Report on the Habilitation Thesis of RNDr. Šimon Budzák, PhD.

The presented Habilitation Thesis consists of a relatively short part (51 pages including the list of 110 references) written in Slovak and an impressive collection of 13 scientific articles coauthored by Dr. Budzák in 2014-2020. The articles were published in the very top international scientific journals including Chemical Science, Angewandte Chemie, Journal of the American Chemical Society etc. All articles have gone through a through the peer review process and there are no doubts as to the high quality of scientific research done by Dr. Budzák. Most of the published works were done in collaboration with experimentalists, which can be challenging for a computational chemist. Besides being an expert in his own field, he must have deep understanding of the subject in general and possess good communication skills. Judging by the success of his collaboration, Dr. Budzák meets all necessary requirements.

In the main text the author presents his view on the fascinating field of photochemistry and describes his own contribution to the area. The content of the work includes the list of used notations, introduction, the goals of the habilitation thesis, a chapter devoted to the physical and chemical aspects of the interaction of molecules with light, an overview of available quantum-chemical methods used in photochemistry, a summary of the results of his work, and conclusions. From the first pages of the Introduction, starting with the 6000-year old history of using dyes and the beginning of photochemistry as a science towards the end of the previous century, then describing the progress made in the last 20-30 years, he keeps the reader captivated.

In the next chapter, he explains the physics of photochemical processes. He gives a comprehensive picture of photochemical phenomena. His explanations are clear, complete and not overburden by unnecessary details. In the overview of computational methods employed in photochemistry he covers the area from the semi-empirical approaches still in use to post-Hartree-Fock methods (up to CC), with DFT and its modifications lying in-between. In the space of just a few pages he manages not only to describe the methods themselves but also analyze their advantages and disadvantages for photochemistry. Computational tools for simulation of solvent effects are portrayed in a separate subsection.

The part summarizing the results of author's works is the longest in the thesis. The high level of the presented research has been addressed above. Here I would like to comment on the quality of presentation. As everywhere else in the thesis, the explanations are relatively short, clear and comprehensive. In this chapter the author shares his fascination with photochemistry and his enthusiasm is infectious.

The submitted Habilitation Thesis is an exceptionally well-written work. It demonstrates the high level of the author as a scientist, his deep understanding of the subject and his great skills as a story-teller. He is able to clearly explain complex concepts with minimal words while remain rigorous and keeping his audience captivated. All these are excellent qualities for teaching students. The candidate satisfies all the requirements needed for

habilitation in Theoretical and computational chemistry and the thesis is excellent. It can be accepted as the base for the habilitation procedure. I suggest that after successful defense Dr. Budzák can be granted the title "Associate professor in Theoretical and computational chemistry" (docent v odbore „Teoretická a počítačová chémia").

Without doubting the quality of the presented work, I suggest the following questions for the discussion:

1. When describing "spin-flip" DFT methods, you indicated the possibility of high spin-contamination. Can you comment on whether it is typical for a particular type of DFT functionals (GGA, hybrids etc.) or it is common for all of them? Does it depend on the class of molecules (light-element compounds, transition-metal complexes etc.)?
2. CAS-based methods: Did you ever encounter problems with the convergence of the results with respect to the size of the active space?
3. Can you comment on the role of relativistic effects, both scalar and spin-orbit, in photochemistry?
4. When spin-orbit effects are involved, spin-forbidden transitions are no longer forbidden. What is your view on the potential use of the now-available relativistic TD-DFT methods in photochemistry?

In Bratislava, 27.1.2022 Olga Malkin, DrSc.