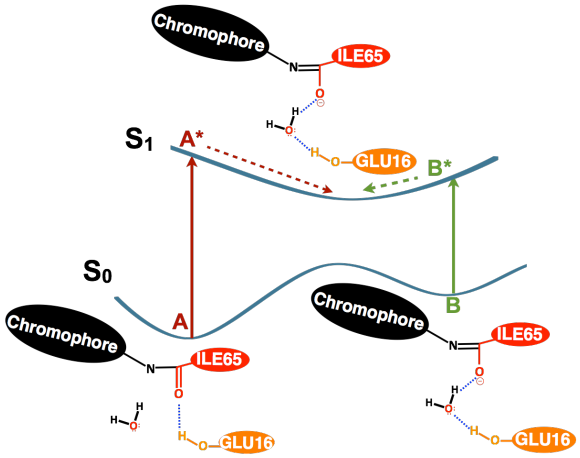
On the nature of an extended Stokes shift in mPlum fluorescent protein

Shirin Faraji

University of Groningen, Theoretical Chemistry, Zernike Institute for Advanced Materials, 9747 AG, Groningen, The Netherlands

E-mail: s.s.faraji@rug.nl

Far-red fluorescent proteins (FPs) enable deep-tissue in vivo imaging [1]. Combination of FPs with large and small Stokes shifts can be used in single-excitation/dual-emission multicolor applications. The atomic-level understanding of excited-state relaxation causing Stokes shift is still incomplete, which hinders the design of new FPs with desired properties. Our recent study [2] using the state-of-the-art hybrid quantum mechanics/molecular mechanics (QM/MM) scheme revealed that the large Stokes shift observed in mPlum is due to the excited-state relaxation of the chromophore and the flexibility of its hydrogen-bond network. The following amino acids pay the most important role: ILE65 and GLU11. The MD simulations reveal two ground-state populations with *direct* (Chro…ILE65…GLU11) and *water-mediated* (Chro…ILE65…Wat231…GLU11) hydrogen bond patterns. In the excited state, both populations relax to an emitting state with *water-mediated* (Chro…ILE65…Wat231…GLU11) hydrogen bond pattern.



The most recent time-resolved experimental findings reported two relaxation times for mPlum: 4 and 71 ps [3-4]. In this presentation the nature of the fluorescence response function of mPlum chromophore will be explored by means of excited-state *ab initio* molecular dynamics (AIMD) simulations. A quantitative description of the experimentally observed relaxation time-scales will be provided.

References

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