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## A series of lanthanide(III) complexes constructed from Schiff base and $\beta$ -diketonate ligands

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### ABSTRACT

A series of lanthanide (III) complexes constructed from Schiff base and  $\beta$ -diketonate ligands have been synthesized by the same method. They are mononuclear complex [Ln(hfac)<sub>3</sub>(L)] (Ln = Nd (**1**); Sm (**2**); Eu (**3**)); tetranuclear complex [Gd<sub>4</sub>(OAc)<sub>2</sub>L<sub>3</sub>(hfac)<sub>10</sub>] (**4**); dinuclear–mononuclear cocrystal [Dy(hfac)<sub>2</sub>(L)]<sub>2</sub>(OAc)·[Dy(hfac)<sub>4</sub>] (**5**); mononuclear–mononuclear cocrystal [Yb(hfac)<sub>2</sub>(L)]·[Yb(hfac)<sub>4</sub>] (**6**) (L = *N,N'*-bis(pyridine)-1,2-ethanediamine, hfac = hexafluoroacetylacetonate). The complexes **1–3** and **6** exhibit characteristic metal-centred emission not only in solid state but also in solvent. Lifetimes and quantum yields of luminescence are also determined.

### Introduction

The study of lanthanide complexes has gained great recognition over the last decade owing to their fascinating topological structures,<sup>1</sup> photoluminescence<sup>2</sup> and magnetism<sup>3</sup>. The photophysical properties of lanthanide ions are markedly dependent on their environment. For the lanthanide ions the f–f transitions are the Laporte forbidden which results in very low absorption coefficients. In order to overcome this, suitable organic ligands as chromophores have been used to act as antennas which can sensitize the lanthanide ions.<sup>4</sup> Moreover, ligands containing high-energy oscillators, such as C–H and O–H bonds, are able to quench the metal excited states nonradiatively, thereby leading to lower luminescence intensities and shorter excited-state lifetimes. Thus the replacement of C–H bonds with C–F bonds is important in the design of new lanthanide luminescent complexes with efficient emission properties.  $\beta$ -diketonate ligands such as 2-thenoyltrifluoroacetate (tta),

hexafluoroacetylacetonate (hfac) are used to act as an antenna to effectively transfer light energy to the metal for sensitized lanthanide emission, because they affords the fully allowed  $\pi-\pi^*$  transitions, thus leading to a possible energy transfer. Therefore,  $\beta$ -diketonates are ideal candidates as light-harvesting chromophores for sensitization of visible and NIR luminescence from Ln(III) ions.<sup>5</sup> Generally, complexation of  $\beta$ -diketonates to Ln(III) ions gives the corresponding neutral, unsaturated complexes such as  $\text{Ln}(\text{hfac})_3 \cdot 2\text{H}_2\text{O}$ , for the trivalent rare-earth ions commonly prefer high coordination numbers (typically 8 or 9). Thus only  $\beta$ -diketonate ligands affording a neutral complex can not protect Ln(III) ions from solvent molecules which can quench emissions. Moreover,  $\text{Ln}(\text{hfac})_3 \cdot 2\text{H}_2\text{O}$  units are almost non-emissive if irradiated with an excitation wavelength above 325 nm.<sup>6</sup> Therefore, other well designed chromophores should take part in the coordination to form more stable complexes.<sup>7</sup> A large number of highly coordinated mononuclear complexes of lanthanide  $\beta$ -diketonates which contain several nitrogen donors such as 1,10-phenanthroline,<sup>8</sup> 2,2'-bipyridine,<sup>9</sup> 2-(2-pyridyl)benzimidazole<sup>10</sup> have been reported. Our strategy to obtain luminescent complexes consists in using aromatic chelating nitrogen donors which can stabilize Ln(III) centres and transfer the energy efficiently to the lanthanide ions, potentially enhancing the luminescent properties. With this in mind, we have chosen to investigate the Schiff base ligand as a chelating ligand in lanthanide chemistry due to its bridging properties *via* the N-donor in pyridine and its fluorescence properties.<sup>11</sup> Our recent studies have focused on the use of a variety of Schiff base ligands to coordinate to Ln(III) atoms to improve lanthanide luminescence.<sup>12</sup> From the lighter to the heavier lanthanides, a series of complexes constructed from Schiff base (L = *N,N'*-bis(pyridine)-1,2-ethanediamine) and  $\beta$ -diketonate ligand (hexafluoroacetylacetonate) have been synthesized by the same method. (Scheme 1) To our surprise, they have the following structures: (i) mononuclear; (ii) tetranuclear; (iii) dinuclear–mononuclear cocrystal; (iv) mononuclear–mononuclear cocrystal. Although numerous  $\beta$ -diketonate lanthanide complexes have been prepared<sup>13</sup>, most nitrogen donors with two or three N-donors result in mononuclear structure. In this paper, the flexible Schiff base ligands act as neutral bridging ligands between the metal centres and the presence of bridging OAc<sup>-</sup> units resulting in the formation of various structures.

**Table 1** Crystallographic data for complexes 1–6

Crystal data	1	2	3	4	5	6
CCDC Number	969261	974866	975131	981053	974256	980754
Empirical formula	C <sub>29</sub> H <sub>17</sub> NdF <sub>18</sub> N <sub>4</sub> O <sub>6</sub>	C <sub>29</sub> H <sub>17</sub> SmF <sub>18</sub> N <sub>4</sub> O <sub>6</sub>	C <sub>29</sub> H <sub>17</sub> EuF <sub>18</sub> N <sub>4</sub> O <sub>6</sub>	C <sub>96</sub> H <sub>58</sub> F <sub>60</sub> Gd <sub>4</sub> N <sub>12</sub> O <sub>24</sub>	C <sub>69</sub> H <sub>36</sub> Dy <sub>3</sub> F <sub>48</sub> N <sub>11</sub> O <sub>16</sub>	C <sub>44</sub> H <sub>20</sub> F <sub>36</sub> N <sub>4</sub> O <sub>12</sub> Yb <sub>2</sub>
Formula weight	1003.71	1009.82	1011.43	3532.54	2674.59	1826.72
Temperature (K)	293	293	293	293	293	293
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71069	0.71073
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic	Triclinic	Orthorhombic
space group	Cc	Cc	Cc	P-1	P-1	Pcca
<i>a</i> (Å)	16.990(3)	16.975(3)	16.936(3)	17.7010(5)	12.440(5)	23.313(5)
<i>b</i> (Å)	18.475(4)	18.527(4)	18.506(4)	19.2428(4)	20.322(5)	11.450(2)
<i>c</i> (Å)	11.966(2)	11.936(2)	11.923(2)	23.1401(7)	20.819(5)	24.062(5)
$\alpha$ (°)	90	90	90	67.657(2)	70.278(5)	90
$\beta$ (°)	92.92(3)	93.47(3)	93.65(3)	83.186(2)	74.202(5)	90
$\gamma$ (°)	90	90	90	63.229(2)	79.033(5)	90
<i>V</i> (Å <sup>3</sup> )	3751.1(12)	3746.9(12)	3729.3(12)	6495.6(3)	4739(3)	6423(2)
<i>Z</i>	4	4	4	2	2	4
Calculated density (Mg/m <sup>3</sup> )	1.777	1.790	1.801	1.806	1.874	1.889
Absorption coefficient (mm <sup>-1</sup> )	1.519	1.702	1.817	2.169	2.499	3.054
<i>F</i> (000)	1956	1964	1968	3414	2570	3488
$\theta$ range	3.26 to 25.00	3.26 to 24.99	3.26 to 25.00	3.13 to 25.00	3.16 to 25.00	3.12 to 25.00
Limiting indices	-19<= <i>h</i> <=20 -21<= <i>k</i> <=9 -14<= <i>l</i> <=14	-18<= <i>h</i> <=20 -17<= <i>k</i> <=22 -14<= <i>l</i> <=11	-20<= <i>h</i> <=19 -22<= <i>k</i> <=11 -14<= <i>l</i> <=13	-21<= <i>h</i> <=19 -22<= <i>k</i> <=21 -27<= <i>l</i> <=26	-14<= <i>h</i> <=14 -24<= <i>k</i> <=24 -24<= <i>l</i> <=24	-27<= <i>h</i> <=15 -13<= <i>k</i> <=13 -11<= <i>l</i> <=28
Reflections collected	6495	6527	6683	51737	34230	15271
Completeness to $\theta = 27.48^\circ$	99.8 %	99.8 %	99.8 %	99.7 %	99.8 %	99.8 %
Data / restraints / parameters	4757 / 9 / 524	4586 / 9 / 524	4594/23/524	22799/87/1747	16671/1187/ 1499	5655/35/440
Goodness-of-fit on <i>F</i> <sup>2</sup>	0.962	0.988	1.045	1.087	1.041	1.079
Final R indices [ <i>I</i> >2 $\sigma$ ( <i>I</i> )]	R <sub>1</sub> = 0.0356 wR <sub>2</sub> = 0.0838	R <sub>1</sub> = 0.0360 wR <sub>2</sub> = 0.0877	R <sub>1</sub> = 0.0431 wR <sub>2</sub> = 0.1179	R <sub>1</sub> = 0.0550 wR <sub>2</sub> = 0.1431	R <sub>1</sub> = 0.0520 wR <sub>2</sub> = 0.1106	R <sub>1</sub> = 0.0541 wR <sub>2</sub> = 0.1405
R indices (all data)	R <sub>1</sub> = 0.0547 wR <sub>2</sub> = 0.0915	R <sub>1</sub> = 0.0514 wR <sub>2</sub> = 0.0968	R <sub>1</sub> = 0.0546 wR <sub>2</sub> = 0.1270	R <sub>1</sub> = 0.0857 wR <sub>2</sub> = 0.1611	R <sub>1</sub> = 0.0826 wR <sub>2</sub> = 0.1297	R <sub>1</sub> = 0.0771 wR <sub>2</sub> = 0.1546

## Experimental section

**Materials and Measurements.** All operations were performed in an open atmosphere. The lanthanide precursors, Ln(hfac)<sub>2</sub>(OAc)(H<sub>2</sub>O)<sub>2</sub> (Ln = Nd, Sm, Eu, Gd, Dy and Yb) were prepared according to a literature procedure previously described.<sup>14</sup> The Schiff base ligand was obtained from the reaction between 1,2-ethylenediamine and pyridylaldehyde according to the reported procedure.<sup>15</sup> Other chemicals were commercially available and generally used as supplied. Elemental (C, H and N) analyses were performed on a Perkin-Elmer 2400 analyzer. IR spectra were conducted on Perkin-Elmer 60000 spectrophotometer. UV spectra were recorded on Shimadzu UV2240 spectrophotometer. Fluorescence spectra for complexes were recorded on a FLSP920 spectrophotometer equipped with a xenon lamp and quartz carrier at room temperature. Luminescence lifetimes were recorded on a single photon counting spectrometer with a microsecond pulse lamp as the excitation. The overall quantum yields of both samarium and europium complexes were measured in MeOH about 5 × 10<sup>-5</sup> M at room temperature and cited relative to a water solution of Ru(bpy)<sub>3</sub>Cl<sub>2</sub> (bpy = 2,2'-bipyridine, Φ = 0.028),<sup>16</sup> and through the following expression:

$$\varphi_{\text{overall}} = \frac{n_{\text{ref}}^2 A_{\text{ref}} I}{n_{\text{ref}}^2 A I_{\text{ref}}} \varphi_{\text{ref}} \quad (1)$$

In eq 1,  $n$ ,  $I$ , and  $A$  denote the refractive index of solvent, the area of the emission spectrum, and the absorbance at the excitation wavelength, respectively, and  $\varphi_{\text{ref}}$  represents the quantum yield of the standard Ru(bpy)<sub>3</sub>Cl<sub>2</sub> solution. The quantum yields of complexes **1** and **4** in methanol solutions are estimated by the equation  $\Phi_{\text{Ln}} = \tau_{\text{obs}}/\tau_0$ , in which  $\tau_{\text{obs}}$  is the observed emission lifetime and  $\tau_0$  is the radiative or 'natural' lifetime with  $\tau_0 = 2$  ms for Yb(III).

### Syntheses of complexes 1–6

All six complexes were synthesized by the same method. The synthesis of complex **1** is described herein. Nd(hfac)<sub>2</sub>(OAc)(H<sub>2</sub>O)<sub>2</sub> (0.066 g, 0.1mmol) was dissolved in 20 mL n-hexane and refluxed for ten minutes. 5 mL CH<sub>2</sub>Cl<sub>2</sub> solution of L (0.024 g, 0.1 mmol) was added, and the mixture was heated for 30 min at around 60 °C. Crystals of **1** suitable for X-ray analysis were isolated by cooling the solution to room temperature and keeping the filtrate in a refrigerator at 4 °C for a week. Anal. Calcd

**(1)** for  $C_{29}H_{17}NdF_{18}N_4O_6$  (yield: 0.059 g, 58%): C, 34.70; H, 1.71; N, 5.58. Found: C, 34.55; H, 1.74; N, 5.48. IR (KBr pellet,  $cm^{-1}$ ): 1656 (vs), 1598 (s), 1550 (s), 1482 (m), 1445 (s), 1252 (vs), 1136 (vs), 1009 (vs), 792 (vs). UV-Vis spectrum in  $CH_3OH$  [ $\lambda_{max}$  (nm)]: 203, 236, 301.

**2** (Ln = Sm) Anal. Calcd (**2**) for  $C_{29}H_{17}SmF_{18}N_4O_6$  (yield: 0.053 g, 52.6%): C, 34.49; H, 1.71; N, 5.58. Found: C, 34.29; H, 1.70; N, 5.52. IR (KBr pellet,  $cm^{-1}$ ): 1661 (s), 1630 (w), 1532 (s), 1469 (vs), 1442 (w), 1255 (vs), 1142 (vs), 801 (s). UV-Vis spectrum in  $CH_3OH$  [ $\lambda_{max}$  (nm)]: 203, 236, 301.

**3** (Ln = Eu) Anal. Calcd (**3**) for  $C_{29}H_{17}EuF_{18}N_4O_6$  (yield: 0.057 g, 56.4%): C, 34.44; H, 1.69; N, 5.54. Found: C, 34.40; H, 1.74; N, 5.51. IR (KBr pellet,  $cm^{-1}$ ): 1656 (vs), 1599 (s), 1530 (s), 1252 (m), 1199 (w), 1137 (s), 1008 (w), 791 (vs). UV-Vis spectrum in  $CH_3OH$  [ $\lambda_{max}$  (nm)]: 203, 236, 301.

**4** (Ln = Gd) Anal. Calcd (**4**) for  $C_{96}H_{59}F_{60}Gd_4 N_{12}O_{24}$  (yield: 0.041 g, 49.3%): C, 32.63; H, 1.68; N, 4.76. Found: C, 32.66; H, 1.58; N, 4.62. IR (KBr pellet,  $cm^{-1}$ ): 1657 (vs), 1599 (s), 1531 (s), 1256 (s), 1146 (w), 1139 (vs), 1100 (w), 793 (vs). UV-Vis spectrum in  $CH_3OH$  [ $\lambda_{max}$  (nm)]: 203, 236, 301.

**5** (Ln = Dy) Anal. Calcd (**5**) for  $C_{69}H_{36}Dy_3F_{48} N_{11}O_{16}$  (yield: 0.041 g, 46%): C, 30.99; H, 1.36; N, 5.76. Found: C, 30.91; H, 1.37; N, 5.68. IR (KBr pellet,  $cm^{-1}$ ): 1658 (vs), 1600 (m), 1529 (m), 1499 (s), 1387 (w), 1254 (vs), 1206 (vs), 1010 (m), 797 (vs). UV-Vis spectrum in  $CH_3OH$  [ $\lambda_{max}$  (nm)]: 203, 236, 301.

**6** (Ln = Yb) Anal. Calcd (**6**) for  $C_{44}H_{20}Yb_2F_{36}N_4 O_{12}$  (yield: 0.039 g, 42.9%): C, 29.93; H, 1.10; N, 3.07. Found: C, 29.96; H, 1.02; N, 3.06. IR (KBr pellet,  $cm^{-1}$ ): 1655 (vs), 1603 (s), 1536 (s), 1479 (w), 1446 (w), 1256 (vs), 1143 (vs), 798 (vs). UV-Vis spectrum in  $CH_3OH$  [ $\lambda_{max}$  (nm)]: 203, 236, 301.

### X-ray crystallography

Crystallography: Diffraction intensity data for single crystals of complexes were collected on a Rigaku R-Axis RAPID imaging-plate X-ray diffractometer at 293 K. The structures were solved by the direct method and refined by the Full-matrix least squares on  $F^2$  using the SHELXTL-97 software package.<sup>17, 18</sup> All non-hydrogen atoms were refined with anisotropic displacement parameters. CCDC 969261, 974866, 975131, 981053, 974256 and 980754 for complexes **1–6** contain the supplementary

crystallographic data for this paper. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk).

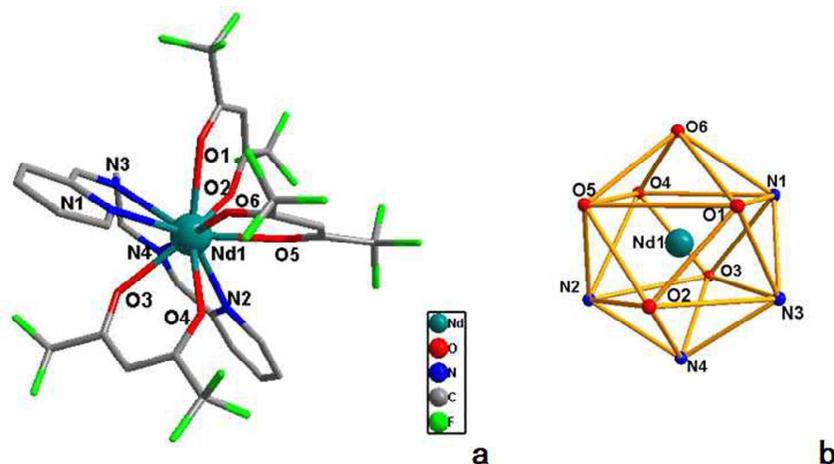
## Results and discussion

### Syntheses

Complexes **1–6** were synthesized by reactions of the Schiff base ligand with the precursor  $\text{Ln}(\text{hfac})_2(\text{OAc})(\text{H}_2\text{O})_2$  in a molar ratio of 1:1 carried out in  $\text{CH}_2\text{Cl}_2/\text{n-hexane}$  at ambient temperature. (Scheme 1) Crystals suitable for X-ray analysis were obtained by cooling the solution to room temperature and keeping the filtrate in a refrigerator at 4 °C for a week. Complexes **1–6** are stable in air and moderately soluble in polar organic solvent such as methanol, ethanol and DMF.

### Structural descriptions of complexes **1–3**

X-ray crystallographic analysis has revealed that complexes **1–3** are isomorphic. Taking **1** as example, the unit cell of complex **1** crystallized in a monoclinic space group *Cc*. The perspective view of the molecular structure of **1** is shown in Fig. 1. Crystallographic details are provided in Table 1, and selected bond lengths of the coordination environment of the metal centres are listed in Table S1. In the  $[\text{Nd}(\text{hfac})_3(\text{L})]$  unit, each hfac anion provides two donor oxygen atoms coordinating to the Nd(III) ion, and the other four coordination sites of Nd(III) are occupied by the four N atoms from Schiff base to complete the 10-coordinated environment  $\text{NdO}_6\text{N}_4$  forming a dicapped square antiprism. The square antiprism is composed of O1, O4, O5, N1, O2, N2, O3 and N3 atoms. The N4 and O6 atoms are at the apices of each square pyramid. (Fig. 1b) The Nd–O (hfac) distances range from 2.461(7) to 2.548(8) Å while the Nd–N distances range from 2.621(8) to 2.714(9) Å.

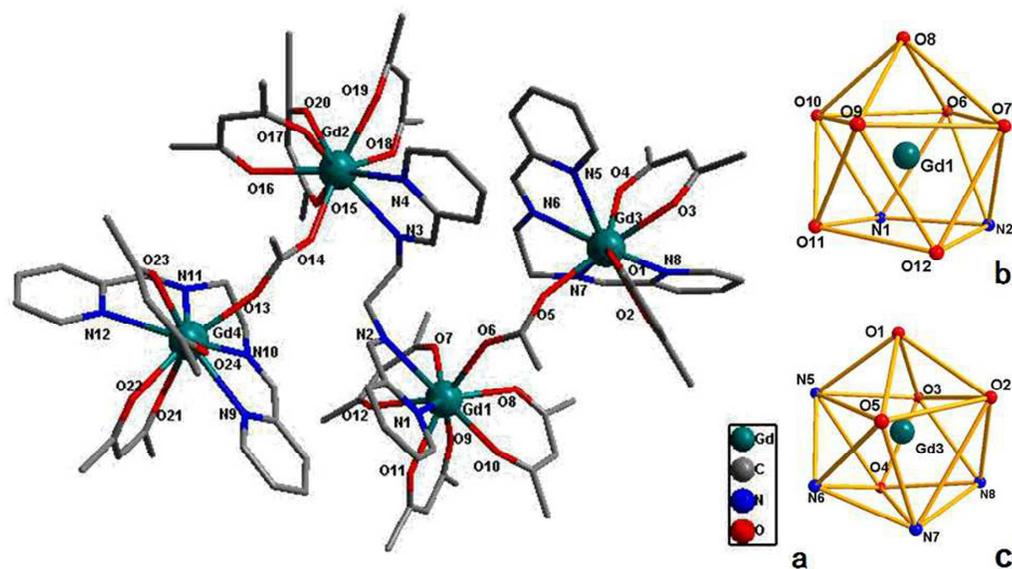


**Fig. 1** a) The crystal structure of **1**, hydrogen atoms are omitted for clarity. Color code: dark green (Nd), blue (N), red (O), gray (C), green (F); b) A perspective view of the coordination polyhedron for the Nd(III) ions in **1**.

#### Structural description of complex **4**

X-ray crystallographic analysis showed that complex **4** crystallizes in a triclinic space group  $P-1$ . Crystallographic details are provided in Table 1, and selected bond lengths of the coordination environment of the metal centres are listed in Table S2. As shown in Fig. 2, the complex **4** contains four independent Gd ions, three Schiff base ligands, two  $\text{OAc}^-$  that connect two Gd ions in a bis-monodentate fashion respectively, and ten hfac without any solvent molecules. One Schiff base ligand displays a curved configuration in which the backbone nitrogen atoms (N1, N2, N3 and N4) link Gd1 and Gd2 ions with the  $\text{Gd1}\cdots\text{Gd2}$  distance 7.600 Å. Gd1 and Gd3 are bridged by one  $\text{OAc}^-$  in which the  $\text{Gd1}\cdots\text{Gd3}$  distance is 6.631 Å. Another  $\text{OAc}^-$  bridged Gd2 and Gd4 with the  $\text{Gd2}\cdots\text{Gd4}$  distance 6.530 Å. Gd1 and Gd2 exhibit 9-coordinated environments from two N atoms from the bridging Schiff base ligand, six O atoms from three hfac molecules, and one O atom from  $\text{OAc}^-$ , forming a monocapped square antiprism with O8 at the capped position. (Fig. 2b) The square antiprism is composed of O9, O7, O6, O10, O11, O12, N2 and N1 atoms. Gd3 and Gd 4 are also 9-coordinated with four N atoms from one Schiff base ligand, four hfac O atoms, and one  $\text{OAc}^-$  O atom. The coordination environment of the Gd(III) ion can be best described as a tricapped trigonal prismatic geometry. The distorted trigonal prism is

composed of O5, N7, O2, N5, O4 and O3 atoms. The O1, N6 and N8 atoms are at the apices of each square pyramid (the angle O1–Gd3–N6 is  $116.7^\circ$ , O1–Gd3–N8 is  $126.3^\circ$ , N6–Gd3–N8 is  $117.0^\circ$ ). (Fig. 2c) The distances from Gd3 to the centres of two triangles (the N7–O2–O5 plane and the O4–O3–N5 plane) are respectively 1.55 and 1.178 Å. The Gd–O (hfac) distances range from 2.359(17) to 2.503(14) Å, Gd–O (OAc<sup>-</sup>) distances range from 2.322(15) to 2.353(14) Å while the Gd–N distances range from 2.53(2) to 2.68(2) Å.

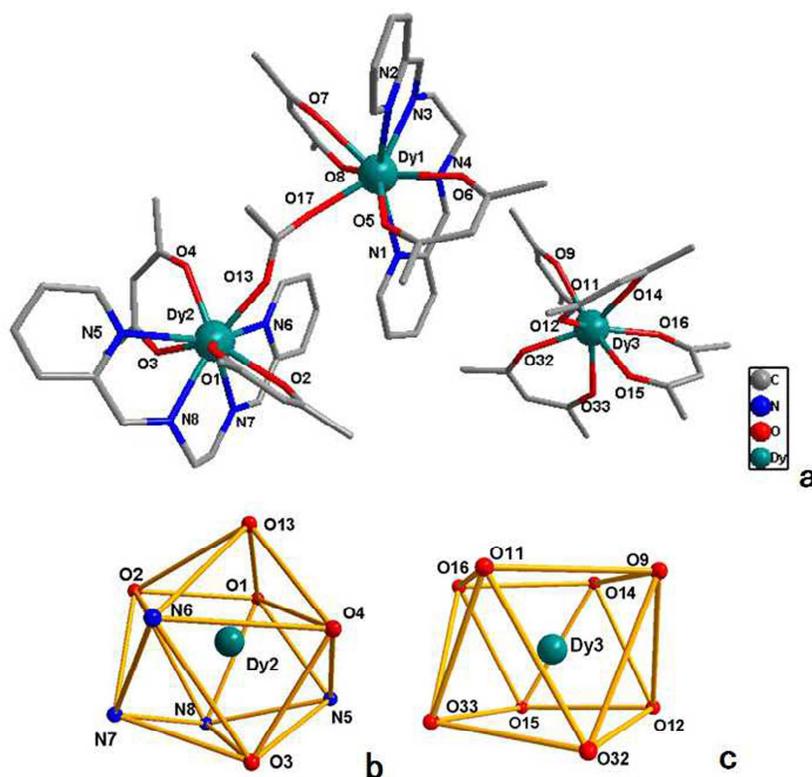


**Fig. 2** The crystal structure of **4**, hydrogen and fluorine atoms are omitted for clarity. Color code: dark green (Gd), blue (N), red (O), gray (C); b) A perspective view of the coordination polyhedra for the Gd1 or Gd2 ion in **4**; c) A perspective view of the coordination polyhedra for the Gd3 or Gd4 ion in **4**.

### Structural description of complex **5**

X-ray crystallographic analysis showed that complex **5** crystallizes in a triclinic space group  $P-1$ . The asymmetric unit of the structure of  $[\text{Dy}(\text{hfac})_2(\text{L})]_2(\text{OAc}) \cdot [\text{Dy}(\text{hfac})_4]$  (**5**) contains one dinuclear  $[\text{Dy}(\text{hfac})_2(\text{L})]_2(\text{OAc})$  unit, one mononuclear  $[\text{Dy}(\text{hfac})_4]$  unit. The dinuclear and mononuclear units are shown in Fig. 3. Crystallographic details are provided in Table 1, and selected bond lengths of the coordination environment of the metal centres are listed in Table S3. In the dinuclear  $[\text{Dy}(\text{hfac})_2(\text{L})]_2(\text{OAc})$  unit, two metal centres are bridged by one OAc<sup>-</sup> in which the Dy1...Dy2 distance is 6.479 Å. The Dy1 and Dy2 in the dinuclear unit are

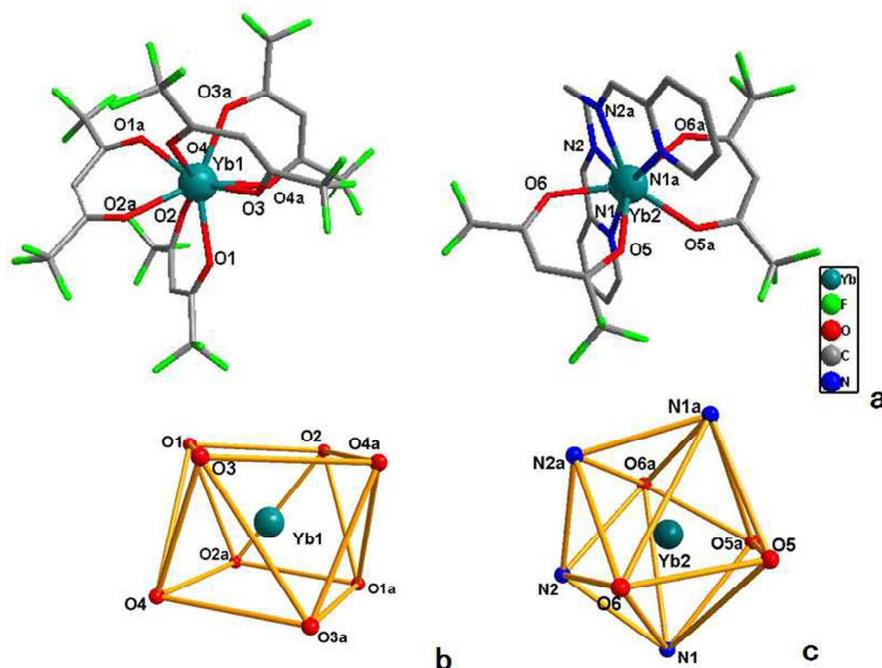
9-coordinated with four N atoms from one Schiff base ligand, four hfac O atoms, and one OAc<sup>-</sup> O atom, giving a tricapped trigonal prismatic geometry. The distorted trigonal prism is composed of O3, N6, O4, N8, O2 and O1 atoms. The N5, N7 and O13 atoms are at the apices of each square pyramid (the angle O13–Dy2–N5 112.5°, O13–Dy2–N7 128.6°, N7–Dy2–N5 118.9°). (Fig. 3b) The distances from Dy2 to the centres of two triangles (the O3–O4–N6 plane and the N8–O1–O2 plane) are respectively 1.73 and 1.70 Å. The metal centre in the mononuclear [Dy(hfac)<sub>4</sub>] unit is 8-coordinated with eight O atoms from four hfac. The coordination environment of the Dy(III) ion can be best described as a square antiprism geometry. (Fig. 3c) The square antiprism is composed of O16, O11, O9, O14, O15, O33, O32 and O12 atoms. The Dy–O (hfac) distances range from 2.311(6) to 2.419(5) Å, Dy–O (OAc<sup>-</sup>) distances range from 2.267(5) to 2.285(5) Å while the Dy–N distances range from 2.501(7) to 2.621(8) Å are comparable to those found in the literature.<sup>19</sup>



**Fig. 3** The crystal structure of **5**, hydrogen and fluorine atoms are omitted for clarity. Color code: dark green (Dy), blue (N), red (O), gray (C); b) A perspective view of the coordination polyhedron for the Dy1 or Dy2 ion in **5**; c) A perspective view of the coordination polyhedron for the Dy3 ion in **5**.

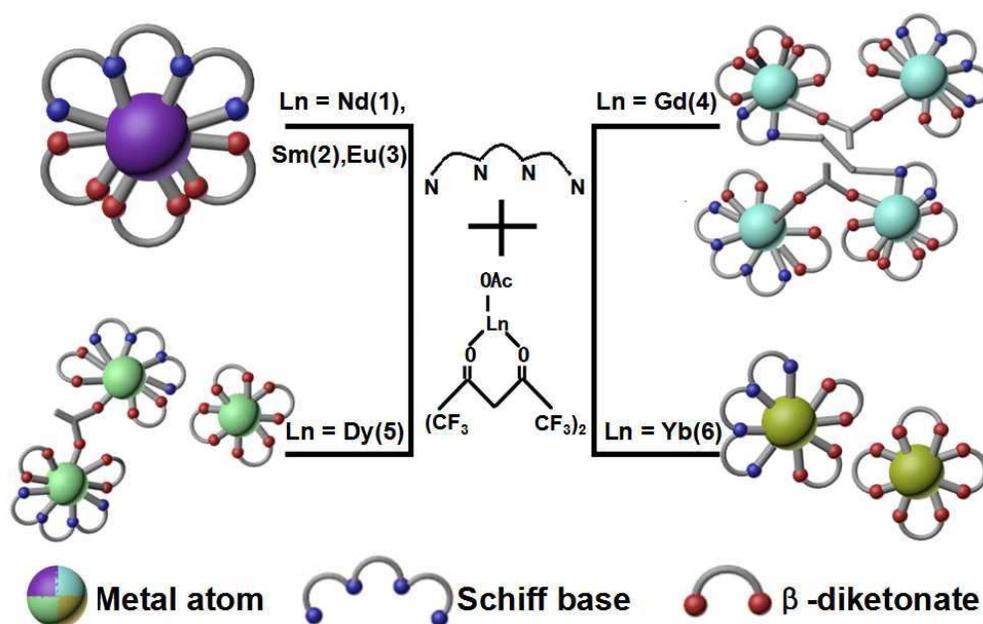
### Structural description of complex **6**

X-ray crystallographic analysis showed that complex **6** crystallizes in an orthorhombic space group *Pcca*. In the asymmetric unit of the structure of  $[\text{Yb}(\text{hfac})_2(\text{L})] \cdot [\text{Yb}(\text{hfac})_4]$ , one mononuclear  $[\text{Yb}(\text{hfac})_2(\text{L})]$  unit is cocrystallized with one mononuclear  $[\text{Yb}(\text{hfac})_4]$  moiety. The two mononuclear units are shown in Fig. 4. Crystallographic details are provided in Table 1, and selected bond lengths of the coordination environment of the metal centres are listed in Table S4. The metal centre in the mononuclear  $[\text{Yb}(\text{hfac})_4]$  unit is 8-coordinated with eight O atoms from four hfac, giving a square antiprism geometry. (Fig. 4b) The square antiprism is composed of O1, O2a, O3, O4, O1a, O2, O3 and O4 atoms. The ytterbium (III) centre in the mononuclear  $[\text{Yb}(\text{hfac})_2(\text{L})]$  unit is 8-coordinated with four N atoms from one Schiff base ligand and four O atoms from two hfac molecules, giving a dodecahedron geometry. (Fig. 4c) The Yb–O (hfac) distances range from 2.272(7) to 2.349(6) Å while the Yb–N distances range from 2.401(7) to 2.459(7) Å are comparable to those found in the literature.<sup>20</sup>



**Fig. 4** The crystal structure of **6**, hydrogen atoms are omitted for clarity. Color code: dark green (Yb), blue (N), red (O), gray (C); b) A perspective view of the coordination polyhedron for the Yb1 ions in **6**; c) A perspective view of the coordination polyhedron for the Yb2 ions in **6**.

Scheme 1. Schematic representation of the complexes 1–6



In a comparison of complexes 1–6 (Scheme 1), the bond distances of Ln–O and Ln–N declined from the lighter to the heavier lanthanides. In 1–3, the Ln(III) ions (Nd, Sm and Eu) with a larger ionic radius are ten-coordinated to four N atoms from Schiff base ligand and six O atoms from Hfac forming mononuclear structure. The Gd(III) ion with a medium radius in 4 is nine-coordinated in which flexible Schiff base ligands act as neutral bridging ligands between the metal centres and the presence of bridging OAc<sup>−</sup> units resulting in the formation of tetranuclear structure. In 5, the OAc<sup>−</sup> acts as a bridging ligand between two Dy(III) ions resulting in dinuclear–mononuclear cocrystal. In 6, the coordination sphere of the Yb(III) ions with a smallest radius are exclusively occupied by eight O(N) atoms forming mononuclear–mononuclear cocrystal. It is noteworthy that complexes 1–6 have been synthesized by the same method, which unambiguously indicates that the ion radius dominated the structures of complexes 1–6.

### Luminescent properties

The UV-vis absorption data of L, Eu(hfac)<sub>2</sub>(OAc)(H<sub>2</sub>O), 1, 4, 5 and 6 are presented in Fig. 5. In MeOH, L consists of three main absorption at *ca.* 202, 235, 271 nm, which are assigned to the  $\pi$ - $\pi^*$  transition of pyridine chromophores and the imine group. For Eu(hfac)<sub>2</sub>(OAc)(H<sub>2</sub>O), there is only a single intense absorption band at *ca.* 303 nm

assigned as intra-ligand  $\pi-\pi^*$  (acac) transitions. As for **1**, **4**, **5** and **6**, there are three similar sets of absorption bands at *ca.* 203, 236 and 301 due to the intra-ligand transitions of L and Hfac ligands, respectively.

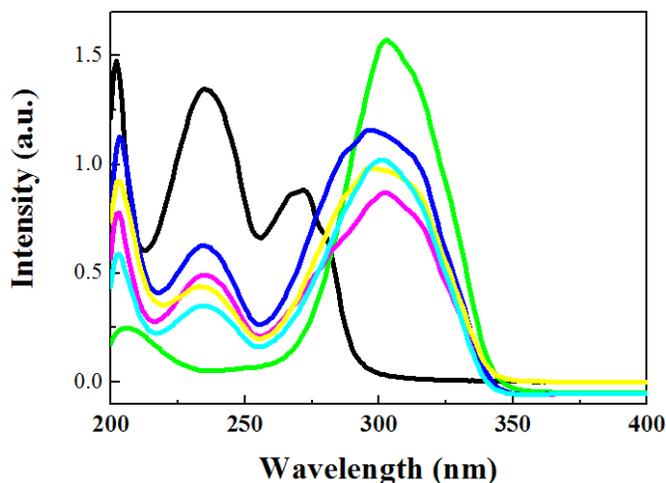
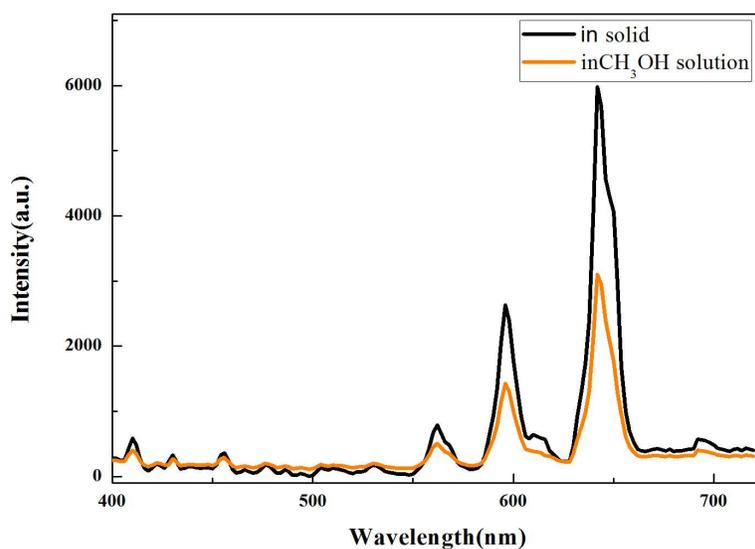


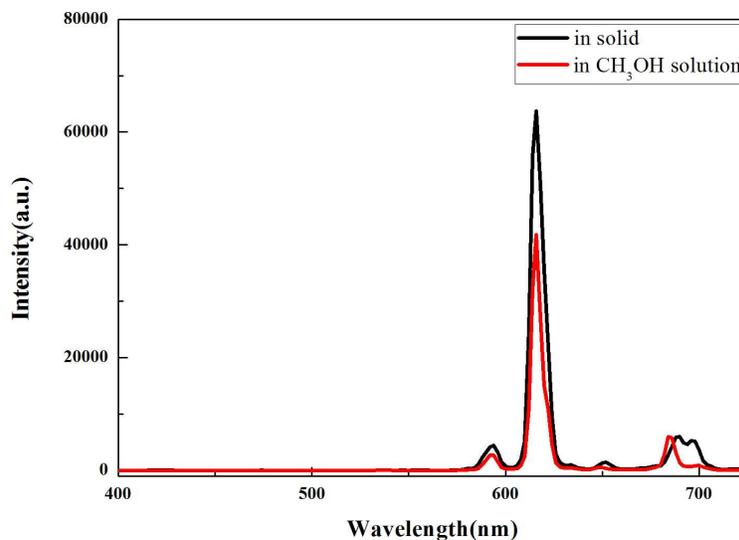
Fig. 5 The UV-vis absorption spectra of L (black),  $\text{Eu}(\text{hfac})_2(\text{OAc})(\text{H}_2\text{O})_2$  (green), **1** (magenta), **4** (blue), **5** (yellow) and **6** (cyan)

The luminescent spectra of complexes **2** and **3** both in solid state and methanol solution ( $10^{-5} \text{ mol}\cdot\text{L}^{-1}$ ) have been recorded at room temperature. (Fig. 6 and 7) For the Schiff base ligand, the broad emission band observed from 275 to 510 nm can be attributed to the  $\pi \rightarrow \pi^*$  transition of the ligand. (Fig. S3) When excited at 325 nm where the ligand absorption mainly took place, the emission spectrum of complex **2** exhibits five major peaks at 565, 601, 645 and 704 nm of Sm(III) emissions. The emissions at 565 nm can be assigned to  ${}^4\text{G}_{5/2} \rightarrow {}^6\text{H}_{5/2}$ , 601 nm and 615 nm to  ${}^4\text{G}_{5/2} \rightarrow {}^6\text{H}_{7/2}$ , 645 nm to  ${}^4\text{G}_{5/2} \rightarrow {}^6\text{H}_{9/2}$ , 704 nm to  ${}^4\text{G}_{5/2} \rightarrow {}^6\text{H}_{11/2}$ . When complex **3** was excited at 315 nm where the ligand absorption mainly took place, typical emission of Eu(III) ion were detected. The emission spectrum of complex **3** exhibits a single narrow band at 615 nm. Five typical emission bands of Eu(III) ion are observed, 580 nm ( ${}^5\text{D}_0 \rightarrow {}^7\text{F}_0$ ), 592 nm ( ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ ), 615 nm ( ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ ), 650 nm ( ${}^5\text{D}_0 \rightarrow {}^7\text{F}_3$ ) and 679 nm ( ${}^5\text{D}_0 \rightarrow {}^7\text{F}_4$ ). For these luminescent lanthanides, the solid state emission spectra are almost identical to their solution spectra in complexes **2** and **3**. However, the fluorescence intensities of two complexes in solid state are stronger than in solution.

This may be due to the excited state of the lanthanide ions which is efficiently quenched by interactions with high-energy vibrations groups of organic solvent. The lifetime values for the excited energy levels in complexes **2** and **3** were determined from their luminescence decay profiles at room temperature (Fig. S4-S7). The lifetime of **2** in solid and methanol solution is respectively 40.1  $\mu\text{s}$  and 37.7  $\mu\text{s}$ . The lifetime of **2** is 921.9  $\mu\text{s}$  in solid state and 941.6  $\mu\text{s}$  in solution. In MeOH, the fluorescence quantum yields ( $\Phi_{em}$ ) for **2** and **3** were 0.16% and 4.57%, respectively.



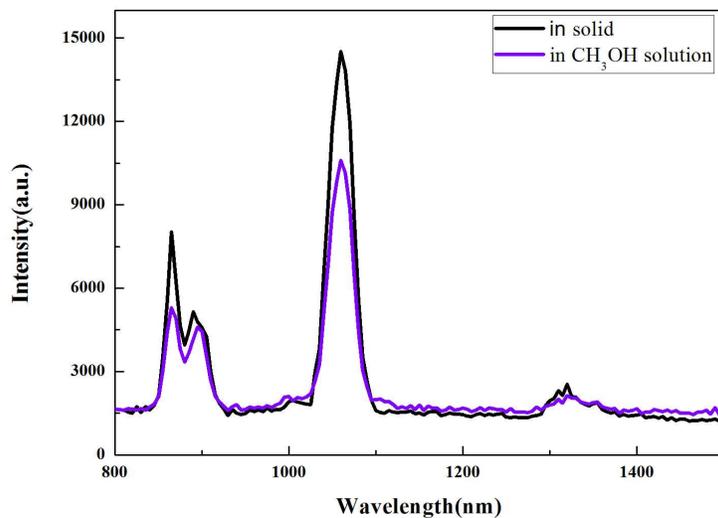
**Fig. 6** The luminescent emission spectra of **2** in solid state and MeOH solution at room temperature.



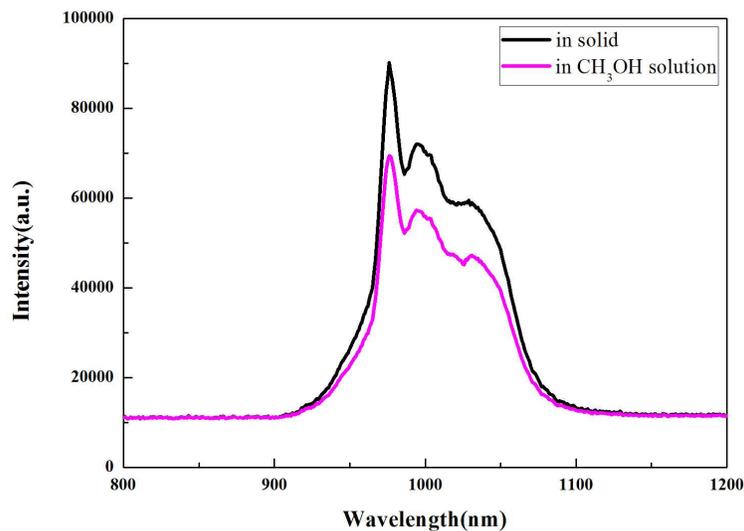
**Fig. 7** The luminescent emission spectra of **3** in solid state and MeOH solution at room temperature.

### NIR Luminescence

The NIR emission spectra for the complexes **1** and **6** were measured not only in solid state but also in MeOH ( $10^{-5}$  M) at room temperature. When complex **1** was excited at 325 nm where the ligand absorption mainly took place, three Nd(III) NIR emission bands were detected and assigned to the  ${}^4F_{3/2} \rightarrow {}^4I_{j/2}$  ( $j = 9, 11, 13$ ) transitions in complex **1**. The emission band at 1060 nm is the most intensive of all four bands. (Fig. 8) The emissions at 865 and 895 nm can be assigned to  ${}^4F_{3/2} \rightarrow {}^4I_{9/2}$ , 1060 nm to  ${}^4F_{3/2} \rightarrow {}^4I_{11/2}$  and 1320 nm to  ${}^4F_{3/2} \rightarrow {}^4I_{13/2}$  transitions of Nd(III). When complex **6** was excited at 325 nm where the ligand absorption mainly took place, the typical emission band of Yb(III) was not a single sharp transition in which well-split NIR emission peaks are observed (Fig. 9). The emission band centred at 976 nm was assigned to the transition of  ${}^2F_{5/2} \rightarrow {}^2F_{7/2}$ . Two other broad bands centred at 993 and 1028 nm were also observed. Similar splitting in Schiff base ytterbium complex has been reported previously,<sup>12b</sup> and in early spectroscopic studies on Yb(III)  $\beta$ -diketonate compounds it was suggested that crystal field splitting is the origin of the structure in the emission spectra.<sup>21</sup> For the NIR luminescent lanthanides, the solid state emission spectra are almost identical to their solution spectra in **1** and **6**. However, the fluorescence intensities of two complexes in solid state are stronger than in solution. Moreover, for complex **6**, the respective NIR luminescent decay curves obtained from time-resolved luminescent experiments can be fitted mono-exponentially with time constant of microseconds (9.9  $\mu$ s for **6** at 976 nm), and the intrinsic quantum yield  $\Phi_{Ln}$  (0.50% for **6**) of the Ln(III) emission may be estimated by  $\Phi_{Ln} = \tau_{obs}/\tau_0$ , where  $\tau_{obs}$  is the observed emission lifetime and  $\tau_0$  is the “natural lifetime”, viz 2.0 ms for Yb(III) ions.<sup>22</sup> (Fig. S8) The lifetime of **6** in solid is 9.3  $\mu$ s lower than that in MeOH (Fig. S9). Unfortunately, unlike complex **6**, the NIR luminescence quantum yield and lifetime of the Nd(III) ion for complex **1** are too weak to be detected in solid state and solvent at room temperature.



**Fig. 8** The luminescent emission spectrum of **1** in solid state and MeOH solution at room temperature.



**Fig. 9** The luminescent emission spectrum of **6** in solid state and MeOH solution at room temperature.

**Table 2** Emission data of compounds **1–3** and **6**.

Complexes	Medium	$\lambda_{\text{ex}}/\text{nm}$	$\lambda_{\text{em}}/\text{nm}(\tau_{\text{em}})$	$\Phi_{\text{em}}(\%)$	Transition type
<b>1</b>	Solid	358	1060(weak)		865, 895 nm ( $^4\text{F}_{3/2} \rightarrow ^4\text{I}_{9/2}$ ),
	CH <sub>3</sub> OH	301	1060(weak)		1060 nm ( $^4\text{F}_{3/2} \rightarrow ^4\text{I}_{11/2}$ ), 1320 nm ( $^4\text{F}_{3/2} \rightarrow ^4\text{I}_{13/2}$ ) 565 nm ( $^4\text{G}_{5/2} \rightarrow ^6\text{H}_{5/2}$ ),
<b>2</b>	Solid	358	645(40.1 $\mu\text{s}$ )		601 nm, 615 nm ( $^4\text{G}_{5/2} \rightarrow ^6\text{H}_{7/2}$ ),
	CH <sub>3</sub> OH	301	645(37.7 $\mu\text{s}$ )	0.16%	645 nm ( $^4\text{G}_{5/2} \rightarrow ^6\text{H}_{9/2}$ ), 704 nm ( $^4\text{G}_{5/2} \rightarrow ^6\text{H}_{11/2}$ ) 580 nm ( $^5\text{D}_0 \rightarrow ^7\text{F}_0$ ), 592 nm ( $^5\text{D}_0 \rightarrow ^7\text{F}_1$ ),
<b>3</b>	Solid	358	615(921.9 $\mu\text{s}$ )		615 nm ( $^5\text{D}_0 \rightarrow ^7\text{F}_2$ ),
	CH <sub>3</sub> OH	301	615(941.6 $\mu\text{s}$ )	4.57%	650 nm ( $^5\text{D}_0 \rightarrow ^7\text{F}_3$ ), 679 nm ( $^5\text{D}_0 \rightarrow ^7\text{F}_4$ )
<b>6</b>	Solid	358	976(9.3 $\mu\text{s}$ )		
	CH <sub>3</sub> OH	301	976 (9.9 $\mu\text{s}$ )	0.50%	976, 993, 1028 nm ( $^2\text{F}_{5/2} \rightarrow ^2\text{F}_{7/2}$ )

## Conclusions

In summary, we have successfully demonstrated the application of a “two-ligand” approach to the construction of functional four types lanthanide complexes. From the lighter to the heavier lanthanides in complexes **1–6**, the coordination numbers for the lanthanide ions are declined from 10 to 8. The structures of all lanthanide complexes depend on the ion radius. Except for the Gd(III) and Dy(III) complexes, all complexes display the typical emission spectra of lanthanide ions. Further studies focused on this synthetic method and the improvement in luminescence properties by the construction of novel lanthanide complexes with  $\beta$ -diketonate and nitrogen donor ligands are in progress.

## Acknowledgments

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A series of lanthanide (III) complexes constructed from Schiff base and  $\beta$ -diketonate ligands have been synthesized by the same method. They are mononuclear complex  $[\text{Ln}(\text{hfac})_3(\text{L})]$  ( $\text{Ln} = \text{Nd}$  (1);  $\text{Sm}$  (2);  $\text{Eu}$  (3)); tetranuclear complex  $[\text{Gd}_4(\text{OAc})_2\text{L}_3(\text{hfac})_{10}]$  (4); dinuclear–mononuclear cocrystal  $[\text{Dy}(\text{hfac})_2(\text{L})]_2(\text{OAc}) \cdot [\text{Dy}(\text{hfac})_4]$  (5); mononuclear–mononuclear cocrystal  $[\text{Yb}(\text{hfac})_2(\text{L})] \cdot [\text{Yb}(\text{hfac})_4]$  (6) ( $\text{L} = N,N'$ -bis(pyridine)-1,2-ethanediamine,  $\text{hfac} =$  hexafluoroacetylacetonate). The complexes 1–3 and 6 exhibit characteristic metal-centred emission not only in solid state but also in solvent. Lifetimes and quantum yields of luminescence are also determined.

