

Influence of Silver Nanoparticles on the Luminescent Property of Europium Complex

Hideki Nabika and Shigehito Deki

Faculty of Engineering, Graduate School of Science & Technology, Kobe University,

Rokkodai, Nada, Kobe 657-8501, Japan

Fax: 81-78-803-6186, e-mail: deki@kobe-u.ac.jp

Luminescent properties of europium complex with pyridine-3,5-dicarboxylic acid (PyDC), which shows Förster-type energy transfer from excited state of PyDC to the resonant level of europium ion, were investigated in the presence of polymer-protected Ag nanoparticles in N,N-dimethylformamide (DMF). High temperature reduction of AgNO₃ in DMF led to the coalescence growth of Ag nanoparticle rather than Ostward ripening. Intensity ratio between two emission bands of europium complex, $I(^5D_0 \rightarrow ^7F_2) / I(^5D_0 \rightarrow ^7F_1)$, increased with the increase of Ag concentration, suggesting that Ag nanoparticle interacts with the europium complexes and affects the coordination structure around europium ion, whereas the luminescence intensity was found to be decreased above a certain Ag concentration.

Key words: Ag nanoparticle, europium complex, luminescence, surface enhancement

1. INTRODUCTION

Luminescent lanthanide ions are of fundamental and technological interest because of their intense and narrow-width emission band, and their potential applications as light-emitting diode (LED) [1], laser materials [2,3], and fluoroimmunoassay [4,5]. Especially for the detection of DNA based on luminescence resonance energy transfer (LRET), lanthanide chelates are useful as fluorescent labels, because the intrinsic fluorescence intensity of DNA is very weak [6]. To achieve highly luminescent europium complex, much effort has been devoted by chelating lanthanide ion with several types of organic molecules [5,7]. The overall quantum yield of these lanthanide chelates is dependent on several radiative and non-radiative transitions, including energy transfer efficiency in the case of energy transfer complex. The investigations on such a lanthanide chelate reported so far have mainly focused on the improvement of individual transition efficiency, in which the coordination structure around lanthanide ion such as the coordination number, distance between lanthanide ion and ligand, and ligand field symmetry, have been intensively studied.

To enhance the luminescence intensity of lanthanide materials, metal colloid or metallic surface would have a possibility to be a useful tool. It is well known that such a small metal particles exhibit strong enhancement of Raman or fluorescence intensity from the molecules nearby the surface of metal, known as surface enhanced Raman (fluorescence) phenomenon, and they play a special role in surface-enhanced spectroscopy [8]. The strongest enhancement of Raman signal is obtained from the molecules directly adsorbed on the metal surface, whereas the maximum fluorescence intensity is observed at a certain distance from the surface [9]. Because the fluorescence enhancement is affected by both the amplified incident electromagnetic field (positive effect)

and the non-radiative deactivation due to damping of dipole oscillation by the surface (negative effect) [10]. In addition, optical absorption due to the surface plasmon resonance (SPR) of metallic colloid in the visible region is also thought to be responsible for the decrease in the total luminescence intensity.

In the present report, first we will describe about the preparation method of Ag nanoparticle by using of DMF as both solvent and reducing agent, and then we will report on the effect of nano-sized Ag particle on the luminescent properties of europium complex by dissolving Ag colloid into europium complex solution.

2. EXPERIMENTAL

Chemicals; AgNO₃ (99.8%) and polyvinylpyrrolidone (PVP, MW 10,000) were used as Ag nanoparticle precursor and protective agent, respectively. Pyridine-3,5-dicarboxylic acid (PyDC) was used as the ligand for europium ion. N,N-dimethylformamide (DMF, 99.5%) and dimethyl sulfoxide (DMSO, 99%) were used without further purification.

Preparation; Under refluxing DMF (90 ml) containing PVP (1.713 g) at 145°C, 10 ml of 100 mM AgNO₃ DMSO solution was added by dropwise with vigorous stirring, and the reaction mixture was kept at this temperature. The color of the solution turned into yellow and then deep red within 3 min after the addition of AgNO₃ solution. After the reaction solution was cooled to room temperature, they were centrifuged at 12,000 rpm for 1 hour to remove excess PVP, and the precipitates were redissolved in DMF to obtain the sample solution with desired concentration.

Eu₂O₃ was dissolved in distilled water by adding appropriate HCl solution, and then this solution was concentrated to recrystallize as EuCl₃. Obtained EuCl₃

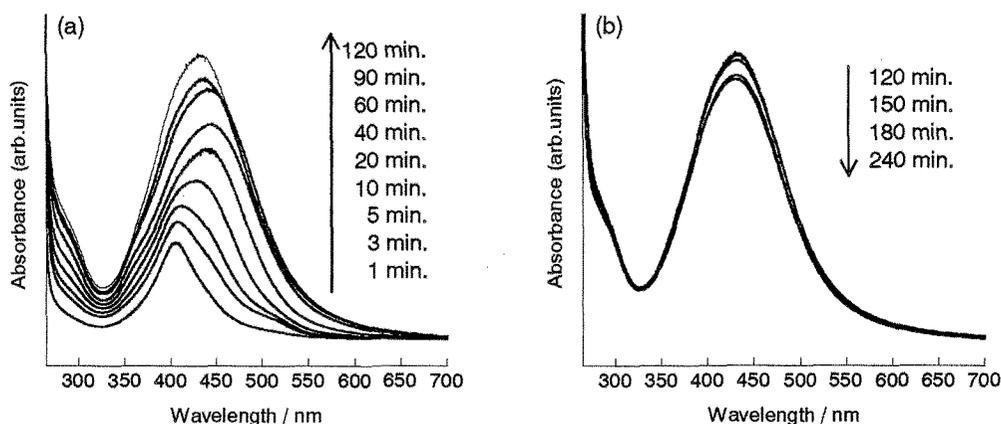


Fig.1 Time evolution of the optical absorption spectra during the reduction of AgNO_3 in DMF. (a) 1 - 120 min; (b) 120 - 240 min after the addition of AgNO_3 solution.

crystal was then dissolved in DMF, and PyDC was also dissolved into EuCl_3 solution.

Characterization; Optical absorption spectra were measured with a U-3300 spectrofluorometer (HITACHI) by using of 10 mm optical path length quartz cuvettes. Because of the high absorbance of the prepared Ag colloidal solution, the sample solution was diluted with DMF to the appropriate concentration for the optical absorption measurement. The morphology and the size distribution were obtained by transmission electron microscope (TEM), JEOL JEM-2010, with the accelerating voltage of 200 kV. For luminescence measurement, Ag colloidal solution and Eu^{3+} -PyDC solution was mixed at various composition, keeping the final concentration of Eu^{3+} -PyDC with $[\text{Eu}^{3+}] = 331.8 \mu\text{M}$, $[\text{PyDC}] = 663 \mu\text{M}$. Measurement was carried out by

using FP-6500 spectrofluorometer (JASCO) with 90° configuration. The excitation wavelength used in this study was 276 nm, corresponding to the excitation wavelength of PyDC.

3. Results and Discussion

3.1 Characterization of PVP-protected Ag nanoparticle;

In our preparation condition, the reduction of AgNO_3 and the formation of Ag nanoparticle started immediately after the addition of AgNO_3 solution into refluxed DMF, which can be seen as the appearance of SPR band of Ag nanoparticle (Fig. 1). The absorbance of SPR band continuously increased up to 120 min after the addition

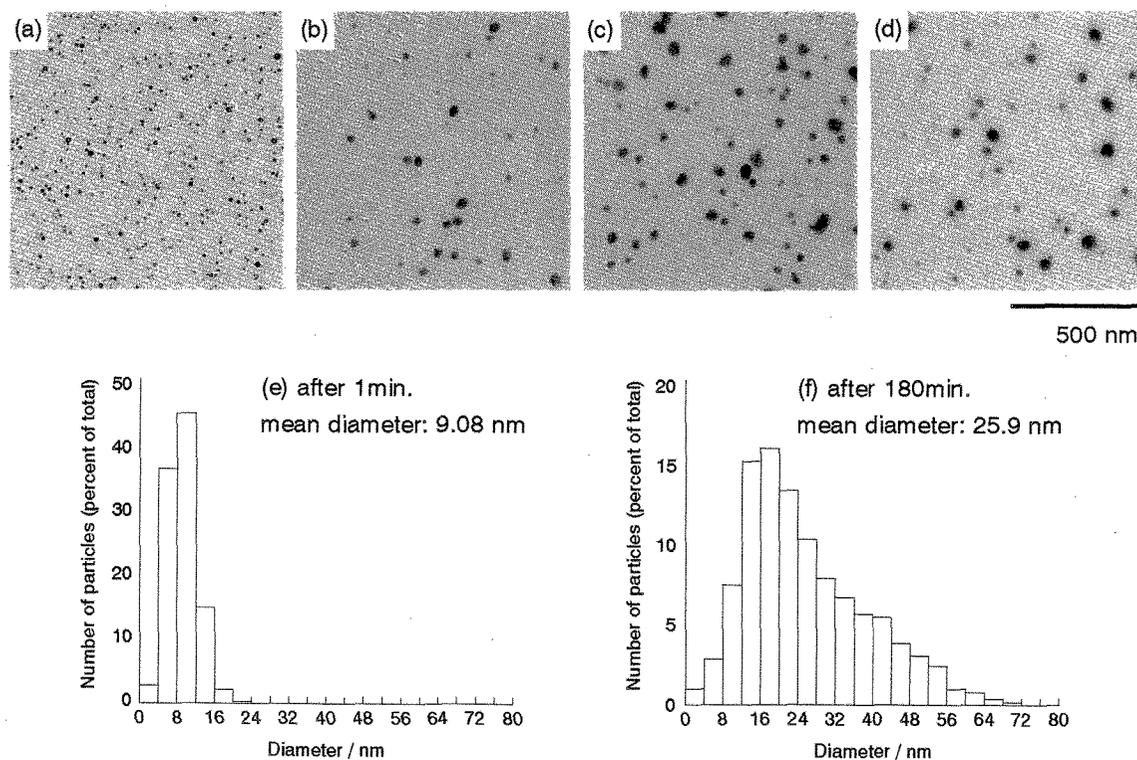


Fig.2 TEM images of Ag nanoparticles. (a) 1 min, (b) 40 min, (c) 90 min, (d) 180 min after the addition of AgNO_3 solution into DMF, and size distributions of the sample after (e) 1 min and (f) 180 min.

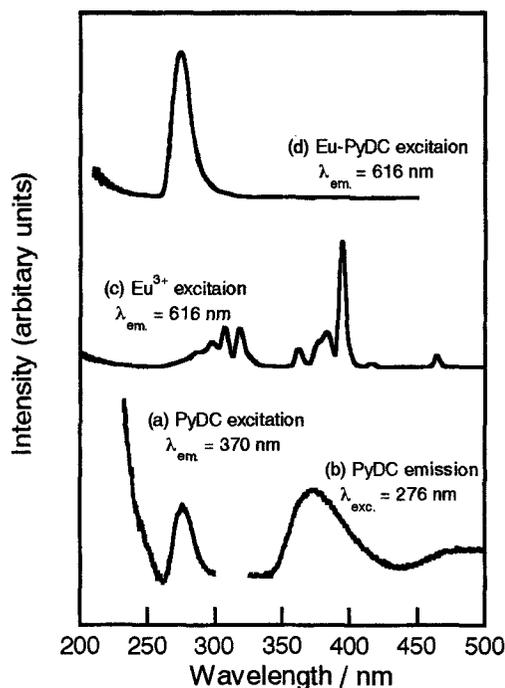


Fig.3 (a) Excitation spectrum of PyDC, (b) emission spectrum of PyDC, (c) excitation spectrum of Eu^{3+} ion, (d) excitation spectrum of Eu^{3+} -PyDC. All sample were measured in DMF.

of AgNO_3 solution (Fig.1(a)), indicating that the nucleation and/or particle growth proceeded, whereas slight decrease was observed from 120 min to 180 min (Fig.1(b)). The SPR peak position red-shifted up to 90 nm, and then blue-shifted. There are no distinct change in both peak position and absorbance of SPR band after 180 min. In addition to the intense SPR band, small shoulder was observed during the initial stage of the reaction around 525 nm, indicating the aggregation formed in the reaction solution. However, this shoulder vanished after 10 min, and therefore these aggregates are thought to be consumed for coalescence or Ostward ripening, both of which are frequently observed in high temperature aging like this study. Particle growth of Ag nanoparticles was characterized by using TEM observation (Fig.2). The mean diameter increased during the reaction from 9.1 nm after 1 min to 25.9 nm after 180 min, and there were no more obvious growth after 150 min to 300 min. It is also noted that they contain some particles larger than 50 nm in the samples after 120 min. The size distribution of the sample after 180 min shows typical log-normal distribution (Fig.2(f)), indicating that coalescence growth mode are favorable in the present system [11]. We used the sample after 180 min for further experiment, because there were no obvious changes on the particle diameter and morphology after 180 min, from the results of optical absorption measurements and TEM observations.

3.2 Effect of Ag nanoparticle on luminescent properties of europium complex.

Europium complex used in this study, Eu^{3+} -PyDC, is an energy-transfer complex, in which the incident energy transfers from excited state of PyDC to the resonant level

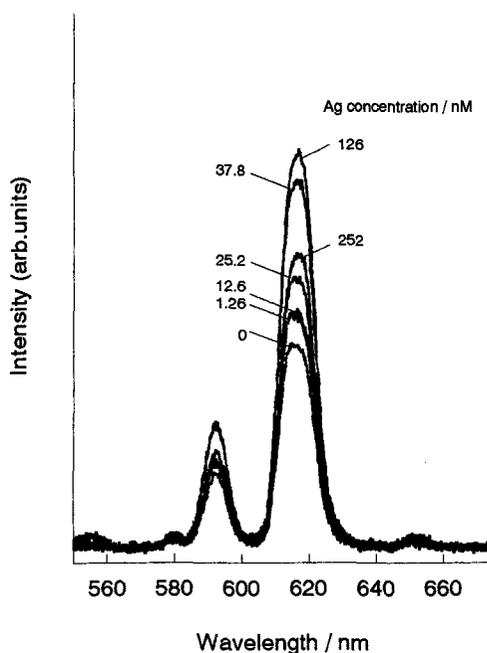


Fig.4 Luminescence spectra of Eu^{3+} -PyDC in DMF with and without Ag nanoparticles.

of Eu^{3+} ion. This was confirmed by comparing the electronic spectra of PyDC, Eu^{3+} ion, and Eu^{3+} -PyDC complex (Fig.3). The excitation spectrum of Eu^{3+} -PyDC shows a broad peak around 275 nm, corresponding to the excitation band of PyDC, while there are no obvious peak at around 394 nm assigned to the excitation band of Eu^{3+} ion (${}^7\text{F}_0 \rightarrow {}^5\text{L}_6$ transition), which was observed in the excitation spectrum of Eu^{3+} solution. We can deduce from this result that the strongest luminescence from europium complex would be obtained through the energy transfer from PyDC to europium ion under indirect excitation for PyDC.

Luminescence spectra of Eu^{3+} -PyDC with and without Ag nanoparticles are shown in Fig.4. There are two distinct peaks in this wavelength region; electric dipole ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ transition at 592 nm and magnetic dipole allowed ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ transition at 618 nm. Obviously, the luminescence intensity was enhanced with the addition of Ag

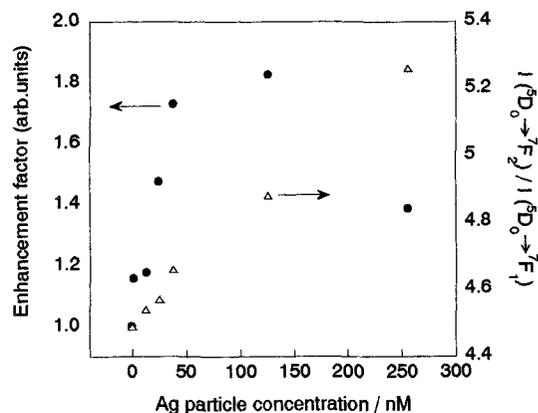


Fig.5 Variation of the enhancement factor and the intensity ratio, $I({}^5\text{D}_0 \rightarrow {}^7\text{F}_2) / I({}^5\text{D}_0 \rightarrow {}^7\text{F}_1)$, with the Ag particle concentration.

nanoparticles up to ~ 100 nM, which is shown in Fig.5 as an enhancement factor. Although the maximum enhancement factor obtained in the present study was only *ca.* 1.8 at the Ag concentration of 126 nM, it would be improved by changing the particle diameter or morphology. It is also important to describe that the intensity ratio between ${}^5D_0 \rightarrow {}^7F_2$ and ${}^5D_0 \rightarrow {}^7F_1$ transition, $I({}^5D_0 \rightarrow {}^7F_2) / I({}^5D_0 \rightarrow {}^7F_1)$, varied with the addition of Ag nanoparticles, which are also included in Fig.5. The intensity ratio between these two bands provides an important information on the coordination structure around europium ion, because ${}^5D_0 \rightarrow {}^7F_2$ transition is very sensitive to the first coordinative environment around europium ion. The intensity ratio increased in proportion to the Ag colloid concentration and does not show the saturation up to 250 nM. This result indicates that Ag nanoparticle interacts with europium ion and/or PyDC, resulting in the distortion of the first coordination structure around europium ion. In spite of the continuous increase in the intensity ratio, enhancement factor decreased above ~ 100 nM. There are two possible explanations on this decrease. One is the re-absorption of the emitted light from europium complex by Ag nanoparticle dissolved in DMF, although the absorbance is low in this emission wavelength region relative to that of SPR band. Another plausible explanation is that PyDC may directly adsorb on the surface of Ag nanoparticle, resulting in the quenching of PyDC excited state. It is well-known that the molecules directly adsorbed on the metallic surface would be quenched due to the damping of dipole oscillation by the metallic surface [9]. Both two mechanisms are possible when the Ag concentration is enough high, however further investigation is necessary to clarify the mechanism for the decrease in the enhancement factor observed at high Ag concentration region.

4. Conclusion

We have prepared Ag nanoparticle with a diameter of about 25 nm by using of DMF as both solvent and reducing agent in the presence of PVP. In this method, coalescence growth mode was favorable rather than Ostward ripening. The luminescent properties of Eu-PyDC complex were strongly affected with the presence of PVP-protected Ag nanoparticle in terms of both luminescence intensity and intensity ratio between ${}^5D_0 \rightarrow {}^7F_2$ and ${}^5D_0 \rightarrow {}^7F_1$ transition. Although the maximum enhancement factor obtained in the present study was only 2, it would be improved by changing the particle diameter or morphology. Continuous increase in $I({}^5D_0 \rightarrow {}^7F_2) / I({}^5D_0 \rightarrow {}^7F_1)$ with the increase of Ag concentration suggests the electrostatic interaction between Ag nanoparticle and Eu^{3+} -PyDC complex.

References

- [1] M. D. McGehee, T. Bergstedt, C. Zhang, A. P. Saab, M. B. O'Regan, G. C. Bazan, V. I. Srdanov, A. J. Heeger, *Adv. Mater.*, **11**, 1349 (1999)
- [2] N. Sabbatine, M. Guardigli, J. M. Lehn, *Coord. Chem. Rev.*, **123**, 201 (1993)
- [3] C. Piguet, J. C. G. Bunzli, G. Bernardinelli, G. Hopfgartner, A. F. Williams, *J. Am. Chem. Soc.*, **115**, 8197 (1993)
- [4] V. M. Mikkala, M. Helenius, I. Hemmilä, J. Kankare, H. Takalo, *Helv. Chim. Acta* **76**, 1361 (1993)
- [5] A. K. Saha, K. Kross, E. D. Kloszewski, D. A. Upson, J. L. Toner, R. A. Snow, C. D. V. Black, V. C. Desai, *J. Am. Chem. Soc.* **115**, 11032 (1993)
- [6] S. Sueda, J. Yuan, K. Matsumoto, *Bioconjugate Chem.*, **11**, 827 (2000)
- [7] G. Bobba, S. D. Kean, D. Parker, A. Beeby, G. Baker, *J. Chem. Soc., Perkin Trans. 2*, 1738 (2001)
- [8] G. Chumanov, K. Sokolov, B. W. Gregory, T. M. Cotton, *J. Phys. Chem.*, **99**, 9466 (1995)
- [9] J. Kummerlen, A. Leitner, H. Brunner, F. R. Aussenegg, A. Wokaun, *Molecular Phys.*, **80** (5), 1031 (1993)
- [10] A. Campion, A. R. Gallo, C. B. Harris, H. J. Robota, P. M. Whitmore, *Chem. Phys. Lett.*, **73**, 447 (1980)
- [11] C. G. Granqvist, R. A. Buhrman, *J. Catalysis*, **42**, 477 (1976)

(Received December 20, 2002; Accepted March 1, 2003)