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A robust cage-based framework for highly selective purification of natural gas

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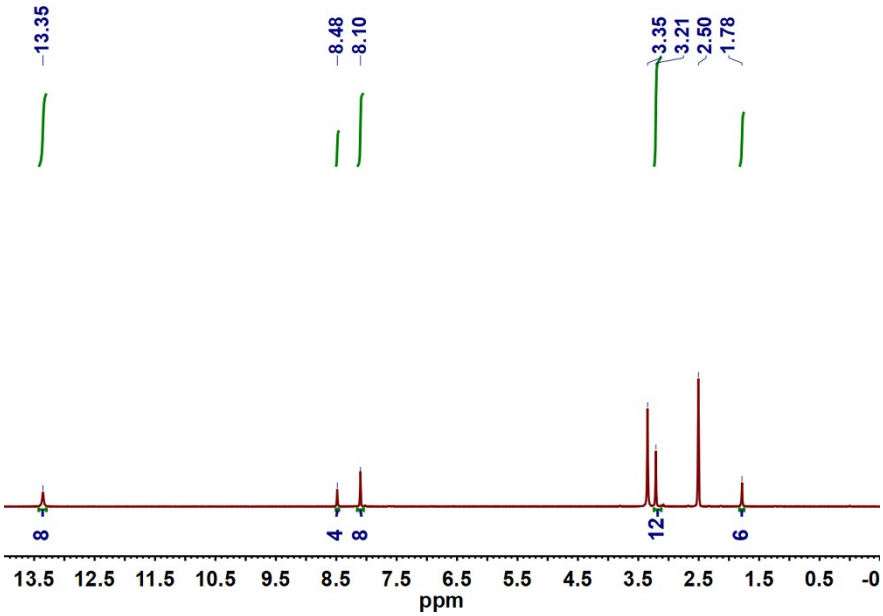
Experimental section

Materials and methods

All reagents and solvents used in synthetic studies are commercially available and used as supplied without further purification. The ligand H_8BTDTA (5',5''-bis(3,5-dicarboxyphenyl)-2',2'',4',6''-tetramethoxy-4'',6'-dimethyl-[1,1':3',1'':3'',1'''-quaterphenyl]-3,3''',5,5'''-tetracarboxylic acid) is synthesized according to the previous reference. Elemental analyses for C, H, N are carried out on a German Elementary Vario EL III instrument. ^{1}H NMR spectra are obtained on a Burker AVANCE 400 (400 MHz) for spectrometer. Single crystal X-ray diffraction experiments are carried on a SuperNova diffractometer equipped with Cu-Kα radiation (λ = 1.5418 Å) by using a ω scan mode. PXRD patterns are collected by an Empyrean X-ray diffractometer using Cu Kα radiation. To collect the PXRD patterns at different temperatures, the sample is heated in air to the anticipated temperature and maintained for 20 min. Thermogravimetric analyses are recorded on a NETZSCH STA 449C unit at a heating rate of 10 ^{o}C min^{-1} under nitrogen atmosphere. Gas sorption isotherms of activated **FJI-H19** are measured on a Micromeritics ASAP 2020 surface area analyser. The breakthrough experiments for mixed gas CH_4 / C_2H_6, CH_4 / C_3H_8 and CH_4 / n-C_4H_{10} (85±0.5 /15±0.5) are carried out at a flow rate of 5 ml / min which controlled by CS200 Sevenstar, (295 K, 1 bar) through using a home-built setup coupled with a mass spectrometer (ominstar). Activated **FJI-H19** powder (71.40 mm and 326.8mg) is packed into stainless-steel column ϕ 2.66 X 105.30 mm in glove box. Before the breakthrough experiments, the correction factors of CH_4 / C_2H_6, CH_4 / C_3H_8 and CH_4 / n-C_4H_{10} (85±0.5 /15±0.5) are first performed, respectively. And the binary mixture gas with a flow rate of 5 ml / min (295 K, 1 bar) is introduced through the bypass line with a resistance. After that a He flow (5 ml / min at 295 K and 1 bar) is introduced to the adsorption column to clean the system. And the sample is activated at 80 ^{o}C with 5 ml / min He flow for 24 h. Then the CH_4 / C_2H_6, CH_4 / C_3H_8 and CH_4 / n-C_4H_{10} binary mixture gas is first stabilized by flowing through the alternative vent line for 30 min before introducing it as a step input to the adsorption column, respectively. Meanwhile, the breakthrough of UiO-66 and MOF-5 are also carried out under the same condition. The results indicate that the separation effect of **FJI-H19** is better than those of UiO-66 and MOF-5 (Fig. 4, S9 and S10).

Synthesis of 5',5''-bis(3,5-dicarboxyphenyl)-2',2'',4',6''-tetramethoxy-4'',6'-dimethyl-[1,1':3',1'':3'',1'''-quaterphenyl]-3,3''',5,5'''-tetracarboxylic acid (H_8BTDTA)

5',5''-bis(3,5-bis(ethoxycarbonyl)phenyl)-2',2'',4',6''-tetramethoxy-4'',6'-dimethyl-[1,1':3',1'':3'',1'''-quaterphenyl]-3,3''',5,5'''-tetracarboxylate (3.5 g, 3 mmol) is dissolved in 20 mL of THF, to which 10 mL of 6 M NaOH aqueous solution is added. The mixture is stirred under reflux for 10 h, before the solvent is removed using a rotary evaporator. The white solid is dissolved in water and is acidified with 6 M HCl to yield gray white precipitate. The precipitate is filtered, washed with water, and dried in an oven at 80 ^{o}C for 10 h to give the H_8BTDTA. Yield: 3.0 g, 86%. ^{1}H NMR (400 MHz, DMSO-d_6, δ): 1.78 (s, 6H), 3.21 (s, 12H), 8.10 (s, 8H), 8.48 (s, 4H), 13.35 (s, 8H).



Scheme 1 The NMR spectra of the H_8BTDTA ligand

Synthesis of FJI-H19

$Cu(NO_3)_2 \cdot 2H_2O$ (24 mg) and H_8BDTA (10 mg) are dissolved in a mixture of 1 ml DMF, 0.185 ml H_2O, 0.33 ml EtOH and 40 ul HCl in a 10 mL pyrex vial. The solution is heated at 85 °C for 5 day to yield 8 mg of blue–green crystals ($([Cu_2(BTDTA)_{0.5} \cdot (H_2O)_2]_n \cdot (solvent)_x$,Yield 62% with respect to H_8BDTA). To obtain the full desolated **FJI-H19**, the synthesized sample was soaked in MeOH for 3 days and then CH_2Cl_2 for 3 days. Then the sample was heated at 80 ℃ for 10 hours in the dynamic high vacuum. This fully activated sample is ready for the adsorption tests. Theoretically, the activated **FJI-H19** has no obvious weight loss upon heating. Because the activated sample is very water-sensitive, it absorbs four water molecules before the elemental analysis experiment. The above result matches well with TG analysis. Elemental analyses calculated (%) for $[Cu_2(BTDTA)_{0.5} \cdot (H_2O)_2]_n \cdot 2nH_2O$: C 44.52, H 3.44. Found: C 45.92, H 3.46.

[CCDC 1586943 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.]

Synthesis of UiO-66 and MOF-5

UiO-66 and MOF-5 are prepared according to the previous references, respectively.[1, 2] And After breakthrough experiments, the N_2 adsorption are also performed, respectively, which are similar to the previous reports (Fig. S11 and S12).

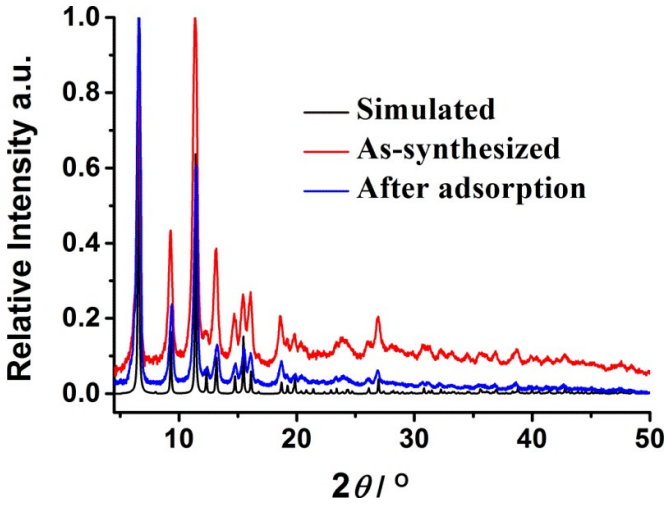


Fig. S1 The PXRD patterns of **FJI-H19**.

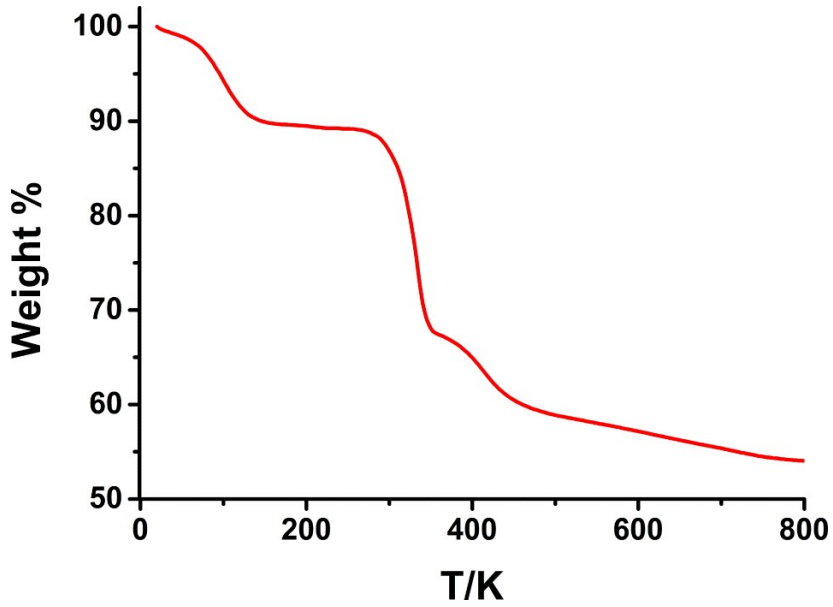


Fig. S2 The thermogravimetric analysis of activated **FJI-H19.**

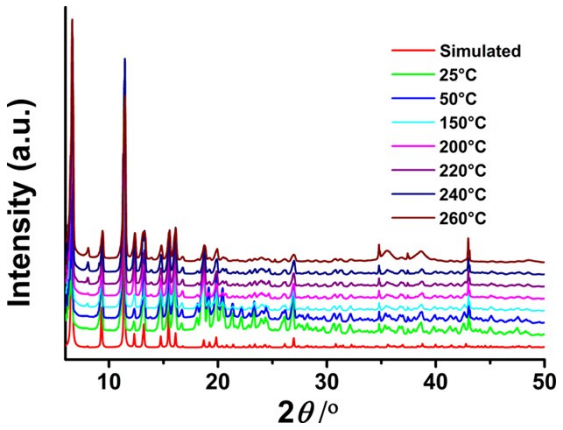


Fig. S3 The variable-temperature PXRD of **FJI-H19** in air atmosphere

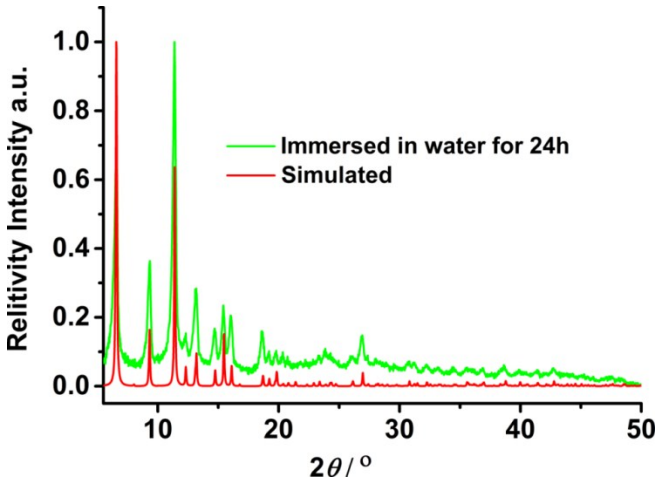


Fig. S4 The PXRD of **FJI-H19** simulated and soaked in water for 24h.

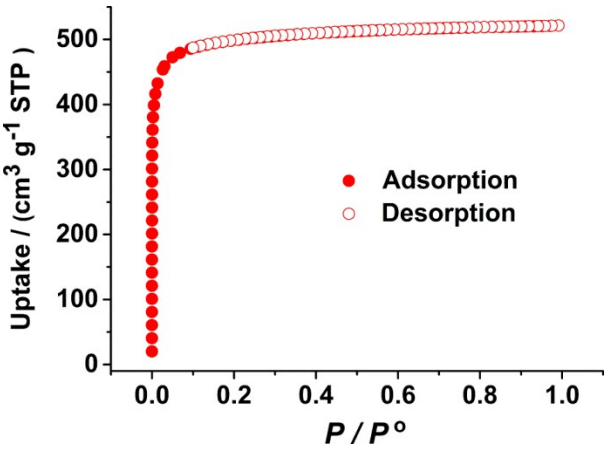


Fig. S5 The N_2 sorption isotherms of **FJI-H19** at 77K and 1 bar.

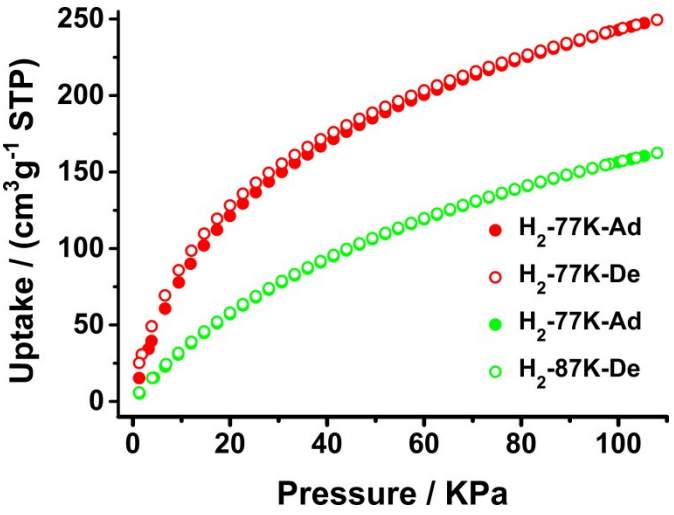


Fig. S6 The H_2 sorption isotherms of **FJI-H19** at 77 K and 87 K under 1bar.

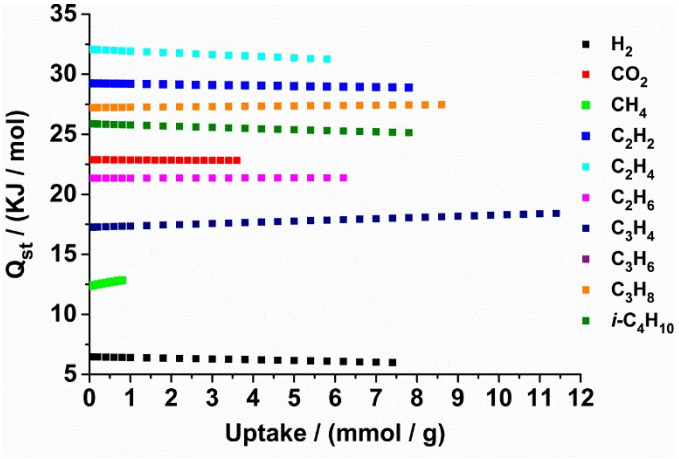


Fig. S7 The isosteric heats of adsorption for various gases in **FJI-H19**.

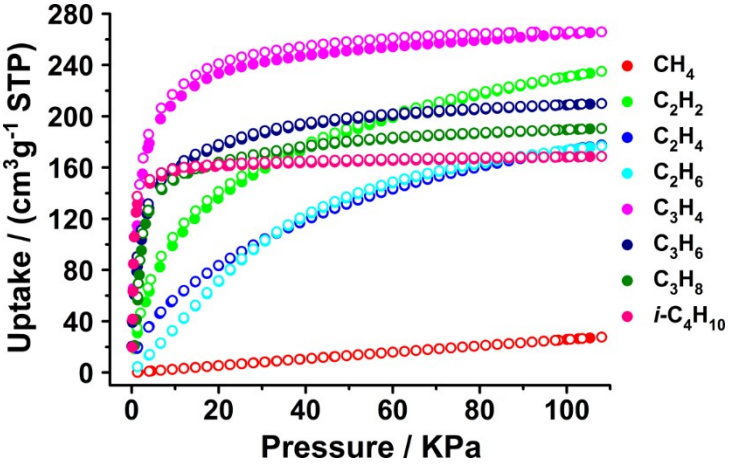


Fig. S8 The gas sorption isotherms of **FJI-H19** at 273 K under 1 bar

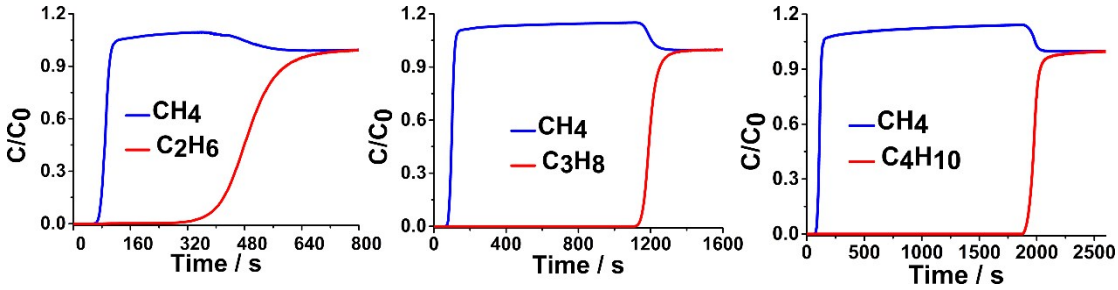


Fig. S9 A binary mixture of CH_4 / C_2H_6, CH_4 / C_3H_8 and CH_4 / *n*-C_4H_{10} (85 / 15) are flown through a fixed bed of UiO-66, respectively

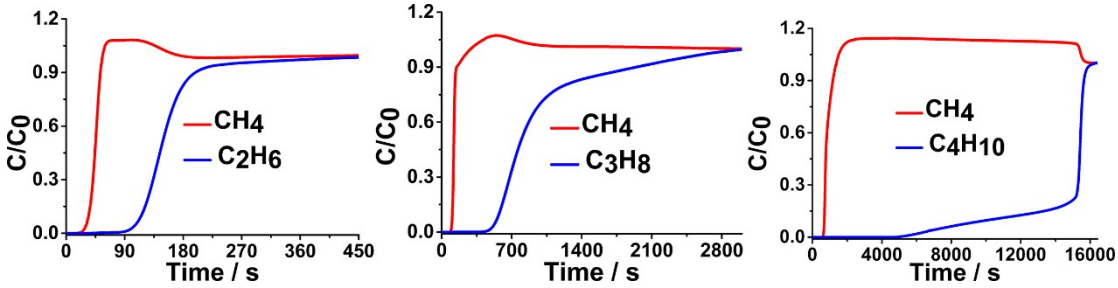


Fig. S10 A binary mixture of CH_4 / C_2H_6, CH_4 / C_3H_8 and CH_4 / *n*-C_4H_{10} (85 / 15) are flown through a fixed bed of MOF-5, respectively.

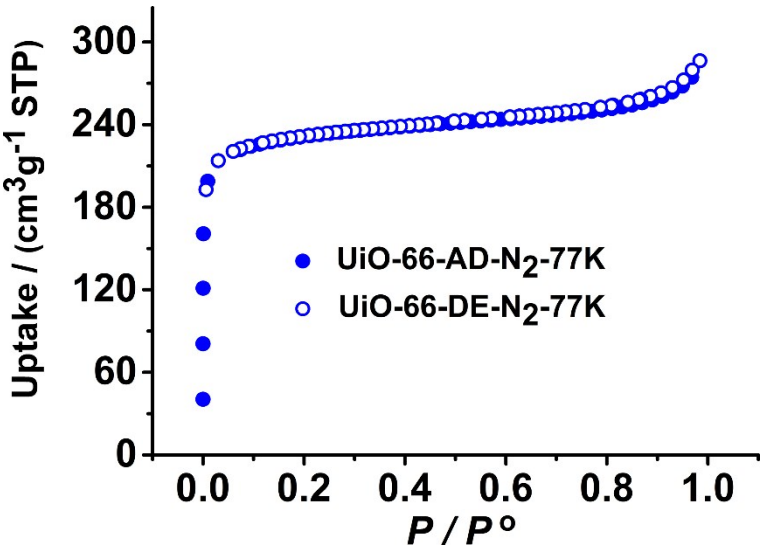


Fig. S11 After breakthrough experiments, the N_2 sorption isotherms of UiO-66 at 77K and 1 bar.

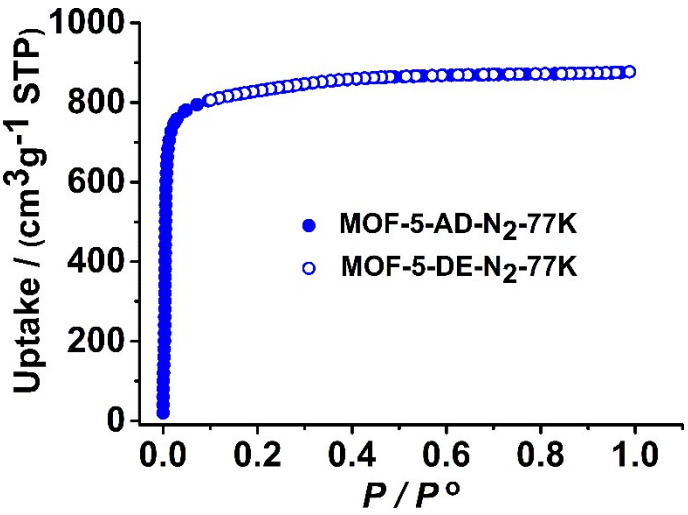


Fig. S12 After breakthrough experiments, the N_2 sorption isotherms of MOF-5 at 77K and 1 bar.

Table 1 Crystal data of **FJI-H19** (CCDC number：1586943)

Identification code	**FJI-H19**
Empirical formula	$C_{25}H_{19}Cu_2O_{12}$
Formula weight	638.48
Temperature	100(2) K
Wavelength	1.54184 Å
Crystal system	Tetragonal
Space group	*P*4/*nmm*
Unit cell dimensions	a = 18.9546(5) Å
Volume	4849.1(3) $Å^3$
Z	4
Density (calculated)	0.875 mg/m^3
Absorption coefficient	1.390 mm^{-1}
F(000)	1292
Completeness to theta = 67.684°	99.8 %
Reflections collected	13690
Data / restraints / parameters	2670 / 0 / 111
Goodness-of-fit on F^2	0.977
Final R indexes [I > 2sigma(I)]	R_1 = 0.0591, wR_2 = 0.1609
Final R indexes [all data]	R_1 = 0.0831, wR_2 = 0.1789
Largest diff. peak/hole / e $Å^{-3}$	0.785 / -0.402

Reference:

1 H. Wu, Y. S. Chua, V. Krungleviciute, M. Tyagi, P. Chen, T. Yildirim and W. Zhou, *J. Am. Chem. Soc.*, 2013, **135**, 10525-10532.

2 S. S. Kaye, A. Dailly, O. M. Yaghi, J. R. Long, *J. Am. Chem. Soc.*, 2007, **129**, 14176-14177.