Electronic Supporting Information

Coexistence of self- and inter-penetration in two (3,6)-connected porous coordination polymers

Qingxia Yao, a Yerong Fan, a Zhan Wang, a Wenzeng Duan, a Suna Wang, a Yunwu Li, a Dacheng Li,*,a,b Qingfu Zhang, a Yuchang Du, a Jianmin Dou a

a School of Chemistry and Chemical Engineering, and Shandong Provincial Key Laboratory of Chemical Energy Storage and Novel Cell Technology, Liaocheng University, Liaocheng 252000, PR China
b Institute of BioPharmaceutical Research, Liaocheng University, Liaocheng 252000, PR China
E-mail: dougroup@163.com; lidacheng62@163.com

S1 - Materials and Instruments
All chemicals except the ligand were purchased and used without further purification. The ligand was synthesized according to the literature.31
IR spectra were recorded on a Nicolet-5700 FT-IR spectrophotometer with KBr pellets in the region of 4000 - 400 cm⁻¹. The powder X-ray diffraction (PXRD) data were collected on a Bruker D8 Advance diffractometer with Cu Kα radiation (λ = 1.5418 Å) and a graphite monochromater at 298 K. Elemental analysis (C, H, and N) were performed on a Perkin-Elmer 2400 II analyzer. Thermogravimetric analysis (TGA) and mass spectrum was performed under nitrogen atmosphere on a Netzsch STA 449F5-QMS403C simutaneous TG/DSC-QMS analyzer with a heating rate of 20 °C/min. The nitrogen adsorption-desorption isotherm was redcorded on a Quantachrome Autosorb iQ analyzer. The photoluminescence spectra were measured on a Perkin-Elmer LS-55 spectrofluorometer.

S2 - Single crystal X-ray diffraction
Single crystal X-ray diffraction data were recorded at room temperature on a Bruker SMART-1000 CCD diffractometer with graphite-monochromated with with Mo Kα radiation (λ = 0.71073 Å) in the o scan mode. Data reduction was performed using the SAINT program.32 The structure was solved by direct methods and refined by full-matrix least-squares methods with SHELX program.33 All non-hydrogen atoms were refined with anisotropic displacement parameters, while the hydrogen atoms on the organic ligand were placed in idealized positions with isotropic displacement parameters. The large pore volume of the compound as well as disorders of guest molecules (DMF, H₂O, and cyclohexanol) in the pores precluded location of these guest molecules. The PLATON/SQUEEZE program was used to remove scattering contribution from disordered guest molecules and to produce solvent-free diffraction intensities, which were used in the final structure refinement.34 Full crystallographic data for 1-Tb have been deposited with the CCDC 1476203.

References
Fig. S1 Coordination environment around Tb$^{3+}$ in 1-Tb.

S3 - Powder X-ray diffraction

Fig. S2 Simulated and experimental powder X-ray diffraction patterns (PXRD) of 1-Tb and 1-Dy. The patterns are identical, indicating the compounds are isostructural.
Fig. S3 PXRD patterns of the simulated (black line), as-synthesized 1-Tb (red line), the activated 1-Tb heated at 200 °C for 6 hours (green line), and recovered 1-Tb exposed to vapour of different solvents at 35 °C for 36 hours: water (blue line); DMF (cyan line); cyclohexanol (magenta line); MeOH, EtOH, THF, acetone, PE, EA, CH₂Cl₂ (grey lines).
Fig. S4 PXRD patterns of the simulated (black line), as-synthesized 1-Dy (red line), the activated 1-Tb heated at 200 °C for 6 hours (green line), and recovered 1-Tb exposed to vapour of different solvents at 35 °C for 36 hours: water (blue line); DMF (cyan line); cyclohexanol (magenta line); MeOH, EtOH, THF, acetone, PE, EA, CH₂Cl₂ (grey lines).
**S4 - Fourier-Transform infrared spectrum**

![FT-IR spectrum of 1-Tb and 1-Dy](image)

Fig. S5 The FT-IR spectrum of 1-Tb and 1-Dy.

**S4 - Simultaneous thermogravimetric analysis and mass spectrum**

Simultaneous thermogravimetric analysis (TGA) and mass spectrum was performed under nitrogen atmosphere on a Netzsch STA 449F5-QMS403C. TGA plot (green line) shows the sample loses all solvents (water, DMF, cyclohexanol) with a weight loss of 30.4% before 320 °C. There is almost no mass loss between 320-560 °C. Upon heating up to 560 °C, it starts to decompose.

Mass spectrum (pink lines) with \(m/z\) value of 18 (water), 73 (DMF), 100 (cyclohexanol) respectively were simultaneously recorded. The vertical axis represents the relative ion abundance of different molecules; the horizontal axis is the temperature. For \(m/z\) value of 18, mass spectrum shows a big peak appears between ca. 120-180 °C, indicating the water molecules release at this temperature range; For \(m/z\) value of 73, mass spectrum shows three big peaks appears between ca. 100-300 °C, indicating DMF molecules release at this broad temperature range; For \(m/z\) value of 100, mass spectrum shows a big peak appears between ca. 60-300 °C, indicating cyclohexanol molecules release at this broad temperature range.
Fig. S6 TGA plot (green line) and Mass spectrum (pink line) with $m/z$ value of 18 (water) of 1-Tb.

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Fig. S7 TGA plot (green line) and Mass spectrum (pink line) with $m/z$ value of 73 (DMF) of 1-Tb.
Fig. S8 TGA plot (green line) and Mass spectrum (pink line) with m/z value of 100 (cyclohexanol) of 1-Tb.

Fig. S9 TGA plots of as-synthesized 1-Tb (black line), and recovered samples exposed in the vapour of H$_2$O, DMF, cyclohexanol at 35 °C for 36 hours: 1-Tb-recovered from H$_2$O (red line); 1-Tb-recovered from DMF (blue line); 1-Tb-recovered from cyclohexanol (cyan line). These results indicate that not only the types but also the content of the guest molecules play important roles in recovering the crystallinity of the samples.
**S5 - Nitrogen adsorption measurement**

The sample for N$_2$ adsorption was exchanged with CH$_2$Cl$_2$, 20 mL × 3 times for 3 days and then activated by heating at 300 °C overnight. The nitrogen adsorption-desorption isotherm was recorded at 77 K on a Quantachrome Autosorb iQ analyzer.

![Nitrogen adsorption-desorption isotherm](image)

**Fig. S10** Nitrogen adsorption-desorption isotherm of 1-Tb at 77 K.

**S6 - Solid-state fluorescence emission**

![Solid-state excitation and emission spectra](image)

**Fig. S11** Solid-state excitation (dotted line) and emission spectra (solid line, excited at 325 nm) of the ligand, 1-Tb, and 1-Dy respectively at room temperature.
Fig. S12 Emission spectra of 1-Tb in different analytes upon 325 nm excitation.
Analytes were prepared as follows: 5.0 mg powdered 1-Tb was suspended in 20.0 mL DMF and ultrasonicated for 45 min to give suspension. To 1.0 mL such suspension was added 1.0 mL other different solvents, including fresh DMF, H₂O, MeOH, EtOH, MeCN, CH₂Cl₂, CHCl₃, THF, DMSO, EtAc, and 5 drops of NB (nitrobenzene). The emission spectra of each analyte were recorded at 325 nm.