

Figure SI.1: Molecular structure of peridinin



Figure SI.2: Absorption spectrum of PCP with OD of 0.6/20µm at 480 nm



Figure SI.3: Normalized decay-associated difference spectra (DADS)

estimated from global analysis of time-resolved data of PCP with excitation at 480 nm, with lifetimes of 60 fs (dashed black), 150 fs (black), 2 ps (red), 11.5 ps (blue), 1 ns (green) and a non-decaying component (magenta). Vertical lines indicate estimated standard deviation.



Figure SI.4 Kinetic model applied with target analysis of the 480 nm excitation data for PCP. The scheme shows the connectivity among the molecular species (boxes), the life time in picoseconds (brackets) and the percentage distribution at each branch point.



Figure SI.5 Concentration profiles corresponding to SADS shown in Fig. 6 resulting from the global analysis of the 480 nm excitation data for PCP. The IRF (150 fs FWHM) is also shown.



Figure SI.6 Spectral fit of the ICT SADS.

The carbonyl bleach is located at 1745 ± 2 cm⁻¹ and its FWHM is 16 ± 3 cm⁻¹.

Table SI.1Estimated location and FWHM of carbonyl bleach ofcarotenoid SADS, in cm⁻¹

species	location	FWHM
S2	1748	15
Hot S1	1745	14
ICT	1745	16
S1	1750	10
Triplet	1748	14

	Chl- <i>a</i> 601			Chl- <i>a</i> 602	
Amino Acid	Distance (Á)	to	Amino Acid	Distance (Á)	to
His66	4.4	II Pyr.Ring	His229	3.4	II Pyr.Ring
Tyr136	12.5	10a-Ester	Tyr302	11.2	10a-Ester
	13.4	9-keto		12.0	9-keto
Tyr108	12.7	10a-Ester	Tyr270	12.7	10a-Ester
	12.2	9-keto		12.0	9-keto
Asn89	6.8	10a-Ester	Asn251	6.8	10a-Ester
	8.7	9-keto		8.8	9-keto
Ser14	11	10a-Ester	Ser177	10	10a-Ester
	14	9-keto		13	9-keto
H ₂ O78	5.4	10a-Ester	H ₂ O 55	5.6	10a-Ester
	6.9	9-keto		6.9	9-keto
			Ser174	11.6	10a-Ester
				13.7	9-keto
			Tyr247	8.0	10a-Ester
				11.3	9-keto
			Tyr270	12.2	10a-Ester
				15.4	9-keto

 Table SI.2
 Main polar residues that surround the two Chl-a;

identifying a group of residues that are conserved for both Chl-a molecules, while other additional polar residues are only present in the binding site that hosts the Chl-a 602