

Photoinduced dynamics in weakly coupled equivalent chromophores

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Dendrimers are arrays of coupled chromophores, with the energy of each unit depending on backbone structure and conformation. Light harvesting and energy funneling properties are strongly dependent on their highly branched conjugated architecture. Herein, the photoexcitation and subsequent ultrafast electronic energy relaxation and redistribution of a first generation dendrimer (Ph₃PG-1)[2] is analyzed combining theoretical and experimental studies. Ph₃PG-1 consists of three linear phenylene-ethynylene (PE) units, or branches, attached in *meta* position to a central group opening the possibility of inter-branch energy transfer. Excited state dynamics are explored using either time-resolved spectroscopy and non-adiabatic excited state molecular dynamics simulations (NA-ESMD)[1]. Our results indicate a subpicosecond loss of anisotropy due to an initial exciton delocalization, induced by couplings among branches, followed by a random exciton self-trapping on different units. The absence of an energy gradient leads to an ultrafast energy redistribution among isoenergetic chromophore units. We observe final similar probabilities for each branch to retain significant contributions of the lowest excited-state electronic transition density. The observed unpolarized emission is attributed to the contraction of the electronic wavefunction in a single branch rather than corresponds to its expansion over the whole dendrimer.

On the other hand, NA-ESMD approach was applied to investigate photoexcited dynamics and relaxations pathways in a spiro-link conjugated polyfluorene at room (T=300K) and low (T=10K) temperatures. These dimeric aggregates consist of two perpendicularly oriented weakly interacting α -polyfluorenes oligomers. The negligible cou-

pling between the monomer chains results in an initial absorption band composed of equal contributions of the two lowest excited electronic states, each localized on one of the two chains. After photoexcitation, an efficient ultrafast localization of all the electronic population to the lowest excited state is observed on the timescale of about 100 fs. Both internal conversion between excited electronic states and vibronic energy relaxation on a single electronic state contribute to this process. Thus, photoexcited dynamics of the polyfluorene dimer follows two distinct pathways with substantial temperature dependence of their efficiency. One relaxation channel involves resonance electronic energy transfer between the monomer chains, whereas the second pathway concerns the relaxation of the electronic energy on the same chain that has been initially excited due to electron-phonon coupling. Our numerical simulations analyze the effects of molecular geometry distortion during the electronic energy redistribution and suggest spectroscopic signatures reflecting complex electron-vibrational dynamics.

References

- [1] "Nonadiabatic Excited-State Molecular Dynamics: Modeling Photophysics in Organic Conjugated Materials", T. Nelson, S. Fernandez-Alberti, A. Roitberg, and S. Tretiak, *Accounts of Chemical Research*, 47(4), 1155-1164 (2014)
- [2] Fude Feng, Seoung Ho Lee, Sevnur Kömürlü, Tracy D. McCarley, Adrian Roitberg, Valeria D. Kleiman and Kirk S. Schanze. *Conjugated Polyelectrolyte Dendrimers: Aggregation, photophysics and amplified quenching*. *Langmuir American Chemical Society* (2012).