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REVIEW REPORT

on doctoral dissertation by MSc **Alejandro Iglesiasa Reguanta**

entitled: *Intermolecular Interactions Between Fluorophores Carrying BF/BF_2 Group and Halogenated Fluorobenzenes.*

The doctoral dissertation by MSc Alejandro Reguant was prepared in the research group of Prof. Borys Ośmiałowski, at the Faculty of Chemistry, Nicolaus Copernicus University in Toruń. The content of the dissertation indicates that the second supervisor is Dr. Josep Maria Luis from the Institute of Computational Chemistry and Catalysis, University of Girona (Catalonia, Spain). This arrangement complies with the provisions of the Polish Higher Education and Science Act, Article 190, paragraph 1.

The research problem forming the basis of the doctoral dissertation concerns the description of the influence of intermolecular interactions, particularly halogen bonds, on the physical properties of organic fluorine-substituted boranes. The chemical compounds selected for the study represent an important and intriguing class of substances exhibiting properties characteristic of dyes. The studies presented in the dissertation aim to predict and potentially design the properties of dyes from this group. As the Author specifies in the opening pages of Chapter 3, the dissertation has two principal objectives. The first is to estimate the stability of

halogen bonds in complexes formed by dye molecules with perfluorohaloarenes and to determine the effect of these interactions on the (photo)physical properties of the complexes. The second goal is to develop and apply a new methodology to identify the physical origin of changes in infrared spectra resulting from the formation of complexes stabilized by halogen bonds.

The dissertation follows a classical structure. It is introduced with a literature review, followed by a section detailing the Doctoral Candidate's original research results.

In the **Introduction**, the Author acquaints the reader with general knowledge about organic dyes, beginning with their earliest practical applications and seamlessly transitioning to contemporary understanding. In the second chapter of this section, the Author focuses the reader's attention on chromophores from the group of organoboron derivatives. The Author discusses the photophysical properties of these compounds, referencing descriptions based on quantum chemistry theory. Additionally, the potential applications of this class of compounds in modern industry are presented. Finally, the Author introduces the reader to the field of research on halogen bonding. Here, one can find a historical overview, which later transitions into a concise summary of the current state of knowledge in this area. It is worth noting that the content of the literature review is supported by over 100 references to external sources.

The next chapter provides a description of the methodology used in the study. Since the work is primarily computational (*in silico*), the Author focuses on describing selected computational chemistry methods, especially the schemes for determining intermolecular interaction energies. Particularly interesting in this section is the part concerning the determination of energy components dependent on an external electric field. During the research described later, it was found that the influence of the electric field is not negligible for the spectroscopic properties of the studied systems. Consequently, a sophisticated interaction energy decomposition scheme was applied, allowing the consideration of the external factor, which in this case is the electric field.

The main part of the dissertation consists of two chapters discussing the Author's original research results. In the initial stage of the study, the Author analyzed complexes of fluoroboron derivatives of N,N-dimethylaniline with perfluorohalobenzene C6F5X (where X=F, Cl, Br, I). Computational methods were used to analyze in detail the complexes graphically represented in the schemes on pages 29 and 33. The obtained results were compared with experimental observations, including emission and absorption fluorescence spectra measurements, as well as IR and NMR spectroscopy. Some measurements were performed using titration methods.

As a result of these studies, it was found that for complexes with pentafluoroiodobenzene, the studied dye molecules exhibited noticeable changes in

spectroscopic properties, such as a slight red shift in the maximum absorption wavelength and a significant red shift in the maximum emission wavelength. This observation was explained by electron charge transfer resulting from the formation of halogen bonding, which, in turn, increased the overall charge transfer within the dye molecule. This is an important observation demonstrating the far-reaching impact of halogen bonding on the electronic structure of the studied systems.

Consistent with the stated research objective, the Author focuses primarily on halogen bonding. Meanwhile, the graphical representations of the studied complexes may, in some cases, suggest the simultaneous presence of weak hydrogen bonds of the C-H…F type. For instance, the structure of complex A-5 from Figure 4.6 illustrates a scenario where the presence of a nonlinear halogen bridge might result from the concurrent formation of a C-H…F hydrogen bond. One could assume that, in the absence of interactions other than halogen bonding, the halogen bond in complex A-5 (as well as in many others in the studied series) would be perfectly linear. Although weak, these potentially coexisting interactions might also play a role in complex formation; however, this aspect is not particularly emphasized in the dissertation.

I would be curious to hear the Doctoral Candidate's opinion on whether the applied research methodology could separate the potential individual contributions of these two distinct interactions and whether the mentioned hydrogen bonds might, in fact, participate in modulating the analyzed physical properties.

In the next step, the Author conducted a decomposition of the energy of the studied intermolecular interactions in the context of the influence of individual components on the spectroscopic properties reflected in IR spectroscopy spectra. The development and subsequent application of this innovative approach to selected real systems allowed, among other things, the observation of a linear relationship between the components of interaction energy and the intensity of recorded vibrational spectra.

The doctoral dissertation submitted for my review represents a comprehensive collection of scientific research results in the field of computational and structural chemistry. Various computational methods were successfully applied in the study, with critical selection of computational experiment conditions and equally critical formulation of conclusions from the conducted research. The Doctoral Candidate skillfully tailored the research methodology to the needs of the analysis and applied it effectively, achieving the stated research objective. It is also worth emphasizing that the quantum chemical computation results were meticulously compared with experimental data. This provides a complete picture of the addressed research problem, ensuring the high standard of the obtained results and final conclusions.

Considering the significant application potential of the analyzed chemical compounds, I can confidently conclude that the reviewed doctoral dissertation meets

all scientific and customary standards expected of such works. Undoubtedly, the conclusions derived from this study represent a valuable contribution to the field.

In conclusion, I am pleased to state that the reviewed doctoral dissertation is a testament to the Author's high competence in the broadly understood field of computational chemistry. I have no doubt that the dissertation submitted for evaluation fully meets the requirements specified in the Act of July 20, 2018 – Law on Higher Education and Science (current reference to the legal act: consolidated text DzU of 2023, item 742, with amendments). Therefore, I recommend to the High Council of the Scientific Discipline of Chemical Sciences at the Faculty of Chemistry, Nicolaus Copernicus University in Toruń, that MSc Alejandro Iglesias Reguant be allowed to proceed to the subsequent stages of the doctoral process.

Furthermore, considering the high standard of the conducted research and its exceptional cognitive quality, which has resulted in measurable outcomes in the form of a series of scientific publications in renowned international journals, I also propose to the High Council of the Scientific Discipline of Chemical Sciences at the Faculty of Chemistry, Nicolaus Copernicus University in Toruń, that the doctoral dissertation of MSc Alejandro Iglesias Reguant be awarded distinction.

Marcin Palusiak.