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Lanthanide perchlorate complexes with 1,4-bis(phenylsulfinyl)butane: structures and luminescent properties

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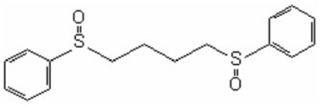
Five representative lanthanide coordination compounds with a disulfoxide ligand [**L** = 1,4-bis(phenylsulfinyl)butane], $[Ln(\mathbf{L})_4](ClO_4)_3$ (Ln = La, **1**; Eu, **2**; Gd, **3**; Tb, **4**; Yb, **5**), have been synthesized and structurally characterized by single-crystal X-ray diffraction. These compounds have isostructural mononuclear structures, in which the ligand **L** coordinates to the metal ions through O donors in chelating coordination mode. The luminescence studies of **2** and **4** in the solid state and solution exhibit the usual metal-centred emission spectra arising from ligand-to-metal energy transfer, and their intensity and lifetimes are increased compared to those of previously reported analogous complexes $\{[Ln(\mathbf{L})_2(DMF)_4](ClO_4)_3 \cdot nH_2O\}_\infty$ (Ln = Eu, $n = 4$, **6**; Ln = Tb, $n = 3$, **7**). The stability of these complexes in solution was also investigated.

Introduction

The study of lanthanide coordination compounds has attracted much attention owing to their interesting structural features and potential applications as functional materials (luminescent stains, contrast agents for magnetic resonance imaging, multifunctional asymmetric catalysis, *etc.*) and as ideal probes in the studies of biological systems.[1] In particular, those containing Eu^{III} and Tb^{III} have long-lived emission and strong luminescence. But a perfect lanthanide luminescent probe has to overcome two difficulties arising from the particular low oscillator strengths of *f–f* transitions and the easy de-excitation of the Ln^{III} excited states. Luckily, encapsulation of the Ln^{III} ions using pre-organized ligands can compensate these disadvantages so as to achieve well-protected environments and provide good emission properties. In addition, the occurrence of an antenna effect allows sensitization of metal-centered luminescence *via* energy transfer from an aromatic ligand, which acts as a light harvester. Accordingly, those lanthanide complexes with chromophoric ligands are interesting for research on light-conversion devices.[2,3] Most of the research efforts in this area have so far been focused on the design and synthesis of lanthanide complexes having organic chromophores and protected metal-centered environments.[4]

1,4-Bis(phenylsulfinyl)butane (**L**) is a bidentate and structurally flexible ligand containing an aromatic chromophore. Some of its copper and lanthanide coordination compounds have been reported by us.[5–8] In order to further study the structures and photophysical properties of the lanthanide complexes with this ligand, we have synthesized five lanthanide perchlorate complexes, $[Ln(\mathbf{L})_4](ClO_4)_3$ (L = La, **1**; Eu, **2**; Gd, **3**; Tb, **4** and Yb, **5**), and established their structures by elemental analyses, IR spectra and X-ray single crystal diffraction, as well as investigating the luminescent properties of **2** and **4**. In these complexes the ligand **L** coordinates to the Ln^{III} center through O-donors in bidentate chelate fashion, which to our knowledge may be the first examples of structurally determined disulfoxide complexes with all the ligands taking on the O-donor chelating coordination mode. The effect of solvent coordination in the related complexes, $\{[Ln(\mathbf{L})_2(DMF)_4](ClO_4)_3 \cdot nH_2O\}_\infty$ (Ln = Eu, $n = 4$, **6**; Ln = Tb, $n = 3$, **7**),[6] leading to the differences in structures and spectroscopic properties is also discussed by comparing with **2** and **4**.



L

Experimental

Materials and general methods

All chemicals and solvents used in the syntheses were of analytical grade and used without further purification. The solvents for analyses were further purified by standard methods. 1,4-Bis(phenylsulfinyl)butane (**L**) was synthesized as previously described.[8] Mp: 106–108 °C. ^1H NMR ($CDCl_3$): δ 1.85 (t, 4H, SCH_2CH_2), 2.80 (t, 4H, SCH_2), 7.58–7.67 (m, 10H, Ph). The complexes, $\{[Ln(\mathbf{L})_2(DMF)_4](ClO_4)_3 \cdot nH_2O\}_\infty$ (Ln = Eu, $n = 4$, **6**; Ln = Tb, $n = 3$, **7**] were prepared as crystals according to our published work.[6]

Melting point measurements were made on an X-4 melting point meter. Elemental analyses were performed on a Perkin–Elmer 240C analyzer. IR spectra were recorded on an FT-IR 170SX (Nicolet) spectrometer in the range of 4000–400 cm^{-1}. ^1H NMR spectra were recorded on a Bruker AC-P500 spectrometer (300 MHz) at 25 °C with tetramethylsilane as the internal reference. Thermal analyses were performed using a Netzsch TG 209 instrument.

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Preparation of the crystals of [Ln(L)$_4$](ClO$_4$)$_3$ (Ln = La, Eu, Gd, Tb and Yb)

Caution! While we have experienced no problems in handling Ln^{III} perchlorates, these should be handled with great caution due to the potential for explosion.

Single crystals of [Ln(**L**)$_4$](ClO$_4$)$_3$ were obtained by layered diffusion of a methanol solution (10 mL) of Ln(ClO$_4$)$_3$·nH$_2$O (0.1 mmol) into a chloroform solution (10 mL) of **L** (0.4 mmol) using triethylorthoformate (6 mL) as a "buffer layer" and also as dehydrating reagent. Colorless crystals were obtained over a few days.

[La(L)$_4$](ClO$_4$)$_3$ (1). Yield: 73%. Anal. calcd. for $C_{64}H_{72}Cl_3LaO_{20}S_8$ (%): C, 46.22; H, 4.36; found: C, 46.07; H, 4.53. ^{1}H NMR (CD$_3$CN): δ 1.87–2.05 (m, 2H), 2.08–2.25 (m, 2H), 2.91–3.07 (m, 4H), 7.45–7.53 (m, 8H), 7.58–7.64 (m, 2H). IR (KBr pellet, cm^{-1}): 3060w, 2937w, 1635w, 1581w, 1444w, 1093s, 1003m, 988s, 756m, 692m. DTA (peak temperature, °C): 201, 467 and 564.

[Eu(L)$_4$](ClO$_4$)$_3$ (2). Yield: 72%. Anal. calcd. for $C_{64}H_{72}Cl_3EuO_{20}S_8$ (%): C, 45.82; H, 4.33; found: C, 45.64; H, 4.51. ^{1}H NMR (CD$_3$CN): δ 1.93–1.97 (m, 1H), 2.10–2.22 (m, 3H), 2.48–2.80 (very weak smooth peak), 7.30 (s, 4H), 7.58 (t, 1H), 7.72 (t, 2H), 7.90 (t, 1H), 8.06 (s, 2H). IR (KBr pellet, cm^{-1}): 3063w, 2954w, 1653w, 1478w, 1445w, 1098s, 1008m, 993s, 750m, 689m; (0.2 mm MeCN film, deducting background peaks from MeCN, cm^{-1}): 3066w, 1632m, 1101s, 1004m, 990m, 754m, 692m. DTA (peak temperature, °C): 186, 443 and 472.

[Gd(L)$_4$](ClO$_4$)$_3$ (3). Yield: 80%. Anal. calcd. for $C_{64}H_{72}Cl_3GdO_{20}S_8$ (%): C, 45.68; H, 4.32; found: C, 45.89; H, 4.16. IR (KBr pellet, cm^{-1}): 3064w, 2940w, 1581w, 1445w, 1094s, 1003m, 987s, 758m, 692m. DTA (peak temperature, °C): 216, 482 and 590.

[Tb(L)$_4$](ClO$_4$)$_3$ (4). Yield: 74%. Anal. calcd. for $C_{64}H_{72}Cl_3TbO_{20}S_8$ (%): C, 45.63; H, 4.31; found: C, 45.46; H, 4.72. IR (KBr pellet, cm^{-1}): 3061w, 2951w, 1653w, 1582w, 1445w, 1090s, 1005m, 989s, 750m, 689m. DTA (peak temperature, °C): 195, 490 and 546.

[Yb(L)$_4$](ClO$_4$)$_3$ (5). Yield: 64%. Anal. calcd. for $C_{64}H_{72}Cl_3YbO_{20}S_8$ (%): C, 45.29; H, 4.28; found: C, 45.43; H, 4.01. IR (KBr pellet, cm^{-1}): 3061w, 2936w, 1581w, 1445w, 1094s, 1003m, 988s, 757m, 692m. DTA (peak temperature, °C): 182, 423 and 464.

Crystal structure determinations of 1–5

Single crystal X-ray diffraction studies of **1**–**5** were carried out with a Bruker Smart 1000 diffractometer with Mo-Kα radiation (λ = 0.71073 Å). Empirical absorption corrections were applied using the SADABS program.[9] All the structures were solved by direct methods (Bruker SHELXTL).[10a] The non-hydrogen atoms were obtained in successive difference Fourier syntheses. The final refinements were performed by full-matrix least-squares methods on F^2 by the Bruker SHELXTL program package.[10b] Hydrogen atoms were included in calculated position and refined with isotropic thermal parameters riding on the parent atoms. Crystallographic data are summarized in Table 1.

It is noteworthy that although we attempted to resolve the crystal structures of these compounds in the $I4/mmm$ space group (Platon suggestion), the rough sketch could not be fixed. The I–4 space group was then selected, in which the resolutions were successful. These structures show positional disorder of the skeletal atoms of **L**, which were solved and refined with a 1:1 site occupancy (see Fig. 1) for the two ligand conformations.†

Photoluminescence and lifetime measurements

UV/vis spectra were obtained on a Hewlett–Packard 8452A diode array spectrophotometer. Steady-state emission and excitation spectra at room temperature and 77 K were obtained on a Spex Fluorolog-2 model F111 fluorescence spectrophotometer with or without Corning filters. The 77 K solid-state emission and excitation spectra were recorded with solid samples loaded in a quartz tube inside a quartz-walled optical Dewar flask filled with liquid nitrogen. For solution emission and excitation spectral studies, the solutions were prepared in a 10 mL Pyrex bulb connected to a side-armed 1 cm quartz cuvette and sealed from the atmosphere by a Rotaflo HP6/6 quick-release Teflon stopper. The solutions were degassed with no fewer than four freeze-pump-thaw cycles. Emission-lifetime measurements were performed using a conventional laser system. The excitation source was the 355 nm output (third harmonic) of a Spectra Physics Quanta-Ray Q-switched GCR-150-10 pulsed Nd-YAG laser.

Results and discussion

General characterization and solution structure

The preparations of **1**–**5** were achieved by the reaction of ligand **L** with the lanthanide perchlorates in the presence of dehydrating reagent using the layered-diffusion method. The IR spectra of the five compounds in the solid state showed sharp bands at 987–993 cm^{-1} resulting from the stretching vibration of the S=O group. The shift of ν(S=O) to lower wave numbers compared to that of free ligand **L** (1035 cm^{-1})[8] suggests coordination through the O of the S=O moieties of **L**. All complexes are air-stable and decomposition starts at about 200 °C. The complexes are soluble in DMF, DMSO and acetonitrile, slightly soluble in ethanol and methanol, but insoluble in acetone and water.

Owing to the structural similarity of all complexes, **2** was selected for investigation of the IR spectrum in MeCN solution. Subtracting background peaks, the IR spectrum of **2** in MeCN gives rise to characteristic vibrations very similar to those in the solid state. The sharp band at 990 cm^{-1} corresponds to the band at 993 cm^{-1} (solid state), while no band was observed near 1035 cm^{-1} [ν(S=O) for free ligand], which indicates that the complex does not break down in MeCN solution. In order to further explore the stability of these complexes in solution, the ^{1}H NMR of **1** and **2** in deuterate MeCN were investigated. For **1** two multi-peaks at δ 1.87–2.05 and 2.08–2.25 are assigned to the resonance of C–(CH$_2$)$_2$–C, and that at 2.91–3.07 to the resonance of S–CH$_2$–. Two multi-peaks at δ 7.45–7.53 and 7.58–7.64 are assignable to the resonances of Ph–H. The splitting of such resonance peaks and a small shift to lower field compared to those of the free ligand are probably attributable to the metal ion coordination to the ligand. For **2** the peaks at δ 1.93–1.97 and 2.10–2.22 correspond to the resonance of C–(CH$_2$)$_2$–C; however, no obvious peak but only a very weak smooth peak is observed at δ 2.48–2.80 for the resonance of S–CH$_2$–. In addition, the Ph–H resonances are divided into five peaks (δ 7.30, 7.58, 7.72, 7.90, 8.06) and shifted to lower field. This behavior may be attributed to the disturbance caused by the paramagnetic ion Eu^{3+} coordinated to the ligand. The differences of the ^{1}H NMR spectra between **1** (diamagnetic compound) and **2** (paramagnetic compound) probably help to further confirm that the

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† CCDC reference numbers 200615–200617, 221546 and 221547. See http://www.rsc.org/suppdata/nj/b3/b308473f/ for crystallographic data in .cif or other electronic format.

Table 1 Crystal data and structure refinement parameters for **1**–**5**

	1	**2**	**3**	**4**	**5**
Formula	$C_{64}H_{72}Cl_3LaO_{20}S_8$	$C_{64}H_{72}Cl_3EuO_{20}S_8$	$C_{64}H_{72}Cl_3GdO_{20}S_8$	$C_{64}H_{72}Cl_3TbO_{20}S_8$	$C_{64}H_{72}Cl_3YbO_{20}S_8$
FW	1662.96	1676.01	1681.30	1682.97	1697.09
T/K	293(2)	293(2)	293(2)	293(2)	293(2)
Crystal system	Tetragonal	Tetragonal	Tetragonal	Tetragonal	Tetragonal
Space group	$I\bar{4}$	$I\bar{4}$	$I\bar{4}$	$I\bar{4}$	$I\bar{4}$
a/Å	14.508(2)	14.488(2)	14.469(2)	14.449(4)	14.426(2)
b/Å	14.508(2)	14.488(2)	14.469(2)	14.449(4)	14.426(2)
c/Å	17.559(4)	17.490(4)	17.509(4)	17.537(5)	17.487(4)
U/Å^3	3696(1)	3671(1)	3666(1)	3661(2)	3640(1)
Z	2	2	2	2	2
μ/mm^{-1}	0.981	1.260	1.311	1.372	1.694
Unique reflect..	3236	3204	3215	3215	3195
Obsd reflect..	2574	3070	2950	2628	3188
R_{int}	0.0462	0.0533	0.0359	0.0548	0.0320
R^a [$I > 2\theta(I)$]	0.0873	0.0674	0.0707	0.0651	0.0669
wR^b (all data)	0.2432	0.1745	0.1902	0.1709	0.1651

^{a} $R = \Sigma\|F_o| - |F_c\|/\Sigma|F_o|$. ^{b} $wR = \{\Sigma[w(F_0^2 - F_c^2)^2]/\Sigma w(F_0^2)^2\}^{1/2}$.

structures of these complexes are preserved when dissolved in MeCN.

Crystal structures of 1–5

The complexes **1**–**5** have isostructural mononuclear structures. A representative molecular structure plot of **4** is shown in Fig. 2 with only one of the disordered occupancies appearing. In these complexes, each metal ion is located at the crystallographic $2/m$ site and one-quarter of the molecule is crystallographically independent. The central ion is coordinated by eight O atoms of four distinct **L** ligands in a distorted dodecahedral geometry. Each bidentate ligand coordinates to the central ion in chelating mode to form a nine-membered ring. In these complexes, the conformation of the sulfoxide oxygen coordination can be considered as a trans-trans arrangement, which is common for sulfoxide complexes with O coordination.[11] As shown in Table 2, there are one relatively shorter and one longer Ln–O bonds in each chelate ligand probably due to the steric crowding in the coordination sphere. Comparing this series of complexes with the 2D structural complexes **6** and **7**,[6] in which the DMF takes part in the coordination, shows that the solvent plays an important role in controlling the structures of such complexes.

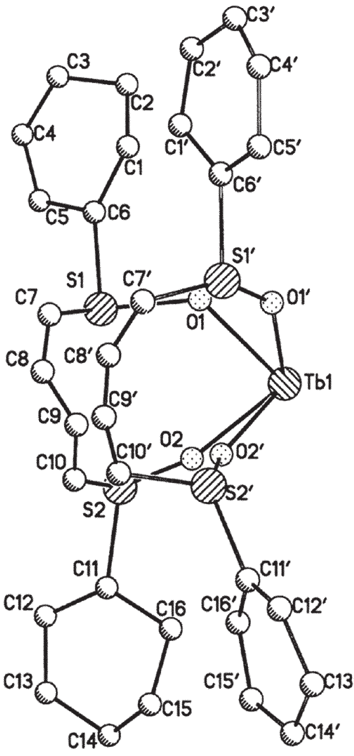

Fig. 1 Labeled ORTEP diagram for the asymmetric unit of **4**, showing the two disordered components (**1**, **2**, **3** and **5** are identical); hydrogen atoms and perchlorate ions were omitted for clarity.

Luminescent properties of 2 and 4

The electronic absorption spectra of **2**, **4**, **6** and **7** in MeCN show absorption bands at *ca.* 238–274 nm (Table 3), similar to those observed in the free ligand. Only a very slight shift of the absorption energy was observed from the 211 (ε = 7409 L mol^{-1} cm^{-1}), 239 (ε = 4709 L mol^{-1} cm^{-1}) and 272 (ε = 606 L mol^{-1} cm^{-1}) nm bands of the free ligands,[8] consistent with their origins as ligand-centered transitions.

The excitation and emission spectra and the lifetimes of **2** and **4** in the solid state and in MeCN solution have been studied. Selected emission spectra are shown in Figs. 3 and 4. The emission spectra of the complexes $\{[Eu(\mathbf{L})_2(DMF)_4](ClO_4)_3\cdot 4H_2O\}_\infty$ (**6**) and $\{[Tb(\mathbf{L})_2(DMF)_4](ClO_4)_3\cdot 3H_2O\}_\infty$ (**7**), were also measured under the same conditions for comparison of the emission properties as a function of ligand-to-metal molar

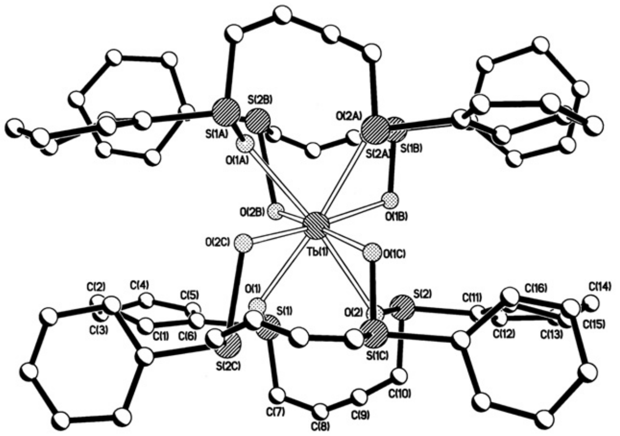

Fig. 2 Crystal structure of the complex cation of $[Tb(\mathbf{L})_4]^{3+}$, showing one disordered component (other analogs are identical).

Table 2 Selected bond distances (Å) and angles (°) for complexes **1**–**5**

	1	**2**	**3**	**4**	**5**
Ln(1)–O(1)	2.46(2)	2.38(3)	2.42(9)	2.64(5)	2.34(4)
Ln(1)–O(2)	2.35(8)	2.27(2)	2.37(3)	2.32(8)	2.34(2)
Ln(1)–O(1′)	2.51(6)	2.21(2)	2.46(5)	2.27(8)	2.29(9)
Ln(1)–O(2′)	2.44(8)	2.52(1)	2.42(2)	2.36(7)	2.52(2)
O(1)–Ln(1)–O(2)	69.6(3)	72.8(6)	70.1(3)	71.0(2)	71.0(2)
O(1′)–Ln(1)–O(2′)	70.8(2)	70.8(5)	70.7(6)	71.9(3)	70.9(3)

ratio (see Table 3). Their excitation spectra (in solid state and in MeCN solution) show a broad band in the *ca.* 250–350 nm range, characteristic of the π–π* transitions of ligand **L**. The emission spectra of **2** and **4** show the typical narrow emission bands of Eu^{III} and Tb^{III} in the solid state and in acetonitrile solution. For the solid-state emission spectrum of **2**, four bands are resolved, corresponding to the $^5D_0 \rightarrow {}^7F_J$ ($J = 1$–4) transitions of Eu^{III}. It is noteworthy that the emission intensity of the band arising from $^5D_0 \rightarrow {}^7F_2$ is weaker than that of $^5D_0 \rightarrow {}^7F_1$ in the solid state. While the solid-state emission spectra of **2** at room temperature and 77 K closely resemble each other, those in MeCN solution are different, with only one band corresponding to the $^5D_0 \rightarrow {}^7F_2$ emission. This indicates that the solvent may play an important role in affecting the coordination environments of Ln^{III} and give rise to a single emission band. In the solid-state emission spectra of **4** at room temperature and 77 K, one band at 543 nm due to $^5D_4 \rightarrow {}^7F_5$ emission was observed in the 450–650 nm region, with another broad band at *ca.* 400 nm, which is likely to be a ligand-centered emission. In solution, four emission bands corresponding to the $^5D_4 \rightarrow {}^7F_J$ ($J = 3$–6) transition were observed.

Luminescence lifetime data for the $^5D_0$ (Eu^{III}) and $^5D_4$ (Tb^{III}) levels measured in the solid state at room temperature and 77 K are listed in Table 3. Very little effect of temperature on the lifetime is observed. The absence of any significant temperature effect on the lifetime may be taken as an indication that a large number of vibration quanta participate in non-radiative decay processes.[12]

Comparison of the emission spectra and lifetimes of **2** and **6** as well as **4** and **7** show that in general, **2** and **4** show relatively stronger emission intensity and a longer emission lifetime than those of the corresponding **6** and **7**. This may be ascribed to the presence of a larger number of aromatic-containing ligands around the metal center and the absence of solvent molecules directly coordinated to the lanthanide center, which would enhance the energy transfer sensitization of the lanthanide emission as well as reduce the deactivation of its excited state *via* non-radiative processes.

Table 3 Absorption and emission features of **2**, **4**, **6** and **7**

Compound	Absorption (MeCN) λ_{abs}/nm (ε/L mol^{-1} cm^{-1})	State (T), Emission λ_{em}/nm	Lifetime/ ms
2	244 (29, 650)	Solid (RT): 591, 612, 650, 697	1.80
	266 (7, 775)	Solid (77 K): 591, 612, 650, 698	1.82
	274 (4, 430)	MeCN solution (RT), 615	
4	244 (29, 780)	Solid (RT): 400, 543	2.14
	266 (7, 285)	Solid (77 K): 543	1.87
	274 (4, 605)	MeCN solution (RT): 488, 543, 584, 619	
6	238 (15, 465)	Solid (RT): 591, 612, 650, 697	1.63
	266 (3, 110)	Solid (77 K): 591, 612, 699	0.02, 1.05[a]
	274 (1, 905)	MeCN solution (RT): 591, 612, 697	
7	238 (17, 475)	Solid (RT): 400, 490, 543, 591, 619	1.47
	266 (2, 955)	Solid (77 K): 488, 543	1.54
	274 (1, 790)	MeCN solution (RT): 488, 543, 584, 619	

[a] Double exponential.

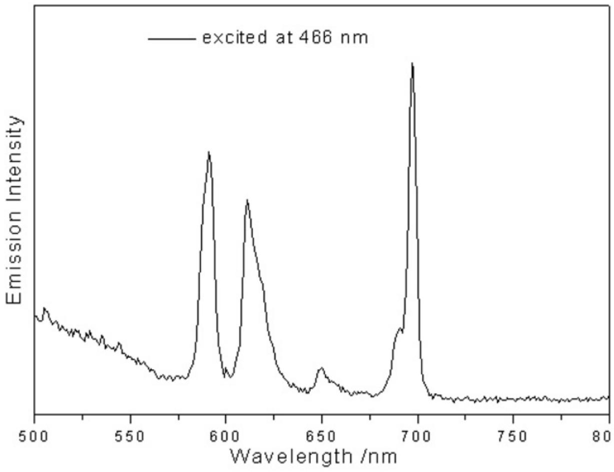

Fig. 3 Emission spectrum of **2** in the solid state.

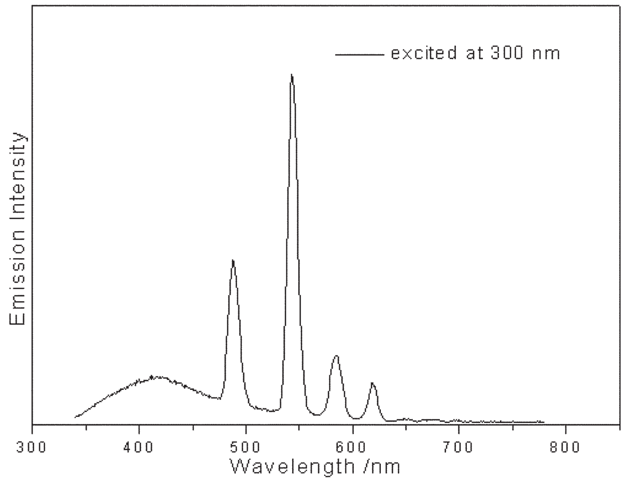

Fig. 4 Emission spectrum of **4** in MeCN solution.

Conclusion

In summary, five lanthanide perchlorate complexes with a disulfoxide ligand were obtained. These complexes have isostructural mononuclear structures. The strong emission and long luminescent lifetimes of the Eu^{III} and Tb^{III} complexes **2** and **4** show that the ligand may be useful for preparing luminescent materials. Ligand-to-metal molar ratios and solvent have important influences on the luminescent properties of such complexes. The IR and ^{1}H NMR spectra of the complexes in MeCN show that these complexes are stable in solution.

Acknowledgements

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