Supporting Information

Dynamic Microporous Indium(III)-4,4'-Oxybis(benzoate) Framework Material with High Selectivity for the Adsorption of CO_2 over N_2

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General Procedures.

All the syntheses were performed in 20 mL glass vial under autogenous pressure. Reagents were purchased commercially and used without further purification. Thermal analysis was carried out on a Netzsch STA449C thermal analyzer at a temperature range of 30 to 550 °C under dinitrogen atmosphere with a heating rate of 10 °C·min^{-1}. X-ray powder diffraction experiments were performed in a Rigaku Dmax 2500 instrument with an ultra 18Kw Cu rotating anode point source. Gas adsorption measurement was performed in the ASAP (Accelerated Surface Area and Porosimetry) 2020 System.

X-ray Crystallography

The diffraction data was collected on a Bruker Smart Apex CCD diffractometer with graphite monochromated Mo Kα radiation (λ = 0.71073Å) at 293 K. Absorption corrections was applied by SADABS.[1] The structure was solved by direct methods and refined with full-matrix least-squares technique using SHELXTL.[2] All non-hydrogen atoms were refined with anisotropic displacement parameters. The total interstitial solvent molecule contents of **1** were determined by TGA.

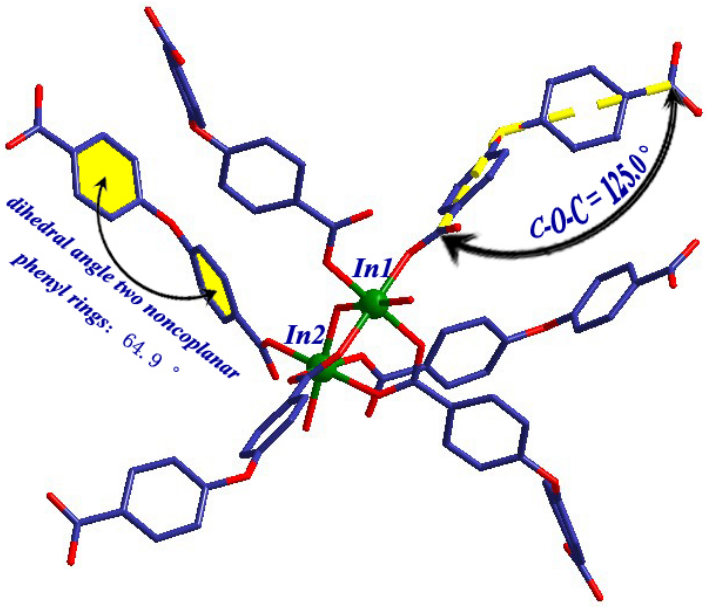

Figure S1 The coordination environment of In atoms in **1**. (Each In atom is shown at 50% probability in the asymmetric unit. Some equivalent atoms have been generated to complete the In(III) coordination, H atoms in benzene rings omitted for clarity without.)

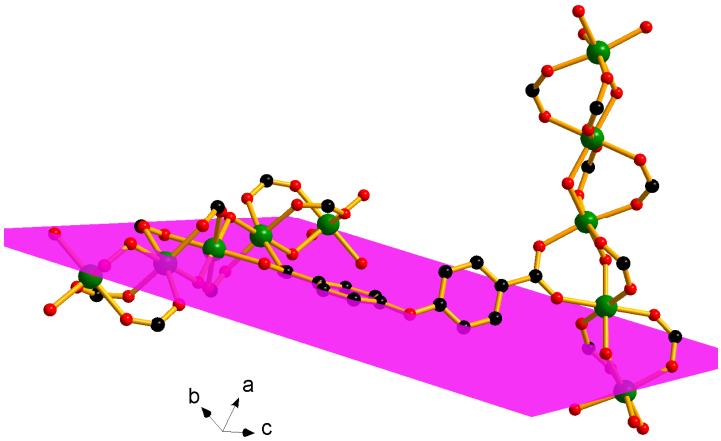

Figure S2. The connectivity between two chains in **1**.

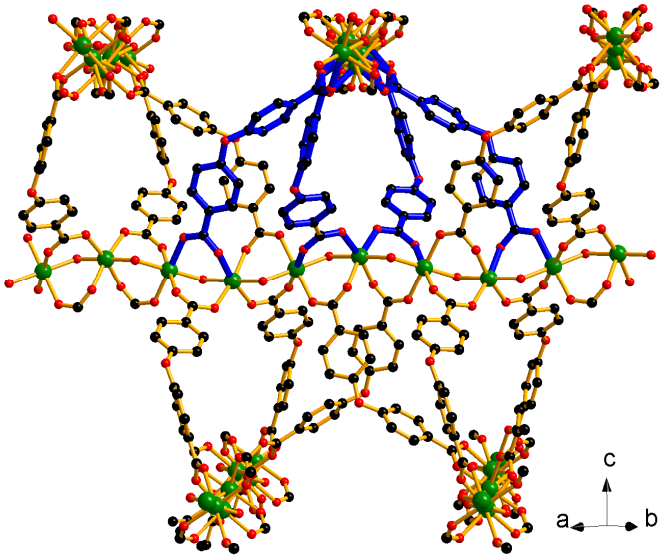

Figure S3. The connectivity between chains in **1**.

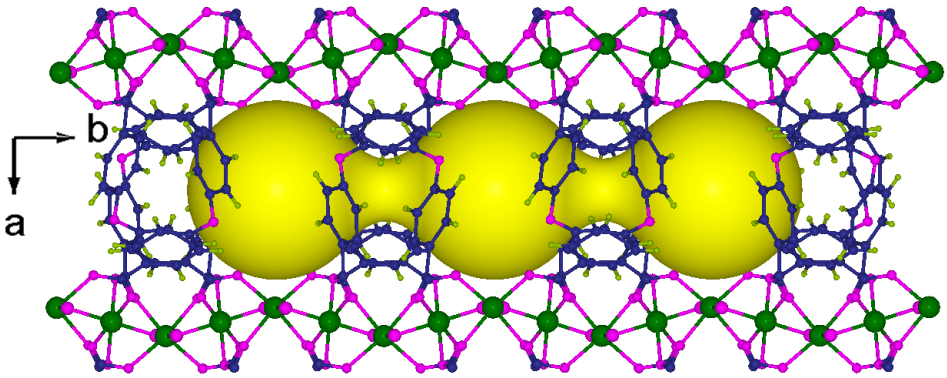

Figure S4. The linkage between adjacent cages in **1**. The yellow entity delegates the large pores and small windows.

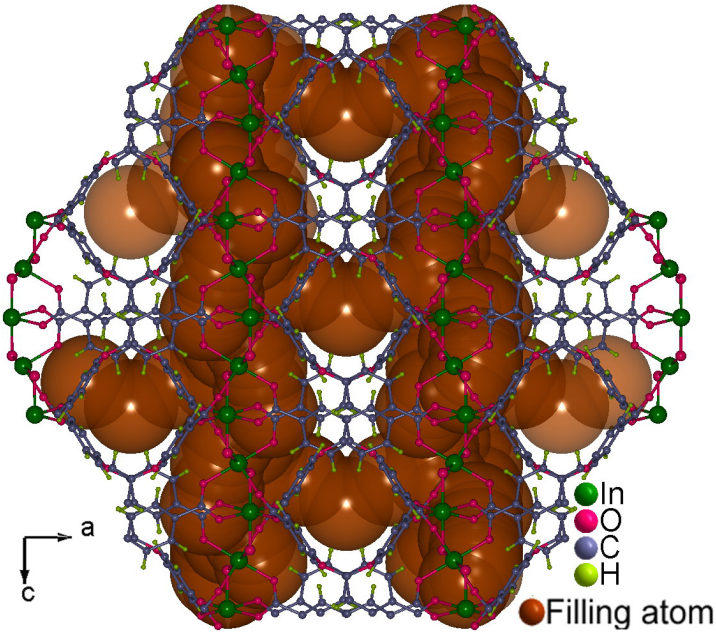

Figure S5. The 3D framework of **1**, showing free spaces (presented by the brown filling atoms) in the framework.

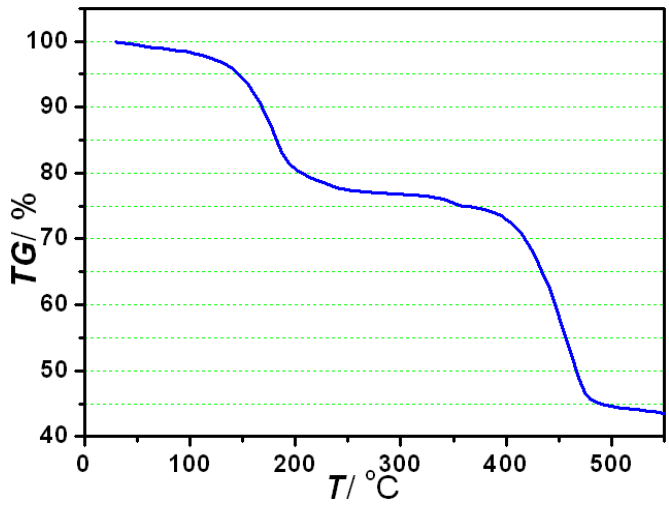

Figure S6. The TG curve of **1**

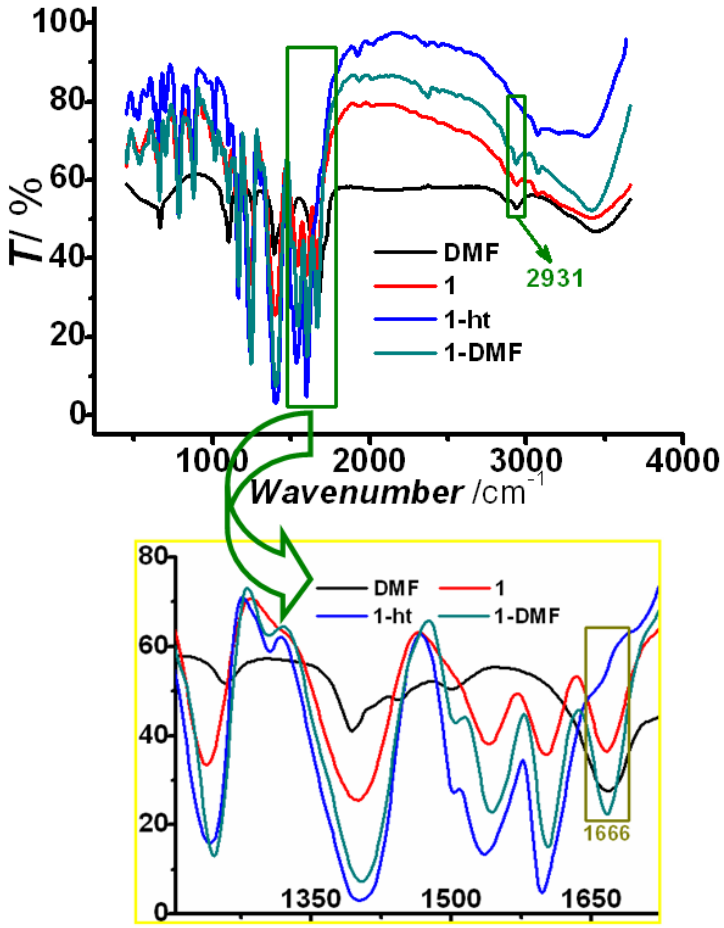

Figure S7. The IR spectra of **1**, DMF, **1-ht** and **1-DMF**.

From the IR spectra of **1**, DMF, **1-ht** and **1-DMF** (Figure S7), two characteristic absorption peaks ($\nu^{C=O}$ = 1666 cm^{-1} and ν^{C-H} = 2931 cm^{-1}) of DMF molecule are presented in the IR spectra of **1** and **1-DMF**, but they are absent in the IR spectra of **1-ht**. The results indicate that all guest DMF molecules in **1** can be removed after dried under vacuum at 180 °C for 7 hour to give a desolvated form **1-ht**. After immersed **1-ht** in DMF, the IR spectra of **1-DMF** is the same as that of **1**, which further demonstrate reversible transformation between **1** and **1-ht**.

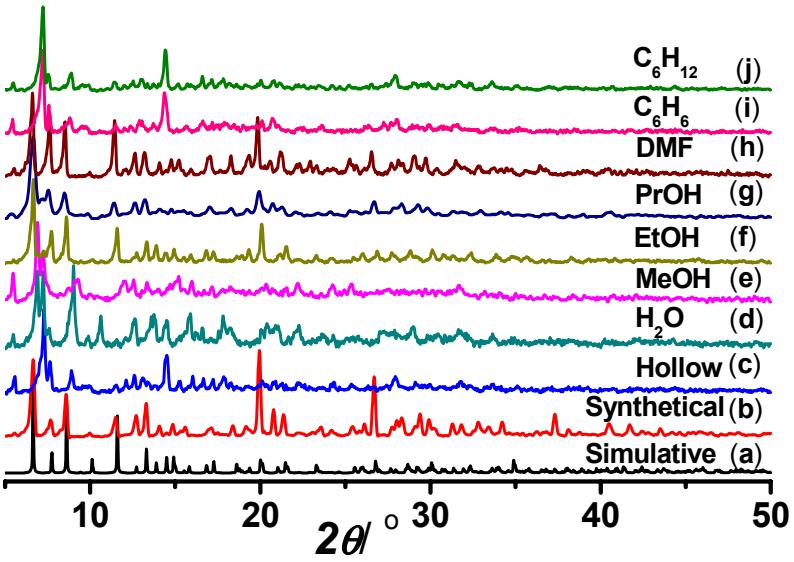

Figure S8. XRPD patterns of (a) simulated **1**, (b) as-synthesized **1**, (c) guest-free of **1**, dried crystals **1** immersed in water (d), methanol (e), ethanol (f), propanol (g), DMF (h), benzene (i) and cyclohexane (j).

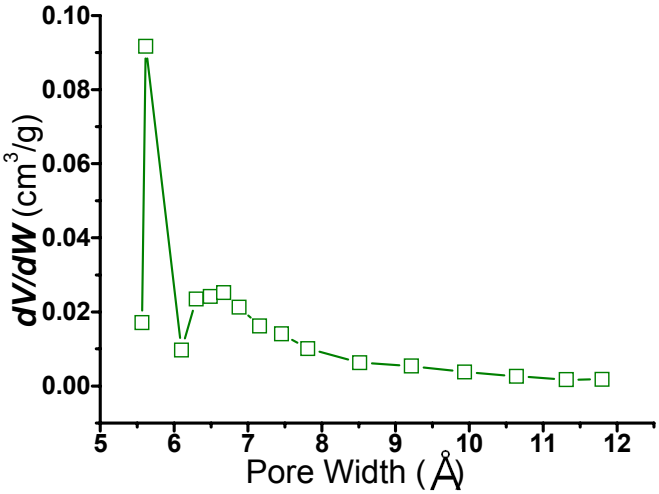

Figure S9 pore size distribution based on Horvath–Kawazoe (H–K) model.

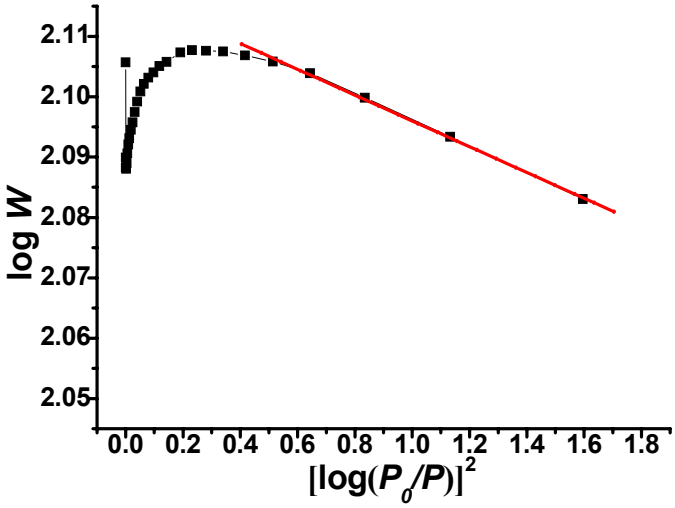

Figure S10 The D-R plot of N_2 adsorption isotherm for **1-ht**

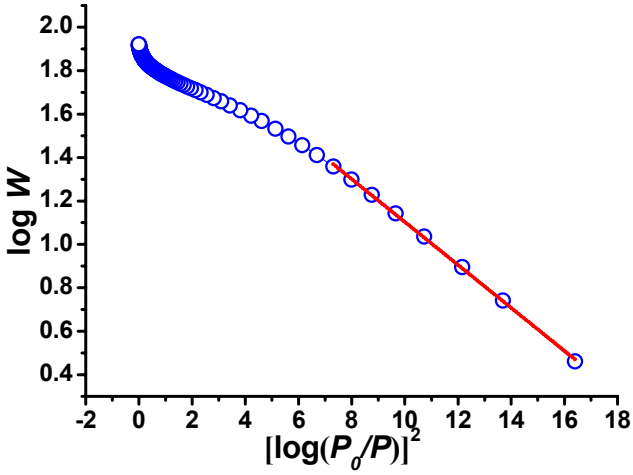

Figure S11 The D-R plot of N_2 adsorption isotherm for **1-ht**

On the other hand, the micropore filling of gas is well described by the Dudinin-Radushkevich (D-R) equation:

$$\ln W = \ln W_0 - (A/\beta E_0)^2 \qquad A = RT\ln(P_0/P) \qquad (1)$$

in which W and W_0 are the amount of adsorption at P/P_0 and the saturated amount of adsorption, respectively. A is the adsorption potential, and β and E_0 are the affinity coefficient and characteristic adsorption energy, respectively. The D-R plot shows a linear relationship existing at higher P/P_0 region, from which the value of βE_o is obtained. Furthermore, the value of βE_o allows the calculation of the isosteric heat of adsorption, $q_{st,\Phi=1/e}$, at the fractional filling of $1/e$ using eq. 2 where ΔH_v is the heat of vaporization of the bulk liquid.[3] The value for ΔH_v for N_2 at 77 K is 5.58 kJ/mol, and thus the value of $q_{st,\Phi=1/e}$ of **1** for N_2 is 12.23 kJ/mol, very close to that of activated carbon (ca. 12 kJ/mol). (Fig. 6)

$$q_{st,\Phi=1/e} = \Delta H_v + \beta E_o \qquad (2)$$

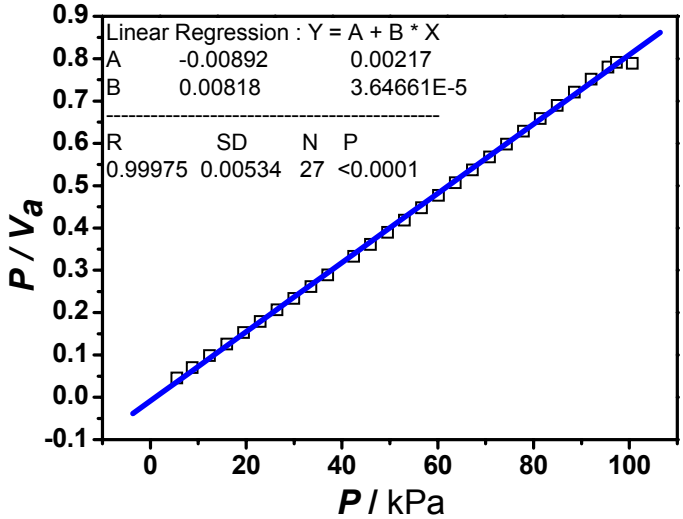

Figure S12 Langmuir plots of N_2 sorption isotherm for **1-ht** at 77K.

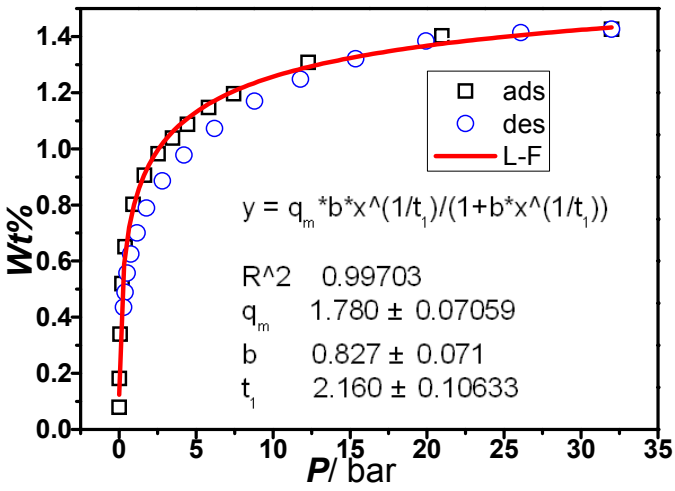

Figure S13. H_2 adsorption isotherms for 1-ht recorded at 77 K, and the red solid line is the fitting of the H_2 adsorption isotherm of 1-ht using Langmuir-Freundlich equation.

The high-press H_2 adsorption experiments were also measured for **1-ht** at 77 K, which showed type I behavior with small hysteresis (Fig. S13). The rapid increase in H_2 uptake at low-pressures is consistent with a strong interaction between H_2 molecules and the pore walls, possibly due to the presence of large cages with small windows. As a result, **1-ht** exhibited an excess gravimetric hydrogen uptake of nearly 1.43% uptakes around 32 atm. By fitting of the Langmuir-Freundlich (L-F) equation to the adsorption isotherm, the saturated H_2 uptake for **1-ht** is estimated to be 1.78%.

References

[1] G. M. Sheldrick, SADABS; Siemens Analytical X-ray Instrument Division, Madison, Wiscconsin, USA, 1996.

[2] G. M. Sheldrick, Universität Göttingen, Germany, 1997.

[3] D. Li, and K. Kaneko, *J. Phys. Chem. B,* 2000, **104**, 8940-8945.