Supplementary Material (ESI) for Chemical Communications
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Supporting Information for

A Novel Microporous MOF with the Capability of the Selective Adsorption of Xylenes

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General Methods: Methanol, benzene, toluene, *m,o,p*-xylene were rapidly purified with CaH_2. The other chemicals and solvents used without further purification. The elemental analyses were carried out on a PerkinElmer 240C element analyzer. Powder X-ray diffraction (XRD) data were collected on Scintag X1 diffractometer with Cu-K_α (λ = 1.5418Å) at 40kV, 35mA. Fourier-Transform infrared spectra were obtained with a Nicolet Impact 410 FT-IR spectrometer using KBr disks dispersed with sample powders in the 4000–400 cm^{-1} range. A Perkin-Elmer TGA 7 thermogravimetric analyzer was used to obtain thermogravimetric analysis (TGA) curve in air with a heating rate of 10ºC/min.

Preparation of JUC-77•DMF ([In(OH)(OBA)]•DMF):

H_2OBA (4,4'-Oxybis(benzoic acid)) (0.043 g, 0.17 mmol) and $In(NO_3)_3$ (0.01 g, 0.03 mmol) were dissolved in DMF (7 mL), and then 2-methyl-1-butanol (2 mL) and HNO_3 (2M 0.55 mL) were added into the mixture. After stirring a little time, placed in a glass bottle and then heated at 85ºC for 72h，yield yellowy or colorless block crystals, which were filtered, and dried under the vacuum. Yield: 67% based on the $In(NO_3)_3$, IR (KBr pellet, cm^{-1}): 1664 (C=O (DMF)), 1598 (C=C (aromatic)), 1238 (C-O-C (OBA^{-2})), 698 (p-disubstituted aromatic). elemental analysis calcd (%) for $InC_{17}H_{15}NO_7$ (460.11): C 44.34%, H 3.26%, N 3.04%; found: C 44.63% H 3.52% N 3.37%. The DMF molecular was determined by TGA and FT-IR (see Fig.S2, S4)

Preparation of JUC-77 ([In(OH)(OBA)]):

JUC-77·DMF was immersed in dried-methanol for 14h to remove the guest molecular-DMF. To make sure the DMF being exchanged by methanol completely, the compound was treated as above for five times. And then heated at 90°C under vacuum for 12h. IR (KBr pellet, cm^{-1}) 1598 (C=C (aromatic)), 1238 (C-O-C (OBA^{-2})), 698 (p-disubstituted aromatic). elemental analysis calcd (%) for InC14H9O6(388.03): C 43.41%, H 2.07%; found: C 43.53%, H 2.12% TGA, IR, and powder X-ray diffraction(see Fig. S3, S4, S5) were used to examine that the channel is open and the sample remained the structure.

Crystallography data:

Yellowy or colorless, block-shaped crystal of $InC_{14}H_9O_6$ (JUC-77 M = 388.03) was selected for X-ray structural analysis on a Bruker SMART CCD diffractometer at 298

K. The complex crystallized in the space group *Fddd* (No.70), orthorhombic, a=19.2396(9), b=20.3017(9), c=46.143(2) Å, V= 18023.4(14) $Å^3$, Z=32, λ=0.71073 Å, ρ_{calcd} = 1.144 Mg/m^3. A total of 28635 reflections were collected, of which 5280 were unique (R_{int} = 0.0588). Final *GooF* = 1.000, R_1 = 0.0698, wR_2 = 0.2191. The structure was solved and refined by full matrix least-squares on F^2 values (SHELXL-97).[1] Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were fixed at calculated positions and refined using a riding mode. The routine SQUEEZE was applied to the structures in order to remove diffuseelectron density associated with badly disordered DMF molecules.[2]

Low-pressure gas and vapor sorption measurements:

The gas and vapor sorption-desorption experiments were performed by using Belsorp-max. The sample was treated at 90 ºC under vaccum for 12h before the measurement. N_2 used was of 99.999% purity, and the liquid such as benzene, toluene, *m-, o-, p*-xylene were dried with CaH_2. All the vapor sorption-desorption isotherms were measured at 298 K. Surface area was determined from the N_2 gas isotherm measured at 77 K. Before each vapor sorption measurement, the sample was treated as mentioned above to make sure the channel open. And the weight of the sample was measured again precisely. And then the N_2 sorption was performed to prove that the channel was empty and the sample was not decomposed.

High-pressure H_2 and CH_4 gas sorption measurements:

The high-pressure H_2 sorption isotherm of JUC-77 was measured at 77 K using the RUBOTHERM magnetic suspension balance (Ankersmid B.V., Netherlands). in the range of 0 - 50 bar for H_2. Before the H_2 sorption measurements, the sample JUC-77 was heated at 70 ºC under vacuum for 12h. The sample density was determined from He isotherm measured at 77 K. And the CH_4 sorption isotherm of JUC-77 was measured at 298 K in the range of 0 - 70 bar, the sample was treated in the same way that for H_2 sorption. The sample density was determined from He isotherm measured at 298 K. The amount the uptake is 2.37 wt% and 6.63 wt% respectively. (see Fig. S7, S8)

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[1]. SHELX-97, Program for Structure Refinement, G. M. Sheldrick, University of Göttingen, Göttingen (Germany), 1997.

[2]. A. L. Spek, J. Appl. Crystallogr., 2003, 36, 7.

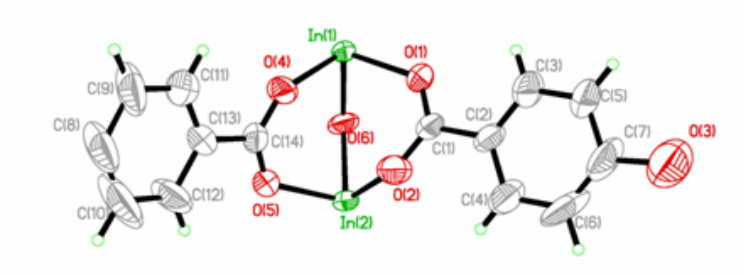


Fig. S1 ORTEP drawing of the asymmetric unit for JUC-77.

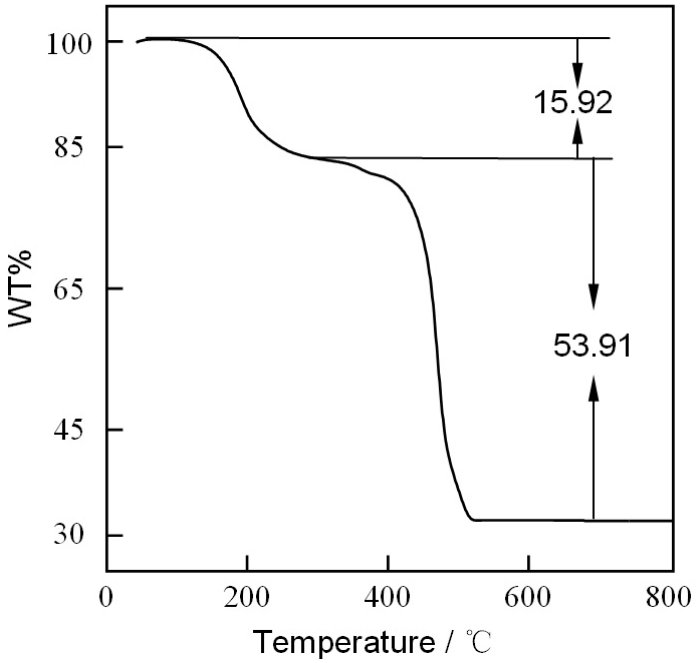


Fig. S2 TGA measurements for as-synthesized JUC-77·DMF indicates tow steps of weight loss. At first, 15.92% weight loss within 250 ºC corresponding to one guest DMF per formula unit, and weight loss of 53.91% for decomposition of JUC-77 between 250 and 520 ºC, then no weight loss after 520 ºC, 30.17% last for In_2O_3 (30.166% for calculation).

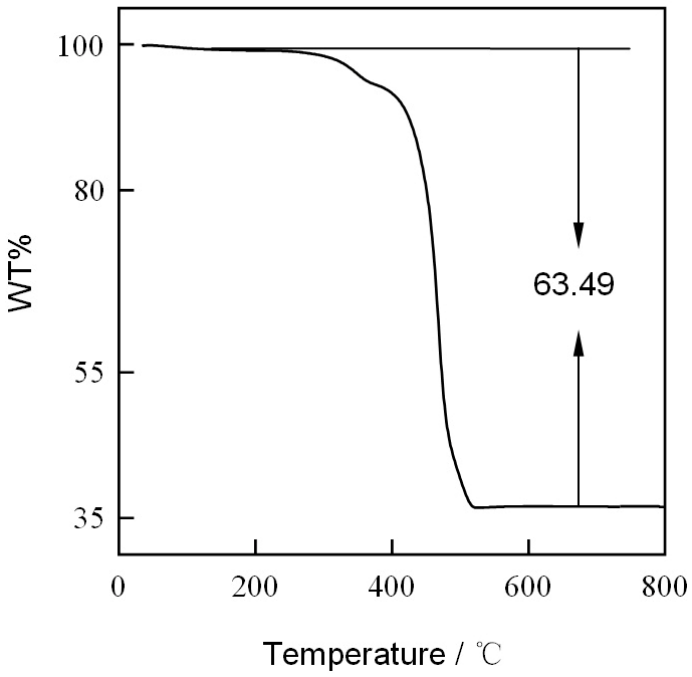


Fig. S3 TGA measurements for as-synthesized JUC-77. Decomposition of JUC-77 began at 250 ºC. The residue was In_2O_3 (experimental: 36.51% and calculated: 35.86%)

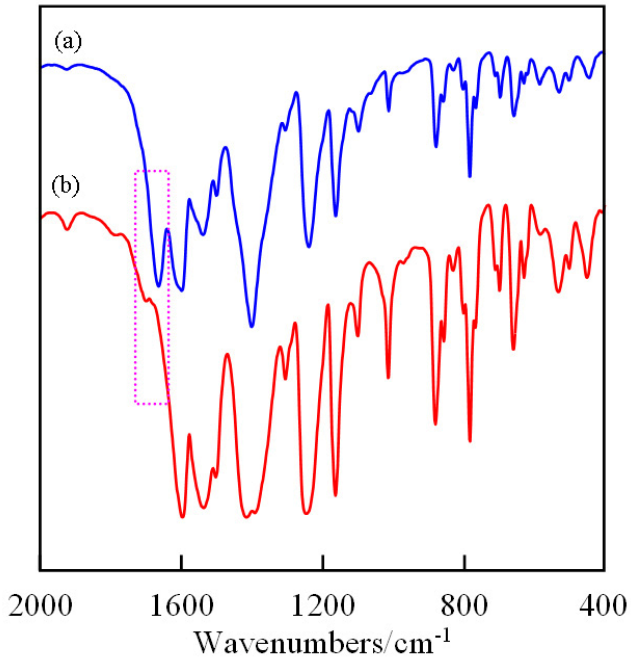


Fig. S4 FT-IR spectra of JUC-77·DMF(a) and JUC-77(b). 1664 cm^{-1} ($C{=}O_{DMF}$) is only found in the curve (a). That implies the guest was removed completely.

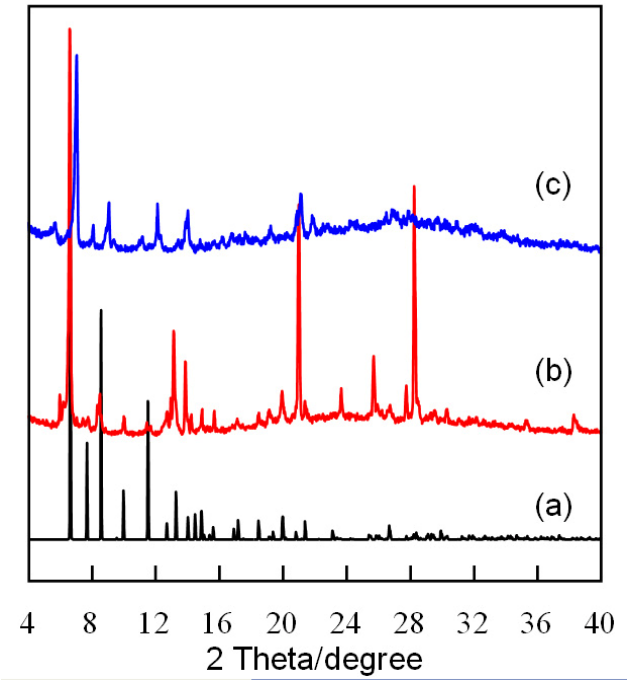


Fig. S5 Powder XRD patterns of the JUC-77: (a) simulated, (b) as-synthesized and (c) activated after all the sorption measurements. (a) and (b) represent the LP forms of JUC-77, (c) represents the NP form of JUC-77.

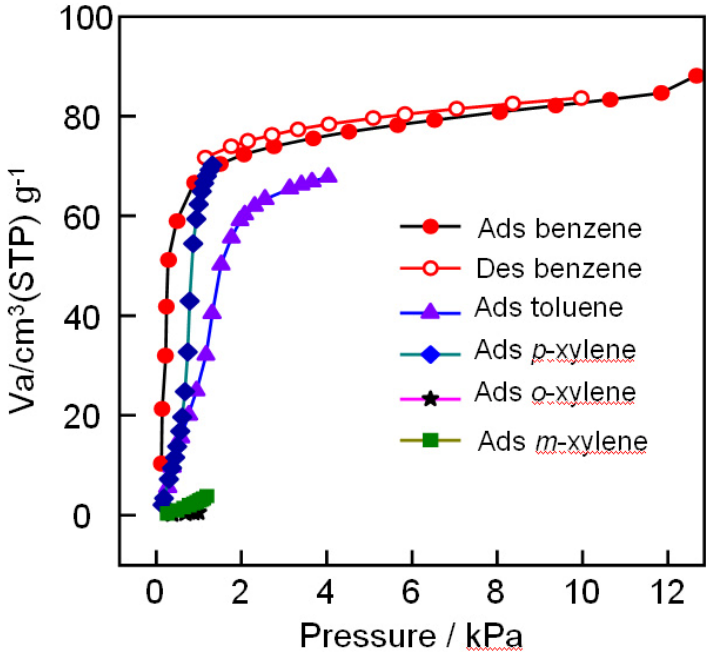


Fig. S6 Vapor adsorption and desorption of JUC-77 with benzne and the vapor adsorption of toluene, xylenes at 298 K. x axis is saturation pressure of benzene, toluene, pX, oX, mX respectively.

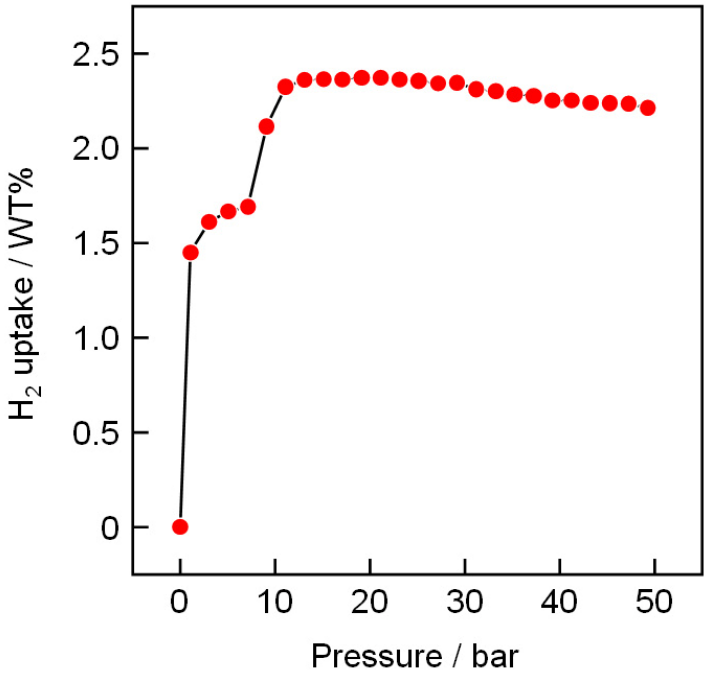


Fig. S7 High pressure H_2 gas sorption was measured at 77 K. In the range 0 - 50 bar, the isotherm indicates two step-adsorption behavior, firstly, it sorbs 1.69 wt% of H_2 at 7.1 bar, and then reaches saturation in the 7.1 - 50 bar region, the amount of the uptake is 2.37 wt%.

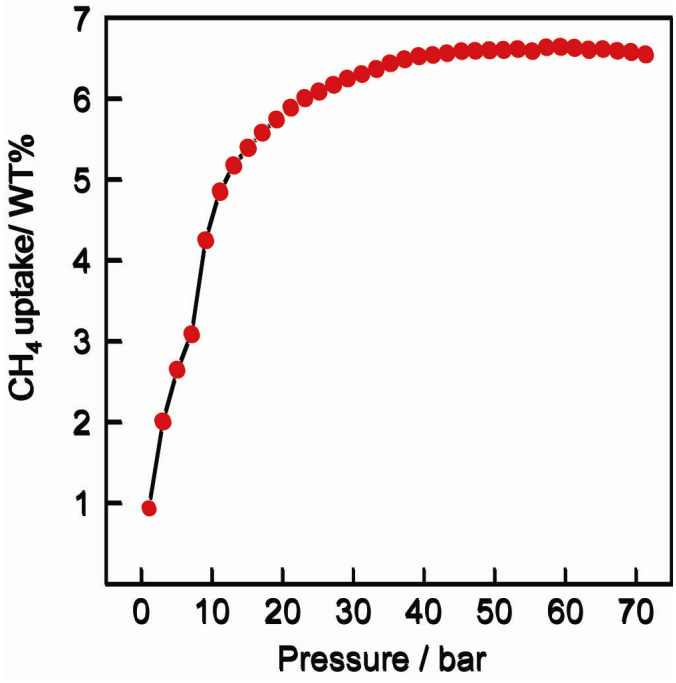
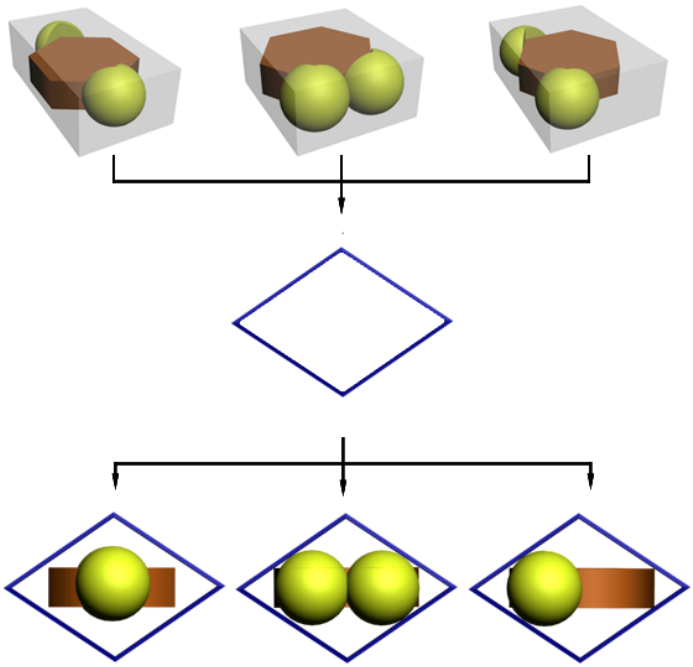


Fig. S8 High pressure CH_4 gas adsorption at 298 K.



Scheme. S1 Smallest minimum dimensions (cuboid in gray) of pX, oX, mX respectively (up); section of the channel (middle); comparison of the size of xylene isomers and section of the channel (bottom). yellow ball: methyl group; hexahedron in brown: aromatic

Table S1 Crystallographic Data for compounds 1

Empirical formula	$InC_{14}H_9O_6$
Formula weight	388.03
Crystal system	Orthorhombic
Space group	*Fddd*
a（Å）	19.2396(9)
b（Å）	20.3017(9)
c（Å）	46.143(2)
α(deg)	90
β(deg)	90
γ(deg)	90
V（Å^3）	18023.4(14)
Z	32
T（K）	298(2) K
λ（Å）	0.71073
ρ_{calcd}(Mg/m^3)	1.144
F(000)	6080
GooF on F^2	1.000
Theta range for data collection(deg.)	1.52 to 25.00
Completeness to theta = 25.00	100.0 %
[a]R_1 [$I > 2\sigma(I)$]	0.0698,
[b]$_wR_2$	0.2191

[a]$R_1 = \Sigma||Fo| - |Fc||/\Sigma|Fo|$, [b]$wR_2 = [\Sigma w(Fo^2 - Fc^2)/ \Sigma w(Fo^2)^2]^{1/2}$

Table S2 Selected Bond lengths [Å] and angles [deg]

In(1)-O(6)#1	2.071(3)	In(2)-O(6)	2.071(2)
In(1)-O(6)	2.071(3)	In(2)-O(6)#2	2.071(2)
In(1)-O(1)#1	2.172(3)	In(2)-O(5)	2.163(3)
In(1)-O(1)	2.173(3)	In(2)-O(5)#2	2.163(3)
In(1)-O(4)#1	2.161(3)	In(2)-O(2)	2.161(3)
In(1)-O(4)	2.161(3)	In(2)-O(2)#2	2.161(3)
O(6)#1-In(1)-O(6)	179.996(1)	O(6)-In(2)-O(6)#2	179.06(15)
O(6)#1-In(1)-O(1)#1	87.28(10)	O(6)-In(2)-O(5)	90.63(11)
O(6)-In(1)-O(1)#1	92.72(10)	O(6)#2-In(2)-O(5)	89.97(11)
O(6)#1-In(1)-O(1)	92.72(10)	O(6)-In(2)-O(5)#2	89.97(11)
O(6)-In(1)-O(1)	87.28(10)	O(6)#2-In(2)-O(5)#2	90.63(11)
O(1)#1-In(1)-O(1)	180.00(15)	O(5)-In(2)-O(5)#2	100.31(15)
O(6)#1-In(1)-O(4)#1	89.79(10)	O(6)-In(2)-O(2)	92.61(11)
O(6)-In(1)-O(4)#1	90.22(10)	O(6)#2-In(2)-O(2)	86.69(11)
O(1)#1-In(1)-O(4)#1	86.40(10)	O(5)-In(2)-O(2)	88.46(11)
O(1)-In(1)-O(4)#1	93.60(10)	O(5)#2-In(2)-O(2)	170.83(11)
O(6)#1-In(1)-O(4)	90.21(10)	O(6)-In(2)-O(2)#2	86.69(11)
O(6)-In(1)-O(4)	89.78(10)	O(6)#2-In(2)-O(2)#2	92.61(11)
O(1)#1-In(1)-O(4)	93.60(10)	O(5)-In(2)-O(2)#2	170.83(11)
O(1)-In(1)-O(4)	86.40(10)	O(5)#2-In(2)-O(2)#2	88.46(11)
O(4)#1-In(1)-O(4)	179.999(1)	O(2)-In(2)-O(2)#2	82.91(16)

Symmetry transformations used to generate equivalent atoms:

#1 -x+2,-y+1,-z+2; #2 -x+9/4,-y+5/4,z;

#3 x-1/4,-y+3/2,z+1/4; #4 x+1/4,-y+3/2,z-1/4;