STEADY-STATE AND FEMTOSECOND TIME-RESOLVED OPTICAL SPECTROSCOPIC STUDIES OF PERIDININ DERIVATIVES

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Abstract

Peridinin is a highly substituted carotenoid characteristic of the Peridiniales group of dinoflagellates whose structure features an unusual C_{37} carbon skeleton rather than the typical C_{40} system present in most carotenoids. One of its most surprising properties is the fact that the lifetime of the lowest excited singlet state is strongly dependent on solvent environment ranging from 7 ps in the strongly polar solvent, trifluoroethanol, to 172 ps in the nonpolar solvents, cyclohexane and benzene.[1] This behavior is highly anomalous for carotenoids which generally show very little dependence of their S_1 spectral properties and lifetimes on solvent environment. The findings suggest that the environment of protein-bound peridinin may modulate its light-harvesting efficiency in vivo. This study is aimed at uncovering the molecular features of peridinin that control its excited state properties and dynamics. We have begun an investigation of synthetically-modified peridinins and report here our findings on *13,14-cis*-PerAcEs compared to natural peridinin. The spectroscopic properties and dynamic behavior of HPLC-purified *13,14-cis*-PerAcEs in methanol and hexane were studied by steady-state absorption, fluorescence, fluorescence excitation, and transient absorption spectroscopy at room temperature. Low temperature (77K) absorption and fluorescence experiments of *13,14-cis*-PerAcEs in EPA (5:5:2 v/v/v ether: isopentane: ethanol, EPA) were also done. The investigation shows differences in absorbance maximum, vibrational structure, fluorescence emission maximum and dynamics compared to natural peridinin. The data will be discussed in terms of specific structural features that control the spectroscopic and dynamic behavior of peridinin.

Objective

To perform systematic modifications to the structure of peridinin in order to:

- Examine the effect of the structural changes on the spectral properties
- Elucidate the factors controlling the dynamics of the excited states of peridinin and peridinin derivatives

Results

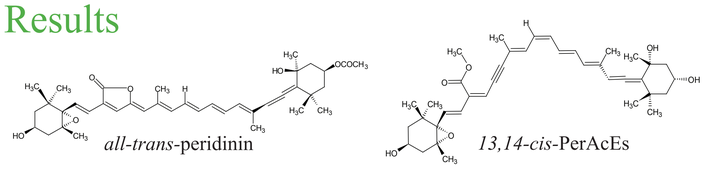

Figure 1. *Structures of peridinin and 13,14-cis-PerAcEs.*

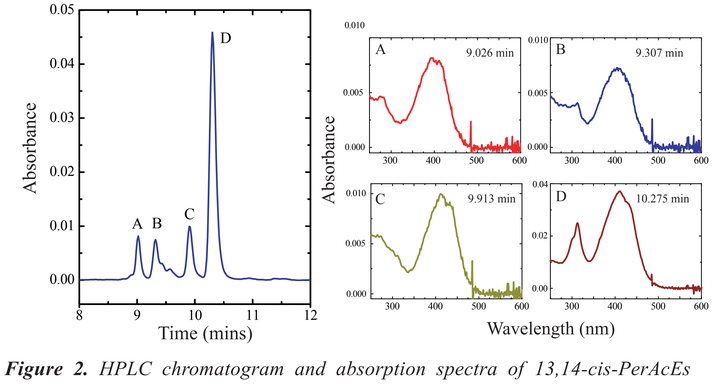

Figure 2. *HPLC chromatogram and absorption spectra of 13,14-cis-PerAcEs monitored at 410 nm using a C_{30} column. Isocratic elution with acetonitrile: methanol:water (87:10:3 v/v/v) at a 0.5 mL/min flow rate.*

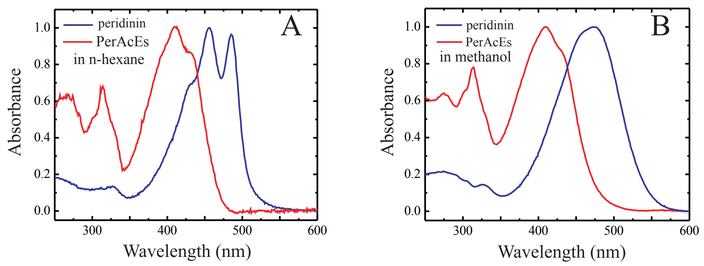

Figure 3. *Absorption spectra of peridinin and 13,14-cis-PerAcEs in (A) n-hexane and (B) methanol at room temperature.*

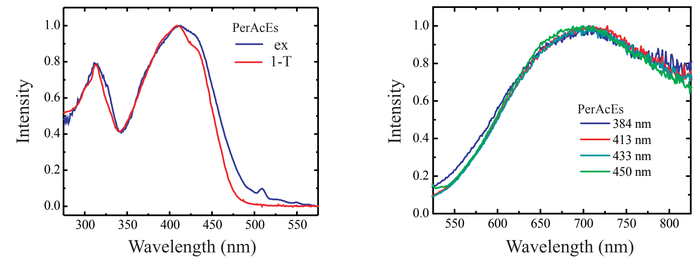

Figure 4. *Fluorescence excitation (ex) (690 nm detection) and 1-T (T is transmittance) spectra of 13,14-cis-PerAcEs in methanol. The spectra were normalized at the λ_{max}.*

Figure 5. *Fluorescence spectra of 13,14-cis-PerAcEs in methanol excited at different wavelengths. The spectra were normalized at the λ_{max}.*

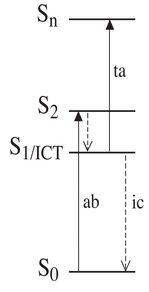

Figure 6. *Energy level diagram of the low-lying singlet states of carotenoids.* (ic) *internal conversion* (ab) *absorption;* (ta) *transient absorption* (ICT) *intramolecular charge transfer.*

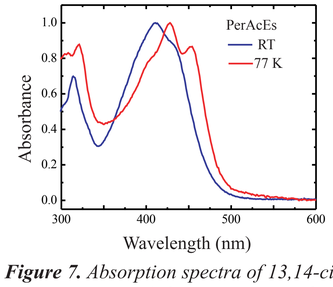

Figure 7. *Absorption spectra of 13,14-cis - PerAcEs in EPA (ether:isopentane:ethanol 5:5:2 v/v/v) at room temperature (RT) and 77 K.*

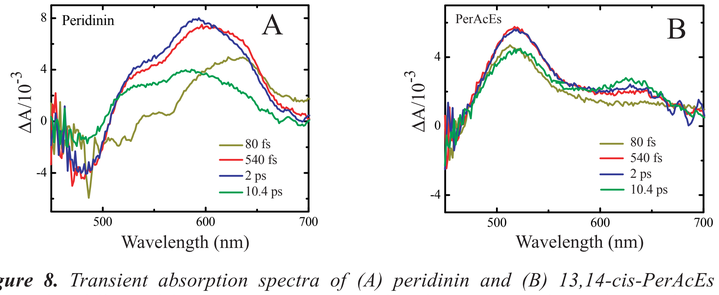

Figure 8. *Transient absorption spectra of (A) peridinin and (B) 13,14-cis-PerAcEs in methanol at different delay times. Excitation wavelength was 490 nm for perdinin and 400 nm for 13,14-cis-PerAcEs.*

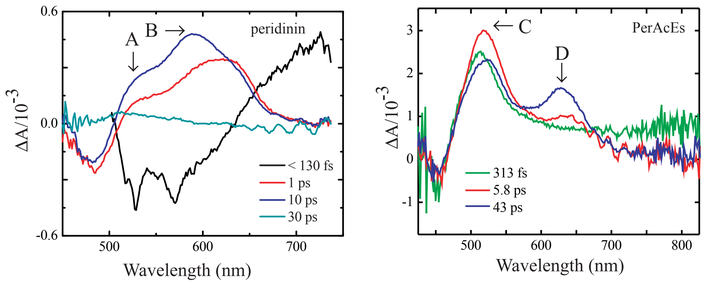

Figure 9. *Evolution Associated Difference Spectra (EADS) of (A) peridinin and (B) 13,14-cis-PerAcEs in methanol.*

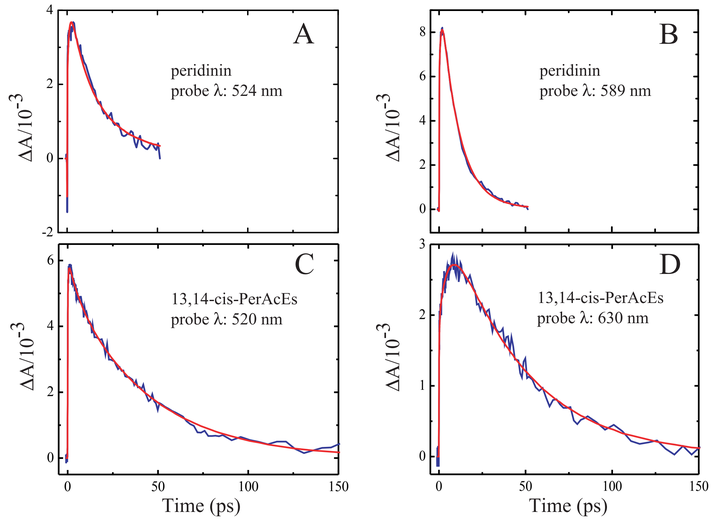

Figure 10. *Transient absorption kinetics at the maximum of the $S_1 \rightarrow S_n$ and $S_{ICT} \rightarrow S_n$ bands (A and B) of peridinin and (C and D) of 13,14-cis-PerAcEs in methanol.*

Summary of observations

- The absorption maximum of *13,14-cis*-PerAcEs is blue-shifted by ~60 nm compared to that of peridinin, and unlike peridinin shows no solvent dependance.
- The fluorescence spectrum of *13,14-cis*-PerAcEs is broad and has a maximum at ~690 nm similar to peridinin.
- The transient absorption spectrum of *13.14-cis*-PerAcEs in methanol shows two peaks at 520 nm and 630 nm that build up at different times.
- The $S_{1/ICT}$ lifetime of *13,14-cis*-PerAcEs in methanol is ~43 ps which is four times longer than that of peridinin.

Reference

1. Bautista, J. A.; Connors, R. E.; Raju, B. B.; Hiller, R. H.; Sharples, F. P.; Gosztala, D.; Wasielewski, M. R.; Frank, H. A. *J. Phys. Chem. B* **1999**, 103, 8751.

Acknowledgments

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