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In situ generation of fluorescent macrocyclic europium(II) complexes via zinc reduction

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ABSTRACT

We report *in situ* generation of macrocyclic Eu(II) complexes upon zinc reduction which readily emitted visible light *via* $5d \rightarrow 4f$ transitions. The nature of a co-existing anion significantly controlled the reduction rate of the Eu(III) complex and the fluorescence intensity of the generated Eu(II) complex. Among the examined anions, Cl^-, Br^-, and I^- effectively offered intense Eu(II) fluorescence, while OAc^- and NO_3^- elongated the time for completion of reduction and weakened the fluorescence. Since the generated macrocyclic Eu(II) complexes were stable under N_2 atmosphere, this *in situ* reduction is a useful method to prepare fluorescent Eu(II) complexes.

1. Introduction

Although divalent europium ion shows optically allowed transitions between *4f* and *5d* orbitals to give a broad emission band in the visible region, a limited number of Eu(II) complexes were reported to emit intense fluorescence. Due to the vulnerability to molecular oxygen and the strong reducing power of the Eu(II) species, preparation and utilization of Eu(II) complexes in solution have been restricted. Adachi and coworkers had combined a series of macrocyclic ligands with $EuCl_2$ prepared from Eu_2O_3 and revealed that the complexation with macrocyclic ligands drastically enhanced the fluorescence intensities in MeOH [1]. Typically, 18-crown-6 formed 1:1 Eu(II) complex which showed the 160-times enhanced fluorescence comparing with $EuCl_2$ itself [1]. Starynowicz et al. [2] reduced Eu(III) complex with 18-crown-6 by electrolysis and obtained the crystal structure of its Eu(II) complex. Since the Eu(II) has large ionic radius and adopts high coordination number, its macrocyclic complexes still have available coordination sites for incoming anions and solvent molecules. A similar fluorescence enhancement was reported with Sm(II)–18-crown-6 and Sm(II)–(15-crown-5)$_2$ complexes[3].

In this paper, we report *in situ* preparation of macrocyclic Eu(II) complexes in MeOH and significant effects of anions on the generation and fluorescence properties of Eu(II) complexes. As a convenient synthetic method of Eu(II) complexes, we applied zinc reduction of $Eu(OTf)_3$ complexes with 18-crown-6 and cryptand[2.2.2]. When several tetrabutylammonium salts were added prior to reduction to the MeOH solution, some additional anions offered ternary Eu(II) complexes with different fluorescent properties.

2. Experimental

2.1. *Chemicals and reagents*

$Eu(OTf)_3$, 18-crown-6, and cryptand[2.2.2] were respectively purchased from Sigma–Aldrich Japan K. K., Tokyo Chemical Industry Co. Ltd, and Merck Ltd. Japan, and used as received. The employed tetrabutylammonium salts were also commercially available from Sigma–Aldrich Japan K. K. (Br^-, I^-, OAc^-, and NO_3^-), Tokyo Chemical Industry Co. Ltd. (Cl^- and SCN^-), and Wako Pure Chemicals Industries Ltd. (F^- as trihydrate). Spectroscopic grade MeOH was purchased from Nacalai Tesque Inc. and used without further purification for all the measurements.

2.2. *In situ generation of macrocyclic Eu(II) complexes in MeOH*

2.2.1. *Eu(II)–18-crown-6 complex*

A 2-ml MeOH solution containing $Eu(OTf)_3$ (5.0×10^{-4} M), 18-crown-6 (5.0×10^{-3} M), and nBu_4NX (2.5×10^{-3} M) was prepared. This solution was transferred to 1-cm quartz cell where excess amount of zinc powder (ca. 100 mg) and a stirring bar were added. The cell was then capped with a rubber septum. The solution was vigorously stirred for longer than 20 min with N_2 gas bubbling. The N_2 gas for de-aeration was passed through the methanol before introducing in the cell to avoid vaporization of the solvent. The zinc reduction was monitored by following the absorption bands of Eu(II) species around 250 and 330 nm.

2.2.2. *Eu(II)–cryptand[2.2.2] complex*

An equimolar mixture of $Eu(OTf)_3$ and cryptand[2.2.2] was stirred at room temperature for longer than 8 h, and then the zinc reduction was similarly carried out.

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The final concentrations were [Eu(OTf)$_3$] = 5.0 × 10^{-4} M, [cryptand] = 5.0 × 10^{-4} M, and [nBu$_4$NX] = 2.5 × 10^{-3} M.

2.3. UV–vis and fluorescence measurements

UV–vis absorption spectra were recorded on a Hitachi U-4500 or a Scinco S-3100 spectrometer. Fluorescence spectra were recorded on a PerkinElmer LS-55 spectrometer. The Eu(II) complexes were excited at 330 nm where the absorbance of the Eu(II) absorption band was ca. 0.2. Excitation and emission slits were set to 5.0 and 2.5 nm, respectively. The obtained fluorescence spectra were not corrected.

2.4. Cyclic voltammetry

Cyclic voltammograms for macrocycle–Eu complexes were measured in MeOH with a Hokuto Denko HSV-100 electrochemical analyzer. The working electrode was a glassy carbon electrode and the counter electrode was a platinum wire. The reference electrode was a Ag$^+$/Ag electrode. The scan rate was 50 mV s^{-1}.

3. Results and discussion

3.1. Macrocyclic complexation

Thermodynamic and structural studies on macrocyclic Eu(II) complexes are limited due to the facile oxidation of Eu(II) species with molecular oxygen. Starynowicz et al. reported the crystal structure of bisperchlorato(18-crown-6)europium(II) by electrochemical reduction [2]. In the complex, the 18-crown-6 located in the equatorial plane and the two perchlorate anions coordinated to the Eu(II) from the opposite sides. Tóth and coworkers [4] reported Sr(II)–cryptand[2.2.2](H$_2$O)(OTf)$_2$.This is an effective reference, because the ionic radius of Sr(II) (r = 1.26 Å) is similar to that of Eu(II) (r = 1.25 Å). The Sr(II) ion was completely wrapped in the cryptand cavity and further coordinated by one water and one OTf$^-$ anion to give a 10-coordinated complex. Stability constants of the Eu(II) complexes with 18-crown-6 and cryptand[2.2.2] were not determined in MeOH, but those of the corresponding of SrCl$_2$ complexes were determined: 18-crown-6 complex, log K = 3.76; cryptand[2.2.2] complex, log K = 4.89 [5]. We employed 5 × 10^{-4} M Eu(OTf)$_3$ solution containing 10 equiv. of 18-crown-6 or 1 equiv. of cryptand[2.2.2] in the following experiments. Under the employed conditions, considerable amounts of Eu(II)–macrocycle complexes are expected to be generated (Fig. 1).

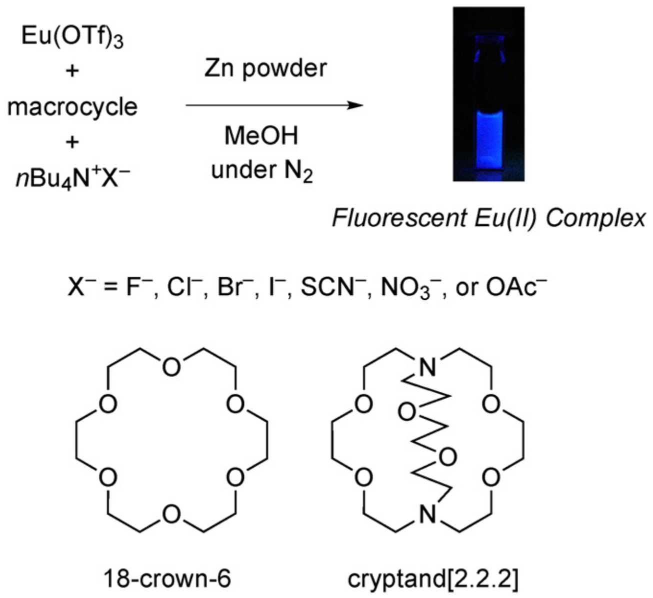

Fig. 1. *In situ* preparation of Eu(II) complex in MeOH.

3.2. In situ preparation of Eu(II) complexes in MeOH

Reduction of Eu(III) complex by zinc was monitored by following the broad absorption bands of *4f* → *5d* transitions of Eu(II) center. When a MeOH solution of Eu(III) salt and macrocyclic ligand was mixed with zinc powder, characteristic absorption bands of the Eu(II) species appeared around 250 and 330 nm, indicating that zinc reduction of Eu(III) complex occurred (see Fig. 2a and b). The reduction rate of each Eu(III) complex was dependent on a combination of macrocycle and co-existing anion. The reduction of Eu(OTf)$_3$–18-crown-6 complex completed after 40 min, while the addition of 5 equivalents of Cl$^-$ or SCN$^-$ to the solution effectively accelerated the reduction and 15 min were enough to obtain the Eu(II) complex quantitatively. OAc$^-$ and NO$_3$$^-$ anions gave no influence on the reduction rates, but the observed UV signals were somewhat broader than other Eu(II) complexes. When cryptand[2.2.2] was employed, the absorption spectral changes were similarly observed, but the reduction rates were more strongly dependent on the natures of the added anions. When an equimolar mixture of Eu(OTf)$_3$ and cryptand[2.2.2] was treated by zinc powder, the absorbance increase at 250 nm continued for longer than 120 min. Addition of Cl$^-$, Br$^-$, I$^-$, SCN$^-$, or OAc$^-$ anion shortened the required time to 30 min for completing the reaction, while 80 min was required for the reduction in the presence of NO$_3$$^-$ anion. In the presence of F$^-$ anion, however, no Eu(II) absorption band appeared at all in both complexes.

As shown in Fig. 2a and b, 18-crown-6 and cryptand[2.2.2] gave different absorption maxima of the Eu(II) species, but the added anions gave only slight changes. The molar extinction coefficients and the wavelength of the absorption maxima observed here were consistent with the values reported by Adachi and coworkers [1], where pure EuCl$_2$ was first prepared and then used for complexation with macrocyclic ligands under inert atmosphere: λ_{max} (nm) (ε (mol^{-1} cm^{-1})) of *in situ* generated 18-crown-6–EuBr$_2$ complex were 256 (1.7 × 10^3) and 326 (4.6 × 10^2) [6]. Literature values were 256 (1723) and 325 (477). Both macrocyclic complexes showed quasi-reversible cyclic voltammograms of Eu^{3+}/Eu^{2+} in MeOH containing 0.1 M nBu$_4$N(OTf) [7]. The cathodic peak potential (E_{pc}) was −0.70 V (vs Ag$^+$/Ag) for 18-crown-6–Eu(OTf)$_3$ complex. The addition of SCN$^-$, OAc$^-$, or NO$_3$$^-$ anion gave more negative E_{pc} values: −0.73 (SCN$^-$), −0.84 (NO$_3$$^-$), and −1.12 V (OAc$^-$). Cryptand[2.2.2]–Eu(OTf)$_3$ complex showed much broader peaks and addition of Cl$^-$, Br$^-$, or SCN$^-$ gave the similar voltammogram, while OAc$^-$ and NO$_3$$^-$ anion gave two reduction peaks (−1.13 and −0.74 V for OAc$^-$; −0.98 and −0.62 V for NO$_3$$^-$). When F$^-$ anion was added, both macrocyclic complexes showed no signal in the employed scan range (0 to −1.6 V). Since the F$^-$ anion is known to bind strongly with Eu(III) ion, zinc may not have enough power to reduce its F$^-$ complex. Since Eu(II) absorption bands appeared and the voltammograms were observable, the employed other anions did not prevent the zinc reduction of the Eu(III) complexes.

3.3. Eu(II) fluorescence

Fluorescence spectra of *in situ* generated Eu(II) complexes were measured by exciting Eu(II) absorption band at 330 nm (Fig. 2c and d). The cryptand[2.2.2] complexes showed fluorescence at longer wavelength than the 18-crown-6 complexes. The natures of the added anions gave no influences on the fluorescence wavelengths, but greatly affected the fluorescence intensities. Addition of Cl$^-$, Br$^-$, and I$^-$ gave intense fluorescence signals, while SCN$^-$, OAc$^-$, and NO$_3$$^-$ anions decreased the fluorescence intensities. The fluorescence measurements were repeated several times within 10 min, but no decrease in intensity was observed unless the solution was exposed to the air. The Eu(II) fluorescence disappeared within a

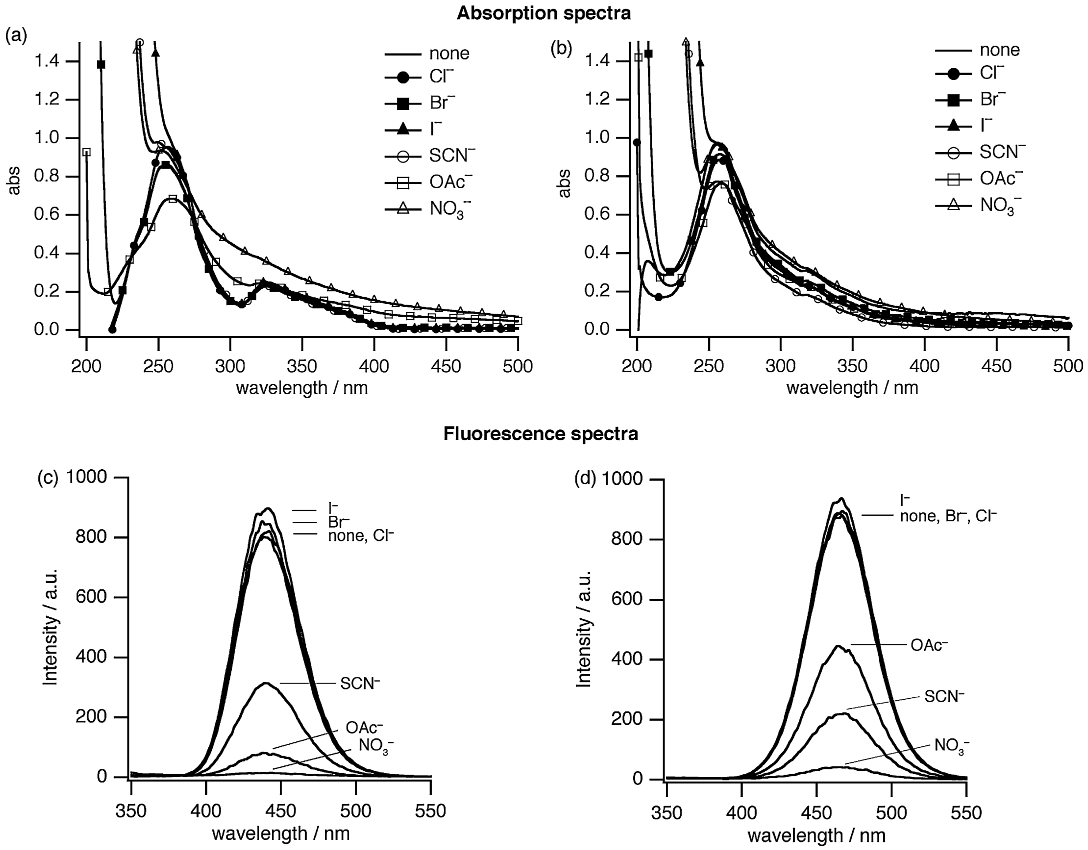

Fig. 2. UV–vis absorption spectra of (a) Eu(II)–18-crown-6 and (b) Eu(II)–cryptand[2.2.2] complexes and fluorescence spectra of (c) Eu(II)–18-crown-6 and (d) Eu(II)–cryptand[2.2.2] complexes after zinc reduction. Markers were put on every 15 points to distinguish the lines. $[Eu(OTf)_3] = 5.0 \times 10^{-4}$ M, [18-crown-6] = 5.0×10^{-3} M or [cryptand[2.2.2]] = 5.0×10^{-4} M, $[nBu_4NX]$ = 0 (none) or 2.5×10^{-3} M; d = 1 cm; MeOH; room temperature; excitation at 330 nm.

minute after contact with air even when the excess amount of zinc remained in the quartz cell.

4. Conclusion

Fluorescent Eu(II) complexes with 18-crown-6 and cryptand[2.2.2] ligands were *in situ* prepared by zinc reduction of the mixture containing ligand, $Eu(OTf)_3$ and external anion. Cl^-, Br^-, and I^- promoted the efficient generation of the fluorescent Eu(II) complexes with both macrocycles. Thus, the appropriate combination of macrocyclic ligand and coordinating anion enabled *in situ* preparation of fluorescent Eu(II) complex.

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