ULTRAFAST SOLVATION DYNAMICS OF FLAVODOXIN IN THREE OXIDATION STATES

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We report here the complete characterization of the dynamic solvation processes at the FMN binding site of flavodoxin in three oxidation states. The local solvation dynamics of flavodoxin are investigated by examining the fluorescence transients and time-resolved emission spectra of the prosthetic FMN chromophore. Our results show a great difference between these three oxidation states. In oxidized state, the solvation processes is featured by a multi-exponential decay in 1 ps, 28 ps, and 670 ps. The solvation rate significantly slows down in semiquinone state due to the presence of the hydrogen bond between the N(5)H of FMN and the backbone carbonyl oxygen of G61. In hydroquinone state, the solvation rate is similar to that in the oxidized state, but with much larger stabilization energy. This result was supported by our MD simulations in which we observed more polar environment of FMN binding site in hydroquinone state due to the more water entry into the pocket through the repulsion between the negative charged flavin cofactor and nearby residues.