

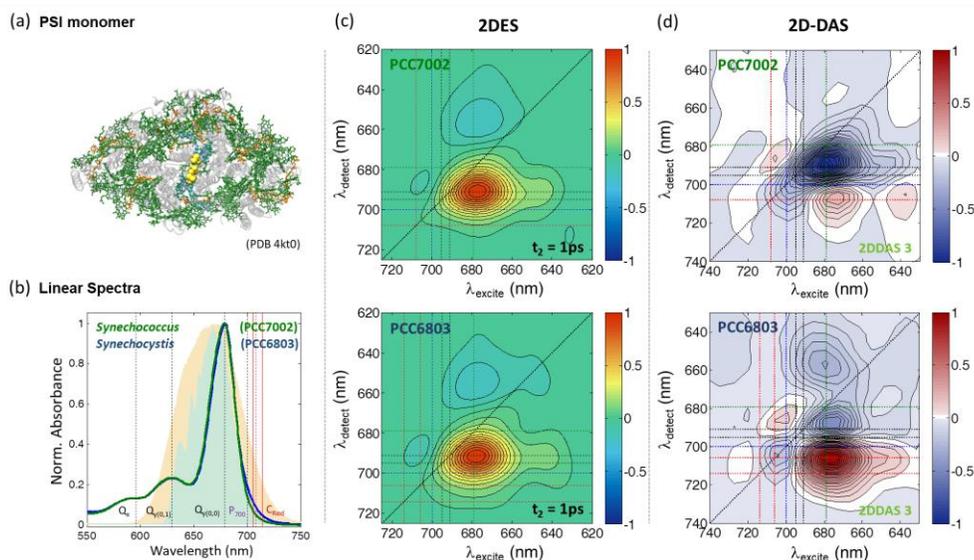
OA2.4 - Ultrafast two-dimensional electronic spectroscopic studies of Cyanobacterial photosystem I complexes

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Photosystem I (PSI) is a large natural light harvesting complex involved in the oxygenic photosynthesis, and is known to be one of nature's most efficient energy converters. In its trimeric form PSI consists of ~300 light harvesting chlorophylls surrounding reaction centers. The structural complexity of PSI leads to spectral congestion and overlap of temporal processes on the femtosecond and picosecond timescales. For these reasons, there still remain unanswered questions regarding the photoinitiated processes of PSI complexes. In order to alleviate some of the spectral congestion and gain further insight into energy transfer and electron transfer in PSI complexes we applied 2D Electronic Spectroscopy (2DES) to PSI complexes isolated from two different Cyanobacterial species: *Synechococcus* sp. (PCC 7002) and *Synechocystis* sp. (PCC 6803). The two PSI complexes were selectively chosen as they have a different number of the red chlorophylls. Red chlorophylls are red-shifted chlorophyll molecules that lie to lower energies than the reaction center and act to compete with energy transfer to the reaction center. Applying a global analysis to interpret the 2DES spectra we gain further insight into energy transfer and equilibration involving the red chlorophylls. Our analysis extracted 5 components with time constants ranging from 45 fs to ~2 ns along with the 2D-Decay Associated Spectra (2D-DAS). In comparing the 2D-DAS spectra of PCC 6803 and PCC 7002 we observe similar pathways of energy transfer, equilibration, and trapping for the two PSI complexes, but different timescales.



(a) structure of PSI monomer from *Synechocystis* PCC 6803 (PDB code 4kt0) (b) linear absorption spectra of PCC 7002 (green) and PCC 6803 (blue), the spectra of pump (green area) and probe (yellow area) pulses (c) 2DES spectra at $t_2 = 1$ ps and (d) third component of 2DDAS for PCC 7002 (top) and PCC 6803 (bottom)