Two-dimensional electronic spectroscopy of biomimetic light-harvesting antennas

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The structural features that could support quantum phenomena in photosynthesis are quite difficult to unravel in complex biological light-harvesting systems. We designed self-assembling chromophore–peptide conjugates in order to mimic natural antennas and we followed their excitonic states dynamics with two-dimensional electronic spectroscopy.

Light-harvesting in photosynthesis is a touchstone in the lively research field devoted to demonstrate that quantum phenomena could affect biological events [1]. LH2 of purple bacteria is an astonishing example of how Nature designs protein scaffolds and arranges light-harvesters excitonically interacting [2]. The striking efficiency of energy transfer among the chromophores in the antenna complexes towards the reaction center aroused the hypothesis that quantum phenomena can affect the early stages of photosynthetic machinery. The leading spectroscopic technique to investigate and follow ultrafast excited state dynamics like energy transfer is two-dimensional electronic spectroscopy (2D-ES).

We designed model systems of light-harvesting complexes by self-assembling chromophore-peptide conjugates via tuning of the polarity of the solvent. The chromophores form an excitonic stack in the core of the aggregate, while the peptide component creates a scaffold that protects the hydrophobic excitonic part from the polar solvent. 2D-ES experiments revealed spectral signatures that are not detectable in the monomers alone and that are attributable to electronic coherences (Fig.1).

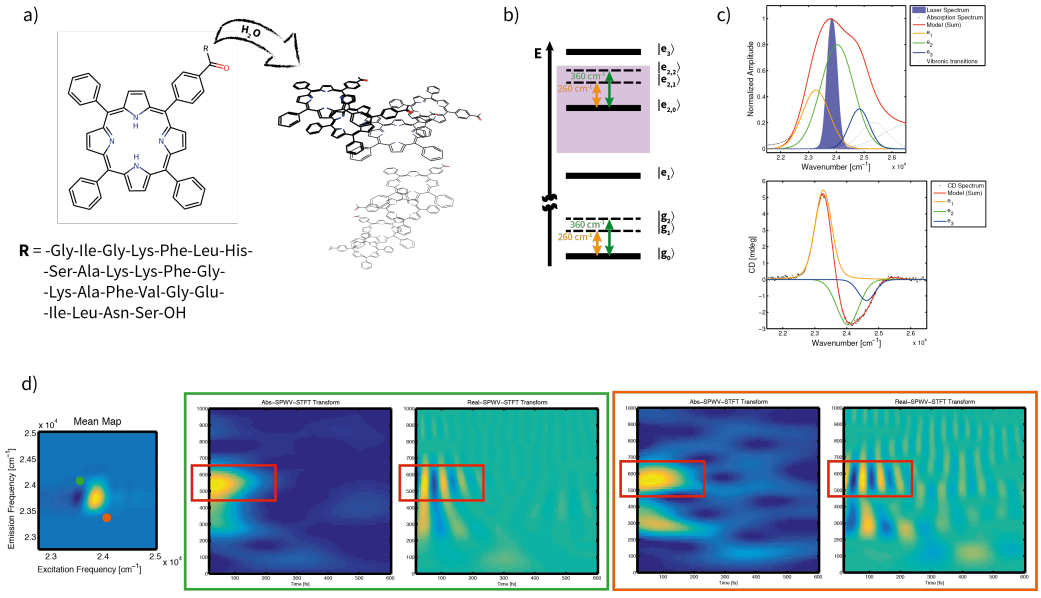

Fig.1 a) Structure of one of the chromophore-peptide conjugates. b) Energy levels diagram of the most relevant electronic and vibrational states of the system. The purple area denotes the spectral region investigated in 2DES. c) Comparison between the absorption spectra of the monomer (in MeOH) and the aggregate (in H_2O/MeOH 9:1 solution) at 295 K. Multi-Gaussian fits of the CD and absorption spectra of the aggregate are reported. In section d) a novel bilinear time-frequency representation is applied at coordinates (ω_1, ω_3) where electronic coherences $|e_1\rangle\langle e_2|$ and $|e_2\rangle\langle e_1|$ are expected and reveals short living beatings (highlighted in red) with ω_2 = 520 cm^{-1}.

[1] Engel, G. S.; Calhoun, T. R.; Read, E. L.; Ahn, T.-K.; Mančal, T.; Cheng, Y.-C.; Blankenship, R. E.; Fleming, G. R. *Science* **2007**, *446*, 782.

[2] Cherezov, V.; Clogston, J.; Papiz, M. Z.; Caffrey, M. *J. Mol. Biol.* 2006, *357*, 1605.