Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

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Version of record first published: 16 May 2011

To cite this article: Fuyuki Ito, Ryuichi Ohta, Yukie Yokota, Kosei Ueno, Hiroaki Misawa & Toshihiko Nagamura (2011): Polarization Dependence for Enhancement of Near-Infrared Fluorescence Intensity by Local Surface Plasmon Resonance from Arranged Gold Nanoblocks, Molecular Crystals and Liquid Crystals, 538:1, 265-271

To link to this article: http://dx.doi.org/10.1080/15421406.2011.564085

Mol. Cryst. Liq. Cryst., Vol. 538: pp. 265–271, 2011

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2011.564085

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Polarization Dependence for Enhancement of Near-Infrared Fluorescence Intensity by Local Surface Plasmon Resonance from Arranged Gold Nanoblocks

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The polarization dependence of excitation light for fluorescence enhancement of near-infrared dyes immobilized in hydrophobic DNA thin film on glass substrates with regularly arranged Au nanoblocks was investigated. The enhancement factor for S-polarized excitation was about 1.2 to 1.5 times as large as that for P-polarized excitation. P-polarized light contributed to the excitation of plasmon band both of horizontal and vertical direction of Au nanoblocks. The vertical direction corresponds to the short axis for height direction which has the absorption in visible region did not contribute the excitation of IR780. When the absorption band of Au array and the fluorescence band of IR780 were overlapped, the fluorescence enhancement did not depend on the polarization of excitation light. It is suggested that the fluorescence quenching originates from the 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.

Keywords Array of gold nanoblocks; fluorescence enhancement; local surface plasmon resonance; near-infrared fluorescence dye; polarization of excitation light

Introduction

Strong photon-molecule coupling fields using local surface plasmon from metal nano structures are widely developed to enhance the fluorescence intensity [1–4]. In particular, near-infrared (NIR) fluorescence dyes are widely used in biochemical and medical fields for in vivo imaging [5]. The NIR fluorescence dyes, however, have several disadvantages such as low fluorescence quantum yield, low stability, and

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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. To overcome these disadvantages, very efficient excitation energy transfer from porphyrin to NIR fluorescence dyes along the DNA double strand was investigated [6]. We also reported the application of confined and electric field enhanced light at surface plasmon resonance (SPR) condition to highly sensitive fluorescence detection of dyes in DNA ultrathin films deposited on a metal film and to high performance nitrogen oxides gas sensing [7]. These results demonstrated that DNA chain is one of the most powerful tools for nanoassemblies and will give novel concepts of materials design. We have very recently been reported to enhance NIR fluorescence by localized SPR (LSPR) from metal nanostructures using the regularly arranged gold (Au) nanoblocks (Au array) which show specific absorption in the NIR region [8]. Average total fluorescence intensity was larger by about 1.1 to 2.5 times depending on the Array structure. The fluorescence enhancement depends on the location of LSPR absorption. In this paper, we investigate polarization dependence which relates to the plasmon band of Au array to clarify the factor of the fluorescence enhancement.

Experimental

Regularly arranged Au nanoblocks (Au arrays) were fabricated by the electron beam lithography on glass plates [9–10]. Three types of Au arrays with designed dimensions of $100 \times 100 \times 40$ nm (Array 1, 2, 3) were prepared as schematically shown in Figure 1(a). The actual sizes of Au blocks were evaluated as 100 nm for Array 1, 110 nm for Array 2, and 150 nm for Array 3 from absorption spectra. The distances between Au blocks were 200 nm for Array 1, 190 nm for Array 2, 150 nm for Array 3 as schematically shown in Figure 1 for Array 1. As a NIR fluorescence dye, 2-[2-[2-Chloro-3-[(1,3-dihydro-3,3-dimethyl-1-propyl- 2H-indol-2-ylidene)ethylidene]-1-cyclohexen-1-yl]ethenyl]-3,3-dimethyl-1-propylindolium iodide (IR780; Aldrich Co. Ltd., Figure 1(b)) was selected. Hydrohobic DNA (H-DNA) was prepared by exchanging sodium ions with hexadecyltrimethylammonium ions according to the reported method [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 Hitachi U-4100 spectrometer. Fluorescence

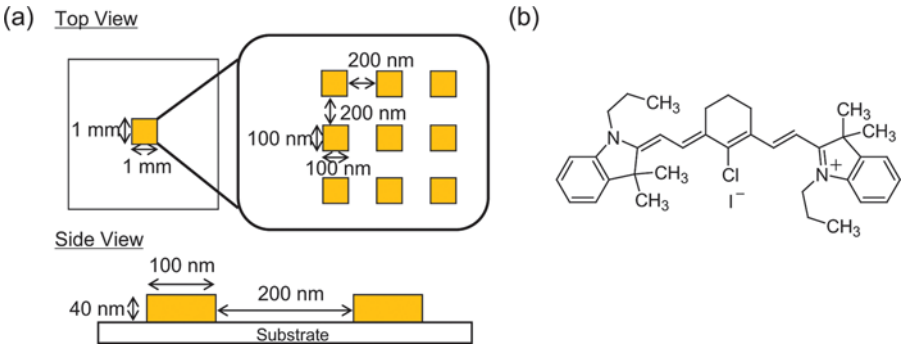

Figure 1. (a) Schematic representation of regularly arranged gold nanoblocks (Array 1), (b) the molecular structure of IR780.

spectra were measured by Hitachi F-4500 fluorescence spectrophotometer. The CW lasers (633, 675, and 788 nm) were used as excitation light. The polarization of excitation light was controlled by a film polarizer. The incident angle for the sample was set on 40°.

Results and Discussion

The absorption and fluorescence spectra of IR780 in H-DNA thin film were shown in Figure 2(a). The absorption spectrum of IR780 in H-DNA thin film shows peak around 800 nm with a shoulder around 730 nm. The fluorescence peak located at 817 nm. The absorption (extinction) spectra of Au arrays exhibit two peaks as shown in Figure 2(b), which were reported previously [8]. The peaks of Au array located around 460 and 700 nm for Array 1, 460 and 730 nm for Array 2, and 460 and

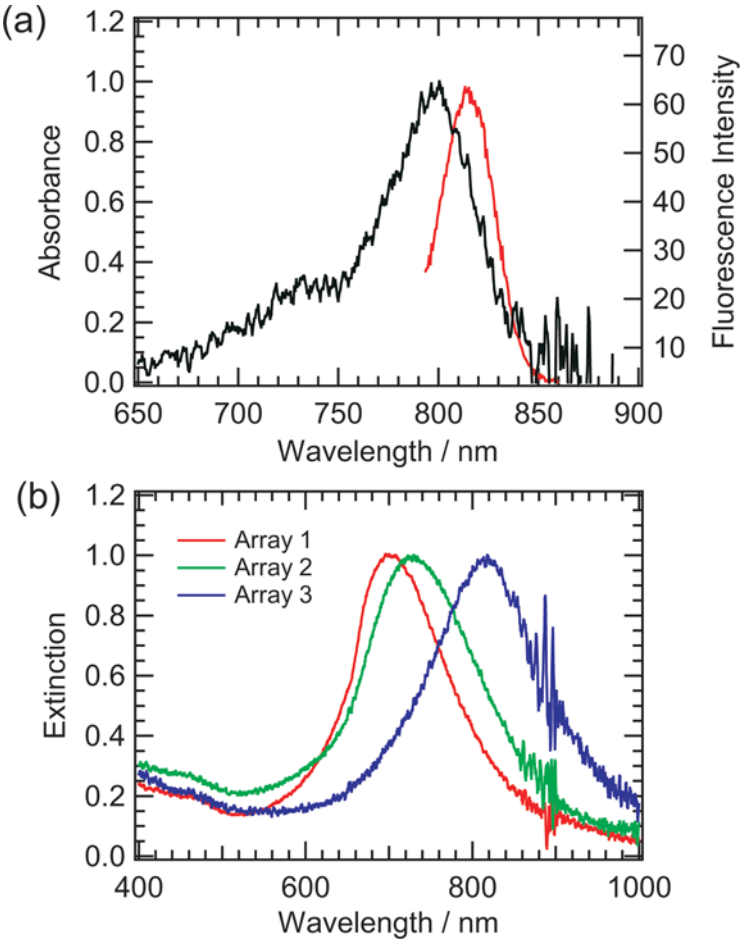

Figure 2. (a) Absorption and fluorescence spectra of IR780 in H-DNA thin film. The excitation wavelength was 780 nm. (b) Extinction spectra of three Au arrays.

820 nm for Array 3. 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 is expected between the Au nanoblocks separated by ca. 150 to 200 nm.

Figure 3 shows schematic representation of polarized excitation light for the Au array. P- and S- polarization are the vector of electric field which defined as parallel and perpendicular to the plane of incidence, respectively. If the incident angle θ is not equal to zero, the P-polarization can excite the plasmon band of Au nanoblocks for both vertical and horizontal direction. In the present condition, $\theta = 40°$, then the ratio of P-polarized light for horizontal and vertical direction of Au nanoblocks is estimated to be 1:0.839 from the ratio of sine to cosine. S-polarization, on the other hand, can only excite for the horizontal direction.

Figure 4 shows fluorescence enhancement factors for IR780 in H-DNA thin films on Array 1, 2, and 3 excited for P- and S-polarized light at 675 and 788 nm together with the absorption spectra of the arrays. In the case of Array 1, the fluorescence was enhanced by about 1.6 and 2.5 times than that in the absence of the Au nanoblocks for P- and S-polarization, respectively. The enhancement factor for Array 2 was similar to that for Array 1. 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 0.6 to 1.2 times of that on a glass plate. The dependence of excitation wavelength and polarization were scarcely observed in Array 3. The peak of absorption band in Array 3 is located at the fluorescence maximum wavelength of IR780. Such overlap between absorption and fluorescence bands is presumed to

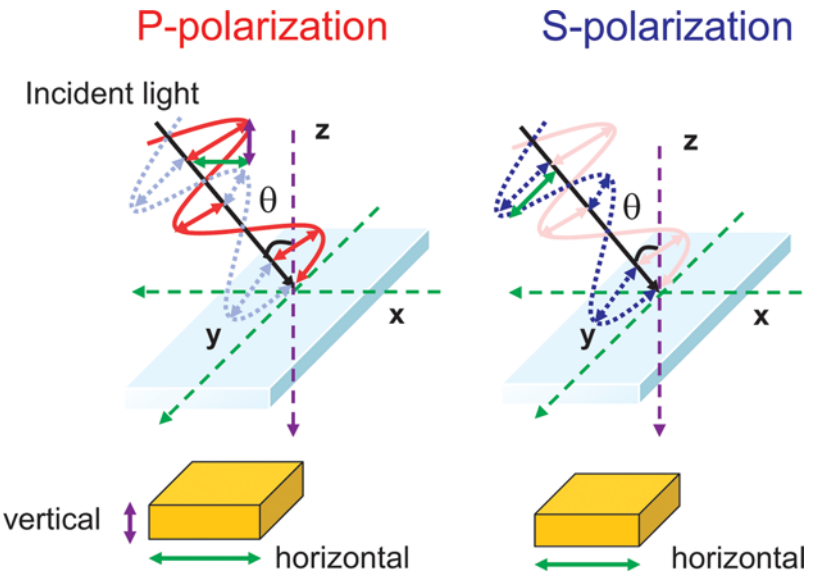

Figure 3. Schematic representation of the polarized light and Au nanoblock.

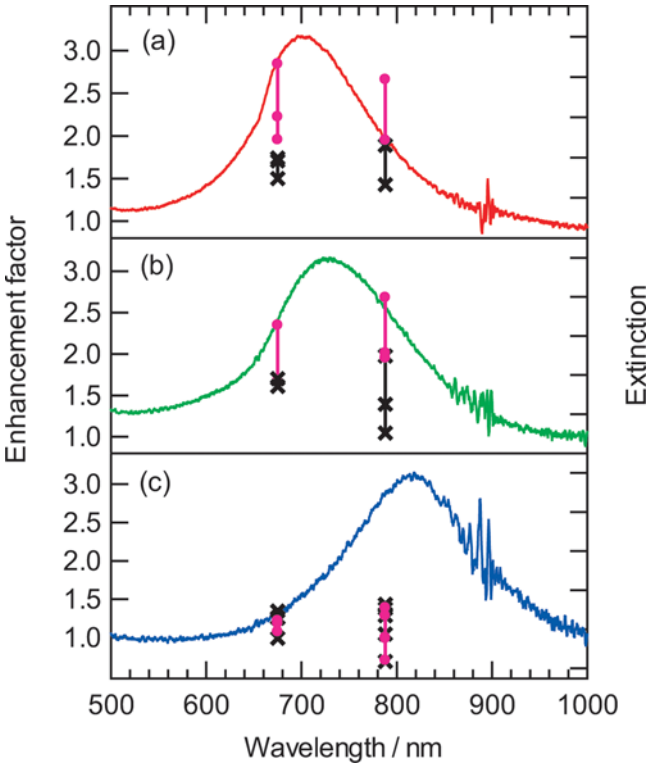

Figure 4. Observed enhancement factors of fluorescence intensity for IR780 in H-DNA thin films on (a) Array 1, (b) Array 2, and (c) Array 3 excited at P-(○, pink plot) and S-polarized (×, black plots) 633, 675 and 788 nm light together with the extinction spectra of the arrays.

result in the fluorescence quenching of the dye due to efficient energy transfer from the excited state of IR780 to Au nanoblocks rather than the fluorescence enhancement, which were reported previously [8].

The excitation wavelength and polarization dependence for the enhancement factor by Array 1, 2, and 3 are summarized in Table 1. The enhancement factor for S-polarized excitation was about 1.2 to 1.5 times larger than that for P-polarized light in the case of Au array 1 and 2. P-polarized light contributed to the excitation of plasmon band both of horizontal and vertical direction of Au nanoblocks. The vertical direction corresponds to the short axis for height direction which has the absorption in visible region did not contribute the excitation of IR780. It is assumed that the fluorescence enhancement due to the excitation of vertical direction is unity, and that excitation light only contribute the projection for the horizontal direction. The apparent enhancement factor E_f can be defined by the Eq. (1):

$$E_f = \frac{1}{1.839}n + \frac{0.839}{1.839} \times 1 \tag{1}$$

Table 1. Enhancement factor of fluorescence intensity for polarized light and excitation wavelength

	Array 1		Array 2		Array 3	
λ_{ex}/nm	675 nm	788 nm	675 nm	788 nm	675 nm	788 nm
P-polarization Obs.	1.7	1.7	1.6	1.5	1.2	1.2
Calcd.*	2.2	2.2	1.9	1.9	1.4	1.4
S-polarization	2.3	2.3	2.2	2.0	1.2	1.1

*Estimated from Eq. (1).

where n is the enhancement factor due to the projection of horizontal direction for Au nanoblocks excited by P-polarization. The second term corresponds to the projection of vertical direction. The fraction values were described above. The calculated enhancement factors due to the horizontal direction by P-polarization were described in Table 1. The calculated n values were almost equal to the enhancement factor due to the excitation by S-polarization. These experimental results suggested that the observed fluorescence enhancement by the Au arrays originated from the resonance of photo-electric field along the plasmon band of transverse and longitudinal mode. It is also required to fit the direction of enhanced photo-electric field by Au arrays and the dipole moment of IR780. On the other hand, the fluorescence quenching is independent of the polarization of excitation light. This phenomenon was strongly supported that the quenching originates from the 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.

Conclusion

We investigated polarization dependence of excitation light for fluorescence enhancement of the NIR dye by regularly arranged but independent Au nanoblocks. The enhancement factor for S-polarized excitation was about 1.2 to 1.5 times as large as that for P-polarized light about Au array 1 and 2. The calculated enhancement factor due to the projection of horizontal direction values was identical to that due to the excitation by S-polarization, suggesting that the observed fluorescence enhancement by the Au arrays originated from the resonance of photo-electric field along the plasmon band of transverse and longitudinal mode. The dependence of excitation wavelength and polarization were scarcely observed in Array 3, which means the fluorescence quenching originates from the 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.

Acknowledgment

This work partly supported by Grant-in-Aid on Priority Area (470: Strong Photon-Molecule Coupling Fields: No. 20043027 and 21020028) from the Ministry

of Education, Culture, Sports, Science, and Technology (MEXT) of the Japanese Government.

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