Electronic supplementary information for

Highly porous and robust ionic MOFs with nia topology constructed by octahedral ligand and trigonal prismatic metal cluster

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1. General characterization:

All the chemical reagents used were bought from commercial source without further purification, unless otherwise noted. Powder X-ray diffractions (PXRD) were carried out on Scintag X1 diffractometer with Cu-Kα (λ = 1.5418 Å) at 40 kV, 35 mA. The elemental analyses were carried out on a PerkinElmer 240C element analyzer. Thermogravimetric analysis (TGA) curves were collected on a Perkin-Elmer TGA 7 thermogravimetric analyzer with a heating rate of 10 ºC/min at air. UV/Vis absorption spectra were recorded on a UV-2450 UV-Vis (SHIMADZU) spectrophotometer.

2. Crystal synthesis

JUC-101: $(In_3O)\cdot(TDCPB)\cdot(3H_2O)\cdot(xGuest)$

In a 20 ml capped vessel, $In(NO_3)_3 \cdot 4.5H_2O$ (20 mg) and TDCPB (10 mg) were added to a mixture of DMF (1.0 ml), DMSO (2.0 ml), methanol (1.0 ml) and 10 drops of aqueous HNO_3 solution (2.0 mol/L). After ultrasonic diffusion for 2 minutes, it was heated at 85 ^oC for 48 hours to obtain the product with colorless block crystal. Elemental analysis for JUC-101: C, 38.34; H, 6.361; N, 1.301; S, 16.04.

JUC-102: $(Mn_3OH)\cdot(TDCPB)\cdot(3H_2O)\cdot(xGuest)$

In a 20 ml capped vessel, $MnCl_2$ (30 mg) and TDCPB (10 mg) were added to a mixture of DMF (3.0 ml) and 4 drops of concentrated HBF_4 solution. After ultrasonic diffusion for 2 minutes, it was heated at 85 ^oC for 48 hours to obtain the product with pale pink block crystal. Elemental Analysis for JUC-102: C, 46.39; H, 4.789; N, 6.804.

Attention: The guests in JUC-101 and JUC-102 contain solvents and counter ions.

3. Crystallography data determination

Block crystals of JUC-101 and JUC-102 were picked for X-ray structural analysis on a Bruker SMART CCD diffractometer with a Mo-Kα radiation source (λ = 0.71073 Å) at 293 K. 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. It is unable to locate the H atoms of the water molecule and OH^-, but the H atoms were added in the cif doc. The large volume fractions of disordered ions or solvents in the lattice

pores could not be modelled in terms of atomic sites and were treated using the SQUEEZE routine[2] in the PLATON software package[3].

Table S1 Crystal data and structure refinement for JUC-101 and JUC-102 single crystals.

Complex	JUC-101	JUC-102
Empirical formula	$C_{66}H_{42}In_3O_{16}$	$C_{66}H_{43}Mn_3O_{16}$
Formula weight	1435.41	1256.77
Temperature (K)	293(2)	293(2)
Crystal system, Space group	Hexagonal, *P*-62*c*	Hexagonal, *P*-62*c*
Unit cell dimensions	$a = b = 19.4356(9)$ Å $c = 27.893(3)$ Å $\alpha = \beta = 90°$ $\gamma = 120°$	$a = b = 20.0962(3)$ Å $c = 26.9145(9)$ Å $\alpha = \beta = 90°$ $\gamma = 120°$
Volume (Å^3)	9124.8(11)	9413.4(4)
Z, Calculated density (g/cm^3)	2, 0.520	2, 0.441
Absorption coefficient (mm^{-1})	0.399	0.220
F(000)	1414	1270
Crystal size (mm)	0.6 × 0.4 × 0.4	0.5 × 0.5 × 0.5
θ range for data collection (°)	1.21 to 28.39	1.17 to 28.34
Limiting indices	$-25 \le h \le 25$ $-25 \le k \le 25$ $-37 \le l \le 20$	$-25 \le h \le 26$ $-26 \le k \le 26$ $-26 \le l \le 35$
Reflections collected / unique	56282 / 7764 $R_{int} = 0.0429$	58035 / 8015 $R_{int} = 0.0624$
Completeness to θ	28.39, 99.8 %	28.34, 100.0 %
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	0.852 and 0.826	0.896 and 0.896
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	7764 / 0 / 135	8015 / 27 / 135
Goodness-of-fit on F^2	0.978	0.944
Final *R* indices [$I > 2\text{sigma}(I)$]	$R_1 = 0.0217$ $wR_2 = 0.0416$	$R_1 = 0.0370$ $wR_2 = 0.0488$
R indices (all data)	$R_1 = 0.0262$ $wR_2 = 0.0422$	$R_1 = 0.0567$ $wR_2 = 0.0514$
Flack parameter	0.007(12)	0.042(11)
Largest diff. peak and hole (e.Å^{-3})	0.368 and -0.531	0.412 and -0.256
CCDC	851215	851216

4. Gas sorption-desorption measurements

The sample was treated at room temperature under vacuum for 2 h and 80 ºC for another 12 h before the measurement. The N_2, H_2, CO_2 and CH_4 sorption-desorption experiments were performed on an Autosorb-iQ2-MP-AG machine. N_2, H_2, CO_2 and CH_4 used were of 99.999% purity. Surface area was determined by the N_2 gas isotherm measured at 77 K. The H_2 sorption-desorption isotherms were collected at 77 K and 87 K. The CO_2 and CH_4 sorption-desorption isotherms were recorded at 298 K. High pressure H_2 adsorption isotherm were carried out by a PCT PRO E&E machine.

5. Dye release experiments of JUC-102

JUC-102 crystals were immersed in saturated dye solution in DMF for 44 h, thus obtaining dye@JUC-102 crystals. Then dye@JUC-102 crystals of 6.5 mg were put into two 10 mm cuvettes with 3 ml pure DMF and 3 ml saturated NaCl solution in DMF, respectively. UV-Vis spectra were recorded after different time interval until 44 h.

6. Bond valence sum (BVS) analysis

Table S2，BVS analyses of In, Mn and O atoms

		BVS	Assignment
JUC-101	In	3.17	In^{3+}
	μ_3-O	2.14	O^{2-}
JUC-102	Mn	2.08 (Mn^{2+})	Mn^{2+}
		1.90 (Mn^{3+})	
		1.99 (Mn^{4+})	
	μ_3-O	1.25	OH^-

The oxidation state of a particular atom can be taken as the nearest integer to the value. The O atom is not protonated if the BVS is ~1.8-2.2, mono-protonated if the BVS is ~1.0-1.2, and doubly-protonated if the BVS is ~0.2-0.4.[4]

References

[1] SHELX-97, Program for Structure Refinement, G. M. Sheldrick, University of Göttingen, Göttingen (Germany), 1997; A. L. Spek, *J. Appl. Crystallogr.,* **2003**, 36, 7.

[2] P. v.d. Sluis and A.L. Spek, *Acta Crystallogr., Sect. A*, 1990, 46, 194.

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

[4] A Supramolecular Aggregate of Four Exchange-Biased Single-Molecule Magnets, T. N. Nguyen, W. Wernsdorfer, K. A. Abboud, and G. Christou, *J. Am. Chem. Soc.*, **2011**, 133, 20688.

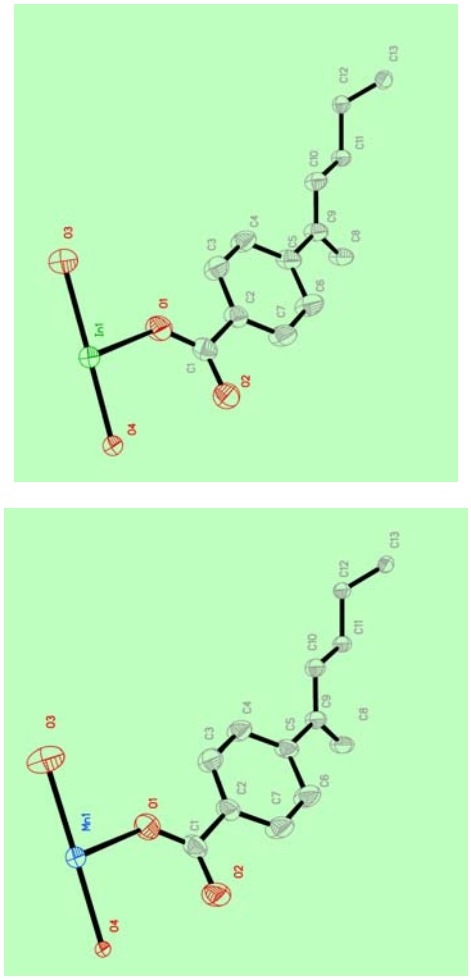


Fig. S1 Asymmetric units of JUC-101 (upper) and JUC-102 (down). (The ellipsoids are drawn at the 30% probability level. H atoms are omitted for clarity)

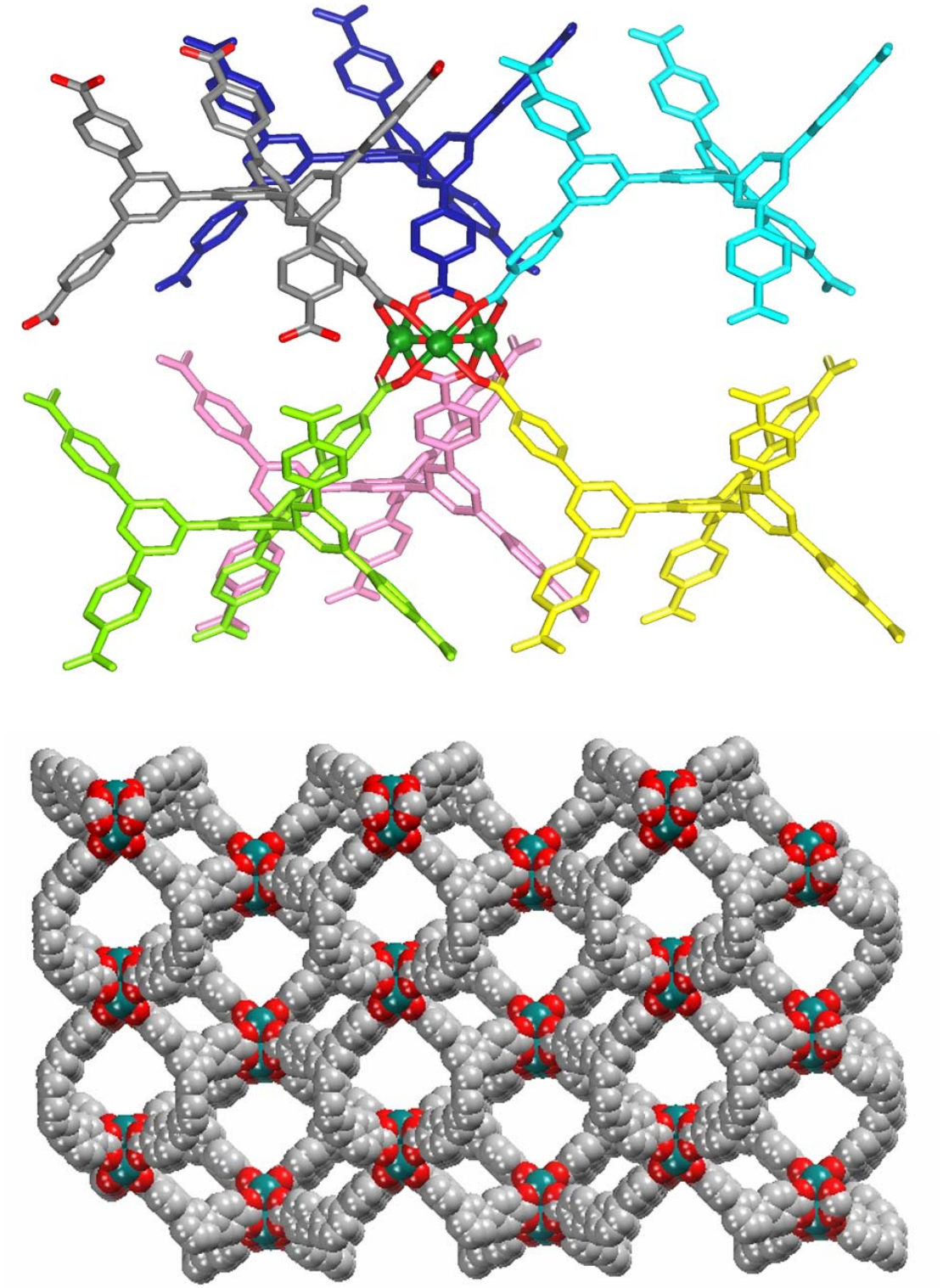
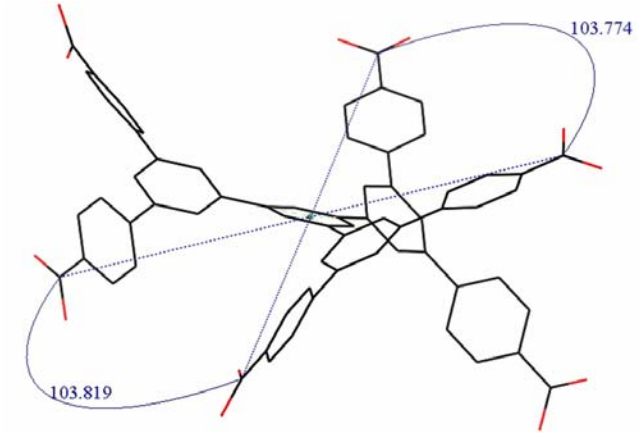
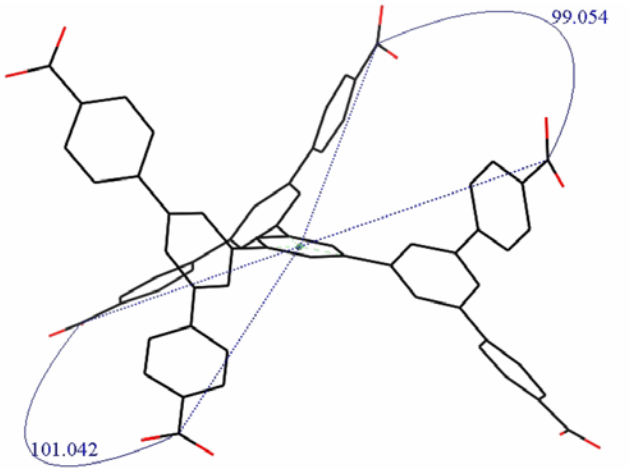


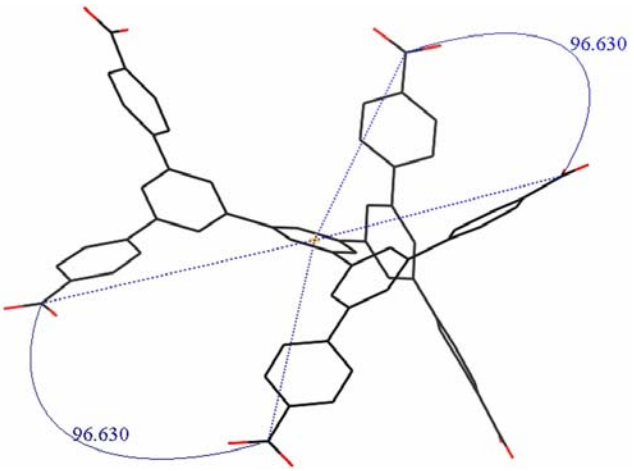
Fig. S2 The structural unit of a metal cluster with six connected ligands (upper) and the stacked structure in single crystal (down).



Calculated



L in JUC-100 (Zn_4O)



L in JUC-101 (In_3O)

Fig. S3 The structures of the six-node TDCPB ligand (calculated; in JUC-100; in JUC-101).

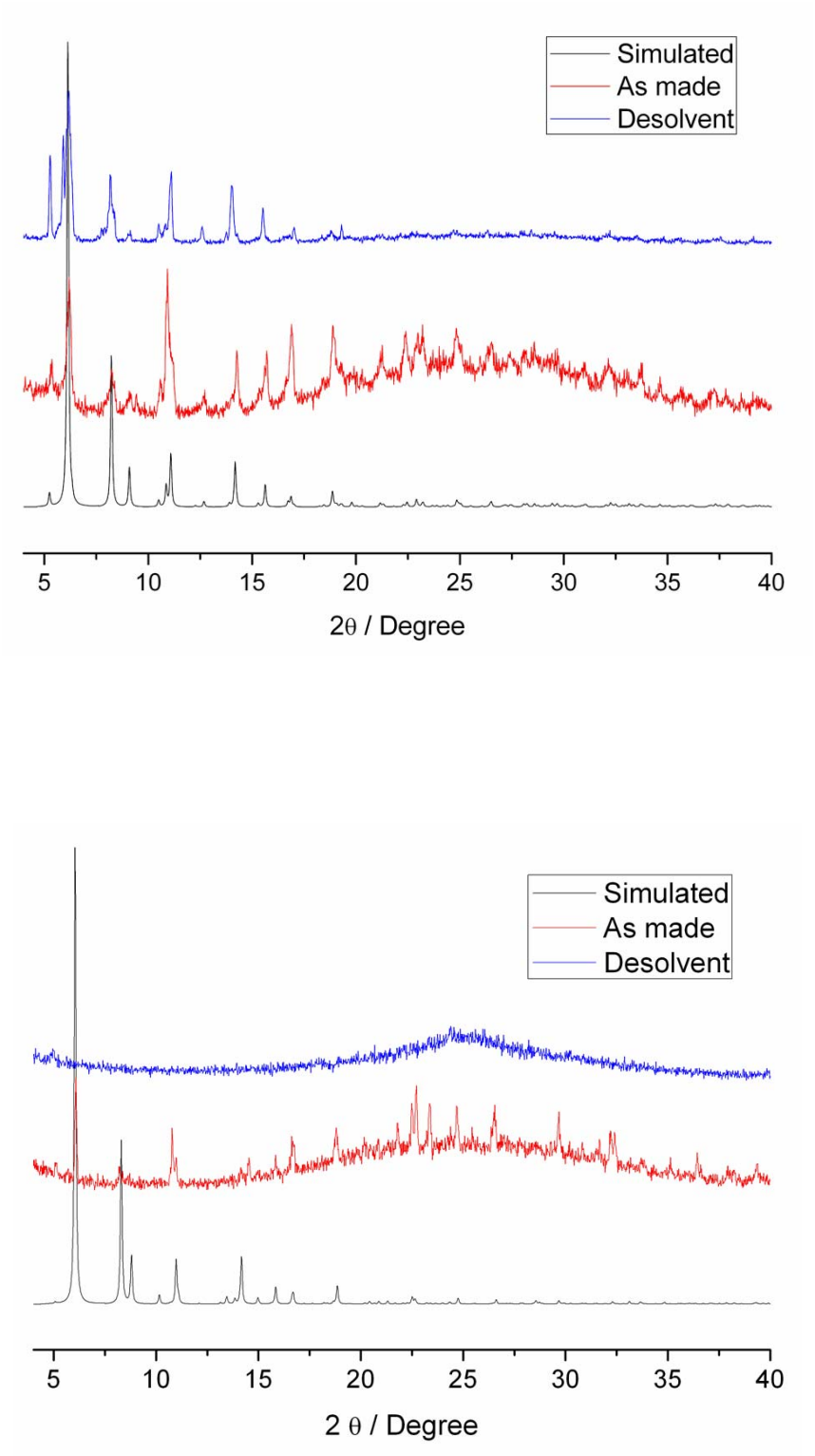


Fig. S4 XRD patterns of JUC-101 (upper) and JUC-102 (down).

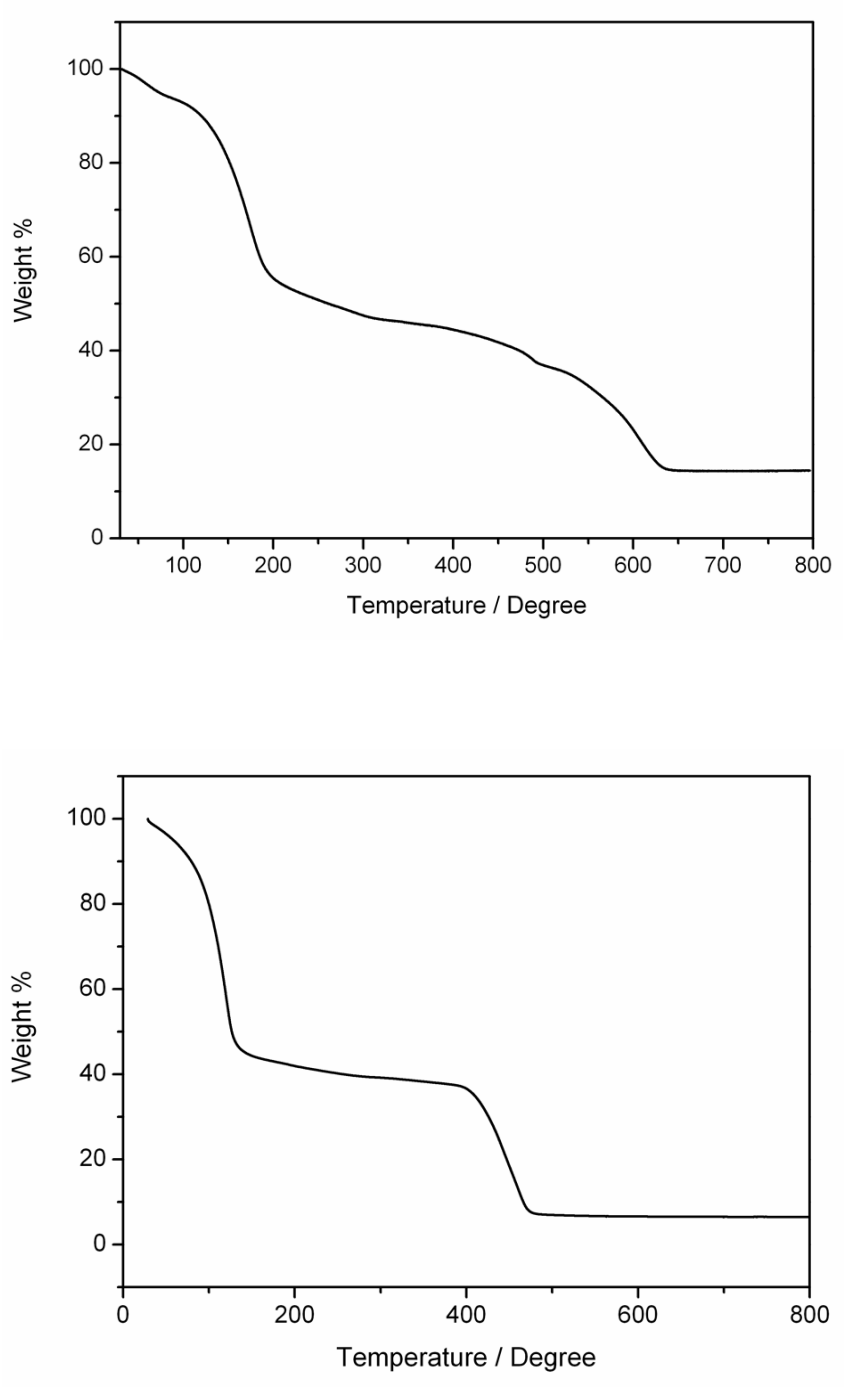


Fig. S5 TG curves of JUC-101 (upper) and JUC-102 (down).

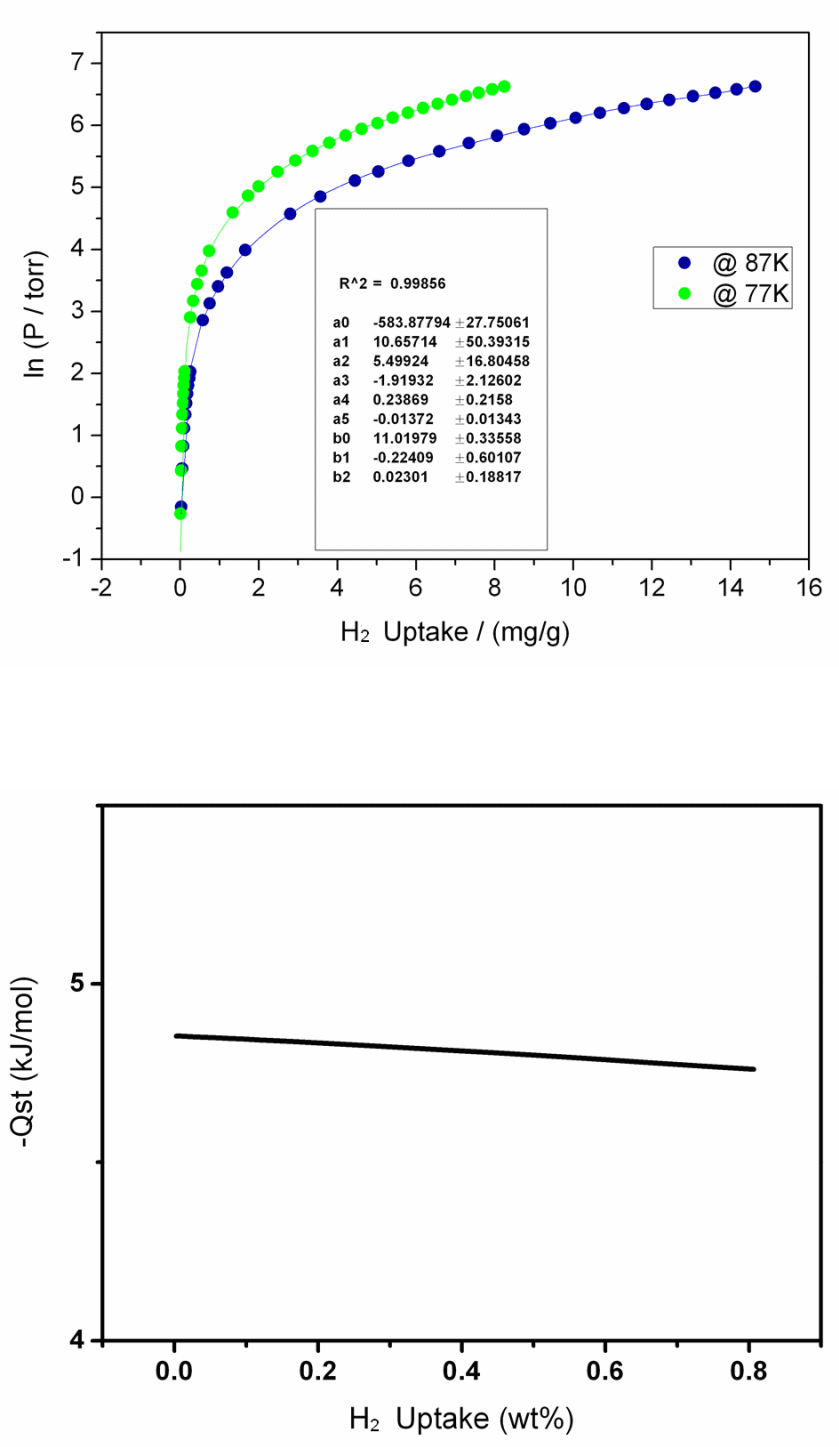


Fig. S6 The curve fits of H_2 enthalpy of JUC-101.

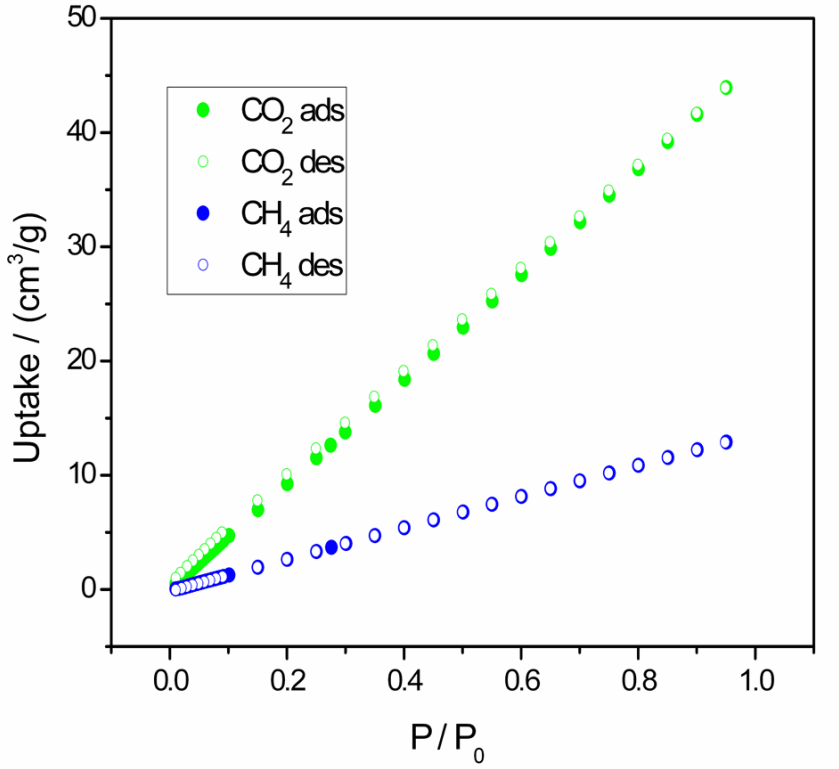


Fig. S7 CO_2 and CH_4 uptake of JUC-101 at 298 K.