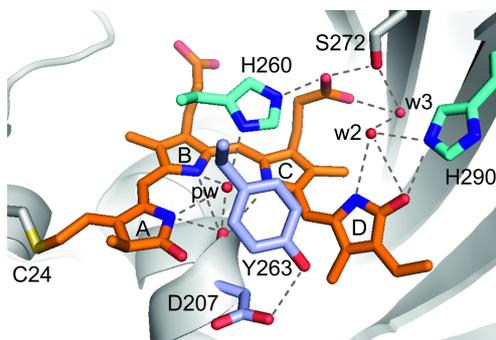


## BILIVERDIN RADICAL FORMATION IN BACTERIOPHYTOCHROME PROTEINS

H. Lehtivuori<sup>1</sup>, E. Maximowitsch<sup>2</sup>, H. Takala<sup>3</sup>, N. V. Tkachenko<sup>4</sup>, T. Domratcheva<sup>2</sup> and J. A. Ihalainen<sup>5</sup>

<sup>1</sup>University of Jyväskylä, Nanoscience Center, Department of Physics, Jyväskylä, Finland, <sup>2</sup>Max Planck Institute for Medical Research, Department of Biomolecular Mechanisms, Heidelberg, Germany, <sup>3</sup>University of Jyväskylä, Nanoscience Center, Department of Biological and Environmental Sciences, Jyväskylä, Finland, <sup>4</sup> University of Helsinki, Institute of Biomedicine, Anatomy, Helsinki, Finland, <sup>5</sup>Tampere University of Technology, Department of Chemistry and Bioengineering, Tampere, Finland  
email: heli.lehtivuori@jyu.fi

Phytochromes control a multitude of reactions. It is a photoreceptor, a pigment that plants, and some bacteria and fungi, use to detect light. It is sensitive to light in the red and far-red region of the visible spectrum. Phytochrome photocycle between red and far-red sensing state starts with excitation of the biliverdin molecule. The decay of the red excited state occurs through one of three competing processes: (i) fluorescence [1,2], (ii) photoproduct (signaling), and (iii) non-radiative. Up to date, both signaling and non-radiative pathways of the excited states are undefined [2]. Thereby, detailed knowledge on the ultra-fast timescale photodynamics is vital for understanding the signaling mechanism of phytochromes.



By utilizing ultra-fast transient absorption spectroscopy and quantum-chemical methods, we demonstrate the charge transfer states being central in the excited state decay processes of the phytochromes [3]. We probed experimentally in a hitherto unexplored near-infrared spectral region, providing insight about the photoinduced radical formation of the biliverdin. The quantum chemical calculations indicate at least two electron transfer processes between biliverdin molecule and amino acid side chains. This study elucidates the origin of the complex excited-state decay processes and serves as a basis for the future studies of the signaling processes in phytochromes. In addition, the identified charge transfer pathways offer a new strategy in increasing fluorescence yield of phytochromes [1].

[1] H. Lehtivuori, S. Bhattacharya, N. M. Angenent-Mari, K. A. Satyshur, and K. T. Forest, *Front. Mol. Biosci.* **2**, 65 (2015)

[2] J. A. Ihalainen, H. Takala and H. Lehtivuori, *Front. Mol. Biosci.* **2**, 75 (2015)

[3] H. Lehtivuori, E. Maximowitsch, H. Takala, N. V. Tkachenko, T. Domratcheva and J. A. Ihalainen, *manuscript under preparation*