Electronic Supplementary Material (ESI) for Dalton Transactions.

Insight into Fluorescence Enhancement of Coordinated Water-containing Lanthanide Metal-Organic Frameworks by Guest Molecules

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In the structure of compound **1a**, the carboxylate C-O bond lengths are in the range of 1.229(8)-1.260(6)Å except for the uncoordinated protonated carboxylate group of the **L** ligand which have a longer (C8-O4: 1.311(10) Å) and a shorter (C8-O3: 1.212(10) Å) bond lengths, further confirming the single bond of C8-O4 and the double bond of C8-O3.

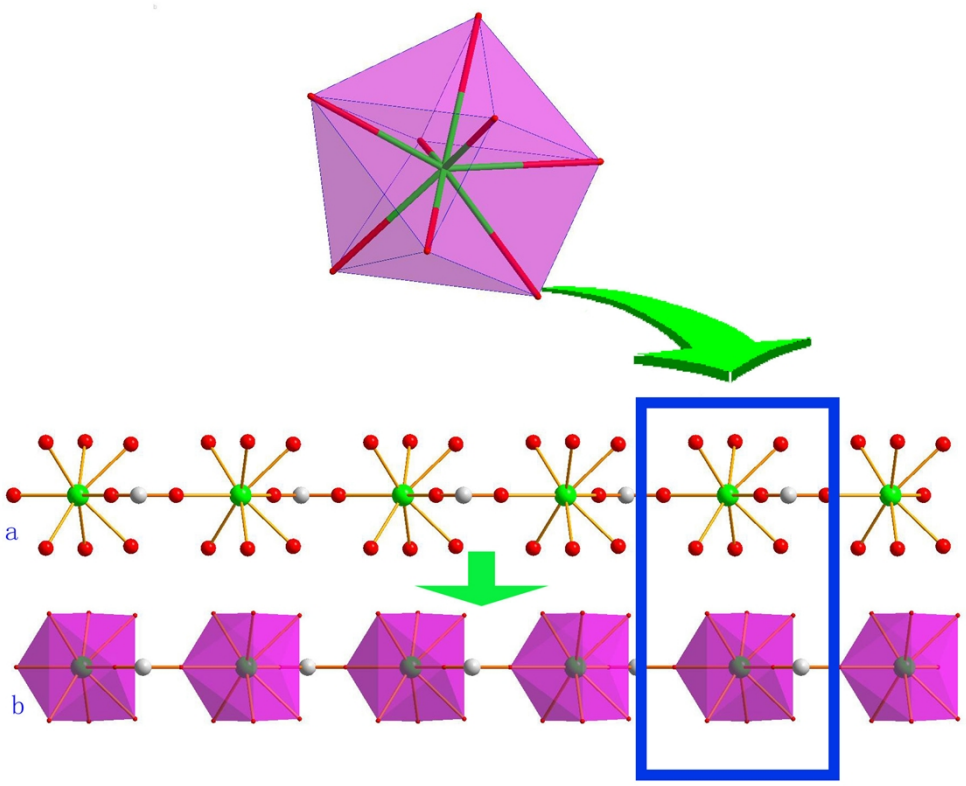

Fig. S1. 1D inorganic hybrid chains of Tb^{3+} in the frameworks of **1a** (viewing from c direction)

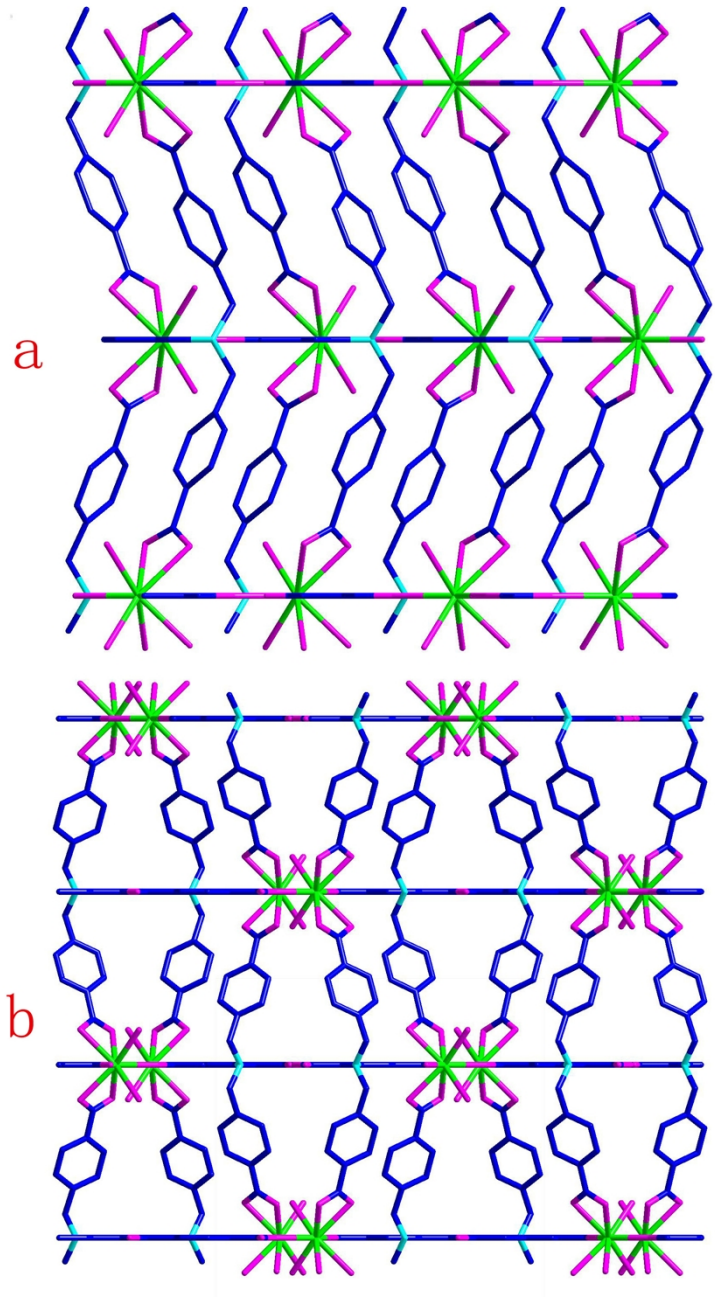

Figure S2. (**a**) Viewing along the *c* direction (**b**) viewing along the *a* direction (after interpenetration) of the 3D framework of **1a**

For the purpose of comparison, the desolvated $[Ln(HL)(H_2O)_2]$ (Ln = Tb **1cn**, Ln = Eu **2cn**) were synthesized. **1cn** and **2cn** were obtained by heating **1c** and **2c** at 160°C in vacuum for 12 hours, respectively. Based on the following powder X-ray diffraction patterns for **1a-1cn** and **2a-2cn**, the structures of **1cn** and **2cn** should be different from those of **1a-d** and **2a-d**. Also, we took much time to try to obtain a satisfactory elemental analysis for **1cn** and **2cn**, unfortunately it was unsuccessful due to **1cn** and **2cn** being very sensitive to moisture.

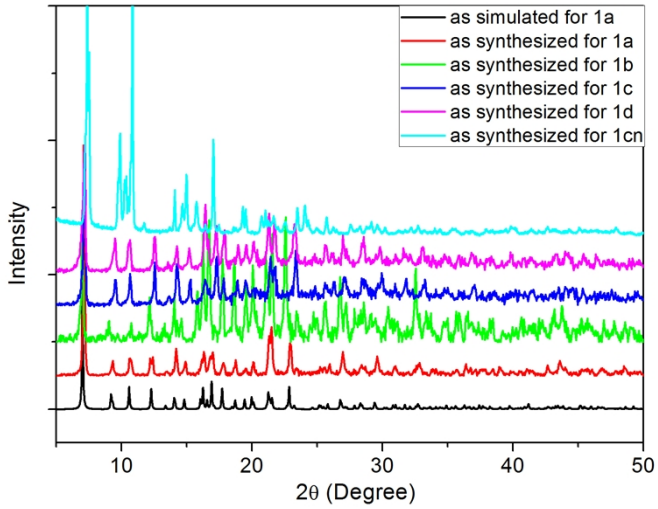

Figure S3A. The powder X-ray diffraction (PXRD) patterns for 1a-1cn

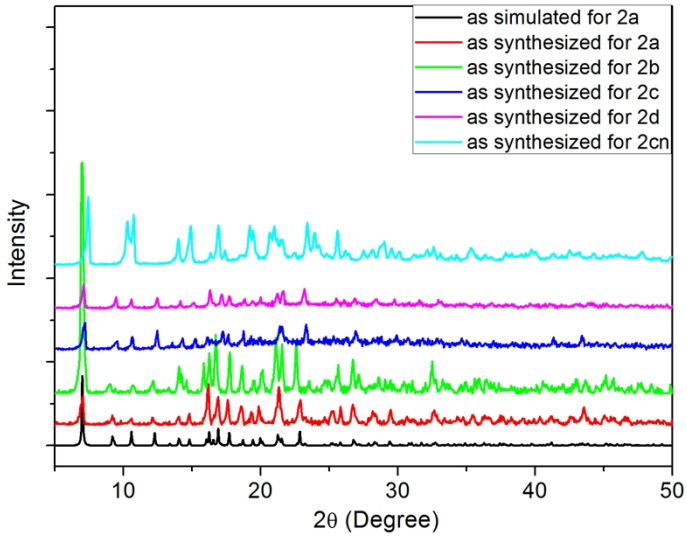

Figure S3B. The powder X-ray diffraction (PXRD) patterns for 2a-2cn

The TGA curves for compounds 1a-1cn and 2a-2cn are shown in figures S4A and S4B. The weight loss for them are: 1a: 27.1% (found: 27.9%), 1b: 28.7% (found: 29.3%), 1c: 23.8% (found: 24.9%), 1d: 24.0% (found: 25.4%), 1cn: 5.6% (found: 5.9%), 2a: 27.0% (found: 27.6%), 2b: 28.9% (found: 29.4%), 2c: 24.1% (found: 24.4%), 2d: 24.2% (found: 25.1%), 2cn: 5.7% (found: 6.1%).

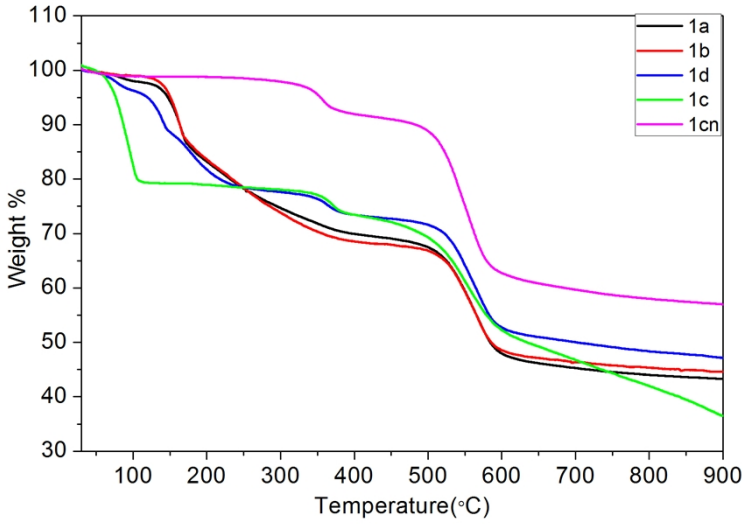

Figure S4A. The TGA curves for 1a-1cn

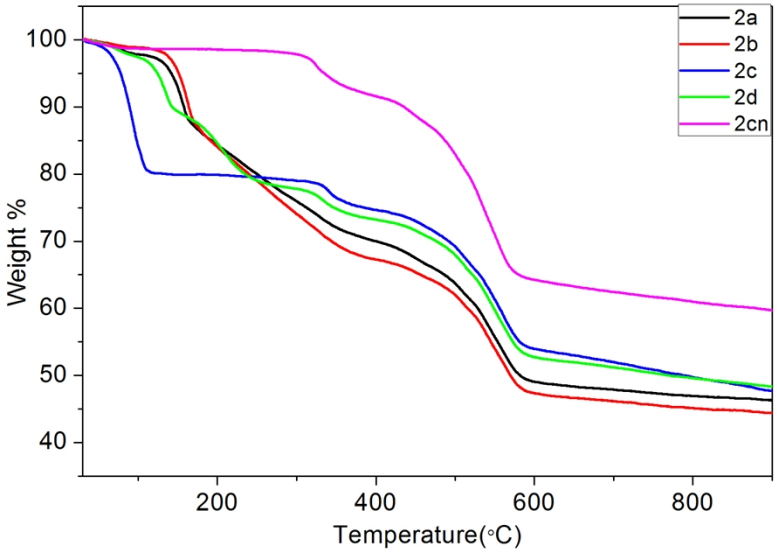

Figure S4B. The TGA curves for 2a-2cn

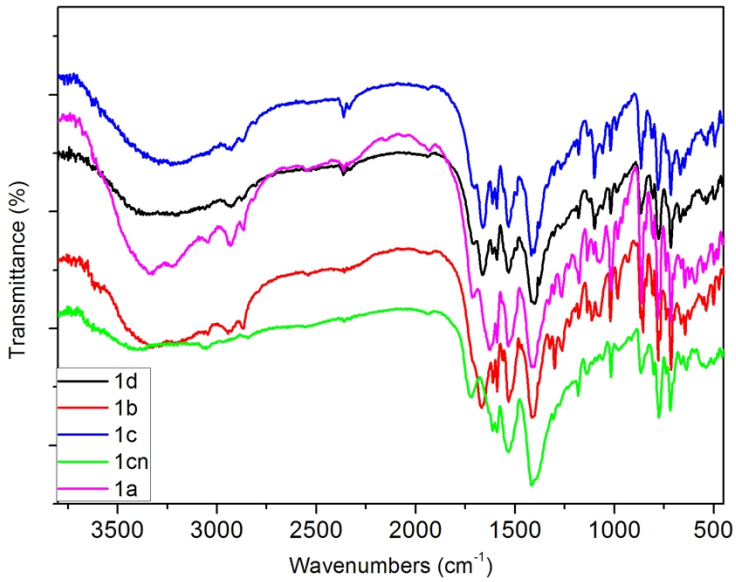

Figure S5. The IR spectra for 1a-1cn

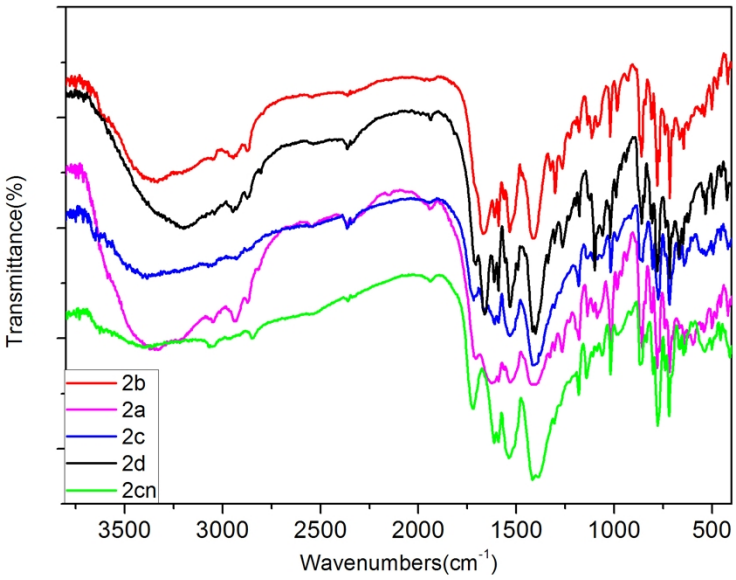

Figure S6. The IR spectra for 2a-2cn

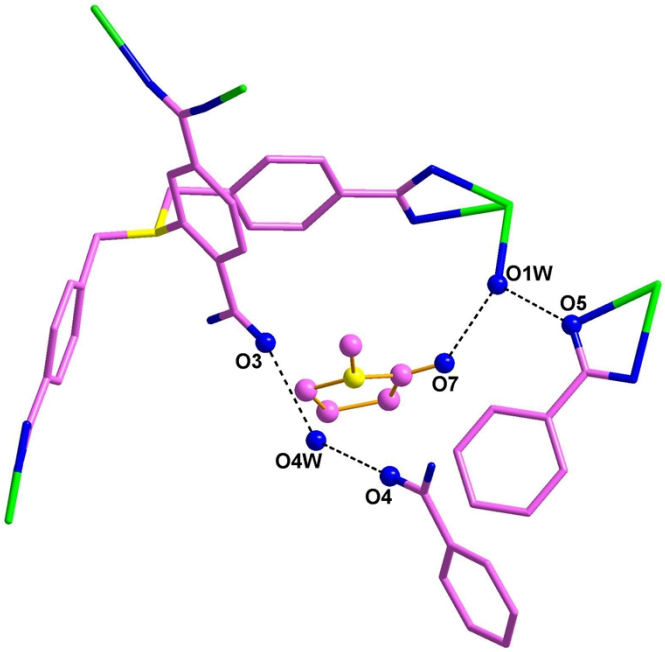

Figure S7. The hydrogen bonds in 1b (all the hydrogen atoms were delete for clearly clarification**)**

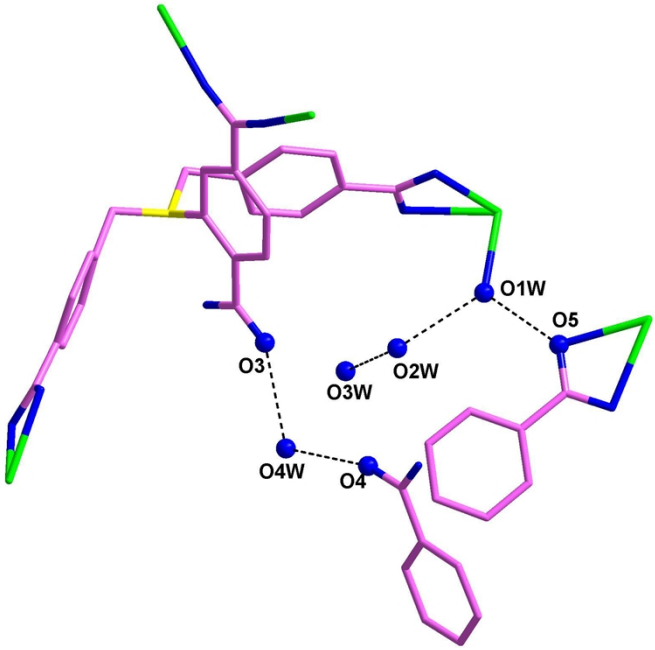

Figure S8. The hydrogen bonds in 1c (all the hydrogen atoms were delete for clearly clarification**)**

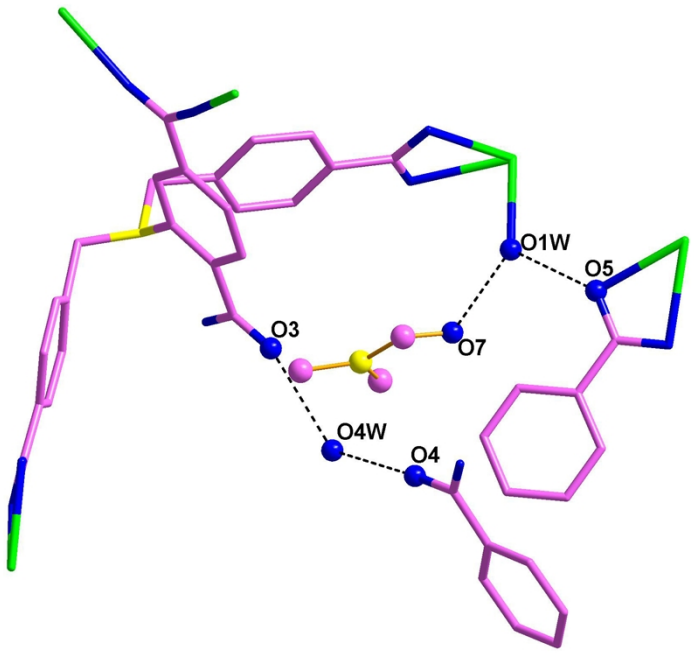

Figure S9. The hydrogen bonds in 1d (all the hydrogen atoms were delete for clearly clarification**)**

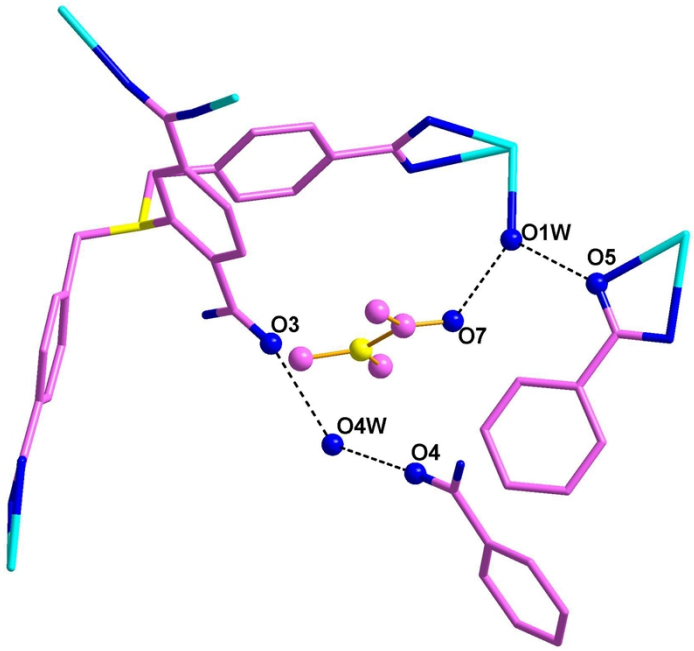

Figure S10. The hydrogen bonds in 2a (all the hydrogen atoms were delete for clearly clarification**)**

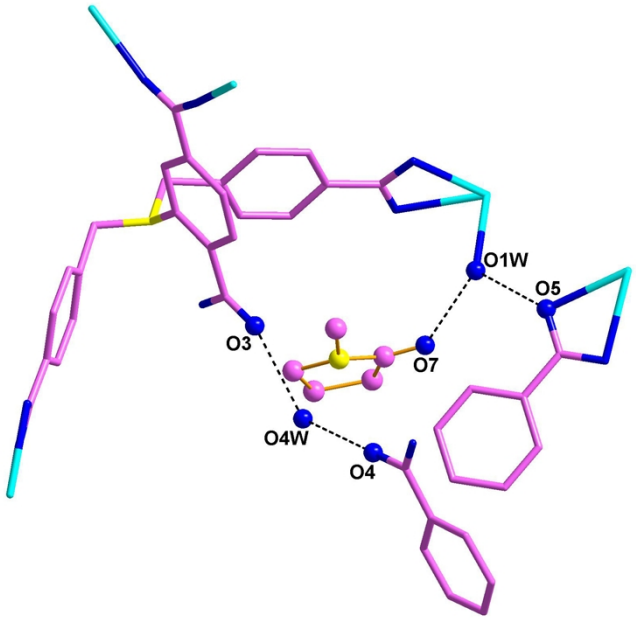

Figure S11. The hydrogen bonds in 2b (all the hydrogen atoms were delete for clearly clarification**)**

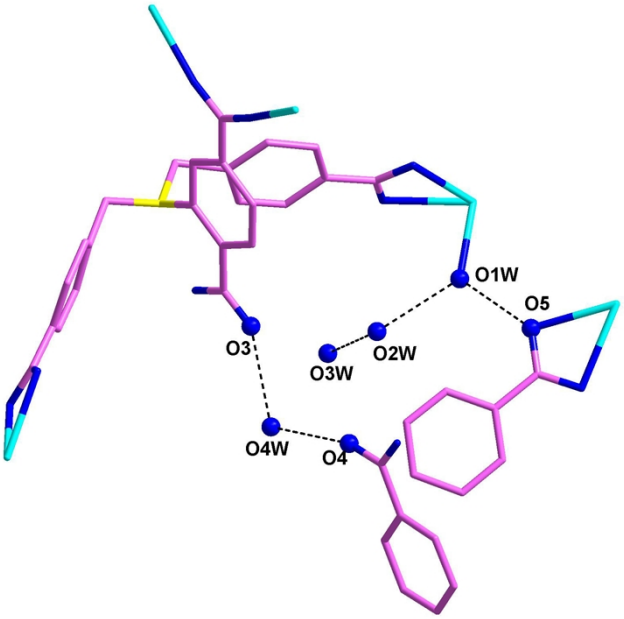

Figure S12. The hydrogen bonds in 2c (all the hydrogen atoms were delete for clearly clarification**)**

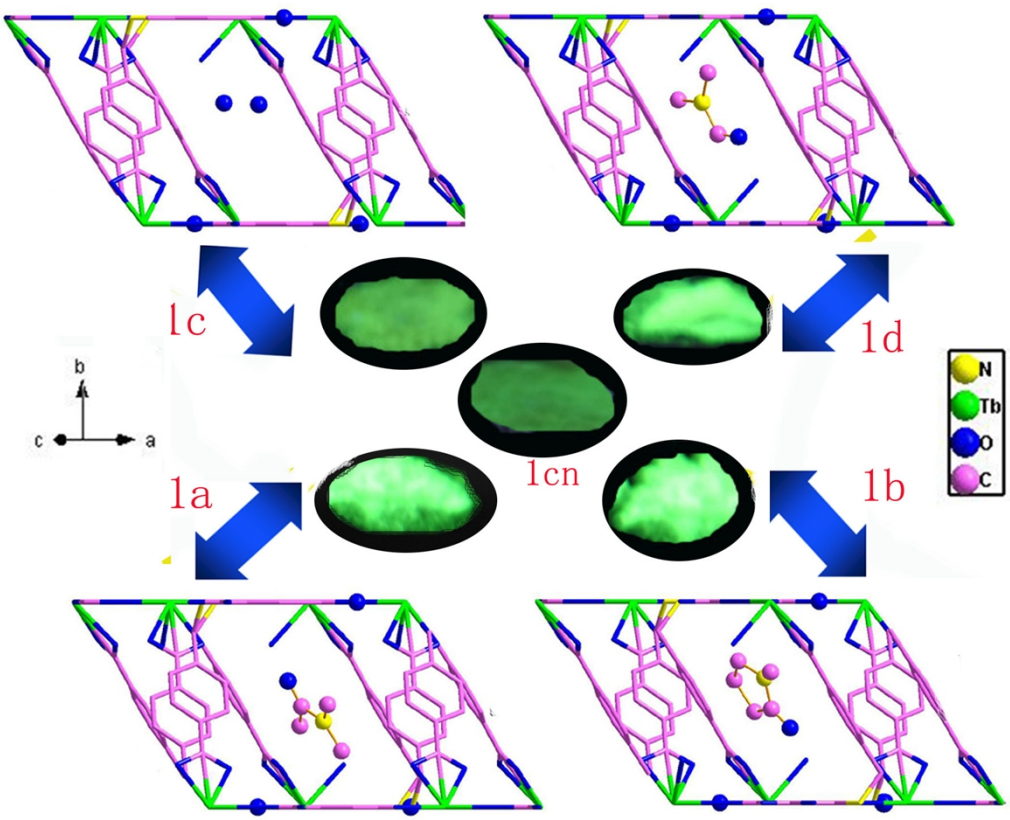

Fig. S13. The frameworks and luminescence photos of **1a-1d**: guest molecules (DMA, NMP, H_2O and DMF) are filling in the frameworks (viewing from [101] direction).

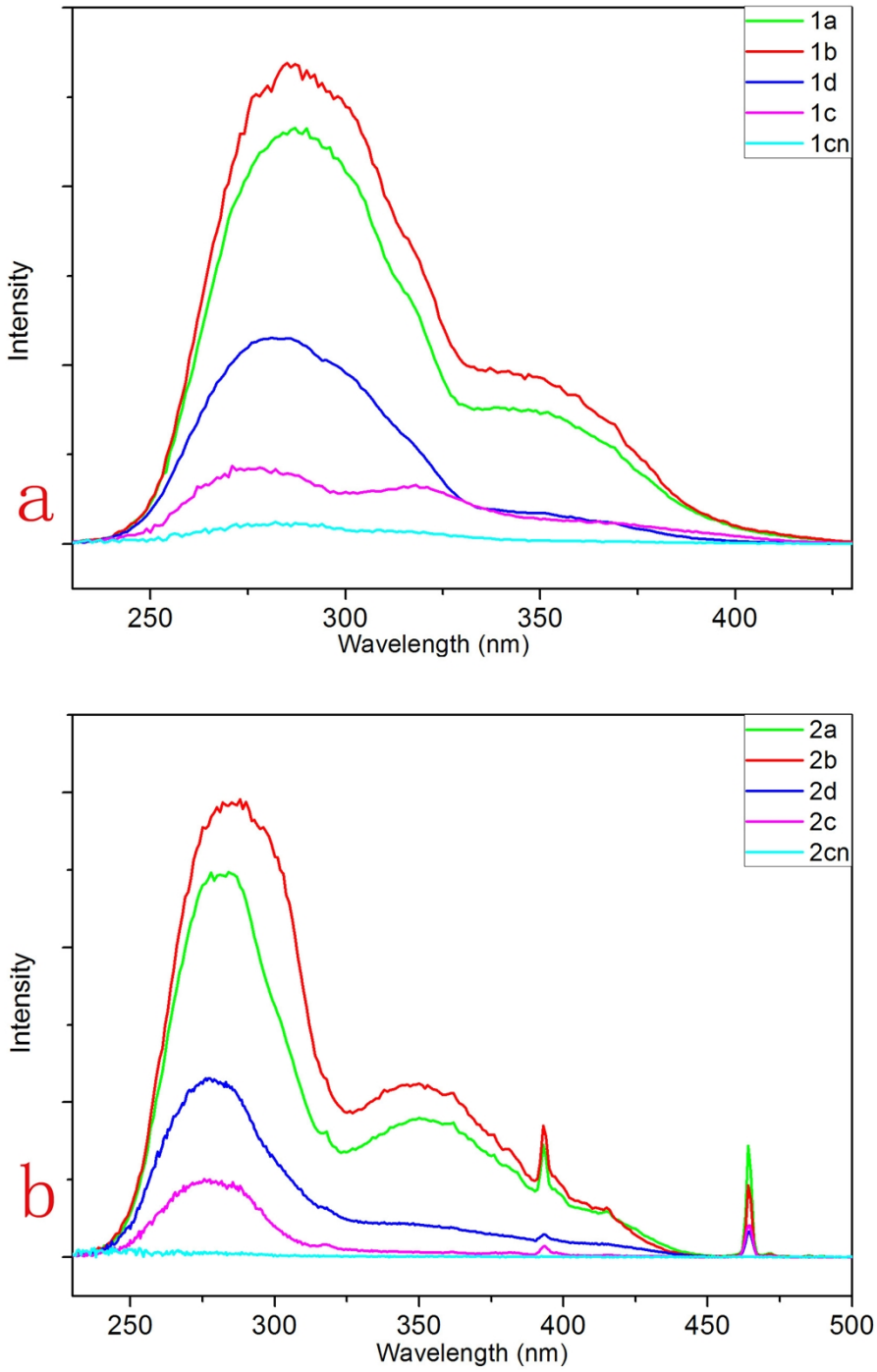

Figure S14. Room-temperature excitation spectras of 1a-1cn and 2a-2cn in the solid state

Table S1. Hydrogen bonds strength data for all of the compounds

sample	1a	1b	1c	1d	2a	2b	2c
O1W H1WB O5	2.842(5)	2.838(11)	2.815(10)	2.800(9)	2.834(4)	2.832(11)	2.829(9)
O4W H4WB O3	2.83(2)	2.764(4)	3.04(4)	2.77(5)	2.804(17)	2.81(4)	3.00(3)
O4W H4WA O4	2.954(19)	2.915(5)	3.37(4)	3.04(5)	2.905(18)	2.90(4)	3.42(4)
O1W H1WA O7	---	2.678(17)	---	2.59(5)	---	2.644(17)	---
O1W H7B O7A	2.610(8)	---	---	---	2.614(7)	---	---
O1W H7B O7B	2.760(2)	---	---	---	2.767(16)	---	---
O2W H2WA O3W	---	---	2.620(3)	---	---	---	2.62(2)
O2W H2WB O1W	---	---	2.770(2)	---	---	---	2.761(16)

The luminescence quantum yield for **1cn** and **2cn** were also measured, as shown in Table S2. As expected, the luminescence of desolvated **1cn** is very weak, and its luminescence quantum yield is only 1.8%. This can be ascribed to the vibration quenching of the coordinated water to the luminescent Tb^{3+} ions, because the high-energy vibrations associated with the hydroxyl groups of water can couple with the excited electronic states of the lanthanide ions. It should be noted, however, that the luminescence intensity of **1c**, which corresponds to **1cn** with guest solvent H_2O molecules, increases. The unusual phenomenon can be understood by the hydrogen bond existing between the frameworks and the guest water molecules (Figure **S8**), because the strong interaction between the OH groups and the guest water molecules by hydrogen bond suppresses the quenching effect of the OH group on the luminescence of lanthanide. Compared to compound **1cn**, the luminescence of desolvated compound **2cn** is too weak to be detected.

Table S2. Comparison of quantum yields and lifetimes of **1cn** and **2cn** with **1a-1d** and **2a-2d**

	Φ_{QY}(%) ±1%	τ (ms)
1a	42.6	0.644
1b	56.5	0.621
1c	13.9	0.528
1d	23.9	0.568
1cn	1.8	0.561
2a	12.5	0.314
2b	15.7	0.315
2c	3.1	0.286
2d	8.7	0.309
2cn	ND*	0.279

*ND means can't be detected