Supplementary Information

Dynamic Response of a Flexible Indium Based Metal-Organic Framework to Gas Sorption†

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1. Experimental Procedures

1.1 Materials and Measurements. All the solvents and reagents for synthesis are reagent grade and purchased commercially without further purification. Elemental analyses were performed with a German Elementary Varil EL III instrument. IR spectrum was recorded in the range 4000-400 cm^{-1} with a Magna 750 FT-IR spectrometer using KBr pellets. The powder X-ray diffraction (PXRD) were recorded by a RIGAKU-DMAX2500 X-ray diffractometer using Cu Kα radiation (λ = 0.154 nm) at a scanning rate of 5°/min for 2θ ranging from 5° to 50°. Thermogravimetric analysis (TGA) was carried out on a NETZSCH STA 449C instrument. The sample and reference (Al_2O_3) were enclosed in a platinum crucible and heated at a rate of 10 °C/min from room temperature to 1000 °C under nitrogen atmosphere. Gas adsorption measurements were performed on an ASAP 2020 Surface Area and Pore Size Analyzer.

1.2 Syntheses of complex 1. A mixture of H_4TCPBDA (0.1 mmol, 66 mg) and $InCl_3$•$4H_2O$ (0.1 mmol, 29 mg) in *N,N'*-dimethylformamide (DMF) (10 mL) with an additional 100 μL HCl was sealed in a 25 mL Teflon-lined bomb at 120 °C for 3 days. Then the mixture was cooled to room temperatrure, yielding colorless block crystals which were collected and repeatedly washed with DMF three times. Phase purity of the crystals was confirmed by powder X-ray diffraction (PXRD). Yield: 74% (based on H_4TCPBDA). Elemental analyses calcd (%) for $C_{41}H_{42}N_3O_{14}In$: C 53.78, H 4.62, N 4.59; found (%): C 53.62, H 4.58, N 4.68. IR data (KBr disk, ν cm^{-1}): 3396 (w), 1593 (s), 1492 (m), 1382 (s), 1317 (s), 1267 (S), 1174 (m), 1107 (w), 1010 (w), 821 (w), 783 (m), 709 (w), 536 (w).

1.3 X-ray Crystallography. Data collections for complexes **1** and **1a** were performed on Rigaku-CCD diffractometers equipped with graphite monochromated Cu-Kα radiation (λ = 1.541984 Å) by using the ω-scan mode at 100 K. All absorption corrections were applied using the *CrystalClear* program. The structure was solved by direct methods. The metal atoms were located from the E-maps, and other non-hydrogen atoms were derived from the successive difference Fourier peaks. The structure was refined on F^2 by full-matrix least-squares using the *SHELXTL*-97 program package.[S1] All non-hydrogen atoms were refined anisotropically except some disordered atoms, and hydrogen atoms of the

organic ligands were generated theoretically onto the specific atoms and refined isotropically with fixed thermal factors. The free solvent molecules are highly disordered in complexes **1** and **1a**, and attempts to locate and refine the solvent peaks were unsuccessful. The diffused electron densities resulting from these molecules were removed using the *SQUEEZE* routine of *PLATON*. [S2] The structures were then refined again using the data generated. The final formula of complex **1** was determined by combining with thermogravimetric analysis (TGA) and elemental analyses. Crystal data are summarized in Table S1.

Table S1 Crystal Data and Structure Refinements for complexes **1** and **1a**.

complex reference	**1**	**1a**
chemical formula	$C_{40}O_8H_{24}N_2In$	$C_{40}O_8H_{24}N_2In$
formula weight	775.43	775.43
temperature (K)	100(2)	100(2)
crystal system	Monoclinic	Monoclinic
space group	*C2/c*	*I2/c*
a (Å)	28.286 (4)	26.9793 (6)
b (Å)	20.942 (3)	21.3293 (4)
c (Å)	27.586 (1)	26.4721 (5)
α (°)	90.00	90.00
β (°)	120.80	97.00
γ (°)	90.00	90.00
V (Å^3)	14037 (2)	15119 (5)
Z	8	8
F (000)	3128	4496
R_{int}	0.040	0.039
no. of reflections measured	42886	14694
no. of independent reflections	13842	11291
goodness of fit on F^2	1.009	1.071
final *R*1 values [$I > 2\sigma(I)$]	0.0597	0.0587
final *wR* (F^2) values [$I > 2\sigma(I)$]	0.1928	0.1792

2. Additional X-ray Crystal Structure

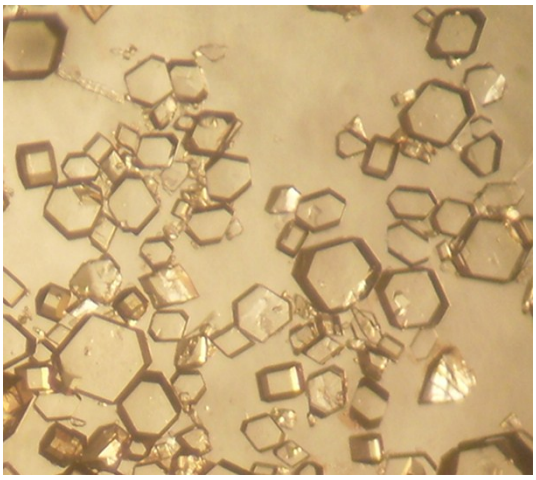

Fig. S1 Photographic crystals of complex **1**.

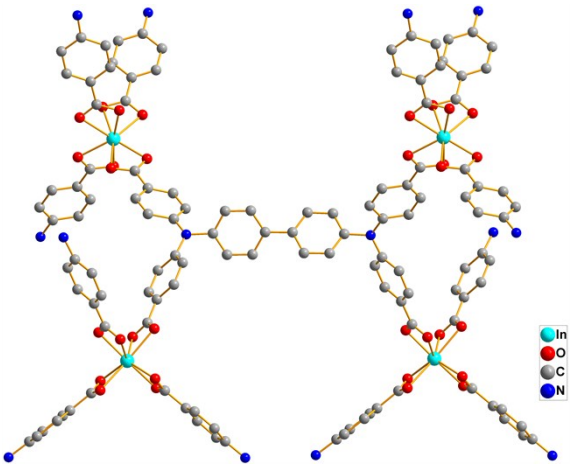

Fig. S2 Coordination environment for In(III) atoms and the ligand H_4TCPBDA in complex **1**. H atoms were omitted for clarity.

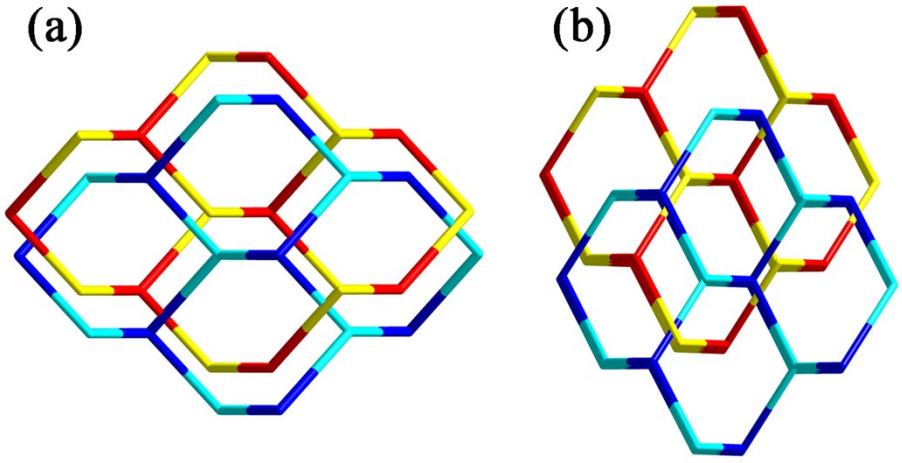

Fig. S3 Two-fold interpenetrating neb topologies of complex **1** (a) and **1a** (b) along the b-axis to illustrate a significant subnetwork shifting transition.

Table S2 Selected Bond Lengths (Å) and Angles (deg) for complex **1**[a].

In(1)-O(4)i	2.182 (3)	In(1)-O(2)	2.266 (2)
In(1)-O(7)ii	2.216 (2)	In(1)-O(6)iii	2.274 (3)
In(1)-O(1)	2.249 (3)	In(1)-O(8)ii	2.288 (3)
In(1)-O(5)iii	2.0988 (18)	In(1)-O(3)i	2.468 (4)
N(1)-C(5)	1.407 (5)	N(2)-C(27)	1.397 (5)
N(1)-C(8)	1.418 (5)	N(2)-C(34)	1.408 (5)
N(1)-C(15)	1.422 (5)	N(2)-C(24)	1.434 (5)
O(4)i-In(1)-O(7)ii	88.85 (10)	O(4)i-In(1)-O(6)iii	80.24 (13)
O(4)i-In(1)-O(1)	170.41 (12)	O(7)ii-In(1)-O(6)iii	82.85 (10)
O(7)ii-In(1)-O(1)	86.73 (10)	O(1)- In(1)-O(6)iii	90.77 (10)
O(4)i-In(1)-O(5)iii	85.65 (10)	O(5)iii-In(1)-O(6)iii	57.92 (9)
O(7)ii-In(1)-O(5)iii	140.75 (11)	O(2)- In(1)-O(6)iii	131.53 (10)
O(1)-In(1)-O(5)iii	92.41 (10)	O(4)i-In(1)-O(8)ii	88.59 (11)
O(4)i-In(1)-O(2)	130.74 (12)	O(7)ii- In(1)-O(8)ii	58.16 (10)
O(7)ii-In(1)-O(2)	126.01 (9)	O(1)-In(1)-O(8)ii	96.27 (10)
O(1)-In(1)-O(2)	58.24 (9)	O(5)iii-In(1)-O(8)ii	159.89 (10)
O(5)iii-In(1)-O(2)	84.97 (9)	O(2)- In(1)-O(8)ii	84.26 (10)
O(6)iii-In(1)-O(8)ii	139.70 (9)	O(5)iii-In(1)-O(3)i	76.08 (11)
O(4)i-In(1)-O(3)i	55.27 (12)	O(2)-In(1)-O(3)i	75.54 (10)
O(7)ii-In(1)-O(3)i	130.03 (12)	O(6)iii- In(1)-O(3)i	117.93 (10)
O(1)-In(1)-O(3)i	133.28 (10)	O(8)ii- In(1)-O(3)i	84.80 (10)
C(5)-N(1)-C(8)	122.88 (3)	C(27)-N(2)-C(34)	124.06 (3)
C(5)-N(1)-C(15)	119.66 (3)	C(27)-N(2)-C(24)	115.28 (3)
C(8)-N(1)-C(15)	115.62 (3)	C(34)-N(2)-C(24)	118.38 (3)

[a] Symmetry codes: (i) 1-x, -1/2+y, 1/2-z; (ii) 1-x, 1/2+y, 1/2-z; (iii) 1-x, 2-y, 1-z.

Table S3 Selected Bond Lengths (Å) and Angles (deg) for complex **1a**[b].

In(1)-O(6)i	2.075 (4)	In(1)-O(8)iii	2.303 (3)
In(1)-O(1)	2.200 (3)	In(1)-O(4)ii	2.305 (2)
In(1)-O(3)ii	2.230 (3)	In(1)-O(2)	2.325 (3)
In(1)-O(7)iii	2.250 (3)	O(1)-C(1)	1.261 (4)
O(3)-C(12)	1.268 (5)	O(8)-C(31)	1.261 (5)
O(4)-C(12)	1.256 (5)	O(2)-C(1)	1.248 (4)
N(1)-C(5)	1.407 (4)	N(2)-C(27)	1.397 (5)
N(1)-C(8)	1.417 (5)	N(2)-C(34)	1.403 (5)
N(1)-C(15)	1.436 (4)	N(2)-C(24)	1.423 (4)
O(6)i-In(1)-O(1)	95.28 (17)	O(6)i-In(1)-O(4)ii	85.88 (13)
O(6)i-In(1)-O(3)ii	92.12 (17)	O(1)-In(1)-O(4)ii	137.60 (9)
O(1)-In(1)-O(3)ii	79.86 (10)	O(3)ii-In(1)-O(4)ii	57.76 (9)
O(6)i-In(1)-O(7)iii	120.47 (18)	O(7)iii-In(1)-O(4)ii	85.73 (9)
O(1)-In(1)-O(7)iii	127.61 (10)	O(8)iii-In(1)-O(4)ii	88.72 (10)
O(3)ii-In(1)-O(7)iii	129.91 (12)	O(6)i-In(1)-O(2)	99.46 (13)
O(6)i-In(1)-O(8)iii	174.44 (14)	O(1)-In(1)-O(2)	56.87 (9)
O(1)-In(1)-O(8)iii	89.63 (12)	O(3)ii-In(1)-O(2)	135.87 (9)
O(3)ii-In(1)-O(8)iii	86.15 (13)	O(7)iii-In(1)-O(2)	78.97 (9)
O(7)iii-In(1)-O(8)iii	57.62 (10)	O(8)iii-In(1)-O(2)	85.42 (10)
C(1)-O(1)-In(1)	95.0 (2)	C(12)-O(4)-In(1)iv	89.3 (2)
C(12)-O(3)-In(1)iv	92.4 (2)	C(1)-O(2)-In(1)	89.5 (2)
C(31)-O(8)-In(1)v	90.1 (2)	C(31)-O(7)-In(1)v	92.2 (2)
C(5)-N(1)-C(8)	119.90 (3)	C(27)-N(2)-C(34)	120.82 (3)
C(5)-N(1)-C(15)	121.59 (3)	C(27)-N(2)-C(24)	119.18 (3)
C(8)-N(1)-C(15)	118.38 (3)	C(34)-N(2)-C(24)	120.00 (3)

[b] Symmetry codes: (i) x, 1+y, z; (ii) x, 1-y, 1/2+z; (iii) -1/2+x, 1/2-y, z; (iv) x, 1-y, -1/2+z; (v) 1/2+x, 1/2-y, z.

3. Infrared (IR) Spectra

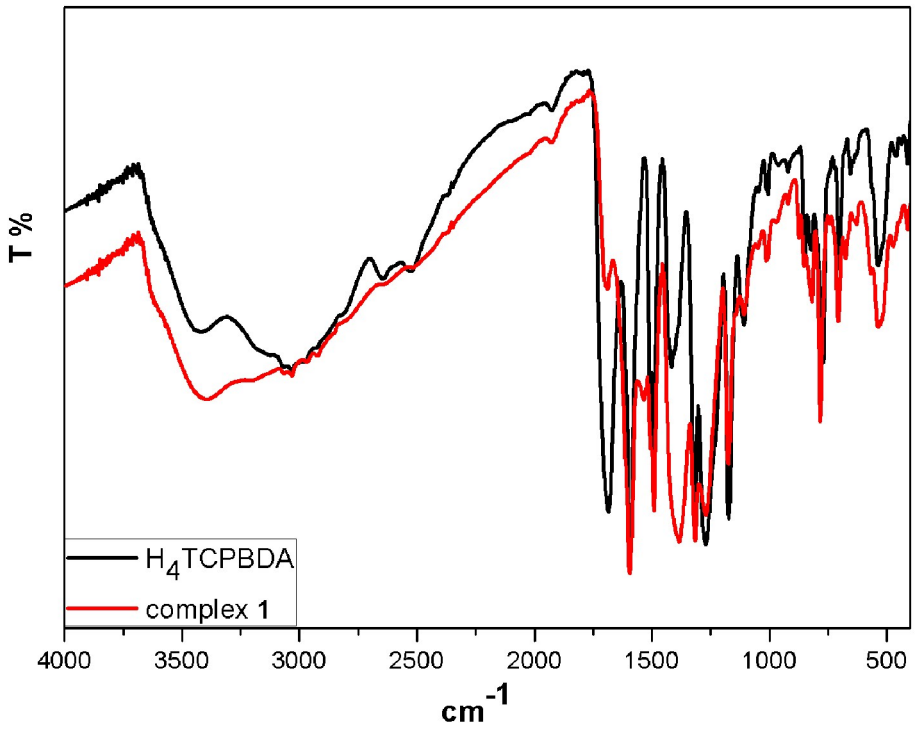

Fig. S4 IR spectra for the ligand H_4TCPBDA and complex **1**.

4. Powder X-Ray Diffraction (PXRD)

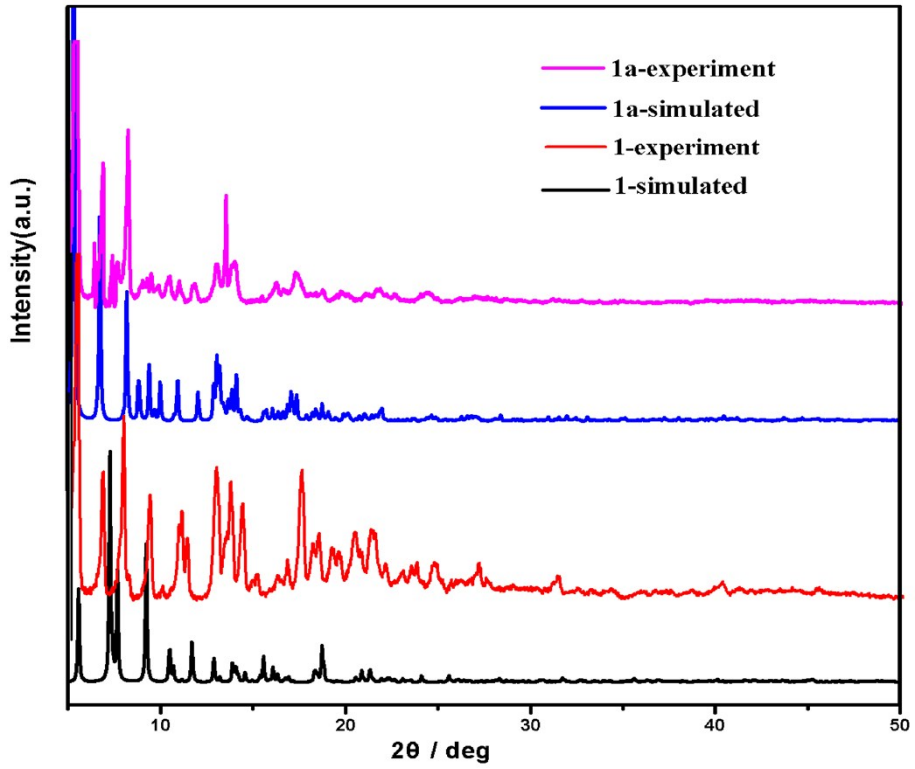

Fig. S5 PXRD patterns of complexes **1** and **1a**.

5. Thermogravimetric Analysis (TGA)

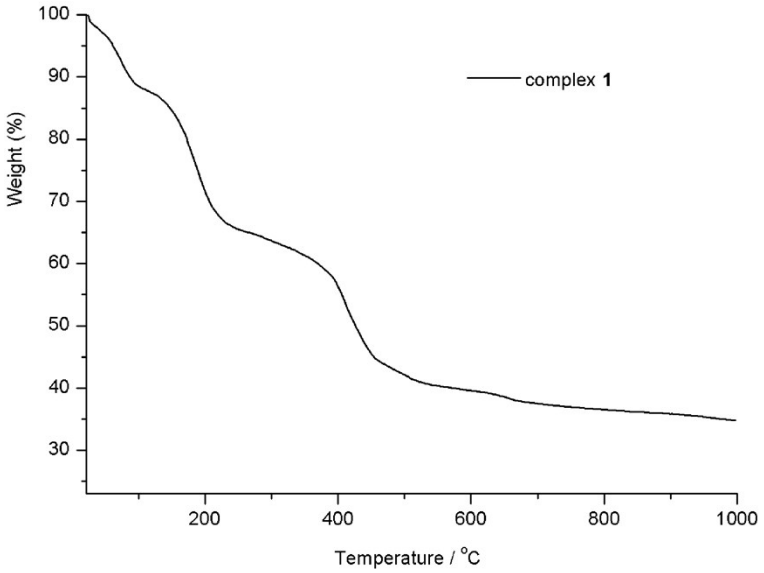

Fig. S6 The TGA Curve of complex **1**.

The thermal stability of complex **1** was investigated using thermogravimetric analysis (TGA) from 25-1000 °C under a flow of nitrogen. The TGA curve of complex **1** shows that the first weight loss of 11.44% was from 25 to 100 °C, wich corresponds to the loss of the free H_2O molecules (calcd, 11.81%).

6. Gas Sorption Test

N_2, Ar, H_2, CO_2 and CH_4 Isotherms. All the N_2, Ar, H_2, CO_2 and CH_4 isotherms for complex **1** were determined using an IGA gravimetric adsorption apparatus at the Fujian Institute of Research on the Structure of Matter in a clean ultra high vacuum system. Before measurements, about 100 mg acetone-exchanged samples were loaded into the sample basket with the adsorption instrument (ASAP 2020) and then degassed under dynamic vacuum at 80 °C for 10 h to obtain the fully desolvated samples. The N_2 and Ar sorption measurements were performed at 77 K and 87 K, respectively; the H_2 sorption measurement was performed at 77 K and 87 K; the CO_2 and CH_4 sorption measurement was performed at 273 K and 295 K.

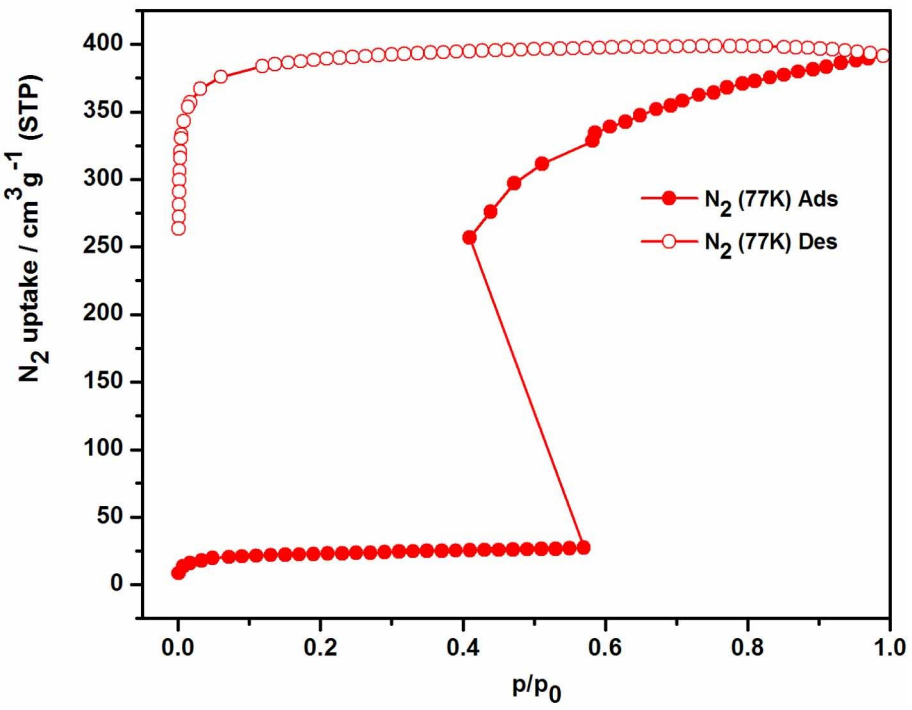

Fig. S7 N_2 sorption isotherm for complex **1** at 77 K.

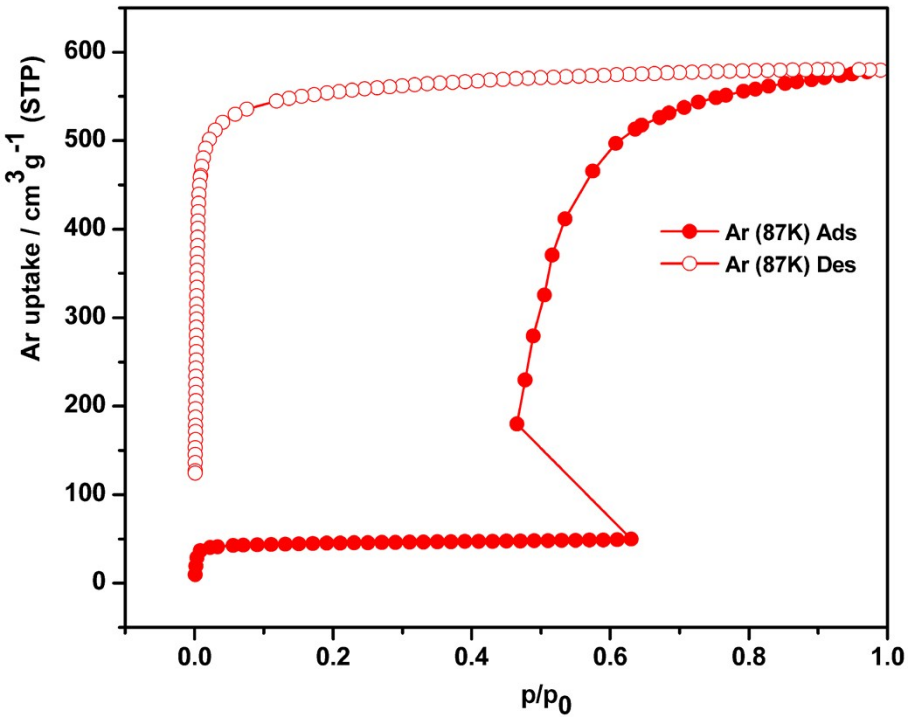

Fig. S8 Ar sorption isotherm for complex **1** at 87 K.

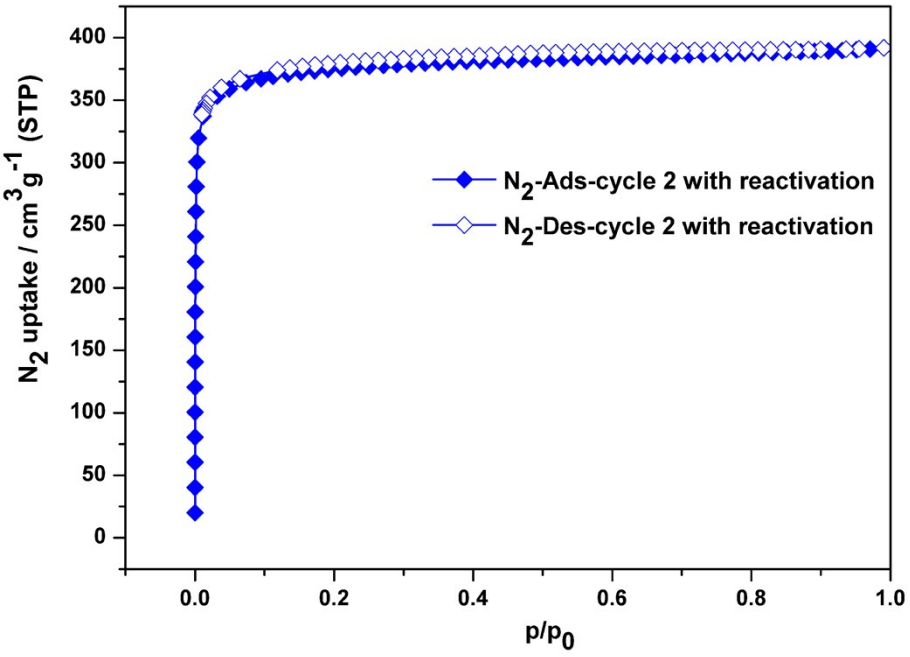

Fig. S9 The isotherm of second cycle N_2 sorption at 77 K for complex **1** with reactivation.

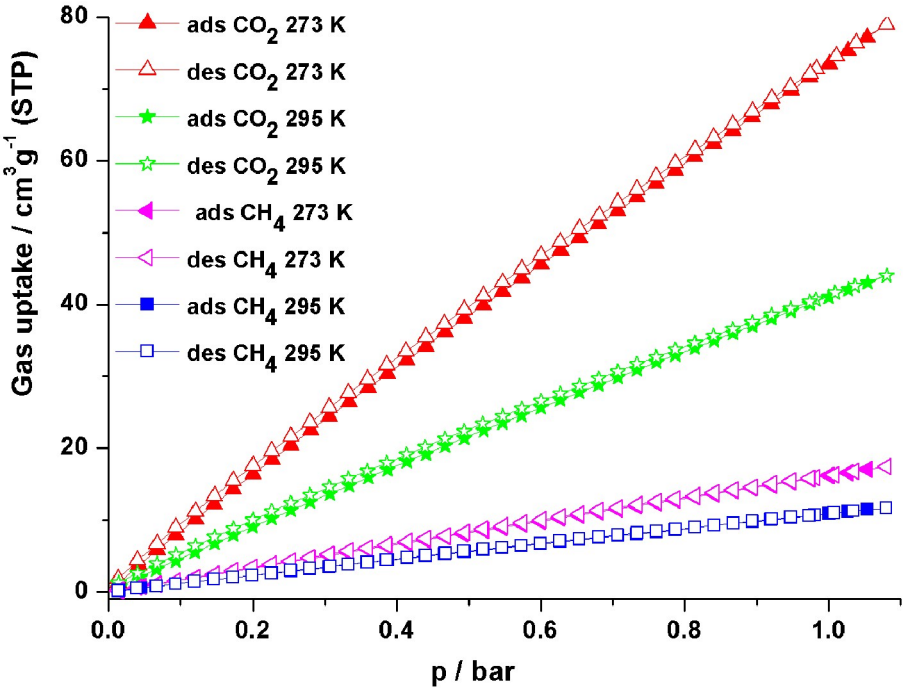

Fig. S10 CO_2 and CH_4 sorption isotherms for complex **1** at 273 K and 295 K.

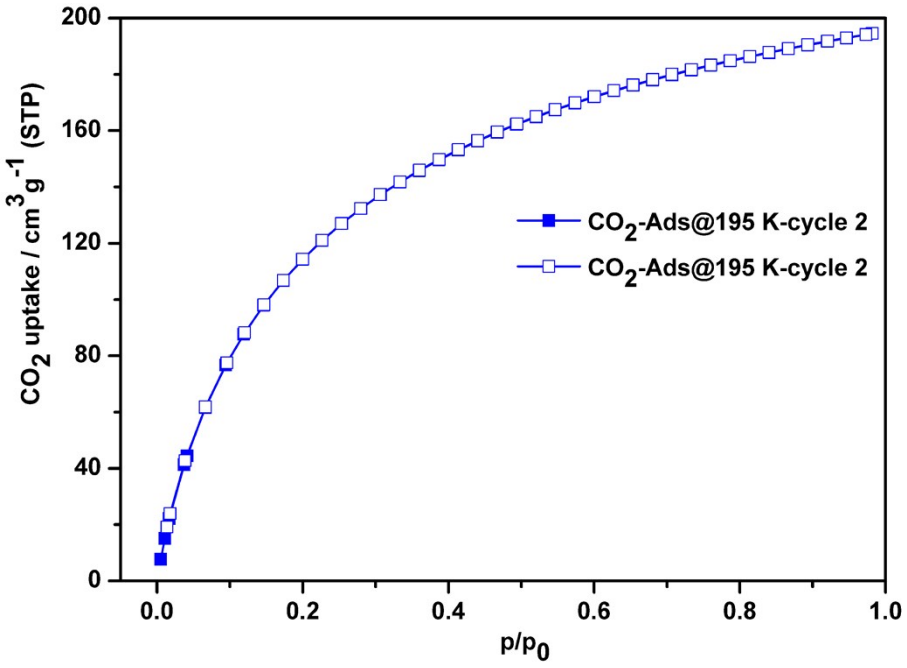

Fig. S11 The isotherm of second cycle CO_2 sorption at 195 K for complex **1**.

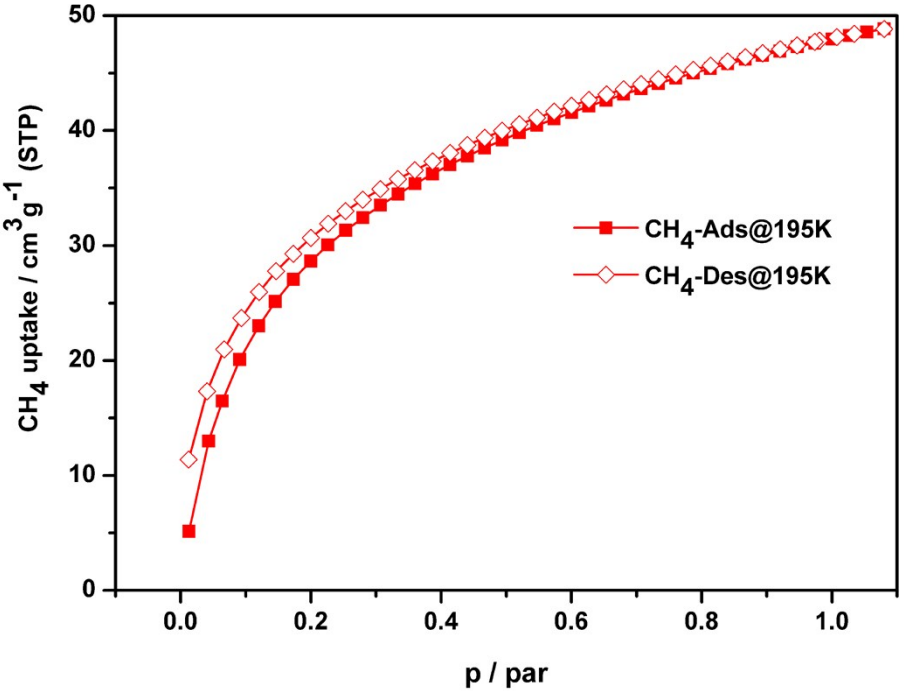

Fig. S12 CH_4 sorption isotherm for complex **1** at 195 K.

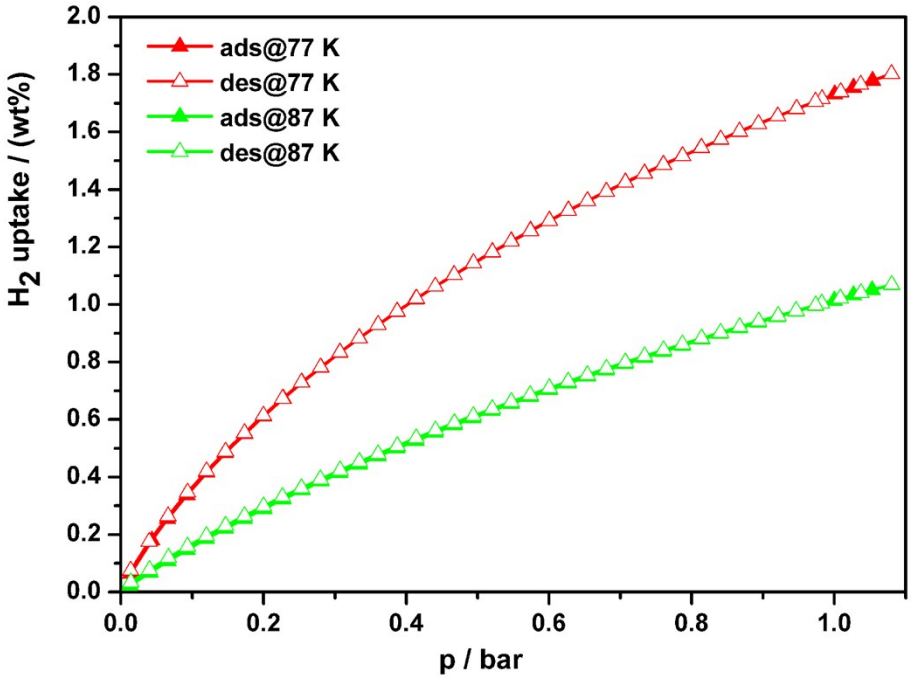

Fig. S13 H_2 sorption isotherms for complex **1** at 77 K and 87 K.

The adsorption heat (Q_{st}) of hydrogen for the desolvated complex **1** is fitted by Virial method using the data obtained from 77 K and 87 K with the following Equation: [S3]

$$\ln(P) = \ln(N) + \frac{1}{T}\sum_{i=0}^{m} a_i * N_i + \frac{1}{T}\sum_{j=0}^{m} a_j * N_j$$

N: adsorbed quantity (mg/g);

P: pressure (mmHg);

T: temperature (K);

a_i, b_j: constant;

R: 8.314 $J \cdot mol^{-1} \cdot K^{-1}$;

The isosteric enthalpy of adsorption (Q_{st}):

$$Q_{st} = \ln(P) = -R * \sum_{i=0}^{m} a_i * N_i$$

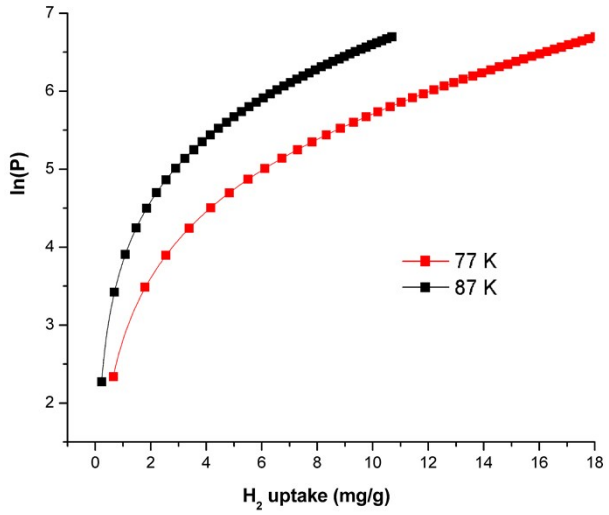

Fig. S14 Nonlinear curve fitting of H_2 sorption isotherms for complex **1** at 77 K and 87 K.

Table S4 Fit curve equation and factor.

		Value	Standard Error
ln(P)	a0*	-692.09598	1.45304
	a1*	20.297	0.54695
	a2*	-1.62181	0.0628
	a3*	0.08257	0.00651
	a4*	-0.00353	3.93245E-4
	a5*	6.09524E-5	8.60328E-6
	b0*	11.68092	0.01716
	b1*	-0.1326	0.00624
	b2*	0.00816	4.98583E-4
	k	77	0
	a0*	-692.09598	1.45304
	a1*	20.297	0.54695
	a2*	-1.62181	0.0628
	a3*	0.08257	0.00651
	a4*	-0.00353	3.93245E-4
	a5*	6.09524E-5	8.60328E-6
	b0*	11.68092	0.01716
	b1*	-0.1326	0.00624
	b2*	0.00816	4.98583E-4
	k	87	0

y=ln(x)+1/k*(a0+a1*x+a2*x^2+a3*x^3+a4*x^4+a5*x^5)+(b0+b1*x+b2*x^2)

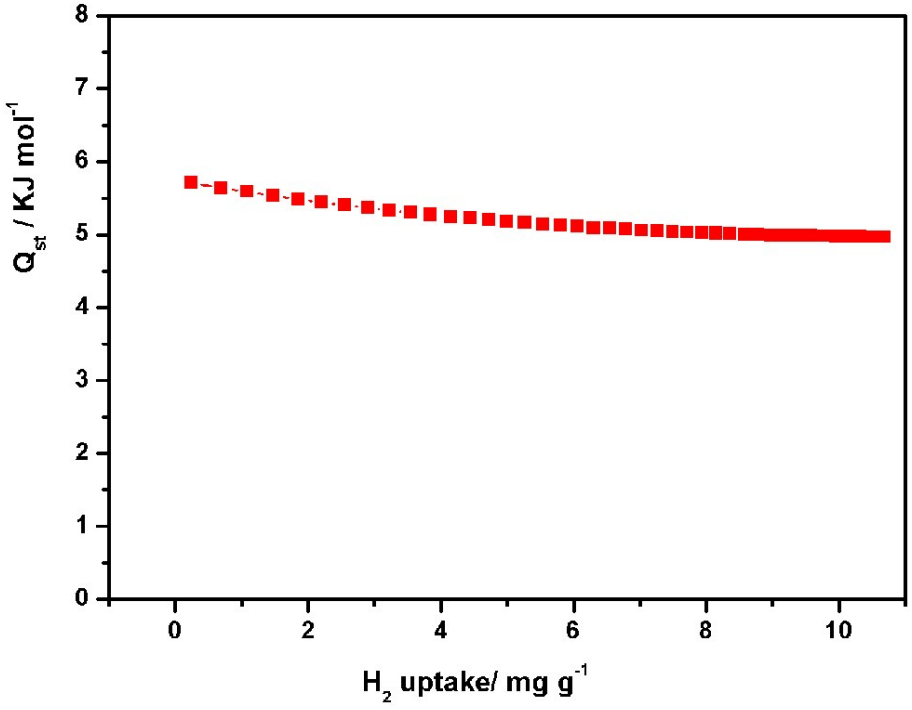

Fig. S15 Heats of sorption isotherms for H_2 in complex **1**.

7. References

(S1) Sheldrick, G. M. SHELXS 97, *Program for crystal Structure Solution* and *Program for crystal Structure Refiniement*, 1997, University of Göttingen.

(S2) P. van der Sluis and A. L. Spek, *Acta Cryst. Sect. A.* 1990, **46**, 194-201.

(S3) J. L. C. Rowsell and O. M. Yaghi, *J. Am. Chem. Soc.,* 2006, **128**, 1304-1315.