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Review of the PhD thesis „Theoretical investigation of Light-Driven Electron Transfer in Molecular Photosensitizers" by Aoussaj Sbai

The PhD dissertation entitled *"Theoretical Investigation of Light-Driven Electron Transfer in Molecular Photosensitizers"* was prepared by Aoussaj Sbai under the supervision of Prof. dr hab. Julien Guthmuller at Gdansk University of Technology.

The dissertation investigates the photophysical properties of boron-dipyrromethane (BODIPY) derivative systems used as molecular light-harvesting units, employing advanced quantum-chemical simulations. The primary objective of the work was to elucidate how electron-transfer pathways affect the efficiency of energy conversion processes. This research topic is of considerable scientific importance due to the growing global demand for efficient renewable-energy technologies capable of reducing carbon dioxide emissions while meeting the increasing energy needs of modern society.

The most significant achievement of the dissertation is the comprehensive theoretical characterization of the electronic and photophysical mechanisms governing BODIPY-based photosensitizers for hydrogen production and light-harvesting applications. The work successfully demonstrates how substituents, solvent effects, charge-transfer states, and triplet-state formation influence photocatalytic efficiency and excited-state dynamics. An important contribution of the thesis is the combination of advanced quantum-chemical methods with detailed photophysical analysis to verify the proposed research hypotheses and identify the key factors controlling non-radiative decay and electron-transfer processes. The dissertation also

provides a systematic evaluation of computational approaches, particularly TDDFT-based vibronic models, and assesses their reliability in reproducing experimental spectra and photophysical behavior. The obtained results provide valuable guidelines for the rational design of more efficient and stable organic photosensitizers for renewable-energy technologies, especially in the fields of photocatalytic hydrogen evolution and photovoltaic applications.

The thesis was prepared in a conventional form as a classical dissertation comprising eight chapters. Chapter 1 provides a general introduction, presenting the scientific background, motivation, and objectives of the research, together with the hypotheses formulated for the study. Chapter 2 describes the physicochemical properties of BODIPY dyes and their derivatives. Chapter 3 presents the theoretical foundations of the quantum-chemical methods applied in the investigation of the structural, electronic, and photophysical properties of BODIPY dyes. The chapter discusses the fundamental concepts of quantum mechanics, the Born–Oppenheimer approximation, Hartree–Fock theory, density functional theory (DFT), and time-dependent density functional theory (TDDFT). In addition, it describes solvation models and photophysical processes such as absorption, emission, intersystem crossing, and electron-transfer dynamics. This chapter constitutes a comprehensive theoretical introduction to the computational methods employed throughout the dissertation.

Chapters 4–7 contain the original research results obtained by the PhD candidate, whereas Chapter 8 summarizes the most important findings and outlines perspectives for future studies based on the presented results. Chapter 4 focuses on the computational investigation of neutral BODIPY dyes used as photosensitizers for hydrogen production. The chapter analyzes the singlet and triplet excited states of the dyes and examines how solvents and different substituents, such as OH and NO_2 groups, influence their electronic and photophysical properties. Particular attention is devoted to relaxation pathways and electron-transfer mechanisms, determining whether the investigated systems efficiently promote hydrogen evolution or undergo deactivation processes.

Chapter 5 presents computational studies of reduced BODIPY dyes and investigates their electronic and photophysical properties. The chapter examines spin-density distribution, the influence of different exchange–correlation functionals, and the effects of substituents and solvent environments on the energy levels of the reduced compounds. Furthermore, it discusses the optimization of excited-state geometries and analyzes how these factors affect photoinduced electron transfer and the efficiency of hydrogen-production systems.

Chapter 6 is devoted to the photophysical properties of the BOD-Ph compound and to the evaluation of different computational vibronic-coupling methods. Theoretical absorption and

emission spectra obtained using the adiabatic Hessian (AH) and vertical Hessian (VH) models are compared with experimental data. The chapter also analyzes radiative and non-radiative rate constants, including internal conversion and intersystem crossing processes, in order to determine which computational approach provides the most accurate description of the photophysical behavior of the studied system.

Chapter 7 investigates down-conversion materials used in semitransparent perovskite solar cells by means of TDDFT calculations. The chapter analyzes the electronic structure as well as the absorption and emission properties of selected down-conversion layers in order to identify the factors influencing their photovoltaic performance. The theoretical results are compared with experimental data to evaluate the efficiency of these materials and their potential applications in renewable-energy technologies.

The results presented in Chapters 4–7 are of considerable importance because they provide a detailed theoretical understanding of the electronic and photophysical processes governing the efficiency of BODIPY-based photosensitizers and related energy-conversion materials. The studies clarify how substituents, solvent effects, excited-state dynamics, and electron-transfer pathways influence light-harvesting efficiency. A particularly valuable and innovative aspect of the dissertation is the comprehensive investigation of both neutral and reduced BODIPY systems using advanced quantum-chemical approaches combined with detailed photophysical analysis. The research hypotheses concerning the role of substituents, charge-transfer states, vibronic effects, and triplet-state formation in controlling photocatalytic activity were systematically verified by means of TDDFT and high-level electronic-structure calculations. Another important contribution is the comparative evaluation of different vibronic-coupling models and their capability to reproduce experimental spectra and non-radiative processes. The obtained results provide valuable guidelines for the rational design of new organic photosensitizers characterized by improved stability, longer-lived excited states, and enhanced photocatalytic activity. Moreover, the comparison of different computational approaches allows the identification of the most reliable theoretical methods for predicting photophysical behavior, which is highly relevant for future studies in photocatalysis, photovoltaics, and renewable-energy applications. The results obtained by Aoussaj Sbai have already been published in two scientific papers, including articles in the journals Phys. Chem. Chem. Phys. 26 (2024) 25925, and ACS Applied Materials & Interfaces, 16 (2024) 6352.

The dissertation contains a substantial number of cited references as well as a well-prepared list of abbreviations, both of which significantly facilitate the reading of the thesis.

The work appears to be theoretically and computationally very solid; nevertheless, several potential shortcomings and limitations may be identified:

1. Most of the results are based on the quantum-chemical calculations, whereas the experimental validation appears relatively limited. This may restrict the full verification of the theoretical predictions in real photocatalytic systems.
2. The analysis mainly concerns selected BODIPY derivatives. Although this enables an in-depth investigation of the underlying mechanisms, it limits the broader generalization of the conclusions to other classes of organic photosensitizers.
3. The author points out that different exchange–correlation functionals lead to different energetic and spectroscopic results. Consequently, some conclusions may depend on the particular computational methodology adopted in the study.
4. The chapter devoted to quantum-chemical methods is very extensive and, at times, resembles a textbook presentation. For some readers, this may disturb the balance between the theoretical introduction and the discussion of the original scientific results.

While reading the dissertation, several questions and comments arose:

1. Why were the geometries of the BODIPY derivatives optimized using the B3LYP functional, despite the well-known tendency of this functional to underestimate certain interatomic bond lengths?
2. What were the main criteria for selecting the exchange–correlation functionals employed in the TDDFT calculations? How can the variations in the vertical excitation energies (VEE) presented in Table 4.1, depending on the computational method used, be explained? These differences are not trivial and cannot be fully justified solely on the basis of standard DFT/ab initio methodology considerations.
3. In the first paragraph on page 67, the author states: *"For the T1 triplet state, ... the results show that MN15 provides the best agreement, with a deviation of about 0.2 eV."* It is not entirely clear to which reference values these deviations were compared. What experimental or theoretical data served as the benchmark for this analysis?
4. Why are the radiative decay constants (k_r) reproduced relatively well, whereas the internal conversion rates (k_{IC}) are not, even when experimental ΔE values are taken into account?
5. In Chapter 7, why was a different solvent employed compared with the systems discussed in the previous chapters? Additionally, which computational methodology was applied in these calculations?

6. In Chapter 7, the photoconversion efficiency of the DPABA and TPETPA molecules was investigated in solution and compared with experimental data. How would the photophysical activity of these molecules be affected if the TFEVE polymer matrix were explicitly taken into account?

The dissertation is generally well written and demonstrates a good command of scientific English. However, several editorial and stylistic issues can be noticed throughout the text. Some sentences are overly long and syntactically complex, which reduces readability and clarity. For example, the sentence *"This value is approximate since it is assumed that vibrational, rotational, or collisional deactivation..."* is grammatically correct, but stylistically a more natural formulation would be: *"This value is only an approximation because ..."*. Overall, the above critical comments and questions do not affect my positive assessment of the dissertation.

Conclusions

In my opinion, the doctoral dissertation submitted by Ms. Aoussaj Sbai fulfills the customary scientific standards as well as the formal requirements specified in the Polish Act on Higher Education and Science (Dz. U. 2018, poz. 1668, with the later amendments). Therefore, I recommend that Ms. Aoussaj Sbai be admitted to the subsequent stages of the doctoral procedure.

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