3Tp04

Protein-Driven Photoisomerization Reaction of Proteins

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Introduction

The photoactive yellow protein (PYP) was discovered in 1985 and its X-ray structure was reported in 1995. There has been a growing interest in PYP, which is a small water-soluble globular protein containing 125 amino acid residues. The photoisomerization of PYP triggers the photocycle, which is essential for the negative phototactic response to blue light. The photoisomerization reaction of PYP is a good model system for the study of the structure-function relationship of the protein for the following reasons: (1) the 3D structure of PYP is determined at a high atomic resolution. (2) and its ultrafast reaction process can be completely traced by a computer simulation. (3) the features of the photoisomerization in the native PYP are strikingly different from the reaction of the *p*-coumaric acid chromophore in solution environments. This means that the microenvironment of the *p*-coumaric acid in the native PYP plays a significant role in the efficient photoisomerization reaction. To elucidate the structure-function relationship of PYP as an efficient photosensory protein, we used computational methods. The contribution of each atom, namely, *the partial atomic driving force,* was quantitatively evaluated by the atom-by-atom separation of the driving force for the reaction. With the aid of computer graphics, the constituent atoms are labeled in different colors

PYP chromophore structure

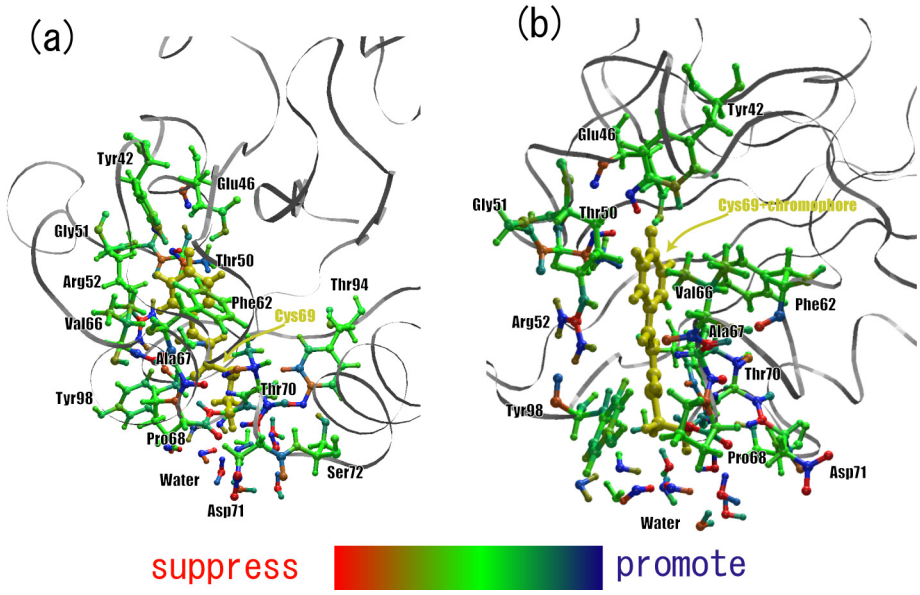
The photoisomerization reaction of the chromophore takes place at the C7=C8 bond. Then, how does the protein environment control the photoreaction of PYP? To study this problem, we calculated the bond-twisting force using a hybrid Quantum Mechanical/Molecular Mechanics method. We found that the force was largest at the C7=C8 bond among all of the backbone bonds of the *p*-coumaric acid. Furthermore, we separated the force, which is acting immediately after light illumination, into different contributions from (1) the internal component of the chromophore itself, and the chromophore-protein interaction. As a result, we found that the latter was much greater than the former. These observations imply that the ultrafast, bond-selective photoisomerization of PYP is driven by the protein-chromophore interaction during the initial stage of the reaction.

Partial atomic driving force

To understand the photoisomerization mechanism of PYP, we separated the bond-twisting force at the C7=C8 bond into different contributions from the constituent atoms of PYP. It should be noted that the ten different conformations of PYP taken from the molecular dynamics trajectory exhibit force profiles strikingly similar to each other. This observation implies that the photoisomerization mechanism of PYP is strongly conserved during the thermal fluctuation of the protein.

Structure-function relationship at a glance

To understand the photoisomerization mechanism of PYP, we drew a color picture of the molecule. Each atom is shown in different colors depending on their different contributions to the bond-twisting force at the C7=C8 bond. We observed that the functionally important atoms are localized around the chromophore. As a result of this analysis, we revealed the reaction mechanism of PYP.



Functional atoms hunt. To find functionally important atoms, the constituent atoms are shown in different colors depending on their partial atomic driving forces for the photoisomerization reaction. The functionally important atoms with a large positive (negative) partial atomic driving force are shown in blue (red), while atoms with small partial atomic driving force are shown in green.