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Published on Web 02/24/2004

Carotenoid and Pheophytin on Semiconductor Surface: Self-Assembly and Photoinduced Electron Transfer

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Carotenoids play several important roles in natural photosynthesis. They act as antenna by transferring singlet energy to chlorophylls and as photoprotective pigments by transferring triplet energy out of the chlorophyll system, thereby preventing chlorophyll-sensitized singlet oxygen production.[1] Carotenoids also quench chlorophyll fluorescence under high light conditions and participate in electron-transfer processes in the reaction center.[2] To mimic the functions of carotenoids in natural systems, synthetic carotenoid−tetrapyrrole dyads have been studied and shown to exhibit efficient carotenoid energy transfer and tetrapyrrole fluorescence quenching via electron transfer.[3] However, in natural photosynthetic membranes, carotenoids and chlorophylls are not covalently linked but are held in suitably close proximity by proteins via noncovalent interactions. Herein we report that under certain condition, carotenoid and pheophytin *a* can self-assemble into a supramolecular system on the surface of nanocrystalline TiO_2. Excitation of the carotenoid initiates electron injection, leading to the formation of a carotenoid radical cation, while excitation of the pheophytin moiety results in ultrafast electron transfer from the carotenoid to the excited pheophytin, leading to the formation of a long-lived charge-separated state. The triplet carotenoid is also produced via primary charge recombination within 30 ns.

Molecules used in this study are depicted in Scheme 1. Carotenoid **1** (*trans*-8′-apo-β-caroten-8′-oic acid)[4] is used to achieve efficient attachment to the TiO_2 surface.[4−6] Sensitization of the nanocrystalline TiO_2 film (average particle size ∼13 nm, ∼1 μm thickness)[6] was carried out by immersing a thin glass plate with the film into a hydrated ethanol solution of 0.2 mM **1** and **2** (pheophytin *a*)[7] for 10 h under argon atmosphere. The steady-state absorption spectrum recorded for the sensitized film is shown in Figure 1. The absorption maximum of the carotenoid is blue-shifted (to ∼400 nm) in comparison with that in solution, the vibrational structure disappeared, and a new absorption peak appeared at 670 nm. The spectral blue-shift and loss of vibrational structure are due to aggregation[8] of **1** on the TiO_2 surface, leading to a monolayer formation as recently reported for carotenoids on films.[5] Since **1** has no absorption at $\lambda > 600$ nm either in solution or on films,[4,5] the new peak at 670 nm must be due to the Q_y absorption of **2**,[9] indicating that **2** was immobilized onto the TiO_2 film. Interestingly, however, molecule **2** cannot be attached without the presence of **1** due to its weak interaction with the hydrophilic oxide surface.[7] The same situation occurs when the carotenoid molecules are not tightly packed on the surface. Consequently, **2** cannot be attached directly to the TiO_2 surface, but to the self-assembled monolayer of **1**. Since the long phytyl chain is more hydrophobic and needs much smaller space than the tetrapyrrole ring, we propose that the phytyl chain penetrates inside the carotenoid layer while the tetrapyrrole ring is exposed to the external surface, as observed by Hata and co-workers on silica film where chlorophyll is immobilized in surfactant assemblies.[10]

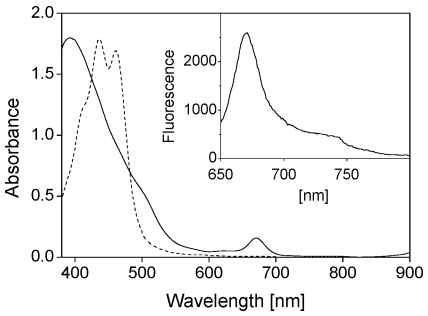
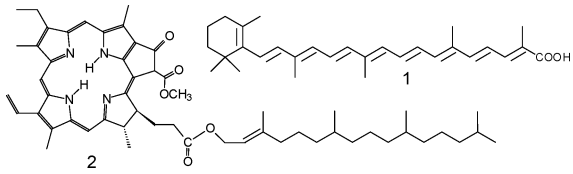


Figure 1. Steady-state absorption spectra of the carotenoid−pheophytin film (solid line) and **1** in ethanol (dashed line). The inset displays the fluorescence spectrum obtained by excitation of the film at 610 nm.

Scheme 1. Structures of the Studied Molecules



The spectral position of both absorption and fluorescence (λ_{max} = 670 nm, Figure 1 inset) spectra of **2** exhibit the characteristic features of monomeric pheophytin in solution,[9] signaling that no aggregation of pheophytin is present. In addition, no indication of the Q_y absorption band for aggregated **2** (695 nm)[11] was observed. To learn about the assembly details of the system, the extinction coeffecient (ϵ) of **1** in the aggregated form was determined to be $\sim 7 \times 10^4$ by dissociating the film containing only **1** with pure ethanol. This is a somewhat lower value than that of the monomer (1×10^5).[5] According to the absorption spectrum in Figure 1 and ϵ of **2** at the peak of the Q_y band (6×10^4),[9] the molar ratio of **1** and **2** self-assembled on TiO_2 film is estimated to be approximately 8.6:1. This ratio remained the same even after substantial prolongation of the sensitization process.

Excitation of the pheophytin−carotenoid-TiO_2 film (**2**−**1**-TiO_2) at the carotenoid moiety with a 7-ns laser pulse at 450 nm gives rise to a carotenoid radical cation ($\mathbf{1}^{\bullet+}$)[4] readily detected via its maximum at 860 nm (data not shown). As shown in our studies of TiO_2 film[12] or TiO_2 colloidal solution[4] containing only **1**, the radical is formed as a consequence of ultrafast ($>10^{12}$ s^{-1}) electron injection from the carotenoid S_2 state into the conduction band of TiO_2. Most interestingly, however, excitation of the pheophytin moiety at 670 nm also results in the immediate formation of $\mathbf{1}^{\bullet+}$, which is long-lived (microsecond−millisecond), and its decay is characterized by multiexponential decay kinetics (Figure 2). To elucidate the mechanism of $\mathbf{1}^{\bullet+}$ formation, kinetics with better time resolution were measured by means of a femtosecond transient absorption

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10.1021/ja031775l CCC: $27.50

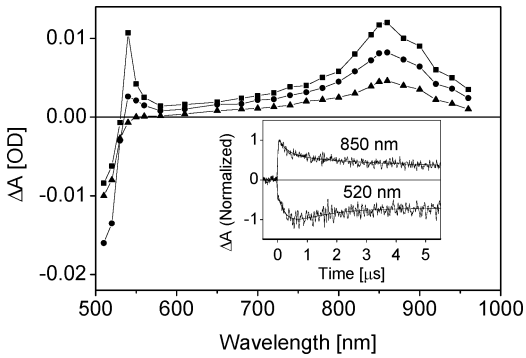

Figure 2. Time-resolved absorption difference spectra recorded after pulsed laser excitation of the deoxygenated carotenoid−pheophytin film at 670 nm: 0.1 μs (■), 0.5 μs (●), 5 μs (▲). Inset: Kinetic traces at selected wavelengths after 670-nm laser light excitation.

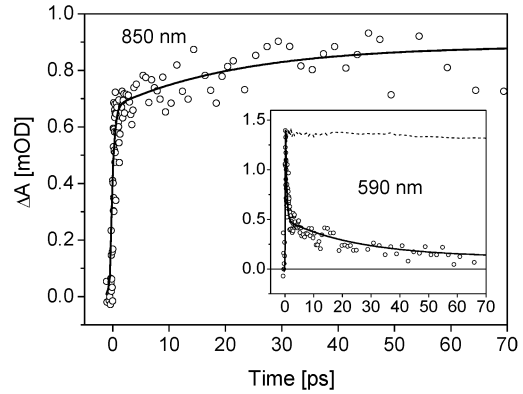

Figure 3. Picosecond kinetics of the **2**−**1**-TiO_2 system recorded at 850 nm, corresponding to the formation of $\mathbf{1}^{\bullet+}$. Inset shows decay of the pheophytin excited state in the **2**−**1**-TiO_2 system recorded at 590 nm. Kinetic trace at 590 nm measured for pheophytin in solution is shown for comparison (dashed line).

setup,[4] providing a 120-fs excitation pulse at 670 nm. Resulting kinetic traces recorded at 850 and 590 nm, corresponding to the absorption of $\mathbf{1}^{\bullet+}$ and excited-state absorption of pheophytin (^{1}**2**), respectively, are shown in Figure 3. Fitting of the 850 nm kinetics yields two rise components of <1 ps (∼60%) and 20 ps (∼40%), demonstrating ultrafast formation of $\mathbf{1}^{\bullet+}$. The same time constants are extracted from kinetics recorded at 590 nm, indicating that $\mathbf{1}^{\bullet+}$ is generated as a result of reductive quenching of ^{1}**2** by **1**, forming a charge-separated state ($\mathbf{2}^{\bullet-}$−$\mathbf{1}^{\bullet+}$-TiO_2). The reductive quenching of ^{1}**2** is further confirmed by comparison of ^{1}**2** in solution and in the **2**−**1**-TiO_2 system (Figure 3). The long-lived nature of the charge-separated state can be understood in terms of delocalization of positive charge in $\mathbf{1}^{\bullet+}$ over the conjugated backbone of the carotenoid,[13] moving the positive charge away from the pheophytin moiety that is assumed to be located at the end of **1**. In addition, our recent experiments on TiO_2 film sensitized by **1** suggest that a hopping of positive charge among aggregated carotenoid molecules may be possible,[12] allowing further separation of charges in $\mathbf{2}^{\bullet-}$−$\mathbf{1}^{\bullet+}$-TiO_2. According to this scheme, efficient large-distance separation of charges is the reason for the observation of a long-lived carotenoid radical. Intriguingly, however, no bleaching of pheophytin is observed on a longer time scale, suggesting that $\mathbf{2}^{\bullet-}$ recovers back to the parent molecule prior to recombination with $\mathbf{1}^{\bullet+}$, or, in other words, that back recombination between $\mathbf{1}^{\bullet+}$ and $\mathbf{2}^{\bullet-}$ is not the dominant pathway. Although we cannot give an unambiguous explanation of this phenomenon, it is possible that $\mathbf{2}^{\bullet-}$ is able to inject an electron into the TiO_2 conduction band through the carotenoid layer. Since the phytyl tail is supposed to penetrate the carotenoid layer, reaching close to the TiO_2 surface, the high driving force of $\mathbf{2}^{\bullet-}$ to give up an electron may lead to electron transfer through the carotenoid layer under the condition that the positive charge is transferred far enough to prevent direct back recombination. This scenario is also supported by the multiexponential decay of $\mathbf{1}^{\bullet+}$ on the μs time scale (Figure 2), which is characteristic of electron recombination between TiO_2 and $\mathbf{1}^{\bullet+}$.[4]

Nevertheless, a certain fraction of $\mathbf{1}^{\bullet+}$ undergoes electron recombination with $\mathbf{2}^{\bullet-}$ to form the triplet state of **1**, as demonstrated by the fast (≤30 ns) formation of the **1** triplet state[4] with an absorption maximum at 540 nm (Figure 2). The formation of the triplet state of **1** must result from initial charge recombination between $\mathbf{1}^{\bullet+}$ and $\mathbf{2}^{\bullet-}$, because the above-mentioned picosecond reductive quenching makes the pathway of pheophytin-to-carotenoid triplet energy transfer[3b] inaccessible. The rather short lifetime of ^{3}**1** (0.3 μs) observed here relative to that in bulk solution[3,4] may result from interaction between **1** and **2** at the TiO_2 surface and also from presence of oxygen in the **2**−**1**-TiO_2 system.

In conclusion, our results demonstrate that a self-assembled carotenoid−pheophytin system leads to an efficient reductive quenching of the pheophytin moiety, suggesting that a similar mechanism can operate also in natural photosynthetic systems. This conclusion is in line with recent calculations on chlorophyll fluorescence quenching by carotenoids via electron transfer.[14] Moreover, the formation of a long-lived charge-separated state indicates that such a "self-assembling" strategy may be also considered for novel dye-sensitized solar cell constructions[15] and other artificial systems aiming to mimic the electron-transfer chain in natural photosynthesis.

Acknowledgment. We thank the Swedish Energy Agency and the Swedish Research Council (VR) for financial support.

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JA031775L