CHARLES UNIVERSITY PRAGUE
faculty of mathematics and physics

Prague, January 18, 2016

Subject: Supervisor's Review of Ph.D. Thesis of David Paleček

The Ph.D. thesis of David Paleček deals with the employment of methods of optical spectroscopy to investigation of excitation energy transfer and quenching in natural photosynthetic systems as well as their artificial analogues proposed for light harvesting. The joint Ph.D. studies were conducted at Faculty of Mathematics and Physics of the Charles University in Prague, the Czech Republic and the Chemical Center of Lund University, Sweden under supervision of prof. Donatas Zigmantas.

The part of research taking place in Prague focused on usage of low-temperature spectroscopy of high spectral resolution (hole-burning spectroscopy and fluorescence line narrowing) to study excitation quenching in artificial bacteriochlorophyll aggregates mimicking the light harvesting systems of photosynthetic green sulfur bacteria. The research confirmed the role of quinones in redox-dependent excitation quenching, however, weaker than in the natural light harvesting complexes. The results suggested that the quenching mechanism involves also the higher excitonic states and that the quenching competes with the ultrafast excitonic relaxation.

The cutting-edge experimental equipment for multidimensional electron spectroscopy at the Lund University was used to study primary processes of excitation energy transfer in reaction centers of photosynthetic purple bacteria. The thesis describes a journey from discovery of coherences lasting longer than the lifetimes of the excited states to the feasible explanation of their vibrational origin by proposing a new form of mechanism of excitation transfer. The explanation disproves former beliefs of the electronic nature of the coherences since the proposed mechanism of Energy Transfer-Induced Coherence Shift (ETICS) preserves the coherence of vibrational states.

The thesis starts with two chapters providing an overview of the studied systems and the two-dimensional electron spectroscopy. The fourth chapter summarizes the main results of the work, the principle of the newly proposed mechanism of ETICS. The individual results are presented as reprints of three articles published in prestigious scientific journals and five manuscripts. Overall, the thesis is of a high scientific value and meets or even exceeds the requirements for Ph.D. thesis.

David Paleček mastered the both extremely demanding experimental techniques during his study. Moreover, he mastered also the interpretation of the two-dimensional spectroscopy data, which requires a detailed understanding of the theoretical foundations of the experimental method.

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David Paleček demonstrated the ability of independent scientific work, a critical evaluation of the obtained results and their presentation at a high level. In my opinion, David Paleček fully deserves award of the Ph.D. degree.

doc. RNDr. Roman Dědic, Ph.D.