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POLITECHNIKA GDAŃSKA BIURO RADY DZIEDZINY NAUKOWEJ NAUKI ŚCISLE	
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Podpis	.....

Wrocław, 28. 04. 2026

The referee report on doctoral dissertation of Mr. Aoussaj Sbai under the title “Theoretical investigation of Light-Driven Electron Transfer in Molecular Photosensitizers”.

The discovery of MODIPY dyes characterized by exceptional fluorescence properties led to their wide application as effective markers. The demand for renewable and clean solar energy also correlates with these compounds as sensitizers and solar light harvesting tools important for different solar energy technologies. The presented doctorate dissertation by PhD Candidate Aoussay Sbai proves His ambitions to be part of endeavors towards enrichment of present knowledge leading the practical use of solar power.

The little review on BODIPY (Chapters 1 and 2) indicates that light-driven water splitting systems offer a sustainable and pollution free energy source, and the idea of a water splitting by employing dye-sensitized photocatalysts stands behind studies performed by Candidate. Artificial photosynthesis is probably a major approach which can overcome fossil fuel dependency, especially in the form of light-driven hydrogen evolution for solar fuel production. The initial absorption of (sun)light and the supply of photoelectrons by the photosensitizer is essential for any further applications in a solar energy conversion. Other possibilities including DSSC solar cells also exist and are subject of an extensive research. The theoretical support of the field is needed since the progress in efficient technologies of acquisition of solar energy is far from being satisfying. The quantum chemical modeling may provide a real help in the design of solar energy applications by providing missing physical and chemical data enhancing ideas on processes taking place. Determined consistent (experimental and theoretical) thermodynamic, structural and spectroscopic data can provide the proper start for the further modeling and more important for a rational design. The presented review constitutes a loose collection of general information, without structures and reaction schemes

potentially taking place e.g. in the H<sub>2</sub> production. Presented detailed data do not form the consistent logical essay friendly for a potential reader.

The presented research goals (subchapter “Research goals”) are clear, ambitious and well defined, although seem to promise to much.

The chapter “Literature Review on Quantum Methods” is probably the longest part of the dissertation and covers more than one hundred years of quantum mechanics and quantum chemistry. The most of the material is already available in academic books and hard work invested by Author in probably not needed, especially that Candidate has not contributed to the development of presented concepts. However, often adopted QC approaches are based on particular assumptions and selected ones need to be justified and at least detailed warnings should be included in the report for potential users of produced data. The extended experience accumulated by Candidate could be very useful for His followers would be materialized in the written form. The formal law requirement that “The doctoral dissertation presents the candidate's general theoretical knowledge in the discipline and the ability to conduct independent scientific work” referee may judge based on Candidate’s actual scientific work.

The Author’s own research contribution to actual knowledge on solar energy related science is presented in four paragraphs. Two sister ones are related to “Computational Investigation of ... a) Neutral and b) Reduced BODIPY Dyes”. The philosophy behind studies is approximately expressed as “... dye chromophores require a thorough understanding of the underlying electronic states ...” in processes of interest. In short, the studies are performed for single molecules or anions in the gas phase and DCM solvent. The systems examined include iodine substituted BODIPY dyes differing by their substituents (-phenyl, -phenylOH and -phenylNO<sub>2</sub>) at the meso position of the BODIPY core (BOD). The properties of interest are related to electronic excited states: singlets and triplets for molecules and doublets for their reduced form. The logic of the presentation is unclear. The reported data is restricted to electronic transition diagrams what makes reading of dissertation difficult. The collection of information resulting from computations being already in hands of Candidate includes extended data on chemical structures, electron density distribution and structure of wavefunction which are critical for the interpretation of experimental findings and for building own concepts on physics and chemistry being observed. The corresponding publication (ref. 162), which has already passed through tough editorial reviewing process, covers little part of available material. The presented study is focused mostly on methodological

comparison of two theoretical approaches (TDA)-TDDFT and DLPNO-STEOM-CCSD), the generalization of findings however is restricted due to a very small training set. Drown conclusions are rather modest, however fit in the framework of assumed “Research goals”. The available literature on electronic excited states properties of BODIPY dyes is reach and the presented material constitutes original contribution to it.

The Chapter 6, according to its title “Photophysical properties for BOD-Ph” presents very detailed studies on simulation of absorption and emission spectra  $S_0$  to  $S_1$  taking into account different models of vibronic-coupling. The very systematic and detailed study is focused on methodological approaches and more important, drown conclusions may provide useful tips when such studies are performed.

The last research chapter provides theoretical support for the search for efficient dawn-conversion materials for perovskite solar cells. The theoretical studies are performed for single molecules PDABA and TPETPA which are important due to their down-conversion capabilities and subsequent application in PSCs. In cooperation with experimental partners theoretical findings are already published (Ref. 188). The computations were carried out according to present standards of theory and provide information on properties of electronic states. The results agree reasonably with experimental findings. More important in the conclusion section of the publication Authors confirms the importance of theoretical part stating that “...The TDDFT calculations effectively estimated the vertical transitions between the singlet excited state  $S_0 \leftrightarrow S_1$  and the associated Stokes shifts, revealing that the molecular environment significantly influences the spectral properties of the down-conversion films.” Since the geometry of the ground state is not reported the referee wonders if the N center is planar?

The “Summary” included at the end of dissertation is informative, detailed and precise. It states that “various quantum-chemical approaches were employed to assess the photoinduced electron-transfer mechanism in three BODIPY dyes. Actually, the list of dyes includes BOD-Ph and its two derivatives BOD-PhOH and BOD-PhNO<sub>2</sub>. The ”Summary” emphasizes rather methodological character of work (QC approaches) with some appeals to problems related to solar energy technology. In “Perspectives” Doctoral Candidate see mostly the potential progress in applying more advanced theoretically and computationally approaches and it is probably His perspective for the postdoctoral life.

Overall, the presented doctoral dissertation is based on the large collection of data reporting extended hard work. On the other side the work makes an impression of not completely finished. The use of produced results is restricted especially on the chemical side of the performed study. The selected compounds: BOD-Ph and its derivatives with “push” and “pull” substituents referring to classical chemical concepts, are not explored deeper e.g. through available electron density distribution. The molecular structures, particularly dihydral BOD-Ph angle, are not explored. More important both these effects may compete with critical influence on electronic spectra in a single molecule but also in condensed phases. Above mentioned effects may be interesting when designing processes and devices exploiting solar energy.

Despite the remarks presented above I state that the presented doctoral dissertation confirms reasonable theoretical knowledge and proper scientific skills for performing scientific studies required for a candidates for a doctoral degree. In conclusion, I declare that the submitted dissertation meets the conditions required by law (art. 187 ust. 1-2 ustawy z dnia 20 lipca 2018. Prawo o szkolnictwie wyższym i nauce (Dziennik Ustaw z 2023 r. poz. 742 z późniejszymi zmianami).

I therefore request that the Candidate Aoussaj Sbai be admitted to the further stages of the doctoral procedure.

Szozepan Roszal