OPTICAL SPECTROSCOPIC STUDIES OF PERIDININ AND PERIDININ-CHLOROPHYLL-PROTEIN (PCP) COMPLEXES

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Abstract

Peridinin is a C_{37} carotenoid found in the Peridinin Chlorophyll-Protein (PCP) from marine dinoflagellates including Amphidinium carterae. An unusual property of peridinin is that its lowest excited singlet state (S_1) lifetime depends strongly on solvent polarity, e.g. the S_1 lifetime is 161 ps in *n*-hexane and 12 ps in methanol. It remains to be elucidated whether a physiological role exists for this behavior. Steady-state and ultrafast time-resolved optical spectroscopic studies were done on purified peridinin, two synthetic peridinin derivatives, and recombinant wild type and mutant N-domain PCPs refolded in the presence of peridinin and chlorophyll-*a*. The investigation of the isolated molecules provide information as to what structural features are responsible for the spectroscopic properties of peridinin. Spectral deconvolution of the steady-state absorption spectra of the refolded PCP complexes reveal the band profiles of the underlying peridinins. Ultrafast time-resolved experiments on the proteins show subtle differences between the complexes suggestive of the robust nature of the pigment-protein complex architecture.

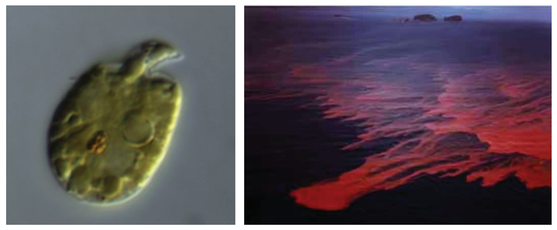


Figure 1. *(left) A. carterae. (Edmund Nash and C. J. Howe, Cambridge University, UK - http://www.bio.cam.ac.uk/~howelab/research.htm). (right) Alexandrium fundyense bloom off the coast of Maine. (WHOI, Woods Hole, MA, US - www.whoi.edu/redtide)*

Objectives

- Examine the effect of structural changes on the spectral properties of the individual molecules
- Elucidate the factors controlling the dynamics of the excited states of peridinin
- Assign the deconvolved spectral bands of peridinin to specific structures in the PCP complex
- Understand the effect of changes in amino acids on the spectroscopic and energy transfer characteristics of PCP

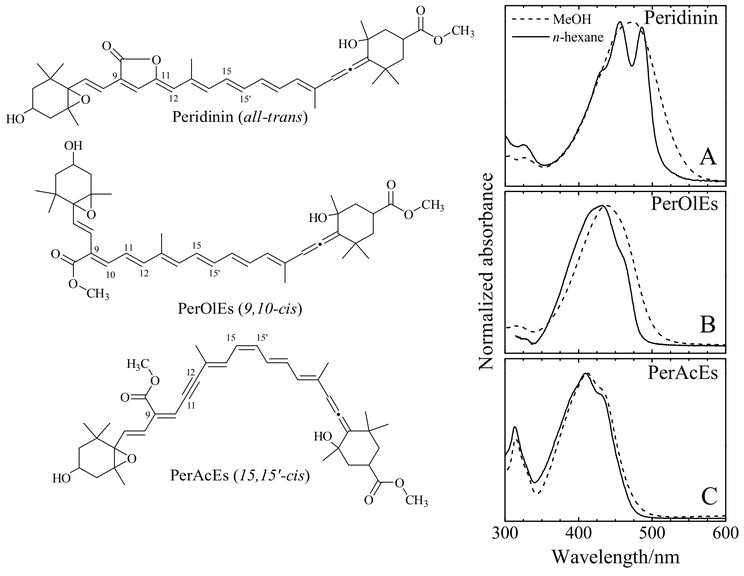


Figure 2. *Structures and steady-state absorption spectra of peridinin and two synthetic derivatives.*

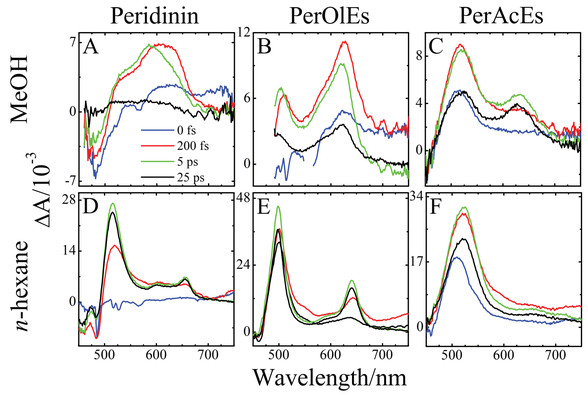


Figure 3. *Transient absorption spectra of peridnin and synthetic derivatives in methanol and n-hexane taken at different delay times.*

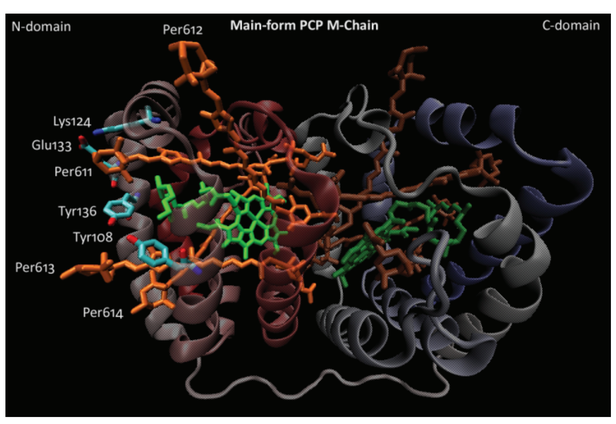


Figure 4. *Structure of main-form Peridinin-chlorophyll-protein (PCP) with the positions of the mutated amino acid residues and peridinins indicated on the N-domain side of the PCP monomer. The mutants (given below) were tested against a 'control' refolded N-domain PCP (RFPCP) for changes in spectral properties: Glu133Gln (EQ), Tyr108Phe/Tyr136Phe (YFYF), Glu133Lys/Lys124Phe (EKKF), Glu133Lys/Lys124Asn (EKKN).*

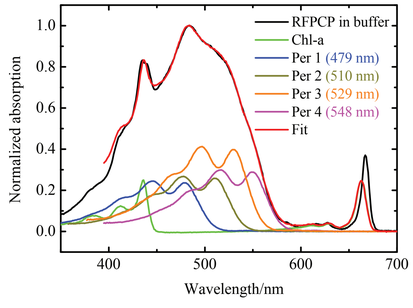


Figure 5. *Spectral deconvolution of the steady-state absorption spectrum of RFPCP into the underlying peridinin and chlorophyll-a spectra. Numbers in parentheses denote the position of the 0-0 vibronic of the peridinin spectrum.*

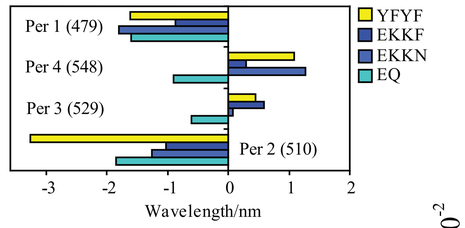
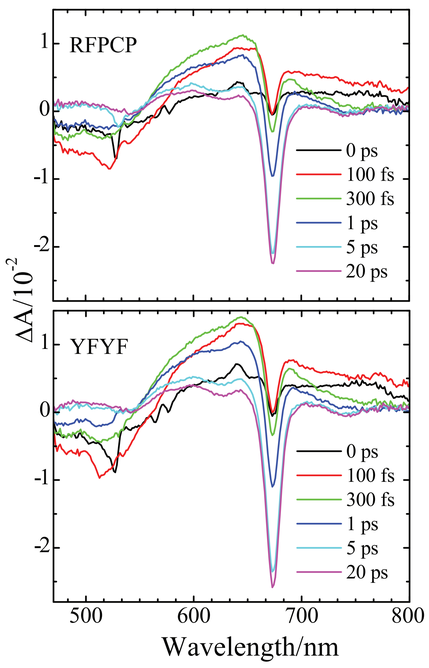


Figure 6. *Wavelength shifts of deconvolved peridinins in the various mutants relative to RFPCP.*



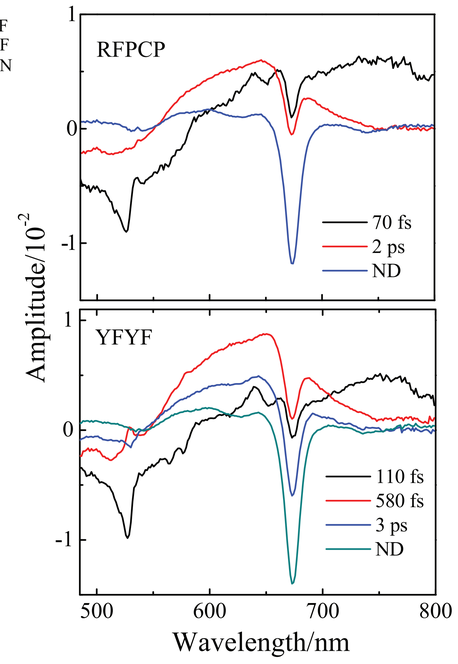


Figure 8. *(above) Evolution-associated difference spectra (EADS) obtained from global fitting of transient spectra of RFPCP and the double-mutant YFYF.*

Figure 7. *(right) Representative transient spectra of RFPCP and the double-mutant YFYF in 60% glycerol-buffer at room temperature.*

Conclusions

- The lactone ring in peridinin is the primary source of the solvent-dependent spectra and dynamics of the molecule.
- Transitions involving an intramolecular charge transfer state dominate the transient absorption spectra of the molecules in methanol, whereas in *n*-hexane the transitions originate primarily from the S_1 state.
- Spectral deconvolutions of the various PCP complexes reveal the underlying band structure of the peridinins. Mutations alter the spectra of select peridinins.
- Global fitting of the transient data from the mutants require an extra EADS component compared to RFPCP for a good fit. The interpretation of these effects is on-going.

Reference

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Acknowledgments

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