Insight Into the Spectral Tuning and Excited State Dynamics of Proteorhodopsin by QM/MM Simulation

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Retinal proteins are used for various biotechnological applications due to their favorable light-sensitive properties. These proteins have the retinal chromophore in common, however, the specific interaction with the altering protein environment can alter. The retinal-protein interaction can change the absorption maximum. The so called spectral tuning mechanism is responsible for covering a wide range of the visible spectrum. In this contribution we will focus on a particular member of this family, Proteorhodopsin (PR) and study it using hybrid quantum mechanics/molecular mechanics (QM/MM) simulations.

Proteorhodopsin is a photoactive proton pump found within marine bacteria which was first discovered in 2000.[1] PR has been suggested to play a large role in marine photoactivated processes due to their wide presence in marine life and their unique ability to absorb sunlight.[2, 3] PR has two major variants which exhibit an environmental adaptation in their absorption maximum to the ocean's depth. The green-absorbing PR (GPR, λ_{max} = 520 nm) is mainly found in microbes at the surface of water whereas the blue-absorbing PR (BPR, λ_{max} = 490 nm) is distributed at the deeper region in the ocean.[4] The amino acid at position 105 controls the color tuning of the two variants, where an L to Q substitution causes a ~25 nm green to blue color-shift in addition to affecting the geometric properties of the retinal chromophore.[5–7] We investigated the green-blue shift using QM/MM simulations. The L to Q mutation produces a positive electrostatic interaction near C14-C15 of retinal, which in turn destabilizes the S_1 state explaining the spectral shift.

Following the light absorption the retinal chromophore is undergoing a photoisomerization. We have studied also this process in PR. QM/MM simulations showed an increased steric interaction between the hydrogen at the C14 of the isomerizing bond and the hydroxyl group at the neighbouring tyrosine 200. This interaction plays an important role in the outcome of the photoisomerization.

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