

## Fabrication and Photoelectrochemical Properties of Polythiophene-Porphyrin Composite Films

Tsuyoshi Akiyama, Keitaro Kakutani<sup>1</sup> and Sunao Yamada

Department of Applied Chemistry, Kyushu University, 6-10-1, Hakozaki, Higashi-ku, Fukuoka, 812-8581, Japan

Phone: +81-92-642-3582 E-mail: t-akitcm@mbox.nc.kyushu-u.ac.jp

<sup>1</sup>Department of Materials Physics and Chemistry, Graduate School of Engineering, Kyushu University

### 1. Introduction

Solar energy conversion is one of promising approaches for the creation of clean energy systems. Organic dyes are very useful in terms of light collection efficiency in the UV-visible-near IR region, as have been verified by a dye-sensitized solar cell developed by Grätzel et. al.<sup>1</sup> Meanwhile, self-assembled monolayers of electron donor (D) - acceptor (A) pairs have been extensively investigated as novel photoelectric molecular devices.<sup>2-6</sup>

In order to increase the overall photocurrent generation efficiency of those assemblies, increase in the number of immobilized photoexcited dyes in the satisfactorily conductive media is basically important.<sup>7,8</sup> Furthermore, the combination of an organic conductive polymer and a photoexcited dye has been expected to realize a novel and easily constructive photoelectric molecular device. Especially, polythiophenes are well known conductive polymers and have been useful for organic electric devices. On the other hand, the porphyrins have been considerably important owing to their high extinction coefficient and have been used as the models for photosynthetic reaction center. Several films of conjugated polythiophenes and porphyrins have been prepared and have been applied for the electrochemical devices.<sup>9,10</sup> For the preparation of polythiophene-porphyrin composites with covalent bonding, meso-tetrathienylporphyrin seems to be one of the good candidates. Furthermore, porphyrin cation is easy to be scavenged by polythiophene, because the oxidation potential of polythiophene is lower than that of porphyrins.

We report here, fabrication and photoelectrochemical properties of polythiophene-porphyrin composite films as novel photoelectric devices.

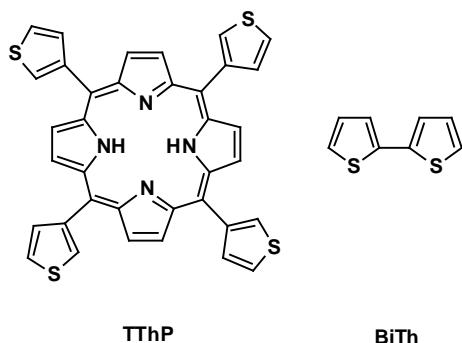
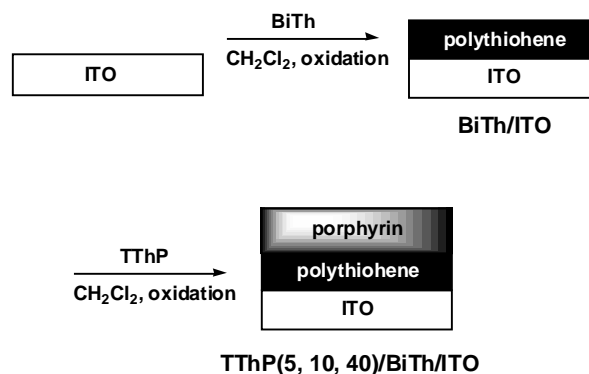


Figure 1. Structures of tetrathienylporphyrin and bithiophene

### 2. Experimental

Tetrathienylporphyrin, **TThP**, was synthesized from pyrrole and 3-thiophenealdehyde according to the previous procedures.<sup>11</sup> Formation and purity of **TThP** was confirmed by <sup>1</sup>H-NMR, elemental analysis, and TOF-mass spectrum.



Scheme 1. Fabrication of polythiophene-porphyrin composite film on ITO electrode

Modified electrodes with polythiophene-porphyrin composites were prepared by sequential two steps of the electrochemical polymerization (Scheme 1). At first, the polythiophene-modified electrode was prepared in a three-electrode electrochemical cell containing  $1 \times 10^{-3} \text{ mol dm}^{-3}$  bithiophene (**BiTh**) and  $0.1 \text{ mol dm}^{-3} \text{ Bu}_4\text{NPF}_6$  in  $\text{CH}_2\text{Cl}_2$ . A bare indium-tin-oxide (ITO) electrode was used as a working electrode, and a platinum wire electrode as a counter and Ag wire electrode as a reference. The applied potential to the working electrode was scanned between 0 V and +2 V with a speed of 0.05 V/s for 10 times. Then, the ITO electrode was removed from the solution, followed by washing with enough amount of  $\text{CH}_2\text{Cl}_2$ , and dried in the air, to give polythiophene-modified electrode (**BiTh/ITO**). Next, **TThP** was assembled on **BiTh/ITO** by using electrochemical polymerization. In this case, **BiTh/ITO** was used as the working electrode and the electrolyte solution containing in  $1 \times 10^{-3} \text{ mol dm}^{-3}$  **TThP** was used. The applied potential was scanned between 0 V and +2 V with 0.05 V/s for 5, 10 and 40 times, to give **TThP(5)/BiTh/ITO**, **TThP(10)/BiTh/ITO** and **TThP(40)/BiTh/ITO**, respectively.

Photocurrent measurements (Figure 2) were carried out using a three-electrode electrochemical cell containing  $0.1 \text{ mol dm}^{-3} \text{ NaClO}_4$  and saturated  $\text{O}_2$  in an aqueous

solution at room temperature. The light from a Xenon (300W) lamp was passed through a monochromator and irradiated the modified electrode. Photocurrent action spectra were measured by changing the excitation wavelength at 0V. The light irradiated the film from the rear side of the modified electrode by using a glass fiber.

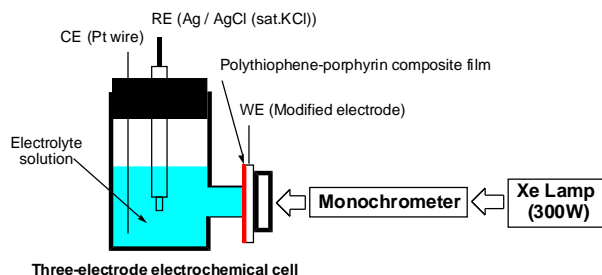


Figure 2. Photocurrent measurement setup

### 3. Results and Discussion

The amount of **TThP** in **TThP(5, 10 or 40)/BiTh/ITO** was confirmed by the absorption spectrum of the composite film. It increased with increasing scanning cycles for electrochemical for polymerization in the **TThP** solution.

Cathodic photocurrents were observed in each modified electrode. The photocurrent action spectra of **TThP(5, 10 or 40)/BiTh/ITO** strongly suggested the formation of the polythiophene-porphyrin composite film and the photochemical cooperation of **TThP** and polythiophene for the photocurrent responses. Figure 3 shows potential dependences of photocurrents for **TThP(5, 10 or 40)/BiTh/ITO**. Photocurrents increased with increasing the scanning cycles and also with the amount of

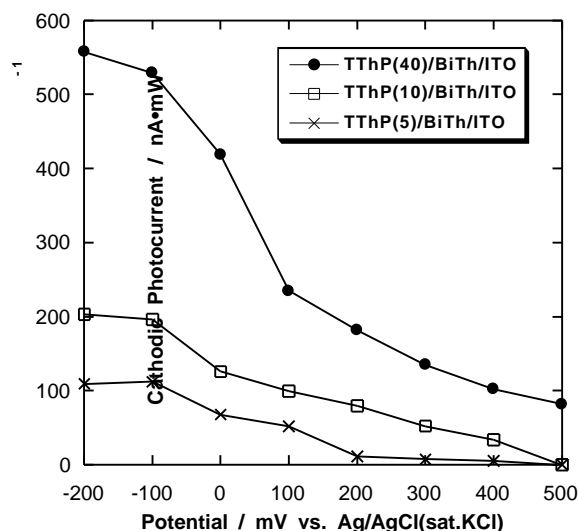


Figure 3. Photocurrents of each modified electrode at several applied potentials

**TThP**. Larger cathodic photocurrents were observed in the negatively applied potentials for each modified electrode.

These results suggest that the porphyrin moiety predominantly contributes to the photocurrent generation. The possible mechanism for photocurrent generation is the combination of three electron-transfer processes; 1) electron transfer from the photoexcited porphyrin moiety to oxygen in the bulk, 2) the scavenging of the porphyrin cation by the polythiophene, and 3) electron supply from the electrode to polythiophene.

### 4. Conclusion

We have shown fabrication and photoelectrochemical properties of polythiophene-porphyrin composite films on the ITO electrodes. Optimization of experimental conditions for fabricating the best polythiophene-porphyrin composite films in terms of photocurrent generation is in progress.

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