

A SYNTHETIC SYSTEM MIMICKING THE ENERGY TRANSFER AND CHARGE SEPARATION OF NATURAL PHOTOSYNTHESIS*

DEVENS GUST and THOMAS A. MOORE

Department of Chemistry, Arizona State University, Tempe, AZ 85287 (U.S.A.)

Summary

A synthetic molecular triad consisting of a porphyrin P linked to both a quinone Q and a carotenoid polyene C has been prepared as a mimic of natural photosynthesis for solar energy conversion purposes. Laser flash excitation of the porphyrin moiety yields a charge-separated state $C^{+}-P-Q^{-}$ within 100 ps with a quantum yield of more than 0.25. This charge-separated state has a lifetime on the microsecond time scale in suitable solvents. The triad also models photosynthetic antenna function and photo-protection from singlet oxygen damage. The successful biomimicry of photosynthetic charge separation is in part the result of multistep electron transfers which rapidly separate the charges and leave the system at high potential, but with a considerable barrier to recombination.

1. Introduction

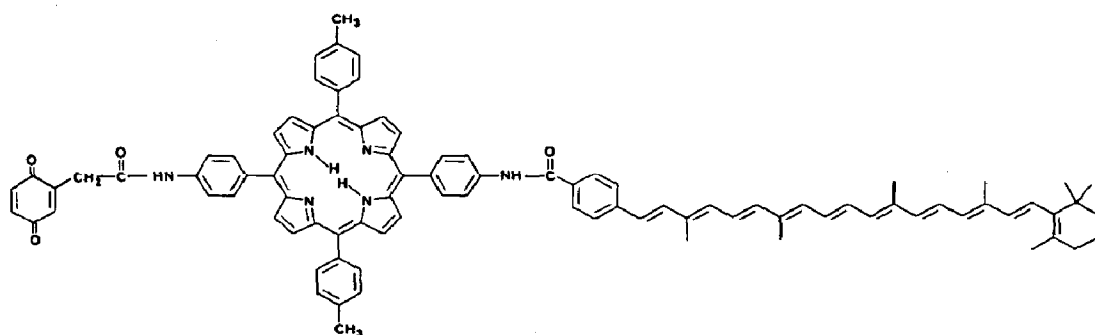
The efficiency, durability and adaptability of natural photosynthesis make it an attractive target for mimicry by those investigating artificial methods for the conversion of sunlight into chemical potential energy. Any attempt at the design of an artificial photosynthetic system requires, of course, some understanding of the details of the natural process. In general terms, the central event in a photosynthetic reaction center is the light-driven transfer of an electron from a donor to an acceptor. This step converts light to chemical energy and thus increases the chemical potential of the system. Subsequent electron transfer steps separate the electron and the hole so that the lifetime before charge recombination is sufficiently long to permit oxidation and reduction reactions by additional species which regenerate the photocatalytic center. These secondary redox reactions mark the beginning of a cascade of dark reactions which ultimately lead, in green plants, to the oxidation of water and the reduction of carbon dioxide. Preceding the photodriven *electron* transfer are *energy* transfer processes in

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which excitation is channeled from various antenna molecules to the reaction center. In addition, the reaction center includes protective elements to prevent photochemical degradation of its sensitive components. The incorporation of all three of these processes (photodriven charge separation, antenna function and photoprotection) into an artificial photosynthetic system is clearly desirable, and this has been the goal of our research.

Although the details of the photosynthetic apparatus of most organisms are not as yet fully understood, it is known that the primary excited species and electron donor is chlorophyll in some form. Quinones play a role as electron acceptors. Carotenoid polyenes are present in all natural photosynthetic assemblies and serve several functions. They act as antennae which absorb light in regions of the solar spectrum where chlorophyll is not effective and transfer singlet excitation energy to chlorophyll. In addition, they play a photoprotective role. Chlorophyll triplets react with oxygen to generate singlet oxygen, which is an extremely reactive and therefore harmful substance. Carotenoid polyenes prevent damage from singlet oxygen by quenching chlorophyll triplet states prior to their interaction with oxygen. This triplet energy transfer process generates the carotenoid triplet (a harmless species) and ground state chlorophyll. Carotenoids may also photoprotect by quenching singlet oxygen itself. Finally, it is known that carotenoid polyenes may act as electron donors in photosynthetic systems under some conditions, although the importance of such donor behavior with regard to the main electron flow is unknown.

It is clear from the above discussion that an artificial biomimetic photosynthetic system demonstrating photodriven charge separation, antenna function and photoprotection requires at least a chlorophyll derivative, a quinone and a carotenoid. As will be shown below, our work demonstrates that it is possible to build a functioning model system utilizing *only* these three components. Our model consists [1] of molecular triad I

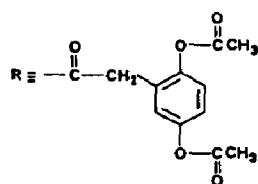
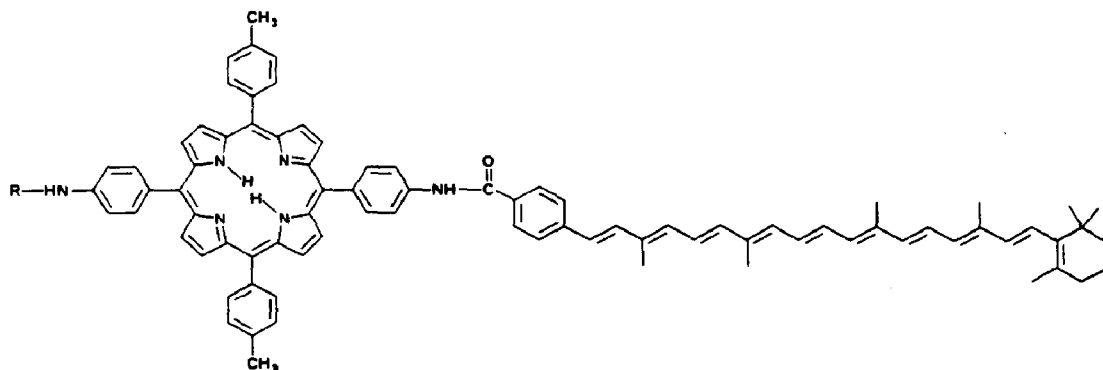


I

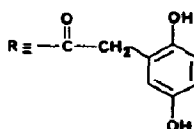
whose center is a synthetic porphyrin. The porphyrin serves as a model for the chlorophylls of natural photosynthesis. Covalently attached to the porphyrin are a quinone electron acceptor and a synthetic carotenoid polyene. The synthesis, structure and photophysics of this molecule are discussed below.

2. Synthesis and structure

The synthesis of I involved the preparation of the carotenoid, quinone and porphyrin precursors and their linkage via amide bonds. The 7'-apo-7'-(4-carboxyphenyl)- β -carotene was made using the Wittig reaction of the ylide of 4-carbomethoxybenzyltriphenylphosphonium bromide with β -apo-8'-carotenal, followed by saponification of the methyl ester. The 5,15-bis(4-aminophenyl)-10,20-bis(4-methylphenyl)porphyrin was prepared by reduction of the corresponding dinitro porphyrin, and the amide linkage between this material and the carotenoid was effected with dicyclohexylcarbodiimide and 4-dimethylaminopyridine. The linkage of the resulting carotenoporphyrin to 2,5-diacetoxyphenylacetic acid using the same reagents yielded II, in which the hydroquinone is protected as the diacetate. Treatment with potassium borohydride in methanol-methylene chloride yielded hydroquinone III, which could be oxidized to I using 2,3-dichloro-5,6-dicyano-1,4-benzoquinone or a variety of other reagents:



II



III

The 500 MHz ^1H nuclear magnetic resonance (NMR) spectra of I, II and III support the assigned structures. Figure 1, for example, shows the spectrum of I in deuteriochloroform (CDCl_3). Resonances for all protons could be assigned using decoupling data and spectra of model compounds. The NMR spectra also yielded conformational information. The porphyrin moiety in an external magnetic field gives rise to large aromatic ring currents, and these currents in turn can cause large changes in the chemical shifts of protons near the porphyrin ring [2]. For example, a proton situated above the plane of the porphyrin and over the center of the macrocycle will experience a large upfield chemical shift change, whereas a proton in the

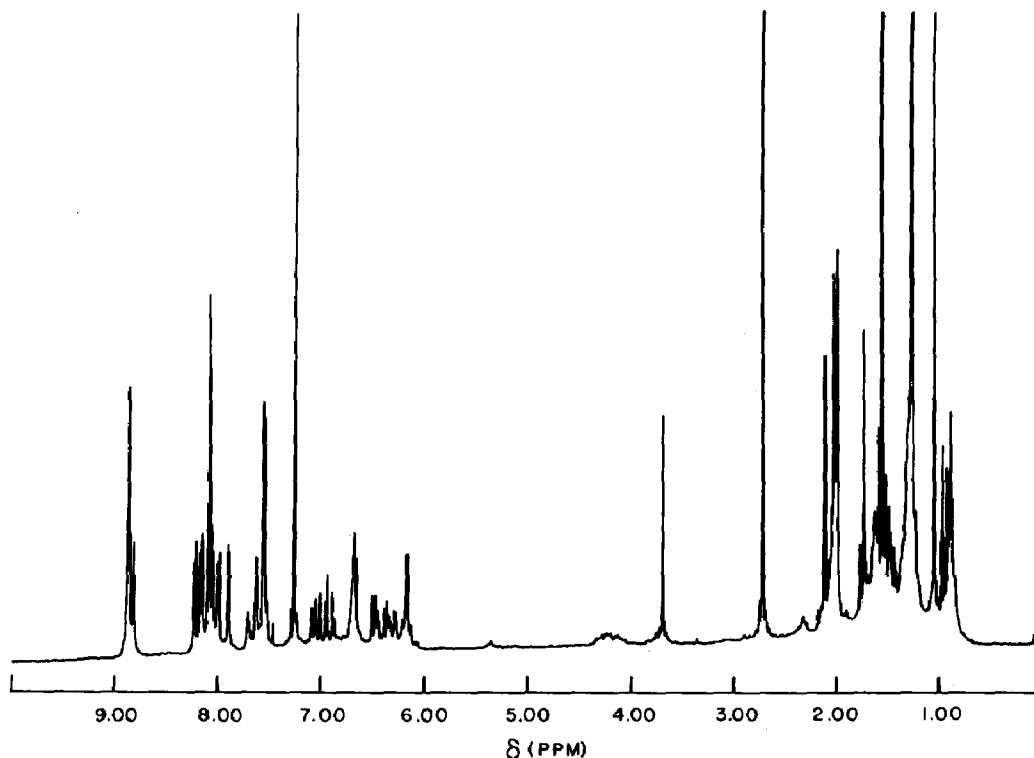


Fig. 1. The 500 MHz ¹H NMR spectrum of triad I in CDCl₃. Chemical shifts δ are in parts per million down field from tetramethylsilane. The porphyrin NH protons at about -2.8 ppm are not shown. Spectra were obtained on a Bruker WM-500 spectrometer.

plane of the porphyrin will experience a downfield shift. Quantitative calculations of these effects [1, 2] yield extended conformations for I - III, such as that shown in Fig. 2. The carotenoid and quinone moieties lie near the plane of the porphyrin ring and are extended away from the macrocycle, rather than folded over it. Thus, these two moieties are well separated in space. As will be shown below, independent conformational information of this type is indispensable for relating structural features to energy or electron transfer function. This is especially true in molecules in which the chromophores of interest are connected by linkages which can, in principle, assume any of a variety of conformations.

3. Photophysical properties

3.1. Charge separation

The absorption spectrum of I in methylene chloride solution is basically a superposition of the spectra of the component chromophores and includes the porphyrin Soret and Q bands, a carotenoid absorption centered at about 470 nm and a weak quinone band in the 240 nm region. Excitation of a

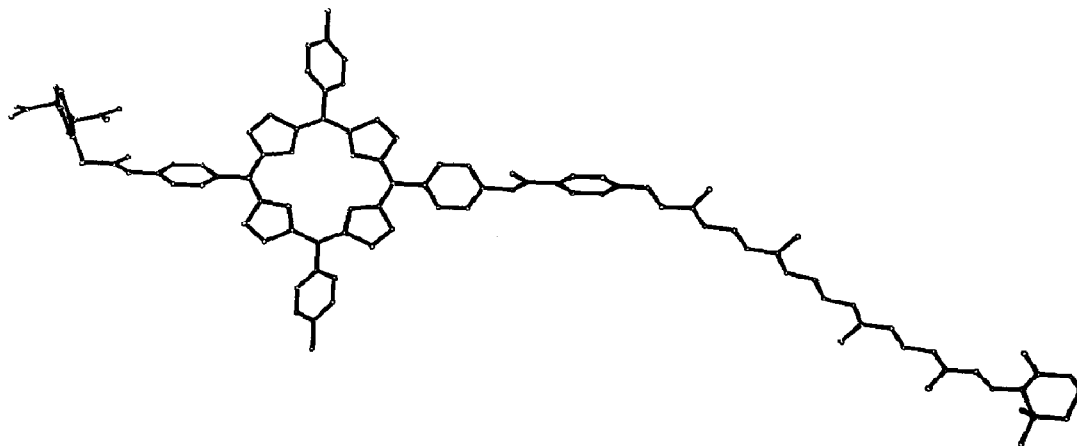
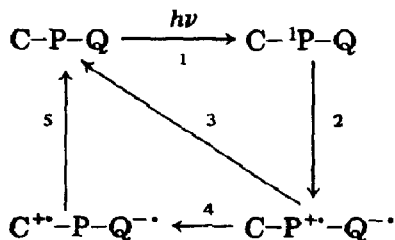


Fig. 2. Time-averaged solution conformation of triad II as calculated from the chemical shift changes induced by the porphyrin aromatic ring current. The hydrogen atoms are not shown. The conformation is an extended one with the protected hydroquinone moiety to the left and the carotenoid to the right. Only one of the possible conformations about the $\text{CH}_2\text{-CO}$ bond is shown, but others are also populated [1].

methylene chloride solution of I with a 10 ns flash of 600 nm laser light yields the transient absorption spectrum shown in Fig. 3. This spectrum, with $\lambda_{\text{max}} \approx 970$ nm, is highly characteristic of the carotenoid radical cation. This is also demonstrated by Fig. 3, which shows cation spectra for II and a model carotenoid obtained from pulse radiolysis experiments. Similar laser flash spectroscopic studies of II and III (in which the quinone is replaced by hydroquinone) yielded no carotenoid radical cations. Thus, it is clear that in the laser flash experiment the carotenoid is acting as an electron donor, but only in the presence of the quinone. In addition, the excitation wavelength ensures that the initial excitation must reside in the porphyrin singlet state. We propose the following scheme to explain these results (C \equiv carotenoid; P \equiv porphyrin; Q \equiv quinone):



Step 1 is simply the excitation of the porphyrin to its first excited singlet state. As has been observed in other covalently linked porphyrin-quinone systems the porphyrin singlet readily donates an electron to the quinone to yield $\text{C-P}^{++}\text{-Q}^{--}$ (step 2). This state can collapse back to the

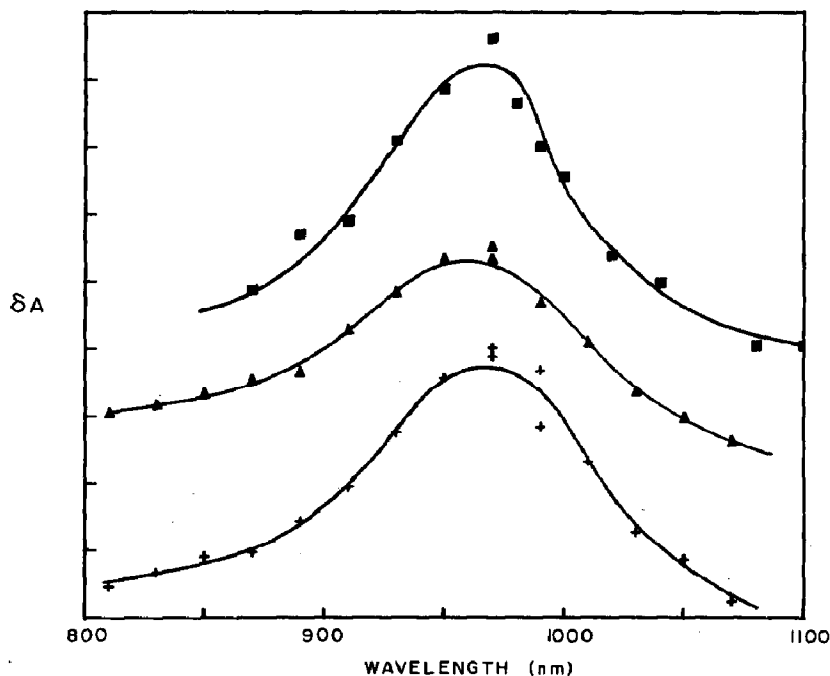


Fig. 3. Transient absorption spectra of carotenoid cation radicals in the region 800 - 1100 nm (solutions in methylene chloride were 10^5 M): ■, spectrum following 10 ns, 600 nm laser flash excitation of triad I; ▲, spectrum 2 μ s after pulse radiolysis of argon-flushed II; +, spectrum 4 μ s after pulse radiolysis of the aniline amide of 7'-apo-7'-(4-carboxyphenyl)- β -carotene. (The ΔA scales for the three spectra are different, and the baselines have been offset for clarity.)

ground state with the evolution of heat (step 3). Rapid charge recombination of this type is, of course, undesirable from the point of view of solar energy conversion because it precludes the harvesting of solar energy as chemical potential energy. In I, however, the transfer of an electron from the carotenoid moiety to the porphyrin (step 4) competes with the back reaction (step 3) to generate a new charge-separated state $C^{+}-P-Q^{-}$. This new state gives rise to the carotenoid radical cation absorption observed following flash excitation. Ultimately this new state will also return to the ground state (step 5) in the absence of competing reactions.

The photodriven charge separation in I thus mimics the photosynthetic system where an excited tetrapyrrole reduces an acceptor and is in turn reduced by a donor species. However, the success of this system as a photosynthesis model will depend on the rates of processes 2 - 5, the quantum yield of charge separation and the amount of energy conserved in the final $C^{+}-P-Q^{-}$ state. Each of these questions will be considered in turn.

The initial photochemical steps following excitation of I are very fast and must be studied on the picosecond time scale. Figure 4 shows the transient absorption kinetics for I in methylene chloride saturated with tetra-*n*-butylammonium tetrafluoroborate salt, following excitation with a 27 ps

pulse of 532 nm light. An absorption at 600 nm appears with the response time of the instrument and decays within about 100 ps. This signal represents the formation of the porphyrin singlet state (step 1), its conversion to $C-P^{+}-Q^{-}$, which also absorbs in this spectral region [3, 4] (step 2), and the decay of the $C-P^{+}-Q^{-}$ state (steps 3 and 4). Concurrent with the decay of the 600 nm absorption is the rise of the carotenoid cation absorption at 950 nm (step 4). The growth is complete within 100 ps, and decay of the $C^{+}-P-Q^{-}$ state is not observable on the picosecond time scale. On the nanosecond time scale, the decay of the carotenoid cation can be easily measured (Fig. 5). In methylene chloride the half-life is 170 ns, whereas addition of tetra-*n*-butylammonium tetrafluoroborate increases this value to about 2.5 μ s. The lifetime is about 3 μ s in acetonitrile.

The quantum yield of the $C^{+}-P-Q^{-}$ state may be estimated if the appropriate extinction coefficients are estimated from those for related compounds [1]. In methylene chloride alone the quantum yield of carotenoid cation radical is about 0.04, and addition of the salt raises this value to more than 0.25.

The energetics of the system are also of importance because charge separation alone is of little value if little energy is conserved. On the basis of the electrochemically determined oxidation and reduction potentials for unlinked carotenoid [5 - 7] and quinone [8] precursors, it is estimated that the $C^{+}-P-Q^{-}$ state lies more than 1.1 V above the ground state. The

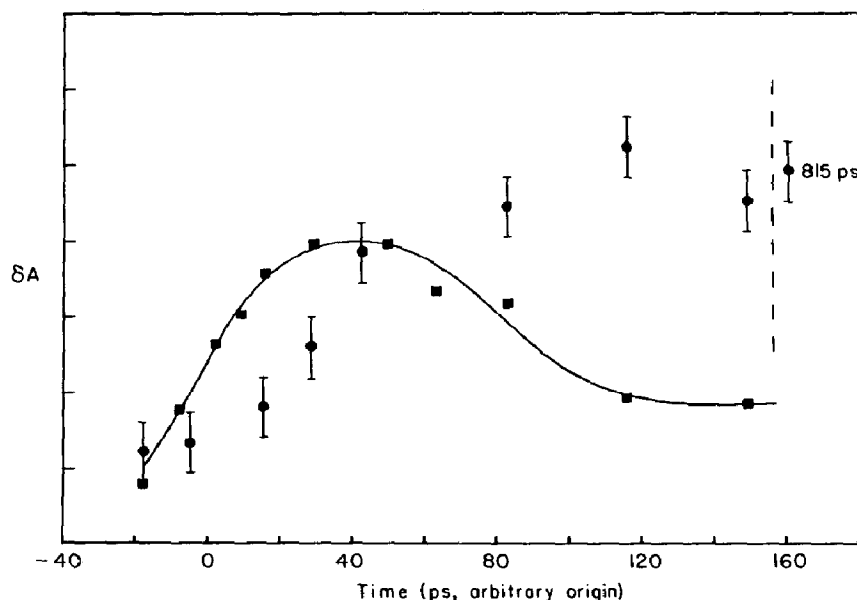


Fig. 4. Transient absorption kinetics for 10^{-4} M I in methylene chloride saturated with tetra-*n*-butylammonium tetrafluoroborate following a 27 ps pulse of 532 nm light. The probe light was the picosecond continuum and was analyzed after the sample cell (1 mm) using Pomfret interference filters (bandwidth, 3 nm) centered at 600 nm (■) and 950 nm (●) ($\delta A = 0.10$ per division). Each point is an average of four laser flashes.

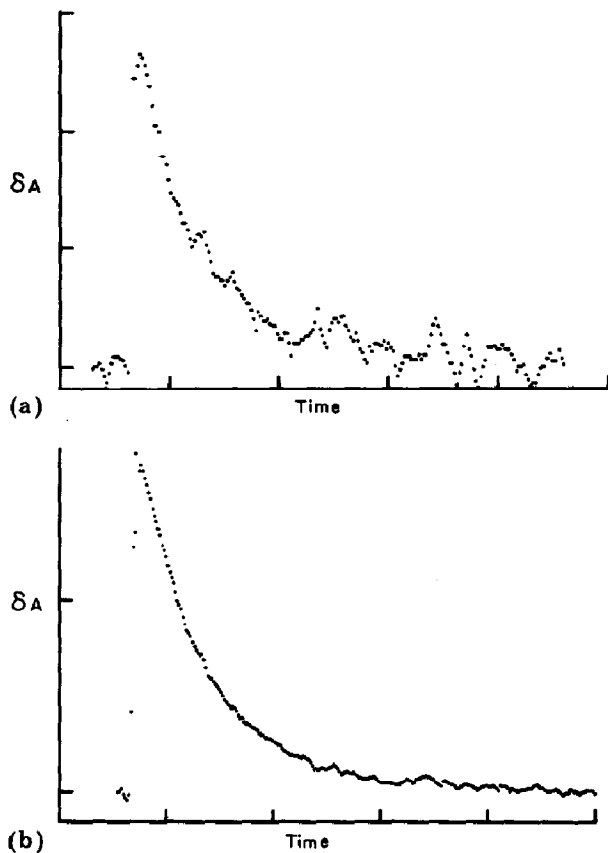


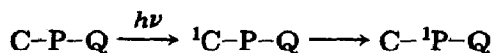
Fig. 5. Transient absorption kinetics at 940 nm for 10^{-5} M I (path length, 1 cm): (a) in methylene chloride (400 ns per division; $1.0 \times 10^{-4} \Delta A$ per division); (b) for the same sample in methylene chloride approximately 50% saturated with tetra-*n*-butylammonium tetrafluoroborate (4 μ s per division; $1.0 \times 10^{-3} \Delta A$ per division). (The sample was excited by a 10 ns, 600 nm laser pulse.)

porphyrin first excited singlet state lies at about 1.9 eV. The C^+-P-Q^- species is therefore a high energy state which has preserved much of the energy inherent in the exciting photon as chemical potential.

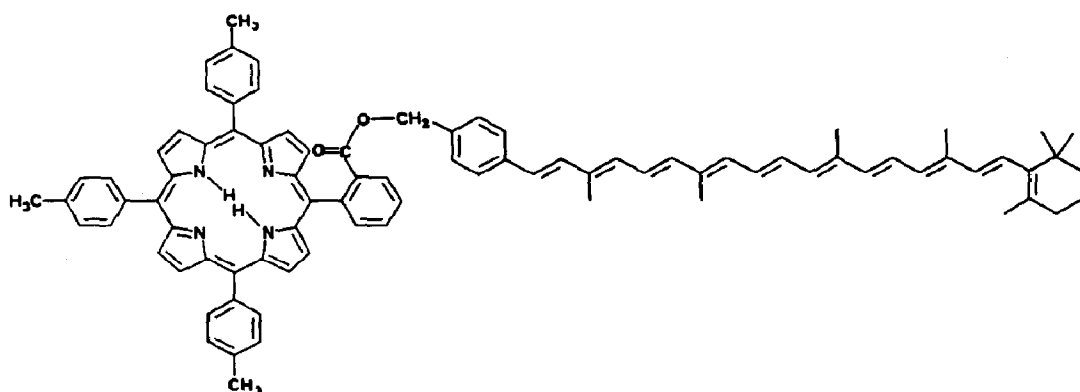
The triad I is thus a successful model for some of the most important charge separation steps of natural photosynthesis. We shall return to this point after discussing its usefulness as a model for antenna function and photoprotection.

3.2. Antenna function

Carotenoid antenna function consists of the absorption of light and the transfer of singlet excitation to chlorophyll or, in the case of I, to the porphyrin moiety:



Such energy transfer may be detected by measuring the fluorescence excitation spectrum. Carotenoids do not fluoresce detectably, and if light absorbed by the carotenoid gives rise to porphyrin fluorescence, singlet transfer must have occurred. Such experiments with I are not possible because the electron transfer dominates the decay of 1P . However, studies of II show that singlet energy transfer does occur to the extent of about 10%. This relatively small number is in fact quite significant when it is realized that the normal lifetime of a carotenoid excited singlet state is at most a few picoseconds due to rapid internal conversion. Thus, any process which can compete with vibrational degradation must be extremely fast. It is reasonable to assume that the successful mimicry of carotenoid antenna function in II is due to the interaction between the chromophores provided by the partial conjugation of the carotenoid to the porphyrin π electron system via the amide linkage and the *meso* aromatic ring. In other carotenoporphyrin systems [9 - 12], higher energy transfer efficiencies have been determined. For example, in IV

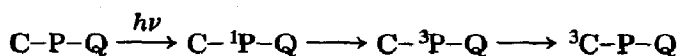


IV

a singlet transfer efficiency of about 25% was found [10]. The high efficiency in this case is due to a folding of the carotenoid chain over the porphyrin so that the two π electron systems are in intimate (to within about 4 Å) contact.

3.3. Photoprotection

As mentioned above, photoprotection from singlet oxygen damage is necessary because chlorophyll or porphyrin triplet states are excellent sensitizers for singlet oxygen production. Carotenoid polyenes can protect against singlet oxygen damage by quenching the tetrapyrrole triplet before it interacts with O₂:



Triplet energy transfer in II and III can easily be studied using laser flash spectroscopy because the porphyrin triplet-triplet absorption maximum is at about 440 nm, whereas that for the carotenoid is at about 540 nm. Thus,

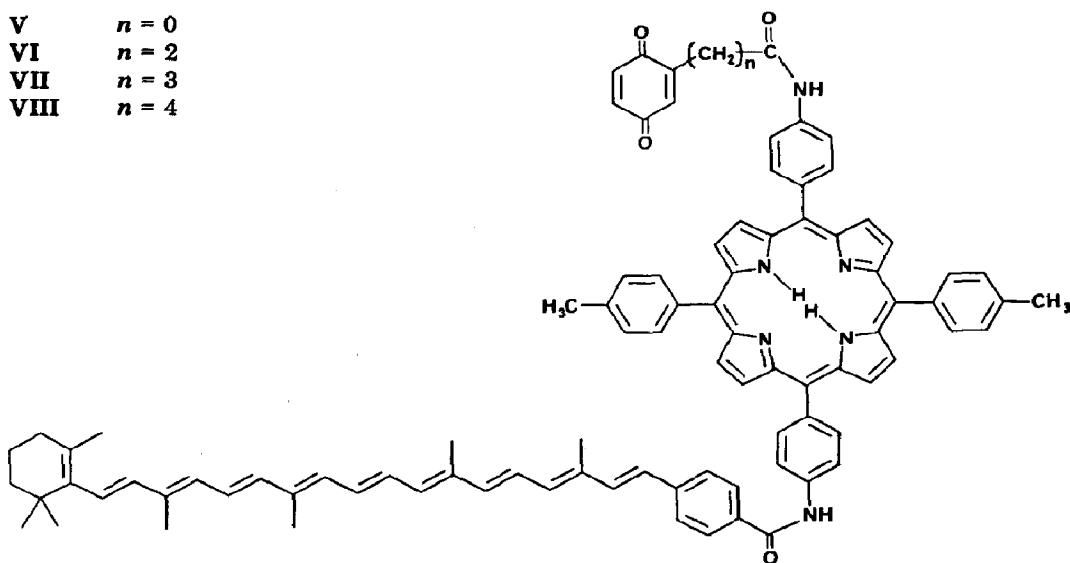
decay of the porphyrin triplet after excitation accompanied by growth of the carotenoid triplet indicates triplet transfer. For II, triplet transfer occurs at a rate of more than $1 \times 10^8 \text{ s}^{-1}$, as measured from the rise of the carotenoid triplet. (It should be noted that the rapid internal conversion of the carotenoid singlet precludes intersystem crossing in the carotenoid itself.) This rate is much faster than the diffusion-controlled reaction of the porphyrin triplet with dissolved oxygen, and photoprotection is therefore complete.

Fast and efficient triplet energy transfer requires an electron exchange mechanism. In the case of II, transfer is again facilitated by partial conjugation between the chromophores. In carotenoporphyrin systems which lack this conjugation, rapid triplet transfer can still occur [11, 13] via stacked conformations in which the π electron systems are in contact (IV), via transfer across formally saturated linkages or via molecular motions which momentarily achieve conformations with good orbital overlap.

3.4. Additional triads

Although triad I and its relatives have demonstrated electron, singlet energy and triplet energy transfer, the rates, and therefore the efficiencies, of these processes did not always equal those observed in natural photosynthesis. In order to improve the efficiencies, more must be known about the precise spatial (conformational) and energetic requirements for these processes. With this goal, we have recently synthesized triads V - VIII

V	$n = 0$
VI	$n = 2$
VII	$n = 3$
VIII	$n = 4$



in which the linkages between the components vary in length and flexibility. 500 MHz ^1H NMR studies again show that VI - VIII adopt extended conformations. Thus, the effect of additional $-\text{CH}_2-$ groups is to separate the

porphyrin and quinone in space. This would be expected to slow down the initial electron transfer (step 2). Indeed, fluorescence lifetime studies reveal that, whereas the porphyrin singlet state of I has totally decayed within a few hundred picoseconds of excitation (see Fig. 4), the fluorescence lifetimes of VII and VIII in methylene chloride are 1.4 ns and 2.2 ns respectively. This slowing of step 2, although it will reduce the quantum yield of $C-P^{+}-Q^{-}$, might also be expected to retard the back reaction 3 and thus to favor step 4. Similarly, the lifetime of the final charge-separated state $C^{+}-P-Q^{-}$ might also be extended. The actual effect of these modifications is currently being determined.

4. Conclusions

Triad I not only carries out photodriven two-step charge separation, but also yields the final charge-separated state at high potential, in reasonable yield and with an exceptionally long lifetime. There are several apparent reasons for this successful mimicry of aspects of the natural photosynthetic process. The charge separation steps involve transfer of an electron from a chromophore to a directly attached species which is relatively close in space. In addition, since we are dealing with excited states in the initial charge separation, the energetics of transfer are favorable. Thus, the generation of the $C-P^{+}-Q^{-}$ state and its conversion to $C^{+}-P-Q^{-}$ are fast and efficient. In contrast, the radical electrons in the final $C^{+}-P-Q^{-}$ state are no longer adjacent and are in fact very far apart in space because the conformation is still presumably an extended one in which the quinone and carotenoid are separated by the neutral porphyrin. Thus, direct recombination will be very slow and might under some circumstances depend on relatively infrequent intramolecular motions which would bring the radicals closer together. Alternatively, recombination could in theory be a two-step process via $C-P^{+}-Q^{-}$ or $C^{+}-P-Q^{-}$. However, formation of either of these intermediates from $C^{+}-P-Q^{-}$ would be energetically unfavorable. In this connection it is interesting to note that natural photosynthetic systems also use rapid multi-step electron transfers to separate the radical cation (hole) and anion (electron) and thereby to slow the recombination (back) reaction.

Carotenoid antenna function and photoprotection from singlet oxygen are also mimicked by I. Although antenna function is not particularly efficient with this molecule (it approaches 100% in some green plant preparations), other carotenoporphyrins (such as IV) demonstrate up to 25% transfer of singlet excitation. Suitable structural modifications may therefore allow the antenna function in a triad to be increased while its charge separation properties are maintained. Photoprotection from singlet oxygen in II is very efficient because of the rapid triplet transfer from the porphyrin to the carotenoid. Such photoprotection is important in green plants (and in artificial systems as well) at high light levels where the reaction center is excited while the acceptor is still reduced from prior excitation. Triads such

as VII and VIII, in which initial charge separation is relatively slow, will also generate some porphyrin triplet state and will benefit from carotenoid photoprotection.

Further work will include not only probing the structural and photo-physical parameters affecting the lifetime, energy and quantum yield of the charge-separated state in triads, but also attempting to carry out the next steps of artificial photosynthesis through oxidation and reduction reactions with $C^{+}-P-Q^{-}$ and additional species. In particular, photodriven charge separation across a bilayer lipid membrane has been accomplished with concomitant reduction of an electron acceptor ($Fe(CN)_6^{3-}$) on one side and oxidation of an electron donor (ascorbic acid) on the opposite side. Our preliminary results indicate that the carotenoid moiety conducts through the phospholipid bilayer and thus gives rise to vectorial electron transport which mimics that found in the energy-conserving processes in bacterial and higher plant photosynthesis.

Acknowledgments

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