Journal of Alloys and Compounds 408–412 (2006) 1017–1021

Journal of
ALLOYS
AND COMPOUNDS

www.elsevier.com/locate/jallcom

Efficient microwave synthesis of luminescent europium(III) complexes with polypyridine and the study of electrospectrochemistry

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Received 30 July 2004; received in revised form 20 November 2004; accepted 28 November 2004

Abstract

We have developed an efficient synthetic method of photosensitive Eu(III)–polypyridine complexes, assisted with microwave irradiation. We succeeded in obtaining pure complexes in a shorter time with a 70% or more yield by reflux synthesis in ethyleneglycol under microwave irradiation and report their physicochemical properties.

The results of the absorption spectra of the complexes in ethyleneglycol solution are obtained. All the Eu(III) complexes exhibit a very strong spectral absorption at 397 and 664 nm. These bands are attributed to intraligand $\pi \rightarrow \pi^*$ transition and $n \rightarrow \pi^*$ charge transfer transition. A general feature in the spectra of Eu(III) ion is a shift of absorption bands toward lower energy on complex formation. “Nephelauxetic effect; β”. We calculated the values of β, $b^{1/2}$ (measure of covalent), and δ% (Sinha’s parameter) of Eu(III)–polypyridine complexes. The values of $b^{1/2}$ was in the ligand order: (pyre) > (tpy) > (bpyca)>(biq), (dmbpy) > (bpy). The fluorescent intensity of Eu(III) complex with bpyca ligand was strong enhanced by about 7.56 times when compared with that of Eu(III) ion, and for strong Eu(III) complex with tpy ligand it was enhanced by about 30 times. The dominant fluorescent transition of intramolecular energy transfer (IMET) process takes place from chelate absorption band state in Eu(III)–polypyridine to the J manifold of ^{7}F, which is a spin forbidden type and the role of the triplet state is enormously important.

The formula of Nicolson–Shain was used for the analysis of an electrode reaction parameter. From the analytic results of C–V, the transfer coefficient (α), the diffusion coefficient (D, cm^2/s), the standard rate constants, k^0f (cm/s) of the electrode reaction for Eu(III) complexes with polypyridine were obtained. And the formation constants (K_f) were also discussed.

Keywords: Spectroscopy; Luminescence; Eu(III); Polypyridine; Microwave synthesis

1. Introduction

Recently, the study of the coordination compounds of the trivalent rare earth ions (RE^{3+}) continues to be an active research area, which may be attributed to the luminescent properties of these compounds and their application as optical signal amplifier, electroluminescent devices and luminescent probes in biological system [1–5]. The intraconfigurational 4f–4f transitions parity forbidden and their emission and absorption spectra exhibit weak intensity [6]. However, some organic ligands in coordination compounds can act as an “antenna”, absorbing and transferring energy efficiently to the rare earth ion and consequently increasing their luminescence yield [7]. Additionally, polypyridine ligands show strong interest in the investigation of the coordination mode of the ligand–metal bond. Based on the infrared spectroscopy the metal–ligand interaction through the heterocyclic nitrogen atom has also been observed. The rare earth metals still attract attention because the demound as new material such a case as an optical lens, metallurgy, a catalyst and fluorescent paint of the cathode-ray tube of a color television. Eu(III) are applied to red fluorescent substance, Nd(III), Sm(III) and

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doi:10.1016/j.jallcom.2004.11.094

Ce{(III) or (IV)} show characteristics which is excellent as a magnetic material and are contributing to a powerful miniaturization. Furthermore, it is used for electric products, such as a cellular phone, fine ceramics, superconductivity, the mini disk (MD), etc., in the high-tech field. There are also many example of research and characterization of the new material synthesis for the improvement in analysis sensivity in the field of separation analytical chemistry have performed as measurements of the excitation and emission spectra at room (298 K) and the cyclic voltammogram in the acetonitril or *N*,*N*-dimethylformamide for europium(III)–polypyridine complexes.

2. Experimental

2.1. Reagents

Ethyleneglycole, acetonitril, dimethylformamide and acetone were purchased from Aldrich Co. and used as received. Polypyridine ligands: 2,2′-bipyridine (bpy), dimethylbipyridine (dmbpy), terpyridine (tpy), bispyridinoethylene (pyre), 2,4,6-tripyridil-*s*-triazin (tptz), bipyridine-4,4′-dicarboxylic acid (bpyca), and biquinoline (Biq) were purchased from Aldrich Co.

The rare earth photosensitive polypyridine complexes were prepared by an efficient synthetic method, assisted with microwave irradiation from a mixture of 3.5 equiv. of each polypyridine ligand and 1 equiv. of $EuCl_3 \cdot 6H_2O$ in 10 ml ethyleneglycol solution dissolved. The ethyleneglycol solvent was evaporated to yield white crystal, which were dried under vacuum. A white precipitate washed with distilled water to remove the each excess ligand and recrystallized with acetone–ethanol, yielding 70% of Eu(III)–polypyridine complexes.

2.2. Apparatus

The excitation and emission spectra at room temperature (298 K) were measured using a spectrophotometer (Hitachi U-3010 and Hitachi F-2500 or Unisoku Co.). Electrochemical measurements were performed at 25 °C under an inert nitrogen atmosphere. A three-electrode cell configuration controlled by a BAS-CV50W potentiostat was used. The formula of Nicolson–Shain was used for the analysis of an electrode reaction's parameter.

2.2.1. Absorption spectroscopic study

Molar extinction coefficient is shown in the peak wavelength of the absorption spectra obtained below as a result of measurement (Table 1). Although big absorption was not seen in a visible light domain since each sample was almost transparently and colorlessly near when it was used as solution, absorption spectrum of the charge transfer from Eu(III) to Eu(II), to near 396 nm was seen, and although it was small also to the long wavelength side, absorption spectrum of the europium(III) complex with polypyridine was seen. Moreover, big absorption was seen in the purple exterior. It will be using the Jorgensen's formula of the following, which dealt with Nephelauxetic effect (electronic cloud expansion effect of each complex) [7]. Based on the theory of Shinha [8]:

$$\beta = \frac{1}{n}\sum\left(\frac{\nu_{\text{complex}}}{\nu_{\text{aquo}}}\right), \quad n = 1 \tag{1}$$

$$b^{1/2} = \left[\frac{1}{2}(1-\beta)\right]^{\frac{1}{2}} \tag{2}$$

$$\delta\% = \left[\frac{1-\beta}{\beta}\right] \times 100 \tag{3}$$

The value to which ν_{complex} is the frequency of each complex at peak, and ν_{aquo} is the values of the frequency of $EuCl_3 \cdot 6H_2O$ at peak. The result calculated based on these formulas is shown in Table 1. Covalent bond nature parameter, the value of β, shows that the value of the complex of pyprz and tptz is both small. From this, it can be judged that these two have the wavelength shift with more lower energy but it turns out that the value of $b^{1/2}$ and $\delta\%$ becomes large, and coordinating nature becomes large. From the amount of $b^{1/2}$ mixture of 4f orbital is shown to be well connected with increase of coordinating nature. Furthermore, π–π* absorption of a polypyridine ligand at ultraviolet region is very large as molar extinction coefficient is seen.

Table 1
Covalence parameter and absorption spectrum data of europium(III)–polypyridine complexes

Complexes	ν (cm^{-1})	β	δ	$b^{1/2}$
$Eu(bpy)_3Cl_3$	18939	0.807	23.92	0.31
$Eu(bpyca)_3Cl_3$	18265	0.778	28.54	0.33
$Eu(dmbpy)_3Cl_3$	18695	0.796	25.63	0.32
$Eu(tpy)_3Cl_3$	18021	0.768	30.21	0.34
$Eu(pyre)_3Cl_3$	16731	0.713	40.25	0.38
$Eu(Biq)_3Cl_3$	18580	0.791	26.42	0.32

$\beta = \nu_{\text{complex}}/\nu_{\text{aqua}}$ (Nephelauxetic effect), $\delta\% = (1-\beta)/\beta \times 100$ (Sinha's parameter), and $b^{1/2}$ is the Choppin's parameters.

2.2.2. Fluorescence spectroscopic method

Since a fluorescence spectrum is seen by quite strong intensity from the observation data of a fluorescence spectrum, it is expected that it can be used for rare earth analysis.

A fluorescence spectrum and its peak wavelength are shown in Tables 2a–g. Moreover, from the calculation value of Judd [6], the kind of transition state of each peak wavelength is identifying, and is simultaneously shown in

Table 2a
Fluorescent spectroscopic data of europium(III) chloride

E (cm^{-1})	λ (nm)	Intensity (%)	ΔE (cm^{-1})	Assignment
17241	580	1	0	$^5D_0 \rightarrow {}^7F_0$
16779	596	2.53	462	$^5D_0 \rightarrow {}^7F_1$
16234	616	5.44	1007	$^5D_0 \rightarrow {}^7F_2$
14205	704	2.38	3036	$^5D_0 \rightarrow {}^7F_4$

Table 2b
Fluorescent spectroscopic data of $Eu(bpy)_3Cl_3$

E (cm^{-1})	λ (nm)	Intensity (%)	ΔE (cm^{-1})	Assignment
17241	580	1	0	$^5D_0 \rightarrow {}^7F_0$
17182	582	2.91	59	
16779	596	7.63	462	$^5D_0 \rightarrow {}^7F_1$
16260	615	16.57	981	$^5D_0 \rightarrow {}^7F_2$
16051	623	12.32	1190	
15244	656	1.68	1997	$^5D_0 \rightarrow {}^7F_3$
14205	704	6.71	3036	$^5D_0 \rightarrow {}^7F_4$

Table 2c
Fluorescent spectroscopic data of $Eu(tpy)_3Cl_3$

E (cm^{-1})	λ (nm)	Intensity (%)	ΔE (cm^{-1})	Assignment
17241	580	1	0	$^5D_0 \rightarrow {}^7F_0$
17153	583	9.35	88	
16863	593	25.96	378	$^5D_0 \rightarrow {}^7F_1$
16722	598	32.99	519	
16234	616	78.46	1007	$^5D_0 \rightarrow {}^7F_2$
15267	655	4.47	1974	$^5D_0 \rightarrow {}^7F_3$
14409	694	7.11	2832	$^5D_0 \rightarrow {}^7F_4$
14225	703	31.48	3016	

Table 2d
Fluorescent spectroscopic data of $Eu(dmbpy)_3Cl_3$

E (cm^{-1})	λ (nm)	Intensity (%)	ΔE (cm^{-1})	Assignment
17241	580	1	0	$^5D_0 \rightarrow {}^7F_0$
17153	583	9.67	88	
16779	596	16.46	462	$^5D_0 \rightarrow {}^7F_1$
16207	617	30.28	1034	$^5D_0 \rightarrow {}^7F_2$
15244	656	5.13	1997	$^5D_0 \rightarrow {}^7F_3$
14388	695	5.71	2853	$^5D_0 \rightarrow {}^7F_4$
14225	703	13.33	3016	

Table 2e
Fluorescent spectroscopic data of $Eu(phen)_3Cl_3$

E (cm^{-1})	λ (nm)	Intensity (%)	ΔE (cm^{-1})	Assignment
17241	580	1	0	$^5D_0 \rightarrow {}^7F_0$
17153	583	9.35	88	
16863	593	25.96	378	$^5D_0 \rightarrow {}^7F_1$
16779	596	11.03	462	
16234	0	36.33	1007	$^5D_0 \rightarrow {}^7F_2$
15267	655	1.31	1974	$^5D_0 \rightarrow {}^7F_3$
14430	693	2.14	2811	$^5D_0 \rightarrow {}^7F_4$
14425	703	12.64	3016	

Table 2f
Fluorescent spectroscopic data of $Eu(Biq)_3Cl_3$

E (cm^{-1})	λ (nm)	Intensity (%)	ΔE (cm^{-1})	Assignment
17241	580	1	0	$^5D_0 \rightarrow {}^7F_0$
16807	595	2.1	434	$^5D_0 \rightarrow {}^7F_1$
16207	617	3.76	1034	$^5D_0 \rightarrow {}^7F_2$
16026	624	2.93	1215	
15267	655	0.34	1974	$^5D_0 \rightarrow {}^7F_3$
14184	705	1.66	3057	$^5D_0 \rightarrow {}^7F_4$

Table 2g
Fluorescent spectroscopic data of $Eu(tptz)_3Cl_3$

E (cm^{-1})	λ (nm)	Intensity (%)	ΔE (cm^{-1})	Assignment
17241	580	1	0	$^5D_0 \rightarrow {}^7F_0$
16892	592	1.9	349	$^5D_0 \rightarrow {}^7F_1$
16722	598	2.25	519	
16447	608	0.59	794	$^5D_0 \rightarrow {}^7F_2$
16234	616	4	1007	
16051	623	3.96	1190	
15267	655	0.44	1974	$^5D_0 \rightarrow {}^7F_3$
14225	703	2.34	3016	$^5D_0 \rightarrow {}^7F_4$

the above tables. For example, a fluorescence spectrum of $Eu(tpy)_3Cl_3$ is shown in Fig. 1. It is seen that the fluorescence spectrum is mainly sharp near 597, 616, and 700 nm. These peaks are the spectrum of the red fluorescence of europium. If this becomes a complex, intensity will increase number of times from the time only of single ion. Symmetry (Oh) actually is not kept up, and then these peaks are considered to overlap and appear. It was shown that the crystal-field splitting of the relevant levels of Eu(III) in D_3 symmetry together with the transitions allowed for electric dipolar selection rules ($^5D_0 \rightarrow {}^7F_{0,2,4}$). The energy difference of a transition state set to ΔE as a criterion, 580 nm (17,241 cm^{-1}). The transition state was identified by combining the values of ΔE in Tables 2a–g. It turns out that the direction becomes stronger having made into the complex with two big red fluorescence spectra, 595 and near 616 nm, rather than the time of europium single ion. Especially $Eu(tpy)_3Cl_3$ has the largest fluorescence intensity as shown in Fig. 1 and it increases by about 15 times when compared with that of a single ion. The mechanism of red fluorescence is shown in Fig. 2. The dominant fluorescent transition of intermolecular energy transfer (IMET) process takes place from chelate absorption band state in Eu(III)–polypyridine to the J manifold of ^7F, which is a spin forbidden type and the role of triplet state is enormously important. If a complex absorbs the excitation light (318 nm), seen with the absorption spectrum, the electronic ground state of polypyridine ligand will go up to singlet excite state S_2^* first and then it gradually falls and moves to triplet state T_1^*. It falls from there to $^5D_0$ of Eu(III). Fluorescence is

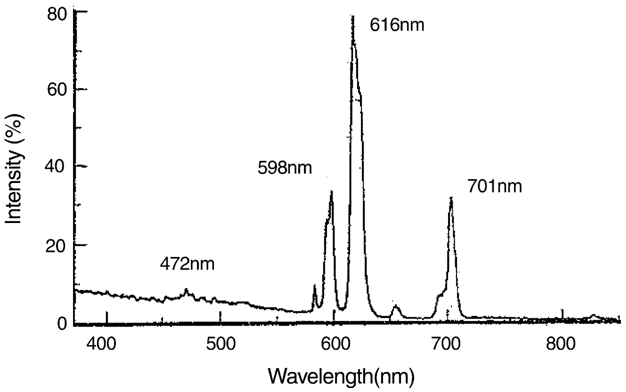

Fig. 1. Fluorescence spectrum of Eu(III)–$(tpy)_3Cl_3$ complex.

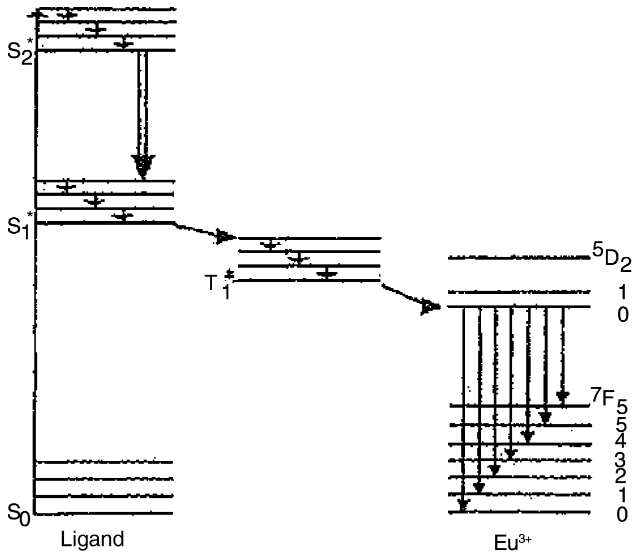

Fig. 2. Schematic diagram of the polypyridine ligand to Europium(III) energy transfer mechanism.

emitted when falling to levels of $^7F_0 \rightarrow {}^7F_6$. The peaks near 595 nm are due to the fluorescence of $^5D_0 \rightarrow {}^7F_2$, peak near 700 nm due to the fluorescence of $^5D_0 \rightarrow {}^7F_4$ and the peak near 616 nm are due to the fluorescence of $^5D_0 \rightarrow {}^7F_3$ (refer to Tables 2a–g).

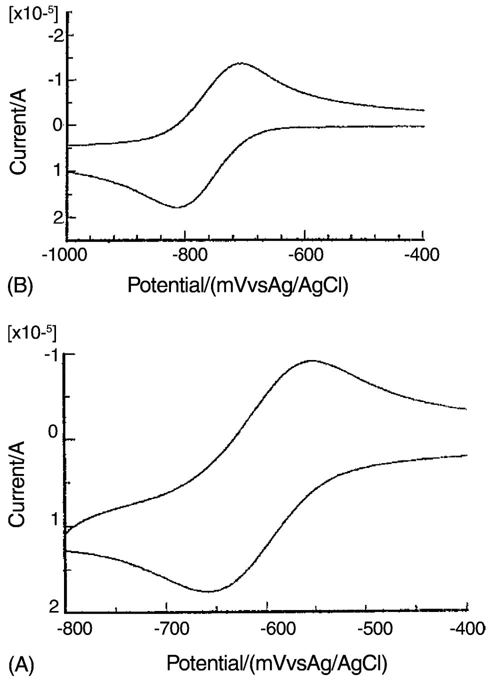

Fig. 3. Cyclic voltammogram of europium chloride (A) and Eu(III)–(tpy)$_3$Cl$_3$ (B) in DMF solution, involving 0.1 mol dm^{-3} (Bu)$_4$NClO$_4$. Glassy carbon electrode was used. Scan rate 100 mV/s.

2.2.3. *Cyclic voltammetry of europium(III)–polypyridine complexes*

The cyclic voltammograms were obtained at scan speed of 50–600 mV/s, from the peak potential difference ($\Delta E_p = E_{pa} - E_{pc}$) shown below, since this system was an irreversible electrode reaction system. It used the formula of Nicholson–Shain for the analysis of the electrode reaction parameters [9]. The following equations were used:

$$E_p = E_0 - \frac{RT}{\alpha n F}\{0.78 + \ln(D_0 \alpha a)^{1/2} - \ln k_s\} \tag{4}$$

where E_p is a function of scan rate v shifting (for a reduction) in a negative direction by an amount ($30/\alpha$, mV) for each 10-fold increase in v, E^0 is a reversible half-wave potential of europium–polypyridine complexes indicating $[(\alpha E_{pc} + (1-\alpha)E_{pa}]/2$, where R is the gas constant (8.314 J/mol) and T is the absolute temperature (Kelvin scale), α the transfer coefficient, F the Faraday constant (96,485 C), k_s the standard electrode rate constant (cm/s), n the number of electron with reduction or oxidation, and D_0 is the diffusion coefficient of oxidant (cm^2/s).

A plot of E_p versus $\log a$ $(= nFv/RT)$ will become linear, α was obtained from the slope of the plot. The rate constant k_s and the diffusion coefficient D_0 were also calculated from the intercept of tangent to the curve and the slope of the peak current of reduction equation (5), respectively:

$$i_{pc} = 299(\alpha n)^{1/2} A D_0^{1/2} C^* v^{1/2} \tag{5}$$

where C^* and A are the concentration of oxidant and surface area of glassy carbon electrode (0.0707 cm^2/s).

For example, cyclic voltammograms of europium chloride and Eu(tpy)$_3$Cl$_3$ are shown in Fig. 3.

Table 3
Cyclic voltammetric data of europium(III)–polypyridine complexes

Complexes	Transfer coefficient (α)	Diffusion coefficients D_0 (cm^2/s)	Rate constants k_s (cm/s)	Reversible half-wave potentials ($E^{1/2}$)(V)	Stability constants log K
EuCl$_3$·6H$_2$O	0.77	5.49×10^{-6}	8.86×10^{-3}	−0.317	1
Eu(byp)$_3$Cl$_3$	0.73	4.49×10^{-6}	1.51×10^{-4}	−0.383	10.11
Eu(tpy)$_3$Cl$_3$	0.78	8.64×10^{-6}	9.25×10^{-5}	−0.396	4.43
Eu(dmbpy)$_3$Cl$_3$	0.57	5.40×10^{-6}	3.84×10^{-4}	−0.372	9.93
Eu(pyre)$_3$Cl$_3$	0.47	1.10×10^{-6}	5.77×10^{-4}	−0.37	9.89
Eu(phen)$_3$Cl$_3$	0.29	1.14×10^{-6}	1.08×10^{-3}	−0.358	9.68
Eu(biq)$_3$Cl$_3$	0.76	1.37×10^{-6}	2.195×10^{-4}	−0.386	10.16
Eu(tptz)$_3$Cl$_3$	0.81	3.52×10^{-6}	5.16×10^{-4}	−0.362	9.75

The stability constants were calculated by Lingane's equation:

$$(E^{\mathrm{r}}_{1/2}) - (E^{\mathrm{r}}_{1/2})_{\mathrm{EuCl_3}} = -\frac{0.0591}{n} \log K_{\mathrm{f}} - p\left(\frac{0.0591}{n}\right) \log C_x \qquad (6)$$

The transfer coefficient (α), diffusion coefficient (D_0, cm^2/s), standard rate constant (k_{s}, cm/s) and stability constant (K_{f}) are shown in Table 3. The magnitude of the rate constants k_{s} is in the order: $\mathrm{EuCl_3{\cdot}6H_2O} > \mathrm{Eu(phen)_3Cl_3} > \mathrm{Eu(pyre)_3Cl_3} > \mathrm{Eu(tptz)_3Cl_3} > \mathrm{Eu(Biq)_3Cl_3} > \mathrm{Eu(dmbpy)_3Cl_3} > \mathrm{Eu(bpy)_3Cl_3} > \mathrm{Eu(tpy)_3Cl_3}$, and the magnitude of the stability constant K_{f} is in the order: $\mathrm{Eu(Biq)_3Cl_3} > \mathrm{Eu(pby)_3Cl_3} > \mathrm{Eu(dmbpy)_3Cl_3} > \mathrm{Eu(pyre)_3Cl_3} > \mathrm{Eu(phen)_3Cl_3} > \mathrm{Eu(tptz)_3Cl_3} > \mathrm{Eu(tpy)_3Cl_3}$.

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