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Chromophore structure in a long-lived intermediate of heliorhodopsins: switching of a hydrogen bonding partner of protonated Schiff base

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Abstract

Heliorhodopsin (HeR) is a novel class of retinal proteins discovered in 2018 [1]. HeR contains an all-*trans*-retinal as a chromophore, which is covalently bound to a lysine residue through a protonated Schiff base linkage. Although amino acid sequences of HeR are largely different from those of type-1 rhodopsins, a family of HeR shares the seven-transmembrane helix motif. Photoexcitation of the all-*trans*-retinal chromophore results in isomerization to a 13-*cis* form. This isomerization initiates a photocycle involving a series of intermediates, which are similar to those observed for type-1 rhodopsins. HeR has a long-lived intermediate in its photocycle, which is named the O intermediate, suggesting that the function of HeR is light sensing. In order to understand the functional role of the O intermediate, we investigated the chromophore structure in two HeRs, HeR 48C12 and *T. archaeon* HeR, using time-resolved resonance Raman spectroscopy.

We measured resonance Raman spectra of the O intermediate of the two HeRs in H₂O and D₂O (Figure 1). The observed spectra of the O intermediate of the both HeRs showed that the chromophore configuration is 13-*cis* and 15-*anti* and that the polyene chain around the Schiff base is distorted. A comparison of frequencies and bandwidths of the C=N stretch bands of the O intermediate in H₂O and D₂O solutions indicated that the Schiff base is protonated and hydrogen-bonded to a water molecule. The latter feature is in contrast to that the hydrogen bond partner is amino acid residue in the unphotolyzed state [2]. Therefore, it is likely that the protein structure around the Schiff base is much altered in the transition from the O intermediate to the unphotolyzed state. This alternation may be a reason for the long lifetime of the O intermediate, which is essential to signal transduction.

Fig. 1: Resonance Raman spectra of HeRs. Traces (a) and (b) show the spectra of O intermediate of HeR 48C12 in H₂O and D₂O, respectively. Traces (c) and (d) show the spectra of O intermediate of *T. archaeon* HeR of O intermediate in H₂O and D₂O, respectively.

Keywords: rhodopsin, retinal chromophore, resonance Raman spectroscopy

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