

One-Electron Reduction of  $\text{Eu}^{3+}$  Ions Induced by the Irradiation of  $\gamma$ -Ray or UV-Light. The Fluorescence Properties of  $\text{Eu}^{2+}$  Ions in an Ethanol Matrix

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Irradiation of  $\gamma$ -ray or UV-light induced an efficient one electron reduction of  $\text{Eu}^{3+}$  ions in a low temperature matrix of ethanol.  $\text{Eu}^{2+}$  ions produced by these processes showed a strong fluorescence which is affected by the circumstances at low temperatures.

We have reported on the photochemical reduction of  $\text{Eu}^{3+}$  ions in organic solvents and the application of an  $\text{Eu}^{3+}/\text{Eu}^{2+}$  photoredox system to organic synthesis.<sup>1)</sup> These ions are known to have characteristic fluorescence properties which have been applied to the fields of cathode-ray tubes, fluorescent lamps, and so on.<sup>2)</sup> However, the fluorescences of these ions are very weak in a solution because of a vibrational interaction between an excited Eu-ion and solvent molecules. Recently, it has been reported that the complexation of  $\text{Eu}^{2+}$  ions with crown ethers or cryptands enormously increases the fluorescence intensity and the effect was due mainly to the protection of  $\text{Eu}^{2+}$  from the collision of methanol molecules by coordinating ligands and to the removal of the solvating OH group from  $\text{Eu}^{2+}$ .<sup>3a)</sup>

On the other hand, we have used low temperature rigid matrix method for the investigation of active intermediates in which the intermediates are isolated in the matrix and stabilized.<sup>4)</sup> In this paper, we report the one electron reduction of  $\text{Eu}^{3+}$  ions by the irradiation of  $\gamma$ -ray or UV-light in a low temperature ethanol matrix and the fluorescence properties of  $\text{Eu}^{2+}$  ions produced by these processes.

An ethanol solution of  $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$  ( $5 \text{ mmol dm}^{-3}$ ) was irradiated by  $^{60}\text{Co}$   $\gamma$ -ray for 2 h at 77 K (Dose: 30 kGy).<sup>5)</sup> The color of the solution was changed to purple after the  $\gamma$ -irradiation due to the trapped electrons formed. Upon photobleaching with a light  $>600 \text{ nm}$ , new absorption bands with  $\lambda_{\text{max}}$  at 260 nm and 325 nm were formed (Fig. 1. 2) which

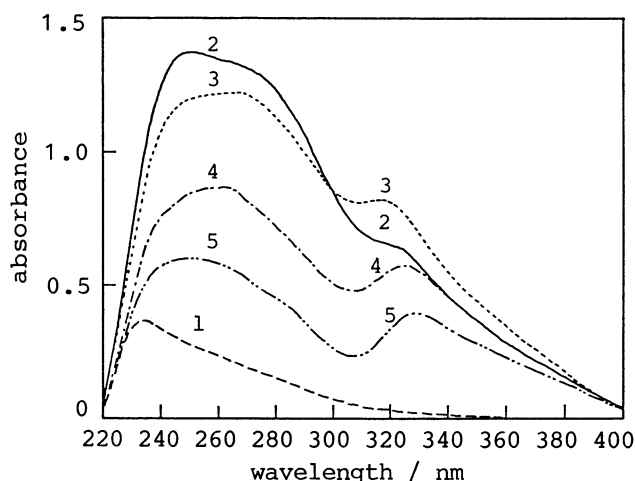


Fig. 1. Changes of the absorption spectra during the annealing of the ethanol matrix irradiated at 77 K.

$[\text{EuCl}_3 \cdot 6\text{H}_2\text{O}] = 5 \text{ mmol dm}^{-3}$

dose: 30 kGy; light pass: 1 mm

1: before irradiation

2: after irradiation at 77 K

3-5: after annealing (3: 100 K, 5: 300 K)

are assigned to  $\text{Eu}^{2+}$  ions. Therefore, it is clear that  $\text{Eu}^{3+}$  ions were reduced by the capture of trapped electrons.

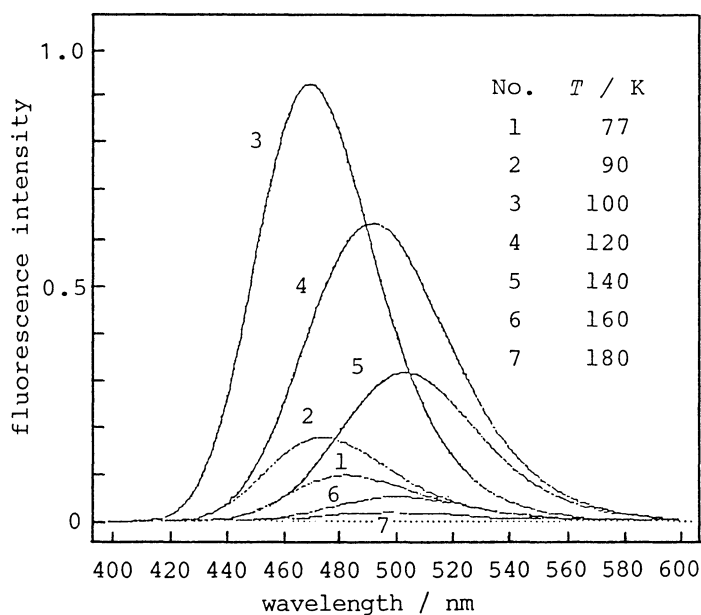


Fig. 2. Fluorescence spectra of an ethanol matrix  $\gamma$ -irradiated at 77 K and after annealing up to 180 K.  $[\text{EuCl}_3 \cdot 6\text{H}_2\text{O}] = 5 \text{ mmol dm}^{-3}$ ; dose: 30 kGy; excitation wavelength: 300 nm

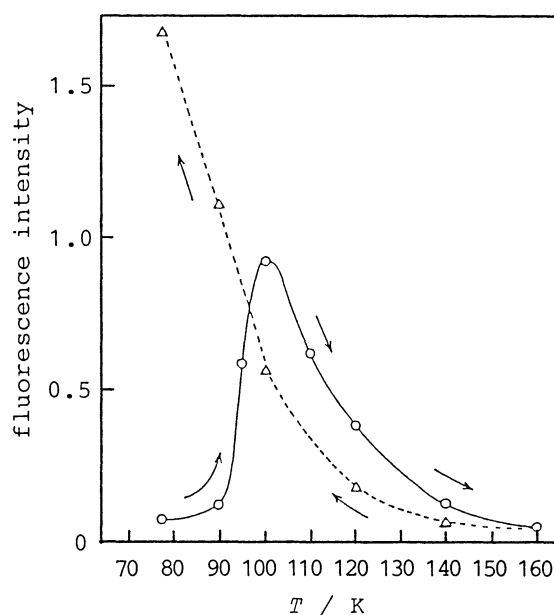


Fig. 3. Changes in the fluorescence intensity at the  $\lambda_{\text{max}}$  on annealing up to 160 K (---o---) and re-cooling (—o—) of the matrix  $\gamma$ -irradiated at 77 K.  $[\text{EuCl}_3 \cdot 6\text{H}_2\text{O}] = 5 \text{ mmol dm}^{-3}$ ; dose: 30 kGy; excitation wavelength: 300 nm

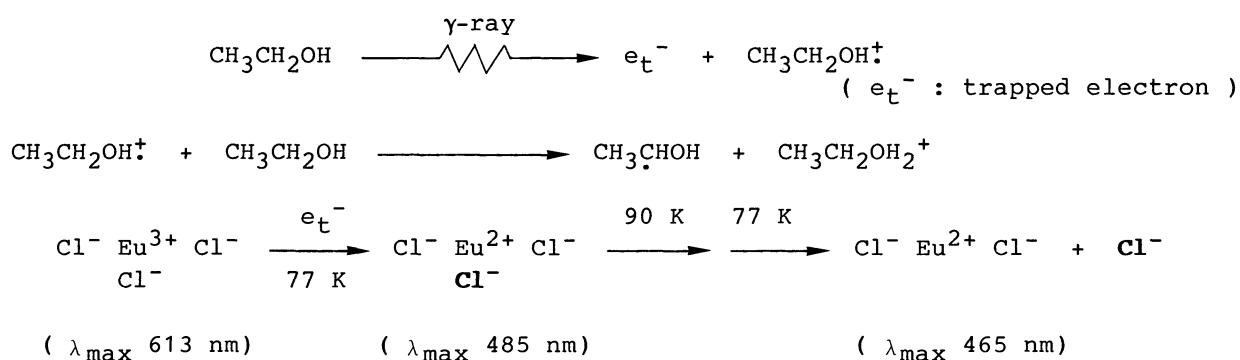
Table 1. Fluorescence property of  $\text{Eu}^{2+}$  ion in an ethanol matrix at 77 K before and after annealing

	Immediately after irradiation	After annealing <sup>a)</sup>
Relative intensity	1	20
$\lambda_{\text{max}}/\text{nm}$	485	465
Lifetime /ns	74 (3%) 460 (23%) 910 (74%)	780 (100%)

a) The  $\gamma$ -irradiated matrix was re-cooled to 77 K immediately after annealing up to 90 K.

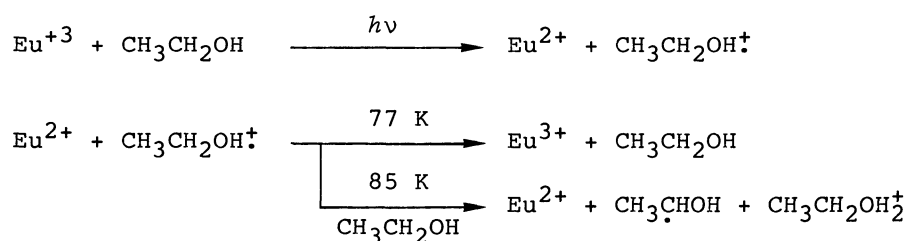
Figure 2 shows the fluorescence spectra of the  $\gamma$ -irradiated matrix at 77 K and after the annealing of the irradiated matrix up to 180 K. At 77 K, the fluorescence was very weak and its maximum was observed at 485 nm. Annealing to 100 K resulted in an increase of the intensity and a blue-shift of the maximum to 465 nm. However, further annealing resulted in a decrease of the intensity and the red-shift of the maximum which are attributable to a melting of the matrix. On the other hand, a cooling of the melted matrix increased the intensity (Fig. 3).

Therefore, it was suggested that the initial annealing of the matrix induced an irreversible change of the fluorescence property of  $\text{Eu}^{2+}$  ions produced by the  $\gamma$ -irradiation at 77 K in a matrix. Absorption spectra also show an irreversible change by annealing (Fig. 1. curves 2-5) in which an isosebestic point was observed upto 100 K (Fig. 1. curves 2-3). Once the matrix melts,  $\text{Eu}^{2+}$  ions showed a reversible change along to the dashed curve in Fig. 3 and it agreed closely with that of  $\text{Eu}^{2+}$  ions independently synthesized showing a strong fluorescence at 460 nm.<sup>3a)</sup> The fluorescence properties of  $\text{Eu}^{2+}$  ions in the present system are summarized in Table 1. The measurement of the fluorescence lifetime of  $\text{Eu}^{2+}$  ions after the  $\gamma$ -irradiation at 77 K indicated the presence of three components. After the annealing and successive re-cooling to 77 K, only a single component with a lifetime of 780 ns was observed. The lifetime agreed with a reported value of  $\text{Eu}^{2+}$  ions in an ethanol matrix at 77 K.<sup>3a)</sup> These results suggest that the  $\text{Eu}^{2+}$  ions produced by  $\gamma$ -irradiation in a 77 K matrix were fixed in rather unstable states which make the fluorescence process inefficient. Upon the annealing, the  $\text{Eu}^{2+}$  ion relaxes to stable conditions and becomes to indicates normal fluorescence properties. ESR analysis showed the formation of H atoms and hydroxyethyl radicals ( $\text{CH}_3\dot{\text{C}}\text{HOH}$ ) but the fine structure and the intensity did not show any change by the annealing in spite of the conspicuous change of the fluorescence. This fact suggests that these radical species had little responsibility for the change of the fluorescence. Addition of crown ether is known to reduce the interaction of  $\text{Eu}^{2+}$  ions with solvent molecules and counter ions, and the effects might enhance the fluorescence intensity of  $\text{Eu}^{2+}$  ions in solution as reported by Adachi et al.<sup>3a-c)</sup> Then, such an effect of crown ether was investigated in the present system. Ethanol solution of  $\text{EuCl}_3$  (20 mmol  $\text{dm}^{-3}$ ) and 18-crown-6 ether (60 mmol  $\text{dm}^{-3}$ ) was irradiated at 77 K. Strong fluorescence of  $\text{Eu}^{2+}$ -crown complex was observed at around 440 nm even immediately after the  $\gamma$ -irradiation at 77 K and this maximum wavelength agreed with that of the sample after annealing and successive re-cooling to 77 K. The experiment by use of  $\text{Eu}(\text{ClO}_4)_3$  gave results similar to that of  $\text{EuCl}_3$ . These observation led us to conclude that these phenomena were caused by the interaction of  $\text{Eu}^{2+}$  ions and  $\text{Cl}^-$  ions which are present in an excess by one electron reduction of  $\text{EuCl}_3$  and fixed in a close vicinity to the  $\text{Eu}^{2+}$  ions as shown in Scheme 1. After annealing, this interaction disappeared on diffusion of the excess  $\text{Cl}^-$  ions, and the sample showed a normal fluorescence.<sup>3a)</sup>



Scheme 1.

One electron reduction of  $\text{Eu}^{3+}$  ions and the fluorescence of  $\text{Eu}^{2+}$  ions were also observed by photoirradiation at a low temperature. A strong blue fluorescence of  $\text{Eu}^{2+}$  ions was observed after a few minutes photoirradiation at 85 K. At 77 K, however, no fluorescence of  $\text{Eu}^{2+}$  ions was observed which suggests the inefficient reduction of  $\text{Eu}^{3+}$  ions. It was concluded that the one electron reduction of  $\text{Eu}^{3+}$  ions was induced only in a rather high temperature matrix in which a molecular diffusion was allowed. In the photo-induced electron transfer reaction,  $\text{Eu}^{3+}$  ion might obtain an electron from the neighbor matrix molecule or the counter ions. Therefore, the back electron transfer process between the geminate pairs seems faster than the diffusion or ion-molecule reactions of one of the geminate pairs.



**Scheme 2.**

We thank the Ministry of Education, Science and Culture of Japan for a Grant-in-Aid for Scientific Research (No. 62750785).

#### References

- 1) A. Ishida, S. Toki, and S. Takamuku, J. Chem. Soc., Chem. Commun., 1985, 1481; A. Ishida, S. Toki, and S. Takamuku, Chem. Lett., 1986, 117.
- 2) J. M. P. J. Versteegen, J. Electrochem. Soc., 121, 1623 (1974).
- 3) a) G. Adachi, K. Sorita, K. Kawata, K. Tomokiyo, and J. Shiokawa, J. Less-Common Met., 93, 81 (1983); b) G. Adachi, K. Tomokiyo, K. Sorita, and J. Shiokawa, J. Chem. Soc., Chem. Commun., 914 1980; c) G. Adachi, K. Sorita, K. Kawata, K. Tomokiyo, and J. Shiokawa, Inorg. Chim. Acta, 109, 117 (1985).
- 4) S. Takamuku, H. Kigawa, H. Suematsu, S. Toki, K. Tsumori, and H. Sakurai, J. Phys. Chem., 86, 1861 (1982).
- 5) Commercially available  $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$  was dried under high vacuum prior to use. Ethanol was distilled over  $\text{CaH}_2$ . Crown ethers were used without further purifications. Radiation source was a  $^{60}\text{Co}$  of the Institute of Scientific and Industrial Research of Osaka University. Photoirradiations were carried out by a 150 W high pressure Xe lamp. Absorption spectra and fluorescence spectra were recorded on a spectro multi-channel photodetector (Ohtsuka electronics MCPD-100) and a spectrofluorophotometer (Hitachi 850), respectively. Fluorescence lifetimes were measured with a single-photon counting apparatus (Horiba NAES-1100 time-resolved spectro fluorophotometer). ESR spectra were recorded on Varian E-series spectrometer. A cryostat was made by Oxford Instruments. The sample solutions were evacuated and sealed in Suprasil cells and irradiated at 77 K. The samples irradiated at 77 K were photobleached with light  $>600$  nm before the fluorescence measurements. Photoirradiations were carried out in a cryostat at several temperatures.

(Received June 7, 1988)