Ultra-fast Energy Transfer from Monomer to Dimer within a Trimeric Molecule

Using artificial system to model the photosynthetic process has been attracting intense research interests. Natural photosynthetic apparatus use very limited kinds of pigments to harvest the solar energy. To harvest more solar energy in a broader spectral region under the limited condition, nature adopts the strategy of pigment aggregation, for the aggregated pigments having a varied absorption spectrum depending on the aggregated pigment number, hence of the extended spectral region. The peripheral light-harvesting complex LH2 in the photosynthetic bacteria is a good example of illustrating such a strategy. Within the LH2 protein frame, there are two concentric bacterio chlorophyll (BChl) rings, one composed of monomeric BChl molecules absorbing at 800 nm, another of dimeric BChl molecules absorbing at 850 nm. Solar energy is transferred from the monomeric ring to the dimeric ring, i. e. , from the monomer to the dimer.

Dr. Li Xiyou's group in the Department of Chemistry, Shandong University, has designed a trimeric perylenetetracarboxylic diimide (PDI) molecule, with three PDI molecules covalently connected by a melamine. By molecular simulation, it was found that two of the three PDI molecules can assume a face-to-face conformation capable of forming a dimeric structure, while the third one appended acts as a monomer, which partially resembles the structural block in the LH2 complex. The existence of dimeric and monomeric structures within the trimer was further supported by the absorption spectroscopic and NMR evidences, while fluorescence measured revealed a possibility of energy transfer from the monomer to the dimer.

Dr. Weng Yuxiang's group in Beijing National Laboratory of Condensed Matter Physics, Institute of Physics of CAS investigated the energy transfer from the monomer to the dimer within the trimeric perylenetetracarboxylic diimide (PDI) molecule by using the femto-second time-resolved transient absorption spectroscopy, in cooperation with the former group. Based on the fact that the UV-visible absorption spectra for the monomer and dimer are overlapped, they proposed a monomer/dimer co-exciation model. By using the single value decomposition method, they resolved the individual absorption spectra of the transient species, and the decay dynamics were obtained by global fitting. Finally, they obtained a monomer to dimer energy transfer time constant of 0. 8 ps, very close to a similar process within the LH2 complex (0. 8—0. 9 ps). This work was published in *J. Am. Chem. Soc.* 2009, 131(1) pp. 30—31.

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