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# Preparation, crystal structure and luminescent properties of lanthanide picrate complexes with N-benzyl-2-{2'-[(benzyl-methyl-carbamoyl)-methoxy]biphenyl-2-yloxy}-N-methyl-acetamide (L)

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#### Abstract

A new amide-based ligand derived from biphenyl, *N*-benzyl-2-{2'-[(benzyl-methyl-carbamoyl)-methoxy]-biphenyl-2-yloxy}-*N*-methylaceamide (L) was synthesized. Solid complexes of lanthanide picrates with this new ligand were prepared and characterized by elemental analysis, conductivity measurements, IR and electronic spectroscopies. The molecular structure of  $[Eu(pic)_3L]$  shows that the Eu(III) ion is nine-coordinated by four oxygen atoms from the L and five from two bidentate and one unidentate picrates. All the coordinate picrates and their adjacent equivalent picrates form intermolecular  $\pi$ - $\pi$  stacking. Furthermore, the  $[Eu(pic)_3L]$  complex units are linked by the  $\pi$ - $\pi$  stacking to form a two-dimensional (2-D) netlike supramolecule. Under excitation, the europium complex exhibited characteristic emissions. The lifetime of the <sup>5</sup>D<sub>0</sub> level of the Eu(III) ion in the complex is 0.22 ms. The quantum yield  $\Phi$  of the europium complex was found to be  $1.01 \times 10^{-3}$  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) ion. © 2007 Elsevier B.V. All rights reserved.

Keywords: Lanthanide picrate complexes; Luminescent properties;  $\pi - \pi$  Stacking; Crystal structure

#### 1. Introduction

Fluorescence spectroscopy has become a powerful tool for monitoring biological events and elucidating the structure and function of biomolecules [1]. The sensitivity and time-resolved nature of fluorescence, in addition to the ready availability of necessary equipment, has made fluorescence spectroscopy a popular choice for studying biological processes. Recently, lanthanides have found wide success as luminescent probes [2,3]. Due to their long (ms) luminescence lifetimes, sharp emission spectra with large Stokes shifts (>200 nm), and unpolarized luminescence, lanthanide ions demonstrate features not common in the typical organic fluorophores.

Amide-based crown ethers offer many advantages in extraction and analysis of the rare earth ions because of their ring-like coordination structure and terminal group effects [4,5]. The open-chain crown ethers containing amide groups possess suitable molecular structure: a chain with inflexible terminal groups. Therefore, they are excellent reagents for activating ion-selective electrodes and extracts of rare earth ions [6]. However, fluorescence properties on open-chain crown ethers with lanthanide complexes have

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been rarely reported [7]. Our group is interested in the supramolecular coordination chemistry of lanthanide ions with amide-based crown ethers that have strong coordination capability to the lanthanide ions and terminal group effects [8]. As a part of our systematic studies, here we introduced biphenyl groups as the basic molecular frame and obtained a new open-chain crown ether ligand, Nbenzyl-2-{2'-[(benzyl-methyl-carbamoyl)-methoxy]-biphenyl-2-yloxy}-N-methyl-acetamide (L), and reported the synthesis, crystal structure and luminescent properties of the lanthanide picrate complexes with the new ligand. The crystal structure of the complex  $Eu(pic)_3L$  shows that the Eu(III) ion could be effectively encapsulated and protected by one coordinated ligand and three coordinated picrates. The  $\pi$ - $\pi$  stacking formed by the equivalent picrates, are very important for the assembly of the complex molecule units into a two-dimensional (2-D) netlike supermolecule and thus enhance the fluorescence intensity of the complex in solid state. Under excitation, the europium complex exhibited characteristic emissions. The lifetime of the  ${}^{5}D_{0}$  level of the Eu(III) ion in the complex is 0.22 ms. The quantum yield  $\Phi$  of the europium complex was found to be  $1.01 \times 10^{-3}$  with quinine sulfate as reference. And the lowest triplet state energy level of the ligand which was calculated from the phosphorescence spectrum of the Gd complex 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) ion.

# 2. Experimental

# 2.1. Materials

Lanthanide picrate [9] and *N*-methyl-*N*-benzylchloroacetamide [10] were prepared according to literature methods. All commercially available chemicals were of A.R. grade and were used without further purification.

#### 2.2. Methods

The metal ion was determined by EDTA titration using xylenal orange as indicator. C, H and N were determined using an Elementar Vario EL. Conductivity measurement was carried out with a DDS-307 type conductivity bridge using  $10^{-3}$  mol dm<sup>-3</sup> solution at 25 °C. IR spectra were recorded on Nicolet FT-170SX instrument using KBr discs in the 400–4000 cm<sup>-1</sup> region. <sup>1</sup>H NMR spectrum was measured on a Varian Mercury plus 300 M spectrometer in CDCl<sub>3</sub> solution with TMS as internal standard. Fluorescence and phosphorescence measurements were made on a Hitachi F-4500 spectrophotometer.

# 2.3. Synthesis of the ligand

The synthetic route for the ligand is shown in Scheme 1. Anhydrous  $K_2CO_3$  (5.6 g, 41 mmol) was added into the 20 mL DMF solution of 2,2'-dihydroxybiphenyl (1.86 g, 10 mmol) at 100 °C. After 1 h, a solution of *N*-methyl-*N*benzylchloroacetamide (5.92 g, 30 mmol) in 10 mL DMF was added dropwise to the mixture and maintained at 100 °C for 7 h. When cool, distilled water (60 ml) was added and the turbid solution was extracted with chloroform (3 × 40 mL). The combined organic phases were washed with water and dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed and the residue was chromatographed to afford the ligand L; Yield: 80%.

# 2.4. Synthesis of the lanthanide picrate complexes

To a solution of 0.2 mmol lanthanide picrate in 5 ml of ethanol was added dropwise the solution of 0.2 mmol L in 10 ml of ethanol. The mixture was stirred at room temperature for 6 h. The precipitated solid complex was filtered, washed with ethanol and dried in vacuum over  $P_2O_5$  for 48 h. All the complexes were obtained as yellow powders in a yield of 85–90%. Slowly evaporating a solution of the europium complex in CHCl<sub>3</sub>/CH<sub>3</sub>CH<sub>2</sub>OH at room temperature, resulted in the formation of block crystals after 2 months.

#### 2.5. Crystal structure determination

X-ray diffraction data of Eu(pic)<sub>3</sub>L was collected on a Bruker SMART CCD diffractometer, using graphitemonochromatized Mo K $\alpha$  ( $\lambda = 0.71073$  Å) at 293(2) K. The structures were solved by direct method and refined by full matrix least-squares techniques on  $F^2$  with all nonhydrogen atoms treated anisotropically. All calculations



Scheme 1. The synthetic route for the ligand L.

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 Table 1

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

Complex	Analysis (%)	$\Lambda_{\rm m}~({\rm cm}^2~\Omega^{-1}~{\rm mol}^{-1})$			
	С	Н	Ν	Ln	
La(pic) <sub>3</sub> L	44.67(45.08)	3.04(2.86)	11.37(11.57)	10.23(10.44)	41.6
Nd(pic) <sub>3</sub> L	44.72(44.91)	3.02(2.84)	11.36(11.53)	10.51(10.78)	35.2
Eu(pic) <sub>3</sub> L	44.24(44.64)	2.68(2.83)	11.26(11.46)	11.16(11.31)	37.4
Gd(pic) <sub>3</sub> L	44.12(44.48)	2.97(2.82)	11.21(11.42)	11.24(11.64)	40.5
Tb(pic) <sub>3</sub> L	44.08(44.41)	2.68(2.81)	11.15(11.40)	11.37(11.77)	39.8
Y(pic) <sub>3</sub> L	46.49(46.84)	2.74(2.97)	12.11(12.02)	6.72(6.95)	43.7

were performed with the program package SHELXTL. The hydrogen atoms were assigned with common isotropic displacement factors and included in the final refinement by using geometrical restrains.

# 3. Results and discussion

# 3.1. Properties of the discussion

Analytical data for the complexes listed in Table 1, indicate that all the complexes conform to a 1:3:1 metal-to-picrate-to-L stoichiometry  $Ln(pic)_3L$ . The complexes are soluble in DMF, DMSO, acetonitrile, acetone, ethyl acetate and CHCl<sub>3</sub>, but slightly soluble in ethanol and methanol. The molar conductances of the complexes in acetone (see Table 1) indicates that all the complexes act as nonelectrolyte [11], implying that all the picrate groups are in the coordination sphere.

Table 2

Crystal data and structure refinements for e	europium picrate complex	
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	1 1 1
Empirical formula	C <sub>101</sub> H <sub>77</sub> Cl <sub>3</sub> Eu <sub>2</sub> N <sub>22</sub> O <sub>50</sub>
Temperature (K)	293(2)
Crystal color	yellow
Crystal size (mm)	$0.35 \times 0.30 \times 0.22$
Formula weight	2809.12
Crystal system	triclinic
Space group	$P\bar{1}$
a (Å)	12.4779(16)
b (Å)	15.014(3)
<i>c</i> (Å)	17.4846(18)
α (°)	69.982(15)
$\beta$ (°)	81.329(11)
γ (°)	72.769(14)
$V(\text{\AA}^3)$	2935.2(8)
Ζ	1
$D_{\text{calc}} (\text{Mg/m}^3)$	1.589
F(000)	1414
Radiation, graphite-monochromatized, $\lambda$ (Å)	0.7107
Reflections collections	24405
Independent reflection	11600
$\theta$ Range for data collection (°)	2.94-26.50
Index range	$-15 \leqslant h \leqslant 15$ ,
	$-18 \leqslant k \leqslant 18$ ,
	$-21 \leqslant l \leqslant 20$
Goodness-of-fit on $F^2$	1.029
$R \left[ I \ge 2\sigma(I) \right]$	R = 0.0443, wR = 0.1166
R (all data)	R = 0.0604, wR = 0.1213
Largest difference in peak and hole ( $e Å^{-3}$ )	1.2050.544

# 3.2. Crystal structure of $Eu(Pic)_{3}L$

A summary of crystallographic data and details of the structure refinements are listed in Table 2. The selected bond lengths and bond angles are given in Table 3.

The single-crystal X-ray analysis of the complex  $Eu(Pic)_3L$  reveals that the Eu(III) ion is coordinated with 9 oxygen donor atoms, five of which belong to two bidentate and one unidentate picrates and the remaining four to the tetradentate ligand L (Fig. 1). The coordination polyhedron around Eu(III) ion is a distorted tricapped trigonal prism (Fig. 2). The ligand wraps around the metal ion with its oxygen atoms and forms a ring-like coordination structure together with the Eu atom. The two phenyl rings about the central bond in the molecule have a drastic twisting, with the dihedral angle between them being 55.70°. The La–O (C=O) distances (mean 2.367 Å) are significantly shorter than the La–O (C=O) bond is stronger than the La–O (C–O–C) bond.

In the complex, the requirement of high coordination number of the lanthanide ion is satisfied by the tetradentate ligand, two bidentate and one unidentate picrates, thus, no coordinated solvent molecules exist in the complex, which can efficiently quench lanthanide luminescence, this is important in the design of supramolecular photonic devices [12].

Table 3	
Selected bond lengths (Å) and bond angles (°) for Eu(pic	:)3L

Eu(1)–O(15)	2.288(3)	Eu(1)–O(2)	2.476(3)
Eu(1)-O(12)	2.317(3)	Eu(1)–O(6)	2.499(3)
Eu(1)-O(5)	2.323(3)	Eu(1) - O(3)	2.575(3)
Eu(1)–O(1)	2.361(4)	Eu(1)–O(22)	2.612(4)
Eu(1)–O(4)	2.374(3)		
O(15)-Eu(1)-O(12)	85.60(13)	O(5)-Eu(1)-O(6)	66.07(11)
O(12)-Eu(1)-O(5)	81.96(13)	O(1)-Eu(1)-O(6)	78.21(12)
O(15)-Eu(1)-O(1)	94.06(14)	O(15)-Eu(1)-O(3)	73.23(11)
O(5)-Eu(1)-O(1)	76.40(12)	O(1)-Eu(1)-O(3)	74.47(11)
O(15)-Eu(1)-O(4)	82.50(13)	O(4)-Eu(1)-O(3)	61.59(10)
O(12)-Eu(1)-O(4)	76.84(12)	O(2)-Eu(1)-O(3)	66.73(10)
O(5)-Eu(1)-O(2)	75.12(11)	O(12)-Eu(1)-O(22)	63.67(13)
O(1)-Eu(1)-O(2)	63.06(12)	O(5)-Eu(1)-O(22)	68.10(12)
O(4)-Eu(1)-O(2)	89.96(11)	O(4)-Eu(1)-O(22)	65.31(12)
O(15)-Eu(1)-O(6)	70.70(12)	O(2)-Eu(1)-O(22)	69.81(12)
O(12)-Eu(1)-O(6)	71.35(12)		



Fig. 1. ORTEP diagram (30% probability ellipsoids) show the coordination sphere of [Eu(pic)<sub>3</sub>L]. Hydrogen atoms are omitted for clarity.

Interestingly, all the three coordinated picrates in the complex molecule stretch out like three hands and capture their equivalent picrates of the adjacent molecules to form  $\pi$ - $\pi$  stacking [13] with the dihedral angles between them being 0°, 0° and 0°, and the distances between their centroids being 3.779 Å, 3.917 Å and 3.647 Å, respectively, thus, producing a two-dimensional (2-D) netlike supramolecule as shown in Fig. 3.

# 3.3. IR spectra

The main infrared bands of the ligand and its complexes are presented in Table 4. The "free" ligand L exhibit two



Fig. 2. Coordination polyhedron of Eu(III) ion in Eu(pic)<sub>3</sub>L.

absorption bands at 1667 and 1110 cm<sup>-1</sup> which are assigned to v(C=O) and v(C=O-C), respectively. In the complexes, the bonds shift by ca. 51 and  $28 \text{ cm}^{-1}$  towards lower wave numbers, thus indicating that the C=O and ether O-atoms take part in coordination to the metal ions. The larger shift for v(C=O) in the spectrum of the complex suggests that the Ln-O (carbonyl) bond is stronger than the Ln-O (ether) bond. The OH out-of-plane bending vibration of the free Hpic at  $1151 \text{ cm}^{-1}$  disappears in the spectrum of the complex indicating that the H atom of the OH group is replaced by Ln(III). The vibration v(C-O) at  $1265 \text{ cm}^{-1}$  is shifted towards higher frequency by ca.  $9 \text{ cm}^{-1}$  in the complex. This is due to the following two effects. First, the hydrogen atom of the OH group is replaced by Ln(III), increasing the  $\pi$ -bond character in the C–O bond. Secondly, coordination of the oxygen atom of L to Ln(III) causes the  $\pi$ -character to be weakened. The free Hpic has  $v_{as}$  (NO<sub>2</sub>) and  $v_s$  (NO<sub>2</sub>) at 1555 and 1342 cm<sup>-1</sup>, respectively, which splits into two bands at  $1578, 1542 \text{ cm}^{-1}$  and  $1359, 1331 \text{ cm}^{-1}$  in the complex. This indicates that some of the O-atoms in the nitro group of Pic<sup>-</sup> take part in coordination [14].

# 3.4. <sup>1</sup>H NMR spectra and mass spectra

L: <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.33–6.96 (m, 18H, ArH and C<sub>12</sub>H<sub>8</sub>–), 4.62 (s, 2H, –O–CH<sub>2</sub>–CO–), 4.59 (d, J = 5.4 Hz, 2H, –N–CH<sub>2</sub>–), 4.49 (s, 2H, –O–CH<sub>2</sub>–CO–), 4.36 (d, J = 24 Hz, 2H, –N–CH<sub>2</sub>–), 2.81–2.68 (m, 6H, –CH<sub>3</sub>).



Fig. 3. The 2-D layers of  $[Eu(pic)_3L]$  generated by intermolecular  $\pi - \pi$  stacking interactions. All the N-methylbenzylamines are omitted for clarity.

Table 4					
The most important IR	bands of the	rare earth	picrate	complexes (c	$cm^{-1}$ )

Complex	v(C=O)	v(С–О–С)	v(C–O)	$v_{as}$ (-NO <sub>2</sub> )	$v_s (-NO_2)$
Hpic			1265	1555	1342
L	1667	1110			
La(pic) <sub>3</sub> L	1615	1081	1273	1576, 1542	1360, 1329
Nd(pic) <sub>3</sub> L	1615	1082	1273	1577, 1541	1357, 1330
Eu(pic) <sub>3</sub> L	1616	1082	1274	1577, 1542	1359, 1331
Gd(pic) <sub>3</sub> L	1616	1082	1274	1578, 1542	1359, 1331
Tb(pic) <sub>3</sub> L	1616	1082	1274	1578, 1542	1360, 1331
Y(pic) <sub>3</sub> L	1618	1082	1275	1578, 1542	1359, 1331

[La(pic)<sub>3</sub> · L]: <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  8.89 (s, 6H, pic-), 7.36–7.04 (m, 18H, ArH and C<sub>12</sub>H<sub>8</sub>–), 4.68 (m, 4H, –N– CH<sub>2</sub>–), 4.38 (s, 2H, –O–CH<sub>2</sub>–CO–), 4.22 (s, 2H, –O– CH<sub>2</sub>–CO–), 2.80–2.73 (m, 6H, –CH<sub>3</sub>).

The <sup>1</sup>H NMR spectra of the "free" ligand L, the diamagnetic Ln(III) picrate complex La(Pic)<sub>3</sub>L were measured in CDCl<sub>3</sub>. The spectrum of L exhibits two multiplets at ca. 7.26 and 2.75 ppm, two doublets at 4.59 ppm (J = 5.4 Hz) and 4.36 ppm (J = 24 Hz), and two singlets at 4.62 and 4.49 ppm assigned to C<sub>12</sub>H<sub>8</sub>- and -C<sub>6</sub>H<sub>5</sub> protons, -CH<sub>3</sub> protons, two groups of -N-CH<sub>2</sub>- protons, two groups of -O-CH<sub>2</sub>-CO- protons, respectively.

Upon coordination, the proton signal of  $-O-CH_2-CO$ in the lanthanum complex is shifted to higher field by ca.0.25 ppm, and the signal of  $-N-CH_2-$  moves to lower field. This is probably due to the inductive effect of Ln– O(L) bonds and a change in the conformation of the ligand in the complexes. The proton signal of the OH group in free HPic disappears in the complexes, indicating that the H atom of the OH group is replaced by Ln(III). The benzene ring protons of the free HPic exhibit a singlet at 9.12 ppm. Upon coordination, the signal moves to higher field. Only one singlet is observed for the benzene ring protons of the three coordination picrate groups, indicating fast exchange among the groups in solution [15].

The mass spectrum of L shows a molecular ion at m/z = 509 (M+H), confirming the molecular formula of L as  $C_{32}H_{32}N_2O_4$ . Above the mass of  $C_{12}H_8$  (m/z = 152) are observed two major fragment ions at m/z = 330 (M – [-O-CH<sub>2</sub>-CO-NC<sub>6</sub>H<sub>5</sub>(C<sub>2</sub>H<sub>5</sub>)]) and 181 (M-[-CO-NC<sub>6</sub>H<sub>5</sub>(C<sub>2</sub>H<sub>5</sub>)]-[-O-CH<sub>2</sub>-CO-NC<sub>6</sub>H<sub>5</sub>(C<sub>2</sub>H<sub>5</sub>)]).

#### 3.5. Electronic spectra

The electronic spectra in the visible region of the Ln(III) complexes exhibit alternations in intensity and shifts in position of the absorption bands relative to the corresponding Ln(III) aquo ions. The shift has been attributed by Jorgensen to the effect on the crystal field of interelectronic repulsion between the 4f electrons, and is related to the covalent character of the metal–ligand bond, assessed by Sinha's parameter ( $\delta$ ), the nephelauxetic ratio ( $\beta$ ) and the bonding parameter ( $b^{1/2}$ ) [16]. Absorption spectra of the Eu(III) complex was registered in chloroform solution at room temperature and the covalent parameters were calculated (Table 5). The values of  $\beta$ , which are less

Table 5Covalent parameters for the neodymium picrate complex

Complex	Frequency (cm <sup>-1</sup> )	Assignment	Covalent parameters
Nd(pic) <sub>3</sub> L	11261	${}^{4}I_{9/2} - {}^{4}F_{3/2}$	$\beta = 0.9984$
	12469	${}^{4}F_{5/2}$	$\delta = 0.1603$
	13405	${}^{4}F_{7/2}$	$b^{1/2} = 0.0283$
	14771	${}^{4}F_{9/2}$	
	17212	${}^{4}G_{5/2}$	
	17414	${}^{2}G_{7/2}$	
	19048	${}^{4}G_{7/2}$	



Fig. 4. The emission spectrum of the europium picrate complex in solid state at room temperature.

than unity, and positive values of  $\delta$  and  $b^{1/2}$  support the existence of partial covalent bonding between metal and ligand [17].

# 3.6. Luminescence study in solid state and in solutions at room temperature

The emission spectra of  $[Eu(pic)_3L]$  at room temperature in the solid state (the excitation and emission slit widths were 1.0 nm, Fig. 4) and solution (the excitation and emission slit widths were 10.0 nm, Fig. 6) were recorded. The emission spectra are similar to each other and show characteristic emission bands of an Eu(III) ion at about 592 and 614 nm, corresponding to  ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$  and  ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$  transitions. The fluorescence intensities at 614 nm are stronger than those at 592 nm, so that the peak height at 614 nm was used to measure the fluorescence intensities of an Eu(III) complex. The fluorescence characteristics of the europium complex in solid state and in CHCl<sub>3</sub>, ethyl acetate, acetone, acetonitrile, and DMF solutions (concentration:  $1.0 \times 10^{-3}$  mol L<sup>-1</sup>) are listed in Table 6. It can be seen that the Eu complex shows strong emission when excited with 421 nm in the solid state. The intensity ratio value  $\eta ({}^{5}D_{0} \rightarrow {}^{7}F_{2}/{}^{5}D_{0} \rightarrow {}^{7}F_{1})$  is 2.8, indicating a low symmetry for the electrostatic field surrounding Eu(III) [18]. This conclusion agrees with the crystal structure of the complex.



Fig. 5. The time-resolved fluorescence spectroscopy of the europium complex at 77 K.



Fig. 6. The emission spectrum of the europium picrate complex in different solutions at room temperature.

Table 6 Fluorescence data for the europium picrate complex

Complex	Solvent	$\lambda_{\rm ex} ({\rm nm})$	$\lambda_{\rm em} (\rm nm)$	RFI	Assignment
Eu(pic) <sub>3</sub> L	solid state	421	593	178	${}^5D_0 \rightarrow {}^7F_1$
			614	491	$^5D_0 \rightarrow {}^7F_2$
	CHCl <sub>3</sub>	461	592	67	${}^{5}D_{0} \rightarrow {}^{7}F_{1}$
	5		613	433	${}^{5}\text{D}_{0} \rightarrow {}^{7}\text{F}_{2}$
	AcOEt	461	592	32	${}^{5}D_{0} \rightarrow {}^{7}F_{1}$
			613	155	$^5D_0 \rightarrow {}^7F_2$
	acetone	461	593	24	$^5D_0 \rightarrow {}^7F_1$
			613	117	$^5D_0 \rightarrow {}^7F_2$
	acetonitrile	461	592	16	$^{5}D_{0} \rightarrow ^{7}F_{1}$
			614	52	$^5D_0 \rightarrow {}^7F_2$
	DMF				

The result of luminescence lifetime study by timeresolved laser-induced fluorescence spectroscopy of the europium complex obtained at 77 K is shown in Fig. 5. The lifetime of the  ${}^{5}D_{0}$  level of the Eu(III) ion in the complex obtained from the delayed curve is 0.22 ms.

From Table 6, it also can be seen that in DMF solution, the fluorescence of europium was quenched which is contributed to the decomposition of the complex in this solvent, and in the other four solvents, the complex has the similar excitation and emission wavelengths. In CHCl<sub>3</sub> solution the europium picrate complex has the strongest luminescence, followed by ethyl acetate and then acetone and acetonitrile. This is due to the coordinating effects of the solvents, namely solvate effect [19] where vibrational quenching of the complex excited state may occur through high energy oscillators on the solvent molecule.

The fluorescence intensity of the europium complex in solution is much lower than the one in solid state. We consider this is on one hand due to the breakage of the  $\pi$ - $\pi$  stacking formed by coordinated equivalent picrates which favor to the energy transfer for europium [20], and on the other hand due to the coordinating effects of solvents.

The fluorescence quantum yield  $\Phi$  of the europium picrate complex in CHCl<sub>3</sub> (concentration:  $1.0 \times 10^{-5}$  mol L<sup>-1</sup>) was found to be  $1.01 \times 10^{-3}$  with quinine sulfate as Ref. [21].

Compared with the europium complex, the characteristic fluorescence of the terbium complex was not determined, either in solid state or in solutions. The reason is probably that the energy gap between the triplet state levels of the ligand and the lowest resonance level of the europium favor to the energy transfer process for europium. In order to acquire the triplet excited state  $T_1$  of the ligand 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 the ligand L, which was calculated from the shortest wavelength phosphorescence band [22] of the corresponding Gd(III) complexes, is  $21930 \text{ cm}^{-1}$ . This energy level is above the lowest excited resonance level  ${}^{5}D_{0}$  of Eu(III)  $(17\,300\,\text{cm}^{-1})$  and  ${}^{5}\text{D}_{4}$  (20500 cm $^{-1}$ ) of Tb(III). Thus the absorbed energy could be transferred from ligand to the Eu or Tb ions. The triplet state energy level  $T_1$  of this ligand L matches better to the lowest resonance level of Eu(III)  $(\Delta v = 4630 \text{ cm}^{-1})$  than Tb(III)  $(\Delta v = 1430 \text{ cm}^{-1})$ ion, because such small  $\Delta v(T_1 - {}^5D_4)$  could result in a back-energy transfer process from the excited resonance level  ${}^{5}D_{4}$  of Tb(III) to the triplet state energy level T<sub>1</sub> of this ligand L and quench the luminescence of the Tb picrate complex [23].

# 4. Conclusion

In summary, six new lanthanide picrate complexes  $LnL(Pic)_3$  (Ln = La, Nd, Eu, Gd, Tb, Y) of a new openchain crown ether ligand *N*-benzyl-2-{2'-[(benzyl-methylcarbamoyl)-methoxy]-biphenyl-2-yloxy}-*N*-methyl-acetamide (**L**) were obtained and structurally characterized. The crystal structure of  $[Eu(pic)_3L]$  shows that the Eu(III) ion is nine-coordinated by four oxygen atoms from the **L** and five from two bidentate and one unidentate picrates. The coordinate picrates can form intermolecular  $\pi$ - $\pi$  stacking, which is very important for the assembly of the complex molecule units into a two-dimensional (2-D) netlike supermolecule, and thus enhance the fluorescence intensity of the europium complex in solid. The lifetime of the  ${}^{5}D_{0}$  level of the Eu(III) ion in the complex is 0.22 ms. The quantum yield  $\Phi$  of the europium complex was found to be  $1.01 \times 10^{-3}$  with guinine 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) ion. To sum up, we designed a new open-chain crown ether ligand which can form stable complexes with lanthanide picrates and sensitize Eu(III) emission. Further studies of the ligand are under way.

#### 5. Supplementary material

CCDC 635705 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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