Molecular Dynamics Study of Light-Harvesting Molecules with Electronic Transition

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Harvesting energy from sunlight is of paramount importance for the solution of the global energy problem, for which synthetic supramolecules such as light-harvesting dendrimers are attracting great attention. In these molecules, electronic excitation energy due to photoexcitation of antennas located on the periphery of the molecules is rapidly transported to the photochemical reaction centers at the cores of the molecules, which in turn perform useful work such as photosynthesis and molecular actuation [1]. Though such energy transfer is conventionally attributed to either dipole-dipole interactions (Forster mechanism) or the overlapping of donor and acceptor electronic wave functions (Dexter mechanism), atomistic mechanisms of rapid electron transport in these dendrimers remain elusive.

In order to identify atomistic mechanisms of rapid energy transport after photoexcitation of a light-harvesting dendrimer, we perform quantum-mechanical molecular dynamics simulations. To incorporate nonadiabatic electronic transitions, the fewest-switches surface-hopping (FSSH) method [2] along with the Kohn-Sham (KS) representation of time-dependent density functional theory (TDDFT) is used. The simulated system consists of a zinc-porphyrin core and a benzyl ether-type antenna. In the antenna, there are three aromatic rings connected by ether oxygen atoms, out of which one aromatic ring is directly connected to the zinc-porphyrin core. The periodic boundary condition is employed with a suprecell of dimensions $18 \times 18 \times 24$ Å$^3$, which is large enough to avoid the interaction between periodic images of the molecule.

Our simulation reveals the key role of thermal molecular motions that
significantly accelerate the energy transport based on the Dexter mechanism. An essential feature of the electronic structure to support the rapid electron transfer is the existence of unoccupied levels in the peripheries just above the unoccupied level in the core (LUMO+2), and that of occupied levels in the peripheries just below HOMO of the core. Crossings of these energy levels occur due to thermal fluctuation even in the ground state. When energy levels cross or approach each other, the wave function spreads over the entire molecule as shown in Figure 1(c) and 1(d).

Upon photoexcitation, the motion of aromatic rings connected by ether bonds enhances the lowering of the energy of the photoexcited state, thereby promoting such crossings further. We discuss the atomic mechanisms of energy transport in detail based on TDDFT-FSSH simulations.

**References**
