Excitation Energy Transfer Dynamics of LHCII complexes

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We use ultrafast ultrafast pump-probe, 3rd order 2D electronic (2DES) and 5th order 3D electronic (3DES) spectroscopies to study the excitation energy transfer dynamics of plant light-harvesting complex II, LHCII. Studies on solubilized natural and mutant trimers, as well as aggregates will be presented.

Light-harvesting antenna systems such as LHCII, the primary light-harvesting complex in plants, are essential for the photosynthetic process that eventually powers the biological world. The excitation energy transfer (EET) processes in light-harvesting systems are therefore of strong interest to scientists.

3rd order 2D electronic spectroscopy (2DES) was performed on solubilized LHCII trimers to study the EET dynamics of the Chl *b* band to the Chl *a* band [1,2]. The complex multistep EET processes were further studied using 5th order 3D electronic spectroscopy (3DES) [3]. 2DES was also used to study the equilibration dynamics within the Chl *a* band.

LHCII aggregates provide a good *in vitro* model of LHCII in the quenched state. 2DES of LHCII trimers and aggregates were performed and compared. 2D decay-associated spectra (DAS) from global analyses of the 2D spectra show differences in their EET dynamics [2].

Studies were also conducted on LHCII mutants where certain amino acids have been changed. The mutagenesis leads to changes in the pigment conformation in LHCII which affects the EET dynamics.

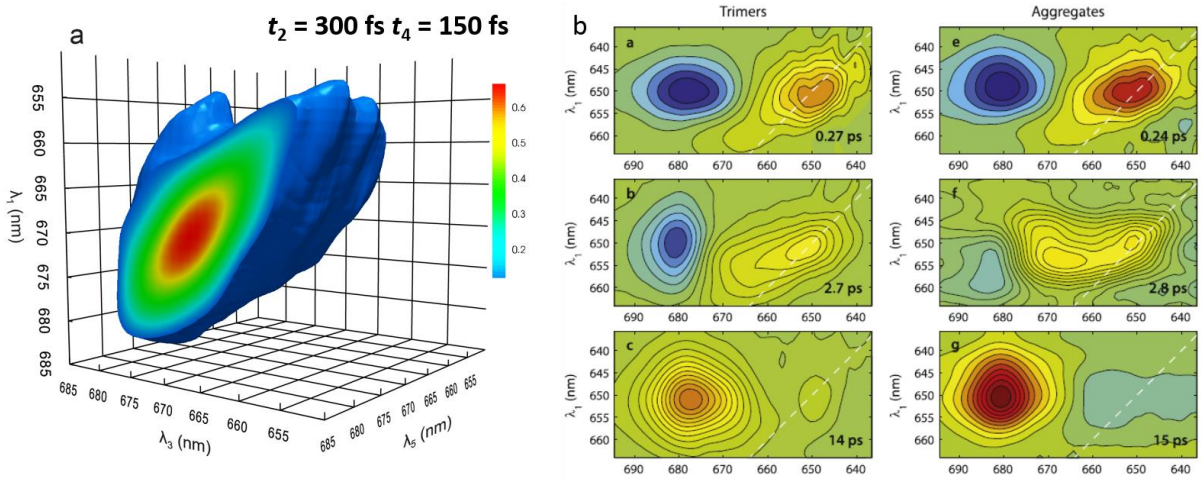

Fig.1 (a) 5th order 3D electronic spectrum of solubilized LHCII trimers at waiting/population times t_2 = 300 fs and t_4 = 150 fs. The off-diagonal feature is a direct observation of a two-step excitation energy transfer process. (b) 2D DAS of LHCII trimers (left column) and aggregates (right column) resulting from global lifetime analysis of a series of 2D spectra at t_2 from 150 to 800 fs with four exponential decay components (The longest decay component is not shown here). The decay lifetimes are indicated on the plots.

[1] K.L. Wells, P.H. Lambrev, Z. Zhang, G. Garab and H.-S. Tan, Phys. Chem. Chem. Phys. **16**, 11640 (2014).
[2] M.M. Enriquez, P. Ahktar, C. Zhang, G. Garab, P.H. Lambrev and H.-S. Tan, J. Chem. Phys. **142**, 212432 (2015).
[3] Z. Zhang, P.H. Lambrev, K.L. Wells, G. Garab, H.-S. Tan, Nat. Comm. **6**, 7194 (2015).