Unique structure of the retinal chromophore enabling sodium ion transport in the sodium ion-pumping protein KR2

Mizutani, Yasuhisa

2020

Mizutani, Y. (2020). Unique structure of the retinal chromophore enabling sodium ion transport in the sodium ion-pumping protein KR2. Proc. Of the 7th Asian Spectroscopy Conference (ASC 2020). doi:10.32655/ASC_8-10_Dec2020.22

<https://hdl.handle.net/10356/144239>

https://doi.org/10.32655/ASC_8-10_Dec2020.22

© 2020 Nanyang Technological University.

Downloaded on 26 Apr 2023 15:25:52 SGT

Unique Structure of the Retinal Chromophore Enabling Sodium Ion Transport in the Sodium Ion-Pumping Protein KR2

Yasuhisa Mizutani

*Department of Chemistry, Graduate School of Science, Osaka University,
1-1 Machikaneyama, Toyonaka, Osaka 560-0043, Japan*

E-mail: mztan@chem.sci.osaka-u.ac.jp

Abstract

Active ion transport across membranes is vital to maintaining the electrochemical gradients of ions in cells and is mediated by transmembrane proteins. Photoexcitation of some microbial rhodopsins leads to ion transport across membranes. They contain all-*trans*-retinal as a chromophore, which is covalently bound to a lysine residue through a protonated Schiff base linkage and surrounded by seven transmembrane α helices. Absorption of a photon results in the chromophore isomerization and leads to a cyclic reaction. To reveal mechanism in ion pumping, it is essential to elucidate sequential changes in the chromophore structure in a photocycle. Resonance Raman spectroscopy enables us to examine the evolution of the structural changes of the retinal chromophore and the protein moiety.[1-7]

We conducted a comprehensive time-resolved resonance Raman spectroscopic study of the structures of the retinal chromophore during the photocycle of the sodium ion pump *Krokinobacter* rhodopsin 2 (KR2).[3] The protein functions as a light-driven outward sodium ion pump across the cell membrane to generate an electrochemical potential gradient. We succeeded in determining the structure of the chromophore in the unphotolyzed state and in the K, L, M, and O intermediates, by overcoming the problem that only a small fraction of the M intermediate is accumulated in the KR2 photocycle. The Schiff base in the retinal chromophore forms a strong hydrogen bond in the unphotolyzed state and in the K, L, and O intermediates, and is deprotonated in the M intermediate. Formation of this strong hydrogen bond facilitates deprotonation of the Schiff base, which is necessary for the sodium ion to move past the Schiff base. The polyene chain in the chromophore of KR2 is twisted in all the states of the photocycle: the portion near the Schiff base is largely twisted in the unphotolyzed state and in the K intermediate, whereas the middle portion of the polyene chain becomes largely twisted in the L, M, and O intermediates. During the photocycle, the twisted structure of the polyene chain and the strong hydrogen bond at the Schiff base are advantageous for transient relocation of the Schiff base proton. The obtained resonance Raman data clarified the unique structural features of the KR2 chromophore, which are not accessible by other methods.

Keywords: time-resolved resonance Raman spectroscopy, light-driven ion pumps

References:

- [1] M. Mizuno and Y. Mizutani, In *Recent Progress in Colloid and Surface Chemistry with Biological Applications*, American Chemical Society: **2015**; Vol. 1215, pp 329-353.
- [2] Y. Mizutani, *Bull. Chem. Soc. Jpn.*, **2017**, 90, 1344.
- [3] N. Nishimura, M. Mizuno, H. Kandori, and Y. Mizutani, *J. Phys. Chem. B*, **2019**, 123, 3430.
- [4] A. Otomo, M. Mizuno, M. Singh, W. Shihoya, K. Inoue, O. Nureki, O. Bj, H. Kandori, Y. Mizutani, *J. Phys. Chem. Lett.*, **2018**, 9, 6431.
- [5] T. Shionoya, M. Mizuno, T. Tsukamoto, K. Ikeda, H. Seki, K. Kojima, M. Shibata, I. Kawamura, Y. Sudo, and Y. Mizutani, *J. Phys. Chem. B*, **2018**, 122, 6945.
- [6] K. Sato, T. Yamashita, H. Ohuchi, A. Takeuchi, H. Gotoh, K. Ono, M. Mizuno, Y. Mizutani, S. Tomonari, K. Sakai, Y. Imamoto, A. Wada and Y. Shichida, *Nature Commun.*, **2018**, 9, 1255.
- [7] M. Mizuno, Y. Shimoo, H. Kandori, Y. Mizutani, *Struct. Dynam.*, **2019**, 6, 054703.