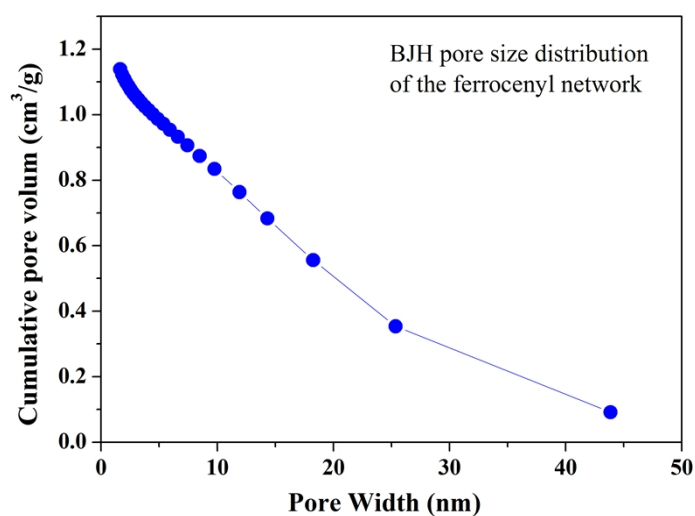


Figure S5: The CO₂(A) and CH₄(B) isotherms at 273 K and 298 K (symbols) and the

virial equation fits (lines) for FNOPs-1

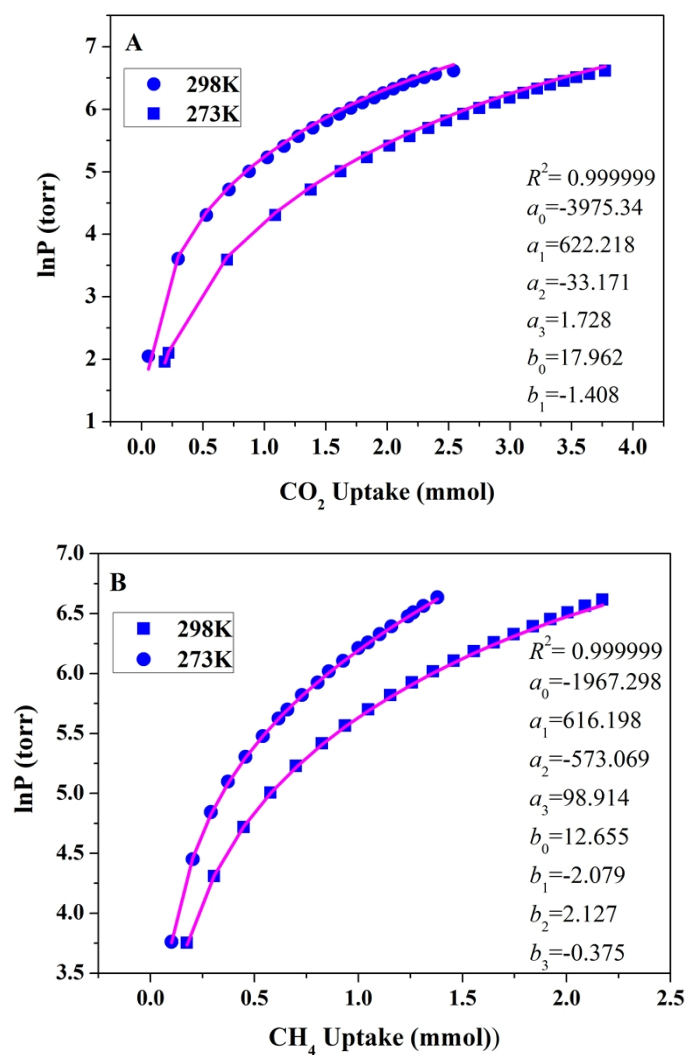
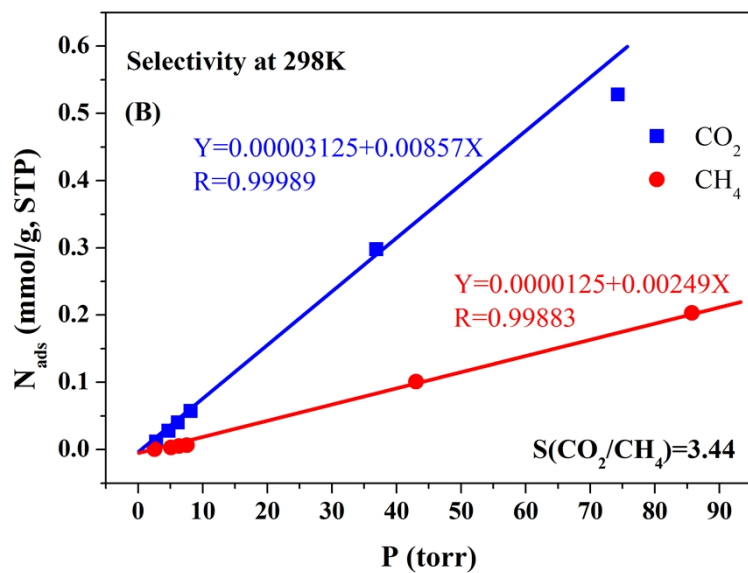
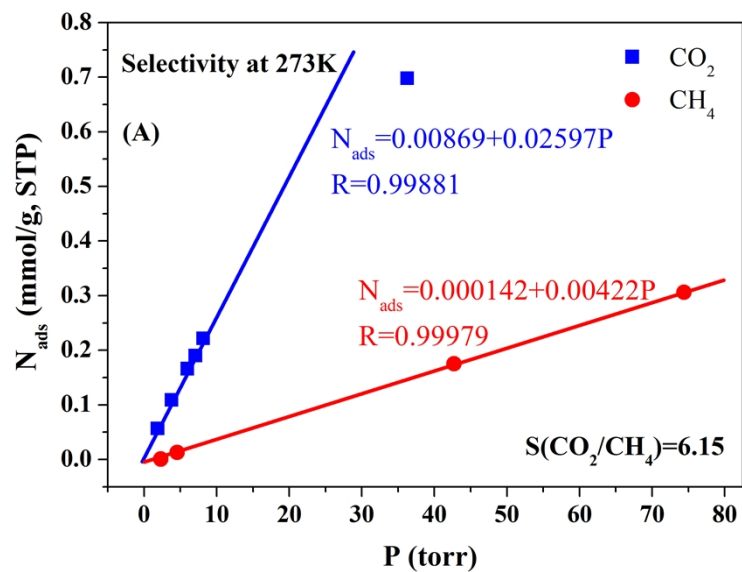


Figure S6 The fitting initial slope for CO₂ and CH₄ isotherms for FNOPs-1 collected at 273 K (A)

and 298 K (B). (N_{ads} =gases uptake, and R=related coefficient)



References

- 1) P. Ganesan, X. Yang, J. Loos, T. J. Savenije, R. D. Abellon, H. Zuilhof, E. J. R. Sudhölter, J. Am. Chem. Soc., 2005, 127, 14530.
- 2) G. G. A. Balavoine, G. Doisneau, T. Fillebeen-Khan, J. Organomet. Chem., 1991, 412, 381.
- 3) J. L. C. Rowsell, O. M. Yaghi, J. Am. Chem. Soc., 2006, 128, 1304.
- 4) P. Huanhua, J. A. Ritter, P. B. Balbuena, Langmuir 1998, 14, 6323.