Hierarchical Assembly of Porphyrins and Fullerenes for Solar Cells

by Taku Hasobe, Shunichi Fukuzumi, and Prashant V. Kamat

The rapid consumption of fossil fuels has created unacceptable environmental problems such as greenhouse effects, which may lead to disastrous climatic consequences. Thus, renewable and clean energy such as that obtained by using solar cells is required to maintain the quality of human life as well as the environment. Progress is being made in the development of heterojunction organic solar cells, which possess an active layer of a conjugated donor polymer and an acceptor fullerene.[1] In these polymer blends, efficient photoinduced electron transfer occurs at the donor-acceptor interface, and intimate mixing of donor and acceptor is therefore beneficial for efficient charge separation.[1,2] For efficient transport of the positive charge carriers through the donor phase and of electrons via the acceptor phase to the electrodes, a phase-segregated network is required.

The need to develop next-generation solar cells has stimulated renewed interest in the design of efficient, low-cost organic solar cells. A most promising strategy is the development of organic solar cells that mimic natural photosynthesis. Energy from sunlight is captured by photosynthetic π-pigments (primarily chlorophylls and carotenoids) which cover the wide spectral range of solar radiation.[3] Light energy is absorbed by individual π-pigments but is not used immediately by these π-pigments for energy conversion. Instead, the light energy is transferred to chlorophylls that are in a well-organized protein environment where the actual energy conversion event starts via electron transfer processes.

The artificial photoconversion devices developed so far have a limited degree of self-organization, whereas the components in the natural system are highly organized in quaternary protein structures. Thus, the construction of efficient photovoltaic devices requires an enhanced light-harvesting efficiency of well-organized chromophore molecules over as much of the solar spectrum as possible together with a highly efficient conversion of the harvested light into electrical energy.

Metal hybrids of organic molecules assembled as two- or three-dimensional (3D) architectures provide routes to the design of materials with electrical, optical, and photochemical properties having potential applications in nanophotonics, lithography, and sensing. The possibility of tailoring the optoelectronic properties of metal nanoparticles by organizing chromophores of specific properties and functions on gold nanoparticles leads to the design of photoresponsive organic-inorganic nanohybrids. Such an organization of a densely packed photoresponsive shell encapsulating the nanoparticle core offers exciting opportunities for the design of light energy conversion devices.[4]

Organized inorganic-organic nanohybrids, with hierarchical superiority in architecture, may be developed by assembling monolayers of organic molecules containing functional groups, such as amines, thiols, isothiocyanates, and silanes, onto the 3D surface of metal nanoparticles.[5] Such monolayer-protected metal clusters (MPCs) prepared by adopting the two-phase extraction procedure can be functionalized with chromophores by place-exchange reactions. For example, porphyrin-alkanethiolate monolayer protected-gold nanoclusters (H_2PC_nMPC) form spherical shape clusters that can be employed as light harvesting antenna. They exhibit high light-harvesting capability and suppress undesirable energy transfer quenching of the porphyrin singlet excited state by the gold surface relative to the bulk gold. Organized porphyrin molecules on gold nanoparticle possess a void space between the porphyrin moieties that facilitate interaction with fullerenes. Thus, a combination of H_2PC_nMPC and C_{60} provides an ideal system for fulfilling an enhanced light-harvesting efficiency of chromophores throughout the solar spectrum and a highly efficient conversion of the harvested light via the high-energy state of the charge separated complex by photoinduced electron transfer.

Fullerenes hold a great promise as a spherical electron acceptor on account of their small reorganization energy in electron transfer reactions.[6] Porphyrins are excellent candidates to capture photons and promote efficient electron transfer with small reorganization energies.[7] In addition, the rich and extensive absorption features of porphyrin systems guarantee increased absorption cross sections and an efficient use of the solar spectrum. Porphyrins and fullerenes readily undergo charge transfer interactions and form a supramolecular complex in solutions as well as in the solid state.[8]

The supramolecular chemistry approach as a means of assembling donor (porphyrin) and acceptor (C_{60}) for light energy conversion has been studied extensively by us and this article represents an overview of earlier published work.[9-12] Composites of donor and acceptor moieties (*e.g.*, porphyrin and fullerene) in the form of clusters when assembled as a 3D network on a conducting surface provide a means to achieve efficient photocurrent generation.

Electrophoretic Deposition of Cluster Films

Porphyrin (H_2PC_nMPC and H_2P-ref) and C_{60} (Fig. 1) are soluble in nonpolar solvents such as toluene, but sparingly soluble in polar solvents such as acetonitrile. When a concentrated solution of C_{60} or porphyrin in toluene is mixed with acetonitrile by fast injection, the molecules aggregate and form stable clusters. The final solvent ratio of mixed solvent employed in the present experiments was 3:1 (v/v)

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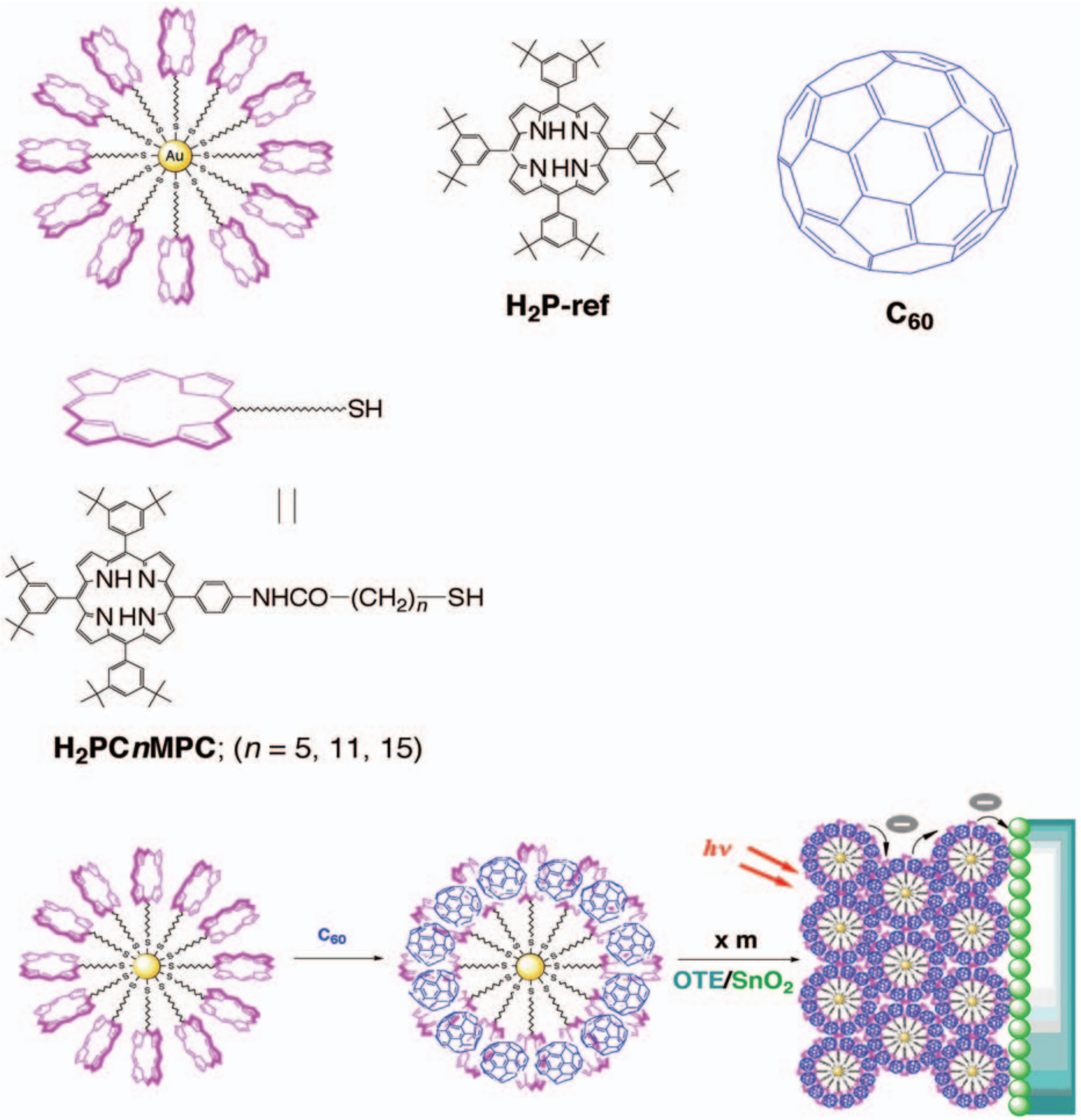

FIG. 1. *Hierarchical assembly of H_2PC_nMPC and C_{60} in the form of clusters and their assembly on a SnO_2-coated conducting glass electrode.*

acetonitrile:toluene. The same strategy can be extended to prepare mixed or composite molecular clusters consisting of H_2PC_nMPC (or H_2P-ref) and C_{60} molecules. Mixed cluster aggregates may be prepared by mixing an equimolar solution of porphyrin H_2PC_nMPC or H_2P-ref and C_{60} in toluene (0.5 mL) and then injecting it into a pool of acetonitrile (1.5 mL). These optically transparent composite clusters are stable at room temperature and can be converted back to their monomeric forms by diluting the solution with toluene.

A known amount of porphyrin derivatives, C_{60} or mixed cluster solution in acetonitrile/toluene (3/1, v/v, 2 mL) is transferred to a 1 cm optical cuvette in which two optically transparent electrodes (viz., OTE/SnO_2 and OTE) are kept at a distance of 6 mm using a Teflon spacer. A dc voltage (200 V) is applied between these two electrodes using a Fluke 415 power supply. The deposition of the film is visible as the solution becomes colorless with simultaneous brown coloration of the OTE/SnO_2 electrode. The OTE/SnO_2 electrode coated with mixed H_2PC_nMPC and C_{60} clusters is referred to as OTE/SnO_2/$(H_2PC_nMPC + C_{60})_m$.

The absorption spectra of $H_2PC_{11}MPC$ and C_{60} in neat toluene are compared with that of $[(H_2PC_{11}MPC+C_{60})_m]$ clusters in acetonitrile/toluene (3/1, v/v) in Fig. 2. The composite clusters $[(H_2PC_{11}MPC+C_{60})_m]$ in the mixed solvent (spectrum a) exhibit much broader and more intense absorption in the visible and near-infrared (near-IR) regions than those of parent $H_2PC_{11}MPC$ (spectrum b) and C_{60} (spectrum c) in toluene. This demonstrates that the composite clusters of $H_2PC_{11}MPC$ and C_{60} are superior as light absorbers to the single component clusters of $H_2PC_{11}MPC$ or C_{60}, because the composite clusters absorb throughout the visible part of the solar spectrum. Similar trends are also observed for other chromophore functionalized metal particles, viz., H_2PC_5MPC and $H_2PC_{15}MPC$.

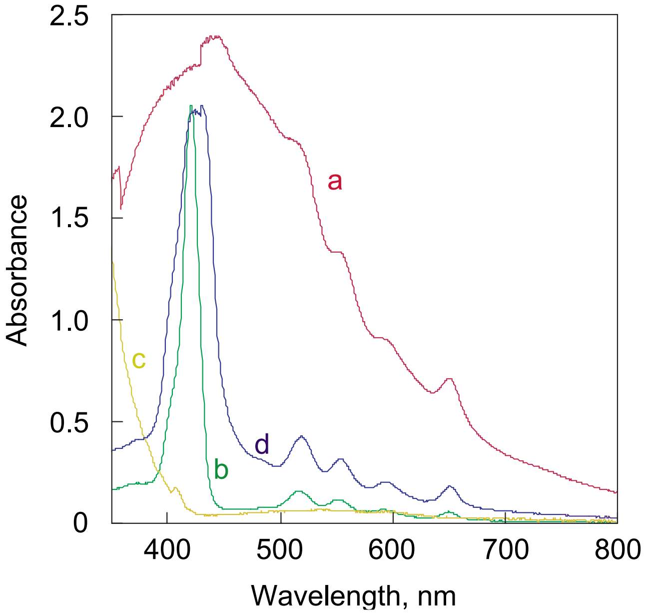

Fig. 2. *Absorption spectra of (a) $(H_2PC_{11}MPC+C_{60})_m$ clusters in acetonitrile/toluene (3/1, v/v); $[H_2P] = 0.19$ mM $[C_{60}] = 0.31$ mM, (b) $H_2PC_{11}MPC$ in toluene; $[H_2P] = 18$ µM, (c) C_{60} in toluene; $[C_{60}] = 150$ µM, and (d) $(H_2PC_{11}MPC)_m$ in acetonitrile/toluene (3 /1, v/v); $[H_2P] = 0.19$ mM.*

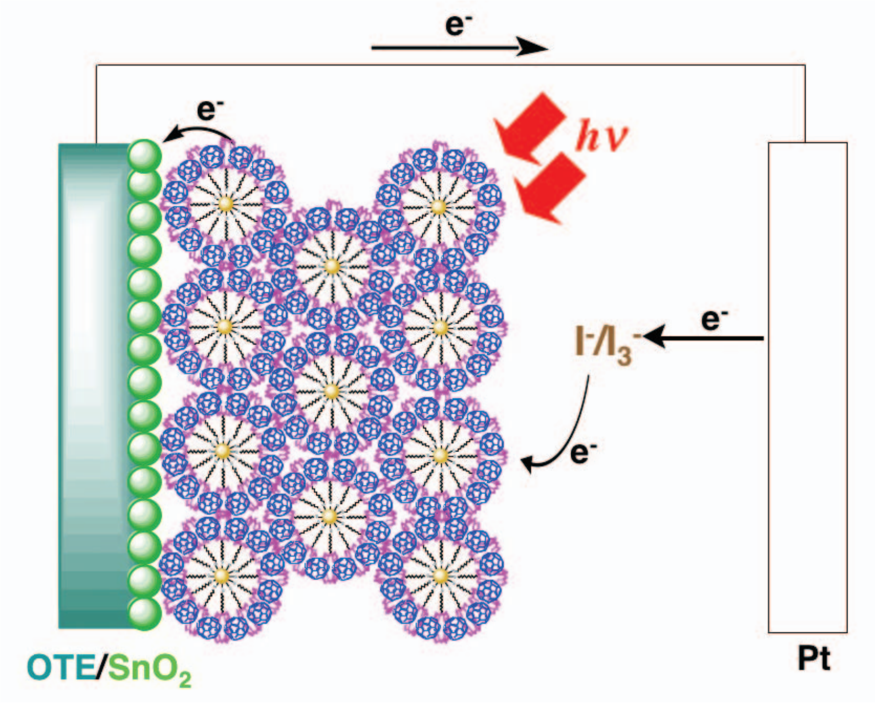

Fig. 3. *Operation of a photoelectrochemical solar cell using hierarchical assembly of fullerenes and porphyrins.*

Porphyrin-Fullerene Assemblies for Solar Cells

To evaluate the photoelectrochemical performance of the $(H_2PC_nMPC+C_{60})_m$ films cast on SnO_2 electrodes, we employed the OTE/SnO_2/$(H_2PC_nMPC+C_{60})_m$ electrode as a photoanode in a photoelectrochemical cell. Photocurrent measurements were performed in acetonitrile containing NaI (0.5 M) and I_2 (0.01 M) as redox electrolyte using a Pt gauge counter electrode as shown in Fig. 3. Photocurrent action spectra of $(H_2PC_nMPC+C_{60})_m$ clusters were recorded by varying the excitation wavelength (Fig. 4). The incident photon-to-photocurrent conversion efficiency (IPCE) values were calculated by normalizing the photocurrent values for incident light energy and intensity[10,11,13]

$$\text{IPCE}\ (\%) = 100 \times 1240 \times I_{sc} / (I_{inc} \times \lambda) \quad [1]$$

where I_{sc} is the short-circuit photocurrent (A/cm^2), I_{inc} is the incident light intensity (W/cm^2), and λ is the wavelength (nm). The overall response of OTE/SnO_2/$(H_2PC_nMPC+C_{60})_m$ parallels the broad absorption spectral features, indicating the involvement of both H_2PC_nMPC and C_{60} in the photocurrent generation.

Experiments on C_{60} with a constant concentration of $H_2PC_{11}MPC$ and measuring the resultant photocurrent exhibit a remarkable increase with increasing the relative ratio of C_{60} to reach the maximum IPCE of 28% at 490 nm with the initial relative ratio of $[H_2P]$:$[C_{60}]$ = 38:62. Considering the well-established photodynamics of the porphyrin-fullerene system, the porphyrin excited singlet state is expected to be quenched by C_{60} via electron transfer in the porphyrin-C_{60} complex rather than by the gold nanoclusters via energy transfer. The length of the linker molecule also influenced the IPCE. Figure 4 shows the effect of the alkanethiolate chain length on the IPCE values.[11] Comparision of the photocurrent action spectra indicate that the higher IPCE and the broader photoresponse are attained with the longer chain length of H_2PC_nMPC. In particular, OTE/SnO_2 /$(H_2PC_{15}MPC+C_{60})_m$ exhibits the maximum IPCE value (54%) and very broad photoresponse (up to ~1000 nm), thus extending the response to the near-IR region. In OTE/SnO_2/$(H_2PC_{15}MPC+C_{60})_m$, a long methylene spacer of $H_2PC_{15}MPC$

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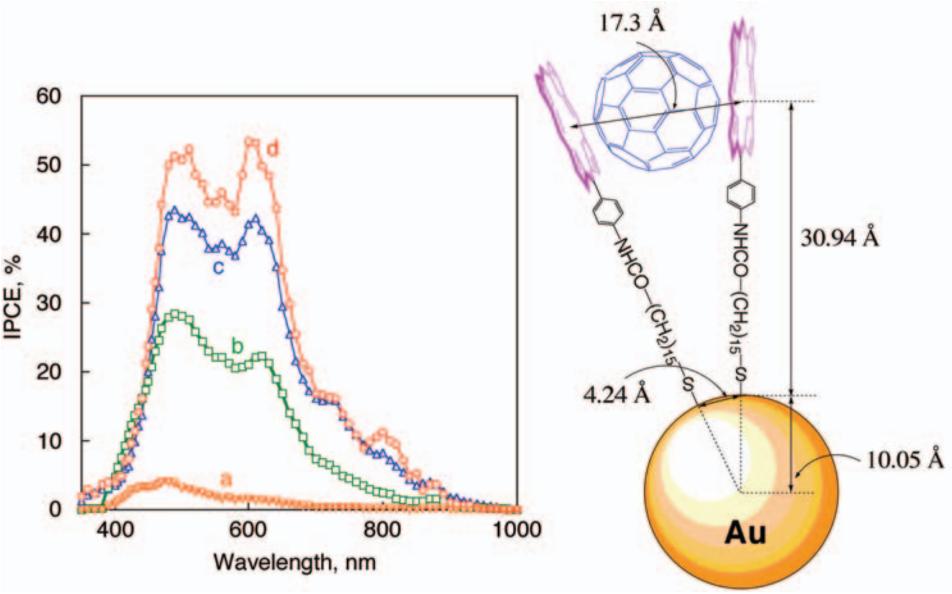


Fig. 4. *Photocurrent action spectra of OTE/SnO$_2$/(H$_2$PC$_n$MPC+C$_{60}$)$_m$ electrode ([H$_2$P] = 0.19 mM; (a) n = 5, [C$_{60}$] = 0.31 mM; (b) n = 11, [C$_{60}$] = 0.31 mM; (c) n = 15, [C$_{60}$] = 0.31 mM; (d) n = 15, [C$_{60}$] = 0.38 mM. Electrolyte; 0.5 M NaI and 0.01 M I$_2$ in acetonitrile.*

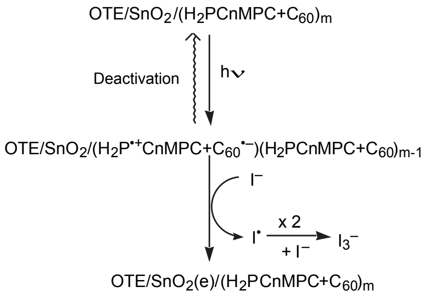
allows sufficient space for the insertion of fullerene molecules and interaction with the neighboring two porphyrin moieties (see illustration of insertion of C$_{60}$ between the porphyrin rings of H$_2$PC$_{15}$MPC in Fig. 4).[11]

The power conversion efficiency (η) of the photochemical solar cell may be evaluated by varying the load resistance (Fig. 5).[11] A drop in the photovoltage and an increase in the photocurrent are observed with decreasing load resistance. The OTE/SnO$_2$/ (H$_2$PC$_{15}$MPC+C$_{60}$)$_m$ system has a much larger fill factor (*FF*) of 0.43, open-circuit voltage (V_{oc}) of 380 mV, short-circuit current density (I_{sc}) of 1.0 mA cm^{-2}, and the overall η of 1.5% at input power (W_{in}) of 11.2 mW cm^{-2}.

A porphyrin octamer with a polypeptidic backbone [P(H$_2$P)$_8$] in Fig. 6 has also been utilized to construct porphyrin-fullerene assemblies for solar cells.[14] The OTE/SnO$_2$/(P(H$_2$P)$_8$ +C$_{60}$)$_m$ system also has a large fill factor (*FF*) of 0.47, V_{oc} of 300 mV, short-circuit current density (I_{sc}) of 0.31 mA cm^{-2}, and the overall η of 1.3% at W_{in} of 3.4 mW cm^{-2}.[15]

Photocurrent Generation Mechanism

The photocurrent generation may be initiated by photoinduced charge separation from the porphyrin singlet excited state (^{1}H$_2$P*/H$_2$P$^{\bullet+}$ = -0.7 V *vs.* the normal hydrogen electrode NHE) to C$_{60}$ (C$_{60}$/C$_{60}^{\bullet-}$ = -0.2 V *vs.* NHE) in porphyrin-C$_{60}$ supramolecular complex rather than via direct electron injection to conduction band of SnO$_2$ (0 V *vs.* NHE) system, which is energetically more favorable (*vide infra*). The electron transfer from ^{1}H$_2$P* to C$_{60}$ competes well with the energy transfer to the gold nanoparticles. While the reduced C$_{60}$ injects electrons into the SnO$_2$ nanocrystallites, the oxidized porphyrin (H$_2$P/H$_2$P$^{\bullet+}$ = 1.2 V *vs.* NHE) undergoes the electron transfer reduction with iodide ion (I$_3^-$/I$^-$ = 0.5 V *vs.* NHE) in the electrolyte.[11]



Concluding Remarks

Organized supramolecular assemblies of multiporphyrin arrays with fullerene molecules as 3D network provide ideal systems for fulfilling an enhanced light-harvesting efficiency of chromophores throughout the solar spectrum. Efficient conversion of the harvested light into the higher energy state of the charge separated complex is achieved by photoinduced electron transfer through such assemblies. There are two essential factors in the efficient photocurrent generation. One is charge separation between porphyrin and fullerene and the other is the resulting hole and electron transport in the thin film. The example of porphyrin and fullerene moieties anchored on a gold surface demonstrates the importance of molecular organization in facilitating efficient charge separation. Three-dimensional steric control between porphyrin and fullerene in the supramolecular systems contributes to both the efficient formation of charge separation and the hole and electron transport in the thin film. Further development of supramolecular assemblies of multiporphyrin arrays with fullerene molecules will certainly contribute to the emergence of efficient light energy conversion systems. Semiconductor nanoparticles and carbon nanotubes also may serve as a support for organizing supramolecular assemblies and facilitate light energy conversion. Our recent efforts have demonstrated success in guiding the porphyrin assembly through single-wall carbon nanotubes.[16] ■

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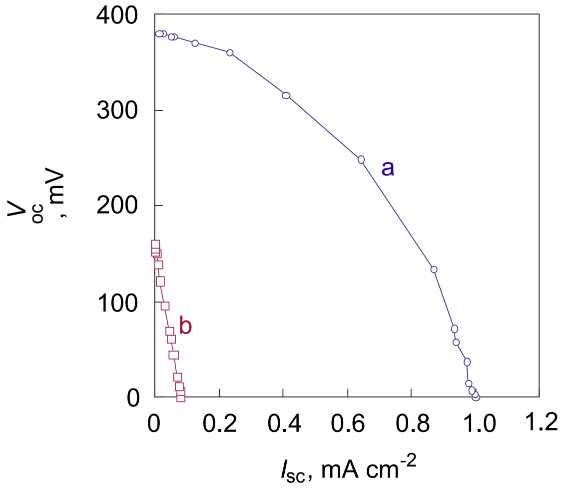
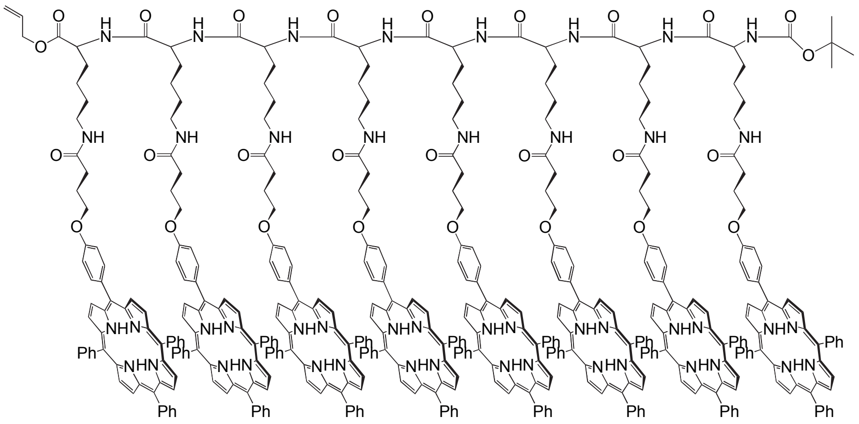


FIG. 5. *Current-voltage characteristics of (a) OTE/SnO_2/($H_2PC_{15}MPC+C_{60}$)$_m$ electrode and (b) OTE/SnO_2/($H_2Pref+C_{60}$)$_m$ electrode prepared from cluster solution of ([H_2P] = 0.19 mM; [C_{60}] = 0.38 mM) under visible light illumination (λ > 400 nm); electrolyte 0.5 M NaI and 0.01 M I_2 in acetonitrile; input power: 11.2 mW/cm².*



$P(H_2P)_8$

FIG. 6. *Porphyrin-peptide octamer [$P(H_2P)_8$] employed for construction of organic solar cells composed of multiporphyrin/C_{60} supramolecular assemblies.*

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