Synthesis of Natural Carotenoid–Modified Pyropheophorbide Dyads for Investigation of Carotenoid–Chlorophyll Excited State Interactions

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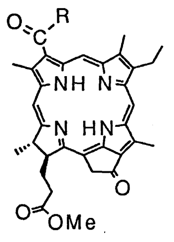
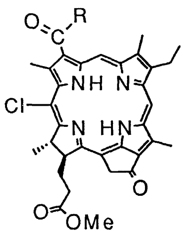
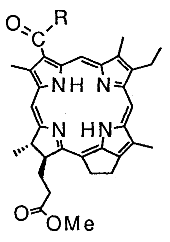
Two sets of new fucoxanthin or zeaxanthin-linked pyropheophorbides were prepared to compare the intramolecular excited-state interactions. Fucoxanthin acts as a better antenna toward pyropheophorbide by transferring singlet energy from its S_1-state, while zeaxanthin is a poorer antenna and quenches the S_1-state of the pyropheophorbide possibly by reverse energy transfer.

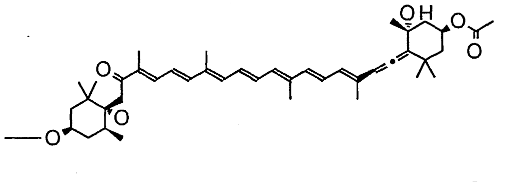
Carotenoids have been considered to play crucial roles in photosynthesis through interactions with chlorophylls.[1] Covalently-linked synthetic models have proved to be quite useful for understanding of biological functions of carotenoids.[2] However, only scattered attention has been paid to the structural diversity of the natural carotenoids in the model approach. Quite recently, we have reported the synthesis of fucoxanthin-pyropheophorbide and zeaxanthin-pyropheophorbide and have revealed marked functional differences between the two carotenoids: fucoxanthin is superior to zeaxanthin in the singlet-singlet energy transfer from carotenoid to pyropheophorbide and zeaxanthin is a stronger quencher of the S_1-state of pyropheophorbide.[3] These results seem to support a proposal that fucoxanthin acts mainly as the antenna and zeaxanthin acts as a light-intensity regulator by quenching the S_1-state of chlorophylls.[4] In order to extend this strategy and get more useful information, we need related models where the pyropheophorbide moiety is chemically modified to allow the examination on the effects of changes in the energy levels of the excited pyropheophorbides and of the hypothetical ion pair states upon the excited-state interactions between the pyropheophorbide and the carotenoid, since most of the natural carotenoids are dipole-forbidden and their energy levels remain unsettled.

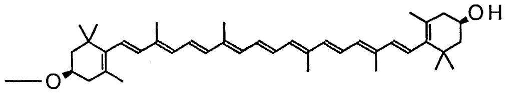

1a-d

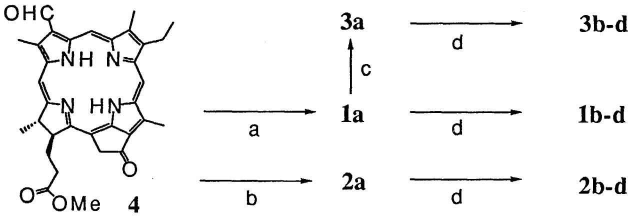

2a-d


3a-d

a) R = —OH b) R = —OMe

c) R =


d) R =




Scheme 1. a) $NaClO_2$, H_2NSO_3H, 2-methyl-2-butene/ THF, H_2O, rt, b) $NaClO_2$, H_2NSO_3H/ THF, H_2O, rt, c) CF_3CO_2H, $NaBH_4$/ CH_2Cl_2, MeOH rt, d) fucoxanthin, zeaxanthin, or MeOH, 2-chloro-1-methylpyridinium iodide, 4-(N,N-dimethylamino)pyridine/ CH_2Cl_2, reflux.

The synthetic routes starting from pyropheophorbide-*d* methyl ester **4**[5] to three carboxylic acids are shown in Scheme 1. The formyl group of **4** was transformed into carboxylic group by the oxidation with $NaClO_2$ in the presence of 2-methyl-2-butene as a chlorine scavenger at room temperature. In the absence of 2-methyl-2-butene, the 20-meso position was effectively chlorinated to give **2a**. The carbonyl group in the five membered ring of **1a** was selectively reduced with $NaBH_4$-CF_3CO_2H to give **3a**. The carboxylic acids **2a** and **3a** were coupled with fucoxanthin and zeaxanthin with 2-chloro-1-methylpyridinium iodide and 4-dimethylaminopyridine to give **2c**, **2d**, **3c**, and **3d** in 12, 20, 27, and 30% yields, respectively. These new dyads gave ^1H NMR and FAB mass spectra, which were fully consistent with the assigned structures.

Table 1 summarized the optical and electrochemical properties of these models. The absorption spectra of the dyads are all the simple sums of the respective chromophores, indicating weak interactions in the ground state. The S_1 energy level of the pyropheophorbide moiety determined from the absorption and fluorescence spectra is in the order of $\mathbf{2} \approx \mathbf{1} < \mathbf{3}$, while the first one-electron reduction potential measured by cyclic voltammetry is in the order of $\mathbf{3} < \mathbf{1} < \mathbf{2}$.

First, the intramolecular singlet-singlet energy transfer from the carotenoid to the chlorin has been examined by measuring the corrected steady-state fluorescence excitation spectra by monitoring the fluorescence from the pyropheophorbides (Figure 1). The observed decrease in the energy-transfer efficiency in the order of **2c** > **1c** > **3c** in the fucoxanthin-series can be accounted for in termes of the energy transfer from the S_1-state (2.00 eV) of the fucoxanthin to the S_1-state of the pyropheophorbide, since the fucoxanthin S_1-state emits fluorescence[6] and the spectral overlap between the fucoxanthin fluorescence and the pyropheophorbide absorption decreases in this order (Table 1).

Table 1. Physical properties of models

compd.	$E(S_1)^a$ /eV	$e_r{}^b$ /V	τ^c /ns	$k_q{}^d$ /s^{-1}	Ω^e /cm^{6}mol^{-1}
1b	1.81	-1.32	8.2		
1c			6.8	0.3×10^8	8.5×10^{-14}
1d			3.9	1.3×10^8	3.4×10^{-14}
2b	1.80	-1.24	2.4		
2c			2.3	0.2×10^8	9.2×10^{-14}
2d			1.8	1.4×10^8	4.3×10^{-14}
3b	1.89	-1.67	6.6		
3c			6.2	0.1×10^8	2.6×10^{-14}
3d			1.9	3.7×10^8	2.5×10^{-14}

^{a}The energy of the S_1-state of pyropheophorbide. ^{b}The first reduction potential against ferrocene/ferrocenium in CH_3CN solutions containing 0.1 M tetraethylammonium chloride. ^{c}Fluorescence lifetimes in THF solutions. ^{d}Rate constants of the fluorescence quenching determined by the following equation $k_q = 1/\tau - 1/\tau_0$, where τ and τ_0 are the fluorescence lifetimes of methyl esters **1-3b** and of carotenoid-linked models **1-3c** and **1-3d**, respectively. ^{e}Spectral overlap between the fluorescence of fucoxanthin (S_1) or zeaxanthin (S_2) and the absorption of pyropheophorbide.

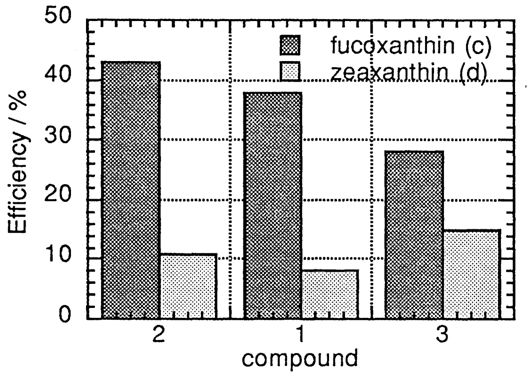


Figure 1. Efficiencies of singlet-singlet energy transfer from carotenoids to pyropheophorbides.

On the contrary, the observed energy-transfer efficiency in the zeaxanthin-series is rather puzzling. The S_1-state of zeaxanthin is strictly dipole-forbidden, probably precluding a Förster type energy-transfer, and its energy level has not been established yet. Recently ca. 1.80 eV or a lower value has been proposed for isoelectronic β-carotene on the basis of extrapolation of the energy levels of shorter polyenes.[7] The most efficient energy-transfer in **3d** in the zeaxanthin-series may encourage a possibility of the energy transfer from the emissive S_2-state of the zeaxanthin, although the S_2-state must be very short-lived.[6,8]

Secondly, we have examined the fluorescence quenching of the pyropheophorbides. As was the case of the previous results[3], the fluorescence is almost not quenched in the fucoxanthin-series but is substantially quenched in the zeaxanthin-series. The rate constants of the chlorin fluorescence quenching have been determined from the fluorescence lifetimes of the dyads taken for selective excitation at the pyropheophorbide chromophores. All the fluorescence decays of the dyads have been deconvoluted with single exponential functions, from which we have determined the fluorescence lifetimes and the rate constants of the fluorescence quenching (Table 1).

The fact that zeaxanthin is a better electron donor than fucoxanthin[9] may suggest the possibility of the electron transfer quenching, where the S_1-state of pyropheophorbide is an electron acceptor and the attached carotenoid is an electron donor. However, much efficient quenching in **3d** in comparison to **1d** and **2d** is not consistent with the electron transfer mechanism. Rather these results can be accounted for in terms of the singlet-singlet energy transfer from the pyropheophorbide to the zeaxanthin, in line with our previous results.[3,10]

Covalently-linked natural carotenoid-pyropheophorbide molecules provide a new opportunity for the detailed studies on the excited-state interactions of carotenoids and chlorophylls. We can change the S_1 energy level of pyropheophorbides by chemical modification and thereby may approach to the real location of the elusive 2^1Ag state of carotenoids. Studies on ultrafast excited-state dynamics of the present molecules are now in progress and will be reported elsewhere.

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