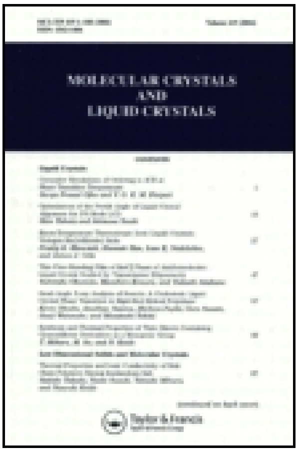

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Hironobu Tahara [a], Hiroaki Yonemura [b], Satoko Harada [a] & Sunao Yamada [b]

[a] Department of Materials Physics and Chemistry, Graduate School of Engineering, Kyushu University, Fukuoka, Japan

[b] Department of Applied Chemistry, Faculty of Engineering, Kyushu University, Fukuoka, Japan

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Magnetic Field Effects on Photoelectrochemical Reactions of a Porphyrin-Viologen Linked Compound in an Ionic Liquid

HIRONOBU TAHARA,[1] HIROAKI YONEMURA,[2]
SATOKO HARADA,[1] AND SUNAO YAMADA[2]

[1]Department of Materials Physics and Chemistry, Graduate School of Engineering, Kyushu University, Fukuoka, Japan
[2]Department of Applied Chemistry, Faculty of Engineering, Kyushu University, Fukuoka, Japan

*Magnetic field effects (MFEs) on photoelectrochemical reaction of a porphyrin-viologen linked compound with six methylene group (**ZnP(n)V(n = 6)**) were examined in an ionic liquid (**[BMIM][BF$_4$]**) using two-electrode cell. A stable anodic photocurrent is produced by irradiating **ZnP(6)V** in **[BMIM][BF$_4$]** with visible light, and the photocurrent clearly increased in the presence of a magnetic field. The MFEs are explained by radical pair mechanism. The magnitude of the MFEs is larger than those in electrodes modified with **ZnP(n)V(n = 4,6,8)** as Langmuir-Blodgett films. The results are most likely ascribed to the properties of **[BMIM][BF$_4$]**.*

Keywords Ionic liquid; magnetic field effect; photoelectrochemical reaction; porphyrin; viologen

Introduction

The mechanisms of photochemical reactions in the condensed phase have been explained by invoking magnetic field effects (MFEs) on reaction kinetics or yields [1]. Consequently, the magnetic field is expected to provide a novel means of controlling photoinduced electron-transfer and the subsequent processes. Previously, we examined MFEs on the photoelectrochemical reactions of photosensitive electrodes modified with zinc-tetraphenylporphyrin (ZnP)-viologen (V^{2+}) linked compounds [**ZnP(n)V (n = 4,6,8)**] as Langmuir-Blodgett (LB) films [2–4] and with semiconductor nanoparticles [5,6]. Recently, to demonstrate the use of C_{60} in a photonic nanodevice we studied MFEs on the photoelectrochemical reactions of photosensitive electrodes modified with nanoclusters containing a positively charged C_{60} derivative and methylphenothiazine [7].

Address correspondence to Hiroaki Yonemura, Department of Applied Chemistry, Faculty of Engineering, Kyushu University, 744 Motooka, Nishi-ku, Fukuoka 819-0395, Japan. E-mail: yonemura@mail.cstm.kyushu-u.ac.jp

Ionic liquids (ILs) are currently the focus of extensive investigation because they possess unique properties (negligible vapor pressure, high viscosity, high ionic conductivity, and high thermal, chemical, and electrochemical stabilities etc.) [8]. However, MFEs on the photoelectrochemical reactions in ILs have not yet been examined. In this study, we examined photoelectrochemical reaction of a ZnP–V^{2+} linked compound with six methylene group (**ZnP(n)V(n = 6)**) in an IL (**[BMIM][BF$_4$]**) using two-electrode cell.

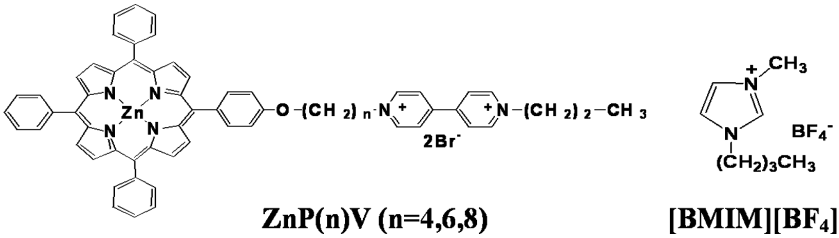
Experimental

Amphiphilic ZnP–V^{2+} linked compound [**ZnP(6)V**] (Fig. 1) was synthesized as reported in the previous paper [2]. **[BMIM][BF$_4$]** (Figure 1) (TCI or Merck) and triethanolamine (TEOA) (Wako) were used without further purification. Cyclic voltammetry and differential pulse voltammetry were carried out on a ALS 420 model EQCM instrument (BAS) using the three-electrode cell. Photoelectrochemical measurements were performed using two-electrode cell containing an ITO electrode as a working electrode and a platinum electrode as a counter electrode by irradiation with a 150 W Xe lamp (Hamamatsu Photonics L2274) through a monochorometer with a potentiostat (Huso HECS-318C) in the presence of TEOA (0.1 M) as a sacrificial electron donor under nitrogen atmosphere [2–7]. MFEs on the photocurrent ($\geq$370 nm) were measured as described in our previous publications [5–7].

Results and Discussion

Electrochemical and Photoelectrochemical Reactions in IL

Redox potentials of **ZnP(6)V** in **[BMIM][BF$_4$]** were measured by cyclic voltammetry and differential pulse voltammetry measurements. Two redox couples were observed ($E_{1/2}(\mathrm{ZnP}^{\cdot +}/\mathrm{ZnP}) = 0.39$ V and $E_{1/2}(V^{2+}/V^{\cdot +}) = -0.81$ V vs. $\mathrm{Fc}^{+}/\mathrm{Fc}$). The redox potentials are different from those ($E_{1/2}(\mathrm{ZnP}^{\cdot +}/\mathrm{ZnP}) = 0.76{\sim}0.78$ V and $E_{1/2}(V^{2+}/V^{\cdot +}) = -0.49{\sim}-0.50$ V vs. Ag/AgCl) in the electrodes modified with **ZnP(n)V (n = 4,6,8)** as LB films [2–4]. The Gibbs free energy driving forces (ΔG) for the intramolecular electron-transfer reactions of **ZnP(6)V** in **[BMIM][BF$_4$]** from the singlet excited state ($^1\mathrm{ZnP}^*$) and the triplet excited state ($^3\mathrm{ZnP}^*$) of the ZnP to V^{2+} using the redox potentials of the ZnP and V^{2+} moieties were estimated to be -0.84 eV and -0.33 eV, respectively. These results indicate that the intramolecular electron-transfer reactions of **ZnP(6)V** in **[BMIM][BF$_4$]** from the $^1\mathrm{ZnP}^*$ and the



ZnP(n)V (n=4,6,8) **[BMIM][BF$_4$]**

Figure 1. Molecular Structures of ZnP–V^{2+} linked compounds (**ZnP(n)V (n = 4,6,8)**) and an ionic liquid (**[BMIM][BF$_4$]**).

^{3}ZnP* to V^{2+} are thermodynamically favorable as similar to the LB-modified electrodes [2–4].

Irradiating **ZnP(6)V** in **[BMIM][BF$_4$]** with visible light ($\geq$370 nm) creates a stable anodic photocurrent using the two-electrode cell. The photocurrent action spectrum of **ZnP(6)V** agrees well with the absorption spectrum of the ZnP moiety of **ZnP(6)V** in **[BMIM][BF$_4$]**. Therefore, the results of the photocurrent action spectrum and the above thermodynamical properties indicate that the photocurrent are attributable to the photoexcitation of the ZnP moiety (^{1}ZnP* and ^{3}ZnP*) of **ZnP(6)V**.

MFEs on the Photocurrents in IL

We examine the MFEs on the photoelectrochemical reaction of **ZnP(6)V** in **[BMIM][BF$_4$]**. The photocurrent increased with increasing magnetic field and became a constant above 50 mT. The magnitude of MFEs on the photocurrent is expressed as

$$Q = (I(B) - I(0))/I(0) \times 100, \tag{1}$$

where I(0) and I(B) are the photocurrent in the absence and presence of the magnetic field (B), respectively, as reported in the previous papers [2–7]. The Q value (%) increases with magnetic field for lower magnetic fields ($B \leq 50$ mT) and is constant for higher magnetic fields ($B \geq 50$ mT) (Fig. 2). The MFEs were similar to those in the LB-modified electrodes [2–4]. The above thermodynamic results suggest the photogeneration of triplet radical pairs, ^{3}(ZnP$^{+}\cdot$—V$^{+}\cdot$) via an intramolecular electron-transfer process from ^{3}ZnP* to V^{2+}. Therefore, the MFEs are explained by the photogenerated triplet radical pair (radical pair mechanism) [1], as similar to the previous papers [2–4].

The intersystem crossing process from ^{3}(ZnP$^{+}\cdot$—V$^{+}\cdot$) to singlet radical pairs, ^{1}(ZnP$^{+}\cdot$—V$^{+}\cdot$) becomes the rate-determining step for the triplet radical pair decay via reverse electron-transfer to the ground state. Under sufficiently strong magnetic fields ($B \geq 50$ mT), intersystem crossing is controlled by relaxation from triplet

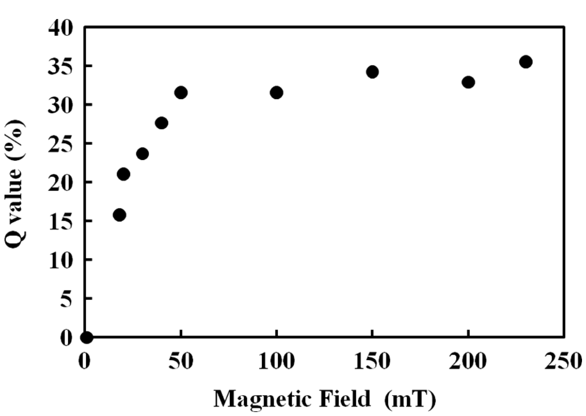


Figure 2. Magnetic field dependence of the Q values of **ZnP(6)V** in **[BMIM][BF$_4$]** using the two-electrode cell.

sublevels to the corresponding singlet [2–4]. As intersystem crossing is suppressed by the magnetic field, the lifetime for the photogenerated radical pair increases and the probability of electron-transfer from the reduced viologen ($V^{\cdot +}$) to the ITO electrode increases. As a consequence, the photocurrent increases in the presence of a magnetic field, as shown in Figure 2. The above mechanism is also supported by the result that the MFEs on the lifetime of photogenerated radical pairs for **ZnP(6)V** in **[BMIM][BF$_4$]** were observed [9]. The magnitude of the MFEs (Q_{max} = ca. 35%) in the present study is larger than those (Q_{max} = ca. 15%) in the previous papers [2–4]. It is probably responsible for the unique properties of **[BMIM][BF$_4$]** as an IL. Further investigations on the mechanism of the MFEs and the effect of the IL on the MFE in the present system using the other methods including time-resolved ESR measurement are now in progress.

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