

Effect of second ligand on the luminescence of Samarium (III) dibenzoylmethane complexes: Syntheses, crystal structures, thermal analysis and luminescence study

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Abstract. The ternary complexes of Sm(III) with dibenzoylmethane (dbm) were synthesized by introducing 1,10-phenanthroline (phen), 4,7-dimethyl-1,10-phenanthroline (dmphen), 3,4,7,8-tetramethyl-1,10-phenanthroline (tmphen), 4,7-diphenyl-1,10-phenanthroline (dpphen), 2,2-bipyridyl (bpy), 4,4'-dimethyl-2,2-bipyridyl (4,4-dmbpy), 5,5'-dimethyl-2,2-bipyridyl (5,5-dmbpy) and 4,4'-di-tert-butyl-2,2-bipyridyl (4,4-dtbbpy) as a second ligand. The complexes were isolated and characterized by elemental analysis (CHN), thermogravimetric analysis (TGA), IR spectroscopy, luminescence spectroscopy and single crystal X-ray diffraction. Structural study shows that in all complexes Sm(III) is in square antiprism geometry. All complexes emit strong luminescence under ultraviolet excitation. The strongest emission is at 643 nm which can be assigned for $^4G_{5/2}$ to $^6H_{9/2}$ transition, equivalent to energy of 15550 cm^{-1} . The addition of the second ligand has increased the emission intensity of the complexes while the transition is maintained.

Keywords. Samarium(III); ternary complexes; crystal structure; luminescence; emission.

1. Introduction

Lanthanide coordination complexes have gained an interest due to their broad applications in light emitting diodes,¹ fluorescent probes,² sensors,³ bioimaging utilities,⁴ time-resolved luminescent immunoassays,⁵ and anion sensing.⁶ In particular, the photoluminescent properties of lanthanide complexes are notable due to their unique properties such as sharp emission bands, long emission lifetime and large Stokes shift.⁷

The lanthanide ions are characterized by a partially filled $4f$ shell that is well shielded by fully filled $5s^2$ and $5p^6$ orbitals. Although the photoluminescence by lanthanide ions is an efficient process, it suffers from a weak light absorption. Due to the low molar absorption coefficient, only a small amount of radiation can be absorbed by $4f$ electrons. The luminescence intensity is not only proportional to the luminescence quantum yield, but also to the amount of light absorbed. However, the problem of weak light absorption can be overcome by the so-called “antenna effect”.⁸ Intense metal-centered luminescence can be observed for lanthanide complexes with organic ligands upon excitation. Due to the intense absorption bands of organic chromophores, more light can be absorbed by the organic ligand

than by the lanthanide ion itself. Thus, an appropriate organic ligand such as β -diketones will increase the luminescence of lanthanide through intramolecular energy transfer from the triplet energy state of the organic ligand to the excited $4f$ states of the lanthanide ion. Although the addition of β -diketones will increase emission intensity, the major problem from the use of the lanthanide β -diketones is due to the difficulty in obtaining the product in anhydrous form.⁹ In general, the β -diketone chelates are obtained in hydrated form, in which the water molecules act as effective luminescence quenchers due to the OH oscillators. A convenient way to improve the light emission properties of lanthanide β -diketones is the substitution of water molecules in the coordination shell with neutral donor ligands (second ligand). The exclusion of water molecules and judicious choice of ligands can minimize the deactivation of lanthanide ion excited state by vibronic modes. Ligands such as 2,2'-bipyridyl (bpy) and 1,10-phenanthroline (phen) are amongst the commonly used ones.¹⁰

According to the energy transfer and intramolecular energy mechanism,^{11,12} upon irradiation of ultraviolet light (UV), the organic ligand of the lanthanide complex is excited from ground state (S_0) to a vibrational level of the first excited singlet state (S_1). There are three possibilities. Firstly, the molecule undergoes fast internal

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conversion to lower vibrational levels of the S_1 state. Secondly, S_1 can be deactivated radiatively to the S_0 (molecular luminescence) and finally, the molecule can undergo non-radiative intersystem crossing from the S_1 to the triplet state (T_1). The T_1 can either be deactivated radiatively to the S_0 by the spin-forbidden transition $T_1 \rightarrow S_0$ (molecular phosphorescence) or undergo a non-radiative transition from the T_1 to an excited state of the lanthanide ion.¹²

Nowadays, many studies have been done on the luminescence properties of europium (Eu), terbium (Tb) and ytterbium (Yb) by varying the first and second ligand.^{13–15} These lanthanide ions are frequently reported due to the intense emission peak in photoluminescence with narrow spectral band and theoretical quantum yield of 100%.¹⁶ For Samarium (Sm), the emission is weaker than europium due to the smaller difference in the energies of the first excited state $^4G_{5/2}$ and the nearest lower-lying level $^6F_{11/2}$, thus nonradiative deactivation most probably will happen.¹⁷ The Sm(III) can exhibit high color purity and known as reliable luminescent sources, with emission peaks of green (565nm), orange (605 nm) and red (643 nm). The selectivity of the appropriate ligand will significantly increase the luminescence properties of the Samarium. Hence, the properties of coordination complexes of Sm(III) are worth investigating.

2. Experimental

All syntheses were carried out with commercially available reagents and were used as received. All measurements were performed in ambient condition unless stated. The elemental (CHN) analysis of all complexes was carried out with Perkin Elmer 2400 Series II elemental analyser. The infrared absorption spectra were recorded using Perkin Elmer System 2000 FT-IR. The spectra of the complexes and free ligands in KBr pellets were recorded in the range of 400 – 4000 cm^{-1} . Thermogravimetric analysis was carried out using Perkin Elmer thermogravimetric analyser (TGA/SDTA^e, METTLER TOLEDO). Samples for TGA were weighed in the range of 15–20 mg and were heated at 20°C/min for the range of 30–900°C in the nitrogen atmosphere. The luminescence spectra were recorded with Perkin Elmer LS55. The configuration was set at 15 nm and 20 nm for excitation and emission slit widths, respectively, 1% attenuator emission filter for all complexes. Complexes dissolved in DMSO (0.01 mol/L) were used for the analysis. The spectra were recorded using 418 nm as excitation wavelength and emission in the range of 500 to 700 nm.

2.1 Synthesis

2.1a Synthesis of $[Sm(dbm)_3(phen)](1)$: In a three-neck round bottom flask, dibenzoylmethane (0.673 g, 3 mmol) and phen (0.198 g, 1 mmol) were dissolved in hot methanol (20 mL). To the solution mixture, 3 mL of sodium hydroxide (0.1 M) was added. The temperature of the reaction mixture was maintained at 50–60°C in which then $Sm(NO_3)_3 \cdot 6H_2O$ (0.445 g, 1 mmol) in methanol (20 mL) was added dropwise with stirring for 30 min. After two hours, the reaction mixture was cooled to room temperature and the resulting precipitate was filtered using vacuum filtration, washed with distilled water and cold ethanol. The product was air dried overnight. Yield: 0.252 g, 40%. Anal. Calc. for $C_{57}H_{41}N_2O_6Sm$: C, 68.44%; H, 4.13%; N, 2.80%. Found: C, 68.50%; H, 3.83%; N, 2.71%. IR (cm^{-1}): 3056w, 1593s, 1548s, 1518s, 1478s, 1456m, 1411s, 1308w, 1308w, 1220w, 722m.

2.1b Synthesis of $[Sm(dbm)_3(4,7-dmphen)](2)$: The preparation was similar to **1** except that 4,7-dimethylphenanthroline (0.208 g, 1 mmol) was used instead of phen. White product was dissolved in a mixture of DMSO/DMF (10 mL, 50/50 v/v) and left for slow evaporation. Colorless crystals of **2** were obtained after a month. Yield: 0.855 g, 25%. Anal. Calc. for $C_{59}H_{45}N_2O_6Sm$: C, 68.91%; H, 4.41%; N, 2.72%. Found: C, 68.85%; H, 4.35%; N, 2.78. IR (cm^{-1}): 3057w, 1595s, 1549s, 1519s, 1478s, 1458m, 1412s, 1221w, 1067w, 721m.

2.1c Synthesis of $[Sm(dbm)_3(tmphen)](3)$: The preparation was similar to **1** except that 3,4,7,8-tetramethylphenanthroline (0.236 g, 1 mmol) was used instead of phen. Yield: 0.090 g, 26%. Anal. Calc. for $C_{61}H_{49}N_2O_6Sm$: C, 69.35%; H, 4.68%; N, 2.65%. Found: C, 69.35%; H, 4.28%; N, 2.64%. IR (cm^{-1}): 3056w, 1593s, 1549s, 1518s, 1478s, 1459m, 1413s, 1308w, 1218w, 1067w, 1024w, 723m.

2.1d Synthesis of $[Sm(dbm)_3(dpphen)](4)$: The preparation was similar to that for **1** except that 4,7-diphenylphenanthroline (0.208 g, 1 mmol) was used instead of phen. Yield: 0.088 g, 26%. Anal. Calc. for $C_{69}H_{49}N_2O_6Sm$: C, 71.91%; H, 4.29%; N, 2.43%. Found: C, 70.46%; H, 3.76%; N, 2.53%. IR (cm^{-1}): 3059w, 1594s, 1549s, 1518s, 1478s, 1457m, 1410s, 1309w, 1219w, 723m.

2.1e Synthesis of $[Sm(dbm)_3(bpy)](5)$: In a three-neck round bottom flask, dibenzoylmethane (0.673 g, 3 mmol) and 2,2-bipyridyl (0.156 g, 1 mmol) were dissolved in

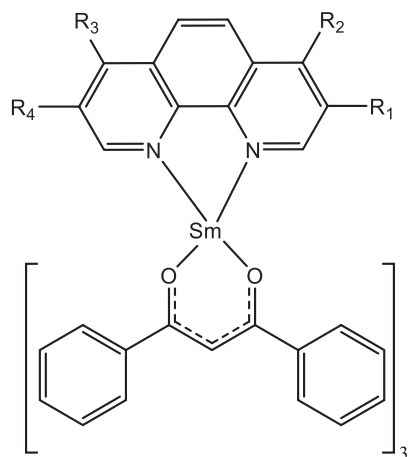
hot ethanol (20 mL). To the solution mixture, 3 mL of sodium hydroxide (0.1 M) was added. The temperature of the reaction mixture was maintained at 50-60°C in which then $\text{Sm}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (0.445 g, 1 mmol) in methanol (20 mL) was added dropwise with stirring for 30 min. After two hours, the reaction mixture was cooled to room temperature and the resulting precipitate was filtered using vacuum filtration, washed with distilled water and followed by cold ethanol. The product was air dried overnight. Yield: 0.331 g, 45%. Anal. Calc. for $\text{C}_{55}\text{H}_{41}\text{N}_2\text{O}_6\text{Sm}$: C, 67.66%; H, 4.23%; N, 2.87%. Found: C, 68.61%; H, 3.98%; N, 2.65%. IR (cm^{-1}): 3059w, 1594s, 1547s, 1518s, 1478s, 1458m, 1408s, 1309w, 1220w, 1066w, 718m.

2.1f *Synthesis of [Sm(dbm)₃(4,4-dmbpy)] (6)*: The preparation was similar to **5** except that 4,4'-dimethyl-2,2'-bipyridyl (0.218 g, 1 mmol) was used instead of bpy. The product was dissolved in a mixture of DMSO/DMF (10 mL, 50/50 v/v) and left for slow evaporation. Colorless crystals of **6** were obtained after a month. Yield:

0.082 g, 25%. Anal. Calc. for $\text{C}_{57}\text{H}_{45}\text{N}_2\text{O}_6\text{Sm}$: C, 68.12%; H, 4.48%; N, 2.79%. Found: C, 67.96%; H, 4.14%; N, 2.76%. IR (cm^{-1}): 3059w, 1595s, 1550s, 1518s, 1478s, 1458m, 1413s, 1306w, 1220w, 1068w, 724m.

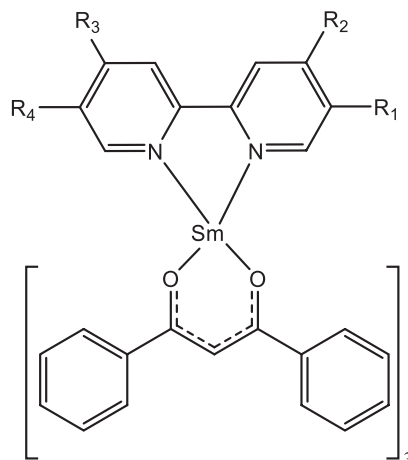
2.1g *Synthesis of [Sm(dbm)₃(5,5-dmbpy)] (7)*: The preparation was similar to **5** except that 5,5'-dimethyl-2,2'-bipyridyl (0.218 g, 1 mmol) was used instead of bpy. The product was dissolved in a mixture of DMSO/DMF (10 mL, 50/50 v/v) and left for slow evaporation. Colorless crystals of **7** were obtained after a month. Yield: 0.095 g, 27%. Anal. Calc. for $\text{C}_{57}\text{H}_{45}\text{N}_2\text{O}_6\text{Sm}$: C, 68.12%; H, 4.48%; N, 2.79%. Found: C, 68.33%; H, 4.17%; N, 2.65%. IR (cm^{-1}): 3059w, 1594s, 1550s, 1519s, 1478s, 1458m, 1414s, 1309w, 1220w, 1023w, 725m.

2.1h *Synthesis of [Sm(dbm)₃(4,4-dtbbpy)] (8)*: The preparation was similar to **5** except that 4,4'-di-tert-butyl-2,2'-bipyridyl (0.268 g, 1 mmol) was used instead of



Scheme 1. Schematic diagram for the synthesized complexes **1** – **4**.

- 1** = $\text{R}_1 = \text{R}_2 = \text{R}_3 = \text{R}_4 = \text{H}$
- 2** = $\text{R}_2 = \text{R}_3 = \text{CH}_3$; $\text{R}_1 = \text{R}_4 = \text{H}$
- 3** = $\text{R}_1 = \text{R}_2 = \text{R}_3 = \text{R}_4 = \text{CH}_3$
- 4** = $\text{R}_2 = \text{R}_3 = \text{C}_6\text{H}_5$; $\text{R}_1 = \text{R}_4 = \text{H}$



Scheme 2. Schematic diagram for the synthesized complexes **5** – **8**.

- 5** = $\text{R}_1 = \text{R}_2 = \text{R}_3 = \text{R}_4 = \text{H}$
- 6** = $\text{R}_2 = \text{R}_3 = \text{CH}_3$; $\text{R}_1 = \text{R}_4 = \text{H}$
- 7** = $\text{R}_1 = \text{R}_4 = \text{CH}_3$; $\text{R}_2 = \text{R}_3 = \text{H}$
- 8** = $\text{R}_2 = \text{R}_3 = t\text{-Bu}$; $\text{R}_1 = \text{R}_4 = \text{H}$

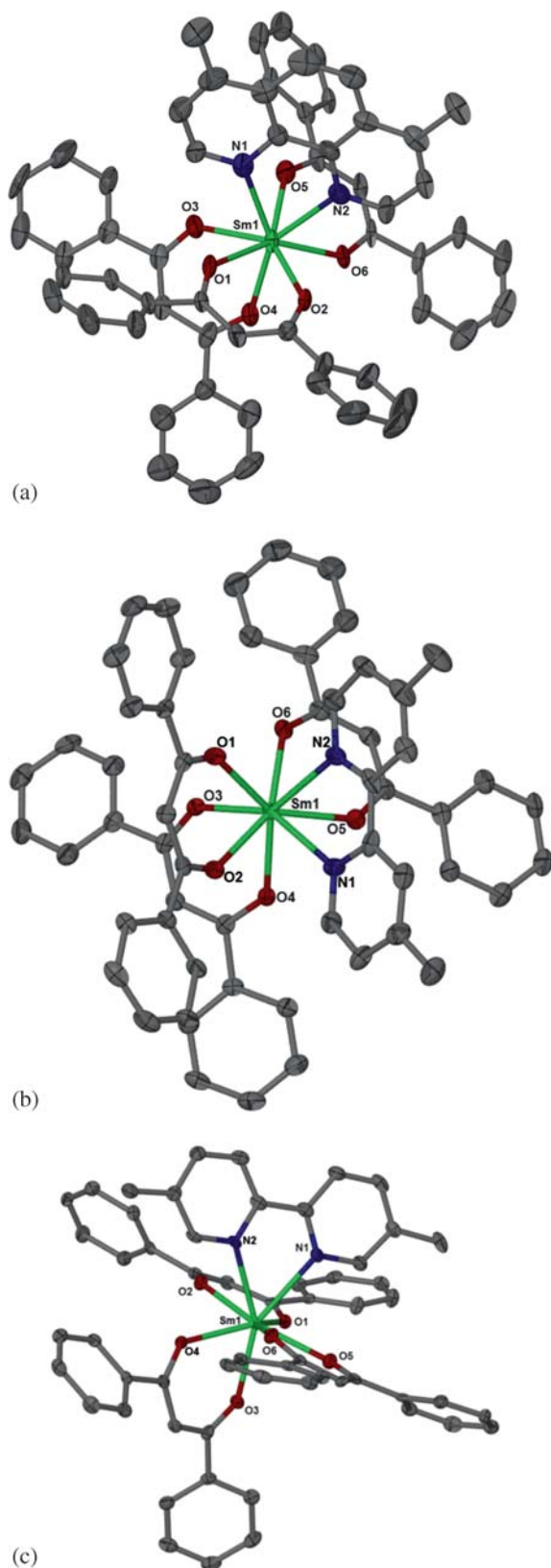


Figure 1. Molecular structures of, (a) $[\text{Sm}(\text{dbm})_3(4,7\text{-dmphen})]$ (**2**), (b) $[\text{Sm}(\text{dbm})_3(4,4\text{-dmpy})]$ (**6**) and (c) $[\text{Sm}(\text{dbm})_3(5,5\text{-dmbpy})]$ (**7**) with ellipsoids shown at 50% probability. Hydrogen atoms are omitted for clarity.

bpy. Yield: 0.087 g, 25%. Anal. Calc. for $\text{C}_{65}\text{H}_{57}\text{N}_2\text{O}_6\text{Sm}$: C, 69.52%; H, 5.28%; N, 2.57%. Found: C, 72.41%; H, 5.61%; N, 3.13%. IR (cm^{-1}): 3059w, 2963w, 1595s, 1548s, 1516s, 1458m, 1410s, 1304w, 1220w, 1023w, 741m.

2.2 Crystallographic details

Crystals were mounted on fine glass fibre using viscous hydrocarbon oil. Data were collected on Oxford CrysAlis Pro, equipped with graphite monochromated Mo-K α ($\lambda = 0.71073 \text{ \AA}$). Data collection temperatures were maintained at 100 K using open flow N_2 cryostreams. Data collection and processing was carried by the CrysAlis^{Pro} software.

Solutions were obtained by direct methods using SHELXS 97, followed by successive refinements using full matrix least squares method against F^2 using SHELXL 97.¹⁸ The program X-seed was used as graphical SHELX interface.¹⁹

2.2a $[\text{Sm}(\text{dbm})_3(4,7\text{-dmphen})]$ (**2**): $\text{C}_{59}\text{H}_{45}\text{N}_2\text{O}_6\text{Sm}$: $M = 1029.93$, colorless, $0.50 \times 0.30 \times 0.20 \text{ mm}^3$, monoclinic, $P2_1/n$, $a = 12.5315(10)$, $b = 19.113(2)$, $c = 19.993(2)$, $\hat{a} = 90$, $\hat{a} = 98.934(8)$, $\hat{a} = 90$, $V = 4730.6(8)$, $Z = 4$, $\tilde{n}_{\text{calc}} = 1.446 \text{ g cm}^{-3}$, $F_{000} = 2096$, 25440 reflections collected, 8385 unique ($R_{\text{int}} = 0.1066$), Final $\text{GooF} = 1.159$, $RI = 0.1177$, $wR2 = 0.2121$, R indices based on 6034 reflections with $I > 2\sigma(I)$, 615 parameters, 0 restraints, $\mu = 1.297$.

2.2b $[\text{Sm}(\text{dbm})_3(4,4\text{-dmbpy})]$ (**6**): $\text{C}_{57}\text{H}_{45}\text{N}_2\text{O}_6\text{Sm}$: $M = 1004.31$, colorless, $0.50 \times 0.40 \times 0.30 \text{ mm}^3$, orthorhombic, $Pbca$, $a = 19.1810(8)$, $b = 20.1166(8)$, $c = 24.1827(8)$, $\hat{a} = 90$, $\hat{a} = 90$, $\hat{a} = 90$, $V = 9331.1(6)$, $Z = 8$, $\tilde{n}_{\text{calc}} = 1.430 \text{ g cm}^{-3}$, $F_{000} = 4088$, 51314 reflections collected, 10767 unique ($R_{\text{int}} = 0.0626$), Final $\text{GooF} = 1.044$, $RI = 0.0427$, $wR2 = 0.0946$, R indices based on 7590 reflections with $I > 2\sigma(I)$, 597 parameters, 0 restraints, $\mu = 1.313$.

2.2c $[\text{Sm}(\text{dbm})_3(5,5\text{-dmbpy})]$ (**7**): $\text{C}_{57}\text{H}_{45}\text{N}_2\text{O}_6\text{Sm}$: $M = 1004.36$, colorless, $0.35 \times 0.25 \times 0.05 \text{ mm}^3$, monoclinic, $P2_1/n$, $a = 13.7841(6)$, $b = 18.7636(10)$, $c = 17.5332(9)$, $\hat{a} = 90$, $\hat{a} = 91.429(5)$, $\hat{a} = 90$, $V = 4533.4(4)$, $Z = 4$, $\tilde{n}_{\text{calc}} = 1.474 \text{ g cm}^{-3}$, $F_{000} = 2044$, 36887 reflections collected, 10482 unique ($R_{\text{int}} = 0.0680$), Final $\text{GooF} = 1.042$, $RI = 0.0415$, $wR2 = 0.0798$, R indices based on 7630 reflections with $I > 2\sigma(I)$, 597 parameters, 0 restraints, $\mu = 1.352$.

3. Results and Discussion

3.1 Synthesis and crystal structure

Reaction of $\text{Sm}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, dibenzoylmethane and bidentate *N*-donor ligand in 1:3:1 molar ratio in the presence of NaOH afforded the formation of eight coordinated Sm(III) complexes namely $[\text{Sm}(\text{dbm})_3(\text{phen})]$ (**1**), $[\text{Sm}(\text{dbm})_3(4,7\text{-dmphen})]$ (**2**), $[\text{Sm}(\text{dbm})_3(\text{tmphen})]$ (**3**), $[\text{Sm}(\text{dbm})_3(4,7\text{-dpphen})]$ (**4**), $[\text{Sm}(\text{dbm})_3(\text{bpy})]$ (**5**), $[\text{Sm}(\text{dbm})_3(4,4\text{-dmbpy})]$ (**6**), $[\text{Sm}(\text{dbm})_3(5,5\text{-dmbpy})]$ (**7**) and $[\text{Sm}(\text{dbm})_3(4,4\text{-dtbbpy})]$ (**8**). Structure for complex **1**, however has been reported and known to be the first crystal structure of this kind of molecule.²⁰ Similar compound was prepared in this current work in order to investigate and compare the luminescence properties for the entire series. Colorless crystals of **2**, **6** and **7** suitable for single crystal X-ray diffraction were obtained by slow evaporation in a mixture of DMSO/DMF. Attempts to obtain crystals for other complexes were unsuccessful although similar reaction procedure was repeated. Even though no crystal structures were obtained for complexes **3**, **4**, **5** and **8**, other characterization methods used in this work such as IR and elemental analyses data support the formation of the proposed complexes. While the crystal structure of **1** is known, we propose that the structure of **3**, **4**, **5** and **8** having similar arrangement of atoms as those in **2**, **6** and **7** with the only difference being the type of bidentate *N*-donor ligand that was used in each reaction procedure (schemes 1 and 2). In addition, the formation of **1** also confirmed via unit cell determination of the single crystal that is similar to those reported structure.

3.2 Crystal structure

Compounds $[\text{Sm}(\text{dbm})_3(4,7\text{-dmphen})]$ (**2**) and $[\text{Sm}(\text{dbm})_3(5,5\text{-dmbpy})]$ (**7**) crystallise in the monoclinic space group $P2_1/n$ while complex $[\text{Sm}(\text{dbm})_3(4,4\text{-dmbpy})]$ (**6**) crystallises in orthorhombic space group $Pbca$ with the entire molecule in the asymmetric unit (figures 1a, 1b and 1c). In all the complexes, Sm(III) adopted square antiprism geometry in which the metal center is surrounded by six oxygen atoms of three dbm ligands and two nitrogen atoms of the co-ligand. In the absence of potential hydrogen bonding donor, the supramolecular interaction of these metal complexes is dominated by $\pi - \pi$ interaction between phenyl rings either with face-to-face or edge-to-face interactions.^{21,22} Such an example

Table 1. Selected bond lengths [Å] and angles [°] for **2**, **6** and **7**.

	2	6	7
Sm1-O1	2.297(3)	2.331(3)	2.242(5)
Sm1-O2	2.319(3)	2.345(2)	2.353(3)
Sm1-O3	2.319(3)	2.353(2)	2.342(3)
Sm1-O4	2.325(3)	2.362(2)	2.377(3)
Sm1-O5	2.330(3)	2.369(2)	2.359(3)
Sm1-O6	2.332(3)	2.414(3)	2.376(3)
Sm1-N1	2.537(4)	2.600(3)	2.609(3)
Sm1-N2	2.567(4)	2.619(3)	2.625(3)
O5 Sm1 O2	147.7(3)	136.16(10)	100.16(9)
O2 Sm1 O3	137.7(3)	86.05(10)	149.06(8)
O2 Sm1 O4	80.2(3)	73.08(10)	138.55(8)
O3 Sm1 O6	120.6(3)	74.33(10)	129.85(8)
O4 Sm1 O1	63.3(12)	138.82(10)	148.34(8)
O6 Sm1 N1	132.3(3)	133.06(11)	141.49(9)
O5 Sm1 N2	78.3(3)	78.93(3)	151.92(9)

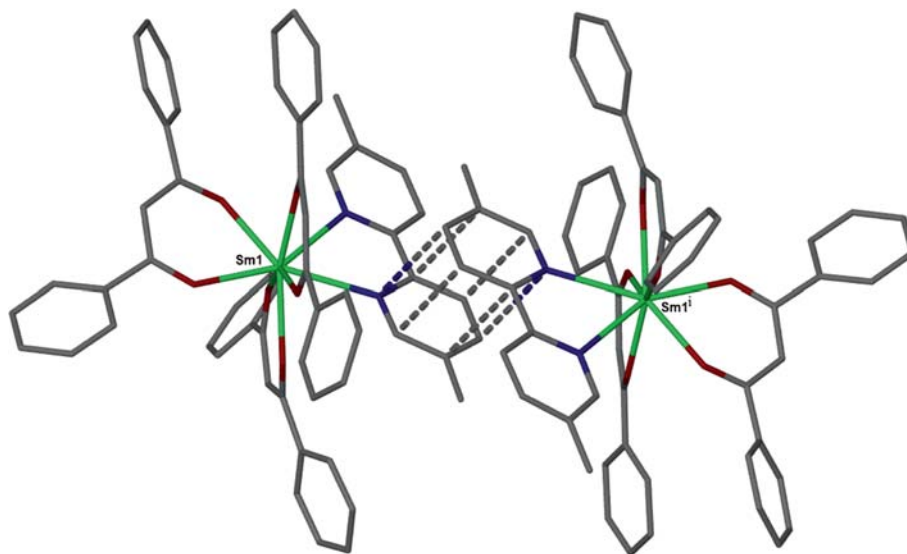


Figure 2. The face-to-face $\pi - \pi$ interaction (back to back) between two phenyl rings in **7** and the distance between two centroids is 3.582(6) Å.

is illustrated in complex **7** with significant face-to-face $\pi - \pi$ interaction of two adjacent molecules (back to back) with the separation being 3.582(6) Å (figure 2). The average distance of Sm-O and Sm-N bond lengths for **2**, **6** and **7** are relatively similar to one another, in agreement with those reported before (table 1).^{23–25}

3.3 Thermal properties of Sm(III) complexes

The thermogram for all Sm(III) complexes shows that all the complexes are thermally stable as the decomposition process occurs critically at temperature more than 300°C (table 2). The number of steps for decomposition of each complex is different. Compounds **1** and **4** show three steps of decomposition while **3** shows two steps of decomposition. Complexes **6** and **7** show five steps of decomposition while **5** and **8** show four steps of decomposition. Complex **2** shows most steps of

decomposition which is six. The TGA-DTG curve of **2** shows a small weight loss in the first and second steps of decomposition in the range of 0.4819% to 2.2149% from 31.43°C to 251.65°C while **4**, **6** and **7** show a small weight loss in the first step only in the range of 1.1077% to 2.1147% from 31.30°C to 210.55°C, that could be due to the loss of entrapped solvent molecules.²⁶ Compounds **1**, **3**, **5** and **8** show a large weight loss in the first step in the range of 21.6375% to 55.6736% from 31.30°C to 524.87°C. Compounds **4**, **6** and **7** experience large weight loss in their second step, about 18.1674% to 57.3702% from 109.04°C to 510.44°C while **2** undergoes a large weight loss of 29.6460% from 251.65°C to 476.55°C. The large weight loss in the range of 250°C to 600°C could be caused by the decomposition of organic ligands.²⁷ This observation is due to scission of first ligand (dbm) into smaller fragments which then is followed by the scission of phen or bpy derivatives into smaller fragments.

Table 2. Temperature range, percentage of weight loss, residue and critical degradation temperature (CDT) for **1–8**.

Compounds	Stage	Temp. Range (°C)	Weight loss(%)	Residue (%)	CDT(°C)
1	1	31.30 – 492.46	55.6736	44.3392	442
	2	492.46 – 542.22	7.6098	36.7293	
	3	542.22 – 907.43	19.0629	17.6664	
2	1	31.43 – 140.33	0.4819	99.5562	410
	2	140.33 – 251.65	2.2149	97.3413	
	3	251.65 – 476.55	29.6460	67.6953	
	4	476.55 – 537.52	4.2522	63.4431	
	5	537.52 – 614.11	7.5911	55.8519	
	6	614.11 – 906.61	7.1121	48.7389	
3	1	31.49 – 524.87	47.4813	52.5296	430
	2	524.87 – 907.50	19.2189	33.3107	
4	1	31.40 – 175.77	2.1147	97.9544	450
	2	175.77 – 510.04	57.3702	40.5842	
	3	510.04 – 907.03	21.5272	19.0570	
5	1	31.40 – 347.94	21.6375	78.3659	435
	2	347.94 – 485.20	31.7429	46.6230	
	3	485.20 – 530.78	5.5225	41.1004	
	4	530.78 – 906.42	14.7562	26.3443	
6	1	31.37 – 166.20	1.2571	8.7573	420
	2	166.20 – 363.63	20.3260	78.4313	
	3	363.63 – 502.44	36.6647	42.7666	
	4	502.44 – 545.95	5.8348	36.9318	
	5	545.95 – 906.59	12.4156	24.5162	
7	1	131.43 – 210.55	1.6866	98.3099	440
	2	210.55 – 380.55	23.5001	74.8097	
	3	380.55 – 500.86	36.5018	38.3079	
	4	500.86 – 547.90	7.3124	30.9955	
	5	547.90 – 906.79	10.8408	20.1548	
8	1	31.62 – 382.91	47.5890	52.3666	435
	2	382.91 – 487.81	29.4404	22.9262	
	3	487.81 – 541.78	7.2201	15.7060	
	4	541.78 – 901.17	15.0390	0.6671	

Table 3. Emission intensity of **1-8** and values of ΔE .

Complexes	Intensity	Triplet energy state (cm^{-1})	ΔE (${}^3\pi\pi^* \rightarrow {}^4G_{5/2}$)
[Sm(dbm) ₃ H ₂ O]	50.8	20250	2520
1	253.59	22880	4880
2	90.36	21551	3551
3	93.61	21691	3691
4	83.28	20900	2900
5	126.54	22300	4300
6	70.5	–	–
7	99.5	–	–
8	101.3	–	–

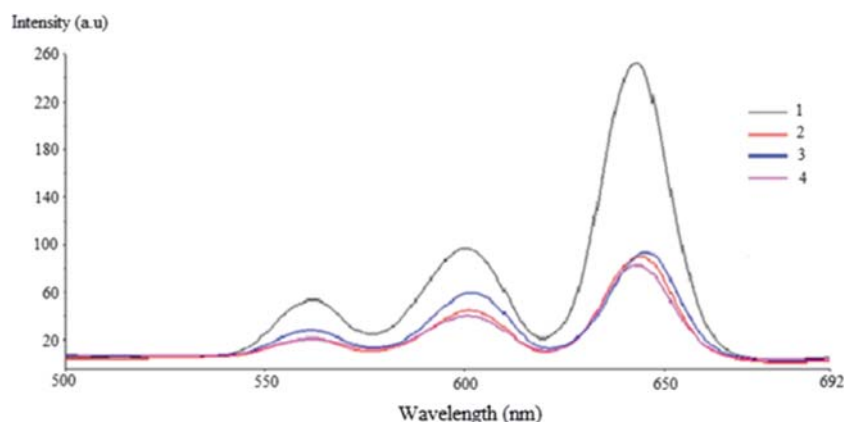
3.4 Luminescence properties of Sm(III) complexes

Generally Samarium(III) is known for weak luminescence due to a very weak absorption of light (small Å).²⁸ However, a suitable organic ligand that coordinates to Sm(III) will increase the luminescence of this element through the transfer of the intramolecular energy from the triplet energy state of the organic ligand to the excited $4f$ states of the Sm(III). According to the intramolecular energy transfer mechanism,^{29,30} energy transfer efficiency depends on two processes. Firstly, energy transfer from lowest triplet energy state of the ligand to the emissive energy level of the Ln(III) by Dexter's resonance exchange interaction.^{31,32} Secondly, inverse energy transfer from Ln(III) ion to the organic ligand by a thermal deactivation mechanism.³³ Small energy difference (ΔE) between triplet excited state of the ligand and excited state of Ln(III) ion will result in back energy transfer.³⁴

From our work, orange luminescence was observed for Sm(III) ternary complexes, **1** - **8**. Due to the difficulty to compare the emission intensities between solid samples, since intensity depends on the grinding and homogeneity of the sample, all the spectra were measured by using solution in DMSO (0.01 mol/L).

The Sm(III) complexes shows emission bands at 565 nm, 605 nm and 643 nm which can be assigned to ${}^4G_{5/2} \rightarrow {}^6H_J$ transitions, where $J = 5/2, 7/2$ and $9/2$, respectively. However, the transition of ${}^4G_{5/2} \rightarrow {}^6H_{9/2}$ is the most dominant.³⁵ All the ternary complexes have a higher intensity compared to [Sm(dbm)₃H₂O]³⁶ (table 3). This result indicated that the addition of second ligand in the form of N, N' -type bidentate ligand will enhance the emission intensity of the complexes.

For phen and its derivative, the emission intensity decreased in the order **1**>**3**>**2**>**4** (figure 3) while for bpy and its derivatives, the intensity decreased in the order **5**>**8**>**7**>**6** (figure 4). In order to explain the difference between the emission intensity of ternary Sm(III) complexes, the energy difference between the triplet energy levels and the excited state of Sm(III) is calculated. From the literature, the excited state energy of Sm(III) ion is 18000 cm^{-1} .^{37,38} The triplet excited energy state of free ligands are: dbm (20520 cm^{-1}),³⁹ phen (22880 cm^{-1}),⁴⁰ bpy (22300 cm^{-1}),⁴¹ dmphen (21551 cm^{-1}),⁴² tmphen (21691 cm^{-1}),⁴² dpphen (20900 cm^{-1})⁴⁰, respectively. There is no data for triplet energy state for 4,4-dmbpy, 5,5-dmbpy and 4,4-dtbbpy. The triplet energy of all ligands is higher than the excited energy state of Sm(III) which then

**Figure 3.** Luminescence spectra for **1-4** in DMSO (0.01 mol/L).

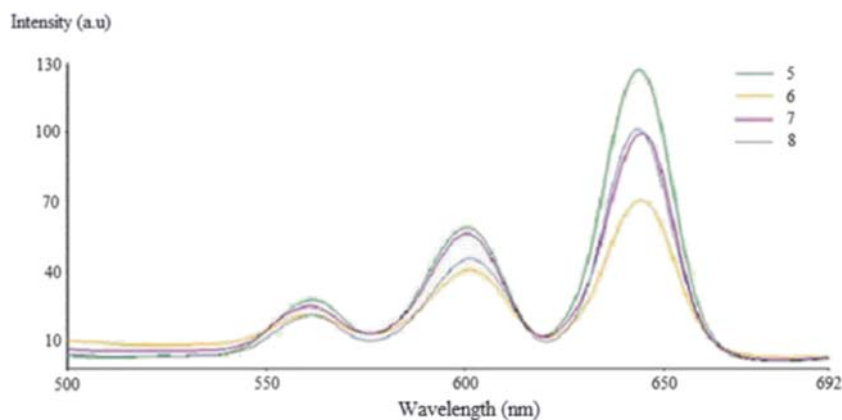


Figure 4. Luminescence spectra for **5-8** in DMSO (0.01 mol/L).

results in the luminescence emission. The ΔE (${}^3\pi\pi^* \rightarrow {}^4G_{5/2}$) calculated for each second ligand is phen (4880 cm^{-1}), bpy (4300 cm^{-1}), tmphen (3691 cm^{-1}), dmphen (3551 cm^{-1}) and dpphen (2900 cm^{-1}). The trend in the ΔE is in good concordance with the difference in the emission intensity of the complexes. It can be deduced that the emission intensity is proportional to the ΔE . Although there is no data for triplet energy state of 4,4-dmbpy, 5,5-dmbpy, 4,4-dtbbpy, but from the trend of phen derivatives, the addition of alkyl group to the ring may decrease the excited triplet state of the ligands and result in the low emission intensity.

4. Conclusions

A series of Sm(III) ternary complexes were synthesized and fully characterized. Crystal structure of **2**, **6** and **7** were determined and Sm(III) shows a square antiprism geometry in all the complexes. Crystal structure analysis indicates that without potential hydrogen bonding acceptor and donor sites, π - π interaction between the adjacent molecules play an important role in stabilizing the structure. Luminescence studies show that under excitation at 418 nm all Sm(III) ternary complexes emit characteristic orange luminescence and the strongest emission is at 643 nm which can be assigned to ${}^4G_{5/2}$ to ${}^6H_{9/2}$ transition. For phen and its derivative, the emission intensity decreased in the order of **1** > **3** > **2** > **4** while for bpy and its derivatives, the intensity decreased in the order of **5** > **8** > **7** > **6**.

Supplementary Information

CCDC 1062168-1062170 contain supplementary crystallographic data for **2**, **6** and **7**. These data can be

obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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