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Novel femtosecond photoreactions in flavo-enzymes

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In exceptional cases, flavo-enzymes perform functional light-driven catalysis, such as in fatty acid photodecarboxylase (FAP) [1]. Yet most display light-independent functions, although in these photophysical processes also occur. Such processes can have photoprotective functions, and may also be exploited for photocatalysis or photoswitching applications [2]. This contribution highlights recent ultrafast spectroscopic studies on short-lived photoproducts in "nonphotoactive"flavoproteins exploring various redox and ligation states. They include the discovery of two hitherto unknown photoreactions that occur on the timescale of a few hundred femtoseconds or less.
First, we observed quasi-instantaneous (<100 fs) photo-oxidation of anionic flavin radicals in various flavoprotein oxidases, and subsequent charge re-separation in a few tens of picoseconds [3]. We will show that such a non-functional photoreaction also occurs in FAP, where it surprisingly involves hydrated electron intermediates.
Second, we studied the charge-transfer complex formed by the flavin ring system and the substrate-analog inhibitor methylthioacetate in monomeric sarcosine oxidase [4]. Here, upon population of the photo-excited CT state, with near-unity quantum yield a state spectroscopically identical to the non-complexed enzyme is formed in ~300 fs in a barrierless process. This implies that all CT interactions are vanished on this timescale. The initial CT complex is subsequently recovered in a strongly thermally activated way on the nanosecond timescale. These are properties of a highly efficient red-absorbing photoswitch. The possible ultrafast structural changes associated with this unprecedented process are discussed, as well as new in-depth characterizations of the process, and possible extensions of this system (the characteristics of which have recently been shown to be highly sensitive to the structural details of the system [5]), for practical applications [6].

References

1. A. Aleksandrov; A. Bonvalet; P. Müller; D. Sorigué; F. Beisson; L. Antonucci; X. Solinas; M. Joffre; M.H. Vos, Angew. Chem. Int. Ed. 2024, 63, e202401376.
2. B. Zhuang; U. Liebl; M.H. Vos, J. Phys. Chem. B 2022, 126, 3199.
3. B. Zhuang; R. Ramodiharilafy; U. Liebl; A. Aleksandrov; M.H. Vos, Proc. Natl. Acad. Sci. U.S.A. 2022, 119, e2118924119.
4. B. Zhuang; M.H. Vos, J. Am. Chem. Soc. 2022, 144, 11569.
5. B. Zhuang; G. Ran; W. Zhang; F. Gai, Chem. Sci. 2025, in press.
6. B. Zhuang; U. Liebl; M.H. Vos; M. Sliwa, ChemPhotoChem 2025, e202500012.

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