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Photophysical properties of tetranuclear Eu(III) complexes in polyphenylsilsesqioxane (PPSQ)

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Abstract

The tetranuclear europium(III) complexes, $[Eu_4(\mu\text{-}O)(L_1)_{10}]$ (L_1 = 2-hydroxy-4-octyloxybenzophenone, **1**) and $[Eu_4(\mu\text{-}O)(L_2)_{10}]$ (L_2 = 2-hydroxy-4-dodecyloxybenzophenone, **2**), were incorporated into the thermostable polyphenylsilsesqioxane (PPSQ) which had a high transparency. The emission bands of both Eu(III) complexes in PPSQ were observed at 578, 590, 615, 653 and 700 nm by the excitation of the ligands at 380 nm. The emission lifetimes were determined to be 0.38 ms for **1** and 0.39 ms for **2**, which were found to be longer than those in THF-d_8 (0.10 ms for **1** and 0.11 ms for **2**). The tetranuclear Eu(III) complexes doped in the PPSQ polymers were stable up to the condition of 250 °C.

Keywords: Polymers; Luminescence; Thermal study

1. Introduction

In recent years, Eu(III)-doped polymers have received considerable attention because of their potential applications for luminescent displays and plastic optical devices [1,2]. Some research groups have extensively studied on the design and synthesis of luminescent Eu(III) complexes for achieving desirable luminescent properties in polymer matrices [3–13]. The plastics containing thermostable luminescent compounds are required, because the current manufacturing processes for the devices include curing processes at temperatures up to 250 °C [14]. We have previously reported on the synthesis of highly thermostable tetranuclear Eu(III) complexes, $[Eu_4(\mu\text{-}O)(L_1)_{10}]$ and $[Eu_4(\mu\text{-}O)(L_2)_{10}]$ using UV absorption reagents, 2-hydroxy-4-octyloxybenzophenone L_1 and 2-hydroxy-4-dodecyloxybenzophenone L_2, as the ligands, which are commonly utilized as the plasticizers in manufacturing plastic products (Fig. 1a) [15].

Polyphenylsilsesqioxane (PPSQ) (Fig. 1b) has received considerable interest in the microelectric industry due to high thermal resistance over 500 °C, high chemical and mechanical stability and low dielectric constants. As PPSQ has also high optical transparency, PPSQ has been suggested as a promising material for wafer-scale optical wave guide interconnect [16]. For the purpose of fabricating luminescent polymers which are applicable for optoelectonic devices, we have focused here on the photophysical properties of the Eu(III) complexes in PPSQ by comparison with those in THF-d_8 shown in our earlier study [15].

Here, we report on the thermostable luminescent polymer (PPSQ) including the tetranuclear Eu(III) complexes with L_1 or L_2. The photophysical properties of **1** and **2** in PPSQ, i.e., the emission spectra, and the emission lifetimes were measured. The photophysical characteristics of the tetranuclear Eu(III) complexes in PPSQ and the high thermostability of the luminescent polymers are demonstrated.

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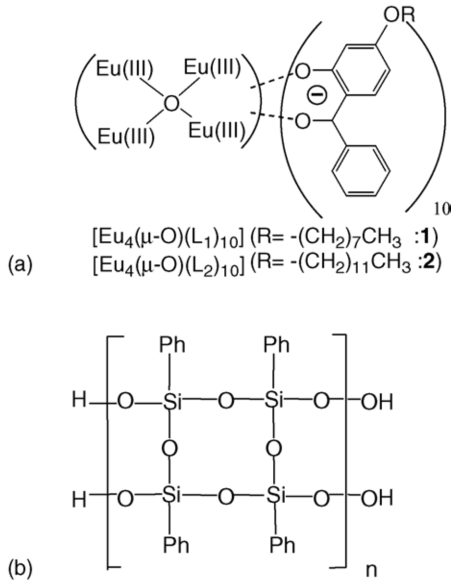

Fig. 1. Chemical structures of the tetranuclear Eu(III) complexes (a) and the PPSQ polymer (b).

2. Experiment

2.1. Apparatus

Infrared spectra of complexes were obtained using a Perkin-Elmer FT-IR 2000 spectrometer. ^{1}H NMR data were obtained with a JEOL EX-270 spectrometer, where chemical shifts were determined using tetramethylsilane (TMS) as an internal standard. Elemental analyses (C, H) were performed with a Perkin-Elmer 240C. The contents of the metal ions were determined by EDTA titration using xylenolorange as an indicator. FAB-MASS spectra were measured by a JEOL JMS-700. Thermal studies were carried out using DSC-60 differential scanning calorimeter.

2.2. Materials

Europium nitrate hexahydrate (99.9%) was obtained from Rhodia Co. Inc. 2-Hydroxy-4-octyloxybenzophenone was purchased from Wako Pure Chemical Industries Ltd. 2-Hydroxy-4-dodecyloxybenzophenone was received from Hekisa Chemical Co. Inc. THF-d_8 was obtained from Wako Pure Chemical Industries Ltd. All other chemicals were reagent grade and were used as purchased. The Eu(III) complexes **1** and **2** were characterized as previously reported in our study [15].

2.3. Preparation of $[Eu_4(\mu\text{-}O)(L_1)_{10}]$ (L_1 = 2-hydroxy-4-octyloxybenzophenone, **1**)

2-Hydroxy-4-octyloxybenzophenone (0.600 g, 1.84 mmol) was dissolved in 40 ml methanol and triethylamine (0.190 g, 1.84 mmol) was added to this solution with stirring at 40 °C. To the yellowish solution, $Eu(NO_3)_3 \cdot 6H_2O$ (0.328 g, 0.735 mmol) in 5 ml methanol was then added dropwise with further stirring for 20 min. Yellowish oily product was obtained. The resulting compound was then crystallized using acetone to give dark yellow crystals. The yield was 30%. ^{1}H NMR (270 MHz, $CDCl_3$): δ12.7 (1H, s), δ7.6–7.2(6H, m), δ6.5–6.4(2H, d), δ4.0(2H, t), δ1.8(2H, m), δ0.9(2H, t). IR (KBr, cm^{-1}): (ν_{CH}) 2922, ($\nu_{C=C}$) 1596, ($\nu_{Ph\text{–}O}$) 1243. Calcd. for $[Eu_4(L_1{}^-)_{10}O^{2-}]$ ($C_{210}H_{250}O_{31}Eu_4$): C, 65.04%, H, 6.50%, Eu, 15.67%. Found: C, 64.90%, H, 6.39%, Eu, 15.41%. FAB MS: *m*/*z* 3552 $[Eu_4(L_1{}^-)_9O^{2-}]^+$.

This complex was highly soluble in non-polar solvents such as hexane, chlorofolm and dichloro-methane.

2.4. Preparation of $[Eu_4(\mu\text{-}O)(L_2)_{10}]$ (L_2 = 2-hydroxy-4-dodecyloxybenzophenone, **2**)

This complex was prepared in a way similar to that of **1** using 2-hydroxy-4-dodecyloxybenzophenone instead of 2-hydroxy-4-octyloxybenzophenone as a ligand. The yield was 30%. ^{1}H NMR($CDCl_3$): δ12.7(1H, s), δ7.6–7.3(6H, m), δ6.5–6.4(2H, d), δ4.0(2H, t), δ1.8(2H, m), δ0.9(2H, t). IR (KBr, cm^{-1}): (ν_{CH}) 2924, ($\nu_{C=C}$) 1608, ($\nu_{Ph\text{–}O}$) 1247. Calcd. for $[Eu_4(L_2{}^-)_{10}O^{2-}]$ ($C_{250}H_{330}O_{31}Eu_4$): C 67.49%, H 7.25%, Eu 13.65%. Found: C 67.50%, H 7.45%, Eu 13.49%. FAB MS: *m*/*z* 4056 $[Eu_4(L_2{}^-)_9O^{2-}]^+$.

The complex was highly soluble in non-polar solvents such as hexane, chlorofolm and dichloromethane.

2.5. Thermostability of Eu(III) complex

The DSC spectra of **1** and **2**, and their ligands (L_1 and L_2) are shown in Fig. 2 [15]. The peaks around 50 °C of the DSC spectra of ligands L_1 and L_2 were assigned to the melting point of each ligand. The endothermic peaks around 50 °C for **1** and **2** were not observed, suggesting that the samples did not contain free ligands. The ligands, L_1 and L_2, were decomposed around 250 °C. In contrast, the decomposition points of **1** and **2** were found to be at 309 °C for **1** and 320 °C for **2**, respectively. The decomposition points were in agreement with those of the TG analyses.

2.6. Preparation of the PPSQ thin films including Eu(III) complexes

The polymer thin films containing Eu(III) complexes were prepared as following: polyphenylsilsesqioxane (PPSQ, Mw ≒ 141,000) was dissolved in anisole (15 wt.%) and the mixtures with Eu(III) complexes were obtained (Eu(III) complexes: 10 wt.%, PPSQ: 90 wt.%). The glass substrates coated with the polymers were then fabricated by a cast method and heated for 5 min in an oven. The excitation spectra of those Eu(III) complexes in PPSQ showed the broad peaks around 380 nm which are assigned to the π–π^* transitions of the ligands.

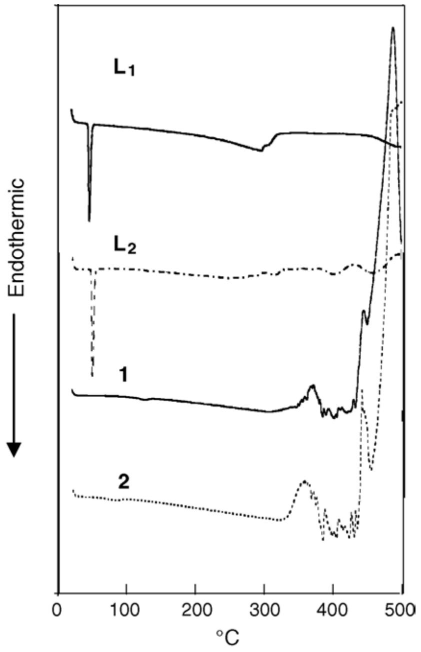

Fig. 2. DSC runs of the tetranuclear Eu(III) complexes and the ligands L_1 and L_2.

2.7. Optical measurements

The emission spectra were measured at room temperature using a JOBIN YVON Fluorolog R-3 spectrofluorometer system. The spectra were corrected for detector sensitivity and lamp intensity variations.

3. Results and discussion

3.1. Photophysical properties

The emission spectra of **1** and **2** in PPSQ thin films are shown in Fig. 3a. The emission peaks for **1** and **2** were observed around 578, 590, 615, 653 and 700 nm, which were assigned to the 4f–4f transitions of Eu(III) ($^5D_0 \rightarrow {}^7F_i$: $i = 0, 1, 2, 3, 4$), respectively. The spectra of **1** and **2** were normalized with respect to the $^5D_0 \rightarrow {}^7F_1$ (magnetic dipole transition). The most intense peaks corresponding to the electronic dipole transition ($^5D_0 \rightarrow {}^7F_2$) were observed at 615 nm for both complexes. The geometrical structures of the Eu(III) complexes are often related with the intensity ratios. The relative intensities ($^5D_0 \rightarrow {}^7F_1$ transition: $^5D_0 \rightarrow {}^7F_2$ transition) of the Eu(III) complexes were 1:7.7 for **1** and 1:9.1 for **2**. In our previous study, the ratios in THF-d_8 for **1** and **2** were found to be 1:13 and 1:14, respectively [16]. The matrices, THF-d_8 and PPSQ, produced remarkable differences in the relative intensities for both Eu(III) complexes. These results suggest that the site symmetries of the Eu(III) in PPSQ are higher than those in THF-d_8. The higher ratios for **2** might be caused by the longer alkyl chains of the ligand (L_2).

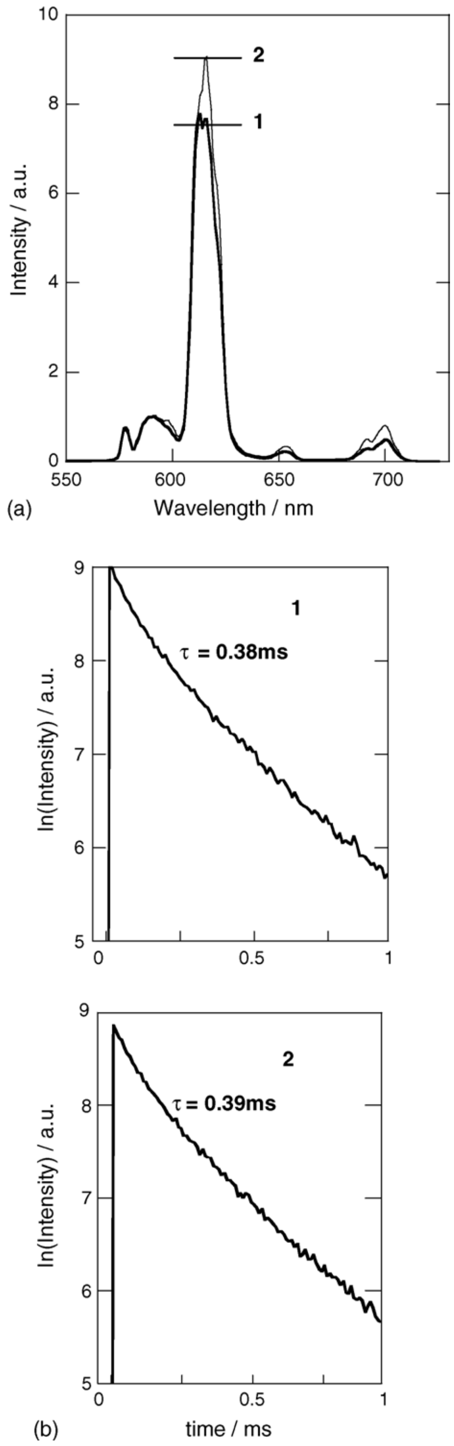

Fig. 3. (a) Emission spectra of the Eu(III) complexes **1** and **2** in PPSQ films on a glass substrate. Excitation at 380 nm. The spectra of **1** and **2** were normalized at the $^5D_0 \rightarrow {}^7F_1$ (magnetic dipole transition). (b) Emission lifetimes of the Eu(III) complexes **1** and **2** in PPSQ.

The emission lifetime studies of the films were also conducted by irradiation at the π–π^* transition of the ligand (380 nm). For both complexes, the emission lifetimes obtained by the single exponential analysis were 0.38 ms for **1** and 0.39 ms for **2**, respectively (Fig. 3b). On the other hand,

Table 1
The emission lifetimes (τ) of the Eu(III) complexes **1** and **2** in PPSQ after heating at different temperatures

Temperatures (°C)	Emission lifetimes,[a] τ (ms)	
	1	**2**
25[b]	0.38	0.39
150	0.40	0.42
200	0.38	0.40
250	0.37	0.36

[a] The emission lifetimes were measured by irradiation at 380 nm.
[b] Control experiment.

we previously reported their emission lifetimes by the ligand excitation in THF-d_8 (0.10 ms for **1** and 0.11 ms for **2**) [16]. The longer lifetimes observed in PPSQ films were consistent with the results of the higher site symmetries of the Eu(III) complexes discussed in connection with the emission intensity ratios. The photophysical properties of the Eu(III) complexes in other polymers such as polymethylmethacrylate (PMMA) are in investigation for understanding the effect of the polymer structures upon the Eu(III) luminescent properties.

3.2. Thermal studies on the luminescent properties

The luminescent PPSQ thin films heated at 150, 200 and 250 °C were prepared in order to test the thermostability at high temperatures. The emission lifetimes of the samples were measured for **1** and **2** (Table 1). The emission lifetimes of the samples were not changed by high temperature treatments and stayed at 0.38–0.40 ms for **1** and 0.36–0.40 ms for **2**. Consequently, the Eu(III) complexes were found to be stable up to 250 °C in PPSQ films. We also tested the thermostability of the mononuclear Eu(III) complex, Eu(hfa)$_3$·2H$_2$O in PPSQ for comparison which has the decomposition temperature of 220 °C in air [15]. The mononuclear Eu(III) complex in PPSQ decomposed below 250 °C so that we could not measure the emission lifetime. The tetranuclear Eu(III) complexes having high decomposition temperatures (over 300 °C) in air also showed the thermostabilities in the PPSQ polymer.

4. Conclusions

The incorporation of the tetranuclear Eu(III) complexes **1** and **2** into the PPSQ polymer provided the following distinct results on the photophysical properties: (i) longer emission lifetimes in PPSQ compared with those in THF-d_8 and (ii) higher thermostability of the tetranuclear Eu(III) complexes in PPSQ than the mononuclear Eu(hfa)$_3$ complex. These types of thermostable lanthanide(III) complexes can be promising candidates as luminescent compounds for plastic optical materials which open up further development of plastic industrial fields.

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