Electronic Supporting Information

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

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S1 - Materials and Instruments

All chemicals except the ligand were purchased and used without further purification. The ligand was synthesized according to the literature.[S1]
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 diffractionmeter 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 diffractionmeter with graphite-monochromated with with Mo Kα radiation (λ = 0.71073 Å) in the ω scan mode. Data reduction was performed using the SAINT program.[S2] The structure was solved by direct methods and refined by full-matrix least-squares methods with *SHELX* program.[S3] 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, H_2O, 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.[S4] Full crystallographic data for **1-Tb** have been deposited with the CCDC 1476203.

References

S1 H. J. Park, D.-W. Lim, W. S. Yang, T.-R. Oh, M. P. Suh, *Chem. Eur. J.*, 2011, **17**, 7251.
S2 Bruker AXS, *SAINT Software Reference Manual*, Madison, WI, 1998.
S3 G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 2008, **64**, 112.
S4 A. L. Spek, *J. Appl. Crystallogr.*, 2003, **36**, 7.

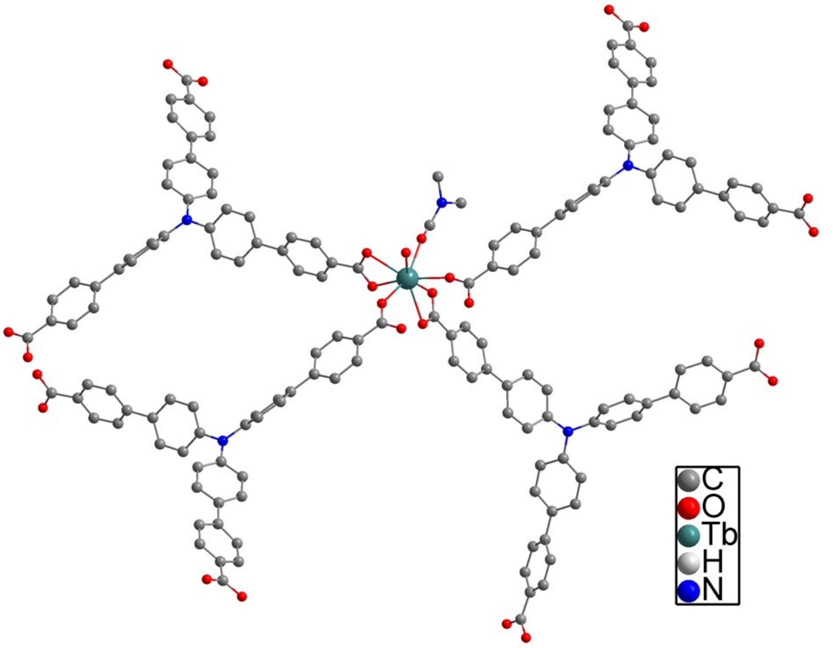


Fig. S1 Coordination environment around Tb^{3+} in **1-Tb**.

S3 - Powder X-ray diffraction

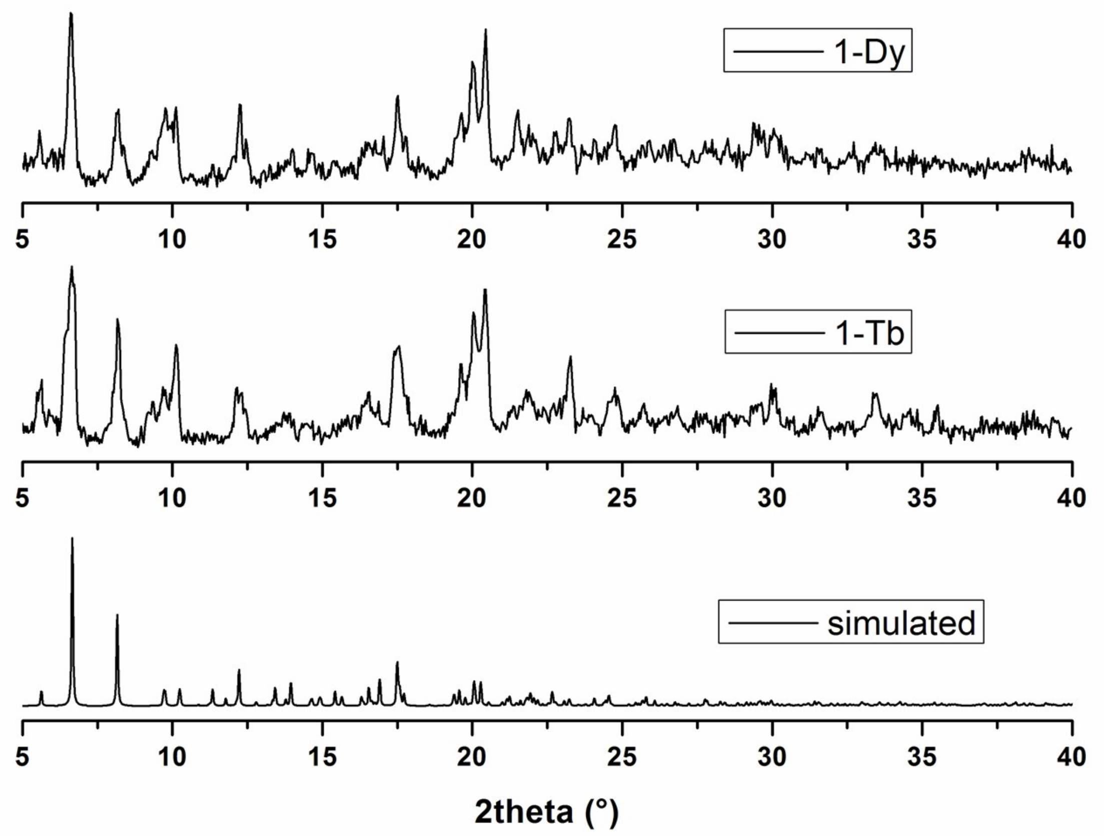


Fig. S2 Simulated and experimental powder X-ray diffraction patterns (PXRD) of 1-Tb and 1-Dy. The patterns are identical, indicating the compounds are isostructual.

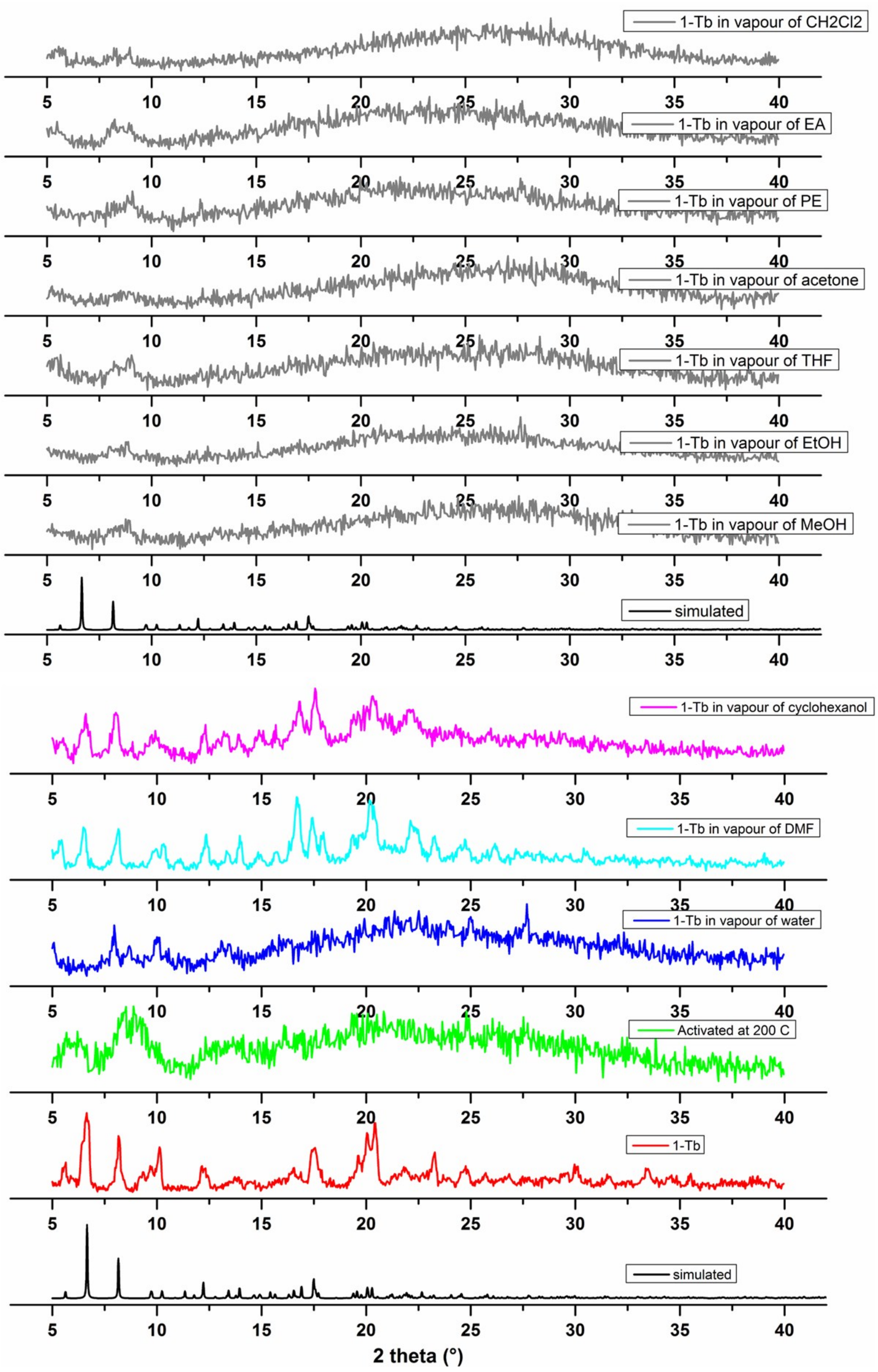


Fig. S3 PXRD patterns of the simulated (black line), as-synthesized 1-Tb (red line), the activated 1-Tb heated at 200 °C for 6 hours (green line), and recovered 1-Tb exposed to vapour of different solvents at 35 °C for 36 hours: water (blue line); DMF (cyan line); cyclohexanol (magenta line); MeOH, EtOH, THF, acetone, PE, EA, CH_2Cl_2 (grey lines).

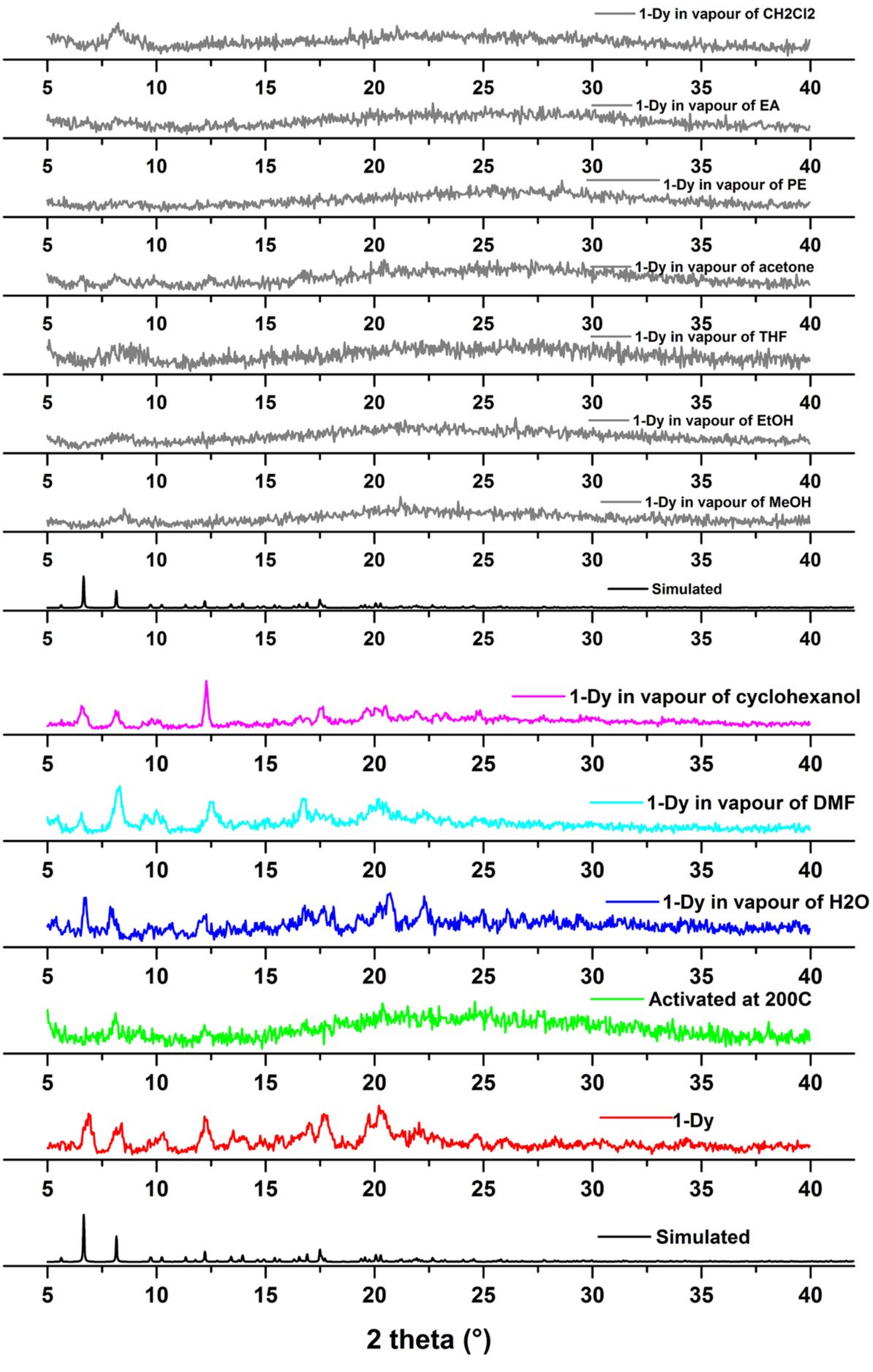


Fig. S4 PXRD patterns of the simulated (black line), as-synthesized 1-Dy (red line), the activated 1-Tb heated at 200 °C for 6 hours (green line), and recovered 1-Tb exposed to vapour of different solvents at 35 °C for 36 hours: water (blue line); DMF (cyan line); cyclohexanol (magenta line); MeOH, EtOH, THF, acetone, PE, EA, CH_2Cl_2 (grey lines).

S4 - Fourier-Transform infrared spectrum

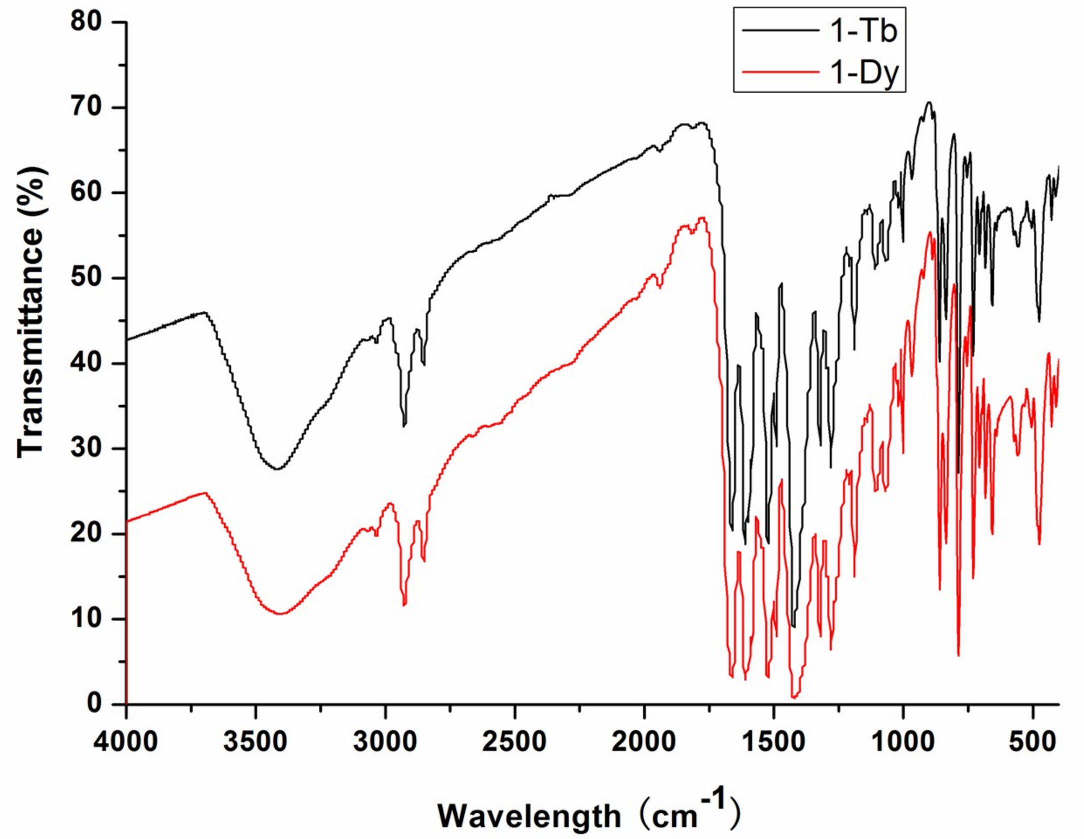


Fig. S5 The FT-IR spectrum of 1-Tb and 1-Dy.

S4 - Simutaneous thermogravimetric analysis and mass spectrum

Simutaneous 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 weitht loss of 30.4% before 320 °C. There is almost no mass loss between 320-560 °C. Upon heating up to 560 °C, it startes to decompose.

Mass spectrum (pink lines) with *m/z* value of 18 (water), 73 (DMF), 100 (cyclohexanol) respectively were simutaneously 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 apprears 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 apprears between ca. 100-300 °C, indicating DMF molecules release at this borad temperature range; For *m/z* value of 100, mass spectrum shows a big peak apprears between ca. 60-300 °C, indicating cyclohexanol molecules release at this broad temperature range.

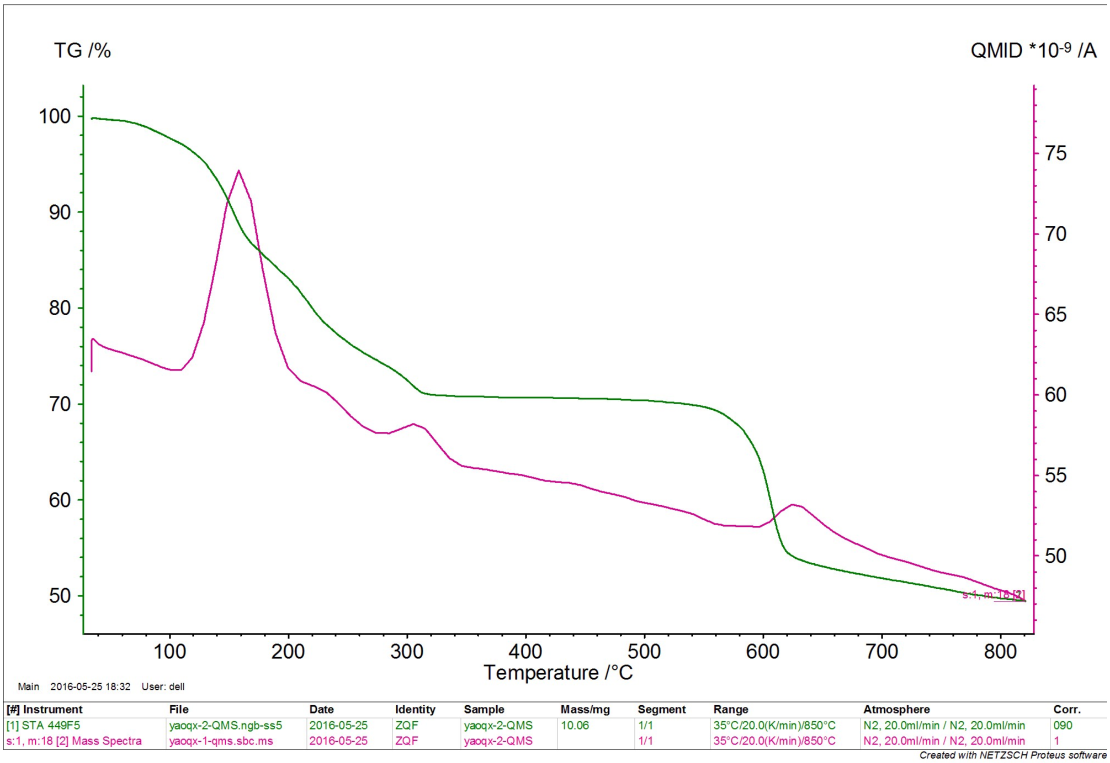


Fig. S6 TGA plot (green line) and Mass spectrum (pink line) with *m/z* value of 18 (water) of 1-Tb.

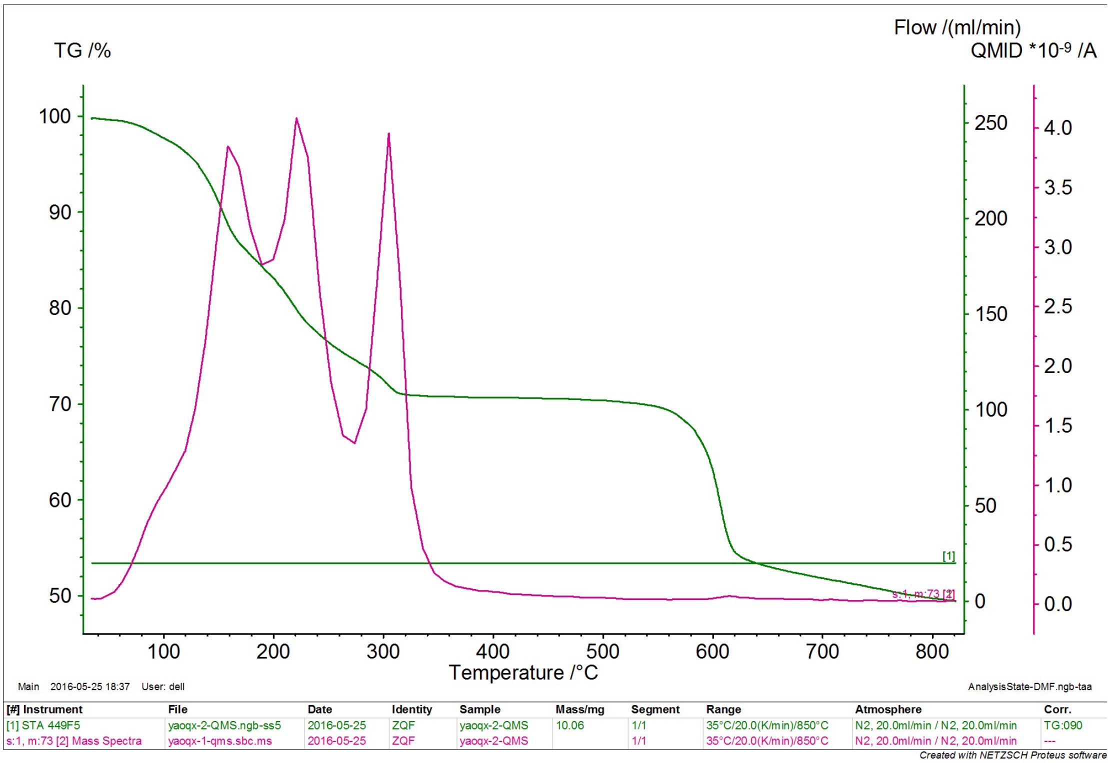
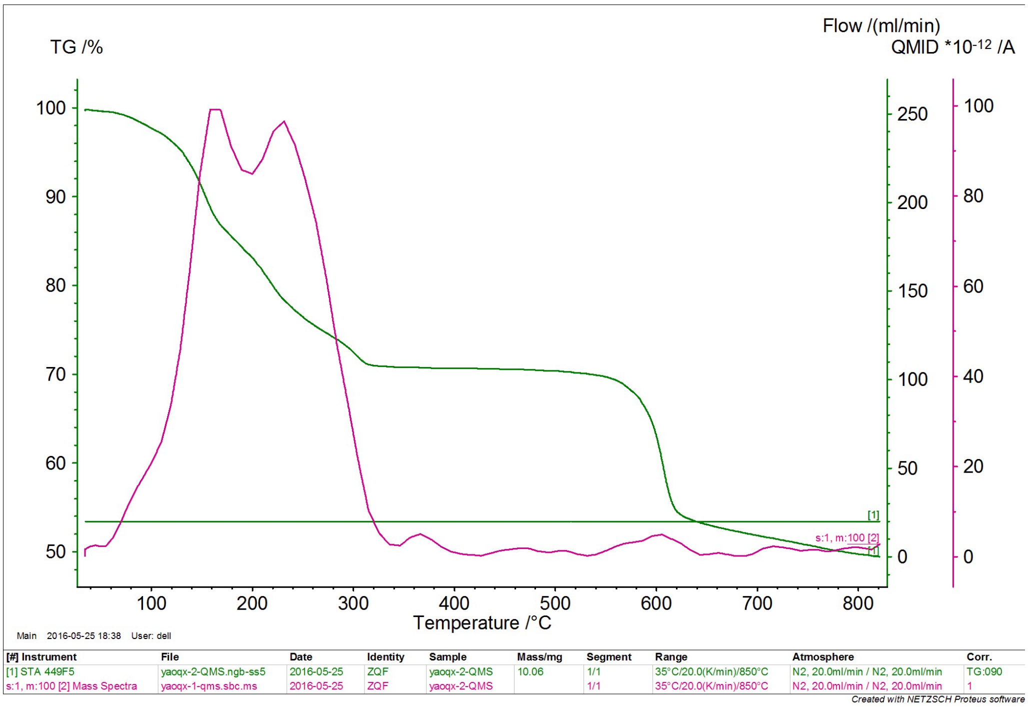


Fig. S7 TGA plot (green line) and Mass spectrum (pink line) with *m/z* value of 73 (DMF) of 1-Tb.



[#] Instrument	File	Date	Identity	Sample	Mass/mg	Segment	Range	Atmosphere	Corr.
[1] STA 449F5	yaoqx-2-QMS.ngb-ss5	2016-05-25	ZQF	yaoqx-2-QMS	10.06	1/1	35°C/20.0(K/min)/850°C	N2, 20.0ml/min / N2, 20.0ml/min	TG:090
s:1, m:100 [2] Mass Spectra	yaoqx-1-qms.sbc.ms	2016-05-25	ZQF	yaoqx-2-QMS		1/1	35°C/20.0(K/min)/850°C	N2, 20.0ml/min / N2, 20.0ml/min	1

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

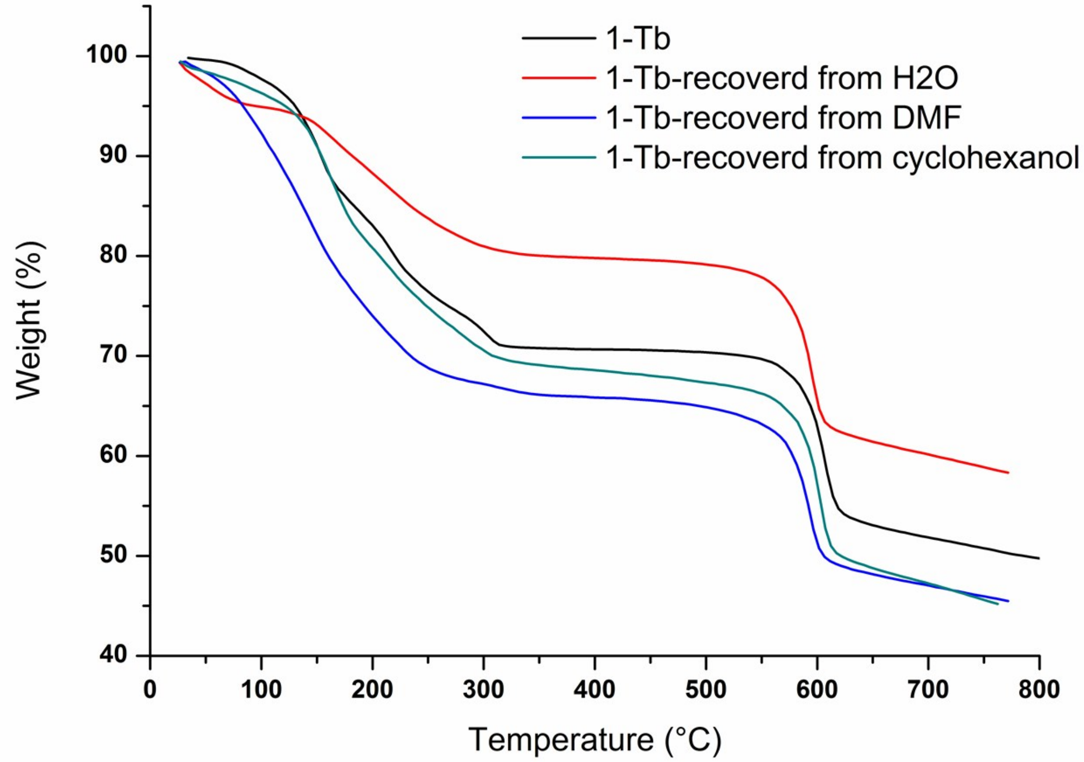


Fig. S9 TGA plots of as-synthesized 1-Tb (black line), and recovered samples exposed in the vapour of H_2O, DMF, cyclohexanol at 35 °C for 36 hours: 1-Tb-recoverd from H_2O (red line); 1-Tb-recoverd from DMF (blue line); 1-Tb-recoverd from cyclohexanol (cyan line). These results indicate that not only 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_2Cl_2, 20 mL × 3 times for 3 days and then activated by heating at 300 °C overnight. The nitrogen adsorption-desorption isotherm was redcorded at 77 K on a Quantachrome Autosorb iQ analyzer.

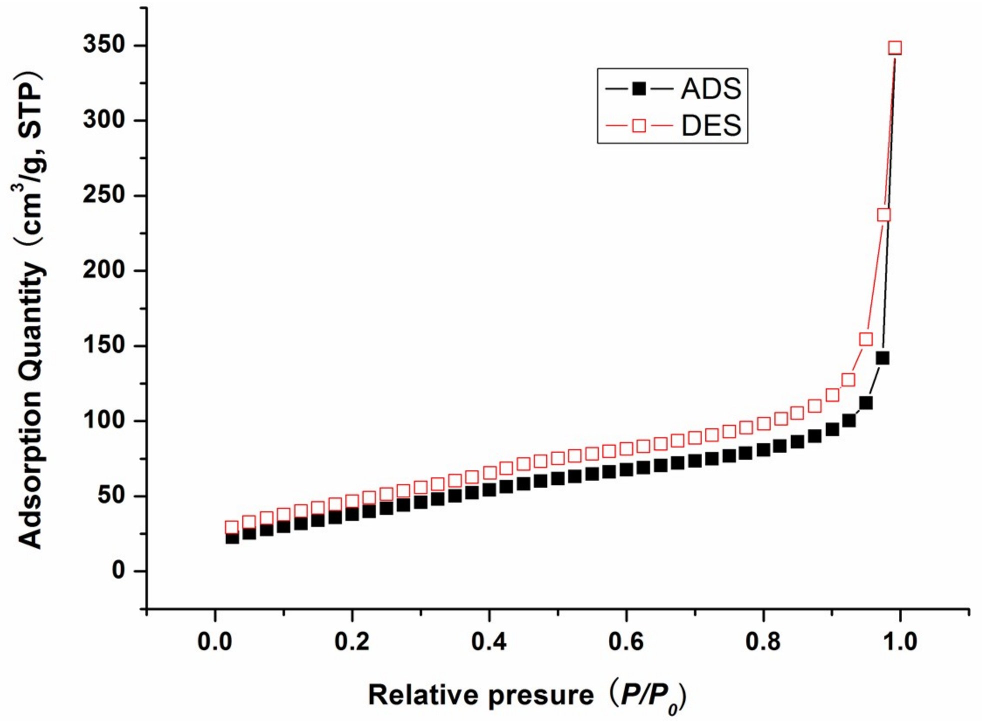


Fig. S10 Nitrogen adsorption-desorption isotherm of **1-Tb** at 77 K.

S6 - Solid-state fluorescence emission

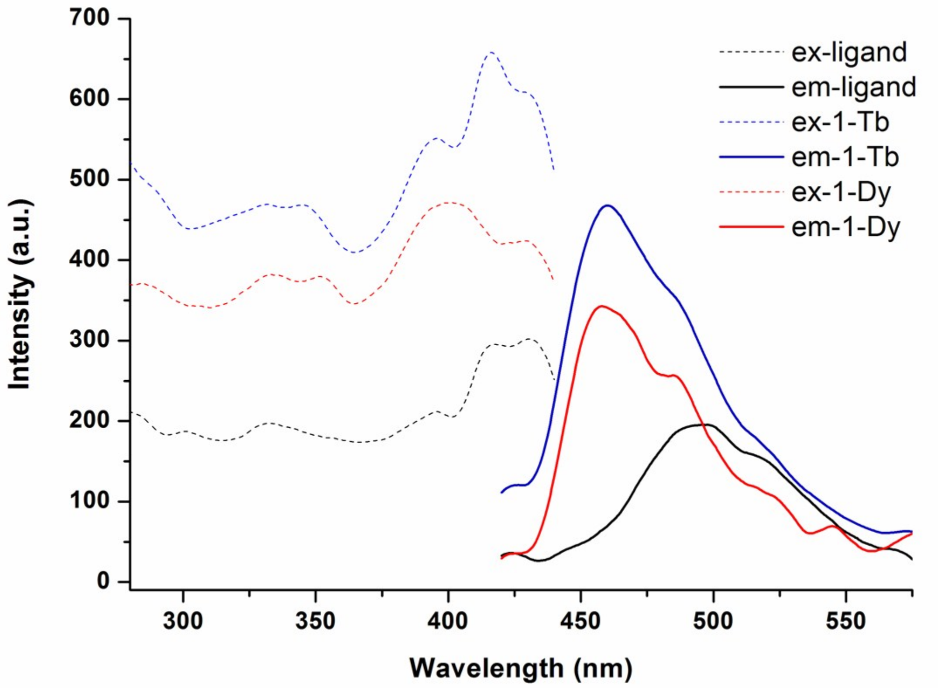


Fig. S11 Solid-state excitation (dotted line) and emission spectra (solid line, excited at 325 nm) of the ligand, **1-Tb,** and **1-Dy** respectively at room temperature.

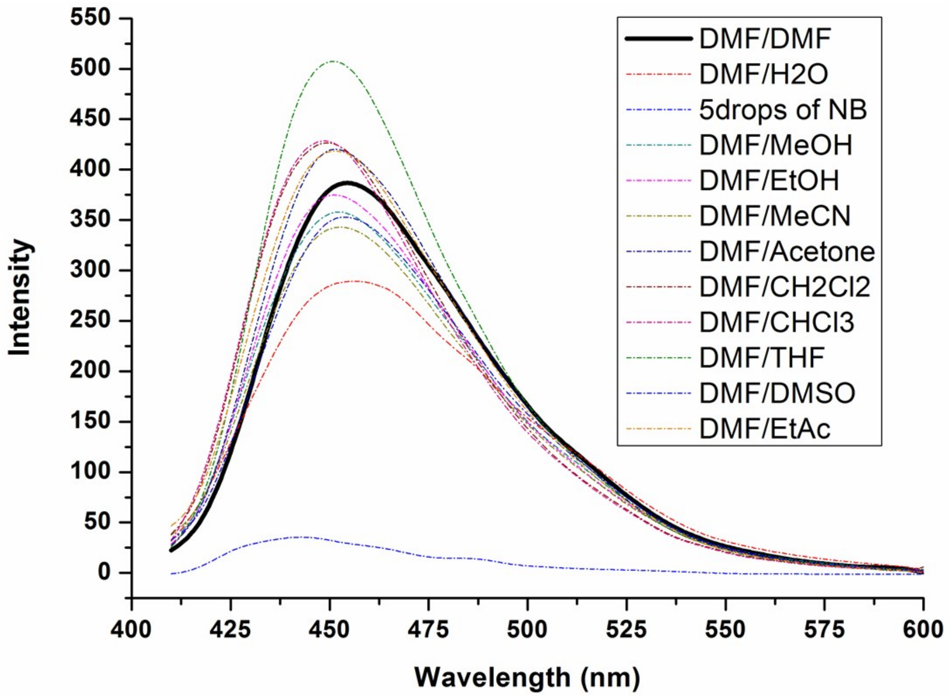


Fig. S12 Emission spectra of **1-Tb** in different analytes upon 325 nm excitation.

Analytes were prepared as follow: 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, H_2O, MeOH, EtOH, MeCN, CH_2Cl_2, $CHCl_3$, THF, DMSO, EtAc, and 5drops of NB (nitrobenzene) . The emission spectra of each analyte were recorded at 325 nm.