J. Am. Chem. Soc. **2001,** *123,* 4855−4856

Efficient Photocurrent Generation in Novel Self-Assembled Multilayers Comprised of [60]Fullerene−Cationic Homooxacalix[3]arene Inclusion Complex and Anionic Porphyrin Polymer

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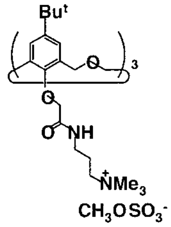
Received January 29, 2001



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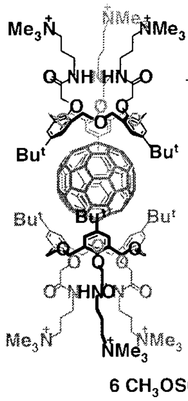

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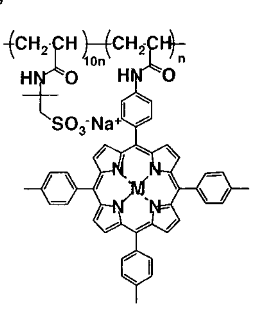

3 (M = 2H)
4 (M = Zn)

The ready availability of [60]fullerene and its homologues as novel electron-pool π-systems has increasingly invited exploration of their outstanding new physical and chemical properties. In particular, the preparation of fullerene thin films is of great interest from both a fundamental and a practical point of view.[1,2] However, the challenge has lain in overcoming the high aggregation tendency of the carbon sphere.[3] One approach is to introduce either thin-layer-forming substituents (such as long aliphatic groups)[4] or surface-adsorptive substituents (such as trimethoxysilyl or mercapto groups)[5,6] into fullerenes. These fullerene derivatives can be deposited on electrode surfaces 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, because the fullerene layers tend to generate long-lived charge-separated states. However, only a few studies have so far been reported for these systems because of their synthetic difficulty in covalently linking all of the thin-layer-forming substituent, donor unit, and acceptor units in one molecular system. It thus occurred to us that a self-assembled method which is easily prepared by alternate adsorption of donor and acceptor layers will offer a promising prospect for the formation of the multilayer photocurrent generation system on electrode.[7] Previously, we reported that a hexacationic homooxacalix[3]arene−[60]fullerene 2:1 complex[8,9] can be deposited on an anion-coated gold surface as a monolayer (or at least as a monolayer-linked ultrathin film): as expected, this membrane showed an efficient redox response in cyclic voltammometry and a photoelectrochemical response under visible light irradiation.[10] Here, we report the facile preparation of a novel [60]fullerene−porphyrin bilayer stabilized by the electrostatic force and the efficient photocurrent generation. The main characteristics of the present system are (1) unmodified [60]fullerene can be assembled as a ultrathin layer because of the encapsulation in cationic homooxacalix[3]arenes, so that sufficient π-conjugate system necessary for efficient electron transfer is retained in it, and (2) all [60]fullerene molecules are insulated from each other by encapsulation.

The preparation of **2** monolayer on an indium−tin oxide (ITO) electrode was similar to that on a gold electrode described in the previous paper.[10,11] The modified ITO electrode was immersed into an aqueous solution containing **3** or **4** (0.37 mg mL^{-1}, respectively).[12] After 20 min, the electrode was washed with ultrapure water and dried with a nitrogen stream (Figure 1).

We measured the UV−vis absorption spectrum of the ITO electrode coated with **2**, **2**−**3**, or **2**−**4** (Figure S2; the broad absorption band at 480−720 nm is caused by the light scattering). The spectrum of **2** displays an absorption maximum at $\lambda_{\max}$ 350 nm, which corresponds to the [60]fullerene absorption in a calixarene−[60]fullerene complex (Abs$_{350}$ = 6.8 × 10^{-3}, Abs$_{400}$ = 2.8 × 10^{-3}) (Figure S2a). From the [60]fullerene absorption ($\epsilon_{341} = 4.8 \times 10^4$), the surface concentration by **2** can be estimated to be 1.4 × 10^{-10} mol cm^{-2}. On the other hand, the bilayers of **2**−**3** and **2**−**4** have an additional absorption maximum at 420 nm (Abs$_{420}$ = 7.6 × 10^{-3}) (Figure S2b) and 428 nm (Abs$_{428}$ = 1.04 × 10^{-2}) (Figure S2c), respectively, which corresponds to the Soret band in the polymer-sustained porphyrin. The red-shift and peak broadening in these Soret bands are similar to those in the porphyrins aggregated on an ITO electrode or in solution.[13] The results support the view that the porphyrin layer is laid on the **2** layer owing to the attractive electrostatic force. On the other hand, the Q-bands appear overlapping with broad absorption at 480−720 nm. From the porphyrin absorption ($\epsilon_{416} = 1.0 \times 10^5$ for **3** and $\epsilon_{423} = 1.9 \times 10^5$ for **4** in water), the surface concentration by **3** and **4** can be estimated to be 7.6 ×

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(11) It is known that the surface of the ITO electrode is very rough, which is not suitable to discussions on the homogeneity of the deposited membranes. Thus, we have evaluated it with the surface of a gold electrode: the SEM and AFM observations have established that the deposited membrane shows the micrograph very similar to the gold surface itself. The result indicates that 3-D aggregate is not formed on the surface. The AFM micrograph is shown in Figure S1.

(12) Synthetic details and characterization data relating to **3** and **4** can be found in the Supporting Information.

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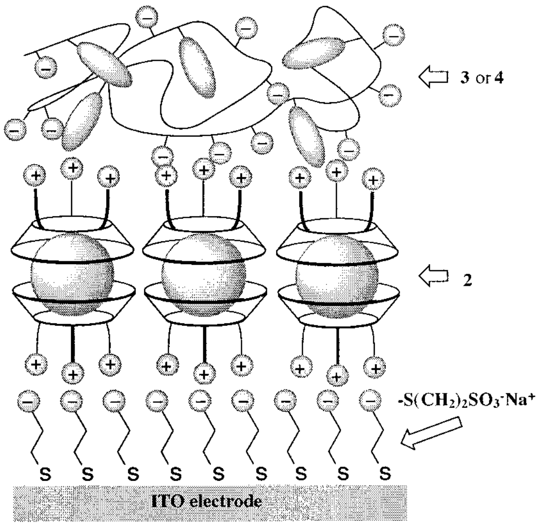

Figure 1. Schematic representation of self-assembled multilayers of sodium 3-mercaptoethanesulfonate (first layer), **2** (second layer), and **3** or **4** (third layer) on an ITO electrode.

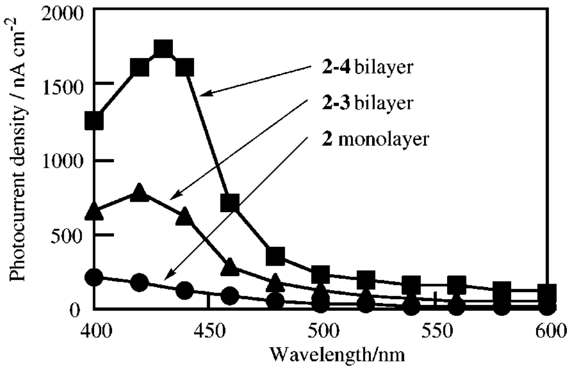

Figure 2. Photocurrent action spectra of **2**, **2**−**3**, and **2**−**4** systems on an ITO electrode at 25 °C (1 mW cm^{-2}, 0.1 M Na_2SO_4 solution containing 50 mM ascorbic acid, pH 3.5).

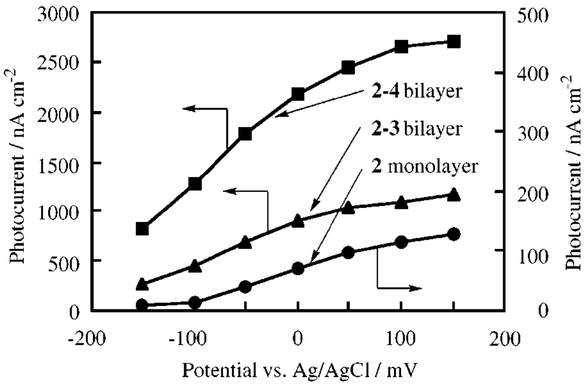

Figure 3. Photocurrent vs bias potential applied to **2** ($\lambda = 400 \pm 16$ nm, 0.56 mW cm^{-2}), **2**−**3** ($\lambda = 420 \pm 16$, 1.36 mW cm^{-2}), and **2**−**4** ($\lambda = 430 \pm 16$, 1.53 mW cm^{-2}) systems on an ITO electrode under monochromatic illumination (0.1 M Na_2SO_4 solution containing 50 mM ascorbic acid, pH 3.5).

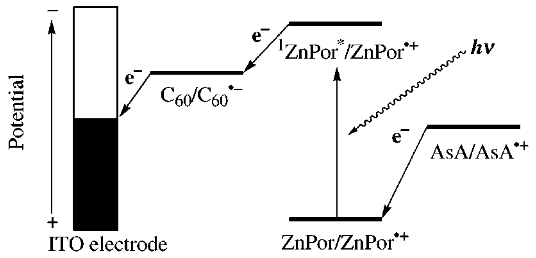

Figure 4. Schematic diagram of the **2**−**4** system. The electrolyte solution contains an electron sacrificer (ascorbic acid: AsA).

10^{-11} and 5.5×10^{-11} mol cm^{-2}, respectively, in terms of the concentrations of porphyrin units. The surface concentration by porphyrin units in **3** and **4** can be estimated to be 0.5 and 0.4 equiv for **2**, respectively, from their absorbance intensity. Since the absorbance at 350 nm corrected by subtracting the absorbance of **3** or **4** is scarcely decreased by the adsorption treatment, one may assume that **2** did not peel off from the ITO electrode in the deposition process of **3** or **4**.

Photocurrent measurements were carried out for **2** monolayer, **2**−**3** bilayer, and **2**−**4** bilayer deposited on the modified ITO electrode in 0.1 M Na_2SO_4 solution containing 50 mM 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 M NaCl) reference electrode.[10] The solution was adjusted to pH 3.5. Figure 2 shows that the action spectra for **2** monolayer, **2**−**3** bilayer, and **2**−**4** bilayer between 400 and 600 nm. It is clearly seen from Figure 2 that the action spectra for **2**−**3** bilayer and **2**−**4** bilayer are markedly increased as compared with that for **2** monolayer. Especially, the increased photocurrent density at 420 nm shows that the porphyrin units of **3** and **4** efficiently act as the photoactive species. On the other hand, the photocurrent of **2**−**3** bilayer and **2**−**4** bilayer is generated at a potential above the first reduction $\{E(C_{60}/C_{60}^{\bullet -})\}$ then increases as the bias voltage becomes more positive (Figure 3). One can conclude, therefore, that it is generated by the electron transfer from the C_{60} to the ITO electrode. These results show that our noncovalently linked system features the photocurrent flow of porphyrin units → C_{60} units → electrode as in the case of the covalently linked dyad or triad systems reported previously (Figure 4).[13,14] The stable anodic photocurrents from this electrolyte to the ITO electrode appeared immediately after the irradiation of the ITO electrode with $\lambda = 400 \pm 16$ (0.56 mW cm^{-2}), 420 ± 16 (1.36 mW cm^{-2}), and 430 ± 16 nm light (1.53 mW cm^{-2}) for **2** monolayer, **2**−**3** bilayer, and **2**−**4** bilayer, respectively. These photoresponsive phenomena could be repeated many times reversibly and the films were sufficiently robust. The quantitative quantum yield can be estimated to be 10, 14, and 21% for **2** monolayer, **2**−**3** bilayer, and **2**−**4** bilayer, respectively. Surprisingly, the value (21%) for the **2**−**4** dyad system is comparable with that (25%) for Sakata's triad system, which has been recorded as the highest quantum yield.[13,14]

In conclusion, the present paper demonstrates that (i) the [60]-fullerene−porphyrin bilayer film can be easily prepared by adsorption of hexacationic **2** and then anionic **3** or **4** onto the anion-covered Au surface and (ii) these films generate a photocurrent response to visible light irradiation. The high quantum yield is related to the inherent function of [60]fullerene encapsulated in cationic homooxacalix[3]arenes and suggests that our self-assembled method is very useful for a novel and simple preparation of photocurrent generators. These studies, which are currently under investigation in this laboratory, can be further extended into triads and tetrads by a convenient alternate adsorption method.

Acknowledgment. We thank Mr. H. Horiuchi for his skill in preparing specially designed glass cells. This work was supported by TOREST (Target Oriented Research for Embryonic Science and Technology) 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.

Supporting Information Available: Synthetic scheme of **3** and **4** and absorption spectra of **2**, **2**−**3**, and **2**−**4** systems (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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