External Electric Field Effects on Emission of a Dendrimer-encapsulated Gold Nanocluster in a Polymer Film

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External electric field effects on emission spectrum of a dendrimer-encapsulated gold cluster in a PVA film have been examined with electric field modulation spectroscopy. Besides the Stark shift, a field-induced quenching of the emission is observed, indicating the field-induced enhancement of the rates of nonradiative processes from the emitting state.

Luminescent probes are very important in investigations in various fields of science. A number of luminescent probes have been prepared for specific applications, and colloidal II–IV semiconductor nanoparticles, which show large emission quantum yields, have received much attention as luminescent probes.[1,2] Recently, it has been reported that sub-nm gold (Au) clusters encapsulated with poly(amidoamine) (PAMAM) dendrimers show strong emission with an emission yield up to ca. 70%.[3,4] Such a high-emissive atomic Au cluster can be prepared by slow reduction of gold salts in the presence of PAMAM as a stabilizing agent, and the size of the cluster can be tuned with the relative Au:PAMAM concentration and the dendrimer generation. The potential application of the atomic Au clusters for biological labeling has been reported.[5]

The electroemission spectrum (plots of the electric-field-induced change in emission intensity as a function of wavelength) has been widely used to examine electronic structures and molecular dynamics following photoexcitation.[6–8] Measurements of electroemission spectra provide unique information on the difference in electric dipole moment and molecular polarizability between the ground and excited states. In the present study, therefore, we have measured the electroemission spectrum of PAMAM-encapsulated Au_8 clusters in a poly(vinyl alcohol) (PVA) film.

The PAMAM-encapsulated Au_8 cluster was prepared through the slow reduction of $HAuCl_4$ in aqueous PAMAM solution, according to a literature procedure.[3,4] The aqueous solution of 5.0×10^{-4} mol dm^{-3} of the fourth generation hydroxy- and amine-terminated PAMAM was mixed with that of 1.5×10^{-3} mol dm^{-3} of $HAuCl_4$ with volume ratio of 1:1, which created the Au_8 cluster. The Au_{13} cluster was also preferentially generated using the second generation PAMAM. PVA (molecular mass 146000–186000) was purified by precipitation with water and methanol. A certain amount of aqueous solution of PVA containing the PAMAM-encapsulated Au_8 cluster was cast on an ITO-coated quartz substrate by spin coating. A semitransparent aluminum film was then deposited on the polymer film. The ITO and aluminum films were used as electrodes.

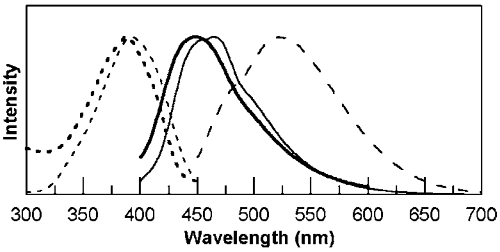

Figure 1. Emission (solid line) and excitation (doted line) spectra of the PAMAM-encapsulated Au_8 cluster in aqueous solution (narrow line) and in PVA (thick line). Emission spectrum of the Au_{13} cluster in aqueous solution is also shown by a dashed line. Excitation wavelength was 385 and 433 nm for the Au_8 and Au_{13} clusters, respectively. Emission wavelength for the excitation spectra of the Au_8 cluster was 463 nm.

Electroemission spectra were measured using electric field modulation spectroscopy.[6–8] A sinusoidal ac voltage with a modulation frequency of 40 Hz was applied between the electrodes, and the value of the field-induced change in emission intensity was detected with a lock-in amplifier at the second harmonic of the modulation frequency. A dc component of the emission intensity was simultaneously observed. The polymer film was cooled using a cryogenic refrigerating system, and the temperature was varied until ca. 40 K.[7] Hereafter, electroemission spectrum is abbreviated as E–E spectrum. The strength of applied fields is represented by rms. Fluorescence decay measurements were carried out using a time-correlated single-photon counting system.[8]

The emission and excitation spectra of the PAMAM-encapsulated Au_8 cluster in aqueous solution and in a PVA film are shown in Figure 1. The excitation spectrum was monitored at the wavelength of the emission maximum, and the measurements in aqueous solution were done at neutral pH. The emission and excitation maxima in aqueous solution are 463 and 385 nm, respectively, which are almost the same as those of the Au_8 cluster reported previously.[3,4] Both emission and excitation spectra in aqueous solution show a red shift in comparison with those in PVA, implying some polar character at the emitting state of the Au_8 cluster.

The emission spectrum of the Au_{13} cluster in aqueous solution is also shown for comparison. It is seen that the wavelength of the emission maximum is strongly dependent of the size of the cluster. It is also noted that the excitation intensity due to PAMAM is observed in the 300–325 nm region in PVA, which may be ascribed to the energy transfer from PAMAM to the Au_8 core.

The E–E spectrum of the PAMAM-encapsulated Au_8 cluster in PVA has been observed, as shown in Figure 2c. The emission spectrum and its derivative spectra are also shown in Figures 2a and 2b, respectively. The magnitude of the E–E intensity is proportional to the square of the applied field strength. A field-induced quenching of the emission is dominant in the E–E spectrum. The field-induced change in excitation spectrum at the wavelength of the emission maximum exhibits a negative

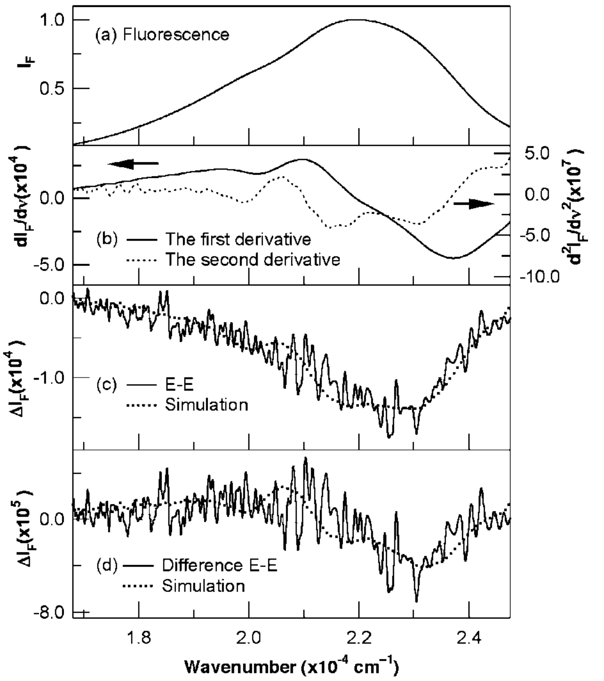

Figure 2. Emission spectrum (a) and its first and second derivative spectra (b) and electroemission spectrum (c) of the PAMAM-encapsulated Au_8 cluster in PVA at 291 K. The difference electroemission spectrum is shown in (d). Applied field strength was $0.9\,MV\,cm^{-1}$ and excitation wavelength was 380 nm.

constant value in the entire spectral region of 320–440 nm, suggesting that the observed field-induced quenching does not arise from the absorption change due to the electric field.

In the present study, the PAMAM-encapsulated Au_8 cluster can be regarded as randomly distributed in a PVA film. On the assumption that the original isotropic distribution in PVA is maintained in the presence of an electric field, the E–E spectrum may be given by a sum of the zeroth, first, and second derivatives of the emission spectrum.[6] Actually, as shown in Figure 2c, the observed E–E spectrum is well fitted by a linear combination of the derivative spectra. From the component of the zeroth derivative spectrum, the magnitude of the field-induced quenching of the emission of the PAMAM-encapsulated Au_8 cluster was evaluated to be ca. 0.01% at $0.9\,MV\,cm^{-1}$. The observed field-induced quenching is attributed to the field-induced enhancement of the rates of nonradiative processes from the emitting state. It has been shown that charge-transfer (CT) dynamics is significantly influenced by an electric field.[6] Then, the field-induced enhancement of the nonradiative process observed in the present study may suggest that the emitting state of the cluster has a CT character to some extent. In analogy to photophysical properties of a molecule,[9] the observed emission could be assigned to the fluorescence from the lowest excited singlet state because the observed emission lifetime of the prepared cluster is ca. 7 ns in a film, which is in the range of fluorescence lifetime generally observed. The CdS nanoparticles also exhibit the field-induced quenching,[8] the magnitude of which is much higher than the present PAMAM-encapsulated Au_8 cluster. This result arises from strong CT character of the emitting state of the CdS nanoparticles.

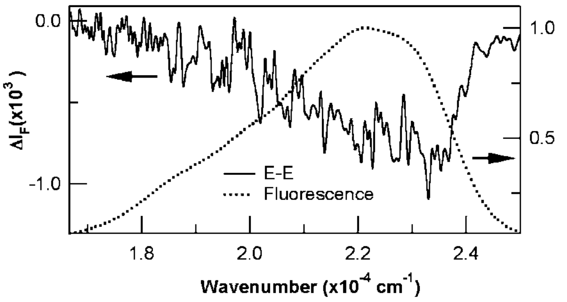

Figure 3. Electroemission (solid line) and emission (dotted line) spectra of the PAMAM-encapsulated Au_8 cluster in PVA at 40 K. Applied field strength was $0.8\,MV\,cm^{-1}$ and excitation wavelength was 380 nm.

The first and second derivative components in the E–E spectrum can be evaluated by subtracting the contribution of the field-induced emission quenching (the zeroth derivative component) from the E–E spectrum. The obtained difference E–E spectrum is shown in Figure 2d. The shape of the difference E–E spectrum is similar to that of the first derivative spectrum, although the small contribution of the second derivative spectrum is necessary to reproduce the difference E–E spectrum, as shown in Figure 2d. This result is very different from that of the CdS nanoparticles.[8] The shape of the electroabsorption of the CdS nanoparticles is similar to the second derivative of the absorption spectrum, which results from the very large difference in electric dipole moment between the ground and excited states. From the coefficient of the first derivative spectrum, the magnitude of the difference in molecular polarizability between the ground and emitting states of the PAMAM-encapsulated Au_8 cluster is estimated to be ca. 6 Å^3, by assuming that the molecular polarizability is isotropic.[6]

The dominance of the field-induced quenching was also observed in the E–E spectrum at 40 K, as shown in Figure 3. The magnitude of the field-induced quenching at 40 K is ca. 0.07% at $0.8\,MV\,cm^{-1}$, suggesting that the field-induced quenching is enhanced with lower temperature. We are now making efforts to measure the E–E spectrum of the Au_8 cluster in a wider temperature region.

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