光機能性蛋白質にみられるカラーチューニング機構に関する理論的研究

Color Tuning Mechanism in Photofunctional Proteins: A SAC-CI Theoretical Study

Jun-ya Hasegawa

Department of Synthetic Chemistry and Biological Chemistry, Graduate School of Engineering, Kyoto University

The present talk summarizes some recent SAC-CI theoretical studies on the photoabsorption spectral tuning mechanism in photobiological systems [1-5]. The role of light is roughly classified into the energy resource and the information. In the former case, green plants and some bacteria have the photosynthetic units in which the photon energy is efficiently converted into the chemical energy [1]. In the latter case, since light is defined by spectrum (wavelength and intensity), controlling photo-absorption energy is essential for photo-functional proteins in our vision, plants, and some bacterial ion pumps. Fluorescent proteins have got significant attention in the field of molecular imaging. It is therefore very important to investigate how these proteins control the excitation energies of the chromophore included.

In our recent studies, SAC-CI calculations successfully reproduced the absorption energy of various retinal proteins, and the color-tuning mechanism was clarified for rhodopsin, bacteriorhodopsin, sensoryrhodopsin, and visual cone pigment [2]. For the emission from fluorescent proteins, role of protein environment was investigated [3]. For firefly luciferin, the yellow-green luminescence had long been recognized as the fluorescence from the enol-oxyluciferin. A recent experiment and our calculations suggested that keto-oxyluciferin can produce the yellow-green luminescence with the help of the protein environment [4].

Depending on the protein environments, some chromophores, retinal and oxyluciferin for examples, significantly change their photoabsorption energies. On the basis of our theoretical analysis, we found a common feature in the character of the electronic transitions and the protein electrostatic environment. On the basis of the proposed color-tuning mechanisms, we also performed theoretical mutagenesis [4].

References

[1] J. Hasegawa and H. Nakatsuji, “Exploring Photo-Biology and Bio-Spectroscopy with the SAC-CI (Symmetry-Adapted Cluster-Configuration Interaction) Method”, in “Radiation Induced Molecular Phenomena in Nucleic Acid: A Comprehensive Theoretical and Experimental Analysis”, Ed., by M. Shukla and J. Leszczynsk, pp. 93-124, Springer, 2008; M. Ehara, J. Hasegawa, H. Nakatsuji, “SAC-CI Method Applied to Molecular Spectroscopy”, in "Theory and Applications of Computational Chemistry: The First 40 Years, A Volume of Technical and Historical Perspectives", Ed. by C. E. Dykstra, G. Frenking, K. S. Kim, and G. E. Scuseria, pp. 1099-1141, Elsevier, Oxford, 2005.

[2] K. Fujimoto, S. Hayashi, J. Hasegawa, and H. Nakatsuji, “Theoretical Studies on the Color-Tuning Mechanism in Retinal Proteins”, J. Chem. Theo. Comp. vol. 3, pp. 605-618, 2007; K. Fujimoto, J. Hasegawa, S. Hayashi, and H. Nakatsuji, “On the color-tuning mechanism of Human-Blue visual pigment: SAC-CI and QM/MM study”, K. Fujimoto, J. Hasegawa, S. Hayashi, and H. Nakatsuji, Chem. Phys. Letters, vol. 432, pp. 252-256, 2006; K. Fujimoto, J. Hasegawa, H. Nakatsuji, “Origin of color tuning in human red, green, and blue cone visual pigments: SAC-CI and QM/MM study”, Chem. Phys. Letters, vol. 462, pp. 318-320, 2008; K. Fujimoto, J. Hasegawa, and H. Nakatsuji, to be submitted.

[3] J. Hasegawa, K. Fujimoto, B. Swerts, T. Miyahara, H. Nakatsuji, “Excited States of GFP Chromophore and Active Site Studied by the SAC-CI method: Effect of Protein-environment and Mutations”, J. Comp. Chem., vol. 28, pp. 2443-2452, 2007.

[4] N. Nakatani, J. Hasegawa, H. Nakatsuji, J. Am. Chem. Soc. 129, 8756-8765 (2007); N. Nakatani, J. Hasegawa, and H. Nakatsuji, submitted.