Molecular mechanism of vision

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The retinal protonated Schiff-base (RPSB) in its all-trans form is found in bacterial rhodopsins, whereas visual rhodopsin proteins host 11-cis RPSB. In both cases, photoexcitation initiates ultrafast sub-picosecond isomerization of the retinal chromophore, leading to proton transport, storage of chemical energy or signaling. At the same time, the isolated RPSB exhibits much slower excited-state decay, in particular, in its all-trans form.

By using a combination of ultrafast time-resolved action-absorption spectroscopy and high-level electronic structure theory, we disclose the ways, by which the photoinduced dynamics of isolated RPSB can be both significantly accelerated and, most notably, steered. The excited-state decay is rendered from a slow picosecond to ultrafast sub-picosecond in the synthetically engineered locked retinal chromophore (L-RSB), becoming as fast as inside the evolutionary optimized retinal-binding protein pocket. Moreover, the unidirectional full rotation of L-RSB from all-trans to 9-cis and from 9-cis to all-trans proceeds in two distinct photoinduced steps, both of which are ultrafast.

As a result, we get a rotary molecular motor, which addresses most, if not all, current challenges in the design principles of molecular motors featuring a double-bond axle. Furthermore, we introduce a theoretical model for interpreting experimental results on gas-phase retinal isomerization in the ground electronic state. We redefine the experimental value and show that the ground-state isomerization barrier of RPSB is as high as in the protein environment. This work is supported by the RSF (project no. 22-13-00126).