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MODELING OF INTER-CHLOROPHYLL COUPLINGS IN THE PHOTOSYNTHETIC FCP COMPLEX

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Photosynthesis has always been one of the most essential processes throughout the development of life on Earth and still has this crucial role today: it allows not only thousands of bacteria, algae and plants to exist but also the codependent animal species to survive. About the same amount of photosynthesis processes are carried out on land and in water, however, it is possible to find photosynthetic organisms in such extremes as deserts or 80 meters deep into the sea [1]. However, one of the most important, but oftentimes forgotten type of photosynthesis–carrying organisms are diatoms – microalgae comprising phytoplankton and accounting for nearly 20 % of global carbon dioxide fixation [2]. Moreover, diatoms have an exceptional light-harvesting complex, fucoxanthin-chlorophyll protein (FCP), which differs from the light-harvesting complex found in higher plants, as it has such chromophores as chlorophyll *c* and fucoxanthin, which guarantee light absorption in the blue-green visible region available in water. Nonetheless, the first crystallographic structure from *Pheodactylum tricornutum* diatom was identified only in 2019 [3], which can allow developing a more thorough theoretical understanding of FCP.

In this study, the Protein Database structure of FCP retrieved from *Phaeodactylum tricornutum* [3] was used to model the first excited state of chlorophylls (Chl) and use these results to determine their interaction energy. The first excited state of chosen Chl *a* and *c* pigments was modeled using TD-DFT level of theory with different functionals and basis sets. The best suited functional and basis set combination proved to be CAM-B3LYP/6-31G(d) and the phytyl tail of pigments was cropped as it had very little impact on transition dipole moment direction and its absolute value. Then first excited states of all of the chlorophylls from FCP were modeled with CAM-B3LYP/6-31G(d) at TD-DFT level and the transition dipole moments were calculated. The Chl *a* and *c* transition dipole moment ratio was found to be close to the expected value from experimental results: between 2.6 and 2.7, depending on chlorophyll *c* subtype. Then structural information about the alignment of pigments in the protein was used to model interaction of pigments applying point dipole approximation. These calculations indicate that the strongest interactions occur within the crystallographically determined Chl clusters: there is always at least one strong interaction between Chl *c* and *a* and within Chl *a* pair. The Förster energy transfer analysis showed that the inverse energy transfer rate is 1-5 ps in the same chlorophyll cluster, which is a result of strong interchromophore interactions. Moreover, these results also indicate fast energy transfer between chlorophyll *c* and *a*, which is a few picosenconds long and coincides with previous experimental results.

References

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