Signal Transduction on the Nanosecond Time Scale: Early Structural Events in the Photocycle of a Xanthopsin

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Photoactive yellow protein (PYP) is a member of the xanthopsin family of eubacterial blue light photoreceptors. On absorption of light, PYP enters a photocycle that ultimately transduces the energy contained in a light signal into an altered biological response. Time-resolved x-ray crystallography was used to determine the structure of the short-lived, red-shifted, intermediate state denoted [pR], which develops within 1 ns after photoelectronic excitation of the chromophore of PYP by absorption of light. Laue data with nanosecond time resolution was collected at white beam station ID-9 at the ESRF. A structural model was built to account for several features in the |F1ns| - |Fdark| difference Fourier map. This model shows that the [pR] state possesses the cis conformation of the 4-hydroxyl cinnamic thioester chromophore, and that the process of trans to cis isomerization is accompanied by the specific formation of new H-bonds that replace those broken upon excitation of the chromophore. Regions of flexibility that comprise the chromophore binding pocket serve to lower the activation energy barrier between the dark state, denoted pG, and [pR], and help initiate entrance into the photocycle. The combination of new H-bonds and steric hinderance in the [pR] structure serve to explain why the chromophore does not simply undergo immediate thermal relaxation down to the pG state, and hence why PYP has a high quantum yield of entrance into the photocycle. This study provides direct structural evidence for the initial processes of transduction of light energy, ultimately into a physiological signal.