Letter

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A Modular Photocurrent Generation System Based on Phospholipid-Assembled Fullerenes

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A modular photoconversion system based on phospholipid-incorporated fullerene is reported. It relies on the noncovalent formation of a lipid bilayer on an electrode to achieve precise placement of fullerene and can be quickly implemented in aqueous media. Photosensitizing dyes can be conveniently added to the system to achieve higher conversion efficiency. It is suggested that amphiphilic lipids are attractive materials for organic solar cells because of their versatility in molecular assembly and chemical conjugation.

Fullerenes have been frequently included in building artificial photoconversion systems owing to their unique electrical and photochemical properties,[1–4] including their narrow HOMO–LUMO gap, long-lived photoinduced charge separation, and low reorganization energy associated with the electron/energy transfer. To facilitate light-to-electrical energy conversion, a stable fullerene-on-electrode structure often needs to be constructed, which can be realized by a variety of synthesis and immobilization strategies,[5–9] such as self-assembly, film casting, and electrodeposition. On the other hand, fullerenes are extremely hydrophobic, which largely limits their handling and chemical modification to organic media. Presumably, decoration of pristine fullerenes with hydrophilic functional groups can produce water-soluble fullerene complexes, but heavily functionalized fullerenes only display weakened photoconversion efficiency due to their perturbed electronic structure.[3,10] A very interesting alternative is based on the use of amphiphilic species such as surfactants and phospholipids. As these molecules form colloids such as micelle and liposome in water via self-assembly, they can host fullerenes within the hydrophobic region of the final structure.[11,12] This strategy has been successfully used to build fullerene-based photoconversion devices. For example, in their pioneering work,[13–15] Mauzerall and his co-workers systematically studied the photoconducting and photosensitizing behaviors of fullerenes embedded in planar lipid bilayers. More recently, Tien and his colleagues[16,17] extended this approach by forming fullerene-incorporated lipid bilayers on solid electrode surfaces. In both cases, fullerenes are expected to exist in aggregates in lipid because of the use of pristine fullerene and organic solvent in the preparation.

We report herein a new approach to modular photocurrent generation by using amphiphilic fullerene C_{60} derivatives assembled in phospholipids. Compared to most previous photoconversion systems based on supramolecular fullerene complexes, our approach relies on noncovalent formation of a lipid bilayer on an electrode to achieve precise placement of fullerene and therefore can be quickly implemented in aqueous media. Furthermore, photosensitizing dyes can be conveniently added to the system to achieve higher conversion efficiency, which, to our knowledge, has not been explored in previous electrode-immobilized lipid/fullerene systems. In order to achieve efficient solar energy capture and conversion, new strategies must be developed to organize multiple photoactive components on electrode surfaces.[18] In this regard, we suggest that amphiphilic lipids are attractive materials because of their versatility in molecular assembly and chemical conjugation.

To maximize homogeneous dispersion of fullerenes in lipids, we adopted an extrusion-based liposome formation method,[19] in which the fullerene/lipid mixture is repeatedly pushed through a series of polycarbonate membranes of defined pore size. Less than 0.2% (mol % vs total lipids) C_{60} was incorporated into the lipid bilayer portion of the liposome this way, since the nanoporous membranes rejected most of the lipid/fullerene aggregates. It has been shown previously that high fullerene loading in liposomes could be achieved by using hydrophilic fullerene monoadducts.[20] Following this strategy, we tested whether monomalonic fullerene (Figure 1, C_{63} hereafter) could be similarly employed to increase the loading and suppress aggregation in liposomes prepared by extrusion. This was found to be the case: when C_{63} was used instead of C_{60} in the preparation, up to 3% (mol %) fullerenes could be quantitatively incorporated into the liposome

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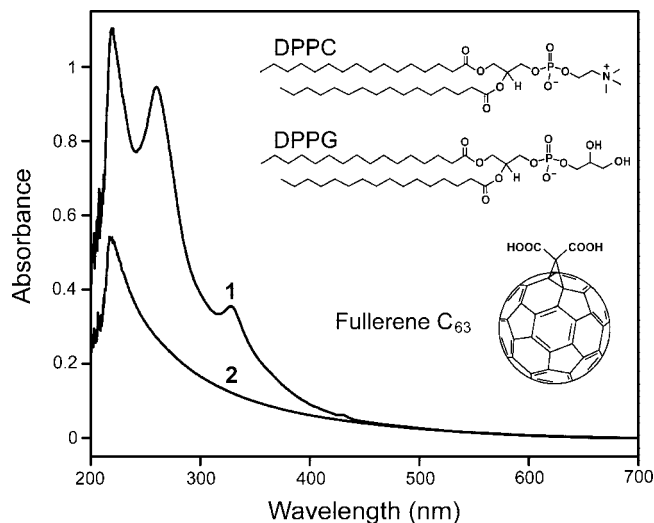
Figure 1. UV−vis absorption spectra of DPPC/DPPG (80/20, mole ratio) liposome with/without 3% (mol %) fullerene C_{63} (**1** and **2**, respectively). DPPC, 1,2-dipalmitoyl-*sn*-glycero-3-phosphocholine; DPPG, 1,2-dipalmitoyl-*sn*-glycero-[phosphor-*rac*-1-glycerol] (sodium salt). To make fullerene-incorporated liposome, the lipid/fullerene mixture in HEPES buffer (10 mM, 0.1 M NaCl, pH 7.7) was first homogenized by sonication for 2 h and then extruded consecutively by membranes with pore size of 400 and 80 nm at 45 °C. A more detailed procedure is given in the Supporting Information.

(vide infra). The ground-state absorption spectrum of the C_{63}−liposome complex reveals several key features of the system (Figure 1). While the main absorption peaks at 260 and 328 nm are typical for C_{60} fullerenes, the small peak at 429 nm is characteristic of [6,6]-closed-ring bridged fullerenes[21] including C_{63}. Importantly, the absence of noticeable features at ~450 nm indicates that aggregation of fullerene C_{63} in lipids is minimal.[11,20]

Lipid vesicles can fuse onto flat hydrophilic surfaces to form a uniform lipid bilayer structure.[22] Owing to their excellent stability and preserved lipid fluidity, these solid-supported lipid bilayers have been increasingly used as biological membrane models and biotechnological building blocks.[23] With our fullerene-incorporated liposomes, it thus becomes possible to construct a uniform fullerene layer on a conducting surface[24,25] and test its light conversion behavior. Our hypothesis here is that the amphiphilic fullerene C_{63} is placed at a relatively fixed position in the lipid bilayer. That is, the hydrophobic bulk of C_{63} preferentially stays in the hydrocarbon region, whereas its malonic group aligns itself with the polar headgroup of the lipid. Considering their relative size and concentration used in the preparation, we propose that the lipid bilayer would accommodate two loose C_{63} layers along its vertical dimension (Scheme 1). Upon irradiation, these photoexcited fullerenes will either pass electrons to or take electrons from the indium tin oxide (ITO) electrode on which the lipid bilayer is formed, resulting in a cathodic or anodic photocurrent.

As shown in Figure 2a (curve at the top), the photoconversion cell comprising C_{63}/lipid/ITO generated a stable anodic photocurrent of 40 nA/cm^2, when irradiated with blue light under no

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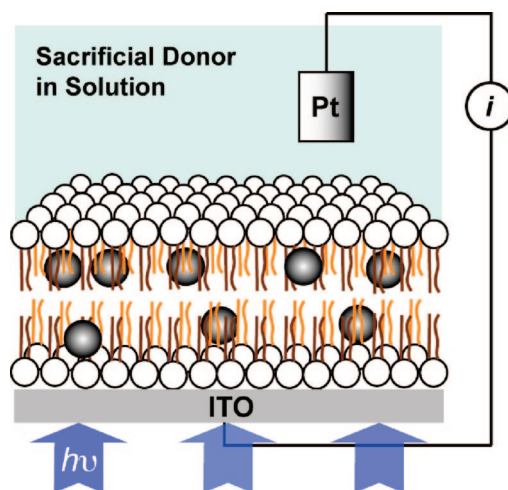
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## Scheme 1. Experimental Design[a]

[a] The system is based on fullerene C_{63}-incorporated lipid bilayer supported on indium tin oxide (ITO) electrode. A 3-electrode setup containing ITO, Pt, and Ag/AgCl (not shown) electrodes was used. The preparation of fullerene-containing lipid bilayer on ITO is described in the Supporting Information.
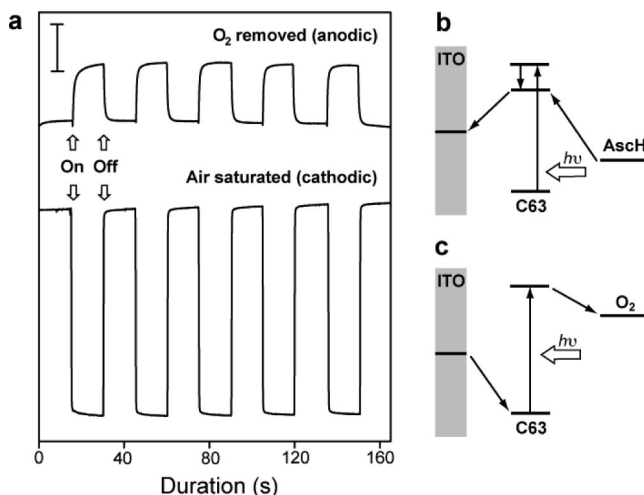
Figure 2. Photocurrent generation from fullerenes incorporated in lipid bilayers and proposed mechanisms. (a) Photocurrent responses from cells configured with fullerene C_{63} in the absence/presence of oxygen. The scale bar represents 30 nA/cm^2. All cells were irradiated by a filtered light beam (480 ± 15 nm, 29.5 mW/cm^2) from a Hg lamp switched on and off every 15 s by a mechanical shutter. The supporting electrolytes contain 50 mM ascorbic acid in HEPES buffer (pH 7.7). (b,c) Proposed mechanism of anodic (and cathodic) photocurrent generation.

bias vs the cell open-circuit potential (V_{oc}) in an oxygen-free ascorbic acid (AscH$^-$) solution. Only negligible photocurrent was obtained when either fullerene C_{63} was omitted from the lipid bilayer or a lipid/C_{60} mixture was used instead to form the lipid bilayer (not shown). The striking difference in performance between fullerenes C_{63} and C_{60} highlights the importance of orderly distribution of fullerenes in lipids in achieving efficient photoconversion. Because C_{60} lacks the amphiphilicity that C_{63} exhibits, it tends to form aggregates and precipitate in lipids, resulting in low inclusion in the lipid bilayer. By contrast, C_{63} can be quantitatively incorporated into the lipid matrix (Figure 3a). Anodic photocurrent generation from fullerene films under an oxygen-free condition has been observed previously by other workers,[26−28] and a similar mechanism is proposed in Figure 2b.

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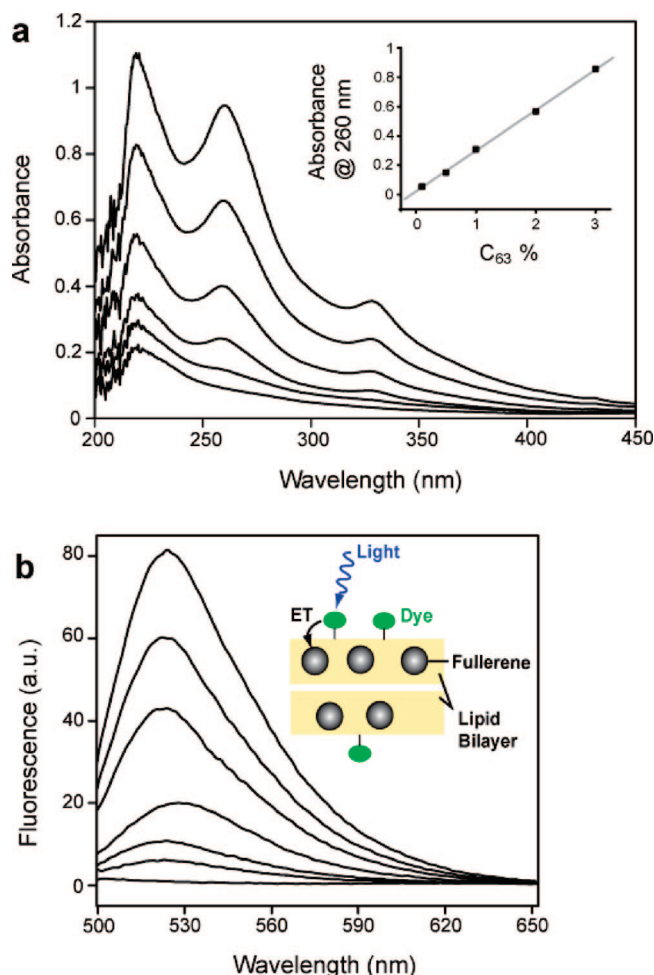
Figure 3. Spectroscopic characterization of liposomes that contain both fullerene and fluorescein dye. (a) Quantitative incorporation of fullerene C$_{63}$ in liposomes as monitored by UV−vis absorption spectroscopy. Spectra (from bottom to top) are obtained from liposomes containing 0%, 0.1%, 0.5%, 1%, 2%, and 3% fullerene C$_{63}$. Inlet: UV absorbance at 260 nm vs amount of fullerene in liposome. The liposomes were dispersed in 10 mM HEPES buffer (0.1 M NaCl, pH 7.7). (b) Fluorescence emission (ex. 460 nm) spectra of DPPC/DPPG (80/20) liposome solutions containing 0.1% fluorescein and various quantities of C$_{63}$ (0%, 0.1%, 0.5%, 1%, 2%, and 3%, from top to the second at bottom). The spectrum at the bottom was obtained from the DPPC/DPPG (80/20) liposome of the same concentration but containing no fluorescein. Inlet: schematic of photoinduced electron transfer across lipid bilayer.

Specifically, the ground-state fullerene species is directly excited to a singlet excited state, which then relaxes to its triplet excited state via intersystem crossing. Following this step, the triplet excited fullerene takes an electron from ascorbic acid in solution and concomitantly donates one electron to the external ITO electrode. On the other hand, when oxygen was present in the solution, an otherwise identical photocell gave a cathodic photocurrent of 120 nA/cm^2 (curve at bottom, Figure 2a). The presence of ascorbic acid is essential for the cathodic photocurrent generation. For instance, the photocurrent increased linearly with AscH$^-$ concentration up to 0.2 M. In addition, when 10 mM Fe(CN)$_6$$^{4-}$ ($E° = 0.16$ V vs Ag/AgCl) was used to replace AscH$^-$ ($E° = -0.19$ V) from the solution, the cathodic photocurrent dropped to ∼3 nA/cm^2. On the basis of these results as well as

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previous reports[3,29,30] on similar photochemical systems, we believe that ascorbic acid can execute dual functions in cathodic photocurrent generation. First, it is the sacrificial electron donor responsible for the oxidation reaction occurring at the counter electrode, on which Fe(CN)$_6$$^{4-}$ plays a similar role but less efficiently due to its more positive oxidation potential. Second, it effectively drives the overall reaction to the right and thus induces higher photocurrent production (Figure 2c), by scavenging the reactive oxygen intermediates generated from reactions between charge-separated fullerenes and oxygen. More experiments are underway to further verify this hypothesis. A conversion efficiency of 5% could be obtained for air-saturated DPPC/DPPG/C$_{63}$ (80/20/3, mol ratio) photocells, using 0.2 M AscH$^-$ and violet illumination (405 ± 5 nm, 9.2 mW/cm^2), with no bias vs V_{oc} (see Supporting Information).

We then reasoned that more efficient photoconversion from our system might be realized by using dye-sensitized photocurrent generation mechanism. While fullerene C$_{63}$ only absorbs visible light weakly, proper visible-absorbing dye molecules can sensitize the photoconversion process by passing the harvested light energy to fullerenes via photoinduced electron transfer (PET).[2-4] To test this feasibility in our lipid-based system, we first prepared liposomes that contain both fullerene and DOPE-conjugated fluorescein (1,2-dioleoyl-*sn*-glycero-3-phosphoethanolamine-*N*-(carboxyfluorescein)) using the same extrusion method. Fluorescein-based dyes[31,32] have been used together with TiO$_2$ to build dye-sensitized solar cells. Moreover, fluorescein-fullerene dyads[33] have been studied previously in organic media, and the corresponding fluorescence quenching was attributed to an intramolecular fluorescein-to-fullerene PET process. As shown in Figure 3b, addition of 0.1% C$_{63}$ into liposomes containing an equal amount of fluorescein quenches the latter's fluorescence by 25%, indicating a viable electronic coupling between lipid-assembled dye ($E° = -1.2$ V) and fullerene molecules ($E° = -0.61$ V). As more fullerenes were added into the liposomes, higher levels of quenching were obtained. The highest C$_{63}$ concentration tested, 3%, led to 95% quenching of the fluorescein fluorescence. These results thus point to the possibility of generating higher photocurrents in a lipid-assembled fullerene system with organic dyes.

Lipid bilayers containing both fullerene and fluorescein could be similarly formed on the ITO surface using liposomes containing both species. As shown in Figure 4, when 1% fluorescein alone was added to the ITO-supported lipid bilayer in the presence of oxygen and AscH$^-$, a cathodic photocurrent of 60 nA/cm^2 was observed. Mechanistically, the photoexcited fluorescein species can take electrons from the external electrode to generate fluorescein anionic radicals,[34] which will then be quenched by oxygen in solution via electron transfer. When 3% fullerene C$_{63}$ was coassembled with 1% fluorescein in the lipid bilayer, a cathodic photocurrent of 520 nA/cm^2 was obtained, which corresponded to a 770% (or 330%) increase in photocurrent as compared to that from the photocell containing fluorescein (or C$_{63}$) only. Underlying this synergistic photoconversion is the efficient PET between lipid-assembled fluorescein and fullerene,

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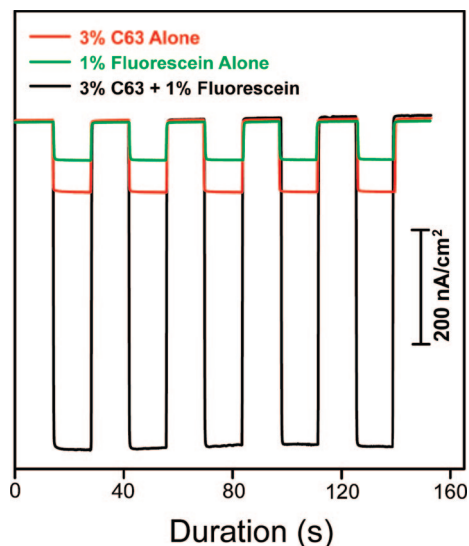(32) Hottori, S.; Hasobe, T.; Ohkubo, K.; Urano, Y.; Umezawa, N.; Nagano, T.; Wada, Y.; Yanagida, S.; Fukuzumi, S. *J. Phys. Chem. B* **2004**, *108*, 15200–15205.
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Figure 4. Photocurrents obtained from ITO-supported lipid bilayers containing 1% DOPE-fluorescein, 3% C_{63}, or both. The cells were irradiated by a filtered light beam (480 ± 15 nm) from a Hg lamp switched on and off every 15 s. The supporting electrolytes contain 50 mM ascorbic acid in air-saturated HEPES buffer (pH 7.7).

as well as the retarded charge recombination exhibited by fullerenes after charge separation. In the photocell containing fluorescein only, other photochemical processes such as back electron transfer and triplet−triplet annihilation can compete with the forward photoconversion process and thus limit the obtainable photocurrents. These competing processes, however, can be effectively suppressed, as the PET between fluorescein and fullerene redirects fluorescein-absorbed light energy to the fullerene acceptor. Another factor that can also play an active role in enhancing photocurrent is the spatial organization of the photoactive species in the lipid membrane. While fluorescein moieties in the assembly are directly exposed to the aqueous phase, the bulk of fullerenes is expected to be buried to a large extent in the lipid bilayer. As a result, a vectorial electron transfer path is established between fluorescein and fullerene upon photoexcitation (inlet, Figure 3b). Finally, liposomes are known to stabilize the triplet excited state of well-assembled fullerene species,[20] thus favoring high photocurrent generation.

Thus, we have established a new strategy for efficient photocurrent generation by using phospholipids to assemble and immobilize fullerenes on electrodes. Quantitative addition and systematic variation of photosensitizing agents to the lipid assembly can be readily achieved, which potentially enables new photoconversion models to be constructed through modular design. Further performance improvement of such systems, for example, by modifying the physical/chemical properties of lipids and dyes used, might lead to solar cells of practical value.

Supporting Information Available: Materials and experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.