

## **Photodynamics of light harvesting molecules: energy transfer, localization, molecular scrambling and state-specific vibrations**

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**Abstract:** Solar energy conversion starts with the harvest of light, and its efficacy depends on the spatial transfer of the light energy to where it can be transduced into other forms of energy. Harnessing solar power as a clean energy source requires the continuous development of new synthetic materials that can harvest photon energy and transport it without significant losses.

Firstly, we investigate photoexcited dynamics and relaxation pathways in a variety of light-harvesting molecules using Non-Adiabatic Excited State Molecular Dynamics (NA-ESMD). We aim to achieve a detailed comprehension of the ultrafast intramolecular electronic and vibrational energy transfer that takes place after photoexcitation. Within our NA-ESMD framework[1], *direct* nonadiabatic molecular dynamics simulations can be applied to describe photoinduced dynamics in large organic conjugated molecules involving multiple coupled electronic excited states. Such NA-ESMD simulations are performed by combining the molecular dynamics with quantum transitions (MDQT) approach with “on the fly” analytical calculations of excited state energies, gradients, and non-adiabatic couplings terms.

With chemically-controlled branched architectures, dendrimers are ideally suited for light harvesting, since they consist of arrays of chromophores with relative positioning and orientations to create energy gradients and to spatially focus excitation energies. The spatial localization of the energy delimits its efficacy and has been a point of intense research for synthetic light harvesters. We therefore present results of combined theoretical experimental studies elucidating ultrafast electronic energy transfer on different phenylene-ethynylene dendrimers (PPE), leading to either unidirectional energy transfer onto an energy sink including an ultrafast collapse of the photoexcited wave function[2], and exciton self-trapping on different units including an ultrafast spatial scrambling among isoenergetic chromophore units[3]. Besides, the use of multiconfigurational Ehrenfest method[4] is discussed and compared to surface-hopping approach[4] in this kind of molecules.

Secondly, we study the internal conversion and vibrational relaxation processes in chlorophylls[5]. Excited state trajectories are analyzed in terms of the ground state equilibrium normal modes[6]. Our analysis of the time evolution of the average mode energies uncovers that only a small subset of the medium-to-high frequency normal modes actively participate in the electronic relaxation processes. These active modes are characterized by the highest overlap with the nonadiabatic coupling vectors (NACRs) during the electronic transitions. Further statistical analysis of the nonadiabatic transitions reveals that the electronic and vibrational energy relaxation occurs via two distinct pathways with significantly different time scales. Besides, we investigate excitation energy transfer and exciton localization dynamics in a chlorophyll dimer system at the interface of two monomers of light-harvesting complex II (LHCII) trimer. The energy relaxation occurs more efficiently in the dimer than the monomer. The strength of thermal fluctuations

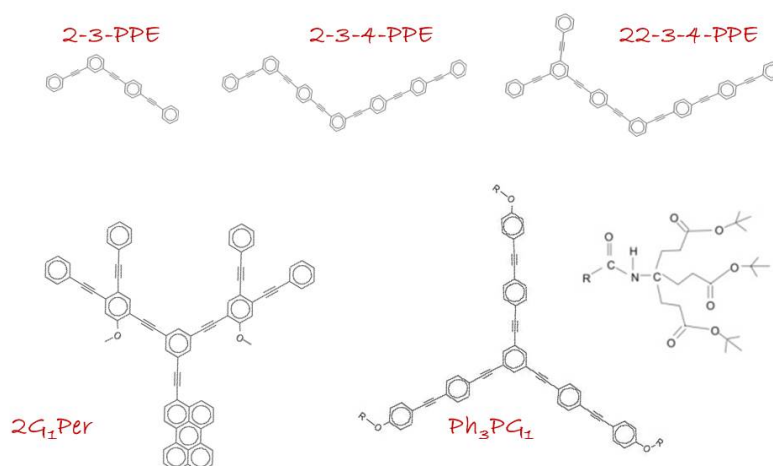


# XIX SBQT

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exceeds intraband electronic coupling between the states belonging to a certain band, producing localized states on the individual chromophores.



**Figure 1.** Models of PPE dendrimers

Therefore, time evolution of spatial electronic localization during internal conversion reveals transient trapping on one of the Chla monomers participating in the events of intermonomeric energy exchange. At the moment of quantum transition, the states become near-degenerate promoting Frenkel-exciton-like delocalization and inter-chromophore energy transfer. As energy relaxation occurs, redistribution of the transition density between two monomers leads to the final spatial scrambling of the exciton.

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