Review-Two Different Multiple Photosynthetic Reaction Centers Using Either Zinc Porphyrinic Oligopeptide-Fulleropyrrolidine or Free-Base Porphyrinic Polypeptide-Li+@C 60 Supramolecular Complexes

Nathalie Solladié, Shunichi Fukuzumi, Kei Ohkubo, Francis d'Souza, Régis Rein, Kenji Saito, Vincent Troiani, Hongjin Qiu, Suresh Gadde, Tetsuya Hasegawa

ECS The Electrochemical Society
Advancing solid state & electrochemical science & technology

Review—Two Different Multiple Photosynthetic Reaction Centers Using Either Zinc Porphyrinic Oligopeptide-Fulleropyrrolidine or Free-Base Porphyrinic Polypeptide-Li+@C$_{60}$ Supramolecular Complexes

View the article online for updates and enhancements.

Review—Two Different Multiple Photosynthetic Reaction Centers Using Either Zinc Porphyrinic Oligopeptide-Fulleropyrrolidine or Free-Base Porphyrinic Polypeptide-Li+@C$_{60}$ Supramolecular Complexes

Nathalie Solladié,[1,z] Shunichi Fukuzumi,[2,3,4] Kei Ohkubo,[2,3] Francis D'Souza,[5,6] Régis Rein,[1] Kenji Saito,[2] Vincent Troiani,[1] Hongjin Qiu,[1] Suresh Gadde,[5] and Tetsuya Hasegawa[2]

[1]*CNRS, LCC (Laboratoire de Chimie de Coordination), 205 route de Narbonne, 31077 Toulouse (France) and Université de Toulouse, UPS, INPT, 31077 Toulouse, France*
[2]*Department of Material and Life Science, Graduate School of Engineering, Osaka University, ALCA and SENTAN, Japan Science and Technology Agency (JST), 2-1 Yamada-oka, Suita, Osaka 565-0871, Japan*
[3]*Department of Bioinspired Science, Ewha Womans University, Seoul, 120-750, Republic of Korea*
[4]*Faculty of Science and Technology, Meijo University, ALCA and SENTAN, Japan Science and Technology Agency (JST), Nagoya, Aichi 468-8502, Japan*
[5]*Department of Chemistry, Wichita State University, 1845 Fairmount, Wichita, Kansas 67260-0051, United States of America*
[6]*Department of Chemistry, University of North Texas, 1155, Union Circle, #305070, Denton, Texas 76203-5017, United States of America*

An overview of two successful examples of photosynthetic reaction center models combined with light-capturing antenna chromophores is presented. In the first example, supramolecular complexes are formed between flexible zinc porphyrinic oligopeptides and fulleropyrrolidine bearing either a pyridine or imidazole functionalized C$_{60}$ via a coordination bond plus $\pi-\pi$ interactions. The excited energy migration occurs between porphyrin units followed by charge separation. The charge separation (CS) lifetimes of the supramolecular oligopeptide complexes have been elongated by increasing the generation of the porphyrins, enabling us to attain the longest lifetime (0.84 ms) for the P(ZnP)$_8$-ImC$_{60}$ supramolecular system in PhCN solution at 298 K, ever reported for supramolecular complexes. In the second example, free-base porphyrin polypeptides (P(H$_2$P)$_n$; n = 4 and 8) form supramolecular complexes with Li$^+$@C$_{60}$ in PhCN, in which the binding is much stronger than C$_{60}$. Efficient energy migration occurs between porphyrins in P(H$_2$P)$_n$. The triplet CS states derived from ^{3}Li$^+$@C$_{60}$ had long lifetimes due to spin-forbidden back electron transfer. The triplet CS lifetime becomes longer upon increasing the number of H$_2$P due to the charge migration among porphyrins. The present study provides valuable insight into the energy and electron transfer processes leading to long-lived charge separated states in artificial photosynthetic antenna-reaction center models.

In natural photosynthetic systems, the solar energy is collected by pigment molecules attached to the light harvesting complexes. In these units, the chlorophylls are held in a favored spacing and orientation by fairly short α-helical polypeptides.[1–3] When a photon hits one of the chlorophylls, the absorbed energy spreads extremely rapidly to the others until the reaction center is reached within the cell membrane where the solar energy is converted into chemical energy used by the cell to grow. In this way, the energy contained in a single photon is conducted in a very short time and with minimal loss of energy from the point where it is absorbed to where it is needed.

Extensive effort has so far been devoted to mimicking light harvesting and charge separation processes in natural photosynthesis.[4–20] Multiporphyrin arrays have been employed as light-harvesting units.[21–36] Light-harvesting and charge-separation units have been combined by coordination bonds between metalloporphyrins and electron acceptor moieties bearing Lewis base ligands.[36–44] Thus, metal centres were required for the construction of supramolecular complexes between porphyrins acting as light harvesting units and electron acceptors containing Lewis base ligands for coordination to the metal centres.[36–44]

To mimic the natural light harvesting antennae, we synthesized 15 years ago a family of porphyrin-functionalized α-polypeptide such as the octamer (Fig. 1).[45] A peptidic backbone was chosen owing to the remarkable ability of peptides to establish secondary structures such as α-helices, that renders reasonable to expect, beyond a certain degree of oligomerisation, a helical spatial arrangement of the chromophores. Such a conformation should induce an overlap of the porphyrins, which may then undergo sufficient electronic coupling to promote a good exciton migration along the set of porphyrins. It has been the first results presented at the ECS meeting in 2003. . Since then, these polypeptides have been extensively studied and many properties have been highlighted.[46–51] In the present mini-review, we focuss on the preparation and study of multiple reaction centers.

Mimicking the natural photosynthetic process requires both synthesis of the light-harvesting and charge-separation units, which should be linked by covalent or noncovalent bonding.[8–12,52–54] Non-covalent bonding is certainly more favorable as compared to covalent bonding from the viewpoint of mimicking the biological photosystems, in which non-covalent interaction plays a pivotal role to regulate the energy- and electron-transfer processes, and easy access toward construction of a variety of donor-acceptor systems.[16–19,54–60] A variety of multiporphyrin arrays have so far been utilized as the light-harvesting units to mimic efficient energy transfer in the photosynthesis.[50,51,61–64] Among multi-porphyrin arrays, porphyrin oligomers with oligopeptidic backbones in which porphyrins are held in a favored spacing and orientation by fairly short helical oligopeptides have merited special attention in relevance to the natural light-harvesting complex in which chlorophyll and oligopeptides are well-organized in the protein.[65,66] We highlight in this mini-review the elaboration of two different multiple photosynthetic reaction centres using either zinc

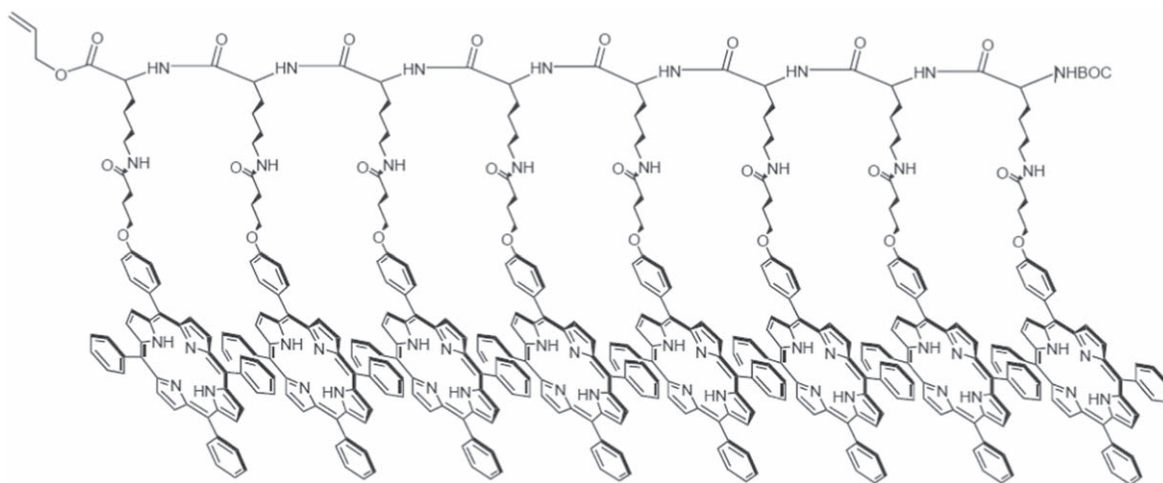[z]E-mail: nathalie.solladie@lcc-toulouse.fr

Figure 1. Family of polypeptide with various numbers of porphyrin units [P(ZnP)$_n$; n = 2, 4, 8]. P(ZnP)$_8$ is represented here.

porphyrinic oligopeptide–fulleropyrrolidine or free-base porphyrinic polypeptide–Li+@C60 supramolecular complexes.

Results and Discussion

Multiple photosynthetic reaction centers using zinc porphyrinic oligopeptide–fulleropyrrolidine supramolecular complexes.—We first synthesized multiple photosynthetic reaction centers composed of light-harvesting multiporphyrin units and charge-separation units, which have been combined by using non-covalent binding including coordination bond and π−π interaction. Zinc porphyrinic oligopeptides with various numbers of porphyrin units [P(ZnP)$_n$; n = 2, 4, 8][48,49,65,66] are used as light harvesting multiporphyrin units, which are bound to electron acceptors of fulleropyrrolidine bearing a pyridine (PyC$_{60}$)[67] or imidazole coordinating ligand (ImC$_{60}$)[48,49] as shown in Fig. 2.

The laser flash photolysis of the supramolecular complexes of P(ZnP)$_n$ with PyC$_{60}$ and ImC$_{60}$ has revealed the formation of the long-lived charge-separated (CS) state. The details of synthesis of porphyrin–peptide oligomers have been reported previously.[65,66] The UV–visible spectra of P(ZnP)$_8$ in benzonitrile (PhCN) at 298 K changed upon addition of PyC$_{60}$, where the Soret band is red-shifted with an isosbestic point at 436 nm. The absorbance change exhibits a saturation behavior with increasing PyC$_{60}$ concentration. This indicates that PyC$_{60}$ forms a 1: 1 supramolecular complex with the ZnP moiety of P(ZnP)$_8$.[39] It has well been established that such nitrogenous bases readily bind to zinc porphyrins with a 1: 1 stoichiometry.[68]

As P(ZnP)$_8$ forms the supramolecular complex with PyC$_{60}$, the fluorescence of P(ZnP)$_8$ is strongly quenched by the intra-supramolecular electron transfer from the singlet excited state of the ZnP moiety (^{1}ZnP*) in P(ZnP)$_8$ to bound PyC$_{60}$ (i.e., static quenching) and not by an intermolecular electron transfer from ^{1}ZnP* to unbound PyC$_{60}$ (i.e., dynamic quenching).[39] In fact, if the fluorescence quenching is analyzed by the Stern-Volmer equation of bimolecular electron transfer [Eq. 1], the rate constant of bimolecular photo-induced electron transfer is estimated as $6 \times 10^{13} \, M^{-1} \, s^{-1}$, which is significantly larger than the diffusion rate constant in PhCN ($5.6 \times 10^9 \, M^{-1} \, s^{-1}$).

$$(I_0/I) = 1 + k_{et}\tau [PyC_{60}] \qquad [1]$$

The values of the formation constants (K) of zinc porphyrinic oligopeptides and C$_{60}$ derivatives (PyC$_{60}$ vs ImC$_{60}$) determined by the absorption spectral change are listed in Table I. In the case of PyC$_{60}$ as an electron acceptor, the K value increases with increasing number of zinc porphyrins in an oligopeptide unit. No supramolecular complex formation was observed in the case of zinc tetraphenylporphyrin with C$_{60}$ derivatives[67] or the porphyrinic

oligopeptides with pristine C$_{60}$ in PhCN.[48,49] The strong association between P(ZnP)$_8$ and C$_{60}$Py may originate from the strong π−π interaction between two zinc porphyrins and C$_{60}$Py in addition to the axial coordination of C$_{60}$Py to the zinc porphyrin. In the case of ImC$_{60}$, however, the highest K value was obtained for the P(ZnP)$_4$-ImC$_{60}$ complex. This indicates that ImC$_{60}$ is much more strongly bound by the oligopeptide, P(ZnP)$_4$, than PyC$_{60}$.

It should be noted that the apparent formation constants determined from the fluorescence quenching are significantly larger than those determined from the UV–vis spectral change, and the difference in such association constants increases with increasing generation of porphyrinic oligopeptides. This indicates that the excited energy migration between the porphyrin units occurs efficiently prior to the electron transfer to the bound C$_{60}$ moiety. Such difference in the formation constants is more enhanced in the P(ZnP)$_n$-ImC$_{60}$ supramolecular complexes as compared to that of PyC$_{60}$ (Table I). For example, an extremely efficient energy transfer may occur in the P(ZnP)$_8$-ImC$_{60}$ system judging from the large difference in the K values determined by the absorption change and by the fluorescence quenching (1.5×10^4 vs $3.3 \times 10^5 \, M^{-1}$). We have also checked the structural change of the oligopeptidic backbone when the porphyrinic oligopeptide forms the supramolecular complex with C$_{60}$ derivatives by the circular dichroism spectroscopy, which exhibited the Cotton effect originating from the porphyrin Soret band at 431 nm.

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 the formation of the CS state as indicated by the transient absorption spectra in Fig. 3a. The absorption band due to PyC$_{60}$$^{.-}$ is clearly observed at 1000 nm together with that due to ZnP$^{.+}$ at 630 nm after laser excitation where only the ZnP moiety is excited (Fig. 3a). The CS state detected decays obeying first-order kinetics (Fig. 3b): the first order plots at different initial CS concentrations afford linear correlations with the same slope (inset of Fig. 3b). If there is any contribution of intermolecular back electron transfer from unbound PyC$_{60}$$^{.-}$ to ZnP$^{.+}$, the second-order kinetics would be involved for the decay time profile. In fact, the corresponding second-order plots (Fig. 3c) 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)$_n$: n = 2, 4] and fullerene derivatives (PyC$_{60}$ and ImC$_{60}$) were also determined and listed in Table I. The CS lifetime
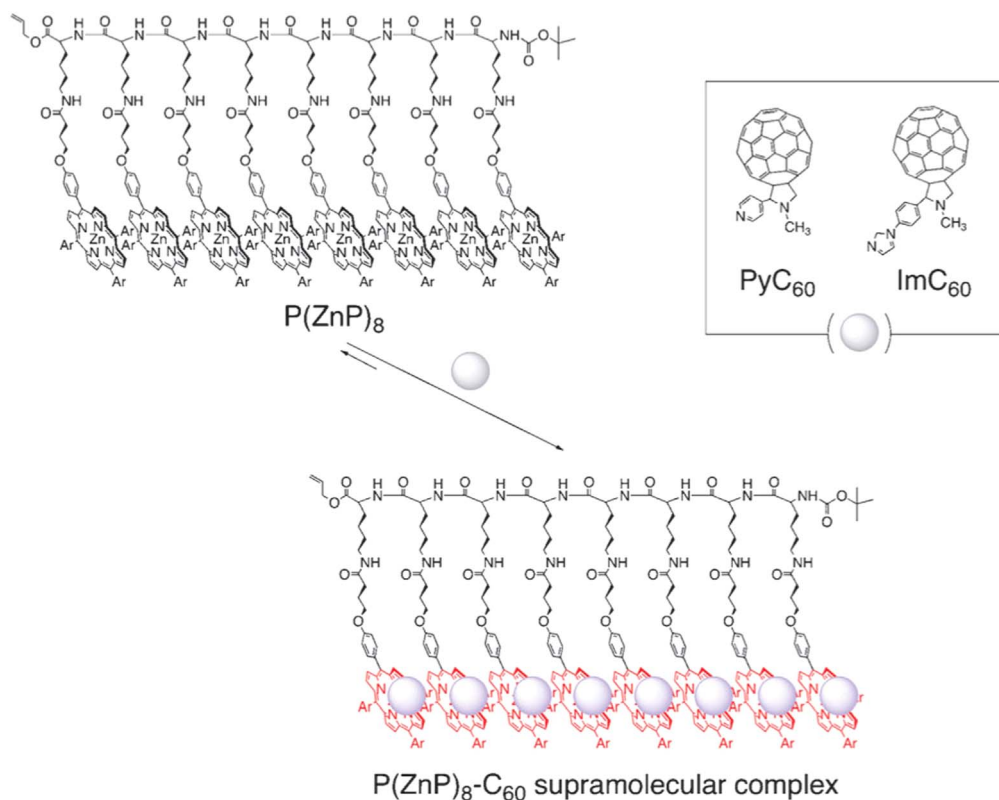
Figure 2. Illustration of a supramolecular complex composed of the porphyrin–peptide octamer P(ZnP)$_8$ and PyC$_{60}$ or ImC$_{60}$. Ar =3,5-(t-Bu)$_2$C$_6$H$_3$.

Table I. Formation constants (K), lifetimes and quantum yield of the CS state of the supramolecular complexes in PhCN at 298 K.

		K^a/M^{-1}		τ_{CS} a)
Porphyrin	Acceptor	UV–vis	Fluorescence	ms^{-1}
P(ZnP)$_8$	PyC$_{60}$	2.3×10^4	1.5×10^5	0.70
P(ZnP)$_4$	PyC$_{60}$	5.2×10^3	1.2×10^4	0.40
P(ZnP)$_2$	PyC$_{60}$	4.0×10^3	9.0×10^3	0.34
P(ZnP)$_8$	ImC$_{60}$	1.5×10^4	3.3×10^5	0.84
P(ZnP)$_4$	ImC$_{60}$	5.9×10^4	8.5×10^4	0.38

a) Experimental error within 5%.

becomes longer with increasing generation of porphyrinic oligopeptides. This may result from efficient hole migration between the porphyrin units following photo-induced electron transfer in the supramolecular complex.

Thus, we have succeeded in attaining the longer CS lifetime by increasing the generation of porphyrinic oligopeptides. Such a long-lived CS state was also confirmed by the ESR measurements under photo-irradiation of the supramolecular complex of P(ZnP)$_8$ with PyC$_{60}$ or ImC$_{60}$ in frozen PhCN at 173 K.[48,49] Under photo-irradiation, the isotropic ESR signals corresponding to the zinc porphyrin radical cation and fullerene radical anion are clearly observed at g = 2.002 and 2.000, respectively.[16,55]

In conclusion, multiple photosynthetic reaction centers combined with light-capturing antenna chromophores have successfully been constructed using supramolecular complexes formed between flexible porphyrinic oligopeptides and fulleropyrrolidine bearing a pyridine (PyC$_{60}$) or imidazole (ImC$_{60}$) ligand via a coordination bond plus $\pi-\pi$ interaction. The excited energy migration occurs between porphyrin units followed by charge separation. The CS lifetimes of the supramolecular oligopeptide complexes have been

elongated by increasing the generation of the porphyrins, enabling us to attain the longest lifetime (0.84 ms) for the P(ZnP)$_8$-ImC$_{60}$ supramolecular system in PhCN solution at 298 K ever reported for supramolecular complexes.

Multiple photosynthetic reaction centers of porphyrinic polypeptide–Li$^+$@c$_{60}$ supramolecular complexes.—In the latter example, metal centers were required for the construction of supramolecular complexes between porphyrins acting as light harvesting units and electron acceptors containing Lewis base ligands for coordination to the metal centers.[35–44] As such there have been only a few reports on supramolecular complexes of free baseporphyrin arrays and electron acceptors without Lewis base ligands, in which the binding is rather weak.[56,57] We thus focused on the construction of supramolecular complexes of free base porphyrin polypeptides (P(H$_2$P)$_n$: n = 4 and 8) with lithium ion-encapsulated C$_{60}$ (Li$^+$@C$_{60}$) (Fig. 4),[69–71] in which binding is much stronger than the case of C$_{60}$ in benzonitrile (PhCN). The photo-dynamics were studied by femtosecond and nanosecond laser-induced transient absorption and fluorescence lifetime measurements.

Free base porphyrin polypeptide (P(H$_2$P)$_n$) were synthesized and characterized as reported previously.[65,66] Upon mixing a PhCN solution of Li$^+$@C$_{60}$ with that of P(H$_2$P)$_8$, the intensity of the Soret band decreased with an increasing concentration of Li$^+$@C$_{60}$. A Soret band was slightly red-shifted from 425 to 427 nm by the addition of Li+@C$_{60}$ to the solution. From the net absorption change at 425 nm in which the absorption due to Li$^+$@C$_{60}$ was subtracted, a linear Benesi–Hildebrand plot[72] was obtained, indicating that each porphyrin unit of P(H$_2$P)$_8$ forms a 1: 1 supramolecular charge-transfer complex with Li$^+$@C$_{60}$ independently with approximately the same binding constant of the unit of M^{-1}. The binding constant at 298 K was determined from the intercept and the slope to be 2.1×10^4 M^{-1}, which is significantly larger than that of C$_{60}$ (5.3×10^3 M^{-1}).[48] The stronger binding of Li$^+$@C$_{60}$ as compared with C$_{60}$ may result from the stronger electron acceptor ability of Li$^+$@C$_{60}$, which facilitates the charge-transfer interaction
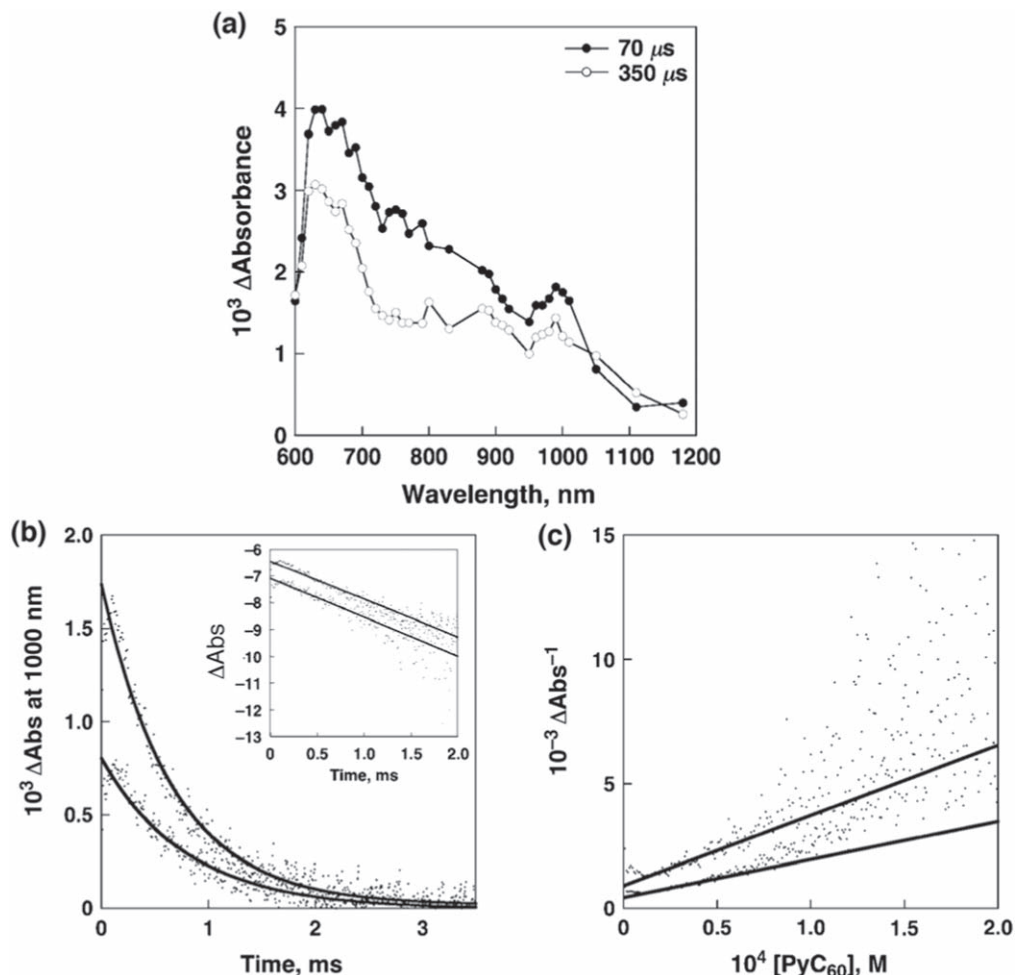
Figure 3. (a) Transient absorption spectra of P(ZnP)$_8$ (2.9 × 10^{-6} M) in the presence of PyC$_{60}$ (4.9 × 10^{-3} M) in deaerated PhCN at 298 K taken at 70 (solid line with black circles) and 350 ms (solid line with white circles) after laser excitation at 561 nm (4 mJ pulse^{-1}), respectively. (b) Time profiles of the absorption at 1000 nm due to PyC$_{60}$.– with different laser powers (4 and 1 mJ pulse^{-1}) at 298 K. Inset: first-order plots. (c) Second-order plots.

as reported for the stronger charge-transfer binding of Li$^+$@C$_{60}$ with corannulene.[73] Similarly the binding constant of the supramolecular complex of P(H$_2$P)$_4$ was determined from the spectral titration to be 6.2 × 10^3 M^{-1}. In the case of P(H$_2$P)$_2$ and P(H$_2$P)$_1$, however, the spectral change was too small to be able to determine the binding constants accurately. The binding constants are summarized in Table II. Thus, multiporphyrins may facilitate charge transfer interactions through the encapsulation of Li+@C$_{60}$ by multiple porphyrins.

Fluorescence of P(H$_2$P)$_8$ was quenched by the addition of a PhCN solution of Li$^+$@C$_{60}$. A Benesi-Hildebrand plot for fluorescence quenching afforded the apparent binding constant of the supramolecular complex of P(H$_2$P)$_8$ with Li+@C$_{60}$ being 8.5 × 10^4 M^{-1}, which is significantly larger than the value determined from the absorption spectral titration (2.1 × 10^4 M^{-1}). Similarly the apparent binding constant of P(H$_2$P)$_4$ with Li$^+$@C$_{60}$ was determined from the fluorescence quenching to be 1.6 × 10^4 M^{-1}, which is also larger than the value determined from the absorption spectral titration (Table II). Such larger apparent binding constants determined from the fluorescence quenching than those determined from the absorption spectral titration indicate that energy migration occurs between the singlet excited state of H$_2$P (^{1}H$_2$P*) and adjacent H$_2$P in P(H$_2$P)$_n$ (n = 4 and 8).

The energy migration rate constant was determined by the fluorescence lifetime measurements of P(H$_2$P)$_8$ with Li$^+$@C$_{60}$. The fluorescence of ^{1}P(H$_2$P)$_8$* exhibited a single exponential decay with the lifetime of 11 ns. In the presence of Li$^+$@C$_{60}$, the decay of

^{1}P(H$_2$P)$_8$* is well analyzed by three exponentials with lifetimes of 100 ps, 3.0 ns and 11 ns. The fast component corresponds to the lifetime of ^{1}H$_2$P* in the supramolecular complex with Li$^+$@C$_{60}$. 95% of the fast component agrees with that predicted by the binding constant determined from the absorption spectral titration. The third component has the same lifetime as that without Li$^+$@C$_{60}$, corresponding to the fluorescence lifetime of ^{1}(H$_2$P)$_8$*. The second component corresponds to energy migration between ^{1}H$_2$P* and the adjacent H$_2$P. 5% of the sum of the first and second components agrees with that predicted from the binding constant determined from fluorescence quenching.

Femtosecond laser-induced transient absorption spectra of P(H$_2$P)$_8$ were recorded in the absence and presence of Li$^+$@C$_{60}$ (Fig. 5). In each case, only the singlet-singlet absorption of ^{1}P(H$_2$P)$_8$* was observed, because H$_2$P was exclusively excited at the excitation wavelength (425 nm) in Fig. 5. The decay of ^{1}P(H$_2$P)$_8$* exhibits a fast component with a lifetime of 6 ps. A similar fast component was observed for ^{1}P(H$_2$P)$_4$* and ^{1}P(H$_2$P)$_2$*. In the case of P(H$_2$P)$_1$, however, no fast component was observed. The ratio of the fast component increased upon increasing the number of H$_2$P in P(H$_2$P)$_n$. 96% of the fast component of P(H$_2$P)$_8$ decreased upon decreasing the laser intensity (Fig. 5b). These results indicate that the fast component results from the singlet–singlet annihilation of two ^{1}H$_2$P* moieties in P(H$_2$P)$_n$ (n = 4 and 8).

In the presence of Li$^+$@C$_{60}$ (20 mM), the decay of ^{1}P(H$_2$P)$_8$* exhibited three exponentials with lifetimes of 6 ps, 90 ps and 2 ns. The first fast component resulted from the singlet-singlet
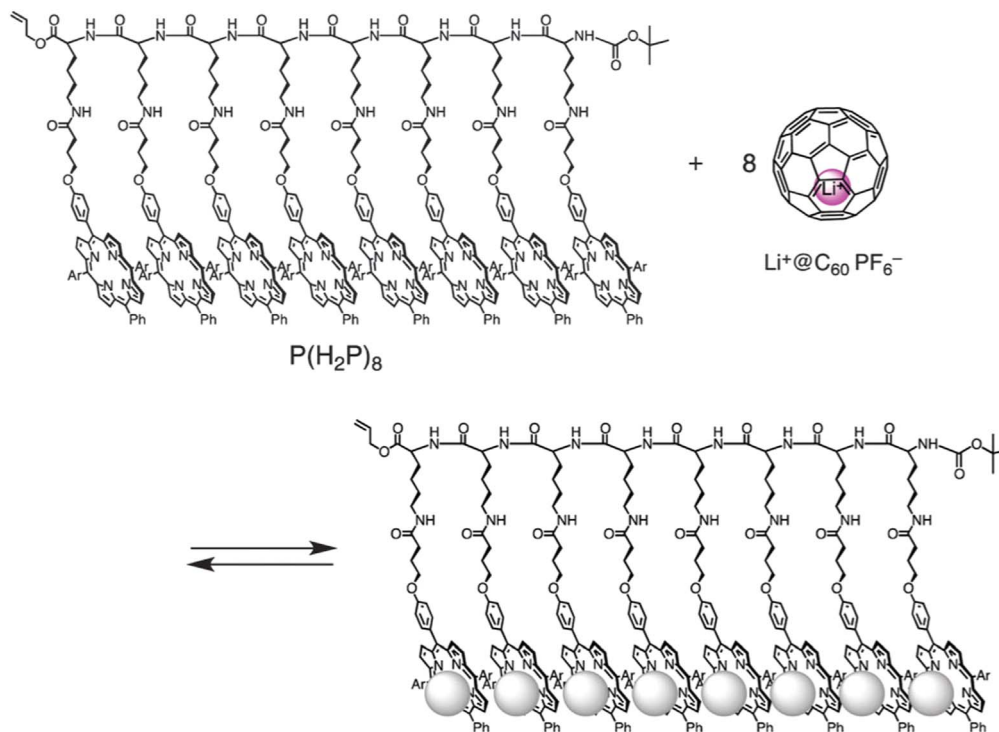
Figure 4. Supramolecular formation of peptide porphyrin oligomers with Li+@C$_{60}$. Ar = 3,5-di-*tert*-butylphenyl.

Table II. Association constant (K, M^{-1}) of P(H$_2$P)$_n$ with Li+@C$_{60}$ and C$_{60}$ in PhCN determined from UV–vis absorption and fluorescence spectral titration.

Porphyrin	Li$^+$@C$_{60}$ UV–vis	Fluorescence	C$_{60}$[b] UV–vis	Fluorescence
P(H$_2$P)$_1$	—[a]	1.1×10^4	—[a]	—[a]
P(H$_2$P)$_2$	—[a]	1.1×10^4	—[a]	—[a]
P(H$_2$P)$_4$	6.2×10^3	1.6×10^4	$2.7 \times 10^{3[b]}$	$9.5 \times 10^{3[b]}$
P(H$_2$P)$_8$	2.1×10^4	8.5×10^4	$5.3 \times 10^{3[b]}$	$2.2 \times 10^{4[b]}$

a) Too small to determine accurately. b) Taken from Ref. 48.

annihilation as observed without Li$^+$@C$_{60}$. The second component (90 ps) may result from electron transfer from ^{1}H$_2$P* to Li$^+$@C$_{60}$ in the supramolecular complex. Because the transient absorption due to the charge-separated state (H$_2$P$^{\cdot+}$ and Li$^+$@C$_{60}^{\cdot-}$) was not observed

in Fig. 5a, where only the singlet-singlet absorption of ^{1}H$_2$P* is seen, back electron transfer may be much faster than the forward electron transfer. The third component may correspond to the energy migration between ^{1}H$_2$P* and the adjacent H$_2$P, because its lifetime agrees with the lifetime of energy migration in the fluorescence lifetime measurements. In the presence of high concentration of Li$^+$@C60 (120 mM), the component of electron transfer from ^{1}H$_2$P* to Li$^+$@C$_{60}$ in the supramolecular complex increased. The three component decay was also observed for P(H$_2$P)$_4$ and P(H$_2$P)$_2$ with Li$^+$@C$_{60}$. In the case of P(H$_2$P)$_1$, only single exponential decay with a lifetime of 11 ns was observed in the absence and presence of Li$^+$@C$_{60}$ because the binding of Li$^+$@C$_{60}$ to P(H$_2$P)$_1$ was negligible.

Nanosecond laser-induced transient absorption spectra of P(H$_2$P)$_8$ with Li$^+$@C$_{60}$ (40 mM) at the excitation wavelength of 532 nm are shown in Fig. 6, where the transient absorption band at 730 nm due to the triplet excited state of Li$^+$@C$_{60}$ (^{3}Li$^+$@C$_{60}$*) is observed together with the absorption band at 1035 nm due to
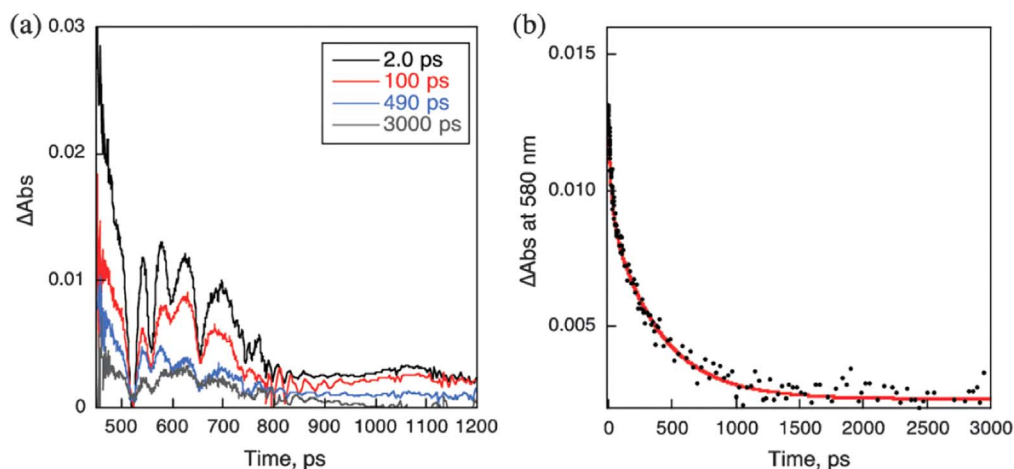

Figure 5. (a) Transient absorption spectra of P(H$_2$P)$_8$ (5.2 × 10^{-6} M) with Li$^+$@C$_{60}$ (2.0 × 10^{-5} M) in deaerated PhCN observed after femtosecond laser flash excitation. Excitation wavelength: 425 nm. (b) Decay time profile at 580 nm with a three-exponential decay curve fitting.

Li$^+$@C$_{60}$$^{\cdot-}$.[46] The decay of the absorption at 730 nm coincides with the appearance of Li$^+$@C$_{60}$$^{\cdot-}$. Thus, electron transfer from P(H$_2$P)$_8$ to ^{3}Li$^+$@C$_{60}$* occurs to produce the triplet charge-separate (CS) state of P(H$_2$P)$_8$$^{\cdot+}$ and Li$^+$@C$_{60}$$^{\cdot-}$. The transient absorption due to P(H$_2$P)$_8$$^{\cdot+}$ is overlapped with that of ^{3}Li+@C$_{60}$* in the 600–700 nm region. The photoexcitation of 532 nm resulted in the excitation of Li$^+$@C$_{60}$ leading to the formation of ^{3}Li$^+$@C$_{60}$* via intersystem crossing. The decay of the absorbance at 1035 nm due to Li$^+$@C$_{60}$$^{\cdot-}$ obeyed first-order kinetics with the lifetime of 210 ms (Fig. 6b). Thus, back electron transfer from Li$^+$@C$_{60}$$^{\cdot-}$ to P(H$_2$P)$_8$$^{\cdot+}$ occurs in the supramolecular complex. The lifetime is long because of the spin-forbidden back electron transfer in the triplet CS state.

Similarly the triplet CS states derived from ^{3}Li$^+$@C$_{60}$* were observed for P(H$_2$P)$_n$ (n = 4, 2, and 1) with Li$^+$@C$_{60}$. The rate constants of electron transfer from ^{1}H$_2$P* to Li$^+$@C$_{60}$ and the energy migration in the supramolecular complexes of P(H$_2$P)$_n$ with Li$^+$@C$_{60}$ are summarized in Table III together with the lifetimes of the triplet CS states. The CS lifetime increases upon increasing the number of H$_2$P in P(H$_2$P)$_n$. Such an increase in the CS lifetime may result from the charge migration between H$_2$P$^{\cdot+}$ and the adjacent H$_2$P in P(H$_2$P)$_n$$^{\cdot+}$. The energy diagram of photoexcitation of P(H$_2$P)$_n$ with Li$^+$@C$_{60}$ is given in Scheme 1. The energies of the excited state of porphyrin and Li$^+$@C$_{60}$ were determined by UV–vis, fluorescence and phosphorescence spectral measurements. The energy of the CS state was determined to be 0.82 eV in PhCN from the one-electron oxidation potential of porphyrin (+0.96 V vs SCE) and reduction potential of Li$^+$@C$_{60}$ (+0.14 V vs SCE) by the electrochemical measurements. Femtosecond laser excitation of the

supramolecular complex of P(H$_2$P)$_8$ with Li$^+$@C$_{60}$ at 425 nm resulted in electron transfer from H$_2$P to the bound Li$^+$@C$_{60}$ to produce the singlet CS state and energy transfer from ^{1}H$_2$P* to the adjacent H$_2$P, followed by electron transfer to Li$^+$@C$_{60}$, when it is bound H$_2$P. The singlet CS state decays rapidly to the ground state. Nanosecond laser excitation at 532 nm resulted in the formation of the singlet excited state of excess Li$^+$@C$_{60}$, followed by intersystem crossing to produce ^{3}Li$^+$@C$_{60}$*, to which intermolecular electron transfer occurs from H$_2$P to produce the triplet CS state with a long lifetime because of the spin-forbidden back electron transfer to the ground state.

We can thus confirm that free base porphyrin polypeptides (P(H$_2$P)$_n$; n = 4 and 8) form supramolecular complexes with Li$^+$@C$_{60}$ in PhCN, in which the binding is much stronger than C$_{60}$. Efficient energy migration occurs between porphyrins in P(H$_2$P)$_n$. Although the lifetimes of the singlet CS states were too short to be detected, the triplet CS states derived from ^{3}Li$^+$@C$_{60}$ had long lifetimes because of the spin-forbidden back electron transfer. The triplet CS lifetime becomes longer upon increasing the number of H$_2$P due to the charge migration among porphyrins. The present study provides valuable insight into the energy and electron transfer in multiple reaction centers.

Conclusions

In conclusion, multiple photosynthetic reaction centers combined with light-capturing antenna chromophores have successfully been constructed using supramolecular complexes formed between
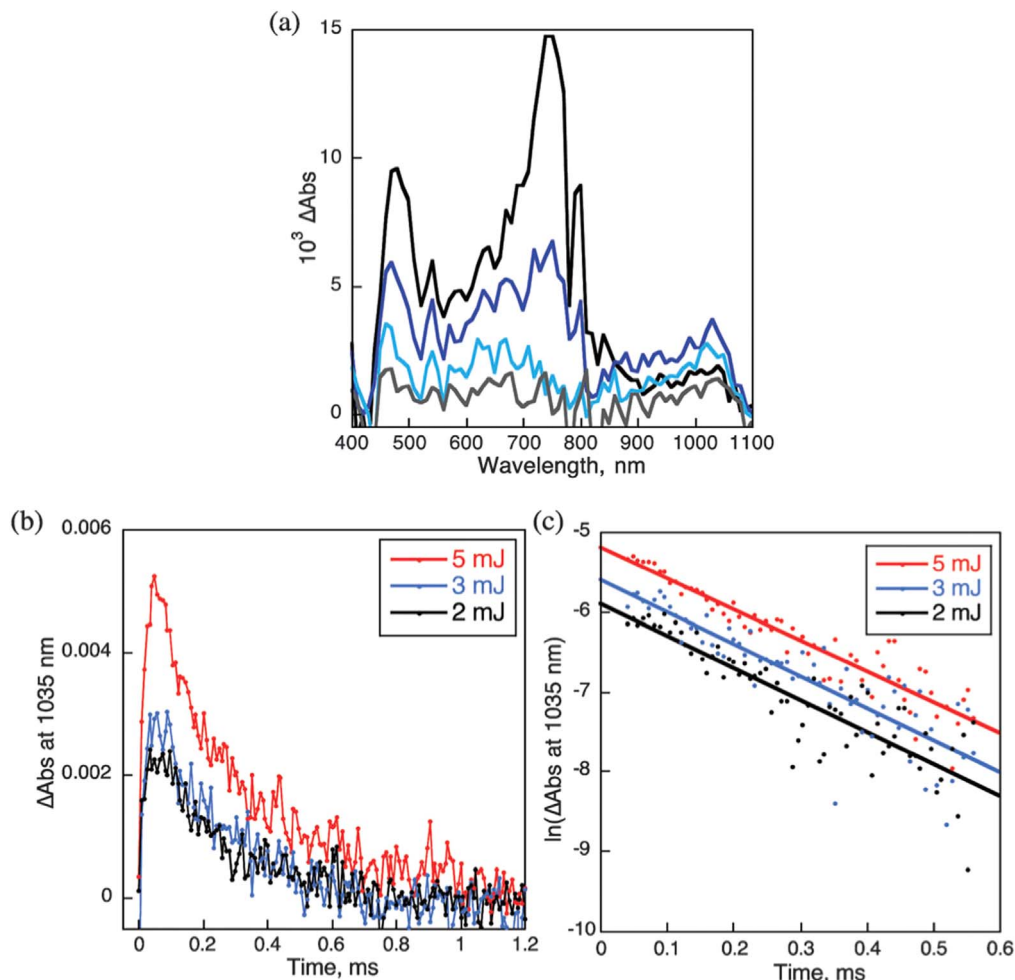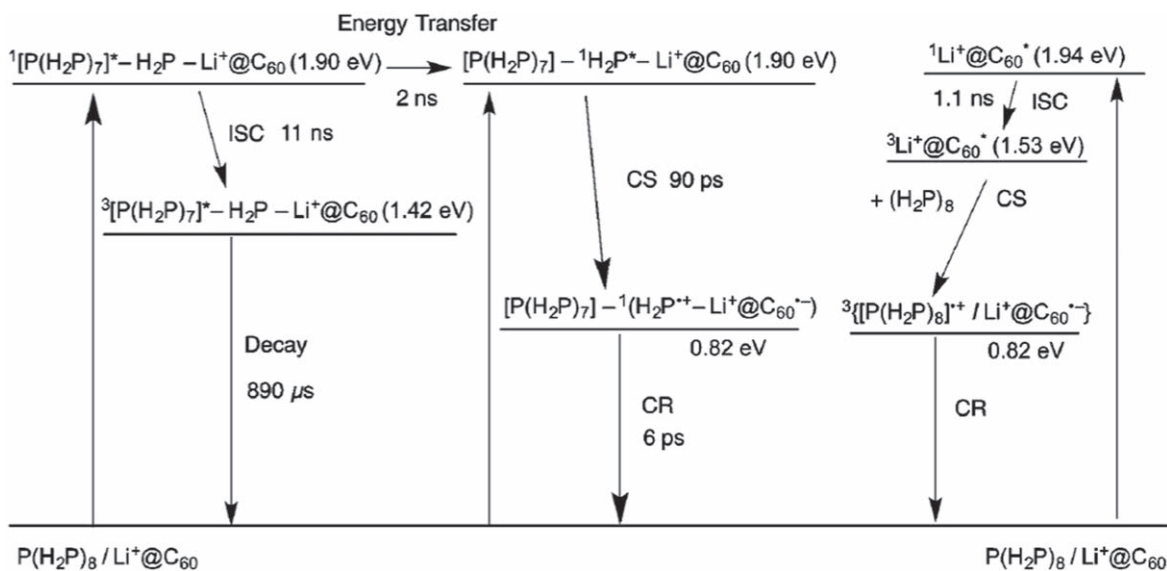

Figure 6. (a) Transient absorption spectra of P(H$_2$P)$_8$ (2.6 × 10^{-6} M) with Li$^+$@C$_{60}$ (4.0 × 10^{-5} M) in deaerated PhCN observed after nanosecond laser flash excitation taken at 8 (black), 32 (blue), 96 (sky blue) and 200 ms (gray). Excitation wavelength: 532 nm. (b) Decay time profile at 1035 nm with the different laser pulse intensities (2–5 mJ pulse^{-1}). (c) First-order plots.

Scheme 1. Reaction course of photo-induced charge separation and charge recombination in the supramolecular complex between $P(H_2P)_8$ and $Li+@C_{60}$ with the values of energy levels.

Table III. Rate constants of intra- and inter-molecular photo-induced electron transfer (k_{ET} and k_{et}) and lifetimes ($\tau(CS)$) and quantum yields ($\Phi(CS)$) of the charge-separated state.

Porphyrin	k_{ET}, $M^{-1} s^{-1}$	k_{et}, $M^{-1} s^{-1}$	τ_{CS}, μs	Φ_{CS}
$P(H_2P)_1$	7.7×10^5	1.7×10^9	—a)	0.70
$P(H_2P)_2$	6.7×10^4	1.8×10^9	—a)	0.34
$P(H_2P)_4$	9.5×10^4	8.0×10^8	160	0.16
$P(H_2P)_8$	1.5×10^5	1.5×10^8	210	0.13

a) Bimolecular decay in the radical ion pair.

flexible porphyrinic oligopeptides and fulleropyrrolidine bearing a pyridine (PyC_{60}) or imidazole (ImC_{60}) ligand via a coordination bond plus $\pi-\pi$ interaction. The excited energy migration occurs between porphyrin units followed by charge separation. The CS lifetimes of the supramolecular oligopeptide complexes have been elongated by increasing the generation of the porphyrins, enabling us to attain the longest lifetime (0.84 ms) for the $P(ZnP)_8$-ImC_{60} supramolecular system in PhCN solution at 298 K ever reported for supramolecular complexes.

In the first exemple, metal centers were required for the construction of supramolecular complexes between porphyrins acting as light harvesting units and electron acceptors containing Lewis base ligands for coordination to the metal centers. As such there have been only a few reports on supramolecular complexes of free base porphyrin arrays and electron acceptors without Lewis base ligands, in which the binding is rather weak. Our second study confirms that free base porphyrin polypeptides ($P(H_2P)_n$; n = 4 and 8) form supramolecular complexes with $Li^+@C_{60}$ in PhCN, in which the binding is much stronger than C_{60}. Efficient energy migration occurs between porphyrins in $P(H_2P)_n$. Although the lifetimes of the singlet CS states were too short to be detected, the triplet CS states derived from $^3Li^+@C_{60}$ had long lifetimes because of the spin-forbidden back electron transfer. The triplet CS lifetime becomes longer upon increasing the number of H_2P due to the charge migration among porphyrins.

Acknowledgments

ORCID

Nathalie Solladié https://orcid.org/0000-0001-6530-6391
Shunichi Fukuzumi https://orcid.org/0000-0002-3559-4107
Kei Ohkubo https://orcid.org/0000-0001-8328-9249
Francis D'Souza https://orcid.org/0000-0003-3815-8949

References

1. W. Kuehlbrandt, *Nature (London)*, **374**, 497 (1995).
2. G. McDermott, S. M. Prince, A. A. Freer, A. M. Hawthornthwaite-Lawless, M. Z. Papiz, R. J. Cogdell, and N. W. Isaacs, *Nature (London, U. K.)*, **374**, 517 (1995).
3. T. Pullerits and V. Sundstroem, *Acc. Chem. Res.*, **29**, 381 (1996).
4. R. E. Blankenship, M. T. Madigan, and C. E. Bauer (ed.), *Anoxygenic Photosynthetic Bacteria* (Springer , Dordrecht) 2 (1995).
5. K. D. Karlin (ed.), *Molecular Level Artificial Photosynthetic Materials* (Wiley, New York) 44 (1997).
6. R. A. Wheeler, *Introduction to the Molecular Bioenergetics of Electron, Proton, and Energy Transfer, ACS Symposium Series*, **883**, 1 (2004).
7. W. Leibl and P. Mathis, *Electron Transfer in Photosynthesis. Series on photo-conversion of solar energy*, **2**, 117 (2004).
8. D. Gust, T. A. Moore, and A. L. Moore, *Acc. Chem. Res.*, **42**, 1890 (2009).
9. G. Bottari, G. de la Torre, D. M. Guldi, and T. Torres, *Chem. Rev.*, **110**, 6768 (2010).
10. V. Sgobba and D. M. Guldi, *Chem. Soc. Rev.*, **38**, 165 (2009).
11. M. R. Wasielewski, *Acc. Chem. Res.*, **42**, 1910 (2009).
12. S. Fukuzumi, *Phys. Chem. Chem. Phys.*, **10**, 2283 (2008).
13. F. D'Souza and O. Ito, *Chem. Commun.*, **4913** (2009).
14. F. D'Souza and O. Ito, *Coord. Chem. Rev.*, **249**, 1410 (2005).
15. C. B. Kc and F. D'Souza, *Coord. Chem. Rev.*, **322**, 104 (2016).
16. S. Fukuzumi et al., *Chem. Commun.*, **47**, 7980 (2011).
17. T. Kojima, T. Honda, K. Ohkubo, M. Shiro, T. Kusukawa, T. Fukuda, N. Kobayashi, and S. Fukuzumi, *Angew. Chem. Int. Ed.*, **47**, 6712 (2008).
18. S. Fukuzumi, T. Honda, K. Ohkubo, and T. Kojima, *Dalton Trans.*, **3880** (2009).
19. T. Kojima, K. Hanabusa, K. Ohkubo, M. Shiro, and S. Fukuzumi, *Chem.—Eur. J.*, **16**, 3646 (2010).
20. S. Fukuzumi, *Functional Organic Materials*, ed. Dr. Thomas, J. J. Muller, and U. H. F. Bunz (Wiley-VCH, Verlag GmbH) Chap. 13, p. 465 (2007).
21. T. Tanaka and A. Osuka, *Chem. Soc. Rev.*, **44**, 943 (2015).
22. H.-W. Jiang, T. Tanaka, H. Mori, K. H. Park, D. Kim, and A. Osuka, *J. Am. Chem. Soc.*, **137**, 2219 (2015).
23. N. Aratani, D. Kim, and A. Osuka, *Acc. Chem. Res.*, **42**, 1922 (2009).
24. J. Yang, M.-C. Yoon, H. Yoo, P. Kim, and D. Kim, *Chem. Soc. Rev.*, **41**, 4808 (2012).
25. T. Miyatake and H. Tamiaki, *Coord. Chem. Rev.*, **254**, 2593 (2010).

26. S. Sengupta and F. Würthner, *Acc. Chem. Res.*, **46**, 2498 (2013).
27. T. S. Balaban, *Acc. Chem. Res.*, **38**, 612 (2005).
28. H.-J. Son et al., *J. Am. Chem. Soc.*, **135**, 862 (2013).
29. I. Cohen-Ofri, M. van Gastel, J. Grzyb, A. Brandis, I. Pinkas, W. Lubitz, and D. Noy, *J. Am. Chem. Soc.*, **133**, 9526 (2011).
30. J. L. R. Anderson et al., *Chem. Sci.*, **5**, 507 (2014).
31. F. A. Tezcan, B. R. Crane, J. R. Winkler, and H. B. Gray, *Proc. Natl. Acad. Sci. U. S. A.*, **98**, 5002 (2001).
32. T. Koshiyama, M. Shirai, T. Hikage, H. Tabe, K. Tanaka, S. Kitagawa, and T. Ueno, *Angew. Chem. Int. Ed.*, **50**, 4849 (2011).
33. R. A. Miller, N. Stephanopoulos, J. M. McFarland, A. S. Rosko, P. L. Geissler, and M. B. Francis, *J. Am. Chem. Soc.*, **132**, 6068 (2010).
34. L. S. Witus and M. B. Francis, *Acc. Chem. Res.*, **44**, 774 (2011).
35. Y. S. Nam, T. Shin, H. Park, A. P. Magyar, K. Choi, G. Fantner, K. A. Nelson, and A. M. Belcher, *J. Am. Chem. Soc.*, **132**, 1462 (2010).
36. M. Endo, M. Fujitsuka, and T. Majima, *Chem.—Eur. J.*, **13**, 8660 (2007).
37. S. Fukuzumi and K. Ohkubo, *J. Mater. Chem.*, **22**, 4575 (2012).
38. S. Fukuzumi, K. Ohkubo, and T. Suenobu, *Acc. Chem. Res.*, **47**, 1455 (2014).
39. S. Fukuzumi, K. Saito, K. Ohkubo, V. Troiani, H. Qiu, S. Gadde, F. D'Souza, and N. Solladié, *Phys. Chem. Chem. Phys.*, **13**, 17019 (2011).
40. A. Takai, C. P. Gros, R. Guilard, and S. Fukuzumi, *Chem.—Eur. J.*, **15**, 3110 (2009).
41. A. Takai, C. P. Gros, J.-M. Barbe, and S. Fukuzumi, *Phys. Chem. Chem. Phys.*, **12**, 12160 (2010).
42. A. Takai, C. P. Gros, J.-M. Barbe, and S. Fukuzumi, *Chem.—Eur. J.*, **17**, 3420 (2011).
43. Y. Pareek and M. Ravikanth, *RSC Adv.*, **4**, 7851 (2014).
44. V. S. Nair, Y. Pareek, V. Karunakaran, M. Ravikanth, and A. Ajayaghosh, *Phys. Chem. Chem. Phys.*, **16**, 10149 (2014).
45. N. Solladié et al., *J. Porphyrins Phthalocyanines*, **7**, 270 (2003).
46. P. Ceroni, G. Bergamini, N. Aubert, V. Troiani, and N. Solladié, *ChemPhysChem*, **6**, 2120 (2005).
47. T. Hasobe, P. V. Kamat, V. Troiani, N. Solladié, T. K. Ahn, S. K. Kim, D. Kim, A. Kongkanand, S. Kuwabata, and S. Fukuzumi, *J. Phys. Chem. B*, **109**, 19 (2005).
48. T. Hasobe et al., *J. Mater. Chem.*, **17**, 4160 (2007).
49. M. Fujitsuka, M. Hara, S. Tojo, A. Okada, V. Troiani, N. Solladié, and T. Majima, *J. Phys. Chem. B*, **109**, 33 (2005).
50. M. Fujitsuka, D. W. Cho, N. Solladié, V. Troiani, H. Qiu, and T. Majima, *J. Photochem. Photobiol., A*, **188**, 346 (2007).
51. K. Saito, V. Troiani, H. Qiu, N. Solladié, T. Sakata, H. Mori, M. Ohama, and S. Fukuzumi, *J. Phys. Chem. C*, **111**, 1194 (2007).
52. D. Gust, T. A. Moore, and A. L. Moore, *Acc. Chem. Res.*, **34**, 40 (2001).
53. D. M. Guldi, G. M. A. Rahman, F. Zerbetto, and M. Prato, *Acc. Chem. Res.*, **38**, 871 (2005).
54. S. Fukuzumi and T. Kojima, *J. Mater. Chem.*, **18**, 1427 (2008).
55. M.-S. Choi, T. Yamazaki, I. Yamazaki, and T. Aida, *Angew. Chem. Int. Ed.*, **43**, 150 (2004).
56. M. Tanaka, K. Ohkubo, C. P. Gross, R. Guilard, and S. Fukuzumi, *J. Am. Chem. Soc.*, **128**, 14625 (2006).
57. A. Takai, M. Chkounda, A. Eggenspiller, C. P. Gros, M. Lachkar, J.-M. Barbe, and S. Fukuzumi, *J. Am. Chem. Soc.*, **132**, 4477 (2010).
58. J. L. Sessler, B. Wang, and A. Harriman, *J. Am. Chem. Soc.*, **115**, 10418 (1993).
59. J. L. Sessler, E. Karnas, S. K. Kim, Z. Ou, M. Zhang, K. M. Kadish, K. Ohkubo, and S. Fukuzumi, *J. Am. Chem. Soc.*, **130**, 15256 (2008).
60. F. D'Souza, E. Maligaspe, K. Ohkubo, M. E. Zandler, N. K. Subbaiyan, and S. Fukuzumi, *J. Am. Chem. Soc.*, **131**, 8787 (2009).
61. A. Tsuda and A. Osuka, *Science*, **293**, 79 (2001).
62. Y. Nakamura, I.-W. Hwang, N. Aratani, T. K. Ahn, D. M. Ko, A. Takagi, T. Kawai, T. Matsumoto, D. Kim, and A. Osuka, *J. Am. Chem. Soc.*, **127**, 236 (2005).
63. C. Maeda, P. Kim, S. Cho, J. K. Park, J. M. Lim, D. Kim, J. Vura-Weis, M. R. Wasielewski, H. Shinokubo, and A. Osuka, *Chem.–Eur. J.*, **16**, 5052 (2010).
64. A. Satake and Y. Kobuke, *Org. Biomol. Chem.*, **5**, 1679 (2007).
65. N. Solladié, A. Hamel, and M. Gross, *Tetrahedron Lett.*, **41**, 6075 (2000).
66. F. Aziat, R. Rein, J. Peon, E. Rivera, and N. Solladié, *J. Porphyrins Phthalocyanines*, **12**, 1232 (2008).
67. F. D'Souza, P. M. Smith, S. Gadde, A. L. McCarty, M. J. Kullman, M. E. Zandler, M. Itou, Y. Araki, and O. Ito, *J. Phys. Chem. B*, **108**, 11333 (2004).
68. J. K. M. Sanders, N. Banpos, Z. Clude-Watson, S. L. Darling, J. C. Hawaley, H. J. Kim, C. C. Mak, and S. J. Webb, *The Porphyrin Handbook* (Academic, San Diego) 3, p. 1 (2000).
69. S. Aoyagi et al., *Nat. Chem.*, **2**, 678 (2010).
70. Y. Kawashima, K. Ohkubo, and S. Fukuzumi, *Chem.—Asian J.*, **10**, 44 (2015).
71. S. Fukuzumi, K. Ohkubo, Y. Kawashima, D. S. Kim, J. S. Park, A. Jana, V. M. Lynch, D. Kim, and J. L. Sessler, *J. Am. Chem. Soc.*, **133**, 15938 (2011).
72. H. Benesi and J. Hildebrand, *J. Am. Chem. Soc.*, **71**, 2703 (1949).
73. M. Yamada, K. Ohkubo, M. Shionoya, and S. Fukuzumi, *J. Am. Chem. Soc.*, **135**, 13240 (2014).