

Elucidation and Control of Ultrafast Intramolecular Charge Transfer Dynamics of Marine Photosynthetic Pigments

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Abstract: Ultrafast Intramolecular Charge Transfer (ICT) state dynamics of fucoxanthin have been investigated by femtosecond pump-probe measurements. A modification of conjugated polyene chain length of fucoxanthin enabled us to clarify and control an ICT character.

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1. Introduction

Carotenoids (Cars) are essential pigment for light-harvesting and photoprotection in natural photosynthesis. They absorb light in the blue-green region of the spectrum and transfer to chlorophyll rapidly and efficiently in their photosynthetic antennas [1]. The excited states of Cars are described by a three-electronic level system (S_0 , S_1 , and S_2) [2]. The optically allowed S_2 ($1^1B_u^+$) state is generated by a one-photon transition from the S_0 ground state ($1^1A_g^-$), and rapidly decays to the lower-lying S_1 ($2^1A_g^-$) state with ~ 100 fs. A nonradiative relaxation from S_1 to S_0 is comparatively slower (ps-ns), while the S_1 - S_0 transition is optically forbidden [2]. The optically forbidden character (S_1) of Cars appears to not function as an effective energy donor in terms of a weak Coulomb interaction. In fact, energy transfer from the Car S_1 state to chlorophyll is often inefficient [1]. On the other hand, Cars containing a carbonyl group in their polyene backbone generate the intramolecular charge transfer (ICT) state below S_1 in polar environments, forming the strongly coupled S_1 /ICT state as shown in Fig. 1(A) [3]. Consequently, the S_0 - S_1 /ICT transition dipole moment of carbonyl Cars increases due to their charge transfer character, and efficient energy transfer from carbonyl Cars to chlorophyll *a* via S_1 /ICT is realized in photosynthetic antennas [4,5]. The present study focused on the ICT character of the carbonyl Cars fucoxanthin (fx) from marine algae that could be correlated to its conjugated polyene chain lengths. Femtosecond pump-probe spectroscopic measurements with 100 fs time-resolution were performed on the fx homologues with varying numbers of conjugated double bonds n (4–8).

2. Experimental

Femtosecond pump-probe spectroscopic measurements were carried out using a mode-locked Ti:Sapphire laser system [6]. Excitation pulses were obtained from an optical parametric amplifier or by the second harmonic generation. A white continuum probe pulse was generated using a 5.0 mm sapphire plate. The instrument response function was determined to be ~ 100 fs. Sample preparations of the fx homologues with $n=4\sim 8$ are described elsewhere [7]. Samples were dissolved in three different solvents: methanol, acetone and cyclohexane.

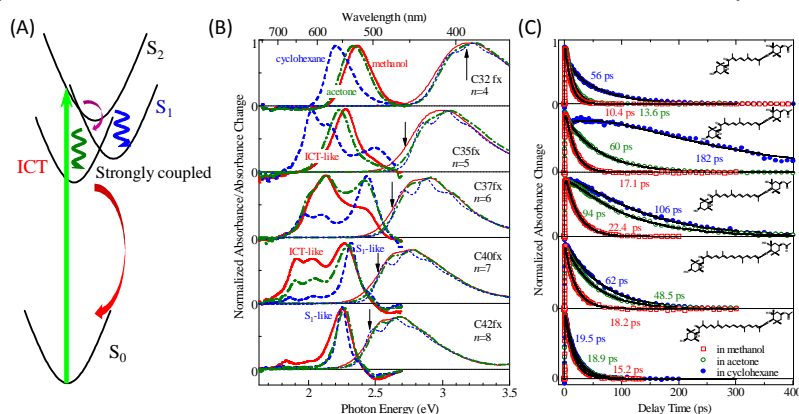


Fig.1. (A) A schematic representation of energy diagram of fucoxanthin. (B) Steady-state and PIA spectra at 3.0 ps of the fx homologs. Arrows indicate excitation energies. (C) Kinetic traces of the S_1 /ICT state. Insets show the chemical structures of the fx homologs.

3. Results and Discussion

Fig. 1(B) represents the steady-state and photo-induced absorption (PIA) spectra of the fx homologues. The steady-state absorption bands, corresponding to the S_0 - S_2 transitions, red-shifted with an increase in n [2]. In the PIA spectra, the native fx (C40fx) in cyclohexane shows a monotonic S_1 - S_n transient absorption [1], while an additional band just below the S_1 transient absorption band, assigned to the ICT-like band [3], increased with solvent polarity, suggesting that the ICT state is stabilized in polar environments. In the longest C42fx, the only S_1 -like transient absorption band appeared even in polar solvents, due to insufficient stabilization of the ICT state. In contrast, both of the S_1 and ICT-like transient absorption bands were observed clearly in the shorter C37fx in all solvents; the transient absorption bands of C35fx and C32fx became monomeric in polar solvents. The monomeric absorption bands of C32fx and C35fx observed in polar solvents were assigned to the ICT-like transient absorption. In addition, the ICT-like transient absorption band predominated and the stimulated emission from S_1 /ICT was observed in the shortest C32fx, even in cyclohexane.

Fig. 1(C) shows the kinetic traces of the S_1 /ICT transient absorption of the fx homologues. The solid lines represent the best-fit curves for the rise and decay phases convoluted with the instrumental response function. In all fx homologs, the S_1 /ICT lifetimes decreased with an increase in solvent polarity, while the S_1 /ICT lifetimes did not exhibit a monotonic dependence on n , *i.e.*, they had the longest lifetimes with $n=6$ in polar solvents (methanol: 22.4 ps and acetone: 94 ps) or with $n=5$ in nonpolar solvent (cyclohexane: 182 ps). The S_1 nonradiative relaxation rates of Cars without a carbonyl group are well explained by the energy gap law [1]. Figure 2 plots the nonradiative relaxation rates of S_1 /ICT as a function of $1/(2n+1)$ as well as those for S_1 of β -carotene homologues ($n=7\sim 15$). The solid line in Fig. 2 denotes the best-fit curve using the energy gap law for β -carotene homologues, as reported previously [8]. The S_1 /ICT lifetimes of fx homologues should also obey the energy gap law if the S_1 /ICT decay cannot be enhanced by the coupling of the ICT state. However, the S_1 /ICT lifetimes clearly deviate from the energy gap law with a decrease in n , suggesting that the S_1 /ICT decay of the shorter fx homologs ($n<8$ for methanol and $n<6$ for acetone and cyclohexane) can be enhanced by the strong coupling of the S_1 and ICT states, even in a nonpolar solvent. From the results, it is confirmed that the ICT property of fx become stronger with a decrease of n and that the shortest C32fx homologue exhibits a strong ICT character even in a nonpolar solvent. In conclusion, the conjugation length dependence of the S_1 /ICT state dynamics of the fx homologues demonstrates that the S_1 /ICT property of fx can be systematically controlled by a modification of its conjugated polyene length [9].

4. References

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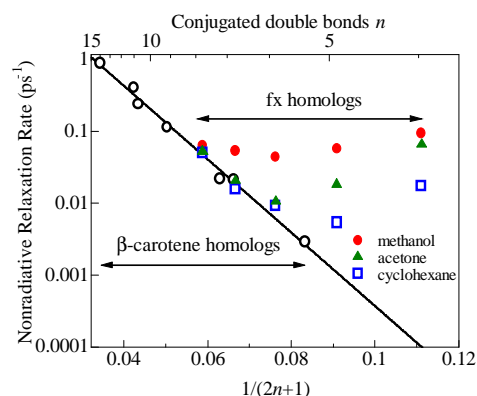


Fig. 2. The nonradiative relaxation of S_1 /ICT for fx homologs and S_1 for β -carotene homologues as a function of $1/(2n+1)$ or n .