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Surface-enhanced luminescence from Eu^{3+} complex nearby Ag colloids

H. Nabika and S. Deki[a]

Department of Chemical Science and Engineering, Faculty of Engineering, Graduate School of Science and Technology, Kobe University, Rokkodai, Nada, Kobe 657-8501, Japan

Abstract. The effect of colloidal dispersion of silver on the luminescent properties of Eu (III) complex with pyridine-3,5-dicarboxylic acid (PyDC) was investigated. The luminescence from Förster type europium complex was enhanced several times with the presence of Ag colloid and the enhancement factor showed Ag concentration dependence. The observed enhancement effect was discussed in view of surface-enhancement effect and optical absorption due to surface plasmon resonance, both arising from excitation of surface plasmon polariton. The coordination structure around Eu (III) ion was also affected with the presence of Ag colloid, which induced the change in the intensity ratio between two emission bands of $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ transitions of Eu (III) ion.

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1 Introduction

Luminescent properties of lanthanide (III) ion have been a subject of great interest, because of their potential applications as optical signal amplification [1], light-emitting diode (LED) [2] and fluoroimmunoassay [3,4]. Among of various lanthanide materials, many experimental and theoretical investigations have been reported on the luminescent properties of europium complex, in which high-efficient luminescence from Eu (III) ion is obtained through energy transfer between ligand excited state and resonant energy level of Eu (III) ion. Much effort has been devoted to achieve highly luminescent europium materials by complexation with several types of organic molecules [5,6] or polymer [7,8], doping into sol-gel derived matrix [9,10] or semiconductor nanoparticles [11], and intercalation into layered material [12]. The overall quantum yield of these europium complexes depends on the efficiency of individual radiative or non-radiative energy transition: the efficiency of ligand excitation, the intersystem crossing efficiency, the energy transfer efficiency, and the luminescent efficiency of Eu (III) ion. The investigations reported so far have mainly focused on the improvement of these efficiencies, in which the coordination environment around Eu (III) ion such as coordination number, the distance between ligand and central Eu (III) ion, and symmetry around Eu (III) ion, have been intensively discussed.

In the present study, we describe novel procedure to enhance the luminescence from europium complex, based on the surface-enhanced fluorescence (SEF). Colloidal films or suspensions of metal nanoparticles have been received considerable attention and it is well known that they play a special role in surface-enhanced spectroscopy [13]. For example, surface-enhanced Raman scattering (SERS) is well-known and several mechanisms have been suggested for surface enhancement effect [14]. SEF is also one of surface-enhancement phenomena based on the large electromagnetic field arising from the excitation of surface plasmon polariton (SPP), which is independent of the kind of the molecules bound to metallic surface. Especially the distance between metallic surface and fluorophore is an important factor for SEF, because the fluorescence enhancement is the results from competition between the amplified incident field around metallic surface and non-radiative relaxation due to damping of the dipole oscillators by metallic surface [15]. Recently, growing attention has been paid for the application of SEF to biophysical or biomedical use [16–19]. Also, the surface-enhancement effect on the fluorescence from Eu (III) ion doped into glass [20] or Eu (III) complex adsorbed onto Ag-island surface [21], has been reported so far, and they observed enhanced luminescence or shortened lifetime of Eu (III) ion with the presence of Ag. The aim of the present study is to apply SEF effect to the conventional solution system containing europium complexes, in which we can prepare the sample simply by mixing of Eu (III) complex solution and Ag colloidal solution. The effect of the presence of Ag

[a] e-mail: deki@kobe-u.ac.jp
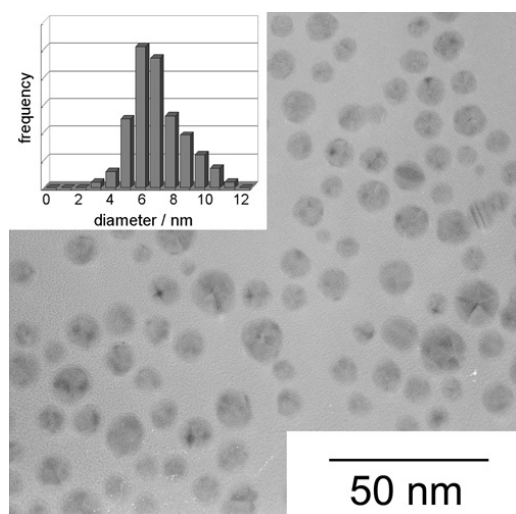
**Fig. 1.** TEM image and the corresponding size distribution of purified Ag nanoparticles.

colloid on the luminescent properties of Eu (III) complex was investigated.

2 Experimental procedure

Ag colloid was prepared by the reduction of $AgNO_3$ with $NaBH_4$ in the presence of polyvinylpyrrolidone (PVP). PVP (33.4 mg) and $AgNO_3$ (25.7 mg, 0.15 mmol) were dissolved in N,N-dimethylformamide (DMF) to obtain 100 ml solution, followed by the addition of 60 ml of 0.83 mM $NaBH_4$(DMF) solution under vigorous stirring. The color of the solution changed to deep orange immediately after the addition of $NaBH_4$. The reaction mixture was left for 12 h with rapid stirring to ensure complete reaction. Centrifuging (14 000 rpm) gave a brown DMF-soluble precipitates, and supernatant containing excess PVP and $NaBH_4$-derived impurities was extracted. The precipitates were again dissolved into DMF. This purification procedure was repeated three times. Morphology and size distribution of Ag colloid was obtained by using of a JEM-2010 (JEOL) transmission electron microscope (TEM), operating at 200 kV. Europium composite was obtained by dissolving equimolar pyridine-3,5-dicarboxylic acid (PyDC) and $EuCl_3$ into DMF to obtain 25 μM solution. For luminescence measurement, Ag colloidal solution and Eu-PyDC solution was mixed at various compositions and luminescence measurements were performed with JASCO FP-6500 spectrofluorometer with 90° configuration.

3 Results and discussion

Representative TEM image of purified Ag colloids shows the presence of small Ag particles with an average diameter of 7.5 nm (Fig. 1). It was also confirmed that the morphology and size distribution showed no significant change
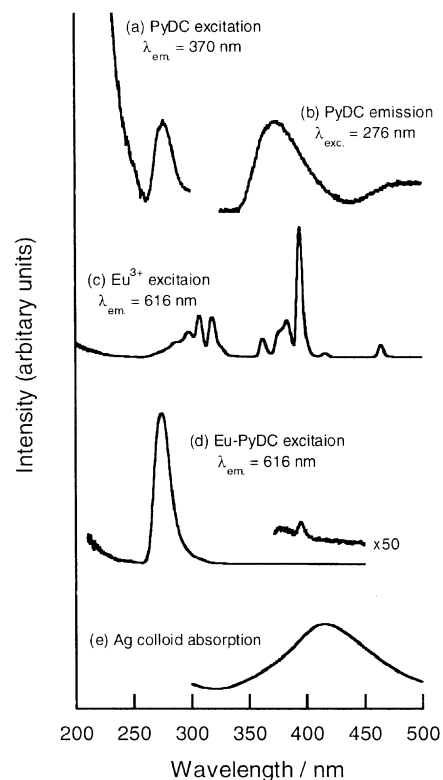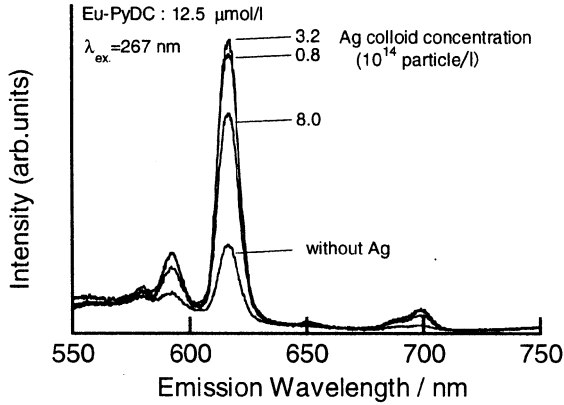

Fig. 2. Electronic spectra of PyDC, Eu (III) ion, Eu-PyDC complex, and Ag colloid dissolved in DMF.

before and after mixing with Eu-PyDC solution, and the Ag colloids were stable at room temperature in DMF at lease four months.

PyDC shows broad emission band centered at around 370 nm (Fig. 2b) with the excitation maximum at 276 nm (Fig. 2a). The excitation spectrum of Eu (III) ion dissolved in DMF was obtained by monitoring $^5D_0 \rightarrow {}^7F_2$ transition at 616 nm, in which several sharp bands characteristic of the f-f transitions of Eu (III) ion were observed and the most intense excitation band was $^7F_0 \rightarrow {}^5L_6$ transition at 394 nm (Fig. 2c). Comparing between the PyDC emission spectrum and the Eu (III) ion excitation spectrum, it can be clearly seen that there is an overlap between the emission band of PyDC and the excitation band of Eu (III) ion in the wavelength region of 350 nm to 400 nm. For well-known antenna-functionalized europium composites in which energy transfer occurs from triplet state of ligand to Eu (III) resonant level by a Dexter resonant exchange mechanism [22], triplet state of antenna chelate should be energetically higher (several thousands cm^{-1}) than the resonant luminescence state of Eu (III) ion, to satisfy the efficient irreversible energy transfer [23]. On the other hand, Förster model suggests that the overlap between emission of ligand and absorption of Eu (III) ion, observed in the present study, is enough to induce energy transfer between them [24].

The excitation spectrum of Eu-PyDC complex was also obtained by monitoring $^5D_0 \rightarrow {}^7F_2$ transition at 616 nm (Fig. 2d), in which an asymmetric peak at around

Fig. 3. Emission spectra of Eu-PyDC with and without Ag colloids.

Table 1. Normalized intensity ($^5D_0 \rightarrow {}^7F_2$) and intensity ratio between two emission bands.

Ag colloid concentration (10^{14} particles/l)	normalized intensity	$\frac{I(^5D_0 \rightarrow {}^7F_2)}{I(^5D_0 \rightarrow {}^7F_1)}$
without	1.00	8.16
0.8	3.79	7.26
3.2	3.94	7.04
8.0	2.89	7.40

274 nm and quite small peak at 394 nm ($^7F_0 \rightarrow {}^5L_6$ transition) were observed. The asymmetric peak observed at 274 nm is thought to be attributable to the excitation of PyDC. These results indicate that more intense emission from Eu (III) would be obtained under ligand excitation than direct excitation of Eu (III) ion, through the energy transfer from excited PyDC to the resonant level of Eu (III) ion.

The influence of the existence of Ag colloids on the emission from Eu-PyDC was investigated with several Ag concentrations (Fig. 3). All the spectrum was obtained at room temperature and under ligand excitation ($\lambda_{ex} = 267$ nm). Five emission peaks centered at 580, 592, 616, 650, and 698 nm, assigned to $^5D_0 \rightarrow {}^7F_0$, $^5D_0 \rightarrow {}^7F_1$, $^5D_0 \rightarrow {}^7F_2$, $^5D_0 \rightarrow {}^7F_3$, and $^5D_0 \rightarrow {}^7F_4$ transition, respectively, were observed. We can see the increase in intensity by the presence of Ag colloids, while the emission wavelength remains unchanged. The normalized intensity of $^5D_0 \rightarrow {}^7F_2$ transition was summarized in Table 1, in which enhancement factor increased at a certain Ag concentration and then was followed by a rapid decrease. Since some kinds of small metallic colloid shows characteristic absorption band in visible region, the decrease in the enhancement factor observed in the most concentrated sample is regarded as the results of re-absorption due to surface plasmon resonance (SPR) of Ag colloids. As shown in Figure 2e, the absorption of Ag colloids dissolved in DMF covers over wide wavelength region from 350 nm to 500 nm, which is the similar region to the resonant energy level between PyDC and Eu (III) ion. If we assume the Förster mechanism, considering the dipole-dipole interaction between donor and acceptor [24], SPR absorption in the resonant energy region is unlikely to be competitive with the energy transfer process. However, Ag colloids also absorb higher wavelength region (not shown), which would result in the absorption of the emitted light from Eu (III) ion, although the absorbance is very low. Therefore, SPR absorption of Ag colloids must be taken into consideration, and the observed enhancement factor seems to be the results from delicate balance of SPR and SEF. Since both SEF and SPR strongly depend on Ag particle diameter, concentration, and surrounding medium, systematic

studies are required to elaborate the relation between SEF and SPR with respect to the condition of Ag colloid for further improvement of overall enhancement effect and is currently under investigation in our group.

Among five emission lines observed in Figure 3, the emission from $^5D_0 \rightarrow {}^7F_2$ electric dipole transition is the strongest. This transition is very sensitive to the first coordinative environment around europium ion, otherwise the magnetic dipole allowed $^5D_0 \rightarrow {}^7F_1$ transition would not be affected by the environment and their emission intensity is often used as internal standard. The intensity ratio between $^5D_0 \rightarrow {}^7F_2$ transition and $^5D_0 \rightarrow {}^7F_1$ transition, $I(^5D_0 \rightarrow {}^7F_2)/I(^5D_0 \rightarrow {}^7F_1)$, is therefore an useful indication of symmetry around Eu (III) ion. The results for all samples with and without Ag colloids are included in Table 1, in which the intensity ratio decreased by the addition of Ag colloids. The decrease in the intensity ratio suggests the increase in the symmetry or decrease in the polarization of Eu (III) ion. Because the transition probability of electric dipole $^5D_0 \rightarrow {}^7F_2$ transition would be depressed under higher symmetric environment that reduce the polarization of Eu (III) ion. In the present study, there are two possibilities to induce ligand field distortion; (i) Ag colloids directly affect the ligand field around Eu (III) ion, (ii) Ag colloids interact with PyDC, not directly with Eu (III) ion, resulting in the changes in the coordination structure around Eu (III) ion. Hayakawa *et al.* reported for Eu (III) ion and Ag precipitates co-doped silica glass that the intensity ratio, $I(^5D_0 \rightarrow {}^7F_2)/I(^5D_0 \rightarrow {}^7F_1)$, showed no significant change with the presence of Ag particle, and they concluded that any obvious changes were not induced by the presence of Ag particles in the ligand field around Eu (III) ion [20]. According to their observation, it can be concluded for the present study that Ag colloids interact with PyDC and this interaction induces the changes in the ligand field around Eu (III) ion, resulting in the decrease in the intensity ratio.

4 Conclusion

Enhancement of luminescence from europium complex was obtained with the presence of Ag colloid with the diameter of 7.5 nm in DMF. Observed enhancement factor depended on the concentration of Ag colloid, and the overall emission enhancement is regarded as the results of both surface enhancement effect and SPR absorption of Ag colloids, although SPR absorption is unlikely to be competitive with dipole-dipole type energy transfer process. Ag colloids also affected the coordination structure

around Eu (III) ion through the interaction with PyDC molecules.

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