

**PHOTOVOLTAIC CELLS COMPOSED OF FULLERENE CLUSTERS AND A MOLECULAR DYAD WITH AN EXTREMELY LONG LIFETIME OF THE ELECTRON-TRANSFER STATE**

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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 millisecond and even into second range. However, the synthetic difficulty has precluded the development of low-cost photovoltaic devices using such model compounds of the photosynthetic reaction center. In addition, a significant amount of energy is lost during the multi-step electron-transfer processes in both natural and artificial long-range charge separation.

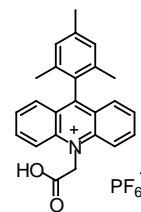
In order to avoid such wasting energy loss, we have recently designed and synthesized a simple dyad, 9-mesityl-10-methylacridinium ion (Acr<sup>+</sup>-Mes), which exhibits extremely slow charge-recombination of the electron-transfer state.<sup>1</sup> We report herein a unique organic photovoltaic cell composed of fullerene clusters and the molecular dyad with an extremely long lifetime of the electron-transfer state.

First, we synthesized Acr<sup>+</sup>-Mes with carboxylic acid (Acr<sup>+</sup>-Mes-COOH) to deposit the dyad on OTE/SnO<sub>2</sub>. The chemical structure of Acr<sup>+</sup>-Mes-COOH is shown in Figure 1.

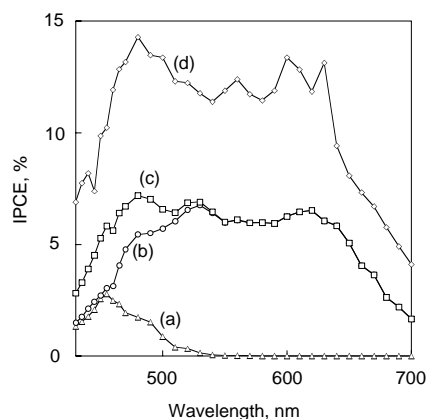
The dyad (Acr<sup>+</sup>-Mes-COOH) was adsorbed by immersing OTE/SnO<sub>2</sub> electrode in 2 × 10<sup>-3</sup> M ethanol solution overnight to prepare OTE/SnO<sub>2</sub>/Acr<sup>+</sup>-Mes-COOH electrode. However, the absorption property is poor due to the low extinction coefficient of Acr<sup>+</sup>-Mes-COOH. In order to improve the light-harvesting efficiency, we further deposited fullerene (C<sub>60</sub>) clusters electrophoretically on OTE/SnO<sub>2</sub>/Acr<sup>+</sup>-Mes-COOH electrode (denoted as OTE/SnO<sub>2</sub>/Acr<sup>+</sup>-Mes-COOH+(C<sub>60</sub>)<sub>n</sub>).

Photoelectrochemical measurements were performed using a standard two-electrode system consisting of a working electrode and Pt wire gauze electrode in air-saturated acetonitrile containing 0.5 M NaI and 0.01 M I<sub>2</sub>. The maximum IPCE (incident photon-to-photocurrent efficiency) value of OTE/SnO<sub>2</sub>/Acr<sup>+</sup>-Mes-COOH (spectrum a in Figure 2) is only 2 % (445 nm), whereas the IPCE value of OTE/SnO<sub>2</sub>/Acr<sup>+</sup>-Mes-COOH+(C<sub>60</sub>)<sub>n</sub> (spectrum d in Figure 2) reaches 15%. The IPCE value of OTE/SnO<sub>2</sub>/Acr<sup>+</sup>-Mes-COOH+(C<sub>60</sub>)<sub>n</sub> is much higher than the sum of the two individual IPCE values of the individual systems (OTE/SnO<sub>2</sub>/Acr<sup>+</sup>-Mes-COOH and OTE/SnO<sub>2</sub>/(C<sub>60</sub>)<sub>n</sub>; spectrum c in Figure 2) in the visible region. The long lifetime of the electron-transfer state (Acr<sup>+</sup>-Mes<sup>+</sup>)<sup>1</sup> produced upon the photoexcitation ensures electron transfer from Acr<sup>+</sup> to C<sub>60</sub>, leading to the efficient photocurrent generation. The formation of C<sub>60</sub> radical anion was confirmed by nanosecond laser flash photolysis measurements.

In summary, we have constructed novel supramolecular photovoltaic cells using molecular nanocluster assemblies of fullerene and a simple molecular dyad with an extremely long lifetime of the electron-transfer state.



**Figure 1.** Chemical structure of Acr<sup>+</sup>-Mes-COOH.



**Figure 2.** Photocurrent action spectra of (a) OTE/SnO<sub>2</sub>/Acr<sup>+</sup>-Mes-COOH and (b) OTE/SnO<sub>2</sub>/(C<sub>60</sub>)<sub>n</sub> electrodes, (c) the sum of the action spectra of OTE/SnO<sub>2</sub>/Acr<sup>+</sup>-Mes-COOH and OTE/SnO<sub>2</sub>/(C<sub>60</sub>)<sub>n</sub> electrodes, and (d) photocurrent action spectrum of OTE/SnO<sub>2</sub>/Acr<sup>+</sup>-Mes-COOH + (C<sub>60</sub>)<sub>n</sub> electrode.

**References**

- [1] Fukuzumi, S.; Kotani, H.; Ohkubo, K.; Ogo, S.; Tkachenko, N. V.; Lemmetyinen, H. *J. Am. Chem. Soc.* **2004**, *126*, 1600.