On the Excitation Energy Transfer Dependency on Pigment–Protein Interactions in the Fenna–Matthews–Olsen Complex.

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Most models of dissipative energy transfer in protein–pigment complexes assume that the local environments of each chromophore are identical, despite the often significant local differences in protein structure. In this contribution I will introduce the use of a model where chromophore excitation energies depend on their surroundings. The model is developed using results from ground state molecular mechanics simulations together with a partial charge difference calculation for the long–range contributions to the chromophore excitation energies fluctuations. The widely studied Fenna–Matthews–Olsen (FMO) [1, 2] "excitonic wire" protein–pigment complex is used as a benchmark system. I will show how the resulting chromophore dependent spectral densities, and the local differences in environmental fluctuations determined by these quantities, influence energy transfer processes in this system. In particular, the calculations reveal that chromophores that are close to the protein–water interface experience strongly dissipative environmental interactions characterized by solvent reorganization energies that can be as much as two–three times those of chromophores that are buried deep in the hydrophobic protein scaffolding. Using a linearized density matrix quantum propagation method [3] the inhomogeneous system–bath model obtained from the site–dependent spectral density calculations give results consistent with experimental dissipation and dephasing rates. [4]

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