

VIBRONICALLY MEDIATED EXCITON TRANSFER IN PERYLENE DIMERS

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Exciton transfer in molecular dyads depends critically on the spatial arrangement of donor and acceptor. Orthogonal perylene bisimide dimers exhibit transfer faster than expected from Förster theory. We show how the interplay of electronic dynamics with underdamped high frequency vibrational modes acts as a mechanism for fast transfer.

Small artificial systems that mimic key features of larger photosynthetic units are important benchmarks for new theoretical approaches to natural light harvesters. In our communication we focus on perylene bisimide dyads (PBD, see Fig. 1 (a)), a donor-acceptor system prepared in two different geometric arrangements, generously provided by Prof. H. Langhals. The parallel configuration implies a strong dipole-dipole coupling resulting in ultrafast transfer times, in perfect agreement with standard Redfield theory [1]. Orthogonally arranged dipoles however suggest uncoupled chromophores, yet unexpectedly fast excitation transfer was observed. Noise-assisted geometry modifications were invoked to explain such findings [2]. In our simulations we treat PBD as a vibronic dimer, [3] a model where the quantum dynamics of electronic transitions and high frequency vibrational modes are combined. We used absorption, fluorescence (Fig. 1 (b)), pump-probe spectra (Fig.1 (c) and two-dimensional electronic spectra to parametrize the model and show that it reproduces key features observed in experiments. In particular, the interplay between electronic and vibrational dynamics result in fast transfer even for weakly coupled chromophores, much faster than suggested by the standard Förster theory. Adding ab initio analysis of inter-molecular couplings we evaluate the role of the solvent in distorting the molecular arrangements dynamically, and the contribution of the linker molecule to an effective coupling between the donor and acceptor. In comparison to noise-assisted transfer [2], vibronic coupling predicts experimental transfer rates at realistic values of the coupling strength J , supported by quantum chemical calculations. In summary, we discuss vibronic coupling as a highly efficient transfer mechanism for bi-chromophoric systems.

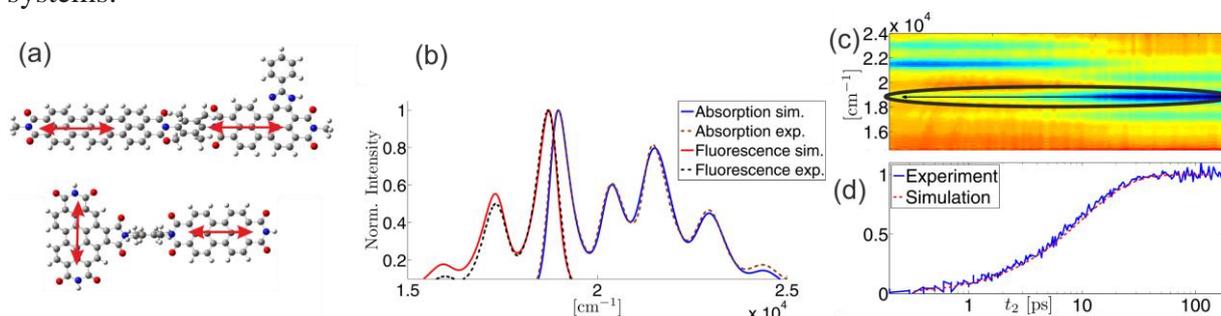


Fig. 1 (a) Parallel (top) and orthogonal (bottom) perylene subunits within the dimers. (b) Absorption and fluorescence from the orthogonal dimer and corresponding numerical fits. (c) Spectrally dispersed pump-probe signal (d) pump-probe data at the acceptor fluorescence peak (blue) in comparison to simulated dynamics (red).

References

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