Photoluminescent Properties of Eu(III) in the Composite Heterocyclic Ligands/Crown Ether Systems

Hong-Guo Liu,[†,§] Kiwan Jang,[‡] Xu-Sheng Feng,[§] Changdae Kim,[#] Young-Jae Yoo,[†] and Yong-Ill Lee[†,*]

[†]*Department of Chemistry and* [‡]*Department of Physics, Changwon National University, Changwon 641-773, Korea*
[*]*E-mail: yilee@sarim.changwon.ac.kr*
[§]*Key Laboratory for Colloid & Interface Chemistry of Education Ministry, Shandong University, Jinan 250100, China*
[#]*Department of Physics, Mokpo National University, Mokpo 534-729, Korea*
Received April 14, 2005

Composite systems of $Eu(phen)_2Cl_3(H_2O)_2$, Eu(DN-bpy)$phenCl_3(H_2O)_2$ and Eu(DB-bpy)$phenCl_3(H_2O)_2$ (DN-bpy: 4,4'-Dinonyl-2,2'-dipyridyl; DB-bpy: 4,4'-Di-*tert*-butyl-2,2'-dipyridyl) with crown ethers of Benzo-15-crown-5 (B15C5), Benzo-18-crown-6 (B18C6), 18-crown-6 (18C6), Dibenzo-18-crown-6 (DB18C6) and Dibenzo-24-crown-8 (DB24C8) were fabricated successfully and characterized by using photoluminescent spectroscopy and luminescent lifetime measurements. All composites formed show high luminescence mainly in red region. It was found that the heterocyclic ligands such as phen, DN-bpy and DB-bpy as well as the crown ethers have great influences on the photoluminescent properties of Eu^{3+} ion. The environment around Eu^{3+} ion in the composite systems changes greatly,presumably the variation of the first coordination sphere. The Eu^{3+} ion occupies higher symmetrical environment and in more than one kind of symmetrical site in the composite systems studied in this work.

Key Words : Europium complex, Crown ether, Photoluminescence, Heterocyclic ligand

Introduction

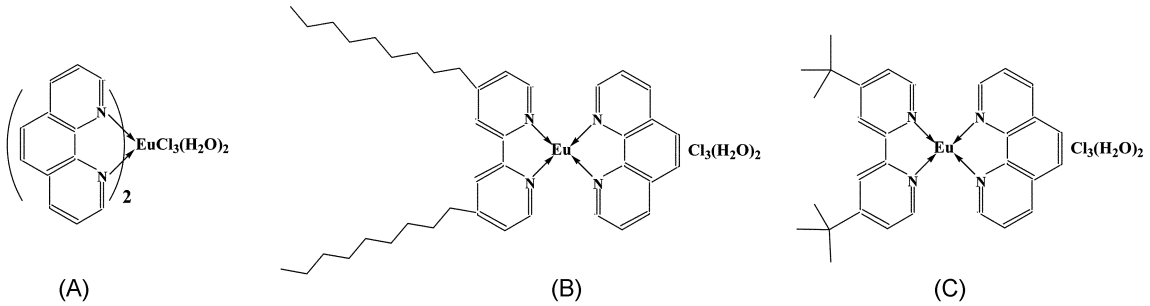
Eu(III) complexes with macrocyclic ligands, such as crown ethers, cryptands, cyclodextrins and calixarenes have been studied extensively because of their unique luminescent properties and potential applications.[1] The central Eu^{3+} ion is incorporated in the cavities of the ligands, which protects the Eu^{3+} from the interaction with small ligands, such as H_2O. It is well known that H_2O can quench the fluorescence of Eu(III). Some europium/crown ether binary complexes were synthesized and the structures and properties were characterized.[2-5] As we know, β-diketones and heterocyclic ligands, such as *phen* and *bpy* can absorb UV-light and transfer the energy to Eu^{3+} ions effectively in the complexes; then the luminescent quantum yields of Eu(III) enhance greatly.[6]

Although the characteristic chemistry of crown ethers involving complexation of ether oxygens with various ionic species has been well documented, its adaptation for the development of photoluminescent materials was not carried out yet except a few studies on the photoluminescence of ternary complexes of Eu^{3+}/crown ether/β-diketone.[7-9] In this paper, the composite systems of $Eu(phen)_2Cl_3(H_2O)_2$, Eu(DN-bpy)$phenCl_3(H_2O)_2$ and Eu(DB-bpy)$phenCl_3(H_2O)_2$ with various crown ethers, B15C5, B18C6, 18C6, DB18C6 and DB24C8 were fabricated and their photoluminescent properties were characterized. The influences of ligands on the luminescent properties of Eu(III) were investigated systematically by the use of photoluminescent spectroscopy and luminescent lifetime measurements.

Experimental Section

Reagents and samples. Eu_2O_3 (99.95%), 1,10-Phenanthroline, phen (99+%), 4,4'-Dinonyl-2,2'-dipyridyl, DN-bpy (97%), 4,4'-Di-tert-butyl-2,2'-dipyridyl, DB-bpy (98%), Benzo-15-crown-5, B15C5 (98%), Benzo-18-crown-6, B18C6 (98%), 18-crown-6, 18C6 (99.5+%), Dibenzo-18-crown-6, DB18C6 (98%) and Dibenzo-24-crown-8, DB24C8 (98%) were purchased from Aldrich Chemical Company and used without further purification. The complexes $Eu(phen)_2Cl_3(H_2O)_2$, Eu(DN-bpy)$phenCl_3(H_2O)_2$ and Eu(DB-bpy)$phenCl_3(H_2O)_2$ (shown in Scheme 1) were synthesized according to the literature methods[10] and dried in air at room temperature. The elemental analysis of the complexes results: $Eu(phen)_2Cl_3(H_2O)_2$: C: 43.0% (44.0%); H: 3.30% (3.08%); N: 8.59% (8.56%); Eu(DN-bpy)phen-$Cl_3(H_2O)_2$: C: 55.0% (54.4%); H: 6.91% (6.39%); N: 6.35% (6.34%); Eu(DB-bpy)$phenCl_3(H_2O)_2$: C: 48.3% (48.5%); H: 5.39% (4.88%); N: 7.51% (7.54%). The values in parentheses are calculated ones. The synthesized complexes were characterized further by FTIR and UV-vis spectroscopy which show different features from those of the ligands,[11,12] presumably the formation of the complexes.

Sample preparation and characterization. Composite systems of the complexes with the crown ethers were prepared by dissolving these components with an equal molar ratio into ethanol/chloroform. The samples for photoluminescent spectroscopy and luminescent lifetime measurements were prepared by casting the organic solutions onto clean glass slides. The solvent was allowed to evapo-



Scheme 1. Molecular structures of the europium complexes; (A) $Eu(phen)_2Cl_3(H_2O)_2$, (B) $Eu(DN\text{-}bpy)phenCl_3(H_2O)_2$ and (C) $Eu(DB\text{-}bpy)phenCl_3(H_2O)_2$.

rate in air at room temperature.

Photoluminescent spectra were obtained by use of a PC 2000 spectroscope (Ocean Optics Inc) with the excitation at 325 nm using a He-Cd laser (Omnichrome, LC-500). Decay curves were accomplished by monitoring the 612-614 nm emission by using 300 MHz-digital oscilloscope (LeCroy 9310, Switzerland) and triple grating monochromator (Spectra Pro-750 ARC Actron, Research Corporation, MA) under the excitation at 355 nm dye laser (Spectron SL 4000B/G, Spectron laser systems, UK) at room temperature.

Results and Discussion

$Eu(phen)_2Cl_3(H_2O)_2$/crown ether systems. Typical emission spectra of pure $Eu(phen)_2Cl_3(H_2O)_2$ and the composite systems with various crown ethers were shown in Figure 1. As can be seen, five emission bands corresponding to $^5D_0 \rightarrow {}^7F_{0,1,2,3,4}$ transitions of Eu^{3+} appear in each spectrum. All the spectra observed are similar to one another. The comparison of the intensities between "hypersensitive" electric dipole ($^5D_0 \rightarrow {}^7F_2$ transition) and magnetic dipole ($^5D_0 \rightarrow {}^7F_1$ transition) were considered for evaluating the micro environment around Eu^{3+} ion. The intensity ratios of $I(^5D_0 \rightarrow {}^7F_2)/I(^5D_0 \rightarrow {}^7F_1)$ values for the composites are illustrated in Table 1 and are very close to one another ranging from 3.4 to 3.8. However, the luminescent lifetimes (τ_1 and τ_2) of $^5D_0$ level of Eu^{3+} ions in these systems show different features compared to those of Eu complex, $Eu(phen)_2Cl_3(H_2O)_2$. The decay curves were fitted by bi-exponential functions and the measured lifetime values are listed in Table 2. It can be seen that the composite systems containing B15C5, B18C6 and 18C6 give similar results and those containing DB18C6 and DB24C8 are comparable each other. The luminescent lifetimes of the composites of DB18C6 and DB24C8 are much shorter than those of B15C5, B18C6 and 18C6. These

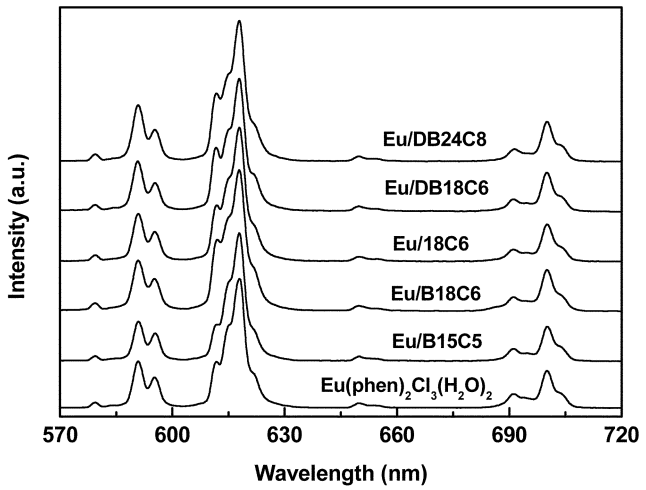


Figure 1. Typical emission spectra of $Eu(phen)_2Cl_3(H_2O)_2$ and the composite systems with crown ethers.

Table 1. Relative intensities of $^5D_0 \rightarrow {}^7F_2$ and $^5D_0 \rightarrow {}^7F_1$ emission bands

Systems	$I(^5D_0 \rightarrow {}^7F_2)/I(^5D_0 \rightarrow {}^7F_1)$
$Eu(phen)_2Cl_3(H_2O)_2$/B15C5	3.8
$Eu(phen)_2Cl_3(H_2O)_2$/B18C6	3.7
$Eu(phen)_2Cl_3(H_2O)_2$/18C6	3.7
$Eu(phen)_2Cl_3(H_2O)_2$/DB18C6	3.8
$Eu(phen)_2Cl_3(H_2O)_2$/DB24C8	3.4
$Eu(phen)_2Cl_3(H_2O)_2$	3.6
$Eu(DN\text{-}bpy)phenCl_3(H_2O)_2$/B15C5	2.7
$Eu(DN\text{-}bpy)phenCl_3(H_2O)_2$/B18C6	3.1
$Eu(DN\text{-}bpy)phenCl_3(H_2O)_2$/18C6	3.3
$Eu(DN\text{-}bpy)phenCl_3(H_2O)_2$/DB18C6	2.2
$Eu(DN\text{-}bpy)phenCl_3(H_2O)_2$/DB24C8	2.1
$Eu(DN\text{-}bpy)phenCl_3(H_2O)_2$	3.3
$Eu(DB\text{-}bpy)phenCl_3(H_2O)_2$/B15C5	3.3
$Eu(DB\text{-}bpy)phenCl_3(H_2O)_2$/B18C6	3.3
$Eu(DB\text{-}bpy)phenCl_3(H_2O)_2$/18C6	4.0
$Eu(DB\text{-}bpy)phenCl_3(H_2O)_2$/DB18C6	2.1
$Eu(DB\text{-}bpy)phenCl_3(H_2O)_2$/DB24C8	2.4
$Eu(DB\text{-}bpy)phenCl_3(H_2O)_2$	2.4

Table 2. Lifetime data of $^5D_0$ level of Eu^{3+} in the composite systems of $Eu(phen)_2Cl_3(H_2O)_2$ with crown ethers

System	τ_1 (μs)	τ_2 (μs)
B15C5	277	123
B18C6	301	80
18C6	266	117
DB18C6	214	39
DB24C8	200	25
Eu complex	175	1153

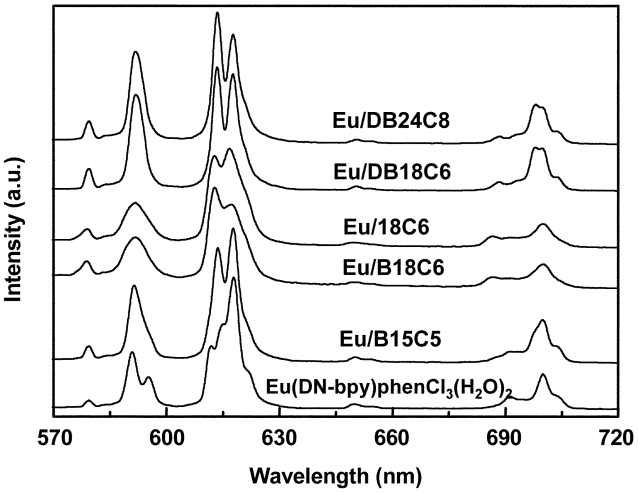


Figure 2. Typical emission spectra of Eu(DN-bpy)phen$Cl_3(H_2O)_2$ and the composite systems with crown ethers.

Table 3. Lorentzian fitting data of the $^5D_0 \rightarrow {}^7F_0$ emission bands and lifetime data for the composite systems of Eu(DN-bpy)phen$Cl_3(H_2O)_2$ with crown ethers

System	λ (nm)	ν (cm^{-1})	Δν (cm^{-1})	τ (μs)
B15C5	579.74	17249	−125	329
	578.84	17276	−98	117
B18C6	579.47	17257	−117	240
	578.48	17287	−87	72
	576.66	17341	−33	10
18C6	579.50	17256	−118	195
	578.53	17285	−89	75
	577.02	17330	−44	20
DB18C6	579.67	17251	−123	192
	578.76	17278	−96	32
DB24C8	579.68	17251	−123	190
	578.78	17278	−96	28
Eu complex	579.67	17251	−123	328
	578.78	17278	−96	36

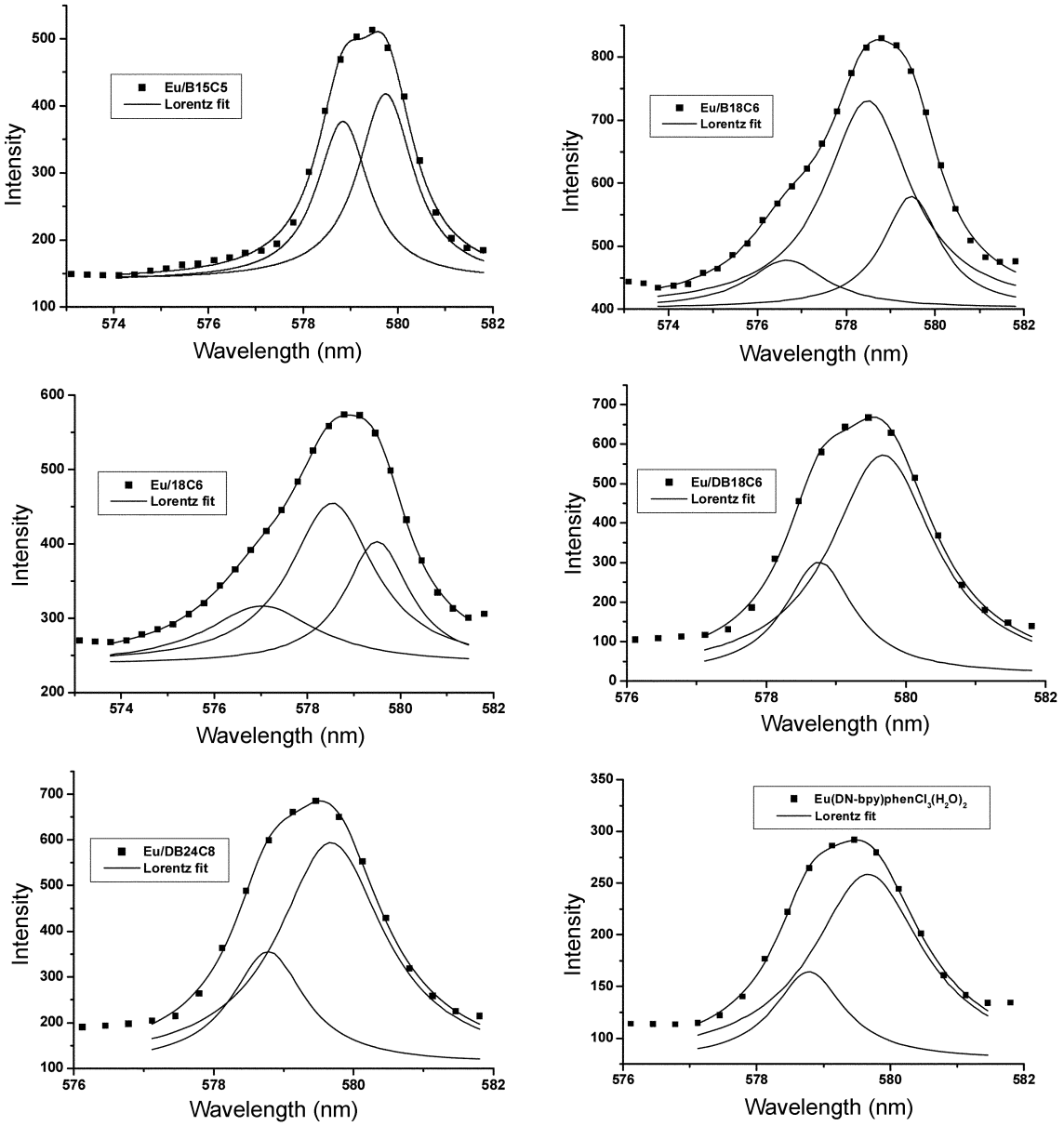


Figure 3. Lorentzian fitting curves of $^5D_0$-$^7F_0$ emission bands for Eu(DN-bpy)phen$Cl_3(H_2O)_2$ and the composite systems with crown ethers.

experimental results indicate that the crown ethers have different effects on the PL properties of Eu^{3+} ions depending on the molecular structure of crown ethers.

Eu(DN-bpy)phen$Cl_3(H_2O)_2$/crown ether systems. Figure 2 shows the emission spectra of Eu(DN-bpy)phen$Cl_3(H_2O)_2$ and its composite systems with crown ethers. Generally, five emission bands were observed for both the Eu complex and composites. The spectrum profiles of the composites have quite different features compared to those of the Eu complex. As can be seen in Figure 2, two and four emission peaks can be distinguished for $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ transitions, respectively in the spectrum of Eu(DN-bpy)-phen$Cl_3(H_2O)_2$. While, only one for $^5D_0 \rightarrow {}^7F_1$ and two peaks for $^5D_0 \rightarrow {}^7F_2$ were appeared for the composite systems. It also can be noticed that the spectra for the composite systems with B18C6 and 18C6 are similar to each other and so do to those with DB18C6 and DB24C8. These results indicate that crown ethers have great influences on the PL properties of Eu^{3+} ions related to their structures. The $I(^5D_0 \rightarrow {}^7F_2)/I(^5D_0 \rightarrow {}^7F_1)$ values of the composite systems with DB18C6 and DB24C8 shown in Table 1 are much less than that of the complex, indicating that the Eu^{3+} ions occupy higher symmetrical environments in the composite systems.

The decay curves of the $^5D_0$ level of Eu^{3+} in these composite systems can be fitted by bi- or tri-exponential functions. The data presented suggest that more than one kind of symmetrical sites of Eu^{3+} ions in composites. The lifetime values listed in Table 3 are similar to each other for the systems with B18C6 and 18C6, or with DB18C6 and DB24C8. For Eu^{3+} ion, the emitting state $^5D_0$ and the ground state $^7F_0$ are non-degenerated and cannot be split by the ligand field. Therefore, $^5D_0 \rightarrow {}^7F_0$ transition can be used as a probe to detect different environments, because one symmetrical site gives only one $^5D_0 \rightarrow {}^7F_0$ emission peak. The $^5D_0 \rightarrow {}^7F_0$ or $^7F_0 \rightarrow {}^5D_0$ transition band can be resolved into individual peaks by Guassian[13] or Lorentzian function.[14] According to Horrocks *et al.*,[15] the most accurate description can be obtained for solid complexes with the Lorentzian function. Figure 3 presents the Lorentzian fitting curves for $^5D_0 \rightarrow {}^7F_0$ transition bands. The detail data are summarized in Table 3. The $^5D_0 \rightarrow {}^7F_0$ transition bands in the spectra of the composite systems with B15C5, DB18C6 and DB24C8 can be resolved into two peaks, while those of the systems with B18C6 and 18C6 can be resolved into three peaks. The differences between these curves imply the influences of the crown ethers on the PL properties of Eu^{3+} ions. It can be induced either fluxional Eu(III) environments or the presence of several sites with only slightly different environments from rather broadening of the components in Table 3, as observed for lanthanide dinuclear complexes with *p*-nitrocalix[8]arene.[13]

The transition energy of $^5D_0 \rightarrow {}^7F_0$ transition can be related to the first coordination sphere around Eu^{3+} ion by the *nephelauxetic effect*[14]; $\Delta\nu = \nu - \nu_0$, where ν is the experimental value, ν_0 represents the ν-value of the gaseous Eu^{3+} ion with no coordinating atoms and ν_0 value was chosen as 17374 cm^{-1}.[16] The $\Delta\nu$ value also reflects the first coordination sphere around Eu^{3+} ions. From the $\Delta\nu$ values listed in Table 3, the environment around Eu^{3+} ions in the composite systems change greatly with comparison to those of the complex, which can postulate the variation of the first coordination sphere as a result of the interaction between the crown ethers and Eu^{3+} ions.

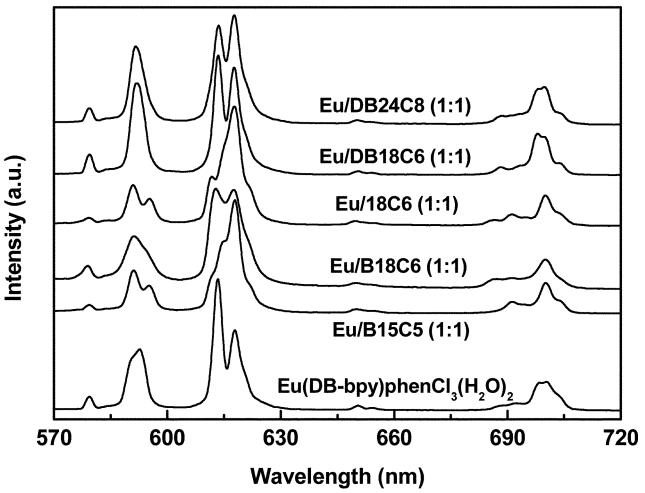


Figure 4. Typical emission spectra of Eu(DB-bpy)phen$Cl_3(H_2O)_2$ and the composite systems with crown ethers.

Table 4. Lorentzian fitting data of the $^5D_0 \rightarrow {}^7F_0$ emission bands and lifetime data for the composite systems of Eu(DB-bpy)phen$Cl_3(H_2O)_2$ with crown ethers

System	λ (nm)	ν (cm^{-1})	Δν (cm^{-1})	τ (μs)
B15C5	579.67	17251	−123	213
	578.76	17278	−96	95
	575.96	17362	−12	19
B18C6	579.51	17256	−118	200
	578.71	17283	−91	122
	576.77	17338	−36	34
18C6	579.84	17246	−128	277
	578.93	17273	−101	106
	576.61	17343	−31	24
DB18C6	579.66	17251	−123	182
	578.75	17279	−95	27
DB24C8	579.67	17251	−123	190
	578.78	17278	−96	23
Eu complex	579.63	17252	−122	229
	578.71	17280	−94	112

Eu(DB-bpy)phen$Cl_3(H_2O)_2$/crown ether systems. The emission spectra of the composite systems of Eu(DB-bpy)phen$Cl_3(H_2O)_2$ with crown ethers are also different from that of the pure complex, as shown in Figure 4. The spectra of the systems with DB18C6 and DB24C8 are similar to each other, so are the spectra of the systems with B15C5 and 18C6, showing different influences related to their structures of crown ethers. The $I(^5D_0 \rightarrow {}^7F_2)/I(^5D_0 \rightarrow {}^7F_1)$ data listed in Table 1 give this trend, too. The luminescent decay curves of $^5D_0$ level of Eu^{3+} ions in these systems

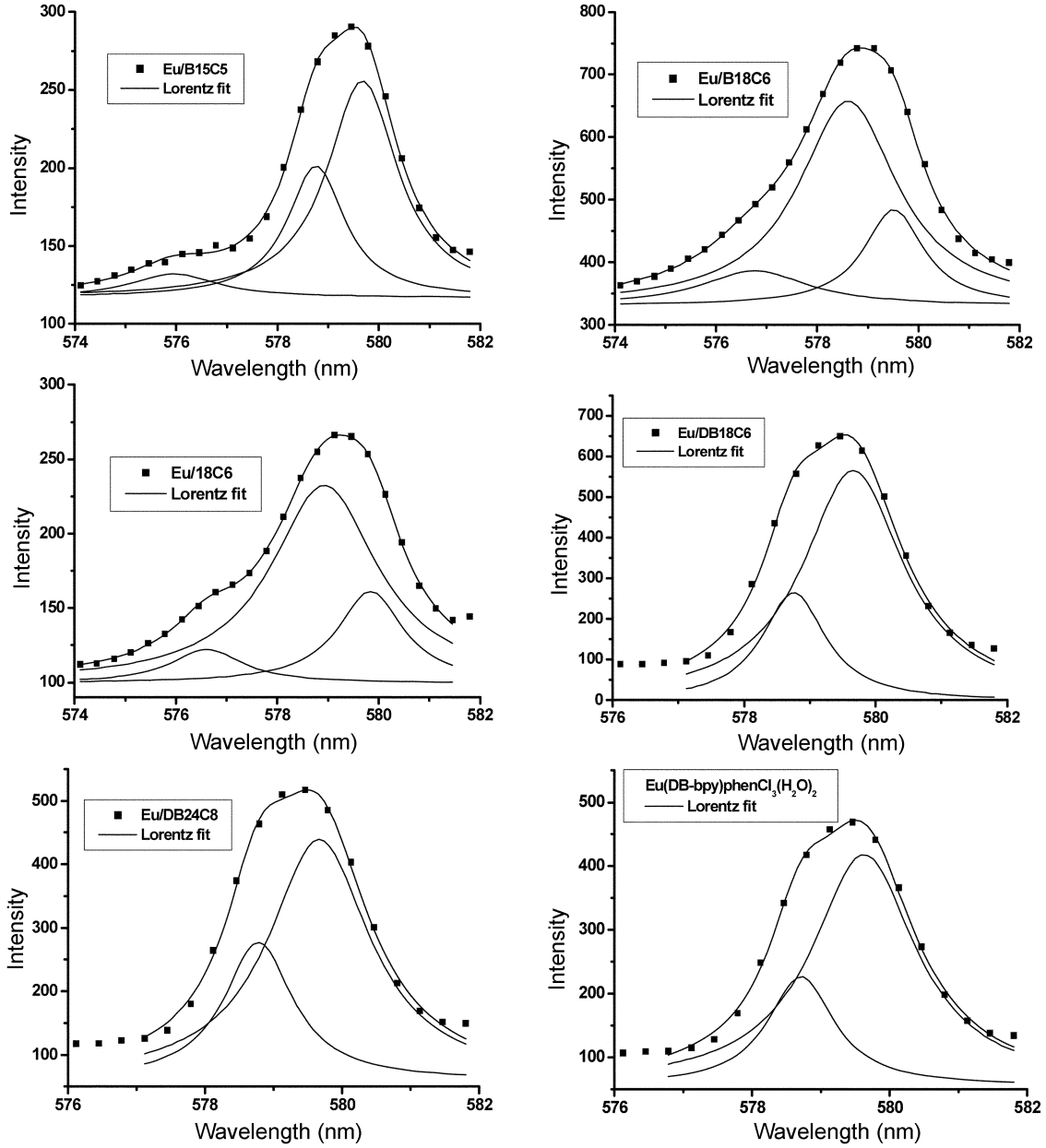


Figure 5. Lorentzian fitting curves of $^5D_0$-$^7F_0$ emission bands for Eu(DB-bpy)phen$Cl_3(H_2O)_2$ and the composite systems with crown ethers.

were fitted by bi- or tri-exponential functions and the lifetime data are summarized in Table 4. Figure 5 shows the $^5D_0 \rightarrow {}^7F_0$ emission bands of the composite systems of Eu(DB-bpy)phen$Cl_3(H_2O)_2$ with crown ethers fitted by Lorentzian function. For the systems with B15C5, B18C6 and 18C6, the $^5D_0 \rightarrow {}^7F_0$ emission bands can be resolved into three peaks, and two peaks can be obtained for the other systems. This result agrees with the PL spectral features of $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ bands, the relative intensities of the two bands and the lifetime data. Just like the systems containing Eu(DN-bpy)phen$Cl_3(H_2O)_2$, the emission peaks are broad, indicating the presence of several sites with only slightly different coordination environments. The different peak positions listed in Table 4 mean that the crown ethers have great influences on the first coordination sphere around Eu^{3+} ions according to *nephelauxetic effect*.

Conclusions

Experimental results obtained in this work show that not only the crown ethers but also the heterocyclic ligands; phen, DN-bpy and DB-bpy, have great influences on the PL behaviors of Eu^{3+} ions. It should be attributed to different molecular structures, such as different substituted alkyl chains in the heterocyclic ligands, the different numbers of oxygen atoms and the benzene rings of the crown ethers. Moreover, the difference in molecular structure leads to various interaction abilities and first coordination sphere of Eu(III). The work presented here validates the PL properties

of the composite heterocyclic ligands/crown ether systems and can provides the useful information for some applications including the broadening of $^5D_0 \rightarrow {}^7F_2$ emission band for laser tuning and the inhomogeneous broadening of $^5D_0 \rightarrow {}^7F_0$ transition for hole-burning materials.

Acknowledgments. The authors gratefully acknowledge the support by the Korea Research Foundation (Grant No.; KRF 2000-005-Y00071) and Changwon National University.

References

1. Bünzli, J.-C. G.; Pigust, C. *Chem. Rev.* **2002**, *102*, 1897.
2. Bünzli, J.-C. G.; Pradervand, G.-O. *J. Chem. Phys.* **1986**, *85*, 2489.
3. Hassaballa, H.; Steed, J. W.; Junk, P. C.; Elsegood, M. R. J. *Inorg. Chem.* **1998**, *37*, 4666.
4. Saleh, M. I.; Salhin, A.; Saad, B.; Fun, H.-K. *J. Mol. Struc.* **1999**, *475*, 93.
5. Yamamura, T.; Sugiyama, W.; Hotokezaka, H.; Harada, M.; Tomiyasu, H.; Nakamura, Y. *Inorg. Chim. Acta* **2001**, *320*, 75.
6. You, B.; Kim, H. J.; Park, N. G.; Kim, Y. S. *Bull. Korean Chem. Soc.* **2001**, *22*, 9.
7. Brito, H. F.; Malta, O. L.; Carvalho, C. A. A.; Menezes, J. F. S.; Souza, L. R.; Ferraz, R. *J. Alloys Comp.* **1998**, *275-277*, 254.
8. Meguro, Y.; Kitatsuji, Y.; Kimura, T.; Yoshida, Z. *J. Alloys Comp.* **1998**, *271-273*, 790.
9. Brito, H. F.; Malta, O. L.; Souza, L. R.; Menezes, J. F. S.; Carvalho, C. A. A. *J. Non-Cryst. Solids* **1999**, *247*, 129.
10. Jin, T.; Tsutsumi, S.; Deguchi, Y.; Machida, K.; Adachi, G. *J. Alloys Comp.* **1997**, *252*, 59.
11. Liu, H.-G.; Lee, Y.-I.; Feng, X.-S.; Xiao, F.; Zhang, L.; Chen, X.; Jang, K.; Seo, H.-J. *Colloids Surf. A* **2005**, *257-258*, 301.
12. Liu, H.-G.; Lee, Y.-I.; Qin, W.-P.; Jang, K.; Kim, S.; Feng, X.-S. *J. Appl. Polym. Sci.* **2004**, *92*, 3524.
13. Bünzli, J.-C. G.; Ihringer, F. *Inorg. Chim. Acta* **1996**, *246*,195.
14. Carlos, L. D.; Ferreira, R. A. S.; Bermudez, V. D. Z.; Molina, C.; Bueno, L. A.; Ribeiro, S. J. L. *Phys. Rev. B* **1999**, *60*, 10042.
15. McNemar, C. W.; Horrocks Jr, W. D. *Appl. Spectros.* **1989**, *43*, 816.
16. Frey, S. T.; Horrocks Jr, W. D. *Inorg. Chim. Acta* **1995**, *229*, 383.