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Description	



# **Supramolecular nanostructured assemblies of different types of porphyrins with fullerene using TiO<sub>2</sub> nanoparticles for light energy conversion**

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## Abstract

TiO<sub>2</sub> nanoparticles were modified with porphyrin derivatives, 5-[4-benzoic acid]-10,15,20-tris[3,5-di-*tert*-butylphenyl]-21*H*,23*H*-porphyrin (**Ar-H<sub>2</sub>P-COOH**), 5-[4-benzoic acid]-10,20-tris[3,5-di-*tert*-butylphenyl]-21*H*,23*H*-porphyrin (**H-H<sub>2</sub>P-COOH**), and 5,10,15,20-tetra[4-benzoic acid]-21*H*,23*H*-porphyrin (**H<sub>2</sub>P-4COOH**). The porphyrin-modified TiO<sub>2</sub> nanoparticles were deposited on nanostructured OTE/SnO<sub>2</sub> electrode together with nanoclusters of fullerene (C<sub>60</sub>) in acetonitrile/toluene (3:1, v/v) using an electrophoretic deposition technique to afford the porphyrin-modified TiO<sub>2</sub> composite electrode denoted as OTE/SnO<sub>2</sub>/(porphyrin-modified TiO<sub>2</sub> nanoparticle+C<sub>60</sub>)<sub>n</sub>. The porphyrin-modified TiO<sub>2</sub> composite electrodes have efficient light absorbing properties in the visible region, exhibiting the photoactive response under visible light excitation using I<sub>3</sub><sup>-</sup>/I<sup>-</sup> redox couple. The incident photon to photocurrent efficiency (IPCE) values of supramolecular nanostructured electrodes of porphyrin-modified TiO<sub>2</sub> nanoparticles with fullerene [OTE/SnO<sub>2</sub>/(**Ar-H<sub>2</sub>P-COO-TiO<sub>2</sub>+C<sub>60</sub>**)<sub>n</sub>, OTE/SnO<sub>2</sub>/(**H-H<sub>2</sub>P-COO-TiO<sub>2</sub>+C<sub>60</sub>**)<sub>n</sub> and OTE/SnO<sub>2</sub>/(**H<sub>2</sub>P-4COO-TiO<sub>2</sub>+C<sub>60</sub>**)<sub>n</sub>] are much larger than those of the reference systems of porphyrin-modified TiO<sub>2</sub> nanoparticles without C<sub>60</sub> [OTE/SnO<sub>2</sub>/(**Ar-H<sub>2</sub>P-COO-TiO<sub>2</sub>**)<sub>n</sub>, OTE/SnO<sub>2</sub>/(**H-H<sub>2</sub>P-COO-TiO<sub>2</sub>**)<sub>n</sub> and OTE/SnO<sub>2</sub>/(**H<sub>2</sub>P-4COO-TiO<sub>2</sub>**)<sub>n</sub>]. In particular, the maximum IPCE value (41%) is obtained for OTE/SnO<sub>2</sub>/(**H-H<sub>2</sub>P-COO-TiO<sub>2</sub>+C<sub>60</sub>**)<sub>n</sub> under the bias potential of 0.2 V vs. SCE. This indicates that the formation of supramolecular complexes between porphyrins and fullerene on TiO<sub>2</sub> nanoparticles plays an important role in improvement of the light energy conversion properties.

## Introduction

Increasing attention has been attracted toward the solar energy to current conversion to develop inexpensive and efficient solar cells.<sup>1-6</sup> The construction of such efficient photovoltaic devices requires an enhanced light-harvesting efficiency of chromophore molecules throughout the solar spectrum together with a highly efficient conversion of the harvested light into electrical energy.<sup>1-6</sup>

Porphyrinoid chromophores have been involved in a number of important biological electron-transfer systems including the primary photochemical reactions of chlorophylls in the photosynthetic reaction centers.<sup>7</sup> Rich and extensive absorption features of porphyrinoid systems result in increased absorption cross-sections and an efficient use of the solar spectrum.<sup>8-10</sup> In purple photosynthetic bacteria, visible light is thereby harvested efficiently by the antenna complexes composed of a wheel-like array of chlorophylls.<sup>11</sup> Since porphyrins contain an extensively conjugated two-dimensional  $\pi$ -system, they are suitable not only for synthetic light-harvesting systems, but also for efficient electron transfer, because the uptake or release of electrons results in minimal structural and solvation change upon electron transfer.<sup>12</sup> In contrast with the two-dimensional porphyrin  $\pi$ -system, fullerenes contain an extensively conjugated three-dimensional  $\pi$  system.<sup>13-15</sup> Buckminsterfullerene ( $C_{60}$ ), for example, is described as having a closed-shell configuration consisting of 30 bonding molecular orbitals with 60  $\pi$ -electrons,<sup>13-15</sup> which is also suitable for the efficient electron-transfer reduction because of the minimal changes of structure and solvation associated with the electron transfer.<sup>16</sup> Judging from the excellent light harvesting properties of porphyrins and the efficient electron-transfer properties of both porphyrins and fullerenes, combination of porphyrins and fullerenes seems to be ideal for fulfilling an enhanced light-harvesting efficiency of chromophores throughout the solar spectrum and a highly efficient conversion of the harvested light into the photocurrent generation. In

addition, porphyrins are known to form supramolecular complexes with C<sub>60</sub>, which contain closest contacts between one of the electron-rich 6:6 bonds of the guest fullerene and the geometric center of the host porphyrins.<sup>17-20</sup> The strong interaction between porphyrins and fullerenes is likely to be a good driving force for the formation of supramolecular complexes between porphyrins and C<sub>60</sub>.<sup>21</sup> Self-assembled monolayers (SAMs) of fullerenes and porphyrins have thereby merited special attention as artificial photosynthetic materials and photonic molecular devices.<sup>22-24</sup> However, such monolayer assemblies possess poor light-harvesting capability, affording only low values of the incident photon-to-photocurrent efficiency (IPCE). In addition, the synthetic difficulty has precluded practical application of such artificial photosynthetic model compounds to develop low-cost photovoltaic devices.

In order to overcome these problems, we have previously reported a simple and new approach to prepare composite clusters of porphyrins and fullerene in a mixture of polar and nonpolar solvents, which are assembled as multilayers on a nanostructured SnO<sub>2</sub> electrode using an electrophoretic deposition technique.<sup>25</sup> The photoelectrochemical properties of the composite systems of porphyrins and fullerene are superior to those of the single component system.<sup>25a</sup> In particular, multi-porphyrin arrays such as porphyrin dendrimers and porphyrin-modified gold nanoclusters with fullerenes exhibit much improved photoelectrochemical properties as compared with the composite clusters of monomeric porphyrin and fullerene.<sup>26</sup>

On the other hand, assembly of dye-modified TiO<sub>2</sub> nanoparticles on electrodes using the electrophoretic deposition technique has also been reported to be useful for preparation of organic thin films to obtain good electron acceptor materials.<sup>3c,d,27,28</sup> The electrophoretic deposition of dye-modified TiO<sub>2</sub> nanoparticles on electrodes is an attractive method for preparation of organic multilayer films. However, assembly of porphyrin-modified TiO<sub>2</sub>

nanoparticles on electrodes using the electrophoretic deposition technique has yet to be applied to construct the supramolecular electrodes with C<sub>60</sub>.

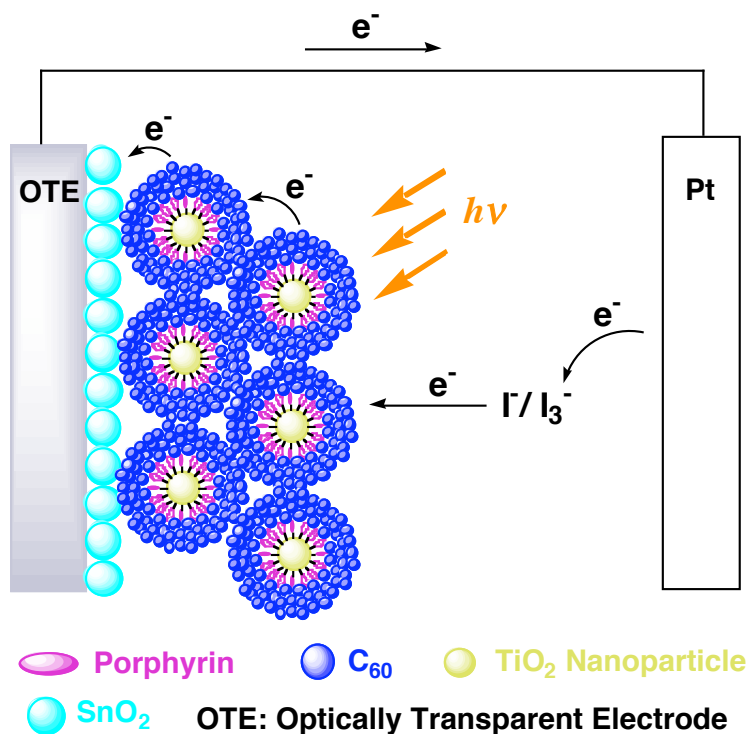
We report herein a new type of organic solar cells based on composite nanoclusters of porphyrin-modified TiO<sub>2</sub> nanoparticles and fullerene and the photoelectrochemical properties, which are different depending on the type of porphyrins shown in Figure 1: 5-[4-benzoic acid]-10,15,20-tris[3,5-di-*tert*-butylphenyl]-21*H*,23*H*-porphyrin (**Ar-H<sub>2</sub>P-COOH**), 5-[4-benzoic acid]-10,20-di[3,5-di-*tert*-butylphenyl]-21*H*,23*H*-porphyrin (**H-H<sub>2</sub>P-COOH**), 5,10,15,20-tetra[4-benzoic acid]-21*H*,23*H*-porphyrin (**H<sub>2</sub>P-4COOH**). The porphyrin (**H<sub>2</sub>P**) moieties are modified with carboxylic acid group (**Ar-H<sub>2</sub>P-COOH**, **H-H<sub>2</sub>P-COOH** and **H<sub>2</sub>P-4COOH** in Figure 1) in order to be assembled on TiO<sub>2</sub> nanoparticles [denoted as **Ar-H<sub>2</sub>P-COO-TiO<sub>2</sub>**, **H-H<sub>2</sub>P-COO-TiO<sub>2</sub>** and **H<sub>2</sub>P-4COO-TiO<sub>2</sub>** in Figure 1, respectively].

### Figure 1

The porphyrin-modified TiO<sub>2</sub> nanoparticles and fullerene nanoclusters are deposited as thin films on optically transparent electrode (OTE) of nanostructured SnO<sub>2</sub> (OTE/SnO<sub>2</sub>) using an electrophoretic method as shown in Scheme 1. We examined the photoelectrochemical properties of composite cluster system using porphyrin-modified TiO<sub>2</sub> nanoparticles (**Ar-H<sub>2</sub>P-COO-TiO<sub>2</sub>**, **H-H<sub>2</sub>P-COO-TiO<sub>2</sub>** and **H<sub>2</sub>P-4COO-TiO<sub>2</sub>**) and fullerene (C<sub>60</sub>) on OTE/SnO<sub>2</sub> electrode [denoted as OTE/SnO<sub>2</sub>/(**Ar-H<sub>2</sub>P-COO-TiO<sub>2</sub>**+C<sub>60</sub>)<sub>n</sub>, OTE/SnO<sub>2</sub>/(**H-H<sub>2</sub>P-COO-TiO<sub>2</sub>**+C<sub>60</sub>)<sub>n</sub> and OTE/SnO<sub>2</sub>/(**H<sub>2</sub>P-4COO-TiO<sub>2</sub>**+C<sub>60</sub>)<sub>n</sub>, respectively] relative to the reference systems containing porphyrin-modified TiO<sub>2</sub> nanoparticles without C<sub>60</sub> [OTE/SnO<sub>2</sub>/(**Ar-H<sub>2</sub>P-COO-TiO<sub>2</sub>**)<sub>n</sub>, OTE/SnO<sub>2</sub>/(**H-H<sub>2</sub>P-COO-TiO<sub>2</sub>**)<sub>n</sub> and OTE/SnO<sub>2</sub>/(**H<sub>2</sub>P-4COO-TiO<sub>2</sub>**)<sub>n</sub>]. The morphology and light energy conversion

properties including the mechanism of these composite cluster systems are described in full detail in this paper.

**Scheme 1**



## Experimental Section

**General.** Chemicals used in this study are of the best grade available, supplied by Tokyo Chemical Industries, Wako Pure Chemical, or Sigma Aldrich Co. <sup>1</sup>H NMR spectra were recorded on a JNM-AL300 (JEOL) instrument at 300 MHz. Matrix-assisted laser desorption/ionization (MALDI) time-of-flight (TOF) mass spectra were measured on a Kratos Compact MALDI I (Shimadzu). TiO<sub>2</sub> nanoparticles (P25, *d* = 21 nm) were purchased from Nippon Aerogel Co. **H<sub>2</sub>P-4COOH** was purchased from Sigma Aldrich Co. Preparation of **Ar-H<sub>2</sub>P-COOH** and **H-H<sub>2</sub>P-COOH** have been described elsewhere.<sup>29,30</sup>

**Preparation of TiO<sub>2</sub> nanoparticles modified with porphyrin moieties.** TiO<sub>2</sub> nanoparticles modified with porphyrin moieties (**Ar-H<sub>2</sub>P-COO-TiO<sub>2</sub>**, **H-H<sub>2</sub>P-COO-TiO<sub>2</sub>** and **H<sub>2</sub>P-4COO-TiO<sub>2</sub>**) were prepared by immersing warmed TiO<sub>2</sub> nanoparticles (80 ~ 100 °C) in acetonitrile (10 mL) containing  $3.0 \times 10^{-4}$  mol dm<sup>-3</sup> of **Ar-H<sub>2</sub>P-COOH**, **H-H<sub>2</sub>P-COOH** and **H<sub>2</sub>P-4COOH** for 12 h, respectively. After adsorbing **Ar-H<sub>2</sub>P-COOH**, **H-H<sub>2</sub>P-COOH** and **H<sub>2</sub>P-4COOH**, TiO<sub>2</sub> nanoparticles were filtered, and the subsequent washing with acetonitrile and drying afforded **Ar-H<sub>2</sub>P-COO-TiO<sub>2</sub>**, **H-H<sub>2</sub>P-COO-TiO<sub>2</sub>** and **H<sub>2</sub>P-4COO-TiO<sub>2</sub>**, respectively. The dye molecules were completely desorbed from TiO<sub>2</sub> nanoparticles into solution by immersing the dye-modified TiO<sub>2</sub> nanoparticles in methanol overnight. The amounts of **Ar-H<sub>2</sub>P-COOH**, **H-H<sub>2</sub>P-COOH** and **H<sub>2</sub>P-4COOH** adsorbed on TiO<sub>2</sub> nanoparticles relative to the total weight were determined as  $2.98 \times 10^{-5}$ ,  $2.98 \times 10^{-5}$ , and  $2.97 \times 10^{-5}$  mol/g, respectively.<sup>28</sup> The molecular packing densities of porphyrins on TiO<sub>2</sub> nanoparticles are approximately the same.

**Electrophoretic deposition of composite clusters on electrode.** C<sub>60</sub> is soluble in nonpolar solvents such as toluene. In mixed solvents (acetonitrile/toluene), however, they aggregate to form large size clusters with diameter of 100 nm - 300 nm.<sup>31</sup> The C<sub>60</sub> cluster and TiO<sub>2</sub> nanoparticles were electrophoretically deposited onto SnO<sub>2</sub> films under an applied potential as reported previously.<sup>28,31</sup>

Nanostructured SnO<sub>2</sub> films were cast on an optically transparent electrode (OTE) by using a dilute (1-2%) colloidal solution (Alfa Chemicals), followed by annealing of the dried film at 673 K. Details about the electrode preparation and its properties have been described elsewhere.<sup>32</sup> These films are highly porous and electrochemically active to conduct charges across the film. The SnO<sub>2</sub> film electrode (OTE/SnO<sub>2</sub>) and an OTE plate were introduced in a 1 cm path length cuvette and were connected to positive and negative terminals of the power supply, respectively. A known amount (~2 mL) of C<sub>60</sub>, porphyrin-



modified TiO<sub>2</sub> nanoparticles (**Ar-H<sub>2</sub>P-COO-TiO<sub>2</sub>**, **H-H<sub>2</sub>P-COO-TiO<sub>2</sub>** and **H<sub>2</sub>P-4COO-TiO<sub>2</sub>**), or the mixed cluster suspension in acetonitrile/toluene (3/1, v/v) immediately after the ultrasonication was transferred to a 1 cm cuvette in which two electrodes (viz., OTE/SnO<sub>2</sub> and OTE) were kept at a distance of ~6 mm using a Teflon spacer. A dc voltage (500 V) was applied between the two electrodes for 2 min using a Fluke 415 power supply. The deposition of the film can be visibly seen as the solution becomes colorless with simultaneous brown coloration of the SnO<sub>2</sub>/OTE electrode. The SnO<sub>2</sub>/OTE electrodes coated with porphyrin-modified TiO<sub>2</sub> nanoparticles (**Ar-H<sub>2</sub>P-COO-TiO<sub>2</sub>**, **H-H<sub>2</sub>P-COO-TiO<sub>2</sub>** and **H<sub>2</sub>P-4COO-TiO<sub>2</sub>**) and C<sub>60</sub> clusters are referred to OTE/SnO<sub>2</sub>/(**Ar-H<sub>2</sub>P-COO-TiO<sub>2</sub>+C<sub>60</sub>**)<sub>n</sub>, OTE/SnO<sub>2</sub>/(**H-H<sub>2</sub>P-COO-TiO<sub>2</sub>+C<sub>60</sub>**)<sub>n</sub>, and OTE/SnO<sub>2</sub>/(**H<sub>2</sub>P-4COO-TiO<sub>2</sub>+C<sub>60</sub>**)<sub>n</sub>, respectively.

The UV-visible spectra were recorded on a Shimadzu 3101 spectrophotometer. Images were recorded using a Hitachi H600 transmission electron microscope. The morphology of the mesoporous electrodes was characterized by a scanning electron micrograph (SEM; JEOL, JSM-6700F).

**Photoelectrochemical measurements.** Photoelectrochemical measurements were performed using a standard three-compartment cell consisting of a working electrode and Pt wire gauze counter electrode and saturated calomel reference electrode (SCE). All photoelectrochemical measurements were performed in acetonitrile containing 0.5 mol dm<sup>-3</sup> NaI and 0.01 mol dm<sup>-3</sup> I<sub>2</sub> with a Keithley model 617 programmable electrometer. A collimated light beam from a 150 W Xenon lamp with a 400 nm cut-off filter was used for excitation of the composite cluster films cast on SnO<sub>2</sub> electrodes. A Bausch and Lomb high intensity grating monochromator was introduced into the path of the excitation beam for selecting wavelength. A Princeton Applied Research (PAR) model 173 potentiostat and Model 175 universal programmer were used for recording I-V characteristics. The IPCE

values were calculated by normalizing the photocurrent values for incident light energy and intensity using eqn. (1),<sup>25</sup>

$$\text{IPCE (\%)} = 100 \times 1240 \times I_{\text{sc}} / (W_{\text{in}} \times \lambda) \quad (1)$$

where  $I_{\text{sc}}$  is the short circuit photocurrent (A/cm<sup>2</sup>),  $W_{\text{in}}$  is the incident light intensity (W/cm<sup>2</sup>), and  $\lambda$  is the wavelength (nm).

## Results and discussion

**Preparation of the composite cluster films of porphyrin-modified TiO<sub>2</sub> nanoparticles and C<sub>60</sub>.** Porphyrins and C<sub>60</sub> are soluble in nonpolar solvents such as toluene, but much less soluble in polar solvents such as acetonitrile.<sup>25,26</sup> By the proper choice of polar to nonpolar solvent, we can achieve a controlled aggregation in the form of the composite nanoclusters. Detailed information of composite nanoclusters of porphyrins and C<sub>60</sub> has been described elsewhere.<sup>25,31</sup> TiO<sub>2</sub> nanoparticles were electrophoretically deposited onto the electrode in suspended solution.<sup>28</sup> Upon subjecting the resultant cluster suspension to a high electric dc field (500 V for 2 min), mixed porphyrin-modified TiO<sub>2</sub> nanoparticles (**Ar-H<sub>2</sub>P-COO-TiO<sub>2</sub>**, **H-H<sub>2</sub>P-COO-TiO<sub>2</sub>** and **H<sub>2</sub>P-4COO-TiO<sub>2</sub>**) and fullerene clusters [(**H<sub>2</sub>P-COO-TiO<sub>2</sub>+C<sub>60</sub>**)<sub>n</sub>] were deposited onto an optically transparent electrode (OTE) of a nanostructured SnO<sub>2</sub> electrode (OTE/SnO<sub>2</sub>), to afford the modified electrode. As the deposition continues we can visually observe decoloration of the solution, accompanied by coloration of the electrode that is connected to positive terminal of the dc power supply. A mixed cluster suspension of porphyrin-modified TiO<sub>2</sub> nanoparticles (**Ar-H<sub>2</sub>P-COO-TiO<sub>2</sub>**, **H-H<sub>2</sub>P-COO-TiO<sub>2</sub>** and **H<sub>2</sub>P-4COO-TiO<sub>2</sub>**) and C<sub>60</sub> were prepared in the

total concentration range from 0.025 to 0.13 mmol dm<sup>-3</sup> (molecular ratio of **H<sub>2</sub>P**:C<sub>60</sub> = 1:5) in acetonitrile/toluene (3/1, v/v). In this case, the mixed clusters were first prepared using different amounts of **H<sub>2</sub>P** on TiO<sub>2</sub> nanoparticle and C<sub>60</sub> to maintain their molar ratio as 1:5. The absorption spectrum of OTE/SnO<sub>2</sub>/(**H<sub>2</sub>P-4COO-TiO<sub>2</sub>+C<sub>60</sub>**)<sub>n</sub> shows that incident light is absorbed strongly in the visible and near-infrared regions (spectrum a in Figure 2). A broad absorption is observed in OTE/SnO<sub>2</sub>/(**H<sub>2</sub>P-4COO-TiO<sub>2</sub>+C<sub>60</sub>**)<sub>n</sub> in the visible region as compared with the reference system without C<sub>60</sub> [OTE/SnO<sub>2</sub>/(**H<sub>2</sub>P-4COO-TiO<sub>2</sub>**)<sub>n</sub>]. Such a broad absorption property of OTE/SnO<sub>2</sub>/(**H<sub>2</sub>P-COO-TiO<sub>2</sub>+C<sub>60</sub>**)<sub>n</sub> may be ascribed to charge-transfer (CT) absorption between porphyrins and C<sub>60</sub>.<sup>25,26,33</sup> Absorption properties of OTE/SnO<sub>2</sub>/(**Ar-H<sub>2</sub>P-COO-TiO<sub>2</sub>+C<sub>60</sub>**)<sub>n</sub> and OTE/SnO<sub>2</sub>/(**H-H<sub>2</sub>P-COO-TiO<sub>2</sub>+C<sub>60</sub>**)<sub>n</sub> are similar to that of OTE/SnO<sub>2</sub>/(**H<sub>2</sub>P-4COO-TiO<sub>2</sub>+C<sub>60</sub>**)<sub>n</sub>.

## Figure 2

**Morphology of OTE/SnO<sub>2</sub>/(H-H<sub>2</sub>P-COO-TiO<sub>2</sub>+C<sub>60</sub>)<sub>n</sub>.** Scanning electron micrograph (SEM) was used to examine the morphology of the OTE/SnO<sub>2</sub>/(**H-H<sub>2</sub>P-COO-TiO<sub>2</sub>+C<sub>60</sub>**)<sub>n</sub> film as shown in Figure 3. The OTE/SnO<sub>2</sub>/(**H-H<sub>2</sub>P-COO-TiO<sub>2</sub>+C<sub>60</sub>**)<sub>n</sub> film is composed of closely packed clusters of about 20-200 nm size with a networked structure, which may result from a supramolecular CT interaction between **H<sub>2</sub>P** and C<sub>60</sub> on TiO<sub>2</sub> nanoparticles. In contrast with the OTE/SnO<sub>2</sub>/(**H-H<sub>2</sub>P-COO-TiO<sub>2</sub>+C<sub>60</sub>**)<sub>n</sub> film, the OTE/SnO<sub>2</sub>/(C<sub>60</sub>)<sub>n</sub> film without porphyrin-modified TiO<sub>2</sub> nanoparticles contain a large size (100 – 300 nm) of nanoclusters as reported previously.<sup>28,31b</sup> Based on these SEM images we can conclude that TiO<sub>2</sub> nanoparticles play an important role in the cluster formation on the films.

### Figure 3

**Photoelectrochemical properties of the composite cluster films of porphyrin-modified TiO<sub>2</sub> nanoparticles and C<sub>60</sub> on OTE/SnO<sub>2</sub> electrodes.** The photoelectrochemical performance was examined using the composite cluster films of porphyrin-modified TiO<sub>2</sub> nanoparticles (**Ar-H<sub>2</sub>P-COO-TiO<sub>2</sub>**, **H-H<sub>2</sub>P-COO-TiO<sub>2</sub>**, and **H<sub>2</sub>P-4COO-TiO<sub>2</sub>**) and C<sub>60</sub> as a photoanode in a photoelectrochemical cell. Photocurrent measurements were performed in acetonitrile containing NaI (0.5 mol dm<sup>-3</sup>) and I<sub>2</sub> (0.01 mol dm<sup>-3</sup>) as redox electrolyte and Pt gauge counter electrode. The photovoltage and photocurrent responses recorded following the excitation of OTE/SnO<sub>2</sub>/**(H-H<sub>2</sub>P-COO-TiO<sub>2</sub>+C<sub>60</sub>)<sub>n</sub>** electrode the visible light region ( $\lambda > 400$  nm) are shown in Figure 4A and B, respectively. The photocurrent response is prompt, steady and reproducible during repeated on/off cycles of the visible light illumination. The short circuit photocurrent density ( $I_{sc}$ ) is 0.095 mA/cm<sup>2</sup>, and open circuit voltage ( $V_{oc}$ ) is 240 mV were reproducibly obtained during these measurements. Blank experiments conducted with OTE/SnO<sub>2</sub> (i.e., by excluding composite clusters **(H-H<sub>2</sub>P-COO-TiO<sub>2</sub>+C<sub>60</sub>)<sub>n</sub>**) produced no detectable photocurrent under the similar experimental conditions. These experiments confirmed the important role of **(H-H<sub>2</sub>P-COO-TiO<sub>2</sub>+C<sub>60</sub>)<sub>n</sub>** assembly towards harvesting light energy and generating photocurrent during the operation of a photoelectrochemical cell.

### Figure 4

The charge separation in the OTE/SnO<sub>2</sub>/**(H-H<sub>2</sub>P-COO-TiO<sub>2</sub>+C<sub>60</sub>)<sub>n</sub>** electrode can be further modulated by the application of an electrochemical bias potential. Figure 5 shows *I-V* characteristics of the OTE/SnO<sub>2</sub>/**(H-H<sub>2</sub>P-COO-TiO<sub>2</sub>+C<sub>60</sub>)<sub>n</sub>** and OTE/SnO<sub>2</sub>/**(H-H<sub>2</sub>P-COO-TiO<sub>2</sub>)<sub>n</sub>** electrodes under the visible light illumination. The photocurrent increases as

the applied potential is scanned towards more positive potentials. Increased charge separation and the facile transport of charge carriers under a positive bias potential are responsible for enhanced photocurrent generation. The ratio of net photocurrent generation of OTE/SnO<sub>2</sub>/(**H-H<sub>2</sub>P-COO-TiO<sub>2</sub>+C<sub>60</sub>**)<sub>n</sub> at +0.2 V *vs.* SCE to that of OTE/SnO<sub>2</sub>/(**H-H<sub>2</sub>P-COO-TiO<sub>2</sub>+C<sub>60</sub>**)<sub>n</sub> at 0 V *vs.* SCE (Figure 5A) is much larger than the case of OTE/SnO<sub>2</sub>/(**H-H<sub>2</sub>P-COO-TiO<sub>2</sub>**)<sub>n</sub> (Figure 5B). This demonstrates that C<sub>60</sub> works as an electron acceptor in the supramolecular complex to enhance the photocurrent generation. At potentials greater than +0.4 V *vs.* SCE, the direct electrochemical oxidation of iodide interferes with the photocurrent measurement.

### Figure 5

A series of photocurrent action spectra were recorded in order to evaluate the photoresponse of the composite clusters towards the photocurrent generation. First, we measured the photocurrent action spectra of OTE/SnO<sub>2</sub>/(**Ar-H<sub>2</sub>P-COO-TiO<sub>2</sub>**)<sub>n</sub>, OTE/SnO<sub>2</sub>/(**H-H<sub>2</sub>P-COO-TiO<sub>2</sub>**)<sub>n</sub> and OTE/SnO<sub>2</sub>/(**H<sub>2</sub>P-4COO-TiO<sub>2</sub>**)<sub>n</sub> as shown in Figure 6. Photocurrent generation is observed under no applied bias potential using a standard two-compartment cell consisting of a working electrode and Pt wire gauze counter electrode to attain 2~6% of maximum IPCE values (spectra a in Figure 6A, 6B and 6C, respectively). We also measured the photocurrent action spectra of OTE/SnO<sub>2</sub>/(**Ar-H<sub>2</sub>P-COO-TiO<sub>2</sub>**)<sub>n</sub>, OTE/SnO<sub>2</sub>/(**H-H<sub>2</sub>P-COO-TiO<sub>2</sub>**)<sub>n</sub> and OTE/SnO<sub>2</sub>/(**H<sub>2</sub>P-4COO-TiO<sub>2</sub>**)<sub>n</sub> under an applied bias potential of 0.2 V *vs.* SCE using a standard three-compartment cell as a working electrode along with Pt wire gauze counter electrode and saturated calomel reference electrode (SCE) (spectra b in Figure 6A, 6B and 6C, respectively). The maximum IPCE value (~20%) is obtained for OTE/SnO<sub>2</sub>/(**H<sub>2</sub>P-4COO-TiO<sub>2</sub>**)<sub>n</sub>, which is much larger than those of

OTE/SnO<sub>2</sub>/(Ar-H<sub>2</sub>P-COO-TiO<sub>2</sub>)<sub>n</sub> (~3.5%) and OTE/SnO<sub>2</sub>/(H-H<sub>2</sub>P-COO-TiO<sub>2</sub>)<sub>n</sub> (~6%). This demonstrates that the difference in the IPCE values results from different electron injection properties from the excited state of porphyrins to the conduction band of TiO<sub>2</sub> semiconductor nanocrystallites. From the structural point of view between porphyrin moieties and TiO<sub>2</sub> nanoparticles, porphyrin moieties definitely lie on the TiO<sub>2</sub> surface because of four-point connection in the case of H<sub>2</sub>P-4COO-TiO<sub>2</sub>, whereas porphyrin moieties may stand on the TiO<sub>2</sub> surface in the cases of OTE/SnO<sub>2</sub>/(Ar-H<sub>2</sub>P-COO-TiO<sub>2</sub>)<sub>n</sub> and OTE/SnO<sub>2</sub>/(H-H<sub>2</sub>P-COO-TiO<sub>2</sub>)<sub>n</sub> as shown in Figure 1. The close distance between porphyrins and TiO<sub>2</sub> surface in H<sub>2</sub>P-4COO-TiO<sub>2</sub> relative to that of Ar-H<sub>2</sub>P-COO-TiO<sub>2</sub> or H-H<sub>2</sub>P-COO-TiO<sub>2</sub> may result in an efficient electron transfer from the excited state of the porphyrin moiety of H<sub>2</sub>P-4COO-TiO<sub>2</sub> to the conduction band of TiO<sub>2</sub> semiconductor nanocrystallites.

### Figure 6

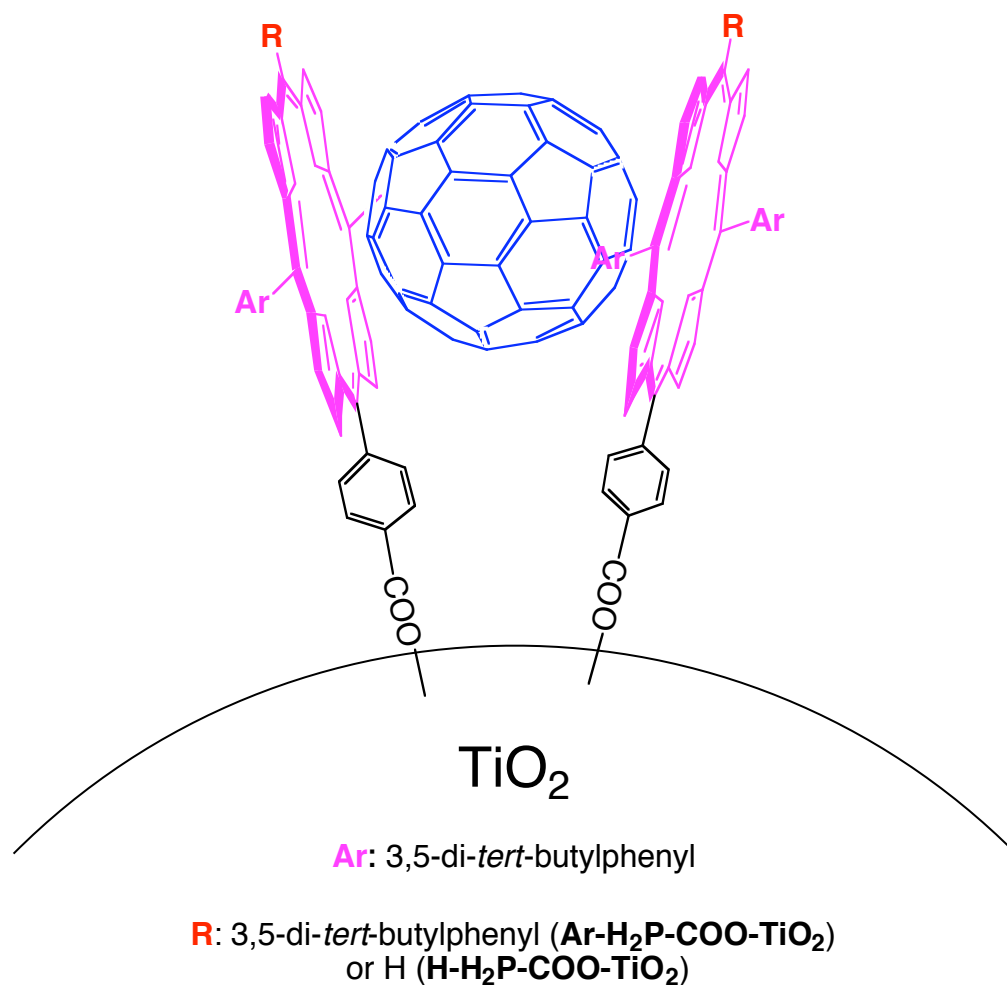
We have also measured the photocurrent action spectra of OTE/SnO<sub>2</sub>/(Ar-H<sub>2</sub>P-COO-TiO<sub>2</sub>+C<sub>60</sub>)<sub>n</sub>, OTE/SnO<sub>2</sub>/(H-H<sub>2</sub>P-COO-TiO<sub>2</sub>+C<sub>60</sub>)<sub>n</sub> and OTE/SnO<sub>2</sub>/(H<sub>2</sub>P-4COO-TiO<sub>2</sub>+C<sub>60</sub>)<sub>n</sub> in order to evaluate the effect of C<sub>60</sub> on the IPCE values as shown in Figure 7. IPCE values of these composite cluster systems under an applied bias potential of 0.2 V vs. SCE become larger than those under no applied potential, as observed for porphyrin-modified TiO<sub>2</sub> nanoparticle films without C<sub>60</sub> (Figure 6). The IPCE values of composite cluster electrodes (Figure 7A, B and C) also become larger than those of the individual systems [OTE/SnO<sub>2</sub>/(C<sub>60</sub>)<sub>n</sub> (Figure 7D) or OTE/SnO<sub>2</sub>/(porphyrin-modified TiO<sub>2</sub> nanoparticle)<sub>n</sub> (Figure 6)]. In particular, the maximum IPCE value of OTE/SnO<sub>2</sub>/(H-H<sub>2</sub>P-COO-TiO<sub>2</sub>+C<sub>60</sub>)<sub>n</sub> under the bias of 0.2 V vs. SCE (~42%) is much larger than the sum of two

individual IPCE values (spectrum c in Figure 7B: ~12%) of OTE/SnO<sub>2</sub>/(**H-H<sub>2</sub>P-COO-TiO<sub>2</sub>**)<sub>n</sub> (spectrum b in figure 6B) and OTE/SnO<sub>2</sub>/(C<sub>60</sub>)<sub>n</sub> (spectrum b in Figure 7D) with the same concentrations of **H<sub>2</sub>P** and C<sub>60</sub>. This indicates that the interaction between **H<sub>2</sub>P** and C<sub>60</sub> contributes significantly to an increase in the IPCE value.

### Figure 7

We have further compared the action spectrum of OTE/SnO<sub>2</sub>/(**H-H<sub>2</sub>P-COO-TiO<sub>2</sub>+C<sub>60</sub>**)<sub>n</sub> with those of OTE/SnO<sub>2</sub>/(**Ar-H<sub>2</sub>P-COO-TiO<sub>2</sub>+C<sub>60</sub>**)<sub>n</sub> and OTE/SnO<sub>2</sub>/(**H<sub>2</sub>P-4COO-TiO<sub>2</sub>+C<sub>60</sub>**)<sub>n</sub>. It should be noted that the molecular packing densities of porphyrins on TiO<sub>2</sub> nanoparticles are approximately the same in OTE/SnO<sub>2</sub>/(**H-H<sub>2</sub>P-COO-TiO<sub>2</sub>+C<sub>60</sub>**)<sub>n</sub>, OTE/SnO<sub>2</sub>/(**Ar-H<sub>2</sub>P-COO-TiO<sub>2</sub>+C<sub>60</sub>**)<sub>n</sub> and OTE/SnO<sub>2</sub>/(**H<sub>2</sub>P-4COO-TiO<sub>2</sub>+C<sub>60</sub>**)<sub>n</sub> (vide supra). In the case of comparison between OTE/SnO<sub>2</sub>/(**H-H<sub>2</sub>P-COO-TiO<sub>2</sub>+C<sub>60</sub>**)<sub>n</sub> and OTE/SnO<sub>2</sub>/(**Ar-H<sub>2</sub>P-COO-TiO<sub>2</sub>+C<sub>60</sub>**)<sub>n</sub> under the bias of 0.2 V vs. SCE, the IPCE value of OTE/SnO<sub>2</sub>/(**H-H<sub>2</sub>P-COO-TiO<sub>2</sub>+C<sub>60</sub>**)<sub>n</sub> (spectrum b in Figure 7B) is much larger than that of OTE/SnO<sub>2</sub>/(**Ar-H<sub>2</sub>P-COO-TiO<sub>2</sub>+C<sub>60</sub>**)<sub>n</sub> (spectrum b in Figure 7A). The absence of 3,5-di-*tert*-butylphenyl substituent at the 15-*meso* position of porphyrin ring in **H-H<sub>2</sub>P-COO-TiO<sub>2</sub>** may enhance the interaction with C<sub>60</sub>, which can be inserted between two porphyrin rings of the porphyrin assembly on TiO<sub>2</sub> nanoparticles (Scheme 2), as compared with **Ar-H<sub>2</sub>P-COO-TiO<sub>2</sub>** in which the *meso* positions are fully substituted. The stronger interaction between the less bulky porphyrins and C<sub>60</sub> leads to an increase in the IPCE value. Such a sandwiched structure of C<sub>60</sub> inserted between two porphyrin rings in Scheme 2 may be impossible in the case of OTE/SnO<sub>2</sub>/(**H<sub>2</sub>P-4COO-TiO<sub>2</sub>+C<sub>60</sub>**)<sub>n</sub> because of the four-point connection of the porphyrin ring onto the TiO<sub>2</sub> surface. This may be the reason why the IPCE values of OTE/SnO<sub>2</sub>/(**H<sub>2</sub>P-4COO-TiO<sub>2</sub>**)<sub>n</sub> under an applied bias potential of 0.2 V vs.

SCE (spectrum b in Figure 7C) are smaller than those of OTE/SnO<sub>2</sub>/(**H-H<sub>2</sub>P-COO-TiO<sub>2</sub>**)<sub>n</sub> (spectrum b in Figure 7B).<sup>34</sup> Based on these results, we can conclude that three dimensional steric control between donor and acceptor moieties is a key factor for construction of efficient organic solar devices.



**Scheme 2.** Illustration of supramolecular assembly between porphyrins and C<sub>60</sub> in (**Ar-H<sub>2</sub>P-COO-TiO<sub>2</sub>**+C<sub>60</sub>)<sub>n</sub> and (**H-H<sub>2</sub>P-COO-TiO<sub>2</sub>**+C<sub>60</sub>)<sub>n</sub>.



**Power conversion efficiency.** The power conversion efficiency ( $\eta$ ) of the photoelectrochemical cell was determined by varying the load resistance with use of eqn. (2),<sup>25a</sup>

$$\eta = ff \times I_{sc} \times V_{oc} / W_{in} \quad (2)$$

where the fill factor ( $ff$ ) is defined as  $ff = P_{max} / (V_{oc} \times I_{sc})$ ;  $P_{max}$  is the maximum power output of the cell,  $V_{oc}$  is the open circuit photovoltage,  $I_{sc}$  is the short circuit photocurrent. A decrease in the photovoltage accompanied by an increase in the photocurrent is observed with decreasing the load resistance as shown in Figure 8. The detailed characteristics of the

### Figure 8

O<sub>TE</sub>/SnO<sub>2</sub>/(**H-H<sub>2</sub>P-COO-TiO<sub>2</sub>**)<sub>n</sub>, O<sub>TE</sub>/SnO<sub>2</sub>/(**H-H<sub>2</sub>P-COO-TiO<sub>2</sub>+C<sub>60</sub>**)<sub>n</sub> and O<sub>TE</sub>/-SnO<sub>2</sub>/(**H<sub>2</sub>P-4COO-TiO<sub>2</sub>+C<sub>60</sub>**)<sub>n</sub> electrodes are summarized in Table 1. The  $I_{sc}$  and  $V_{oc}$  values of O<sub>TE</sub>/SnO<sub>2</sub>/(**H-H<sub>2</sub>P-COO-TiO<sub>2</sub>+C<sub>60</sub>**)<sub>n</sub> are much larger than those of O<sub>TE</sub>/SnO<sub>2</sub>/(**H-H<sub>2</sub>P-COO-TiO<sub>2</sub>**)<sub>n</sub>, leading to more than 4 times improvement of the  $\eta$  value (0.11%) as compared with that of O<sub>TE</sub>/SnO<sub>2</sub>/(**H-H<sub>2</sub>P-COO-TiO<sub>2</sub>**)<sub>n</sub> (0.025%). Furthermore, the  $\eta$  value of highly organized O<sub>TE</sub>/SnO<sub>2</sub>/(**H-H<sub>2</sub>P-COO-TiO<sub>2</sub>+C<sub>60</sub>**)<sub>n</sub> using TiO<sub>2</sub> nanoparticles is about 3 times larger than that of non-organized composite cluster system of porphyrin and fullerene without TiO<sub>2</sub> nanoparticles, which was reported previously (~0.03%).<sup>25a,26a,b</sup> The  $\eta$  value of O<sub>TE</sub>/SnO<sub>2</sub>/(**H<sub>2</sub>P-4COO-TiO<sub>2</sub>+C<sub>60</sub>**)<sub>n</sub> (0.10%) is about the same as that of O<sub>TE</sub>/SnO<sub>2</sub>/(**H-H<sub>2</sub>P-COO-TiO<sub>2</sub>+C<sub>60</sub>**)<sub>n</sub> (0.11%).

**Table 1**

**Photocurrent generation mechanism.** The photocurrent generation mechanism in composite cluster systems of porphyrin and fullerene has previously been reported to be initiated by ultrafast electron transfer from the singlet excited state of porphyrin to  $C_{60}$  in the femtosecond time domain.<sup>25,26</sup> In the case of the reference systems without  $C_{60}$  [OTE/SnO<sub>2</sub>/(Ar-H<sub>2</sub>P-COO-TiO<sub>2</sub>)<sub>n</sub>, OTE/SnO<sub>2</sub>/(H-H<sub>2</sub>P-COO-TiO<sub>2</sub>)<sub>n</sub>, and OTE/SnO<sub>2</sub>/(H<sub>2</sub>P-4COO-TiO<sub>2</sub>)<sub>n</sub>], the photoexcitation of H<sub>2</sub>P moiety results in electron injection from the singlet excited state of the dye into the conduction band and/or trap states of TiO<sub>2</sub> nanoparticles to produce the porphyrin radical cation (H<sub>2</sub>P<sup>•+</sup>). The electrons collected on TiO<sub>2</sub> nanoparticles are furthermore injected into SnO<sub>2</sub> nanocrystallites ( $E_{CB} = 0$  V vs. NHE)<sup>25a</sup> to produce the photocurrent in the circuit. The resulting porphyrin radical cation (H<sub>2</sub>P<sup>•+</sup>) produced in the photoinduced electron injection to the conduction band of TiO<sub>2</sub> is reduced by electrolyte (I<sub>3</sub><sup>-</sup>/I = 0.5 V vs. NHE) in the multilayer film.<sup>25</sup> At the counter electrode, the electron reduces the oxidized electrolyte (I<sub>3</sub><sup>-</sup>), leading to the photocurrent generation.

In the cases of OTE/SnO<sub>2</sub>/(H-H<sub>2</sub>P-COO-TiO<sub>2</sub>+C<sub>60</sub>)<sub>n</sub>, OTE/SnO<sub>2</sub>/(H-H<sub>2</sub>P-COO-TiO<sub>2</sub>+C<sub>60</sub>)<sub>n</sub> and OTE/SnO<sub>2</sub>/(H<sub>2</sub>P-4COO-TiO<sub>2</sub>+C<sub>60</sub>)<sub>n</sub>, not only TiO<sub>2</sub> nanoparticles, but also C<sub>60</sub> molecules (C<sub>60</sub>/C<sub>60</sub><sup>•-</sup> = -0.2 V vs. NHE)<sup>25a</sup> act as an electron acceptor, leading to the enhancement of the photocurrent generation efficiency in composite cluster systems (porphyrin-modified TiO<sub>2</sub> nanoparticle and C<sub>60</sub>) as compared with the systems without C<sub>60</sub>. The major pathway contributing to the enhanced photocurrent generation is the intermolecular charge transfer between excited H<sub>2</sub>P and C<sub>60</sub> within the supramolecular complex to produce H<sub>2</sub>P<sup>•+</sup> and C<sub>60</sub><sup>•-</sup>. Photoinduced electron transfer from the porphyrin singlet excited state (<sup>1</sup>H<sub>2</sub>P<sup>\*</sup>) to C<sub>60</sub> is thermodynamically feasible as evident from the oxidation potential of <sup>1</sup>H<sub>2</sub>P<sup>\*</sup> (<sup>1</sup>H<sub>2</sub>P<sup>\*</sup>/H<sub>2</sub>P<sup>•+</sup> = -0.7 V vs. NHE),<sup>25</sup> which is more negative than the reduction potential of C<sub>60</sub> (C<sub>60</sub>/C<sub>60</sub><sup>•-</sup> = -0.2 V vs. NHE).<sup>25a</sup> Such photoinduced electron

transfer from the excited porphyrins to  $C_{60}$  has been well established by earlier studies.<sup>16,26</sup>

$C_{60}^{\bullet-}$  is also generated from the interaction between excited  $C_{60}$  ( $C_{60}^*$ ) and iodide ions present in the electrolyte. Collectively, these  $C_{60}^{\bullet-}$  species accumulated in clusters transfer electrons to  $SnO_2$  nanocrystallites ( $E_{CB} = 0$  V vs. NHE),<sup>25,31</sup> to produce the current in the circuit. The regeneration of  $H_2P$  ( $H_2P/H_2P^{2+} = 1.2$  V vs. NHE)<sup>25</sup> is achieved by the triiodide/iodide couple ( $I_3^-/I^- = 0.5$  V vs. NHE)<sup>25</sup> present in the electrolyte system. The improvement of IPCE values under an applied bias potential of 0.2 V vs. SCE relative to the corresponding systems under no applied potential results from an increase of driving force of electron transfer from  $C_{60}^{\bullet-}$  to  $SnO_2$  nanocrystallites using a standard three-compartment cell.

## Conclusion

We have successfully constructed supramolecular photovoltaic cells composed of molecular nanocluster assemblies of porphyrin and fullerene, which are well organized with  $TiO_2$  nanoparticles. The IPCE values of the composite cluster systems of porphyrins and  $C_{60}$  with  $TiO_2$  nanoparticles [OTE/ $SnO_2/(H-H_2P-COO-TiO_2+C_{60})_n$ , OTE/ $SnO_2/(H-H_2P-COO-TiO_2+C_{60})_n$  and OTE/ $SnO_2/(H_2P-4COO-TiO_2+C_{60})_n$ ] are improved as compared with the reference systems [OTE/ $SnO_2/(H-H_2P-COO-TiO_2)_n$ , OTE/ $SnO_2/(H-H_2P-COO-TiO_2)_n$  and OTE/ $SnO_2/(H_2P-4COO-TiO_2)_n$ ]. The largest  $\eta$  value is achieved in OTE/ $SnO_2/(H-H_2P-COO-TiO_2)_n$  (0.11%) composed of the porphyrin-modified  $TiO_2$  nanoparticles and  $C_{60}$  clusters.

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34. The IPCE values in Figure 7C are particularly smaller than those in Figure 7B in the longer wavelength region because of the more unfavorable interaction between **H<sub>2</sub>P-4COO-TiO<sub>2</sub>** and C<sub>60</sub> as compared with that between **H-H<sub>2</sub>P-COO-TiO<sub>2</sub>** and C<sub>60</sub>.

**Table 1.** Performance characteristics of OTE/SnO<sub>2</sub>/(H-H<sub>2</sub>P-COO-TiO<sub>2</sub>)<sub>n</sub>, OTE/SnO<sub>2</sub>/(H-H<sub>2</sub>P-COO-TiO<sub>2</sub>+C<sub>60</sub>)<sub>n</sub>, and OTE/SnO<sub>2</sub>/(H<sub>2</sub>P-4COO-TiO<sub>2</sub>+C<sub>60</sub>)<sub>n</sub>

System	$V_{oc}$ (mV)	$I_{sc}$ (mA cm <sup>-2</sup> )	$ff$	$\eta$ (%) <sup>a</sup>
(H-H <sub>2</sub> P-COO-TiO <sub>2</sub> ) <sub>n</sub>	160	0.035	0.31	0.025
(H-H <sub>2</sub> P-COO-TiO <sub>2</sub> +C <sub>60</sub> ) <sub>n</sub>	240	0.095	0.33	0.11
(H <sub>2</sub> P-4COO-TiO <sub>2</sub> +C <sub>60</sub> ) <sub>n</sub>	220	0.11	0.29	0.10

<sup>a</sup>Electrolyte: 0.5 mol dm<sup>-3</sup> NaI and 0.01 mol dm<sup>-3</sup> in acetonitrile; white light illumination ( $\lambda$  > 400 nm); input power; 6.8 mW cm<sup>-2</sup>.

## Figure Captions

**Figure 1.** TiO<sub>2</sub> nanoparticles modified with porphyrin dyes and the reference compounds employed in this study.

**Figure 2.** (A) Absorption spectra of (a) OTE/SnO<sub>2</sub>/(H<sub>2</sub>P-4COO-TiO<sub>2</sub>+C<sub>60</sub>)<sub>n</sub> ([H<sub>2</sub>P] = 0.025 mmol dm<sup>-3</sup>, [C<sub>60</sub>] = 0.13 mmol dm<sup>-3</sup>), (b) OTE/SnO<sub>2</sub>/(H<sub>2</sub>P-4COO-TiO<sub>2</sub>)<sub>n</sub> ([H<sub>2</sub>P] = 0.025 mmol dm<sup>-3</sup>), (c) H<sub>2</sub>P-4COOH in toluene/*tert*-butanol (v/v, 1/1) (10 μmol dm<sup>-3</sup>) and (d) C<sub>60</sub> in toluene (15 μmol dm<sup>-3</sup>).

**Figure 3.** SEM (scanning electron micrograph) image of OTE/SnO<sub>2</sub>/(H-H<sub>2</sub>P-COO-TiO<sub>2</sub>+C<sub>60</sub>)<sub>n</sub> ([H<sub>2</sub>P] = 0.025 mmol dm<sup>-3</sup>, [C<sub>60</sub>] = 0.13 mmol dm<sup>-3</sup>).

**Figure 4.** (A) Photovoltage and (B) photocurrent generation at OTE/SnO<sub>2</sub>/(H-H<sub>2</sub>P-COO-TiO<sub>2</sub>+C<sub>60</sub>)<sub>n</sub> ([H<sub>2</sub>P] = 0.025 mmol dm<sup>-3</sup>, [C<sub>60</sub>] = 0.13 mmol dm<sup>-3</sup>) under illumination of white light (λ > 400 nm); electrolyte: 0.5 mol dm<sup>-3</sup> NaI and 0.01 mol dm<sup>-3</sup> I<sub>2</sub> in acetonitrile; input power: 6.8 mW cm<sup>-2</sup>.

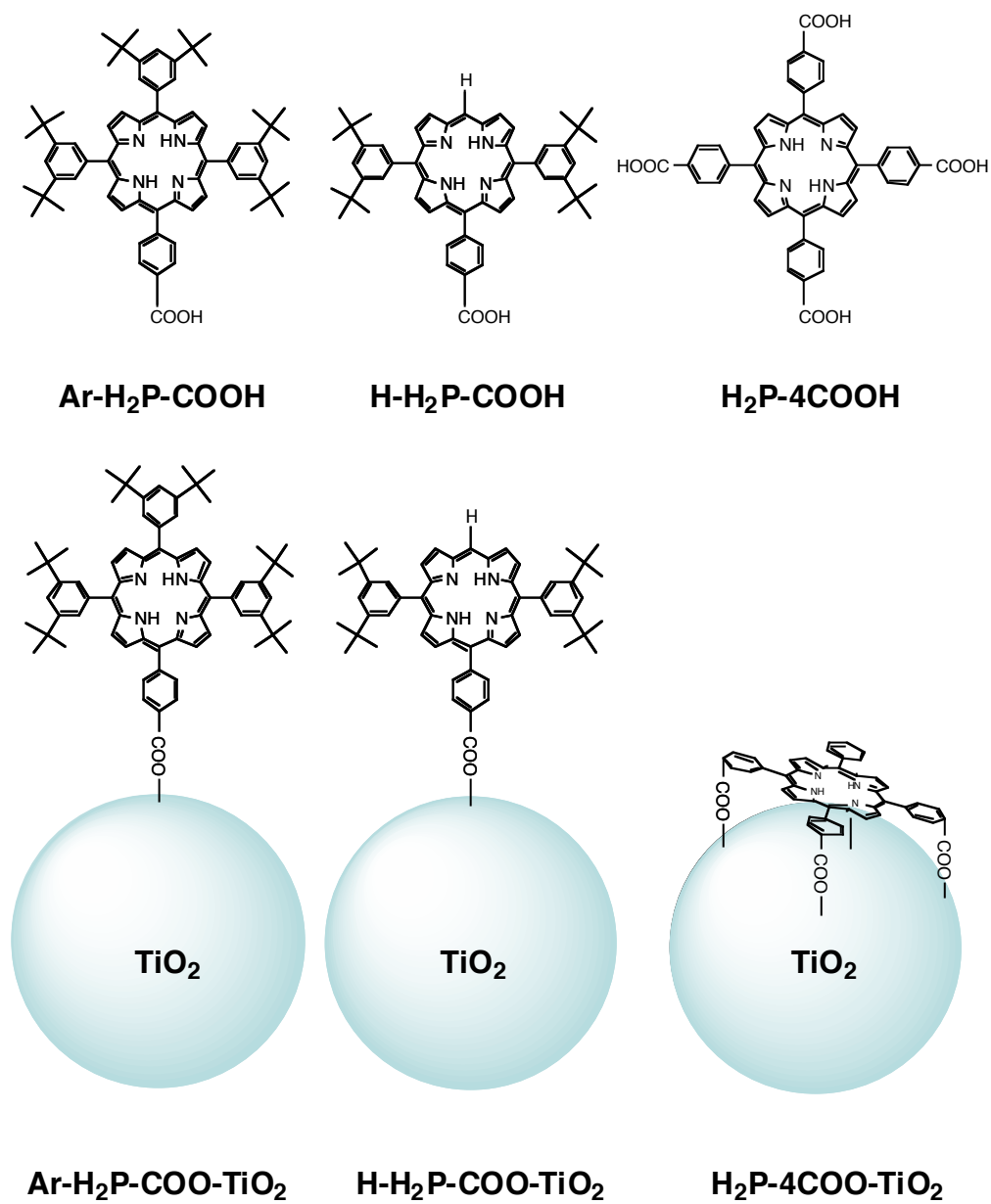
**Figure 5.** *I-V* characteristics of (A) OTE/SnO<sub>2</sub>/(H-H<sub>2</sub>P-COO-TiO<sub>2</sub>+C<sub>60</sub>)<sub>n</sub> ([H<sub>2</sub>P] = 0.025 mmol dm<sup>-3</sup>, [C<sub>60</sub>] = 0.13 mmol dm<sup>-3</sup>) and (B) OTE/SnO<sub>2</sub>/(H-H<sub>2</sub>P-COO-TiO<sub>2</sub>)<sub>n</sub> ([H<sub>2</sub>P] = 0.025 mmol dm<sup>-3</sup>) under illumination of white light (λ > 400 nm); electrolyte: 0.5 mol dm<sup>-3</sup> NaI and 0.01 mol dm<sup>-3</sup> I<sub>2</sub> in acetonitrile; input power: 27.8 mW cm<sup>-2</sup>.

**Figure 6.** (A) Photocurrent action spectra of OTE/SnO<sub>2</sub>/(Ar-H<sub>2</sub>P-COO-TiO<sub>2</sub>)<sub>n</sub> ([H<sub>2</sub>P] = 0.025 mmol dm<sup>-3</sup>) (a) with no applied bias potential and (b) at an applied bias potential of 0.2 V vs. SCE. (B) Photocurrent action spectra of OTE/SnO<sub>2</sub>/(H-H<sub>2</sub>P-COO-TiO<sub>2</sub>)<sub>n</sub> ([H<sub>2</sub>P] = 0.025 mmol dm<sup>-3</sup>) (a) with no applied bias potential and (b) at an applied bias potential of 0.2 V vs. SCE. (C) Photocurrent action spectra of OTE/SnO<sub>2</sub>/(H<sub>2</sub>P-4COO-TiO<sub>2</sub>)<sub>n</sub> ([H<sub>2</sub>P] = 0.025 mmol dm<sup>-3</sup>) (a) with no applied bias potential and (b) at an applied bias potential of 0.2 V vs. SCE. electrolyte: 0.5 mol dm<sup>-3</sup> NaI and 0.01 mol dm<sup>-3</sup> I<sub>2</sub> in acetonitrile.

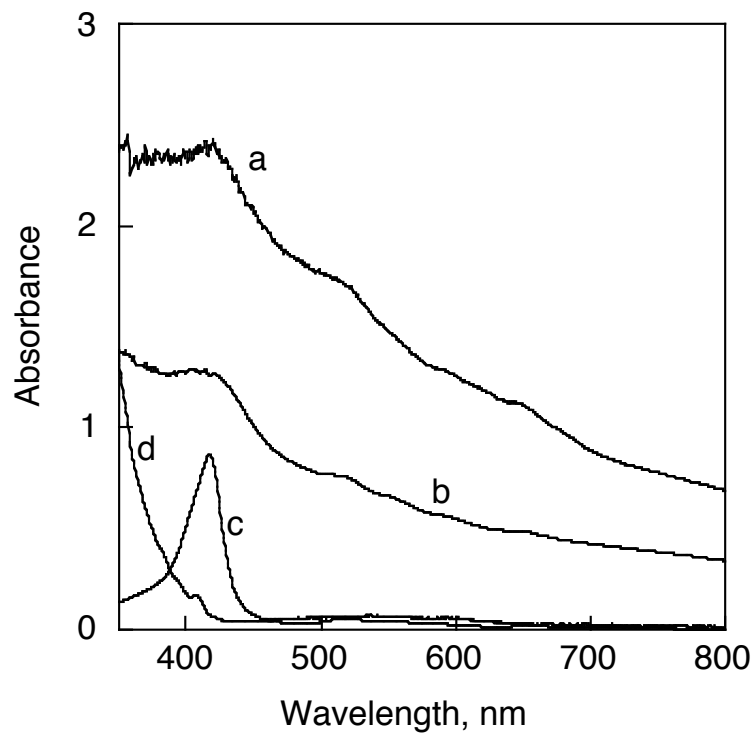
**Figure 7.** (A) Photocurrent action spectra of OTE/SnO<sub>2</sub>/(Ar-H<sub>2</sub>P-COO-TiO<sub>2</sub>+C<sub>60</sub>)<sub>n</sub> ([H<sub>2</sub>P] = 0.025 mmol dm<sup>-3</sup>, [C<sub>60</sub>] = 0.13 mmol dm<sup>-3</sup>) (a) with no applied bias potential and (b) at an applied bias potential of 0.2 V *vs.* SCE. (B) Photocurrent action spectra of OTE/SnO<sub>2</sub>/(H-H<sub>2</sub>P-COO-TiO<sub>2</sub>+C<sub>60</sub>)<sub>n</sub> ([H<sub>2</sub>P] = 0.025 mmol dm<sup>-3</sup>, [C<sub>60</sub>] = 0.13 mmol dm<sup>-3</sup>) (a) with no applied bias potential and (b) at an applied bias potential of 0.2 V *vs.* SCE. (c) Sum of two individual IPCE values of OTE/SnO<sub>2</sub>/(H-H<sub>2</sub>P-COO-TiO<sub>2</sub>)<sub>n</sub> (spectrum b in Figure 6B) and OTE/SnO<sub>2</sub>/(C<sub>60</sub>)<sub>n</sub> (spectrum b in Figure 7D) at an applied bias potential of 0.2 V *vs.* SCE. (C) Photocurrent action spectra of OTE/SnO<sub>2</sub>/(H<sub>2</sub>P-4COO-TiO<sub>2</sub>+C<sub>60</sub>)<sub>n</sub> ([H<sub>2</sub>P] = 0.025 mmol dm<sup>-3</sup>, [C<sub>60</sub>] = 0.13 mmol dm<sup>-3</sup>) (a) with no applied bias potential and (b) at an applied bias potential of 0.2 V *vs.* SCE. (D) Photocurrent action spectra of OTE/SnO<sub>2</sub>/(C<sub>60</sub>)<sub>n</sub> ([C<sub>60</sub>] = 0.13 mmol dm<sup>-3</sup>) (a) with no applied bias potential and (b) at an applied bias potential of 0.2 V *vs.* SCE. electrolyte: 0.5 mol dm<sup>-3</sup> NaI and 0.01 mol dm<sup>-3</sup> I<sub>2</sub> in acetonitrile.

**Figure 8.** Power characteristics of (a) OTE/SnO<sub>2</sub>/(H-H<sub>2</sub>P-COO-TiO<sub>2</sub>+C<sub>60</sub>)<sub>n</sub> ([H<sub>2</sub>P] = 0.025 mmol dm<sup>-3</sup>, [C<sub>60</sub>] = 0.13 mmol dm<sup>-3</sup>) and (b) OTE/SnO<sub>2</sub>/(H-H<sub>2</sub>P-COO-TiO<sub>2</sub>)<sub>n</sub> ([H<sub>2</sub>P] = 0.025 mmol dm<sup>-3</sup>) under white light illumination ( $\lambda > 400$  nm); electrolyte: 0.5 mol dm<sup>-3</sup> NaI and 0.01 mol dm<sup>-3</sup> I<sub>2</sub> in acetonitrile; input power: 6.8 mW cm<sup>-2</sup>.

Figure 1



**Figure 2**



**Figure 3**

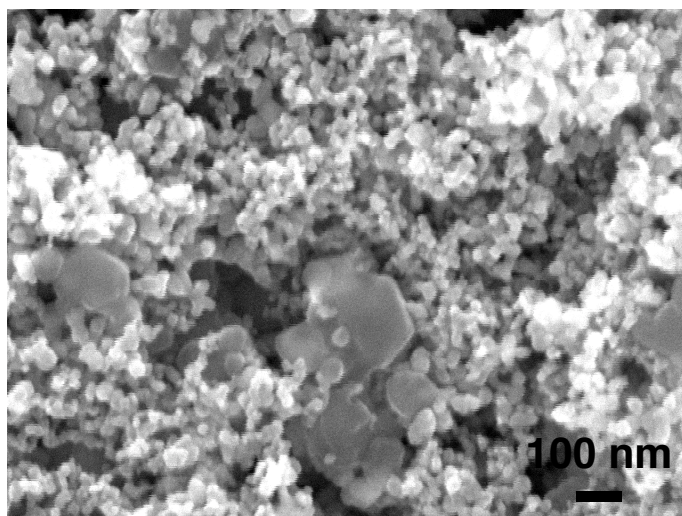


Figure 4

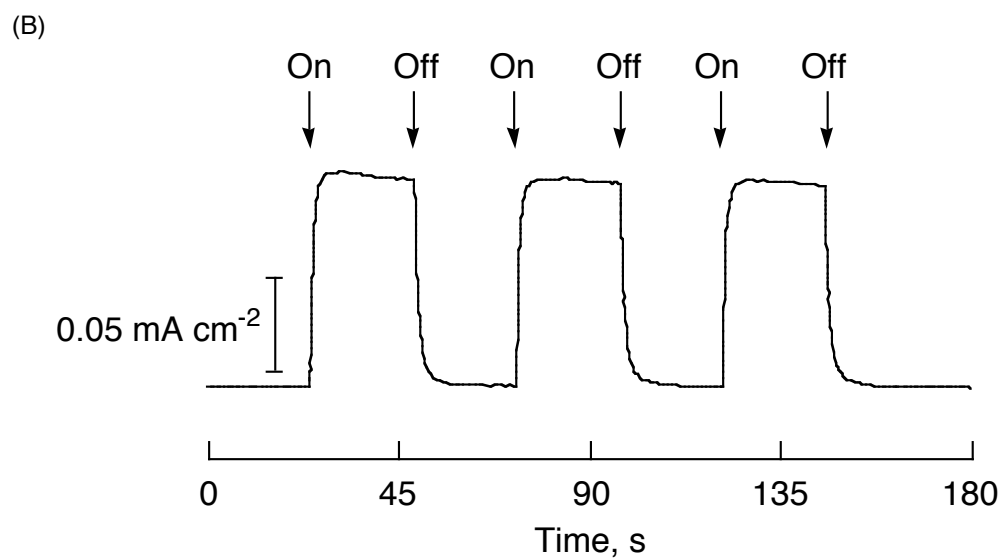
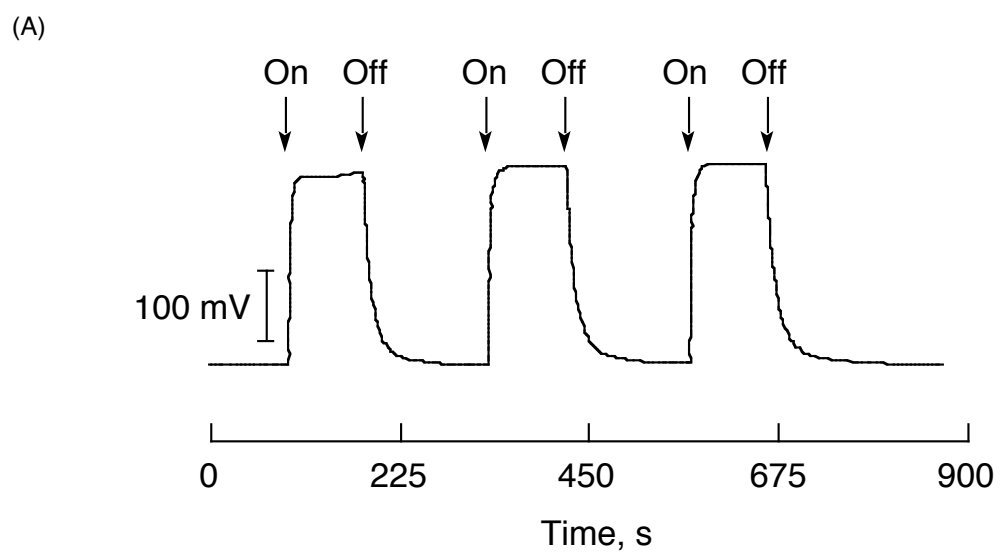




Figure 5

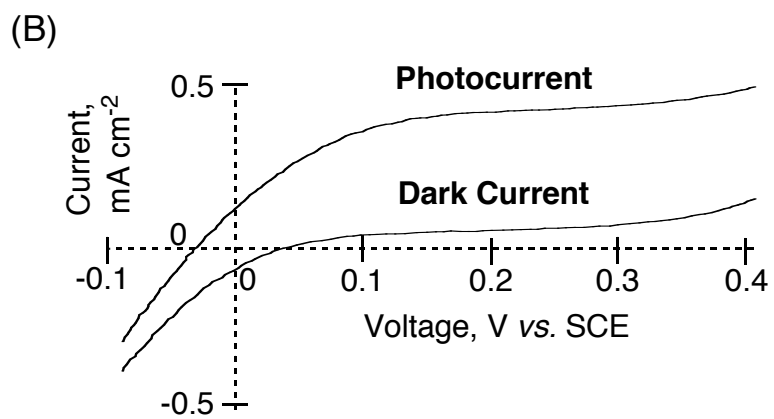
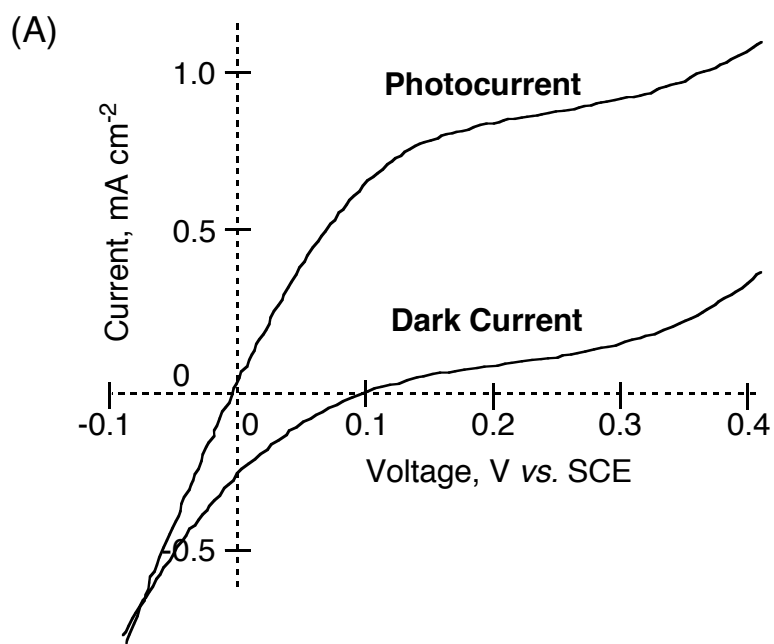


Figure 6

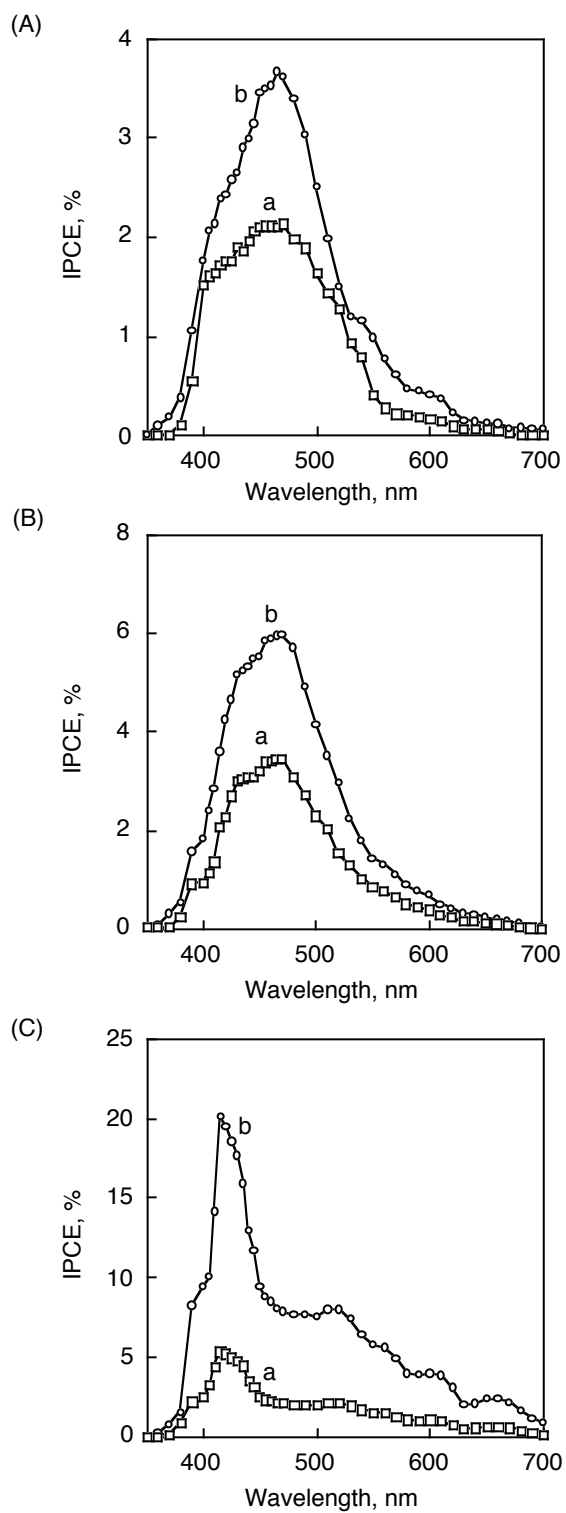


Figure 7

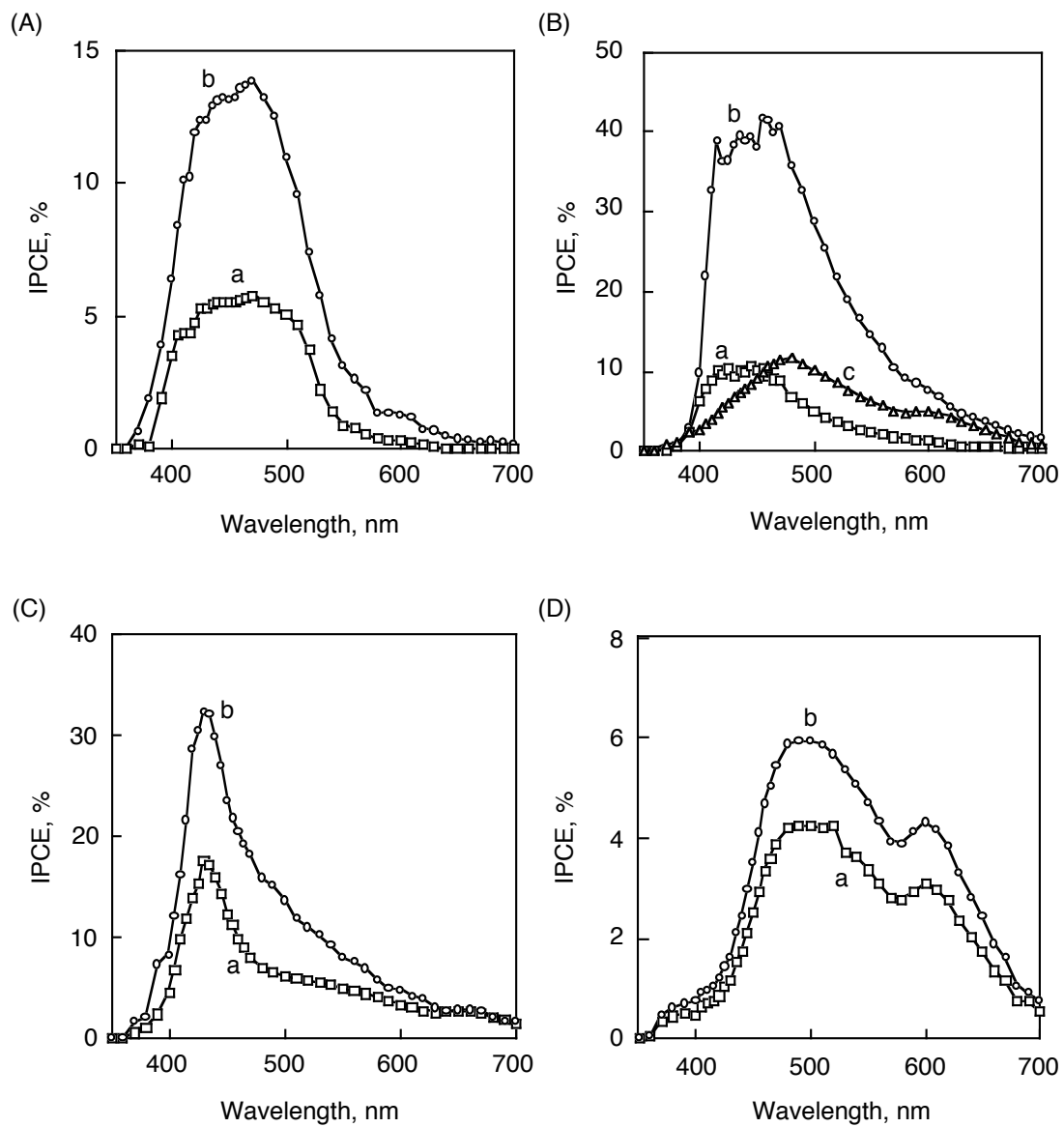


Figure 8

