CHEMISTRY LETTERS, pp. 1131-1134, 1994.

Luminescence Properties of Divalent Europium Complexes of Polymer Ligands Containing [2.2.2] and [2.2.1] Cryptand Units

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Divalent europium (Eu^{2+}) complexes with polymer ligands containing 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane ([2.2.2] cryptand) and 4,7,13,16,21-pentaoxa-1,10-diazabicyclo[8.8.5]tricosane ([2.2.1] cryptand) have been synthesized. The complexes emitted ca. 450 nm luminescence by ultra violet excitation. A Eu^{2+}-[2.2.2] cryptate-attaching polymer had high luminescence efficiency and its maximum relative emission intensity was ca. 19% with respect to an NBS standard, $CaWO_4$:Pb.

Recently, several studies[1-5] have performed on synthesis of organic polymers containing rare earth ions. Banks *et al.* and Okamoto *et al.*[6-10] have developed intense red and green light-emitting polymeric materials containing Eu^{3+} and Tb^{3+} complexes of β-diketone, respectively. Blue is the remaining one among the three primary colors of light, and so we have recently been focusing on new organic blue-emitting materials activated by divalent europium ions which formed complexes with several kind of organic molecules.[11-17] Some cryptand monomer complexes of Eu^{2+} have been reported to exhibit 450~470 nm emission under UV radiation.[16] This finding easily reminds us of mixing the complexes with a polymer matrix to develop a polymer phosphor of blue emission. This idea, however, dose not work because the complex dissociates to a Eu^{2+} ion and cryptand in this matrix. A path to avoid this drawback is to use a polymer containing cryptand moieties as a ligand. In this work, the methacrylate analogues containing [2.2.2] and [2.2.1] cryptands as coordination groups have been synthesized and polymerized with methylmethacrylate (MMA) in various ratios. We have reported here the luminescence properties of Eu^{2+} complexes of these cryptand-attaching polymers.

copoly(MA[2.2.2]/MMA)
m:n=1:6.8 m:n=1:79
m:n=1:24 m:n=1:100
m:n=1:50
PMA[2.2.2]
m:n=1:0

copoly(MA[2.2.1]/MMA)
m:n=1:5.6 m:n=1:46

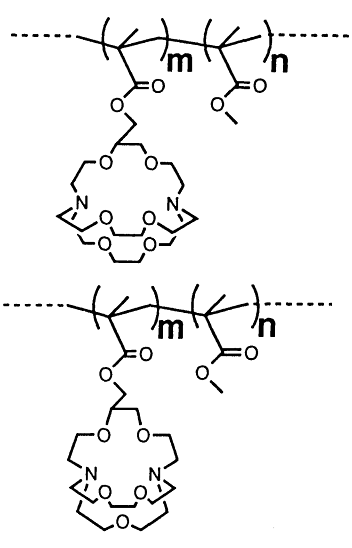

Fig. 1. Schematic representation of polymer ligands used.

The synthetic polymer-supported [2.2.2] cryptand(**1**): PMA[2.2.2] and copoly(MA[2.2.2]/MMA), and [2.2.1] cryptand (**2**): copoly(MA[2.2.1]/MMA), are shown in Fig.1. A synthetic route similar to the others was previously described.[17,18] The ratio of cryptand moiety to MMA (m:n) was determined by elemental analysis, see Fig.1. The polymers obtained were insoluble in methanol, ethanol, acetone,chloroform and THF. They only swelled in acetone and in chloroform. The insolubility of the polymer obtained in this work is probably due to their high molecular weights and/or high networking.[19]

The divalent europium cryptate-attaching polymers: Eu^{2+}-**1** and Eu^{2+}-**2** complexes, were prepared as follows. Firstly, an amount (ca. 40 mg) of powdered **1** or **2** was soaked in an anhydrous $EuCl_2$ metanolic solution[20] in a nitrogen flushed box for 12 h and then it was separated from the mother liquors by decantation and dried in vacuum at room temperature for 2 h. The luminescence measurement has been described previously for similar solid powder samples.[11] After the complexes were dissociated by hydrochloric acid, the $EuCl_2$ concentration in the polymer was determined by means of atomic absorption spectrometry, after the complexes were dissociated by hydrochloric acid.

The europium cryptate complex formation was confirmed by shifting in ν(C-O-C) vibrations occurred at 1130 cm^{-1} and 1120 cm^{-1} in the metal free polymer ligands (**1**) and (**2**), respectively, to lower wave numbers[21] in the solid polymers containing Eu^{2+}. The Eu^{2+} ion whose ionic diameter is 0.25 nm[22] can be encapsulated completely in the [2.2.2] cryptand cage: (cavity size 0.28 nm[23]). By complexing with a Sr^{2+} ion which has the same valence and a similar ionic diameter in comparison with a Eu^{2+} ion, all ^{13}C-NMR signals of the complex assigned to carbon of [2.2.2] cryptand shifted toward a high magnetic field, the finding of which suggests that the Sr^{2+} , namely, Eu^{2+}, is located at the center of the cavity of [2.2.2] cryptand. However the cavity of [2.2.1] cryptand (diameter: 0.22 nm[23]) is slightly smaller than the ionic diameter of a Eu^{2+} ion. Accordingly, a cage of [2.2.1] cryptand can only partially encapsule a Eu^{2+} ion in it, and the Eu^{2+} ion in the [2.2.1] cryptand complexes coordinates with some molecules of methanol whose ν(O-H) vibrations bring about a nonradiative transition of an excited Eu^{2+} ion.[24] In other words, the emission intensity of the Eu^{2+} complex with ligand(**2**) becomes for less than that with ligand(**1**).

Table 1. Luminescence properties of Eu^{2+} polymer complexes

Polymer Ligand	$[EuCl_2]^{a)}$	$L/M^{b)}$	$\lambda^{c)}$	$I^{d)}$	$\tau^{e)}$
	wt%		nm	%	ns
PMA[2.2.2]	18.7	2.04	453	2.90	429
copoly(MA[2.2.2]/MMA)(m:n=1:6.8)	13.4	1.26	452	5.22	481
copoly(MA[2.2.2]/MMA)(m:n=1:24)	5.77	1.26	450	13.8	497
copoly(MA[2.2.2]/MMA)(m:n=1:50)	2.38	1.67	450	16.2	520
copoly(MA[2.2.2]/MMA)(m:n=1:79)	2.06	1.26	449	19.3	536
copoly(MA[2.2.2]/MMA)(m:n=1:100)	1.41	1.48	449	16.1	533
copoly(MA[2.2.1]/MMA)(m:n=1:5.6)	6.30	3.34	445	1.40	381
copoly(MA[2.2.1]/MMA)(m:n=1:46)	3.43	1.25	438	1.97	402

a)$EuCl_2$ concentration in the polymer complex. b)Ratio of [2.2.2] (ligand) to Eu^{2+} (metal). c)Emission peak wavelength. d)Relative emission intensity with respect to that for $CaWO_4$:Pb(NBS1026). e)Luminescence lifetime (Horiba Time-Resolved Spectrofluorometer, NAES-1100).

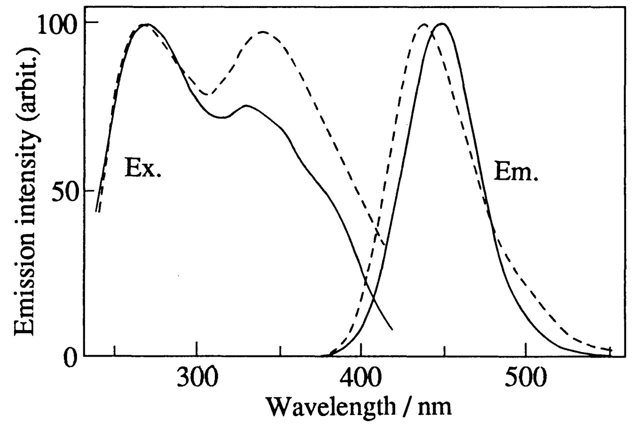

Fig. 2. Emission (Em.) and excitation (Ex.) spectra for the Eu^{2+}-polymer complexes.
(—) Eu^{2+}-copoly(MMA[2.2.2]/MMA)(m:n=1:79)
(···) Eu^{2+}-copoly(MMA[2.2.1]/MMA)(m:n=1:46).

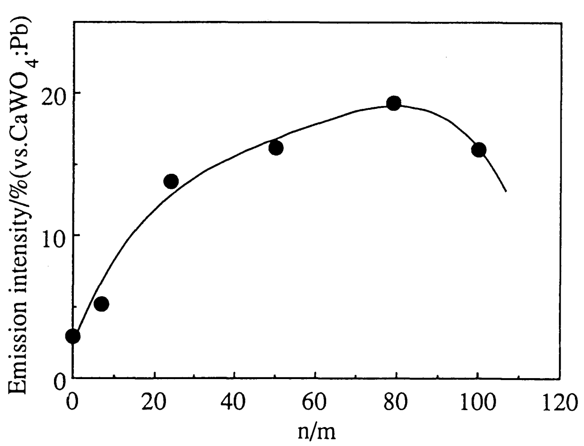

Fig. 3. The dependence of the emission intensities for Eu^{2+} complexes of the polymer containing [2.2.2] cryptand on the ratio of MMA to [2.2.2] cryptand moiety in the polymer (n/m).

The excitation and emission spectra for Eu^{2+}-**1** and Eu^{2+}-**2** complexes are shown in Fig.2 at the respective optimal $EuCl_2$ concentrations for the maximum emission intensity. A Eu^{2+} ion is known to emit various colors of luminescence based on the $4f^65d^1 \rightarrow 4f^7$ transition, which is very sensitive to the surroundings because of the participation of the outer-orbital 5d electron25,26).Both Eu^{2+}-**1** and Eu^{2+}-**2** complexes exhibited aiming blue emissions whose emission peak wavelength do not coincide, owning to the difference in surroundings around a Eu^{2+} ion, i.e. the structures of the Eu^{2+} cryptate-attaching polymer.

The spectroscopic data obtained for the various Eu^{2+} polymer complexes are summarized in Table 1. The maximum relative emission intensities27) for Eu^{2+}-**1** and Eu^{2+}-**2** complexes were ca. 19% and ca. 2.0% of that for the NBS standard, $CaWO_4$:Pb(NBS1026),28,29) respectively.The cavity size of [2.2.1] cryptand is too small to enclose a Eu^{2+} ion, so that the solvent molecules, i.e. methanol which comes into play as an effective quencher, bind to a Eu^{2+} ion on the unoccupied coordination sites of it. On the other hand, a [2.2.2] cryptand cage can shield a Eu^{2+} ion from molecules of methanol effectively, because it has the suitable cavity size to enclose a Eu^{2+} ion in it. The emission intensity for the Eu^{2+}-**1** complex, therefore, was much higher than that for the Eu^{2+}-**2** complex.

The authors found that the emission intensity for the Eu^{2+}-**1** complex was also depended on the "mole" ratio of MMA to [2.2.2] cryptand moiety (n/m). The relationships between n/m of the polymer ligand (**1**) and the emission intensity was in the following order, Eu^{2+}-**1**(m:n=1:79) > Eu^{2+}-**1**(m:n=1:50) ≅ Eu^{2+}-**1**(m:n=1:100) > Eu^{2+}-**1**(m:n=1:24) »Eu^{2+}-**1**(m:n=1:6.8) > Eu^{2+}-**1**(m:n=1:0). This phenomenon can be mainly elucidated by the concentration quenching. For the case of m:n=1:10, the Eu^{2+} concentration is too much and for m:n=1:100, the Eu^{2+} concentration is too small for a high luminescence efficiency. The value of m:n=1:79 is the most suitable one. In addition, increase in quantity of [2.2.2] cryptand moiety causes the enhancement of absorption of UV and visible light, leading to decrease in excitation rate and in emission intensity.

Eu^{2+} ions in cryptand complexes are 5 times stabler than that in the crown ether analogues under storage in a silica-geled desiccator.

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19) A 15-crown-5-methyl methacrylate-MMA copolymer: copoly(MA15C5/MMA), synthesized by solution polymerization method was soluble in THF and its molecular weights were determined to be Mn=5.5×10^4 and Mw=8.3×10^4 reported in Ref. 12. So that the molecular weight of the polymer synthesized in this work is estimated to be more than 5×10^4.

20) Methanol was purified and degassed through repetition of freeze-pump-thaw cycles to prevent from the oxidation of Eu^{2+} to Eu^{3+} during the formation of complexes.

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27) The emission intensity is expressed as area of the band of emission under UV-Vis. excitation light.

28) The quantum efficiency of the $CaWO_4$:Pb(NBS1026) is 76% under 254 nm excitation.

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(Received March 16, 1994)