Fabrication and Photochemical Characterization of Organic Dye-Metal Oxide Hybrid Langmuir Blodgett Film

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Langmuir-Blodgett (LB) film of tetra-t-butyl-Zn-phthalocyanine (Pc), dicitratodiperoxotitanate complex (TAS) and ditetradecylviologen (V) triad was fabricated on thin glass waveguide as a cascade electron transfer model. The arrangement of the layer as Pc-TAS-V was successfully controlled by LB process. Monolayer of Pc or V was stabilized with TAS layer due to a multiple electrostatic interaction at air-water interface. Photoinduced electron transfer from the Pc to V through the TAS layer in Pc-TAS-V triad system was measured directly using waveguide spectroscopy. Electron transfer in the opposite layering sequence, V-TAS-Pc, was negligible. According to these results, direction of the electron transfer can be controlled in the triad by controlling the layering sequence using the hybrid LB procedure.

Keywords: Langmuir-Blodgett film, photocurrent, phthalocyanine, viologen, dicitratodiperoxotitanate complex

1. Introduction
Langmuir-Blodgett films have been focused as molecular assembly in which layering sequence of components can be controlled arbitrary. The sophisticated architecture of multi-layered LB films has been applied to vectorial electron transfer. Supramolecular system with redox active units [1-3] or amphiphilic polymers with photoactive side chains [4-6] successfully assembled to achieve the vectorial electron transfer.

Hybrid LB films of organic amphiphiles with inorganic nanosheets are also stable photoactive multilayers [7-9]. The inorganic sheet works as a smooth 2D scaffold in the hybrid LB films (Fig. 1). However, the ordinary smectite clays are insulators, so that it should disturb electron transfer between the adjacent organic layers passing through the clay nanosheet [10].

Redox couple of Co$^{2+/3+}$ incorporated artificially in the clay nanosheet can mediate the electron transfer [11]. Hybrid LB film with titanate nanosheet was the first example of LB films with oxide semiconductor nanosheet, which can effectively mediate electron transfer through the layer[12]. The nanosheet can cover almost all the surface in the monolayer, though there are some part of niche areas should be left uncovered due to a geometric principle. Smooth LB films of vanadium oxide hydrate with higher coverage were fabricated from a distearyldimethyl ammonium and vanadate hybrid [13]. The monomeric vanadate precursor ions are reversibly polymerized to vanadium oxide hydrate polyions.

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Redox potential of the vanadium oxide layer unfortunately too positive to mediate a cascade electron transfer from ruthenium complex to violagen acceptor. More negative potential of the mediating unit in inorganic sheet should be required for the cascade electron transfer. An inorganic layer with $\text{Ti}^{3+/4+}$ units with no defects will be an ideal mediating layer for the cascade electron transfer. In this paper, we will report the first example of hybrid LB film of dye-titanium complex-acceptor triad monolayer, in which a cascade photoinduced electron transfer was directly observed using a waveguide spectroscopy.

2. Method

2.1 Materials

Dicitratodiperoxotitanate complex ammonium salt (TAS) was purchased from Furuuchi Chemical and used as received. Hydrochloric acid, sodium hydroxide, tetradecyl bromide, (Wako Pure Chemical) and 4,4'-bipyridine was used as received. Tetra-$t$-butyl-Zn-phthalocyanine (Pc) was synthesized after the reported procedure [14]. Ditetradecylviologen dibromide was synthesized by substituting quartinization of 4,4'-bipyridine with tetradecyl bromide [15]. $^1$H-NMR($\sigma$/ppm in CDCl$_3$): 9.2(d, $J = 7.1$ Hz, 4H), 8.9(d, $J = 6.8$ Hz, 4H), 4.7(d, $J = 15.2$ Hz, 4H), 2.1(t, $J = 14.1$ Hz, 4H), 1.4(m, 44H), 0.9(t, $J = 13.6$ Hz, 6H).

2.2 Fabrication of hybrid LB film

As a typical procedure to fabricate DSA-TAS hybrid, chloroform solution of Pc (1 mM) was spread on aqueous solution of TAS (20 $\mu$M) at 18°C in a LB trough. After compressing the hybrid monolayer on the air-water interface, the monolayer was transferred on a solid substrate, such as Si wafer (Nilaco) or soda glass (Matsunami) at constant pressure. The substrate was cleaned using conc. sulfuric acid - 30 % aqueous hydrogen peroxide solution (1:1).

2.3 Equipments

$^1$H-NMR was measured on Bruker Avance 400 MHz FT-NMR spectrometer. Langmuir-Blodgett films were fabricated on Nippon Laser Electronics LB-400 trough system. Surface morphology was observed on SII SPM-3800N using Olympus OMCL-TR400PSA-3 cantilever ($k=0.09\text{Nm}^{-1}$). Shimadzu UV-2400PC spectrophotometer was used to record absorption spectra. Waveguide spectroscopy was carried out using System Instruments SIS-50-SS spectrophotometer. As a light source for excitation of the Pc monolayer, a photodiode with emission maximum at ca. 640 nm was used. Electrochemical measurement was carried out on ALS 650 system using Ag/Ag$^+$ reference electrode and platinum wire counter electrode in DMF solution of 0.1 M lithium perchlorate.

3. Results and Discussions

3.1 Surface pressure-area isotherm

A chloroform solution of tetra-$t$-butyl-Zn-phthalocyanine (Pc) was spread on water or 20 $\mu$M TAS aqueous solution. During compression process, surface pressure was plotted against occupied area per molecule in the monolayer on the aqueous solution as shown in Fig. 2(a). Limiting area on pure water was 75 $\text{Å}^2$ [16], whereas it decreased to 63 $\text{Å}^2$ on TAS solution. A projected area of Pc molecule in an edge-on alignment, 60 $\text{Å}^2$, is comparable to the observed limiting area, suggesting an edge-on type alignment in the hybrid monolayer. TAS can closely interact with Pc to assist aggregation of the Pc in the monolayer, although the Pc molecule has no apparent cationic charge.

Notable effect of the TAS ion was observed in tetradecyl viologen (V)-TAS hybrid LB film. Limiting area for original LB film of V is 183 $\text{Å}^2$ [17], however it decreased to 118 $\text{Å}^2$ on TAS solution probably due to much stronger Coulomb interaction between viologen dication and TAS$^4$.  

Fig. 2 Surface pressure - area isotherms for (a) Pc-TAS and (b) V-TAS hybrid monolayers. Solid lines and broken lines represent deposition process on water and the TAS solutions, respectively.
Based on these isotherms, hybrid LB films of Pc-TAS and V-TAS hybrid LB films were deposited at 20 mN m\(^{-1}\) and 25 mN m\(^{-1}\), respectively.

### 3.2 Surface morphology of Pc-TAS and V-TAS hybrid LB films

Pc-TAS hybrid monolayer was transferred onto Si (100) wafer under the constant pressure with almost quantitative transfer ratio. Surface morphology of the deposited film was observed with AFM. Fig. 3 shows surface morphology of intrinsic Pc (a) and Pc-TAS (b) monolayers over 1000 nm x 1000 nm squared area. There are some bumps on the surface, however the roughness is less than 2 nm over the observed area except for the intrinsic Pc monolayer due to strong characteristics of aggregation. Surface roughness over the observed area is less than 2 nm in average, which is comparable to the edge-to-edge dimension of Pc. Considering the size of Pc molecule and TAS complex [18], the hybrid LB film could be smooth enough for controlling the electron transfer through the layer.

Surface morphology of the V-TAS hybrid and intrinsic V monolayers are shown in Fig. 3 (c) and (d). Surface roughness of these layers are 1.2 – 1.3 nm, which are smaller than the chain length of the ditetradecyl viologen molecule. These results support that the monolayer of V-TAS and intrinsic V have good smoothness. Smaller effect of TAS on the surface morphology of the V probably due to flexibility of the tetradecyl alkyl chains on the less dense packing in of the viologen even in the tightly interacting V-TAS hybrid.

### 3.3 Absorption spectrum and redox potentials of Pc and V

Absorption spectrum of DMF solution of Pc was measured (Fig. 4). It shows the single and strong Q-band at 675 nm with extinction coefficient of 2.4 x 10\(^5\) M\(^{-1}\) cm\(^{-1}\), which is a typical spectrum for isolated phthalocyanine with high symmetry [19]. The big extinction coefficient is an advantage in efficient absorption of excitation light even in the monolayer film. In addition, normalized fluorescence spectrum of the Pc in the same solution was shown in Fig. 4. It shows small Storks shift due to rigid aromatic structure of the phthalocyanine ring. The potential difference between HOMO and LUMO levels can be estimated as 1.86 eV based on the longer edge of the absorption spectrum (705 nm).

Oxidation potential of the Pc was measured by cyclic voltammetry in DMF solution of LiClO\(_4\). It showed a reversible redox peaks at 0.33 V (p\(_{ox}\)) and 0.25 V (p\(_{red}\)) vs. Ag/Ag\(^+\) reference and an irreversible second oxidation peak at 0.80 V vs. Ag/Ag\(^+\). The first equilibrium potential was estimated as 0.29 V vs. Ag/Ag\(^+\). No redox peaks was observed in the range between 0 V and -1 V vs. Ag/Ag\(^+\), so that Pc is electrochemically stable in the range. Reduction potential of ditetradecyl viologen was measured by the same procedure. It showed reversible redox peak at -0.83 V (p\(_{red}\)) and -0.77 V (p\(_{ox}\)) vs. Ag/Ag\(^+\). The equilibrium reduction potential of -0.80 V vs. Ag/Ag\(^+\) was obtained. No redox peak was observed between

![Fig. 3 Surface morphology of Pc and V hybrid monolayers deposited on Si wafer](image)

(a) Pc, (b) Pc-TAS hybrid, (c) V and (d) V-TAS hybrid monolayers.

![Fig. 4 Absorption and fluorescence spectra of Pc in DMF solution. Solid line represents absorption spectrum and dotted line represents fluorescence spectrum (\(\lambda_{ex}= 650\) nm). Absorbance and fluorescence intensity are normalized.](image)
-0.7 V and 0 V vs. Ag/Ag⁺, which shows the viologen is electrochemically stable in the potential range.

3.4 Photoinduced electron transfer in V-TAS-Pc triad monolayer

The V-TAS-Pc and the Pc-TAS-V triad layer were fabricated by LB process on slab type waveguide [20] for the measurement of spectral change due to reduction of viologen during irradiation process. A schematic models of the layers are shown in Fig. 5 (a) and (b). Considering the obtained redox potential of Pc and V, energy diagrams for the two types of triad layer are shown in Fig. (c) and (d), corresponding to the sequence of Fig. 5(a) and (b), respectively. A cascade electron transfer models are shown for the layering sequence.

For monitoring photoinduced electron transfer, the V-TAS-Pc triad layer was deposited on a slab type waveguide. Fig. 6(a) shows the transient change in absorption spectra of V-TAS-Pc hybrid for several minutes under irradiation with 640 nm LED. The broad absorption band around 400 nm was observed immediately on irradiation. The absorption band is a typical one for a viologen cation radical, an one-electron reduced form of viologen dication. The broadening of the band is probably due to aggregation of the viologen in the hybrid LB film [15]. The increase of the 400 nm-band, however, was saturated after 2 min irradiation and broad breaching was observed.

around 450-600 nm. The oxidized form of Pc⁺ shows absorption band around 450-600 nm [21], which is comparable to the absorption band of the breaching, suggesting that the electron transfer process is saturated. On the other hands, the Pc-TAS-V triad system showed negligible change in the transient spectra as shown in Figure 6(b) even after irradiation for 9 minutes. Oxidation potential of EG is more positive than the reduction potential of the viologen, therefore, the first electron transfer from EG to V is thermodynamically prevented endothermic process. The exothermic process from EG to the HOMO of the excited Pc is not efficient because it is separated by the long alkyl chain of V layer as shown in Fig. 5(d). This is an evidence to show that a cascade electron transfer is controlled depending on the layering sequence.

Excited state of Pc will efficiently donate an electron to the adjacent TAS layer (process II) because it is a static and slightly endothermic process. Following electron transfer to the viologen dication reduced it to a cation radical V⁺. The sacrificial electron transfer from ethylene glycol (EG) to the oxidized Pc⁺ should be inefficient because the outermost surface of the Pc layer is hydrophobic, on which hydrophilic EG will scarcely contact.

The light source for this experiment is an LED lamp, so that the time resolution of the transient experiment should be in the order of several
seconds. The timescale of the equipment is too slow to observe the fast electron transfer of the step II after the excitation. The electron transfer was confirmed by efficient fluorescence quenching of the Pc by TAS. We could monitor a photostationary state, where the oxidized Pc⁺ will be present. Only a limiting number of acceptor molecules are available in the V-TAS-Pc triad monolayer because it is isolated from another V layer deposited directly on the glass substrate by the insulating long alkyl chains of V (Fig 5(b)) [22]. On measuring the spectral change using our equipment, the 400 nm band corresponds to V⁺ ▪ will increase first, but it will be saturated soon when all of the viologen in the monolayer is reduced to V⁺, then the Pc⁺ will be reduced again to Pc by the sacrificial electron donation from EG. These hypotheses can reasonably explain the results in the spectral change. Transient spectroscopy with short time resolution to observe fast electron transfer is in underway.

4. Conclusion
V-TAS–Pc hybrid film was fabricated by a modified LB method as an artificial model of a cascade photoinduced electron transfer. In contrast, the electron transfer in the reversed layering sequence, Pc-TAS-V, was negligible. A vectorial electron transfer from Pc to viologen via TAS in the V-TAS-Pc triad monolayer was observed by waveguide spectroscopy. The hybrid layering structure is expected as a fundamental architecture for a nanorectifier or an artificial photosynthetic model.

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References