An Error in Determination of Photoinduced Electron Transfer Rates in Langmuir-Blodgett Films

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In Langmuir-Blodgett (LB) films consisting of viologen (V^{2+}) - pyrene (Py) dyads, the accumulation of viologen cation radical ($V^{+\bullet}$) was observed during UV irradiation under N_2. The additional quenching due to energy transfer by the colored $V^{+\bullet}$ resulted in an error in determination of photoinduced electron transfer rates between the V^{2+} and Py moieties in the LB films. This type of error can be generally expected in LB films and self-assembled monolayers.

The photochemical oxidation of LB films containing 6-(1-(8-decyl)pyrene)-hexanoic acid[1] in the presence of molecular oxygen was reported previously.[2] The pyrene quinones were determined as the photo-oxidative products by FT-IR. We observed a larger decrease in the fluorescence intensity of the pyrene derivative with increasing the elapsed time after the beginning of the irradiation with UV light under air. The photo-oxidative products acted as the energy acceptors and diminished the fluorescence intensity of the pyrene moieties quite efficiently by Förster-type energy transfer quenching. Inhibition of the photo-oxidation was observed under N_2. Thus it is important to keep the LB films under N_2 or an inert atmosphere when the fluorescence spectra or the intensities are measured.

However, even under the inert atmosphere made by the flow of N_2, considerable decrease of fluorescence intensities with elapsed time of UV irradiation was observed for LB films consisting of one of electron acceptor-sensitizer (A-S) dyads (**1** - **4**) as shown in Figure 1. Moreover, the recovering of fluorescence intensities were clearly observed when the irradiated samples were transferred into air.

Figure 2(a) shows two slightly different absorption spectra of a LB film containing the compound **4** measured under N_2 before (solid line in the inset) and after (dotted line in the inset) 5 min UV (350 nm) irradiation under N_2. The dashed curve in the inset illustrates an absorbance difference spectrum between the two absorption spectra. It is clear from comparison of the absorption difference spectrum with the spectrum of a methyl viologen cation radical solution produced electrochemically[3] that viologen cation radical accumulated in the LB film during UV irradiation under N_2. A fluorescence band of the pyrene moiety (Figure 2(b)) around 400 nm well overlaps with the absorption band of viologen cation radical. These results suggest that the photoproduced viologen cation radical acted as the energy transfer quencher for the excited pyrene moiety and diminished the fluorescence intensity as observed in Figure 1. In addition, the viologen cation radical is known to be reoxidized readily to viologen by oxygen in air.[4] This is the reason why recovering of the fluorescence intensity was observed upon exposure to air.

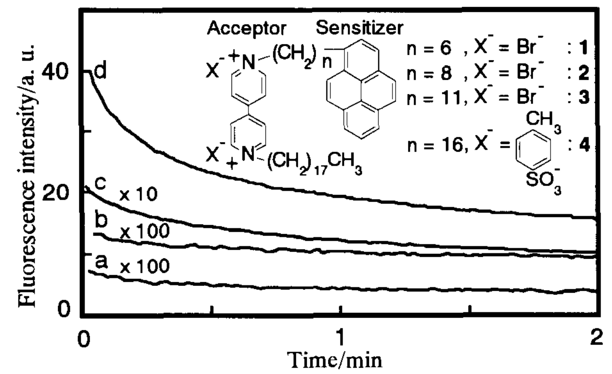

Figure 1. The changes in the fluorescence intensities of LB films consisting of one of the A-S dyads, **1** (curve a), **2** (curve b), **3** (curve c) and **4** (curve d), and arachidic acid (AA) (molar ratio, 1:10) as functions of elapsed time. The intensities of the curves a and b and the curve c are magnified by a factor of 100 and 10, respectively.

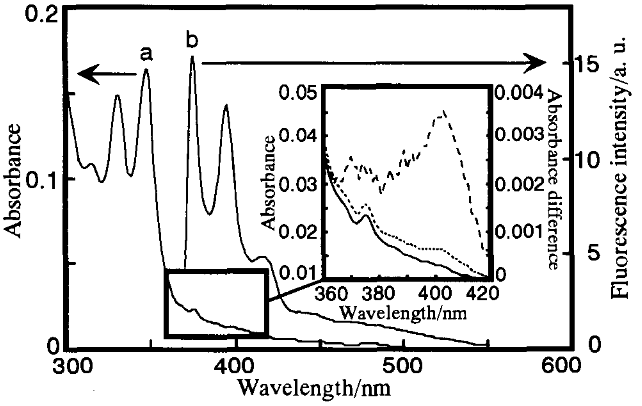

Figure 2. a) UV-vis absorption spectra of the mixed LB film of A-S dyad **4** - AA (molar ratio 1:10, 122 layers). Absorption spectra measured after 5 minutets UV irradiation at 350 nm (dotted curve) and absorption difference spectra (dashed curve) between the two curves, dotted and solid, are also shown (inset). b) Fluorescence spectra of the mixed LB film of **4** - AA (81 layers).

Photochromic LB films have been mainly studied by the use of reversible changes in color induced by photo-isomerization. Recently Yamazaki et al. succeeded in switching interlayer energy transfer between energy donor and acceptor layers by inserting a photochromic layer.[5] The charge separated state $V^{+\bullet}$ - $Py^{+\bullet}$ produced by the photo-induced intramolecular electron transfer of a V^{2+}-Py dyad molecule was not expected to be so stable as the photochromic material because $V^{+\bullet}$ -$Py^{+\bullet}$ would disappear rapidly due to the fast intramolecular back electron transfer. However, the accumulation of viologen cation radical was evidently observed in the LB film containing the V^{2+}-Py dyad as shown in Figure 2.

The accumulation of viologen cation radical can be explained by the same mechanism introduced to explain very long decay time (> 10 s) of photoinduced surface potential of the LB films containing A-S dyad or electron acceptor-sensitizer-electron donor (A-S-D) triad observed with a scanning surface potential microscope (SSPM).[6] The observed change in the photoinduced surface potential arises from the change in the number of the charge separated species in the LB films. Thus the prolonged decay indicated that some separated charges existed even 10 s after shutting the irradiation down. This can not be explained by the charge separation and recombination within one dyad or one triad molecule. Such long lifetimes of the separated charges can be interpreted by assuming succeeding lateral intermolecular charge migration among the acceptor or the donor moieties after the perpendicular intramolecular charge separation within a molecule. Namely, the rapid migration of the photo-created radical anions ($A^{-\cdot}$) by exchange electron among the acceptor (A) moieties or cations ($S^{+\cdot}$ or $D^{+\cdot}$) among the electron donor (S or D) moieties can separate the charge further distantly.

The more pronounced decay of fluorescence intensity, which corresponds to the more efficient accumulation of viologen cation radical, was observed with an increase in the bridge chain length of A-S dyad (Figure 1). This relationship is consistent with the mechanism described above. Namely, the longer lifetime of the charge-separated state of the dyad with the longer bridge chain increases the lateral migration efficiency to form the long-lived separated charge.

Figure 3 schematically illustrates photochemical events of two types of multi-layered LB films deposited on gold optically transparent electrodes (OTEs), i.e. AuOTE/A/S/D and AuOTE/D/S/A, investigated in the early stage of our research for electrochemical photodiodes.[7] The LB films were composed of three layers of different surfactant derivatives containing one of the functional moieties of A (viologen, V^{2+}), S (pyrene, Py) and D (ferrocene, Fc). As shown in Figures. 3(a) and 3(b), an anodic and a cathodic photoelectron flow through the outer circuit produce a ferrocene cation and a viologen cation radical, respectively. The viologen cation radical acts more efficiently than the ferrocene cation as the photochromic energy acceptor because absorbance of the viologen cation radical around the wavelength of fluorescence band of pyrene is approximately a hundred times larger than that of ferrocene cation.[3,8] In fact, the anodic photocurrents observed on the AuOTE/A/S/D system were very stable and almost the same current was recorded repeatedly over 1 h, while the cathodic currents observed on the AuOTE/D/S/A system were decayed appreciably within ten repetitions of the stepped illumination. These results are likely to be explained in terms of the more efficient energy transfer quenching by the viologen cation radical than the ferrocene cation.

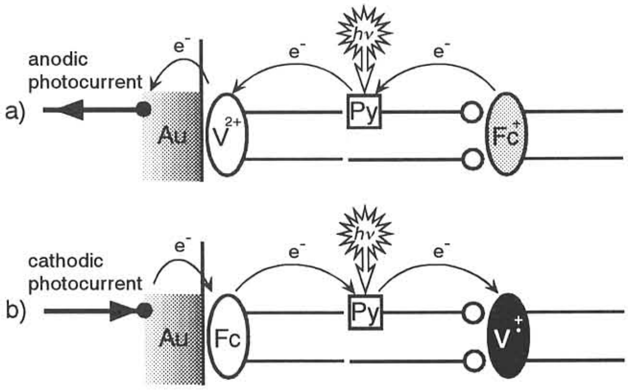

Figure 3. Schematical illustrations of photochemical events of two types of multi-layered LB films. a) AuOTE/A/S/D system. b) AuOTE/D/S/A system.

Not only viologen but also many other compounds which are capable as electron acceptors or donors can be changed into energy acceptors owing to photochromism via photoinduced electron transfer. The accumulation of the photochromic energy acceptor should be taken into account especially when the fluorescence lifetime measurement is employed to study electron transfer kinetics in highly concentrated systems such as LB films and self-assembled monolayers because averaging of high-speed repetitive measurements is ordinary used for attaining a high S/N ratio.

In conclusion it is important to avoid the above described unfavorable photochromism for fabrication of more efficient molecular photodevices such as molecular photodiodes and artificial photosynthetic systems.

References and Notes

1 This compound was synthesized and used as a mixture of three regioisomers, i. e. 6-(1-(8-decyl)pyrene)-hexanoic acid, 6-(1-(6-decyl)pyrene)-hexanoic acid, and 6-(1-(3-decyl)pyrene)-hexanoic acid (6.2 : 3.2 : 0.6 in a molar ratio).
2 M. Fujihira, T. Kamei, M. Sakomura, Y. Tatsu, and Y. Kato, *Thin Solid Films,* **179**, 485 (1989).
3 T. Watanabe and K. Honda, *J. Phys. Chem.,* **86**, 2617 (1982).
4 J. A. Farrington, M. Ebert, E. J. Land, and K. Fletcher, *Biochim. Biophys. Acta,* **314**, 372 (1973).
5 I. Yamazaki and N. Ohta, *Pure & Appl. Chem,* **67**, 209 (1995).
6 M. Fujihira, M. Sakomura, D. Aoki, and A. Koike, *Thin Solid Films,* **273**, 168 (1996).
7 M. Fujihira, K. Nishiyama, and H. Yamada, *Thin Solid Films,* **132**, 77 (1985).
8 O. Traverso and F. Scandola, *Inorg. Chim. Acta,* **4**, 493 (1970).