Modeling Charge Transfer States in Phycobilisomes

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Abstract

Phycobilisomes are giant (~6 MDa) light-harvesting pigment-protein complexes of cyanobacteria and certain algae, responsible for harvesting sunlight and regulating the flow of absorbed energy to provide the photochemical reaction centres with a constant energy throughput. Single-molecule spectroscopy studies have identified the presence of strongly red-shifted and quenched emission states and they were hypothesised to originate from charge-transfer states residing on phycocyanobilin pigments in the core of phycobilisomes. The quenched states were suggested to be an important, rapidly activated photoprotective mechanism to protect the organism against high solar illumination. An investigation into the molecular origin of these states, the role of the background charge, amino-acid residues around the pigments, and the geometrical configuration of the pigments requires the use of atomistic simulations involving a state-of-the-art QM/MM computational microscope. In this work, the ground-state geometries of the trimeric core units of phycobilisomes retrieved from *Synechocystis* PCC 6803 and *Synechococcus* PCC 7002 were optimized using Density Functional Theory (DFT) employing the CAM-B3LYP exchange-correlation functional together with the 6-31+G* basis set. Linear-response time-dependent DFT (TD-DFT) was used to calculate the excited-state geometries. The results demonstrated that the coupling between the energy states in TD-DFT spectra would serve as a screening tool as a charge transfer states in light-harvesting pigments. Accordingly, care should be taken in considering the natural transition orbitals (NTOs) for CTS analysis. Therefore, a complete analysis of charge transfers energies, hole-electron distance, NTOs, and optimized charge transfer states are needed to confirm the presence of charge transfer states. Amino acids around the D-ring of the bilin have a strong potential to serve as electron acceptor.