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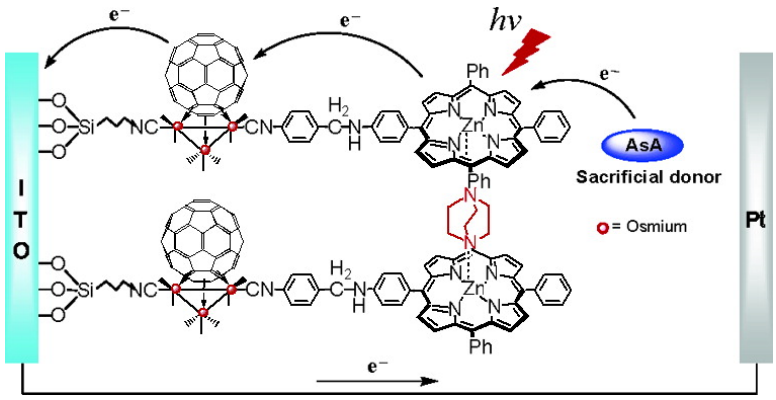

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Unusually High Performance Photovoltaic Cell Based on a [60]Fullerene Metal Cluster−Porphyrin Dyad SAM on an ITO Electrode

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Photoinduced electron transfer (ET) in donor−acceptor (D−A) molecular systems has received considerable attention for applications such as optoelectronics, photonics, sensors, and other nanoscale molecular devices.[1] Coupled with porphyrins and/or ferrocenes as electron donors, C_{60}-containing systems such as dyad and triad have recently been demonstrated as the most prominent photovoltaic devices in artificial photosynthetic cells.[2] The most intriguing characteristics of C_{60} as an electron acceptor are that it accelerates photoinduced charge separation and slows down charge recombination in the ET process, mainly because of its relatively low-lying LUMO and small reorganization energy.[3] Recently, we have reported that C_{60}−metal cluster complexes show remarkable stabilities in the reduced state and strong electronic communication between C_{60} and metal cluster centers.[4]

Self-assembled monolayers (SAMs) and multilayer thin films with potential gradients have proven to be promising in mimicking the natural photosynthetic apparatus and fabricating efficient photovoltaic cells.[5] Herein we report the preparation of a novel C_{60}−porphyrin dyad structure $Os_3(CO)_7(CNR)(CNR')(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-}C_{60})$ (**ZnP**−**C$_{60}$**; R = $(CH_2)_3Si(OEt)_3$, R′ = ZnP) (Scheme S1),[6] in which a triosmium carbonyl cluster moiety links C_{60} and a porphyrin unit and 3-(triethoxysilyl)propyl isocyanide is employed as a surface-anchoring ligand. Compound **ZnP**−**C$_{60}$** forms an ideal SAM (abbreviated as **(ZnP)**−**C$_{60}$/ITO**; see the inset in Figure 1) with an almost full surface coverage on the ITO electrode in the presence of diazabicyclooctane (**DABCO**), which exhibits well-defined electrochemical responses and remarkably high photocurrent generation in C_{60}-based photovoltaic cells.

The UV/vis spectrum of **(ZnP)**−**C$_{60}$/ITO** shows that the characteristic Soret band becomes broader and the λ_{max} value of B bands is red-shifted by 11 nm relative to that of **ZnP**−**C$_{60}$** in CH_2Cl_2 (Figure 1). The broadening and bathochromic shift indicate moderate perturbation within SAMs mainly due to **DABCO** binding and porphyrin aggregates.[7] The red shift of the B band implies that the axial **DABCO** binding to the d_{z^2} orbitals of zinc lowers the porphyrin singlet excited state and also enhances the porphyrin surface coverage on ITO (vide infra).

The cyclic voltammogram (CV) of **(ZnP)**−**C$_{60}$/ITO** (Figure 2) reveals three well-resolved redox waves at −1.17, −1.47, and −1.92 V ($E_{1/2}$) with relative areas of 1:1:3.1. Importantly, the overall feature of CV of **(ZnP)**−**C$_{60}$/ITO** is similar to that of **ZnP**−**C$_{60}$** in solution. The first and second waves are successive one-electron reductions localized on C_{60}. The third wave corresponds to an overlapped pattern of two-electron reduction of the C_{60}−triosmium cluster moiety and one-electron reduction of the porphyrin moiety (Figure S1).[6] Two successive waves are also observed at 0.29 and 0.48 V ($E_{1/2}$) for **(ZnP)**−**C$_{60}$/ITO** due to the first and second oxidations of the porphyrin moiety (Figure S2).[6] The monolayer surface coverage (Γ) of **(ZnP)**−**C$_{60}$/ITO** is estimated to be 1.8×10^{-10} mol cm^{-2} from the integrated charge of the first reduction peak at −1.17 V, which is comparable to $\sim 1.9 \times 10^{-10}$ mol cm^{-2} for a closely packed monolayer of C_{60}.[8] The coverage of **(ZnP)**−**C$_{60}$/ITO** is three times higher than that of **ZnP**−**C$_{60}$/ITO** (SAM without **DABCO**, 0.6×10^{-10} mol cm^{-2}, Figure S3[6]), which is consistent with the data in UV/vis spectra and AFM images (Figure S4).[6] Well-ordered structural confinement via strong interaction of metalloporphyrin with a bifunctional base **DABCO** may be responsible for such high surface coverage.

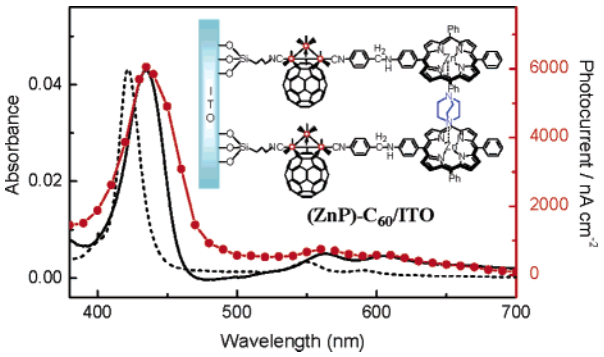

Figure 1. Absorption spectra of **ZnP**−**C$_{60}$** (···) in CH_2Cl_2 and **(ZnP)**−**C$_{60}$/ITO** (—), and the action spectrum of **(ZnP)**−**C$_{60}$/ITO/AsA/Pt** (red line) with 0.96 mW cm^{-2} light at 100 mV bias vs Ag/AgCl. Inset shows the molecular structure of **(ZnP)**−**C$_{60}$/ITO** (the red atoms are osmium atoms, and carbonyl ligands are omitted for clarity).

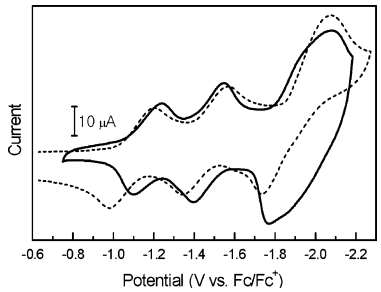

Figure 2. Cyclic voltammograms of **ZnP**−**C$_{60}$** in chlorobenzene (···) and **(ZnP)**−**C$_{60}$/ITO** in CH_2Cl_2 (—) with 0.1 M Bu_4NPF_6 as an electrolyte at a scan rate of 0.5 V s^{-1}.

Photocurrent measurements for SAMs were carried out using ascorbic acid (**AsA**) as a sacrificial electron donor by the typical reported procedures.[2c,5d,6] A stable anodic photocurrent appears

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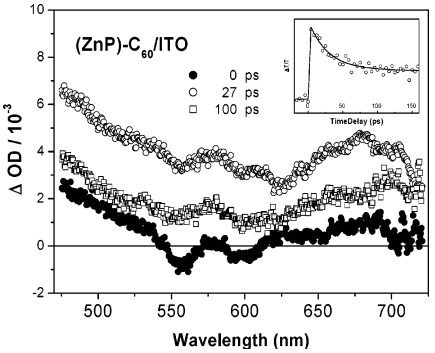

Figure 3. Transient absorption spectra of **(ZnP)−C_{60}/ITO** at 0 (●), 27 (□), and 100 (○) ps time delays with photoexcitation at 400 nm. Inset shows the transient absorption kinetic profiles at 430 nm.

immediately upon irradiation of the ITO electrode with 435 nm light (0.96 mW cm^{-2}), and the response is reversibly repeated (Figure S5).[6] The action spectrum of **(ZnP)−C_{60}/ITO/AsA/Pt** cell matches well with the absorption spectrum of **(ZnP)−C_{60}/ITO** in the 380−700 nm region (Figure 1), indicative of Zn(II)porphyrin as a photoactive sensitizer for the photocurrent generation. The anodic photocurrent increases in proportion to an increase of the positive bias of the ITO electrode (Figure S6).[6] The quantum yields for **ZnP−C_{60}/ITO/AsA/Pt** and **(ZnP)−C_{60}/ITO/AsA/Pt** cells are estimated to be 10.4 and 19.5%, respectively, based on the number of photons absorbed by the chromophores. To the best of our knowledge, the present **(ZnP)−C_{60}/ITO/AsA/Pt** cell exhibits the highest quantum efficiency ever reported for molecular photovoltaic cells (dyad 6%,[5c,d] triad 11%[5d]), based on the covalently linked D−A dyad structure on ITO.

The fluorescence lifetimes of various SAMs were measured by using time-correlated single-photon counting technique with excitation at 420 nm (Figure S7 and Table S1).[6] The fluorescence decay of SAM on the ITO surface was monitored at 605 nm corresponding to Zn(II)porphyrin emission. The fast components of fluorescence lifetimes of **ZnP−C_{60}/ITO** (12 ps) and **(ZnP)−C_{60}/ITO** (27 ps) are shorter than those of corresponding reference SAMs without C_{60} such as **ZnP−Os/ITO** and **(ZnP)−Os/ITO** (52 and 66 ps, respectively).[6] This observation implies a strong quenching of the porphyrin singlet excited state by the C_{60} ligand via intramolecular electron transfer in C_{60}-containing SAMs. A slightly longer fluorescence lifetime of **(ZnP)−C_{60}/ITO** (27 ps) compared with that of **ZnP−C_{60}/ITO** (12 ps) may be attributed to the fact that the complexation of **DABCO** between the two Zn(II)porphyrins precludes aggregation with adjacent porphyrins. Furthermore, this structural confinement increases the donor−acceptor separation. The moderate fluorescence lifetimes of our SAMs, **ZnP−C_{60}/ITO** and **(ZnP)−Os/ITO** (Table S1),[6] are believed to arise from self-quenching in aggregated porphyrins, based on previous results that the fluorescence lifetimes of **ZnP** reference molecules on ITO and slide glass are similar.[5c] These fast ET processes in **(ZnP)−C_{60}/ITO** seem to be responsible for the high performance in photocurrent generation.

The femtosecond transient absorption decay profiles of **ZnP−C_{60}/ITO** and **(ZnP)−C_{60}/ITO** with excitation at 400 nm were also measured to confirm the intramolecular electron transfer from the porphyrin singlet excited state to C_{60} on ITO. The ground-state bleaching recovery profiles of **ZnP−C_{60}/ITO** and **(ZnP)−C_{60}/ITO** at 430 nm could be fitted as double exponential decays, 12 and 92 ps and 27 ps and 2.4 ns (inset in Figure 3), respectively. The fast components are in good agreement with the fluorescence lifetimes of **ZnP−C_{60}/ITO** (12 ps) and **(ZnP)−C_{60}/ITO** (27 ps). In addition, the transient absorption spectrum acquired at 27 ps time delay for **(ZnP)−C_{60}/ITO** reveals a broad absorption band in the 630−720 nm region and an absorption tail extending to 600 nm with apparent ground-state bleaching signals at 560 and 600 nm (Figure 3). The former is consistent with the spectral feature of porphyrin cation radical **ZnP**$^{\bullet+}$,[9] and the latter corresponds to the characteristic absorption of the **DABCO** cation,[10] in which both absorption increase and decay change at the same rate. This confirms the generation of **[DABCO-ZnP]**$^{\bullet+}$ with ca. 27 ps rise and a few hundred picosecond decay time. The positive charge can be distributed over both moieties, instead of being localized exclusively on **ZnP** or **DABCO**, which may lower the charge recombination rate leading to an increase in the photocurrent generation efficiency.[9]

In conclusion, we have successfully constructed highly ordered, nearly fully covered [60]fullerene metal cluster−porphyrin dyad SAM on the ITO surface with an aid of **DABCO** binding in **(ZnP)−C_{60}/ITO**, which leads to the unusually high photocurrent generation efficiency in the **(ZnP)−C_{60}/ITO/AsA/Pt** cell. We have provided direct spectroscopic evidence for the formation of **[DABCO−ZnP]**$^{\bullet+}$ in the photoinduced ET process of **(ZnP)−C_{60}/ITO**. Further improvement of our C_{60}−metal cluster systems is under active investigation for the artificial photosynthetic applications.

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Supporting Information Available: Synthetic procedures of **ZnP−C_{60}**, photoelectrochemical data of **(ZnP)−C_{60}/ITO**, CVs of **(ZnP)−C_{60}/ITO** and related compounds in solution, AFM image, and fluorescence decay profiles of **(ZnP)−C_{60}/ITO**. This material is available free of charge via the Internet at http://pubs.acs.org.

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