Electronic Supplementary Information

Rational design of phosphonocarboxylate meta-organic frameworks for light hydrocarbon separations

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1. General experimental materials and methods

All chemicals and solvents purchased were analytical grade and used without further purification. Ligand H₃hpda was synthesized according to form literature^{1, 2}(the procedure was showed in Scheme S1). Single-crystal X-ray diffraction data of compound FJI-C3 and FJI-C5 were collected with a SuperNova CCD-based diffractometer equipped with graphite-monochromated Cu K α radiation by using a ω-scan at 100 K. Elemental analyses of C, H and N were tested using a Vario MICRO EL III elemental analyzer. Infrared (IR) spectra were recorded on a PerkinElmer Spectrum in the range of 4000–400 cm⁻¹ using KBr pellets. Thermogravimetric analyses (TGA) were performed under a nitrogen atmosphere with a heating rate of 10 °C min⁻¹ using an SDT Q600 thermogravimetric analyzer. Powder X-ray diffraction (PXRD) data were gleaned on a MiniFlex600 diffractometer with Cu K α radiation($\lambda = 1.54056$ Å) at room temperature, and the recording speed was 5° min⁻¹ over the 2 θ range of 4–50° at room temperature. ¹H NMR spectra were recorded at ambient temperature on a BRUKER AVANCE III spectrometer; chemical shifts were referenced to TMS in the solvent signal in d_6 -DMSO. Gas adsorption measurement was performed in the ASAP 2020 System. Purity and homogeneity of the bulk product of FJI-C3 and FJI-C5 were determined by comparison of the simulated and experimental X-ray powder diffraction patterns.

2. Synthesis of materials

Synthesis of the ligand of H₃hpda

Synthesis of ligand H_3 hpda (H_3 hpda =4,4'-(hydroxyphosphoryl) dibenzoic acid).



Scheme S1. Process of synthesis of the ligand H₃hpda

A mixture of di-p-tolylphosphine oxide (2.0 g, 8.7mmol), potassium hydroxide (0.7 g, 12.5 mmol), and water (0.7 mL) in ethanol (15 mL) is refluxed for 4 h 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 intermediate product di-p-tolylphosphinic acid (Yield 1.73g~81%). In the next moment, total intermediate product (1.73 g, 7.0 mmol) is solved with pyridine (12 mL). To this mixture, KMnO₄ (20 g, 126.7 mmol) is added portionwise with little water at a rate to maintain refluxing. Then remove 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 1.98g~92%).

¹H NMR (400 MHz, DMSO) δ 13.21 (s, 1H), 8.02 (dd, J = 8.2, 2.7 Hz, 1H), 7.85 (dd, J = 11.6, 8.2 Hz, 1H). ³¹P NMR (162 MHz, DMSO) δ 21.28 (s). ¹³C NMR (101 MHz, DMSO) δ 167.24 (s), 141.28 (s), 133.54 (s), 131.73 (d, J = 10.0 Hz), 129.55 (d, J = 12.5 Hz).

3. Crystal structures

b



Fig. S1 3D crystal structure of FJI-C3





Fig.S2 3D crystal structure of FJI-C5

4. Thermogravimetric Analyses (TGA)



Fig. S3 Thermogravimetric curve of FJI-C3



Fig. S4 Thermogravimetric curve of FJI-C5

According to the TG curve of FJI-C3, the continual sharp weight loss

from 30 to 150 °C was caused by the removal of uncoordinated water and DMF). The coordinated water and DMF then start to lose gradually from 150 °C. Similarly, for **FJI-C5**, the rapid 26.5% weight loss was also caused by the uncoordinated guest molecules. Then a mild loss from 210 °C may be attribute to the coordinated water.

$\mathbf{L}_{as c=0}$

5. IR spectra

Fig. S5 IR spectra of FJI-C3 (blue) and ligand (red).



Fig. S6 IR spectra of FJI-C5 (blue) and ligand (red).

The peaks in the range of 2345-2781 cm⁻¹ can be assigned to the vibrations of the P–O–H groups of ligand. The lack of these bands in the spectra of **FJI-C3** and **FJI-C5** indicate the absence of P–O–H groups which match well the crystallographic analyses where the P–O–H groups deprotonated and coordinated with metal ions. The P=O group gives the absorption band at ~1120-1242 cm⁻¹, while the bands at ~1662 and ~1400cm⁻¹ could be ascribed to the asymmetric and symmetric stretch vibrations of the dicarboxylate groups for **FJI-C3** and at ~1670 and ~1418 for **FJI-C5** ^{3, 4}. The deformation vibration bands of the benzene rings $v(_{Ar-H})$ are observed in the region of 720–740 cm⁻¹.

6. Gas Adsorption and Selectivity Measurements

The as-synthesized sample of **FJI-C3** and **FJI-C5** were directly degassed at 423 K for 6 h under ultrahigh vacuum before gas sorption measurements.

The adsorption heat (Qst) defined as

$$O_{st} = \frac{RT^2(\partial lnp/\partial T)}{\partial t}$$

is determined by using pure component C_2H_2 , C_2H_4 , C_2H_6 , CH_4 isotherms fitting by Virial method.

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

$$S_{i/j} = (q1/q2)/(p1/p2)$$

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



Fig. S7 Le Bail refinement of the PXRD patterns of the bulk solid of (a) FJI-C3 and (b) FJI-C5, experimental (black) and simulated (red). R_{wp} : the weighted profile R-factor calculated for the full pattern; R_p : the

unweighted profile R-factor calculated for the full pattern

CCDC number	1444652	1444653
Chemical formula	C31H26Cu3N1O15P2	C28H16Mg3O16P2
Fomula weight	905.1	743.3
Crystal system	monoclinic	orthorhombic
Space group	$P2_1/n$	Pnnm
a/Å	12.9967(9)	11.3418(9)
b/Å	19.0728(14)	13.5168(15)
c/Å	20.6874(17)	15.8624(14)
α (°)	90.00(0)	90.00(0)
β(°)	103.374(6)	90.00(0)
γ (°)	90.00(0)	90.00(0)
Ζ	4	2
Temperature/K	293	293
Wacelength/Å	1.54051	1.54051
2θ range/o	4.000-50.000	4.000-50.000
R_p	0.0369	0.067
R_{wp}	0.0592	0.111
R _{exp}	0.0244	0.0174
GOF	2.42	6.36

Table S1 Crystal data and refinement details for FJI-C3 and FJI-C5



Fig. S8 PXRD patterns of FJI-C3 before and after gas adsorption.



Fig. S9 PXRD patterns of FJI-C5 before and after gas adsorption.

8. Comparison of selectivity

Table S2. Comparison of C₂H₄/CH₄ and C₂H₆/CH₄ selectivity FJI-C3

MOFs	C ₂ H ₄ /CH ₄	C ₂ H ₆ /CH ₄	References
FJI-C3	23.7	39.9	This work
FJI-C5	19.0	33.3	This work
USTA-35a	8	13.5	5
BUT-52	14.4	13.7	6
FIR-7a-ht.	8.6	14.6	7
JLU-Liu22		14.4	8
JLU-Liu5		17.6	9
JLU-Liu6		20.4	9
USTA-33a	12	16	10

and FJI-C5 with recently reported MOFs.

9. Crystallographic data

Table S3. Crystallographic data and structure refinement for FJI-C3:

Compound	FJI-C3
Chemical formula	$C_{31}H_{26}Cu_3NO_{15}P_2$
Radiation type	Cu K_{α}
Formula mass	905.09
Crystal system	Monoclinic
Space group	$P2_1/n$
<i>a</i> (Å)	12.8613 (1)
<i>b</i> (Å)	18.9007 (2)

20.5254 (2)
90.000
102.991 (1)
90.000
4861.77 (8)
173
4
0.033
0.046
0.123
1.020
1444652

Table S4.Crystallographic data and structure refinement for **FJI-C5**:

Compound	FJI-C5
Chemical formula	$C_{28}H_{16}Mg_3O_{16}P_2$
Radiation type	$\operatorname{Cu} K_{\alpha}$
Formula mass	743.28
Crystal system	Orthorhombic
Space group	Pnnm
<i>a</i> (Å)	11.3020 (2)
<i>b</i> (Å)	13.5426 (2)

<i>c</i> (Å)	15.7763 (2)
α (°)	90.000
$\beta(^{\circ})$	90.000
γ(°)	90.000
Unit cell volume /Å ³	2414.70 (6)
Temperature (K)	173
Ζ	2
R _{int}	0.045
Final R_1 values (I>2 σ (I))	0.074
Final wR (F ₂) values (I> $2\sigma(I)$)	0.203
Goodness of fit on F ²	1.09
CCDC number	1444653

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