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Synthesis and Properties of Europium Complexes with β-Diketone Ligands for Organic Electroluminescent Devices

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Europium complexes with new β-diketone ligands with fluorene for organic electroluminescent (EL) devices have been synthesized and their properties examined. The absorption spectra of the complexes were varied by changing the conjugated system of the β-diketone; also, the energy transfer from the host material to the europium complexes and the intramolecular energy transfer have been improved. Concerning the volatility, the thermal properties of the europium complexes were improved by using phenanthroline derivatives. We fabricated organic EL devices using the synthesized complexes, and investigated the luminance of the devices.

Rare-earth complexes, particularly europium complexes, have been studied because of their potential use as laser materials. The fluorescence of europium complexes and their properties were reported by Weissman,[1] who discovered an internal energy transfer from coordinated ligands to the central metal ion. For europium complexes, β-diketonates are often used because they are easily synthesized and show high emission.[2,3] However, the fluorescent intensity of europium β-diketonates and their triplet-state levels depend strongly on the substituents of the β-diketonates.[4,5]

Recently, europium β-diketonates have been applied for organic electroluminescent (EL) devices,[6—10] as well as for planer microcavity emitters[11] because the europium β-diketonates exhibit a sharp red emission peak. However, high luminance has not yet been achieved in these devices because of the efficiency and stability of the europium β-diketonates. In organic EL devices using the europium β-diketonates as dopants, it is thought that light emission occurs by the following path. The energy of the carrier recombination is generated and transferred from the host material to a singlet excited state of the ligand (β-diketone). The energy is then transferred to the triplet excited state of the ligand via intersystem crossing, from where it is finally transferred to the central Eu^{3+} ion. There are two main problems associated with this process with respect to device operation which must be considered: (1) the efficiency of energy transfer from the host material to the europium β-diketonates, and (2) the efficiency of energy transfer from the triplet-state levels of the europium β-diketonates to the Eu^{3+} ion. Additionally, the thermal properties of the europium β-diketonates must also be considered.

The efficiency of energy transfer from host materials to europium β-diketonates depends on the overlap between the fluorescent spectra of the host materials and the absorption spectra of the europium β-diketonates.[8] In our previous report, the efficiency of energy transfer from the host material to the europium β-diketonates in solution was discussed.[12] Since the efficiency of energy transfer was changed by the absorption spectra of the europium β-diketonates, we need to design absorption spectra suitable for the host materials. The absorption spectra of the europium β-diketonates are determined principally by the β-diketone substituents.[13] More concretely, the absorption peaks of β-diketones containing aromatic groups are found at longer wavelengths than those of aliphatic substituted β-diketones.

The efficiency of energy transfer from the ligand to the central Eu^{3+} ion depends on the correlation of the relative positions of the triplet ligand levels and the rare-earth ion levels.[14] The triplet state of the ligand is also characteristic of the β-diketone substituents.

Concerning the thermal properties of the europium β-diketonates, the complexes should preferably readily evaporate, since EL devices are often fabricated by vapor-deposition. However, most of the europium β-diketonates developed for the organic laser materials cannot be deposited. On the other hand, some complexes, e.g., $[Eu(tta)_3(phen)]$ (tta = 2-thenoyltrifluoroacetone, phen = 1,10-phenanthroline), can form films by vapor deposition because coordinating to phen introduces volatility.[8]

In this paper we report on newly synthesized europium complexes with β-diketone ligands, and examine their energy levels and efficiency of energy transfer in order to select europium β-diketonates suitable for organic EL devices. Furthermore, we discuss the design of molecular structures that form films by vapor deposition, and report on the thermal properties of some europium β-diketonates and the properties of their films.

Experimental

Preparation of β-Diketones. Some β-diketonates (flta, flpa, flha, dnm) were synthesized by the Claizen condensation method (Scheme 1). The selected ethyl acetate and selected methyl ketone were added into a solution of sodium methoxide in diethyl ether and stirred at room temperature for 48 h. The other β-diketones were purchased.

Preparation of 2-Fluorencarbonyltrifluoroacetone (flta). A mixture of ethyl trifluoroacetate (10 mmol), sodium methoxide (11 mmol) and 50 ml of dry diethyl ether was stirred. After adding 10 mmol of 2-acetylfluorene, the reaction mixture was stirred for 48 h at room temperature. After the solution was acidified with a HCl solution, the product was extracted with ether and dried with $MgSO_4$. IR (neat) 1786, 1599, 1448, 1304, 1144, 796 cm^{-1}; ^1HNMR $\delta = 3.99$ (s, 2H, CH_2), 6.64 (s, 1H, CH), 7.40—8.14 (m, 7H, CH).

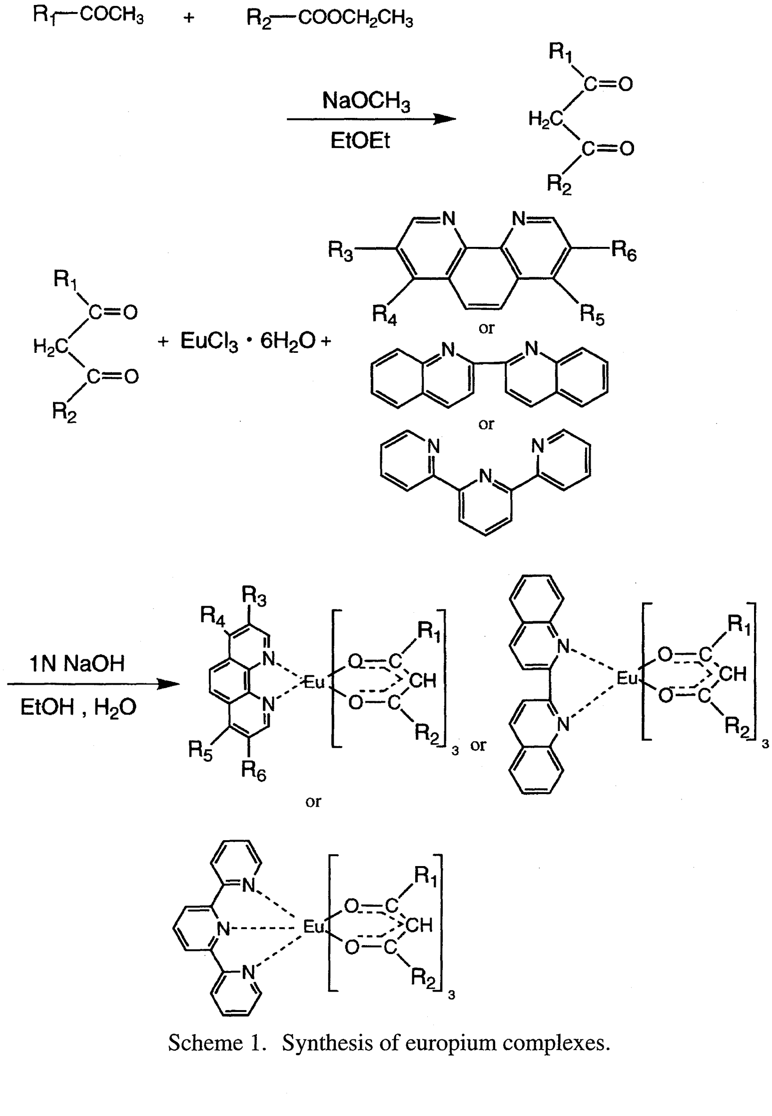
Preparation of 2-Fluorencarbonylmethylpentafluoroethylketone (flpa). In the same way as flta, flpa was prepared from ethyl pentafluoroacetate and 2-acetylfluorene. IR (neat) 1582, 1450, 1326, 1219, 1010, 868 cm^{-1}; ^1HNMR $\delta = 3.99$ (s, 2H, CH_2), 6.70 (s, 1H, CH), 7.40—8.14 (m, 7H, CH).

Preparation of 2-Fluorencarbonylmethylheptafluoropropylketone (flha). In the same way as flta, flha was prepared from ethyl heptafluoroacetate and 2-acetylfluorene. IR (neat) 1678, 1607, 1348, 1232, 1118, 775 cm^{-1}; ^1HNMR $\delta = 3.95$ (s, 2H, CH_2), 6.68 (s, 1H, CH), 7.40—8.14 (m, 7H, CH).

Preparation of Di(2-naphthoyl)methane (dnm). In the same way as flta, dnm was prepared from 2-naphthoyl ethyl ester and 2-acetonaphthone. IR (neat) 3058, 1776, 1610, 1540, 1433, 791 cm^{-1}; ^1HNMR $\delta = 7.1$ (s, 1H, CH), 7.50—8.07 (m, 14H, Naph).

Preparation of Europium Complexes. The europium complexes were synthesized by the conventional method.[2)] A solution of β-diketone and either phen or phen derivatives in ethanol were made, and a NaOH solution was then added while stirring. $EuCl_3 \cdot 6H_2O$ (1 mmol) was dissolved in 10 ml of pure water; this solution was then added dropwise to the β-diketone solution. The mixture was stirred at 60 °C for 1 h and then cooled. The product was collected by filtration and washed in ethanol and pure water.

Preparation of [Eu(tta)$_3$(phen)]. A solution of 3 mmol 2-thenoyltrifluoroacetone (tta) and 1 mmol 1,10-phenanthroline (phen) in 20 ml of ethanol were made, and 3 mmol of a 1 M NaOH solution (1 M = 1 mol dm^{-3}) was then added while stirring. A solution of 1 mmol $EuCl_3 \cdot 6H_2O$ in 10 ml of pure water was added dropwise to the tta and phen solution. The mixture was stirred at 60 °C for 1 h and then cooled. The product was collected by filtration and washed in ethanol and pure water. Then, the complex was purified by recrystallization, and vacuum drying. IR (neat) 1601, 1413, 1309, 1142, 787 cm^{-1}; ^1HNMR $\delta = 6.16$ (s, 3H, CH=), 6.49 (d, 3H, CH=), 6.95 (d, 3H, CH=), 8.51 (d, 2H, CH=), 9.54 (s, 2H, CH=), 10.18 (d, 2H, CH=), 10.35 (s, 2H, CH=).



Scheme 1. Synthesis of europium complexes.

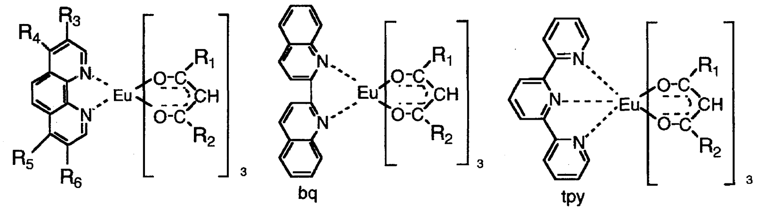
The other complexes were prepared in the same way as [(Eu(tta)$_3$(phen)].

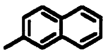
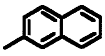
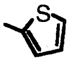
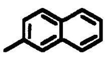
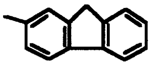
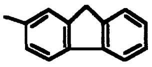
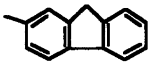
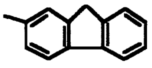
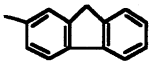
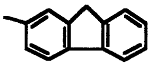
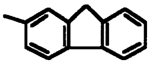
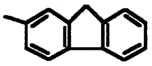
Apparatus. The absorption spectra were recorded on a Shimadzu UV-2500PC. The photoluminescence spectra were recorded on a Hitachi F-3010 fluorescence spectrophotometer. The melting points were determined by a Rigaku THERMOFLEX TAS300, and the IR spectra were recorded on a Bio-Rad FTS-60. ^{1}H NMR spectra were measured on a JEOL α-400 in CDCl$_3$ using TMS as an internal standard.

Results and Discussion

The absorption and thermal properties of the europium β-diketonates are summarized in Table 1. The complexes exhibited absorption peaks at between 340 and 370 nm. The absorption peak was varied by changing the major ligand (β-diketone); the absorption spectra of [Eu(nta)$_3$(phen)], [Eu(flta)$_3$(phen)], and [Eu(dbm)$_3$(phen)] solutions are shown in Fig. 1. The absorption peaks of [Eu(nta)$_3$(phen)] are clearly at shorter wavelengths than those of [(Eu(flta)$_3$(phen)] and [Eu(dbm)$_3$(phen)]. This is due to a decreased conjugation of the β-diketone. That is, the conjugation of fluorene was increased compared to that of naphthalene. On the other hand, the absorption peaks were shifted only little upon changing the substituents of the β-diketone from CF$_3$ to C$_2$F$_5$ or C$_3$F$_7$, as shown in Fig. 2. The absorption spectra of [Eu(flta)$_3$(phen)], [Eu(flpa)$_3$(phen)], and [Eu(flha)$_3$(phen)] were similar because the conjugation was not changed. In these complexes, only the alkyl chain was changed. Similarly, the absorption peaks shifted only little by changing the second ligand (Fig. 3). These results indicated that the absorption spectra are only characteristic of the aromatic groups of the β-diketones. Hence, it is necessary to change the aromatic group of the β-diketone in order to synthesize the required

Table 1. Schematic Drawing and Thermal Properties of Europium Complexes, and Absorption Peaks of Europium Complexes in THF; Dibenzoylmethane (dbm), 4,7-Diphenyl-1,10-phenanthroline (dpphen), 4,7-Dimethyl-1,10-phenanthroline (dmphen), 3,4,7,8-Tetramethyl-1,10-phenanthroline (tmphen), 2,2′-biquinoline (bq), 2,2′ : 6′,2′-terpyridine (tpy)



	R1	R2	R3	R4	R5	R6	mp (°C)	λ_{max}(nm)
[Eu(dbm)$_3$(phen)]			H	H	H	H	185	353
[Eu(dnm)$_3$(phen)]			H	H	H	H	—	370
[Eu(tta)$_3$(phen)]		CF$_3$	H	H	H	H	249	343
[Eu(nta)$_3$(phen)]		CF$_3$	H	H	H	H	221	336
[Eu(flta)$_3$(phen)]		CF$_3$	H	H	H	H	—	349
[Eu(flpa)$_3$(phen)]		C$_2$F$_5$	H	H	H	H	—	342
[Eu(flha)$_3$(phen)]		C$_3$F$_7$	H	H	H	H	230	351
[Eu(flha)$_3$(dpphen)]		C$_3$F$_7$	H			H	—	350
[Eu(flha)$_3$(dmphen)]		C$_3$F$_7$	H	CH$_3$	CH$_3$	H	—	353
[Eu(flha)$_3$(tmphen)]		C$_3$F$_7$	CH$_3$	CH$_3$	CH$_3$	CH$_3$	—	345
[Eu(flha)$_3$(bq)]		C$_3$F$_7$					—	350
[Eu(flha)$_3$(tpy)]		C$_3$F$_7$					—	350

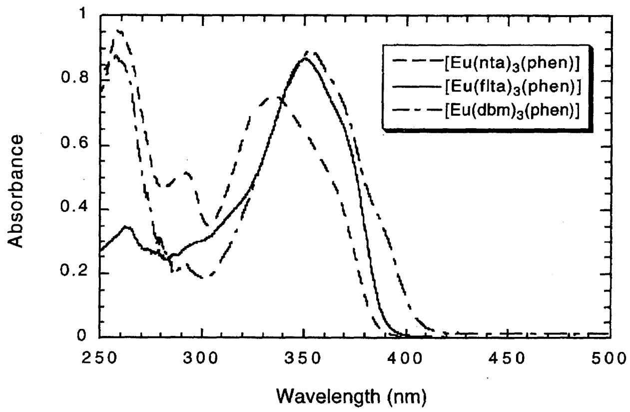


Fig. 1. The absorption spectra of europium complexes in THF; [Eu(nta)$_3$(phen)] (broken line), [Eu(flta)$_3$(phen)] (solid line), [Eu(dbm)$_3$(phen)] (dashed-and-dotted line).

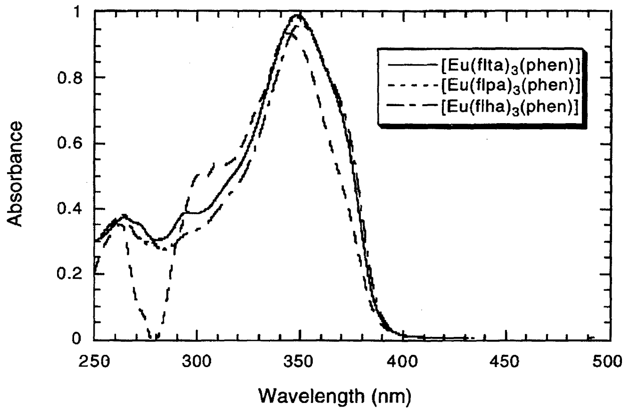


Fig. 2. The absorption spectra of europium complexes in THF; [Eu(flta)$_3$(phen)] (solid line), [Eu(flpa)$_3$(phen)] (broken line), [Eu(flha)$_3$(phen)] (dashed-and-dotted line).

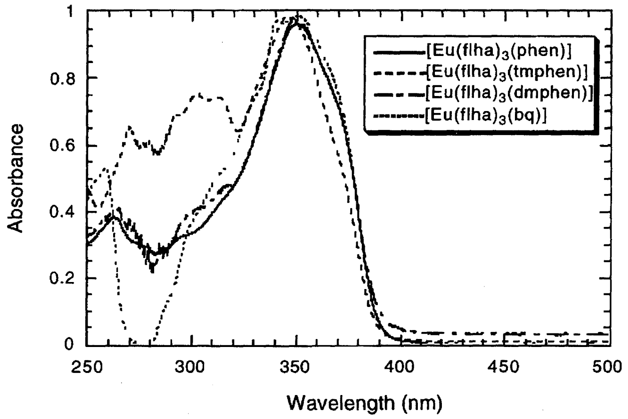


Fig. 3. The absorption spectra of europium complexes in THF; [Eu(flha)$_3$(phen)] (solid line), [Eu(flha)$_3$(tmphen)] (broken line), [Eu(flha)$_3$(dmphen)] (dashed- and- dotted line), [Eu(flha)$_3$(bq)] (dotted line).

europium β-diketonates.

The efficiency of the intramolecular energy transfer was very sensitive to the energy levels of the triplet state of the β-diketonates. The triplet-state levels of the ligands were determined from the phosphorescence spectra of the corresponding gadolinium complexes.[5] The energy levels of Eu^{3+} and the triplet-state levels of the β-diketones are shown in Fig. 4. The energy levels of the ligands (tta, dbm, flta, flpa, flha) lay near to 20500 cm^{-1}. That is, the efficiency of the energy transfer from the ligand to Eu^{3+} was almost equal for these complexes. In complexes with β-diketone ligands with fluorene, the fluorescence intensity decreased slightly in the ligands in the order flha > flpa > flta, because the quantum yields decreased slightly in the ligands in the order flha (0.180) > flpa (0.151) > flta (0.143). The quantum yields

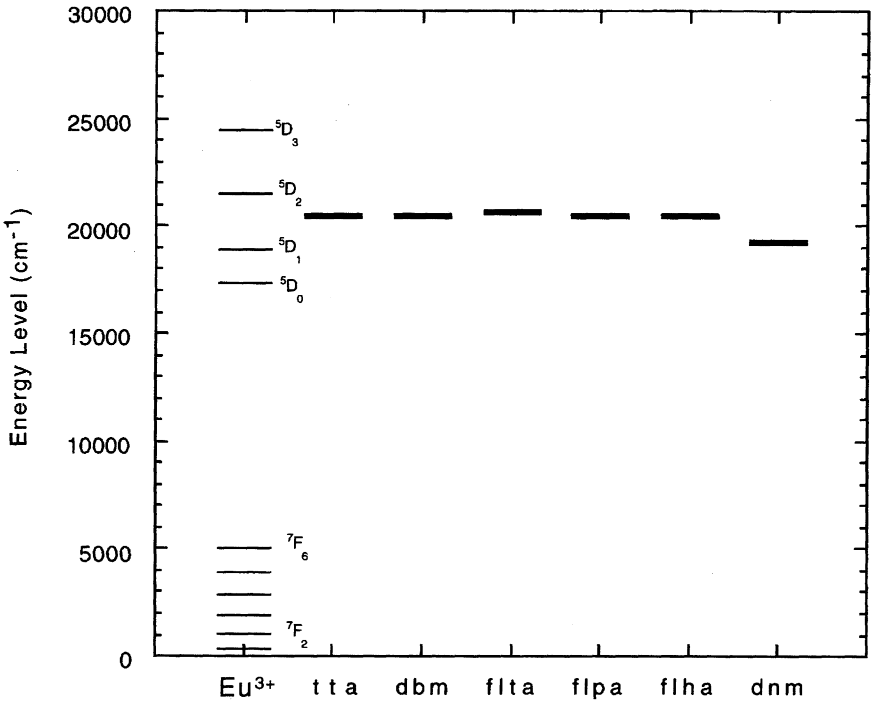


Fig. 4. The triplet state levels of ligands.

(Φ) of the complexes were calculated with a standard quantum yield of Φ = 0.209 for [Eu(nta)$_3$(topo)$_2$] in benzene (topo = trioctylphosphine oxide).[4] However, because it was not significant, these results insisted that the efficiency of the energy transfer from the ligand to Eu^{3+} was almost equal in spite of changing the substituents of the β-diketone from CF$_3$ to C$_2$F$_5$ or C$_3$F$_7$. On the other hand, di(2-naphtoyl)methane (dnm), which showed an absorption peak at the longest wavelength, had a triplet state level at 19000 cm^{-1}. When the conjugation of the β-diketone was increased, the absorption peak was red shifted and the triplet-state level was at lower energy. The fluorescence intensity of [Eu(dnm)$_3$(phen)] was therefore the lowest, since the dnm triplet-state level is closer to the ^{5}D$_1$ level of the Eu^{3+} ion, and the fluorescence was quenched by the thermal-deactivation mechanism.[5]

To investigate the thermal properties of the europium β-diketonates, the complexes were decomposed by heating. Although some complexes were decomposed at elevated temperature without melting, some did melt. The thermal properties were different due to the intermolecular forces between neighboring complexes. The intermolecular forces can be changed by replacing the major or the second ligands. However, when the major ligand (β-diketone) is changed, the absorption spectrum of the complex is also changed. We would like to change the thermal properties of the complex, while keeping the desired absorption spectra. To achieve this, we changed the second ligand or a part of the β-diketone, but kept the conjugated group fixed. The films of [Eu(flta)$_3$(phen)] and [(Eu(dnm)$_3$(phen)] could not be formed by vapor deposition. We then designed molecular structures with a higher fluorine content that could be used to form films by vapor deposition. When we changed the ligand from CF$_3$ to C$_3$F$_7$, the thermal property of the complex ([Eu(flta)$_3$(phen)]) was improved. A thin film of the complex could then be formed by vapor deposition, while keeping the desired absorption spectrum (Fig. 2) and the triplet-state level (Fig. 4). The fluorescence spectra and absorption spectra of the films formed by vapor deposition were similar to the spectra of the solutions. The absorption spectrum of the [Eu(flha)$_3$(phen)] film is shown in Fig. 5. The peak of phen (270 nm) became more intense than the β-diketone peak (350 nm) when compared with the absorption spectrum of the solution. The spectrum of the film resulted from the dissociation of the ligand or the different orientation of the molecular dipole moments between the solution and the film. The NMR spectrum of the film indicated that the second ligand was slightly dissociated by vapor deposition. We then changed from phen to phen derivatives (dpphen, dmphen, tmphen, bq and tpy) to increase the volatility of the complexes (dpphen = 4,7-diphenyl-1,10-phenanthroline, dmphen = 4,7-dimethyl-1,10-phenanthroline, tmphen = 3,4,7,8-tetramethyl-1,10-phenanthroline, bq = 2,2′-biquinoline, tpy = 2,2′ : 6′,2′-terpyridine). The thermal properties of these complexes were changed, while still keeping the absorption properties (Fig. 3). Since the complexes with dpphen, dmphen, tmphen included the phenyl group or methyl group, the complexes had steric hindrance, the complex with bq was free to rotate about the C–C bond next to the nitrogen atom. The steric hindrance or the degree of freedom should prevent dissociation. In the complex with tpy the bonding number was changed from an eight-coordinate complex to a nine-coordinate complex, and hence the thermal properties were also expected to improve. However, the thermal stability was decreased in the complexes coordinated with tmphen and bq (Fig. 6), and we could not form a film of the complex coordinated with tpy by vapor deposition. The figure shows thermogravimetry (TG) curves of europium complexes, and TG decreased the temperature rise. The NMR spectra of the complexes after increasing the temperature indicated that the second ligand was dissociated. On the other hand, the thermal stability was increased in the complex coordinated with dpphen (Fig. 6). Moreover, the film of [Eu(flha)$_3$(dpphen)] could be formed by vapor deposition and the volatility was higher compared to that of [Eu(flha)$_3$(phen)]. We therefore suggest that in bulky complexes the large phen derivative (dpphen) is responsible for the increased volatility because the bonding strength between europium and the nitrogen atoms of dpphen derivatives

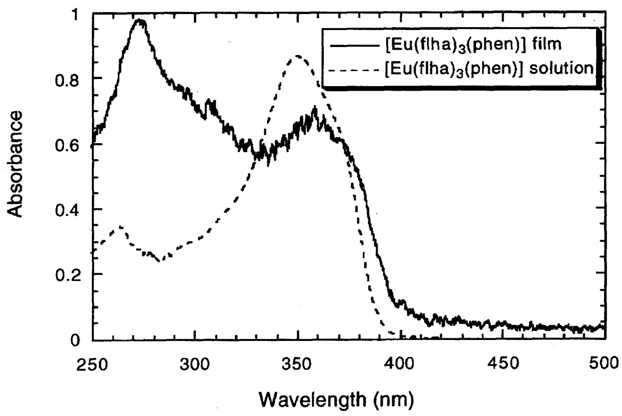


Fig. 5. The absorption spectrum of the thin film of [Eu(flha)$_3$(phen)] and the absorption spectrum of [Eu(flha)$_3$(phen)] in THF.

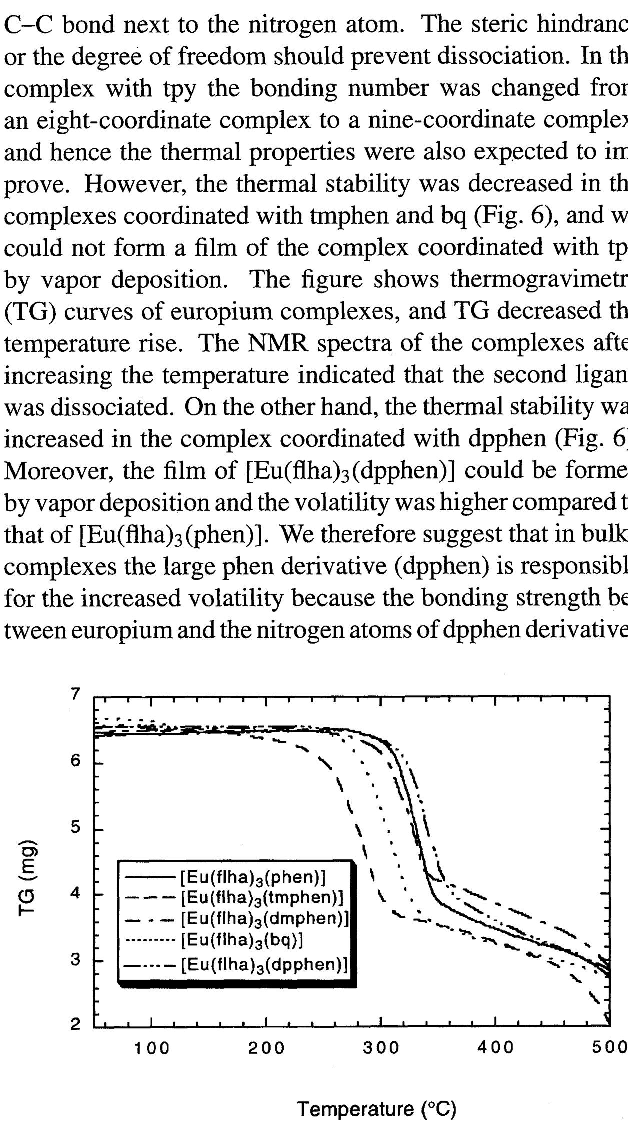


Fig. 6. TG curves of europium complexes; [Eu(flha)$_3$(phen)] (solid line), [Eu(flha)$_3$(tmphen)] (broken line), [Eu(flha)$_3$(dmphen)] (dashed-and-dotted line), [Eu(flha)$_3$(bq)] (dotted line), [Eu(flha)$_3$(dphen)] (dashed-and-three-dotted line).

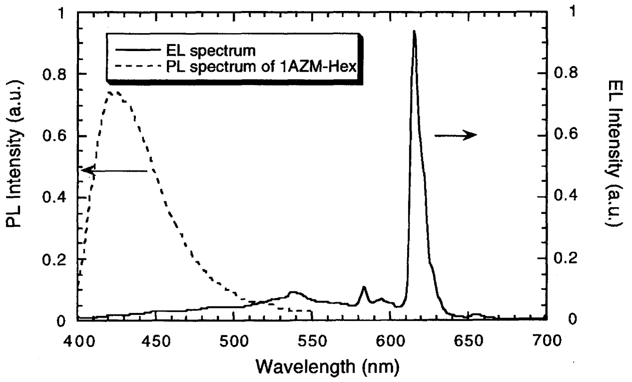


Fig. 7. The PL spectrum of 1AZM-Hex in THF (broken line), and the EL spectrum of the device using the europium complexes doped in 1AZM-Hex (solid line).

is stronger than that for phen, because the electron density is higher due to an electron-donating characteristic.

We fabricated organic EL devices using europium complexes as a guest. The device structure was indium-tin oxide (ITO)/*N*,*N*′-diphenyl-*N*,*N*′-(3-methyl phenyl)-1,1′-biphenyl-4,4′-diamine (TPD) (500 Å)/a europium complex doped in 1AZM-Hex (500 Å)/Mg. The host material, 1AZM-Hex, was a zinc complex reported by Sano and co-workers.[7] The zinc complex exhibited a blue emission peak at 440 nm and the EL devices exhibited a red emission peak at 615 nm (Fig. 7). The luminance of the organic EL device using [Eu(flha)$_3$(dpphen)] improved the thermal stability was measured to be 10 cd m^{-2}. The luminance of an organic EL device using [Eu(nta)$_3$(phen)] which had an absorption peak at shorter wavelength and had a high quantum yield of (Φ = 0.225), was measured to be 5 cd m^{-2}. On the other hand, the luminance of the organic EL device using [Eu(dbm)$_3$(phen)], which had an absorption peak at a longer wavelength, was measured to be 9 cd m^{-2}. The fluorescent spectra of the 1AZM-Hex and the absorption spectra of [Eu(dbm)$_3$(phen)] were much overlapped; however, the luminance was low because the fluorescence intensity of [Eu(dbm)$_3$(phen)] was low. The [Eu(flha)$_3$(dpphen)] had high quantum yields and had an absorption peak at a longer wavelength; however, the luminance was quite the same as that of [Eu(dbm)$_3$(phen)] in devices using 1AZM-Hex as a host.

In order to obtain higher luminance, we need to use a host material which possesses a higher emission energy than the energy of 1AZM-Hex; must also other factors, such as the purity of the complex and the device structure, must also be considered. Furthermore, a greater improvement of the thermal stability and the dissociation of the ligand must be considered.

Conclusion

Europium complexes coordinating some β-diketones and phen derivatives were synthesized. The fluorescent properties, triplet-state levels, and thermal properties were examined. The complexes had different absorption spectra and triplet-state levels achieved by changing the β-diketones. With respect to the energy transfer from the host to the guest, the overlap was improved by red shifting the absorption spectra. Furthermore, the volatilities of europium β-diketonates were improved by synthesizing new ligands. We developed a thermal stable complex, [Eu(flha)$_3$(dpphen)], which showed high emission. However, in order to obtain high-luminance organic EL devices, we need to improve not only the efficiency and the volatility of the complex, but also consider other factors, such as the purity of the complex and the device structure.

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