J. Phys. Chem. A **2007,** *111,* 12141−12145

Density Functional Theory Investigation of Novel Eu(III) Complexes with Asymmetric Bis(phosphine) Oxides

Fumihiko Aiga,* Hiroki Iwanaga, and Akio Amano

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

Received: August 25, 2007

Recently, we have developed novel Eu(III) complexes with three β-diketonates and one asymmetric bis(phosphine) oxide whose light emission intensity is drastically increased. In this paper, one of these complexes is investigated by the density functional theory calculation. Sixteen isomers of this complex have been considered. The ratio of the existence for the most stable isomer (**B1_1a**) is found to be about 51%, and the sum of the ratio of the existence for the six most stable isomers (**B1_1a**, **B1_3a**, **B1_8a**, **B1_2a**, **B1_1b**, and **B1_5a**) is about 100%, assuming the Boltzmann distribution ($T = 300$ K). The coordination structures of the six most stable isomers in the ground states are similar, and we can expect asymmetric ligand fields for them, favorable for the efficient light emission. Vertical excitation energies and oscillator strengths for each isomer have been obtained by the time-dependent density functional theory. With the red-shift of the wavelength and the interpolation by Gaussian convolution, both the calculated absorption spectra for the most stable isomer **B1_1a** and the calculated absorption spectra for the ensemble average of the isomers are found to be similar to the experimental fluorescence excitation spectra. The efficiency of energy transfer from the triplet excited state to the Eu(III) ion is considered by calculating ΔE_{ET} (difference between the adiabatic excitation energy of the complex for the lowest triplet state and the emission energy of the Eu(III) ion for $^5D_0$ to $^7F_2$). The characters for the lowest triplet states for the isomers are investigated by the spin density distributions of the triplet states.

1. Introduction

Eu(III) complexes have been extensively investigated as luminescent materials.[1−10] The long luminescent lifetimes of Eu(III) ions are due to the forbidden character of their intra-4f transitions, which result in low absorption coefficients.[11] 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.[1,4,12] The photophysical pathway of this sensitization process involves the excitation of the ligand(s), intersystem crossing to the triplet state of the ligand(s), energy transfer (ET) to Eu(III) ion, and subsequent emission of the Eu(III) ion.

Eu(III) complexes have been applied to luminescent devices such as lasers[13,14] and organic light-emitting diodes (OLED).[15,16] We have developed a light-emitting diode (LED) device by using the Eu(III) complex with three β-diketonates and two different phosphine oxides in the fluorescence layer of the LED,[17−19] and we have investigated these complexes by the density functional theory (DFT) calculation.[20] These complexes are highly soluble and have strong emission intensities. However, ligand exchange of phosphine oxide ligands was detected by ^{31}P NMR analysis.[18] Ligand exchange has an undesirable effect on the durability of Eu(III) complexes. Therefore, recently, we have developed novel Eu(III) complexes with three β-diketonates and one asymmetric bis(phosphine) oxide.[21] We have introduced a bis(phosphine) oxide, which consists of two different phosphine oxides, in order to prevent ligand exchange. The molecular structure of the bis(phosphine) oxide is designed to be asymmetric to attain a large emission intensity and large solubility. The sharpness of the ^{31}P NMR spectra suggests that ligand exchange is prohibited and emission intensity is drastically increased.[21] Nakamura et al. reported Eu(III) complexes with three β-diketonates and one symmetric bis(phosphine) oxide,[7,8,10] which have narrow emission bands due to the degeneration of Stark levels. These complexes show large stimulated emission cross sections.

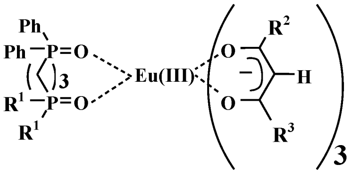
In this paper, we report the DFT investigation of the Eu(III) complexes with three β-diketonates and one asymmetric bis(phosphine) oxide, depicted in Figure 1. As well as the model complex **BM1**, we have investigated the real complex **B1**.[21] Eu(III) complexes have been theoretically investigated by semiempirical molecular orbital calculations[22−27] and ab initio quantum chemical calculations.[20,28−33] Since f orbitals do not play a major role in Eu−ligand bonds,[28] we have used the effective core potential (ECP) including 4f^n electrons for Eu by Dolg et al.,[34] and we have calculated the excited states by time-dependent density functional theory (TDDFT). Therefore, in this paper, we do not consider the excited states for intra-4f 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 bis(phosphine) oxides for the ground and excited states.

This paper is organized as follows. In section 2, the computational details are described. In section 3, the ground states of the 16 isomers of **B1** are characterized, and in section 4, the excited states are characterized. Section 5, which is the final section, is devoted to concluding remarks.

---

* To whom correspondence should be addressed. E-mail: fumihiko.aiga@toshiba.co.jp.

10.1021/jp076820g CCC: \$37.00



B1: R^1=*n*-Bu, R^2=C_3F_7, R^3=*t*-Bu
BM1: R^1=Me, R^2=R^3=H

Figure 1. Molecular structures of real complex **B1** and model complex **BM1**.

2. Computational Details

The calculations were carried out with the Gaussian 03 package.[35] For singlet ground states, 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. For singlet excited states, the excitation energies and oscillator strengths at the optimized geometry in the ground state were obtained by TDDFT calculations with the B3LYP functional. For the lowest triplet states, DFT calculations were performed by using the B3LYP functional. Geometry optimization was carried out, and the adiabatic excitation energy was obtained, with the difference between the energy of the lowest triplet state at the optimized geometry for the triplet state and the energy of the singlet ground state at the optimized geometry for the singlet state, which is the ΔSCF method.[30,32]

Considering that f orbitals do not play a major role in Eu−ligand bonds[28] and in order to reduce the computational cost, we used the large-core quasi-relativistic ECP, having $46 + 4f^n$ electrons, for Eu by Dolg et al.[34] 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

First, we obtained the optimized geometry for the model complex **BM1** in the ground state, where the *t*-Bu group and the C_3F_7 group in β-diketonate were replaced by a H atom and the *n*-Bu group in the phosphine oxide was replaced by a methyl group, which is the same rule taken in our previous paper.[20] The initial geometry of **BM1** was given from the geometry of **M3** at structure B in our previous paper,[20] whose two phosphine oxides were replaced by the bis(phosphine) oxide. The optimized geometry of **BM1** is illustrated in Figure 2.

Then, we constructed the initial geometries for the real complex **B1**[21] by replacing one H atom in the β-diketonate of **BM1** by a *t*-Bu group and the other H atom by a C_3F_7 group. Since there are two ways of replacing H atoms in each β-diketonate of **BM1**, eight isomers for complex **B1** were considered. We call these isomers **B1_1a**, **B1_2a**, ..., and **B1_8a**, respectively. Finally, we constructed the initial geometries for the other eight isomers by interchanging Ph with *n*-Bu in bis(phosphine) oxides of **B1_1a**, **B1_2a**, ..., and **B1_8a**, respectively. We call these isomers **B1_1b**, **B1_2b**, ..., and **B1_8b**, respectively. Therefore, we considered 16 isomers.

The energy *E*r (kcal/mol) for the 16 isomers of **B1** relative to the most stable isomer **B1_1a** is given in Table 1. The ratio *R*r of the existence relative to the most stable isomer **B1_1a** and the absolute ratio *R*a of the existence, assuming the Boltzmann distribution ($T = 300$ K) with respect to *Er*, are also shown. The ratio of the existence for the most stable isomer **B1_1a** is found to be about 51%, and the sum of the ratio of the existence for the six most stable isomers (**B1_1a**, **B1_3a**, **B1_8a**, **B1_2a**, **B1_1b**, and **B1_5a**) is about 100%. Therefore, it follows that the other 10 isomers scarcely exist.

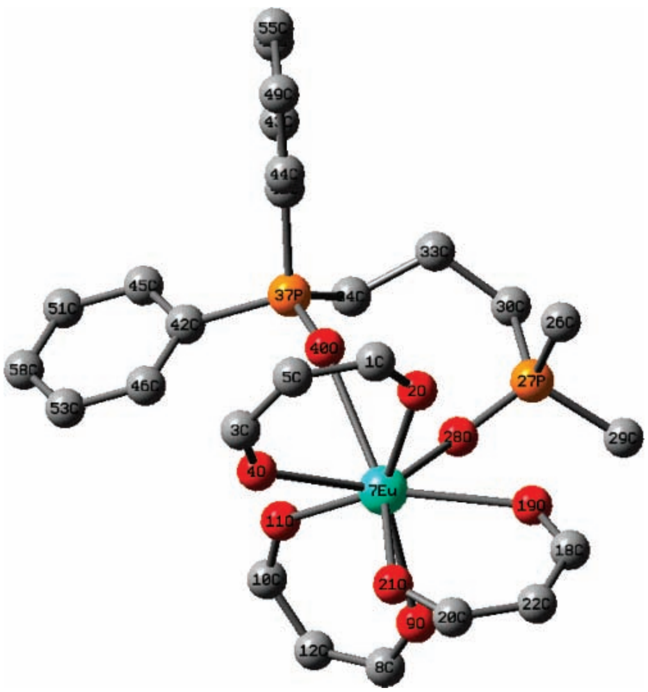


Figure 2. The optimized geometry of **BM1**. (H atoms are excluded.)

TABLE 1: The Energy *E*r (kcal/mol) for the 16 Isomers of B1 Relative to the Most Stable Isomer B1_1a; the Ratio *R*r of the Existence Relative to the Most Stable Isomer B1_1a, and the Absolute Ratio *R*a of the Existence, Assuming the Boltzmann Distribution ($T = 300$ K) with Respect to *Er*, Are Also Shown

	*E*r	*R*r	*R*a
B1_1a	0.00	1.000	0.509
B1_3a	0.53	0.412	0.210
B1_8a	0.74	0.289	0.147
B1_2a	0.90	0.222	0.113
B1_1b	2.27	0.022	0.011
B1_5a	2.42	0.017	0.009
B1_6a	5.27	0.000	0.000
B1_3b	5.74	0.000	0.000
B1_4a	6.41	0.000	0.000
B1_7a	7.22	0.000	0.000
B1_7b	9.59	0.000	0.000
B1_8b	9.76	0.000	0.000
B1_4b	10.47	0.000	0.000
B1_2b	10.64	0.000	0.000
B1_5b	11.83	0.000	0.000
B1_6b	12.11	0.000	0.000

Calculated bond lengths between Eu and O and Mulliken charges for Eu and O for **B1** at the optimized geometry for the six most stable isomers are given in Table 1S (Supporting Information). The substituents C_3F_7 or *t*-Bu are connected to the carbon atoms C1, C3, C18, C20, C8, and C10 of **BM1** in Figure 2. Δ*R* is the variation of bond length from the corresponding value for **BM1**, and Δ*q* is the variation of charge. Since Δ*R* and Δ*q* are very small, we consider that **BM1** is a good model for **B1** concerning the ground-state coordination structure around the Eu atom. Actually, the bond lengths of the model complex, composed by the same rule as that for **BM1** in our previous paper,[20] are in good agreement with those of the corresponding real complex determined by Hasegawa et al.[6] with single-crystal X-ray diffraction. **B1_1a**, **B1_8a**, and **B1_5a** have the bonds with shorter lengths (2.397, 2.378, and 2.396 Å,

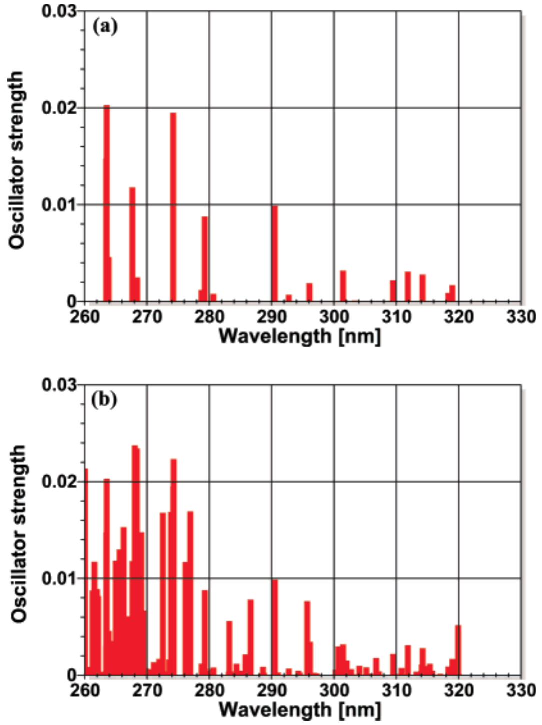


Figure 3. Calculated electronic spectra for the most stable isomer **B1_1a** (a) and the calculated electronic spectra for the ensemble average of the isomers (b).

respectively) than the bond length in the Eu(III) complex having three β-diketonates and two phosphine oxides in our previous paper.[21] Therefore, we can expect a more asymmetric ligand field for **B1**, favorable for the efficient light emission.

4. Excited States

Calculated electronic spectra for the most stable isomer **B1_1a** are illustrated in Figure 3a. The calculated electronic spectra for the ensemble average of the isomers, which are obtained by multiplying the oscillator strength of each isomer by *R*a for each isomer and superimposing all spectra, are illustrated in Figure 3b. Calculated electronic spectra for other isomers in the six most stable isomers are illustrated in Figure 1S (Supporting Information). For each isomer, the 30 lowest singlet excited states are considered. The difference of spectra between isomers is found to be large.

Comparison of the experimental fluorescence excitation spectra[21] with the calculated electronic spectra for the most stable isomer **B1_1a** is illustrated in Figure 4a, where calculated spectra are red-shifted by 73 nm, transition energies and oscillator strengths are interpolated by a Gaussian convolution with a σ of 0.1 eV, and oscillator strengths are normalized to the experimental intensity of the fluorescence excitation spectra at 335 nm, as well as in refs 31 and 36. Comparison with the calculated spectra for the ensemble average of the isomers is illustrated in Figure 4b, where calculated spectra are also red-shifted by 73 nm, transition energies and oscillator strengths are interpolated by a Gaussian convolution with a σ of 0.09 eV, and oscillator strengths are normalized to the experimental intensity of the fluorescence excitation spectra at 335 nm. Both the calculated absorption spectra for the most stable isomer **B1_1a** and the calculated absorption spectra for the ensemble average of the isomers are found to be similar to the experimental fluorescence excitation spectra. In order to make a more complete comparison in the short wavelength region below 330 nm, calculation of higher excited states than the 30th may be needed. From the above, there are two possibilities. One possibility is that **B1_1a** exists alone as the only isomer of **B1** in the solution, and the other possibility is that several isomers can exist as the ensemble of the Boltzmann distribution in the solution. We cannot determine which possibility is more probable by this measurement of fluorescence excitation spectra. The mixture of the several isomers is favorable for the high solubility. Although excited states, populated by light absorption, can relax through various processes, the relaxation processes of the excited states of **B1** here can be considered to be almost the same since the calculated absorption spectra are similar to the experimental fluorescence spectra. Of course, it is better to obtain the experimental absorption spectra, but it was difficult. Because the absorption coefficient of **B1** is very large, it is necessary to prepare a dilute solution or to prepare the measurement equipment with a thin cell. However, in dilute solutions, the ligands of **B1** may dissociate, and we could not prepare the measurement equipment with a thin cell. Therefore, we could not obtain the experimental absorption spectra. Concerning the calculated absorption spectra, it is better to calculate the Franck−Condon factor,[37] and this is a subject for future work.

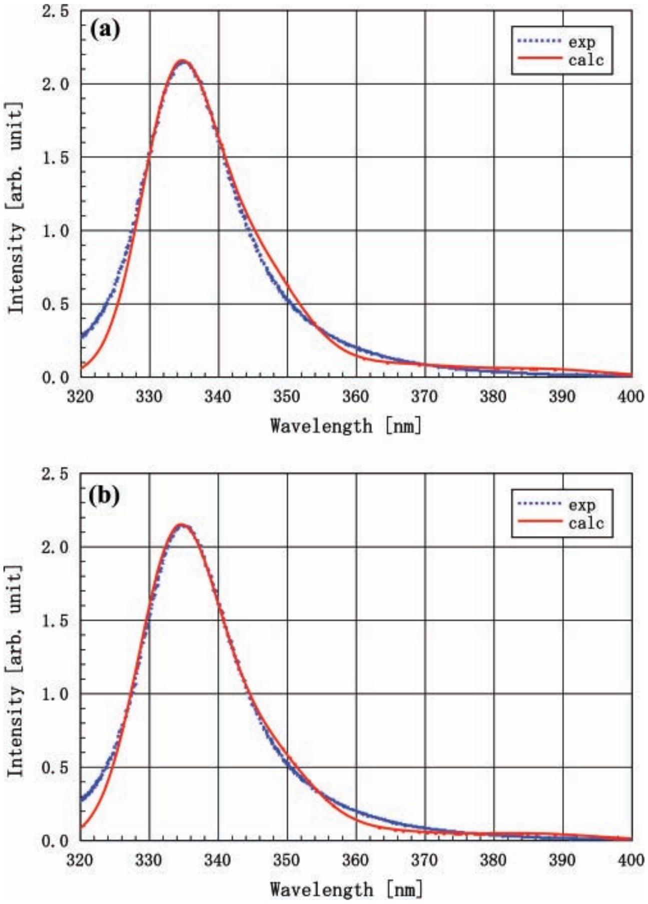


Figure 4. Comparison of the experimental fluorescence excitation spectra with the calculated electronic spectra for the most stable isomer **B1_1a** (a) and the calculated spectra for the ensemble average of the isomers (b).

The calculated bond length between Eu and O and the Mulliken charge for Eu and O for **B1** at the optimized geometry of the lowest triplet state for the six most stable isomers are given in Table 2S (Supporting Information). As well as the values from Table 1S, ΔR and Δq are very small, and the coordination structure of the lowest triplet state of **B1** is found to be similar to that for the singlet ground state of **B1**.

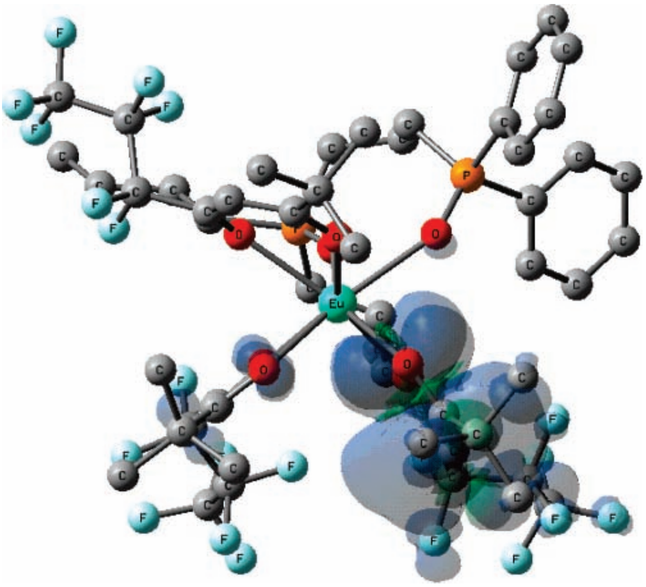


Figure 5. The spin density distribution for **B1_1a** at the optimized geometry of the lowest triplet state.

TABLE 2: Calculated Adiabatic Excitation Energy of the Lowest Triplet State Ex_t and ΔE_{ET} (eV) for the Six Most Stable Isomers

	Ex_t	ΔE_{ET}
B1_1a	2.71	0.70
B1_3a	2.65	0.63
B1_8a	2.66	0.65
B1_2a	2.61	0.59
B1_1b	2.64	0.62
B1_5a	3.28	1.26

The calculated adiabatic excitation energies of the lowest triplet state Ex_t and ΔE_{ET} (difference between Ex_t and the emission energy of Eu(III) ion for $^5D_0$ to $^7F_2$) (eV) for the six most stable isomers are given in Table 2. For efficient sensitization, there is an empirical rule that ΔE_{ET} must be larger than 3500 cm^{-1} (=0.43 eV).[1] For all isomers in Table 2, ΔE_{ET} satisfies this rule. In order to evaluate the efficiency of energy transfer quantitatively, we have to calculate the probability for the non-adiabatic transitions between excited states of complexes. In order to estimate the efficiency for emission of the Eu(III) ion quantitatively, we have to deal with the intra-4f transitions. These are also subjects for future work.

In Table 2, Ex_t for **B1_5a** is especially large in comparison with those for other isomers. Therefore, we have investigated the character of the triplet states for these isomers. The spin density distribution for the most stable isomer **B1_1a** at the optimized geometry of the lowest triplet state is illustrated in Figure 5, and the spin density distributions for other isomers are illustrated in Figure 2S (Supporting Information). The spin density distributions for isomers other than **B1_5a** are localized on one β-diketonate. On the other hand, the spin density distribution for **B1_5a** is delocalized on two β-diketonates. Therefore, the lowest triplet state of **B1_5a** can be characterized not only by the intra-β-diketonate excitation but also by the charge transfer from one β-diketonate to the other β-diketonate. The lowest triplet states for isomers other than **B1_5a** can be characterized by the intra-β-diketonate excitation.

5. Conclusions

We have employed DFT calculations to theoretically investigate a novel Eu(III) complex with three β-diketonates and one asymmetric bis(phosphine) oxide. Sixteen isomers of this complex have been considered. The ratio of the existence for the most stable isomer **B1_1a** is found to be about 51%, and the sum of the ratio of the existence for the six most stable isomers (**B1_1a**, **B1_3a**, **B1_8a**, **B1_2a**, **B1_1b**, and **B1_5a**) is about 100%, assuming the Boltzmann distribution (T = 300 K). Vertical excitation energies and oscillator strengths for each isomer have been obtained by TDDFT. With the red shift of the wavelength and the interpolation by Gaussian convolution, both the calculated absorption spectra for the most stable isomer **B1_1a** and the calculated absorption spectra for the ensemble average of the isomers are found to be similar to the experimental fluorescence excitation spectra.

Acknowledgment. The authors would like to thank Dr. T. Ushirogouchi, Dr. K. Takaoka, Dr. H. Asai, Dr. T. Sato, and Dr. S. Uchikoga.

Supporting Information Available: Additional tables and figures. 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.; Berbardinelli, G.; Imbert, D.; Bunzil, J.-C. G.; Morgantini, P.-Y.; Werber, 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) Nakamura, K.; Hasegawa, Y.; Wada, Y.; Yanagida, S. *Chem. Phys. Lett.* **2004**, *398*, 500.
(8) Nakamura, K.; Hasegawa, Y.; Kawai, H.; Yasuda, N.; Wada, Y.; Yanagida, S. *J. Alloys Compd.* **2006** *408*−*412*, 771.
(9) Hasegawa, Y.; Kawai, H.; Nakamura, K.; Yasuda, N.; Wada, Y.; Yanagida, S. *J. Alloys Compd.* **2006** *408*−*412*, 669.
(10) Nakamura, K.; Hasegawa, Y.; Kawai, H.; Yasuda, N.; Kanehisa, N.; Kai, Y.; Nagamura, T.; Yanagida, S; Wada, Y. *J. Phys. Chem. A* **2007**, *111*, 3029.
(11) Carnall, W.T. In *Handbook on the Physics and Chemistry of Rare Earths*; Gschneider, K.A., Eyring, L. R., Eds.; North-Holland: Amsterdam, The Netherlands, 1979; Vol. 3, p 171.
(12) 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: The Netherlands, 1996; Vol. 23, p 69.
(13) Kuriki, K.; Koike, Y.; Okamoto, Y. *Chem. Rev.* **2002**, *102*, 2347.
(14) Hasegawa, Y.; Wada, Y.; Yanagida, S.; Kawai, H.; Nagamura, T. *Appl. Phys. Lett.* **2003**, *83*, 3599.
(15) Uekawa, M.; Miyamoto, Y.; Ikeda, H.; Kaifu, K.; Nakaya, T. *Bull. Chem. Soc. Jpn*. **1998**, *71*, 2253.
(16) Kido, J.; Okamoto, Y. *Chem. Rev.* **2002**, *102*, 2357.
(17) Iwanaga, H.; Amano, A.; Aiga, F.; Harada, K.; Oguchi, M. *J. Alloys Compd.* **2006**, *408*−*412*, 921.
(18) Iwanaga, H.; Amano, A.; Oguchi, M. *Jpn. J. Appl. Phys.* **2005**, *44*, 3702.
(19) Iwanaga, H.; Amano, A.; Furuya, F.; Yamasaki, Y. *Jpn. J. Appl. Phys.* **2006**, *45*, 558.
(20) Aiga, F.; Iwanaga, H.; Amano, A. *J. Phys. Chem. A* **2005**, *109*, 11312.
(21) Iwanaga, H.; Aiga, F.; Amano, A. *Mater. Res. Soc. Symp. Proc.* **2007**, *965*, S03-12.
(22) De Andrade, A. V. M.; Da Costa, N. B., Jr.; Simas, A. M.; De Sa, G. F. *Chem. Phys. Lett.* **1994**, *227*, 349.
(23) De Andrade, A. V. M.; Longo, R. L.; Simas, A. M.; De Sa, G. F. *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 1835.
(24) Batista, H. J.; Longo, R. L. *Int. J. Quantum Chem.* **2001**, *90*, 924.
(25) Vila-Nova, S. P.; Pereira, G. A. L.; Albuwuerque, R. Q.; Mathis, G.; Bazin, H.; Autiero, H.; de Sa, G. F.; Alves, A., Jr. *J. Lumin.* **2004**, *109*, 173.
(26) Freire, R. O.; Rocha, G. B.; Simas, A. M. *Inorg. Chem.* **2005**, *44*, 3299.

(27) Pavithran, R.; Saleesh Kunar, N. S.; Biju, S.; Reddy, M. L. P.; Junior, S. A.; Freire, R. O. *Inorg. Chem.* **2006**, *45*, 2184.

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

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

(30) Gutierrez, F.; Tedeschi, C.; Maron, L.; Daudey, J. P.; Poteau, R.; Azema, J.; Tisnes, P.; Picard, C. *Dalton Trans.* **2004**, 1334.

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

(32) Guillaumont, D.; Bazin, H.; Benech, J.-M.; Boyer, M.; Mathis, G. *ChemPhysChem* **2007**, *8*, 480.

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

(34) Dolg, M.; Stoll, H.; Savin, A; Preuss, H. *Theor. Chim. Acta* **1989**, *75*, 173.

(35) 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.; Bakken, V.; 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. 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 D.01; Gaussian, Inc.: Pittsburgh, PA, 2004.

(36) Fantacci, S.; Angelis, F. D.; Sellon, A. *J. Am. Chem. Soc*. **2003**, *125*, 4381.

(37) Santoro, F.; Lami, A.; Improta, R.; Barone, V. *J. Chem. Phys.* **2007**, *126*, 184102.