Electronic Supplementary Material (ESI) for *CrystEngComm*

Supporting information

Two microporous metal-organic frameworks with double-walled tubular structures consisted of nested coaxial double-stranded helices

Qiang Gao,[ab] Ming-Yan Wu,[a] You-Gui Huang,[a] Lian Chen,[a] Wei Wei,[ab] Qing-Fu, Zhang,[a] Fei-Long Jiang,[a] Mao-Chun Hong*[a]

[a]*Key Laboratory of Optoelectronic Materials Chemistry and Physics, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou 350002, China*

Tel: +86-591-83792460 Fax: +86-591-83794946

E-mail: hmc@fjirsm.ac.cn

[b]*Graduate school of Chinese Academy of Science, Beijing, China*

Experimental Section

Synthesis of **1**: A mixture of $InCl_3 \cdot 4H_2O$ (58.0 mg, 0.2mmol), H_2aip (36.0mg, 0.2mmol) and imidazole (34mg, 0.5mmol), H_2O (5ml) and ethanol (5ml) was placed in 30-ml Teflon-lined stainless steel autoclave, and the autoclave was sealed, heated to 110 ˚C under autogenous pressure for 96h, and then cooled to room temperature at $6°C \cdot h^{-1}$. Colorless crystalline product was filtered, washed with distilled water, and dried at ambient temperature. Yield: (75% based on $InCl_3$). Anal. Calcd for $C_8H_{12}NO_8In$ (%): C, 26.30; H, 3.31; N,3.84; found (%): C, 26.38; H, 3.26; N, 3.89. IR (KBr): 3432(br, s),2970(w), 1618(s), 1573(s), 1483(w), 1445(w), 1414(m), 1382(s), 1114(w), 964(w), 784(m), 722(w)cm^{-1}.

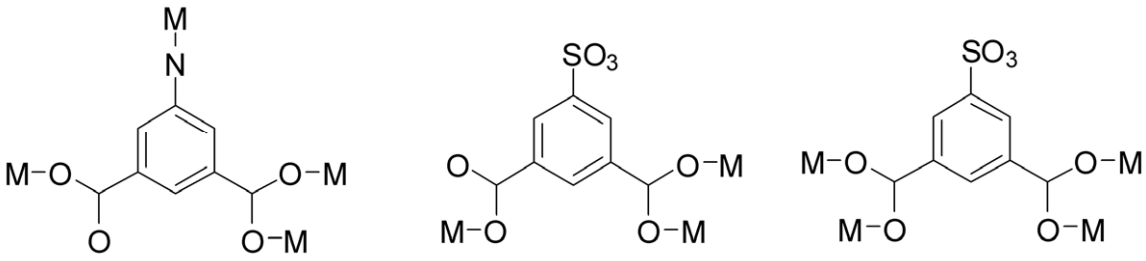
Synthesis of **2**: A mixture of $InCl_3 \cdot 4H_2O$ (58.0 mg, 0.2mmol), NaH_2sip (53.6mg, 0.2mmol) and 2-picoline (0.1ml, 1.0mmol), H_2O (2ml) and ethanol (6ml) was placed in 30-ml Teflon-lined stainless steel autoclave, and the autoclave was sealed, heated to 90 ˚C under autogenous pressure for 72h, and then cooled to room temperature at $6°C \cdot h^{-1}$. Colorless crystalline product was filtered, washed with distilled water, and dried at ambient temperature. Yield: (80% based on $InCl_3$). Anal. Calcd for $C_{16}H_{16}O_{19}S_2In_2$ (%):C, 23.84; H, 2.00; found (%): C, 23.89; H, 1.92. IR (KBr): 3444(br, s), 2952(w), 1610(s), 1553(s), 1449(m), 1378(s), 1199(s), 1120(s), 1048(s), 777(m), 630(m)cm^{-1}.

Different organic bases (imidazole and 2-picoline) were added to these two synthesis reaction systems, respectively, which play important roles in the syntheses of the complexes, though they are not included in the final structures. Further researches indicate that in the absence of these two organic bases, or when other kinds of organic bases, such as pyridine, 3- and 4-picoline were used in replacement of the corresponding organic bases, no crystals could be obtained.

Crystallographic Analyses

The intensity data were collected on a Saturn70 CCD diffractometer for **1**, and a Mercury CCD diffractometer for **2**, with graphite-monochromated MoKα radiation (λ = 0.71073 Å) at room temperature. All absorption corrections were performed by using the multiscan program. The structure were solved by direct methods and refined by full-matrix least squares on F^2 with the SHELXTL-97 program. [G. M. Sheldrick, *SHELXTL-97, Program for the Solution of Crystal Structures*, University of Göttingen, Germany, 1997] All non-hydrogen atoms were refined anisotropically, except free water molecules O7 and O8 in **1** and C11 in **2**. All hydrogen atoms belonging to the water molecules and μ_2-OH groups were found in the electron-density map. The

other hydrogen atoms were generated geometrically.



$(\kappa^1\text{-}\kappa^1)\text{-}\kappa^1\text{-}\kappa^1\text{-}\mu_4$ aip

$(\kappa^1\text{-}\kappa^1)\text{-}\kappa^1\text{-}\mu_3$ sip

$(\kappa^1\text{-}\kappa^1)$ - $(\kappa^1\text{-}\kappa^1)$ $\text{-}\mu_4$ sip

Scheme S1. Schematic representation of the coordination modes of aip and sip ligands.

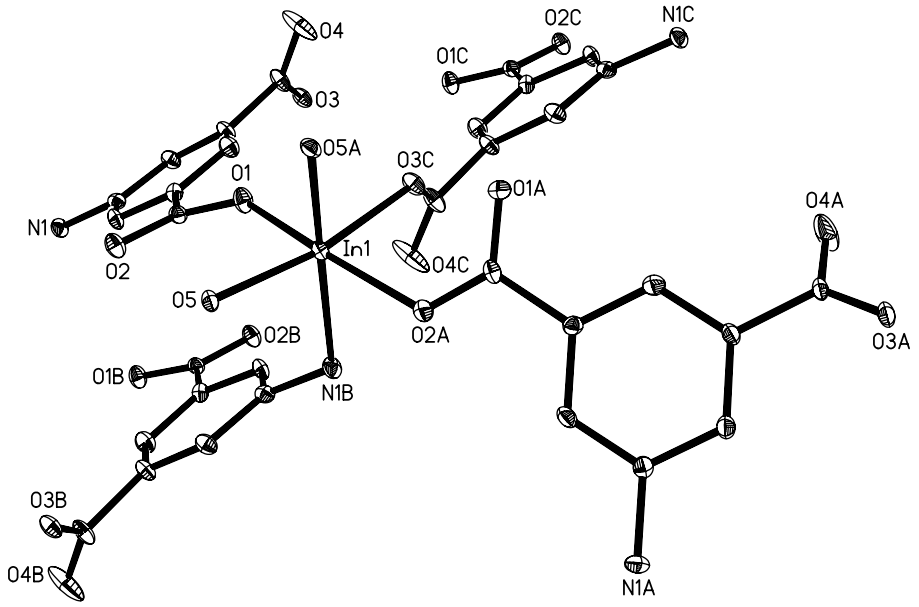


Fig. S1 The coordination environment of In(III) ion in **1** with the thermal ellipsoid at the 30% probability level. hydrogen atoms are omitted for clarity. Symmetry codes: A: 1/3-y, 2/3+x-y, z-1/3, B: 1/3-x, 2/3-y, 5/3-z, C 1/3-x, 2/3-y, 2/3-z.

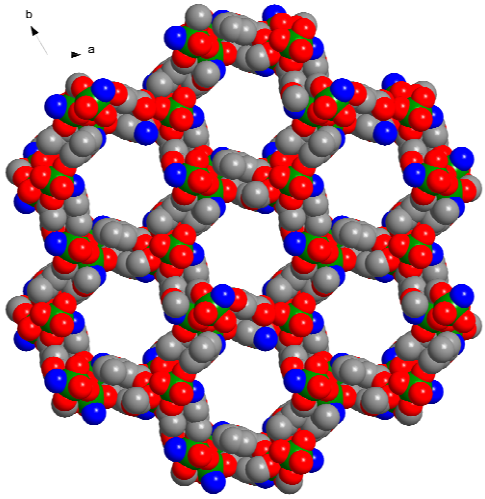


Fig. S2. The space-filling diagram for open-framework structure of **1**. The lattice water molecules and hydrogen atoms are omitted for clarity. Color code: green, In; red, O; blue, N; gray, C atoms.

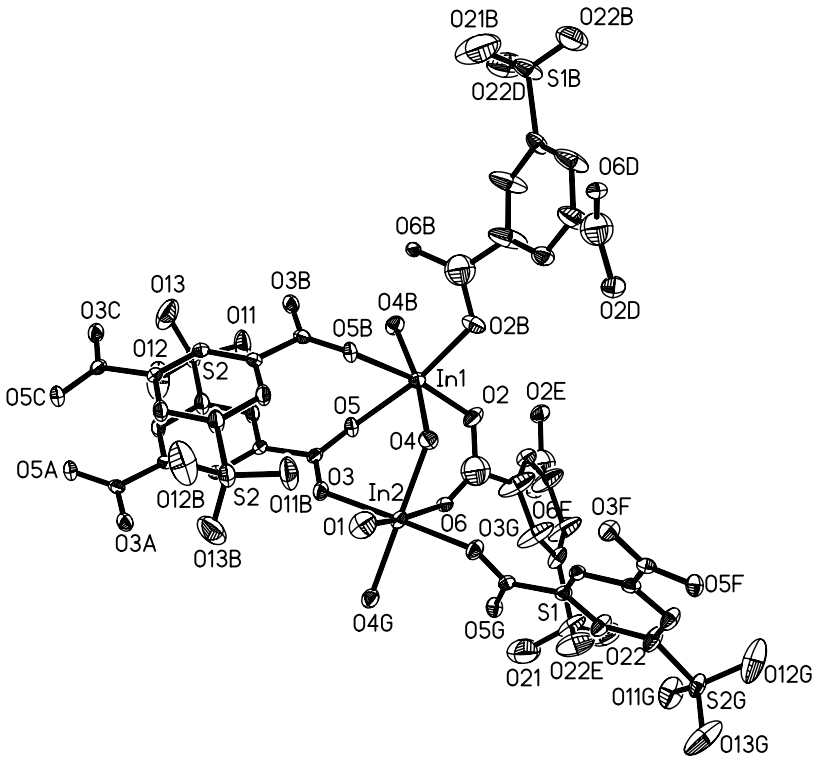


Fig. S3 The coordination environments of In(III) ions in **2** with the thermal ellipsoid at the 30% probability level. Disorder atoms and hydrogen atoms are omitted. Symmetry codes: A: 1-y, 1-x, z, B: y, x, 1-z, C 1-x, 1-y, 1-z; D: y, 1-x+y, 1-z; E: 1-x+y, y, z; F: 2/3+x-y, 1/3+x, 4/3-z; G 2/3+x-y, 4/3-y, 4/3-z..

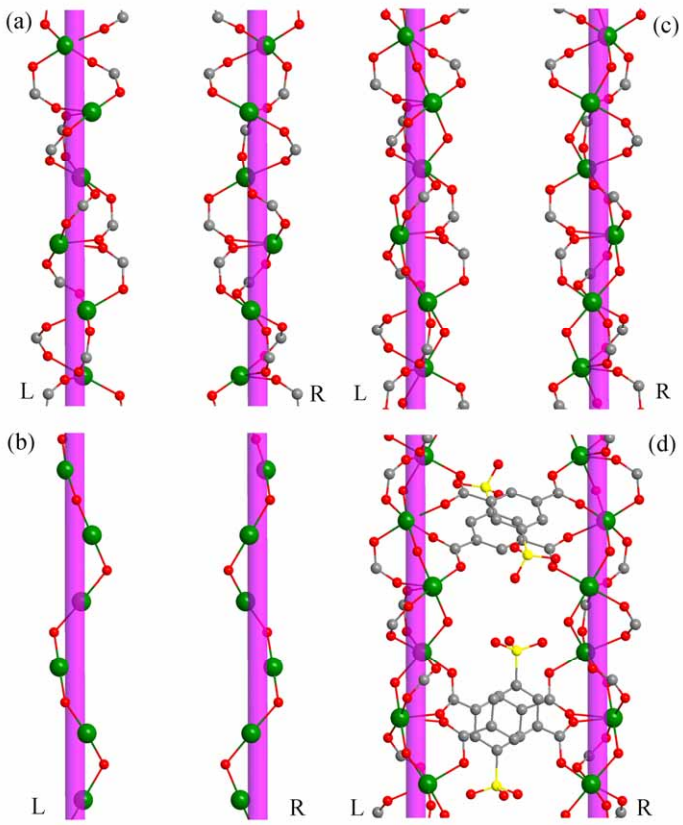


Fig. S4 (a) Ball-and-stick representation of the outer helical chains along *b*-axis in **2**. (b) Ball-and-stick representation of the inner helical chains along *b*-axis. (c) View of the nested coaxial double-stranded helix. (d) Neighbouring helices are interconnected by sip ligands.

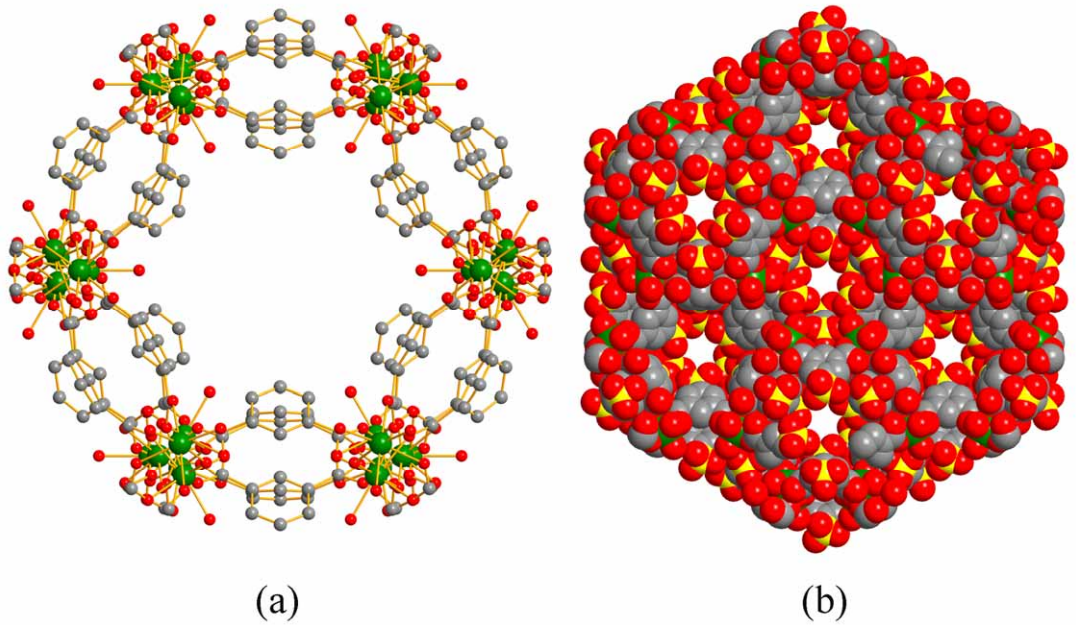


Fig. S5. (a) Ball-and-stick representation of the double-walled cylindrical channel in **2**. Sulfonate anion groups are omitted for clarity. (b) The space-filling diagram for open-framework structure of **2**. The lattice water molecules and hydrogen atoms are omitted for clarity. Color code: green, In; red, O; yellow, S; gray, C atoms.

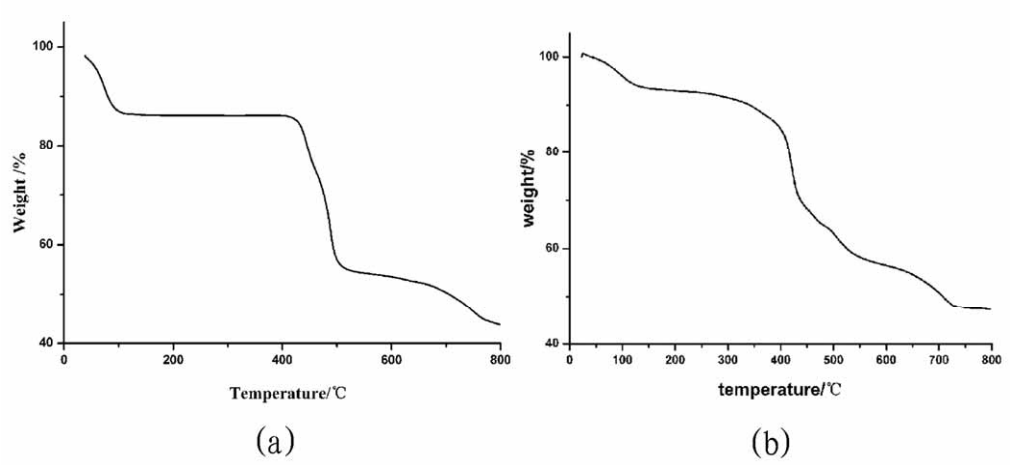


Fig. S6. TG curves for **1** (a) and **2** (b) under N_2 flow.

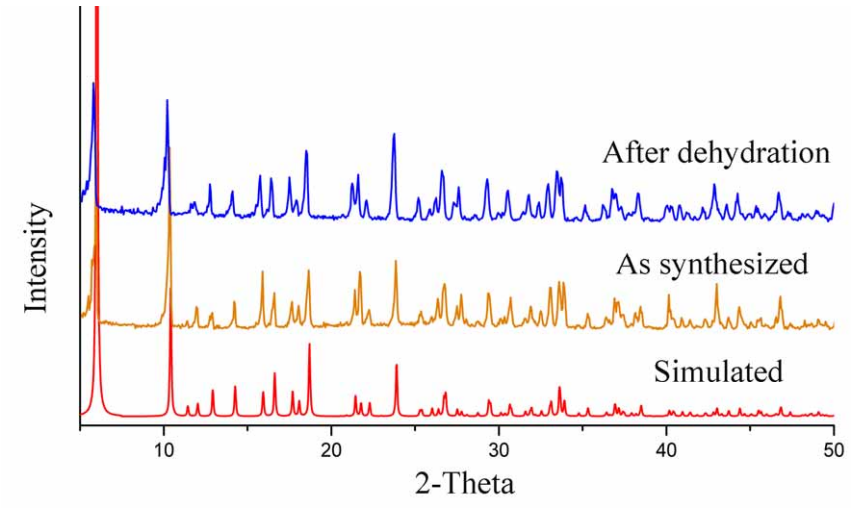


Fig. S7. Powder XRD for **1**. The dehydration process was performed by heating the sample to 150℃ for 5 hours after vacuum.

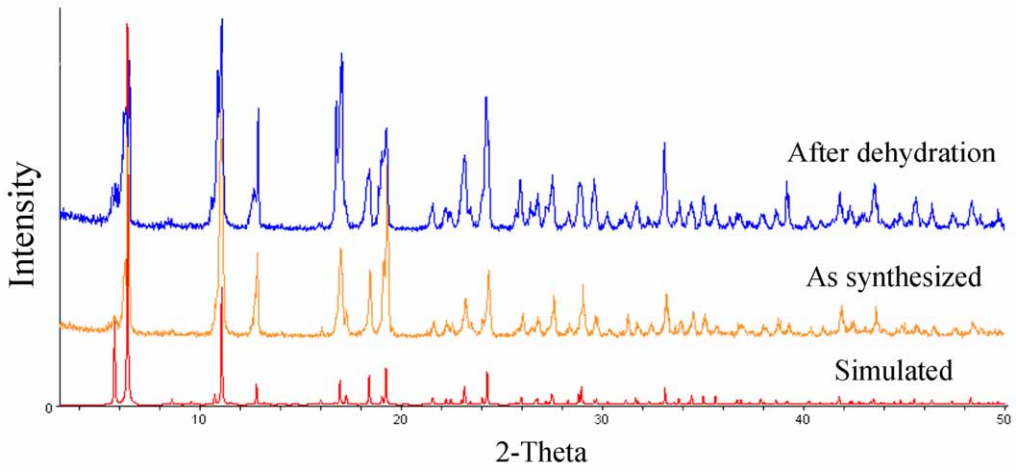


Fig. S8. Powder XRD for **2**. The dehydration process was performed by heating the sample to 120℃ for 10 hours after vacuum.

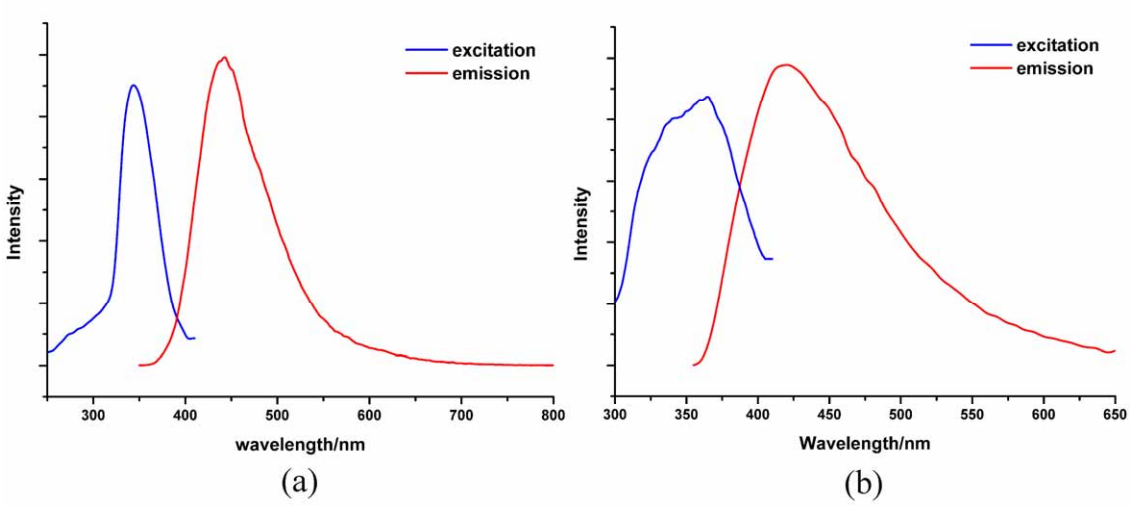


Fig. S9. Photoluminescence spectra of **1** (a) and **2** (b) at room temperature.