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Near-infrared Fluorescence Enhancement by Regularly Arranged Gold Nanoblocks

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Fluorescence intensity of near infrared dyes immobilized in hydrophobic DNA thin film spin-coated on glass substrates with regularly arranged gold (Au) nanoblocks was about 2.5 times larger than that without Au nanoblocks, strongly suggesting the fluorescence intensity was enhanced by increased electric field intensity of excitation light due to local plasmon resonance of Au nanoblocks.

Near-infrared (NIR)-fluorescence dyes have been widely used in biochemical and medical fields for in vivo imaging.[1] The NIR-fluorescence dyes, however, have several disadvantages such as low fluorescence quantum yield, low stability, and low durability compared with visible-fluorescence dyes in aqueous solutions and solid films. These properties mostly originate from the molecular structure with extended π-conjugation. The low fluorescence quantum yield is essentially governed by the Strickler–Berg relation.[2] To overcome these disadvantages, energy transfer from porphyrin to NIR-fluorescence dyes along the DNA double helix was investigated upon excitation at the visible region.[3] Steady-state-fluorescence spectra showed that the NIR fluorescence was enhanced up to 86 times due to the efficient energy transfer from the excited porphyrin in the presence of DNA. The DNA matrix contributes not only to make efficient energy transfer, but also to improve stability and durability of NIR dye by immobilization between base pairs or in the groove. We also reported that confined and electric-field-enhanced light at surface plasmon resonance (SPR) condition can be applied to highly sensitive fluorescence detection of dyes in DNA ultrathin films deposited on a metal film and to high-performance nitrogen oxide gas sensing.[4] We have also been making efforts to enhance NIR fluorescence by localized SPR (LSPR) from metal nanostructures. Recently, fluorescence enhancement by LSPR was reported by several groups.[5–8] In this letter, we report the enhancement of NIR-fluorescence intensity using the regularly arranged gold (Au) nanostructures which show specific absorption in the NIR region without interactions between nanostructures.

The regularly arranged Au nanoblocks (Au arrays) were fabricated by the electron-beam lithography on glass plates.[9,10] The sizes of Au nanoblocks were evaluated as 100 nm for Array 1, 110 nm for Array 2, and 150 nm for Array 3 from absorption spectra and atomic force microscopy. The distances between Au blocks were 200 nm for Array 1, 190 nm for Array 2, 150 nm for Array 3. Figure 1a shows schematic representation of Array 1. As a NIR-fluorescence dye, 2-(2-{2-chloro-3-[(1,3-dihydro-3,3-dimethyl-1-propyl-2*H*-indol-2-ylidene)ethylidene]-1-cyclohexen-1-yl}ethenyl)-3,3-dimethyl-1-propylindolium iodide (IR780; Aldrich Co., Ltd., inset of Figure 2) was selected. Hydrophobic DNA (H-DNA) was prepared by exchanging sodium ions with hexadecyltrimethylammonium

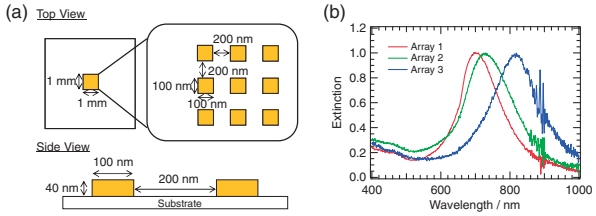

Figure 1. (a) Schematic representation of regularly arranged gold nanoblocks (Array 1), (b) extinction spectra of three Au arrays.

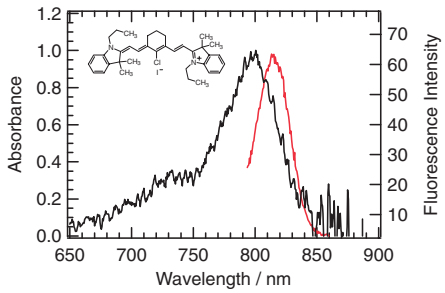

Figure 2. Absorption and fluorescence spectra of IR780 in H-DNA thin film. The excitation wavelength was 780 nm. The inset shows the molecular structure of IR780.

ions according to the reported method.[4,11,12] H-DNA thin films with immobilized dyes were prepared by spin coating on glass plates with Au arrays. The film thickness was 40 nm. UV–vis absorption spectra were measured by a Hitachi U-4100 spectrophotometer. Fluorescence spectra were measured by a Hitachi F-4500 fluorescence spectrophotometer. The CW lasers (633, 675, and 788 nm) were used as excitation light.

The absorption spectrum of IR780 in H-DNA thin film showed a peak around 800 nm with a shoulder around 730 nm. The fluorescence spectrum showed a peak around 817 nm. The absorption (extinction) spectra of Au arrays exhibit two peaks as shown in Figure 1b. The peaks located around 460 and 700 nm, 460 and 730 nm, and 460 and 820 nm for Array 1, 2, and 3, respectively. The visible and NIR absorption peaks can be assigned to the LSPR bands along vertical (height) and horizontal directions, respectively. No plasmon coupling to form such as gap mode was observed between Au nanoblocks separated by 150–200 nm.

Fluorescence spectra of IR780 in H-DNA thin films were measured in the absence and presence of Au arrays. Figure 3 shows fluorescence spectra of IR780 on Array 1, 2, and 3 excited at 675 nm. Average total fluorescence intensity was larger by 2.4, 2.5, and 1.1 times for Array 1, 2, and 3 as compared with that on a glass substrate alone, respectively. These enhancement factors are average values, because observed

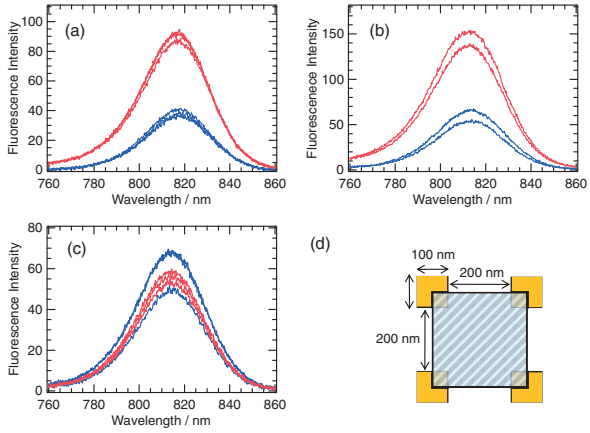

Figure 3. Fluorescence spectra of IR780 in H-DNA thin films on (a) Array 1, (b) Array 2, and (c) Array 3 excited at 675 nm in the presence (red line) and the absence (blue line) of Au array. (d) Schematic representation of Au nanoblocks in the Array 1.

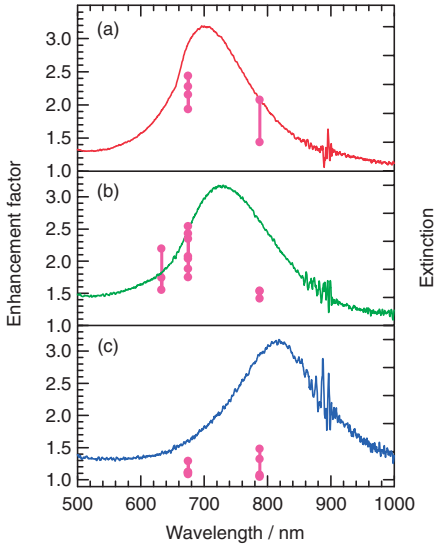

Figure 4. Observed enhancement factors (pink plots) of fluorescence intensity for IR780 in H-DNA thin films on (a) Array 1, (b) Array 2, and (c) Array 3 excited at 633, 675, and 788 nm together with the absorption spectra of the arrays.

fluorescence comes from total area composed of Au array and glass substrate as schematically shown in Figure 3d. Therefore, we estimated the normalized enhancement factor assuming the fluorescence enhancement is effective only on the Au nanoblocks. The fraction of effective area (f_a) of Au in one array unit is 1/9, 121/900, and 1/4 for Array 1, 2, and 3, respectively. The average enhancement factor E_f can be defined by the eq 1:

$$E_f = f_a \times n + (1 - f_a) \times 1 \quad (1)$$

where n is the normalized enhancement factor of Au nanoblocks. The second term corresponds to the glass alone. The normalized enhancement factor was estimated to be 13.6, 12.2, and 1.4, for Array 1, 2, and 3, respectively. These experimental results strongly suggested that the observed fluorescence enhancement by the Au arrays originated from the increase of excitation rate by the enhanced electric field of the incident light by LSPR.

We further investigated the excitation wavelength dependence of fluorescence enhancement. Figure 4 shows fluorescence enhancement factors for IR780 in H-DNA thin films on Array 1, 2, and 3 excited at 633, 675, and 788 nm together with the absorption spectra of the arrays. In the case of Array 1 and 2, the fluorescence was enhanced by about 2.5 times than that in the absence of the Au nanoblocks excited at 675 nm. The wavelength dependence of enhancement-factor values seems to correspond to the absorption spectra of Au arrays. These findings suggested that LSPR mostly affects the absorption process in observed fluorescence enhancement. In the case of Array 3, on the other hand, the enhancement factor is only about 1.0 to 1.5 times of that on a glass plate. The peak of absorption band in Array 3 is located at the fluorescence maximum wavelength of IR780. Such overlap between absorption and fluorescence bands most probably results in the fluorescence quenching of the dye due to efficient energy transfer from the excited state of IR780 to Au nanoblocks or the increased deactivation of excited dye molecules induced by resonance with Au nanoblocks.

In conclusion, we confirmed the fluorescence enhancement of the NIR dye by regularly arranged but independent Au nanoblocks. It was attributed to the electric field enhancement of excitation light by LSPR. The fluorescence quenching was also observed if the overlap between the absorption of Au nanoblocks and the fluorescence of the dye is large. Detailed studies including polarization dependence for the fluorescence enhancement are in progress.

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