Supplementary Information

Alteration of the H-Bond to the A_{1A} Phylloquinone in Photosystem I: Influence on the Kinetics and Energetics of Electron Transfer

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Figure S1. The |D|–|E| (A, C) and |D|+|E| (B, D) FDMR resonance transitions of isolated thylakoids from the wild type (A, B) and the L722W$_{PsaA}$ variant (C, D) recorded at 720 nm. |D| and |E| are the two zero-field splitting parameters that define the difference in the energy levels of the triplet state. Open symbols: untreated, illuminated thylakoids; Closed symbols: thylakoids pre-reduced with 10 mM sodium dithionite and illuminated for 5 minutes at room temperature. The solid lines are fits to the data with a sum of Gaussian line-widths as described in refs. 1,2. Both samples display resonance transitions with maxima at ~715 MHz (|D| - |E|) and ~940 MHz (|D| + |E|) previously assigned to $^3P_{700}$.[3] The FDMR intensity found under reducing conditions represents triplet formation in all of the PS I complexes and the ratio of the intensities for the two sets of conditions gives the percentage of PS I complexes in which $^3P_{700}$ is formed under ambient redox conditions. 9 to 12% of the PS I complexes from the L722W$_{PsaA}$ variant generate triplets compared to the 2 to 4% of PS I complexes from the wild type. Gaussian components: 709/948 MHz; 716/952 MHz; 733/958 MHz. Experimental conditions: emission wavelength, 720 nm; phase, –106°; gain, 100 μV; temperature, 1.8 K; amplitude modulation, 33 Hz.

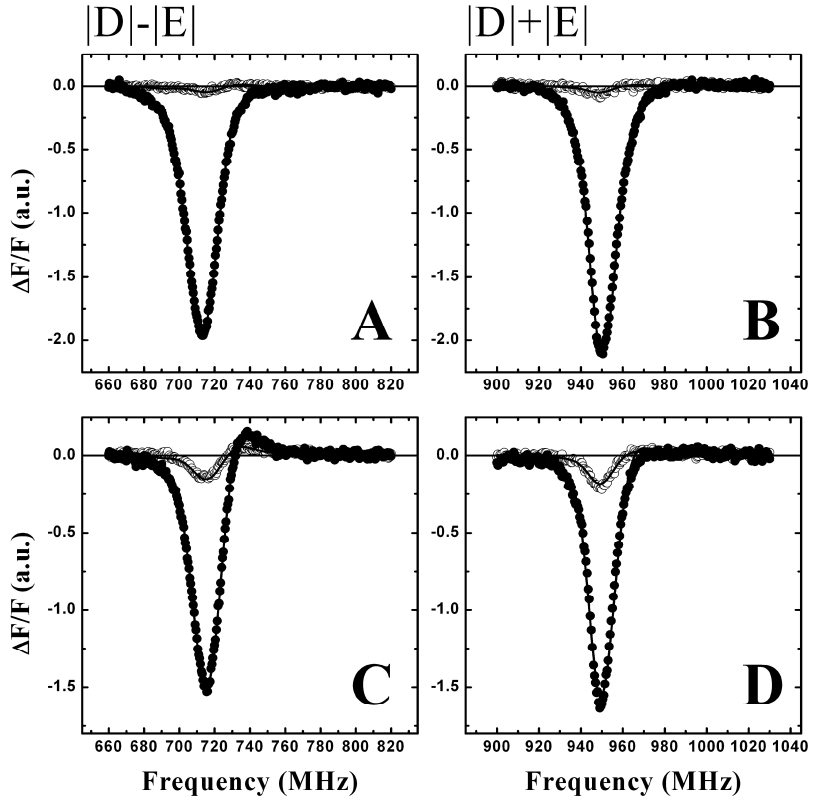


Figure S2. Comparison of the out-of-phase echo modulation of P_{700}^{+} A_{1A}^{-} in PS I from wild type (A) and L722W$_{PsaA}$ (B). Open symbols: experimental data; solid lines: fit; closed symbols: reconstruction of the spectrometer dead time; dashed line: baseline. Fits of the modulation curves as described in ref. 4 yield the following parameters: wild type: dipolar coupling, D = –169.6 µT; exchange coupling, J = 1.68 µT; L722W$_{PsaA}$: D = –169.8 µT; J = 1.70 µT. The dipolar couplings for the wild type and the L722W$_{PsaA}$ variant correspond to distances of 25.42 Å and 25.41 Å between P_{700}^{+} and A_{1A}^{-}, respectively

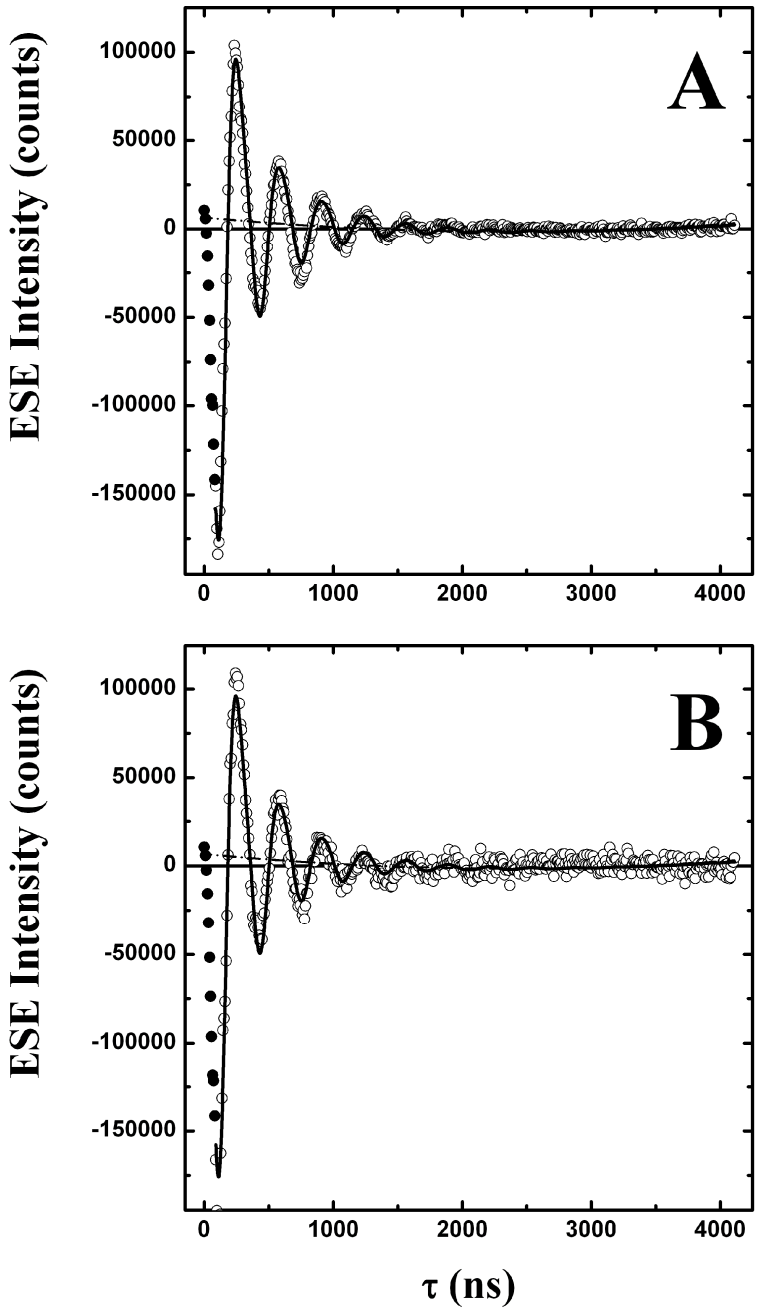
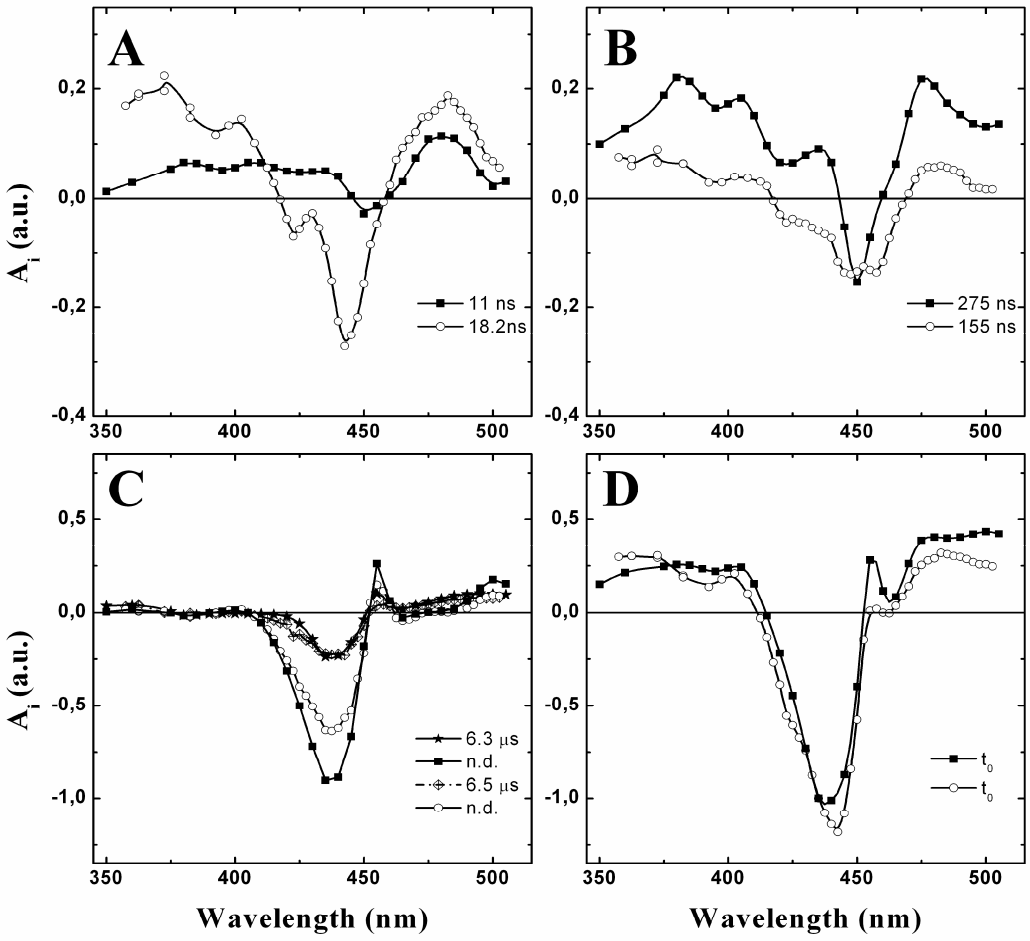


Figure S3. Pump-probe spectroscopy of whole cells of the wild type (closed) and the L722W$_{PsaA}$ variant (open). Spectra of the exponential decays normalized to the initial absorbance change at time zero are shown. Panel A depicts the fast phase due to A_{1B}^- to F_X electron transfer; panel B depicts the slow phase due to A_{1A}^- to F_X electron transfer; panel C shows the reduction of P_{700}^+ together with the non-decaying component; and panel D shows the normalized initial spectra extrapolated to time zero (t_0). The 6-µs component depicted in panel C is attributed to the reduction of P_{700}^+ based on its typical bleaching at 430 nm. The presence of 'Chl-like' bleaching in the ns components of the L722W$_{PsaA}$ variant is due to contribution from P_{700}^+ A_0^- recombination. The DAS obtained with whole cells are similar to those obtained from PS I particles (compare with Fig. 4).



Reference

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