

LETTERS

Enhancing and Quenching Functions of Silver Nanoparticles on the Luminescent Properties of Europium Complex in the Solution Phase

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Luminescent properties of the Eu(dinic) complex, where dinic is dinicotinic acid, were examined in the presence of silver nanoparticles in *N,N*-dimethylformamide. The formation of particle aggregates was observed upon mixing the particle solution with the complex solution, in which the complexes behaved like linker molecules. Luminescent intensity of the complexes was enhanced in the presence of silver nanoparticles, but at only a limited particle concentration region. The observed particle concentration dependences of the luminescent intensity were regarded as the result of a delicate balance between an enhancing and a quenching effect of the silver nanoparticles. In addition to the change in intensity, silver nanoparticles also affected the asymmetric ratio (or monochromaticity) of the europium luminescence. These changes in the luminescent properties of the complex were discussed in terms of the effects of particle aggregates and consequent modifications of the local electromagnetic field, refractive index, and the ligand field around europium ion.

Photoactive lanthanide complexes are of both fundamental and technological interest because of their large Stokes shifts, narrow emission bandwidths, and long emission lifetimes. Due to these characteristics, they are suitable candidates for applications as light-emitting diode (LED),¹ laser materials,^{2,3} and fluoroimmunoassay.^{4–7} Selvin and co-workers reported that luminescent (or lanthanide-based) resonant energy transfer (LRET) can be a novel tool for measuring nanometer scale distances, both in vitro and in vivo, in which LRET relies on energy transfer from a donor lanthanide complex to an acceptor organic dye via a nonradiative dipole–dipole (Förster-type) interaction.^{8–10} A major problem concerning the use of lanthanide complex for fluoroimmunoassay is the quenching due to a coupling with vibrational modes of solvent molecules. To avoid this quenching effect, several kinds of chelating agents have been synthesized.^{6,11,12} On the other hand, nanostructured

metallic surfaces would be promising materials to enhance the luminescence of these lanthanide complexes. Metallic nanostructures have caused a drastic increase in the intensity of Raman scattering or luminescence of ions or molecules in close proximity with the metallic surface.¹³ Recent investigations of the surface enhancement effect have opened up a new methodology for high-sensitivity detection such as single-molecule surface-enhanced Raman spectroscopy (SM-SERS).^{14–16} Lakowicz et al. reported the effects of silver island films on fluorescence properties of DNA, with a quantum yield of 10^{-4} to 10^{-5} , and they observed an intrinsic fluorescence from DNA without any additional label used for the conventional DNA detection method.¹⁷ These remarkable enhancement phenomena stem from a resonant excitation of surface plasmon polaritons confined within a metallic nanostructure and a consequent enhancement in the induced dipole moment of the target molecules.¹³

Pioneering experiments on the luminescence properties of the Eu(III) ion located in close proximity to a metallic surface were

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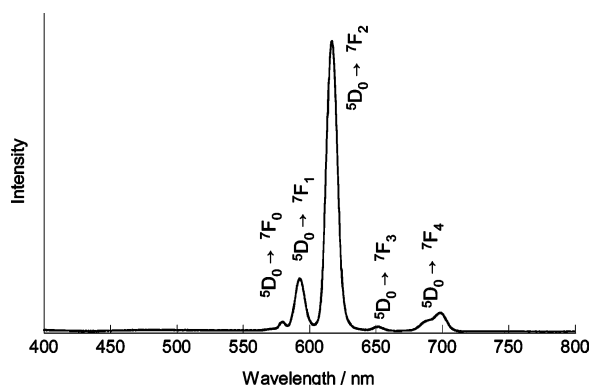


Figure 1. Luminescent spectrum of Eu(dinic) complex dissolved in DMF under ligand excitation (276 nm).

made by Drexhage^{18,19} and recently by Barnes.^{20,21} All these experiments were carried out by depositing Eu(III) complex onto the metallic thin films covered with an organic spacer. Nevertheless, lanthanide complexes are required to be used in the solution phase as luminescent labels for biological applications. In this regard, the use of metallic nanostructures in solution phase as surface enhancers is an attractive challenge, and nanosized metallic particles are promising candidates for this purpose. In this work, we report on the fundamental aspects of the role of metal nanoparticles on the luminescent properties of europium complexes in solution phase using silver nanoparticles of different sizes and shapes.

Spherical Ag nanoparticles of different sizes were synthesized by reducing AgNO₃ with *N,N*-dimethylformamide (DMF).²² Poly(vinylpyrrolidone) (PVP) aqueous solution (10 mL, 10 wt %) was added to DMF (80 mL), followed by an addition of AgNO₃ aqueous solution (10 mL). The mean particle diameter was tuned by changing the reaction temperature (90–110 °C) and the concentration of AgNO₃ solution (0.125–0.250 M). The

reaction was kept for 3 h and the obtained dark-brownish solution was purified by centrifugation at 12 000 rpm for 45 min.

Preparation of rod-shaped silver nanoparticles was made according to the previously reported seed-mediated method.²³ The obtained ruby-red solution containing silver nanorods was centrifuged (8000 rpm, 30 min), and precipitates were dissolved to PVP aqueous solution (10 wt %), and kept at 30 °C for 1 h. This solution was again centrifuged (8000 rpm, 30 min), and precipitates were dissolved into a PVP–DMF solution (10 wt %) and kept at 30 °C for 1 h. To remove excess PVP molecules, purification was made by centrifugation at 6500 rpm for 30 min.

Eu(dinic), where dinic is dinicotinic acid (pyridine-3,5-dicarboxylic acid), complexes were used as luminescent complexes and obtained by dissolving the ligand into EuCl₃ (DMF) solution with a molar ratio of 2:1. The emission spectrum of this solution (Figure 1) exhibits several well-defined emission bands under ligand excitation ($\lambda_{\text{ex}} = 267$ nm), indicating the formation of the complex that exhibits the energy transfer from the ligand to the central Eu(III) ions.

The morphology and size distribution of silver nanoparticles were obtained by a transmission electron microscope (TEM, JEOL JEM-2010, 200 keV). Optical absorption spectra were measured with a U-3300 spectrophotometer (HITACHI) by using a 10 mm optical path length quartz cuvette. Luminescence measurements were performed using a FP-6500 spectrofluorometer (JASCO) with a 90° configuration. The samples for the optical measurements were prepared by mixing the complex solution and the particle solution with keeping the final concentration of Eu(III) ion at 250 μM .²⁴

Three sets of spherical silver nanoparticles with a particle diameter varying from 9.7 to 27.1 nm and rod-shaped silver nanoparticles with an aspect ratio of 1.79 were prepared in the present study. The representative TEM micrographs and size distributions are presented in Figure 2, in which minor axis (*a*-

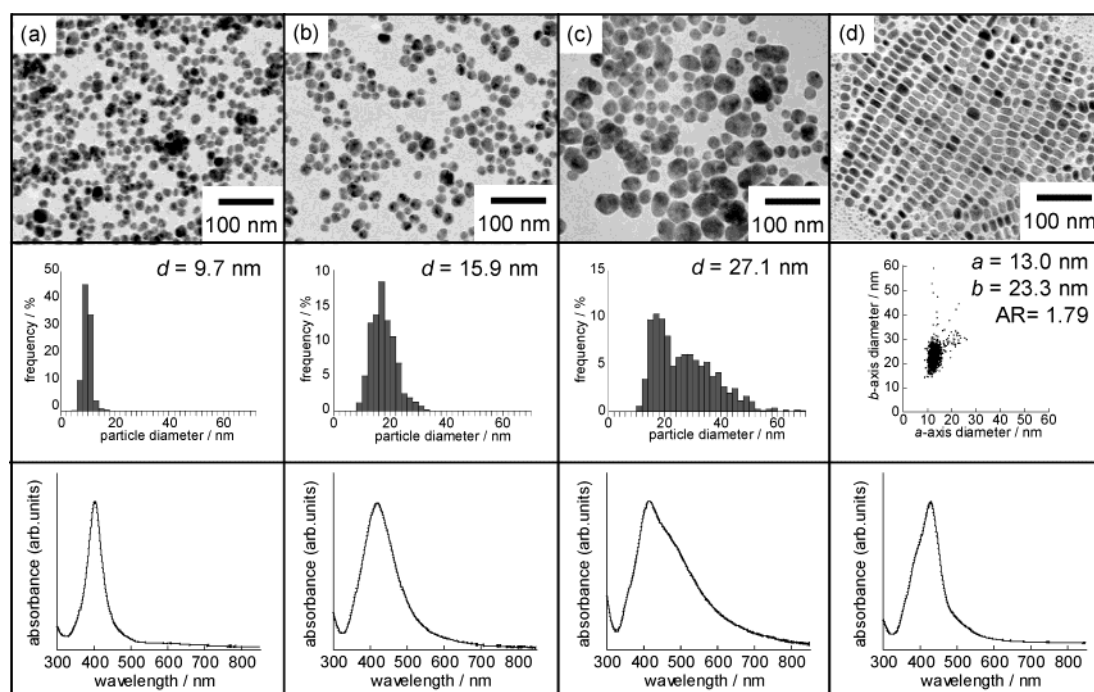


Figure 2. TEM micrographs, size distributions, and optical absorption spectra of spherical silver nanoparticles prepared at (a) 90 °C, [AgNO₃] = 0.125 M, (b) 90 °C, [AgNO₃] = 0.250 M, and (c) 110 °C, [AgNO₃] = 0.250 M and (d) of the rod-shaped silver nanoparticle. The mean diameter, *d*, was obtained by counting at least 500 particles in each sample, and the aspect ratio (AR) calculation for rod sample was done on only spheroidal particles.

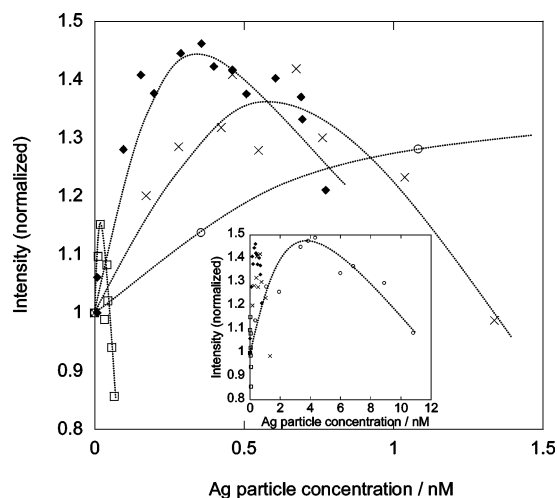


Figure 3. Silver concentration dependence of integrated luminescent intensity, in which the intensity is normalized with the intensity in the absence of Ag nanoparticles (0 nM): spherical particle with $d = 9.7$ nm (○), 15.9 nm (×), and 27.1 nm (□); rod-shaped particle (◆).

axis) and major axis (b -axis) distribution are displayed for rod-shaped sample (Figure 2d). The mean diameter was obtained by counting at least 500 particles in each sample, and the aspect ratio calculation was done on only spheroidal particles. DMF solutions of both spherical and rod-shaped nanoparticles exhibited a bright yellow-orange color, and a distinct optical absorption band is observed around 400 nm in each sample (Figure 2). Rod-shaped nanoparticles are known to exhibit two distinct absorption maxima corresponding to transverse and longitudinal modes of a localized surface plasmon resonance.²⁵ However, the absorption spectrum of the rod-shaped sample prepared in the present study shows a single peak at 428 nm, along with a small shoulder around 400 nm because of the small aspect ratio. Upon adding the complex solution into the nanoparticle solution, the color of the solution immediately changed to pinkish red, accompanying the appearance of a new absorption or scattering band around 500–550 nm. The appearance of the new band at longer wavelength region indicates the formation of particle aggregates in the solution.²⁶ No color or spectral change was observed when only either ligands or europium ions were added into the particle solution, indicating the function of Eu(dinic) complexes as linker molecules, and the complexes are expected to be incorporated in the particle aggregates.

The particle concentration dependence on the emission intensity of the complexes is illustrated in Figure 3, in which the intensity is normalized with the intensity in the absence of Ag nanoparticles (0 nM). Luminescent intensity first increases and then decreases with the increasing particle concentration, and each sample shows a different maximum enhancement factor (g) and the particle concentration at which the intensity reaches the maximum (C_{\max}). It is deduced from this concentration dependence that the silver nanoparticles act as both an enhancer and a quencher for europium luminescence, because the luminescent intensity should decrease monotonically when the metal nanoparticles serve as only the quencher.²⁷ The obtained maximum enhancement factor for each sample is thus regarded as the result of a delicate balance between the enhancement and the quenching effect. The enhancement effect is known to be strongly affected by the size and symmetry of the metallic nanostructure,²⁸ and a comprehensive expression considering both the enhancing and the quenching effects will give detailed information for the particle concentration depen-

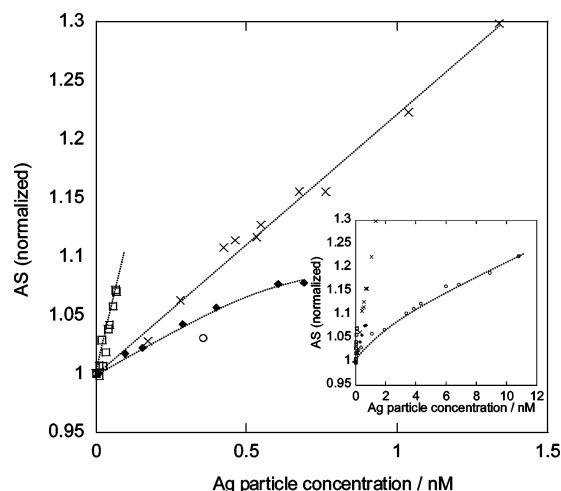


Figure 4. Silver concentration dependence of asymmetric ratio (AS), in which the AS value is normalized with the value in the absence of Ag nanoparticles (0 nM): spherical particle with $d = 9.7$ nm (○), 15.9 nm (×), and 27.1 nm (□); rod-shaped particle (◆).

dence, including the quantitative treatment for g and C_{\max} of each sample.

In contrast to our results, only the quenching effect of metal nanoparticles has been observed in the solution system where gold nanoparticles and semiconductor nanoparticles²⁹ or organic fluorophores²⁷ were co-dissolved. The origin of this difference is attributable to the above-mentioned aggregates formation and the difference in the metal used. The enhancement field around metallic nanostructures is strongly enhanced when two or more particles come into close proximity with each other, and the aggregate effect concerning Raman scattering has been reported.²⁶ As mentioned above, Eu(dinic) complexes are expected to be incorporated into particle aggregates, and thus the fluorescent intensity was effectively enhanced in the present system. Moreover, silver is a well-established material to exhibit remarkable enhancement ability for Raman and fluorescent intensity of molecules. The effectiveness of silver for enhancement phenomenon is widely known and Lakowicz et al. observed enhanced luminescence from $[\text{Ru}(\text{bpy})_3]^{2+}$ complexes,³⁰ where bpy is 2,2'-bipyridyl, in the presence of silver particle islands, whereas Au nanoparticles quench the fluorescence of $[\text{Ru}(\text{bpy})_3]^{2+}$ following the Stern–Volmer relation.³¹

In addition to the changes in the luminescent intensity with the particle addition, we found another effect arising from the addition of Ag nanoparticles. Figure 4 shows the variation in asymmetric ratio (AS) with the particle concentration, where AS is defined as the integrated emission intensity ratio between $^5\text{D}_0 \rightarrow ^7\text{F}_1$ (magnetic dipole transition) and $^5\text{D}_0 \rightarrow ^7\text{F}_2$ (electric dipole transition), $\text{AS} = \int I_{\text{D}_0 \rightarrow \text{F}_2}(\omega) d\omega / \int I_{\text{D}_0 \rightarrow \text{F}_1}(\omega) d\omega$. A variation in the AS value describes two effects of the nanoparticle addition, that is, the modifications of the ligand field and the refractive index around europium ions. The increasing tendency in AS values with the particle concentration indicates the increase in the distortion of the ligand field arising from the interaction with Ag nanoparticles during the aggregate formation.³² The effect of refractive index modification is explained on the basis of the local field effect, which gives the refractive index dependence of the electric dipole transition rate.^{33–35} The macroscopic variation in the refractive index upon particle addition is almost negligible according to the Maxwell–Garnett (MG) effective medium expression, because of quite a low volume fraction of Ag nanoparticles ($\sim 10^{-6}$).³⁶ However, considering that the Eu(dinic) complexes exist in close proximity of Ag nanoparticles, the local refractive index around Eu(dinic)

complexes is different from that of bare Eu(dinic) dissolved in DMF,^{37,38} resulting in the modification of the electric dipole transition rate and thus the change in the AS value. It is also notable that the AS value increased monotonically with the particle concentration, unlike luminescent intensity. The monotonic increase in AS value indicates that the number of Eu(dinic) complex interacting with Ag nanoparticles is not saturated under this concentration condition, which is reasonable because the complex concentration (250 μ M) is markedly higher than that of Ag nanoparticles (<10 nM).

In summary, fundamental aspects of the effects of Ag nanoparticles on the luminescent properties of europium complexes in solution phase have been reported. The luminescent intensity increased in the early stage of the particle addition and then decreased by further addition. This behavior indicates the functions of the silver nanoparticles as both the surface enhancer and the quencher in the solution phase. The observed luminescent intensity is thus regarded as the result of the delicate balance between these two functions of the silver nanoparticles, which is strongly dependent on the particle size and shape. Under our experimental conditions, smaller particles showed larger enhancement factors in the higher particle concentration region, and the rod-shaped nanoparticles exhibited effects comparable to those with the spherical nanoparticles having similar particle diameters. The ligand field and the refractive index around europium ions were also altered due to the presence of the silver nanoparticles, which brought about the change in the AS value. Finally, we pointed out that the observed changes in the luminescent properties are attributable to the formation of the particle aggregates in the solution. It should also be noted that the enhanced luminescence was observed despite the off-resonant condition between the excitation wavelength (276 nm) and the surface plasmon (ca. 400 nm), and these findings suggest that the further luminescence enhancement of the europium complex is expected even in the solution phase by optimizing the design of both nanoparticles and complexes.

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