Long-lived photoinduced charge separation for solar cell applications in supramolecular complexes of multi-metalloporphyrins and fullerenes

Shunichi Fukuzumi* and Kei Ohkubo

Monomers, dimers, trimers, dendrimers and oligomers of metalloporphyrins form supramolecular complexes with fullerene derivatives via electrostatic interactions, π–π interactions and coordination bonds. Photoexcitation of the supramolecular complexes resulted in photoinduced electron transfer from the porphyrin moiety to the fullerene moiety to produce the charge-separated states as revealed by laser flash photolysis measurements. The rate constants of photoinduced charge separation and charge recombination in supramolecular complexes of multi-metalloporphyrins and fullerenes were also determined by laser flash photolysis measurements and the results depending on the number of porphyrins in the supramolecular complexes are discussed in terms of efficiency of photoinduced energy transfer and charge separation as well as the lifetimes of charge-separated states. The photoelectrochemical performances of solar cells composed of supramolecular complexes of monomers, dimers, dendrimers and oligomers of metalloporphyrins with fullerenes are compared in relation to the rate constants of photoinduced charge separation and charge recombination.

1. Introduction

Photosynthesis is one of the most fundamental and indispensable processes in nature, because it converts light energy into chemical energy required to maintain life.1,2 Photosynthesis is initiated by the multistep electron-transfer reactions in the photosynthetic reaction centres following light energy harvesting by antenna chlorophylls, funnelled to a bacteriochlorophyll

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dimer, the so-called special pair, to attain the long-lived charge-separated (CS) state.\textsuperscript{3,2} The redox-active components such as chlorophyll, pheophytin and quinones are appropriately located in the protein matrix by non-covalent interactions.\textsuperscript{1,2} Extensive efforts have so far been devoted to the design of electron donor–acceptor composites using covalently and non-covalently linked systems to form the long-lived CS state upon photoexcitation for artificial photosynthesis.\textsuperscript{3–29}

Porphyrins, which are involved in a number of important biological electron-transfer systems including the primary photophysical reactions of chlorophylls (porphyrin derivatives) in the photosynthetic reaction centres, are particularly attractive building blocks as electron acceptors as well as light-harvesting compounds for the construction of supramolecular electron donor–acceptor composites due to their excellent photophysical and electron-transfer properties.\textsuperscript{8–29} With regard to electron acceptors, fullerenes, which are extensively conjugated three-dimensional \(\pi\) systems, are ideal electron acceptors because of the minimal changes of structure and solvation associated with the electron-transfer reduction.\textsuperscript{30–38}

Thus, combination of porphyrins and fullerenes is regarded as ideal donor–acceptor ensembles, because the combination results in a small reorganization energy, which allows to accelerate photoinduced electron transfer and to slow down charge recombination, leading to the generation of long-lived CS states with high quantum yields.\textsuperscript{39} However, non-covalent binding between monomer porphyrins and fullerenes is usually not strong enough in polar solvents which are generally used for studies on photoinduced electron-transfer reactions.\textsuperscript{64–68} Among non-covalent interactions, an electrostatic interaction is relatively strong in polar solvents.\textsuperscript{69–73} Muti-point binding sites can be introduced by using multi-metalloporphyrins (dimers, trimers, dendrimers and oligomers), allowing strong binding between multi-metalloporphyrins and fullerenes in polar solvents.\textsuperscript{29,30}

In this perspective, we review our recent development on photoinduced charge separation in supramolecular complexes of porphyrin anions and fullerenes, which are strongly bound in polar solvents, towards construction of supramolecular solar cells based on the long-lived photoinduced charge separation.

## 2. Supramolecular complexes of monomer porphyrin sulfonates and \(\text{Li}^+@C_{60}\)

Zinc tetraphenylporphyrin tetrasulfonate anion \([\{(\text{Bu}_4\text{N})_4\text{H}_2\text{TPPS}^+\}]\) forms a strong supramolecular binding with a cationic lithium ion encapsulated fullerene (Li\(^+@C_{60}\))\textsuperscript{74–77} in benzonitrile (PhCN) by electrostatic and \(\pi\)–\(\pi\) interactions (Scheme 1).\textsuperscript{78} The Job’s plots of the absorbance change confirmed the 1:1 stoichiometry between ZnTPPS\(^{4–}\) and Li\(^+@C_{60}\).\textsuperscript{78} Free base tetraphenylporphyrin tetrasulfonate anion \([\{(\text{Bu}_4\text{N})_4\text{H}_2\text{TPPS}^+\}]\) also forms a 1:1 complex with \(\text{Li}^+@C_{60}\). The formation constants \((K)\) of the ZnTPPS\(^{4–}/\text{Li}^+@C_{60}\) and H\(_2\)TPPS\(^{4–}/\text{Li}^+@C_{60}\) complexes were determined from the absorption change to be \(1.6 \times 10^5\) and \(3.0 \times 10^5\) M\(^{-1}\), respectively.\textsuperscript{78} The same formation constants were obtained from the fluorescence quenching of ZnTPPS\(^{4–}\) and H\(_2\)TPPS\(^{4–}\) and by Li\(^+@C_{60}\) in PhCN.\textsuperscript{78}

The occurrence of the photoinduced energy transfer in the supramolecular complex was confirmed by the transient absorption spectra of the ZnTPPS\(^{4–}/\text{Li}^+@C_{60}\) complex measured in PhCN using femtosecond laser flash photolysis (Fig. 1a).\textsuperscript{78} The transient absorption bands taken at 2 ps observed at 620 and 737 nm are assigned to the singlet excited state of ZnTPPS\(^{4–}\). This band decays with the rate constant \((k_{\text{EN}})\) of \(9.7 \times 10^{10}\) s\(^{-1}\) (Fig. 1b) to form the singlet excited state of Li\(^+@C_{60}\) at 100 ps (Fig. 1a). The decay rate constant of ZnTPPS\(^{4–}\) to Li\(^+@C_{60}\) radical anion \((\lambda_{\text{max}} = 670\) nm\) and that of Li\(^+@C_{60}\) radical anion \((\lambda_{\text{max}} = 1035\) nm\)\textsuperscript{78} Thus, the electron transfer from ZnTPPS\(^{4–}\) to Li\(^+@C_{60}\) is much faster than that from the excited state of Li\(^+@C_{60}\) to ZnTPPS\(^{4–}\).

The transient absorption spectra taken by nanosecond laser flash photolysis shown in Fig. 2a demonstrate the formation of ZnTPPS\(^{4–}\) and Li\(^+@C_{60}\) complexes were determined from the transient absorption change to be \(1.6 \times 10^5\) and \(3.0 \times 10^5\) M\(^{-1}\), respectively. The same formation constants were obtained from the fluorescence quenching of ZnTPPS\(^{4–}\) and H\(_2\)TPPS\(^{4–}\) and by Li\(^+@C_{60}\) in PhCN.\textsuperscript{78}

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ZnPSS− to {[^{3}Li^{+}@C_{60}]^{−}}* or from {[^{3}ZnPSS^{4−}]^{−}} to Li^{+}@C_{60} occurs in the supramolecular complex to produce the triplet charge-separated (CS) state. The lifetime of the triplet CS state of the supramolecular complex was determined to be 300 μs for ZnPSS^{4−} from the first-order decay of the CS state (Fig. 2b). It was confirmed that back electron transfer occurred in the supramolecular complex, because the first-order decay rate constant remains the same irrespective of the difference in the laser intensity (inset of Fig. 2b). Similarly the CS lifetime of 310 μs was determined for [{^{1}H_{2}TPPS^{4−}}]^{−}−Li^{+}@C_{60}. This is the longest lifetime of the CS state ever reported for monomer porphyrin/fullerene systems linked non-covalently in solution. The quantum yield of the CS state is determined to be 0.39 using the absorption of the CS state (Li^{+}@C_{60}: ε_{1035} = 7300 M^{-1} cm^{-1}).

The activation enthalpies of the charge-recombination (CR) processes were determined to be 3.0 kcal mol^{-1} for ZnPSS^{4−}−Li^{+}@C_{60} and 5.4 kcal mol^{-1} for H_{2}TPPS^{4−}−Li^{+}@C_{60}. This indicates that there is a significant energy difference between the singlet and triplet CS states and that the CR processes may occur through the thermally activated singlet CS state. The lifetime of the CS state at 77 K is estimated as long as 60 h for H_{2}TPPS^{4−}−Li^{+}@C_{60}. Such a long-lived triplet CS state was detected by the EPR measurements by photoliration of the H_{2}TPPS^{4−}−Li^{+}@C_{60} complex in frozen PhCN as shown in Fig. 3. The spin−spin interaction in the triplet radical ion pair of the supramolecular complex is clearly shown at 77 K, where the fine structure due to the triplet CS state is clearly observed at g = 2. From the zero-field splitting values (D = 52 G for ZnPSS^{4−} and 56 G for H_{2}TPPS^{4−}) the distances (r) between two electron spins were estimated using the relation, D = 27800/J, to be 8.1 and 7.9 Å, respectively. These r values agree with the centre-to-centre distance of a reported crystal structure of porphyrin/C_{60}.

By mixing PhCN solutions of the supramolecular complexes of MTPPS^{4−} and Li^{+}@C_{60} with acetonitrile (MeCN), nanoclusters were produced and they were deposited on an optically transparent electrode (OTE) of nanostructured SnO_{2} (OTE/SnO_{2}) by application of a dc electric field (~100 V cm^{-1}) to construct photovoltaic cells. The (MTPPS^{4−}/Li^{+}@C_{60})_{n} films are composed of closely packed Li^{+}@C_{60} clusters of about 80 nm size, which render a nanoporous morphology to the film as shown in the TEM images in Fig. 4.

The photoelectrochemical measurements of a robust thin film of OTE/SnO_{2}/(MTPPS^{4−}/Li^{+}@C_{60})_{n} were performed using a standard two-electrode system consisting of a working electrode and a Pt wire gauze electrode in air-saturated MeCN containing 0.5 M LiI and 0.01 M I_{2} (Fig. 5). The IPCE (incident photon-to-photocurrent efficiency) values were determined by normalizing the photocurrent values for incident light energy and intensity and using eqn (1).

\[
\text{IPCE (}) = 100 \times \frac{i_{sc}}{(I_{inc} \times \lambda)} \tag{1}
\]
in which the fill factor (FF) is defined as 

\[
\text{FF} = \frac{I_{sc}}{I_{oc} V_{oc}} / W_{in}
\]

where \(I_{sc}\) is the short circuit photocurrent (A cm\(^{-2}\)), \(I_{oc}\) is the incident light intensity (W cm\(^{-2}\)) and \(\lambda\) is the wavelength (nm). The IPCE value of OTE/SnO\(_2\)/(ZnTPPS\(_4\)/Li\(^+\)@C\(_{60}\)) \(_n\) is much higher than the sum of the two individual IPCE values of the individual systems OTE/SnO\(_2\)/(ZnTPPS\(_4\)) \(_n\) and OTE/SnO\(_2\)/(Li\(^+\)@C\(_{60}\)) \(_n\) in the visible region (Fig. 6). The maximum IPCE value of OTE/SnO\(_2\)/(ZnTPPS\(_4\)/Li\(^+\)@C\(_{60}\)) \(_n\) was 77% at 450 nm. Such a high IPCE value indicates that photocurrent generation is initiated via photoinduced electron transfer from ZnTPPS\(_4^+\) to Li\(^+\)@C\(_{60}\), followed by the charge transport to the collective surface of an OTE/SnO\(_2\) electrode (Fig. 5). When ZnTPPS\(_4^+\) was replaced by H\(_2TPPS\(_4\) the IPCE value was observed as 7% at 440 nm probably because of the self-aggregation of H\(_2TPPS\(_4\) without binding with Li\(^+\)@C\(_{60}\).84

The power conversion efficiency (\(\eta\)) of the OTE/SnO\(_2\)/(ZnTPPS\(_4\)/Li\(^+\)@C\(_{60}\)) \(_n\) electrode was calculated by using eqn (2):

\[
\eta = \text{FF} \times \frac{I_{sc}}{I_{oc}} \times V_{oc} / W_{in}
\]

As compared to porphyrin monomers, porphyrin dimers with appropriate linkage can accommodate electron acceptor guest molecules by \(\pi-\pi\) interactions to form sandwich complexes.86–96 For example, a cyclic Ni porphyrin dimer (Ni-CPDPy) linked by butadiyne moieties bearing 4-pyridyl groups (Fig. 7) forms a sandwich complex with C\(_{60}\) (C\(_{60}\)⊂Ni\(_2\)-CPDPy) as shown in the X-ray crystal structure (Fig. 8), where the dimer bites a C\(_{60}\) molecule by tilting the porphyrin rings with respect to each other and there are strong \(\pi-\pi\) interactions between the porphyrin rings and C\(_{60}\).97 The adjacent dimers are linked by hydrogen bonds and \(\pi-\pi\) interactions.97 The C\(_{60}\) molecules are linearly arranged in the inner channel to give a supramolecular peapod.97–102

The linear arrangement of C\(_{60}\) in C\(_{60}\)⊂Ni\(_2\)-CPDPy high electron mobilities of \(\sum_{b+c} = 0.72\) and 0.20 cm\(^2\) V\(^{-1}\) s\(^{-1}\) along the \(b\) and \(c\) axes, respectively, which were determined by flash-photolysis time-resolved microwave conductivity (FP-TRMC) measurements.97 The TRMC technique can evaluate the

3. Supramolecular complexes of cyclic porphyrin dimers with C\(_{60}\) and Li\(^+\)@C\(_{60}\)

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[Fig. 5 Schematic image of photoelectrochemical cell of OTE/SnO\(_2\)/(ZnTPPS\(_4^+\)/Li\(^+\)@C\(_{60}\) and electron-transfer pathways to generate photocurrent.]

[Fig. 6 Photocurrent action spectra of OTE/SnO\(_2\)/(ZnTPPS\(_4^+\)/Li\(^+\)@C\(_{60}\)\(_n\) (red), OTE/SnO\(_2\)/(ZnTPPS\(_4^+\)) \(_n\) (blue), and OTE/SnO\(_2\)/(Li\(^+\)@C\(_{60}\)\(_n\) (black). Electrolyte: 0.5 M LiI and 0.01 M I\(_2\) in MeCN-PhCN (3 : 1 v/v).]

[Fig. 7 Chemical structure of Ni\(_2\)-CPDPy.]

[Fig. 8 Crystal structures of tubular assemblies of C\(_{60}\)⊂Ni\(_2\)-CPDPy. Hydrogen atoms are omitted for clarity.]
intrinsic mobility without being affected by the chemical or physical defects in the material and/or the organic/metal-electrode interfaces.\textsuperscript{103–105} The observed value along the \( b \) axis of the single crystal of \( C_{60} \subset \text{Ni}_{2}-\text{CPDPy} \) is comparable to that of the single crystal of \( C_{60} \) (\( \Sigma \mu = 0.50 \text{ cm}^{2} \text{ V}^{-1} \text{ s}^{-1} \) measured by TOF).\textsuperscript{106} The observed high electron mobility along the \( b \) axis is due to the well-ordered linear arrangement of \( C_{60} \) in the porphyrin nanotube. However, the expected charge-separated state could not be observed in the time-resolved transient absorption spectra of \( C_{60} \subset \text{Ni}_{2}-\text{CPDPy} \) because the singlet excited state of the nickel porphyrin immediately changes to the triplet excited state by intersystem crossing and the low energy triplet excited state of \( C_{60} \) (3\( C_{60}^{*} \)) is formed by energy transfer.\textsuperscript{97} The estimated energy level of the charge-separated state (1.98 eV) is higher than that of 3\( C_{60}^{*} \) (1.60 eV).\textsuperscript{97} When \( \text{Ni}_{2}-\text{CPDPy} \) was replaced by a free base porphyrin dimer (\( \text{H}_{4}\text{-CPDPy} \)), a complete charge-separated state \( \{\text{H}_{4}\text{-CPDPy}^{+} + \text{C}_{60}^{-}\} \) was observed by femtosecond laser flash photolysis of \( C_{60} \subset \text{H}_{4}\text{-CPDPy} \) in the solid state with a lifetime of 470 ps.\textsuperscript{107} The photovoltaic activity of \( C_{60} \subset \text{Ni}_{2}-\text{CPDPy} \) and \( C_{60} \subset \text{H}_{4}\text{-CPDPy} \) was evaluated by using solar cells composed of modified electrodes and \( \Gamma^{-}/\text{I}_{3}^{-} \) solution.\textsuperscript{107} The \( C_{60} \subset \text{H}_{4}\text{-CPDPy} \)-modified electrode exhibited IPCE of 17\% and a power conversion efficiency (\( \eta \)) of 0.33\%, which was more than 16 times larger than that of \( \text{OTE/SmO}_{2}/(C_{60} \subset \text{Ni}_{2}-\text{CPDPy})_{n} \) (0.02\%).\textsuperscript{107} Such a significant enhancement of the \( \eta \) value demonstrates that the formation of highly ordered clusters and the efficient charge separation of \( (C_{60} \subset \text{H}_{4}\text{-CPDPy})_{n} \) contributes to the improvement of the light energy conversion properties.\textsuperscript{107}

When \( C_{60} \) is replaced by \( \text{Li}^{+}@C_{60} \) porphyrin dimers with four long alkoxy substituents on the meso-phenyl groups (MCPDPy(OC\(_{6}\)) in Fig. 9) form strong supramolecular complexes in even a polar solvent such as PhCN.\textsuperscript{108} The association constants (\( K_{\text{assoc}} \)) of \( \text{Li}^{+}@C_{60} \subset \text{MCPDPy}(\text{OC}_{6}) \) in PhCN at 298 K were determined to be 2.6 \( \times \) 10\(^{5} \) M\(^{-1} \) for \( \text{Li}^{+}@C_{60} \subset \text{H}_{4}\text{-CPDPy}(\text{OC}_{6}) \) and 3.5 \( \times \) 10\(^{5} \) M\(^{-1} \) for \( \text{Li}^{+}@C_{60} \subset \text{Ni}_{2}\text{-CPDPy}(\text{OC}_{6}) \).\textsuperscript{108}

Upon laser excitation of \( \text{Li}^{+}@C_{60} \subset \text{Ni}_{2}\text{-CPDPy}(\text{OC}_{6}) \), transient absorption bands due to \( \text{Ni}_{2}\text{-CPDPy}(\text{OC}_{6})^{+} \) and \( \text{Li}^{+}@C_{60}^{-} \) were observed as shown in Fig. 10a.\textsuperscript{108} In this case, electron transfer occurs from \( \text{Ni}_{2}\text{-CPDPy}(\text{OC}_{6}) \) to the triplet excited state of \( \text{Li}^{+}@C_{60} \) (3\( \text{Li}^{+}@C_{60}^{*} \)) rather than from \( 3\text{[Ni}_{2}\text{-CPDPy}(\text{OC}_{6})^{*} \) to \( \text{Li}^{+}@C_{60} \) as indicated by the disappearance of the absorption band at 750 nm due to 3\( \text{Li}^{+}@C_{60}^{*} \), accompanied by the appearance of the absorption band at 1035 nm due to 3\( \text{Li}^{+}@C_{60}^{*} \) (Fig. 10b).\textsuperscript{108} The rate constant of electron transfer from \( \text{Ni}_{2}\text{-CPDPy}(\text{OC}_{6}) \) to \( 3\text{Li}^{+}@C_{60}^{*} \) to produce the CS state was determined from the rise in the absorbance at 1035 nm due to \( \text{Li}^{+}@C_{60} \) to be \( 5.7 \times 10^{7} \) s\(^{-1} \).\textsuperscript{108} The absorbance at 1035 nm due to \( \text{Li}^{+}@C_{60} \) in the CS state decayed obeying first-order kinetics with the same slope irrespective of the difference in
the laser intensity (Fig. 10c). This clearly indicates that the decay of the CS state occurs via intrasupramolecular back electron transfer rather than a bimolecular back electron-transfer reaction between the CS states. The CS lifetime was determined from the slope of the first-order plots in Fig. 10c to be 0.67 ms, which is the longest value ever reported for non-covalent monomer dimer porphyrin-fullerene supramolecules in solution. The CS state was also observed for Li+@C60 ⊂ H4-CPDPy(OC6). The quantum yields of the CS states were estimated to be 0.13 for Li+@C60 ⊂ Ni2-CPDPy(OC6) and 0.32 for Li+@C60 ⊂ H4-CPDPy(OC6) and by means of the comparative method with the absorption intensities of the CS states (Li+@C60 ⊂ ε(1035 nm) = 7300 M⁻¹ cm⁻¹). When Li+@C60 was replaced by pristine C60, no CS states were produced as predicted by their higher energy levels than those of the triplet excited states of CPDPy(OC6) and C60.

The mechanisms of intrasupramolecular photoinduced charge separation in Li+@C60 ⊂ Ni2-CPDPy(OC6) are shown in Scheme 2. The singlet excited state of Ni2-CPDPy(OC6) ([Ni2-CPDPy(OC6)]*) is generated upon photoexcitation of Li+@C60 ⊂ Ni2-CPDPy(OC6) at 420 nm, where the porphyrin moiety is exclusively excited. Even if the Li+@C60 moiety is excited, energy transfer from [Li+@C60]* (Eₐ = 1.94 eV) to Ni2-CPDPy(OC6) (Eₛ = 1.97 eV) occurs to produce [Ni2-CPDPy(OC6)]*. Although electron transfer from [Ni2-CPDPy(OC6)]* to Li+@C60 is energetically possible (Scheme 2), the fast intersystem crossing occurs to generate [Ni2-CPDPy(OC6)]* (kISC > 10¹² s⁻¹). Then, electron transfer occurs from [Ni2-CPDPy(OC6)]* to Li+@C60 with the driving force of 0.30 eV to produce the CS state. The CS state decays slowly via intrasupramolecular BET with the lifetime of 0.67 ms (Scheme 2).

4. Supramolecular complex of a porphyrin tripod with C60

The tripod conformation of a porphyrin trimer (TPZn₃) in Fig. 11 makes it possible to capture a fullerene derivative containing a pyridine moiety (PyC60) inside the cavity strongly by π-π interactions together with the coordination bond between Zn²⁺ and the pyridine moiety (Scheme 3). The association constant of TPZn₃ with PyC60 in toluene determined from the UV-vis absorption spectral titration (Fig. 12a) is much larger as compared with those of the corresponding monomer (MPZn) and dimer porphyrin (DPZn₂). The ¹H NMR signals of TPZn₃ exhibit downfield shifts upon complexation with PyC60, whereas the pyridyl protons of PyC60 exhibit large upfield shifts by the complexation, which is ascribed to the influence of the large porphyrin aromatic ring current. This result clearly shows that the...
pyridyl group of PyC60 coordinates to the central zinc ions of TPZn3. The encapsulation of PyC60 into the cavity of TPZn3 was supported by the DFT-optimized structure (B3LYP/3-21G(*) basis set) in Fig. 12b.113

The occurrence of photoinduced electron transfer from 1TPZn3* to PyC60 was confirmed by femtosecond laser flash photolysis measurements in Fig. 13a, where the transient absorption spectrum due to 1TPZn3* changes as time elapses to afford the absorption bands at 1.Imax = 1000 nm due to the monofunctionalized fullerene radical anion114,115 and at 670 nm due to the one-electron oxidized species of TPZn3 (TPZn3+).113,116,117

In sharp contrast to the TPZn3–PyC60 complex, the transient absorption spectrum of the monomer porphyrin (MPZn) in the presence of PyC60 (Fig. 13b) exhibits the absorbance change due to the energy transfer from 1MPZn* to PyC60 to give the singlet excited state 1PyC60*, followed by the conversion to the triplet excited states 3MPZn* and 3PyC60* at 2800 ps (green line in Fig. 13b), accompanied by the recovery of the ground state.113

The energy diagrams of photodynamics for TPZn3 and MPZn in the presence of PyC60 in toluene are shown in Scheme 4a and 4b, respectively.113 The energy level (1.49 eV) of the CS state (TPZn3+–PyC60−) is lower than the energy level of the triplet excited state of PyC60 moieties (1.56 eV). The rate constant (kET) of photoinduce electron transfer from 1TPZn3* to PyC60 is larger than the rate constant of intersystem crossing. From the rate constant of back electron transfer (kBET = 1.9 × 109 s−1), the lifetime of the CS state is determined to be τCS = 0.53 ns. In contrast, only energy transfer from 1MPZn* to PyC60 occurs to produce 1PyC60*, in competition with intersystem crossing to 3MPZn*.113

TPZn3 also forms a stable 1:1 complex with gold(III) tetra(4-pyridyl)porphyrin (AuTPyP+) in nonpolar solvents.118 The strong binding of TPZn3 with AuTPyP+ results from the encapsulation of AuTPyP+ inside the cavity of TPZn3 through multiple coordination bonds. The efficient quenching of the singlet excited state of TPZn3 occurs via a photoinduced electron-transfer pathway in the TPZn3–AuTPyP+ complex as the case of TPZn3–PyC60 complex.118

5. Supramolecular complexes of porphyrin oligopeptides and C60

Multiple photosynthetic reaction centres composed of light-harvesting multiporphyrin units and charge-separation units were obtained by using both the coordination bond and π–π interaction. Zinc porphyrinic oligopeptides with various numbers of porphyrin units [P(ZnP)n; n = 2, 4, 8]119,120 were used as light-harvesting multiporphyrin units (Fig. 14), which are bound to electron acceptors of fulleropyrrolidine bearing a pyridine (PyC60)113 or imidazole coordinating ligand (ImC60)82 as shown in Fig. 15.121

The binding constant (K) of PyC60 to P(ZnP)n increased with increasing number of zinc porphyrins in an oligopeptide unit.121 No supramolecular complex formation was observed in the case of zinc tetraphenylporphyrin in PhCN.121 The strong binding between P(ZnP)n and PyC60 results from the strong π–π interactions between two zinc porphyrins and PyC60 in addition to the axial coordination of PyC60 to zinc ions of the porphyrins. In the case of ImC60, however, the highest K value was obtained in the P(ZnP)4–ImC60 complex. This
indicates that ImC$_{60}$ is much more strongly bound by the oligopeptide, P(ZnP)$_n$, than PyC$_{60}$. The apparent binding constants ($K$) determined from the fluorescence quenching of P(ZnP)$_n$ were significantly larger than those determined from the UV-vis spectral change, and the difference in the values increased with increasing the generation of porphyrinic oligopeptides (with increasing the number of the porphyrin units). This indicates that the excited energy migration between the porphyrin units occurs efficiently prior to the electron transfer to the bound C$_{60}$ moiety. An extremely efficient energy transfer also occurs in P(ZnP)$_8$–ImC$_{60}$ judging from the large difference in the $K$ values determined by the absorption change and by the fluorescence quenching ($1.5 \times 10^4$ vs. $3.3 \times 10^5$ M$^{-1}$).

The occurrence of photoinduced electron transfer in the supramolecular complex in PhCN was confirmed by the transient absorption spectra of the supramolecular complex of P(ZnP)$_8$ with PyC$_{60}$ using nanosecond laser flash photolysis. The laser photoexcitation at 561 nm of the supramolecular complex of P(ZnP)$_8$ with PyC$_{60}$ results in formation of the CS state as indicated by the transient absorption spectra in Fig. 16a, where the absorption band due to PyC$_{60}^-$ is clearly observed at 1000 nm together with that due to ZnP$^+$ at 630 nm. The CS state detected decays obeying first-order kinetics (Fig. 16b) and the first-order plots at different initial CS concentrations afford linear correlations with the same slope (inset of Fig. 16b). If there is any contribution of intermolecular back electron transfer from unbound PyC$_{60}^-$ to ZnP$^+$, the second-order kinetics would be involved for the decay time profile. In fact, the corresponding second-order plots (Fig. 16c) are clearly non-linear and the initial slope varies depending on the CS concentration. Thus, the decay process is ascribed to back electron transfer in the supramolecular complex rather than intermolecular back electron transfer between ZnP$^+$ and PyC$_{60}^-$. The CS lifetimes of the supramolecular complexes of other porphyrins [P(ZnP)$_n$] and the fullerene derivative (ImC$_{60}$) become longer with increasing generation of porphyrinic oligopeptides (with increasing the number of the porphyrin units). Such elongation of the CS
lifetimes results from efficient hole migration between the porphyrin units following the photoinduced electron transfer in the supramolecular complexes.

Multiple photosynthetic reaction centres have also been constructed using supramolecular complexes of zinc porphyrin dendrimers \([D(ZnP)_{n}: n = 4, 8, 16]\) with PyC\(_{60}\).\(^{122}\) Efficient energy migration occurs more efficiently between the ZnP units of dendrimers prior to the photoinduced electron transfer with increasing the generation of dendrimers to attain an extremely long CS lifetime e.g., 0.25 ms for the D(ZnP)\(_{16}\)–PyC\(_{60}\) complex in PhCN at 298 K.\(^{122}\)

Multiple photosynthetic reaction centres composed of supramolecular complexes of harvesting multiporphyrin units and charge-separation units have enabled us to construct supramolecular organic solar cells by the electrodeposition of mixed porphyrin-peptide oligomers \([P(H_2P)_{n} + C_60]_m\) and \([P(ZnP)_{n} + C_60]_m\) onto an optically transparent electrode (OTE) of a nanostructured SnO\(_2\) electrode (OTE/SnO\(_2\)), to obtain modified electrodes \([P(H_2P)_{n} + C_60]_m\) and \([P(ZnP)_{n} + C_60]_m\) \((n = 1, 2, 4, 8, 16)\).\(^{123}\) The IPCE value increased with increasing the number of porphyrins in a polypeptide unit in both \([P(H_2P)_{n} + C_{60}]_m\) and \([P(ZnP)_{n} + C_{60}]_m\) \((n = 1, 2, 4, 8, 16)\) systems as shown in Fig. 17. Such a good photoelectrochemical performance results from efficient photoinduced electron-transfer from the excited state of the porphyrin unit to C\(_{60}\) in the supramolecular complex with longer CS lifetimes as the number of porphyrins in a polypeptide unit increases \((vide supra)\). The maximum IPCE value of \([P(ZnP)_{16} + C_{60}]_m\) (56%) is larger than that of \([P(H_2P)_{16} + C_{60}]_m\) (48%) probably because of the larger driving force of the photoinduced electron transfer.

The maximum IPCE values of \([P(ZnP)_{16} + PyC_{60}]_m\) (20%) and \([P(ZnP)_{16} + ImC_{60}]_m\) (15%) are much smaller than that of \([P(ZnP)_{16} + C_{60}]_m\) (56%), whereas the binding constant of \(P(ZnP)_{16}–C_{60}\) is smaller than those of \(P(ZnP)_{16}–ImC_{60}\) and \(P(ZnP)_{16}–PyC_{60}\).\(^{123}\) The lower IPCE values of \(P(ZnP)_{16}–ImC_{60}\) and \(P(ZnP)_{16}–PyC_{60}\) systems as compared with that of \(P(ZnP)_{16}–C_{60}\) system may result from the poor electron-transport properties of C\(_{60}\) derivatives due to the steric hindrance of the ligand moiety.\(^{123}\) Thus, a key element for efficient photocurrent generation is mainly the hole and electron transport in...
the thin film rather than the charge separation between porphyrins and C_{60}.^{12,13}

$I/V$ characteristics of (a) (P(H_2P)_{16} + C_{60})_m, (b) (P(H_2P)_8 + C_{60})_m, and (c) (P(H_2P)_4 + C_{60})_m modified electrodes under visible light irradiation ($\lambda > 400$ nm) are shown in Fig. 18. The (P(H_2P)_{16} + C_{60})_m system has a larger fill factor (FF) of 0.47, an open circuit voltage ($V_{oc}$) of 320 mV, a short circuit current ($I_{sc}$) of 0.36 mA cm$^{-2}$, $\eta$ > 400 nm.

The $\eta$ values of the (P(H_2P)_{16} + C_{60})_m system was remarkably enhanced (around 40 times) in comparison with the (P(H_2P)_4 + C_{60})_m modified electrode ($\eta$ = 0.043%) under the same experimental conditions. The $\eta$ value of (P(ZnP)_4 + C_{60})_m is also determined as 1.4% and this value is much larger than that of (P(ZnP)_4 + C_{60})_m (0.047%) as shown in Fig. 18B.^{12,13}

6. Conclusions

As described above, porphyrin monomers, dimers, trimers and oligomers form supramolecular complexes with fullerene derivatives via electrostatic interactions, $\pi$-$\pi$ interactions and coordination bonds. Photoexcitation of the supramolecular complexes resulted in efficient photoinduced electron transfer from the porphyrin moiety to the fullerene moiety to produce the long-lived CS states as revealed by laser flash photolysis measurements. In particular, a supramolecular complex of a cyclic Ni porphyrin dimer with Li@C_{60} [Li@C_{60} \subset Ni_{2-}CPDPy(OC_{6})_{a}] affords a long-lived triplet CS state with 0.63 ms lifetime. A high IPCE value (77% at 450 nm) was achieved for a supramolecular solar cell using the OTE/SnO_2/(ZnTPPS\textsuperscript{4-}/Li@C_{60})_n electrode. The use of porphyrin oligomer peptides has also enabled to construct multiple photosynthetic reaction centres composed of light-harvesting multiporphyrin units and charge-separation units linked by both the coordination bond and $\pi$-$\pi$ interactions, which afforded long-lived CS states. Supramolecular organic solar cells composed of porphyrinic oligopeptides and C_{60} exhibited higher overall power conversion efficiency with increasing the number of porphyrin units. Supramolecular complexes formed between porphyrins and fullerenes in particular Li@C_{60} provide promising materials for more efficient solar energy conversion.

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References

Perspective Dalton Transactions


