Supporting Information

High-Connected Mesoporous Metal–Organic Framework

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Experimental

Materials and methods

All chemicals were commercial and used without further purification. Elemental analyses of C, H, and N were performed on a Perkin-Elmer 2400 Series II analyzer. Infrared spectra (IR) were recorded on a BIO-RAD FTS-6000e spectrometer by using KBr pellets. Powder X-ray diffraction (PXRD) was performed on a Rigaku Rint 2000 X-ray diffractometer with Cu Kα. Thermogravimetric (TG) analyses were performed on a Shimadzu DTG-50 instrument under helium with a heating rate of 5 K min^{-1}. The gas (N_2, H_2, CO_2, and CH_4) adsorption measurements were performed on an automatic volumetric adsorption equipment (Belsorp mini II). Before gas adsorption measurements, samples **1** and **2** were evacuated for 18 h at 100 ^oC and 130 ^oC, respectively.

X-ray crystallography

The collection of crystallographic data of **1** and **2** was carried out on a R-AXIS RAPID II diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at 293 K. The structures were solved by direct methods and refined on F^2 by full-matrix least-squares methods using the SHELXTL package.[1] Generally, the hydrogen atoms of the ligands were generated theoretically onto the specific atoms. The hydrogen atoms connected to oxygen atom (O8) in hydroxyl group and the oxygen atoms (O1w, O2w and O3w) in non-coordinated water molecules were not located in the structural solution, but these hydrogen atoms are included in the formulae of **1** and **2**.

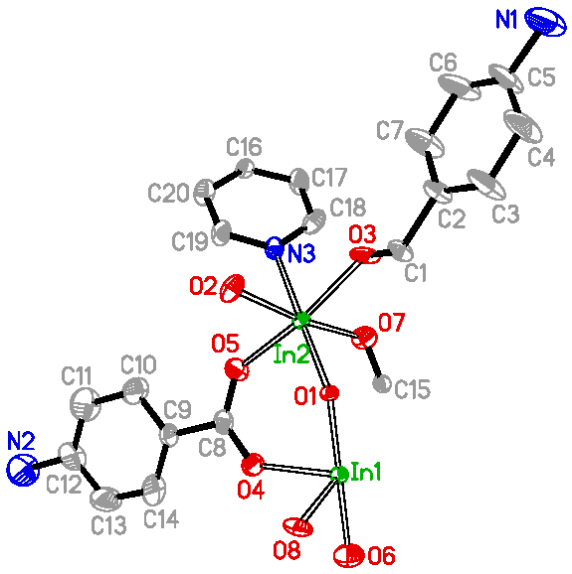

Fig. S1 ORTEP plot of the asymmetric unit of **1** (40% probability ellipsoids). Hydrogen atoms and non-coordinated water molecules are omitted for clarity.

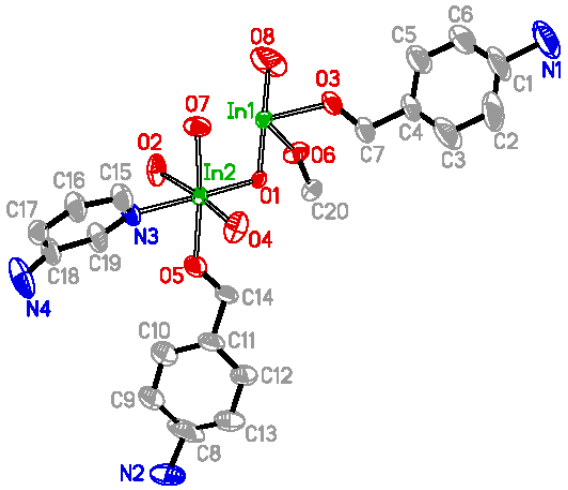

Fig. S2 ORTEP plot of the asymmetric unit of **2** (40% probability ellipsoids). Hydrogen atoms and non-coordinated water molecules are omitted for clarity.

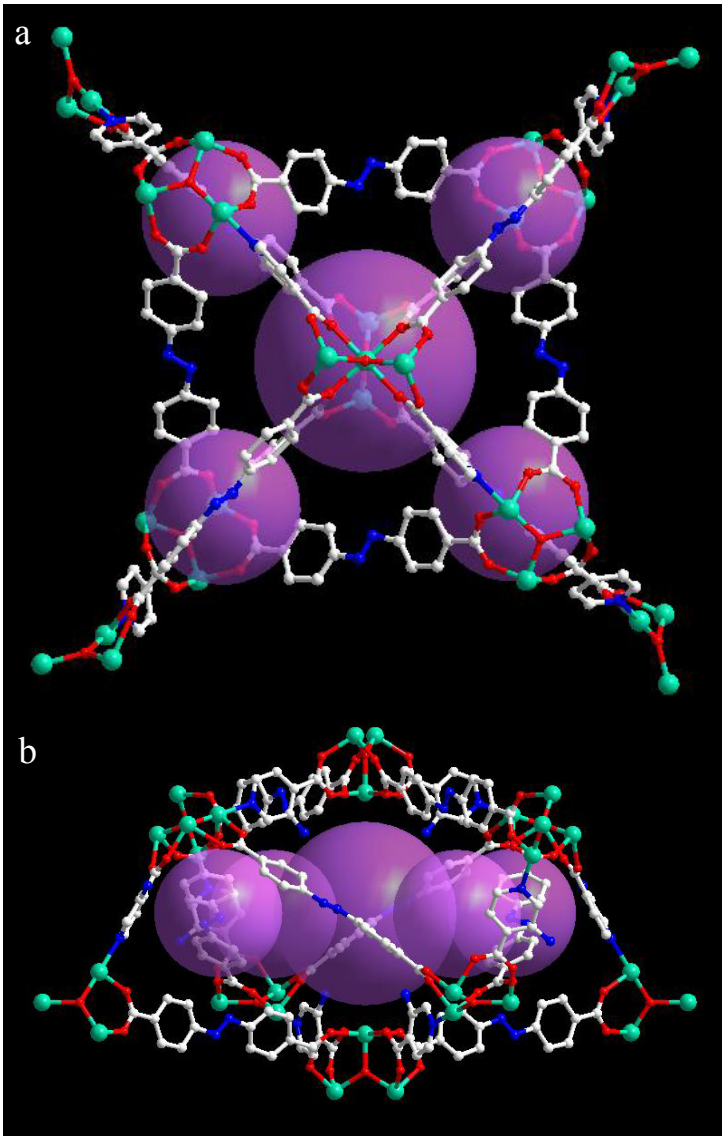

Fig. S3 View of the pore of (a) **1** and (b) **2.** The central big purple sphere indicates tetrahedral cage, and the rest indicate side pockets. Some atoms are omitted for clarity. N blue, O red, C white, In green.

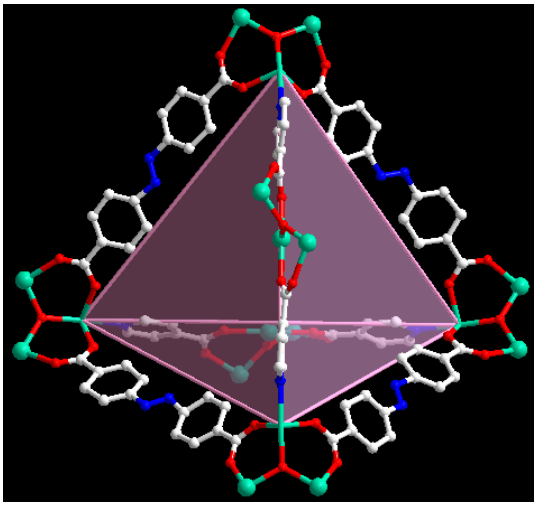

Fig. S4 View of the tetrahedral cage of **1**.The cage contains two different types of edges ($In_3O(IN)_2$ complex and ADC ligand), and their sizes are 17.0 and 18.5 Å (measured between opposite indium atoms).

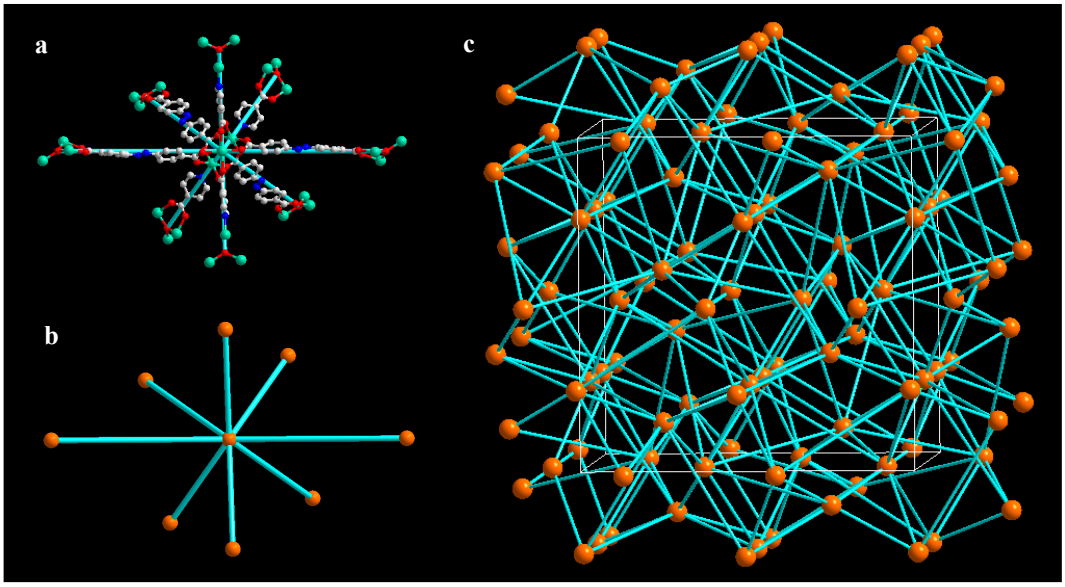

Fig. S5 Schematic views of (a) eight-connected $In_3O(O_2CR)_6X_3$ cluster, (b) the topology of eight-connected $In_3O(O_2CR)_6X_3$ cluster represented as a node, and (c) the topological structure of **1**.

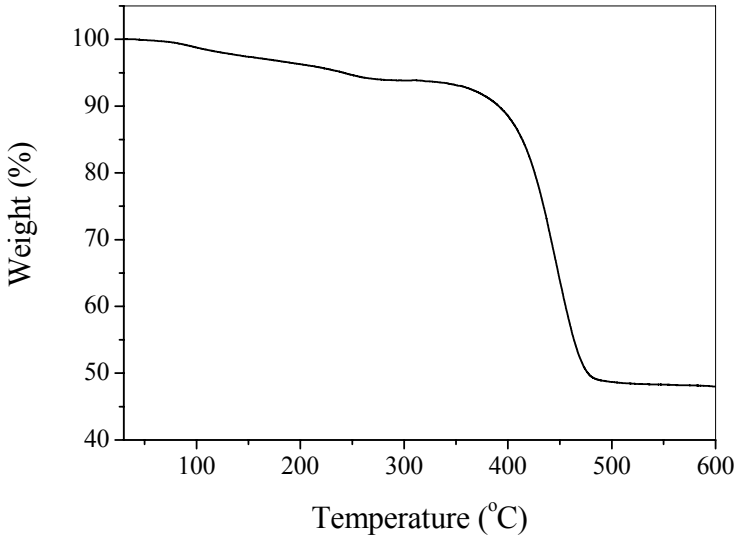

Fig. S6 TG curve of **1**. Conditions: temperature range from 30 °C to 600 °C at 5 °C /min under flow of He gas. The weight loss of 6.45% (calculated 6.77%) from 30 °C to 270 °C corresponds to the removal of H_2O guest molecules.

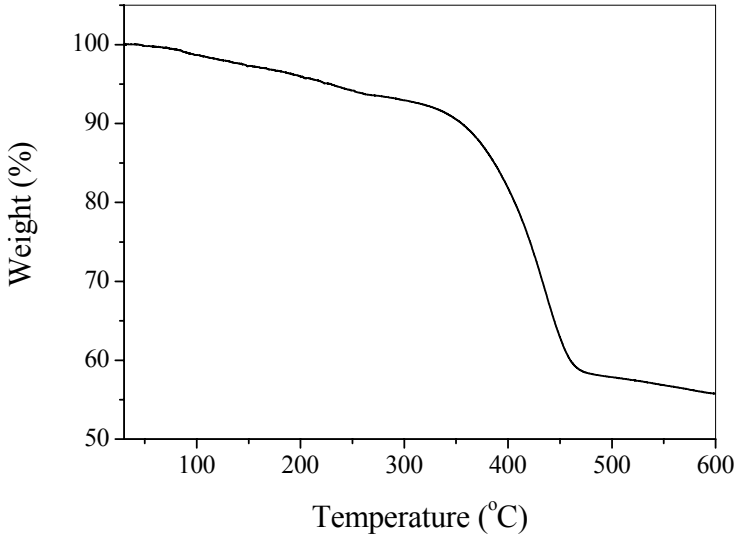

Fig. S7 TG curve of **2**. Conditions: temperature range from 30 °C to 600 °C at 5 °C /min under flow of He gas. The weight loss of 5.58% (calculated 3.89%) from 30 °C to 260 °C corresponds to the removal of H_2O guest molecules.

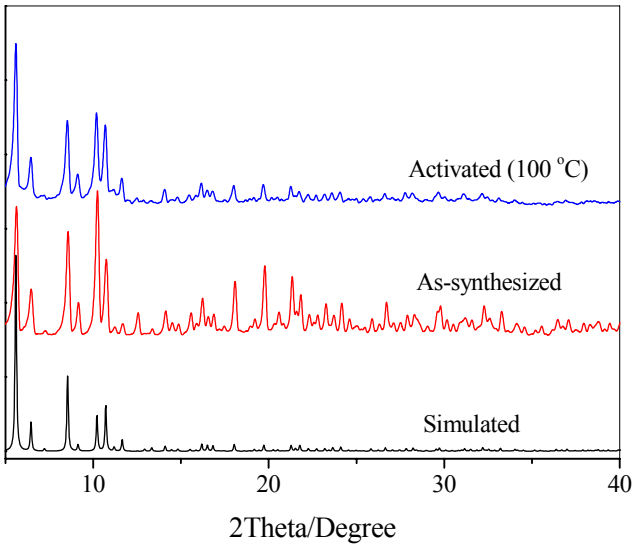

Fig. S8 PXRD pattern of as-synthesized sample and activated sample of **1**. The positions of peaks without significant change confirm that the framework retains when the guest molecules are removed.

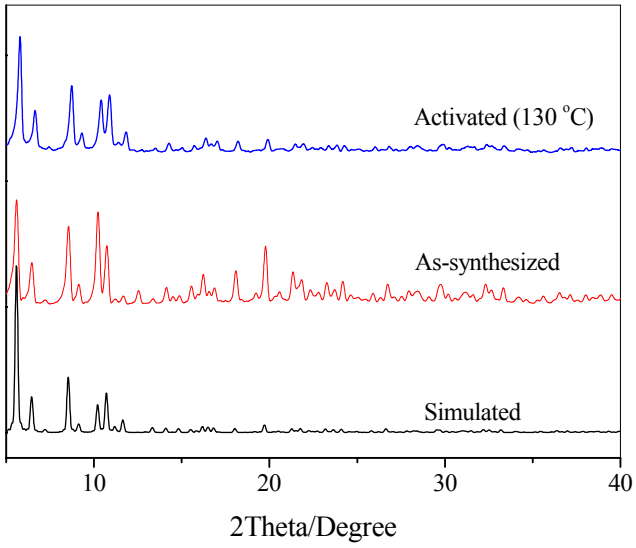

Fig. S9 PXRD pattern of as-synthesized sample and activated sample of **2**. The positions of peaks without significant change confirm that the framework retains when the guest molecules are removed.

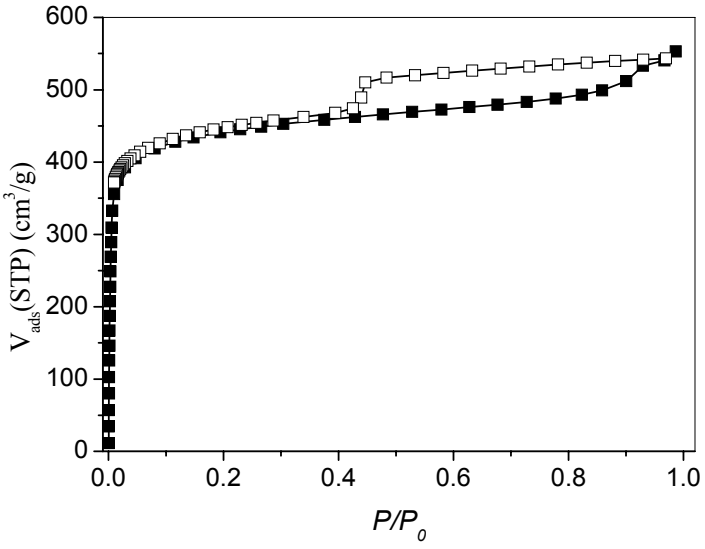

Fig. S10 Ar sorption isotherms at 87 K for **1.**

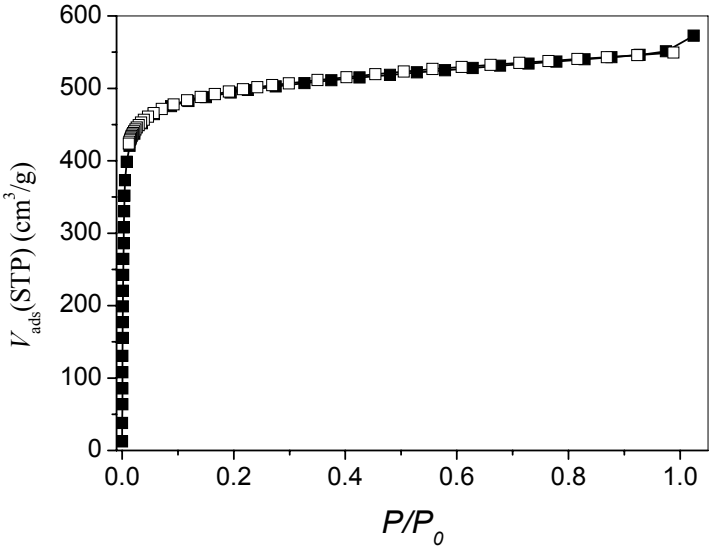

Fig. S11 Ar sorption isotherms at 87 K for **2.**

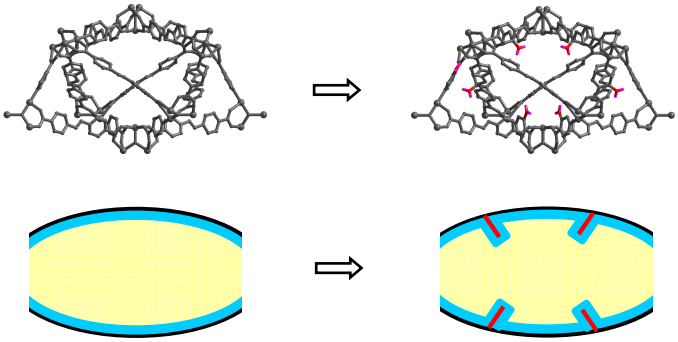

Fig. S12 Schematic illustration of the increase in the surface area of mesopores through the amine functionalization of **1**. The yellow represents the space of mesopore, and the blue represents the surface containing adsorption sites.

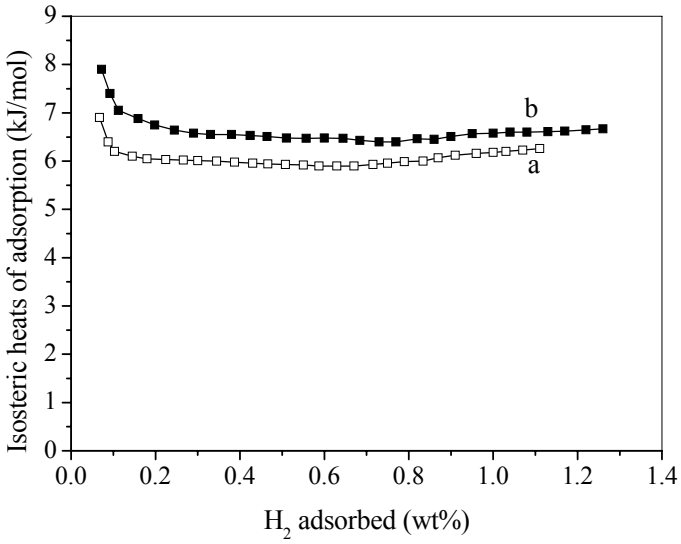

Fig. S13 Isosteric heats of H_2 adsorption for (a) **1** and (b) **2.** Isosteric heats of adsorption as a function of the quantity of hydrogen adsorbed were calculated by using a variant of the Clausius-Clapeyron equation.

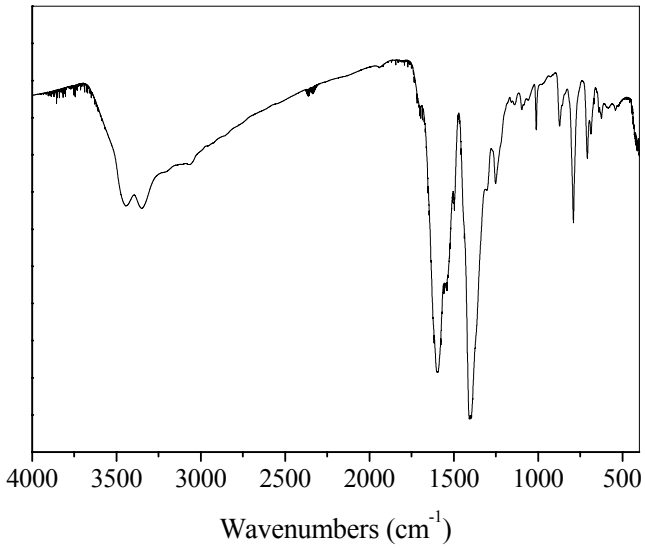

Fig. S14 IR spectrum of **1**. 3442 (m), 3342 (m), 1597 (s), 1404 (s), 1249 (w), 1094 (w), 1011 (w), 867 (w), 794 (m), 713 (w), 623 (w).

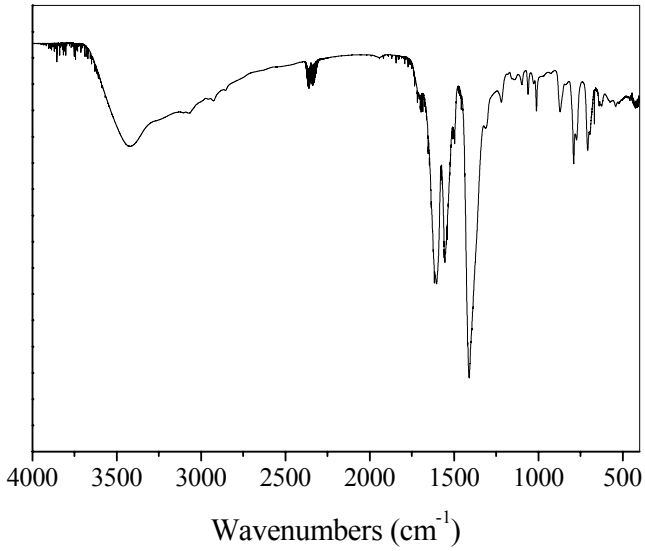

Fig. S15 IR spectrum of **2**. 3424 (m), 1605 (s), 1550 (s), 1413 (s), 1221 (w), 1096 (w), 1012 (w), 867 (w), 795 (m), 703 (m), 630 (w).

Reference

1 (a) G. M. Sheldrick, *SHELXS97*, *A Program for the Solution of Crystal Structures from X-ray Data*, University of Göttingen, 1997; (b) G. M. Sheldrick, *SHELXL97*, *A Program for the Refinement of Crystal Structures from X-ray Data*, University of Göttingen, 1997.