

# Electronic coherences in rhodamine dimers: vibronic coupling and distance dependence

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2D electronic spectroscopy experiments supported by theoretical modeling on rhodamines hetero-dimers characterized by different interpigment distances and electronic interactions have been performed to clarify the role of vibronic coupling in the coherent dynamics of the systems.

The relevance of quantum coherence in the energy migration within biological and artificial multi-chromophoric antenna systems is the object of a lively debate in the literature given the decisive implications that this may have to understand the biological process and engineer artificial materials. [1]. How the coupling with vibrations can prolong, sustain or destroy electronic coherences is still an open question. [2-3]. In this work supramolecular rhodamine heterodimers on a DNA scaffold were suitably engineered to mimic the basic donor-acceptor unit of light-harvesting antennas. Three samples have been designed and prepared, differing for the distance between the two rhodamines moieties. The comparison of the results obtained applying 2D photon echo spectroscopy (2DPE) to these three samples and to the corresponding monomeric forms [4] allowed isolating and identifying features attributable to the evolution of coherent superpositions of donor and acceptor states initially prepared by coherent excitation and contributing to the dynamics of the energy transfer process.[5] Through the support of high level *ab initio* TD-DFT computations of the entire dimer, we could establish that the vibrational modes preferentially optically accessed are not involved in non-adiabatic interactions with electronic transitions. It was thus possible to assess for how long an electronic coherence can survive in a large rigid supramolecular system once it has been created in a controlled manner.

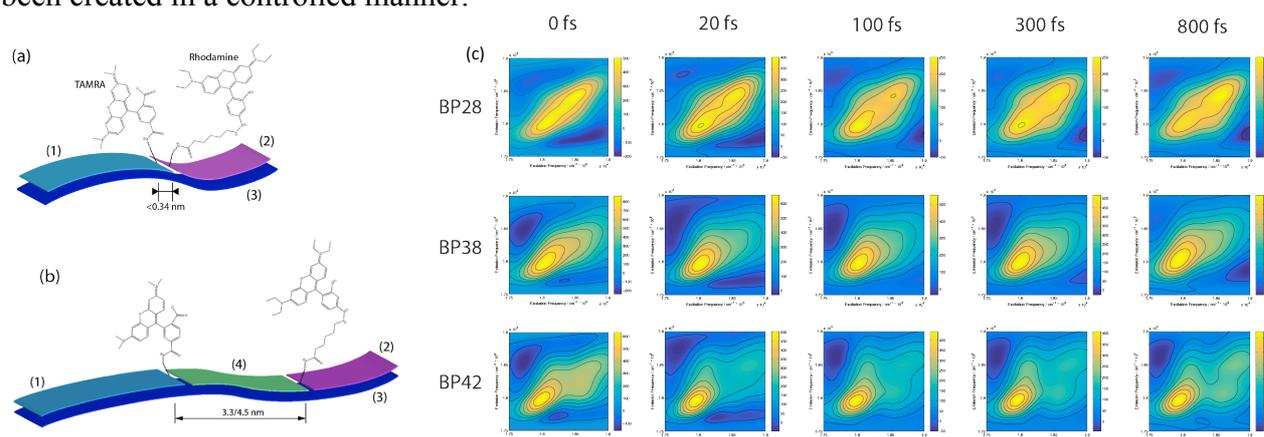


Fig. 1. Schematic representation of the studied species: (a) BP28 dimer and (b) BP38 and BP42 dimers. (c) Real rephasing experimental spectra at selected values of  $t_2$  for the three samples.

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