

A Novel Conformation of PYP Caused by a Vibrational Marker

Jianping Wang*, Pengyun Yu, and Fan Yang

Beijing National Laboratory for Molecular Sciences; Molecular Reaction Dynamics Laboratory, Institute of Chemistry, Chinese Academy of Sciences, Beijing, 100190, P. R. China, Beijing 100190, P. R. China, *jwang@iccas.ac.cn

Upon the binding of a ruthenium carbonyl complex to photoactive yellow protein, large conformation of the protein occurred, as evidenced by several steady-state spectroscopic methods. Ultrafast local structural dynamics of the newly formed conformation were characterized by ultrafast 2D IR spectroscopy.

Novel infrared probes possessing very unique vibrational frequencies and structural sensitivities have often been used as a very important tool for studying local structures and dynamics of proteins. For obvious reasons the ideal case is that the labeling of such vibrational markers does not or only minimally perturbs the structure of proteins. However, this is not always the case- sometime large and interesting conformation occurs as a consequence of the labeling.

In this work, a tricarbonylchloro-glycinato-ruthenium^{II} complex successfully binds to photoactive yellow protein M100A [1] at two separated locations in the form of ruthenium dicarbonyl, which stabilizes the protein at a unique conformation highly resembling its signaling state (the so-called pB state). UV-Vis, CD, linear IR and 2D IR methods were used to characterize the resultant conformation and its local structural dynamics in the two binding sites (Fig. 1).

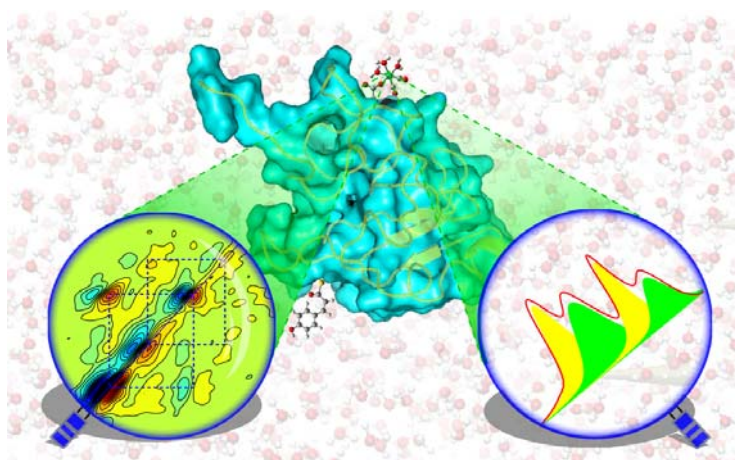


Fig. 1. Linear IR and 2D IR spectra of the ruthenium dicarbonyl complex bound to photoactive yellow protein M100A. Two different binding sites were observed, which show two pairs of C≡O stretching modes in the linear IR spectrum (red curve): the asymmetric stretching (as) and symmetric stretching (ss) C≡O modes at one site in two yellow-shaded peaks, and those at another site in two green peaks. The frequency positions for the four IR peaks are 1952, 1979, 2032, and 2059 cm^{-1} (from left to right) for the as_1 , as_2 , ss_1 , and ss_2 components of the dicarbonyl at two binding sites respectively. Four diagonal peaks and their corresponding pair-wised cross peaks (between as_1 and ss_1 and between as_2 and ss_2 respectively) in the 2D IR spectrum are observed and are in agreement with the assignment of the linear IR spectrum.

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