

# Quenching of Excited J Aggregates on Metals by Surface Plasmon Excitations

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The photocurrent spectrum was measured for a solid-state organic photoelectric cell with ITO and Al electrodes. A large difference was observed between absorption and photocurrent spectra for merocyanine J aggregate Langmuir–Blodgett (LB) films as an organic photoconductor of the cell. The spectra indicate that the J aggregate in the LB film is not responsible for the photocurrent. To confirm the origin, the angular distribution of emission from the metal was measured using a coupler prism under the excitation of the J aggregates. P-polarized directional emission, which distinguishes surface plasmon polaritons (SP), was observed for a coupler prism/Al/LB film system. It is evident that excited J aggregates on metals are quenched by coupling with SP. The quenching seems to have a close relation with the difference between absorption and photocurrent spectra. The emission spectrum was also measured to compare with the fluorescence spectrum of the J aggregate LB film. The fluorescence spectrum was sharper and more Stokes-shifted than the emission based on SP. The emission process via SP seems to be less influenced by relaxation in the J aggregate.

## Introduction

Recently, the number of studies concerning photoelectric cells with organic photoconductive layers are increasing.<sup>1</sup> In many cases, the aim of the study is the realization of a solar cell mimicking photosynthesis, which is expected to possess better performance than conventional inorganic cells.<sup>2</sup> Actually, the yield of photon-to-electron conversion in such cells already exceeds 30% at the optimum conditions.<sup>3</sup>

Dyes are known to form a variety of aggregates.<sup>4</sup> In particular, J aggregates, which show red-shifted sharp absorption spectra, are famous as photosensitizers in photography.<sup>5</sup> J aggregates also interest researchers in nonlinear optics,<sup>6</sup> optical memory,<sup>7</sup> or super radiation.<sup>8</sup> One of their features is that they cause efficient Förster-type energy transfer.<sup>9</sup> Such energy transfer plays an important role in the antenna system of photosynthesis.<sup>10,11</sup>

We have been studying the influence of aggregate formation in the organic photoconductive layer of photoelectric cells. In previous papers, it has been shown that the J aggregate in the photoconductive layer is not responsible for the photocurrent when metal electrodes are directly contacted with the J aggregate layer.<sup>12,13</sup> The possibility of nonradiative energy transfer from excited J aggregates near a metal surface to surface plasmon polaritons (SP) was investigated by Pockrand et al.<sup>14</sup> If similar energy transfer takes place in our system, excited J aggregates will suffer nonradiative decay and the transferred energy will dissipate as thermal energy in the metal.

SP is a type of electromagnetic wave localized at a metal surface. As the dispersion relation of light in air does not match that of SP on the metallic surface, SP cannot interact with light directly.<sup>15</sup> There are two methods to couple SP and light, i.e., use of a coupler prism and formation of a grating-like structure on the metal surface.<sup>15</sup> To verify the excitation of SP, we employed a coupler prism to detect SP as light emission from a metal. p-Polarized directional emission, which distinguishes SP,<sup>16,17</sup> was observed through the coupler prism for a coupler prism/Al/Langmuir–Blodgett (LB) film system when J ag-

gregates in the LB film were excited by laser light irradiation. In the J aggregates, inelastic scattering is caused by energy exchange with molecules; therefore, measurement of emission spectra is quite valuable to investigate the process.<sup>18</sup> Emission spectrum based on SP excitation was measured to compare with the fluorescence spectrum of the J aggregate LB film. The spectral difference reflects the relaxation processes from excited states in the J aggregate.

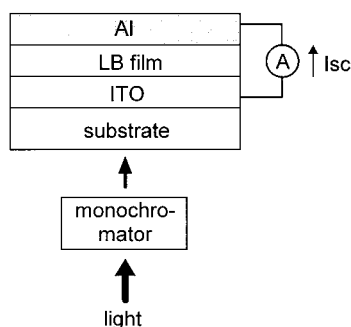
## Experimental Section

**Sample Preparation.** Amphiphilic merocyanine dye (MC) and arachidic acid (AA) were used as film-forming material. MC (NK2746) was purchased from The Japanese Research Institute for Photosensitizing Dyes, Co. Ltd. (Okayama, Japan), and its chemical structure is shown in ref 13. MC was diluted with AA to form stable LB films and the molar mixing ratio was [MC]/[AA] = 1:2. The mixture was dissolved in chloroform at a concentration of about  $1 \times 10^{-3}$  mol/L and spread on water containing about  $4 \times 10^{-4}$  mol/L of CdCl<sub>2</sub>. The pH value was adjusted to about 6.2 adding KHCO<sub>3</sub>, and the temperature was kept at about 20 °C. The monolayers were transferred onto substrate using the vertical dipping technique at a surface pressure of 25 mN/m, and this yielded Y-type LB films.

ITO-coated glass and cover glass were used as substrates for samples of photoelectric and SP measurements, respectively. ITO-coated glass substrates were purchased from Geomatec Co. Ltd. (Yokohama, Japan), and the thickness of the ITO electrode was about 150 nm. Al metal layers were deposited by vacuum evaporation at about  $10^{-4}$  Pa. The film thickness of the Al was monitored using a quartz thickness gauge so as to be about 25 nm.

**Photocurrent.** Measurement of short-circuit photocurrent (*I*<sub>sc</sub>) for the cells of an ITO/11-layer LB film/Al structure as shown in Figure 1 was carried out in air at room temperature. As merocyanine dyes are known to act like p-type semiconductors,<sup>19</sup> ITO/LB film and LB film/Al interfaces form an ohmic contact and a Schottky barrier respectively, and the cells function as Schottky barrier-type photodiodes. The cells were illuminated

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**Figure 1.** Schematic of the layered structure of the photoelectric cell and arrangement for  $I_{sc}$  measurement. An 11-layer merocyanine J aggregate LB film was sandwiched between ITO and Al metal film electrodes.

from the substrate side, i.e., through the substrate and ITO base with monochromatic light of  $100 \mu\text{W}/\text{cm}^2$ . The wavelength of the incident was changed by a monochromator. The current as  $I_{sc}$  from ITO to Al electrodes caused by light irradiation was monitored using an electrometer (Keithley 610C) as a function of wavelength.

**Reflectance.** Figure 2a shows the experimental setup used for the measurement of angular dependence of reflectance. The sample has a glass substrate/Al or a glass substrate/Al/21-layer LB film structures. The substrate was fixed on the flat base of a hemicylindrical BK-7 prism ( $n = 1.522$  at  $\lambda = 488 \text{ nm}$ ) using immersion oil. The arrangement corresponds to Kretschmann configuration, and SP can be excited at the Al/LB film interface.<sup>15</sup> The attenuated total reflection (ATR) prism with the sample was mounted on a computer-controlled goniostage. An Ar laser ( $\lambda = 488 \text{ nm}$ ) was used as the light source, and the light beam was polarized linearly using a Glan–Thomson prism. The p-polarized light beam was modulated by a light chopper of 1 kHz, and the reflected light beam was detected by a photodiode. The incident angle  $\theta$  was changed by rotating the goniostage. The intensity of the reflected light was measured as a function of  $\theta$  using a lock-in amplifier.

**Emission.** Figure 2b shows the experimental setup used for the measurement of angular distribution of light emission based on SP. A hemicylindrical prism made of BK-7 glass was used as a coupler prism to bring out nonradiative SP as light. Samples were prepared on microscope cover glass substrates. Al film as

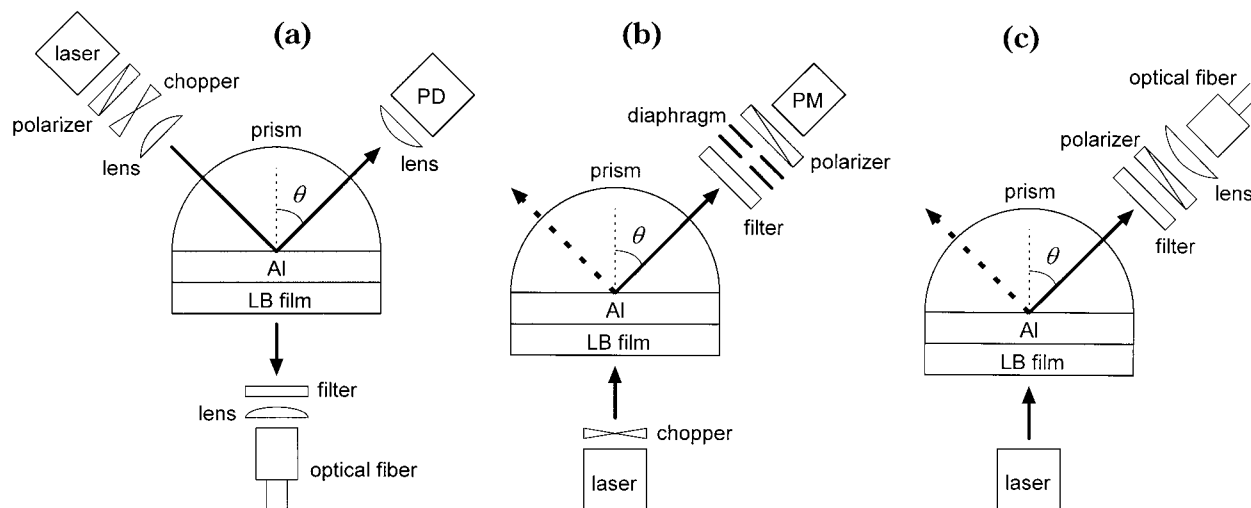
a metal layer and a 21-layer LB film were successively formed on the substrate. The substrate was fixed on the flat base of the prism with the appropriate immersion oil. The Ar laser ( $\lambda = 488 \text{ nm}$ ) was used as the light source for the excitation of J aggregates, the amplitude of which was modulated by the light chopper of 1 kHz. The angle  $\theta$  was changed by the computer-controlled goniostage. The intensity of emitted light was measured as a function of the angle using the lock-in amplifier. The light emission was detected by a photomultiplier through a sharp-cut filter ( $\lambda = 520 \text{ nm}$ ) to eliminate the scattered light of excitation, diaphragms to secure the angular resolution, and a polarizer to examine the polarization of the emitted light. The diameter of the hole of the diaphragms was 1 mm, and the distance between them was 100 mm.

**Spectrum.** The fluorescence spectrum of the J aggregate LB film on the Al metal layer was measured in the configuration of Figure 2a. Unlike conventional methods, fluorescence from J aggregates on the metal film was measured to compare with the emission spectrum based on SP in the same condition, since existence of the metal film is possible to influence the spectrum.<sup>20</sup> The incident angle of the Ar laser was adjusted so as to excite SP at the Al/LB film interface, and the J aggregates were excited by the SP. The spectrum was measured using a multichannel spectrophotometer (Photol, IMUC-7000) through the sharp-cut filter to eliminate the scattered light of excitation, a collection lens, and an optical fiber to guide the fluorescence.

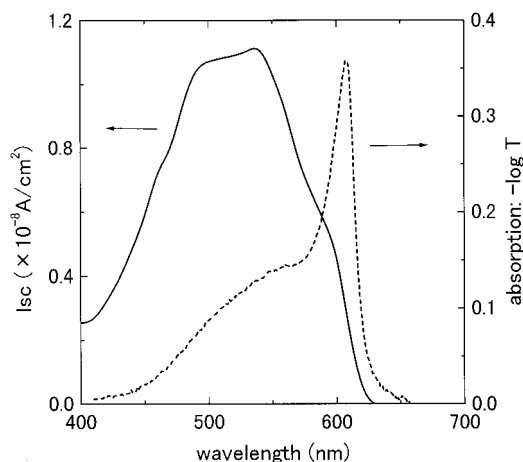
The emission spectrum based on SP was measured in the configuration of Figure 2c. The Ar laser was used as the light source for the excitation of J aggregates in the LB film. The angle  $\theta$  was adjusted so that the intensity of emission came to be maximum. The spectrum was measured using the multichannel spectrophotometer through the coupler prism, the sharp-cut filter to eliminate the scattered light of excitation, the polarizer to eliminate the s-polarized component, the collection lens, and the optical fiber to guide the emission.

## Results

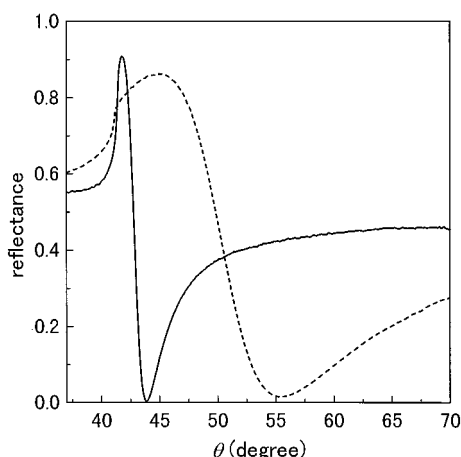
**Absorption and  $I_{sc}$  Spectra.** The solid and the broken lines in Figure 3 show the  $I_{sc}$  and the absorption spectra of the ITO/11-layer LB film/Al cell and the 11-layer LB film, respectively. The absorption spectrum is associated with a sharp red-shifted band at about 610 nm which is assignable to J aggregate. Unlike the absorption spectrum, the maximum in the  $I_{sc}$  spectrum is



**Figure 2.** Schematic of the layered structure of the sample and arrangement for measurements: (a) experimental setup for the measurement of angular distribution of reflectance and fluorescence spectrum excited by SP; (b) experimental setup for the measurement of angular distribution of emission based on SP; (c) experimental setup for the measurement of emission spectrum based on SP. A 21-layer merocyanine J aggregate LB film was formed on an Al metal film.



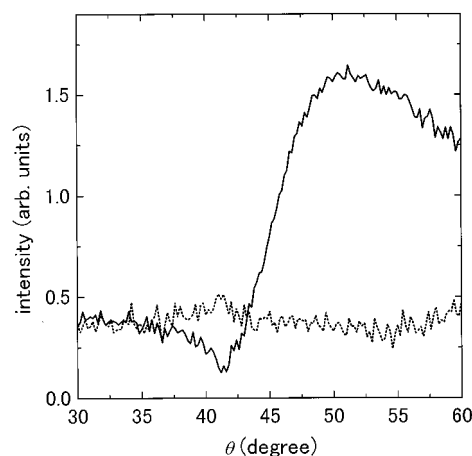
**Figure 3.** Isc spectrum of an ITO/11-layer LB film/Al cell (solid line) and absorption spectrum of an 11-layer LB film (broken line).



**Figure 4.** Measured reflectance for samples of Al film (solid line) and Al/21-layer LB film (broken line) as functions of angle  $\theta$  for p-polarized light of an Ar laser ( $\lambda = 488$  nm).

located at about 530 nm, which corresponds to a monomer band, and only a shoulder is detectable at 600 nm. These spectra indicate that the J aggregates in the LB film are not responsible for the photocurrent. Such disagreement between absorption and Isc spectra is often observed in red-shifted aggregates such as J aggregates.<sup>12,13</sup> Excited J aggregates are known to cause efficient energy transfer, which brings the ability of sensitizer to them.<sup>9</sup> When there is a metal near the excited J aggregates, they can cause energy transfer to the metal by excitation of SP.<sup>14</sup> The nonradiative decay of excited J aggregates by energy transfer to the metal seems to have close relation with the relative predominance of the contribution from the monomer band for the Isc spectrum.

**Reflectance Curves.** The measured reflectance curves for p-polarized light are shown in Figure 4. Solid and broken lines correspond to the Al and the Al/LB film structures, respectively. Dips around  $\theta = 43^\circ$  and  $\theta = 55^\circ$  are due to SP excitation at the Al/air and the Al/LB film interfaces, respectively. It should be noted that the reflectance decreases down to almost 0 and nearly 100% of the incident was absorbed by the metal as SP at each dip. The incident could be efficiently coupled with SP in this case. As is well-known, the position, width, and depth of the dips depend strongly on the nature of the overlayer on the metallic surface.<sup>15,17</sup> The dip for the Al/LB film is located at a higher angle than that for the Al in Figure 4. The higher shift of the dip is reflected in the fact that the real part of

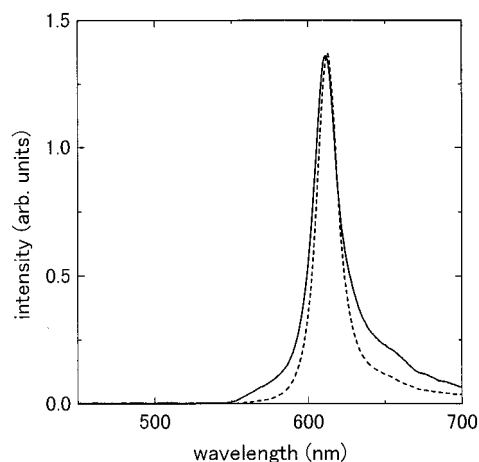


**Figure 5.** Intensities of emission based on SP as functions of angle  $\theta$  for a sample of Al/21-layer LB film: (solid line) p-polarization; (broken line) s-polarization.

dielectric constant of the LB film is larger than that of air. Furthermore, the dip is shallower and broader than that for the Al. The results show that the imaginary part of its dielectric constant, which is closely related to the absorption coefficient of the material, is larger than that of air. The reflectance curve for the Al can be best fitted using the complex dielectric constant of  $-12.0 + i3.50$  at  $\lambda = 488$  nm and the thickness of 24.0 nm for the Al film. The reflectance curve for the Al/LB film can be best fitted using the values of Al, the complex dielectric constant of  $1.75 + i0.05$  at  $\lambda = 488$  nm, and the thickness of 57.0 nm for the LB film. The estimated film thickness for LB films is quite reasonable by comparison with the theoretical value, i.e.,  $2.76 \text{ nm (molecular length of AA)} \times 21 \text{ layers} = 57.96 \text{ nm}$ .<sup>21</sup> The existence of an Al oxide layer on the metal film was ignored, since the very thin layer hardly affects the fitting.<sup>22</sup>

**Emission Curves.** The measured intensities of the emitted light as functions of  $\theta$  for the sample of the Al/LB film structure are shown in Figure 5. Clear dependence for the polarization was observed in the emission curves. While the p-polarized component shows typical angular dependence (directivity), the intensity of the s-polarized component in this angle range is almost constant at about 20% of the peak intensity of the p-polarized component. It is well-known that SP can couple with only p-polarized light.<sup>15,16</sup> Therefore, it is evident that the main component of the observed emission originates from SP which is generated by energy transfer from excited J aggregates. The maximum amount of p-polarized light is emitted at about  $51^\circ$ . In the ideal case, angle positions of dip and peak for reflectance and emission intensities, respectively, show a good agreement.<sup>17</sup> As shown in Figure 4, however, the dip of reflectance for the Al/LB film is located at about  $56^\circ$ . The wavelength for the measurement of reflectance was 488 nm. Although the same wavelength was used for the excitation of J aggregates, the wavelength range for the observation of light emission based on SP was longer than 520 nm, since the sharp-cut filter of 520 nm was introduced to eliminate the scattered excitation light. The difference in the wavelength brings about the disagreement of the angle positions of the dip and the peak in our case.

**Emission Spectra.** The fluorescence and the emission spectra of the Al/LB film are shown in Figure 6. The angles  $\theta$  corresponding to Figure 2 were  $56^\circ$  and  $51^\circ$  for the fluorescence and the emission based on SP, respectively. The spectra were normalized at each peak. A strong sharp fluorescence with a



**Figure 6.** Spectra of emission based on SP (solid line) and fluorescence (broken line) for a sample of Al/21-layer LB film.

small Stokes shift, as shown in Figure 6, is known as the evidence for J aggregate formation.<sup>9</sup> The spectrum of the emission based on SP is similar to that of the fluorescence; however, it is less Stokes shifted and broader than that of the fluorescence. It should be noted that the main component of the emission based on SP is far red-shifted from the excitation wavelength. The large red shift causes the disagreement between the angle positions of the dip and the peak mentioned above.

## Discussion

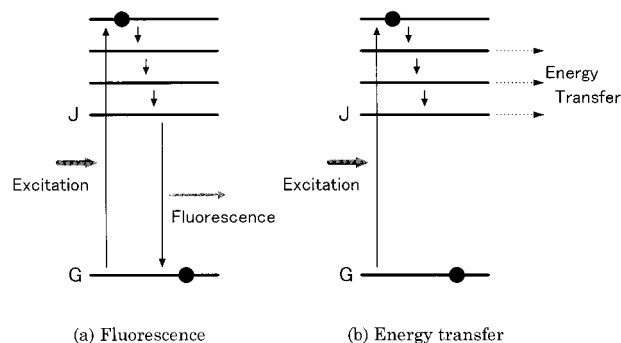
The results presented in the previous section demonstrate the nonradiative energy transfer from excited J aggregates near a metal surface to SP. The excited SP couples with lattice vibration of the metal, and its energy is going to dissipate as thermal energy.<sup>15</sup> Therefore, when there is a metal electrode near excited J aggregates in solar cells, the efficiency of photoelectric conversion due to J aggregates will be lowered by such energy transfer.

The Isc spectrum shown in Figure 3 indicates that the J aggregate is not responsible for the photocurrent. However, the J aggregate can remarkably contribute to the photocurrent when the LB film does not have direct contact with metal electrodes but has an organic hetero junction.<sup>12,23</sup> The fact suggests that the quantum efficiency of the J aggregate is potentially similar to the monomer and the metal electrode plays an important role. Although the nonradiative energy transfer seems to cause the difference between Isc and absorption spectra, we should not neglect possible energy transfer from the excited monomers to the J aggregates to explain the difference based on energy transfer. Efficiency of the Förster-type energy transfer  $\phi$  in LB films is given by

$$\phi = \frac{1}{1 + (d/d_0)^\alpha} \quad (1)$$

where  $d$  is a distance between sensitizer and acceptor layer and  $d_0$  is a critical distance of energy transfer.<sup>9</sup> When the LB film consists of monomers, the exponent  $\alpha$  is 4. On the other hand,  $\alpha$  comes to be 2 when the LB film consists of J aggregates.<sup>9</sup> The different behavior in  $\alpha$  means that excited energy in J aggregates is more easily transferred than that in monomers. The efficiency of energy transfer from monomers to J aggregates or to metal electrodes seems not to be high enough to efficiently prevent charge separation in the excited monomers. Therefore, I believe that the difference in the efficiency brings about the

## SCHEME 1 Illustration of the Energy Level Diagram in J Aggregate and Relaxation Processes from Excited State: (a) Emission of Fluorescence; (b) Energy Transfer to SP



relative predominance of the contribution from the monomer band for the Isc spectrum.

The difference in spectra between fluorescence and emission based on SP seems to reflect the relaxation processes in the excited J aggregates. In the case of fluorescence from J aggregates, the emission process can be explained by Scheme 1a. The excited electrons suffer relaxation with decay and accumulate at the lowest excited state close to the J band. The main part of the fluorescence is due to the transition between the lowest excited and the ground states, which results in a small Stokes shifted sharp spectrum. In contrast to the fluorescence, energy transfer during relaxation, which results in a less Stokes shifted broader spectrum, seems to be possible in the case of SP excitation as shown in Scheme 1b. The scheme means that the processes of the energy transfer and the excitation of SP are faster than those of the fluorescence emission.

## Concluding Remarks

Electrodes in solar cells are indispensable to conduct photocurrent. Metal electrodes are popular for fabrication of solid-state organic solar cells;<sup>2,3</sup> however, we should consider that there is not an electrode like metals, which possess high electron density and plasma frequency, in the system of photosynthesis when we fabricate organic solar cells referring to the photosynthesis. In the present study, we have demonstrated that metal electrodes can play a role of effective acceptor for excited J aggregates. The quenching of excited J aggregates leads to lowering the efficiency of photoelectric conversion. Further study of energy transfer between electrodes and molecules is necessary to improve the performance of organic solar cells.

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