11312 *J. Phys. Chem. A* **2005,** *109,* 11312−11316

Density Functional Theory Investigation of Eu(III) Complexes with β-Diketonates and Phosphine Oxides: Model Complexes of Fluorescence Compounds for Ultraviolet LED Devices

Fumihiko Aiga,* Hiroki Iwanaga, and Akio Amano

*Corporate Research & Development Center, Toshiba Corporation, 1 Komukai-Toshiba-cho,
Saiwai-ku, Kawasaki 212-8582, Japan*

Received: September 20, 2005; In Final Form: October 14, 2005

The density functional theory was employed to investigate Eu(III) complexes with three β-diketonates and two phosphine oxides (complex **M1**: Eu(bdk)$_3$(TPPO)$_2$, complex **M2**: Eu(bdk)$_3$(TMPO)$_2$, and complex **M3**: Eu(bdk)$_3$(TPPO)(TMPO)) deemed to be the model complexes of the fluorescence compounds for the ultraviolet LED devices we have recently developed. For each complex, two minimum energy points corresponding to two different optimized geometries (structures A and B) have been found, and the difference of the energy between two minimum energy points is found to be quite small (less than 1 kcal/mol). Vertical excitation energies and oscillator strengths for each complex at two optimized geometries have been obtained by the time-dependent density functional theory, and the character of the excited states has been investigated. For complex **M3**, the absorption edge is red-shifted, and the oscillator strengths are relatively large. The efficiency of intersystem crossing and energy transfer from the triplet excited state to the Eu(III) ion is considered by calculating ΔE_{ISC} (the energy difference between the first singlet excited state and the first triplet excited state) and ΔE_{ET} (the difference between the excitation energy of the complex for the first triplet excited state and the emission energy of the Eu(III) ion for ^{5}D to ^{7}F).

1. Introduction

Eu(III) complexes have been extensively investigated as luminescent materials.[1−6] The long luminescent lifetimes of Eu(III) ions are due to the forbidden character of their intra-4*f* transitions, which unfortunately result in low absorption coefficients.[7] For this reason, the excited state of a luminescent Eu(III) ion is generally populated by energy transfer from the triplet state of an organic antenna chromophore (ligands).[1,4,8] The photophysical pathway of this sensitization process is schematically represented in Figure 1. The overall process involves excitation of the ligand(s), intersystem crossing (ISC) to the triplet state of the ligand(s), energy transfer (ET) to the Eu(III) ion, and subsequent emission (Em) of the Eu(III) ion.

Eu(III) complexes have been applied to luminescent devices, such as lasers,[9,10] and organic light-emitting diodes (OLED).[11,12] Recently, we have developed a light-emitting diode (LED) device by using the Eu(III) complex with three β-diketonates and two phosphine oxides depicted in Figure 2 (complexes **1**, **2**, and **3**) in the fluorescence layer of the LED,[13−15] and we have achieved the highest luminous intensity reported to date (over 850 mlm) when 20 mA of direct current was applied to the ultraviolet LED (402-nm excitation) by using complex **3**. These results are considered to be due to the properties of complex **3**, particularly, large absorption coefficients as well as the red-shift of absorption spectra, the greatly asymmetric ligand field, and the high solubility in a fluorinated polymer.

In the work reported in this paper, we employed the density functional theory (DFT) to investigate the Eu(III) complexes with three β-diketonates and two phosphine oxides (complex **M1**: Eu(bdk)$_3$(TPPO)$_2$, complex **M2**: Eu(bdk)$_3$(TMPO)$_2$, and complex **M3**: Eu(bdk)$_3$(TPPO)(TMPO)) depicted in Figure 2, which are deemed to be the model complexes for complexes **1**, **2**, and **3**.[13−15] In these model complexes, the *t*-Bu group and the C_3F_7 group in β-diketonate are replaced by a H atom, and the *n*-Oc group in phosphine oxide is replaced by a methyl group. We can investigate the differences of the molecular and electronic structures among these model complexes due to the difference of the phosphine oxide.

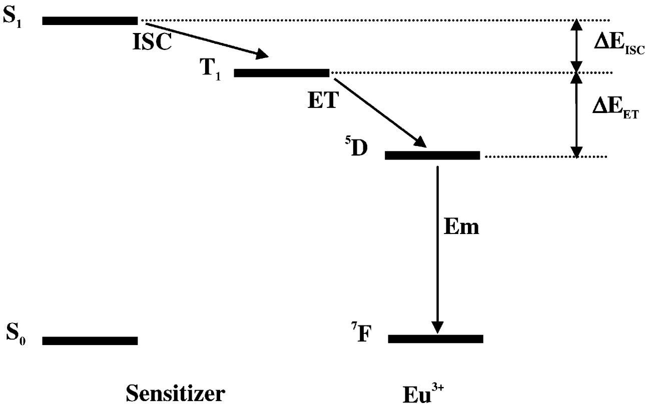


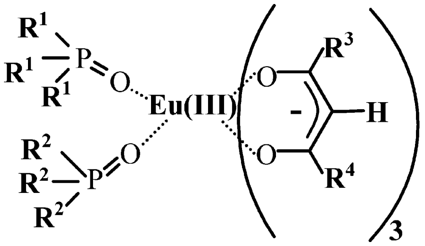
Figure 1. Schematic representation of the photophysical pathway of the sensitization process.

Eu(III) complexes have been theoretically investigated by semiempirical molecular orbital calculations[16−18] and ab-initio quantum chemical calculations.[19−23] Since *f*-orbitals do not play a major role in Eu−ligand bonds,[19] we have used the effective core potential (ECP) including 4f^n electrons for Eu by Dolg et al.[24] as well as ref 20, and we have calculated the excited states by time-dependent density functional theory (TDDFT) as well as ref 21. Therefore, in this paper, we do not consider the excited

---

* E-mail: fumihiko.aiga@toshiba.co.jp.

10.1021/jp0553535 CCC: $30.25



1: R^1=R^2= Ph, R^3=C_3F_7, R^4=*t*-Bu

2: R^1=R^2=*n*-Oc, R^3=C_3F_7, R^4=*t*-Bu

3: R^1=*n*-Oc, R^2=Ph, R^3=C_3F_7, R^4=*t*-Bu

M1: R^1=R^2= Ph, R^3=R^4=H

M2: R^1=R^2=Me, R^3=R^4=H

M3: R^1=Me, R^2=Ph, R^3=R^4=H

H1: R^1=R^2= Ph, R^3=R^4= CF_3

Figure 2. Molecular structures of Eu(III) complexes used in our LED devices (**1**−**3**), and of model complexes (**M1**−**M3**) used for calculations in this paper. Molecular structure of complex H1[6] is also given.

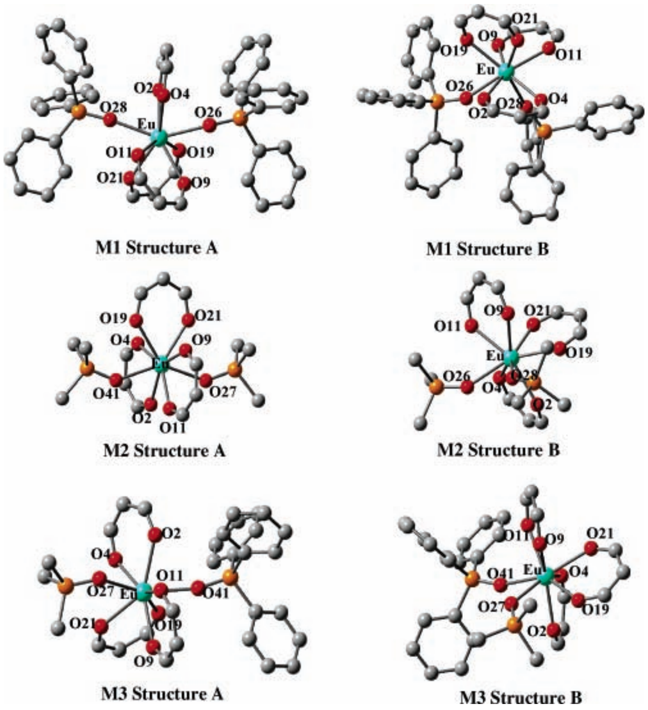
states for intra-4*f* transitions in the Eu(III) ion, and we consider the excited states for ligand excitations. To our knowledge, this work is the first ab-initio investigation of Eu(III) complexes having three β-diketonates and two phospine oxides for ground and excited states.

Eightfold coordinated Eu(III) complexes have a square-antiprism structure,[16] and in this paper, we consider two coordination geometries (structures A and B) for each complex. Structure A corresponds to the structure of complex **H1** (depicted in Figure 2) determined by Hasegawa et al.[6] with single-crystal X-ray diffraction. Structure B corresponds to the structure of the Eu(III) complex with three β-diketonates and one dipyridyl determined by Batista et al.[3] with single-crystal X-ray diffraction. In our model complexes, the dipyridyl ligand is replaced by two phosphine oxides. For structure A, each oxygen atom of phosphine oxide coordinates in another square in the square-antiprism structure; for structure B, each oxygen atom of phosphine oxide coordinates in the adjacent point of a square in the square-antiprism structure.

This paper is organized as follows. In section 2, the computational details are described. In section 3, the optimized geometries corresponding to structures A and B are characterized for each complex in the ground state. In section 4, the electronic structures of excited states are characterized for each complex at structures A and B. The efficiency of intersystem crossing and energy transfer from the triplet excited state to the Eu(III) ion is considered for each complex. In section 5, the concluding remarks are given.

2. Computational Details

The calculations were carried out with the Gaussian 03 package.[25] DFT calculations were performed by using the B3LYP functional. Geometry optimization was carried out without symmetry constraints. The optimized geometry was confirmed to be the minimum energy point by vibrational frequency analysis. The excitation energies and oscillator strengths at the optimized geometry in the ground state were obtained by TDDFT calculations.



M1 Structure A M1 Structure B

M2 Structure A M2 Structure B

M3 Structure A M3 Structure B

Figure 3. Two optimized geometries for complexes **M1**, **M2**, and **M3** (H atoms are excluded.)

Considering the fact that *f*-orbitals do not play a major role in the Eu−ligand bonds[19] and in order to reduce the computational cost, we used a large core quasi-relativistic ECP, having 46+4f^n electrons, for Eu by Dolg et al.[24] For valence orbitals, the (7s6p5d)/ [5s4p3d] basis set was used. For all other atoms, the 6-31G(d) basis set was used.

3. Ground States

The optimized geometries of complexes **M1**, **M2**, and **M3** at both structures A and B in the ground state are illustrated in Figure 3. Since all of the vibrational frequencies are real for each complex at both structures A and B, all of the optimized geometries in Figure 3 correspond to the minimum energy points. Calculated ligand binding energy E_{LB}, ligand affinity E_{LA}, and ligand torsion energy E_{LT} for each complex at both structures A and B are given in Table 1. E_{LB} is calculated with the energy of the free Eu^{3+} ion and free ligand, calculated at the optimized geometry of free ligand, and the energy of the complex. On the other hand, E_{LA} is calculated with the energy of the free Eu^{3+} ion and free ligand, calculated at the geometry in the complex, and the energy of the complex. E_{LT} is $E_{LA} - E_{LB}$. For each complex, the difference of E_{LB} between structures A and B is quite small (less than 1 kcal/mol), and the difference of E_{LA} between two structures is also small. Assuming that the difference of the energy between structures A and B is also small for complexes **1**, **2**, and **3**, we can suppose that complexes **1**, **2**, and **3** can exist at both structures A and B in solution or in the fluorescence layer of LED. For complex **M1**, E_{LB} at structure A is larger than that at structure B. This is in accordance with the fact that the coordination structure of complex **H1** determined by Hasegawa et al.[6] with single-crystal X-ray diffraction is the structure A, not the structure B. For complex **M3**, E_{LB} at structure A is larger than that at structure B, as well as complex **M1**. On the other hand, for complex **M2**, E_{LB} at structure A is smaller than that at structure B.

The bond length between Eu and O and the Mulliken charge for Eu and O for each complex at both structures A and B are given in Table 2. For complex **M1** at structure A, the corresponding bond lengths for complex **H1** determined by

TABLE 1: Calculated Ligand Binding Energy E_{LB}, Ligand Affinity E_{LA}, and Ligand Torsion Energy E_{LT} (kcal/mol)

	E_{LB}		E_{LA}		E_{LT}	
	structure A	structure B	structure A	structure B	structure A	structure B
M1	1094.89	1093.91	1105.28	1108.63	10.39	14.71
M2	1112.44	1113.34	1125.08	1125.11	12.64	11.77
M3	1104.85	1104.59	1116.04	1117.11	11.19	12.52

TABLE 2: Calculated Bond Length between Eu and O, and Mulliken Charge for Eu and O at the Optimized Geometry[a]

	structure A				structure B			
	bond	R(Å)	atom	q	bond	R(Å)	atom	q
M1	Eu−O2(bdk1)	2.469(2.41)	Eu	1.319	Eu−O9(bdk1)	2.434	Eu	1.345
	Eu−O4(bdk1)	2.460(2.39)	O2(bdk1)	−0.513	Eu−O11(bdk1)	2.434	O9(bdk1)	−0.515
	Eu−O9(bdk2)	2.457(2.44)	O4(bdk1)	−0.508	Eu−O19(bdk2)	2.444	O11(bdk1)	−0.504
	Eu−O11(bdk2)	2.427(2.42)	O9(bdk2)	−0.521	Eu−O21(bdk2)	2.407	O19(bdk2)	−0.526
	Eu−O19(bdk3)	2.455(2.41)	O11(bdk2)	−0.505	Eu−O2(bdk3)	2.471	O21(bdk2)	−0.508
	Eu−O21(bdk3)	2.461(2.41)	O19(bdk3)	−0.517	Eu−O4(bdk3)	2.459	O2(bdk3)	−0.518
	Eu−O26(phP1)	2.436(2.32)	O21(bdk3)	−0.519	Eu−O26(phP1)	2.479	O4(bdk3)	−0.520
	Eu−O28(phP2)	2.434(2.31)	O26(phP1)	−0.676	Eu−O28(phP2)	2.484	O26(phP1)	−0.672
			O28(phP2)	−0.674			O28(phP2)	−0.668
M2	Eu−O19(bdk1)	2.490	Eu	1.290	Eu−O2(bdk1)	2.442	Eu	1.294
	Eu−O21(bdk1)	2.490	O19(bdk1)	−0.528	Eu−O4(bdk1)	2.449	O2(bdk1)	−0.518
	Eu−O2(bdk2)	2.443	O21(bdk1)	−0.528	Eu−O19(bdk2)	2.493	O4(bdk1)	−0.505
	Eu−O4(bdk2)	2.446	O2(bdk2)	−0.487	Eu−O21(bdk2)	2.409	O19(bdk2)	−0.525
	Eu−O9(bdk3)	2.446	O4(bdk2)	−0.515	Eu−O9(bdk3)	2.464	O21(bdk2)	−0.512
	Eu−O11(bdk3)	2.443	O9(bdk3)	−0.515	Eu−O11(bdk3)	2.480	O9(bdk3)	−0.504
	Eu−O27(MeP1)	2.438	O11(bdk3)	−0.487	Eu−O26(MeP1)	2.463	O11(bdk3)	−0.529
	Eu−O41(MeP2)	2.438	O27(MeP1)	−0.652	Eu−O28(MeP2)	2.442	O26(MeP1)	−0.647
			O41(MeP2)	−0.652			O28(MeP2)	−0.651
M3	Eu−O2(bdk1)	2.453	Eu	1.306	Eu−O2(bdk1)	2.451	Eu	1.307
	Eu−O4(bdk1)	2.468	O2(bdk1)	−0.519	Eu−O4(bdk1)	2.435	O2(bdk1)	−0.513
	Eu−O19(bdk2)	2.439	O4(bdk1)	−0.497	Eu−O19(bdk2)	2.470	O4(bdk1)	−0.500
	Eu−O21(bdk2)	2.490	O19(bdk2)	−0.521	Eu−O21(bdk2)	2.408	O19(bdk2)	−0.536
	Eu−O9(bdk3)	2.430	O21(bdk2)	−0.530	Eu−O9(bdk3)	2.471	O21(bdk2)	−0.505
	Eu−O11(bdk3)	2.462	O9(bdk3)	−0.511	Eu−O11(bdk3)	2.436	O9(bdk3)	−0.505
	Eu−O27(MeP)	2.431	O11(bdk3)	−0.489	Eu−O27(MeP)	2.475	O11(bdk3)	−0.531
	Eu−O41(PhP)	2.438	O27(MeP)	−0.655	Eu−O41(PhP)	2.469	O27(MeP)	−0.660
			O41(PhP)	−0.675			O41(PhP)	−0.666

[a] For complex **M1** at structure A, the corresponding bond lengths for complex **H1** determined by Hasegawa et al.[6] with single-crystal X-ray diffraction are given in parentheses.

Hasegawa et al.[6] with single-crystal X-ray diffraction are given in parentheses. We cannot find remarkable differences in bond length for complexes **M1**, **M2**, and **M3**. On the other hand, the greater the number of TPPO ligands is, the larger the Mulliken charge of Eu is, and therefore, we can find $q(\text{Eu}; \textbf{M1}) > q(\text{Eu}; \textbf{M2}) > q(\text{Eu}; \textbf{M3})$. This is considered to be due to the strong electron-withdrawing effect of TPPO. However, we cannot find remarkable differences in the Mulliken charge of O for these complexes.

To estimate the calculated structure of complex **H1**, we calculated the free β-diketonate ligand with $R_3 = R_4 = CF_3$ for complex **H1**. The Mulliken charge of O atoms in the free β-diketonate ligand with $R_3 = R_4 = H$ for **M1** is −0.538, and the Mulliken charge of O atoms in the free β-diketonate ligand with $R_3 = R_4 = CF_3$ for complex **H1** is −0.559. On the basis of these Mulliken charges, O atoms in the β-diketonate ligand for complex **H1** are considered to be more attractive to the Eu ion than O atoms in the β-diketonate ligand for complex **M1**, and the bond length between Eu and O in the β-diketonate ligand in complex **H1** is expected to be shorter than that between Eu and O in the β-diketonate ligand in complex **M1** assuming that the steric effect of the CF_3 group is small. This is in accordance with the bond lengths in Table 2. The bond lengths of complex **H1** determined by Hasegawa et al.[6] with single-crystal X-ray diffraction are 0.01−0.12 Å shorter than those of complex **M1**.

4. Excited States

Calculated electronic spectra of complexes **M1**, **M2**, and **M3** at structures A (red line) and B (blue line) for singlet excited states are given in Figure 4. For each complex, the spectrum whose wavelength is smaller than 260 nm, has been cut. The calculated excitation wavelength, oscillator strength, main configurations, and character for the singlet vertical excited states are given in Tables 1S−6S (Supporting Information), where H and L denote HOMO and LUMO, respectively. Complete spectra can be obtained from these tables. For complex **M1**, the absorption edge is red-shifted, but the oscillator strengths are small. For complex **M2**, the oscillator strengths are large, but the absorption edge is blue-shifted. On the other hand, for complex **M3**, the absorption edge is red-shifted and the oscillator strengths are relatively large. Calculated electronic spectra of TPPO (yellow line), TMPO (violet line), and bdk (green line) at the optimized geometry of free ligand are also given in Figure 4. Since the spectra of free ligands are quite different from those of complexes **M1**, **M2**, and **M3**, the electronic structures of excited states for complexes **M1**, **M2**, and **M3** are considered to be different from those for free ligands.

For complexes **M1**, **M2**, and **M3**, the pictorial displays of the extent of mixing in the frontier orbitals, which appear in the main configurations of the wave functions for excited states, are given in Figure 1S (Supporting Information), as well as in ref 26 for the Ru complex. The color codes define the sum of

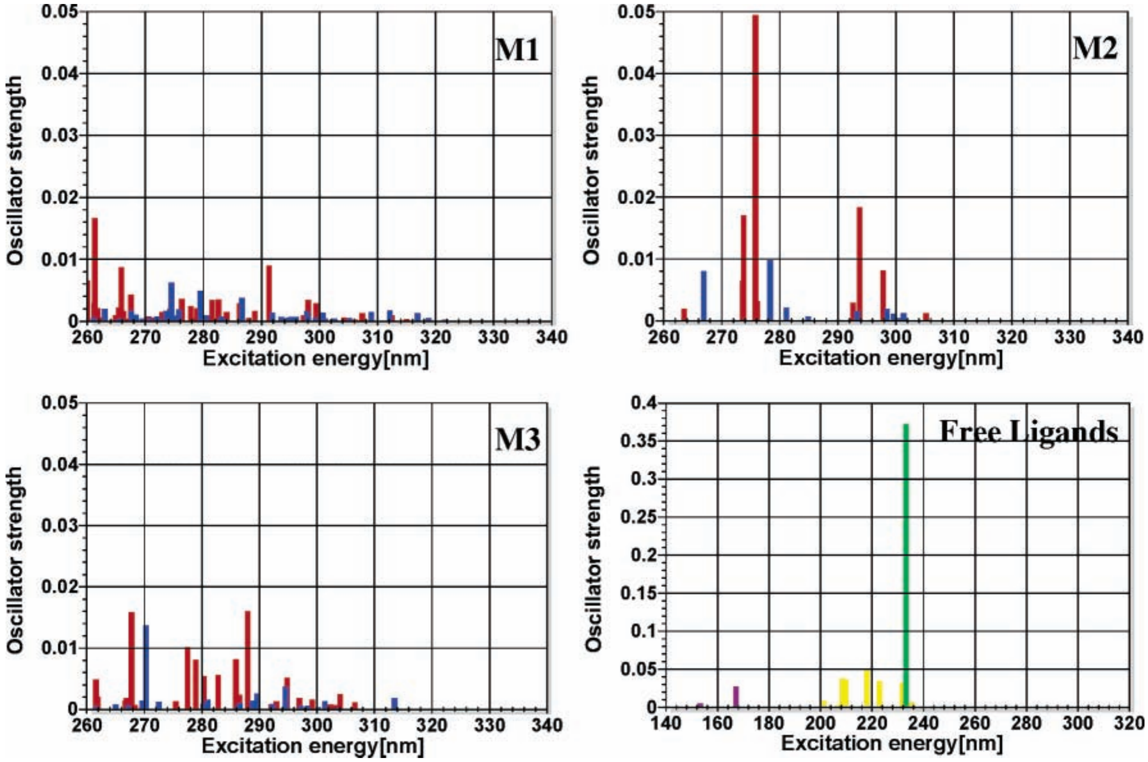


Figure 4. Calculated electronic spectra of complexes **M1**, **M2**, and **M3** at structure A (red line) and structure B (blue line), and calculated electronic spectra of free ligands; TPPO (yellow line), TMPO (violet line), and bdk (green line).

TABLE 3: Calculated Energy Differences ΔE_{ISC} and ΔE_{ET} (eV)

	ΔE_{ISC}		ΔE_{ET}	
	structure A	structure B	structure A	structure B
M1	1.05	0.82	0.87	0.91
M2	1.18	1.22	0.86	0.88
M3	1.16	0.99	0.86	0.89

the squares of the molecular orbital coefficients of the total atomic contributions from Eu and each ligand as denoted. For complexes **M1** and **M3**, the excited states can be characterized by the charge transfer from bdk ligand(s) to TPPO ligand(s). On the other hand, for complex **M2**, the excited states can be characterized by the intra-bdk-ligand(s) excitation. Since each complex has delocalized orbitals among plural ligands, the electronic structure for each complex is considered to be different from that for free ligands.

Finally, we consider the sensitization process for each complex. Calculated energy differences ΔE_{ISC} and ΔE_{ET}, depicted in Figure 1, for each complex at both structures A and B are given in Table 3. ΔE_{ISC} is calculated with the excitation energy difference between the first singlet excited state and the first triplet excited state by TDDFT. ΔE_{ET} is calculated with the excitation energy for the first triplet excited state by TDDFT and the energy difference between ^{5}D and ^{7}F for Eu(III), which is assumed to be 2.016 eV, corresponding to 615 nm. For efficient sensitization, ΔE_{ISC} must be larger than 5000 cm^{-1} (= 0.62 eV), and ΔE_{ET} must be larger than 3500 cm^{-1} (= 0.43 eV)[1]. According to Table 3, complexes **M1**, **M2**, and **M3** satisfy these conditions. To evaluate the efficiency of intersystem crossing and energy transfer quantitatively, we have to calculate the probability for the nonadiabatic transitions between excited states of complexes. This is a subject for future work. For energy transfer, we consider that the theoretical approach by Faustino and co-workers[27] can be used.

To estimate the efficiency for emission of the Eu(III) ion, which is the final stage in Figure 1, we have to deal with the intra-4*f* transitions. This is a subject for future work. From the viewpoint of ab-initio calculation, we consider that the spin−orbit configuration interaction calculation[23] and the response theory approach for phosphorescence[28] can be used. From the viewpoint of Judd−Ofelt analysis[29,30] on the ligand field parameters, we consider that the theoretical approach by Malta and co-workers[31] can be used.

It is possible to calculate complexes **1**−**3**. This is also a subject for future work. Since the structure of β-diketonate in complexes **1**−**3** is not symmetric, it is expected that many coordination structures can exist for complexes **1**−**3**. To estimate the molecular and electronic structures of complexes **1**−**3**, we calculated the free β-diketonate ligand with R_3 = *t*-Bu and R_4 = C_3F_7 for complexes **1**−**3**. The Mulliken charges of O atoms in this β-diketonate are −0.555 and −0.585. Since the Mulliken charges of O atoms in the free β-diketonate ligand with $R_3 = R_4 =$ H for complexes **M1**−**M3** is −0.538, O atoms in the β-diketonate ligand for complexes **1**−**3** is considered to be more attractive to the Eu ion than O atoms in the β-diketonate ligand for complexes **M1**−**M3**, and the bond length between Eu and O in the β-diketonate ligand in complexes **1**−**3** is expected to be shorter than that between Eu and O in the β-diketonate ligand in complexes **M1**−**M3** assuming that the steric effect of the *t*-Bu group and the C_3F_7 group is small. The orbital energy of HOMO for the free β-diketonate ligand with $R_3 = R_4 =$ H for complexes **M1**−**M3** is −0.09 eV, and that for the free β-diketonate ligand with R_3 = *t*-Bu and R_4 = C_3F_7 for complexes **1**−**3** is −1.14 eV. Therefore, the absolute value of excitation energy for complex **1**, **2**, or **3** is expected to be different from that for corresponding model complex (**M1**, **M2**, or **M3**). However, we expect that the comparison of excitation spectra among complexes **1**−**3** is similar to that among complexes **M1**−**M3**.

5. Conclusions

We have employed DFT calculations to theoretically investigate Eu(III) complexes with three β-diketonates and two phosphine oxides (complexes **M1**, **M2**, and **M3**) deemed to be the model complexes for complexes **1**, **2**, and **3**, which are the fluorescence compounds for the ultraviolet LED devices we have recently developed. For each complex, two minimum energy points corresponding to two different optimized geometries (structures A and B) have been found, and the difference of the energy between two minimum energy points is quite small (less than 1 kcal/mol). Assuming that the difference of the energy between structures A and B is also small for complexes **1**, **2**, and **3**, we can suppose that complexes **1**, **2**, and **3** can exist at both structures A and B in solution or in the fluorescence layer of LED.

Vertical excitation energies and oscillator strengths for each complex at two optimized geometries have been obtained by the TDDFT calculation, and the character of the excited states has been investigated. For complex **M3**, the absorption edge is red-shifted, and the oscillator strengths are relatively large. Considering ΔE_{ISC} and ΔE_{ET}, the luminescent ^{5}D state of the Eu(III) ion can be efficiently populated for each complex.

Therefore, we can suppose that complex **M3**, which is the model for complex **3**, is efficient for excitation at the long-wavelength UV region. This supports our experimental result that we have achieved the highest luminous intensity reported to date by using complex **3**.

Acknowledgment. The authors are grateful to Dr. K. Harada for helpful comments and discussions. The authors thank Dr. K. Naito, Dr. T. Ushirogouchi, Dr. S. Uchikoga, Dr. I. Amemiya, Dr. H. Asai, Dr. M. Yamamoto, Dr. S. Saito, and Dr. M. Ishikawa for their encouragement.

Supporting Information Available: Additional tables showing calculated excitation energies, oscillator strengths, and main configurations for singlet excited states and an additional figure showing a pictorial display of the extent of mixing in the frontier orbitals of complexes **M1**, **M2**, and **M3**. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Steemers, F. J.; Verboom, W.; Reinhoudt, D. N.; van der Tol, E. B.; Verhoeven, J. W. *J. Am. Chem. Soc.* **1995**, *117*, 9408.

(2) Latva, M.; Takalo, H.; Mukkala, V.-M.; Matachescu, C.; Rodriguez-Ubis, J. C.; Kankare, J. *J. Lumin*. **1997**, *75*, 149.

(3) Batista, H. J.; De Andrade, A. V. M.; Longo, R. L.; Simas, A. M.; De Sa, G. F.; Ito, N. K.; Thompson, L. C. *Inorg. Chem.* **1998**, *37*, 3542.

(4) Klink, S. I.; Hebbink, G. A.; Grave, L.; Alink, P. G. B. O.; van Veggel, F. C. J. M.; Werts, M. H. V. *J. Phys. Chem. A* **2002**, *106*, 3681.

(5) Senegas, J.-M.; Bernardinelli, G.; Imbert, D.; Bunzil, J.-C. G.; Morgantini, P.-Y.; Weber, J.; Piguet, C. *Inorg. Chem.* **2003**, *42*, 4680.

(6) Hasegawa, Y.; Yamamuro, M.; Wada, Y.; Kanehisa, N.; Kai, Y.; Yanagida, S. *J. Phys. Chem. A* **2003**, *107*, 1697.

(7) Carnall, W. T. In *Handbook on the Physics and Chemistry of Rare Earths*; Gschneider, K. A., Eyring, L. R., Eds.; North-Holland: Amsterdam, 1979; Vol. 3, p 171.

(8) Sabbatini, N.; Guardigli, M.; Manet, I. In *Handbook on the Physics and Chemistry of Rare Earths*; Gschneidner, K. A., Eyling, L. R., Jr., Eds.; Elsevier: Amsterdam, 1996; Vol. 23, p 69.

(9) Kuriki, K.; Koike, Y.; Okamoto, Y. *Chem. Rev.* **2002**, *102*, 2347.

(10) Hasegawa, Y.; Wada, Y.; Yanagida, S.; Kawai, H.; Nagamura, T. *Appl. Phys. Lett.* **2003**, *83*, 3599.

(11) Uekawa, M.; Miyamoto, Y.; Ikeda, H.; Kaifu, K.; Nakaya, T. *Bull. Chem. Soc. Jpn*. **1998**, *71*, 2253.

(12) Kido, J.; Okamoto, Y. *Chem. Rev.* **2002**, *102*, 2357.

(13) Iwanaga, H.; Amano, A.; Aiga, F.; Harada, K.; Oguchi, M. *J. Alloys Compd*., in press.

(14) Iwanaga, H.; Amano, A.; Oguchi, M. *Jpn. J. Appl. Phys.* **2005**, *44*, *3702*.

(15) Iwanaga, H.; Amano, A.; Furuya, F.; Yamasaki, Y. *Jpn. J. Appl. Phys*., in press.

(16) De Andrade, A. V. M.; Da Costa, N. B., Jr.; Simas, A. M.; De Sa, G. F. *Chem. Phys. Lett.* **1994**, *227*, 349.

(17) De Andrade, A. V. M.; Longo, R. L.; Simas, A. M.; De Sa, G. F. *J. Chem. Soc*., *Faraday Trans.* **1996**, *92*, 1835.

(18) Batista, H. J.; Longo, R. L. *Int. J. Quantum Chem.* **2001**, *90*, 924.

(19) Maron, L.; Eisenstein, O. *J. Phys. Chem. A* **2000**, *104*, 7140.

(20) Boehme, C.; Coupez, B.; Wipff, G. *J. Phys. Chem. A* **2002**, *106*, 6487.

(21) Gutierrez, F.; Rabbe, C.; Poteau, R.; Daudey, J. P. *J. Phys. Chem. A* **2005**, *109*, 4325.

(22) Ricca, A.; Bauschlicher, C. W., Jr. *Chem. Phys. Lett.* **2002**, *366*, *623*.

(23) Naleway, C.; Seth, M.; Shepard, R.; Wagner, A. F.; Tilson, J. L.; Ermler, W. C.; Brozell, S. R. *J. Chem. Phys.* **2002**, *116*, 5481.

(24) Dolg, M.; Stoll, H.; Savin, A.; Preuss, H. *Theor. Chim. Acta* **1993**, *85*, 441.

(25) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, revision B.04; Gaussian, Inc.: Pittsburgh, PA, 2003.

(26) Aiga, F.; Tada, T. *J. Mol. Struct.* **2003**, *658*, 25.

(27) Faustino, W. M.; Malta, O. L.; de Sa, G. F. *J. Chem. Phys.* **2005**, *122*, 054109.

(28) Tunell, I.; Rinkevicius, Z.; Vahtras, O.; Sałek, P.; Helgaker, T.; Ågren, H. *J. Chem. Phys.* **2003**, *119*, 11024.

(29) Judd, B. R. *Phys. Rev.* **1962**, *127*, 750.

(30) Ofelt, G. S. *J. Chem. Phys.* **1962**, *70*, 4830.

(31) Malta, O. L.; Brito, H. F.; Menezes, J. F. S.; Gonçalves e Silva, F. R.; Alves, S., Jr.; Farias, F. S., Jr.; de Andrade, A. V. M. *J. Lumin*. **1997**, *75*, 255.