Design of Efficient Electroluminescent Lanthanide(III) Complexes

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The lanthanide complexes have been anticipated to exhibit high efficiency along with a narrow emission spectrum. Photoluminescence for the lanthanide complex is characterized by a high efficiency since both singlet and triplet excitons are involved in the luminescence process. However, the maximum external electroluminescence quantum efficiencies have exhibited values around 1% due to triplet-triplet annihilation at high current. Here, we proposed a new energy transfer mechanism to overcome triplet-triplet annihilation by the Eu complex doped into phosphorescent materials with triplet levels that were higher than singlet levels of the Eu complex. In order to show the feasibility of the proposed energy transfer mechanism and to obtain the optimal ligands and host material, we have calculated the effect depending on ligands as a factor that controls emission intensity in lanthanide complexes. The calculation shows that triplet state as well as singlet state of anion ligand affects on absorption efficiency indirectly.

Keywords : Electroluminescence, Lanthanide complexes, Energy transfer, Triplet-triplet annihilation.

Efficient electroluminescence (EL) device based on thin film organic or conjugated polymeric material is a promising candidate for next generation low-cost, full-color, flat-panel displays[1] and has been studied extensively since Tang and VanSlyke[2,3] reported the first architecture of the double layered organic EL device. These devices are injection type and show a low driving voltage of less than 10V. In these devices, light is generated by the recombination of injected holes and injected electrons in an emitting layer. The lanthanide complexes also have been applied by many groups as emitting materials and have been anticipated to exhibit high efficiency along with a narrow emission spectrum.[4-8] It is known that lanthanide complexes are characterized by highly efficient intra-energy conversion from the ligand singlet (S_1) to the triplet (T_1), and then to the excited state of the central metal ion. The metal ions exhibits sharp spectral bands corresponding to ^5D_x-^7F_x transitions.

This mechanism is characterized by a high (20%-95%) photoluminescence (PL) efficiency for molecules suspended in a dilute solution.[5] Since both singlet and triplet excitons are involved in the luminescence process, it can be possible to obtain very high metal ion excitation efficiency by optimizing energy transfer in solid state systems where the molecule is doped into an appropriate molecular host matrix.

Baldo *et al*.[9,10] have studied the mechanism for energy transfer using a lanthanide complex Eu(TTA)$_3$Phen doped into a charge transport material such as biphenyl-*p*-(*t*-butyl)phenyl-1,3,4 oxadiazole (PBD) or 4,4'-N,N'-dicabazole-biphenyl (CBP) host. Two energy transfer mechanisms was expected: (1) singlet-singlet energy transfer from the host by the Förster mechanism and (2) triplet-triplet energy transfer from the host by the Dexter mechanism. If the energy transfer (2) was active, this allowed extra conversion efficiency from the triplet state. Host material have been selected as blue-fluorescent materials since a Förster-type energy transfer is expected from the host singlet to the ligand singlet.[11] However, the maximum external EL quantum efficiencies(η) using the devices have exhibited values around 1%. Also, with increasing current, a significant decrease of η along with an increase in host emission is observed. Thus, they conclude that bimolecular annihilation due to the CBP-CBP triplet interaction transferred from TTA triplet is the deactivation process at high current.

In this report, we proposed a new energy transfer mechanism of the Eu complex doped into phosphorescent materials with triplet levels that were higher than singlet levels of the Eu complex. Since triplet-triplet annihilation occur between host triplet transferred from the ligand triplet, we need a energy transfer mechanism which can avoid triplet-triplet energy transfer between the host and ligand and at the same time it has to use the triplet state energy of the host. The triplet-triplet energy transfer by the Dexter mechanism is possible due to the host and ligand having the similar energy levels. Thus, in case of using phosphorescent host, we can use triplet states and also, if the triplet level of phosphorescent host is higher than the triplet level of the ligand of the Eu complex, triplet-triplet annihilation can be prevented from energy gap. Expected energy transfer mechanism of the emitting layer of the EL devices is shown in Figure 1.

The difference between the proposed mechanism and the mechanism studied by Forrest group are following: (1) Forrest *et al*. use the fluorescent material as host and we use the phosphorescent material, (2) they expected triplet-triplet energy transfer (Dexter mechanism) and we expect triplet-singlet energy transfer (Förster mechanism).

The efficiency of energy transfer from host triplet to the ligand singlet is given by [11]

$$\eta_{ET} = \frac{k_{ET}}{k_{ET} + k_R + k_{NR}} \qquad (1)$$

where k_{ET} is the rate of the Förster energy transfer from host

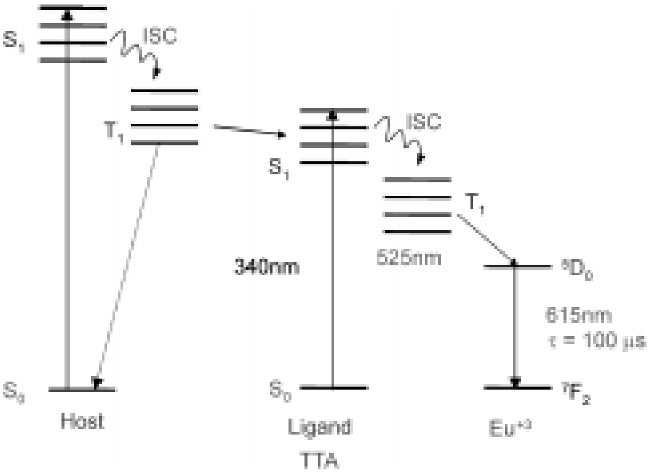


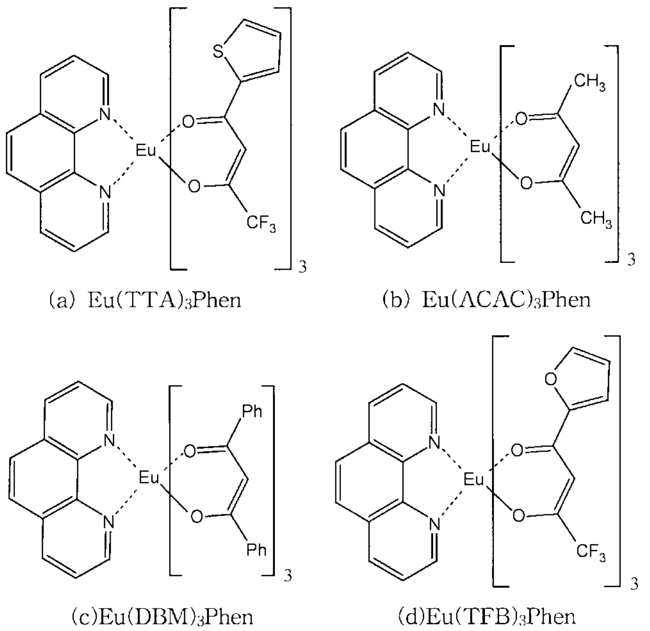
Figure 1. Proposed energy transfer mechanisms of Eu(TTA)$_3$Phen-doped phosphorescent host.

triplet to ligand singlet and k_R and k_{NR} are the radiative and non-radiative rates on the host, respectively. In Förster's theory k_{ET} is proportional to k_R. Thus, if the host is efficiently phosphorescent then it is possible to obtain triplet-singlet energy transfer by the Förster mechanism. Such triplet-singlet energy transfer were shown by Forrest *et al.*[11]

The PL and EL of lanthanide complexes were affected by the structure of the ligand. Therefore, to design optimal ligands and their energy levels which not only displays a good charge carrier but also gives a high luminescent efficiency are important. Thus, the absorption and emission spectrums have calculated by various method and their electronic character, energy transfer, and EL mechanisms are studied through molecular structure of ligand and energy structure calculation. To resolve the energy transfer mechanism, lanthanide complex is dopped to phosphorescent host material and it has been studied through the overlap between emission spectrum of host material and absorption spectrum of guest material. The chemical structure of lanthanide complexes with various ligands are shown in the Figure 2.

Since, the lanthanide complex is absorbed the energy by the anion ligand neither the neutral ligand nor metal ion, the energy absorption process of lanthanide complex mostly depends on the anion ligand. Thus for the simplicity of the calculation, we calculated the optimization of the ligand structure by attaching on the Mg(II) ion. While Eu(III) ion has three anion ligands and one neutral ligand, Mg(II) has only two anion ligands. Using this simple structure the computational time is saved without changing electronic properties of ligands. This was tested by calculating the absorption of ligands with different kinds of metal ion. We found that HOMO-LUMO gap of anion ligand in different metal ions are almost similar through calculation. That is, light absorption of lanthanide complex is absorbed by anion ligand. Based on this fact, anion ligand is calculated with simple metal ion instead of more complex ion to calculate absorption efficiency and PL of the lanthanide complex.

The calculation method was studied with the aid of the HyperChem molecular modelling package[12] at PIII 600 MHz. Semiempirical molecular orbital calculation were done by the PM3 methods for geometry optimizations and electronic transition energies (absorption and fluorescence) were calculated by the ZINDO/S method.[13-15] For the comparison, ab initio (HF/6-31G*) and hybrid HF/DFT (B3LYP/6-31G*) computations for geometry optimizations using Gaussian 94[16] at PIII 1GHz were carried out. The procedure of calculation is following: (1) optimized structure of Mg(II) complexes are calculated by semiempirical PM3 method, ab initio (HF/6-31G*) and hybrid HF/DFT (B3LYP/6-31G*) for absorption efficiency depending on ligands. (2) electronic ground state absorption spectrum based on above structure is obtained through configurational interaction (CI) of ZINDO/S. (3) From this absorption spectrum, energy state and absorption intensity of excited singlet state of anion ligand are found. Triplet states are also calculated using the same procedure except the spin multiplicity. The calculated absorption wavelength of Mg(II) complexes by different geometry optimization methods and experimental results of Eu(III) complexes with same anion ligand are summarized in Table 1.



(a) Eu(TTA)$_3$Phen (b) Eu(ACAC)$_3$Phen

(c)Eu(DBM)$_3$Phen (d)Eu(TFB)$_3$Phen

Figure 2. Chemical structures of Europium complexes.

Compared to calculated and experimental results, it is found that the absorption peak were varied by changing the anion ligand. The absorption peak of ACAC ligand are clearly at shorter wavelengths than those of DBM ligand. This is due to a decreased conjugation of β-diketone. The longer conjugation length of β-diketone anion ligand of lanthanide complexes, absorption spectrum is shifted to long wavelength. Also, the absorption peak of TTA and TFB ligands are shown in between ACAC and DBM ligands because the conjugation length are in between. However, TTA ligand which has two electron withdrawing functional group was shifted to longer wavelength than TFB ligand with one electron donating group. Absorption peak regions are shifted to shorter wavelength changing from electron

Table 1. The Comparison of anion ligands absorption wavelength calculated by PM3 and *ab initio* (HF/6-31*G, B3LYP/6-31G*) (Geometry Optimized) and ZINDO/S(CI) in Mg(II) complexes and experimental results in Eu(III) complexes with same anion ligand

Anion ligand	Exp [nm][17]	Calc. [nm]-singlet		
		PM3/ ZINDO/S (CI)	HF/6-31G* ZINDO/S (CI)	B3LYP/ 6-31G* ZINDO/S(CI)
ACAC	288	286	284	288
TTA	343	338	326	340
TFB	337	336	330	337
DBM	353	327	325	343

Table 2. The table perform geometry optimizations and compute zero-point energy corrections and final total energy values with the identical model chemistry[19] (MAD; mean absolute deviation from experiment)

Model Chemistry	MAD (kal/mol)	StdDev
B3LYP/6-31G*	7.9	9.5
PM3	17.2	14.0
HF/6-31G*	51.0	41.2

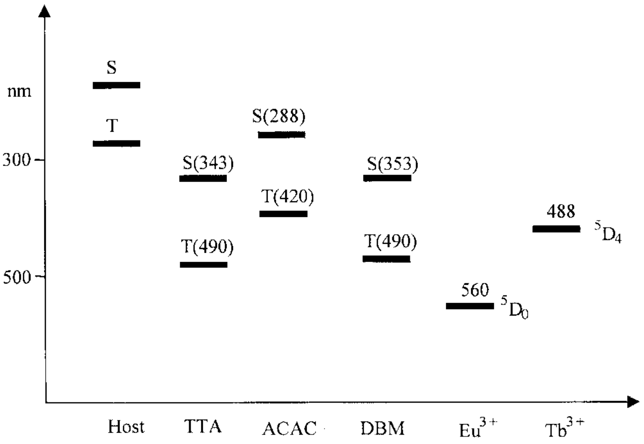


Figure 3. Singlet-triplet state energy level of each ligand and host, Eu^{3+}, Tb^{3+} central metal ion energy levels.

withdrawing to electron donating. The reason can be explained that large resonance effect of electron donating substitute makes π^* state away from n state. If we can calculate absorption spectrum with kinds of ligand, we may see the effect of substitute on absorption characteristics. Thus, we intend to design Eu complex being able to efficient energy transfer by changing conjugation length of β-diketone and/or by substitute functional group in anion ligand of lanthanide complex.[18] From Gaussian 94, the difference between the computed and experimental values and their standard deviations are shown in Table 2. MAD means the average difference between the computed and experimental values ignoring the sign. From Table 1 and 2, B3LYP/6-31G* method is the most robustness method to reproduce experimental data.

As shown Figure 1, EL efficiency of lanthanide complex is very sensitive to the singlet state energy as well as triplet state energy of anion ligand. The reason is that triplet state energy, second ground state of anion ligand of lanthanide complex, gives a larger effect on energy transfer between anion ligand and central metal ion than singlet state energy. Although the efficiency of EL process is effected by singlet state energy of anion ligand, it is also effected by rate constant of inter-system crossing to be triplet state. Because triplet energy state is changed in case of changing substitute of anion ligand, one may find an optimized molecular structure of triplet state by calculating triplet state energy of ligands. Thus, taking the spin multiplicity as triplet, the geometry optimization was carried out by semiempirical PM3 method, ab initio (HF/6-31G*) and hybrid HF/DFT (B3LYP/6-31G*). After the geometry optimization, triplet state energy can be calculated by configurational interaction (CI) from the electronic ground state whose geometry is fixed in the optimized structure of triplet state. Thus triplet state energy can be obtained through this absorption spectrum. Singlet and triplet state energy level of each ligand and Eu^{3+}, Tb^{3+} central metal ion energy levels are shown in Figure 3.

As shown in Figure 3, the triplet of the host phosphorescent materials is higher than the ligand singlet. However, phosphorescence in organic molecules is very few at room temperature. Our first candidate of host material is 2,2,2-triphenylacetophenone (TPAP) and their emission spectrum is around 340 nm. Furthermore, the ligand triplet is higher than the $^5D_0$ levels of the Eu^{3+} ion. This energy structure is planned so as to achieve a smooth energy transfer from the host to the ligand and then emission from the ^5D levels of the Eu^{3+} ion. From the spin multiplicity, the host triplet could be generated three times more than the host singlet. Thus, using this mechanism, EL efficiency can be reached nearly quadruple of the fluorescent EL devices.

In case of Eu^{3+}, the anion ligand (TTA or DBM) absorbs energy and is excited to its singlet state, through inter-system crossing, transit to its triplet state, then intra-molecular energy transfer to the energy level of the Eu^{3+} ion and luminescence is emitted when transition to the ground state occurs. And also in case of Tb^{3+}, efficient luminescence is shown at anion ligand, ACAC. However, in case of Eu^{3+} and anion ligand, ACAC, the energy gap is so big that energy transfer efficiency is decreased and emission efficiency is low. Tb^{3+} and anion ligand, TTA and DBM is hardly transferred to intra-molecular energy states to show no emission, too.

In conclusion, we proposed a new energy transfer mechanism to overcome triplet-triplet annihilation by the Eu complex doped into phosphorescent materials with triplet levels that were higher than singlet levels of the Eu complex. Since triplet-triplet annihilation occur between host triplet transferred from the ligand triplet, we need a energy transfer mechanism which can avoid triplet-triplet energy transfer between the host and ligand and at the same time it has to use the triplet state energy of the host. The triplet-triplet energy transfer by the Dexter mechanism is possible due to the host and ligand having the similar energy levels. Thus, in case of using phosphorescent host, we can use triplet states and also, if the triplet level of phosphorescent host is higher than the singlet level of the ligand of the Eu complex, triplet-triplet annihilation can be prevented from energy gap.

In order to show the feasibility of the proposed energy transfer mechanism and to obtain the optimal ligands, the effect depending on ligands as a factor that controls emission intensity in lanthanide complexes has been calculated. The calculation shows that the longer conjugation length of β-diketone anion ligand of lanthanide complexes, absorption spectrum is shifted to long wavelength. Also triplet state as well as singlet state of anion ligand affects on absorption efficiency indirectly. From comparing between calculation data and experimental data, absorption spectra using hybrid HF/DFT (B3LYP/6-31G*) is the most robustness method to reproduce experimental data. From this proposed mechanism, we may anticipate organic materials with a high quantum efficiency using a suitable phosphorescent host and ligand of Eu complex.

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References

1. Depp, S. W.; Howard, W. E. *Sci. Am.* **1993,** 90.
2. Tang, C. W.; VanSlyke, S. A. *Appl. Phys. Lett.* **1987**, *51*, 913.
3. (a) Tang, C. W.; VanSlyke, S. A.; Chen, C. H. *J. Appl. Phys.* **1989**, *65*, 3610. (b) Jeon, E.-G.; Choy, J. H.; Choi, Q. W.; Kim, H. *Bull. Korean Chem. Soc.* **1985**, *6*, 304. (c) Kang, S.-J.; Jung, Y. S.; Sohn, Y. S. *Bull. Korean Chem. Soc.* **1997**, *18*, 75.
4. Burrought, J. H.; Bradley, D. D. O.; Brown, A. R.; Marks, R. N.; Mackay, K.; Friend, R. H.; Burn, P. I.; Holmes, A. B. *Nature* **1990**, *347*, 539.
5. Kido, J.; Nagai, K.; Okamoto, Y. *J. Alloys and Compounds* **1993**, *192*, 30.
6. Weissman, S. I. *J. Chem. Phys.* **1942**, *10*, 214.
7. Crosby, G. A.; Whan, R. E.; Freeman, J. J. *J. Phys. Chem.* **1962**, *66*, 2493.
8. Dawson, W. R.; Krop, J. L.; Windsor, M. W. *J. Chem. Phys.* **1966**, *45*, 2410 .
9. Baldo, M. A.; Thompson, M. E.; Forrest, S. R. *Pure Appl. Chem.* **1999**, *71*, 2095.
10. Adachi, C.; Baldo, M. A.; Forrest, S. R. *Journal of Appl. Phys.* **2000**, *87*, 8049.
11. Baldo, M. A.; Thompson, M. E.; Forrest, S. R. *Nature* **2000**, *403*, 750.
12. HyperChem 5.0; Dewar, M. J. S., *AM1*; Stewart, J. J. P.; Seiler, F. J., *PM3*; Zerner, M.C., *ZINDO*; Hypercube. Inc.: 1996.
13. Anderson, W. P.; Edwards, W. D.; Zerner, M. C. *Inorg. Chem.* **1986**, *25*, 2728.
14. Anderson, W. P.; Cundari, T. R.; Dargo, R. S.; Zerner, M. C. *Inorg. Chem.* **1990**, *29*, 1.
15. Holmes, A. B.; Bradley, D. D. C.; Brown, A. R.; Burn, P. L.; Burroughes, J. H.; Friend, R. H.; Greenham, N. C.; Gymer, R. W.; Halliday, D. A.; Jackson, R. W.; Kraft, A.; Martens, J. H. F.; Pichler, K.; Samuel, I. D. W. *Synth. Met.* **1993**, *55*, 4031.
16. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. L.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A.; *Gaussian Revision*, B. 3; Gaussian Inc.: Pottsburgh, PA, 1995.
17. Dirr, S.; Johannes, H.; Schobel, J.; Ammermann, D.; Bohler, A.; Kowalsky, W. *SID 97 DIGEST* **1997**, 778.
18. Uekawa, M.; Miyamoto, Y.; Ikeda, H.; Kaifu, K.; Nakaya, T. *Bull. Chem. Soc. Jpn.* **1998**, *71*, 2253.
19. Foresman, J. B. *Exploring Chemistry with Electronic Structure Methods* **1996**, 147.