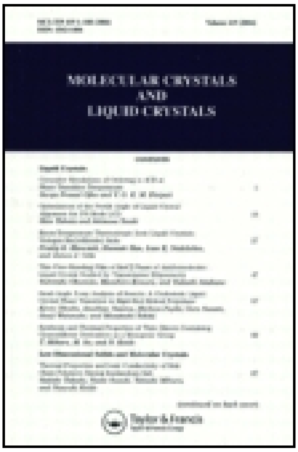


Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

An Influence of Monomeric Porphyrin Structure on the Electropolymerized Photoactive Electrode for Polymer Solar Cells

Kensuke Takechi [a] [b] , Naoko Takahashi [c] , Tohru Shiga [a] , Tsuyoshi Akiyama [d] & Sunao Yamada [d]

[a] Advanced Battery Lab., Toyota Central R&D Labs., Inc., Aichi, Japan

[b] Department of Material Physics and Chemistry, Kyushu University, Fukuoka, Japan

[c] Nano-Analysis Lab., Toyota Central R&D Labs., Inc., Aichi, Japan

[d] Department of Applied Chemistry, Kyushu University, Fukuoka, Japan

Version of record first published: 16 May 2011

To cite this article: Kensuke Takechi, Naoko Takahashi, Tohru Shiga, Tsuyoshi Akiyama & Sunao Yamada (2011): An Influence of Monomeric Porphyrin Structure on the Electropolymerized Photoactive Electrode for Polymer Solar Cells, Molecular Crystals and Liquid Crystals, 538:1, 10-14

To link to this article: http://dx.doi.org/10.1080/15421406.2011.563206

Mol. Cryst. Liq. Cryst., Vol. 538: pp. 10–14, 2011

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2011.563206

An Influence of Monomeric Porphyrin Structure on the Electropolymerized Photoactive Electrode for Polymer Solar Cells

KENSUKE TAKECHI,[1,2] NAOKO TAKAHASHI,[3]
TOHRU SHIGA,[1] TSUYOSHI AKIYAMA,[4] AND
SUNAO YAMADA[4]

[1]Advanced Battery Lab., Toyota Central R&D Labs., Inc., Aichi, Japan
[2]Department of Material Physics and Chemistry, Kyushu University, Fukuoka, Japan
[3]Nano-Analysis Lab., Toyota Central R&D Labs., Inc., Aichi, Japan
[4]Department of Applied Chemistry, Kyushu University, Fukuoka, Japan

We have fabricated and compared photocurrent generation properties of electropolymerized films consisting of 2,2′-bithiophene and a porphyrin derivative, 5,10,15,20-tetra(3-thienyl)-21H,23H-porphyrin or 5,10,15,20-tetra(2-thienyl)-21H,23H-porphyrin. It was found that the location and the concentration of porphyrin moieties in the films were different between the two porphyrin monomers, and the polymer film with the former porphyrin gave larger photocurrent than the latter. The result indicates that the molecular design of the polymer electrode is very important for effective photocurrent generation.

Keywords Electrochemical polymerization; polythiophene; porphyrin; solar cell

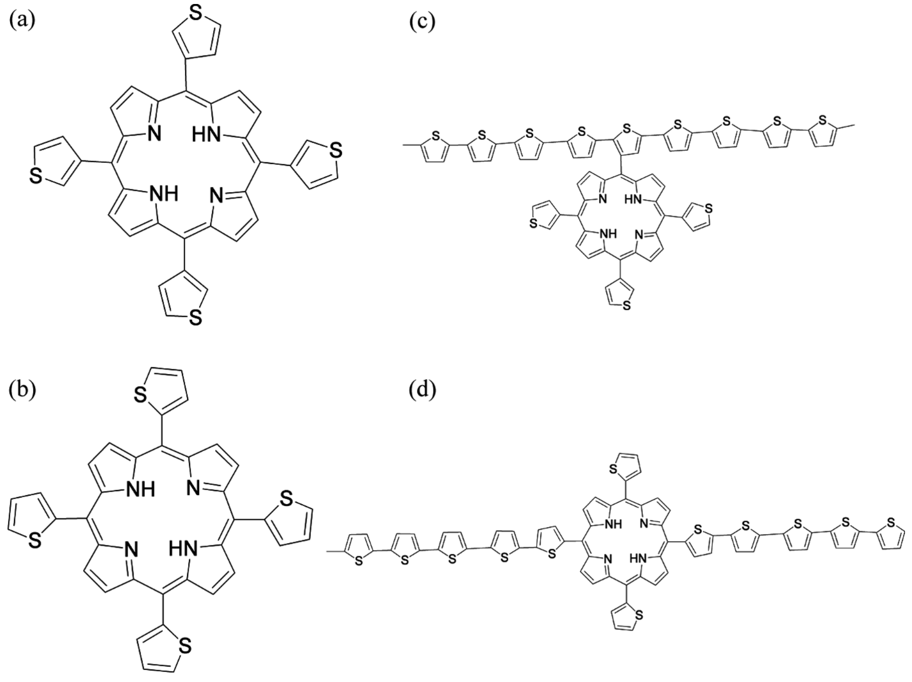
Introduction

A significant improvement in the conversion efficiency and reduced cost of solar cells has been required to meet the demands of future electronics and clean energy generation. Organic solar cells including polymer solar cells are promising candidates along this line. Among them, the polymer solar cell containing a photoactive polymer film is noteworthy because the electrode can be fabricated very easily by well-established methods such as spin coating [1], solution casting [2] and electropolymerization [3–5].

Recently, our group has proposed a uniform photoactive film fabricated by a one-step electropolymerization method from the solution of the monomer of a conducting polymer and photoactive molecules [6–10]. After polymerization, the photoactive monomeric molecules have been confined in the conducting polymer

---

Address correspondence to Kensuke Takechi, Advanced Battery Lab., Toyota Central R&D Labs., Inc., 41-1, Yokomichi, Nagakute, Aichi 480-1192, Japan. Tel.: +81-561-71-7751; Fax: +81-561-63-5743; E-mail: ktakechi@mosk.tytlabs.co.jp



Scheme 1. Molecular structures of (a) **3-TThP** and (b) **2-TThP**, and proposed polymer structures of (c) (**3-TThP + pTh**) and (d) (**2-TThP + pTh**).

structure. The cell with the polymer film consisting of 5,10,15,20-tetra(3-thienyl)-21H,23H-porphyrin (**3-TThP**) and 2,2′-bithiophene exhibits as high as 32% of photon-to-electron conversion efficiency under the monochromatic light (Scheme 1a, c). One of our strategies to achieve high mobility of photoinduced charge carrier is to establish continuous polythiophene (**pTh**) pathway from photoactive molecule to current collecting substance.

In this paper, we have investigated the effect of the orientation of the thienyl moieties in the monomeric porphyrin molecule to elucidate the influence of the **pTh** structure in the electrode. We have found that the photocurrent generation property was remarkably influenced by a small change of the molecular structure. These results must give a useful knowledge in a smart design of the photoactive electrode for polymer solar cells.

Experimental

5,10,15,20-tetra(3-thienyl)-21H,23H-porphyrin **(3-TThP)** and 5,10,15,20-tetra(2-thienyl)-21H,23H-porphyrin **(2-TThP) (**Scheme 1) were synthesized according to the previous procedures [6]. **(TThP + pTh)** polymer electrode was fabricated on the surface of an indium-tin-oxide (ITO) glass (Sanyo Vacuum Industries, $2 \times 2 \times 0.3\,\mathrm{cm}$) in a similar manner as before [6]. A dichloromethane solution containing **3-** or **2-TThP** ($0.25\,\mathrm{mmol\,L^{-1}}$), 2,2′-bithiophene ($1.50\,\mathrm{mmol\,L^{-1}}$) and tetrabutylammonium hexafluorophosphate ($0.1\,\mathrm{mol\,L^{-1}}$) was used as the electrolyte for polymerization. Polymerization was carried out using a potentiostat (Hokuto

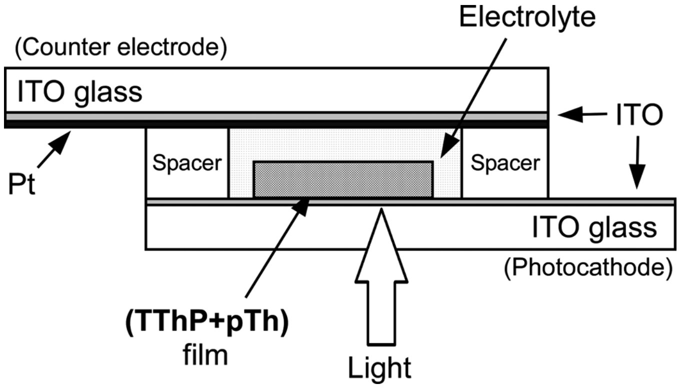


Figure 1. Schematic illustration of the sandwich-type solar cell.

Denko, HA-3001), and the potential applied to the working electrode was scanned between 0 and +2 V at a rate of 20 mV s^{-1} for one cycle. During polymerization, the solution was stirred at a speed of 500 rpm.

Sandwich-type solar cells were fabricated (Fig. 1). A photoactive electrode consisting of the **(TThP + pTh)** polymer film and a counter electrode were attached to each other with a spacer, and the gap between them was filled with an electrolyte. The counter electrode was Pt sputtered on to ITO glass. The electrolyte was a 0.05 mol L^{-1} iodine and 0.5 mol L^{-1} lithium iodide solution in 3-methoxypropionitrile.

UV-visible absorption spectrum and incident photon-to-electron conversion efficiency (IPCE) were measured using same setups of the previous procedures [6].

Results and Discussion

We compared electrochemical properties between the electropolymerized (**2-TThP + pTh**) and (**3-TThP + pTh**) films. In the case of the (**2-TThP + pTh**) film, the thickness was thinner (30 nm) than that of the (**3-TThP + pTh**) film (80 nm) under the same polymerization condition, as could be recognized from the comparison of UV-Vis absorption intensities (Fig. 2b, d). To evaluate concentration of the porphyrin moiety in the polymer films, XPS analyses were carried out (Table 1). The calculated concentration of the porphyrin moieties in the (**2-TThP + pTh**) film was about 1/14 (porphyrin/thiophene), much higher than in the case of (**3-TThP + pTh**) film (1/58). On the other hand, absorption band to the Soret band of porphyrin (440 nm) in the (**2-TThP + pTh**) film was relatively small as compared with that of **pTh** (around 550 nm). These results indicate that the concentration of the porphyrin moiety the surface region of the (**2-TThP + pTh**) film was quite high even though the total concentration was relatively low, because the XPS analysis reflected the surface region of materials.

Schematic illustrations of the expected polymer structure of (**2-TThP + pTh**) and (**3-TThP + pTh**) films are shown in Scheme 1c, d. In the case of (**3-TThP + pTh**) film, porphyrin moieties will be hanged from the **pTh** chain. It must realizes continuous long carrier path for photocurrent generation. In the case of (**2-TThP + pTh**) film, the porphyrin moieties must be located in the central position of the **pTh** chain,

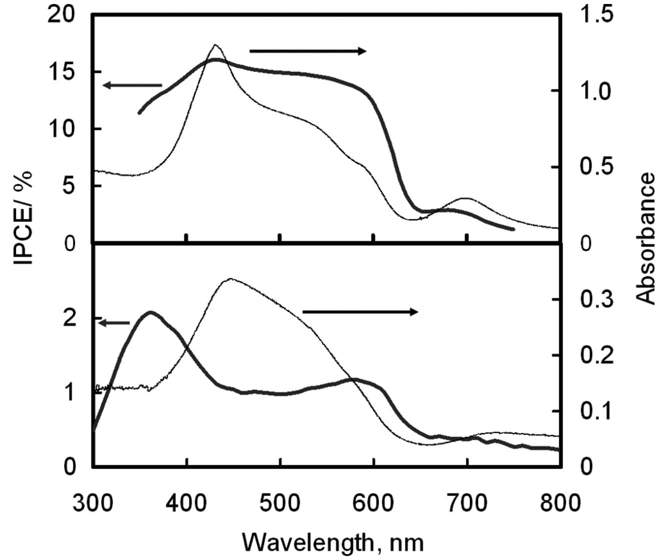


Figure 2. IPCE and absorption spectra of (a, b) (**3-TThP** + **pTh**) and (c, d) (**2-TThP** + **pTh**) films. The light intensity of the monochromatic light was 1.0×10^{16} photon $s^{-1} cm^{-2}$ for IPCE measurements.

Table 1. Atomic ratio and porphyrin/thiophene ratio measured by XPS

Films	C	O	N	S	N/S	Porphyrin/Thiophene
2-TThP + **pTh**	77.74	3.84	2.40	14.95	0.16	1/14
3-TThP + **pTh**	79.95	1.36	0.89	17.6	0.05	1/58

and thus the π-conjugation must be cut off at the position of porphyrin moiety. It must lead to the suppression of the growth of **pTh** chain and the thickness of the film during the polymerization process. As a result, the (**2-TThP** + **pTh**) film must incorporate higher concentration of the porphyrin moieties preferentially in its surface region in the film, even though thinner condition, as compared with the case of (**3-TThP** + **pTh**) film.

Photocurrent action spectra of the (**TThP** + **pTh**) films are shown in Figure 2a, c. Clearly, the IPCE values of (**2-TThP** + **pTh**) film around 440 nm corresponding to the Soret band of the porphyrin moiety were suppressed in contrast to those of the (**3-TThP** + **pTh**) film. This phenomenon can be reasonably explained by the above-described structural proposition, increasing the degree of recombination of photo-induced charge carrier at the porphyrin moieties in the **pTh** chain. In other words, the continuous **pTh** structure from porphyrin moieties to current collecting electrode realized smooth carrier flow in the (**3-TThP** + **pTh**) film.

Conclusions

We have confirmed that the electropolymerized (**2-TThP** + **pTh**) film had completely different photocurrent generation properties as compared with the corresponding

(**3-TThP + pTh**) film. It was found that the small difference of the molecular structure of monomeric porphyrin probably affected the photo-induced carrier transport property. The result indicates that the molecular design of polymer electrode is very important for effective photocurrent generation.

References

[1] Cook, S., Furube, A., & Katoh, R. (2008). *Jpn. J. Appl. Phys.*, *47*, 1238.

[2] Kim, S. S., Na, S. I., Jo, J., Tae, G., & Kim, D. Y. (2007). *Adv. Mater.*, *19*, 4410.

[3] Akiyama, T., Yoneda, H., Fukuyama, T., Sugawa, K., Yamada, S., Takechi, K., Shiga, T., Motohiro, T., Nakayama, H., & Kohama, K. (2009). *Jpn. J. Appl. Phys.*, *48*, 04C172.

[4] Akiyama, T., Fukuyama, T., Sugawa, K., Yoneda, H., & Yamada, S. (2009). *Synthetic Met.*, *159*, 965.

[5] Segawa, H., Wu, F.-P., Nakayama, N., Maruyama, H., Sagisaka, S., Higuchi, N., Fujitsuka, M., & Shimidzu, T. (1995). *Synthetic Met.*, *71*, 2151.

[6] Takechi, K., Shiga, T., Motohiro, T., Akiyama, T., Yamada, S., Nakayama, H., & Kohama, K. (2006). *Sol. Energy Mater. Sol. Cells*, *90*, 1322.

[7] Akiyama, T., Matsushita, M., Kakutani, K., Yamada, S., Takechi, K., Shiga, T., Motohiro, T., Nakayama, H., & Kohama, K. (2005). *Jpn. J. Appl. Phys.*, *44*, 2799.

[8] Sugawa, K., Kakutani, K., Akiyama, T., Yamada, S., Takechi, K., Shiga, T., Motohiro, T., Nakayama, H., & Kohama, K. (2007). *Jpn. J. Appl. Phys.*, *46*, 2632.

[9] Sugawa, K., Akiyama, T., & Yamada, S. (2008). *Thin Solid Films*, *516*, 2502.

[10] Takechi, K., Shiga, T., Akiyama, T., & Yamada, S. (2010). *Photochem. Photobiol. Sci.*, *9*, 1085.