Ln(III) complexes as potential phosphors for white LEDs

Akerboom, S.

6 Triboluminescence of lanthanoid dibenzoylmethanates

A series of lanthanoid coordination compounds with the general formula $HNEt_3[Ln(dbm)_4]$ (Ln = La, Nd, Sm, Eu, Tb, Dy, Ho, Er, Tm, Yb; dbm = dibenzoylmethanate) has been prepared and characterized. Single crystals with Ln = La, Nd and Sm were obtained. Single crystal X-ray diffraction studies reveal that the compounds with Ln = La, Nd crystallize in the space group $P2_1/c$, while the Sm-compound crystallizes in the space group Pc. Based on powder XRD data, the compounds with Ln = Eu - Yb can be described with a monoclinic cell. Photoluminescence studies show that compounds with Ln = Sm, Eu exhibit bright photoluminescence characteristic of the lanthanoid ion upon excitation in the near UV range. Furthermore, $HNEt_3[Sm(dbm)_4]$ has been identified as a novel triboluminescent compound.

(The work in this chapter has been published:
S. Akerboom, M. Meijer, M.A. Siegler, W.T. Fu, E. Bouwman, *J. Lumin.* 145 (2014) 278).

6.1 Introduction

Since the 1950s, molecules based on the beta-diketone structural motif have been found to be good ligands for *Ln*(III) ions, giving rise to stable complexes [1]. The chemical and physical properties of these complexes have been reviewed extensively by Binnemans [2]. When deprotonated, the beta-diketone molecules are monoanionic and, in principle, three ligands are needed to compensate for the charge of the *Ln*(III) ion, giving rise to a neutral complex. In such complexes, the coordination number of the metal is 6, while the lanthanoids normally prefer a higher coordination number, typically 8 or 9 [3, 4]. As a result, the coordination sphere in these complexes is usually saturated by coordination of solvent molecules to the lanthanoid ion, examples include $[Eu(ttfa)_3(H_2O)_2]$, $[Eu(aftfbd)_3(H_2O)_2]$ and $[Eu(ttfa)_3(DMSO)_2]$ (Httfa = 1-(2-thienyl)-4,4,4-trifluoro-1,3-butanedione, Haftbd = (2-acetylfluorene)-4,4,4-trifluoro-1,3-butanedione) [5-7]. These solvent molecules can be replaced by another chelating neutral ligand, such as 1,10-phenanthroline or 2,2'-bipyridine [6, 8, 9]. It is however possible to prepare homoleptic *Ln*(III) complexes with four beta-diketone type ligands when the appropriate conditions are employed during synthesis. As the resulting complex will be monoanionic, a counter ion is needed. Lanthanoid complexes with beta-diketones have interesting photophysical properties, including photoluminescence, laser action and electroluminescence [7, 8, 10-14]. These are a result of the so-called 'antenna-effect', in which the ligand is capable of transferring energy of its excited state to an excited state of the lanthanoid ion. This mechanism provides efficient sensitization of the lanthanoid ion, as direct intra-4f transitions are parity- and often spin forbidden. In 1966, Hurt *et al.* reported that $HNEt_3[Eu(dbm)_4]$ (Hdbm = dibenzoylmethane) exhibits intense luminescence, characteristic of Eu(III), upon fracture of the crystals, a phenomenon known as *triboluminescence* (TrL) [15]. The word derives from the Greek *tribein*, meaning 'to rub' [16]. For the analogous Tb(III) complex, only very weak triboluminescence was observed. Triboluminescence has also been reported for (2-hydroxyethylammonium)$[Eu(dbm)_4]$ and (pyrrolidinium)$[Eu(dbm)_4]$ by Xiong *et al.*[17] and for $[Tb(tmhd)_3$(4-(dimethylamino)pyridine)] (Htmhd = 2,2,6,6-tetramethyl-3,5-heptanedione) and its Sm(III) analog [18]. In these compounds, the luminescence spectrum is characteristic for the lanthanoid ion in the complex. Bulgakov and co-workers have studied triboluminescence for the entire series $[Ln(acac)_3(H_2O)]$, *Ln* = Ce, Pr, Eu, Gd, Tb, but only for the Eu and Tb compounds the TrL spectrum shows emission by the lanthanoid ion [19]. For the other compounds, the TrL-spectra correspond to the $^3\Pi_u$-$^3\Pi_g$ transitions of N_2*. The authors explain the TrL phenomenon as arising from adsorbed molecules of dinitrogen. Excitation of adsorbed dinitrogen molecules can in turn be explained by the generation of an electric field upon fracture of the crystals [18, 19]. In the past, it has often been claimed that noncentrosymmetric crystals are a prerequisite for TrL to occur [20]. Cracking such materials would lead to the buildup of opposite charge on the opposing crystal faces at

voltages high enough to allow for gas discharge. In triboluminescent lanthanoid complexes, the resulting emission can be absorbed by the ligands. Indeed, experiments with Gd(III) complexes show TrL characteristic for the ligand, suggesting that the ligand is acting as an energy-harvesting antenna [21]. As of to date, the compound described by Hurt is still the compound with highest TrL intensity [22]. The present Chapter concerns a systematic investigation of the photo- and triboluminescent properties of some lanthanoid analogues of $HNEt_3[Eu(dbm)_4]$.

6.2 Experimental

6.2.1 General

C, H, N analysis was performed using a Perkin-Elmer 2400 series II analyzer. X–ray powder diffraction was performed on a Philips X'pert diffractometer equipped with an X'cellerator detector. A Perkin-Elmer Spectrum Two FTIR spectrometer equipped with the UATR Two accessory was used to record IR spectra. Photoluminescence spectra were recorded on a Shimadzu RF-5301PC spectrofluoriphotometer. Triboluminescence spectra were recorded using an irradiance calibrated Avantes AvaSpec ULS2048L CCD spectrometer connected to a quartz cuvette holder. The spectrometer was controlled by the AvaSoft 7.7 software, which was programmed to record and save a spectrum every 40 ms while the sample was being crushed in the cuvette using a stainless steel spatula.

6.2.2 Crystal structure determination

Single crystal X-ray diffraction measurements were performed on crystals of [**1**], [**2**] and [**3**]. All reflection intensities were measured at 110(2) K ([**1**] and [**2**]) or 190(2) K ([**3**]) using a SuperNova diffractometer equipped with Atlas detector with Mo-Kα ([**1**], λ = 0.71073 Å) or Cu-Kα ([**2**] and [**3**], λ = 1.5418 Å) radiation (mirror optics) under the program CrysAlisPro (Version 1.171.36.24 Agilent Technologies, 2012). The program CrysAlisPro was used to refine the cell dimensions and for data reduction. The structure was solved with the program SHELXS-97 and was refined on F^2 with SHELXL-97 [23, 24]. Analytical numeric absorption corrections based on a multifaceted crystal model were applied using CrysAlisPro. The temperature of the data collection was controlled using the system Cryojet, manufactured by Oxford Instruments. The H atoms, unless otherwise specified, were placed at calculated positions with isotropic displacement parameters having values 1.2 or 1.5 times *U*eq of the attached C atoms. The H atoms attached to the N atoms of the triethylammonium cations were found from Fourier difference maps, and their atomic coordinates and isotropic thermal factors were refined freely.

Unit cell dimensions of compounds [**4**] - [**10**] have been determined using the Le Bail extraction routine implemented in the Rietica program (version 1.77) [25, 26]. A six term polynomial was used to fit the background, and the peak profile was described by a pseudo-

Voigt function. Lattice refinements of compounds [**4**] - [**10**] were carried out in the space group *I2/a* that has been reported for [**4**] by Sweeting *et al.* in 1987 [20]. Note that the *I2/a* cell can be transformed to a *C2/c* cell, which is the standard setting for space group no. 15.

6.2.3 Synthesis

Lanthanoid chlorides were synthesized by stirring the respective oxides in an excess of concentrated hydrochloric acid at 90 °C in a round bottom flask equipped with a reflux condenser until clear solutions were obtained. Subsequently, the solutions were concentrated to a volume of approximately 10 mL by rotary evaporation, 35 mL of water was added and the resulting mixtures were concentrated *in vacuo* to give the salts as fine powders.

Compounds [**1**] to [**10**] were synthesized according to a general procedure. Hdbm (897 mg, 4.0 mmol) was dissolved in EtOH (10 mL) and NEt_3 (0.56 mL, 4.0 mmol) was added. The yellow solution was heated to 60 °C. The lanthanoid salt $Ln Cl_3 \cdot n H_2O$, assuming $n = 7$ for *Ln* = La, Pr and $n = 6$ for *Ln* = Nd - Yb, (1.0 mmol) was also dissolved in 10 mL EtOH and heated to 60 °C. The lanthanoid salt solution was added slowly to the solution containing the ligand, resulting in a suspension. The suspension was stirred at 60 °C for 2 hours, causing it to redissolve. The erlenmeyer flasks containing the mixtures were closed with a stopper and placed on a bench. Crystals began to appear within a few hours. After 1 day the crystals were collected on a P3 glass frit, washed with cold EtOH and dried in a vacuum oven at 40 °C for one day.

*$HNEt_3[La(dbm)_4]$ ([**1**])*

Starting from $LaCl_3 \cdot 7H_2O$ (371 mg, 1.00 mmol). This reaction mixture was stored at –20 °C for 10 days to promote crystal growth. The product is a pale yellow crystalline solid. Yield: 328 mg (0.29 mmol, 29%). Elemental analysis calcd (%) for $C_{66}H_{60}LaNO_8$ ($HNEt_3[La(dbm)_4]$): C 69.90, H 5.33, N 1.24; found: C 69.98, H 5.75, N 1.25.

*$HNEt_3[Nd(dbm)_4]$ ([**2**])*

Starting from $NdCl_3 \cdot 6H_2O$ (359 mg, 1.00 mmol); product is an orange crystalline solid. Yield: 730 mg (0.64 mmol, 64%). Elemental analysis calcd (%) for $C_{66}H_{60}NNdO_8$ ($HNEt_3[Nd(dbm)_4]$): C 69.56, H 5.31, N 1.23; found: C 69.51, H 5.67, N 1.55.

*$HNEt_3[Sm(dbm)_4]$ ([**3**])*

Starting from $SmCl_3 \cdot 6H_2O$ (365 mg, 1.00 mmol); product is a yellow crystalline solid. Yield: 584 mg (0.51 mmol, 51%). Elemental analysis calcd (%) for $C_{66}H_{60}NO_8Sm$ ($HNEt_3[Sm(dbm)_4]$): C 69.20, H 5.28, N 1.22; found: C 68.87, H 4.94, N 1.27.

*$HNEt_3[Eu(dbm)_4]$ ([**4**])*

Starting from $EuCl_3 \cdot 6H_2O$ (366 mg, 1.00 mmol); product is a yellow crystalline solid. Yield: 901 mg (0.79 mmol, 79%). Elemental analysis calcd (%) for $C_{66}H_{60}EuNO_8$ ($HNEt_3[Eu(dbm)_4]$): C 69.10, H 5.27, N 1.22; found: C 68.80, H 5.88, N 1.20.

*$HNEt_3[Tb(dbm)_4]$ ([**5**])*

Starting from $TbCl_3 \cdot 6H_2O$ (10 mL of a 0.1 M stock solution in ethanol); product is a yellow crystalline solid. Yield: 779 mg (0.67 mmol, 67%). Elemental analysis calcd (%) for $C_{66}H_{60}NO_8Tb$ ($HNEt_3[Tb(dbm)_4]$): C 68.69, H 5.24, N 1.21; found: C 68.67, H 5.66, N 1.23.

*$HNEt_3[Dy(dbm)_4]$ ([**6**])*

Starting from $DyCl_3 \cdot 6H_2O$ (377 mg, 1.00 mmol); product is a pale yellow crystalline solid. Yield: 774 mg (0.81 mmol, 81%). Elemental analysis calcd (%) for $C_{66}H_{60}DyNO_8$ ($HNEt_3[Dy(dbm)_4]$): C 68.47, H 5.22, N 1.21; found: C 68.51, H 5.66, N 1.28.

*$HNEt_3[Ho(dbm)_4]$ ([**7**])*

Starting from $HoCl_3 \cdot 6H_2O$ (379 mg, 1.00 mmol); product is a yellow crystalline solid in daylight and an orange-pink crystalline solid under fluorescent lighting. Yield: 811 mg (0.70 mmol, 70%). Elemental analysis calcd (%) for $C_{66}H_{60}HoNO_8$ ($HNEt_3[Ho(dbm)_4]$): C 68.33, H 5.21, N 1.21; found: C 68.06, H 5.63, N 1.23.

*$HNEt_3[Er(dbm)_4]$ ([**8**])*

Starting from $ErCl_3 \cdot 6H_2O$ (382 mg, 1.00 mmol); product is a pale orange crystalline solid. Yield: 702 mg (0.60 mmol, 60%). Elemental analysis calcd (%) for $C_{66}H_{60}ErNO_8$ ($HNEt_3[Er(dbm)_4]$): C 68.19, H 5.20, N 1.20; found: C 67.98, H 5.67, N 1.26.

*$HNEt_3[Tm(dbm)_4]$ ([**9**])*

Starting from $TmCl_3 \cdot 7H_2O$ (401 mg, 1.00 mmol); product is a yellow crystalline solid. Yield: 561 mg (0.48 mmol, 48%). Elemental analysis calcd (%) for $C_{66}H_{60}NO_8Tm$ ($HNEt_3[Tm(dbm)_4]$): C 68.10, H 5.19, N 1.20; found: C 67.13, H 6.12, N 1.24.

*$HNEt_3[Yb(dbm)_4]$ ([**10**])*

Starting from $YbCl_3 \cdot 6H_2O$ (387 mg, 1.00 mmol); product is a yellow crystalline solid. Yield: 654 mg (0.56 mmol, 56%). Elemental analysis calcd (%) for $C_{66}H_{60}NO_8Yb$ ($HNEt_3[Yb(dbm)_4]$): C 67.86, H 5.18, N 1.20; found: C 67.75, H 5.55, N 1.19.

6.3 Results and discussion

6.3.1 Synthesis

All *Ln*(III) complexes have been synthesized in yields ranging from 29% for the La(III) compound to 83% for the Eu(III) compound. The reactions were performed in hot ethanolic solution to ensure complete dissolution of the lanthanoid salt and ligand and allow for crystallization upon cooling to room temperature. The results of elemental analysis show that all compounds are described by the general formula $HNEt_3[Ln(dbm)_4]$. In addition, the IR spectra obtained for [**1**]- [**10**] are highly similar and resemble the IR spectrum of Hdbm. The strong bands in the 1600 cm^{-1} region are readily assigned to the carbonyl bands of the ligand, while the two bands at 743 and 689 cm^{-1} can be assigned to the out of plane C-H bending of the phenyl groups of the ligand. Compound [**1**] is highly soluble in ethanol, as compared to the other lanthanoid compound; cooling of its reaction mixture did not lead to the formation of a crystalline compound or a precipitate even after several days. Concentration of the mixture to approximately half its initial value eventually led to the formation of a crystalline solid in a low yield relative to the other compounds. The color that is observed for compound [**7**] is strongly dependent on the light source used to illuminate the compound. This is not uncommon for Ho(III) compounds and it is a result of the interplay between the absorption spectrum of the compound and the emission spectrum of the light source [27].

*Structure of **[1], [2] and [3]***

Single crystals of compounds [**1**] ($HNEt_3[La(dbm)_4]$), [**2**] ($HNEt_3[Nd(dbm)_4]$) and [**3**] ($HNEt_3[Sm(dbm)_4]$) were obtained by direct crystallization from the reaction mixture. Their solid-state structures were determined *via* single crystal X-ray crystallography. Crystallographic data for compounds [**1**], [**2**] and [**3**] are given in Table 6.1; selected bond distances and angles are given in Table 6.2. All three compounds crystallize in a monoclinic space group with two crystallographically independent lanthanoid ion sites in the asymmetric unit. As the differences in bond distances and angles of the two independent molecules are negligible, the data for only one of each are provided in Table 6.2. The structure of the $[Ln(dbm)_4]^-$ complex ion is highly similar for all three compounds, with four dbm^- ligands binding in a bidentate mode. The coordination geometry around the central ion is best described as a distorted square antiprism. For [**1**], the La-O bond lengths range from 2.444(2) to 2.556(2) Å, while the Nd-O bond lengths in [**2**] vary between 2.389(2) to 2.503(2) Å. In compound [**3**], Sm-O bond lengths range from 2.358(4) to 2.421(3) Å. These values can be considered normal for this type of bonds [28]. The decrease of the average bond lengths on going from [**1**] to [**3**] are a result of lanthanoid contraction.

Table 6.1: Crystallographic data for compounds [1], [2] and [3].

	[**1**]	[**2**]	[**3**]
formula	$C_{66}H_{60}LaNO_8$	$C_{66}H_{60}NNdO_8$	$C_{66}H_{60}NO_8Sm$
fw	1134.06	1139.39	1145.50
crystal size [mm^3]	0.18 × 0.23 × 0.27	0.24 × 0.26 × 0.33	0.20 × 0.24 × 0.37
crystal color	colorless	colorless	colorless
crystal system	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$ (# 14)	$P2_1/c$ (# 14)	Pc (# 7)
a [Å]	19.0448(3)	19.14645(15)	25.3006(2)
b [Å]	22.2878(2)	22.30120(16)	9.02328(7)
c [Å]	28.0866(4)	27.8550(2)	27.4737(2)
β [°]	109.6946(15)	110.0750(9)	112.5634(11)
V [$Å^3$]	11225.2(3)	11171.15(14)	5792.00(8)
Z	8	8	4
d_{calc} [g/cm^3]	1.342	1.355	1.314
μ [mm^{-1}]	0.818	7.546	8.051
refl. measured / unique	131872 / 22962	87068 / 21347	35745 / 16830
parameters	1383	1383	1523
R1/wR2 [I>2σ(I)]	0.0271 / 0.0656	0.0287 / 0.0794	0.0297 / 0.0714
R1/wR2 [all refl.]	0.0358 / 0.0710	0.0301 / 0.0804	0.0343 / 0.0725
S	1.040	1.080	0.990
$\rho_{min/max}$ [$e/Å^3$]	–1.17 / 0.78	–2.11 / 1.82	–0.82 / 1.53

Table 6.2: Selected bond distances and angles for compounds [1], [2], and [3].

	[**1**]	[**2**]	[**3**]
Bond distance (Å)			
Ln1–O1A	2.4646(18)	2.4088(19)	2.4084(28)
Ln1–O2A	2.5111(17)	2.4512(18)	2.3695(31)
Ln1–O3A	2.4931(22)	2.4307(24)	2.4105(25)
Ln1 -O4A	2.4526(22)	2.4028(23)	2.3582(41)
Ln1 –O5A	2.4586(20)	2.4045(20)	2.4207(32)
Ln1 –O6A	2.5559(19)	2.5028(21)	2.4066(32)
Ln1 –O7A	2.5397(16)	2.4822(16)	2.4051(34)
Ln1 –O8A	2.4589(18)	2.4025(18)	2.3856(30)
Bond angle (°)			
O1A-*Ln1*-O2A	68.948(64)	70.295(72)	71.096(98)
O3A-*Ln1*-O4A	68.500(66)	70.069(73)	70.575(112)
O5A-*Ln1*-O6A	68.489(60)	69.865(63)	70.012(108)
O7A-*Ln1*-O8A	68.459(63)	69.638(65)	70.763(112)
O1A-*Ln1*-O6A	81.986(62)	79.999(67)	76.114(95)
O2A-*Ln1*-O5A	73.274(62)	72.645(66)	72.014(104)
O3A-*Ln1*-O8A	71.252(63)	71.164(68)	79.977(97) (O4A-O8A)
O4A-*Ln1*-O7A	77.639(63)	76.643(69)	72.670(115) (O3A-O7A)
Hydrogen bond distances			
N–H···O	(O5A) 1.91(3)	(O5A) 1.91(3)	(O6A) 1.972(3)
N–H···O	(O8A) 1.92(4)	(O8A) 1.92(4)	(O3B) 1.976(3)

Despite the similar coordination geometries of the lanthanoid ions in structures [**1**] - [**3**], the packing of [**3**] is different from that of [**1**] and [**2**]. In addition, in [**3**] disorder is found for two phenyl groups on one of the independent molecules and for one phenyl group on the other molecule. In all cases the phenyl groups are disordered over two orientations, with relative occupancies of 0.627(5) and 0.373(5), 0.581(6) and 0.419(6) for the first independent molecule and 0.633(15) and 0.367(15) for the second independent molecule. The triethylammonium ion fits in the cavities formed by the packed complexes, as is illustrated in Figure 6.1. In [**1**] and [**2**], hydrogen bonds exist between the triethylammonium hydrogen and O5A and O8A of the ligands of one of the symmetry independent molecules. In [**3**], the ammonium hydrogen forms a hydrogen bond to O6A and O3B; hydrogen bond lengths are given in Table 6.2.

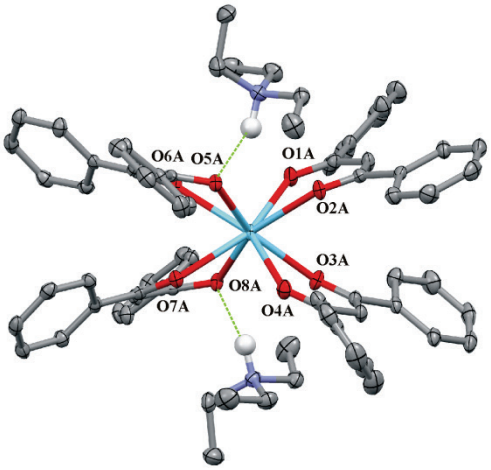

*Figure 6.1: Thermal ellipsoid plot (50% probability contours) of [**1**], ($HNEt_3[La(dbm)_4]$), showing one of the two crystallographically independent La(III) complex anions and two hydrogen bonded $HNEt_3$ cations, as well as the distorted square antiprismatic coordination sphere. Hydrogen bonds between the ammonium hydrogen and the ligands are indicated by a dashed line and the numbering scheme for O atoms is indicated. Other hydrogen atoms have been omitted for clarity.*

Structure of [4] - [10]

X-ray powder diffraction patterns recorded for compounds [**4**] - [**10**] at room temperature appear to be highly similar, and could be indexed with a monoclinic cell in the space group *I2/a* [20]. The room temperature powder XRD patterns for compounds [**1**] - [**2**] could not be indexed in *I2/a*, while this was possible for the pattern recorded for [**3**]. The difference is most likely a result from lanthanoid contraction. Results of the LeBail extraction are given in Table 6.3.

Table 6.3: Results of the LeBail extraction of unit cell dimensions of room temperature powder XRD data.

	S.G.	a (Å)	b (Å)	c (Å)	β (°)	V (Å^3)	Rp	χ^2
[**1**]*	*P2$_1$/c*	19.0448(3)	22.2878(2)	28.0866(4)	109.695(2)	5613	–	–
[**2**]*	*P2$_1$/c*	19.1465(2)	22.3012(2)	27.8550(2)	110.075(1)	5586	–	–
[**3**]	*I2/a*	25.344(5)	9.154(1)	27.618(3)	112.31(1)	5928(2)	3.15	1.53
[**4**]	*I2/a*	25.340(2)	9.1553(6)	27.640(1)	112.210(6)	5936.6(7)	2.90	1.67
[**5**]	*I2/a*	25.171(7)	9.140(1)	27.621(2)	112.100(8)	5901(2)	3.61	3.53
[**6**]	*I2/a*	25.152(3)	9.121(1)	27.642(2)	111.900(8)	5884(1)	3.04	2.26
[**7**]	*I2/a*	25.138(3)	9.1431(6)	27.652(3)	112.000(7)	5892.7(9)	2.59	1.49
[**8**]	*I2/a*	25.129(4)	9.154(1)	27.603(4)	111.80(1)	5896(2)	2.51	1.43
[**9**]	*I2/a*	25.116(4)	9.167(1)	27.640(3)	111.74(1)	5911(1)	2.56	1.53
[**10**]	*I2/a*	25.047(3)	9.1627(8)	27.616(3)	111.560(8)	5894(1)	2.68	1.82

*Notes: * Unit cell dimensions acquired from single crystal measurements; the unit cell volume for these compounds (Z = 8) is divided by 2 for comparison with the data for [**3**] - [**4**] (Z = 4).*

Luminescent properties

When compounds [**1**] - [**10**] are illuminated by a standard laboratory UV lamp at 366 nm, only compounds [**3**] (*Ln* = Sm) and [**4**] (*Ln* = Eu) clearly show visible luminescence. Indeed, room temperature photoluminescence (PL) could only be detected for [**3**] and [**4**]. The photoluminescence spectra for these compounds are given in Figure 6.2 and Figure 6.3. Both compounds show broad excitation bands in the UV to nUV region of the spectrum, indicating ligand-centered excitation. Superimposed on the broad bands, narrow lines corresponding to direct excitation of the luminescent centre can be distinguished. For [**3**], a narrow line at 420 nm ($[^6P_{5/2}, {}^4P_{5/2}] \leftarrow {}^6H_{5/2}$) can be seen, which is characteristic for the Sm(III) ion [29]. The emission spectrum of [**3**] shows lines characteristic for the $^4G_{5/2} \rightarrow {}^6H_J$ transitions of Sm(III) at 565 nm (J = 5/2), 610 nm (J = 7/2), 650 nm (J = 9/2), and 700 nm (J = 11/2). The most intense transition in the emission spectrum is the $^4G_{5/2} \rightarrow {}^6H_{9/2}$ transition, which is mainly of electric dipole (ED) nature. The $^4G_{5/2} \rightarrow {}^6H_{5/2}$ transition in contrast is mainly of magnetic dipole (MD) nature. As a result, its intensity is relatively insensitive to the environment of the Sm(III) ion and can therefore be taken as an internal reference. The fact that the intensity of the $^4G_{5/2} \rightarrow {}^6H_{9/2}$ transition is larger than the intensity of the $^4G_{5/2} \rightarrow {}^6H_{5/2}$ transition indicates that the Sm(III) ion occupies a non-centrosymmetric coordination site, which is in agreement with the structure determined by single X-ray crystallography [2, 30, 31]. The excitation spectrum recorded for [**4**] is similar to that of [**3**], showing an additional narrow line at 395 nm ($[^5L_6, {}^5G_2, {}^5L_7, {}^5G_3] \leftarrow {}^7F_0$) characteristic for direct excitation of the Eu(III) ion [32]. In the emission spectrum, four lines can be seen corresponding to the $^5D_0 \rightarrow {}^7F_J$ transitions of Eu(III) at 595 nm (J = 1), 615 nm (J = 2), 650 nm (J = 3) and 700 nm (J = 4).

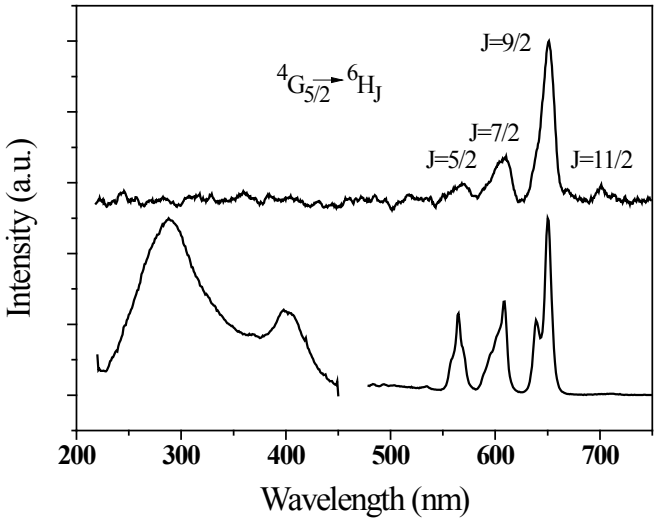

*Figure 6.2: Triboluminescence emission (top) and photoluminescence (bottom) spectra for [**3**] ($HNEt_3[Sm(dbm)_4]$). The excitation spectrum on the bottom left was recorded monitoring the intensity of the $^4G_{5/2} \rightarrow {}^6H_{9/2}$ transition, while the emission spectrum on the bottom right was obtained using an excitation wavelength of 298 nm.*

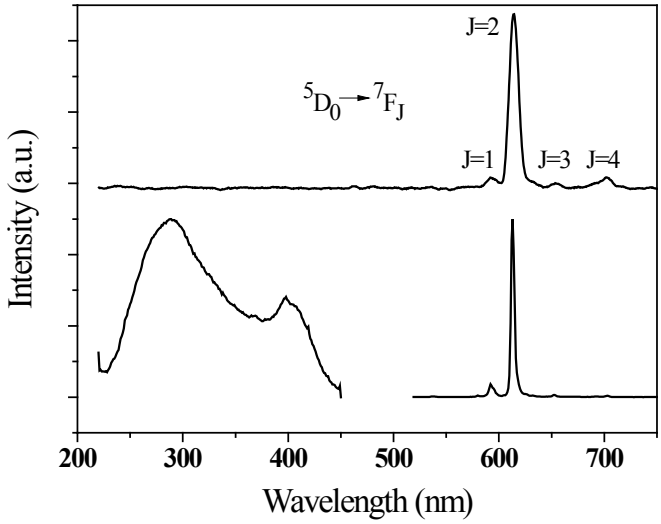

*Figure 6.3: Triboluminescence emission (top) and photoluminescence (bottom) spectra for [**4**] ($HNEt_3[Eu(dbm)_4]$). The excitation spectrum on the bottom left was recorded monitoring the intensity of the $^5D_0 \rightarrow {}^7F_2$ transition, while the emission spectrum on the bottom right was obtained using an excitation wavelength of 380 nm.*

Most of the emission intensity comes from the $^5D_0 \rightarrow {}^7F_2$ ED transition while the $^5D_0 \rightarrow {}^7F_1$ MD transition is weak, which is indicative of the lack of an inversion center on Eu(III). Although visible luminescence is also expected from [**5**] as a result of the Tb(III) $^5D_4 \rightarrow {}^7F_5$ transition at 545 nm, and from [**6**] due to the Dy(III) $^4F_{9/2} \rightarrow {}^6H_{13/2}$ transition at 570 nm, no photoluminescence emission could be detected within the sensitivity of the instrument being used. This observation is readily explained by the fact that the triplet level of the dbm ligands, which is around 20,500 cm^{-1} is too close to or below the resonance levels of Tb(III) ($^5D_4$ at 20,500 cm^{-1}) and Dy(III) ($^4F_{9/2}$ at 21,000 cm^{-1}) [2, 29, 33, 34]. Because of the $4f_0$ configuration of La(III), no luminescence is expected from [**1**], while complexes [**2**] and [**7**] to [**10**] are expected to give luminescence only in the nIR region [2]. Photoluminescence emission spectra were recorded up to the longest possible wavelength of the spectrometer (900 nm), but no emission was detected for [**1**], [**2**] and [**5**] - [**10**]. Triboluminescence (TrL) has also been detected for [**3**] and [**4**], with the TrL spectra showing the same emission lines as the corresponding PL spectra. The TrL spectra for [**3**] and [**4**] are shown in Figure 6.2 and Figure 6.3, respectively. Compound [**4**] is one of the best triboluminescent compounds known, and a TrL spectrum was readily obtained. Compound [**3**] shows fairly bright orange flashes visible to the naked eye upon crushing. The intensity is, however, much lower than that of [**4**]. To our knowledge, triboluminescence has not been reported for compound [**3**]. Differences between the PL and TrL emission spectra in Figure 6.2 and Figure 6.3 mainly result from the differences in resolution and spectral sensitivity of the spectrophotometers used. Interestingly, the only complex to show TrL besides [**4**] is also the only photoluminescent compound. This supports the hypothesis involving excitation of the luminescent center *via* the ligand. Fascinatingly, the ability of [**4**] to show triboluminescence has been linked to the structural disorder of the ligand's phenyl groups by Sweeting *et al.* [20]. Because the structure they report for [**4**] is centrosymmetric, this compound has been the counterexample against the requirement for a non-centrosymmetric space group for TrL to occur for a long time. However, Cotton *et al.* have reinvestigated the structure of [**4**] and found the non-centrosymmetric space group *Ia* [35]. In the structure they describe, disorder is also present for four of the ligand phenyl groups. Compound [**3]** also crystallizes in a non-centrosymmetric space group and has disordered phenyl groups. Thus, as of yet it is unclear whether the relation between TrL and a non-centrosymmetric space group really exists, or if the presence of disorder within the structure provides another pathway to enable TrL.
It is worth mentioning that Fontenot *et al.* have studied the same series of compounds for their triboluminescent properties and published their results roughly simultaneously with the publication of the work described in this Chapter [16, 36]. In their work, they report that the Eu(III) compound shows by far the strongest TrL, followed by the Sm(III) compound. The latter is found to give only 1.8% of the intensity of the Eu(III) compound. This is in qualitative agreement with our observations. However, the authors also report TrL for the Gd(III), Nd(III), Pr(III), Tb(III) and Yb(III) compounds, of which the relative TrL emission

intensity compared to the Eu(III) compound is in between 0.1 and 1%. Our equipment is probably not sufficiently sensitive to detect such weak TrL emissions.

6.4 Conclusion

A series of compounds described by the general formula $HNEt_3[Ln(dbm)_4]$, *Ln* = La, Nd, Sm, Eu, Tb, Dy, Ho, Er, Tm, Yb has been prepared. Single crystal X-ray diffraction studies show that the compounds with *Ln* = La, Nd are isostructural and crystallize in the $P2_1/c$ space group. The Sm-compound on the other hand crystallizes in the *Pc* space group. Bright triboluminescence was detected for this compound, in analogy with the Eu-compound. Because this compound is found to crystallize in a non-centrosymmetric space group, it cannot settle the debate on whether or not centrosymmetry is a prerequisite for TrL to occur.

6.5 References

[1] S.I. Weissman, *J. Chem. Phys.*, 10 (1942) 214-217.

[2] K. Binnemans, *Rare earth beta-diketonates*, in *Handbook on the Physics and Chemistry of Rare Earths*, 2005, Elsevier. 107-272.

[3] L. Armelao, S. Quici, F. Barigelletti, G. Accorsi, G. Bottaro, M. Cavazzini, and E. Tondello, *Coord. Chem. Rev.*, 254 (2010) 487-505.

[4] G. Vicentini, L.B. Zinner, J. Zukerman-Schpector, and K. Zinner, *Coord. Chem. Rev.*, 196 (2000) 353-382.

[5] J.G. White, *Inorg. Chim. Acta*, 16 (1976) 159-162.

[6] H. Wang, P. He, S. Liu, J. Shi, and M. Gong, *Appl. Phys. B: Lasers Opt.*, 97 (2009) 481-487.

[7] H.F. Brito, O.L. Malta, and J.F.S. Menezes, *J. Alloy. Compd.*, 303-304 (2000) 336-339.

[8] L. Huang, L. Cheng, H. Yu, L. Zhou, J. Sun, H. Zhong, X. Li, J. Zhang, Y. Tian, Y. Zheng, T. Yu, J. Wang, and B. Chen, *Physica B*, 406 (2011) 2745-2749.

[9] J.-C.G. Bünzli, E. Moret, V. Foiret, K.J. Schenk, M. Wang, and L. Jin, *J. Alloy. Compd.*, 207-208 (1994) 107-111.

[10] A. Mech, M. Karbowiak, C. Görller-Walrand, and R. Van Deun, *J. Alloy. Compd.*, 451 (2008) 215-219.

[11] R.G. Charles and E.P. Riedel, *J. Inorg. Nucl. Chem.*, 28 (1966) 3005-3018.

[12] Y. Hasegawa, Y. Wada, and S. Yanagida, *J. Photochem. Photobiol., C*, 5 (2004) 183-202.

[13] Y.-g. Lü, G. Li, C.-h. Shi, L.-s. Yu, F. Luan, and F.-j. Zhang, *T. Nonferr. Metal. Soc.*, 20 (2010) 2336-2339.

[14] F. Chen, Z. Bian, and C. Huang, *J. Rare Earth.*, 27 (2009) 345-355.

[15] C.R. Hurt, N. McAvoy, S. Bjorklund, and N. Filipescu, *Nature*, 212 (1966) 179-180.

[16] R. Fontenot, W. Hollerman, K. Bhat, S. Allison, and M. Aggarwal, *Journal of Theoretical and Applied Physics*, 7 (2013) 30.

[17] R.-G. Xiong and X.-Z. You, *Inorg. Chem. Commun.*, 5 (2002) 677-681.

[18] W. Clegg, I. Sage, I. Oswald, P. Brough, and G. Bourhill, *Acta Crystallogr., Sect. C. Cryst. Struct. Commun.*, 56 (2000) 1323-1325.
[19] R.G. Bulgakov, S.P. Kuleshov, A.N. Zuzlov, and R.R. Vafin, *Russ. Chem. Bull.*, 53 (2004) 2712-2714.
[20] L.M. Sweeting and A.L. Rheingold, *J. Am. Chem. Soc.*, 109 (1987) 2652-2658.
[21] E.E.S. Teotonio, G.M. Fett, H.F. Brito, W.M. Faustino, G.F. de Sá, M.C.F.C. Felinto, and R.H.A. Santos, *J. Lumin.*, 128 (2008) 190-198.
[22] R.S. Fontenot, K.N. Bhat, W.A. Hollerman, M.D. Aggarwal, and K.M. Nguyen, *CrystEngComm*, 14 (2012) 1382-1386.
[23] G.M. Sheldrick, *SHELXS–97*, *Bruker AXS Inc., Madison, Wisconsin*, 1997.
[24] G.M. Sheldrick, *Acta Crystallogr., Sect. A. Found. Crystallogr.*, 64 (2008) 112-122.
[25] B.A. Hunter, *Rietica*, *IUCR Powder Diffraction*, 1997.
[26] A. Le Bail, H. Duroy, and J.L. Fourquet, *Mater. Res. Bull.*, 23 (1988) 447-452.
[27] K. Binnemans and C. Görller-Walrand, *Chem. Phys. Lett.*, 235 (1995) 163-174.
[28] A.G. Orpen, L. Brammer, F.H. Allen, O. Kennard, D.G. Watson, and R. Taylor, *J. Chem. Soc. Dalton Trans.*, (1989) S1-S83.
[29] W.T. Carnall, P.R. Fields, and K. Rajnak, *J. Chem. Phys.*, 49 (1968) 4424-4442.
[30] J.H.S.K. Monteiro, I.O. Mazali, and F.A. Sigoli, *J. Fluoresc.*, 21 (2011) 2237-2243.
[31] H.F. Brito, O.L. Malta, M.C.F.C. Felinto, E.E.S. Teotonio, J.F.S. Menezes, C.F.B. Silva, C.S. Tomiyama, and C.A.A. Carvalho, *J. Alloy. Compd.*, 344 (2002) 293-297.
[32] W.T. Carnall, P.R. Fields, and K. Rajnak, *J. Chem. Phys.*, 49 (1968) 4450-4455.
[33] E.E.S. Teotonio, H.F. Brito, G.F. de Sá, M.C.F.C. Felinto, R.H.A. Santos, R.M. Fuquen, I.F. Costa, A.R. Kennedy, D. Gilmore, and W.M. Faustino, *Polyhedron*, 38 (2012) 58-67.
[34] W.T. Carnall, P.R. Fields, and K. Rajnak, *J. Chem. Phys.*, 49 (1968) 4447-4449.
[35] F.A. Cotton, L.M. Daniels, and P. Huang, *Inorg. Chem. Commun.*, 4 (2001) 319-321.
[36] S. Akerboom, M.S. Meijer, M.A. Siegler, W.T. Fu, and E. Bouwman, *J. Lumin.*, 145 (2014) 278-282.