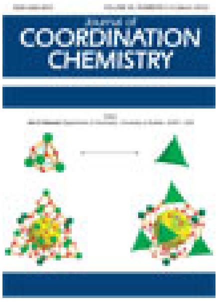

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Synthesis, crystal structure, and luminescence properties of rare-earth complexes with 2,2′-bis[(diethylcarbamoyl)- methoxy]-1,1′-biphenylene

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Synthesis, crystal structure, and luminescence properties of rare-earth complexes with 2,2′-bis[(diethylcarbamoyl)-methoxy]-1,1′-biphenylene

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A new amide-based ligand derived from biphenyl, 2,2′-bis[(diethylcarbamoyl)-methoxy]-1,1′-biphenylene (L), and its complexes of rare-earth picrates were synthesized. Solid complexes of lanthanide picrates (Ln = La, Nd, Eu, Gd, Tb, and Y) with this new ligand were prepared and characterized by elemental analysis, conductivity measurements, X-ray powder diffraction, and infrared spectroscopies. The molecular structure of [Gd(pic)$_3$L] shows that the Gd(III) is eight-coordinate by four oxygen atoms from **L** and the other from one bidentate and two unidentate picrates. Furthermore, [Gd(pic)$_3$L] units are linked by intermolecular hydrogen bonds to generate a 2-D netlike supramolecule. Under excitation, the Eu(III) complex exhibited characteristic emissions of europium. The luminescence properties of the Eu(III) complex in solid state and in CHCl$_3$, acetone, acetonitrile, and DMF were investigated. The lifetime of the $^5D_0$ level of Eu(III) in the complex was 0.26 ms. The quantum yield $\mathbf{\Phi}$ of the europium picrate complex was 6.67×10^{-3} with quinine sulfate as reference. The lowest triplet state energy level of the ligand indicates that the triplet state energy level of the ligand matches better to the resonance level of Eu(III) than Tb(III).

Keywords: Rare-earth picrate complexes; Crystal structure; Hydrogen bonds; Luminescence properties

1. Introduction

Rare-earth coordination chemistry has significance due to their electronic, magnetic and spectroscopic properties, and intriguing structural features [1–7]. Lanthanide complexes have many potential applications such as luminescent sensing and imaging technology, and contract agents for MRI [8–13]. Among the luminescent complexes studied, europium(III) and terbium(III) complexes appear to be most attractive because of their highly monochromic red/green emission in the visible range featuring large Stokes shifts and long emission lifetimes. However, as a consequence of the parity rule (and sometimes due to the change in spin multiplicity), lanthanide ions are very poor at

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absorbing light directly. In order to obtain strongly luminescent complexes, organic molecules, which are able (1) to encapsulate and protect the lanthanide ions from solvent molecules and (2) to absorb energy and transfer it efficiently to the metal, need to be introduced as sensitizers (antenna effect) [14]. Although different types of chelating agents can be used for the preparation of these complexes [15–18], the podand-type ligands (especially amide-type podands) commonly improve the sensitization of the luminescence of Eu(III) or Tb(III). This is due to their efficient contribution to ligand-to-metal energy transfer, and possessing spheroidal cavities and hard binding sites, stabilizing the complexes, and shielding the encapsulated ion from interaction with the surroundings [19]. Our group has been interested in supramolecular coordination chemistry of rare-earth metals with amide-type podands that have strong coordination capability to the lanthanide ions and terminal group effects [20]. As part of our systematic studies, this work reports a new amide-type podand, 2,2′-bis[(diethylcarbamoyl)-methoxy]-1,1′-biphenylene (L), including the synthesis, crystal structure, and luminescent properties of its lanthanide picrate complexes. The crystal structure of $Gd(pic)_3L$ shows that the Gd(III) is effectively encapsulated and protected by one coordinated ligand and three coordinated picrates. Furthermore, $Gd(Pic)_3L$ units are linked by intermolecular $C–H \cdots O$ interactions to form a 2-D supramolecular network. The fluorescent properties of the Eu(III) complex were studied. The lowest triplet state energy level of the ligand which was calculated from the phosphorescence spectrum of the Gd(III) at 77 K indicates that the triplet state energy level of the ligand matches better to the resonance level of Eu(III) than Tb(III).

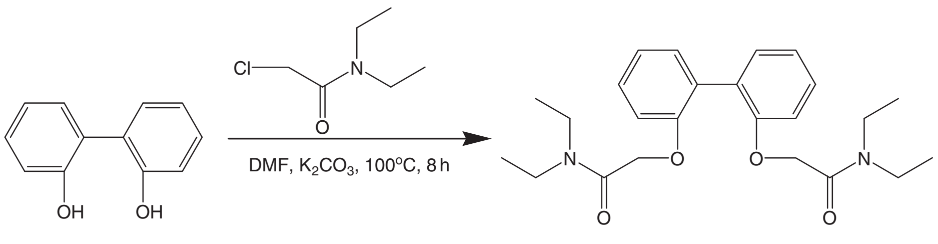
2. Experimental

2.1. *Materials*

Lanthanide picrates [21] and N,N-diethylchloroacetamide [22] were prepared according to literature methods. Other chemicals were obtained from commercial sources and used without purification.

2.2. *Chemical and physical measurements*

The lanthanide ions were determined by EDTA titration using xylenol orange as an indicator. C, H, and N were determined using an Elementar Vario EL analyzer. Conductivity measurements were carried out with a DDS-307-type conductivity bridge using $10^{-3}\,\mathrm{mol\,dm^{-3}}$ solutions in acetone at 25°C. X-ray powder diffraction (XRPD) patterns were obtained on a Rigaku D/Max-II X-ray diffractometer with graphite-monochromated Cu-Kα radiation. Infrared (IR) spectra were recorded on a Nicolet FT-170SX instrument using KBr discs from 400 to $4000\,\mathrm{cm^{-1}}$. ^{1}H NMR spectra were measured on a Varian Mercury plus 300M spectrometer in $CDCl_3$ with TMS as internal standard. Fluorescence and phosphorescence measurements were made on a Hitachi F-4500 spectrophotometer. Luminescence decays were recorded using a pumped dye laser (Lambda Physics model FL2002) as the excitation source.



L

Scheme 1. The synthetic route for **L**.

2.3. *Synthesis of ligand*

The synthetic route for the ligand is shown in scheme 1. Anhydrous K_2CO_3 (5.6 g, 41 mmol) was added into 15 mL DMF solution of 2,2′-dihydroxybiphenyl (1.86 g, 10 mmol) at 100°C. After 1 hour, a solution of N,N-diethylchloroacetamide (4.48 g, 30 mmol) in 10 mL DMF was added dropwise to the mixture and maintained at 100°C for 8 h. When cooled, 60 mL distilled water was poured and the turbid solution was extracted by 40 mL chloroform three times. Organic phase combined was washed with water and dried with anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the crude product was chromatographed to afford **L**; yield: 87%. Anal. Calcd (Found) for $C_{24}H_{32}N_2O_4$: C, 69.64 (69.51); H, 7.59 (7.48); N, 6.45 (6.33) %. ^1H NMR (300 MHz, $CDCl_3$): δ 7.32–7.26(m, 4H, $C_{12}H_8$–), 7.04–6.97(m, 4H, $C_{12}H_8$–), 4.59(q, 4H, –O–CH_2–CO–), 3.32(q, $J = 9.2$ Hz, 4H, –N–CH_2–), 3.20(q, $J = 9.6$ Hz, 4H, –N–CH_2–), 1.06(t, $J = 4.6$ Hz, 6H, –CH_3), 0.92(t, $J = 4.8$ Hz, 6H, –CH_3).

2.4. *Synthesis of complexes*

To a solution of 0.2 mmol lanthanide picrate in 15 mL of ethanol was added dropwise solution of 0.2 mmol **L** in 3 mL of chloroform. The mixture was stirred at room temperature for 6 h. The precipitated solid complex was filtered, washed with ethanol, and dried *in vacuo* over P_2O_5 for 48 h. All the complexes were obtained as yellow powders in 60–80% yield.

2.5. *X-ray crystallography*

For the gadolinium complex, X-ray measurements were performed on a Bruker SMART CCD diffractometer using graphite-monochromated Mo-Kα ($\lambda = 0.71073$ Å) radiation at 293(2) K. The structures were solved by direct methods and refined by full matrix least-squares on F^2 with all nonhydrogen atoms treated anisotropically. All calculations were performed with SHELXTL. Hydrogen atoms were assigned with common isotropic displacement factors and included in the final refinement by using geometric restraints.

Table 1. Analytical and molar conductance data for the complexes (calculated values in parentheses).

Complex	Analysis (%) C	H	N	Ln	Λm ($cm^2\,\Omega^{-1}mol^{-1}$)
$La(pic)_3L$	40.43(40.82)	3.54(3.10)	12.27(12.47)	11.02(11.24)	36.0
$Nd(pic)_3L$	40.27(40.65)	3.51 (3.09)	12.21(12.41)	11.43(11.62)	36.6
$Eu(pic)_3L$	40.15(40.40)	3.47(3.07)	12.15(12.34)	12.04(12.17)	48.7
$Gd(pic)_3L$	40.06 (40.23)	3.42(3.05)	12.06(12.29)	12.27(12.54)	38.7
$Tb(pic)_3L$	39.92(40.17)	3.39(3.05)	12.03(12.27)	12.34(12.66)	39.2
$Y(pic)_3L$	42.28(42.54)	3.56(3.23)	12.79(12.99)	7.28(7.50)	53.1

3. Results and discussion

3.1. *Properties of the discussion*

Analytical data for the complexes (table 1) indicate that all the complexes have 1 : 3 : 1 metal-to-picrate-to-L stoichiometry $Ln(pic)_3L$. The complexes are soluble in DMF, DMSO, acetonitrile, acetone, and $CHCl_3$, and slightly soluble in ethanol and methanol. The molar conductances of the complexes in acetone (see table 1) indicate that all complexes are nonelectrolytes [23], implying that all the picrate groups are in the coordination sphere.

3.2. *X-ray diffraction studies*

X-ray quality crystal of $Gd(pic)_3L$ was obtained after several weeks of slow evaporation of the chloroform–ethanol solution in air at room temperature. A summary of crystallographic data and details of the structure refinements are listed in table 2. Selected bond lengths and angles are given in table S1.

Single-crystal X-ray analysis of $Gd(Pic)_3L$ reveals that the coordination sphere around Gd(III) consists of four oxygen donors coming from a tetradentate L (O1, O2, O3, and O4) and four other oxygen donors coming from one bidentate and two unidentate picrates (O5, O6, O12, and O19) as shown in figure 1. The coordination polyhedron around Gd(III) can be best described as a distorted square antiprism (figure 2). The ligand wraps around the metal with its oxygen atoms forming a ring-like coordination structure with Gd(III). The two phenyl rings about the central bond in the molecule have a drastic twisting, with the dihedral angle between them being 63.95°. The La–O (C=O) distances (mean 2.354 Å) are significantly shorter than the La–O (C–O–C) distances (mean 2.556 Å). This suggests that the La–O (C=O) bond is stronger than the La–O (C–O–C) bond.

In the complex, the high coordination number of the lanthanide ion is satisfied by the tetradentate ligand, two bidentate, and one unidentate picrates, thus, no coordinated solvent exists in the complex, which can efficiently quench lanthanide luminescence; this is important in the design of supramolecular photonic devices [24].

The $[Gd(pic)_3L]$ units are linked *via* the significant intermolecular hydrogen bonds C8–H8 ··· O16 [O16 ··· H8, 2.5190 Å, and C8–H8 ··· O16#1, 139.10°; symmetry code #1: $1/2-x$, $1/2+y$, z] and C11–H11 ··· O14 [O14 ··· H11, 2.5004 Å, and C11–H11 ··· O14#2, 175.24°; symmetry code #2: $-1/2+x$, y, $1/2-z$] to further generate a 2-D supramolecular network as shown in figure 3.

Table 2. Crystal data and structure refinements for Gd(pic)$_3$L.

Empirical formula	$C_{42}H_{38}N_{11}O_{25}Gd$
Temperature (K)	298(2)
Crystal color	Yellow
Crystal size (mm^3)	$0.42 \times 0.38 \times 0.10$
Formula weight	1254.08
Crystal system	Orthorhombic
Space group	*Pbca*
Unit cell dimensions (Å, °)	
a	15.058(1)
b	23.370(2)
c	29.29(2)
α	90
β	90
γ	90
Volume (Å^3), Z	10,308(14), 8
Calculated density (g cm^{-3})	1.616
F(000)	5048
Wavelength (Å)	0.71073
Reflections collected	50,874
Independent reflections	9016
θ range for data collection (°)	1.94–25.01
Index range	$-12 \le h \le 17$; $-27 \le k \le 27$; $-34 \le l \le 34$
Goodness-of-fit on F^2	1.008
$R[I > 2\sigma(I)]$	$R = 0.0787$, $wR = 0.1739$
R(all data)	$R = 0.1755$, $wR = 0.2293$
Largest difference peak and hole (e Å^{-3})	2.547 and −1.306

To explore the other complex structures, XRPD of the La(III), Eu(III) and Tb(III) complexes with **L** were performed. The XRPD patterns (figures S1, S2, and S3) of the complexes showed the main reflections remaining nearly identical with the Gd(III) complex, supporting the notion that these four complexes are isostructural.

3.3. *IR spectra*

The main IR bands of the ligand and its complexes are presented in table 3. The IR spectra of the complexes are similar. The "free" **L** exhibits two absorptions at 1660 and 1120 cm^{-1} which are assigned to ν(C=O) and ν(C–O–C), respectively. In the complexes, the bonds shift by *ca* 47 and 38 cm^{-1} to lower wavenumbers, thus indicating that C=O and ether take part in coordination to the metal ions. The OH out-of-plane bending vibration of free Hpic at 1151 cm^{-1} disappears in spectra of the complexes, indicating that hydrogen of OH is replaced by Ln(III). The ν(C–O) at 1265 cm^{-1} is shifted to higher frequency by *ca* 10 cm^{-1} in the complexes, due to the following two effects. First, the hydrogen of OH is replaced by Ln(III), increasing the π-bond character in the C–O bond. Second, coordination of the oxygen of **L** to Ln(III) causes the π-character to be weakened. The free Hpic has ν_{as} (NO_2) and ν_s (NO_2) at 1555 and 1342 cm^{-1}, respectively; these split into two bands at 1578, 1544 cm^{-1} and 1359, 1330 cm^{-1} in the complexes, indicating that some oxygen atoms in the nitro of Pic$^-$ take part in

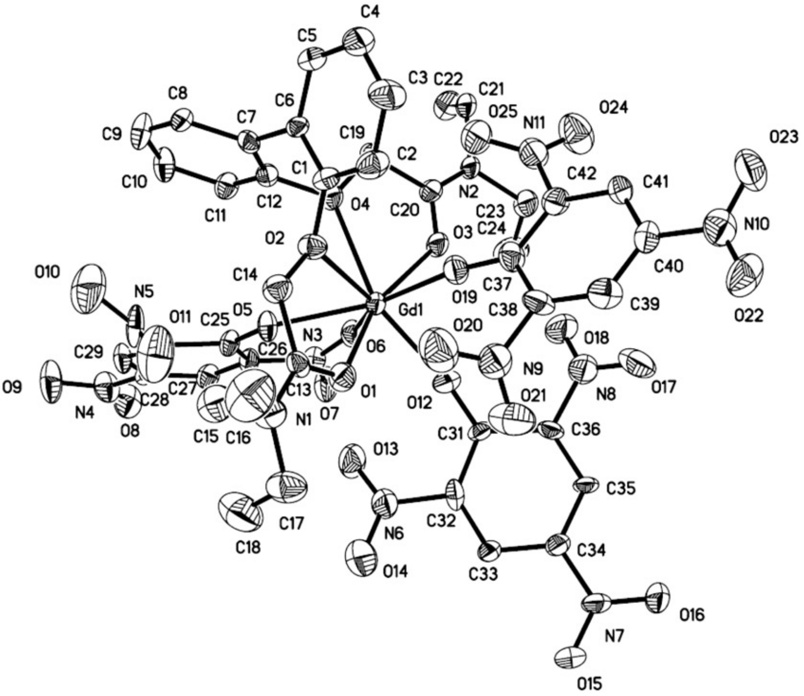


Figure 1. ORTEP diagram (30% probability ellipsoids) showing the coordination sphere of Gd(pic)$_3$L. Hydrogen atoms are omitted for clarity.

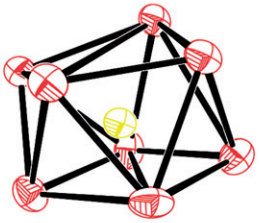


Figure 2. Coordination polyhedron of Gd(III) ion in Gd(pic)$_3$L.

coordination [25]. On the basis of the similarity of their IR spectra, it may be assumed that the complexes have similar structures.

3.4. *Photoluminescence studies*

The emission spectra of [Eu(pic)$_3$L] at room temperature in the solid state (the excitation and emission slit widths were 1.0 nm, figure 4) and in solution (the excitation and emission slit widths were 5.0 nm, concentration: 1.0×10^{-3} mol L^{-1}, figure 5) were recorded; the fluorescence characteristics of the europium complex are listed in table 4. It can be seen that the emission spectrum excited with 451 nm in the solid state shows

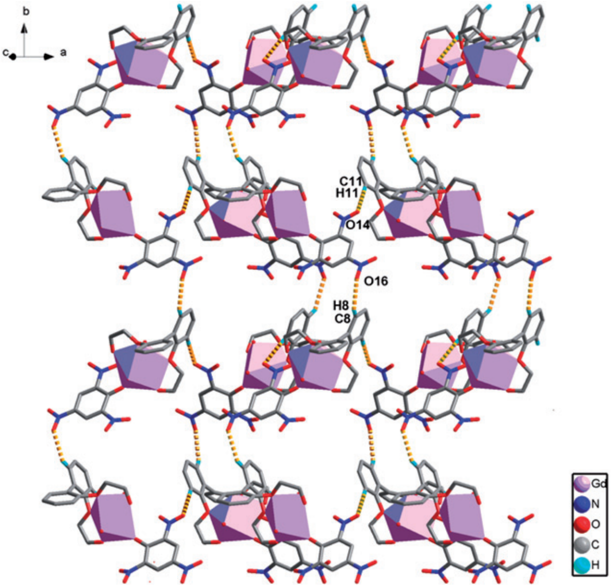


Figure 3. View of the 2-D network of Gd(pic)$_3$L generated by intermolecular hydrogen bonds [C8–H8 $\cdots$ O16#1, symmetry code #1: $1/2-x$, $1/2+y$, z; C11–H11 $\cdots$ O14#2, symmetry code #2: $-1/2+x$, y, $1/2-z$; the hydrogen bonds are indicated by dashed lines] (some atoms of the ligand and picrates are omitted for clarity).

Table 3. The most important IR bands of the rare-earth picrate complexes (cm^{-1}).

Complex	ν(C=O)	ν(C–O–C)	ν(C–O)	ν_{as}(–NO$_2$)	ν_s(–NO$_2$)
Hpic	–	–	1265	1555	1342
L	1660	1120	–	–	–
La(pic)$_3$L	1612	1082	1274	1578, 1542	1358, 1331
Nd(pic)$_3$L	1613	1083	1276	1578, 1543	1359, 1330
Eu(pic)$_3$L	1616	1082	1275	1578, 1544	1360, 1327
Gd(pic)$_3$L	1614	1082	1275	1579, 1542	1359, 1332
Tb(pic)$_3$L	1612	1081	1274	1578, 1545	1357, 1331
Y(pic)$_3$L	1612	1083	1276	1580, 1544	1361, 1332

characteristic emission bands of Eu(III) at 582, 590–596, and 615 nm, which are assigned to $^5D_0 \rightarrow {}^7F_0$, $^5D_0 \rightarrow {}^7F_1$, and $^5D_0 \rightarrow {}^7F_2$ transitions. The dominant emission is centered at 615 nm and corresponds to the hypersensitive $^5D_0 \rightarrow {}^7F_2$ transition, giving the complex an intense red luminescence. Notably, the $^5D_0 \rightarrow {}^7F_2$ transition is much more intense than the $^5D_0 \rightarrow {}^7F_1$ transition; the intensity ratio of the Eu(III) complex for $I(^5D_0 \rightarrow {}^7F_2)/I(^5D_0 \rightarrow {}^7F_1)$ indicates the absence of an inversion center at Eu(III) [26].

The result of luminescence lifetime study by time-resolved laser-induced fluorescence spectroscopy of the Eu(III) complex obtained at 77 K is shown in figure 6. The lifetime of the $^5D_0$ level of the Eu(III) in the complex obtained from the delayed curve is 0.26 ms.

From table 4, it can also be seen that in DMF solution, the fluorescence of europium was quenched which is attributed to decomposition of the complex in this solvent; in the

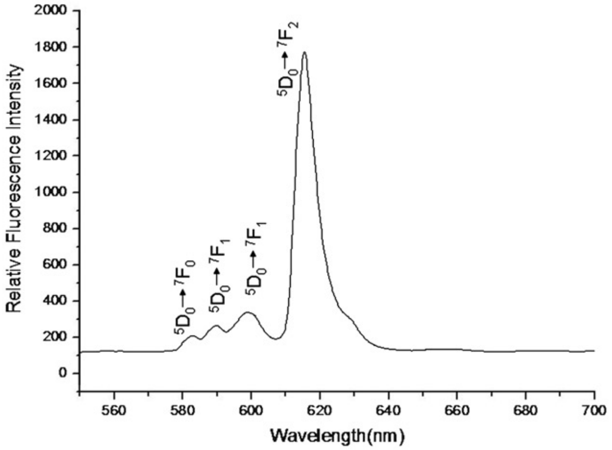


Figure 4. The emission spectrum of the Eu(III) complex in solid state.

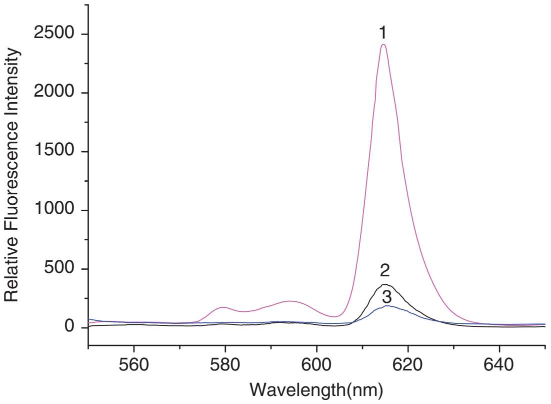


Figure 5. The emission spectrum of the Eu(III) complex in different solutions at room temperature. (1) In $CHCl_3$, (2) in acetone, (3) in acetonitrile.

Table 4. Fluorescence data for the europium complex.

Complex	Solvent	λ_{ex} (nm)	λ_{em} (nm)	RFI	Assignment
$Eu(pic)_3L$	Solid state	451	582	210	$^5D_0 \rightarrow {}^7F_0$
			590	265	$^5D_0 \rightarrow {}^7F_1$
			596	317	$^5D_0 \rightarrow {}^7F_1$
			616	1728	$^5D_0 \rightarrow {}^7F_2$
	$CHCl_3$	462	594	227	$^5D_0 \rightarrow {}^7F_1$
			615	2412	$^5D_0 \rightarrow {}^7F_2$
	Acetone	462	615	369	$^5D_0 \rightarrow {}^7F_2$
	Acetonitrile	462	615	189	$^5D_0 \rightarrow {}^7F_2$
	DMF	–	–	–	–

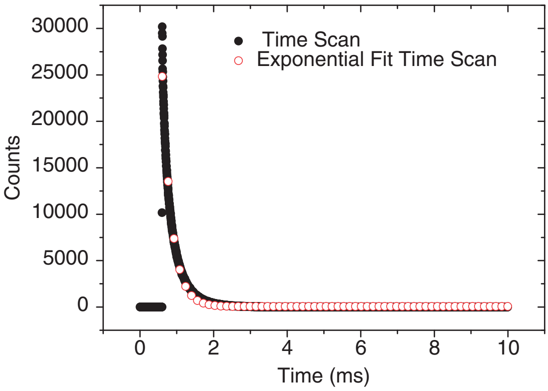


Figure 6. The time-resolved fluorescence spectroscopy of the Eu(III) complex at 77 K.

other three solvents, the complex has similar excitation and emission wavelengths. In $CHCl_3$ the europium picrate complex has the strongest luminescence, followed by acetone and then acetonitrile. This is due to the coordinating effects of the solvents [27], where vibrational quenching of the complex excited state may occur through high energy oscillators on the solvent molecule.

The fluorescence quantum yield **Φ** of the europium picrate complex in $CHCl_3$ (concentration: $1.0 \times 10^{-5}\,\mathrm{mol\,L^{-1}}$) was 6.67×10^{-3} with quinine sulfate as reference [28].

We do not detect any characteristic green emission of central Tb(III) in the Tb(III) complex, either in solid state or in solutions. This phenomenon is probably that the energy gap between the triplet state levels of the ligand and the lowest resonance level of the europium favor energy transfer for europium. In order to acquire the triplet excited state T_1 of **L**, the phosphorescence spectra of the Gd(III) picrate complex was measured at 77 K in a chloroform–methanol–ethanol mixture (v : v : v, 1 : 5 : 5). The triplet state energy levels T_1 of **L**, calculated from the shortest wavelength phosphorescence band [29] of the corresponding Gd(III) complexes, is $21552\,\mathrm{cm^{-1}}$. This energy level is above the lowest excited resonance level $^5D_0$ of Eu(III) ($17{,}300\,\mathrm{cm^{-1}}$) and $^5D_4$ ($20{,}500\,\mathrm{cm^{-1}}$) of Tb(III). Thus the absorbed energy could be transferred from **L** to the Eu or Tb ions. The triplet state energy level T_1 of **L** matches better to the lowest resonance level of Eu(III) ($\Delta\nu = 4252\,\mathrm{cm^{-1}}$) than Tb(III) ($\Delta\nu = 1052\,\mathrm{cm^{-1}}$), because such small $\Delta\nu(T_1–^5D_4)$ could result in a back-energy transfer from the excited resonance level $^5D_4$ of Tb(III) to the triplet state energy level T_1 of **L** and quench the luminescence of the Tb picrate complex [30].

4. Conclusion

We reported the synthesis, structural characterization, and luminescence properties of rare-earth picrate complexes with 2,2′-bis[(diethylcarbamoyl)-methoxy]-1,1′-biphenylene (**L**). The crystal structure of $Gd(pic)_3L$ shows that Gd(III) is eight-coordinate by four oxygen atoms from a ligand and the four other oxygen atoms from a bidentate and two unidentate picrates. The complex units are linked *via* intermolecular hydrogen bonds to form a 2-D netlike supramolecule. The Eu(III) complex exhibited characteristic fluorescence of europium ion. Different solvents affect the fluorescence of europium ions. The lifetime of the $^5D_0$ level of the Eu(III) ion in the complex is 0.26 ms. The quantum yield $\mathbf{\Phi}$ of the Eu(III) complex is 6.67×10^{-3} with quinine sulfate as reference. The lowest triplet state energy level of the ligand indicates that the triplet state energy level of the ligand matches better to the resonance level of Eu(III) than Tb(III). We designed a new amide-type podand that forms stable complexes with lanthanide picrates and sensitize Eu(III) emission, thus may have applications in the field of photonic devices.

Supplementary material

Crystallographic data for the structure reported in this article has been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 840458. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge, CB2 IEZ, UK (Fax: +44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk; http://www.ccdc.cam.ac.uk).

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