EXCITATION ENERGY TRANSFER AND PHOTOREGULATORY MECHANISMS IN INTACT PHYCOBILISOMES USING TWO-DIMENSIONAL ELECTRONIC SPECTROSCOPY

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The phycobilisome is the principal light-harvesting chromoprotein complex in cyanobacteria and red algae. We have employed broadband multidimensional electronic spectroscopy with 6.7-fs laser pulses for the first time to study the excitation energy transfer mechanisms in intact phycobilisomes isolated from *Fremyella diplosiphon*. The results show that excitation energy transfer pathways include delocalized optical excitations of bilin (linear tetrapyrrole) chromophores, which transfer excitation energy along the rods in $<$600 fs. Excitation energy moves more slowly from the rods to the core on the $>$10 ps time scale, indicating that excitation energy is localized on individual bilin chromophores in the allophycocyanin-containing segments of the phycobilisome. The intramolecular charge-transfer character of the β84 chromophore in allophycocyanin would strongly favor dynamic exciton localization upon transfer of excitation energy from the rod segments. This phenomenon contributes to a kinetic bottleneck, which allows photoregulatory mechanisms, including that involving binding of the orange carotenoid protein, to operate efficiently in the core. In phycobilisomes isolated from *Fremyella diplosiphon* grown under red light, in contrast to those grown under white light, the terminal emitting APC680 segments exhibit significantly shorter excited-state lifetimes. These findings further show that trapping bilin sites are accumulated in the core of the phycobilisome during growth as part of a chromatic adaptation response.

(Work supported by grant awards DE-SC0010847 (W.F.B. laboratory) and DE-SC0020606 (C.A.K. laboratory) from the Photosynthetic Systems program of the Office of Basic Energy Sciences, U.S. Department of Energy.)