Light energy conversion

Elucidation of the pumping mechanism of light-driven proton-pumping proteins

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Abstract

In living organisms, energy conversion and material transport occur via proton concentration gradients across membranes. These gradients are established by proteins that actively transport protons, known as proton pumps. Some microorganisms have been found to use outward-facing proton pumps that utilize light energy to transport protons from the cell interior to the exterior. Recently, a protein that inwardly transports protons, in opposition to conventional proteins, has been discovered and garnered considerable attention, despite sharing a similar three-dimensional structure. Nevertheless, the mechanism of inward proton transport remains unclear. We observed the structural changes of the retinal chromophore in schizorhodopsin 4, an inward proton pump, and determined that the sequence of the structural changes is reversed compared to that of conventional proteins, which allows for the transportation of protons in the opposite direction.

Background & Results

We employed time-resolved resonance Raman spectroscopy to observe the structural changes in the retinal chromophore of schizorhodopsin 4. The conventional proton pumps undergo isomerization upon light absorption, deprotonation of the Schiff base, followed by reprotonation, and finally reisomerization. This is shown in Figure 2 (left). However, our study on schizorhodopsin 4 indicates that reisomerization and subsequent reprotonation take place after the deprotonation of the Schiff base (Figure 2, right). Most notably, the sequence of reisomerization and reprotonation is reversed. Additionally, this difference can explain why schizorhodopsin 4 pumps protons in the opposite direction to conventional proton pumps. Conventional proton pumps release protons following photoisomerization of Schiff bases towards the cytoplasmic medium. However, transportation of the protons to the extracellular medium is necessary, and it is believed that the negatively charged amino acid residues on the extracellular side of the chromophore attract the proton released from the Schiff base. The Schiff base that has lost the proton maintain their orientation and accepts a proton from the cytoplasmic medium. Finally, the Schiff base faces extracellular medium upon reisomerization. Schizorhodopsin 4 releases a proton to cytoplasmic medium after the Schiff base is flipped upon isomerization. Then, the chromophore is subsequently reisomerized. The Schiff base is oriented towards the extracellular medium, receiving protons from extracellular medium. Accordingly, the proton transport mechanism has been found to be highly rational for the inward proton transport.

Significance of the research and Future perspective

The results of this study indicate that the sequence of structural changes of the chromophore has an influence on the direction of proton transport. This finding is expected to facilitate the understanding of the principle of proton transport and promote the molecular design of proton pumps by revealing and analyzing the mechanisms of other inward-directed proton pumps.

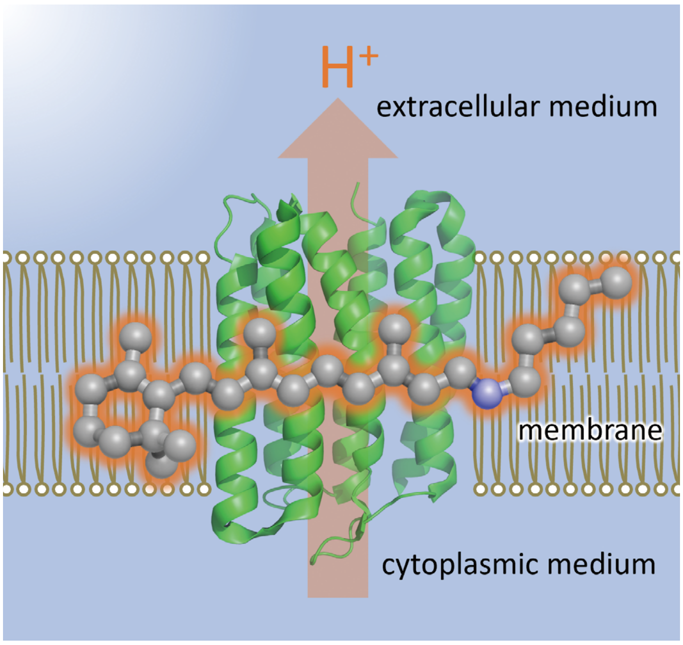

Figure1

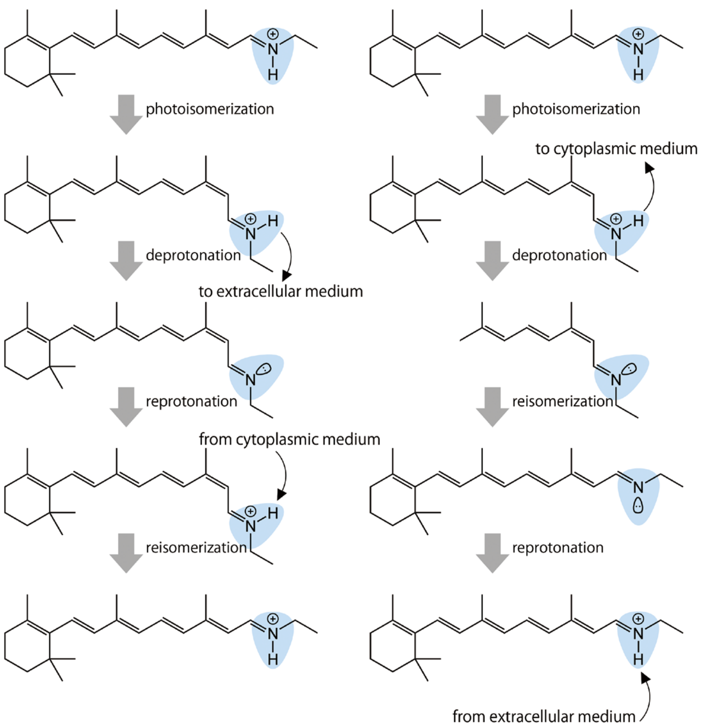

Figure2

Patent

Treatise Hayashi, Kouhei; Mizuno, Misao; Mizutani, Yasuhisa et al. Cis-Trans reisomerization precedes reprotonation of the retinal chromophore in the photocycle of schizorhodopsin 4, Angew. Chem. Int. Ed. 2022, 61, e202203149. doi: 10.1002/anie.202203149

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