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Synthesis and luminescence properties of 2-(benzylcarbamoyl)phenyl derivatives and their europium complexes

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ABSTRACT: Six novel 2-(benzylcarbamoyl)phenyl derivatives were synthesized and characterized by ¹H-NMR, mass spectrometry, infrared spectra and elemental analysis. Their europium complexes were prepared and characterized by elemental analysis, EDTA titrimetric analysis, IR and UV spectra as well as molar conductivity measurements. The luminescence properties of these complexes were investigated and results show that 2-(benzylcarbamoyl)phenyl derivatives possess high selectivity and good coordination with the europium ion. Complex Eu-2-(benzylcarbamoyl)phenyl-2-phenylacetate showed green luminescence that was emitted by the ligand of 2-(benzylcarbamoyl)phenyl-2-phenylacetate, while other complexes showed the characteristic red luminescence of europium ion and also possessed high luminescence intensity. Copyright © 2012 John Wiley & Sons, Ltd.

Keywords: amide ligand; rare earth; complex; synthesis; luminescence properties

Introduction

Rare earth complexes are currently attracting considerable attention due to their special physical and chemical properties; i.e. electric, magnetic and catalytic attributes (1-3). Since rare earth complexes can show narrow emission bands and hypersensitivity to coordination environments, researchers have paid particular attention to their luminescence properties (4). The luminescence intensity of rare earth complexes is strongly dependent on the absorption efficiency of ligands in the UV region, the efficiency of ligand-to-metal energy transfer and the efficiency of rare earth luminescence (5,6). Because of its ring-like coordination structure and terminal group effects (7), the amide compounds have a variable coordination style for rare earth ions. Many studies have reported in recent years on the synthesis of amide rare earth complexes. Ercules et al. (8) synthesized N-(methylpyridyl)acetamide and reported the influence of N-(methylpyridyl)acetamide ligands on the photoluminescent properties of Eu-perchlorate complexes. Liu et al. (9) synthesized a series of ether-amide-type multipodal ligands and their europium complexes. Song et al. (10) synthesized 2.2'-bipydine derivative and its rare earth complexes and investigated their luminescence properties. Luo et al. (11) designed and synthesized novel mono-substituted β -diketone ligands and their rare earth complexes. In this study, six novel 2-(benzylcarbamoyl) phenyl derivatives as well as their intermediates were synthesized and characterized by ¹H nuclear magnetic resonance spectroscopy (¹H-NMR), mass and infrared spectroscopy (MS & IR) and elemental analysis. Their europium complexes were also prepared and characterized by elemental analysis, ethylenediaminetetraacetic acid (EDTA) titration analysis, IR and UV spectra as well as molar conductivity measurements. The luminescence properties and coordination modes of these complexes were investigated. The synthesis route for the 2-(benzylcarbamoyl)phenyl derivatives (L¹⁻⁶) is shown in Scheme 1.

Experimental

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Methods

The carbon, hydrogen, and nitrogen analyses were obtained using an Elementar Vario ELIII elemental analyzer and ¹H-NMR spectrum was measured on a Varian 400 NMR (400 MHz) instrument (both from Agilent Technologies Co. Ltd., Beijing, China) in CDCl₃ solution with tetramethylsilane (TMS) as internal standard. The europium ion was determined by ethylenediaminetetraacetic acid (EDTA) titration using xylenol orange as an indicator. IR spectra in the 4000–400 cm⁻¹ region were measured using KBr pellets on a PerkinElmer spectrometer (PerkinEylmer Chengdu, Chengdu, China). UV spectra were detected on a LabTech UV-2100 (Columbia MO, USA) spectrophotometer using ethyl alcohol to dissolve the samples. Fluorescence spectra were obtained on a Hitachi F-4500 spectrophotometer (Hitachi *Hi-Tech*, Shanghai, China) at room temperature.

Materials

Europium nitrate was prepared according to the literature (12). Benzylamine and aromatic carboxylic acid were of CP grade. Methyl salicylate and other reagents were of AR grade and purchased from commercial suppliers.

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(a) 100°C, reflux, 12 h; (b) SOCl₂, N₂, 60°C, reflux, 5~6 h; (c) CH₂Cl₂, N₂, reflux, 8~9 h



Scheme 1. The synthesis route for 2-(benzylcarbamoyl)phenyl derivatives.

Synthesis

Synthesis of N-Benzylsalicylamide (A). Methyl salicylate (4.08 g, 30 mmol) and benzylamine (3.21 g, 30 mmol) were added into a 100-mL three-necked flask. The mixture was heated to reflux for 12 h, cooled and diluted with 20 mL cold ethyl acetate and a large white solid precipitate was obtained. This compound was filtered, washed three times with ethyl acetate and dried under a vacuum for 24 h. The resulting product was a white solid with the following features: yield, 80%; mp 129-32°C; ¹H-NMR (CDCl₃, 400 MHz); δ , 4.56 (d, 2H, CH₂), 6.50 (s, 1H, NH), 6.75 (t, 1H, ArH), 6.93 (d, 1H, ArH), 7.18-7.32 (m, 7H, ArH), 12.22 (s, 1H, OH); MS (EI) m/z (%), 227 (M, 50), 228 (M + 1, 11); And IR, 1642 (C = O), 3357, 1546, 699 (N-H), 3357 (O-H).

Synthesis of acyl chloride (B^{1-6}). Benzoic acid (3.66 g, 20 mmol) and SOCl₂ (15 mL) were added into a 100-mL single-necked flask.

The mixture was heated to reflux until benzoic acid was completely dissolved. Next, the mixture was refluxed for another 5 h and the SOCl₂ residue was completely distilled under a vacuum resulting in benzoyl chloride (B¹). Methods used for compounds B²⁻⁶ were similar to that for compound B¹.

Synthesis of amide ligands (L¹⁻⁶). 2-(benzylcarbamoyl)phenyl benzoate (L^1). The obtained benzoyl chloride was dissolved in 20 mL dry dichloromethane in a 100 mL single-necked flask. Next, a dichloromethane solution of N-Benzylsalicylamide (4.86 g, 20 mmol) and triethylamine (5 mL) were added to the flask. The mixture was stirred for 8 h at room temperature and then became faint yellow in colour. After adding 30 mL distilled water to the flask, the mixture was neutralized to pH 7-8 with dilute NaHCO₃, extracted with dichloromethane, washed three times with distilled water and evaporated to produce a crude product.

This product was purified over a silica-gel column with the eluent of ethyl acetate/petroleum ether (1:4, v/v). The resulting solution was collected, evaporated and then dried under a vacuum, resulting in a white solid product with the following characteristics: Yield, 45%; Mp, 106-109°C; ¹H-NMR (CDCl₃, 400 MHz), δ , 4.50 (d, 2H, ArCH₂N), 6.60 (s, 1H, NH), 7.11–7.64 (m, 11H, ArH), 7.90 (d, 1H, ArH) and 8.05 (d, 2H, ArH); MS (EI) m/z (%), 331 (M, 5); IR (KBr): 1740, 1630 (C = O), 1202 (C-O-C), 3283, 1570, and 707 (N-H). Analysis data calculated for C₂₁H₁₇NO₃ were: C, 76.12; H, 5.17; N, 4.23. Found: C, 75.22; H, 5.20; N, 4.25. Synthesis methods were similar to those for compound L¹.

2-(benzylcarbamoyl)phenyl-4-methylbenzoate (L²). This crude product was purified over a silica-gel column with the eluent of ethyl acetate/petroleum ether (1:6, v/v), forming a white solid with the following characteristics: Yield, 40%; Mp, 87-90°C; ¹H-NMR (CDCl₃, 400 MHz); δ , 2.46 (s, 3H, ArCH₃), 4.49 (d, 2H, ArCH₂N), 6.65 (s, 1H, NH) and 7.11-7.92 (m, 13H, ArH); MS (ESI) m/z (%), 346.2 (M + 1, 5), 691.4 (2M + 1, 20) and 693.1 (2M + 3, 23); IR (KBr): 1741, 1630 (C = O), 1198 (C-O-C), 3282, 1531 and 692 (N-H). Analytical data calculated for C₂₂H₁₉NO₃ were: C, 76.50; H, 5.54 and N, 4.06. Found: C, 75.55; H, 5.47and N, 4.03.

2-(benzylcarbamoyl)phenyl-4-chlorobenzoate (L³). This product was purified over a silica-gel column with an eluent of ethyl acetate/petroleum ether (1:6, v/v), forming a white solid with the following properties: Yield, 65%; Mp, 108-111°C; ¹H-NMR (CDCl₃, 400 MHz); δ , 4.49 (d, 2H, ArCH₂N), 6.88 (s, 1H, NH), 7.13-7.94 (m, 13H, ArH); MS (EI) m/z (%), 365 (M, 5) and 367 (M + 2, 2); IR (KBr): 1741, 1646 (C = O), 1206 (C-O-C), 3272, 1554 and 691 (N-H). Data for C₂₁H₁₆CINO₃ were: C, 69.95; H, 4.41; N, 3.83. Found: C, 69.85; H, 4.47; N, 3.79.

2-(benzylcarbamoyl)phenyl-4-methoxybenzoate (L⁴). This product was purified over a silica-gel column with an eluent of ethyl acetate/ petroleum ether (1:5, v/v), forming a white solid with the following properties: Yield, 35%; Mp, 87-89°C; ¹H-NMR (CDCl₃, 400 MHz); δ , 3.90 (s, 3H, OCH₃), 4.49 (d, 2H, CH₂), 6.68 (s, 1H, NH), 6.90-7.49 (m, 10H, ArH), 7.91-7.93 (m, 1H, ArH), 7.95 (m, 2H, ArH); IR (KBr): 1741, 1653 (C = O), 1206 (C-O-C), 3273, 1608, 691 (N-H). Data for C₂₂H₁₉NO₄ were: C, 73.12; H, 5.30; N, 3.88. Found: C, 72.29; H, 5.27; N, 3.73.

2-(benzylcarbamoyl)phenyl-3-chlorobenzoate (L⁵). This product was prepared as above and produced a white solid with the following characteristics: Yield, 70%; Mp, 113-115°C; ¹H-NMR (CDCl₃, 400 MHz); δ , 4.29 (d, 2H, CH₂), 6.38 (s, 1H, NH), 7.06-7.82 (m, 13H, ArH); IR (KBr): 1741, 1630 (C = O), 1199 (C-O-C), 3296, 1578, 700 (N-H). Data for C₂₁H₁₆CINO₃ were: C, 68.95; H, 4.41; N, 3.83. Found: C, 68.88; H, 4.54; N, 3.85.

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2-(benzylcarbamoyl)phenyl-2-phenylacetate (L^6). This product was prepared as above producing a red solid with the following properties: Yield, 60%; Mp, 70-72°C; ¹H-NMR (CDCl₃, 400 MHz); δ , 3.69 (s, 2H, CH₂), 4.27 (d, 2H, CH₂), 6.46 (s, 1H, NH), 7.05-7.84 (m, 14H, ArH); IR (KBr): 1748, 1640 (C = O), 1199 (C-O-C), 3311, 1601, 700 (N-H). Data for C₂₁H₁₆ClNO₃ were: C, 76.50; H, 5.54; N, 4.06. Found: C, 75.59; H, 5.49; N, 3.39.

Preparation of the title complexes

Europium nitrate (0.2 mmol) was dissolved in 5 mL ethyl acetate in a 100-mL single-necked flask and 0.2 mmol ligand L dissolved in 15 mL ethyl acetate was added to the flask. The mixture was stirred for 6 h at room temperature and then 5 mL diethyl ether was added one drop at a time. A precipitated solid complex was formed, separated from the solution by suction filtration and washed several times with ethyl acetate. The complex was then dried for 48 h under a vacuum at room temperature.

Results and discussion

Properties of the complexes

Analytical data for the complexes are listed in Table 1. Results of elemental analysis indicated that the composition of the six novel europium complexes conformed to $(EuL^{1-6}(NO_3)_2 \cdot 2H_2O)NO_3 \cdot nH_2O$ (n = 1, 3). L¹⁻⁶ ligands were easily dissolved in DMSO, DMF, THF, chloroform and dichloromethane as well as acetone, methanol, ethanol, diethyl ether and ethyl acetate; however, they hardly dissolved in cyclohexane. All europium complexes were soluble in DMSO, DMF, THF, chloroform, acetone, methanol and ethanol, but only slightly soluble in ethyl acetate and diethyl ether. The molar conductance data of the complexes in acetone indicated that all complexes acted as electrolytes (13).

UV spectral analysis

UV data of the ligands and their complexes are listed in Table 2. Since UV spectra of all complexes were similar, only the UV spectra of $(EuL^4(NO_3)_2 \cdot 2H_2O)NO_3 \cdot H_2O$ and $(EuL^6(NO_3)_2 \cdot 2H_2O)NO_3 \cdot H_2O$ as well as their corresponding ligands were selected, as shown in Figs 1 and 2, respectively. Two absorption peaks of the free ligand L^4 (Fig. 1) appeared at 206 nm and 260 nm, which were assigned to the $n-n^*$ and $n-n^*$ transitions of L^4 . The UV spectrum of $(EuL^4(NO_3)_2 \cdot 2H_2O)NO_3 \cdot H_2O$ was similar to that of L^4 free ligand; the only difference being that the first strong absorption wavelength shifted to 212 nm. This was due to the introduction of europium ion that enlarged the ligand's congjugated system, which

Table 1.	Elemental	analytical	and	molar	conductance	data	of the	com	olexes

Complexes	_	۸ _m			
	С	Н	Ν	Eu	(S cm ² mol ⁻¹)
$(EuL^{1}(NO_{3})_{2}\cdot 2H_{2}O)NO_{3}\cdot H_{2}O$	35.67 (34.87)	3.17 (3.20)	7.89 (7.75)	20.99 (21.01)	110
(EuL2(NO3)2·2H2O)NO3·H2O	34.54 (35.83)	3.33 (3.42)	7.52 (7.60)	19.85 (20.61)	112
(EuL3(NO3)2·2H2O)NO3·3H2O	31.99 (31.77)	2.97 (3.30)	7.04 (7.06)	19.87 (19.14)	105
$(EuL^{2}(NO_{3})_{2}\cdot 2H_{2}O)NO_{3}\cdot H_{2}O$	34.56 (35.07)	3.56 (3.34)	7.69 (7.44)	20.36 (20.17)	130
(EuL ⁶ (NO ₃) ₂ ·2H ₂ O)NO ₃ ·H ₂ O (EuL ⁶ (NO ₃) ₂ ·2H ₂ O)NO ₃ ·H ₂ O	34.76 (33.28) 34.99 (35.83)	2.67 (2.93) 3.56 (3.42)	7.19 (7.39) 7.77 (7.60)	20.45 (20.05) 21.09 (20.61)	138

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Table 2. UV data	of complexes and co	rrespondi	ng ligands
Complexes	λ_{max} (nm)	ligands	λ _{max} (nm)

complexes	And A Court	nganas	And a compared as a compared a
$(EuL^{1}(NO_{3})_{2}\cdot 2H_{2}O)NO_{3}\cdot H_{2}O$	209, 232	L1	206, 231
$(EuL^2(NO_3)_2 \cdot 2H_2O)NO_3 \cdot H_2O$	214, 242	L ²	208, 240
$(EuL^{3}(NO_{3})_{2}\cdot 2H_{2}O)NO_{3}\cdot H_{2}O$	212, 241	L3	208, 240
$(EuL^4(NO_3)_2 \cdot 2H_2O)NO_3 \cdot H_2O$	212, 261	L^4	206, 260
$(EuL^{5}(NO_{3})_{2}\cdot 2H_{2}O)NO_{3}\cdot H_{2}O$	208	L ⁵	206, 235
$(EuL^{6}(NO_{3})_{2}\cdot 2H_{2}O)NO_{3}\cdot H_{2}O$	215	L6	210, 241



Figure 1. UV spectra of a): $(EuL^4(NO_3)_2 \cdot 2H_2O)NO_3 \cdot H_2O$ and b): L^4 .



Figure 2. UV spectra of a): $(EuL^6(NO_3)_2 \cdot 2H_2O)NO_3 \cdot H_2O$ and b): L^6 .

indicated that it was coordinated to the europium ion (14). Two absorption peaks of the free ligand L⁶ (Fig. 2) appeared at 210 nm and 241 nm, which were assigned to the π - π * and n- π * transitions of L⁶. While there was only one absorption peak at 215 nm in the UV spectrum of (EuL⁶(NO₃)₂·2H₂O)NO₃·H₂O, this indicated that L⁶ had coordinated to the europium ion. Data in table 2 and the UV spectra showed that the other ligands had coordinated to europium ion.

IR spectral analysis

IR spectral data of the ligands and their complexes are listed in Table 3. Since the IR spectra of all the complexes were similar,

only the IR spectra of (EuL²(NO₃)₂·2H₂O)NO₃·H₂O and (EuL⁶(NO₃)₂·2H₂O)NO₃·H₂O as well as their corresponding ligands were selected (Figs. 3 and 4, respectively). IR spectra of the free ligands showed bands at 1740–1748 cm⁻¹and 1630– 1653 cm^{-1} , which were assigned to the stretch vibration of the carbonyl group (ν (C = O)), and ν (C-O-C) appeared at 1198–1206 cm^{-1} . In the IR spectra of the complexes (EuL¹⁻⁵(NO₃)₂·2H₂O) NO₃·nH₂O, (n = 1, 3), the absorption band for v(C = O) in the high frequency region remained unchanged but shifted about 8 cm⁻¹ in the low frequency region. As a result, these data indicated that only the oxygen atom of amide carbonyl group was coordinated to the europium ion. The characteristic absorption bands for v(C = O) of ligand L^6 appeared at 1748 cm⁻¹ and 1640 cm⁻¹, which shifted \approx 7–8 cm⁻¹ towards lower wave numbers after formation of the complexes. This indicated that the oxygen atoms of both the amide and carbonyl groups in ligand L⁶ were coordinated to the europium ion. The band for u(C-O-C) remained unchanged. These results clearly showed that the oxygen atom of u(C-O-C) did not take part in coordination with the europium ion.

The characteristic frequencies of the coordinating nitrate groups ($C_{2\nu}$) appeared at \approx 1481 (υ_1), 1324 (υ_4), 1031 (υ_2) and 815 cm⁻¹ (υ_3) (15). In addition, the difference between the two strongest absorption bands of the nitrate groups ($|\upsilon_1 - \upsilon_4|$) was 157 cm⁻¹, indicating that the coordinated nitrate groups in the complexes were bidentate (16). A characteristic absorption band assigned to the free nitrate groups was observed at \approx 1381 cm⁻¹ in the spectra of the complexes (17). This conformed to results of the conductivity experiment. Additionally, broad bands at 3340 cm⁻¹ indicated that H₂O was existent in the complexes, confirming the elemental analysis. The complexes showed medium intensity bands in the regions of 584–599 cm⁻¹, which were assigned to Eu-O modes.

Luminescence studies

The luminescence characteristics of the complexes in solid state were measured at room temperature under a drive voltage of 700 V, and excitation and emission slit widths were 5.0 nm. The fluorescence spectral data of $(EuL^{1-5}(NO_3)_2 \cdot 2H_2O)NO_3 \cdot nH_2O$ (n = 1, 3) are listed in Table 4 and the excitation and emission spectra of $(EuL^4(NO_3)_2 \cdot 2H_2O)NO_3 \cdot H_2O$ are shown in Figs. 5 and 6, respectively. It can be observed in Table 4 and Figs. 5 and 6 that the excitation spectra of $(EuL^{1-5}(NO_3)_2 \cdot 2H_2O)NO_3 \cdot nH_2O$ (*n* = 1, 3) were similar, as measured under 614 nm emission wavelength, and their maximum excitation peaks showed at 395 or 356 nm. Emission spectra of $(EuL^{1-5}(NO_3)_2 \cdot 2H_2O)NO_3 \cdot nH_2O$ (*n* = 1, 3) were also similar and showed characteristic red luminescence of europium ion; the strongest emission peak appeared at 615 nm.

The energy transfer efficiency from ligand to centre ion is one of the key factors that influences the characteristic luminescence properties of rare earth ions. It is shown in Table 4 that all complexes presented the characteristic luminescence of europium ion. This indicated that all the ligands were comparatively good organic chelators for the absorbtion and transfer of energy to the europium ion. The relative luminescence intensity of rare earth complexes is related to the efficiency of the intramolecular energy transfer between the triple levels of the ligand and the emitting level of the rare earth ion, which depends on the energy gap between the two levels. It can be seen in Table 4 that luminescence intensity of $EuL^4(NO_3)_2 \cdot 2H_2O)NO_3 \cdot H_2O$ was much



Table 3. IR spectral data of the ligands and their complexes (cm ⁻¹)									
Complex				υ(<i>NO</i> ³⁻)					υ(Eu-O)
	$\upsilon(C=O)$	υ(<i>Ar-O-C</i>)	v_1	ν_4	v ₂	ν_3	$ v_1 - v_4 $	v ₀	
L ¹	1740, 1630	1202							
$(EuL^{1}(NO_{3})_{2}\cdot 2H_{2}O)NO_{3}\cdot H_{2}O$	1741, 1638	1202	1478	1319	1038	815	159	1376	599
L ²	1741, 1630	1198							
$(EuL^2(NO_3)_2 \cdot 2H_2O)NO_3 \cdot H_2O$	1741, 1639	1198	1481	1308	1038	815	173	1377	599
L ³	1741, 1646	1206							
$(EuL^3(NO_3)_2 \cdot 2H_2O)NO_3 \cdot H_2O$	1741, 1638	1207	1481	1324	1031	815	157	1381	584
L^4	1741, 1653	1206							
$(EuL^4(NO_3)_2 \cdot 2H_2O)NO_3 \cdot H_2O$	1738, 1637	1206	1481	1324	1039	815	157	1384	599
L ⁵	1741, 1630	1199							
$(EuL^{5}(NO_{3})_{2}\cdot 2H_{2}O)NO_{3}\cdot H_{2}O$	1741, 1639	1199	1489	1332	1031	815	157	1381	592
L ⁶	1748, 1640	1199							
$(EuL^{6}(NO_{3})_{2}\cdot 2H_{2}O)NO_{3}\cdot H_{2}O$	1741, 1632	1198	1478	1323	1031	815	155	1385	584



Figure 3. IR spectra of a): $(EuL^2(NO_3)_2 \cdot 2H_2O)NO_3 \cdot H_2O$ and b): L^2 .



Figure 4. IR spectra of a): $(EuL^6(NO_3)_2 \cdot 2H_2O)NO_3 \cdot H_2O$ and b): L^6 .

stronger than that of the other four complexes. It appeared that the triplet levels of the ligand L^4 was in an appropriate level to centre the europium ion and caused an energy transition from ligand to europium ion more easily. This is because the ligand L^4 has an activating group ($-OCH_3$) that donates electrons to the aromatic ring and enlarges the ligand '*n*-conjugated system. Luminescence intensity of (EuL³(NO₃)₂·2H₂O)NO₃·3H₂O was much stronger than that of (EuL²(NO₃)₂·2H₂O)NO₃·H₂O. The reason was that the $p \rightarrow \pi$ conjugation effect between the lone pair electrons of the CI atom and the π -electron of the phenyl ring were stronger than the $\sigma \rightarrow \pi$ hyperconjugation effect between the σ -electron of methylic C-H bond and the π -electron of phenyl ring. L^5 had an acceptable electron substituent (-Cl) that caused the electron density of the phenyl ring to decrease. At the same time, the introduction of the accepting electron group easily resulted in fluorescence quenching. Therefore, the luminescence intensity of EuL⁵(NO₃)₂·2H₂O)NO₃·H₂O was weak. Additionally, the relative intensity of ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ was stronger than that of ${}^{5}D_{0}$ ${}^{7}F_{1}$ in the spectra of complexes, showing that the europium ion was not in a centro-symmetric coordination site (18). However, (EuL⁶(NO₃)₂·2H₂O)NO₃·H₂O showed green luminescence that was emitted by L⁶; its fluorescence spectral data are listed in Table 5. The excitation and emission spectra of (EuL⁶(NO₃)₂·2H₂O)NO₃·H₂O are shown in Figs. 7–10.

As can be seen in Fig. 7, the excitation spectra of the L^6 and its complex were measured under the 614 nm emission wavelength in solid state and the ligand and its complex exhibited broad excitation bands (λ_{max} = 460 nm). Fig. 8 shows the excitation spectra of L⁶ and its complex were measured under 500 nm emission wavelength. Maximum L⁶ excitation peaks and its complex were located at 422 and 308 nm, respectively. Emission spectra of the free ligand L^6 and its complex (EuL⁶(NO₃)₂·2H₂O) NO₃·H₂O can be seen excited at 308 nm in Fig. 9; maximum emission peaks were located at 461 and 460 nm, respectively. Luminescence intensity of the complex was much stronger than that of free ligand L⁶. Emission spectra of free ligand L⁶ and its complex $(EuL^{6}(NO_{3})_{2} \cdot 2H_{2}O)NO_{3} \cdot H_{2}O$ were excited at 422 nm (Fig. 10) and the maximum emission peaks were located at 495 and 491 nm, respectively. The luminescence intensity of the free ligand L⁶ was much stronger than that of the complex.

Analysis of infrared spectra showed that the oxygen atom of the amide carbonyl group in $(EuL^{1-5}(NO_3)_2 \cdot 2H_2O)NO_3 \cdot nH_2O$ (n = 1, 3) was coordinated to the europium ion. However, the oxygen atoms of both the amide and ester carbonyl groups in $(EuL^6(NO_3)_2 \cdot 2H_2O)NO_3 \cdot H_2O$ were also coordinated to the europium ion. The reason for this was that the oxygen atom of the ester carbonyl group in the ligands L^{1-5} was adjacent to the benzene ring, which enlarged the ligand's π -conjugated

Table 4. Fluorescence spectral data of the complexes								
Complex	λ_{ex}	⁵ D ₀ - ⁷ F	: 1	⁵ D ₀ - ⁷ F ₂				
	nm	λ_{em}/nm	l/a.u.	λ_{em}/nm	l/a.u.			
$(EuL^{1}(NO_{3})_{2}\cdot 2H_{2}O)NO_{3}\cdot H_{2}O$	395	590.4	468.3	615.0	1446			
$(EuL^2(NO_3)_2 \cdot 2H_2O)NO_3 \cdot H_2O$	395	589.8	758.3	615.0	1794			
$(EuL^3(NO_3)_2 \cdot 2H_2O)NO_3 \cdot H_2O$	395	589.8	1176	615.0	3489			
$(EuL^4(NO_3)_2 \cdot 2H_2O)NO_3 \cdot H_2O$	356	590.4	1390	615.0	4368			
$(EuL^{5}(NO_{3})_{2}\cdot 2H_{2}O)NO_{3}\cdot H_{2}O$	395	589.8	626	615.0	847.5			



Figure 5. Excitation spectrum of $(EuL^4(NO_3)_2 \cdot 2H_2O)NO_3 \cdot H_2O$; emission wavelength = 614 nm.



Figure 6. Emission spectrum of $(EuL^4(NO_3)_2 \cdot 2H_2O)NO_3 \cdot H_2O$, excitation wavelength = 395 nm.

Table 5. Fluorescence spectral data of L^6 and $(EuL^6(NO_3)_2\cdot 2H_2O)$ $NO_3\cdot H_2O$						
Complex	λ_{ex}/nm	λ_{em}/nm	l/a.u.			
L ⁶	308	461.4	6902			
(EuL ⁶ (NO ₃) ₂ ·2H ₂ O)NO ₃ ·H ₂ O	308	460.0	10000			
L [°]	422	495.2	8707			
(EuL ⁶ (NO ₃) ₂ ·2H ₂ O)NO ₃ ·H ₂ O	422	491.0	5591			



Figure 7. Excitation spectra of a): $(EuL^6(NO_3)_2\cdot 2H_2O)NO_3\cdot H_2O$ and b): $L^6,$ emission wavelength = 614 nm.



Figure 8. Excitation spectra of a): $(EuL^6(NO_3)_2\cdot 2H_2O)NO_3\cdot H_2O$ and b): $L^6,$ emission wavelength = 500 nm.

system and caused the electron density of the ester carbonyl group atom to decrease. Nevertheless, methylene was found between the carbonyl oxygen atom and the benzene ring in L^6 , which decreased the conjugation property and resulted in an electron density increase of the carbonyl oxygen atom. As a result, the oxygen atom of the ester carbonyl group was easy to coordinate with the europium ion. As shown in Figs. 9 and 10, the conjugation effect between carbonyl oxygen atom and benzene ring caused the triplet levels of L^6 to not correspond very well to the emitting level of europium ion, resulting in





Figure 9. Emission spectra of a): $(EuL^6(NO_3)_2 \cdot 2H_2O)NO_3 \cdot H_2O$ and b): L^6 , excitation wavelength = 308 nm.



Figure 10. Emission spectra of a): $(EuL^6(NO_3)_2\cdot 2H_2O)NO_3\cdot H_2O$ and b): $L^6,$ excitation wavelength = 422 nm.

blocked intramolecular energy transfer. As a result, the excited electron of L⁶ returned to the ground state and the complex $(EuL^6(NO_3)_2 \cdot 2H_2O)NO_3 \cdot H_2O$ showed green luminescence.

Conclusions

Six novel 2-(benzylcarbamoyl)phenyl derivatives were synthesized that formed stable solid complexes with the europium ion. The complex (EuL¹⁻⁵(NO₃)₂·2H₂O)NO₃·nH₂O (n = 1, 3) showed the characteristic red luminescence of europium ion. However, the complex (EuL⁶(NO₃)₂·2H₂O)NO₃·H₂O showed green luminescence emitted by L⁶. The conjugation effect of the L⁶ caused its triplet levels to not match very well the emitting level of europium ion, resulting in an inhibition of intramolecular energy transfer. Luminescence intensity of (EuL⁴(NO₃)₂·2H₂O)NO₃·H₂O was much stronger than that of the other four complexes of (EuL¹⁻⁵(NO₃)₂·2H₂O)NO₃·nH₂O (n = 1, 3). These results are useful for designing ligands that possess stronger conjugated systems and higher intramolecular energy transfer efficiency. These complexes are promising candidates for application in sensory materials and luminescent probes.

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