Computational studies of nonadiabatic energy transfer in the 2G1-m-per dendrimer

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The ultrafast sub-picosecond intramolecular energy transfer dynamics of the poly-phenylene ethynylene (PPE) dendrimer 2G1-m-per is studied using the nonadiabatic excited-state molecular dynamics (NA-ESMD[1]) computer software. Dendrimers are synthetic macromolecules with branched repeating units, that are good mimic systems to study the efficient nonadiabatic energy transfer processes present in natural photosynthetic systems. NA-ESMD is a computational package that relies on the collective electronic oscillator (CEO[2]) and the molecular dynamics with quantum transitions (MDQT[3]). With the CEO, analytically calculated quantum mechanical potential is obtained using the AM1 hamiltonian. The fewest-switches surface hopping algorithm of MDQT is applied to treat the nonadiabatic processes. The results show that after a vertical 400 nm photoexcitation, the electronic populations follow cascading relaxation dynamics. Analyses of the transition density (TD) confirm that the excitation energy transfers from the periphery to the core via the unidirectional energy funnel. It is also observed that the TD transfers to the core localized mostly on one of the two G1 branches of the dendrimer. An interesting relationship between the S2 electronic state and the participation number for the carbon and oxygen atoms is observed as well.

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[1] *J Phys Chem B* **2011**, *115*, 5402

[2] *Chem Rev* **2002**, *102*, 3171

[3] *J Chem Phys* **1990**, *93*, 1061