ULTRAFAST DYNAMICS AND ANIONIC ACTIVE STATES OF COFACTOR FLAVIN IN CRYPTOCHROME AND PHOTOLYASE

YA-TING KAO, CHUANG TAN, JIANG LI, LIJUAN WANG, DONGPING ZHONG, *Chemistry, and Biochemistry, Programs of Biophysics, Chemical Physics, and Biochemistry, The Ohio State University, Columbus, Ohio, 43210*.

Flavoproteins perform a variety of important biological functions using different redox states of flavin cofactor. We report here our systematic studies of the dynamics of four redox states of the flavin cofactor in both photolyases and insect Type 1 cryptochromes. With femtosecond resolution, we observed ultrafast photoreduction of oxidized state in subpicosecond and of neutral radical semiquinone in tens of picoseconds through intraprotein electron transfer mainly with a neighboring conserved tryptophan triad. Such ultrafast dynamics excludes their potential role as functional states. In contrast, we find that the anionic semiquinone and hydroquinone have longer lifetimes that are compatible with high-efficiency intermolecular electron transfer reactions. In photolyases, the excited active state has a long (nanosecond) lifetime optimal for DNA-repair function. In insect Type 1 cryptochromes known to be blue-light photoreceptors the excited active form has complex deactivation dynamics on the time scales from a few to hundreds of picoseconds, which is believed to occur through conical intersection(s) with a flexible bending motion to modulate the functional channel. These unique properties of anionic flavins suggest a universal mechanism of electron transfer for initial functional steps of the photolyase/cryptochrome blue-light photoreceptor family.