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High-efficiency Energy Transfer from Carotenoids to a Phthalocyanine in an Artificial Photosynthetic Antenna[¶]

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ABSTRACT

Two carotenoid pigments have been linked as axial ligands to the central silicon atom of a phthalocyanine derivative, forming molecular triad 1. Laser flash studies on the femtosecond and picosecond time scales show that both the carotenoid S_1 and S_2 excited states act as donor states in 1, resulting in highly efficient singlet energy transfer from the carotenoids to the phthalocyanine. Triplet energy transfer in the opposite direction was also observed. In polar solvents efficient electron transfer from a carotenoid to the phthalocyanine excited singlet state yields a charge-separated state that recombines to the ground state of 1.

INTRODUCTION

Carotenoid pigments are ubiquitous in photosynthetic organisms, where the light they absorb drives a significant fraction of the photosynthetic biomass production. In the photosynthetic light harvesting pigment protein complexes examined to date, the carotenoid antenna molecules are found electronically coupled to chlorophylls by relatively short-range interactions that are necessary for efficient singlet energy transfer (1). It is of interest to find ways to use these pigments in artificial photosynthetic assemblies because, in addition to being powerful light absorbers, they can protect systems from oxidative damage and participate in electron transfer processes. In the carotenoid-containing tetrapyrrolebased model systems reported so far, the carotenoid has been covalently linked to the periphery of the tetrapyrrole, where the short-range interactions necessary to promote energy transfer arise from the proximity of the carotenoid π -electron system to π -electrons at the edge of the tetrapyrrole (2–4). Triad 1 was designed to explore singlet energy transfer and photoinduced electron transfer in a system having an alternative molecular geometry in which the carotenoids are almost perpendicular to the plane of the tetrapyrrole and are located at its center.



MATERIALS AND METHODS

Instrumental techniques. ¹H nuclear magnetic resonance (NMR) spectra were recorded on a Unity Inova 500 (Varian, Palo Alto, CA) spectrometer at 500 MHz. The samples were dissolved in deuter-iochloroform with tetramethylsilane as an internal reference. Mass spectra were obtained with a matrix-assisted laser desorption time-of-flight spectrometer (matrix used: sulfur). Ultraviolet–visible absorption spectra were measured on a Cary 500 (Varian Techtron, Australia) UV-VIS-NIR spectrophotometer, and corrected fluorescence excitation and emission spectra were obtained using a Photon Technology International MP-1 (Photon Technology International, Monmouth Junction, NJ) spectrofluorimeter and optically dilute samples (A<0.07). The excitation spectra of silicon 1,4,8,11,15,

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Abbreviations: NMR, nuclear magnetic resonance; THF, tetrahydrofuran.

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18,22,25-octabutoxyphthalocyanine dihydroxide and triad **1** were recorded under identical conditions. The excitation spectrum of silicon 1,4,8,11,15,18,22,25-octabutoxyphthalocyanine dihydroxide, which has some absorption in the carotenoid region (360-530 nm), was used to generate an excitation correction file in the 300-750 nm region by assuming that the absorption and fluorescence excitation spectra were identical.

Fluorescence decays on the picosecond-nanosecond time scale were performed on $\sim 1 \times 10^{-5} M$ solutions by the time-correlated single photon counting method, using an apparatus that has been previously described (5). Fluorescence decays on the femtosecondpicosecond time scale were recorded using the fluorescence upconversion technique and a spectrometer that had been modified to give better time response than previously described (6). Excitation light centered at 489 nm was obtained by frequency-doubling the ca 75 fs near-IR pulses produced by a Tsunami (Spectra-Physics Lasers, Mountain View, CA) 82 MHz mode-locked Ti:sapphire laser pumped by an argon ion laser. Fluorescence decays were recorded at up to 13 wavelengths in the 552-710 nm range using parallel (in the carotenoid S_2 emission region) or magic angle (in the region of the tetrapyrrole emission) polarization. Fluorescence transients were fitted to a sum of two or more exponential decays with a floating background and were convoluted with a Gaussian response function, using the Spectra program.

Transient absorption measurements on the femtosecond–picosecond time scale were made using the pump–probe technique, with systems described previously (7,8). To determine the number of lifetime components in the transient absorption data, singular value decomposition analysis was performed and decay associated spectra derived, as previously described (9). Nanosecond transient absorption measurements were made with excitation from an Opotek (Opotek, Carlsbad, CA) optical parametric oscillator pumped by the third harmonic of a Continuum Surelight (Continuum, Santa Clara, CA) Nd:YAG laser (pulse width ~5 ns, repetition rate 10 Hz). The transient absorbance was measured using a diode detector equipped with 10 nm band-pass interference filters. The detection portion of the spectrometer has been described previously (10).

The solvents used for the spectroscopic work were toluene (>99%), tetrahydrofuran (THF; >99.8%) and pentane (95%) from Merck (Darmstadt, Germany) and EM Science (Gibbstown, NJ) and benzonitrile (99.9%, high-performance liquid chromatography grade) from Aldrich (Milwaukee, WI). The solvents were purified by column chromatography with neutral activated Al_2O_3 (Merck, Type I) or by distillation. THF was refluxed with sodium metal and benzophenone before distillation.

Synthesis. Methyl 8'-apo-β-caroten-8'-oate (3) was prepared according to published procedures and 8'-apo-\beta-caroten-8'-oic acid was prepared by base-catalyzed hydrolysis of 3 (11). The carotenoic acid (182 mg, 0.42 mmol) was dissolved in 4 mL of toluene and 1 mL of pyridine. One drop of thionyl chloride was added to the mixture, which was stirred under argon for 5 min. The solvent was distilled under vacuum, and the acid chloride was kept under high vacuum for ~15 min. A suspension of 16 mg (0.02 mmol) of silicon tetra-tert-butylphthalocyanine dihydroxide (2, Aldrich, mixture of isomers) in 3 mL of 2-picoline was mixed with the carotenoid acid chloride and stirred under argon for 2 h. A portion of 4-dimethylaminopyridine (30 mg) was added to the mixture, which was kept well stirred under argon for an additional period of 36 h at 60°C. The solvent was evaporated under reduced pressure, and the product was purified by column chromatography (silica gel-CH2Cl2) to yield 9.6 mg (19%) of triad 1. Matrix-assisted laser desorption-ionization time-of-flight mass spectrometry; m/z: 1628 (M)+; the NMR spectrum is consistent with the expected structure.

RESULTS

Conformation of triad 1 by NMR

Silicon phthalocyanines are known to induce large shielding effects on the NMR chemical shifts of their axial ligands on account of the ring-current of the macrocycle π -electrons. The isoshielding lines for this effect have been previously calculated (12,13). In this work, a map of the isoshielding



Figure 1. Absorption spectra of triad 1 (—), phthalocyanine 2 (---) and carotenoid 3 (---) in toluene solution and fluorescence emission spectrum of triad 1 (----) with excitation at 610 nm in the same solvent. The spectra of 1 and 2 are normalized at the Q_y absorption band of the phthalocyanine (between 675 and 695 nm). The spectrum of 3 is presented to illustrate peak positions and band-shape; the optical density ordinate is arbitrary.

lines, in conjunction with molecular modeling (AM1, Gaussian 98) and crystal structure data for silicon carboxylatophthalocyanines (14,15) was used to estimate the theoretical changes in chemical shift ($\Delta\delta$) in the ¹H resonances expected for carotenoid protons for different conformations. The differences between the observed ¹H chemical shifts in **1** and the corresponding ¹H resonances in model carotenoid **3** were used to derive the experimental $\Delta\delta$ values. An extended (all*trans* configuration and *s*-*trans* conformation) carotenoid structure positioned above or below the phthalocyanine ring gave the best agreement between the experimental and the theoretical $\Delta\delta$ for the five hydrogen atoms of the carotenoid moiety proximal to the silicon atom (two methyl group hydrogens and three hydrogens on the conjugated chain).

Absorption and fluorescence excitation spectra

The absorption spectrum of model phthalocyanine 2 in toluene, with λ_{max} at 679, 649, 610 and 359 nm, is shown as the dashed line in Fig. 1. This spectrum is typical of a metal phthalocyanine, and only weak absorption is observed in the region where the solar irradiation is highest (between 450 and 550 nm). In triad 1 (solid line, Fig. 1), the addition of the two carotenoid pigments results in a large increase in absorption in the center of the spectrum and a substantial redshift in all the phthalocyanine bands (λ_{max} at 693, 662, 622, 478, 452 and 366 nm). In contrast, the absorption maxima of the carotenoid moiety of 1 are slightly blueshifted compared with model 3 in toluene (λ_{max} at ~482 nm [shoulder] and 456 nm). The fluorescence emission spectrum of the phthalocyanine moiety of 1 (dotted line, Fig. 1) has a maximum at 704 nm. Figure 2 shows the absorption spectrum and the corrected excitation spectrum for the phthalocyanine fluorescence of 1 with emission monitored at 790 nm. The excitation spectrum was normalized to the absorption spectrum at the red-most bands. This spectrum clearly indicates efficient singlet-singlet energy transfer from carotenoid to phthalocyanine.



Figure 2. The absorption spectrum of triad 1 (—) and the corrected fluorescence excitation spectrum (- - -) of an $\sim 1 \times 10^{-7} M$ solution of 1 in toluene. The excitation spectrum has been normalized to the absorption spectrum at the phthalocyanine Q_y band (693 nm). The fluorescence excitation spectrum was corrected in the range of 300–750 nm using a file generated from the absorption and fluorescence excitation spectra of silicon 1,4,8,11,15,18,22,25-octabutoxyphthalocyanine dihydroxide. The apparent energy transfer efficiency in excess of 100% in the region of the shoulder at ~480 nm is likely caused by errors in the correction process.

Carotenoid singlet state dynamics

Using the fluorescence upconversion technique, the lifetime of the strongly allowed second excited singlet state (S₂, $1^{1}B_{u}^{+}$) of the carotenoid, which gives rise to the absorption maximum at ~450 nm, was measured. The S₂ lifetime of model carotenoid **3** in toluene was determined to be 82 ± 3 fs (average of 20 measurements). The emission decay curve at 577 nm is shown in Fig. 3, along with the instrument response function. The average lifetime of the S₂ state of the carotenoid moieties of triad **1** in toluene was found to be 53 ± 3 fs. The lifetime of the lowest excited singlet state (S₁, $2^{1}A_{g}^{-}$) of carotenoid **3** was determined in toluene by pump (489 nm)–probe (555 nm) techniques and found to be 24.4 ± 0.6 ps. The major component of the corresponding lifetime for triad **1** was only 2.6 ± 0.2 ps.

Phthalocyanine singlet state dynamics

To determine the formation kinetics of the S₁ excited state of the phthalocyanine moiety of triad 1 after excitation of the carotenoids at 489 nm, fluorescence upconversion measurements were made at wavelengths longer than 674 nm in two solvents, toluene and THF. As shown in Fig. 4, the rise time of the phthalocyanine fluorescence in toluene at 693 nm is clearly composed of two components, 500 \pm 50 fs and 2.3 \pm 0.2 ps, and the emission does not decay over the 20 ps time scale recorded. In the more polar solvent, THF, the fluorescence is strongly quenched; it decays with a time constant of 6.2 ps. Using the time-correlated single photon counting method, the fluorescence lifetime of 1 was found to be 2.84 ns ($\chi^2 = 1.18$) in toluene, 0.011 ns ($\chi^2 = 1.08$) in THF, 0.004 ns ($\chi^2 = 1.13$) in benzonitrile and 5.43 ns (χ^2 = 1.14) in pentane, whereas the fluorescence lifetime of 2was 5.40 ns ($\chi^2 = 1.01$) in benzonitrile, 5.65 ns ($\chi^2 = 1.19$) in toluene and 6.11 ns ($\chi^2 = 1.10$) in THF (components having amplitudes less than 7% omitted).



Figure 3. Normalized fluorescence decay kinetics at 578 nm of an $\sim 1 \times 10^{-4} M$ solution of triad $\mathbf{1}$ (\bigcirc) and carotenoid $\mathbf{3}$ (\bigtriangledown) in toluene after excitation with parallel polarization at 489 nm. The lines are fits with decay time constants of 55 fs (98% amplitude) and 81 fs (97%), the carotenoid S₂ lifetimes of $\mathbf{1}$ and $\mathbf{3}$, respectively. A 128 fs Gaussian response function is also shown (—).

Triplet state dynamics in triad 1

Figure 5 presents the transient absorption spectrum of phthalocyanine 2 (dashed line) in its lowest excited triplet state in argon-saturated toluene solution measured 400 ns after excitation by a laser flash at 620 nm. The transient spectrum decayed uniformly with a time constant of $150 \pm 15 \,\mu\text{s}$ and could be quenched by oxygen. The transient spectrum of triad 1 taken after excitation by a laser flash at 680 nm is shown by the solid line in Fig. 5. It decayed with a time constant of $4.7 \pm 0.5 \,\mu\text{s}$ and could also be quenched by oxygen.

Charge transfer state dynamics in triad 1

The decay-associated absorption spectrum of triad **1** dissolved in THF and excited at 680 nm is shown in Fig. 6. The prominent absorption in the near-IR (\sim 860 nm) is characteristic of a carotenoid radical cation species having 10 conjugated double bonds (including the carbonyl group). In spectral regions where the transient absorption is positive, decaying species are indicated by positive amplitudes and



Figure 4. Isotropic formation kinetics of the excited S₁ state of the phthalocyanine moiety of triad **1** detected by upconversion of the phthalocyanine fluorescence at 693 nm, after carotenoid excitation at 488 nm with magic angle polarization of an $\sim 1 \times 10^{-4} M$ solution of triad **1** in toluene (\bigcirc) and in THF (\triangledown). The lines are fits with time constants of 500 fs (0.22) and 2.3 ps (0.78) for the rise of the signal in toluene (the values in parentheses indicate relative amplitudes). The decay of the signal in THF was fitted with a 6.2 ps time constant.



Figure 5. Transient absorption spectrum of an $\sim 10^{-3} M$ solution of triad 1 (—) in toluene 4.3 ns after excitation at 680 nm with a laser pulse of ~ 100 fs. Transient absorption spectrum of an argon-saturated $\sim 10^{-5} M$ solution of phthalocyanine 2 (- - -) in toluene 400 ns after excitation at 620 nm with a laser pulse of ~ 5 ns.

rising species by negative amplitudes. This situation is reversed in spectral regions where the transient absorption is negative, e.g. decaying species are indicated by negative amplitudes and rising species (increases in negative absorption) are indicated by positive amplitudes. The transient absorption intensity is large and positive in the near-IR and it is seen to rise and decay with time constants of 6.2 \pm 0.6 and 25 ± 3 ps, respectively. Similarly, the positive transient absorption in the spectral region from 525 to 640 nm rises and decays with the same pair of time constants. At 490 nm the situation is reversed—a bleaching signal grows with a 6.2 ps time constant and recovers in 25 ps. The negative amplitude at 680 nm has the same time constant, 25 ps, and is likewise associated with the recovery of a bleaching signal. Transient spectra of similar shapes were observed when triad 1 was dissolved in toluene. The amplitudes were much smaller, and the time constants for the decay-associated spectra were 2.6 \pm 0.3 ns and 20 \pm 2 ps. In pentane, the fluorescence lifetime of triad 1 was 5.43 ns, and there was no evidence of transient absorption in the near-IR.

DISCUSSION

Conformation and absorption spectra

The fits of observed shifts in the carotenoid ¹H NMR of **1** to the calculated values indicate that the carotenoids are disposed axially from the phthalocyanine with average conformations in which the angle between the carotenoid long axis and the phthalocyanine plane is $\sim 77^{\circ}$. As presented in Fig. 1, the absorption spectrum of triad **1** clearly displays the contributions of the two carotenoids to the spectrum of the phthalocyanine. The spectrum of **1** is not a simple superposition of the model phthalocyanine **2** and carotenoid **3** spectral components. The red-most band at 679 nm in **2** is shifted to 693 nm in triad **1**, and the carotenoid band at 456 nm in model carotenoid **3** is shifted to 452 nm in triad **1**. It is clear from Fig. 1 that a small degree of interchromophore interaction occurs in **1**.



Figure 6. Decay-associated spectra of the transient absorption obtained with an $\sim 10^{-3}$ *M* solution of triad **1** in THF after an ~ 100 fs laser pulse at 680 nm: a 6.2 ps component(—), a 25 ps component (---) and a nondecaying component (···).

Singlet energy transfer

As shown in Fig. 2, essentially complete (>95%) energy transfer from the carotenoid to the phthalocyanine of 1 is indicated by the match between the corrected excitation spectrum for phthalocyanine fluorescence and the absorption spectrum. In order to determine in detail which carotenoid excited states are involved in the flow of energy to the phthalocyanine, the lifetimes of the carotenoid S₂ and S₁ excited states were measured in model carotenoid 3 and in triad 1. Figure 3 shows that the S_2 level of the carotenoid is quenched from 82 fs in 3 to 53 fs in 1. This quenching is attributed to energy transfer and may be used to calculate an efficiency of 35%, which is substantially less than >95% measured by steady state fluorescence excitation. Thus, the contribution of a second path to the flow of energy is suspected and, indeed, indicated by the results of pump-probe measurements of the S1 state lifetime of the carotenoid in triad 1 and model 3 and by the rise time of phthalocyanine fluorescence presented in Fig. 4.

Focusing on the phthalocyanine data in toluene, two components are found, with time constants of 500 fs and 2.3 ps. The 500 fs component is assigned to energy arriving from the S_2 level of the carotenoid. The delay (53 fs vs 500 fs) must be associated with relaxation to the phthalocyanine S_1 state before fluorescence. It is reasonable to assume that internal conversion in the carotenoid from S_2 state to S_1 state is the dominant process competing with energy transfer from S_2 , and a yield of 65% may be assigned to this process. The 2.3 ps component in the rise time of phthalocyanine fluorescence in 1 matches well the S_1 state carotenoid lifetime measured by pump-probe (2.6 ps), and it is assigned to energy transfer from the carotenoid S_1 level. Quenching of the carotenoid S_1 level from 24.4 ps in 3 to 2.6 ps in 1 gives an energy transfer efficiency of 89%. Taking into account that the quantum yield from the S_1 state is only 65%, the quantum yield of energy transfer from S1, based on light absorbed to populate S_2 , is calculated to be 58%. Therefore, the overall quantum yield of energy transfer from carotenoid to phthalocyanine from both S_2 (35%) and S_1 (58%) pathways is \sim 93%, in excellent agreement with the value estimated from steady state fluorescence excitation measurements. Energy flow to the phthalocyanine from both the carotenoid S_2 and S_1 excited states in **1** models very well the same phenomenon found in natural systems (8,16–18).

The observation that both the strongly electric dipole allowed S_2 state and the extremely electric dipole forbidden S₁ state make major contributions, albeit on different time scales, to the singlet energy transfer in 1 has mechanistic implications. To the extent that the carotenoids are perpendicular to the plane of the phthalocyanine, and located at its center, coupling of donor S₂ state and acceptor state transition dipole moments in the Förster sense would be small because of the orientation factor. Moreover, the carotenoid S₁ state transition dipole moment is exceedingly small. Recent theoretical treatment of the electronic coupling considers point dipoles generated by the electronic transition located on each atom of the two chromophores. The interactions between the point dipoles are then summed over the volume of the donor and acceptor to give a coulombic coupling term (17,19). It will be interesting to apply this technique to 1 and to carry out a similar calculation on a carotenophthalocyanine in which the carotenoid is linked to the periphery of the macrocycle and extends away from it.

Theoretical predictions and experimental results have located a carotenoid excited singlet state above S_1 and near S_2 as defined herein. Under the conditions of our experiments (temporal resolution, wavelength range, *etc.*), there is no evidence that this state plays a role in the singlet energy transfer in **1** (20,21).

Triplet energy transfer

The dashed line in Fig. 5 displays the transient absorption spectrum of phthalocyanine 2 in argon saturated toluene solution taken 400 ns after the laser flash at 620 nm. The longlived signal is assigned to the phthalocyanine triplet species on the basis of positive absorption in the 450 to 600 nm region, ground state bleaching and oxygen-dependent decay dynamics. Evidence for fast triplet-triplet energy transfer in triad **1** is shown by the transient spectrum taken 4.3 ns after flash excitation at 680 nm. The ground state bleach in the spectral region \sim 420 to 470 nm and positive ΔA in the 475 to 600 nm region are characteristic of the carotenoid triplet species. The lifetime of 4.7 µs confirms the assignment of this transient to the carotenoid triplet species. Because excitation at 680 nm does not populate carotenoid singlet states, and in any case intersystem crossing in carotenoids is very inefficient, the high yield of triplet carotenoid must be because of intramolecular triplet energy transfer from the phthalocyanine triplet. The carotenoid triplet rise time (data not shown) is the same as the fluorescence lifetime of 1 in toluene, which means that the rate constant for triplet-triplet energy transfer is much larger than that for intersystem crossing in the phthalocyanine moiety of 1. Presumably, triplet-triplet energy transfer is mediated by Dexter electron exchange terms that require orbital overlap between the carotenoid and phthalocyanine moieties to be effective. Therefore, the bridging Si atom must be effective in providing this orbital interaction.

Note that at 4.3 ns after an excitation flash of ~ 100 fs (Fig. 5) the transient absorption shows a strong bleach in the region of the phthalocyanine Q_v band. In spectra taken at

earlier times (not shown) when the population of phthalocyanine singlet species is greater, the Q_y bleach signal is larger; it is composed mostly of depleted ground state population and stimulated emission. On a time scale of 100 ns to several microseconds, long after all the excited and ionic species have decayed except the carotenoid triplet, a similar but smaller Q_y bleach is observed. This apparent decrease in the absorption coefficient of the phthalocyanine Q_y band is associated with a perturbation caused by the attached triplet carotenoid. Such spectral behavior has been observed in natural antenna systems and in other model systems and is further evidence that the chromophores are tightly coupled; *e.g.* there is sufficient electronic coupling to mediate energy transfer on the femtosecond time scale (22–24).

Electron transfer

As shown in Fig. 4, the excited singlet state of the phthalocyanine moiety of 1 in toluene does not decay on the picosecond time scale but is quenched to 6.2 ps in THF. This behavior is characteristic of electron donor-acceptor dyads in which a charge transfer state is close in energy to the local excited singlet state. Therefore, in nonpolar solvents the charge transfer state is slightly higher than the local excited singlet and not accessible, whereas in polar solvents it is lower and populated by electron transfer quenching of the local excited singlet level. In order to verify relaxation of the phthalocyanine S_1 level to a charge transfer state, spectra were taken in the region where the radical ions absorb. In the decay-associated spectra of 1 in THF (Fig. 6), the rise and decay of a strong signal in the near-IR is evident. Concomitantly, the carotenoid ground state bleach at 490 nm rises and decays. The signal at 860 nm is assigned to the formation and decay of the carotenoid radical cation moiety of 1; it forms with a time constant of 6.2 ps and decays in 25 ps. Also present in the decay-associated spectra are rise and decay components characteristic of the sum of the phthalocyanine S_1 state (decaying), the radical anion species (rising and decaying) and the recovery of the ground state. The match of the rise of the carotenoid radical cation spectrum with the decay of the phthalocyanine S_1 level (6.2 ps) establishes electron transfer from the carotenoid to the phthalocyanine S₁ state as a fluorescence quenching mechanism. The charge transfer state forms with a quantum yield near unity, living for 25 ps and decaying to the ground state of triad 1.

Spectra with similar shapes having reduced amplitude were observed in toluene and were fitted to two characteristic time constants, 2.6 ns and 20 ps. On the basis of the 2.8 ns fluorescence lifetime of the phthalocyanine moiety of **1** in toluene, it is tempting to assign the 2.6 ns component in the decay-associated spectra to a pathway for formation of the charge separated state; the 20 ps component would then be the lifetime of that state. However, a 20 ps decay time taken with a 2.6 ns formation time should reduce the amplitude of the transient spectra in toluene by ~150-fold compared with THF. The observed amplitude is reduced by ~20-fold. Thus, the assignment of electron transfer dynamics in toluene awaits further experiments. On the basis of the 2.6 ns formation time, the quantum yield of this pathway is ~50%. Triad **1** dissolved in pentane had a 5.4 ns fluorescence lifetime, and no charge-separated species were observed.

CONCLUSION

Triad **1** exemplifies a compact molecular architecture in which two carotenoid pigments are coupled to a single tetrapyrrole as axial ligands to a centrally coordinated Si atom. This construct demonstrates highly efficient singlet energy transfer from the carotenoids to the tetrapyrrole and fast triplet energy transfer in the reverse direction. In polar solvents, photoinduced electron transfer from one of the attached carotenoids to the S₁ level of the phthalocyanine is efficient and yields a relatively long-lived charge-separated state. It is anticipated that this new class of artificial photosynthetic structures will form the basis of antenna systems and charge relays for artificial reaction centers.

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