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Photoelectrochemical Properties of Supramolecular Composite of Fullerene Nanoclusters and 9-Mesityl-10-carboxymethylacridinium Ion on SnO_2

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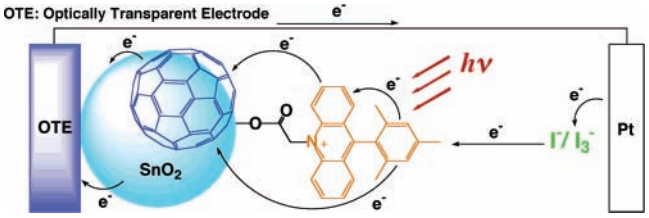
ABSTRACT



The photovoltaic cell composed of both fullerene nanoclusters and 9-mesityl-10-carboxymethylacridinium ion exhibits significant enhancement in the photoelectrochemical performance as well as broader photoresponse in the visible and near-infrared regions as compared with the reference system containing only each component.

Extensive efforts have so far been devoted to develop molecular triads, tetrad, pentads, etc., which can mimic a cascade of electron-transfer steps in the natural photosynthetic reaction center, leading to long-range charge separation with prolonged lifetime of the charge-separated state into second range.[1−5] However, the synthetic difficulty has precluded the development of low-cost photovoltaic devices using such molecular arrays.[6−9] In addition, a significant amount of energy is lost during the multistep electron-transfer processes in both natural and artificial long-range charge separation. To avoid such wasted energy loss, we have

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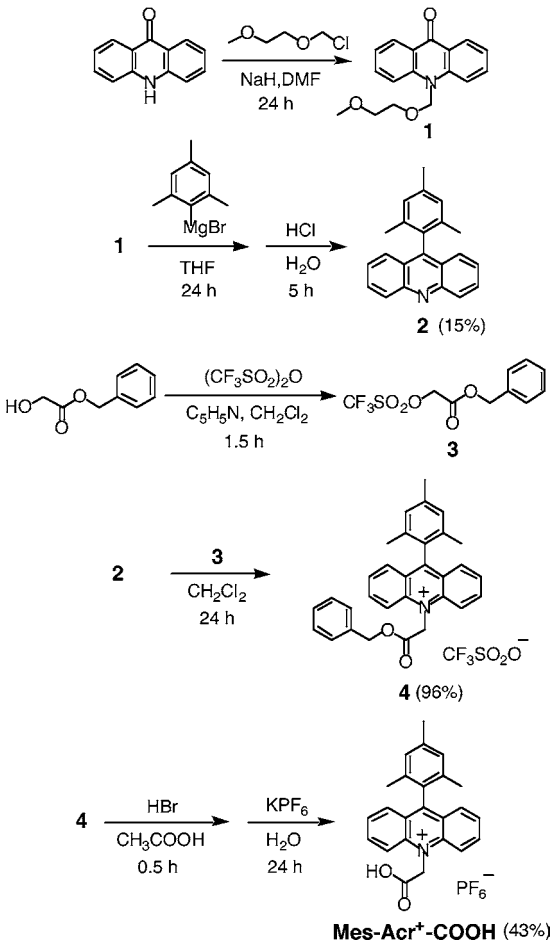
recently designed and synthesized a simple dyad (9-mesityl-10-methylacridinium ion) that exhibits extremely slow charge recombination of the electron-transfer state with remarkably high energy (2.37 eV).[10,11] Such a simple molecular dyad capable of fast charge separation, but extremely slow charge recombination, has obvious advantages with regard to synthetic feasibility, which now allows us to develop a unique organic photovoltaic cell using the molecular dyad with an extremely long lifetime of the electron-transfer state as well as high energy (2.37 eV).[10]

We report herein synthesis of 9-mesityl-10-carboxymethylacridinium ion (Mes-Acr$^+$-COOH) which can be assembled on optically transparent electrode (OTE) of nanostructured SnO_2 (OTE/SnO_2) and the organic photovoltaic cell composed of fullerene nanoclusters and Mes-Acr$^+$-COOH. The photoelectrochemical behavior of the nanostructured SnO_2 film of Mes-Acr$^+$-COOH and fullerene nanoclusters [denoted as OTE/SnO_2/Mes-Acr$^+$-COOH + $(C_{60})_n$] is significantly higher than the single component films of Mes-Acr$^+$-COOH or fullerene clusters (denoted as OTE/SnO_2/Mes-Acr$^+$-COOH or OTE/SnO_2/$(C_{60})_n$).

The general strategy to synthesize Mes-Acr$^+$-COOH is shown in Scheme 1. The synthetic procedure and characterization is given in the Supporting Information (S1−S4).

The synthesized dyad (Mes-Acr$^+$-COOH) was adsorbed by immersing the OTE/SnO_2 electrode in a 2×10^{-3} M ethanol solution overnight to prepare the OTE/SnO_2/Mes-Acr$^+$-COOH electrode. To remove the adsorbed water from the SnO_2 surface, the films were heated to 80 °C before immersion. Figure 1A shows the absorption spectrum of OTE/SnO_2/Mes-Acr$^+$-COOH. The spectrum of OTE/SnO_2/Mes-Acr$^+$-COOH agrees with that of Mes-Acr$^+$-COOH in acetonitrile. This indicates that Mes-Acr$^+$-COOH is successfully deposited on OTE/SnO_2. However, the absorption property is still poor due to the low extinction coefficient of

Scheme 1



Mes-Acr$^+$-COOH. To improve the light-harvesting efficiency, we prepared fullerene (C_{60}) clusters from a C_{60} suspension of the final concentration (0.62 mM) in acetonitrile/toluene (3/1) and deposited them electrophoretically on an OTE/SnO_2/Mes-Acr$^+$-COOH electrode (OTE/SnO_2/Mes-Acr$^+$-COOH + $(C_{60})_n$). As reported previously, C_{60} clusters act as good electron acceptors as well as light-harvesting molecules.[4−6,12] The absorption spectrum of OTE/SnO_2/Mes-Acr$^+$-COOH + $(C_{60})_n$ is shown in Figure 1B. The spectrum of OTE/SnO_2/Mes-Acr$^+$-COOH + $(C_{60})_n$ becomes broader as compared to the spectra of OTE/SnO_2/$(C_{60})_n$ and OTE/SnO_2/Mes-Acr$^+$-COOH, and the absorbance of OTE/SnO_2/Mes-Acr$^+$-COOH + $(C_{60})_n$ is significantly higher than that of OTE/SnO_2/$(C_{60})_n$ alone. This indicates that there is charge-transfer (CT) interaction between the mesityl (donor) moiety of Mes-Acr$^+$-COOH and C_{60} (see Supporting Information: S5).[13]

AFM was used to evaluate the topography of an OTE/SnO_2/Mes-Acr$^+$-COOH + $(C_{60})_n$ film as shown in Figure

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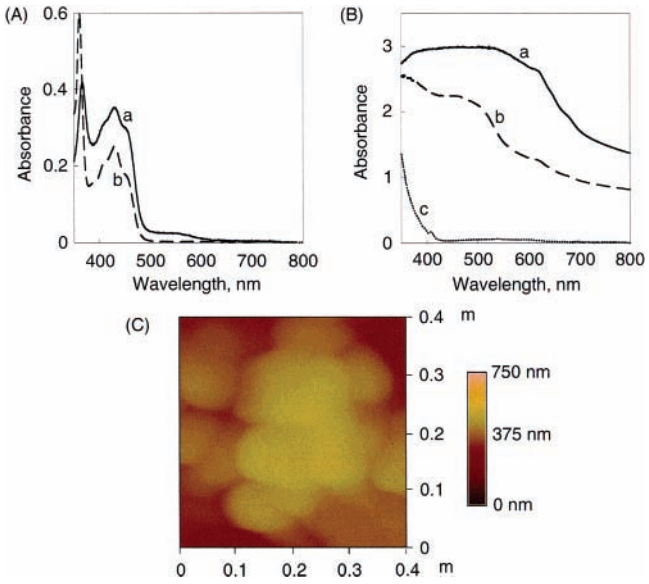

Figure 1. (A) Absorption spectra of (a) OTE/SnO_2/Mes-Acr^+-COOH and (b) Mes-Acr^+-COOH in acetonitrile (4.0×10^{-5} M). (B) Absorption spectra of (a) OTE/SnO_2/Mes-Acr^+-COOH + $(C_{60})_n$, (b) OTE/SnO_2/$(C_{60})_n$, and (c) C_{60} in toluene (1.5×10^{-5} M). (C) AFM image of OTE/SnO_2/Mes-Acr^+-COOH + $(C_{60})_n$ electrode. [C_{60}] = 0.62 mM in acetonitrile/toluene (3/1).

1C. The OTE/SnO_2/Mes-Acr^+-COOH + $(C_{60})_n$ film is composed of closely packed C_{60} clusters of about 100 nm size, which renders a nanoporous morphology to the film. The grape bunch morphology of the cluster assembly thus provides a high surface area to the electrophoretically deposited film of C_{60} clusters. As indicated earlier,[14] charging of fullerene moieties in the dc electric field plays an important role in the growth and deposition process. These films are quite robust and can be washed with organic solvents to remove any loosely bound C_{60} nanoassemblies.

Photoelectrochemical measurements were performed using a standard two-electrode system consisting of a working electrode and a Pt wire gauze electrode in air-saturated acetonitrile containing 0.5 M NaI and 0.01 M I_2. To evaluate the response toward the photocurrent generation, a series of photocurrent action spectra were recorded. The IPCE (incident photon-to-photocurrent efficiency) values were calculated by normalizing the photocurrent values for incident light energy and intensity and using the expression (1)[15]

$$\text{IPCE (\%)} = 100 \times 1240 \times i_{sc}/(I_{inc}\lambda) \qquad (1)$$

where i_{sc} is the short circuit photocurrent (A/cm^2), I_{inc} is the incident light intensity (W/cm^2), and λ is the wavelength (nm). The maximum IPCE value of OTE/SnO_2/Mes-Acr^+-COOH (spectrum a in Figure 2A) is only 2% (445 nm),

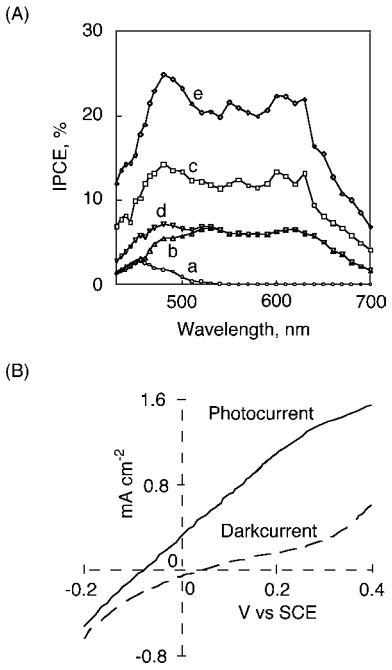

Figure 2. (A) Comparison of photocurrent response (IPCE values) of (a) OTE/SnO_2/Mes-Acr^+-COOH electrode ([C_{60}] = 0.62 mM), (b) OTE/SnO_2/$(C_{60})_n$ electrode ([C_{60}] = 0.62 mM), (c) OTE/SnO_2/Mes-Acr^+-COOH + $(C_{60})_n$ electrode ([C_{60}] = 0.62 mM), (d) the sum of the IPCE response of OTE/SnO_2/Mes-Acr^+-COOH and OTE/SnO_2/$(C_{60})_n$ electrodes ([C_{60}] = 0.62 mM), and (e) OTE/SnO_2/Mes-Acr^+-COOH + $(C_{60})_n$ electrode ([C_{60}] = 0.62 mM) with applied bias potential: 0.2 V vs SCE. (B) I−V characteristics of OTE/SnO_2/Mes-Acr^+-COOH + $(C_{60})_n$ electrode ([C_{60}] = 0.62 mM) under white light (λ > 370 nm) illumination; electrolyte: 0.5 M NaI and 0.01 M I_2 in acetonitrile, input power: 28.3 mW/cm^2.

whereas the IPCE value of OTE/SnO_2/Mes-Acr^+-COOH + $(C_{60})_n$ (spectrum c in Figure 2A) reaches 15% (480 nm).[16] On the other hand, the IPCE value of OTE/SnO_2/Mes-Acr^+-COOH + $(C_{60})_n$ is much higher than the sum of the two individual IPCE values of the individual systems (OTE/SnO_2/Mes-Acr^+-COOH and OTE/SnO_2/$(C_{60})_n$; spectrum d in Figure 2A) in the visible region.

The charge separation in the OTE/SnO_2/Mes-Acr^+-COOH + $(C_{60})_n$ electrode can be further modulated by controlling the applied potential in a standard three-compartment cell as a working electrode along with a Pt wire gauze counter-electrode and a saturated calomel reference electrode (SCE).[15] Figure 2B shows I−V characteristics of the OTE/SnO_2/Mes-Acr^+-COOH + $(C_{60})_n$ electrode under the applied potential and is scanned toward more positive potentials. Increased charge separation and the facile transport of charge carriers under positive bias are responsible for enhanced photocurrent generation. At potentials greater than +0.4 V vs SCE, direct

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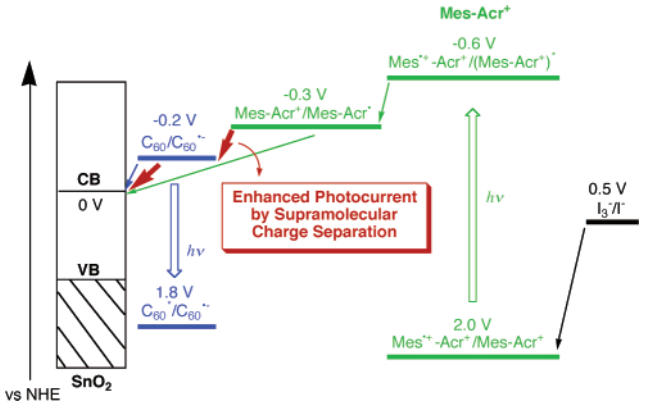
(16) Overall power conversion efficiency (η) of OTE/SnO_2/Mes-Acr^+-COOH + $(C_{60})_n$ electrode is estimated as 0.05% at input power (W_{in}) of 28.3 mW cm^{-2} (λ > 370 nm); see the Supporting Information (S6).

electrochemical oxidation of iodide interferes with the photocurrent measurement. We evaluated the photocurrent action spectra of OTE/SnO_2/Mes-Acr^+-COOH + $(C_{60})_n$ under the electrochemical bias (spectrum e in Figure 2A). The maximum IPCE value is obtained as 25% at an applied potential of 0.2 V vs SCE. Such a high IPCE value indicates that photocurrent is initiated via electron-transfer between excited Mes-Acr^+-COOH and C_{60} clusters, followed by the charge transport to the collective surface of OTE/SnO_2 electrode. The charge transport is significantly improved under the influence of an applied bias.

To clarify the photocurrent generation mechanism, we examined formation of C_{60} radical anion by nanosecond laser flash photolysis measurements. Time-resolved transient absorption spectra of 9-mesityl-10-methylacridinium ion without carboxylic acid **(**Mes-Acr^+)[10] and fullerene in deoxygenated toluene−acetonitrile (1:1, v/v) have clearly exhibited a broad absorption band at about 1050 nm (see the Supporting Information).[17,18] This is diagnostic of the formation of the C_{60} radical anion upon photoirradiation. Thus, electron transfer occurs from the acridinium radical moiety to C_{60}, following photoinduced electron transfer from the mesitylene moiety to the singlet excited state of acridinium ion moiety of Mes-Acr^+, to produce the electron-transfer state of Mes-Acr^+ dyad ($Mes^{\bullet+}$-$Acr^{\bullet}$), which has an extremely long lifetime. The absorption−time profile of the composite cluster (Mes-Acr^+ dyad and C_{60}) in deoxygenated toluene−acetonitrile (1:1) recorded at 1050 nm was carried out (see the Supporting Information: S7). The second-order decay kinetics corresponds to electron transfer from the $C_{60}^{\bullet-}$ to the $Mes^{\bullet+}$ moiety, affording the second-order rate constant of back-electron transfer ($k_{bet} = 2.9 \times 10^9\ M^{-1}\ s^{-1}$).

The mechanism of the photocurremt generation of OTE/SnO_2/Mes-Acr^+-COOH and OTE/SnO_2/Mes-Acr^+-COOH + $(C_{60})_n$ electrodes is summarized in Scheme 2. In the case of

Scheme 2



the OTE/SnO_2/Mes-Acr^+-COOH system, the photocurrent generation is initiated by photoinduced electron transfer in Mes-Acr^+ dyad to produce $Mes^{\bullet+}$-$Acr^{\bullet}$. The reduced acridinium ion ($Acr^{\bullet}$) ($Acr^+/Acr^{\bullet} = -0.3$ V vs NHE)[10] injects electrons into the conduction band of SnO_2 (0 V vs NHE),[15] whereas the oxidized mesityl moiety ($Mes/Mes^{\bullet+} = 2.0$ V vs NHE)[10] undergoes the electron-transfer reduction with the iodide ($I_3^-/I^- = 0.5$ V vs NHE)[15] in the electrolyte solution. On the other hand, in the case of the OTE/SnO_2/Mes-Acr^+-COOH + $(C_{60})_n$ electrode, the long lifetime of the electron-transfer state ($Mes^{\bullet+}$-$Acr^{\bullet}$) ensures efficient electron-transfer from $Acr^{\bullet}$ to C_{60} ($C_{60}/C_{60}^{\bullet-} = -0.2$ V vs NHE)[15] to produce the C_{60} radical anion (vide supra). While the reduced C_{60} clusters inject electrons into the conduction band of SnO_2, the oxidized mesityl moiety ($Mes^{\bullet+}$) undergoes the electron-transfer reduction with iodide ion in the electrolyte. Enhanced IPCE values of OTE/SnO_2/Mes-Acr^+-COOH + $(C_{60})_n$ (spectrum c in Figure 2A), relative to the sum of the two individual IPCE values of the individual systems (spectrum d in Figure 2A), may result from charge-transfer interaction between the mesityl (donor) moiety of Mes-Acr^+-COOH and C_{60} clusters, which appears at the long wavelength region over 500 nm.

In summary, we have constructed supramolecular photovoltaic cells using molecular nanocluster assemblies of fullerene and a simple molecular dyad (Mes-Acr^+) with an extremely long lifetime and a high energy of the electron-transfer state. Remarkable improvement in the photoelectrochemical properties of the composite of Mes-Acr^+ dyad and fullerene nanoclusters has been achieved as compared with each component systems (OTE/SnO_2/$(C_{60})_n$ and OTE/SnO_2/Mes-Acr^+-COOH), due to the extremely long lifetime of the electron-transfer state of Mes-Acr^+-COOH and efficient electron transfer from $Acr^{\bullet}$ to C_{60}, together with the charge-transfer interaction between the mesityl (donor) moiety of Mes-Acr^+-COOH and C_{60} clusters.

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Supporting Information Available: Experimental Section (S1−S4), charge-transfer (CT) absorption spectrum of Mes-Acr^+ with C_{60} (S5), and current−voltage characteristics of OTE/SnO_2/Mes-Acr^+-COOH + $(C_{60})_n$ (S6), and transient absorption spectra of Mes-Acr^+ with C_{60} and the decay profile of absorbance at 1050 nm (S7). This material is available free of charge via the Internet at http://pubs.acs.org.

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