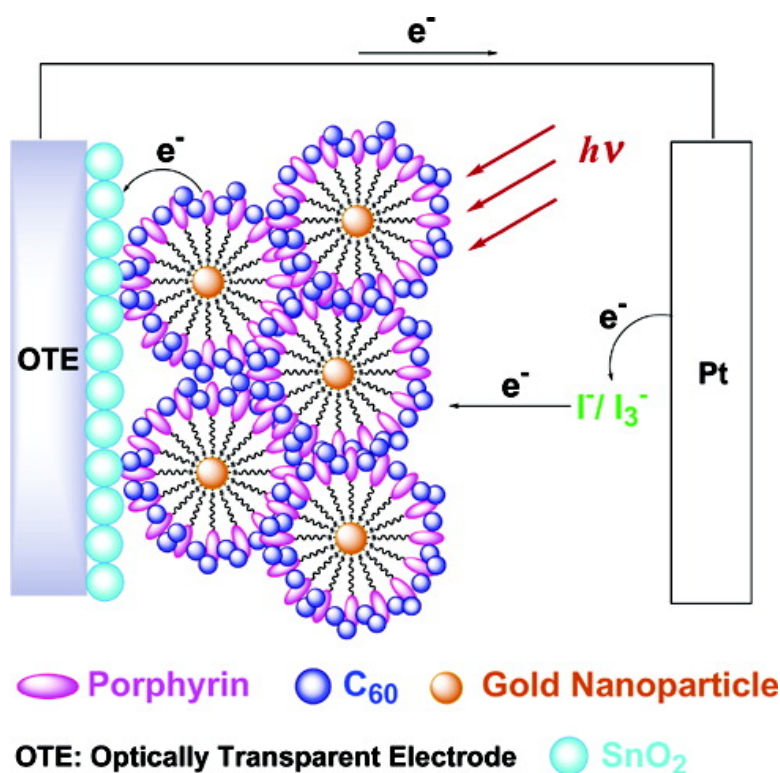


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Quaternary Self-Organization of Porphyrin and Fullerene Units by Clusterization with Gold Nanoparticles on SnO₂ Electrodes for Organic Solar Cells

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The requirement to develop inexpensive renewable energy sources has stimulated new approaches for production of efficient, low-cost organic solar cells that mimic natural photosynthesis in the conversion and storage of solar energy.^{1–5} Although strategies to design artificial photoconversion devices do not necessarily imitate all of the intricacies of natural photosynthesis, the artificial photoconversion devices developed so far have only a low degree of self-organization, whereas the components in the natural system are highly organized in quaternary protein structures.⁶

Herein, we report novel organic solar cells prepared using quaternary self-organization of porphyrin (donor) and fullerene (acceptor) dye units by clusterization with gold nanoparticles on SnO₂ electrodes as shown in Figure 1. First porphyrin-alkanethiolate monolayer protected gold nanoclusters with well-defined size (8–9 nm) and spherical shape H₂PC_{*n*}MPC (*n* = 5, 11)⁷ are prepared (secondary organization) starting from the primary component (porphyrin-alkanethiol).⁸ These nanoparticles form complexes with fullerene molecules (tertiary organization), and they are clusterized in an acetonitrile/toluene mixed solvent (quaternary organization). The clusters are then attached to SnO₂ electrodes by an electrophoretic deposition method.

The quaternary organization of H₂PC_{*n*}MPC and C₆₀ composite clusters [denoted as (H₂PC_{*n*}MPC + C₆₀)_{*m*} (*n* = 5, 11)] was performed by injecting a mixed toluene solution of H₂PC_{*n*}MPC and C₆₀ in acetonitrile/toluene (3/1, v/v).^{9,10} This procedure allows us to achieve the complex formation between H₂PC_{*n*}MPC and C₆₀, and the clusterization at the same time. The clusterization of the H₂PC_{*n*}MPC reference system without C₆₀ [denoted as (H₂PC_{*n*}MPC)_{*m*} (*n* = 5, 11)] or porphyrin and C₆₀ reference system without gold nanoparticles [denoted as (H₂P-ref + C₆₀)_{*m*}; H₂P-ref: 5,15-bis(3,5-di-*tert*-butylphenyl)porphyrin] was also performed in the same manner. The absorption spectra of (H₂PC₁₁MPC + C₆₀)_{*m*} and (H₂PC₁₁MPC)_{*m*} in an acetonitrile/toluene 3:1 mixture are much broader than those in toluene, implying formation of the clusters in the mixed solvent (see Supporting Information Figures S1, S2). The broad long-wavelength absorption in the 700–800 nm regions is diagnostic of the charge-transfer absorption band due to the π -complex formed between the porphyrin and C₆₀.^{11,12}

The TEM image of (H₂PC₁₁MPC + C₆₀)_{*m*} (Figure 1a) displays well-controlled size and shape of larger nanoclusters with a diameter of 300–400 nm. These clusters are in sharp contrast with the TEM image of (H₂PC₁₁MPC)_{*m*} without C₆₀ exhibiting irregular, smaller size (Figure 1b). Judging from the diameter of H₂PC_{*n*}MPC (8–9 nm), one can safely conclude that H₂PC_{*n*}MPC are self-assembled

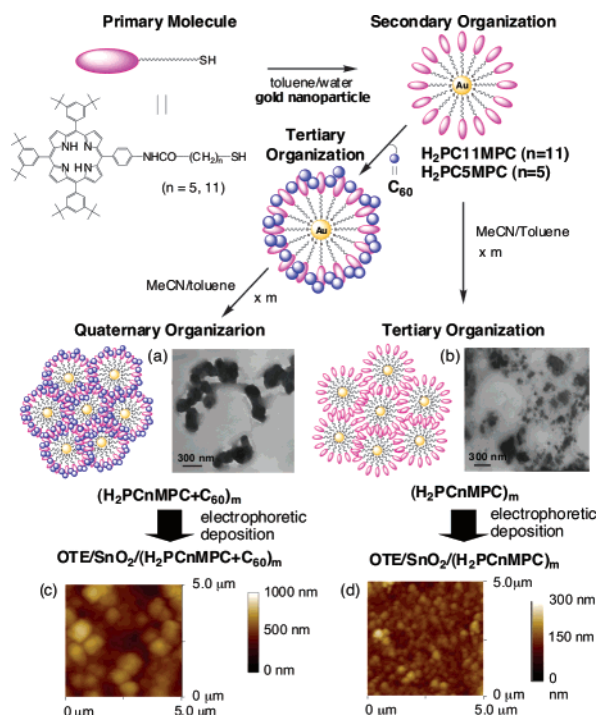


Figure 1. Illustration of high-order organization of porphyrin and C₆₀ units with gold nanoparticles and their TEM image of (a) (H₂PC₁₁MPC + C₆₀)_{*m*} and (b) (H₂PC₁₁MPC)_{*m*}, AFM image of (c) OTE/SnO₂/(H₂PC₁₁MPC + C₆₀)_{*m*} and (d) OTE/SnO₂/(H₂PC₁₁MPC)_{*m*}.

with C₆₀ molecules in the mixed solution to yield large donor–acceptor (D–A) nanoclusters with an interpenetrating network. Upon subjecting the resultant cluster suspension to a high electric (DC) field (200 V for 1 min), mixed H₂PC_{*n*}MPC and C₆₀ clusters [(H₂PC_{*n*}MPC + C₆₀)_{*m*}] and reference clusters [(H₂PC_{*n*}MPC)_{*m*} or (H₂P-ref + C₆₀)_{*m*}] were deposited onto an optically transparent electrode (OTE) of nanostructured SnO₂ electrode (OTE/SnO₂), to give modified electrodes [denoted as OTE/SnO₂/(H₂PC_{*n*}MPC + C₆₀)_{*m*}, OTE/SnO₂/(H₂PC_{*n*}MPC)_{*m*}, and OTE/SnO₂/(H₂P-ref + C₆₀)_{*m*} (*n* = 5, 11)], respectively. The absorptivity of OTE/SnO₂/(H₂PC_{*n*}MPC + C₆₀)_{*m*} is much enhanced as compared with that of OTE/SnO₂/(H₂PC_{*n*}MPC)_{*m*} (Supporting Information Figure S2). These results ensure that incident light is absorbed intensively in the visible and near-infrared regions by OTE/SnO₂/(H₂PC_{*n*}MPC + C₆₀)_{*m*}.

The AFM image of OTE/SnO₂/(H₂PC₁₁MPC + C₆₀)_{*m*} and OTE/SnO₂/(H₂PC₁₁MPC)_{*m*} reveals the cluster aggregation with a regular size (Figure 1c and 1d). These results also suggest that the electric deposition of (H₂PC_{*n*}MPC + C₆₀)_{*m*} and (H₂PC_{*n*}MPC)_{*m*} leads to the association of smaller clusters on a nanostructured SnO₂

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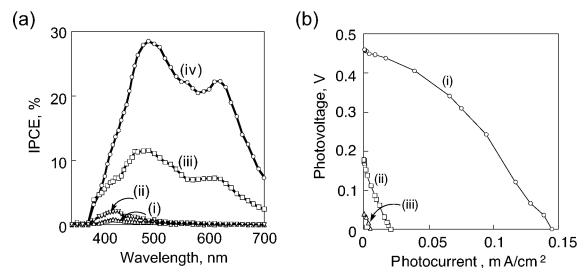


Figure 2. (a) The photocurrent action spectra (IPCE vs wavelength) of OTE/SnO₂/(H₂PC11MPC + C₆₀)_m under short circuit conditions. [H₂P] = 0.19 mM; [C₆₀] = (i) 0 mM, (ii) 0.06 mM, (iii) 0.19 mM, and (iv) 0.31 mM in acetonitrile/toluene = 3/1. (b) Current–voltage characteristics of (i) OTE/SnO₂/(H₂PC11MPC + C₆₀)_m, (ii) OTE/SnO₂/(H₂P-ref + C₆₀)_m, and (iii) OTE/SnO₂/(H₂PC11MPC + C₆₀)_m in the dark. Electrolyte: 0.5 M NaI and 0.01 M I₂ in acetonitrile. Input power: 3.4 mW cm⁻². [H₂P] = 0.19 mM; [C₆₀] = 0.31 mM.

electrode to grow larger ones. The size of OTE/SnO₂/(H₂PC11MPC + C₆₀)_m (700–900 nm) is much larger than that of OTE/SnO₂/(H₂PC11MPC)_m (300–400 nm). This indicates that quaternary organization of the porphyrin and C₆₀ molecules is achieved on SnO₂, allowing formation of the interpenetrating network of the porphyrin and C₆₀ molecules for OTE/SnO₂/(H₂PC11MPC + C₆₀)_m.

Photoelectrochemical measurements were performed with a standard two-electrode system consisting of a working electrode and Pt wire gauze electrode in 0.5 M NaI and 0.01 M I₂ in acetonitrile. Figure 2a showed the incident photon to photocurrent efficiency (IPCE) of the OTE/SnO₂/(H₂PC11MPC + C₆₀)_m system as a function of the initial concentration of the mixed toluene solution containing the porphyrin and C₆₀ moieties ([H₂P]:[C₆₀] = (i) 100:0, (ii) = 75:25, (iii) = 50:50, (iv) = 37:63). IPCE of the OTE/SnO₂/(H₂PC11MPC)_m system exhibits a remarkable increase with increasing the relative ratio of C₆₀ to reach a maximum IPCE of 28% at 490 nm with the initial relative ratio of ([H₂P]:[C₆₀] = 37:63). Considering the well-established photodynamics of the porphyrin-fullerene system,¹³ these results lead to the conclusion that the porphyrin excited singlet state is quenched by C₆₀ via electron transfer in the porphyrin-C₆₀ complex rather than by the gold nanocluster via energy transfer. This is consistent with the results that under the same conditions the IPCE value is 7 times as large as that of OTE/SnO₂/(H₂PC5MPC + C₆₀)_m where the chain length of MPC is too short to accommodate C₆₀ between two porphyrin rings (Supporting Information Figure S3). In this case, the porphyrin excited singlet state is quenched more efficiently by the gold nanocluster due to the short spacer (i.e., *n* = 5) between the porphyrin and the gold nanocluster rather than electron transfer to C₆₀.

Figure 2b shows current–voltage (*I/V*) characteristics of OTE/SnO₂/(H₂PC11MPC + C₆₀)_m, OTE/SnO₂/(H₂PC11MPC)_m, and OTE/SnO₂/(H₂P-ref + C₆₀)_m in the dark and under visible light irradiation ($\lambda > 370$ nm). The OTE/SnO₂/(H₂PC11MPC + C₆₀)_m system has a much larger fill factor (*FF*) of 0.35, open circuit voltage (*V*_{oc}) of 420 mV, short circuit current density (*I*_{sc}) of 0.14 mA cm⁻², and overall power conversion efficiency (η) of 0.61% at an input power (*W*_{in}) of 3.4 mW cm⁻² as compared with the reference systems. The *I/V* characteristics of OTE/SnO₂/(H₂PC11MPC + C₆₀)_m are also remarkably enhanced in comparison with OTE/SnO₂/(H₂P-ref + C₆₀)_m under the same experimental conditions. Furthermore, the IPCE obtained with the (H₂PC11MPC + C₆₀)_m system is more than an order of magnitude greater than the one obtained by sensitizing TiO₂ with (H₂P-ref)_m clusters.¹⁴ These results clearly show the large improvement of photoelectrochemical properties is due to the three-dimensional structure between porphyrin and fullerene.

Photocurrent generation in the present system is initiated by photoinduced charge separation from the porphyrin excited singlet state (H₂P*/H₂P⁺ = -0.7 V vs NHE)¹³ to C₆₀ (C₆₀/C₆₀⁻ = -0.2 V vs NHE)⁹ in the porphyrin-C₆₀ complex rather than direct electron injection to the conduction band of SnO₂ (0 V vs NHE)⁹ system. While the reduced C₆₀ injects electrons into the SnO₂ nanocrystallites, the oxidized porphyrin (H₂P/H₂P⁺ = 1.2 V vs NHE)¹³ undergoes electron-transfer reduction with the iodide (I₃⁻/I⁻ = 0.5 V vs NHE)⁹ in the electrolyte system.

Remarkable enhancement in the photoelectrochemical performance as well as broader photoresponse in the visible and infrared (Figure 2) relative to the reference systems demonstrates that the quaternary organization approach provides a novel perspective for the development of efficient organic solar cells.

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Supporting Information Available: Absorption spectra of OTE/SnO₂/(H₂PC11MPC + C₆₀)_m and the reference systems (S1, S2), photocurrent action spectrum of OTE/SnO₂/(H₂PC5MPC + C₆₀)_m (S3), and experimental section (S4, S5) (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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