Journal of Photochemistry and Photobiology A: Chemistry 219 (2011) 243–249

Contents lists available at ScienceDirect

Journal of Photochemistry and Photobiology A: Chemistry

journal homepage: www.elsevier.com/locate/jphotochem

Synthesis, characterization and luminescence property of ternary rare earth complexes with azatriphenylenes as highly efficient sensitizers

Hui-Juan Sun[a], Xiao-Tao Fu[a], Hai-Bin Chu[a,b,*], Yan Du[a], Xue-Mei Lin[a], Xin Li[a], Yong-Liang Zhao[a,**]

[a] *College of Chemistry and Chemical Engineering, Inner Mongolia University, Hohhot 010021, China*
[b] *SINOPEC Beijing Research Institute of Chemical Industry, Beijing 100013, China*

ARTICLE INFO

Article history:
Received 20 October 2010
Received in revised form 18 February 2011
Accepted 25 February 2011
Available online 3 March 2011

Keywords:
Azatriphenylene
Carboxylate
Rare earth complex
Luminescence intensity
Quantum efficiency

ABSTRACT

A series of novel ternary rare earth complexes showing attractive luminescence properties were prepared with both neutral and anion ligands. Three azatriphenylene neutral ligands, 1,10-phenanthroline (phen), dipyrido [3,2-a: 2′,3′-c] quinoxaline (dpq) and dipyrido [3,2-a: 2′,3′-c] phenazine (dppz) were investigated systematically as sensitizers in the ternary rare earth complexes. Benzoate ions (BA^-) and phenoxyacetate ions (POA^-) were chosen as anion ligands. The compositions of these complexes were characterized by elemental analysis, rare earth coordination titration, molar conductivity measurement, IR spectroscopy, UV–vis absorption spectroscopy, ^{1}H NMR spectroscopy and TGA–DTA. The luminescence spectra, luminescence decay time and quantum efficiency of the complexes were also studied. The very strong luminescence intensities and rather long luminescence lifetimes (typically > 1.0 ms) were achieved for both Eu^{3+} and Tb^{3+} ternary complexes with phen and dpq as neutral ligands. Moreover, high quantum efficiencies (40–60%) were also obtained for Eu^{3+} ternary complexes with phen and dpq as neutral ligands.

1. Introduction

Rare earth compounds have attracted much attention because of their superior luminescent properties, such as long luminescence lifetimes, large Stokes shift and sharp emission profile, and their applications in the fields of catalysis, information technique, display, lighting, nanoscience, agriculture and military [1–4]. However, the luminescence intensities of rare earth ions are relatively weak because f–f electronic transitions of these ions are forbidden by the parity rule.

Direct coordination of the antenna ligands with rare earth ions can effectively sensitize the central ions by ligand-to-metal energy transfer. Both anion ligands and neutral ligands have been recognized widely as effective antenna ligands towards rare earth ions. First, anion ligands, such as β-diketones and aromatic carboxylic acids, not only can form stable complexes with rare earth ions, but also are able to efficiently receive light and transfer energy to rare earth ions [5]. Nonetheless, because of the electrostatic repulsion between anion ligands, anion ligands alone could not meet the high coordination number requirement of rare earth ions. Consequently, solvent molecules are typically evolved in the complexes, resulting in low luminescent efficiencies of rare earth ions. The introduction of certain neutral ligands, such as terphenyl-based compounds, azatriphenylenes and pyridine derivatives, can increase the luminous efficiency of the rare earth complexes. The reason is that the neutral ligands can replace the solvent molecules to coordinate with the central ions as well as eliminate energy loss caused by thermal vibration of solvent molecules [5,6]. Also, they can improve the rigidity and stability of the complex structures, and increase the absorption of light energy and energy transfer efficiency so as to enhance the luminous intensity of the complexes [7,8]. However, rare earth complexes with neutral ligands alone typically exhibit poor luminescence quenched by anions such as hydroxyl ions. Besides, the coordination environment as well as crystal structure of the complexes changes significantly when both anion and neutral ligands are involved. In addition, intramolecular energy transfer process between the two ligands would improve the luminescence efficiency of rare earth complexes. Hence, the design and synthesis of new ternary complexes with both anion and neutral ligands have theoretical significance and application value for excellent luminescent rare earth materials.

The complexes of rare earth ions with aromatic carboxyl acids have optimal luminescence. Phenanthroline (phen) and 2,2′-bipyridine (bipy) are widely used as neutral ligands in ternary complexes [9–12]. In order to get rare earth complexes with strong luminescence, good thermodynamic stability and high quantum efficiency, two neutral azatriphenylene ligands, dipyrido [3,2-a:

---

[*] Corresponding author at: College of Chemistry and Chemical Engineering, Inner Mongolia University, Hohhot 010021, China. Tel.: +86 13624849905.
[**] Corresponding author. Tel.: +86 13624849905; fax: +86 471 4992984.
E-mail addresses: binghai99@gmail.com (H.-B. Chu), hxzhaoyl@163.com (Y.-L. Zhao).

1010-6030/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.jphotochem.2011.02.026

2′,3′-c] quinoxaline (dpq) and dipyrido [3,2-a: 2′,3′-c] phenazine (dppz), were synthesized and a series of novel rare earth ternary complexes were prepared with benzoate ions (BA^-) or phenoxyacetate ions (POA^-) as anion ligands and azatriphenylenes as neutral ligands. Importantly, rather strong luminescence intensities and long lifetimes have been obtained for both Eu^{3+} and Tb^{3+} ternary complexes with phen and dpq as neutral ligands. The high quantum efficiencies have also been achieved for Eu^{3+} ternary complexes with phen and dpq as neutral ligands. Moreover, all these complexes were all non-electrolytes and stable at the room temperature.

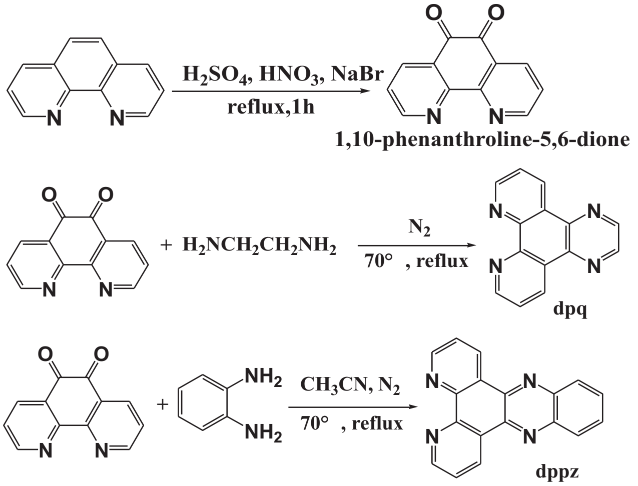
2. Materials and methods

2.1. Materials and general methods

Purities of rare earth oxides are 99.99%. Other reactants and solvents are all of analytical grade if not mentioned. Elemental analysis was performed with a PE-2400 elemental analyzer. The molar concentration of rare earth was determined by EDTA titration method with xylenol orange as indicator. A Nicolet Nexus 670 FT-IR spectrometer using KBr pellet was used to obtain the IR spectra in the range of 4000–400 cm^{-1}. Molar conductivity was measured by DDSJ-308A conductivity meter at room temperature, with N,N-dimethylformamide (DMF) as solvent and the concentration of complexes was 1.0×10^{-3} mol L^{-1}. The thermo gravimetric analysis (TGA) and differential thermal analysis (DTA) were performed by a DTG-50 instrument with a heating rate of 10 °C min^{-1} under a N_2 atmosphere. Absorption spectra were recorded on a Tu-1901 spectrophotometer, using absolute ethanol as solvent and the concentration of the complexes was 1.0×10^{-5} mol L^{-1}. A Bruker 400 MHz NMR spectrometer was used for the acquisition of ^1H NMR spectra in $CDCl_3$ solution. The excitation, emission spectra and luminescence decay time of the obtained complexes were measured using an Edinburgh Instruments FLS920 spectrometer at room temperature. The excitation slit and emission slit widths were all 0.1 nm.

2.2. Synthesis of dpq and dppz

Dpq and dppz were synthesized according to literatures [13–17]. Synthesis routes of the ligands are as follows:



The relevant values of dpq product were consistent with literature values, mp: 299 °C (literature [16] value: 297–299 °C). ^1H NMR (400M-$CDCl_3$), ppm 9.506–9.481 (q, 2H), 9.303–9.288 (q, 2H), 8.989 (s, 2H), 7.822–7.791 (q, 2H); Anal. Found for $C_{14}H_8N_4$: C, 72.07; H, 3.87; N, 24.02; Calcd. C, 72.40; H, 3.47; N, 24.13. The relevant values of dppz product were consistent with literature values, mp: 250–251 °C (literature [13] value: 250 °C). ^1H NMR (400M-$CDCl_3$), ppm 9.650–9.625 (q, 2H), 9.278–9.263 (q, 2H), 8.363–8.338 (q, 2H), 7.937–7.912 (q, 2H), 7.812–7.781 (q, 2H); Anal. Found for $C_{18}H_{10}N_4$: C, 76.23; H, 3.71; N, 19.59; Calcd. C, 76.58; H, 3.57; N, 19.85.

2.3. Preparation of rare earth chloride solution

The solution of rare earth chloride was prepared according to literature [18]. Rare earth chloride was obtained by the reaction of rare earth oxide with dilute solution of HCl, heating dissolved, evaporated, and then dissolved in anhydrous ethanol.

2.4. Synthesis of $RE(C_6H_5COO)_3L$ ($RE^{3+} = Eu^{3+}$, Tb^{3+}; L = phen, dpq, dppz)

0.50 mmol neutral ligand phen was dissolved in absolute ethanol, and then aqueous C_6H_5COONa (0.2162 g, 1.5 mmol) was added. A few minutes later, 0.5 mmol $EuCl_3$ was dropwise added into this mixture with continuous stirring under constant temperature of 70 °C. The pH was readjusted to 6.8 with aqua ammonia. The resulting mixture was stirred at 70 °C for 3 h. The mixture was filtered and the solid was washed twice with absolute ethanol and ether, respectively. After dried at 50 °C for several hours, the complex $Eu(C_6H_5COO)_3$phen was obtained. In the similar way, $Eu(C_6H_5COO)_3$dpq, $Eu(C_6H_5COO)_3$dppz, $Tb(C_6H_5COO)_3$phen, $Tb(C_6H_5COO)_3$dpq and $Tb(C_6H_5COO)_3$dppz were prepared.

2.5. Synthesis of $Eu_{0.5}Ln_{0.5}(C_6H_5COO)_3$dpq ($Ln^{3+} = La^{3+}$, Gd^{3+})

The synthetic procedure for $Eu_{0.5}La_{0.5}(C_6H_5COO)_3$(dpq) was the same as above mentioned, except that an equimolar amount of $EuCl_3$ and $LaCl_3$ were added together. Similar to $Eu_{0.5}La_{0.5}(C_6H_5COO)_3$(dpq), $Eu_{0.5}Gd_{0.5}(C_6H_5COO)_3$(dpq) was synthesized.

2.6. Synthesis of $RE(POA)_3L \cdot 1/2H_2O$ ($RE^{3+} = Eu^{3+}$, Tb^{3+}; L = phen, dpq, dppz)

HPOA (0.2267 g, 1.5 mmol) was dissolved in 5 ml absolute ethanol and aqueous NaOH (1.5 mmol) was added to readjust the pH to 7. Then 0.5 mmol absolute ethanol solution of the second ligand phen was added to this mixture with stirring. A few minutes later, 0.5 mmol $EuCl_3$ was added dropwise into the mixture with continuous stirring under constant temperature of 70 °C. Then $Eu(POA)_3phen \cdot 1/2H_2O$ was obtained similar to the above-mentioned method. Using the same methods, complexes $Eu(POA)_3dpq \cdot 1/2H_2O$, $Eu(POA)_3dppz \cdot 1/2H_2O$, $Tb(POA)_3phen \cdot 1/2H_2O$, $Tb(POA)_3dpq \cdot 1/2H_2O$ and $Tb(POA)_3dppz \cdot 1/2H_2O$ were got.

3. Results and discussion

3.1. Composition analysis and molar conductivity

The theoretical data and the measured data of complexes are shown in Table 1. The results of elemental analyses (C, H, N) and rare earth EDTA titration indicate that the composition of the complexes are $RE(C_6H_5COO)_3L$ ($RE^{3+} = Eu^{3+}$, Tb^{3+}; L = phen, dpq, dppz), $Eu_{0.5}Ln_{0.5}(C_6H_5COO)_3$dpq ($Ln^{3+} = Gd^{3+}$, La^{3+}) and $RE(POA)_3L' \cdot 1/2H_2O$ ($RE^{3+} = Eu^{3+}$, Tb^{3+}; L′ = phen, dpq, dppz). Colors of complexes are white and all the complexes are stable in the air. The complexes are easily dissolved in dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) but difficult to dissolve in water, ethanol and acetone.

The small molar conductance values of rare earth complexes in DMF (Table 1) indicate that only a small fraction of rare earth

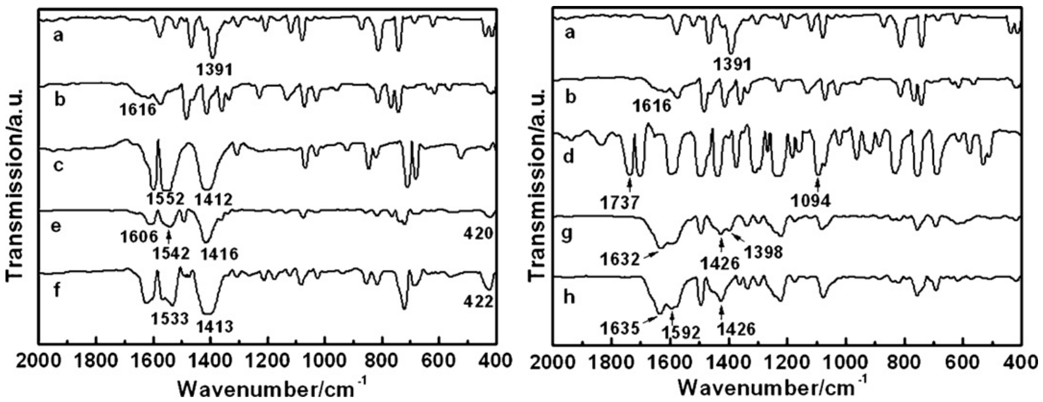


Fig. 1. IR spectra of some ligands and complexes: a, dpq; b, dppz; c, NaBA; d, HPOA; e, Tb(BA)$_3$dppz; f, Eu$_{0.5}$Ga$_{0.5}$(BA)$_3$dpq; g, Eu(POA)$_3$dpq1/2H$_2$O; h, Tb(POA)$_3$dppz1/2H$_2$O.

Table 1
Composition analysis (%) and molar conductivities (S cm^2 mol^{-1}) (25 °C) of the rare earth complexes.

Complex	C%	H%	N%	RE%	λ_m (S cm^2 mol^{-1})
EuL$_3$phen	56.77(56.98)	3.528(3.333)	3.831(4.028)	21.92(21.85)	18.5
TbL$_3$phen	56.19(56.42)	3.292(3.300)	3.792(3.989)	22.65(22.62)	20.7
EuL$_3$dpq	55.87(56.23)	2.806(3.101)	7.256(7.496)	20.54(20.33)	18.2
TbL$_3$dpq	55.37(55.71)	3.358(3.073)	7.331(7.428)	20.93(21.06)	17.6
EuL$_3$dppz	58.58(58.72)	3.463(3.159)	7.135(7.026)	18.98(19.06)	16.2
TbL$_3$dppz	58.05(58.22)	3.336(3.132)	7.321(6.965)	19.84(19.75)	15.4
Eu$_{0.5}$Gd$_{0.5}$L$_3$dpq	55.69(56.03)	3.357(3.090)	7.312(7.470)	20.73(20.61)	16.8
Eu$_{0.5}$La$_{0.5}$L$_3$dpq	56.52(56.72)	3.396(3.129)	7.472(7.562)	19.45(19.63)	15.8
EuL′$_3$phen·1/2H$_2$O	54.17(54.41)	4.225(3.806)	3.376(3.526)	19.02(19.13)	20.3
TbL′$_3$phen·1/2H$_2$O	53.79(53.94)	3.325(3.773)	3.317(3.496)	19.67(19.82)	18.4
EuL′$_3$dpq·1/2H$_2$O	53.53(53.90)	3.501(3.572)	6.411(6.619)	18.06(17.95)	19.2
TbL′$_3$dpq·1/2H$_2$O	53.29(53.47)	3.627(3.543)	6.143(6.566)	18.47(18.62)	16.5
EuL′$_3$dppz·1/2H$_2$O	55.97(56.25)	3.775(3.597)	6.549(6.250)	17.04(16.95)	18.4
TbL′$_3$dppz·1/2H$_2$O	55.47(55.82)	3.612(3.570)	6.188(6.202)	17.46(17.59)	16.5

Remark: the values in brackets are theoretical values; L = BA$^-$, L′ = POA$^-$.

complexes ionize in DMF solution and these complexes are non-electrolytes [19,20].

3.2. IR Spectra

The IR spectra of ligands phen, dpq, dppz, HPOA, NaBA and all the obtained complexes were determined in the range of 4000–400 cm^{-1}, some of which are given in Fig. 1.

Spectra analysis of benzoate series rare earth complexes: IR spectra of ligand NaBA showed ν_{as} at 1552 cm^{-1} and ν_s at 1412 cm^{-1}, which shifted to 1530–1542 cm^{-1} and 1411–1418 cm^{-1} in the complexes, respectively. New bands occurring in the region 411–424 cm^{-1} could be attributed to the RE-O absorption peak, which indicated that the carboxyl group of the benzoate coordinated with RE(III) [21]. For ligand dpq, the $\nu_{(C=N)}$ at 1391 cm^{-1} shifted to the vicinity of 1408 cm^{-1} and overlapped with the ν_s bands of carboxyl in the complexes, indicating that the rare earth ions coordinated with dpq [22,23]. The $\nu_{(C=N)}$ at 1616 cm^{-1} of ligand dppz shifted to 1606 cm^{-1} in the complexes, which indicated that the rare earth ions coordinated with dppz [24,25].

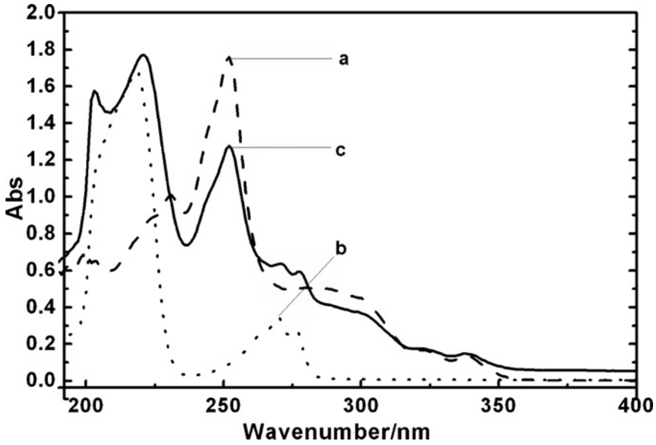


Fig. 2. UV–vis spectra of the ligands and complex: a, dpq; b, HPOA; c, Eu(POA)$_3$dpq1/2H$_2$O. The concentrations are 1.0 × 10^{-5} mol L^{-1}, 3.0 × 10^{-5} mol L^{-1}, 1.0 × 10^{-5}mol L^{-1}, respectively.

Spectra analysis of phenoxyacetate series of rare earth complexes: The bands at 1737 cm^{-1} and 1094 cm^{-1} could be attributed to the $\nu_{(C=O)}$ vibration and $\delta_{(OH)}$ rocking vibration of ligand HPOA, which disappeared after the formation of the complexes. Also, new

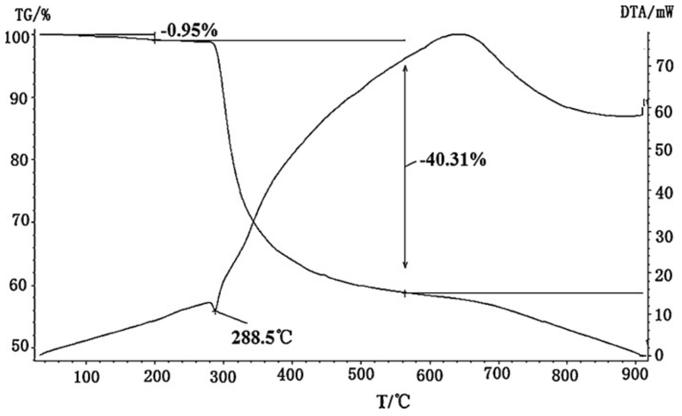


Fig. 3. TG–DTA curves of Tb(POA)$_3$dppz·1/2H$_2$O in N$_2$ atmosphere.

peaks emerged at 1426 cm^{-1} and 1632–1635 cm^{-1}, which could be assigned to the symmetric and antisymmetric stretching vibrations of the carboxylate group, respectively. These changes indicated that the carboxyl coordinated with the rare earth ions in the complexes. After introducing the neutral ligands, the $\nu_{(C=N)}$ at 1391 cm^{-1} of dpq shifted to the vicinity of 1398 cm^{-1} in the complexes, indicating that the rare earth ions coordinated with dpq [22,23]. The $\nu_{(C=N)}$ of ligand dppz at 1616 cm^{-1} shifted to 1592 cm^{-1} in the complexes which revealed the rare earth ions coordinated with dppz [24,25].

3.3. *UV–vis absorption spectra*

The UV–vis absorption spectra of ligands phen, dpq, dppz, HPOA, NaBA as well as all complexes were determined in comparison with absolute ethanol as reference. As shown in Fig. 2, the absorption peak of phenoxyacetate at 219 nm shifted to 221 nm in the complex $Eu(POA)_3dpq·1/2H_2O$, which indicated that the rare earth ions coordinated with phenoxyacetate. The absorption peak of dpq at 251 nm shifted to 252 nm in the complexes, which indicated that dpq was involved in the coordination. The data further confirmed the formation of ternary rare earth complexes.

3.4. *TGA–DTA*

As shown in Fig. 3, the weight loss of the complex $Tb(POA)_3dppz·1/2H_2O$ around the endothermic peak at 288.5 °C is 0.95%, which could be assigned to the theoretical content (0.99%) of the complexes containing 0.5 water molecules. Moreover, it should be coordinated water because of the relative high temperature. The complex begins to decompose at about 300 °C with obvious weight loss. The weight loss of 40.31% is consistent with the theoretical value (40.97%) of the complex that loses one dppz and two carboxyl groups. The aromatic carboxylate ligand was relatively thermally stable [26], thus the weight loss of complex does not stop at 900 °C, indicating that decomposition of the complex has not yet finished.

3.5. *Chemical structure*

Most of the rare earth complexes with phen and carboxylate have a dimeric structure $[RE_2(phen)_2(carboxylate)_6]$ [27–33], while some of the related complexes having substituted benzoate ligand have a monomeric structure. The four ternary complexes $Eu(BA)_3phen$, $Tb(BA)_3phen$, $Eu(POA)_3phen·1/2H_2O$ and $Tb(POA)_3phen·1/2H_2O$ have a dimeric structure as identified by X-ray analysis [9,11,12,34]. However, chemical structures of other complexes with dpq or dppq are still under investigation.

3.6. *Luminescence spectra*

Table 2 gives the data of the excitation and emission spectra of the complexes in the solid state at room temperature. The spectral peak identification is based on the data of the free-ion energy levels given by Carnall et al. [35]. The excitation spectra of the complexes are essentially the same. They all contain a broadband absorption in 250–400 nm, but the strongest absorption peaks are different (see Table 2). The emission spectra of all complexes show a characteristic transitions of RE^{3+} [36,37]. The representative emission spectra of Eu^{3+}, Tb^{3+} complexes are presented in Figs. 4 and 5.

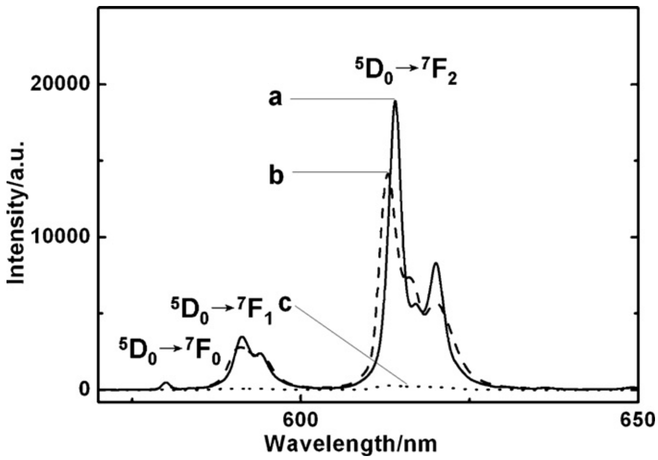


Fig. 4. Photoluminescence spectra of complexes: a, $Eu(BA)_3phen$ (λ_{ex} = 348 nm); b, $Eu(BA)_3dpq$ (λ_{ex} = 359 nm); c, $Eu(BA)_3dppz$ (λ_{ex} = 378 nm).

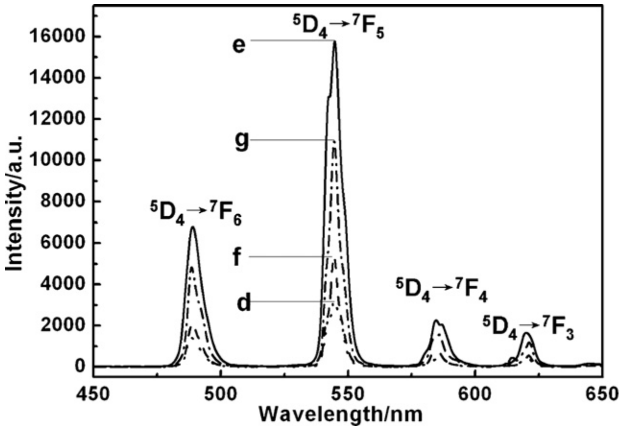


Fig. 5. Photoluminescence spectra of complexes: d, $Tb(BA)_3phen$ (λ_{ex} = 347 nm); e, $Tb(BA)_3dpq$ (λ_{ex} = 355 nm); f, $Tb(POA)_3phen·1/2H_2O$ (λ_{ex} = 356 nm); g, $Tb(POA)_3 dpq·1/2H_2O$ (λ_{ex} = 346 nm).

All europium complexes emit the characteristic luminescence of Eu^{3+}, of which the $^5D_0 \rightarrow {}^7F_1$ belongs to magnetic dipole transition, appearing at nearly 591 nm. $^5D_0 \rightarrow {}^7F_2$ belongs to the electric dipole transition, appearing in the vicinity of 613 nm. It can be seen from Table 2 that the intensities of the electric dipole transitions are stronger than those of the magnetic dipole transitions.

Table 2
Luminescent spectra data of the complexes.

Complex	λ_{ex} (nm)	$^5D_0 \rightarrow {}^7F_1$		$^5D_0 \rightarrow {}^7F_2$		Complex	λ_{ex} (nm)	$^5D_4 \rightarrow {}^7F_6$		$^5D_4 \rightarrow {}^7F_5$	
		λ_{em} (nm)	I_0 (a. u)	λ_{em} (nm)	I_0 (a. u)			λ_{em} (nm)	I_0 (a. u)	λ_{em} (nm)	I_0 (a. u)
EuL_3phen	348	591	3879	614	23,400	TbL_3phen	347	488	1465	545	3232
EuL_3dpq	359	591	2858	613	15,570	TbL_3dpq	355	489	6943	545	16,340
EuL_3dppz	378	589	91	612	287	TbL_3dppz	334	489	68	545	145
$Eu_{0.5}Gd_{0.5}L_3dpq$	359	591	2772	613	15,760	$TbL'_3phen·1/2H_2O$	356	489	2205	544	5535
$Eu_{0.5}La_{0.5}L_3dpq$	354	591	473	613	2437	$TbL'_3dpq·1/2H_2O$	346	488	4962	545	11,200
$EuL'_3phen\ 1/2H_2O$	348	592	4375	617	9889	$TbL'_3dppz\ 1/2H_2O$	348	482	101	545	87
$EuL'_3dpq\ 1/2H_2O$	350	593	2278	614	8124						
$EuL'_3dppz\ 1/2H_2O$	386	593	170	615	555						

Remark: L = BA$^-$, L′ = POA$^-$.

The luminescence emission spectra of the terbium complexes are similar and all can be issued as characteristic luminescence of $^5D_4 \rightarrow {}^7F_6$ (around 488 nm), $^5D_4 \rightarrow {}^7F_5$ (around 545 nm), $^5D_4 \rightarrow {}^7F_4$ (around 585 nm) and $^5D_4 \rightarrow {}^7F_3$ (around 620 nm) transitions. Among them, the intensity of $^5D_4 \rightarrow {}^7F_5$ transition is the strongest.

As can be seen from the luminescence data of the complexes, the luminescence intensities of benzoate series of Eu^{3+} complexes are stronger than phenoxyacetate series of Eu^{3+} complexes. For Eu^{3+} complexes with the same acidic ligand but different neutral ligands, the luminescence intensities of phen complexes and dpq complexes are stronger than those of dppz complexes. The sequence of energy transmission capacity of the neutral ligands is phen > dpq > dppz. For $Eu_{0.5}Ln_{0.5}(C_6H_5COO)_3$dpq ($Ln^{3+} = Gd^{3+}$, La^{3+}), Gd^{3+} was found to enhance the luminescence intensity of Eu^{3+}. However, La^{3+} adding did not enhance the luminescence intensity of Eu^{3+}. The difference between Gd(III) and La(III) ions may result from the different radius of Gd(III) and La(III) ions. The radius of Gd(III) ion (93.8 pm) is similar with that of Eu(III) ion (95 pm). However, the radius of La(III) ion (105 pm) is much larger than that of Eu(III) ion. The luminescence efficiency of the complex may be lowered down because of the structure distortion in the complex $Eu_{0.5}La_{0.5}(C_6H_5COO)_3$dpq [12]. Therefore, only Gd(III) ion enhanced the emission of Eu(III) ion and La(III) did not. The effect of neutral ligands on luminescence intensity of Tb^{3+} complexes is different from that of Eu^{3+} complexes. For the same acidic ligand but different neutral ligands, the sequence of luminescence intensity of the complex is dpq > phen > dppz.

The effect of neutral ligands on the luminescence intensity of central rare earth ions is investigated by energy difference between the triplet states of the ligands and the resonance energy level of the Eu^{3+} and Tb^{3+} ions. According to the energy transfer and intramoleclar energy mechanism [10,38], one of the most important factors influencing the luminescence properties of rare earth complexes is the intramolecular energy transfer efficiency. The energy transfer rate constants are dependent on the energy difference, and there should exist an optimal energy difference. If the energy difference is too large, the energy-transfer rate constant will decrease due to the diminution of the overlap between the energy donor (ligands) and acceptor (rare earth ions). On the contrary, if the energy difference is too small, the energy can backtransfer from the rare earth ions to the triplet state energy of the ligands. In the luminescence theory of rare earth complexes, the requirement for efficient intramolecular energy transfer is that the energy difference lies within the range 2000–5000 cm^{-1} [39,40]. The triplet state energies of neutral ligands phen, dpq, dppz are 21,480 cm^{-1}, 23,800 cm^{-1} and 18,500 cm^{-1} [41,42], respectively. And the lowest excited state energy of Eu^{3+} and Tb^{3+} are 17,500 cm^{-1} and 20,400 cm^{-1} [43], respectively. The triplet state energy of phen matches well with the lowest excited state energy of Eu^{3+} ions (the energy difference is 3980 cm^{-1}), thus phen is able to transfer energy to Eu^{3+} ion effectively. Consequently, the luminescence intensity of Eu^{3+} ions could be effectively enhanced. Similarly, the triplet state energy of dpq matches well with the lowest excited state energy of Tb^{3+} ions (the energy difference is 3400 cm^{-1}). Therefore, the luminescence intensity of the complexes of Tb^{3+} with dpq is strong. However, the triplet state energy of dppz is close to the lowest excited state energy of Eu^{3+} ions and is lower than that of Tb^{3+} ions. Thus the energy easily backtransfers from central ions to dppz, which results in weak luminescence emission of the central rare earth ions.

3.7. *Luminescence lifetime*

The luminescence lifetime of several complexes were determined and their data were shown in Table 3. From the data of Eu^{3+} complexes, the luminescence lifetime of phen or dpq complexes are longer than dppz complexes. Also, the lifetimes (typically > 1.0 ms) are much longer than the reported values in the literatures [8,44–46]. The luminescence lifetime of $Tb(BA)_3$dpq and $Tb(POA)_3dpq{\cdot}1/2H_2O$ were also measured, and corresponding luminescence decay curves and fit curves are shown in Figs. 6 and 7.

Table 3
Luminescent life-time and χ^2 of the complexes.

Complexes	Luminescence lifetime (μs)	χ^2
$Tb(C_6H_5COO)_3$dpq	1235.89	1.172
$Tb(POA)_3dpq{\cdot}1/2H_2O$	1649.75	1.344
$Eu(C_6H_5COO)_3$phen	1255.38	1.402
$Eu(C_6H_5COO)_3$dppz	188.66	1.469
$Eu_{0.5}Gd_{0.5}(C_6H_5COO)_3$dpq	1125.08	1.590
$Eu_{0.5}La_{0.5}(C_6H_5COO)_3$dpq	1194.14	1.649
$Eu(POA)_3phen{\cdot}1/2H_2O$	1675.41	1.655
$Eu(POA)_3dpq{\cdot}1/2H_2O$	1443.04	1.407
$Eu(POA)_3dppz{\cdot}1/2H_2O$	110.74	1.364

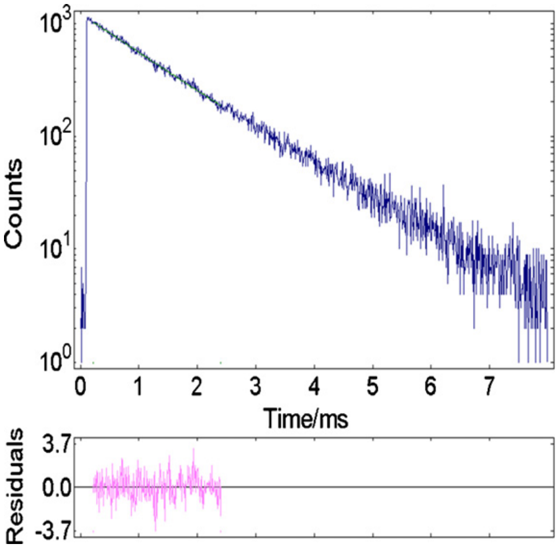


Fig. 6. Luminescence decay curve and fit curve of $Tb(C_6H_5COO)_3$dpq.

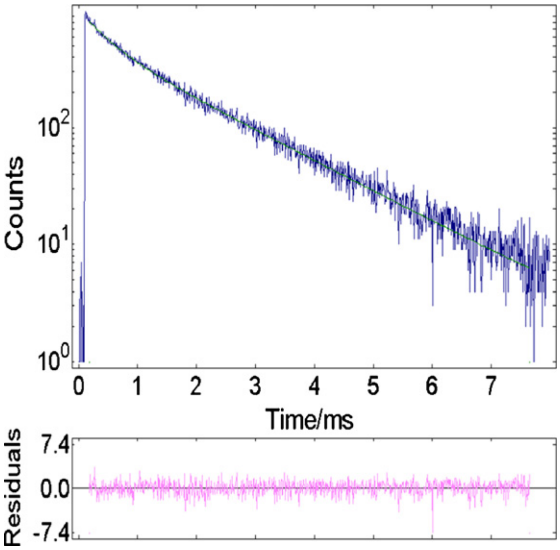


Fig. 7. Luminescence decay curve and fit curve of $Tb(POA)_3dpq{\cdot}1/2H_2O$.

Table 4
Luminescence data of the complexes.

	EuL_3phen	EuL_3dppz	$Eu_{0.5}Gd_{0.5}$ L_3dpq	$Eu_{0.5}La_{0.5}$ L_3dpq	EuL'_3phen·1/2H_2O	EuL'_3dpq·1/2H_2O	EuL'_3dppz 1/2H_2O
ν_{00} (cm^{-1})	17,241	17,271	17,241	17,241	17,241	17,241	17,241
ν_{01} (cm^{-1})	16,920	16,978	16,920	16,920	16,892	16,863	16,863
ν_{02} (cm^{-1})	16,287	16,340	16,313	16,313	16,207	16,287	16,260
ν_{03} (cm^{-1})	16,129	16,207	16,129	16,129	16,129	16,129	16,129
I_{01}	3879	91	2772	473	4375	2278	170
I_{02}	23,400	287	15,760	2437	9889	8124	555
I_{02}/I_{01}	6.03	3.15	5.69	5.15	2.26	3.57	3.26
τ (ms)	1.255	0.189	1.125	1.194	1.675	1.443	0.111
$1/\tau$ (ms^{-1})	0.797	5.291	0.889	0.838	0.597	0.693	9.009
A_r	501.4	369.4	459.1	469.5	264.7	322	311.8
A_{nr}	295.6	4921.6	429.9	368.5	332.3	371	8697.2
η (%)	62.91	7.00	51.64	56.03	44.33	46.46	3.46

Remark: L = BA^-, L′ = POA^-.

3.8. Luminescence decay times (τ) and emission quantum efficiency (η)

The typical decay curves of the Eu^{3+} complexes were measured. According to the emission spectrum and lifetime of the Eu^{3+} first excited level (τ, $^5D_0$), η values of the $^5D_0$ Eu^{3+} excited states were determined. The η can be defined as follows [47]:

$$\eta = \frac{A_r}{(A_r + A_{nr})} \tag{1}$$

Where A_r and A_{nr} are radiative and nonradiative transition rates, respectively. A_r can also be obtained by:

$$A_r = \sum A_{0J} = A_{00} + A_{01} + A_{02} + A_{03} + A_{04} \tag{2}$$

In the above Eq. (2), A_{0J} represents the radiative rates for each $^5D_0 \rightarrow {}^7F_J$ (J = 0–4) transitions of Eu^{3+}. A_{0J} can be calculated from the following equation:

$$A_{0J} = A_{01}\left(\frac{I_{0J}}{I_{01}}\right)\left(\frac{\nu_{01}}{\nu_{0J}}\right) \tag{3}$$

Here, A_{01} is the Einstein's coefficient of spontaneous emission between the $^5D_0$ and $^7F_1$ energy levels. In this experiment, A_{01} can be determined to be about 50 s^{-1} [48]. I_{0J} are the integrated intensities of the $^5D_0 \rightarrow {}^7F_J$ transitions (J = 0–4) with ν_{0J} ($\nu_{0J} = 1/\lambda_J$) energy centers.

The lifetime (τ), radiative (A_r), and nonradiative (A_{nr}) transition rates are related through the following equation:

$$A_{tot} = \frac{1}{t} = A_r + A_{nr} \tag{4}$$

Based on the above four equations, the quantum efficiencies of the europium complexes were calculated and shown in Table 4. From the data of η, it can be seen that the quantum efficiencies of benzoate series of complexes are higher than those of phenoxyacetate series complexes. For the same acidic ligand but different neutral ligands, the quantum efficiencies of phen complexes and dpq complexes are higher than those of dppz complexes. Compared with some reported europium complexes (the quantum efficiencies are typically in the range of 1–25%) [49,50], the quantum efficiencies reported here are much higher.

4. Conclusions

In summary, fourteen ternary rare earth complexes have been prepared with BA^- or POA^- as anion ligands and phen, dpq or dppz as neutral ligands. They have the composition of $RE(C_6H_5COO)_3L$ ($RE^{3+} = Eu^{3+}$, Tb^{3+}; L = phen, dpq, dppz), $Eu_{0.5}Ln_{0.5}(C_6H_5COO)_3$dpq ($Ln^{3+} = Gd^{3+}$, La^{3+}) and $RE(POA)_3L{\cdot}1/2H_2O$ ($RE^{3+} = Eu^{3+}$, Tb^{3+}; L = phen, dpq, dppz). The luminescence spectra show that the Eu^{3+} complexes and Tb^{3+} complexes exhibit good characteristic luminescence emission spectra. For Eu^{3+} or Tb^{3+} complexes of the same acidic ligand but different neutral ligands, the luminescence intensities of phen complexes and dpq complexes are much stronger than those of dppz complexes. The efficient sensitization of phen and dpq ligands may result from the energy match between the triplet state energy of the ligands and the lowest excited state energy of the rare earth ions. Importantly, the high quantum efficiencies and long lifetimes of the Eu^{3+} and Tb^{3+} ternary complexes with phen and dpq as neutral ligands are advantages over many of the ternary rare earth complexes investigated so far.

Acknowledgements

The research work is supported by the National Natural Science Foundation of China (20461002), Natural Science Foundation of Inner Mongolia (200711020203), the Opening Foundation for Significant Fundamental Research of Inner Mongolia (2010KF03) and a fund from Inner Mongolia University.

References

[1] R. Reyes, M. Cremona, E.E.S. Teotonio, H.F. Brito, O.L. Malta, Chem. Phys. Lett. 396 (2004) 54–58.
[2] H.H.S. Oliveira, M.A. Cebim, A.A. Da Silva, M.R. Davolos, J. Alloys Compd. 488 (2009) 619–623.
[3] M. Zhou, H. Fei, Y. Liu, W.F. Li, Prog. Chem. 22 (2010) 201–209.
[4] A.G. Trambitas, T.K. Panda, J. Jenter, P.W. Roesky, C. Daniliuc, C.G. Hrib, P.G. Jones, M. Tamm, Inorg. Chem. 49 (2010) 2435–2446.
[5] S. Lis, M. Elbanowski, B. Makowska, Z. Hnatejko, J. Photochem. Photobiol. A 150 (2002) 233–247.
[6] B.H. Bakker, M. Goes, N. Hoebe, H.J. van Ramesdonk, J.W. Verhoeven, M.H.V. Werts, J.W. Hofstraat, Coord. Chem. Rev. 208 (2000) 3–16.
[7] W.L. Li, Chemistry 8 (1991) 1–9.
[8] Y. Li, Y.L. Zhao, J. Fluoresc. 19 (2009) 641–647.
[9] S.-Y. Niu, B. Yang, J.-Q. Cao, G.-D. Yang, W.-M. Bu, Chem. J. Chin. Univ. 18 (1997) 1917.
[10] B. Yan, H.J. Zhang, S.B. Wang, J.Z. Ni, J. Photochem. Photobiol. A 116 (1998) 209–214.
[11] H. Deng, Y.-P. Cai, H. Chao, C.-L. Chen, C.-W. Jiang, C.-Q. Chen, L.-N. Ji, Chin. J. Chem. 21 (2003) 409.
[12] V.I. Tsaryuk, K.P. Zhuravlev, A.V. Vologzhanina, V.A. Kudryashova, V.F. Zolin, J. Photochem. Photobiol. A 211 (2010) 7–19.
[13] Z.B. Zhang, W.P. Yan, M.G. Fan, Chin. J. Appl. Chem. 22 (2005) 103–104.
[14] M. Ghosh, P. Biswas, U. Florke, Polyhedron 26 (2007) 3750–3762.
[15] J. Dickeson, L. Summers, Aust. J. Chem. 23 (1970) 1023–1027.
[16] J.G. Collins, A.D. Sleeman, J.R. Aldrich-Wright, I. Greguric, T.W. Hambley, Inorg. Chem. 37 (1998) 3133–3141.
[17] A.M.S. Garas, R.S. Vagg, J. Heterocyclic Chem. 37 (2000) 151–158.
[18] C.H. Huang, Coordination Chemistry of Rare Earth, Science Press, Beijing, 1997.
[19] M. Taylor, C. Carter, C. Wynter, J. Inorg. Nucl. Chem. 30 (1968) 1503–1511.
[20] W.J. Gear, Coord. Chem. Rev. 7 (1971) 81–122.
[21] Y.F. Zhao, Y.L. Zhao, F. Bai, Y. Wang, J. Fluoresc. 19 (2009) 179–182.
[22] P. Biswas, S. Dutta, M. Ghosh, Polyhedron 27 (2008) 2105–2112.
[23] C.X. Yuan, L.P. Lu, X.L. Gao, Y.B. Wu, M.L. Guo, Y. Li, X.Q. Fu, M.L. Zhu, J. Biol. Inorg. Chem. 14 (2009) 841–851.
[24] Z.H. Xiao, H.W. Zhu, Z. Chen, Chem. Reagents 28 (2006) 359–360.
[25] Q. Qiao, R.G. Wang, G.Q. Wu, T.D. Tang, Cryst. Res. Technol. 44 (2009) 567–570.

[26] R.F. Wang, S.P. Wang, J.J. Zhang, J. Mol. Struct. 648 (2003) 151–158.
[27] S.P. Yang, H. Yang, X.B. Yu, Z.M. Wang, J. Mol. Struct. 659 (2003) 97–102.
[28] X. Li, Z.Y. Zhang, Y.Q. Zou, Eur. J. Inorg. Chem. (2005) 2909–2918.
[29] L.J. Xu, S.P. Wang, R.F. Wang, J.J. Zhang, J. Coord. Chem. 61 (2008) 237–250.
[30] N. Zhao, S.P. Wang, R.X. Ma, Z.H. Gao, R.F. Wang, H.J. Zhang, J. Alloys Compd. 463 (2008) 338–342.
[31] Z.M. Chen, S.P. Wang, N. Yang, N. Zhao, J.J. Zhang, R.F. Wang, B.H. Zhao, Russ. J. Coord. Chem. 35 (2009) 541–546.
[32] R.X. Ma, Z.M. Chen, Z.H. Gao, S.P. Wang, R.F. Wang, J.J. Zhang, Synth. Met. 159 (2009) 1272–1276.
[33] H.M. Ye, N. Ren, J.J. Zhang, S.J. Sun, J.F. Wang, Struct. Chem. 21 (2010) 165–173.
[34] R.F. Wang, S.P. Wang, S.K. Shi, J.J. Zhang, Chin. J. Struct. Chem. 23 (2004) 1300–1304.
[35] W.T. Carnall, P.R. Fileds, K. Raunaks, J. Chem. Phys. 49 (1968) 4450–4455.
[36] W.S. Liu, M.Y. Tan, Acta Chim. Sin. 48 (1990) 1090–1095.
[37] A.P. Souza, L.C.V. Rodrigues, H.F. Brito, S. Alves, O.L. Malta, J. Lumin. 130 (2010) 181–189.
[38] G.A. Grosby, R.E. Whan, R.M. Alire, J. Chem. Phys. 34 (1961) 743–748.
[39] F.J. Steemers, W. Verboom, D.N. Reinhoudt, E.B. Vandertol, J.W. Verhoeven, J. Am. Chem. Soc. 117 (1995) 9408–9414.
[40] M. Latva, H. Takalo, V.M. Mukkala, C. Matachescu, J.C. RodriguezUbis, J. Kankare, J. Lumin. 75 (1997) 149–169.
[41] E.B. van der Tol, H.J. van Ramesdonk, J.W. Verhoeven, F.J. Steemers, E.G. Kerver, W. Verboom, D.N. Reinhoudt, Chem. -Eur. J. 4 (1998) 2315–2323.
[42] F.F. Chen, Z.Q. Bian, C.H. Huang, J. Chin. Rare Earth Soc. 28 (2007) 385–395.
[43] S.I. Klink, L. Grave, D.N. Reinhoudt, F. van Veggel, M.H.V. Werts, F.A.J. Geurts, J.W. Hofstraat, J. Phys. Chem. A 104 (2000) 5457–5468.
[44] N.M. Shavaleev, R. Scopelliti, F. Gumy, J.C.G. Bunzli, Inorg. Chem. 48 (2009) 6178–6191.
[45] R. Ma, H. Chu, Y. Zhao, Q. Wuren, M. Shan, Spectrochim. Acta A Mol. Biomol. Spectrosc. 77 (2010) 419–423.
[46] Y. Wang, Y.-L. Zhao, H.-H. Li, X.-Y. Wei, R.-J. Ma, Y. Du, Chin. J. Lumin. 31 (2010) 405.
[47] P.C.R. Soares-Santos, H.I.S. Nogueira, V. Felix, M.G.B. Drew, R.A.S. Ferreira, L.D. Carlos, T. Trindade, Chem. Mater. 15 (2003) 100–108.
[48] M.H.V. Werts, R.T.F. Jukes, J.W. Verhoeven, Phys. Chem. Chem. Phys. 4 (2002) 1542–1548.
[49] L.D. Carlos, Y. Messaddeq, H.F. Brito, R.A.S. Ferreira, V.D. Bermudez, S.J.L. Ribeiro, Adv. Mater. 12 (2000) 594–598.
[50] Y. Huang, B. Yan, M. Shao, J. Solid State Chem. 182 (2009) 657–668.