

Enhancement of Light-Energy Conversion Efficiency by Multi-Porphyrin Arrays of Porphyrin–Peptide Oligomers with Fullerene Clusters

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Organic photovoltaic cells using supramolecular complexes of porphyrin–peptide oligomers (porphyrin-functionalized α -polypeptides) with fullerene demonstrate remarkable enhancement in the photoelectrochemical performance as well as broader photoresponse in the visible and near-infrared regions by increasing the number of porphyrin units in α -polypeptide structures. A high power conversion efficiency (η) of 1.3% and a maximum incident photon-to-photocurrent efficiency (IPCE) of 42% were attained using composite clusters of porphyrin–peptide octamer and fullerene. These results clearly show that the formation of a molecular assembly between fullerene and multi-porphyrin arrays with a polypeptide backbone controls the electron transfer efficiency in the supramolecular complex, which is essential for the light-energy conversion.

The requirement to develop inexpensive renewable energy sources has stimulated new approaches for the production of efficient, low-cost organic photovoltaic devices.^{1–3} Photovoltaic devices based on solution-processable conjugated polymers (donor) mixed with fullerene (acceptor) are particularly attractive for the production of low-cost solar cells.³ On the other hand, the light-harvesting complexes in the natural photosynthetic system are composed of chlorophylls (or bacteriochlorophylls) assembled in protein matrices with α -helical polypeptides absorbing light over a wide spectral range.^{4–6} The challenge of creating artificial mimics of these light-harvesting complexes has stimulated the development of routes to a diverse collection of multi-porphyrin arrays.^{7–9} In this context, we have recently reported that composite clusters of multi-porphyrin arrays and fullerene (C_{60}), which were assembled on a nanostructured SnO_2 electrode using an electrophoretic deposition technique, exhibited much enhanced light-energy conversion properties as compared with the nonorganized systems.¹⁰ The multi-porphyrin arrays employed in the composite clusters with C_{60} were

porphyrin dendrimers and porphyrin alkanethiolate monolayer-protected gold nanoparticles. In the case of composite cluster systems composed of porphyrin dendrimers and fullerene, however, the light-energy conversion property decreases with increasing dendritic generations because of the rigid structure of porphyrin dendrimers, which hampers effective interaction between the porphyrin units and C_{60} in the higher dendritic generation.^{10a} In the case of the porphyrin alkanethiolate monolayer-protected gold nanoparticles, on the other hand, the singlet excited state of the porphyrin unit is strongly quenched by energy transfer to the gold nanoparticles.^{10b,11} Thus, multi-porphyrin arrays with rather flexible structure without energy transfer quenching are required to improve the energy conversion efficiency in the composite cluster systems with C_{60} .

We report herein novel photovoltaic cells composed of porphyrin–peptide oligomers (porphyrin-functionalized α -polypeptides; Chart 1)¹² and fullerene clusters, which are deposited on nanostructured SnO_2 electrodes. Such porphyrin oligomers with a polypeptidic backbone are flexible enough to accommodate C_{60} between the porphyrin units, and no quenching of the excited state of porphyrins is observed as compared with the monomer porphyrin, in contrast with the case of porphyrin alkanethiolate monolayer-protected gold nanoparticles. The light-energy conversion efficiency is shown to increase with an increasing number of porphyrins in a polypeptide unit to reach the highest value ($\eta = 1.3\%$ and maximum IPCE = 42%).

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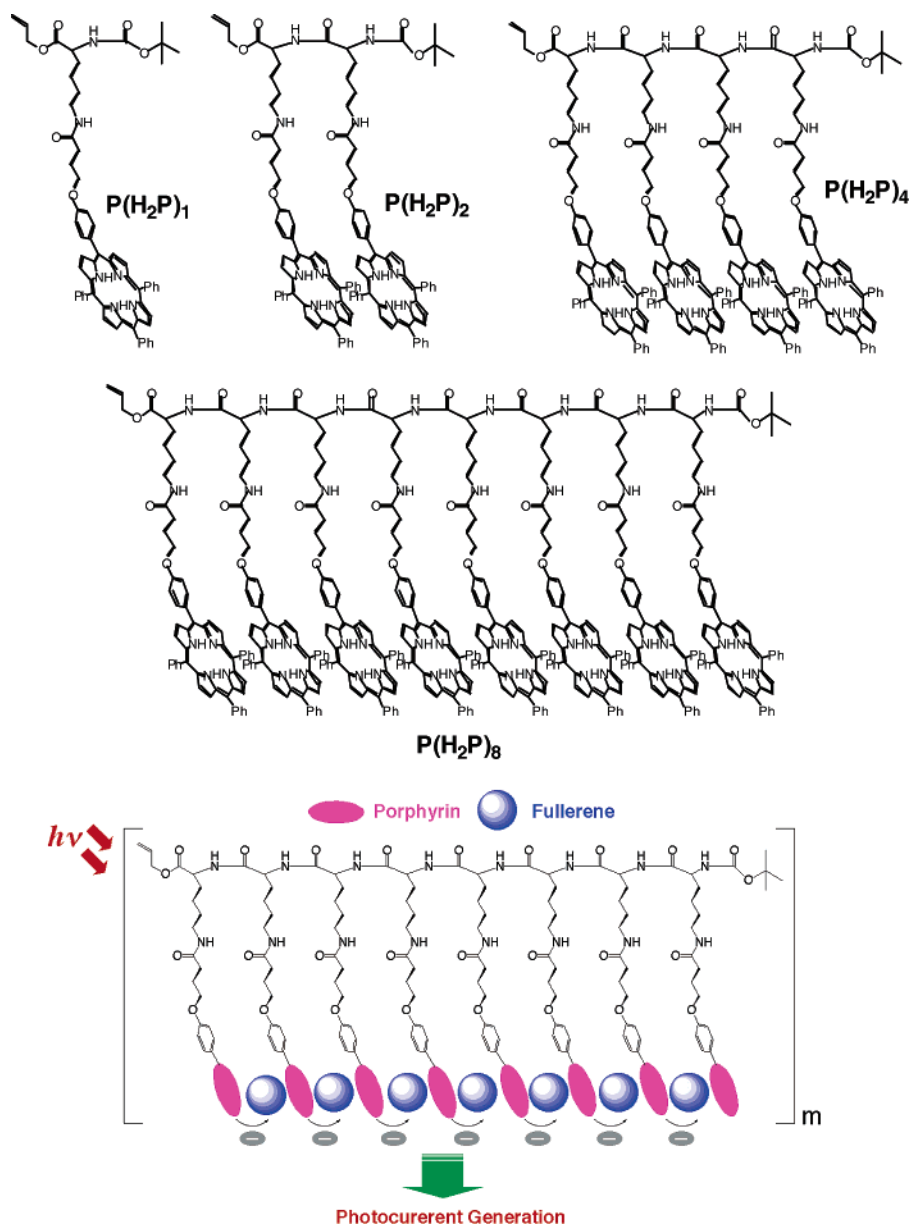
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CHART 1: Porphyrin Compounds Used in This Study and the Illustration of Supramolecular Assembly between Porphyrin–Peptide Oligomers and Fullerenes

The details of synthesis of porphyrin–peptide oligomers have been reported previously.¹² The organization of $P(H_2P)_n$ and C_{60} composite clusters (denoted as $(P(H_2P)_n + C_{60})_m$ ($n = 1, 2, 4, 8$)) was performed by injecting a toluene solution of $P(H_2P)_n$ and C_{60} into acetonitrile/toluene (3/1, v/v).¹³ Herein, the concentration of one porphyrin unit in these composite clusters is taken as constant: $[P(H_2P)_1] = 0.19$ mM, $[P(H_2P)_2] = 0.10$ mM, $[P(H_2P)_4] = 0.048$ mM, and $[P(H_2P)_8] = 0.024$ mM in acetonitrile/toluene = 3/1, whereas the concentration of C_{60} (0.31 mM) is in excess of the concentration of one porphyrin unit in acetonitrile/toluene = 3/1. This procedure allows us to obtain the supramolecular complex between $P(H_2P)_n$ and C_{60} and the clusterization at the same time.

The absorption spectrum of $(P(H_2P)_8 + C_{60})_m$ in acetonitrile/toluene 3:1 mixture (spectrum a in Figure 1A) becomes much broader, and the Soret band in $(P(H_2P)_8 + C_{60})_m$ is red-shifted as compared with the spectrum in toluene (spectrum b and c in Figure 1A). This indicates formation of the supramolecular π -complex between $P(H_2P)_n$ and C_{60} clusters in the mixed solvent.¹⁴ The broad long-wavelength absorption in the 700–

800 nm region is diagnostic of the charge transfer (CT) absorption band due to the strong π -complex formed between porphyrin and C_{60} (see Supporting Information S1).^{14–16} Furthermore, TEM images of $(P(H_2P)_8 + C_{60})_m$ clearly shows the formation of large nanoclusters (Figure 1B). Judging from the molecular scale of $P(H_2P)_n$ and C_{60} , we can conclude that $P(H_2P)_n$ molecules are self-assembled with C_{60} molecules in the mixed solution to yield large donor–acceptor nanoclusters with an interpenetrating network. Additionally, molecular clusters of $(P(H_2P)_n + C_{60})_m$ ($n = 2, 8$) have controlled size and shape as compared with that of $(P(H_2P)_1 + C_{60})_m$ (see Supporting Information S2).

Upon subjecting the resultant cluster suspension to a high electric dc field (500 V for 1 min), mixed $P(H_2P)_n$ and C_{60} clusters ($(P(H_2P)_n + C_{60})_m$) were deposited onto an optically transparent electrode (OTE) of a nanostructured SnO_2 electrode (OTE/ SnO_2) to give modified electrodes (denoted as OTE/ $SnO_2/(P(H_2P)_n + C_{60})_m$ ($n = 1, 2, 4, 8$)).¹³ The absorptivity of the OTE/ $SnO_2/(P(H_2P)_8 + C_{60})_m$ electrode (spectrum d in Figure 1A) is highly enhanced compared with that of the

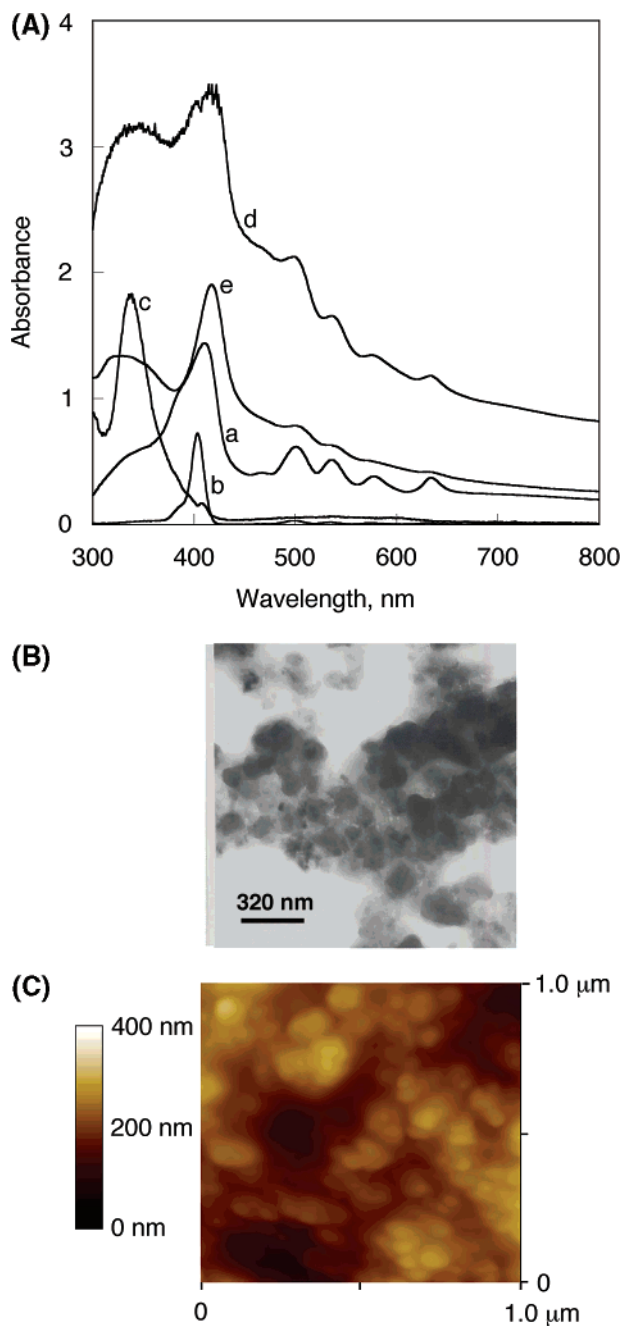


Figure 1. (A) Absorption spectra of (a) (P(H₂P)₈ + C₆₀)_m ([P(H₂P)₈] = 0.024 mM, [C₆₀] = 0.31 mM) in acetonitrile/toluene = 3/1, (b) P(H₂P)₈ in toluene (3.1 μM), (c) C₆₀ in toluene (150 μM), (d) OTE/SnO₂/(P(H₂P)₈ + C₆₀)_m electrode ([P(H₂P)₈] = 0.024 mM, [C₆₀] = 0.31 mM), and (e) OTE/SnO₂/(P(H₂P)₈)_m electrode ([P(H₂P)₈] = 0.024 mM). (B) TEM image of (P(H₂P)₈ + C₆₀)_m ([P(H₂P)₈] = 0.024 mM, [C₆₀] = 0.31 mM). (C) AFM image of OTE/SnO₂/(P(H₂P)₈ + C₆₀)_m electrode ([P(H₂P)₈] = 0.024 mM, [C₆₀] = 0.31 mM).

reference system containing only porphyrin units (OTE/SnO₂/(P(H₂P)₈)_m: spectrum e in Figure 1A).¹³ These results ensure that incident light is absorbed strongly in the visible and near-IR regions by OTE/SnO₂/(P(H₂P)_n + C₆₀)_m due to the supra-molecular π -complex formation between porphyrin and fullerene.^{14–16} The atomic force microscope (AFM) image of OTE/SnO₂/(P(H₂P)₈ + C₆₀)_m reveals that the OTE/SnO₂/(P(H₂P)₈ + C₆₀)_m film is composed of closely packed clusters of 50–100 nm size (Figure 1C).

Photoelectrochemical measurements were performed with a standard two-electrode system consisting of a working electrode and a Pt wire gauze electrode in 0.5 M NaI and 0.01 M I₂ in

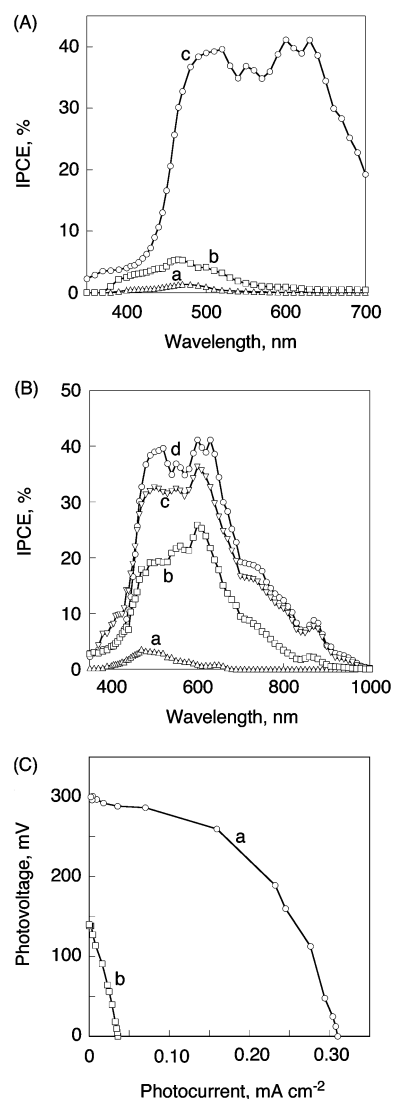


Figure 2. (A) The photocurrent action spectra (IPCE vs wavelength) of OTE/SnO₂/(P(H₂P)₈ + C₆₀)_m electrode at different concentrations of C₆₀; [P(H₂P)₈] = 0.024 mM = constant, (a) [C₆₀] = 0 mM, (b) [C₆₀] = 0.10 mM, and (c) [C₆₀] = 0.31 mM in acetonitrile/toluene = 3/1 (v/v). (B) The photocurrent action spectra (IPCE vs wavelength) of OTE/SnO₂/(P(H₂P)_n + C₆₀)_m under short circuit conditions. (a) [P(H₂P)₁] = 0.19 mM, (b) [P(H₂P)₂] = 0.10 mM, (c) [P(H₂P)₄] = 0.048 mM, and (d) [P(H₂P)₈] = 0.024 mM; [C₆₀] = 0.31 mM in acetonitrile/toluene = 3/1. (C) Current–voltage characteristics of (a) OTE/SnO₂/(P(H₂P)₈ + C₆₀)_m and (b) OTE/SnO₂/(P(H₂P)₁ + C₆₀)_m electrodes. Electrolyte: 0.5 M NaI and 0.01 M I₂ in acetonitrile. Input power: 3.4 mW cm⁻², $\lambda > 400$ nm. [P(H₂P)₈] = 0.024 mM; [P(H₂P)₁] = 0.19 mM; [C₆₀] = 0.31 mM.

air-saturated acetonitrile. Figure 2A shows a significant increase in the IPCE of the OTE/SnO₂/(P(H₂P)₈ + C₆₀)_m electrode with increasing C₆₀ concentration (0–0.31 mM in acetonitrile/toluene) at a constant concentration of P(H₂P)₈ (0.024 mM). This indicates that electron transfer from the excited state of porphyrin to C₆₀ takes place, leading to efficient photocurrent generation.¹³ Figure 2B shows the IPCE of the OTE/SnO₂/(P(H₂P)_n + C₆₀)_m electrode at a constant concentration ratio of porphyrin to C₆₀ ([P(H₂P)₁] = 0.19 mM, [P(H₂P)₂] = 0.10 mM, [P(H₂P)₄] = 0.048 mM, and [P(H₂P)₈] = 0.024 mM; [C₆₀] = 0.31 mM in acetonitrile/toluene = 3/1). The IPCE value of OTE/SnO₂/(P(H₂P)_n + C₆₀)_m ($n = 1, 2, 4, 8$) exhibits a remarkable increase with an increasing number of porphyrins in a polypeptide unit. The OTE/SnO₂/(P(H₂P)₈ + C₆₀)_m system has the maximum IPCE value of 42% at 600 nm as well as a broad

photoresponse, extending into the IR region (up to 1000 nm). Such an effective light-energy conversion is largely ascribed to the polypeptide structure which controls the three-dimensional organization between porphyrin and C_{60} (Chart 1). This suggests that electron transfer properties are improved by increasing the number of porphyrins in a polypeptide unit.

Figure 2C shows current–voltage (I/V) characteristics of $OTE/SnO_2/(P(H_2P)_8 + C_{60})_m$ and $OTE/SnO_2/(P(H_2P)_1 + C_{60})_m$ electrodes under visible light irradiation ($\lambda > 400$ nm). The $OTE/SnO_2/(P(H_2P)_8 + C_{60})_m$ system has a much larger fill factor (FF) of 0.47, open circuit voltage (V_{oc}) of 300 mV, short circuit current density (I_{sc}) of 0.31 mA cm^{-2} , and the overall power conversion efficiency (η) of 1.3% at input power (W_{in}) of 3.4 mW cm^{-2} .¹⁷ The I/V characteristics of $OTE/SnO_2/(P(H_2P)_8 + C_{60})_m$ system is also remarkably enhanced (more than 30 times) as compared with the $OTE/SnO_2/(P(H_2P)_1 + C_{60})_m$ electrode ($\eta = 0.043\%$) under the same experimental conditions.

Photocurrent generation in the present system may be initiated by photoinduced charge separation from the porphyrin excited singlet state ($H_2P^*/H_2P^{*+} = -0.7 \text{ V vs NHE}$)¹³ in the porphyrin–peptide oligomer to C_{60} ($C_{60}/C_{60}^{\bullet-} = -0.2 \text{ V vs NHE}$)¹³ in the porphyrin–peptide oligomer– C_{60} complex rather than direct electron injection to conduction band of SnO_2 (0 V vs NHE) system. The reduced C_{60} injects electrons into the SnO_2 nanocrystallites, whereas the oxidized porphyrin ($H_2P/H_2P^{*+} = 1.2 \text{ V vs NHE}$)¹³ undergoes electron transfer reduction with the iodide ($I_3^-/I^- = 0.5 \text{ V vs NHE}$)¹³ in the electrolyte system.

The formation of the radical cation of porphyrin of $P(H_2P)_8$ and the radical anion of C_{60} upon photoexcitation of the composite cluster of $(P(H_2P)_8 + C_{60})_m$ is confirmed by the electron spin resonance (ESR) measurements performed in frozen acetonitrile/toluene under photoirradiation (see Supporting Information S3). The ESR spectrum consists of two signals, one of which is attributable to $C_{60}^{\bullet-}$ at a small g value ($g = 2.001$),¹⁸ and the other is a porphyrin radical cation at a higher g value ($g = 2.003$).¹⁹ The fluorescence of $OTE/SnO_2/(P(H_2P)_n + C_{60})_m$ ($n = 1, 2, 4, 8$) electrodes was significantly quenched as compared to the corresponding $OTE/SnO_2/(P(H_2P)_n)_m$ without C_{60} because of photoinduced electron transfer quenching.²⁰ The weighted average fluorescence lifetime (τ_{avg}) of $OTE/SnO_2/(P(H_2P)_n)_m$ decreases with an increasing number of porphyrins in a polypeptide unit (S4), in accordance with an increase in the IPCE value in Figure 2B.^{21,22}

The photodynamics of the composite molecular cluster of porphyrin with a polypeptide unit and C_{60} was examined by the femtosecond time-resolved transient absorption spectra. The time-resolved transient absorption spectra of $(P(H_2P)_1 + C_{60})_m$ in acetonitrile/toluene (3/1, v/v) are shown in Figure 3A, where strong transient bleaching (around 660 nm) due to the fluorescence is observed upon laser pulse excitation, and then, the broad absorption appears within 1.9 ps at 440–480 nm. This is characteristic of the triplet excited state of porphyrins.²³ In contrast to the case of $(P(H_2P)_1 + C_{60})_m$, neither the bleaching originating from fluorescence (660 nm region) nor strong absorption of the triplet excited state of porphyrins (440–480 nm) is observed in the case of $(P(H_2P)_8 + C_{60})_m$, but instead, the broad absorption at around 650 nm appears after the laser pulse excitation, as shown in Figure 3B.²⁴ This broad absorption spectrum is a clear indication of formation of the porphyrin radical cation.²⁵ This indicates that electron transfer from the singlet excited state of porphyrins to C_{60} occurs in the supramolecular complex of $(P(H_2P)_8 + C_{60})_m$. Thus, an increase in the number of porphyrin units of the porphyrin–peptide

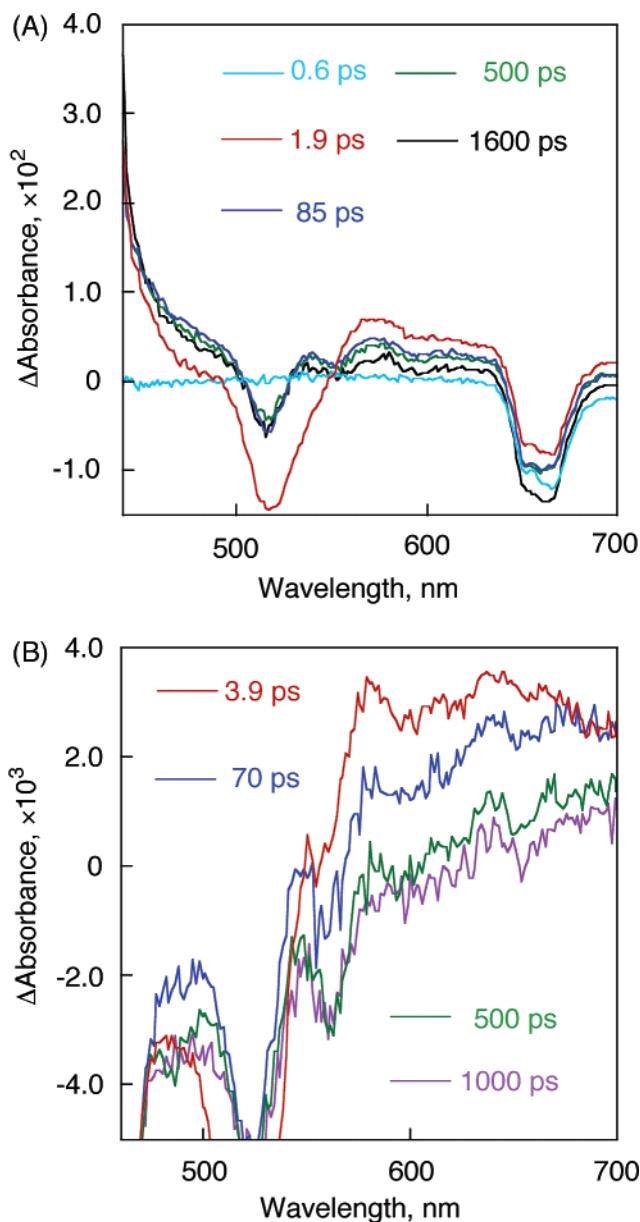


Figure 3. (A) Femtosecond time-resolved absorption spectra of $(P(H_2P)_1 + C_{60})_m$ ($[P(H_2P)_1] = 0.19 \text{ mM}$; $[C_{60}] = 0.31 \text{ mM}$) in argon-saturated acetonitrile/toluene (3/1, v/v) after laser excitation at 387 nm at 298 K. (B) Femtosecond time-resolved absorption spectra of $(P(H_2P)_8 + C_{60})_m$ ($[P(H_2P)_8] = 0.024 \text{ mM}$; $[C_{60}] = 0.31 \text{ mM}$) in argon-saturated acetonitrile/toluene (3/1, v/v) after laser excitation at 387 nm at 298 K.

oligomers has a great effect on the light-energy conversion as well as electron transfer properties in $OTE/SnO_2/(P(H_2P)_n + C_{60})_m$.

In summary, we have successfully constructed a novel organic photovoltaic system using supramolecular complexes of porphyrin–peptide oligomers with fullerene clusters. Such a composite system has an efficient photoresponse in visible and near-IR regions, and the light-energy conversion efficiency increases with an increasing number of porphyrins in a peptide unit to achieve $\eta = 1.3\%$ and maximum IPCE of 42% for the $OTE/SnO_2/(P(H_2P)_8 + C_{60})_m$ electrode. An increase of the light-energy conversion property in this system is ascribed to the enhancement of photoinduced electron transfer properties in the supramolecular assembly, which is confirmed by the fluorescence lifetime measurement and femtosecond laser flash photolysis measurement.

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Supporting Information Available: CT absorption spectra between $\text{P}(\text{H}_2\text{P})_4$ and C_{60} (S1), TEM images of $\text{P}(\text{H}_2\text{P})_1 + \text{C}_{60m}$ and $\text{P}(\text{H}_2\text{P})_2 + \text{C}_{60m}$ (S2), ESR spectrum of photoirradiated $\text{P}(\text{H}_2\text{P})_8 + \text{C}_{60m}$ (S3), fluorescence lifetimes of $\text{OTE}/\text{SnO}_2/\text{P}(\text{H}_2\text{P})_n$ and $\text{OTE}/\text{SnO}_2/\text{P}(\text{H}_2\text{P})_n + \text{C}_{60m}$ ($n = 1, 2, 4, 8$) (S4), femtosecond time-resolved absorption spectra of $\text{P}(\text{H}_2\text{P})_n + \text{C}_{60m}$ ($n = 2, 4$) in acetonitrile/toluene (3/1, v/v), $\text{P}(\text{H}_2\text{P})_8$ in toluene and the time profiles at 650 nm (S5). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (22) The lifetimes of fluorescence of $\text{P}(\text{H}_2\text{P})_n$ in toluene are approximately constant with an increasing number of porphyrins in a polypeptide unit. The lifetimes of fluorescence of $\text{P}(\text{H}_2\text{P})_n$ ($n = 1, 2, 4, 8$) are determined as 11.2, 10.3, 11.8, and 11.1 ns, respectively.
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