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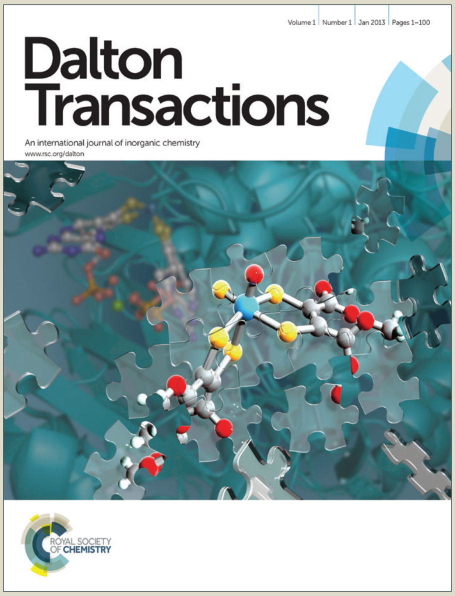

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Insight into Luminescence Enhancement of Coordinated Water-containing Lanthanide Metal-Organic Frameworks by Guest Molecules

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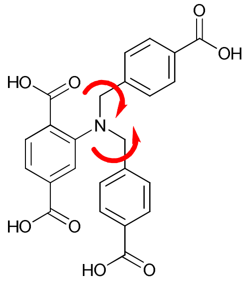
A series of isostructural lanthanide three-dimensional compounds $[Ln(HL)(H_2O)_2]\cdot$guest (Ln = Tb or Eu, H_4L = 2-(N,N-bis(4-methylbenzoic acid)amino)benzoic-1,4-dioic acid, guest = NMP, DMA, DMF or H_2O) were assembled and characterized. Their luminescence intensities and quantum yields increase in the order of the guest molecules: NMP > DMA > DMF > H_2O (NMP = N-methyl-2-pyrrolidone, DMA = N,N-Dimethylacetamide, DMF = N,N-Dimethylformamide). The investigation reveals that the hydrogen-bond formed between the metal-organic frameworks should be responsible for the luminescence enhancement of the compounds.

Introduction

The luminescent Metal-Organic Frameworks (MOFs) with light-emitting building blocks have already proved to be potential new type of solid-luminescent materials for chemical sensing, light-emitting devices (LEDs).[1] The unique luminescent properties with desirable intensities make them most promising candidate materials for application in viable sensing devices.[2] Among the plethora of luminescent ions, lanthanides ions are good candidates for luminescent materials for their long lifetimes and high chromaticities. Great research efforts have been paid on lantanides MOFs during the past few years.

Generally, the luminescence intensity of coordination compound is related to coordinated metal, ligand and temperature, etc. As a special ligand, water is easy to coordinate to lanthanide metal ions. However, it is well known that the luminescence intensity or quantum yield is severely diminished when water is close or coordinates to luminescent metal centers due to the high energy vibrations of O-H bond.[1e,3] To enhance the luminescent intensity or quantum yield of luminescent compounds, an effective way reported by Lehn's and other groups is to employ multidentate ligand such as cryptate to coordinate lanthanide metal center to prevent the coordination of water.[4] For MOFs, a common method to increase their luminescent intensities is to remove or replace the water molecules coordinated to metal centers or located within the voids of a MOF[1g,5]. More recently, it has been reported that the luminescent intensities of some coordinated water-containing MOFs can be enhanced considerably by the guest molecules.[1g,6] Their mechanisms are still unclear, since the structures of the MOFs after exchange of guest molecules are often difficult to be determined. Usually they tend to be very low crystalline and even amorphous phases.[7] A common explanation is that the enhancement of the luminescence is largely due to the interaction between the guest molecules and the coordination ligand. Herein, we report a series of new isostructural coordinated water-containing lanthanide compounds with different guest molecules. Eight isostructural lanthanide compounds formulated as $[Ln(HL)(H_2O)_2]\cdot$guest (Ln = Tb, guest = 2DMA+0.5H_2O **1a**; Ln = Tb, guest = 2NMP+0.5H_2O **1b**; Ln = Tb, guest = 4.5H_2O **1c**; Ln = Tb, guest = 2DMF+0.5H_2O **1d**; Ln = Eu, guest = 2DMA+0.5H_2O **2a**; Ln = Eu, guest = 2NMP+0.5H_2O **2b**; Ln = Eu, guest = 4.5H_2O **2c**; Ln = Eu, guest = 2DMF+0.5H_2O **2d**; DMF = N,N-Dimethylformamide, DMA = N,N-Dimethylacetamide, NMP = N-methyl-2-pyrrolidone) were synthesized using a semirigid ligand, 2-(N,N-bis(4-methylbenzoic acid)amino)benzoic-1,4-dioic acid (**H_4L**). The structure of the ligand is shown in Scheme **1**. It can be seen that the -$N(CH_2\text{-})_2$ linker in **H_4L** can bend and rotate freely when such ligand coordinates to metal centers. They display different luminescence intensities and quantum yields. Moreover, the luminescence properties of the compounds can be reversibly modified by exchange of guest molecule.



Scheme 1. Schematic diagram structures of H_4L.

Experimental section

Materials and characterizations. All reagents and solvents were used as received from commercial suppliers without further purification. The infrared spectra of KBr pellets were recorded in the range of 4000-450 cm^{-1} on a Perkin-Elmer Spectrum One FT-IR spectrometer. Elemental analyses (C, H, and N) were performed with a Vario MICRO CHNOS elemental analyzer. Powder X-ray diffraction (PXRD) data were collected on a Rigaku MiniFlex diffractometer with Cu Kα radiation (λ=1.5406 Å). The solid-state luminescence emission and excitation spectra and liftimes were recorded on FLS920 or FLS980 luminescence spectrophotometer.

Preparation. The ligand 2-(N,N-bis(4-methylbenzoic acid)amino)benzoic-1,4-dioic acid (**H_4L**) was synthesized according to the method described in the literature.[8]

Synthesis of [Tb(HL)(H_2O)$_2$]·2(DMA)·0.5(H_2O) (1a). **H_4L** (0.09 g, 0.2 mmol) was dissolved in a mixture of DMA (4.5 ml) and H_2O (0.5 ml). Then Tb(NO_3)$_3$·6H_2O [0.2 ml, 0.2 mmol, (1.0 M in water)] was added. After that, the solution was sealed in a 20 mL glass vial and heated at 90 °C for 2 days. The reaction system was cooled slowly to room temperature. After filtration and washing with DMA, colorless needle crystals suitable for X-ray structural analysis were collected. **Yield:** ca. 70.3% (based on Tb(NO_3)$_3$). **Anal.** Calcd for $C_{32}H_{35}N_3O_{12.5}$Tb: C, 46.84; H, 4.30; N, 5.12. **Found:** C, 46.78; H, 4.47; N, 5.05.

Synthesis of [Tb(HL)(H_2O)$_2$]·2(NMP)·0.5(H_2O) (1b). Method A: Compound **1b** can be obtained by the same synthetic procedure as that for **1a** except using NMP instead of DMA. Colorless needle crystals were collected. **Method B:** Compound **1b** can also be obtained by heating **1a** in 10 mL NMP at 90 °C for 2 days. **Yield:** ca. 46.8% (based on Tb(NO_3)$_3$). **Anal.** Calcd for $C_{34}H_{39}N_3O_{12.5}$Tb: C, 48.12; H, 4.63; N, 4.95. **Found:** C, 48.04; H, 4.78; N, 4.88.

Synthesis of [Tb(HL)(H_2O)$_2$]·4.5(H_2O) (1c). Compound **1c** can be obtained by heating **1a** or **1b** in 10 mL H_2O at 90 °C for 2 days. **Anal.** Calcd for $C_{24}H_{28}NO_{14.5}$Tb: C, 39.96; H, 3.91; N, 1.94. **Found:** C, 36.74; H, 4.69; N, 1.88.

Synthesis of [Tb(HL)(H_2O)$_2$]·2(DMF)·0.5(H_2O) (1d). Compound **1d** can be obtained by heating **1a** or **1b** in 10 mL DMF at 90 °C for 2 days. **Anal.** Calcd for $C_{30}H_{35}N_3O_{12.5}$Tb: C, 45.24; H, 4.43; N, 5.28. **Found:** C, 45.08; H, 4.61; N, 5.19.

Synthesis of [Eu(HL)(H_2O)$_2$]·2(DMA)·0.5(H_2O) (2a), [Eu(HL)(H_2O)$_2$]·2(NMP)·0.5(H_2O) (2b)), [Eu(HL)(H_2O)$_2$]·4.5(H_2O) (2c)) and [Eu(HL)(H_2O)$_2$]·2(DMF)·0.5(H_2O) (2d)). Compound **2a-2d** can also be obtained by the same synthetic procedure as that for **1a-1d** respectively except using Eu(NO_3)$_3$·6H_2O instead of Tb(NO_3)$_3$·6H_2O. **Yield for 2a:** ca. 71.9%; **Yield for 2b:** ca. 44.6% (based on Tb(NO_3)$_3$). **Anal. Calcd for 2a $C_{32}H_{35}N_3O_{12.5}$Eu:** C, 47.24; H, 4.34; N, 5.16. **Found:** C, 47.15; H, 4.52; N, 5.15; **Anal. Calcd for 2b $C_{34}H_{39}N_3O_{12.5}$Eu:** C, 48.52; H, 4.67; N, 4.99. **Found:** C, 48.38; H, 4.54; N, 4.85; **Anal. Calcd for 2c $C_{24}H_{28}NO_{14.5}$Eu:** C, 40.35; H, 3.95; N, 1.96. **Found:** C, 36.81; H, 4.68; N, 1.82; **Anal. Calcd for 2d $C_{30}H_{35}N_3O_{12.5}$Eu:** C, 45.63; H, 4.67; N, 5.32. **Found:** C, 45.42; H, 4.75; N, 5.21. It should be noted that the elemental analysis difference for **1c** or **2c** between the found and calculated data are attributed to absorb moisture in the air. It can be calculated from the elemental analysis difference that 4 water molecules per chemical formula have been absorbed for both 1c and 2c, being consistent with the TGA results.

X-ray crystallography. Data collection was performed on Rigaku 724HG CCD diffractometer with graphite-monochromated Mo Kα (λ = 0.71073 Å) radiation at room temperature. The collected data were reduced using the program CrystalClear (Rigaku and MSC, 1999) and an empirical absorption correction (multiscan) was applied. The structures were solved by direct methods and refined by the full-matrix least squares on F^2 using the SHELXTL-97 program.[9] All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms attached to carbon atoms were placed in geometrically idealized positions and included as riding atoms (C-H bond fixed at 0.97 Å). Crystallographic and refinement details are summarized in Table **1**. Selected hydrogen-bond lengths for **1a-1d** and **2a-2c** are listed in Table **S1** of the Supporting Information.

(Here is Table 1)

Results and Discussion

Fortunately, the crystals suitable for X-ray single-crystal structure determination of complexes **1a**-**1d** and **2a**-**2c** have been obtained. The crystal structure determination of the compounds provides an important opportunity for more in-depth understanding of the relationship between the luminescent properties and the structures of the MOFs. Since the structures of these compounds are isostructural, only the structure of **1a** is described here. Compound **1a** shows a 3D framework which crystalizes in orthorhombic space group *Pnma*. Every building block is composed of one terbium ion, one **L** ligand, two coordinated water molecules, two free DMA and a half of free water molecules. As shown in Figure **1**, the terbium ion is eight-coordinated to six oxygen atoms of the carboxyl groups from the L ligands and two oxygen atoms of two water molecules. Notably, there exists one free carboxyl group in the L ligand; that is, O3 and O4 do not coordinate any terbium ion. The Tb^{3+} ions are linked through the bridging carboxyl groups of the **L** ligand to construct one-demensional chains (**Figure S1**). Furthermore, the chains link to each other by the flexible **L** ligand to construct a 3D porous frameworks (**Figures 2** and **S2**).

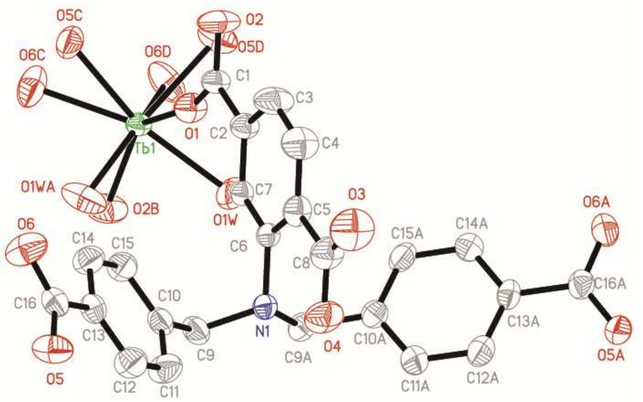


Figure 1. Coordination environment of the Tb^{3+} ion in compound **1a**, all hydrogen atoms are omitted for clarity. Symmetry codes: a: x, 0.5-y, z. b: x, -0.5-y, z. c: 0.5-x, -y, 0.5+z. d: -x, -0.5+y, 2-z. e: 0.5-x, -0.5+y, 0.5+z. f : x, 0.5-y, 0.5+z.

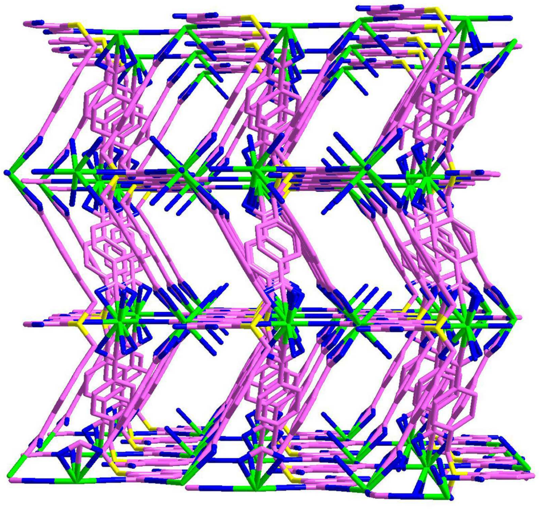


Figure 2. The 3D framework of **1a**.

It is worth noting that the O-H···O distances between the free solvent molecule and the coordinated water molecule or the carboxylate group of the L ligand are 2.59(5)-3.42(4) Å, suggesting the existence of the hydrogen bonds (Figures **3**, **S7-S12** and Table **S1**).

The total solvent-accessible volume of the framework is estimated to be 34.1% according to the PLATON [10] calculation. The high porosity and considerable stability together with the open framework unveil these samples as good candidates for luminescent sensing study. By carefully immersing **1a** in NMP, H_2O and DMF at 90 °C, **1b**, **1c** and **1d** were obtained respectively. Most interestingly, complexes **1a**-**1d** can be converted reversibly by immersing them into the corresponding solvent of DMA, NMP, H_2O or DMF. This makes it possible to reversibly modify the luminescence of the compounds by exchange of guest molecule. Compounds **2a**-**2d** show the similar features to the Tb^{3+} compounds. Moreover, from the crystal structures it can be found that a part of the free water molecules in these compounds are still retained in the frameworks after the guest-exchange process. This may result from the existence of the hydrogen bond between the free carboxyl group in the L ligand (O3, O4) and the part of the free water molecules. Besides water molecules, it can be found from the structures of the compounds (**Figures 3**, **S7, S9-S11**) that there also exists the hydrogen bond between the frameworks and the other guest solvent molecules. This is supported by the fact that the guest molecules of compound **1a** could not be replaced by CH_2Cl_2 and cyclohexane which can't form hydrogen bond with the framework of the MOF compounds, even if compound **1a** was soaked in CH_2Cl_2 or cyclohexane for 7 days.

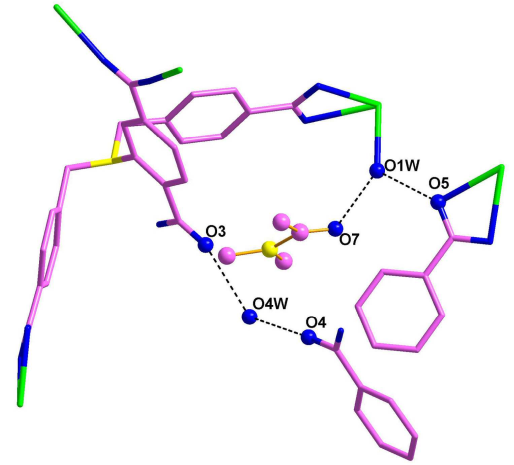


Figure 3. The hydrogen bond in **1a** (the DMA molecules are disordered in the framework, to better understand the structures, we place them in the same position).

The luminescence properties including quantum yields (Φ_{QY}) of **1a-2d** and **2a-2d** were investigated in the solid state at room temperature. The emission spectra are shown in Figures **4**. The luminescence quantum yields (Φ_{QY}) were measured, and the data are listed in Table **2**. As shown in Figure **4**, the emission spectra of the Tb^{3+} compounds exhibit typical emission pattern characteristic of the f-f transitions of isolated Tb^{3+} ions in the visible region. The emission bands can be attributed to the transitions of $^5D_4\rightarrow{}^7F_n$ (n = 6, 5, 4 and 3). They are at 488($^5D_4\rightarrow{}^7F_6$), 543($^5D_4\rightarrow{}^7F_5$), 583($^5D_4\rightarrow{}^7F_4$), and 623 nm ($^5D_4\rightarrow{}^7F_3$) respectively. The most striking green luminescence at 543 nm corresponds to the $^5D_4\rightarrow{}^7F_5$ electronic transition. The luminescence intensities and Φ_{QY} of the Tb^{3+} compounds increase in the order: **1b** (NMP) > **1a** (DMA) > **1d** (DMF) > **1c** (H_2O) (Figures **5** and Table **2**). Obviously, one important factor for the luminescence enhancement should be the hydrogen bond forming between the frameworks and the guest solvent molecules. Of course, the hydrogen bond strength should largely deepened on the relative hydrogen bond acceptor strengths of the guest solvents. Another influence factor may be the molecular rigidity of the guest solvents. Generally, the more rigid a guest solvent molecule is, the higher the luminescence quantum yield of the compound is. This is because the non-radiative processes related to molecular thermal vibrations and rotations are less efficient in more rigid guest molecules. Therefore, the luminescence enhancement order may result from the cooperation of the hydrogen bond between the frameworks and the guest molecules and the rigidity of the guest molecules. To further understand the luminescence properties, temperature dependent luminescence of **1b** was measured from 298 to 100 K. As shown in figure **6**, the intensity of **1b** is enhanced gradually with the decrease of temperature from 280 to 100 K. This can be attributed to the weaker vibration of guest molecules at lower temperature.

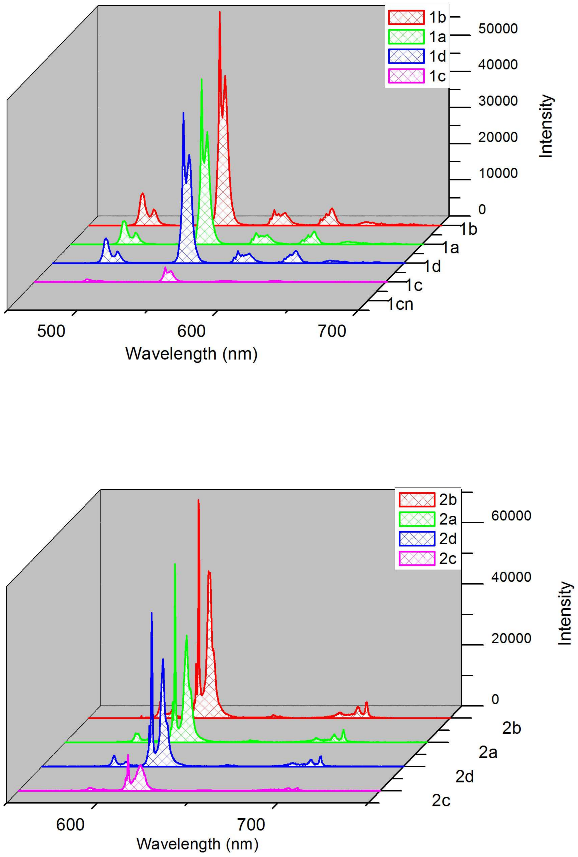


Figure 4. Comparison of the emission intensities of 1a-1d and 2a-2d in the solid state(under excitation at 285 nm)

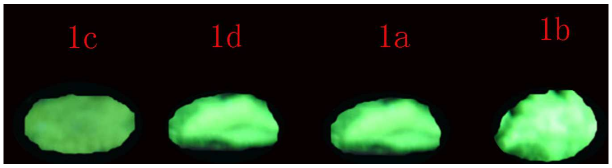


Figure 5. A snapshot of the Tb^{3+} compounds under UV irradiation.

For the Eu^{3+} compounds, the emission spectra of the Eu^{3+} compounds exhibit also four characteristic bands at 590 ($^5D_0 \rightarrow {}^7F_1$), 613 ($^5D_0 \rightarrow {}^7F_2$), 656 ($^5D_0 \rightarrow {}^7F_3$), 704 nm ($^5D_0 \rightarrow {}^7F_4$) among which the intensity of the hypersensitive transition is $^5D_0 \rightarrow {}^7F_2$ at 613 nm. Compounds **2a-2d** also show relatively weaker luminescence and lower Φ_{QY} than the corresponding Tb^{3+} compounds, suggesting the stronger quenching effect of the O-H group on Eu^{3+} than Tb^{3+}. The luminescence intensities and quantum yields of the Eu^{3+} compounds follow the similar order to the Tb^{3+} compounds: **2b** (NMP) > **2a** (DMA) > **2d** (DMF) > **2c** (H_2O) (**Figure 4**) due to the same reasons mentioned above.

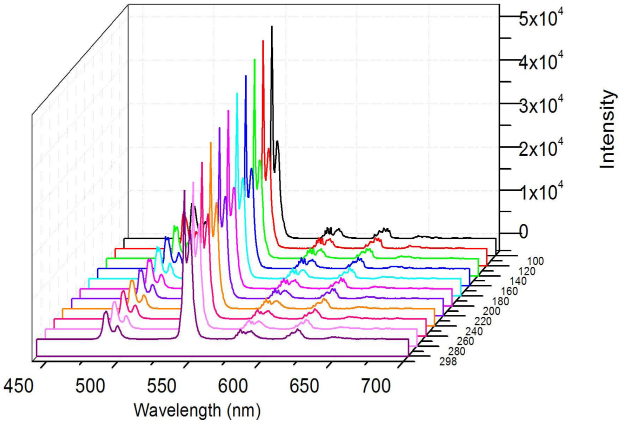


Figure 6. Comparison of the emission intensities of 1b at different temperature.

Table 2. Luminescence quantum yields and lifetimes for compounds 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
2a	12.5	0.314
2b	15.7	0.315
2c	3.1	0.286
2d	8.7	0.309

*ND means can't be detected

Moreover, the luminescence lifetime(τ) of all the compounds were measured, the data are listed in Table 2. It can be seen from Table 2 that compounds **2a-2d** show relatively shorter luminescence lifetimes than the corresponding Tb^{3+} compounds. And, the water containing frameworks **1c** and **2c** show shorter lifetimes with respect to the other guest containing frameworks. However, unlike the luminescence intensities and quantum yields, no change trend for the lifetimes of **1a-1d** and **2a-2d** was observed.

Conclusions

In summary, a series of 3D lanthanide MOFs with the guest DMA, NMP, H_2O and DMF guest molecules were synthesized and characterized. Luminescent studies on these compounds indicate that they exhibit apparently guest-dependent luminescent emissions. The intensities and the quantum yields of these compounds increase in the similar order: **1b** (NMP) > **1a** (DMA) > **1d** (DMF) > **1c** (H_2O) and **2b** (NMP) > **2a** (DMA) > **2d** (DMF) > **2c** (H_2O). Furthermore, the luminescent intensities can be reversibly modified by the guest molecule exchange. For the first time, this investigation reveals that the luminescence enhancement of the water-containing lanthanide MOFs by the guest molecules result from the effect of the hydrogen bond forming between the frameworks and the guest molecules. A challenge in luminescent lanthanide MOFs is to increase quantum yields and overall brightness of emission. Therefore, the introduction of the hydrogen bonding unit into the MOFs and/or increasing the guest molecule rigidity may be an effective new way to approach this goal.

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Notes and references

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Electronic Supplementary Information (ESI) available: crystal data, TGA, PXRD, IR, luminescent data and so on,. CCDC: 1010141 (**1a**) 1009888 (**1b**); 1009889 (**1c**); 1009890 (**1d**); 1009892 (**2a**); 1009891 (**2b**); 1009893 (**2c**). For ESI and crystallographic data in CIF or other electronic format see See DOI: 10.1039/b000000x/

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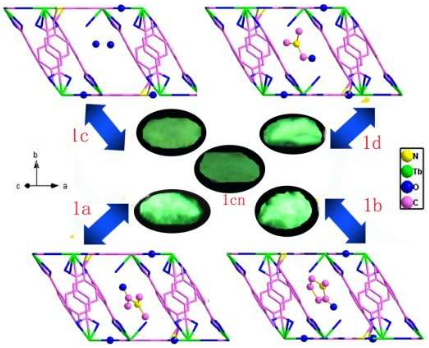
Table 1. Crystallographic data for all of the compounds

Sample	**1a**	**1b**	**1c**	**1d**
formula	$C_{32}H_{35}N_3O_{12.5}Tb$	$C_{34}H_{39}N_3O_{12.5}Tb$	$C_{24}H_{36}NO_{18.5}Tb$	$C_{30}H_{35}N_3O_{12.5}Tb$
*M*r[g mol^{-1}]	820.6	848.6	793.5	796.5
Crystal system	orthorhombic	orthorhombic	orthorhombic	orthorhombic
space group	*Pnma*	*Pnma*	*Pnma*	*Pnma*
a (Å)	10.929	10.913	10.932	10.902
b (Å)	16.586	16.542	16.713	16.715
c (Å)	19.393	19.793	18.893	19.201
V (Å^3)	3515.9	3573.2	3452.0	3499.0
Z	4	4	4	4
D_c (g cm^{-3})	1.550	1.577	1.390	1.512
μ (mm^{-1})	2.077	2.046	2.107	2.084
F (000)	1652	1716	1444	1604
T(K)	295	293	293	293
R_{int}	0.0273	0.0987	0.0485	0.0539
GOF on F^2	1.073	1.046	1.056	1.004
R1,^{a} wR2^b (I>2σ(I))	0.0391,0.1110	0.0782,0.2324	0.0711,0.2382	0.0824,0.2408
R1,^{a} wR2^b (all data)	0.0410,0.1129	0.0931,0.2161	0.0740,0.2437	0.0908,0.2551

Sample	**2a**	**2b**	**2c**
formula	$C_{32}H_{35}N_3O_{12.5}Eu$	$C_{34}H_{39}N_3O_{12.5}Eu$	$C_{24}H_{36}NO_{18.5}Eu$
*M*r[g mol^{-1}]	813.6	841.7	786.5
Crystal system	orthorhombic	orthorhombic	orthorhombic
space group	*Pnma*	*Pnma*	*Pnma*
a (Å)	10.979	10.959	11.048
b (Å)	16.651	16.565	16.702
c (Å)	19.380	19.750	18.739
V (Å^3)	3542.7	3585.4	3457.8
Z	4	4	4
D_c (g cm^{-3})	1.525	1.559	1.374
μ (mm^{-1})	1.835	1.816	1.872
F (000)	1644	1708	1436
T(K)	295	293	293
R_{int}	0.0318	0.0548	0.0500
GOF on F^2	1.047	1.003	1.003
R1,^{a} wR2^b (I>2σ(I))	0.0357,0.1016	0.0772,0.2048	0.0623,0.2081
R1,^{a} wR2^b (all data)	0.0390,0.1053	0.0823,0.2089	0.0670,0.2155

^{a} $R_1 = \sum(F_o - F_c)/\sum F_o$; $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$



The luminescence of novel metal-organic frameworks can be reversibly modified by different guest molecules, the hydrogen-bond formed between the metal-organic frameworks and the guest molecules and the rigidity of the guest molecules should be responsible for the luminescence enhancement of the compounds.