Photocurrent Generation by ITO Electrodes Modified with Self-Assembled Monolayers of Porphyrin-Fullerene Dyads

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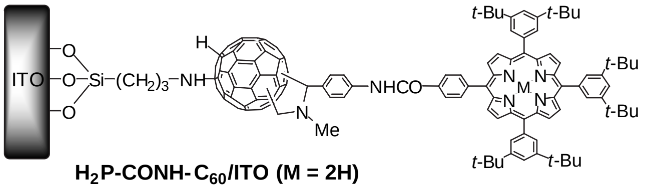
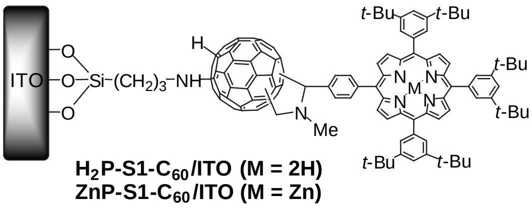
Self-assembled monolayers (SAMs) are highly promising to construct molecular architecture on metal and semiconductor surfaces. SAMs of photoactive chromophores on the flat gold surface have merited special attention as artificial photosynthetic materials and photonic molecular devices. In particular, donor-acceptor linked molecules have been employed in such systems to mimic photosynthetic electron transfer (ET) and energy transfer (EN) on the gold electrode. However, strong EN quenching of the excited states of chromophores by the gold surface has precluded achievement of a high quantum yield for charge separation (CS) on the surface as attained in photosynthesis. In order to surmount such an EN quenching problem, indium-tin oxide (ITO) with high optical transparency (>90%) and electrical conductivity (~10^4 Ω cm) seems to be the most promising candidate as an electrode which may suppress the quenching of the excited states of adsorbed dyes on the surface.[1] Despite these advantages, development of SAMs on the ITO electrode has been limited in that their chemical modification requires carefully controlled conditions which have been difficult to achieve.

We report herein construction of SAMs of porphyrin-fullerene dyads on the ITO electrode. It is expected that efficient photoinduced ET takes place from the porphyrin excited singlet state to the C_{60}, followed by multistep ET, leading to the remarkable enhancement of photocurrent generation in the present system because of small reorganization energy of porphyrin-fullerene systems in photoinduced ET.



H_2P-CONH-C_{60}/ITO (M = 2H)
ZnP-CONH-C_{60}/ITO (M = Zn)



H_2P-S1-C_{60}/ITO (M = 2H)
ZnP-S1-C_{60}/ITO (M = Zn)

Absorption spectra of **H_2P-CONH-C_{60}**/ITO were compared to those of **H_2P-CONH-C_{60}** in THF. The Soret bands of **H_2P-CONH-C_{60}**/ITO become broader than those of **H_2P-CONH-C_{60}** in THF. The λ_{max} value of the Soret band of **H_2P-CONH-C_{60}**/ITO (426 nm) is red-shifted by 6 nm relative to that of **H_2P-CONH-C_{60}** (420 nm) in THF. Similar red-shift and broadening of the Soret bands were observed for **ZnP-CONH-C_{60}**/ITO (6 nm), **H_2P-S1-C_{60}**/ITO (4 nm) and **ZnP-S1-C_{60}**/ITO (7 nm). These results indicate that the porphyrin environments of these SAMs are perturbed moderately, relative to the references in THF, due to the porphyrin aggregation.

Photoelectrochemical measurements were carried out in an argon-saturated 0.1 M Na_2SO_4 aqueous solution containing 50 mM ascorbic acid (AsA) acting as an electron sacrificer using **ZnP-CONH-C_{60}**/ITO as a working electrode, a Pt counter electrode, and an Ag/AgCl (sat. KCl) reference electrode. A stable anodic photocurrent appeared immediately upon irradiation of **ZnP-CONH-C_{60}**/ITO with λ = 430.0 ± 5.0 nm light (500 μW cm^{-2}) at applied potential of +0.15 V vs Ag/AgCl (sat. KCl). When the irradiation was cut off, the photocurrent fell down instantly (Figure 1). Similar photoelectrochemical behavior was observed using **H_2P-CONH-C_{60}**/ITO, **ZnP-S1-C_{60}**/ITO, and **H_2P-S1-C_{60}**/ITO.

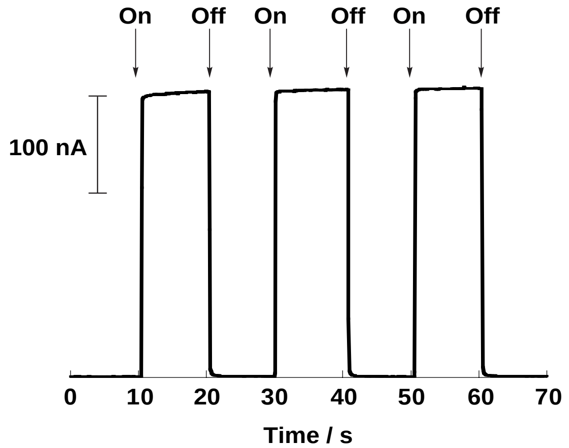


Figure 1. Photoelectrochemical response of ITO/**ZnP-CONH-C_{60}**/AsA/Pt cell with illumination at 420 nm; input power: 500 μW cm^{-2}; applied potential: 150 mV vs Ag/AgCl (sat. KCl).

Taking into account the result of porphyrin-fullerene linked systems on electrodes as well as in solution,[2] it is concluded that an intramolecular ET takes place from $^1P^*$ to C_{60}, followed by intermolecular ET from AsA to $P^{\bullet+}$. On the other hand, an electron is injected from $C_{60}^{\bullet-}$ to the ITO, which eventually leads to the anodic current generation.

(1) Yamada, H.; Imahori, H.; Nishimura, Y.; Yamazaki, I.; Fukuzumi, S. *Chem. Commun.* **2000**, 1921.
(2) Imahori, H.; Tamaki, K.; Guldi, D. M.; Luo, C.; Fujitsuka, M.; Ito, O.; Sakata, Y.; Fukuzumi, S. *J. Am. Chem. Soc.* **2001**, *123*, 2607.