Two Different Charge Separation Pathways in Photosystem II

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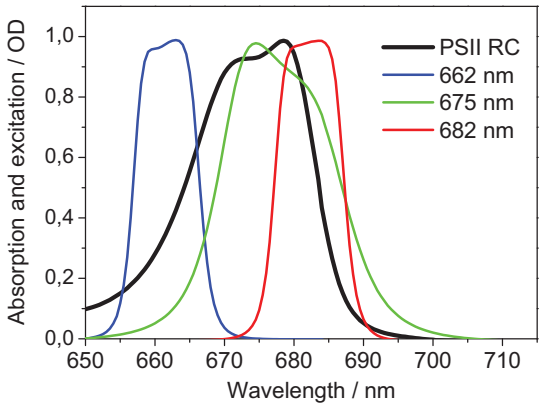
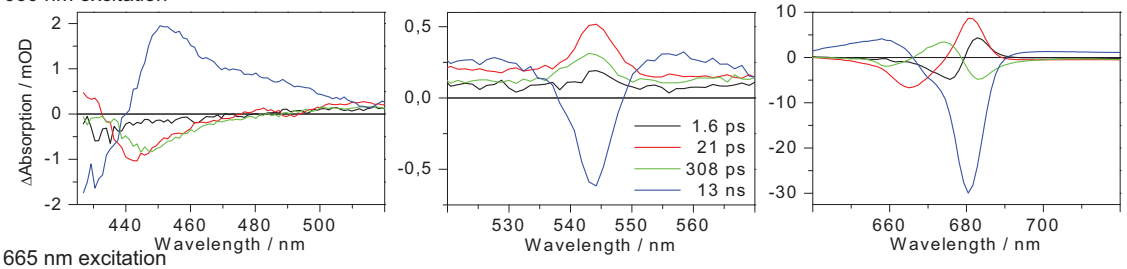
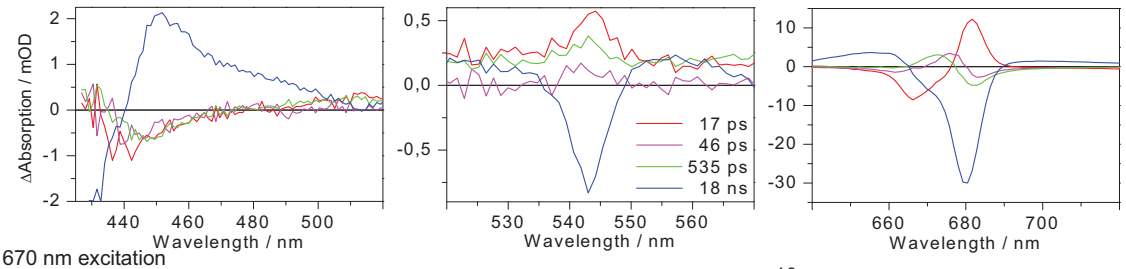


Figure S1. Photosystem II reaction center (PSII RC) absorption spectrum at 77 K (*thick line*) and broad laser excitation profiles (*thin lines*).

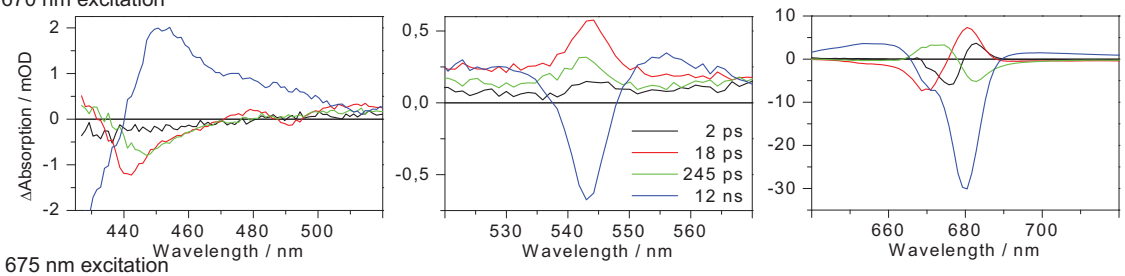
660 nm excitation



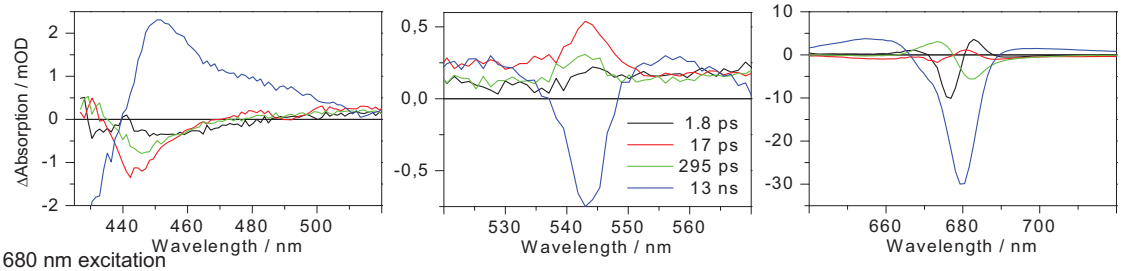
665 nm excitation



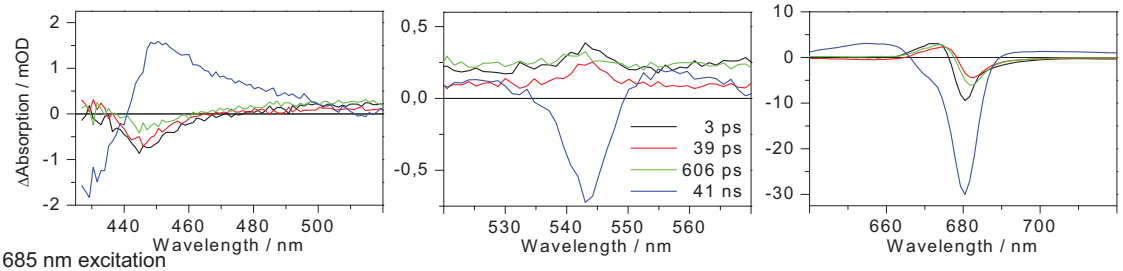
670 nm excitation



675 nm excitation



680 nm excitation



685 nm excitation

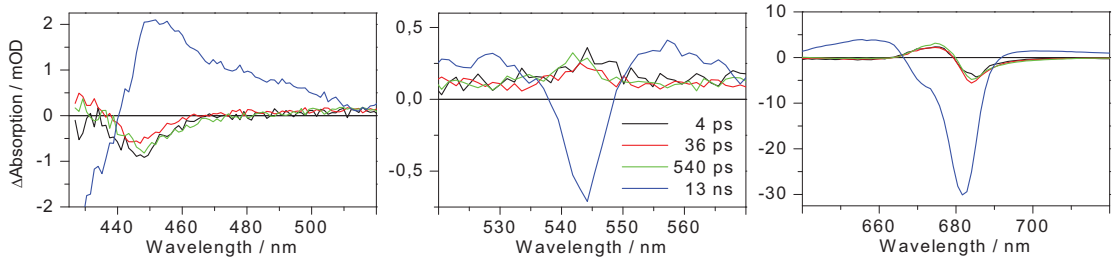


Figure S2. Decay associated difference spectra (DADS) for narrow excitations. (*From top to bottom*) 660 nm, 665 nm, 670 nm, 675 nm, 680 nm and 685 nm excitation and (*from left to right*) Phe anion, Phe Q_x and Q_y absorption regions.

In the 440 – 460 nm region the blue DADS represents the absorption band of the non-decaying Phe anion. The other DADS indicate that two or three rise time scales are present with all excitation wavelengths. In the 535 – 555 nm region the blue DADS represents the final bleach of the Phe Q_x absorption. Likewise, in this region the bleach rises on three time scales. The area of the final bleach appears larger than the sum of the rises because of the direct Phe Q_x bleach upon excitation. In the Q_y region the blue DADS represents the final radical pair where the changes in the position of the bleach are attributed to photoselection. The DADS with lifetimes up to 4 ps correspond to energy equilibration and early charge separation. For 660 – 670 nm excitation the ~20 ps red DADS corresponds to Chl_z decay and energy transfer to the RC core followed by fast charge separation, the small redshift of the bleach with excitation wavelength is attributed to photoselection. Two further slow time scales of ~40 ps and 250 – 600 ps in which there is an additional rise of the final radical pair are present, in fact the green DADS in the Q_y region are remarkably similar in shape for all excitations and similar also to the ~40 ps red DADS for 680 – 685 nm excitation.

Table S1. Lifetimes estimated by global analysis with five parallel decays. Estimated values of all nine experiments have been collated in six columns to lump similar lifetimes.

λ_{exc}(fwhm)	τ_1 / fs	τ_2 / ps	τ_3 / ps	τ_4 / ps	τ_5 / ps	τ_6 / ns
660 nm (5)	145	1.6	21	—	308	13
665 nm (5)	680	—	17	46	535	18
670 nm (5)	199	2	18	—	245	12
675 nm (5)	138	1.8	17	—	295	13
680 nm (5)	205	3	—	39	606	41
685 nm (5)	903	4	—	36	540	13
662 nm (8)	105	1.7	20	—	331	12
675 nm (12)	62	1.3	21	—	257	12
682 nm (8)	105	1.8	—	31	576	14

The estimated relative error is 10 % for τ_2 - τ_5 and 20 % for τ_1. τ_6 is less precisely estimated because of the 3 ns time range, and can best be called *long lived*.

Table S2. Evolution of percentage of pheophytin Q_x bleach estimated by global analysis with a sequential model.

	500 fs	3 ps	20 ps	300 ps	600 ps	20 ns	Δ(300-20ps)
660 nm	29	34	47	80	100	88	33
665 nm	29	36	41	80	100	95	39
670 nm	29	42	49	83	100	96	34
675 nm	47	49	55	85	100	91	30
680 nm	54	60	73	87	100	95	14
685 nm	50	53	71	82	100	88	11

The Phe*/Phe$^-$ formation is calculated from the global analysis (EADS) as the amplitude of the Q_x bleach at 544 nm after background subtraction ($\Delta A_{557nm} = 0$) and expressed as a percentage with respect to the 600 ps component. The estimated relative error is 10 %.

Table S3. Distribution of excitation energy among exciton states for *blue* excitation.

λ_{exc} (fwhm)	$Chlz_{667}$*	$Chlz_{670}$*	$Chl_{D1}Phe_{D1}$*	$P_{D1}P_{D2}Chl_{D1}$*	$Chl_{D1}Phe_{D1}$*	$P_{D1}P_{D2}Chl_{D1}$*
660 nm (5)	25	0	48	27	64	36
665 nm (5)	27	5	51	17	75	25
670 nm (5)	3	27	58	12	83	17
675 nm (5)	0	8	85	7	92	8
662 nm (8)	31	0	55	14	80	20
675 nm (12)	0	12	70	18	80	20

The percentage of excitation energy in the exciton states is estimated by the target analysis of Figure 3 and expressed as a percentage with respect to the total excitation energy delivered to the system. The estimated relative error is 10%.

Table S4. Distribution of excitation energy among exciton states and their contribution to the final state.

	Blue excitation			*Red* excitation
	Initial	After $Chls_z$ ET	Final	Final
$Chls_z$*	33			
RC*	43	48% of 33 = 16	59	60
$Trap_{65}$	14	4% of 33 = 1	15	20
$Trap_{585}$	10	48% of 33 = 16	26	20

The percentage of excitation energy in the exciton states is estimated by the simplified target analysis of Figure 4 and expressed as a percentage with respect to the total excitation energy delivered to the system. The estimated relative error is 10%.