Supporting Information

A Water-Stable Anionic Metal-organic Framework for Highly Selective Separation of Methane from Natural Gas and Pyrolysis Gas

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1. Synthesis of ligands

Synthesis of the ligand of H₅hpdia (H₅hpdia=5,5'-(hydroxyphosphoryl)diisophthalic acid)



Scheme S1. Process of synthesis of the containing phosphorous ligand H₅hpdia

The synthesis of ligand of H₃hpdia is according to former work¹. A mixture of bis(3,5-dimethylphenyl)phosphine oxide (2.0 g, 7.8 mmol), potassium hydroxide (0.7 g, 12.5 mmol), and water (0.7 ml) in ethanol (15 ml) is refluxed for 4h and then remove ethanol by rotary evaporation, following diluted with water (50 ml). The aqueous solution is washed with toluene for three times and then acidified with hydrochloric acid. The white precipitate is filtered off to give medium product bis(3,5-dimethylphenyl)phosphinic acid (Yield 1.8g~85%). In the next moment, total medium product (1.8g, 6.6 mmol) is solved with pyridine (12 ml). To this mixture, KMnO₄ (42 g, 265.7 mmol) is added portionwise with little water at a rate to maintain refluxing. Then remove brown precipitate by filtering, the remained solution is rotary evaporated until the odor of pyridine is no longer evident. Finally, the mixture is acidified with hydrochloric acid and filter to get the white target product (Yield 2.3 g~89%).

¹H NMR (400 MHz, DMSO) δ 13.61 (s, 2H), 8.47 (dd, J = 5.8, 4.2 Hz, 3H). ³¹P NMR (162 MHz, DMSO) δ 13.03(s).

2. X-ray crystallography of compound FJI-C4

Single-crystal X-ray diffraction data of compounds **FJI-C4** were collected with a SuperNova CCD-based diffractometer equipped with graphite-monochromated Cu K α radiation by using a ω -scan at 100 K. All of the structures were solved by direct methods and refined on F² by full matrix least-squares using the SHELXL-97 program package. All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms attached to carbon atoms were added theoretically. Detailed final refinements and structure data of these compounds are presented in Table S2.



Figure S1. Rodlike Single crystal of FJI-C4 under microscope



FigureS2. ORTEP drawing of the asymmetric unit of **FJI-C4**, excluding the guest entities.



Figure S3. The structure of FJI-C4 viewed along *a*, *b*, and *c* axis.



Figure S4. The 3D mode of framework in **FJI-C4** showing square channels viewed along *c* axis with exhibition of its surface area.

3. Thermogravimetric analysis (TGA)



Figure S5. The TGA curves of FJI-C4 under N₂ atmosphere.

4. IR spectrum



Figure S6. The IR spectrum of FJI-C4.

5.¹H NMR spectrum





A ¹H NMR study was performed to determine the number of Me₂NH₂⁺cations per hpdia⁵⁻ unit for samples of **FJI-C4**. ~10 mg of sample was completely dissolved in 20 μ L of DCl (35 wt% in D₂O) and 550 μ L of *d*₆-DMSO.

Result:

¹H NMR (400 MHz, DMSO) δ 8.55 (d, J = 14.0 Hz, 1.04H), 8.46 (dd, J = 11.9, 1.5 Hz, 2.01H), 7.94 (s, 0.68H), 2.89 (s, 2.28H), 2.72 (s, 2.27H), 2.53 (s, 2.99H). Peak assignment,

 $NH_2(CH_3)_2^+$, $\delta 2.53$ (singlet, 2.99 H);

DMF, δ7.94 (s, 0.68H), 2.89 (s, 2.28H), 2.72 (s, 2.27H)

hpdia⁵⁻, δ8.55 (d, J = 14.0 Hz, 1.04H), 8.46 (dd, J = 11.9, 1.5 Hz, 2.01H),

6. Gas adsorption and selectivity measurements

The as-synthesized sample was firstly Soxhlet extracted with acetone at 85 °C for 2 days and then further degassed at 423 K for 6 h under ultrahigh vacuum before gas sorption measurements.

The isosteric heats (Q_{st}) of CO₂ and light hydrocarbons adsorption for **FJI-C4** were estimated from the sorption data measured at 273 and 298 K by Clausius-Clapeyron equation.

Clausius-Clapeyron Equation:

$$\frac{\partial(\ln P)}{\partial(1/T)} = -Q_{st}$$

The Clausius-Clapeyron equation is a standard method for calculation of coverage-dependent Q_{st} using measured temperature-pressure-coverage isotherm data points. Hence, it cannot give Q_{st} at zero coverage, and the Q_{st} at very low surface coverage has a quite large error because the adsorption apparatus cannot work well at very low pressure (e.g. low accuracy of the pressure gauges, leaking, etc.)²

In ideal adsorbed solution theory (IAST), the adsorption isotherm of pure gas is fitted by the single-site Langmuir-Freundlich equation.

$$Y = \frac{A1 * b1 * x^{c1}}{1 + b1 * x^{c1}}$$

- Y: molar loading of species i, mmol/g
- A1: saturation capacity of species i, mmol/g
- b1: constant, Pa⁻¹
- c1: constant

The adsorption selectivity is defined as Si/j = (q1/q2)/(p1/p2),

- Si/j: adsorption selectivity
- qi : the amount of i adsorbed
- pi : the partial pressure of i in the mixture.



Figure S8. H₂ adsorption isotherm at 77 K



Figure S9. CO_2 adsorption isotherms at 273 K and 298 K.



Figure S10. Isosteric heats of CO₂ adsorption for FJI-C4.



Figure S11. Isosteric heats of light hydrocarbon (CH₄, C₂H₂, C₂H₄, C₂H₆, and C₃H₈) for **FJI-C4**.



Figure S12. IAST-predicted selectivity for CO_2/N_2 (15:85), CO_2/N_2 (50:50) and CO_2/CH_4 (50:50) adsorption based on adsorption isotherms of the pure gas for FJI-C4 at 273 K



Figure S13. IAST-predicted selectivity for CO_2/CH_4 (1:1) adsorption based on adsorption isotherms of the pure gas for FJI-C4 at 298 K

The CO₂ selectivity separation is considered to be a promising candidate for reducing CO₂ emissions, namely (i) postcombustion capture from flue gas containing other component gases, predominantly N₂; (ii) separation from natural gas for its reservation (mainly CH₄) are typically contaminated with over 40 % CO₂ and N₂.³ IAST prediction based on the CO₂, CH₄, and N₂ sorption isotherm are present in Figure S11. It shows that, at 1 bar, the estimated CO₂/N₂ selectivity is 46.1 at 273 K from binary mixtures (CO₂/N₂=15:85), which indicated that it hold promise for postcombustion CO₂ capture application. Whereas, at 1 bar, the predicted CO₂/CH₄ selectivity is 12.4 at 273 K and 8.0 at 298 K for equimolar gas-phase mixtures which is high than many metal organic framework.

7. Comparison of selectivities

Table S1. Comparison of C_3H_8/CH_4 , C_2H_2/CH_4 , C_2H_4/CH_4 and C_2H_6/CH_4 selectivities of **FJI-C4** with some other MOFs.

MOFs	C ₃ H ₈ /CH ₄	C_2H_2/CH_4	C ₂ H ₄ /CH ₄	C ₂ H ₆ /CH ₄	References
FJI-C4	293.4	51.0	22.1	39.7	This work
USTA-35a	80	19	8	13.5	4
FIR-7a-ht.	78.8		8.6	14.6	5
JLU-Liu22	271.5			14.4	6
JLU-Liu5	107.8			17.6	7
JLU-Liu6	274.6			20.4	8
USTA-33a		18	12	16	8

8. Powder X-ray diffraction



Figure S14. Powder X-ray diffraction pattern of FJI-C4.

9. Physical parameters of selected gas

Table S2 Polarizability and quadruple moment of light hydrocarbons and carbon dioxide.⁹

Adsorbate	Polarizability $\times 10^{25}$ /cm ³	Quadruple moment $\times 10^{26}$ /esu cm ²
CH ₄	25.93	0
C ₂ H ₆	44.3–44.7	0.65
C ₂ H ₄	42.52	1.50
C ₂ H ₂	33.3–39.3	-
C ₃ H ₆	62.6	-
C ₃ H ₈	62.9–63.7	-
CO ₂	29.11	4.3

10. Crystallographic data for compounds

Table S3.	Crystallographic	data and structure	e refinement for FJI-C4	Ι,
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Compound	FJI-C4	
Chemical formula	C16H6N0O10PZn2	
Radiation type	$\operatorname{Cu} K_{\alpha}$	
Formula mass	519.92	
Crystal system	Orthorhombic	
Space group	Pbcn	
<i>a</i> (Å)	10.7239 (3)	
<i>b</i> (Å)	15.3597 (3)	
<i>c</i> (Å)	17.7316 (3)	
α (°)	90.000	
$\beta(^{\circ})$	90.000	
γ(°)	90.000	
Unit cell volume $/\text{Å}^3$	2920.68 (11)	
Temperature (K)	173	
$\mu (mm^{-1})$	2.87	
Ζ	4	
R _{int}	0.029	
Final R_1 values (I>2 σ (I))	0.032	
Final wR (F ₂) values (I> $2\sigma(I)$)	0.086	
Goodness of fit on F ²	1.06	
CCDC number	1431891	

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