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

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Abstract

Peridinin is a highly-substituted C_{37} carotenoid found in marine dinoflagellates. It is the primary light harvesting component of the peridinin-chlorophyll-complex (PCP) from *Amphidinium carterae*. An unusual property of peridinin is that its S_1 excited state lifetime is dependent on solvent polarity. This has been attributed to the presence of an intramolecular charge transfer state, S_{ICT}, in the excited state manifold of peridinin.[1] The precise nature of this state and its role in light-harvesting is not yet entirely clear. In order to explore this issue, chemically modified peridinins were synthesized and the spectroscopic properties and dynamic behavior of the molecules were studied at room temperature in methanol solution by steady-state absorption, fluorescence, and ultrafast transient absorption spectroscopic techniques. Low temperature (77 K) absorption and fluorescence experiments were also carried out for the molecules dissolved in EPA (5:5:2 v/v/v ether: isopentane: ethanol). The data reveal a number of differences between the behavior of peridinin and the modified molecules including substantial blue shifts in both steady-state and fluorescence emission spectra of the modified peridinins. Ultrafast transient absorption spectroscopy was done to determine the dynamics of the excited states of the molecules. Single wavelength fitting of the data reveal the kinetic components. The data are helping elucidate the structural features that control the spectroscopic properties and dynamics of peridinin.

Objectives

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

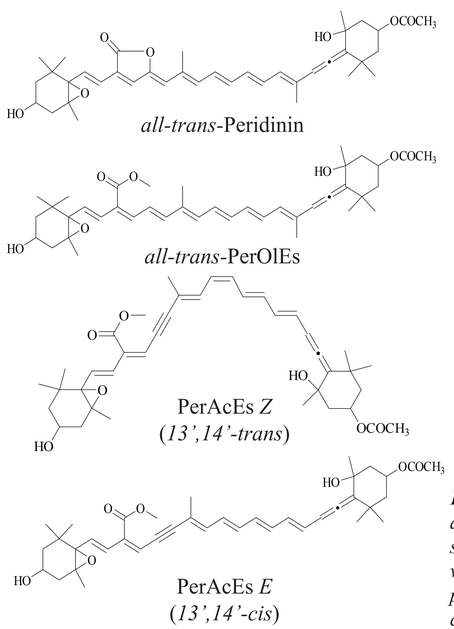

Figure 1. *Structure of peridinin and derivatives.*

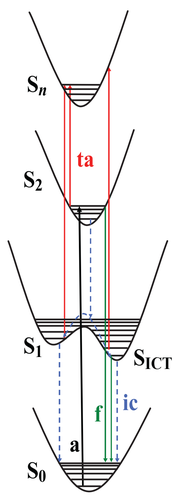

Figure 2. *Energy level diagram of the low-lying singlet states of carotenoids with associated photophysical processes.* (ic) *internal conversion;* (a) *absorption;* (ta) *transient absorption;* (ICT) *intramolecular charge transfer state.*

Steady state absorption and fluorescence

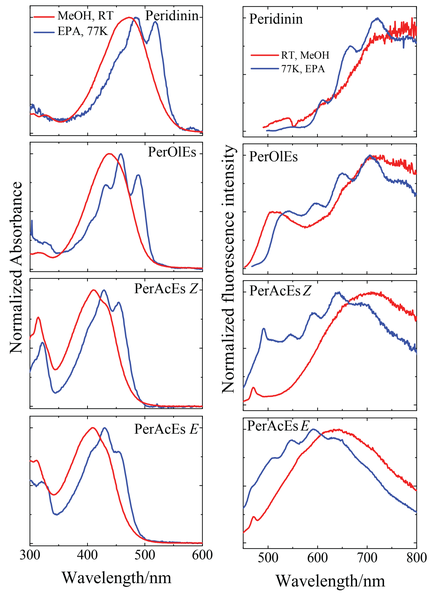

Figure 3. *Steady state absorption and fluorescence spectra of peridinin and derivatives at room temperature and 77 K. The spectra were normalized at the respective λ_{max}. The excitation wavelength for the fluorescence emission was at the λ_{max} of the absorbance spectrum for the RT spectra and at the spectral origin for the 77 K spectra.*

Transient absorption spectra

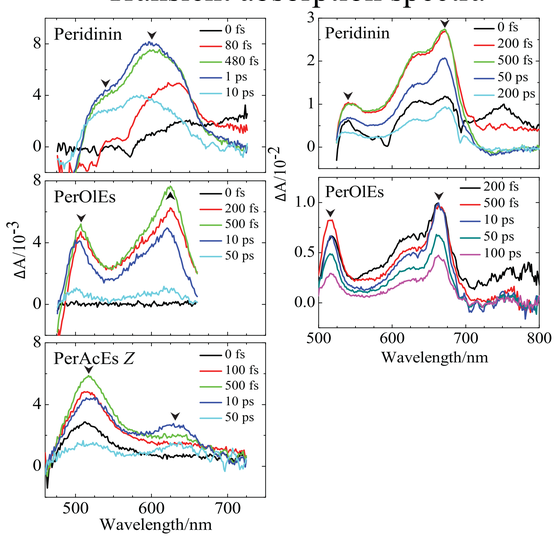

Figure 4. *Transient absorption spectra of peridinin and derivatives in methanol (RT) and EPA (47 K) at different delay times. Excitation wavelength was 400 nm for RT experiments and at the spectral origin for the 47 K experiments. The laser pulse energy was 1μJ.*

Transient absorption kinetics

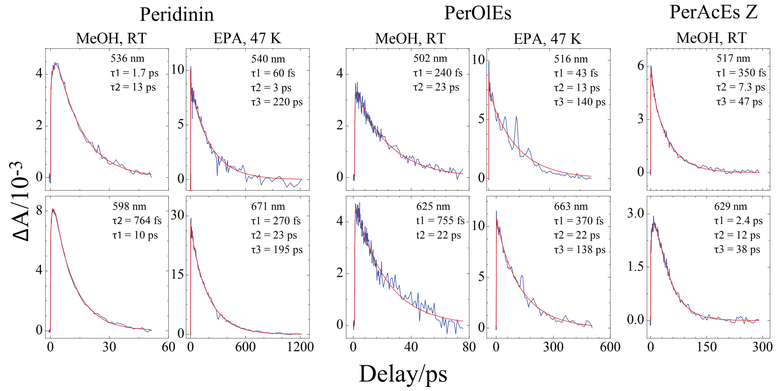

Figure 5. *Single wavelength kinetics from the transient absorption spectra of peridinin and derivatives in methanol (RT) and EPA (47 K).*

Molecule	Transient absorption experiment		Wavelength (nm)	Kinetic components	
	T (K)	solvent		Lifetime (ps)	Contribution (%)
Peridinin	RT	MeOH	536	1.70	-100
				13.2	+100
			598	0.76	-100
				10.4	+100
	47	EPA	540	0.06	-100
				2.99	+17.1
				218	+82.9
			671	0.27	-100
				23.1	+7.9
				195	+92.1
PerOlEs	RT	MeOH	502	0.24	-100
				23.4	+100
			625	0.76	-100
				21.4	+100
	47	EPA	517	0.01	+98.2
				9.78	+0.2
				139	+1.6
			663	0.37	-90.4
				22.4	-9.6
				138	+100
PerAcEs Z	RT	MeOH	517	0.35	-100
				7.26	+17.8
				46.6	+82.2
			629	2.37	-24.2
				12.0	-75.8
				38.2	+100

Table 1. *The lifetimes and percent contributions of kinetic components obtained from single wavelength fits. The transient absorption experiments on peridinin and derivatives were done in methanol (RT) and in EPA (47 K). Signs before the contribution (%) refer to the nature of the components, '+' denotes a decay and '–' denotes a rise.*

Conclusions

- The S_1 lifetime of PerOlEs is longer than that of peridinin due to its higher energy evidenced by the steady state fluorescence
- Further experiments at different temperatures will be required to understand the nature of the excited state decay pathways.

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

This work is supported by grants from the National Institutes of Health (GM-30353) and the University of Connecticut Research Foundation.