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Photosynthetic Reaction Center Mimicry of a "Special Pair" Dimer Linked to Electron Acceptors by a Supramolecular Approach: Self-Assembled Cofacial Zinc Porphyrin Dimer Complexed with Fullerene(s)

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Abstract: Biomimetic bacterial photosynthetic reaction center complexes have been constructed using well-defined self-assembled supramolecular approaches. The "special pair" donor, a cofacial porphyrin dimer, was formed via potassium ion induced dimerization of *meso*-(benzo-[15]crown-5)porphyrinatozinc. The dimer was subsequently self-assembled with functionalized fullerenes via axial coordination and crown ether–alkyl ammonium cation complexation to form the donor–acceptor pairs, mimicking the noncovalently bound entities of the photosynthetic reaction center. The adopted self-assembly methodology yielded supramolecular complexes of higher stability, with defined geometry and orientation. Efficient forward electron transfer from the singlet excited zinc porphyrin dimer to the fullerene entity and relatively slow reverse electron transfer, important steps in the photosynthetic light energy conversion have been achieved in these novel biomimetic model systems.

Keywords: electron transfer • fullerenes • photosynthesis • porphyrinoids • self-assembly

Introduction

Self-assembly directed construction of supramolecules capable of mimicking biological functions is one of the fastest growing areas of research. The potential applications of these self-assembly techniques to the design of molecular systems lay in self-replication, light energy harvesting and nanotechnology.[1] An approach to the development of artificial supramolecular systems capable of performing specific functions is to mimic the features adopted by the natural systems in carrying out the desired tasks. Mimicking the primary events of the reaction centers of photosynthetic bacteria directly involves harvesting solar energy.[2] Structural studies of *R. viridis* and *R. sphaeroides* have revealed membrane-bound protein containing four bacteriochlorophylls, two bacteriopheophytins and two quinones.[3] The primary electron donor, a "special pair" of two bacteriochlorophylls, is held noncovalently apart by about 3.2 Å with a slipped cofacial orientation. These reaction centers employ a sequential multi-step electron transfer strategy to realize the efficient conversion of light energy to chemical energy.

Despite numerous studies for models of the reaction centers of photosynthetic systems,[2] incorporation of a "special pair" into these models has been limited to only a few studies.[4] Majority of these studies utilized covalent bonding of the different entities. Although noncovalent (self-assembly) approach of building donor–acceptor pairs is more biomimetic, it is often difficult to control the distance and orientation due to weak interactions and the associated equilibrium processes. In the present study, we have accomplished building "special-pair" donor–acceptor triads and tetrads utilizing well-defined self-assembly methods without any covalent links to connect different entities. As light harvesting electron-donor, we employed the non-covalently dimerized zinc porphyrin with crown ether voids (**a** in Scheme 1). As electron acceptor, functionalized fullerene (Scheme 1) has been used instead of quinone, due to its inherent properties such

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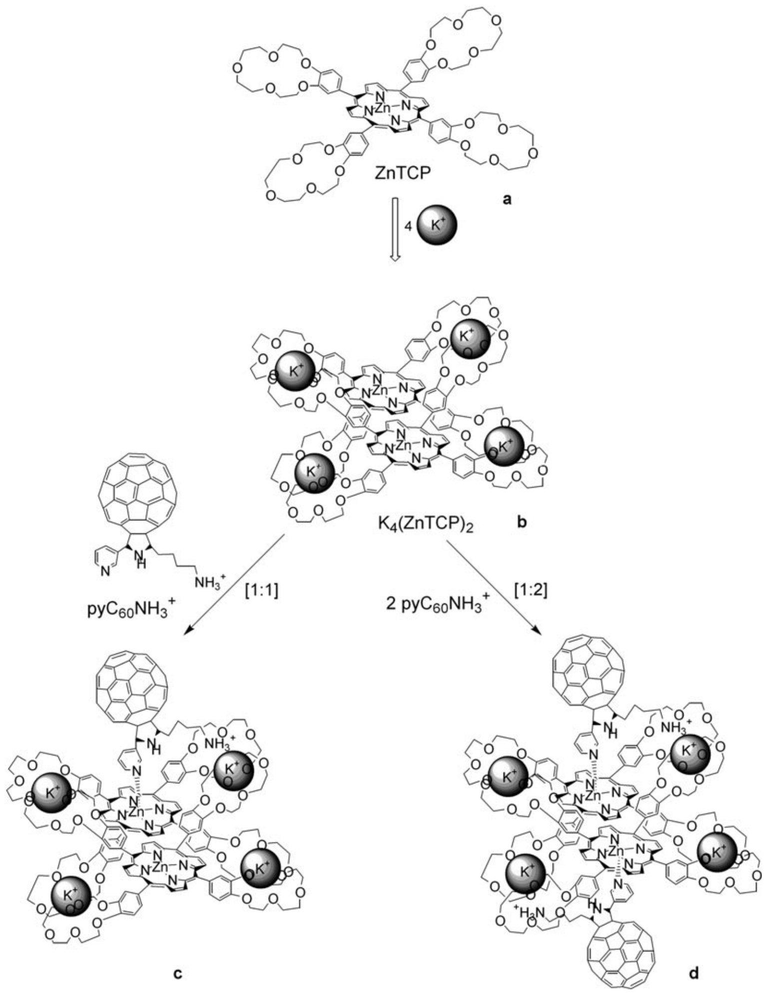

Scheme 1. Construction of the supramolecular "special pair" porphyrin dimer–fullerene triad and tetrad.

as reversible, step-wise addition of up to six electrons and low reorganization energy accompanied with electron transfer processes.[5,6] Our approach shown in Scheme 1 involves, first, potassium cation induced dimerization of zinc *meso*-tetrakis(benzo-[15]crown-5)porphyrin, $K_4[ZnTCP]_2$ (**b** in Scheme 1).[7] Here, due to inconformity of the size differences, the potassium ion is sandwiched between two [15]crown-5 entities from two different porphyrins. As a result of four bis(crown ether)–potassium ion complexes, the resulting porphyrin dimer is expected to be highly stable.[7a] Next, the zinc crown ether porphyrin dimer was self-assembled via axial coordination to pyridine and an alkyl ammonium cation functionalized fullerene $pyC_{60}NH_3^+$.[8b,c] Here, the pyridine binds to the zinc metal center, while the alkyl ammonium cation interacts with one of the crown ether entities (without destroying the K^+–sandwich dimer) via a "two-point" binding motif thus gaining additional stability (**c** in Scheme 1). As shown here, utilization of such well-defined multiple modes of binding in a controlled fashion results in the formation of biomimetic supramolecular complexes, and allows probing photoinduced charge separation from the singlet excited porphyrin dimer, $K_4{}^1[ZnTCP]_2{}^*$ to the fullerene within the supramolecular complex by time-resolved methods.

Results and Discussion

Steady-state absorption studies: Figure 1 (curve i) shows the UV-visible spectrum of zinc tetrakis(benzo-[15]crown-5)porphyrin monomer, ZnTCP, which revealed a Soret band at 434 and visible bands at 562 and 604 nm. Upon addition of K^+ (10 equiv potassium tetrakis(4-chlorophenyl)borate), the Soret band blue-shifted to 415 nm, while the visible bands red-shifted by 2–3 nm (in curve ii, top spectrum). Such spectral behavior was attributed to the cofacial porphyrin dimer formation with strong exciton coupling between the two macrocycles.[9a,b] ESI-mass spectrum, recorded in CH_2Cl_2/CH_3OH confirmed the molecular ion peak of $K_4[ZnTCP]_2$ (at 778 see Supporting Information). From the procedure adopted by Thanabal and Krishnan,[7b] the binding constant for $K_4[ZnTCP]_2$ was evaluated to be K_{dimer} ~$2\times10^{22}\,\text{M}^{-5}$ in benzonitrile. This value is close to that reported for other cation (M = NH_4^+, Ba^{2+}, Cu^{2+} etc.) induced formation of $M_4[ZnTCP]_2$ suggesting very stable porphyrin dimer formation. ESR studies performed on paramagnetic CuTCP exhibited the ESR spectrum (see Supporting Information), in which formation of the ground triplet state was confirmed on addition of K^+, suggesting the formation of $M_4[CuTCP]_2$. From the splitting of these ESR signals, the Cu–Cu distance was found to be 4.2 Å. Job's plot constructed using optical absorption data also confirmed the stoichiometry of the $K_4[ZnTCP]_2$ complex (see Supporting Information for the plot).

Addition of the functionalized fullerenes, $pyC_{60}NH_3^+$ in Scheme 1 to $K_4[ZnTCP]_2$ resulted in a decreased Soret intensity at 415 nm with a small red shift, typical of that expected for axial coordination of pyridine to zinc porphyrin.[8] During the titration with $pyC_{60}NH_3^+$, two isosbestic points were observed at 411 and 420 nm (spectra under curve ii at ca. 415 nm in Figure 1). Addition of excess of fullerene ligands did not cause in breaking the K^+–sandwich dimer since the original zinc porphyrin monomer spectrum could

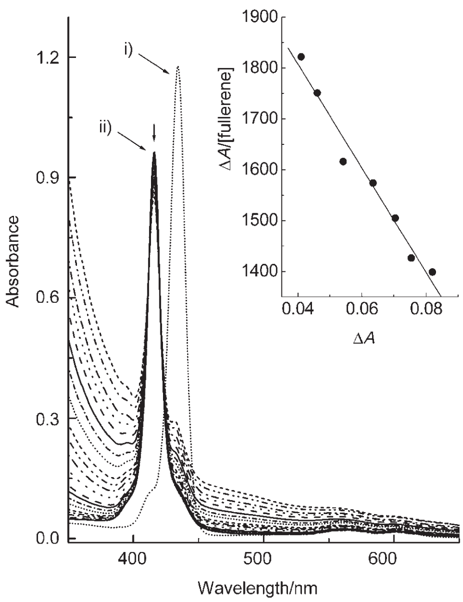

Figure 1. UV-visible spectra of i) zinc tetrakis(benzo-[15]crown-5)porphyrin (2.0 μm), (ii: top at 415 nm) potassium ion induced zinc tetrakis-(benzo-[15]crown-5)porphyrin dimer and (spectra under ii at ca. 415 nm) on increasing addition of fullerene, $pyC_{60}NH_3^+$ (1.3 μm each addition) in benzonitrile. The inset shows a Scatchard plot constructed for evaluating the binding constant.

not be observed under these conditions. The calculated binding constant, $K_{complex}$ was found to be $1.03\times10^4\,M^{-2}$ for the tetrad formation, in which two $pyC_{60}NH_3^+$ are bound to the two zinc centers of $K_4[ZnTCP]_2$ in addition to two of eight crown ethers. Job's plots were constructed to determine the stoichiometry of the supramolecular complex (see Supporting Information for the plot). Such plots revealed a 1:2 supramolecular stoichiometry for the $K_4[ZnTCP]_2$:$(pyC_{60}NH_3^+)_2$ complex being in agreement with the supramolecular structure shown in Scheme 1d. ^{1}H NMR studies performed in $CDCl_3/CD_3OD$ (1:1 v/v) also confirmed coordination of pyridine ligands to the zinc centers in the dimer, that is, the pyridine protons were shielded up to 4 ppm in the supramolecular complex. The magnitude of $K_{complex}$ suggests moderate stability for the supramolecular complex. Our attempts to obtain the molecular ion peak of the supramolecular triad, **c** or tetrad, **d** using ESI-mass technique were not fully successful. Even under mild temperature and ionization conditions, molecular ion peaks corresponding only to $K_4[ZnTCP]_2$ and $pyC_{60}NH_3^+$ were separately observed. Attempts were also made to verify whether the ammonium cation would replace the K^+ sandwiched between the two crown ether entities of the dimer. Such replacement reactions are known in the case of some K^+ complexed crown ether derivatives (1:1 complex),[10a] although in the case of pure [18]crown-6 no selectivity for binding of NH_4^+ over K^+ is observed.[10b] When 10 equivalents of $pyC_{60}NH_3^+$ were added to $K_4[ZnTCP]_2$, the dimer molecular ion peak with four K^+ was still retained in the mass spectrum. It is likely that in the dimer structure, when an alkyl ammonium cation binds to the K^+ sandwiched crown ether dimer, the binding of one of K^+–crown ether entity of the dimer weakens while the another crown ether entity which is not bound to alkyl ammonium cation still holds the bound K^+ resulting in structures **c** and **d** in Scheme 1.

Electrochemical studies: The performed electrochemical studies led us to evaluate the redox potentials and also to probe the integrity of the supramolecular complex. As shown in Figure 2, the differential pulse voltammograms (DPV) of the monomer, ZnTCP revealed the first oxidation and the first reduction peaks located at 0.25 and −1.80 V versus Fc/Fc$^+$, respectively (curve i). Upon forming the dimer, $K_4[ZnTCP]_2$ by the addition of K^+ to the solution of ZnTCP, both oxidation and reduction peaks revealed splitting as a consequence of strongly interacting porphyrin macrocycles.[7c,11] The first split peaks negatively shifted, and appeared at 0.14 V for the oxidation process, and −1.90 V for the reduction process (curve ii). Addition of $pyC_{60}NH_3^+$ to the $K_4[ZnTCP]_2$ dimer solution revealed additional changes in the peak potentials; however, the split oxidation and reduction peaks, signatures for keeping dimer in solution, still retained with considerable broadening in the oxidation region (curve iii). The split porphyrin peaks of the supramolecular complex in Scheme 1 were located at 0.25 and 0.31 V for oxidation, and −1.90 and −2.08 V for reduction, respectively, in addition to peaks at −1.02 and −1.41 V for the reduction of $pyC_{60}NH_3^+$. That is, the porphyrin oxidation was anodically shifted and reduction was cathodically shifted as compared to the redox potentials of $K_4[ZnTCP]_2$. These results clearly demonstrate the existence of a new supramolecule, $pyC_{60}NH_3^+$ bound $K_4[ZnTCP]_2$, as depicted in Scheme 1.

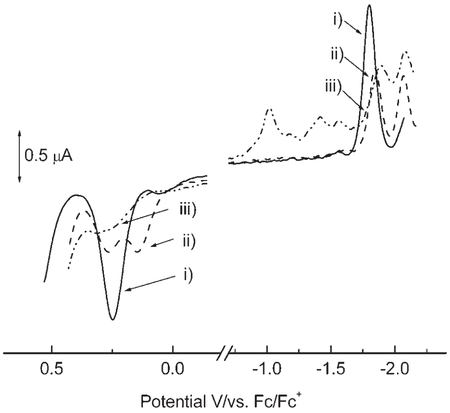

Figure 2. Differential pulse voltammograms (DPV) of i) zinc tetrakis-(benzo-[15]crown-5)porphyrin, ii) zinc tetrakis(benzo-[15]crown-5)porphyrin dimer formed by the addition of potassium ions, and iii) zinc tetrakis(benzo-[15]crown-5)porphyrin dimer -fullerene, $pyC_{60}NH_3^+$ supramolecular complex in benzonitrile, 0.1 M $(n\text{-}C_4H_9)_4NClO_4$. The concentration of porphyrins were ~0.1 mM and the potassium tetrakis(4-chlorophenylborate) used to induce dimerization was ~5 mM. Scan rate = 5 mV s^{-1}, pulse width = 0.25 s, pulse height = 0.025 V.

The free-energy changes for charge separation ($-\Delta G_{CS}$) via K$_4$^{1}[ZnTCP]$_2$* and charge recombination ($-\Delta G_{CR}$) calculated from the electrochemical and emission data of (E_{0-0}=2.0 eV for K$_4$[ZnTCP]$_2$) were found to be about 0.8 eV and about 1.2 eV, respectively, for supramolecules **c** and **d**.[12] The magnitudes of these values suggest charge separation to be near the top region of Marcus parabola curve and charge recombination to be deep in the Marcus inverted region.[6] That is, higher values of k_{CS} and relatively lower values of k_{CR} are expected.[6]

DFT B3LYP/3-21G(*) computational studies: The optimized geometries of the dimer, K$_4$(ZnTCP)$_2$ and the supramolecular donor–acceptor complexes (**c** and **d**) calculated by DFT B3LYP/3-21G$^{(*)}$ method are shown in Figure 3 with the tube and space filling views. In the dimer structure, the two porphyrin rings were stacked with a Zn–Zn distance of 3.9 Å and inter-ring N–N distance of 4.2 Å. The two porphyrin rings lying on top of each other were found to be rotated with respect to one another with N-Zn-Zn-N dihedral angle of 8.9°. These results are in agreement with a blue-shifted Soret peak at 415 nm in Figure 1 (curve ii). The calculated HOMOs and LUMOs for the cation induced dimer were all π-orbitals and were nearly degenerate. As predicted for the closely interacting π-systems, the orbital coefficients were nearly equally localized over both of the porphyrin rings (see Supporting Information). Upon axial coordinating two equivalents of pyC$_{60}$NH$_3^+$ to the dimer, the resulting structure revealed the keeping of both K$_4$[ZnTCP]$_2$ dimer and two newly formed Zn←N bonds (← represents coordinate bond) and two newly formed crown ether−NH$_3^+$ bonds were confirmed as shown in Figure 3b, in which the center-to-center distance r_{C-C} was estimated to be ~10.5 Å and the edge-to-edge distance r_{Ed-Ed} to be ~6.6 Å for **c** and **d**; these distances are close to that reported earlier for ZnTPP←pyC$_{60}$ dyad from X-ray structural studies.[13]

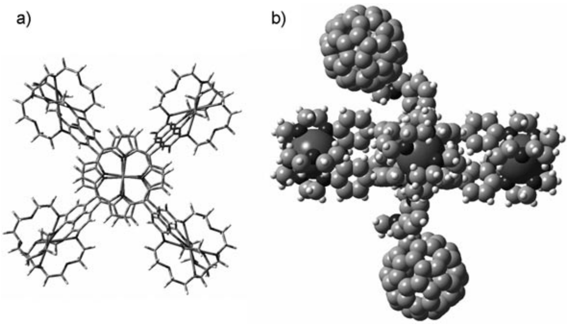

Figure 3. B3LYP/3-21G$^{(*)}$ optimized structure of a) K$_4$[ZnTCP]$_2$ dimer (compound **b** in Scheme 1), and b) bis-pyC$_{60}$NH$_3^+$ complexed K$_4$[ZnTCP]$_2$ dimer (compound **d** in Scheme 1).

The frontier HOMO was found to be on both of the zinc porphyrin macrocycles while the frontier LUMO was on one of the fullerene entity. These results suggest that the photoinduced charge separated state is (K$_4$[ZnTCP]$_2^{\bullet+}$:pyC$_{60}^{\bullet-}$NH$_3^+$) for **c** and (pyC$_{60}$NH$_3^+$:K$_4$[ZnTCP]$_2^{\bullet+}$:pyC$_{60}^{\bullet-}$NH$_3^+$) for **d**.

Steady-state and time-resolved emission studies: Steady-state fluorescence spectrum of ZnTCP showed two emission bands located around 600 and 650 nm similar to that of *meso*-tetraphenylporphyrinatozinc, ZnTPP bearing no crown ether entities. It may also be mentioned here that the addition of size adequate Na$^+$ leading into the formation of Na$_4$[ZnTCP] monomer had no drastic changes in the emission behavior. Interestingly, upon the addition of the size inadequate K$^+$ leading into the formation of the dimer, K$_4$[ZnTCP]$_2$, the fluorescence of zinc porphyrin was quenched over 95 % of its original intensity (static quenching) due to the presence of exciton coupling.[9a,b] Addition of pyC$_{60}$NH$_3^+$ to form supramolecular triad (one equiv) and tetrad (two equiv) caused additional quenching of the already quenched K$_4$[ZnTCP]$_2$ emission. The dimer, K$_4$[ZnTCP]$_2$ formed by the addition of K$^+$ revealed a mono-exponential decay with a lifetime of 1806 ps, which was only slightly shorter than those of ZnTCP and Na$_4$[ZnTCP] with lifetimes of 1970 and 1900 ps, respectively. Unlike the steady-state emission behavior, the lifetime of the dimer was not quenched significantly, suggesting the existence of static quenching in the dimer.[9c] However, efficient quenching of the singlet excited state of zinc porphyrin in the K$_4$[ZnTCP]$_2$ was observed in the supramolecular triad and tetrad formed by the addition of one equivalent and two equivalents of pyC$_{60}$NH$_3^+$ (Figure 4). Both the triad (one equiv) and the tetrad (two equiv) revealed bi-exponential decays with short and long lifetime components; 210 ps (67 %)–2100 ps (33 %) and 170 ps (70 %)– 2200 ps (30 %), respectively. Since the short lifetime component can be predominantly attributed to charge separation in polar benzonitrile,[14] the calculated rate and quantum yield, k_{CS} and Φ_{CS}, under these conditions were found to be 4.3×10^9 s^{-1} and 0.90 and 5.3×10^9 s^{-1} and 0.91 for the triad and tetrad, respectively. The average quantum yield for the fluorescence quenching in the supramolecular tetrad, K$_4$(ZnTCP)$_2$:(pyC$_{60}$NH$_3^+$)$_2$ was found to be 0.61. This value agreed well with the fraction of supramolecular complex (=0.65) evaluated from the binding constant value

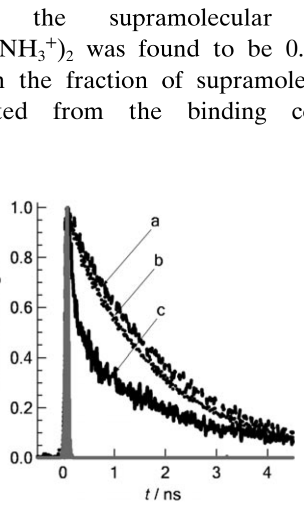

Figure 4. Fluorescence decays of a) ZnTCP (0.1 mM), b) K$_4$[ZnTCP]$_2$ (0.10 mM), and c) K$_4$[ZnTCP]$_2$ (0.10 mM) with PyC$_{60}$NH$_3^+$ (0.11) in benzonitrile, λ_{ex}=410 nm.

($K_{\text{complex}} = 1.03 \times 10^4\,\text{M}^{-2}$ when concentrations of $K_4[ZnTCP]_2$ and $pyC_{60}NH_3^+$ were 7.3×10^{-4} and $1.0 \times 10^{-3}\,\text{M}$, respectively) indicating good agreement between experimentally determined K_{complex} and fluorescence results. A comparison of k_{CS} and Φ_{CS} between the triad and tetrad suggests that the charge separation rate and efficiency for the tetrad are slightly better than those for the triad which could be ascribed to the presence of two acceptor entities for a given donor, dimer entity in the tetrad.

In order to visualize the importance of the cofacial dimer, $K_4[ZnTCP]_2$ as a donor against the monomer ZnTCP, the k_{CS} and Φ_{CS} were measured for a simple dyad formed by self-assembling ZnTCP and $pyC_{60}NH_3^+$ (1:1 ratio) in the studied solvent. The k_{CS} and Φ_{CS} for this dyad were found to be $2.9 \times 10^9\,\text{s}^{-1}$ and 0.85, respectively. In a separate experiment, a dyad was formed using $Na_4[ZnTCP]$ and $pyC_{60}NH_3^+$. The k_{CS} and Φ_{CS} for this dyad were found to be $3.0 \times 10^9\,\text{s}^{-1}$ and 0.86, respectively. These results clearly suggest $K_4[ZnTCP]_2$ dimer being a better electron donor than either of its monomer analogues.

Nanosecond transient absorption spectral investigations: The confirmation of the charge-separated state and evaluation of the charge-recombination rate were performed by the nanosecond transient absorption spectral technique. Upon forming the supramolecular triad, the transient absorption spectrum revealed the characteristic band at 1000 nm of fulleropyrrolidine anion radical, serving as a direct proof of charge separation within the supramolecular triad (Figure 5). The absorption of the radical cation of $K_4(ZnTCP)_2$ dimer, which would be expected to appear in the 600–700 nm region was hidden by the strong triplet state absorptions of the unbound $K_4(ZnTCP)_2$ and $pyC_{60}NH_3^+$ along with the absorption peaks of the supramolecular complex in the 650–900 nm region (see Supporting Information).[15] The time profile of the 1000 nm band showed two-component decay; the initial decay was attributed to $pyC_{60}^{\bullet-}NH_3^+$. The segment of the slow decay part of the 1000 nm band was mainly attributed to the tail of the triplet-state absorption with lifetimes of about 100 µs as revealed in the long time-scale measurements. From the initial fast decay part, the charge-recombination rate (k_{CR}) was evaluated to be $1.0 \times 10^7\,\text{s}^{-1}$ for the triad, which was slightly slower than that for tetrad ($k_{CR} = 2.0 \times 10^7\,\text{s}^{-1}$). For $ZnTCP{:}pyC_{60}NH_3^+$ and $Na_4[ZnTCP]{:}pyC_{60}NH_3^+$ dyads, the k_{CR} values were found to be 1.1×10^7 and $1.0 \times 10^7\,\text{s}^{-1}$, respectively. Although, unlike k_{CS}, no specific trend with respect to k_{CR} could be arrived, the overall k_{CR} values were two orders of magnitude smaller than the k_{CS} values, as predicted from the Marcus theory based on the small reorganization energy and calculated free-energy changes for charge separation and charge-recombination in the presently investigated supramolecular donor–acceptor conjugates.

It may be mentioned here that after the charge recombination, peaks corresponding to the triplet excited state of the fullerene still exist suggesting possibility of electron transfer from the triplet excited state. However, the time-profile of the $C_{60}^{\bullet-}$ in Figure 5b shows fast rise indicating occurrence of electron transfer from the singlet excited state of $K_4[ZnTCP]_2$. Under these conditions, electron transfer from the triplet excited states may be considered to be a minor path.

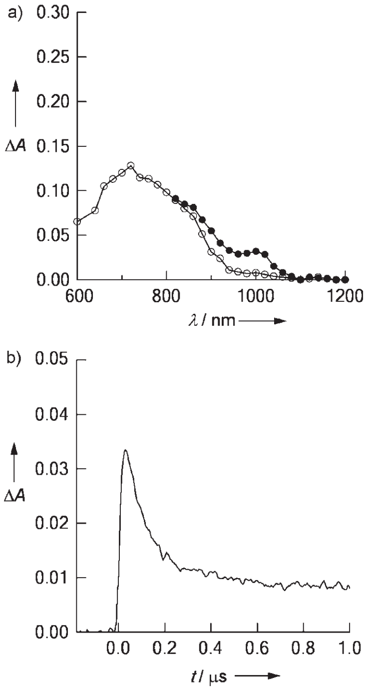

Figure 5. a) Nanosecond transient absorption spectra of $K_4[ZnTCP]_2$ (0.10 mM) with $PyC_{60}NH_3^+$ (0.11 mM) observed by 550 nm laser irradiation at 30 ns (●) and 500 ns (○) time intervals in benzonitrile. b) Time profile monitored at 1000 nm.

Summary

We have assembled exotic supramolecular triad and tetrad as photosynthetic reaction center mimics of "special pair" dimer linked to one or two acceptors. Unlike the previous studies on this area of research, the present supramolecular construction is fully based on well-defined self-assembly methods without utilization of covalent bonding to link the different entities. The structure of these novel supramolecules is deduced from spectroscopic and electrochemical methods. Efficient charge separation from singlet excited zinc porphyrin dimer, $K_4{}^1[ZnTCP]_2^*$ to the complexed fullerene within the supramolecular triad and tetrad was observed and the experimentally measured k_{CR} values suggested these processes to occur in the inverted region of the Marcus parabola curve.

Experimental Section

Chemicals: Fullerene, C_{60} was from SES Research, Houston, TX. The syntheses and characterization of ZnTCP and $PyC_{60}NH_3^+$ are given elsewhere[7c,8b] and were freshly purified over silica gel column prior to the spectral studies. All the chromatographic materials and solvents were procured from Fisher Scientific and were used as received. Tetra-*n*-butylammonium perchlorate, $(n\text{-}C_4H_9)_4NClO_4$ was from Fluka Chemicals. All other chemicals utilized in the synthesis were from Aldrich Chemicals (Milwaukee, WI) and were used as received.

Instrumentation: The UV-visible spectral measurements were carried out with a Shimadzu UV-1650PC spectrophotometer. The fluorescence emission was monitored by using either a Spex Fluorolog-tau or Varian Cary Eclipse spectrometers. Right angle method was utilized. Cyclic voltammograms were recorded on a EG&G Model 263 A potentiostat using a three-electrode system. A platinum or glassy carbon electrode was used as the working electrode. A platinum wire served as the counter electrode and an Ag/AgCl was used as the reference electrode. Ferrocene/ferrocenium redox couple was used as an internal standard. All the solutions were purged prior to electrochemical and spectral measurements using argon gas. The computational calculations were performed using B3LYP/3-21G(*) methods with GAUSSIAN 03 software package[16] on high speed computers.

Time-resolved emission and transient absorption measurements: The picosecond time-resolved fluorescence spectra were measured using an argon-ion pumped Ti/sapphire laser (Tsunami; pulse width = 2 ps) and a streak scope (Hamamatsu Photonics; response time = 10 ps). The details of the experimental setup are described elsewhere.[17] Nanosecond transient absorption spectra in the NIR region were measured by means of laser-flash photolysis; 532 nm light from a Nd/YAG laser (pulse width = 6 ns) was used as the exciting source and a Ge-avalanche-photodiode module was used for detecting the monitoring light from a pulsed Xe lamp for shorter timescale measurements than 5 μs. For longer timescale measurements than 5 μs, the InGaAs photo-diode detector was used to detect the monitoring light from continuous Xe lamp.[17]

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