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Development of ultraviolet LED devices containing europium (III) complexes in fluorescence layer

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Abstract

Relations between molecular structures of europium complexes and their luminescent properties were investigated. Europium complex with β-diketones and two different phosphine oxides **8** was highly soluble in fluorinated medium, and realized largest fluorescence intensities. The luminous intensity of ultraviolet light emitting diodes devices (LEDs) whose fluorescence layer consists of fluorinated polymer and **8** was over 200 mcd (20 mA). Fluorescence compounds of this type are promising for application in next-generation white LEDs. Moreover, we proposed a novel molecular design of europium complex with asymmetric diphosphine dioxide.

Keywords: Phosphors; Luminescence

1. Introduction

White LEDs are attracting much attention because of their large luminance and low weight. In particular, a LED device consisting of near-ultraviolet-light chip and red, green and/or yellow, and blue fluorescence compounds (Fig. 1) has a large color rendering index. However, only a few red inorganic fluorescence compounds have been reported which can be excited efficiently by near-ultraviolet-light. Such red fluorescence compounds are strongly required to realize large luminance white LEDs.

On the other hand, rare-earth complexes, notably europium complexes, have been the subject of remarkable development. The fluorescence spectra of europium complexes hardly shift according to concentration of dyes and properties of matrix polymers. Therefore, they are considered to be suitable for LEDs as fluorescence compounds from the viewpoint of adjusting color balance. Moreover, the sharpness of the intra-f-shell emission lines of trivalent europium ions realizes pure color.

However, because almost all absorption lines of europium ions arise from parity forbidden f–f electronic transitions, their absorption cross sections are small and direct optical excitation is inefficient.

It is known that the emission of rare-earth ions can be enhanced through indirect excitation mechanisms. For europium complexes, β-diketones are often used as ligands because they are easily synthesized and show relatively high emission [1–7].

This paper discusses the relations between molecular structures of europium complexes having β-diketones and their luminescent properties. Spectroscopic analysis of europium complexes was carried out to explain the quite large luminous intensity of some LEDs.

2. Experimental details

2.1. Method of formation of fluorescence layer in LEDs

Each europium complex and fluorinated polymer were mixed together and dissolved in each solvent that can solve it easily. By drying the solution, polymer sheet contain-

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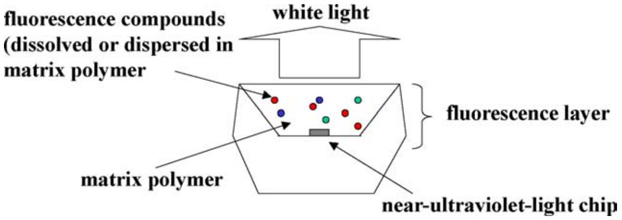


Fig. 1. Structure of ultraviolet-excited white LEDs.

ing europium complex uniformly was obtained. Then the sheet was cut and measured, and stacked on the LED-chip. The LEDs were heated to realize uniform fluorescence layers.

2.2. *Molecular orbital calculation of europium complexes*

We characterized the molecular and electronic structures of europium complexes by density functional theory (DFT) calculations with B3LYP functional. The basis set employed in this work was CEP-4G. Firstly, we obtained optimized geometries in the ground state, and the excitation energies and oscillator strengths at the optimized geometry in the ground state were obtained by time-dependent DFT (TDDFT) calculations. All calculations were performed with the Gausssian 98 program package [8].

2.3. *NMR spectroscopy of europium complexes*

The ^{31}P NMR solution spectra were recorded on a JEOL JNM-LA400W (at 162 MHz) with a repetition time of 3 s. Chemical shifts (δ, ppm) were referenced to H_3PO_4. Vertrel XF (fluorinated solvent, Du Pont-Mitsui Fluorochemicals) was used as solvent.

2.4. *Measurement of fluorescence spectra of fluorescence compounds and luminous intensity of LEDs*

Fluorescence spectra of dilute solution of fluorescence compounds were measured with a Hitachi F3000 spectrofluorescence photometer. Luminous intensities were measured with CAS140B (InstrumentSystems).

2.5. *Europium complexes*

Europium complexes **1**–**5** were purchased from H. W. Sand Corp and **6** from ABCR GmbH & Co., KG.

2.6. *Properties of ultraviolet LEDs without fluorescence layer*

Generating power of LED-chips was 4.52 mW (average) (center wavelength = 395 nm) and 2.77 mW (average) (center wavelength = 402 nm) at 20 mA electric current.

3. Results and discussion

3.1. *Ultraviolet LEDs using previous europium complexes in fluorescence layer*

Matrix polymer of fluorescence layer in LEDs is required to have high transparency of near ultraviolet and visible light, as well as rare C–H, O–H bonds to prevent vibration quenching. Fluorinated polymers are suitable for these purposes [9]. One more important property required is good ability to solve europium complexes. Generally, fluorinated polymer cannot dissolve polar compounds such as metal complexes. To satisfy the need for these properties, we selected CEFRAL FG 700X (acryl graft type fluorinated polymer, purchased from Central Glass Co., Ltd.).

Two types of europium complexes with β-diketones were investigated. Type 1 (Fig. 2) complexes (**1**–**5**) have β-diketones and phenanthroline as ligands, and are mainly used in organic electro-luminescence devices. It was reported that β-diketones and heterocyclic ligands efficiently sensitize trivalent europium ions [5,10,11].

Type 2 (Fig. 2) (**6**) complex has only β-diketones, and is used in security ink (cannot be seen in visible light and can be seen in ultraviolet light).

Ultraviolet LEDs (red) using the above-mentioned europium complexes were fabricated and their luminous intensities were measured.

LEDs using type 1 europium complexes were found to have relatively low luminous intensities (under 45 mcd, 20 mA, λ exc = 395 nm). The large plain condensed rings like phenanthroline often reduce the solubility of compounds. They were not soluble in fluorinated polymer but dispersed as particles. This leads to increasing of light scattering and decreasing of efficiency of light taking out from the LEDs.

On the other hand, type 2 europium complexes are highly soluble in fluorinated polymer. However, they were found to have very low luminous intensity (under 1 mcd, 20 mA, λ exc = 395 nm). This is attributable to small molar absorption coefficient of type 2 complex in ultraviolet light.

3.2. *Study of a new type of europium complexes*

From the results presented in Section 3.1, new type europium complexes are required. Europium complexes with β-diketones and phosphine oxides were reported to be effective for enhancing fluorescence intensity [12].

We propose novel europium complexes having β-diketones and two phosphine oxides. They are even more amorphous due to more asymmetric molecular structures and expected to be more soluble in fluorinated polymers. Also, their absorption coefficients are expected to be larger due to the effects of more asymmetric ligand-fields. These factors should lead to better fluorescence intensity.

To compare fluorescence intensities for the various conditions of europium complexes, solvent **7** (Vertrel XF: fluorinated solvent, Du Pont-Mitsui Fluorochemical Ltd.) (Fig. 3)

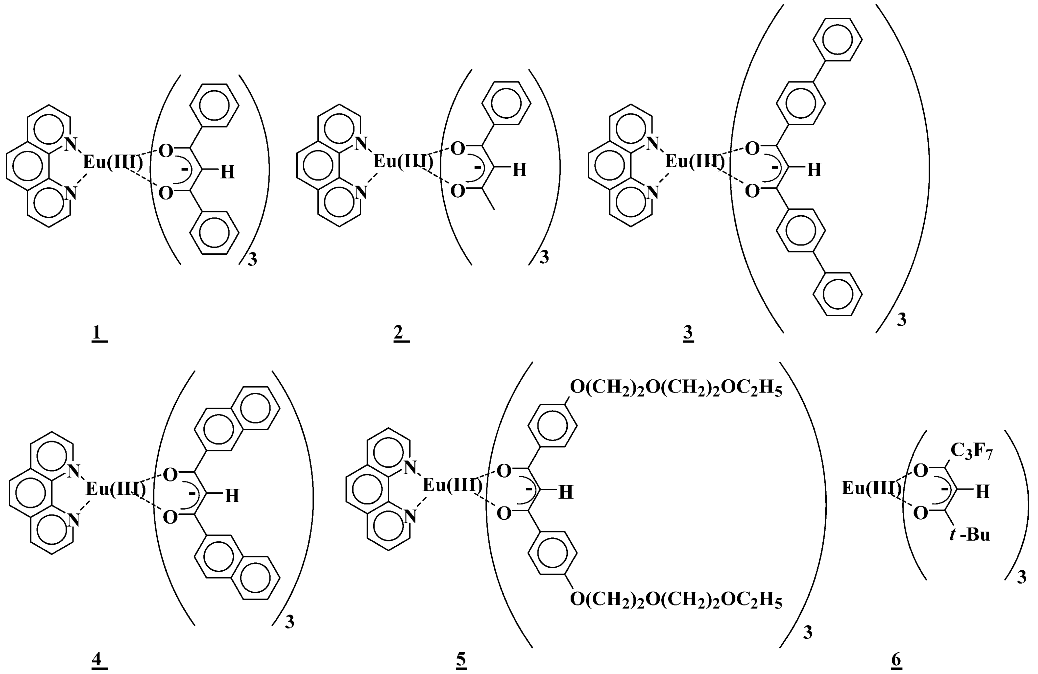


Fig. 2. Molecular structures of europium complexes used in this study (**1**–**5**: type 1; **6**: type 2).

was selected as a model hydrophobic fluorinated polymer. Dilute solution of europium complex **6** and mixtures of **6** and phosphine oxide **9** and/or **10** were made and fluorescence spectra excited by 395 nm light, that is, by the maximum wavelength of LED-chip, were measured (Fig. 4). In the case where a europium complex **6** individuality dissolved in solvent **7**, very small fluorescence intensity was observed. When the mixture of **6** and 2.0 molar equivalent of phosphine oxide **9** or **10** was dissolved, the fluorescence intensity was remarkably enlarged. Moreover, when the mixture of **6** and 1.0 molar equivalent of trioctylphosphine oxide **9** and triphenylphosphine oxide **10** was dissolved (Fig. 3), fluorescence intensity was drastically enlarged. This is explained by the highest solubility of expected europium complex **8** in fluorinated solvent and the large absorption coefficient due to the effects of asymmetric ligand-fields.

3.3. Proof of formation of europium complexes in fluorinated solvent by ^{31}P NMR spectra.

To prove the existence of europium complex **8** in fluorinated solvent **7**, ^{31}P NMR spectra were measured (Fig. 5). The spectrum of the mixture of phosphine oxides **9** and **10** in solvent **7** is shown in the first row in Fig. 5. Sharp signals were obtained for each phosphine oxide. In the third and fourth columns are spectra of the mixtures of **6** and **10**, and

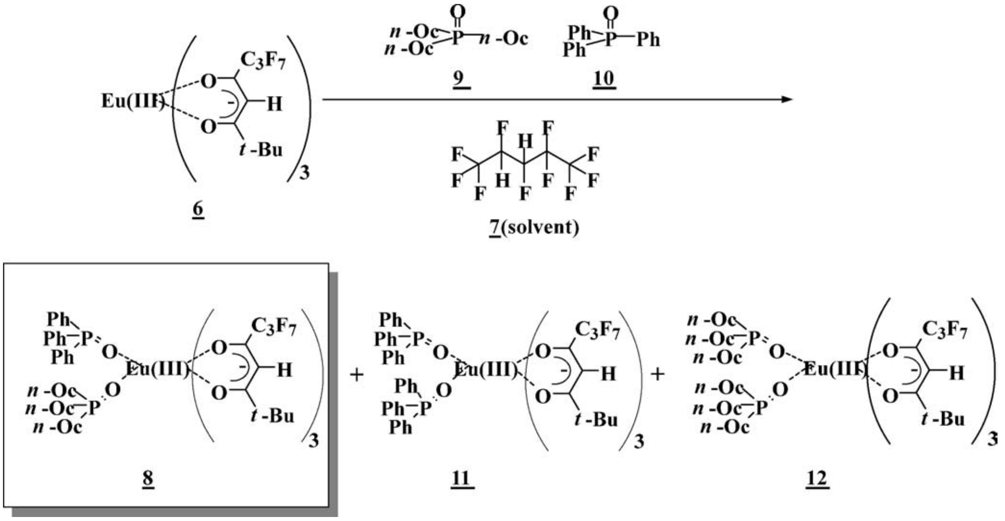


Fig. 3. Expected reaction and molecular structure of europium complex having two phosphine oxides as ligands **8**.

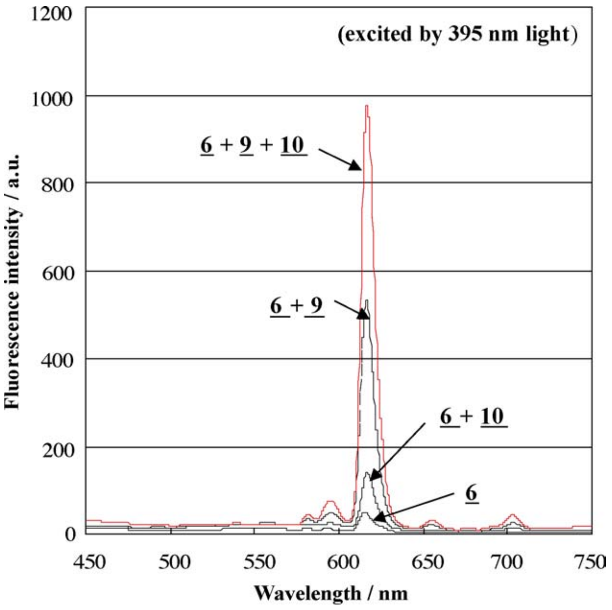


Fig. 4. Fluorescence intensities of europium complexes in fluorinated solvent **7**.

6 and **9**, respectively. The signals D and B, which shifted to upper magnetic fields from the original one, were identified as phosphine oxide ligands [13]. The second row is the spectrum of the mixture of **6**, **9** and **10**. Fore signals, B, B′, D′ and D, were observed toward upper magnetic fields. Signals B and D corresponded with those in the fourth and third row, respectively, and were identified as phosphine oxide ligands of europium complexes **11** and **12** (Fig. 3). Signals B′ and D′ strongly support the existence of europium complex **8** in fluorinated solvent **7**. Signal B′ was identified as trioctylphosphine oxide ligand of **8**, and D′ as triphenylphosphine oxide ligand of **8**.

From the results presented in Sections 3.2 and 3.3, the largest fluorescence intensities were obtained in the case where compounds **6**, **9** and **10** were mixed with fluorinated solvent. In the solvent, europium complex **8** was formed and this is considered to be one of the main factors accounting for the large fluorescence intensity.

3.4. The luminous intensity of ultraviolet LEDs using europium complexes in fluorescence layer

LEDs whose fluorescence layer consisted of the mixture of compounds **6**, **9** and **10** and fluorinated polymer CEFRAL FG 700X were fabricated. The largest luminous intensity in the optimum condition, which is the best datum reported so far, was 186 mcd (red) excited at 395 nm and over 200 mcd (red) at 402 nm ultraviolet light. Luminous intensity of previously reported ultraviolet LEDs (red) is about 60 mcd. Existence of europium complex **8** having two phosphine oxides as ligands is considered to be the main factor to enlarge luminous intensity.

3.5. Molecular orbital calculation of newly proposed europium complexes having asymmetric diphosphine dioxide as ligands

We propose the use of asymmetric diphosphine dioxide ligands to implement different phosphine oxide structures in europium complexes. Moreover, chelate effects of diphosphine dioxide ligands will inhibit ligand exchange, resulting in improved endurance of europium complexes.

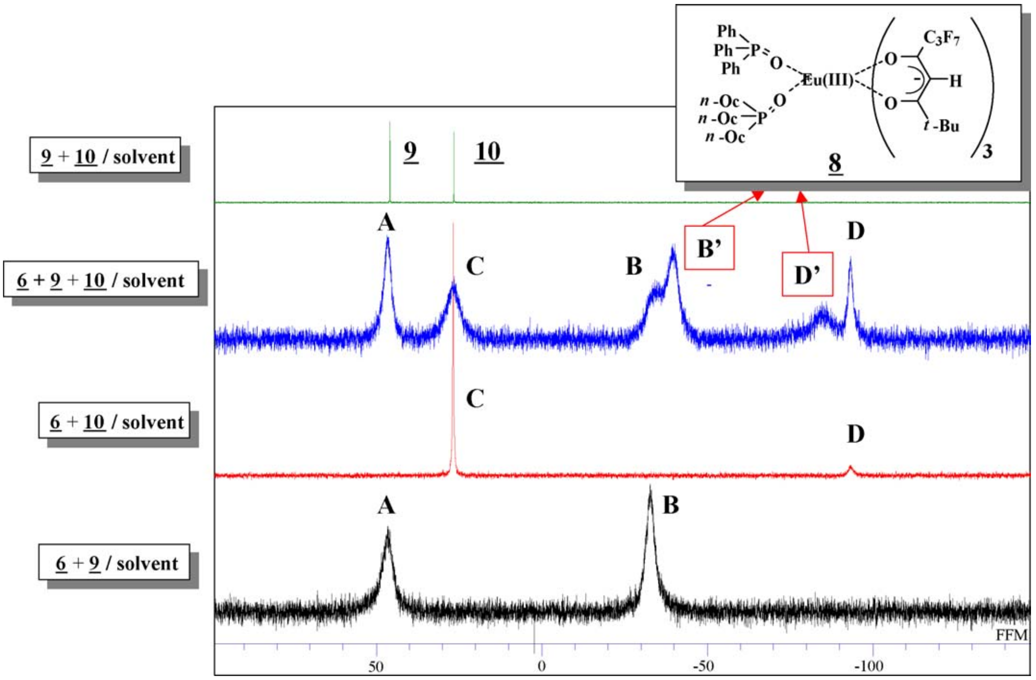
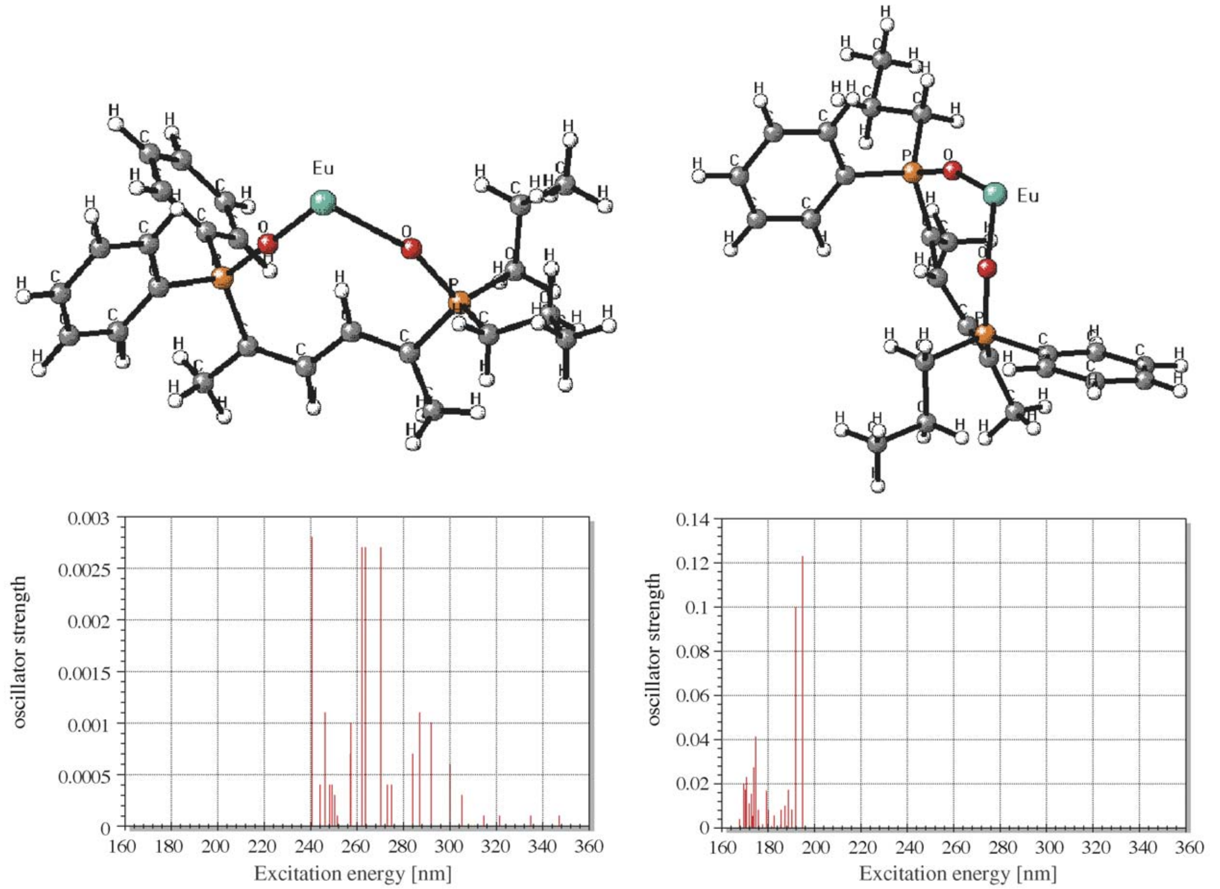


Fig. 5. ^{31}P NMR spectra of europium complexes in fluorinated solvent **7**.



13:Eu(III) $OP(C_6H_5)_2$ C (CH_3)=CH CH=C (CH_3) P $(CH_2CH_2\ CH_3)_2$ O

14: Eu(III) $OP(C_6H_5)(CH_2CH_2CH_3)C(CH_3)$=CH CH=C (CH_3) $P(C_6H_5)(CH_2CH_2CH_3)O$

Fig. 6. The optimized geometry of complex **13** and **14** and their calculated electronic spectra, respectively.

The optimized geometries and calculated electronic spectra of complexes **13** and **14** are shown in Fig. 6. While the oscillator strengths of complex **14** are stronger than those of complex **13**, the corresponding excited states for the spectra of complex **14** are ligand centered excited states. Therefore, they cannot contribute to the europium emission. On the other hand, the corresponding excited states for the spectra of complex **13** are delocalized for both ligand and europium. Therefore, they can contribute to the europium emission. From these results, among diphosphine dioxides, specific molecular structures are effective for enhancing luminous intensity of LEDs.

4. Conclusion

In the case where europium complexes having β-diketones and two phosphine oxides were used as fluorescence compounds of LEDs, the largest luminous intensity was realized. This is considered to be attributable to large absorption coefficient followed by more asymmetric ligand-field and large solubility in fluorinated polymer. Fluorescence compounds of this type are promising for next-generation white LEDs. Moreover, we found that novel europium complex having asymmetric diphosphine dioxide was effective.

References

[1] S. Sato, M. Wada, Bull. Chem. Soc. Jpn. 43 (1970) 1955.
[2] J. Yuan, K. Matsumoto, Anal. Sci. 12 (1996) 31.
[3] L.R. Melby, N.J. Rose, E. Abramson, J.C. Caris, J. Am. Chem. Soc. 86 (1964) 5117.
[4] S. Sato, M. Wada, T. Seki, Jpn. J. Appl. Phys. 7 (1968) 7.
[5] M. Uekawa, Y. Miyamoto, H. Ikeda, K. Kaifu, T. Nakaya, Bull. Chem. Soc. Jpn. 71 (1998) 2253.
[6] J.-C.G. Bunzli, E. Moret, V. Foiret, K.J. Schenk, W. Mingzhao, J. Linpei, J. Alloys Compd. 207 (1994) 107.
[7] A.O. Ribeiro, P.S. Calefi, A.M. Pires, O.A. Serra, J. Alloys Compd. 374 (2004) 151.
[8] Gaussian 98, Revision A.10, Gaussian Inc., Pittsburgh, PA, 2001.
[9] Y. Hasegawa, K. Sogabe, Y. Wada, T. Kitamura, N. Nakashima, S. Yanagida, Chem. Lett. (1999) 35.
[10] G.A. Crosby, R.E. Whan, R.M. Alire, J. Chem. Phys. 34 (1961) 743.
[11] W.R. Dawson, J.L. Kropp, M.W. Windsor, J. Chem. Phys. 45 (1966) 2410.
[12] Y. Hasegawa, M. Yamamoto, Y. Wada, N. Kanehisa, Y. Kai, S. Yanagida, J. Phys. Chem. A 107 (2003) 1697.
[13] F. Embert, A. Mehdi, C. Reye, R.J.P. Corriu, Chem. Mater. 13 (2001) 4542.