Transient absorption measurements of acceptor-sensitizer-donor triad molecules in solutions and Langmuir-Blodgett films

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Abstract

Transient absorption measurements of an acceptor-sensitizer-donor (A-S-D) triad molecule (ASD) that contained viologen, pyrene, and ferrocene as the A, S, and D moieties, respectively, were made in benzonitrile and aqueous micellar solutions, and in a

Langmuir-Blodgett (LB) monolayer assembly. Intramolecular electron transfer reactions were initiated by photo-excitation of the S moiety, which gave rise to the long-lived final charge-separated $A^{\bullet-}$ -S- $D^{+\bullet}$ state. The rate of the backward electron transfer from $A^{\bullet-}$ to $D^{+\bullet}$ was determined from the absorption decay of the viologen cation radical monitored at 600 ~ 700 nm. The estimated lifetime of the final charge-separated state was ca. 60 ns, based on measurements of the solutions. Extremely slow decay (much longer than 600 μ s) of the transient absorption of the viologen cation radical was observed for a mixed ASD LB film with 22-tricosenoic acid (TA). This slow decay observed on a LB film at higher ASD concentrations may be explained by lateral charge migration between adjacent molecules in the monolayer plane.

Key words: transient absorption spectroscopy; triad molecule; intramolecular electron transfer; Langmuir-Blodgett film

1. Introduction

In higher plants, the photosynthetic reaction centers for photosystems I and II (PSI and PSII) are embedded in the thylakoid membranes [1, 2]. PSI and PSII are large protein complexes that contain many functional moieties, including pigments, electron donors,

and electron acceptors, that are held in the appropriate positions and orientations by the protein environment. The controlled alignment and orientation of the moieties play important roles in charge separation in the primary process of photosynthesis. It is of great interest to design artificial photosynthetic molecular devices that mimic this elaborate molecular machinery.

We have been studying artificial photosynthetic reaction centers consisting of amphiphilic acceptor-sensitizer-donor (A-S-D) triad molecules oriented unidirectionally within Langmuir-Blodgett (LB) monolayer assemblies [3]. In an A-S-D triad, three moieties, *i.e.*, an electron acceptor, (A, viologen), a sensitizer (S, pyrene or perylene), and an electron donor (D, ferrocene), are combined by sigma-bonded tunneling bridges at appropriate distances, and they align across the monolayer due to the amphiphilic property of this molecule. On excitation of the S moiety, two-step electron transfer occurs, *i.e.*, from S to A and from D to S, resulting in a charge-separated state, $A^{\bullet-}-S-D^{+\bullet}$. The long-lived charge-separated state can be detected by observing the change in surface potential using scanning surface potential microscopy (SSPM) [4-7] and measuring the photocurrent electrochemically [3, 5]. The dynamics of photo-induced electron transfer in a perylene type A-S-D triad have been examined in a benzonitrile solution using femtosecond transient absorption spectroscopy [8]; however, the yield and lifetime of the

final charge-separated state could not be elucidated in detail because the lifetime of the final charge-separated state was much longer than the limitation of the time scale (< 4 ns) available in that measurement. In this study, transient absorption measurements on longer time scales were made for two types of solution containing a pyrene-type A-S-D triad: benzonitrile solution and an aqueous micellar solution. Although the A-S-D molecule is designed for LB films, the measurements in solution will provide useful information. In addition, the A-S-D embedded in a LB monolayer was also subjected to transient spectroscopy.

2. Experimental details

2.1 Materials

Fig. 1 shows the structural formula of the pyrene-type A-S-D triad molecule (ASD) studied. The ASD consisted of viologen (A), pyrene (S), and ferrocene (D), and was synthesized in our laboratory; the synthetic details will be described elsewhere. ASD is amphiphilic because the viologen A moiety is hydrophilic, while the ferrocene D side is hydrophobic. Benzonitrile (purchased from Aldrich) was selected as the solvent to prepare ASD solutions because of its low boiling temperature (191°C) and the high solubility of the triad molecule. All other chemicals were of reagent grade and used as

received. The LB films were deposited on quartz plates purchased from Fujiwara Scientific Company.

2.2 Preparation of solutions of A-S-D triad

A benzonitrile solution containing 0.1 mM ASD and an aqueous micellar solution of 125 mM n-tetradecyltrimethylammonium bromide (TTAB) containing 0.1 mM ASD were used for steady state and transient measurements. The solvent for the micellar solution was pure water from the Milli-Q system (Millipore). Before the transient absorption measurements, the solutions were deoxygenated under N₂ flow for 30 min with stirring.

2.3 Preparation of ASD LB monolayers

The ASD LB films were formed using a Langmuir trough equipped with an electronic microbalance and a glass Wilhelmy plate (Kyowa Kaimenkagaku, HBM-AP). The quartz substrates were cleaned using a chromic acid mixture. The subphase was pure water (Milli-Q system; Millipore.). The temperature of the subphase was maintained at 15°C. In the LB films, the ASD was diluted in a 1:2 molar ratio with 22-tricosenoic acid (TA) because of the difficulty in forming a stable pure ASD monolayer. A chloroform

solution of the 1:2 mixture of ASD and TA was used to spread the monolayer on an air-water interface. After compressing the monolayer, it was transferred to a quartz substrate at a constant surface pressure of 15 mNm^{-1} . To ensure sufficient absorbance, 45 layers (24 bilayers and 1 monolayer) were formed on both sides of the substrate using Y-type deposition.

2.4 Transient absorption measurements

Fig. 2 shows the experimental set-up used to measure the transient absorption spectra for the solutions and the ASD LB film. The solutions and the LB coated quartz substrate were placed in the transparent cell and kept under deoxygenated condition by N_2 flow. The excitation light source was the third-harmonic light (355-nm) of a Q-switched Nd:YAG laser (5 ns FWHM, Surelite I-10, Continuum). The monitoring light source was a CW Xe lamp (Model 66023, Oriel Instruments), which was monitored with a streak scope with a sweep unit (C2830 and M2548, Hamamatsu Photonics) combined with a cooled CCD camera (C4880-89, Hamamatsu Photonics).

3. Results and Discussion

Fig. 3 presents the surface pressure-area (π - A) isotherms for TA (curve *a*), ASD

(curve *c*) and the binary mixture of them (curve *b*) . The ASD pure monolayer gives a markedly expanded isotherm (curve *c*) with a wide shoulder around 12 mN m^{-1} and the collapse pressure was ca. 27 mN m^{-1} . Although a slight shoulder is still observed at the similar surface pressure (ca. 10 mN m^{-1}), the π -*A* isotherm of the ASD mixed monolayer with TA (curve *b*) exhibited a condensed shape with high collapse pressure of 38 mN m^{-1} . Notably, the curve *b* has no kink around the collapse pressure of the curve *c*. These results suggest that ASD and TA are miscible without phase separations in the mixed monolayer.

Since the molar absorption coefficient of the ferrocene cation radical [9] is very small in the wavelength region of our measurements, the final charge-separated state, $\text{A}^{\bullet}\text{-S-D}^{+\bullet}$, should be detected using the absorption of the viologen cation radical. The maximum peak of the absorption coefficient of the viologen cation radical is normally around 400 nm [10]. In our molecular system, however, strong emission from the pyrene moiety affects the detection of the transient absorption changes around this wavelength. Therefore, we investigated another transient absorption band of the viologen cation radical at 500 ~ 700 nm. Figs. 4(a) - (c) show the transient absorption spectra of the solutions and LB film. Spectra (a) and (b) for the benzonitrile and TTAB micellar solutions, respectively, were accumulated for 100 ns after excitation. As described below,

the viologen cation radical in the LB film has a much longer lifetime. Therefore, the signal (c) for the LB film was accumulated from 50 to 450 μ s after excitation. The signal-to-noise (S/N) ratios of signals (a) and (b) are relatively poor because of the shorter accumulation time, however, the profiles of the signals are substantially the same as that of the transient absorption of the viologen cation radical observed in a perylene-type A-S-D LB film [8].

Figs. 5(a) and (b) show the kinetic traces of the transient absorption intensities of the benzonitrile and TTAB micellar solutions, respectively, accumulated over the wavelength range from 600 to 700 nm. The decay of the signals represents the decrease in the viologen cation radical after photo-excitation via an intramolecular charge recombination process. The figures show that the decay rates of these signals were very similar. The solid lines plotted on the kinetic traces are the single exponential fits. Semilogarithmic plots of the kinetic traces and their best-fit lines are shown in Figs. 6(a) and (b). The lifetimes of the viologen cation radical in the benzonitrile and micellar solutions determined from the single exponential decay fit were 62 and 63 ns, respectively.

It is reasonable to assume that ASD molecules dissolved in micelles would tend to attain a stretched conformation. On the other hand, the alkyl chains in the ASD molecule

would be random conformation in benzonitrile. However, in the charge-separated viologen^{+•}-pyrene-ferrocene^{+•} state, the Coulombic repulsion between the positive charges would prevent the oxidized donor and the reduced acceptor moieties coming closer to each other, therefore the charge recombination via through-space back electron transfer would be suppressed. The similar lifetimes between the micellar and the benzonitrile solutions might suggest that the charge recombinations in both the solutions occur via through-bond back electron transfer.

The kinetic trace of the ASD LB film is shown in Fig. 7. The absorption of the transient species still remained 600 μ s after excitation. Such an extremely prolonged lifetime cannot be attributed to further stretching of the molecular conformation in the LB film. In our previous studies, we observed the slow decay of the separated charges induced by light irradiation for perylene-type A-S-D LB assemblies over a few seconds using scanning surface potential microscopy (SSPM) [4-7]. Similarly, we can explain the present result by assuming further charge separation via lateral diffusion of the photo-created radical anions or cations. If lateral diffusion of the separated charges takes place in the ASD LB film, the viologen cation radical will accumulate [11] under illumination. When the illumination is turned off, the accumulated cation radical should decay via a long-distance intermolecular recombination process, whereas in solution it

only decays intramolecularly.

In the transient measurements, the chemical decompositions due to photo-oxidation of the samples were suppressed by the deoxygenation treatments described in sections 2.2 and 2.4. However, the prolonged lifetime of the radical species might induce the oxidation decompositions of the compound by a trace amount of oxygen remaining in the cell container. The kinetic trace of the ASD LB film seems to contain a non-decaying component. The permanent accumulation of the viologen cation-radical species might be ascribable to the oxidation decomposition of the long-lived ferrocene cation radical species.

Previously, we examined the effect of dilution of perylene-type A-S-D LB monolayers with TA [6]. In that study, a considerable charge accumulated at a dilution ratio of 1:5, whereas no charge accumulation was detected at 1:30. This means that the lateral charge migration process in an A-S-D LB film can be suppressed by lowering the surface concentration of the A-S-D molecule. The surface concentration of ASD in the ASD LB film at the dilution ratio of 1:2 used in this study is sufficiently high to let the charges accumulate. To elucidate the intramolecular recombination rate of the final charge-separated $A^{\bullet}-S-D^{+\bullet}$ state, the ASD LB film should be diluted at a ratio of 1:30 with TA. Unfortunately, however, the transient absorption signals of such diluted LB

films will be too weak to be detected. Efforts are underway to investigate the transient absorption kinetics of diluted LB films.

4. Conclusions

We estimated that the recombination rate of the final charge-separated state of ASD was ca. 60 ns in transient absorption studies of benzonitrile and aqueous TTAB micellar solutions. In the micellar solution, the observed recombination rate should correspond to a stretched conformation of the amphiphilic ASD molecule. The kinetic trace observed for the mixed ASD LB film with TA, in which further charge separation via lateral diffusion of photo-created charges is possible, did not reflect the intramolecular recombination rate. To determine the lifetime of the charge-separated state of ASD in LB films, the lateral charge migration process should be avoided by lowering the surface concentration of the ASD molecule.

Acknowledgement

This work was supported by a Grant-in-Aid for Scientific Research (C) (17550126) from Japan Society of the Promotion of Science.

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Figure captions

Figure 1. Structure of a pyrene-type ASD triad molecule.

Figure 2. Experimental apparatus used to measure transient absorption.

Figure 3. Surface pressure - area isotherms of (a) the pure monolayer of TA, (b) the mixed monolayer of ASD and TA (1:2 in molar ratio), and (c) the pure monolayer of ASD.

Figure 4. Transient absorption spectra of ASD in (a) benzonitrile, (b) an aqueous micellar solution of TTAB, and (c) LB film.

Figure 5. Time dependence of the transient absorption intensity of ASD in (a) benzonitrile and (b) an aqueous TTAB solution.

Figure 6. Semi-logarithmic plot of the time dependence of the transient absorption intensity of ASD in (a) benzonitrile and (b) an aqueous micellar solution of TTAB.

Figure 7. Time dependence of the transient absorption intensity of an ASD LB film.

Fig. 1 Structure of a pyrene-type ASD triad molecule.

Fig. 2 Experimental apparatus used to measure transient absorption.

Fig. 3 Surface pressure-area isotherms of (a) the pure monolayer of TA; (b) the mixed monolayer of ASD and TA (1:2 in molar ratio); (c) the pure monolayer of ASD.

Fig. 4 Transient absorption spectra of ASD in (a) benzonitrile; (b) aqueous micellar solution of TTAB; (c) LB film.

Fig. 5 Time dependence of transient absorption intensity of ASD in (a) benzonitrile; (b) aqueous TTAB solution.

Fig. 6 Semi logarithmic plot of the time dependence of transient absorption intensity of ASD in (a) benzonitrile; (b) aqueous micellar solution of TTAB.

Fig. 7 Time dependence of transient absorption intensity of ASD LB film.