CHEMISTRY LETTERS, pp. 2029-2032, 1990.

Effects of Zinc(II) on Fluorescence Properties of Divalent Europium - Poly(Methacrylate Containing 15-crown-5 Structure) Complex

Nobuyuki HIGASHIYAMA and Gin-ya ADACHI*
Department of Applied Chemistry, Faculty of Engineering, Osaka University, Yamadaoka,
Suita, Osaka 565

The Eu^{2+}-Zn^{2+}-poly(methacrylate containing 15-crown-5 structure) complex excited by U.V. light was found to yield bright blue emission. Its emission intensity was observed to be ca. 50 % of that for $CaWO_4$:Pb (NBS1026), while the emission intensity for Eu^{2+}-poly(methacrylate containing 15-crown-5 structure) was ca. 20 %. The luminescence lifetime gets much longer by virtue of the Zn^{2+} coexistence. This Eu^{2+}-Zn^{2+}-polymer complex will be a new promising blue phosphor.

A divalent europium - monomeric 15-crown-5 complex under U.V. irradiation is well-known to give blue bright emission, which is corresponding to 4f-5d transition.[1-4] Polymerization of the ligand containing 15-crown-5 and preparation of the solid Eu^{2+}-complex with the polymer enables it to become a new phosphor with the characteristics of an organic polymer.

Eu^{2+}-poly(methacrylate containing 15-crown-5 structure) complexes have been synthesized and also found to emit strong blue luminescence.[5-7] Enhancement of the emission intensity is desirable for their practical uses. We have recently studied effects of the coexistence of several metal ions with the Eu^{2+} ion on the fluorescent characteristics. In the present paper, we report on the effects of the zinc ion on the fluorescence properties of the complex. The polymer ligand used, as shown in Fig. 1, was 15-crown-5-methyl methacrylate (MA15C5) - methyl methacrylate (MMA) copolymer, with the 1:10 initial molar ratio of MA15C5 to MMA. The monomer, 15-crown-5-methyl methacrylate (MA15C5), was synthesized in a similar manner which has been reported in Ref. 8. The copolymerization was done by bulk polymerization using α, α'-azobis-isobutylonitrile (AIBN) for 15 h. at 60 °C.

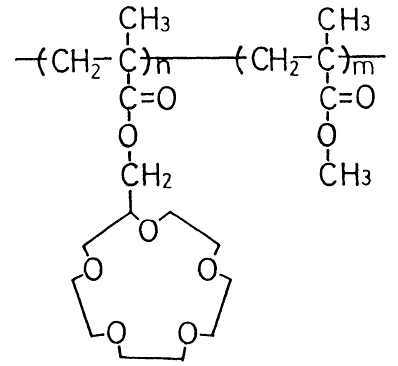

Fig. 1. Copoly(MA15C5-MMA).

$EuCl_2$ was prepared as previously described [2,7] and methanol used was completely degassed by repeated freeze-pump-thaw cycles on a high vacuum line. This process was essential to protect Eu^{2+} against oxidation.

The Eu^{2+}-Zn^{2+}-polymer complexes were prepared by soaking an amount (ca. 60-100 mg) of the powdered (MA15C5-MMA) copolymers in various mixed methanol solutions of $EuCl_2$ and $ZnCl_2$ in a nitrogen flushed box for 1 day. A range of the $EuCl_2$ concentration was from $5x10^{-3}$ M to $1x10^{-1}$ M and the $ZnCl_2$ concentration was $1x10^{-1}$ M or $2x10^{-1}$ M. The Eu^{2+}-Zn^{2+}-polymer complexes were separated from the mother liquors by decantation and then dried in vacuo at room temperature.

The $EuCl_2$ and $ZnCl_2$ concentrations in the polymer complex were determined by EDTA titration and by atomic absorption spectrometry and/or by inductively coupled plasma emission spectrometry (ICP) analysis.

Corrected fluorescence and corrected excitation spectra for freshly prepared powdered samples were obtained by a Shimadzu Absolute Spectrofluorophotometer, Model RF-502, using the automatic compensation and pre-calibration system for the instrumental factors, and also fluorescence lifetimes were measured, as reported previously.[2] The emission intensity is expressed as area of the emission band under UV-visible excitation light and the relative emission intensity was determined by comparison with that for $CaWO_4$:Pb (NBS1026) excited by 254 nm.

Emission and excitation spectra for the Eu^{2+}-Zn^{2+}-copoly(MA15C5-MMA) complex and for the Eu^{2+}-copoly(MA15C5-MMA) complex are illustrated at their respective optimal

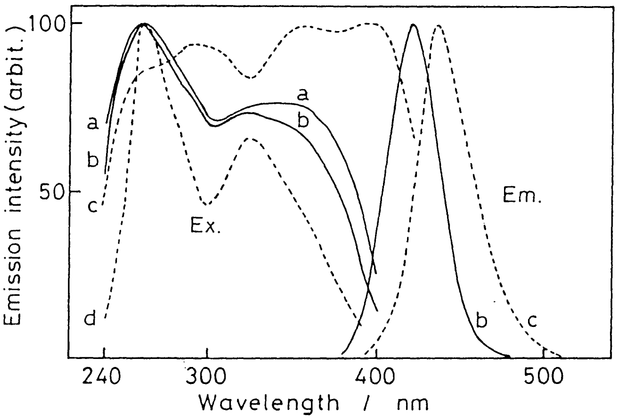

Fig. 2. Emission (Em.) and excitation (Ex.) spectra.
(——) Eu^{2+}-Zn^{2+}-copoly(MA15C5-MMA) complex
a: $[EuCl_2]$=3.92 wt%,
b: $[EuCl_2]$=0.684 wt%
(---) Eu^{2+}-copoly(MA15C5-MMA) complex
c: $[EuCl_2]$=1.07 wt%,
d: $[EuCl_2]$=<0.05 wt%

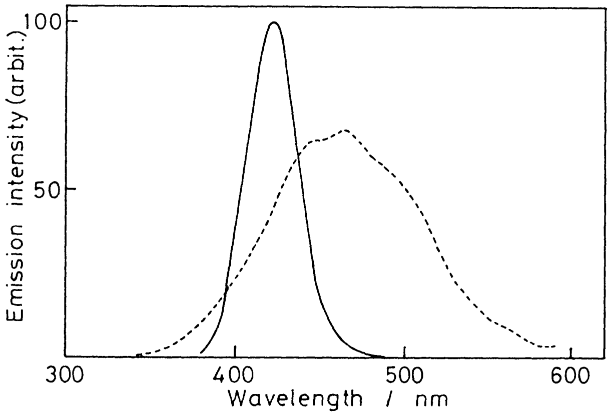

Fig. 3. Comparison of emission spectrum for Eu^{2+}-Zn^{2+}-copoly(MA15C5-MMA) complex ($[EuCl_2]$=0.684 wt%) (——) and that for $CaWO_4$:Pb (NBS1026) (---).

Table 1. Luminescence properties of Eu^{2+}-Zn^{2+}-copoly(MA15C5-MMA) complexes

$[EuCl_2]^{a)}$ in CH_3OH / M	$[ZnCl_2]^{a)}$ in CH_3OH / M	$[EuCl_2]^{b)}$ in Complex / wt%	$[ZnCl_2]^{b)}$ in Complex / wt%	$I^{c)}$ / %	$\lambda^{d)}$ / nm	$\tau^{e)}$ / ns
5×10^{-3}	0	$<0.05^{f)}$	0	7.09	420	610
1×10^{-2}	0	0.0736	0	11.2	432	513
5×10^{-2}	0	1.07	0	23.1	436	477
5×10^{-2}	0	1.93	0	15.9	435	458
1×10^{-1}	0	5.39	0	13.5	437	423
5×10^{-3}	1×10^{-1}	0.148	1.32	27.3	420	678
1×10^{-2}	1×10^{-1}	0.393	1.90	47.5	421	654
5×10^{-2}	1×10^{-1}	1.39	2.34	45.2	421	607
1×10^{-1}	1×10^{-1}	3.92	4.12	30.6	422	531
1×10^{-2}	2×10^{-1}	0.684	3.71	50.5	421	639
1×10^{-2}	1×10^{-1}	0.482	2.48	49.5	420	640

a) Concentration in methanol at the preparation of the complex.
b) Concentration in the polymer complex. c) The relative emission intensity determined by comparison with that (=100%) of $CaWO_4$:Pb (NBS1026).
d) Emission peak wavelength. e) Luminescence lifetime. f) Not measurable.

$EuCl_2$ concentration for the maximum emission intensity in Fig. 2. These broad band emissions are attributed to $4f^65d$-$4f^7$ transition of an Eu^{2+} and the spectra lie in the blue-violet region. This transition is allowed for the emission and absorption of the electric-dipole radiation.

The spectroscopic data obtained for various Eu^{2+}-Zn^{2+}-copoly(MA15C5-MMA) complexes are summarized in Table 1.

Each sample emitting the maximum blue luminescence was prepared by soaking the polymer ligand into the methanol solution of the 1×10^{-2} M $EuCl_2$ and 2×10^{-1} M $ZnCl_2$ concentration for the Eu^{2+}-Zn^{2+}-polymer complex and into the methanol solution of the 5×10^{-2} M $EuCl_2$ concentration for the Eu^{2+}-polymer complex. The $EuCl_2$ and $ZnCl_2$ concentrations for the former were found to be 0.684 wt% and 3.71 wt%, respectively. On the other hand, the $EuCl_2$ concentration for the latter was 1.07 wt%.

There were two peaks in the excitation spectrum for the Eu^{2+}-Zn^{2+}-polymer complex, which were located at ca. 260 nm and 330 nm (Fig. 2). Excitation spectra for Eu^{2+}-Zn^{2+}-polymer complexes with any Eu^{2+} concentration obtained were similar to the absorption spectrum of $EuCl_2$ in methanol.[2,3] On the contrary, in the case of the brightest luminescent Eu^{2+}-polymer complex ($[EuCl_2]$= 1.07 wt%), the excitation spectrum was very different from that for the Eu^{2+}-Zn^{2+}-polymer complex. A peak in the spectrum appeared at ca. 400 nm, as shown in Fig. 2(c). The shape of the excitation spectrum for the Eu^{2+}-polymer complex with a low $EuCl_2$ concentration : <0.05 wt%, however, was very similar to the excitation spectrum for the Eu^{2+}-Zn^{2+}-polymer complex.

The peak wavelength varied from 420 nm to 436 nm for the Eu^{2+}-copoly(MA15C5-MMA) complex, as the $EuCl_2$ concentration increased,[7] while there was less change in the peak wavelength for the Eu^{2+}-Zn^{2+}-polymer complex and it is almost constant at ca. 420 nm (Table 1). This emission wavelength is identical to that for the low $EuCl_2$ concentration Eu^{2+}-polymer complex.

According to these results, it is assumed that the coexistence of Zn^{2+} with Eu^{2+} causes the surroundings of the Eu^{2+} ions in the complex similar to those in the low $EuCl_2$ concentration Eu^{2+}-polymer complex, even if the $EuCl_2$ concentration is relatively high in the Eu^{2+}-Zn^{2+}-polymer complex.

The maximum emission intensity for the Eu^{2+}-Zn^{2+}-polymer complex became ca. 2.5 times as large as that for the Eu^{2+}-complex and was ca. 50 % with respect to that for $CaWO_4$:Pb (NBS1026),[9] whose quantum efficiency was reported to be about 76 %.[10] Figure 3 shows both luminescence spectra for the maximum luminescent Eu^{2+}-Zn^{2+}-polymer complex excited by 261 nm and for $CaWO_4$:Pb (NBS1026) excited by 254 nm. It is clearly demonstrated that the Eu^{2+}-Zn^{2+}-polymer complex emits stronger luminescence at the region of about 420 nm than the standard phosphor.

The luminescence lifetime for the Eu^{2+}-Zn^{2+}-polymer complex is longer than that for the corresponding Eu^{2+}-polymer complex. This result indicates that the enhancement of Eu^{2+} emission caused by Zn^{2+} addition is due to killing non-radiative mechanisms operated on emitting Eu^{2+} states in the original Eu^{2+}-polymer complex.

References

1) G. Adachi, K. Tomokiyo, K. Sorita, and J. Shiokawa, J. Chem. Soc., Chem. Commun., 1980, 914.
2) G. Adachi, K. Sorita, K. Kawata, K. Tomokiyo, and J. Shiokawa, J. Less-Common Met., 93, 81(1983).
3) G. Adachi, H. Fujikawa, K. Tomokiyo, K. Sorita, K. Kawata, and J. Shiokawa, Inorg. Chim. Acta, 113, 87(1986).
4) G. Adachi, H. Fujikawa, and J. Shiokawa, J. Less-Common Met., 126, 147(1986).
5) G. Adachi, H. Nakamura, T. Mishima, and J. Shiokawa, Chem. Express, 2, 341(1987).
6) G. Adachi, H. Nakamura, T. Mishima, and J. Shiokawa, Chem. Express, 2, 727(1987).
7) N. Higashiyama, H. Nakamura, T. Mishima, J. Shiokawa, and G. Adachi, in contribution.
8) T. Maeda, M. Ouchi, K. Kimura, and T. Shono, Chem. Lett., 1981, 1573.
9) NBS Technical Note 417 U.S. Department of Commerce, National Bureau of Standards, 1968, 16.
10) A. Bril and W. Hoekstra, Philips Res. Repts, 16, 356(1961).

(Received August 13, 1990)