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Fucoxanthin— and Peridinin—Pheophorbide-*a* Molecules as a New Light-Harvesting Model

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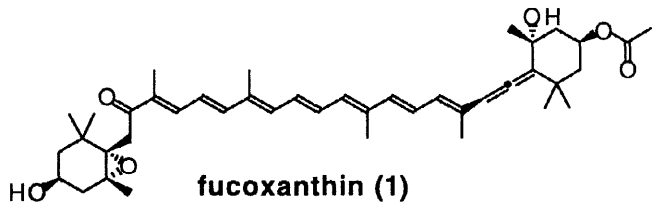
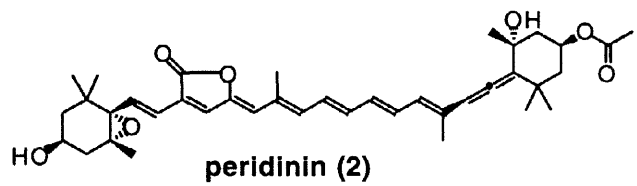
Abstract: In fucoxanthin—pheophorbide-*a* and peridinin—pheophorbide-*a* dyads prepared by trans-esterification at the 13^2 methoxycarbonyl group of methyl pheophorbide-*a*, singlet-singlet energy transfer from the carotenoid to the pheophorbide occurs with 23 and 54% efficiencies, respectively.

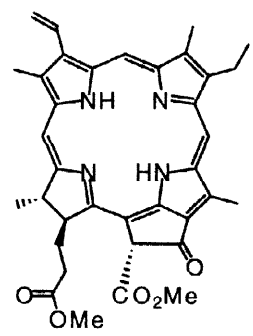
Carotenoids in light-harvesting proteins and reaction centers increase the overall efficiency of photosynthesis by passing absorbed light energy to chlorophylls.[1] Absorbing light in the 450-550 nm region where chlorophyll absorption is weak, carotenoids can undergo rapid singlet-singlet energy transfer to chlorophylls in spite of extremely short lifetimes of singlet excited states of carotenoids (antenna function). On the other hand, under conditions of high light intensity, carotenoids can dissipate excess energy though singlet-singlet energy transfer or can quench the triplet excited states of chlorophylls that sensitize singlet-oxygen generation and thus are harmful to natural cells (photoprotection).



fucoxanthin (1)



peridinin (2)



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Covalently-linked synthetic models have proven to be quite useful for understanding biological functions of carotenoids.[2] However, carotenoids used in model studies have been so far limited to unnatural 7'-apo-7'-aryl-β-carotene.[2,3] Recently, we reported the synthesis of fucoxanthin— and zeaxanthin—pyropheophorbide molecules in which the mechanisms of rapid singlet-singlet energy transfer from the carotenoid to the pyropheophorbide were indeed different between the two carotenoids.[4-6] Considering structural and functional diversity of natural carotenoids, synthetic methods for linking natural carotenoids to chlorophyll pigments that are mild enough not to affect fragile natural carotenoids would be highly desirable.

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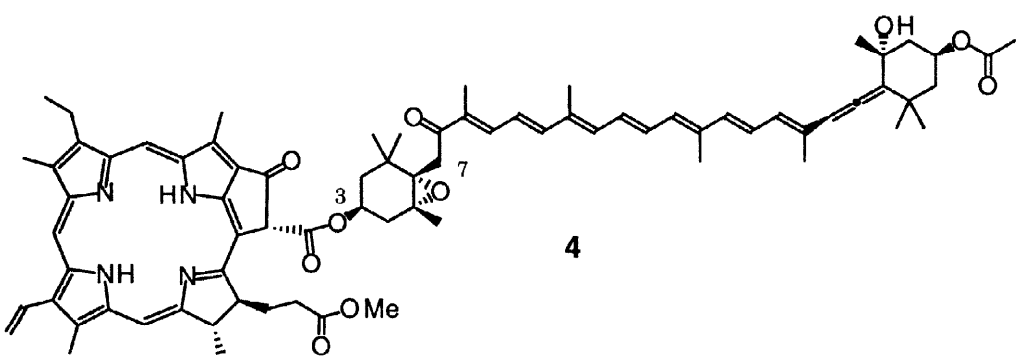
Development of a synthetic unit where singlet-singlet energy transfer from the carotenoid to the chlorophyll occurs in high quantum yield is also an important target in the photosynthetic model approach.

Here we report that fucoxanthin and peridinin are effectively attached to a pheophorbide-*a* pigment under our transesterification conditions, where the methanol moiety at the 13^2 methoxycarbonyl in methyl pheophorbide-*a* is replaced by a variety of primary and secondary alcohols with aid of 2-chloro-1-methylpyridinium iodide (CMPI) and 4-dimethylaminopyridine (DMAP).[7] When a 1:1 mixture of fucoxanthin (**1**) and methyl pheophorbide-*a* (**3**) in toluene was refluxed in the presence of CMPI and DMAP, a new band besides those of **1** and **3** appeared in TLC; byproducts were not detected, indicating that the reaction was fairly clean. After refluxing for 4 h, the reaction mixture was worked up in the usual manner and the separation by silica gel column chromatography gave fucoxanthin—pheophorbide-*a* linked molecule **4** in 29% yield based on the amount of **1** used. Peridinin—pheophorbide-*a* molecule **5** was synthesized under the same conditions in 40% yield. The structures of **4** and **5** were fully characterized by 500 MHz ^{1}H NMR and FAB mass spectra. The FAB mass spectra indicated a parent ion peak at 1233 (Calcd for $C_{77}H_{92}N_4O_{10}$, 1232.6) for **4** and at 1205 (Calcd for $C_{74}H_{84}N_4O_{11}$, 1204.6) for **5**. In the ^{1}H NMR spectrum of **4**, H_3-proton appeared at 5.16 ppm, being 1.34 ppm lower compared with that in **1**, being consistent with an ester linkage at this position, and H_7 methylene protons appeared as a AB quartet at 2.53 and 3.62 ppm (J=19 Hz), indicating a fragile β,γ-epoxy ketone intact in **4**. In the ^{1}H-NMR spectrum of **5**, H_3-proton appeared at 5.20 ppm, being 1.29 ppm lower than that in **2**, and H_7-, H_8-, and H_{10}-protons appeared at 6.93.(d, J=16 Hz), 6.30(d, J=16 Hz), and 6.92 (s) ppm, respectively. Only small upfield shifts were observed for the protons in the carotenoid moieties both in **4** and **5**, suggesting rather stretched conformations in solution. It is worthy to note that all the functional groups in fucoxanthin, peridinin, and methyl pheophorbide-*a* are all preserved in the dyads **4** and **5** and that the carotenoid and the pheophorbide are held at close proximity to permit excited-state interactions within very short lifetimes of excited states of carotenoids. These structural aspects are quite suitable as a model for the study of biological roles of carotenoids in photosynthesis.



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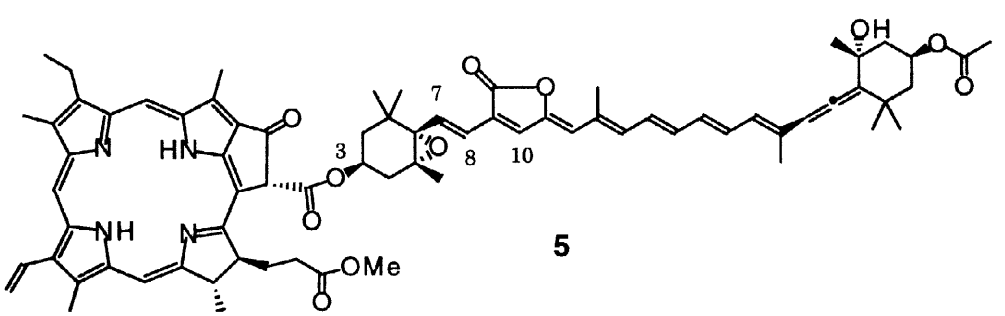

5

Fucoxanthin and peridinin are both important natural carotenoids that are believed to play mainly light-harvesting function in blown algae and photosynthetic dinoflagellates, respectively.[8,9] In contrast to the forbidden nature of $S_1 \rightleftarrows S_0$ transition in many carotenoids, these two carotenoids, whose symmetries are broken, the S_1 state may "borrow" oscillator strength from the S_2 state, making the S_1 state partially dipole-allowed and thus leading to a meaningful rate of Förster-type singlet-single energy transfer from the carotenoid to the pheophorbide. It has been also known that these two carotenoids have the S_1-state energies that are higher enough than those of chlorophyll and pheophorbide and do not quench the S_1-states of chlorophyll and pheophorbide. These features are quite favorable for a light-harvesting carotenoid.

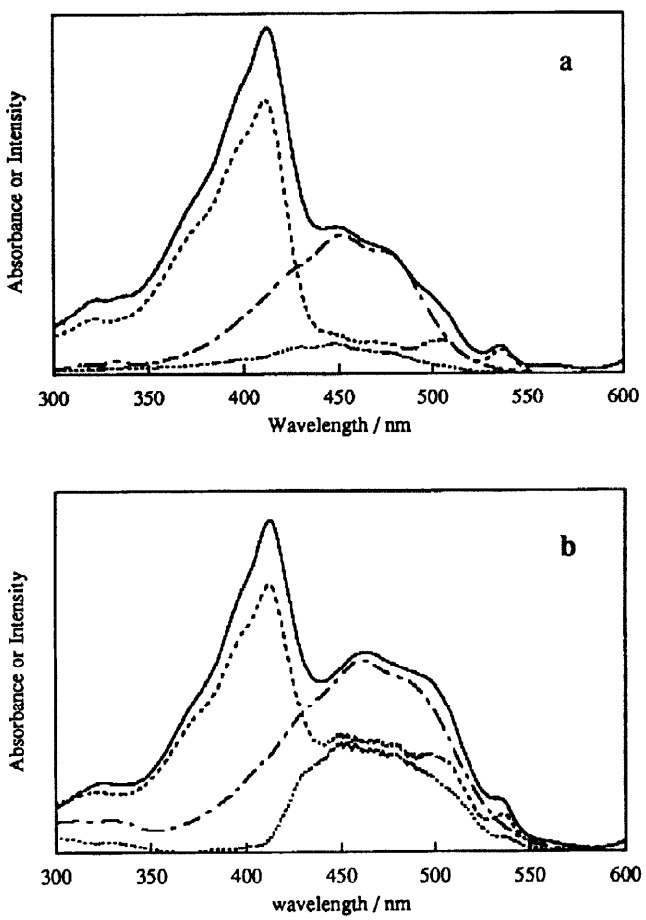

Figure 1. Comparison of the absorption spectra and fluorescence excitation spectra in THF; **4** (a) and **5** (b): the absorption spectra of **4** and **5** (———); the corrected fluorescence excitation spectra of **4** and **5** (— — —); the absorption spectra of **1** and **2** (— · —); the calculated carotenoid absorbance contributing to the fluorescence of pheophorbide (·····).

The absorption spectra of **4** and **5** were, respectively, a simple sum of those of the individual pigments **1** and **3**, and those of **2** and **3**, indicating that the electronic interactions in the ground state are very small both in **4** and **5**. In the steady-state fluorescence spectra of **4** and **5**, the fluorescence emission from the pheophorbide moiety is not quenched by the attached carotenoids, being analogous to the previous case.[4] On the basis of comparison of the absorption spectra and the fluorescence excitation spectra (Figure 1), the

efficiency of singlet-singlet excitation energy transfer from the carotenoid to the pheophorbide has been estimated to be ca. 23 ± 2 and $54 \pm 3\%$ for **4** and **5**, respectively. Most probably, this energy transfer from the S_1 state of symmetry-broken carotenoid to the pheophorbide proceeds via dipole-dipole interaction mechanism (Förster mechanism[10]), where the geometrical parameters (distance and orientation), the spectral overlap, and the lifetime of a donor state (the S_1-state of carotenoid) are key parameters which determine a rate of energy transfer. The similar connections as well as the observed small chemical-shift changes in the carotenoid moieties suggest essentially the similar geometries of the pheophorbide and the carotenoid in **4** and **5**. The fluorescence spectra of fucoxanthin and peridinin are also quite similar in shape and wavelength to each other.[11] Accordingly, the spectral overlap in the Förster equation[10] should be also similar in **4** and **5**. On the other hand, the lifetime of the peridinin S_1-state was reported to be ca. 103 ps,[12] being longer than that of fucoxanthin (60-68 ps).[4,6] Therefore, much larger efficiency in the singlet energy transfer in **5** may be rationalized in terms of a longer lifetime of peridinin S_1-state.

Characterization of the ultrafast excited-state dynamics of **4** and **5** in real time scale that is now in progress will be reported elsewhere.

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