Novel Photodynamics in Phytochrome & Cyanobacteriochrome Photosensory Proteins¹

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The photodynamics of recently characterized phytochrome and cyanobacteriochrome photoreceptors are discussed. Phytochromes are red/far-red photosensory proteins that utilize the photoisomerization of a linear tetrapyrrole (bilin) chromophore to detect the red to far-red light ratio. Cyanobacteriochromes (CBCRs) are distantly related cyanobacterial photosensors with homologous bilin-binding GAF domains, but exhibit greater spectral diversity. The excited-state mechanisms underlying the initial photoisomerization in the forward reactions of the cyanobacterial photoreceptor Cph1 from Synechocystis, the RcaE CBCR from Fremyella diplosiphon, and Npr6012g4 CBCR from Nostoc punctiforme were contrasted via multipulse pump-dump-probe transient spectroscopy. A rich excited-state dynamics are resolved involving a complex interplay of excited-state proton transfer, photoisomerization, multilayered inhomogeneity, and reactive intermediates, and Le Chatelier redistribution. NpR6012g4 exhibits a high quantum yield for its forward photoreaction (40%) that was ascribed to the activity of hidden, productive ground-state intermediates via a “second chance initiation dynamics” (SCID) mechanism.

¹This work was supported by a grant from the Chemical Sciences, Geosciences, and Biosciences Division, Office of Basic Energy Sciences, Office of Science, United States Department of Energy (DOE DE-FG02-09ER16117).