

Host-Guest Complexation Effect on a C₆₀-Porphyrin Light-to-Photocurrent Conversion System

Atsushi Ikeda,^{a,b} Tsukasa Hatano,^c Toshifumi Konishi^b
Jun-ichi Kikuchi,^a and Seiji Shinkai^{a*}

^aGraduate School of Materials Science, Nara Institute of Science and Technology, Takayama, Ikoma, Nara 630-0101, Japan.

^bPRESTO, Japan Science and Technology Corporation.

^cDepartment of Chemistry and Biochemistry, Graduate School of Engineering, Kyushu University, Hakozaki, Higashi-ku, Fukuoka 812-8581, Japan.

There has been great interest devoted to the development of photocurrent generators consisting of organic electron-donor and/or electron-acceptor couples. These electron-donors or electron-acceptors can be deposited on the electrode surface as monolayers by means of Langmuir-Blodgett (LB) membranes and self-assembled monolayers (SAMs). In these approaches, monolayer systems comprised of covalently-linked donor-acceptor molecules, in the form of dyads and triads, can result in the high light-to-photocurrent conversion values. This high efficiency is attributed to the ability of the donor-acceptor layers to generate the long-lived charge-separated-state with high quantum yields. It is very difficult, however, to covalently-link all of the thin-layer-forming substituent, donor unit and acceptor unit in one molecular system by a synthetic procedure. To find a more expeditious and more general means of designing the multilayer photocurrent generator system on the electrode, we have taken advantage of the alternate adsorption method (Figure 1a).¹ A hexacationic homooxacalix[3]arene (1)-C₆₀ 2:1 complex (2) can be deposited on an indium-tin oxide (ITO) electrode with anionic surface as a monolayer and then anionic 3 can be deposited on the ITO electrode (Figure 1a).^{2,3} The largest advantage of the alternate adsorption method is the easiness of the technique utilizing the self-assembling system without decreasing of a quantum yield.

The preparation of thin films with high surface concentration of donor-acceptor molecules is indispensable to achieve the high conversion efficiency, but it inevitably accompanies self-aggregation of chromophores. After photoactivation, the aggregated donor or acceptor molecules on the electrode will be deactivated by self-quenching. In fact, the high-concentration deposition and self-quenching have always been an antinomy problem in the light-to-photocurrent conversion system. It thus occurred to us that the self-aggregation might be suppressed by encapsulation of donor or acceptor in a cavity of macrocyclic host molecules. It was shown by several groups that porphyrin is included in a hydrophobic cavity of cyclodextrin. This fact prompted us to evaluate the insulation effect of

cyclodextrin on the conversion efficiency. This paper addresses the data on this attractive working-hypothesis of added cyclodextrin in the C₆₀-porphyrin dyad system (Figure 1b).

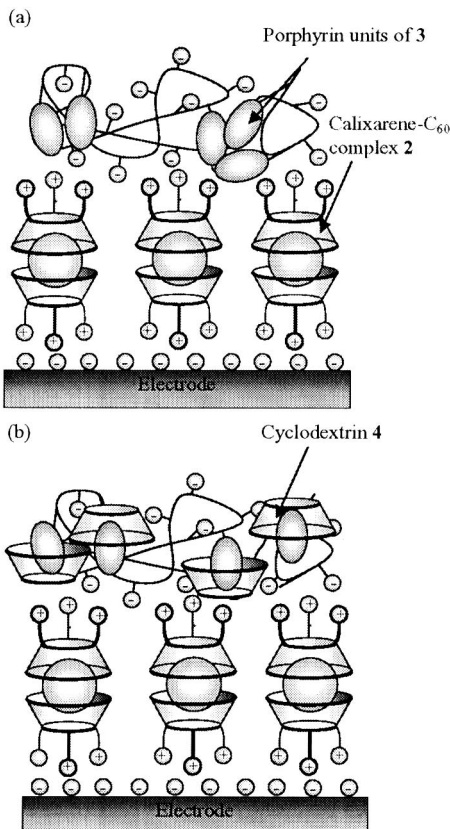


Figure 1 Schematic representation of self-assembled multilayers of 2 (first layer) and 3 or 3-4 complex (second layer) on an ITO electrode.

Photocurrent measurements were carried out for 2 monolayer, 2-3 bilayer, and 2-3-4 bilayer deposited on the ITO electrode. From the action spectra, the photocurrent density for 2-3-4 bilayer is remarkably increased as compared with that for 2-3 bilayer. The quantum yield can be estimated to be 15 and 20% for 2-3 bilayer and 2-3-4 bilayer, respectively, confirming the effectiveness of added cyclodextrin.

In conclusion, the present paper demonstrated that the photocurrent density and the quantum yield in the C₆₀-porphyrin bilayer system are remarkably improved by the addition of cyclodextrin. The achievement of the high quantum yield arises from the isolation of porphyrin units by cyclodextrin utilizing the host-guest interaction.

References

- (1) Ikeda, A.; Hatano, T.; Shinkai, S.; Akiyama, T.; Yamada, S. *J. Am. Chem. Soc.* **2001**, *123*, 4855.
- (2) (a) Ikeda, A.; Hatano, T.; Kawaguchi, M.; Suenaga, H.; Shinkai, S. *Chem. Commun.* **1999**, 1403. (b) Islam, S. D.-M.; Fujitsuka, M.; Ito, O.; Ikeda, A.; Hatano, T.; Shinkai, S. *Chem. Lett.* **2000**, 78.
- (3) Hatano, T.; Ikeda, A.; Sano, M.; Kanekiyo, Y.; Shinkai, S. *J. Chem. Soc., Perkin Trans. 2* **2000**, 909.

