Magnetic Field Effects on Photoelectrochemical Responses of Modified Electrodes with Porphyrin-Viologen Linked Compound as Langmuir Blodgett Film[1]

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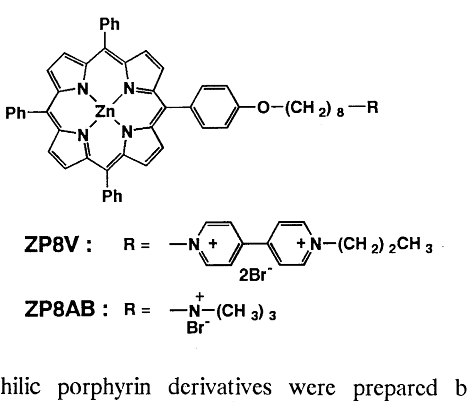
Modified electrodes were fabricated by depositing a monolayer containing porphyrin-viologen linked compound on ITO electrodes by Langmuir-Blodgett method. Visible light irradiation on the modified electrodes afforded stable anodic photocurrents. The photocurrents clearly increased in the presence of magnetic fields. The magnetic field effects on photocurrents, as observed for the first time, are ascribed to the contribution of triplet radical pairs.

Donor(D)-acceptor(A) linked compounds in various organized molecular environments are expected to serve as a model system for studying the electron-transfer reactions in biochemical systems such as photosynthesis. A number of modified electrodes have been constructed by covalently bonded D-A systems.[2] However, the reaction mechanism of photoelectrochemical process of the modified electrodes have not ever been elucidated yet. One of the reasons is shortage of appropriate means for verifying complicated mechanisms.

During the last two decade, the reaction mechanism of photochemical reactions in condensed phase have been elucidated by the magnetic field effects (MFE) on the reaction kinetics or yields.[3] In spite of increasing importance of photochemical reaction at interface, the studies on MFE are rather scarce. The present authors have previously obtained photogenerated radical pairs of D-A linked compounds, and the lifetime of the radical pair was remarkably extended in the presence of magnetic fields (MF).[4,5] The MFE were explained as due to retardation of intersystem crossing of the radical pair as a consequence of Zeeman splitting of triplet sublevels. As a consequence, MF has been expected to provide a novel means of controlling photoinduced electron-transfer and the succeeding processes.

In the present paper, as an application of the MFE, we attempted to observe MFE on photoelectrochemical reaction of modified electrodes with D-A linked compound as Langmuir-Blodgett (LB) film.



Amphiphilic porphyrin derivatives were prepared by the previously reported procedures.[5] Modified electrodes were prepared by depositing the mixed monolayer with porphyrin-viologen linked compound consisting of eight methylene groups as a spacer (**ZP8V**) and arachidic acid (1:10) on ITO electrodes (30 mm × 18 mm) by the use of standard LB method.[6] Photoelectrochemical measurements were carried out by using a three electrode cell (Figure 1). A supporting electrolyte was $NaClO_4$ (0.1 M). The modified electrodes were irradiated with a 500W high-pressure Hg arc lamp through a visible-pass filter (>400 nm). The photocurrents of the modified electrode were measured under a controlled potential at 0 V vs Ag/AgCl with a potentiostat in the presence of triethanolamine (TEOA) (50 mM) as a sacrificial electron donor under nitrogen atmosphere. The action spectra were measured by the light from a 300W Xe lamp passing through a monochorometer. MFE on the photocurrents were measured as shown in Figure 1. The electrode cell was placed at pole-gap (6.6 cm) of an electromagnet. Electric field was applied parallel to MF to avoid influence of magneto-hydrodynamic (MHD) force.[7]

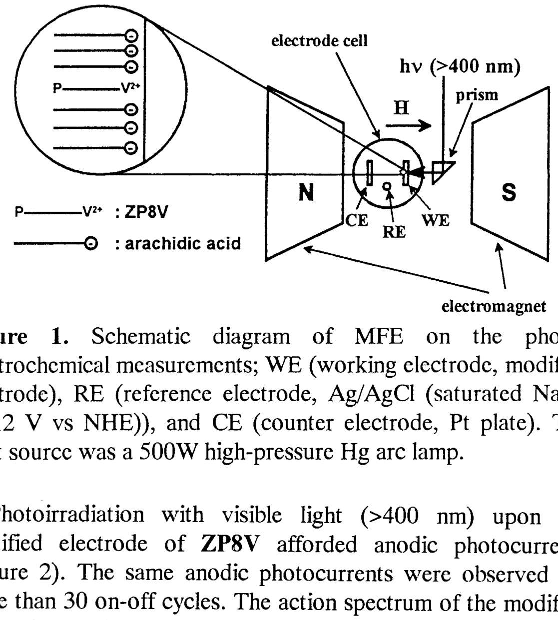


Figure 1. Schematic diagram of MFE on the photoelectrochemical measurements; WE (working electrode, modified electrode), RE (reference electrode, Ag/AgCl (saturated NaCl: 0.212 V vs NHE)), and CE (counter electrode, Pt plate). The light source was a 500W high-pressure Hg arc lamp.

Photoirradiation with visible light (>400 nm) upon the modified electrode of **ZP8V** afforded anodic photocurrents (Figure 2). The same anodic photocurrents were observed for more than 30 on-off cycles. The action spectrum of the modified electrode was in good agreement with the absorption spectrum of the porphyrin moiety of **ZP8V** in LB films. The result strongly indicate that the photocurrents are attributable to the excitation of the porphyrin moiety.

In the presence of MF, the photocurrent clearly increased (Figure 2). The responses were reproducible for a number of times (more than 20 times). The same MFE were observed, when the direction of MF was reversed. These results indicate that the MFE on the photocurrents do not come from MHD effects.[7] The MFE are explained by the photogenerated radical pair (radical pair mechanism[3]) as discussed later.

As a reference system, another modified electrode was prepared by using the porphyrin derivative without viologen moiety (**ZP8AB**). The action spectra of photocurrents were similar to those due to **ZP8V**-modified electrode. Direct electron

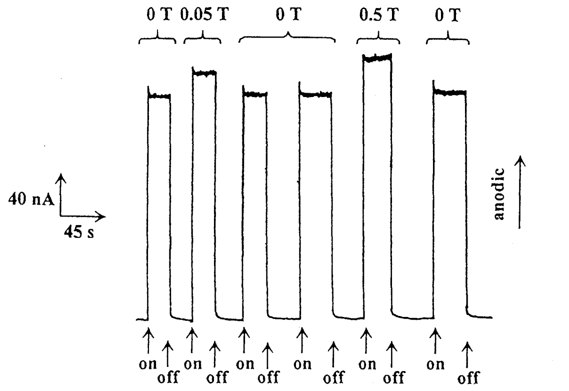


Figure 2. MFE on the photocurrents of the **ZP8V**-modified electrode.

transfer from excited porphyrin to electrode may partly contribute to the photocurrents for **ZP8V**-modified electrode. However, no MFE on photocurrents were observed with **ZP8AB**. The results support that the MFE in **ZP8V**-modified electrode are ascribed to the photogenerated radical pair.

The increment of the photocurrent (Q) increased with MF and became constant value (ca. 15%) at above 0.3 T as shown in Figure 3. The decay rates of radical pair with the same compound in solution previously discovered to decrease with MF and reached a plateau region at above 0.3 T.[5] The MFE on the photocurrents were in the present experiment in good agreement with those on the lifetime of photogenerated radical pairs in solution.

On the basis of these observations, a reaction mechanism is suggested as summarized in Scheme 1. The MFE on photocurrents in porphyrin(P)-viologen(V^{2+}) linked compound were clearly due to photogeneration of triplet radical pairs $^3(P^{+\cdot}$-$V^{+\cdot})$ via intramolecular electron transfer process at the electrode surface. Intersystem crossing process (k_{isc}) will become rate-determining step for the radical pairs to decay via reverse electron transfer. Under high MF, the k_{isc} is controlled by spin flipping relaxation from the triplet sublevels to the singlet radical pair (relaxation mechanism[8]). As the k_{isc} were suppressed with the increase of MF, the reduced viologen $V^{+\cdot}$ will gain better chances of transferring the electron to the electrode. As a consequence, the photocurrents increase in the presence of MF. In other words, the MFE on the photocurrents may be taken as an experimental evidence to indicate that the photoelectrochemical responses of **ZP8V**-modified electrode were ascribed to sequential electron transfer process via viologen moiety as a mediator between porphyrin moiety and ITO electrode.

In a summary, MFE on the photoelectrochemical reaction of the modified electrode was clearly observed, for the first time, by the use of D-A linked compound as LB film on the electrode. These results indicate that electrochemical reaction of D-A pair-modified electrodes will be controlled by the combined use of light and MF. The discovery will lead to an epochmaking means of reaction control involving electrochemical processes in LB films and the related systems such as supramolecular device. Further studies are under progress to evaluate the contributions of singlet radical pair and direct electron transfer from excited porphyrin to electrode to the photocurrents of **ZP8V**-modified electrode.

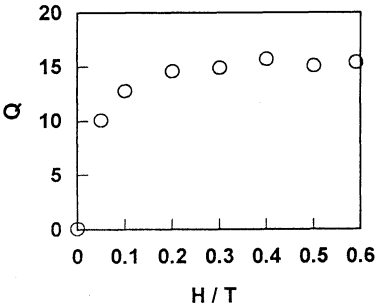
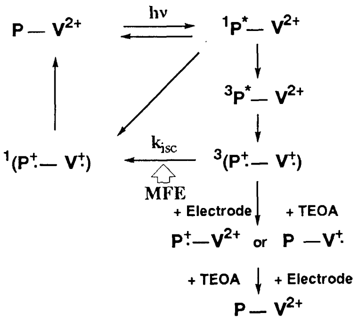


Figure 3. MFE on the fractional increment (Q = (I(H)-I(0))/I(0) × 100) of photocurrent of **ZP8V**-modified electrode. The photocurrent in the presence and absence of magnetic fields is denoted by I(H) and I(0), respectively.



Scheme 1.

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References and Notes

1 Contribution No. 1026 from the Department of Chemical Science and Technology, Faculty of Engineering, Kyushu University.

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6 The monolayer film was fabricated by dipping the substrate into aqueous subphase ($CaCl_2$ (0.3 mM) and $NaHCO_3$ (0.05 mM)) and raising it at a rate of 10 mm min^{-1} at 15 ℃. All of monolayer films were made at a constant surface pressure of 30 mN m^{-1}. The deposition ratio was 1.0±0.1.

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