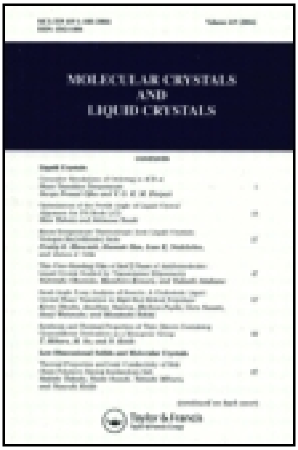

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Magnetic Field Effects on Photoelectrochemical Responses of Modified Electrodes with Langmuir-Blodgett Monolayer Containing Porphyrin-Viologen Linked Compounds

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MAGNETIC FIELD EFFECTS ON PHOTOELECTROCHEMICAL RESPONSES OF MODIFIED ELECTRODES WITH LANGMUIR-BLODGETT MONOLAYER CONTAINING PORPHYRIN-VIOLOGEN LINKED COMPOUNDS

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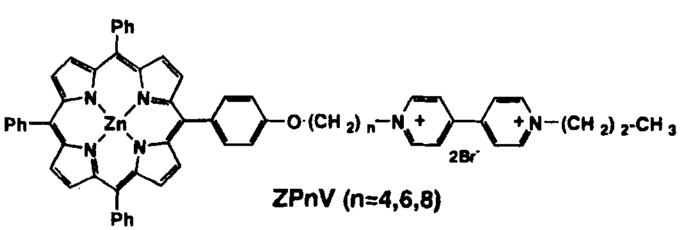
Abstract Modified electrodes were prepared by depositing a monolayer containing porphyrin-viologen linked compounds with various spacer chain-length on ITO electrodes by Langmuir-Blodgett method. Stable anodic photocurrents were observed by visible light irradiation upon the modified electrodes. The photocurrents were clearly enhanced in the presence of magnetic fields. Effects of spacer chain-length on the magnetic field effects are caused by photoactive triplet radical pairs.

INTRODUCTION

Photoinduced electron transfer reaction of donor(D)-acceptor(A) linked compounds in various organized molecular environments has been one of the most investigated subjects in the chemistry of photoresponsive materials. A number of modified electrodes have been constructed by covalently bonded D-A systems.[1]

We have previously obtained photogenerated radical pairs of D-A linked compounds, and found the lifetime of the radical pair was remarkably extended in the presence of magnetic fields (MF).[2]

Recently, as an application of the magnetic field effects (MFE), we had reported MFE on photoelectrochemical reaction of modified electrodes, for the first time, by the use of Langmuir-Blodgett (LB) film of porphyrin-viologen linked compound.[3] In the present paper, the following porphyrin-viologen linked compounds with various spacer chain-length were examined to elucidate the effects of spacer chain-length on the MFE.



ZPnV (n=4,6,8)

PHOTOCURRENTS OF MODIFIED ELECTRODES WITH PORPHRIN-VIOLOGEN LINKED COMPOUNDS

Modified electrodes were prepared by depositing the mixed monolayer with **ZPnV** (n=4,6,and 8) and arachidic acid (AC) (1:10) on ITO electrodes by the use of standard LB method. Photoelectrochemical measurements were carried out by using a three electrode cell. The photocurrents of the modified electrode were measured under a controlled potential at 0 V vs Ag/AgCl in the presence of triethanolamine (50 mM), which serves as a sacrificial electron donor under nitrogen atmosphere.

Photoirradiation with visible light (>400 nm) upon the **ZP8V**-modified electrode afforded anodic photocurrents. The same anodic photocurrents were observed for more than 30 on-off cycles. The action spectrum of the **ZP8V**-modified electrode was shown in Figure 1. The action spectrum was in good agreement with the absorption spectrum of the porphyrin moiety of **ZP8V** in LB films. The result strongly indicates that the photocurrents were due to the excitation of the porphyrin moiety.

Essentially the same phenomena were also observed with other **ZPnV** (n=4 and 6). The photocurrents of **ZP6V**- and **ZP8V**-modified electrodes were about twice as large as those of **ZP4V**-modified electrode. Fluorescence emission from **ZP4V**, on the other hand, was almost half of those from **ZP6V** and **ZP8V**.[4] Therefore, the effects of spacer chain length on photocurrents should be ascribed to triplet state rather than singlet of the excited porphyrin.

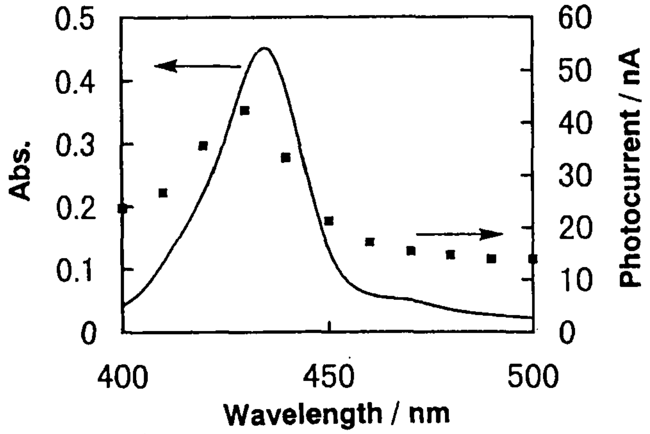


FIGURE 1 Action spectrum of **ZP8V**-modified electrode (■) and absorption spectrum of the mixed LB film (30 layers) of **ZP8V** and AC (1:10) (——).

MFE ON PHOTOCURRENTS OF MODIFIED ELECTRODES

The photocurrent of all modified electrodes were clearly enhanced in the presence of MF. The same MFE were observed, when the direction of MF was reversed. These results indicate that the MFE on the photocurrents are not due to magnetohydrodynamic effects.[5] The MFE are explained by the photogenerated radical pair. As a reference system, another modified electrode was prepared by using the amphiphilic porphyrin derivative with an ammonium head group (**ZP8AB**). The action spectra of photocurrents were similar to those due to **ZPnV**-modified electrode. However, no MFE on photocurrents in **ZP8AB**-modified electrode were observed. [3] The results suggest that the MFE in **ZPnV**-modified electrode are ascribed to the photogenerated radical pair.

The increment of the photocurrent (Q) increased with MF and became constant value at above 0.3 T (Figure 2). The Q value due to **ZP8V**- and **ZP6V**-modified electrodes were twice greater than that due to **ZP4V**-modified electrode. The MFE on the lifetime of radical pairs with **ZP8V** and **ZP6V** are larger than those with **ZP4V** in solution. [2] The effects of spacer chain-length on the MFE were in good agreement with those on the lifetime of radical pairs. Therefore, the MFE on the photocurrents were explained in terms of relaxation mechanism [6] as discussed below.

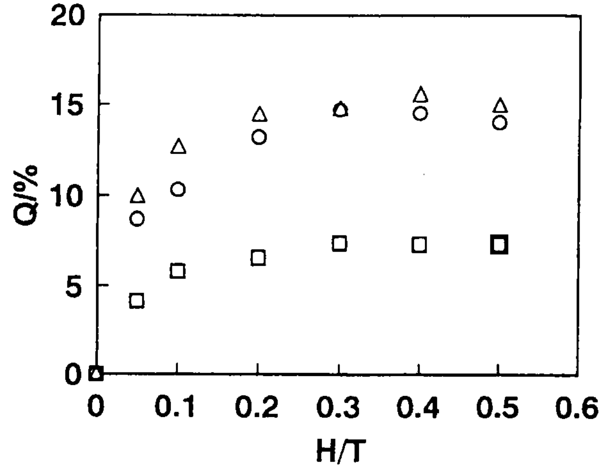


FIGURE 2 MFE on the fractional increment (Q= (I(H)-I(0))/I(0) × 100) of photocurrent of **ZP8V**(△)-, **ZP6V**(○), and **ZP4V**(□)- modified electrodes. The photocurrent in the presence and absence of magnetic fileds is denoted by I(H) and I(0), respectively.

The MFE on photocurrents for **ZPnV** were clearly ascribed to photogeneration of triplet radical pairs via intramolecular electron transfer process at the electrode surface. Intersystem crossing (ISC) process will become rate-determining step for the radical pairs to decay via reverse electron transfer. The ISC process is controlled by relaxation from triplet sublevels to the corresponding singlet. As the ISC process were suppressed with the increase of MF, the reduced viologen in triplet radical pair will gain better chances of transferring the electron to the electrode. As a consequence, the photocurrents increase in the presence of MF.

CONCLUSION

On the basis of spacer chain-length effects on the photocurrents and the MFE, the photocurrents of **ZPn**V-modified electrodes were mainly ascribed to photogeneration of triplet radical pairs via intramolecular electron transfer process at the electrode surface. The effects of spacer chain-length elucidated that the spacer between D and A moieties could be appropriately adjusted to attain a higher efficiency in generation of photocurrents and to enhance MFE. The present MFE will provide an useful means of reaction control involving electrochemical processes in LB films and the related systems such as artificial photosynthetic molecular devices.

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