Spectroscopy and Photocurrent Generation in Nanostructured Thin Films of Porphyrin–Fullerene Dyad Clusters

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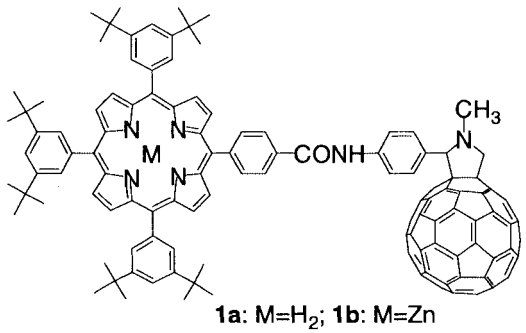
Porphyrin–fullerene dyad cluster films, when cast on nanostructured SnO_2 films, are photoelectrochemically active and generate anodic photocurrent under visible light excitation (maximal IPCE value = ~0.4%).

The development of artificial systems for the conversion of visible light into chemical or electrical energy is an important goal. We have prepared a variety of porphyrin–fullerene linked molecules as ideal components to achieve long-lived charge-separated states efficiently.[1–3] Self-assembled monolayers (SAMs) of such molecules have also revealed efficient photoinduced multistep electron transfer (ET) and energy transfer (EN) on gold surfaces.[1,4,5] In particular, mixed SAMs of boron dye and ferrocene–porphyrin–C_{60} on the gold electrode have established a cascade of photoinduced EN and multistep ET, leading to the production of photocurrent output with the highest quantum yield (50%) ever reported for photocurrent generation at monolayer-modified metal electrodes using donor–acceptor linked molecules.[1,4–6] In this system, however, the incident photon to photocurrent efficiency (IPCE), has been limited by the poor light-harvesting efficiency of the monolayers. An attractive approach has been to utilize nanostructured morphology for the photoactive films where the three-dimensional surface is covered with dye which can absorb the light intensively.[7–12] However, porphyrin–fullerene linked systems exhibiting efficient formation of long-lived charge-separated states have yet to be assembled on three-dimensional surface to examine the photocurrent generation.

We report herein such systems to examine the photophysical and photoelectrochemical properties of porphyrin–fullerene dyad (**1**) cluster on nanostructured SnO_2 films (Figure 1). It is well established that photoinduced ET in **1** occurs from the porphyrin excited singlet state to the C_{60} to generate the radical ion pair with a long-lived lifetime in both polar and nonpolar solvents (quantum yield = 0.99 in benzonitrile).[1–3] Thus, it is expected that photocurrent generation in the present system will be enhanced using electrodeposition of porphyrin–fullerene dyad cluster aggregates on nanostructured SnO_2 films.



1a: M=H_2; **1b**: M=Zn

Figure 1. Porphyrin–fullerene dyads used in this study.

The synthesis and characterization of **1** have been described previously.[2] The cluster suspension of **1** was prepared by injecting a toluene solution of **1** into acetonitrile (acetonitrile/toluene, 19:1 v/v). The absorption spectra of **1a** in toluene and acetonitrile/toluene (19:1 v/v) are compared in Figure 2. The Soret band of **1a** in acetonitrile/toluene is broadened and red-shifted by 16 nm relative to the corresponding spectrum of **1a** in toluene. Similar red-shift and broadening were observed for **1b**. These results indicate the formation of porphyrin–fullerene cluster in the mixed solvent, as in the case of C_{60}–aniline dyad.[11,13] The fluorescence spectra of **1a** in toluene and acetonitrile/toluene 19:1 are also compared under the same experimental conditions. Both the fluorescence spectra are similar in shape and peak position, but the intensity in the latter is reduced by a factor of ~1/4 than the former. Similar behavior was seen for **1b**. Based on the photodynamics of **1** in various solvents,[1–3] photoinduced charge separation (CS) of porphyrin–fullerene cluster may also occur efficiently in the mixed solvent.[13]

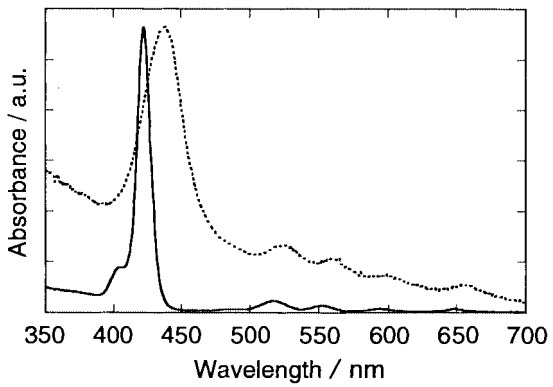


Figure 2. Absorption spectra of **1a** in toluene (solid line) and in 19 : 1 acetonitrile–toluene mixture (v/v) (dotted line).

Time-resolved transient absorption spectra of **1** in deaerated acetonitrile/toluene (19:1 v/v) were measured by nanosecond laser photolysis. Broad and structureless absorption appears

(600–1200 nm) with no characteristic fingerprint of C_{60} anion (1000 nm).[1–3] This broadening is likely to be caused by the strong interaction between the chromophores in the clusters. The decay rates of **1a** and **1b** at 1000 nm were determined as 1.5×10^7 s^{-1} and 7.4×10^7 s^{-1}, respectively, which do not agree with the decay rates of excited triplet states of the freebase porphyrin (2.6×10^3 s^{-1}),[2] zincporphyrin (2.3×10^4 s^{-1}),[2] and the C_{60} (4.0×10^4 s^{-1}).[2] Taking into account the above results, we can conclude that charge-separated state is produced in the porphyrin–fullerene clusters.

The porphyrin–fullerene dyad cluster films when cast on nanostructured SnO_2 films are photoactive and generate anodic photocurrent under standard three-compartment cell containing the working electrode, Pt wire counter electrode, and Ag/AgCl reference electrode (electrolyte: 0.5 M LiI and 1 mM I_2 in acetonitrile; 0 V vs Ag/AgCl).[11] Under visible light illumination ($\lambda > 425$ nm) the OTE (optically transparent electrode)/SnO_2 electrodes modified with **1** yielded a maximum photocurrrent and photovoltage in the range of 28–37 μA and 70–100 mV, respectively. The maximal IPCE values were found to be 0.42% for OTE/SnO_2/**1a** cell and 0.36% for OTE/SnO_2/**1b** cell as shown in Figure 3 and 4. The action spectra of **1** largely agree with the absorption spectra on the nanostructured SnO_2 electrode. This indicates that the porphyrin is a photoactive species for the photocurrent generation.[14] The photocurrent generation may arise via the initial photoinduced CS in the dyad clusters, followed by an electron injection to SnO_2 and subsequent electron relay to the resulting porphyrin radical

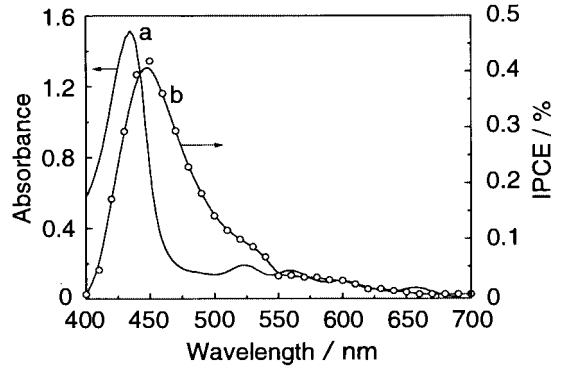


Figure 3. (a) Absorption spectrum and (b) photocurrent action spectrum of OTE/SnO_2/**1a** film electrode.

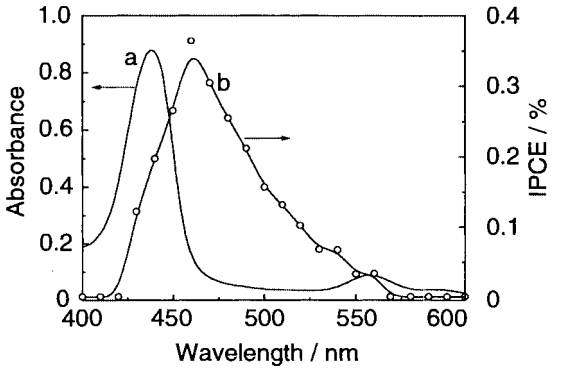


Figure 4. (a) Absorption spectrum and (b) photocurrent action spectrum of OTE/SnO_2/**1b** film electrode.

cation using the I_3^-/I^- couple.[7–9] It should be noted here that light harvesting properties in the present system (maximal absorbance: ~ 1.5 (absorptivity = 97%) for **1a** and ~ 0.9 (absorptivity = 87%) for **1b**) are improved by a factor of ~ 40 and ~ 20, respectively, as compared to the corresponding monolayer system (0.04–0.05).[4–6,15]

In conclusion, we have developed photoelectrochemical cells of porphyrin–fullerene dyad cluster for the first time. The light-harvesting efficiency in the present system is remarkably improved as compared to the corresponding monolayer systems. Although the IPCE value has remained to be improved by controlling the morphology of the films, the present study has provided a promising way for the utilization of porphyrin–fullerene linked molecules in energy conversion devices such as solar cells.

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13 Fullerenes are known to form optically transparent microscopic clusters in mixed solvents at room temperature.[10–12] Since the porphyrin bears bulky *tert*-butyl groups on the *meta* positions of the phenyl groups at the *meso*-positions, the clustering may be ascribed to the strong three-dimensional hydrophobic interactions between the fullerene units or the fullerene and the porphyrin units rather than the porphyrin units.
14 The difference in shape and the peak position between the two spectra may be due to the difference between the actual spectrum obtained in transmission mode in air and the real spectrum on the electrode under the photoelectrochemical conditions, where the dyads are in contact with the electrolyte solution.
15 The quantum yield of photocurrent generation in the present systems is estimated as ~ 0.4%.