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The luminescent properties of divalent europium complexes of crown ethers and cryptands

Jianzhuang Jiang [1], Nobuyuki Higashiyama, Ken-ichi Machida,
Gin-ya Adachi *

Department of Applied Chemistry, Faculty of Engineering, Osaka University, 2-1 Yamadaoka,
Suita, Osaka 565, Japan

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Contents

1. Introduction 2
2. The energy-level and configurational-coordinate diagram of Eu^{2+} ion 4
3. Prepatation, stiochiometry and crystal structure of divalent europium (strontium) complexes 6
   3.1. The preparation of divalent europium crown ether, azacrown ether and cryptand as well as their polymeric derivative complexes 7
   3.2. The stiochiometry and crystal structure of divalent europium crown ether, azacrown ether and cryptand as well as their polymeric derivative complexes 9
4. The spectroscopic properties of divalent europium complexes 11
   4.1. The fluorescent properties of divalent europium crown ether, azacrown ether and cryptand complexes 11
   4.2. The luminescent characteristics of divalent europium poly-crown ether and poly-cryptand complexes 20
   4.3. The color-changeable luminescence characteristics of $Eu^{3+/2+}$-15-crown-5 complexes . . 26
5. Concluding remarks 27
Acknowledgements 27
References 28

Abstract

The luminescent properties of divalent europium complexes with crown ether, azacrown ether, N-pivot-azacrown ether, and cryptand in methanol or water have been systematically investigated under UV irradiation. These divalent europium complexes show greatly enhanced

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* Corresponding author. Fax: +81 68797354.

[1] Permanent address: Department of Chemistry, Shandong University, Jinan 250100, People's Republic of China.

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emission from 417 nm to 488 nm in the visible blue region in comparison with that of the methanol solution of $EuCl_2$. The aqueous solution of $EuCl_2$ is non-luminescent. This obvious distinction in luminescent properties between the macrocyclic ligand-coordinated divalent europium and uncoordinated divalent europium is attributed to the "insulation effect" of Eu^{2+} ion from the solvent molecules of CH_3OH and H_2O by the macrocyclic crown ether or cryptand encapsulation to divalent europium. Moreover, these macrocyclic ligands provide an additional restriction to the electronic charge expansion of the excited Eu^{2+}. This also contributes to the enhancement of the Eu^{2+} luminescence. Among all the investigated macrocyclic ligands, 15-crown-5 (15C5) affords the largest enhancement to the Eu^{2+} emission. The intensity of the Eu^{2+}–15C5 complex is 690 times that of the $EuCl_2$ methanol solution with the same Eu^{2+} concentration. This special emission enhancement effect is related to the particular complex composition of 1:3 (Eu^{2+}:15C5) and corresponding configuration of Eu^{2+}–15C5 complex in methanol. Concerning the mechanism, the luminescence enhancement of divalent europium by complexation with these macrocyclic crown ether or cryptand ligands is found to be initiated from the decrease in non-radiative rate constant rather than from the increase in radiative one.

The divalent europium complexes of methacrylate polymeric polyether derivatives such as 15C5-, 18-crown-6- (18C6), and cryptand [2.2.1]- or [2.2.2]-containing polymer and copolymer have also been prepared. Their luminescent properties in solid state have been studied to aim for practical application. As a similar situation to the simple polyether complexes, the divalent europium complex with 15C5-containing polymer or copolymer shows the largest luminescent enhancement effect. Its emission intensity reaches about 20% that of the commercial inorganic luminescence product $CaWO_4$:Pb (NBS 1026). In addition, the doping effect of several divalent ions, namely Mg, Sr, Ba and Zn in polymeric complexes, has also been investigated according to the luminescence concentration quenching mechanism in solid state luminescence materials. The emission intensity of 15C5-containing polymer europium(II) complex is raised to twice stronger by doping of Zn^{2+} ion.

Keywords: Luminescence; Divalent europium; Crown ether complex; Cryptand complex

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1. Introduction

In the early 1940s, rare earths were found for the first time to have important applications in the preparation industry by the great Australian entrepreneur Carl Auer von Welsbach. Since then, they have been the object of much interest for scientific and technological purposes connected with their special electronic configuration and structure. In recent years, with respect to the development of modern science and technology, rare earths have been found to have more and more important applications in preparing materials with special optic, electronic, thermodynamic and magnetic properties. Among them, applications in powerful tunable laser systems as laser source and in biological systems as luminescent probe are especially based on the closed 4f electronic configuration of the corresponding rare earth elements.

In general, the rare earths have a partially filled 4f subshell which lies inside the $5s^25p^6$ closed subshells of the xenon structure. It is therefore screened from the affect of the surrounding anions or dipolar molecules in crystal, vitreous state or coordination compound by these outer electron subshells. This results in minimal perturbation of the electronic transitions between these 4f orbitals of R^{3+} and thus the relative extreme sharpness of the emission bands derived from these transitions. The sharpness of these emission bands is even comparable to that observed in the spectra of free atoms. The luminescent characteristics on the basis of 4f orbital transitions for the tervalent rare earth ion R^{3+} in crystal and vitreous state materials have attracted much research interest and formed the subject of numerous papers [1–10]. A great number of corresponding fluorescent materials have been practically employed in the modern electronic and optic material industry. For example, the Y_2O_3:Eu^{3+} and Y_2O_3S:Eu^{3+} fluorescent materials have been used extensively as the CRT materials in color TV production based on the sharp emission between the transition of $4f^6(^5D_O)$–$4f^6(^7F_J)$ states [11]. Vitreous Nd-containing materials have been applied as a powerful tunable laser source since the early 1980s [12,13]. Moreover, in the form of coordination complexes, these 4f–4f transitions of R^{3+} are similarly hardly perturbed by the ligand coordination field. This is clearly indicated by their similar narrow absorption and emission bands as in crystal and vitreous state materials. Nevertheless, research on fluorescent tervalent rare earth coordination compounds has also been promoted by the consideration that the tailoring of the bulk properties of coordination compound materials can easily be realized by altering the functional group of coordination ligands.

On the other hand, several rare earth elements such as Eu, Yb and Sm possess another substable oxidation state R^{2+} besides the normal R^{3+} state due to the stable half- or completely-filled 4f electron shell in their divalent oxidation state. The electronic configuration for the lowest excited state of divalent rare earths is thus primarily changed to $4f^{q-1}5d^1$ ($q=7$, 14) rather than $4f^q$ for the normal R^{3+} state. This outer 5d subshell is different from the screened deep-lying 4f electrons. It is easily influenced by the surrounding environment, such as the surrounding anions or ligands, and always split to several sublevels according to its crystal or ligand field symmetry. Therefore, the divalent species takes on greatly different luminescent characteristics from the tervalent analogues originated from the 4f–5d transitions. They usually exhibit more than one wide absorption band due to the splitting of the 5d orbital and a wide emission band because of the broadening of the $4f^{q-1}5d^1$ ($q=7$, 14) excited states. Actually, the luminescent properties as well as the magnetic characteristics of these divalent rare earths in solid state form have been well studied and applied in modern industry [14–33]. However, research on their corresponding coordination compounds was not developed until the quite recent reports of Adachi et al. [34] and Sabbatini et al. [35] in the early 1980s, mainly due to the low stability of these divalent rare earth species towards oxygen, especially in solution.

Shortly after the syntheses of crown ether and cryptands in the late 1960s, it was found that the stability of unusual divalent oxidation state rare earth ions coordinated by these macrocyclic ligands was modified to a large degree through the encapsulation effect of these macrocyclic ligands. This motivated Adachi et al. to try to investigate the luminescent properties for the divalent europium crown ether complexes since 1980 [36–41] as an extension to their previous work on the vitreous divalent europium materials [26–33]. Sabbatini et al. carried out similar research on Eu^{2+} cryptand complexes [35,42].

2. The energy-level and configurational-coordinate diagram of Eu^{2+} ion

Fig. 1 shows the energy-level diagram of the Eu^{2+} ion. It establishes the theoretical basis for the luminescent characteristics of the divalent europium, Eu^{2+}, in crystal as well as in coordination form. It is necessary to note that the excited states of $4f^7$ are too high to be fully overlapped with the broad excited states of $4f^65d^1$ because of the very low energy of the ground state of $4f^7$ for Eu^{2+}. According to the broad range of $4f^65d^1$ excited states of Eu^{2+} in Fig. 1, it is easy to understand the broad absorption and emission bands of Eu^{2+} species. However, a more powerful tool in explaining the presence and efficiency of emission is the configurational-

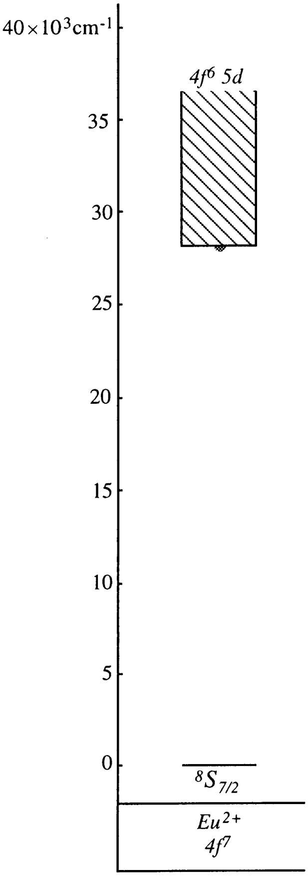


Fig. 1. The energy-level diagram of the Eu^{2+} ion.

coordinate diagram, which is given in Fig. 2 for the divalent europium, Eu^{2+}. The potential energy of the luminescent center, Eu^{2+}, in the crystal lattice or in the coordination ligand field is plotted as a function of the configurational-coordinate r, where r represents the distance of the central Eu^{2+} to the coordination ions or atoms and where only the lowest energy level has been selected and presented here from the continuous broad range of excited state, $4f^65d^1$, for Eu^{2+} ion. At absolute zero temperature, Eu^{2+} occupies the lowest vibrational level of the ground state. It moves to higher vibrational levels with increase in temperature. Due to the absorption of UV radiation, the Eu^{2+} luminescent center is raised to $4f^65d^1$ excited state. The electron charge distribution of Eu^{2+} ion in the $4f^65d^1$ excited state moves somewhat further from the nucleus of the Eu^{2+} ion. The negative charge cloud becomes a little more diffuse. As a consequence, the Eu^{2+} ion assumes a greater positive charge. Therefore the distance between Eu^{2+} and coordination atoms (O and N in crown ether and cryptand complexes) in the excited state becomes smaller than that in the ground state due to the increase of interaction between the excited Eu^{2+} ion and these ligand coordination atoms [43]. This system in the excited state then relaxes towards the lower energy vibrational equilibrium state and those below it to the lowest energy vibrational state by dissipating heat. From these relaxed low energy vibrational states it returns to the ground state, thereby giving emission in a relatively broad range according to the decrease in Eu^{2+}–ligand bond distance, Δr. It thus shows a broad emission band. As the emission transition occurs mainly from the lowest energy vibrational state of the excited level of $4f^65d^1$ to a higher vibrational state of the $4f^7$ ground level due to the different Eu^{2+}–ligand bond distances in ground and excited states, the emission generally lies at a lower energy compared with the absorption. This phenomenon is well known as the Stokes shift in luminescence chemistry [43].

From the configurational-coordinate diagram shown in Fig. 2, one can easily

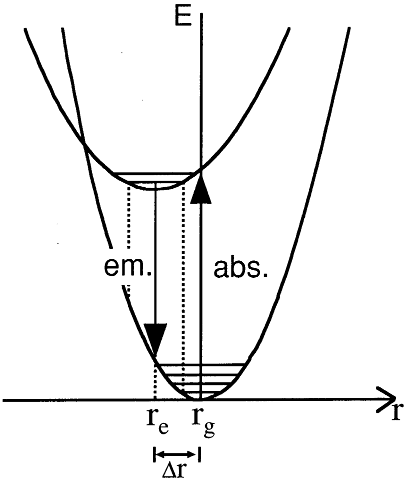


Fig. 2. The configurational-coordinate diagram of Eu^{2+} ion.

understand the luminescence quenching phenomenon initiated by the increase in temperature. As the luminescent center of Eu^{2+} is thermally activated to the intersection point of excited and ground state curves, the system would then non-radiatively return to the ground state by dissipating heat. The luminescence intensity thus decreases with increase of temperature, and the luminescence may completely disappear at a certain value of high temperature. It can be concluded from the configurational-coordinate that the quenching temperature of luminescence is determined by the magnitude of Δr. The larger the absolute value of Δr, the lower the quenching temperature of luminescence. A relative conclusion that the luminescence efficiency at room temperature also depends on the magnitude of Δr can be further deduced.

Another positive effect of the fluorescence of divalent europium by complexation with crown ether or cryptand is reached through the substantial reduction in the non-radiative deactivation process by the macrocyclic ligand encapsulation of divalent europium. These coordinating macrocyclic ligands effectively shield the introduction and perturbation of solvent molecules (H_2O or CH_3OH) from the fluorescent center of Eu^{2+}. They also prevent the progress of photoreaction between H_2O and Eu^{2+} in aqueous solution [44–50].

Concerning research on solid state polymeric polyether complexes, a phenomenon called concentration quenching involved in solid state (crystal or vitreous) luminescence materials should be briefly introduced here. It means that the luminescence intensity of solid state materials decreases with increasing concentration of the corresponding luminescence center. Since the distance between luminescence centers decreases with increase in concentration of the luminescence center, the probability of excitation energy transfer among the excited state luminescence centers may exceed that of emission. The luminescence efficiency thus decreases [43].

3. Preparation, stoichiometry and crystal structure of divalent europium crown ether, azacrown ether and cryptand as well as their polymeric derivative complexes

The rare earth crown ether and cryptand complexes have been intensively studied since the mid 1960s. The research was mainly directed towards the design of a new separation process, the understanding of rare earth coordination chemistry, and the preparation of rare earth luminescence materials. For the most part, this research work has concentrated on tervalent rare earth species. Their synthesis, stoichiometry, structure, thermodynamic properties, electronic absorption spectra, luminescence characteristics, and corresponding applications as spectroscopic probes and separation reagents have been well understood based on extensive investigation. The results have also been summarized in several review papers from different points of view by Bunzli and Wessner [51,52], Bunzli [53], and Adachi and Hirashima [54].

Among these studies, Gansow et al. [55–58] paid attention to the electrochemistry of the cryptand [2.2.1] and [2.2.2] complexes with divalent europium and ytterbium. They found that the cryptand encapsulation for these divalent rare earth ions has a significant effect on their electrochemical properties. The reduction potential of $R^{3+/2+}$–[2.2.1] or –[2.2.2] cryptates in aqueous or methanol solution shifts to less negative values and becomes reversible. This clearly suggests stabilization of the R(II) oxidation state by complexation with these macrocyclic ligands. The crown ether ligands were found to show a similar stabilization effect to these divalent rare earth ions by other investigators [59–66]. The corresponding potential data are given in Table 1.

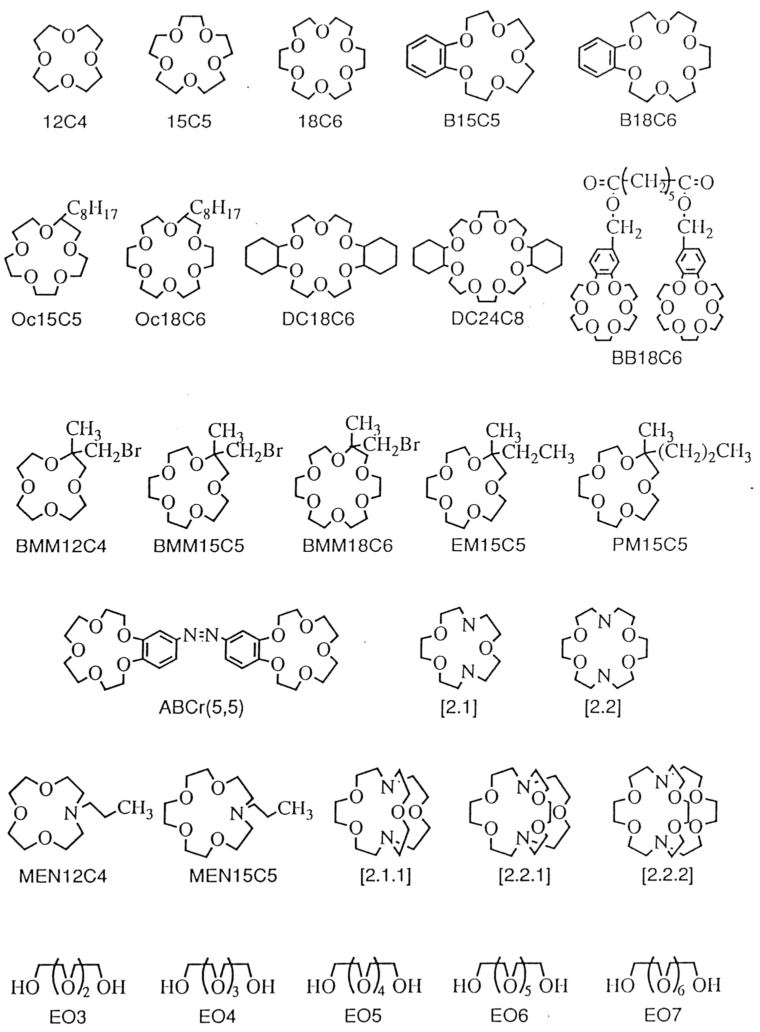
Investigation of the luminescent properties of these divalent europium crown ether and cryptand complexes was a natural result of the intense work on corresponding tervalent rare earth crown ether or cryptand derivatives and the electrochemical research on these divalent rare earth macrocyclic complexes.

3.1. The preparation of divalent europium crown ether, azacrown ether and cryptand as well as their polymeric derivative complexes

The most systematic investigation focused on the corresponding Eu^{2+} crown ether or cryptand complexes in methanol system, and was conducted by Adachi et al. [34,36–41]. They prepared these complexes by adding the divalent europium salt $EuCl_2$ or $EuBr_2$ directly into a highly degassed anhydrous methanol solution containing the required molar amount of corresponding crown ether, azacrown ether or cryptand ligands. These divalent europium halide compounds were prepared according to a previously reported method through the reaction of Eu_2O_3 with NH_4X ($X=Cl$, Br) followed by reduction with H_2 gas. Scheme 1 shows the schematic structure of crown ether, azacrown ether, cryptand, and polyethylene glycol ligands. Sabbatini's group also made an independent contribution to research on the luminescence of divalent europium macrocyclic ligand complexes [35,42]. However, their attention was limited to the related [2.2.1] and [2.2.2] cryptand complexes. They prepared Eu^{2+}–cryptand complex samples by a similar process to that of Adachi et al., but produced the divalent europium salt by means of electrochemical reduction of the tervalent chloride under argon according to the method of Gansow et al. [55–58]. Further efforts towards the practical utilization of these divalent europium complexes as stable luminescent materials led to the preparation and luminescence

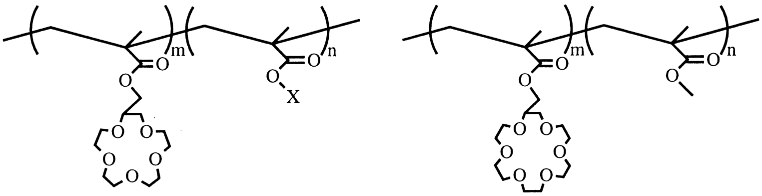
Table 1
The reduction potential data of $Eu^{3+/2+}$ in the crown ether or cryptand complexes

Redox couple	Solvent	Electrolyte	E_f (mV SCE)	Literature
$Eu^{3+/2+}$	H_2O	0.1 M NapTS (pH 3)	−626	[56]
$Eu(2.2.1)^{3+/2+}$	H_2O	0.1 M TEAP	−425	[56]
	H_2O	0.1 M $NaClO_4$	−425	[56]
	H_2O	0.5 M $NaClO_4$ (pH 2–7)	−435	[56]
$Eu(2.2.2)^{3+/2+}$	H_2O	0.1 M TEAP	−205	[56]
	H_2O	0.5 M $NaClO_4$	−215	[56]
$Eu(2B.2.1)^{3+/2+}$	H_2O	0.5 M $NaClO_4$	−370	[56]
$Eu^{3+/2+}$	MeOH	0.05 M TEAP	−260	[62]
$Eu(2.2.1)^{3+/2+}$	MeOH	0.05 M TEAP	−120	[62]
$Eu^{3+/2+}$	MeOH	0.1 M TBAP	−150	[59]
$Eu(15C5)^{3+/2+}$	MeOH	0.1 M TBAP	−65	[59]



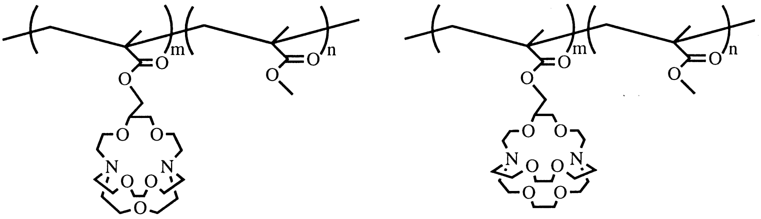
Scheme 1. The schematic structure of the crown ether, azacrown ether, cryptand, and polyethylene glycol ligands.

investigation of polymeric and copolymeric crown ether or cryptand divalent europium complexes, also by Adachi's group [67–74]. First, the monomer as well as the polymer or copolymer containing the crown ether or the cryptand fractions was synthesized according to literature procedures [75–78]. Then the fine ground powder of polymer was treated with a methanol solution of $EuCl_2$ under an inert gas. This is, in fact, a modified procedure for the preparation of the simple complex in solution. Scheme 2 shows the schematic structure of crown ether- or cryptand-containing polymer or copolymer ligands.



copoly(MA15C5/X) copoly(MA18C6/MMA)

X=CH_3	MMA
CH_2CH_3	EMA
$(CH_2)_3CH_3$	BMA
$CH_2CH_2OCH_2$	MAG1
$(CH_2CH_2O)_5CH_3$	MAG5



copoly(MA[2.2.1]/MMA) copoly(MA[2.2.2]/MMA)

PMA15C5 PMA18C6

Scheme 2. The schematic structure of crown ether- or cryptand-containing polymer or copolymer ligands.

3.2. The stoichiometry and crystal structure of divalent europium crown ether, azacrown ether and cryptand as well as their polymeric derivative complexes

In spite of the stabilization effect by complexation with crown ether or cryptand ligands, divalent europium as well as other divalent rare earth complexes is still easily oxidized to the tervalent state. It is difficult to isolate the corresponding divalent rare earth complexes. Only a few examples of 1:1 and 4:3 (metal:ligand) divalent crown ether and cryptand complexes have been described [79–83]. Therefore, stoichiometric and structural information on luminescent divalent europium crown ether and cryptand complexes in aqueous or methanol solution has been deduced by indirect methods only, such as Job's method of continuous variation or a molar ratio method using emission intensity [34,36–40]. Some were further demonstrated by means of NMR using Sr^{2+} instead of Eu^{2+} because they show the same electronic charge and ionic radius. All these methods for determining the stoichiometry of complexes were illustrated through the 15C5 or 18C6 compounds (Table 2).

The compositions listed in Table 2 (as well as the configuration which will be discussed below) of 15C5 and 18C6 complexes in solution were supported by the X-ray single crystal molecular structures of their corresponding Sr^{2+} analogues [83].

Table 2
Stiochiometry and spectroscopic properties of Eu^{2+} complexes with crown, cryptand and polyethylene glycols in methanol

Complex[a]	[Eu]:[ligand][b]	Maximum absorption band (nm)	Maximum emission band (nm)	Relative emission intensity[c]	log K_{st}[d]
Eu^{2+}–12C4	—[e]	252, 322	428	93[f]	—[e]
Eu^{2+}–15C5	1:3 (1:3)[g]	248, 318	432	690	2.36
Eu^{2+}–18C6	4:3 (1:1)[g]	257, 325	446	160	3.76
Eu^{2+}–B15C5	—[e]	267, 327	417	95	—[e]
Eu^{2+}–B18C6	1:1 (1:1)[g]	268, 328	447	9.2	3.62
Eu^{2+}–Oc15C5	—[e]	250, 320	423	690	—[e]
Eu^{2+}–Oc18C6	1:1 (1:1)[g]	258, 324	445	120	3.74
Eu^{2+}–DC18C6	4:3 (1:1)[g]	257, 318	440	87	3.68
Eu^{2+}–DC24C8	1:1	252, 327	443	180	—
Eu^{2+}–BB18C6	2:1 (2:1)[g]	276, 326	448	2.2	3.57
Eu^{2+}–[2.1]	—[e] (1:1)[g]	250, 319	460	130	2.39
Eu^{2+}–[2.2]	3:2 (1:1)[g]	260, 333	469	6.8	3.00
Eu^{2+}–MEN12C4	1:2	257, 306, 320	488	410	—
Eu^{2+}–MEN15C5	1:1	252, 301, 320	472	13	-
Eu^{2+}–[2.1.1]	—[e] (1:1)[g]	249, 327	445	1.0	3.07
Eu^{2+}–[2.2.1]	3:1 (1:1)[g]	254, 333	445	29	3.23
Eu^{2+}–[2.2.2]	1:1 (1:1)[g]	254, 317	468	270	4.89
Eu^{2+}–EO3	—[e]	250, 329	467	2.2	—
Eu^{2+}–EO4	-[e]	251, 327	442	5.0	—
Eu^{2+}–EO5	1:1	252, 320	464	4.2	—
Eu^{2+}–EO6	2:1	252, 321	467	47	—
Eu^{2+}–EO7	2:1	252, 316	458	66	—
$EuCl_2$	—	248, 328	489	1.0	—

[a] The Eu^{2+} concentration is 4.0×10^{-3} M.
[b] The ratio determined by means of the emission intensity molar ratio method.
[c] The relative intensities of the emission were determined by comparison with the intensity of the emission from a $EuCl_2$–methanol solution ($[Eu] = 4.0 \times 10^{-3}$ M).
[d] Stability constant for Sr^{2+} analogues determined by ^1H NMR.
[e] The ratios could not be established.
[f] The value for [Eu]:[ligand] = 1:10.
[g] The ratio obtained by ^1H NMR.

As expected from the size of the Sr^{2+} and 18C6 cavity, the Sr^{2+} ion enters completely into the cavity of 18C6 in the molecule of the complex. It locates in the center of the twisted 18C6 ligand. Two H_2O and one CH_3OH solvent molecule coordinate to this Sr^{2+} ion from the up and down directions of the equatorial center of the Sr^{2+}–18C6 molecule. In the case of 15C5, the Sr^{2+} ion locates out of the equatorial center of the 15C5 ligand because of the smaller size of this ligand compared with that of the Sr^{2+} ion. In the opposite direction to 15C5, three H_2O solvent molecules coordinate to the Sr^{2+} ion. The corresponding divalent europium complexes are expected to possess a similar structure. It is therefore possible for the divalent europium ion in methanol solution to coordinate with two additional 15C5 molecules a little loosely, in addition to the first strongly coordinating one. This has been demonstrated by Job's method of continuous variation or a molar ratio method using intensities and NMR measurement of Sr^{2+}–15C5 complex in deuterated methanol [39].

4. The spectroscopic properties of divalent europium complexes

4.1. The fluorescent properties of divalent europium crown ether, azacrown ether and cryptand complexes

Since the first observation of enhanced blue luminescence of divalent europium by complexation with crown ether in 1980 [34], Adachi et al. have carried out a systematical study in this field [36–41]. Table 2 also lists the spectroscopic characteristics of these divalent europium crown ether, azacrown ether, and cryptand complexes. The data of polyethylene glycol divalent europium complexes are also given for the sake of comparison. In addition, Fig. 3 exhibits the emission and absorption spectra of Eu^{2+}–15C5, Eu^{2+}–18C6, and $EuCl_2$ in methanol. These three samples all

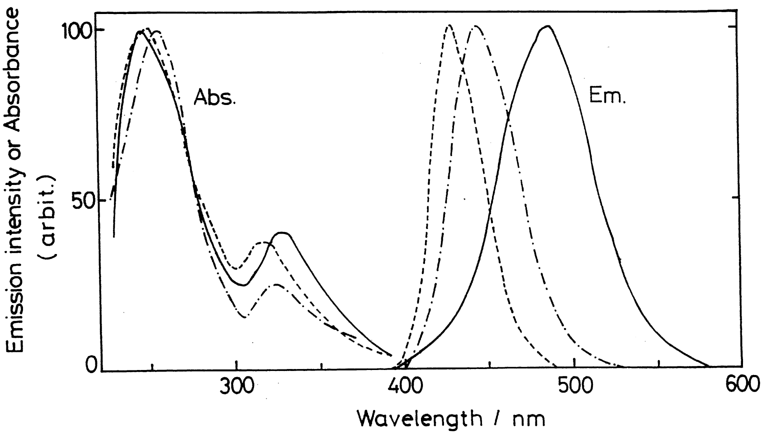


Fig. 3. The emission and absorption spectra of Eu^{2+}–15C5 (- - -), Eu^{2+}–18C6 complex (– · –), and $EuCl_2$ (———) in methanol.

show two absorption bands in the ultra-violet region. This is attributed to the fact that the lowest excited state of Eu^{2+}, $4f^65d^1$, is easily influenced and split by the surrounding environments. In the present situation, the 5d level is split into two levels under the coordination field of crown ether, cryptand or CH_3OH ligand. In contrast, only one emission band is observed in the visible region between 417 and 488 nm for these species. The red shift of the higher energy band and blue shift of the absorption at lower energy of crown ether complexes with respect to those of $EuCl_2$ in methanol suggest a weaker ligand field for crown ether in comparison with that of the CH_3OH ligand. This corresponds well with the experimental results for aqueous cryptand Eu^{2+} complexes obtained by Sabbatini et al. [35,42].

It has been well documented [35,44–51] that an aqueous divalent europium solution does not emit at room temperature, while its methanol solution emits very weakly [34]. The experimental results shown in Table 2 clearly indicate that the formation of Eu^{2+} complexes with macrocyclic crown ether or cryptand ligand obviously enhances the divalent europium emission intensity. The largest enhancement effect was achieved by complexation with the 15C5 ligand. On the contrary, the non-macrocyclic polyethylene glycol enhanced the emission intensity of divalent europium only to a limited degree, far less than the corresponding crown ether or cryptand ligand with similar coordination fractions. This may be explained as follows. In the case of crown ether and cryptand complexes, the coordinating macrocyclic ligand protects the Eu^{2+} ion from collision with the OH group-containing H_2O or CH_3OH molecules [34–40,42,41]. This substantially reduces the non-radiative decay process initiated by vibrationic coupling of the Eu^{2+} excited state $4f^65d^1$ to OH oscillators of H_2O or CH_3OH molecule [34–40,42,41]. The non-macrocyclic polyethylene glycol ligands, however, cannot effectively protect Eu^{2+} from the solvent molecules as their macrocyclic analogues do. Furthermore, they themselves contain OH groups, which induce the non-radiative decay as described above. Because longer chain polyethylene glycols such as the hexa- or hepta-ethylene glycol can surround Eu^{2+} more effectively to form a pseudo-encircled structure complex, they therefore show better luminescence enhancement effect compared with the small size ones.

Within the series of macrocyclic crown ether and cryptand ligands, 15C5 and [2.2.2] provide the largest luminescence enhancement effect in their respective series. This can be explained in terms of their complex composition and molecular configuration in CH_3OH solution according to the configurational-coordinate diagram theory.

As discussed in Section 3, 15C5 forms a 3:1 [(1+2):1] composition complex with divalent europium in methanol solution. The Eu^{2+} ion is encapsulated by one 15C5 ligand and locates slightly away from the equatorial plane of the central complex cation because of the smaller cavity size of 15C5 ($r=0.9$–1.1 Å) compared with the divalent europium diameter ($r=1.09$ Å). The other two ligands are located a little further away from the Eu^{2+} ion in comparison with the first, and enclose this Eu^{2+} as shown in Fig. 4 [36]. This special Eu^{2+}–15C5 composition and configuration in methanol solution provides full protection to the divalent europium from attack by any methanol solvent molecule, thus reducing the non-radiative deactivation

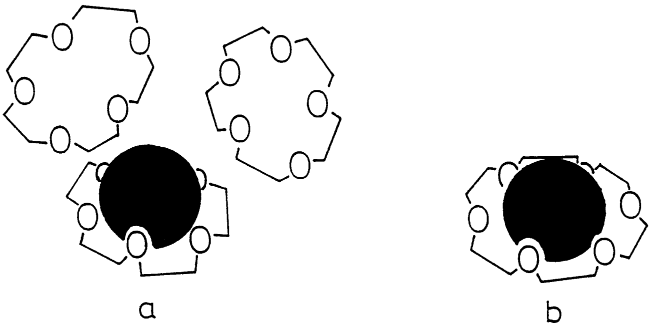


Fig. 4. Structural configuration of Eu^{2+} complex in alcohol solution: (a) Eu^{2+}–15C5; (b) Eu^{2+}–18C6.

process of the Eu^{2+} excited states. This is the main reason why 15C5 showed the largest luminescence enhancement effect among the whole series of crown ether ligands. In other cases, only 1:1 or 4:3 (ligand:europium) composition complexes are formed, whether for the smaller size ligand of 12-crown-4 (12C4) or the larger size ligands of 18C6 and 24-crown-8 (24C8) [79–83]. The solvent methanol molecules can attack and coordinate with the europium ion from the upper side for the small size 12C4 complex because the divalent europium sits above the equatorial plane of the 12C4 molecule. For the larger size ligand of 18C6 or 24C8, they have a large enough cavity to enclose the Eu^{2+} ion completely and thus provide a better encapsulation effect than the smaller size ligand. However, no additional ligands cap the Eu^{2+} ion as in the situation of the 15C5 complex. Methanol solvent molecules can still collide and coordinate with central Eu^{2+} from both above and below, as suggested by analysis of the single crystal structure of the Sr^{2+}–18C6 complex.

The encapsulation effect for luminescence efficiency is further demonstrated by investigation of the benzo-crown ether complexes of Eu^{2+}. Both the emission intensity and lifetime of benzo-15-crown-5 (B15C5) and benzo-18-crown-6 (B18C6) Eu^{2+} complexes decrease strongly with respect to their respective analogues of 15C5 and 18C6 [38]. This fact is attributed to a decrease in flexibility of the benzo-crown ethers, which prevents their effective complexation of the Eu^{2+} ion. For example, a 1:1 (Eu^{2+}:ligand) composition complex was determined for both these benzo-crown ether ligands by the emission intensity ratio method. Compared with the 1:3 (Eu^{2+}:ligand) composition of the 15C5 complex, the encapsulation effect of the B15C5 ligand decreases to a large extent. Moreover, the same 1:1 composition was observed with both the 18C6 and B18C6 ligands. The protection effect of B18C6 afforded to Eu^{2+} from attack by solvent molecules is decreased compared with 18C6 due to its low flexibility. This conclusion is verified by a decrease in the stability constant from 3.76 ($\log K_{st}$) for the 18C6 complex to 3.62 ($\log K_{st}$) for the B18C6 complex measured by the NMR method in methanol solution [38].

The emission characteristics of the organic fluorescence center of a phenyl group around 300 nm in these benzo-crown ether complexes has also been investigated. The emission dependence on the concentration of the complex is shown in Fig. 5 [11,38]. The fact that the phenyl group emission intensity decreases with increase

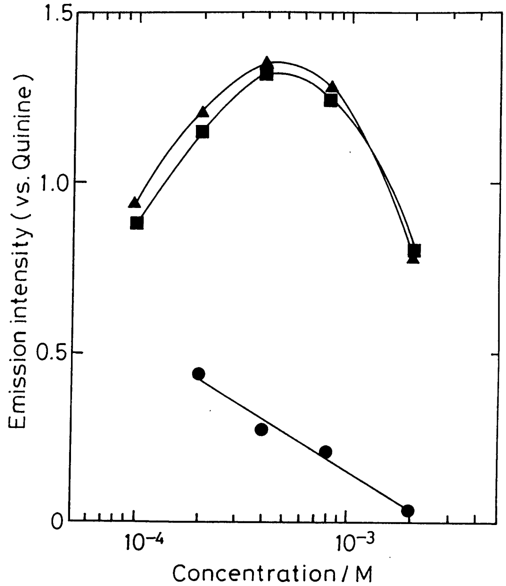


Fig. 5. Dependence of the ligand (phenyl group) emission intensity (ex. 280 nm) on ligand concentration: (a) benzo-18-crown-6 (B18C6) (▲); (b) Sr^{2+}–B18C6 (■); (c) Eu^{2+}–B18C6 (●).

in complex concentration suggests energy transfer from the excited phenyl group to a Eu^{2+} ion. This conclusion is additionally supported by experimental results for the di(benzo-18-crown-6) (BB18C6) complex [11,38]. The enhancement of Eu^{2+} emission intensity by complexation with BB18C6 is very small compared with that of the corresponding 18C6 ligand, and is attributed to the lower encapsulation effect of BB18C6 resulting from its rigid structure and low flexibility as mentioned above.

Another factor responsible for the largest fluorescence enhancement of 15C5 among the series of crown ether ligands is its most appropriate cavity size for the divalent europium diameter (r_{15C5}:$R_{Eu^{2+}} = 1$). The data for macrocyclic ligand cavity size and divalent europium are presented in Table 3 [11]. Upon absorption of UV radiation, the Eu^{2+} is raised to the $4f^65d^1$ excited state. This induces a decrease in the Eu^{2+}–O (N) equilibrium distance. However, the diffusion of the electron charge cloud of the Eu^{2+} excited state is restricted due to the very similar size between 15C5 and Eu^{2+} ion. Δr is thus limited to some degree in the case of the 15C5 complex. According to the aforementioned configurational-coordinate diagram theory, the smaller the absolute value of Δr, the greater the efficiency of fluorescence. In the situation of 18C6 and 24C8 ligands, their larger cavity size provides more space to allow the negative electron charge diffusion of Eu^{2+} in the excited state, thus inducing a larger absolute value of Δr. This is the second reason why the emission efficiency of Eu^{2+}–18C6 and Eu^{2+}–24C8 is lower than that of the Eu^{2+}–15C5 complex.

In the series of cryptand ligands, the cryptand [2.2.1] hole size fits the Eu^{2+} diameter better than that of the cryptand [2.2.2] ligand. It is therefore expected to

Table 3
Cavity sizes of crown ether, cryptand and ionic radius

Ligand	Radius of cavity size (Å)
12C4	0.6
15C5	0.9–1.1
18C6	1.3–1.6
24C8	>2.0
[2.1]	1.1
[2.2.2]	1.4
Sr(II)	1.26[a]
Eu(II)	1.25[a]

[a] Ionic radius (8-coordinated).

give a larger limitation to the diffusion of the Eu^{2+} excited state electron cloud and a relatively better fluorescence enhancement effect than the [2.2.1] ligand. However, the experimental results indicate that cryptand [2.2.2] shows a better fluorescence enhancement effect [11,36]. This is due to the slightly larger hole size of cryptand [2.2.2], which can encapsulate Eu^{2+} completely. This better encapsulation effectively reduces the collision of Eu^{2+} with solvent molecules of CH_3OH or H_2O, showing a higher luminescence efficiency by diminishing the non-radiative decay. On the contrary, in spite of the better limitation on the diffusion of Eu^{2+} excited state electron cloud, the smaller size of cryptand [2.2.1] cannot encapsulate the same size Eu^{2+} completely, as in the situation of one 15C5 ligand. It cannot then protect the Eu^{2+} ion from collision with solvent molecules and consequently reduce the non-radiative decay as effectively as the cryptand [2.2.2] ligand.

The experimental result that the emission intensity of Eu^{2+}–15C5, Eu^{2+}–18C6 and the same concentration of $EuBr_2$ in ethanol solution depends on temperature is in good accord with the emission intensity enhancement results discussed above [11,36]. Fig. 6 exhibits the temperature dependence of the emission intensity for these three samples. At low temperature, all three systems show intensive emission due to the very low non-radiative decay related to the low degree of coupling between the high energy Eu^{2+} excited state and low vibrational energy of the solvent OH group at low temperature. With increase of temperature, the emission intensity decreases greatly for $EuBr_2$ in ethanol. However, the emission intensity of the 18C6 system does not decrease so much because of the protection from collision by solvent molecules afforded by 18C6 encapsulation. The Eu^{2+}–15C5 complex hardly shows any temperature quenching effect until room temperature due to its unique complex configuration in solution and corresponding excellent protection of Eu^{2+} from solvent molecules.

In order to get further information about the cavity size effect towards the enhancement of emission intensity, azacrown ether [2.1], [2.2] and N-pivot lariat azacrown ether 10-(2-methoxyethyl)-1,4,7-trioxa-10-azacyclododecane (MEN12C4), 13-(2-methoxyethyl)-1,4,7,10-tetraoxa-13-azacyclopentadecane (MEN 15C5) were devised and prepared. The emission characteristics of their Eu^{2+}

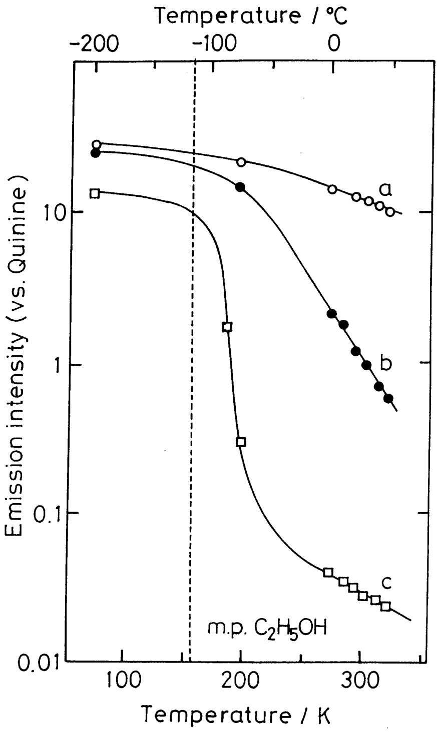


Fig. 6. The temperature dependence of emission intensity of Eu^{2+} complexes: (a) Eu^{2+}–15C5; (b) Eu^{2+}–18C6; (c) $EuBr_2$ in ethanol.

complexes were investigated. The emission of these two Eu^{2+} complexes shifts to longer wavelength. Moreover, a larger emission band width is observed compared with their corresponding unfunctionalized crown ether analogues. A similar characteristic of large emission band width has also been noted in Eu^{2+} complexes of cryptand ligands which also contain N coordination atoms. The energy of the Eu^{2+} excited state, $4f^65d^1$, in these complexes does not differ greatly from that in crown ether complexes as indicated by the similarity in the longer wavelength absorption bands in the Eu^{2+}–[2.1], Eu^{2+}–[2.2], Eu^{2+}–MEN12C4, Eu^{2+}–MEN15C5, Eu^{2+}–crown ether and Eu^{2+}–cryptand complexes. The red shift and broadening of the emission band are attributed to the greater curve of the configurational-coordinate parabola for these N-containing ligands. This is related to the lower electron density and coordination ability of the nitrogen atoms compared with those of oxygen atoms. The limitation on diffusion of the Eu^{2+} excited state electron cloud by these N-containing ligands is also considered weaker than the corresponding crown ether ligands for the same reason.

Apart from the aforementioned reason, the weak luminescence enhancement of azacrown ether of [2.1] and [2.2] to Eu^{2+} fluorescence has also been ascribed to the high vibrational energy of their amine group (–NH–). It couples with the energy of the $4f^65d^1$ excited state of Eu^{2+}, inducing non-radiative decay. The most interesting result is exhibited by the MEN15C5 ligand, which possesses a similar cavity size as 15C5. However, it enhanced only about 13 times the Eu^{2+} emission intensity for Eu^{2+} in methanol, far lower than that of 15C5. The NMR measurement indicates that the O atom in the lariat group takes part in coordination with the divalent europium. This prevents the formation of a [(1+2):1] (ligand:Eu^{2+}) composition complex as in the case of the 15C5 ligand, and thus greatly decreases the protection of Eu^{2+} from solvent molecules. The O atom in the lariat group of MEN12C4 is also found to take part in coordination with the divalent europium; however, NMR measurements disclosed formation of a complex with 2:1 (ligand:Eu^{2+}) composition. This reasonably increases the protection for Eu^{2+} to a larger degree and leads to a great fluorescence enhancement effect. The complex of Eu^{2+} with MEN12C4 shows an emission about 500 times stronger than that of Eu^{2+} in methanol solution [41].

Fig. 7 shows the relationship between the quantum yields and the coordination number to Eu^{2+} ion in methanol solution for the series of crown ether complexes. The larger the coordination number around the divalent europium, the higher the quantum yield of the complex, although there are a few exceptions [36].

An interesting phenomenon of emission intensity dependence on the radiation time was found for the first time in divalent europium crown ether complex with a bromoalkyl group in the ligand. Fig. 8 gives the relationship of the radiation time dependence of emission intensity of 2-bromomethyl-2-methyl-15-crown-5 (BMM15C5) Eu^{2+} complex [11,37]. The emission intensity increases with increasing radiation time and reaches its largest value after about 1 h. However, the emission intensity of the Eu^{2+} complexes with the 2-propyl-2-methyl-15-crown-5 (PM15C5)

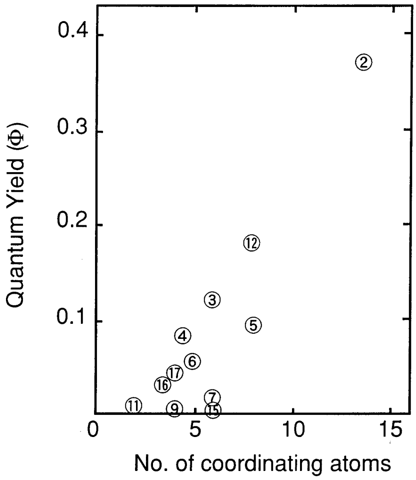


Fig. 7. The relationship between quantum yield and coordination numbers of Eu^{2+} in complexes in methanol with the ligand of: **2**, 15C5; **3**, 18C6; **4**, dicyclohexyl-18-crown-6 (DC18C6); **5**, dicyclohexyl-24-crown-8 (DC24C8); **6**, B15C5; **7**, B18C6; **9**, cryptand [2.2]; **11**, cryptand [2.2.1]; **12**, cryptand [2.2.2]; **15**, pentaethylene glycol (EO5); **16**, hexaethylene glycol (EO6); **17**, heptaethylene glycol (EO7).

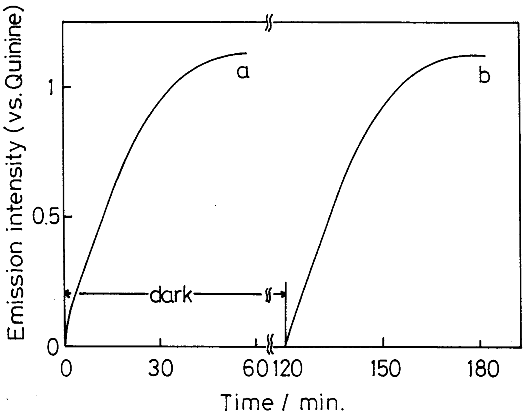


Fig. 8. Time dependence of emission intensity for the Eu^{2+} complex with 2-bromomethyl-2-methyl-15-crown-5 (BM15C5).

and 2-ethyl-2-methyl-15-crown-5 (EM15C5) ligands, which do not contain Br atoms in the chain group, does not show any radiation time dependence. This is explained by the hypothesis that the Br atom in the chain methyl group moves to the center of the crown ether under radiation and simultaneously coordinates with the Eu^{2+} ion together with the oxygen atoms in the crown ether ligand. This hypothesis is also supported by the discovery of a dependence of emission spectra of these bromomethyl–crown ether complexes on time (Fig. 9) [11,37]. With increase of radiation time, the emission band shifts to shorter wavelength. Moreover, the emission fraction in the long wavelength, which is attributed to Eu^{2+} ion uncoordinated

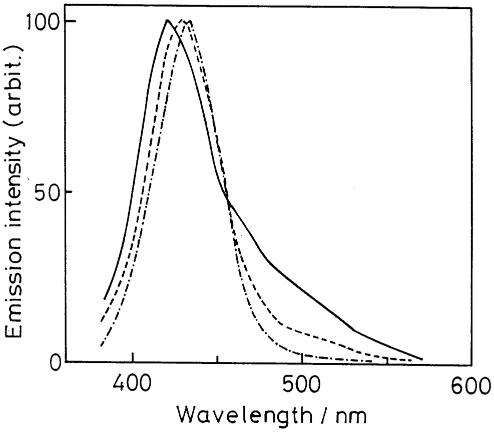


Fig. 9. Time dependence of emission and absorption spectra for the Eu^{2+} complex with 2-bromomethyl-2-methyl-15-crown-5 (BM15C5): (a) before irradiation (———); (b) after 10 min irradiation (- - -); (c) after 60 min irradiation (– · –).

by the macrocyclic ligand, decreases due to the progress of complexation under radiation.

It is well known that azobenzene shows transformation of cis- or trans-isomer upon the interaction of radiation and heat [84]. The azo(benzo-15-crown-5) [ABCr(5,5)] ligand was synthesized to target the development of an optically responsive rare earth luminescence material [85]. The excitation and emission properties, such as the luminescence intensity and configuration of the corresponding divalent europium complex, are well understood on the basis of the transformation of cis- and trans-isomer under radiation at different wavelengths.

The data for the luminescence quantum yields (ϕ), lifetimes (τ), radiative and non-radiative rate constants (κ and κ^*) deduced from the values of ϕ and τ for these Eu^{2+} complexes with crown ether, azacrown ether, cryptand, and polyethylene glycol ligands are given in Table 4. The lifetimes (τ) and radiative rate constants (κ) for all these complexes are of the same order with those of $EuCl_2$ in methanol, with

Table 4
Luminescence quantum yield ϕ, luminescence lifetime τ, radiative and non-radiative rate constants (κ and κ^*) of divalent europium complexes with crown ether, cryptand and polyethylene glycols

Complex[a]	ϕ (%)	τ (ns)	$\kappa \times 10^{-5}$ (s)[b]	$\kappa^* \times 10^{-5}$ (s)[c]
Eu^{2+}–12C4	3.6[d]	300	1.2	32
Eu^{2+}–15C5	28	800	3.5	9.0
Eu^{2+}–18C6	9.4	142	6.6	64
Eu^{2+}–B15C5	1.5	143	1.2	69
Eu^{2+}–B18C6	0.2	28	0.72	360
Eu^{2+}–Oc15C5	2.1	761	2.8	12
Eu^{2+}–Oc18C6	6.7	143	4.7	66
Eu^{2+}–DC18C6	3.8	89	4.3	110
Eu^{2+}–DC24C8	2.9	290	0.099	3.4
Eu^{2+}–BB18C6	0.05	—[e]	—[e]	—[e]
Eu^{2+}–[2.1]	7.1	42[f]	1.7[f]	21[f]
Eu^{2+}–[2.2]	4.6	16[f]	0.29[f]	62[f]
Eu^{2+}–MEN12C4	14	810	1.7	11
Eu^{2+}–MEN15C5	0.31	16	1.9	620
Eu^{2+}–[2.1.1]	0.05	—[e]	—[e]	—[e]
Eu^{2+}–[2.2.1]	1.4	24[f]	0.58[f]	41[f]
Eu^{2+}–[2.2.2]	9.3	200	0.47	4.5
Eu^{2+}–EO3	0.064	—[e]	—[e]	—[e]
Eu^{2+}–EO4	0.14	—[e]	—[e]	—[e]
Eu^{2+}–EO5	0.10	—[e]	—[e]	—[e]
Eu^{2+}–EO6	0.12	43[f]	0.29[f]	23[f]
Eu^{2+}–EO7	0.18	59[f]	0.30[f]	17[f]
$EuCl_2$	0.036	2.1	2.1	5900

[a] The Eu^{2+} concentration is 4×10^{-3} M.
[b] Radiative rate constant.
[c] Non-radiative rate constant.
[d] The value for [Eu]:[ligand] = 1:10.
[e] Not measured.
[f] Not very reliable.

a few exceptions, while the non-radiative rate constants (κ^*) show a great difference among different species of complexes. The divalent europium complexes formed with crown ether, azacrown ether, and cryptand ligands show smaller non-radiative rate constants (κ^*) than $EuCl_2$ in methanol. Their value of κ^* is even smaller compared with that of non-macrocyclic polyethylene glycol Eu^{2+} complexes. Among these macrocyclic ligands, 15C5 brings the smallest non-radiative rate constant value to Eu^{2+} because of the special protection effect of 15C5 ligands to the central europium ion from the collision of methanol molecules. This clearly indicates that the luminescence enhancement of divalent europium from the complexation with macrocyclic ligands is initiated by the decrease in non-radiative rate constant rather than by the increase in radiative rate constant.

4.2. The luminescent characteristics of divalent europium poly-crown ether and poly-cryptand complexes

After intensive studies of the luminescence of divalent europium crown ether and cryptand complexes in solution, Adachi et al. further prepared divalent europium complexes of crown ether- or cryptand-containing polymeric ligand and investigated their fluorescent properties to target the practical application of divalent europium complex luminescence materials [41,67–74].

The various crown ether- and cryptand-containing monomers were synthesized according to literature procedures [75–78]. They were then polymerized independently or copolymerized with another kind of monomer, providing the polymer or copolymer ligands containing crown ether or cryptand fractions. These ligands were treated with $EuCl_2$ methanol solution under nitrogen gas to give the divalent europium polymeric or copolymeric complexes after washing with methanol and drying in vacuo [67–74].

Fig. 10 describes the excitation and emission spectra of Eu^{2+}–PMA15C5 and

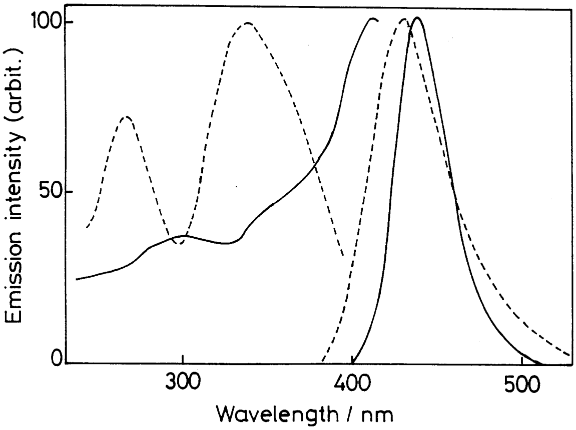


Fig. 10. Excitation and emission spectra of the polymer complex: (a) Eu^{2+}–PMA15C5 (———); (b) Eu^{2+}–PMA18C6 (- - -).

Eu^{2+}–PMA18C6 complexes. They show similar emission characteristics to their related simple complexes in solution. This not only indicates the formation of the similar divalent europium complex both in the polymer form and in solution, but also suggests their similar complex composition and structure. Therefore a similar protection effect of the macrocyclic ligand to the luminescence center Eu^{2+} from the unvaporized methanol molecules in the polymer is also identified. As for the situation in crystal or vitreous luminescent material, concentration quenching occurs with increase of divalent europium concentration. With the increase of divalent europium in polymer or copolymer material, the average distance between the divalent europium ions decreases. The probability of energy transfer between the Eu^{2+} excited states increases with increasing Eu^{2+} concentration. When the Eu^{2+} concentration reaches a critical value which depends on the particular poly-ether species, the probability of this energy transfer exceeds that of emission from the Eu^{2+} excited states.

Fig. 11 shows the dependence of emission intensity of Eu^{2+}–15C5 and Eu^{2+}–18C6 polymeric complexes as well as copolymeric complexes on $EuCl_2$ concentration. Fig. 11 indicates that the 15C5-containing copolymeric complex shows stronger emission intensity than the 15C5-containing polymeric complex. This is rationalized by the fact that introduction of an additional fraction into the polymer increases the distance between the 15C5 fractions and thus the distance between the coordinated Eu^{2+} ions. The larger the ratio of the additional fraction to the 15C5 fraction in the copolymer, the stronger the emission intensity. Fig. 11 also indicates that the emission intensity of 15C5-containing polymer or copolymer Eu^{2+} complex is stronger than that of the corresponding 18C6-containing polymer or copolymer Eu^{2+} complex. This again demonstrates that the composition as well as configuration

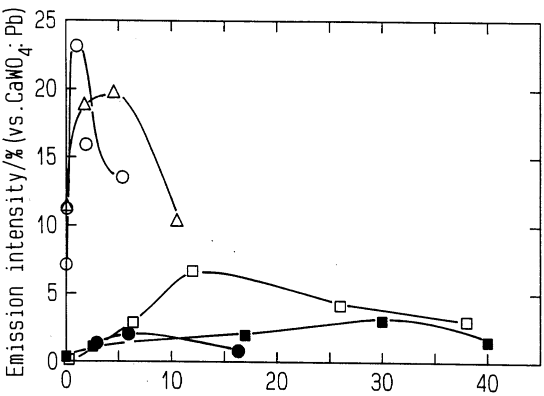


Fig. 11. The dependence of emission intensity of Eu^{2+} polymer or copolymer complex on $EuCl_2$ concentration: (a) Eu^{2+}–PMA15C5 (□); (b) Eu^{2+}–copoly(MA15C5/MMA) (1:5) (△); (c) Eu^{2+}–copoly(MA15C5/MMA) (1:10) (○); (d) Eu^{2+}–PMA18C6 (■); (e) Eu^{2+}–copoly(MA18C6/MMA) (1:10) (●).

of crown ether Eu^{2+} complex in 15C5- and 18C6-containing polymer or copolymer are similar to their respective simple analogues in solution.

Furthermore, besides emission intensity, the emission band position in these polymeric or copolymeric complexes also shows dependence on $EuCl_2$ concentration [71]. Fig. 12 exhibits the relationship between the emission peak wavelength and $EuCl_2$ concentration for 15C5- and 18C6-containing polymeric and copolymeric complexes. With increase of $EuCl_2$ concentration, the emission band especially for the 15C5-containing polymeric and copolymeric complexes shifts to longer wavelength. This suggests that with increase of $EuCl_2$ concentration the Eu^{2+} ions tend to aggregate together instead of dispersing homogeneously over the polymer. This induces a sudden change in the composition and configuration of the Eu^{2+} complexes and thus the emission properties in the 15C5-containing polymer. As the divalent europium ion is fully enclosed in the 18C6 ligand cavity, even in the polymeric complexes, the increase of $EuCl_2$ concentration does not greatly affect construction of the Eu^{2+}–18C6 complex in these 18C6-containing polymeric complexes. Therefore, the dependence of emission band position for 18C6-containing polymeric and copolymeric complexes is not as obvious as for 15C5-containing polymeric and copolymeric complexes. For both 15C5- and 18C6-containing polymeric and copolymeric complexes, the emission characteristics are dominated by free europium ions absorbed by the polymer after reaching a certain large value of $EuCl_2$ concentration.

Several kinds of copolymer with different sizes (Scheme 3) are used to copolymerize with the 15C5-containing monomer to investigate their affect upon the emission characteristics [11,71]. The dependence of emission intensity for these Eu^{2+} copolymeric complexes on $EuCl_2$ concentration is plotted in Fig. 13. With further increase of the size of the additional copolymer fraction the fluorescence enhancement diminishes. Initially, an increase in the size of additional copolymer fraction is helpful in increasing the distance between the Eu^{2+} complexes and thus the emission efficiency,

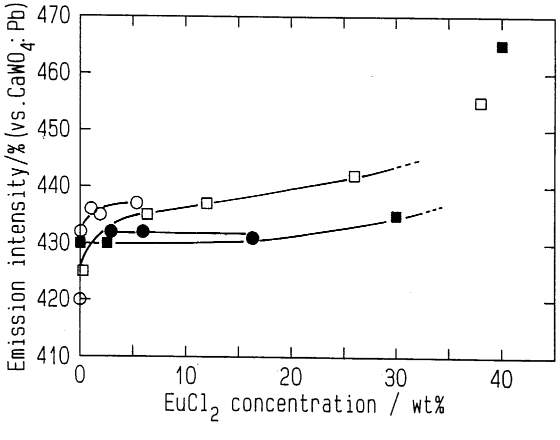
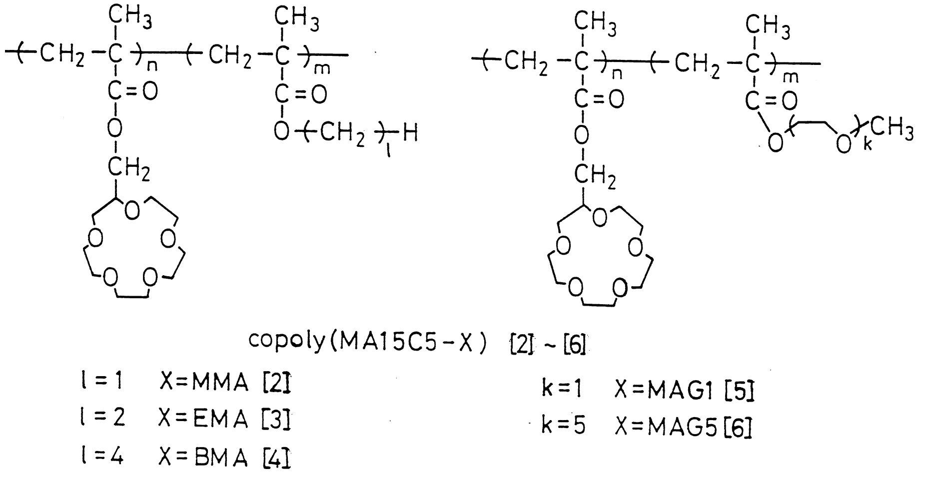


Fig. 12. The dependence of emission peak wavelength of the Eu^{2+} polymer or copolymer complex on $EuCl_2$ concentration: (a) Eu^{2+}–PMA15C5 (□); (b) Eu^{2+}–copoly(MA15C5/MMA) (1:10) (○); (c) Eu^{2+}–PMA18C6 (■); (d) Eu^{2+}–copoly(MA18C6/MMA) (1:10) (●).



Scheme 3. Schematic structure of the 15C5 copolymer: (a) $l=1$, X=MMA; (b) $l=2$, X=EMA; (c) $l=4$, X=BMA; (d) $k=1$, X=MAG1; (e) $k=5$, X=MAG5.

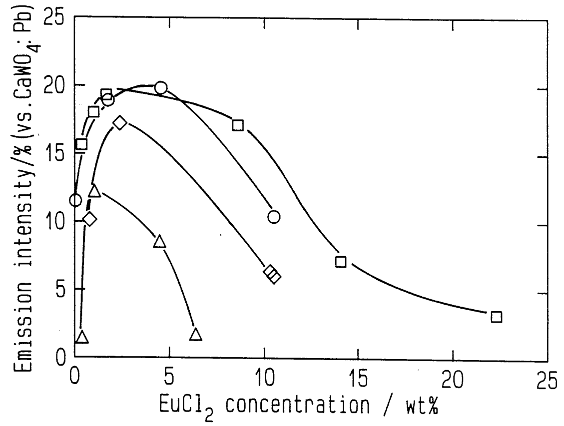


Fig. 13. The dependence of emission intensity of Eu^{2+}–copoly(MA15C5/X) (1:5) complex on $EuCl_2$ concentration: (a) X=MMA (○); (b) X=EMA (□); (c) X=BMA (△); (d) X=MAG1 (◇).

but further increase may prevent the effective complexation of Eu^{2+} with 15C5 fractions due to the increasing steric obstruction.

The dependence of luminescence lifetime of the divalent europium 15C5-containing polymeric and copolymeric complexes on $EuCl_2$ concentration (Fig. 14) [11,71] also supports this viewpoint. Due to reduction in the encapsulation effect of the 15C5 ligand to Eu^{2+} with a structural change in the polymeric complexes and an increase in the energy transfer among the Eu^{2+} species accompanying an increase of $EuCl_2$ concentration, the luminescence efficiency decreases. This is expressed by the decrease in lifetime shown in Fig. 14. Other 15C5-containing polymeric and copolymeric

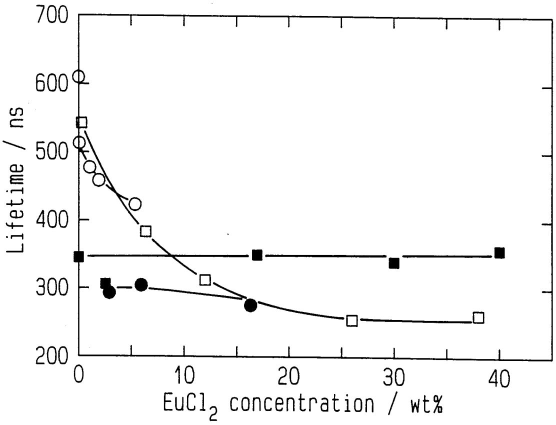


Fig. 14. The dependence of luminescence lifetime of Eu^{2+} polymer or copolymer complex on $EuCl_2$ concentration: (a) Eu^{2+}–PMA15C5 (□); (b) Eu^{2+}–copoly(MA15C5/MMA) (1:10) (○); (c) Eu^{2+}–PMA18C6 (■); (d) Eu^{2+}–copoly(MA18C6/MMA) (1:10) (●).

species display a similar result. However, the lifetime of the 18C6-containing polymeric complexes does not change as greatly as that of the 15C5-containing analogues. This is rationalized by the smaller degree of change in encapsulation to Eu^{2+} for the 18C6 fraction in 18C6-containing polymers associated with the 1:1 (Eu^{2+}:18C6) composition.

The emission characteristics including the lifetime and emission intensity of azacrown ether- or cryptand-containing polymeric complexes are similar to those of their respective simple analogues in methanol or water solution. Similar to their crown ether-containing polymeric analogues, these characteristics also display a dependence on $EuCl_2$ concentration. All these data are organized in Table 5 along with those of crown ether-containing polymeric complexes.

The introduction of additional ions such as alkaline earth metal ions Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, and Group IIB metal ions Zn^{2+} as well as Cd^{2+} into the crown ether-containing polymeric complexes of Eu^{2+} similarly improves the fluorescence characteristics as the introduction of an additional group into the crown ether-containing polymer. The fluorescence properties of 15C5-containing polymeric and copolymeric Eu^{2+} complexes co-doped with the above mentioned divalent ions were investigated [73]. Experimental results indicate that the introduction of additional alkaline earth ions into 15C5-containing polymeric complexes results in an effect on the Eu^{2+} fluorescence similar to that of lowering the Eu^{2+} content in the polymer. The emission intensity for 15C5-containing polymeric Eu^{2+} complexes co-doped with alkaline earth ions is almost the same as that of the undoped polymeric Eu^{2+} complexes. This suggests that the alkaline earth ions exist in a coordinated form displacing Eu^{2+} in the polymer. The bulky Ba^{2+} ions influence the surroundings of the Eu^{2+}–15C5 moieties in the polymer, thus the Eu^{2+} polymeric complexes co-doped with this ion give the smallest emission intensity of all the alkaline earth co-doped ones. The fluorescence properties of the 15C5-containing polymeric

Table 5
Luminescence properties of Eu^{2+} complexes with crown ether- or cryptand-containing polymer or copolymer

Polymer complex	(*m*:*n*)[a]	[EuCl$_2$][b] in MeOH (M)	[EuCl$_2$][c] in polymer (wt%)	Emission			
				I[d] (%)	τ[e] (ns)	λ_{max} (nm)	L/M[f]
Eu^{2+}–copoly(MA15C5/MMA)	(1:5)	0.05	4.55	19.8	430	439	5.3
	(1:10)	0.05	1.07	23.1	447	436	16
Eu^{2+}–copoly(MA15C5/EMA)	(1:5)	0.01	1.01	18.0	476	435	25
Eu^{2+}–copoly(MA15C5/BMA)	(1:5)	0.01	1.05	12.2	418	437	20
Eu^{2+}–copoly(MA15C5/MAG1)	(1:5)	0.01	2.40	17.2	447	439	8.6
Eu^{2+}–copoly(MA15C5/MAG5)	(1:5)	0.005	—[g]	0.17	412	412	—[g]
Eu^{2+}–PMA15C5		0.01	12	6.63	312	437	5.1
Eu^{2+}–copoly(MA18C6/MMA)	(1:10)	0.01	5.98	1.99	304	432	2.6
Eu^{2+}–PMA18C6		0.05	30	3.0	340	435	1.4
Eu^{2+}–copoly(MA[2.2.2]/MMA)	(1:5.5)	0.05	20.7	4.22	378	453	0.83
Eu^{2+}–PMA[2.2.2]			18.7	2.90	429	453	2.04
Eu^{2+}–copoly(MA[2.2.2]/MMA)	(1:79)		2.06	19.3	536	449	1.26

[a] Molar ratio of the monomer containing a crown compound to the other monomer.
[b] EuCl$_2$ concentration in complex formation.
[c] EuCl$_2$ concentration in the polymer complex when emission intensity becomes maximum, determined by EDTA titration.
[d] The maximum relative emission intensity determined by comparison with that (100%) of CaWO$_4$:Pb(NBS1026).
[e] Luminescence lifetime.
[f] Ratio of ligand to Eu.
[g] Not measured.

Eu^{2+} complexes co-doped with Zn^{2+} ions are greatly improved. The maximum fluorescence intensity obtained for 15C5-containing polymeric Eu^{2+} complexes co-doped with Zn^{2+} ions reaches about 50% that for NSB1026, about two times that of 15C5-containing polymeric Eu^{2+} complexes. The lifetime of Eu^{2+} by co-doping with Zn^{2+} is also apparently lengthened. These results suggest that Zn^{2+} behaves differently from the alkaline earth ions in the polymer. Raman spectroscopic measurements indicate that ZnCl$_4^{2-}$ complex anions are formed in the polymer matrix. Judging from the excitation and fluorescence spectra of 15C5-containing polymeric Eu^{2+} complexes co-doped with Cd^{2+} ions, this ion appears to act like Zn^{2+}. However, the improvement of Eu^{2+} fluorescence is not as effective as with Zn^{2+} due to the difficulty in forming the larger ionic size CdCl$_4^{2-}$ complex anions.

The stability of divalent europium is greatly improved by the formation of crown ether-, azacrown ether- or cryptand-containing polymer or copolymer complexes. The Eu^{2+} ion is known to be the most stable divalent lanthanide species, but it may be immediately oxidized on contact with oxygen in air in methanol or aqueous solution. However, the mean half period of the luminescence intensity of polymeric complexes kept in a desiccator was found to be about one day [11,71]. Interestingly, the resistivity of Eu^{2+} ions against oxidation in 15C5-containing polymeric Eu^{2+} complexes co-doped with Zn^{2+} ions was further extremely enhanced compared with that of 15C5-containing polymeric Eu^{2+} complexes, although the reason is not clear [73].

4.3. The color-changeable luminescence characteristics of the $Eu^{3+/2+}$–15-crown-5 complex

Adachi et al. further investigated the color-changeable luminescence characteristics of $Eu^{3+/2+}$–15-crown-5 complexes by modifying the valency of the Eu ion under electrochemical polarization [59]. A similar $Eu^{3+/2+}$–bpy (bpy = 2,2′-bipyridine) system was simultaneously studied for comparison. The formal $Eu^{3+/2+}$ potential for the 15C5 complex is −65 mV, whereas the formal potential for the Eu–bpy system is −200 mV vs. SCE. Compared with the value in $Eu^{3+/2+}$ methanol, −150 mV, the conclusion that complexation with 15C5 improves the stability of divalent europium and the coordination with bpy enhances the stability of tervalent europium can be reached. The luminescence properties for these systems were then studied under electrochemical polarization at −450 and 500 mV, respectively.

Fig. 15(a) shows the emission spectra of $Eu^{3+/2+}$–15C5 methanolic solution con-

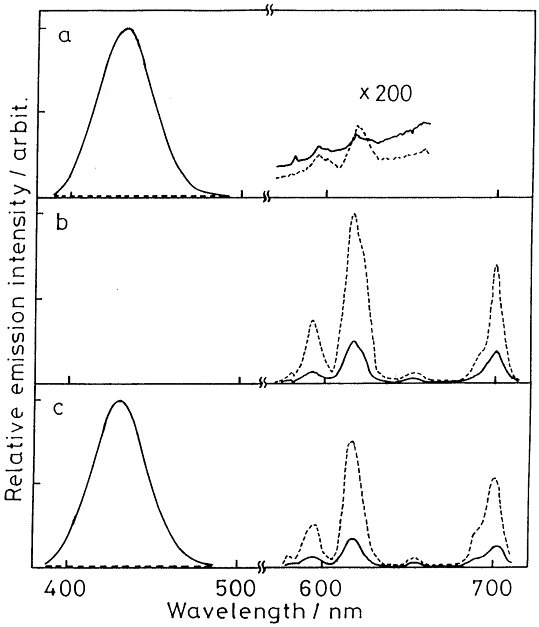


Fig. 15. The emission spectra for the methanolic solution containing: (a) 2 mM $Eu^{3+/2+}$, 6 mM 15C5, and 0.1 M TBAP; (b) 2 mM $Eu^{3+/2+}$, 6 mM bpy, and 0.1 M TBAP, excited by 300 nm after polarization at −450 mV for 30 min (———) and at 500 mV for 30 min (· · ·), respectively; (c) 4 mM $Eu^{3+/2+}$, 6 mM 15C5, 1 mM bpy, and 0.1 M TBAP, excited by 254 nm after polarization at −450 mV for 150 min (———) and at 500 mV for 30 min (· · ·).

taining 2 mM Eu and 6 mM 15C5. The characteristic band of the Eu^{2+}–15C5 complex at 430 nm increases dramatically under polarization at −450 mV. At +500 mV the blue band disappears almost completely and a weak red line spectra corresponding to Eu^{3+}–15C5 grows in. The emission intensity of this red line is quite low compared with that of the blue band. This is attributed to the absence of an effective sensitizer for the luminescence of Eu^{3+} in the 15C5 system. On the other hand, the situation for the $Eu^{3+/2+}$–bpy system contrasts with that of the $Eu^{3+/2+}$–15C5. It exhibits strong red emission lines [Fig. 15(b)] derived from the f–f transitions of the Eu^{3+} ion because bpy ligands act as effective sensitizers; they absorb the radiation energy and then transfer this energy to the central Eu^{3+} ions. However, no blue emission is observed with electrochemical polarization at −450 mV, even for a long time, due to the non-radiative energy transfer from the excited states of Eu^{2+} to bpy ligands. In order to improve the characteristics for the color-changeable phosphor between blue and red, a mixture of $Eu^{3+/2+}$–15C5 and $Eu^{3+/2+}$–bpy complexes in methanol containing 4 mmol $EuCl_2$, 6 mmol 15C5, and 1 mmol bpy was prepared. The emission spectra were checked and are shown in Fig. 15(c). The intense blue emission (430 nm) and red emission (616 nm) with almost the same intensity are observed under anodic and cathodic polarization conditions, respectively. Furthermore, the response time from blue to red is relatively rapid (8 min) under cathodic electrochemical polarization conditions at +500 mV. The recovery of the blue emission under anodic polarization at −450 mV is much slower (more than 150 min).

5. Concluding remarks

Research on rare earth luminescence has been a very active field. The corresponding rare earth luminescence materials have been extensively applied in various important fields of modern science and technology, such as laser sources, solar cell apparatus, and biological probes. However, previous research attention has been focused on the crystal and vitreous fluorescence materials of rare earths with normal tervalent oxidation state. There has been a limited number of publications and applications concerning divalent rare earth materials in the form of inorganic crystal and vitreous states, and in particular about divalent rare earth coordination compound materials. This article systematically summarizes recent progress in research on the fluorescence of divalent europium crown ether and cryptand complexes and their polymeric derivative complexes. Extensive applications with special biological, optic and magnetic interests are expected to develop for these macrocyclic coordination compound materials upon further intensive investigation.

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