Enhancement of Excimer Fluorescence from Thin Dye Film by Single Gold Nanoparticles

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We studied the enhancement of excimer emission from a thin perylene dye film (10-nm thickness) by localized surface plasmon resonance (LSPR) of single gold nanoparticles (GNPs), and observed a large fluorescence enhancement factor of about 25. The absence of excitation wavelength dependence of the enhancement factor indicates that the fluorescence intensity enhancement is mainly due to an increase of the radiative emission rate by LSPR.

In 1946 Purcell suggested that spontaneous emission of molecules could be modified by a resonant coupling with an external electromagnetic (EM) field.[1] Such kind of environmental condition could be observed near noble metal surfaces and nanoparticles due to LSPR which confines the incident light (E_0) into the near field to give rise to a great enhancement of the local EM field (E_{Loc}).[2] Since then, many studies pointed out that combining metallic nanostructures with molecules lead to a modification of the molecular fluorescence.[3–8] Experimental and calculation results pointed out that both molecular absorption and emission processes are modified by LSPR. In case of absorption, the EM field enhancement increases the absorption transition probability for molecules near nanoparticles, leading to an increase of the molecular fluorescence intensity. However, it is more complicated for the fluorescence emission process because LSPR could modify both radiative and nonradiative molecular transition which leads to enhancement and quenching, respectively. Recent work emphasizes that the excitation wavelength, the particle size[9] and the overlap of the LSPR band with the absorption and emission spectra of the dye[10] are crucial for observing a high enhancement factor of the dye fluorescence. In this letter, we present a new approach to study the spectral modifications of a fluorescent dye by a single gold nanoparticle (GNP). In order to see how the LSPR modifies the spectroscopic properties of a dye, we build a core–shell structure using GNP (100 nm diameter) as the core and a thin layer (10-nm thickness) of *N*,*N*′-bis(2,5-di-*tert*-butylphenyl)-3,4,9,10-perylene dicarboximide[11] (PDI) as a shell. The PDI shell exhibits an excimer emission having a large Stokes shift, which allows a good separation of the absorption and the emission spectra. Considering absorption, excitation, and fluorescence spectra of the dye we will try to give more information of the molecular fluorescence modifications by LSPR in such structure.

GNPs (mean diameter of 100 nm, EMGC100; British Biocell) were immobilized on a glass substrate using the same procedure described in another study.[12] We carefully prepared a sample where mean spacing between nanoparticles was larger than 10 μm, which was confirmed from dark-field optical microscope images. A thin PDI (Sigma-Aldrich) film was prepared on the sample substrate by vapor deposition, and the thickness was set to be 10 nm. Fluorescence spectra was measured using a CCD polychromator coupled through an optical fiber to an inverted microscope Olympus IX70 (microscope objective X60, N.A. 0.7 Olympus). By using an imaging pinhole, we detected the fluorescence selectively from a spatial area of 2.2-μm diameter. For the excitation we use a halogen lamp in dark-field configuration and different optical band pass filters for selecting the excitation wavelength. We compared fluorescence spectra from areas with and without GNP on the same sample and examined the fluorescence modification due to the LSPR. For the light-scattering spectra of the single GNPs, we used the same setup described above without optical filters.

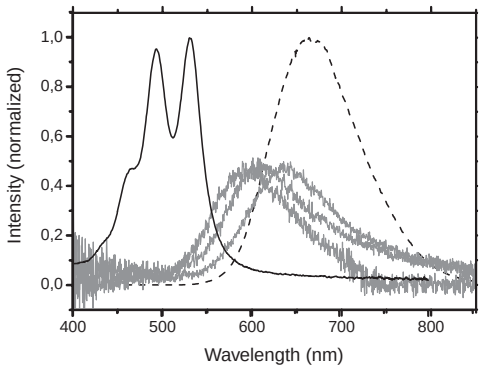

Figure 1. Absorption (black line) and emission spectra (black dashed line) of the PDI dye. The light scattering spectra of different GNPs (gray lines) are included to show the inhomogeneous size distribution of the commercial solution.

Figure 1 presents the absorption and emission spectra of a PDI film vapor-deposited. The absorption spectrum exhibits a vibrational structure with peaks at 490 and 530 nm which are 10 nm shifted compared to a PDI solution. On the other hand, the emission spectrum shows only one broad peak around 650 nm with a large Stokes shift which is characteristic of an excimer emission. Light-scattering spectra of single GNPs are also given in Figure 1 and show peaks from 580 to 620 nm due to the size distribution (between 80 and 120 nm) of the colloid sample.[12] The LSPR band shows a good overlap with the emission spectrum, while a small overlap with the absorption spectrum.

Figure 2 shows a representative result of a single GNP: the fluorescence intensity is higher with GNP than without. Because there is no significant difference in the number of molecules under the observation area (2.2-μm diameter) with and without GNP (100-nm diameter) (see Supporting Information), the increase of the fluorescence intensity is coming from PDI molecules near GNPs. So, we calculate the fluorescence modulation spectrum (blue spectrum on Figure 2) by subtracting fluorescence without GNP from that with GNP. In the case of PDI, this calculated spectrum has the same shape as the fluorescence spectrum of the PDI film. We examined about 20 nanoparticles and always observed the fluorescence enhancement. Moreover, the

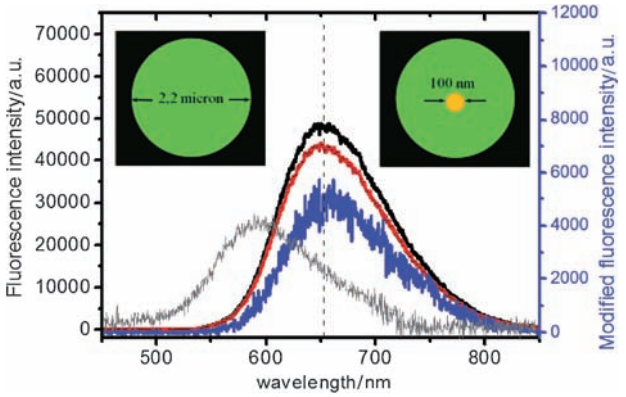

Figure 2. Fluorescence spectra obtained with (black line) and without (red line) GNP and fluorescence modulation spectrum (blue line) of the PDI dye near the GNP. Light-scattering spectra (gray line) of the corresponding GNP are also included. Inset: simple scheme of the experimental setup with and without GNP.

enhancement factor does not show a clear dependence on the particle size. By assuming that the EM field enhancement by LSPR is localized at a distance of 10 nm around the GNP,[13] we obtained the fluorescence enhancement factor[14] to be an average value of 25 ± 5.

The total fluorescence intensity enhancement factor (EF_{MF}) is determined by LSPR modification of both absorption (photoexcitation) and emission processes. It can be evaluated using the relation:[15] $EF_{MF} \approx \eta_{abs} \cdot Q_{Loc}/Q_0$, where Q_{Loc} and Q_0 refer to the fluorescence quantum yield with and without the EM field enhancement, respectively. The photoexcitation process enhancement η_{abs} can be estimated roughly by the relation: $\eta_{abs} \approx |E_{Loc}|^2/|E_0|^2$. In order to determine if the absorption or the fluorescence enhancement is dominant in the present result, we measured excitation wavelength dependence of the EF_{MF}. When the photoexcitation process enhancement is the main mechanism, EF_{MF} is expected to become large at excitation wavelength around the peak of the LSPR band. As shown in Figure 3, the wavelength dependence agrees with the excitation spectrum of thin PDI film, and the enhancement factor keeps roughly a constant value independent of the excitation wavelength. This observation indicates that the photoexcitation process enhancement is not dominant, and we can consider that the increase of the

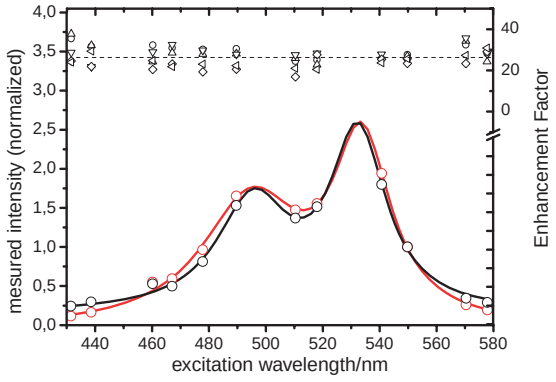

Figure 3. At the bottom: excitation spectra for the PDI dyes near GNP (black) and in thin dye film (red). On top: value of the enhancement factor for each excitation wavelength.

fluorescence intensity is mainly due to modifications of the PDI emission processes by the LSPR. In this case, modifications of the fluorescence spectrum could be expected. But we did not see any clear changes in the fluorescence spectrum (only a small red shift of 3 nm) which could be explained by the small variation of the EM field enhancement for wavelength longer than 600 nm and partially due to the absorption of the PDI fluorescence by the GNP (see Supporting Information).

In conclusion, we have pointed out some advantages of using excimer emission for investigating fluorescence enhancement by LSPR. First of all, excimer emission has a small rate constant of its intrinsic radiative decay, and the quantum yield is also very small in general, so we can expect to observe large fluorescence enhancement as it was pointed out in previous studies.[16,17] Secondly, the large Stokes shift between the absorption and the emission bands is very pleasing for precise "set" of the LSPR band by choosing different particle sizes or shapes. The fluorescence enhancement mechanism can be elucidated precisely by separating the modification of absorption and emission processes by LSPR. In the present study, we see no differences between the excitation and the absorption spectra of PDI. Also no significant dependence of the enhancement factor on the excitation wavelength has been observed, which demonstrates that the observed fluorescence enhancement is due to modification of the emission processes by LSPR.

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