Theoretical study on excitation energy transfer in the light-harvesting complex

Masahiro Higashi[1,2]

[1]Department of Molecular Engineering, Kyoto University, Kyoto 615-8510, Japan
[2]JST, PRESTO, 4-1-8 Honcho, Kawaguchi, Saitama, 332-0012, Japan

In light-harvesting complexes, light energy absorbed by pigments are efficiently transferred to the reaction center of photosystems. The excitation energy transfer (EET) to the reaction center is known to proceed with nearly perfect quantum yield. To maximize the EET efficiency, the protein environment tunes the excitation energies of pigments, defined as the site energies, and their fluctuations, although the detailed mechanism is unknown. The Fenna−Matthews−Olson (FMO) complex is the first light-harvesting complex to be solved by X-ray crystallography and has extensively been studied both experimentally and theoretically. However, none of previous theoretical studies using molecular dynamics (MD) simulations combined with quantum mechanical and molecular mechanical (QM/MM) calculations cannot reproduce the experimental site energies and their fluctuations quantitatively. There are at least two problems in a conventional combination of MD simulations using MM force fields and QM/MM calculations. One is the accuracy of the QM calculation, and the other is the different accuracy of the potential energy surfaces of pigments calculated with the MM force fields and QM/MM methods. To solve the first problem, we have improved the description of excited-state electronic structures of pigment by optimizing the parameter of the CAM-B3LYP density functionals [J. Phys. Chem. B 118:10906–10918 (2014)]. Next, to solve the second problem, we have developed the molecular mechanics with Shepard interpolation correction (MMSIC) method to generate an accurate semi-global potential energy surface of pigment in condensed phase with low computational cost [J. Chem. Theory Comput. 12: 4128–4137 (2016)]. By solving these two problems, we can successfully reproduce the site energies and their fluctuations almost quantitatively. We find that the FMO complex consists of sites with heterogeneous fluctuations extending from fast to slow modulation. We also find that efficient EETs are facilitated by site-dependent fluctuations that enhance the resonance condition between neighboring sites with large site energy differences and circumvent exciton trapping on the pathway to the reaction center [J. Phys. Chem. B 123:9762–9772 (2019)]. Knowledge of site-dependent fluctuations is an important component of understanding optimization of EET in photosynthetic systems.