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Novel Photodynamics in Phytochrome & Cyanobacteriochrome Photosensory Proteins[1]

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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.

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