Pergamon

SCIENCE DIRECT®

Tetrahedron 59 (2003) 3537–3540

TETRAHEDRON

# Host–guest complexation effect of 2,3,6-tri-*O*-methyl-β-cyclodextrin on a $C_{60}$–porphyrin light-to-photocurrent conversion system

Atsushi Ikeda,[a,b,*] Tsukasa Hatano,[c] Toshifumi Konishi,[b] Jun-ichi Kikuchi[a] and Seiji Shinkai[c,*]

[a] *Graduate School of Materials Science, Nara Institute of Science and Technology, Takayama, Ikoma, Nara 630-0101, Japan*
[b] *PRESTO, Japan Science and Technology Corporation (JST), Japan*
[c] *Department of Chemistry and Biochemistry, Graduate School of Engineering, Kyushu University, Hakozaki, Higashi-ku, Fukuoka 812-8581, Japan*

Received 5 February 2003; accepted 12 March 2003

---

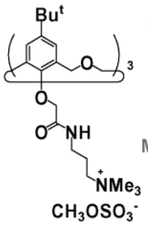
**Abstract**—In a light-to-photocurrent conversion system based on a $C_{60}$–porphyrin bilayer prepared by electrostatic alternate adsorption, porphyrin units in a porphyrin polymer have been isolated by cyclodextrin utilizing the host–guest interaction. In this system, a high quantum yield was achieved by suppression of self-quenching of porphyrin units. © 2003 Elsevier Science Ltd. All rights reserved.

---

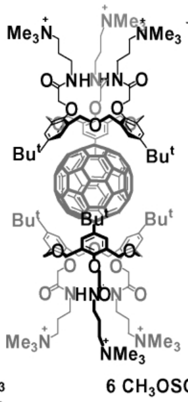
## 1. Introduction

There has been great interest devoted to the development of photocurrent generators consisting of organic electron-donor and electron-acceptor couples.[1] 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).[2] 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.[3] 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.[3] 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 (Fig. 1(a)).[4,5] A hexacationic homooxacalix[3]arene (**1**)–$C_{60}$ 2:1 complex (**2**)[6] can be deposited on an indium–tin oxide (ITO) electrode with anionic surface as a monolayer (or at least as a monolayer-like ultrathin film) and then anionic **3** can be deposited on the ITO electrode (Fig. 1(a)).[4,5] As expected, this dyad system showed a sensitive photoelectrochemical response under visible light irradiation and a high quantum yield

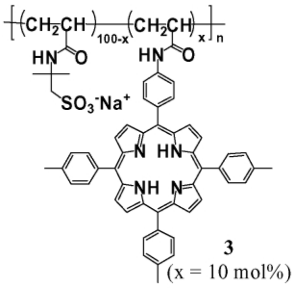
$C_{60}$



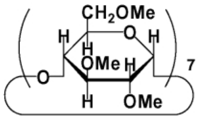
**1**



**2**



**3** (x = 10 mol%)



**4**

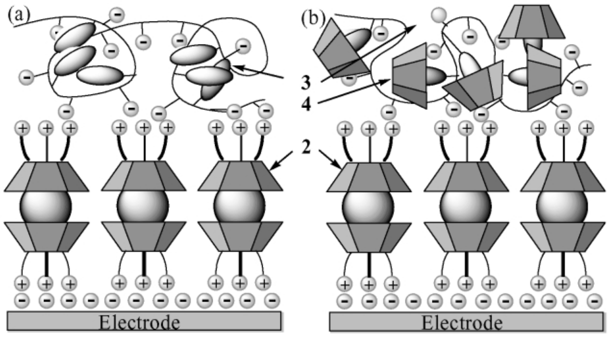


**Figure 1.** Schematic representation of self-assembled multilayers of **2** (first layer) and **3** or **3**–**4** complex (second layer) on an ITO electrode.

---

*Keywords*: fullerenes; calixarenes; porphyrins; cyclodextrins; photocurrent.

* Corresponding authors. Fax: +81-743-72-6099; e-mail: aikeda@ms.aist-nara.ac.jp

doi:10.1016/S0040-4020(03)00417-4

(14%).[4] The largest advantage of the alternate adsorption method is the easiness of the technique utilizing the self-assembly system with maintaining the high 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 induces self-aggregation of chromophores. After photoactivation, therefore, 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 molecules in a cavity of macrocyclic host molecules. It was shown by several groups that porphyrin is included in a hydrophobic cavity of cyclodextrins.[7] This fact prompted us to evaluate the insulation effect of cyclodextrins on the light-to-photocurrent conversion efficiency. This paper addresses the detailed examination of this attractive working-hypothesis in a $C_{60}$–porphyrin dyad system (Fig. 1(b)).

## 2. Results and discussion

### 2.1. Effect of the addition of cyclodextrin in aqueous solution

The UV–Vis and fluorescence spectra of aqueous solution of **3** (porphyrin unit $x$=10 mol%)[8] were measured in the absence and the presence of 2,3,6-tri-*O*-methyl-β-cyclodextrin (**4**) (Fig. 2). In the absence of **4**, a broad absorption band assignable to the Soret band appeared at 390–450 nm and the corresponding fluorescence intensity was very weak. The findings clearly indicate that the porphyrin units of **3** were aggregated with one another.[9] Upon addition of **4** to the aqueous solution of **3**, the Soret band became very sharp and a very strong fluorescence band was observed at 651 nm (Fig. 2). These results imply that pendent porphyrins, aggregated in the aqueous solution, are insulated by inclusion in the cavity of **4**.[10]

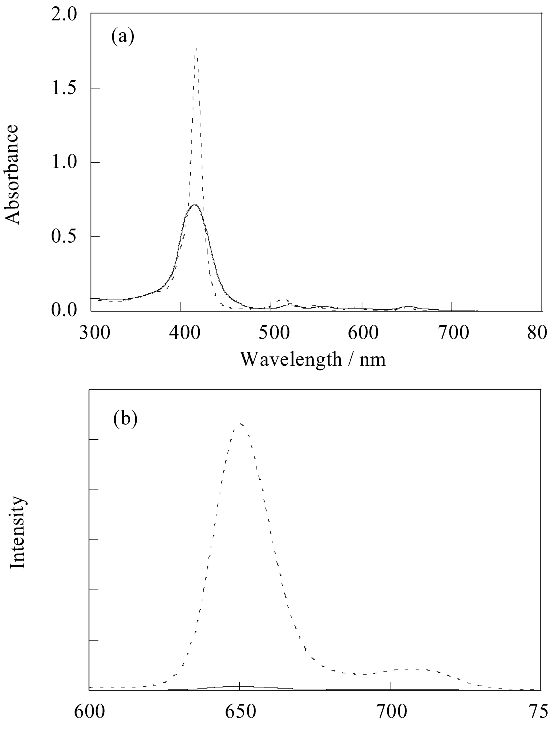


**Figure 2.** (a) Absorption and (b) fluorescence spectra ($\lambda_{ex}$ 407 nm) of **3** (0.25 mg $dm^{-3}$) in the absence (continuous line) and the presence (dashed line) of **4** (8.1 mmol $dm^{-3}$, 100 equiv./porphyrin unit) in water at 25°C.

### 2.2. Effect of the addition of cyclodextrin on ITO electrode

To determine the surface concentration of **2** and **3**, we measured cyclic voltammogram (CV) of the deposited ITO electrode (Fig. 3). From the peak current of the first reduction of $C_{60}$ and oxidation of porphyrin, the surface concentration of **2**, **3** and **3**–**4** complex can be estimated to be $4.8\text{–}6.2\times10^{-10}$, $6.9\times10^{-11}$ and $8.2\times10^{-11}$ mol $cm^{-2}$, respectively, in terms of the concentrations of porphyrin units (Table 1).[11] This result shows that the adsorption of **3** on the electrode coated with **2** is scarcely influenced by the addition of **4**.

We measured the UV–Vis absorption and fluorescence

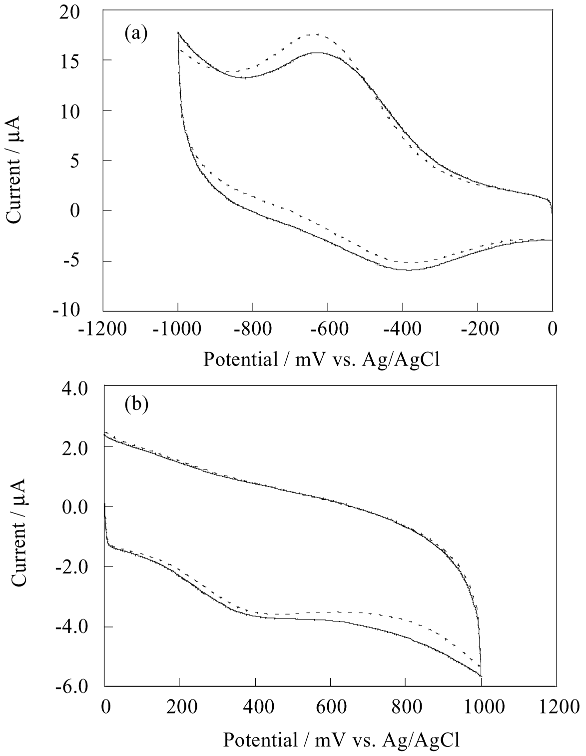


**Figure 3.** Cyclic voltammograms on the ITO electrode coated with **2**–**3** (continuous line) and **2**–**3**–**4** (dashed line) at 25°C; (a) the cathodic reduction of $C_{60}$ and (b) the anodic oxidation of porphyrin unit.

**Table 1**. Surface concentration of **2** and **3** (mol $cm^{-2}$)

| Compounds | **2** Monolayer | **2**–**3** Bilayer | **2**–**3**–**4** Bilayer |
|---|---|---|---|
| **2** | $4.8\times10^{-10}$ | $5.0\times10^{-10}$ | $6.2\times10^{-10}$ |
| **3** | – | $6.9\times10^{-11}$ | $8.2\times10^{-11}$ |

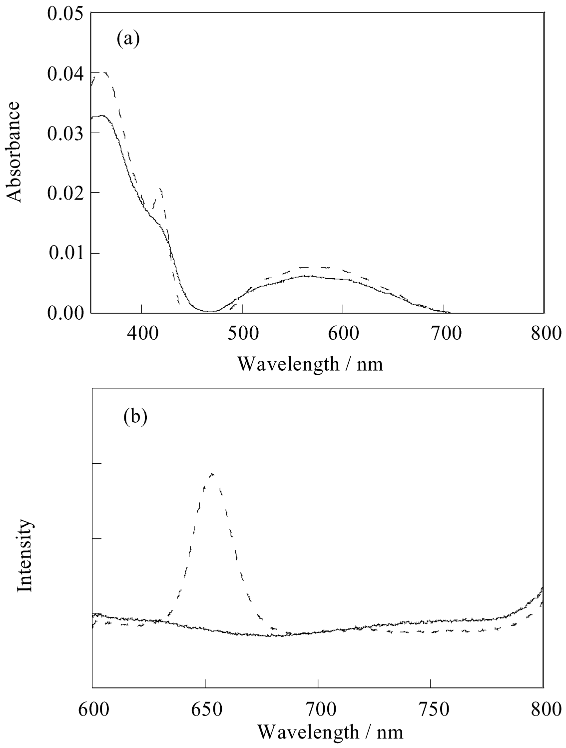


**Figure 4.** (a) Absorption and (b) fluorescence spectra ($\lambda_{ex}$ 418 nm) of **2**–**3** (continuous line) and **2**–**3**–**4** (dashed line) systems on an ITO electrode at 25°C.

spectroscopies of the ITO electrode coated with **2**, **2**–**3** or **2**–**3**–**4** (Fig. 4). The appearance of broad peaks at 350–400 nm and 500–700 nm is due to the light scattering. It is seen from Figure 3 that the peak at 420 nm in the presence of **4** is sharper than that in the absence of **4**, indicating that in **2**–**3**–**4** system, the pendent porphyrin units are included in the cavity of **4** even on the ITO electrode.

### 2.3. Photocurrent generation

Photocurrent measurements were carried out for **2** monolayer, **2**–**3** bilayer and **2**–**3**–**4** bilayer deposited on the ITO electrode (in 0.10 mol dm$^{-3}$ $Na_2SO_4$ solution containing 0.05 mol dm$^{-3}$ ascorbic acid (AsA) as an electron sacrificer using a modified ITO electrode as the working electrode, a Pt counter electrode and a Ag/AgCl (3 mol dm$^{-3}$ NaCl) reference electrode). To avoid the leakage of cyclodextrin from **2**–**3**–**4** bilayer, cyclodextrin **4** was added to the solution (2.0 mmol dm$^{-3}$). The pH of the solutions were maintained to 3.5. Figure 5 shows the action spectra for **2** monolayer, **2**–**3** bilayer and **2**–**3**–**4** bilayer between 400 and 600 nm. It is clearly seen from these action spectra that the photocurrent density for **2**–**3**–**4** bilayer is remarkably increased as compared with that for **2**–**3** bilayer. Especially, the increased photocurrent density at 420 nm shows that the porphyrin units insulated as **3**–**4** complex act as the efficient photoactive species. Undoubtedly, host–guest complexation is able to remarkably suppress the self-quenching of porphyrin chromophores and evolve the long-lived charge-separation-state of the photoactivated porphyrin.[10] 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.[12]

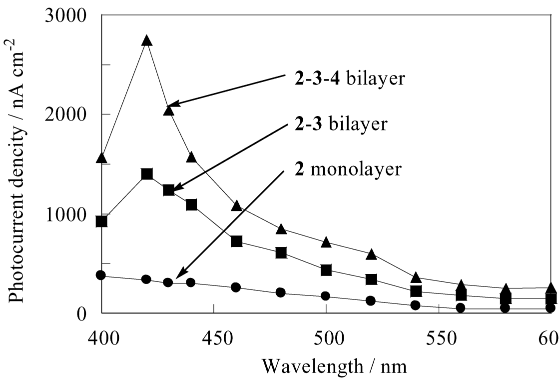


**Figure 5.** Photocurrent action spectra of **2**, **2**–**3** and **2**–**3**–**4** systems on an ITO electrode at 25°C (1 mW cm$^{-2}$, 0.10 mol dm$^{-3}$ $Na_2SO_4$ solution containing 0.05 mol dm$^{-3}$ ascorbic acid, pH 3.5).

## 3. Summary and conclusions

The present paper demonstrated that the photocurrent density and the quantum yield in the $C_{60}$–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. One can therefore propose that the host–guest method is very useful for preparation of photocurrent generators not only by means of alternate layer-by-layer adsorption but also by means of SAM. In addition, one may expect that the durability of photocurrent generators is also improved by the encapsulation of donor and acceptor molecules in the host molecules. Further applications of this new concept are currently continued in these laboratories.

## 4. Experimental

### 4.1. Miscellaneous

UV–visible spectra were measured on Shimadzu UV-3000PC spectrometer. Cyclic voltammetry (CV) was performed on a Windows-driven BAS 100 W electrochemical analyzer.

### 4.2. Materials

$C_{60}$ (>99.5%) was purchased from MER corporation. 2,3,6-Tri-*O*-methyl-β-cyclodextrin was purchased from Wako Pure Chemical Industries, Ltd. The syntheses of compound **1**[6a] and **3**[4] were described previously.

### 4.3. Preparation of ITO electrodes modified $C_{60}$ and porphyrin polymer

The preparation of calixarene–$C_{60}$ complex **2** was reported previously.[5] Complex **2** was deposited from aqueous solution ([**2**]=0.25 mmol dm$^{-3}$, [NaCl]=0.50 mol dm$^{-3}$) on ITO electrode with the anionic surface by pretreatment with 30% aqueous $H_2O_2$ solution/28% aqueous $NH_3$ solution=1:1 at 80°C for 15 min.[13] After washing with ultrapure water and drying with a nitrogen stream, the electrode was immersed in an aqueous solution containing **3**

([**3**]=0.33 g $dm^{-3}$, [NaCl]=0.50 mol $dm^{-3}$) or **3**–**4** complex ([**4**]=0.91 mmol $dm^{-3}$). After 10 min, the electrode was washed with ultrapure water containing **4** (2.00 mmol $dm^{-3}$) and dried with a nitrogen stream again.

CV was performed with three-electrode configuration in aqueous solution containing supporting electrolyte ($Na_2SO_4$, 0.1 mol $dm^{-3}$). The modified ITO electrode was used as the working electrode, the counter electrode being a platinum wire. An Ag/AgCl electrode was used as the reference electrode. The scan rate was 50 mV $s^{-1}$. All measurements were carried out under nitrogen and at 25°C.

### 4.4. Photoelectrochemical measurements

A 500 W Xe arc lamp (USHIO XB-50101AAA, XS-50102AAA) was used as the light source in the photoelectrochemical studies and a monochrometer (Shimadzu SPG 120IR) was used to obtain different wavelengths. The intensity of the light was measured with an energy and power meter (Advantest TQ8210). Photocurrent measurements were carried out in an aqueous $Na_2SO_4$ (0.1 mol $dm^{-3}$) solution by using a three-electrode photoelectrochemical cell, consisting of the modified ITO electrode. All measurements were carried out in the presence of ascorbic acid (0.05 mol $dm^{-3}$) as a sacrificial reagent under a nitrogen atmosphere.

## Acknowledgements

We thank Mr H. Horiuchi for his skill in preparing specially designed glass cells. This work was supported by PRESTO in Japan Science and Technology Corporation (JST) and also by the Grants-in-Aid for Scientific Research (No. 11750749) from the Ministry of Education, Science and Culture of Japan.

## References

1. (a) Murakami, H.; Watanabe, Y.; Nakashima, N. *J. Am. Chem. Soc.* **1996**, *118*, 4484. (b) Nakashima, N.; Kuriyama, T.; Tokunaga, T.; Murakami, H.; Sagara, T. *Chem. Lett.* **1998**, 633. (c) Chen, K.; Caldwell, W. B.; Mirkin, C. A. *J. Am. Chem. Soc.* **1993**, *115*, 1193. (d) Higashi, N.; Inoue, T.; Niwa, M. *Chem. Commun.* **1997**, 1507. (e) Bianco, A.; Gasparrini, F.; Maggini, M.; Misiti, D.; Polese, A.; Prato, M.; Scorrano, G.; Toniolo, C.; Villani, C. *J. Am. Chem. Soc.* **1997**, *119*, 7550. (f) Imahori, H.; Azuma, T.; Ozawa, S.; Yamada, H.; Ushida, K.; Ajavakom, A.; Norieda, H.; Sakata, Y. *Chem. Commun.* **1999**, 557. (g) Akiyama, T.; Miyazaki, A.; Sutoh, M.; Ichinose, I.; Kunitake, T.; Yamada, S. *Colloids Surf.* **2000**, *169*, 137. (h) Chupa, J. A.; Xu, S.; Fischetti, R. F.; Strongin, R. M.; McCauley, J. P., Jr.; Smith, A. B., III.; Blasie, J. K.; Peticolas, L. J.; Beanv, J. C. *J. Am. Chem. Soc.* **1993**, *115*, 4383. (i) Arias, F.; Godínez, L. A.; Wilson, S. R.; Kaifer, A. E.; Echegoyen, L. *J. Am. Chem. Soc.* **1996**, *118*, 6086.
2. (a) Imahori, H.; Yamada, H.; Ozawa, S.; Ushida, K.; Sakata, Y. *Chem. Commun.* **1999**, 1165. (b) Imahori, H.; Yamada, H.; Nishimura, Y.; Yamazaki, I.; Sakata, Y. *J. Phys. Chem. B* **2000**, *104*, 2099. (c) Hirayama, D.; Takimiya, K.; Aso, Y.; Otsubo, T.; Hasobe, T.; Yamada, H.; Imahori, H.; Fukuzumi, S.; Sakata, Y. *J. Am. Chem. Soc.* **2002**, *124*, 532. (d) Imahori, H.; Norieda, H.; Yamada, H.; Nishimura, Y.; Yamazaki, I.; Sakata, Y.; Fukuzumi, S. *J. Am. Chem. Soc.* **2001**, *123*, 100.
3. (a) Lahav, M.; Gabriel, T.; Shipway, A. N.; Willner, I. *J. Am. Chem. Soc.* **1999**, *121*, 258. (b) Luo, C. P.; Guldi, D. M.; Maggini, M.; Menna, E.; Mondini, S.; Kotov, N. A.; Prato, M. *Angew. Chem., Int. Ed.* **2000**, *39*, 3905. (c) Ariga, K.; Lvov, Y.; Kunitake, T. *J. Am. Chem. Soc.* **1997**, *119*, 2224. (d) Lvov, Y.; Ariga, K.; Ichinose, I.; Kunitake, T. *J. Am. Chem. Soc.* **1995**, *117*, 6117.
4. Ikeda, A.; Hatano, T.; Shinkai, S.; Akiyama, T.; Yamada, S. *J. Am. Chem. Soc.* **2001**, *123*, 4855.
5. Hatano, T.; Ikeda, A.; Sano, M.; Kanekiyo, Y.; Shinkai, S. *J. Chem. Soc., Perkin Trans. 2* **2000**, 909.
6. (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.
7. (a) Kano, K.; Tanaka, N.; Minamizono, H.; Kawakita, Y. *Chem. Lett.* **1996**, 925. (b) Kano, K.; Nishiyabu, R.; Asada, T.; Kuroda, Y. *J. Am. Chem. Soc.* **2002**, *124*, 9937. (c) Wang, X.; Pan, J.; Shuang, S.; Zhang, Y. *Supramol. Chem.* **2002**, *14*, 419.
8. A synthetic detail and characterization data relating to **3** can be shown in Ref. 4. The ratio 9:1 sulfonic acid units/porphyrin units in the copolymer was obtained from $^1$H NMR spectroscopy.
9. (a) Kano, K.; Miyake, T.; Uomoto, K.; Sato, T.; Ogawa, T.; Hashimoto, S. *Chem. Lett.* **1983**, 1867. (b) Kano, K.; Nakajima, T.; Takei, M.; Hashimoto, S. *Bull. Chem. Soc. Jpn* **1987**, *60*, 1281. (c) Kano, K.; Minamizono, H.; Kitae, T.; Negi, S. *J. Phys. Chem. A* **1997**, *101*, 6618.
10. Konishi, T.; Ikeda, A.; Asai, M.; Hatano, T.; Shinkai, S.; Fujitsuka, M.; Ito, O.; Tsuchiya, Y.; Kikuchi, J. Submitted for publication.
11. Chidsey, C. E. D.; Bertozzi, C. R.; Putvinski, T. M.; Mujsce, A. M. *J. Am. Chem. Soc.* **1990**, *112*, 4301, and references therein.
12. The absorbance at 430 nm and the photocurrent density in the presence of cyclodextrin is ca. 1.4 and 2.0 times larger than those in the absence of it, respectively. Since the quantum yield is defined as following equation, the quantum yields of **2**–**3**–**4** bilayer is ca. 1.4 times larger than that of **2**–**3** bilayer. $\phi = (i/e)/[I(1 - 10^{-A})]$, $I = (W(\lambda)/(hc)$ where $i$ is the photocurrent density, $e$ is the elementary charge, $I$ is number of photons per unit area and unit time, $\lambda$ is the wavelength of light irradiation, $A$ is absorbance of the adsorbed dyes at $\lambda$ nm, $W$ is light power irradiated at $\lambda$ nm, $c$ is the light velocity, and $h$ is Planck's constant.
13. Tedeschi, C.; Mölhwald, H.; Kirstein, S. *J. Am. Chem. Soc.* **2001**, *123*, 954.