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Reviewer's Report on the Thesis entitled Intermolecular Interactions Between Fluorophores Carrying BF/BF$_2$ Group and Halogenated Fluorobenzenes

by Mr. Alejandro Iglesias Reguant

The doctoral dissertation by Ms. Alejandro Iglesias Reguant has been carried out at the Faculty of Chemistry of the Nicolaus Copernicus University in Toruń (Poland) and University of Girona (Catalonia, Spain) under the scientific supervision of prof. dr hab. Borys Ośmiałowski and Dr Joseph Maria Louis. It formally consists of six main chapters, abstract (in English only), a list of abbreviations, a bibliography, a list of figures, a list of tables, a full list of publications and supplementary data. The overall presentation is given in 110 pages. The first chapter plays an introductory role. It outlines the importance of dyes in organic chemistry and presents cornerstones in the development of key concepts. It also presents its role in the context of some cultural, scientific and artistic aspects related to the development of humanity. Then, the properties of BF/BF$_2$ fluoroborate chromophores were discussed along with the basic concepts explaining the photochemical properties of dyes and their wide application, mainly in molecular electronics. Subsequently, a significant part of the thesis work is devoted to the concept of halogen bond concept. This is very important because the goals involve deeper insight into this kind of intermolecular interaction. In my opinion, this chapter is written in a comprehensive way, so that even a non-specialist can gain a lot from it. The literature part includes 119 publications out of 169 presented in the bibliography. The choice was made carefully, but I would expect a brief review of solid state interactions in analogues of A and B systems. In fact there are not to many systems based on 3a-fluoro-3aH-3,4-dioxa-1,6,9bl^5-triaza-3al^5-boraphenalene or 1,1-difluoro-1H-9l^5,11^5-pyrido[1,2-c][1,3,5,2]oxadiazaborinine (with/or without nitrogen atom in the heterocyclic ring) skeletons, but all of them show very interesting photophysical properties that are tuned by substituents. In this context a contribution by Glotzbach and coworkers [*Journal of Organic Chemistry* **2013**, *78*, 4410] might have also been taken into account. The next two chapters present the methodology and objectives respectively. Theoretical methods, tools and computational strategies are presented very concisely. I appreciate the way this was done, although some of the principles of infrared spectroscopy could be briefly mentioned here. There are two main objectives of the thesis work. The first one concerns comprehensive and extremely detailed computational analysis of the stability of halogen bonding in two kind

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complexes formed by systems containing BF or BF_2 chromofore and perfluorohaloarenes, whereas the other one focuses on development and application of a new methodology to determine the physical origin of spectral feature changes in the infrared spectra upon the formation of molecular complexes. Both are very valuable because they contribute to a deeper understanding of the halogen bond, but in my opinion the latter is a very important achievement because it can serve as a general theoretical tool to explain the spectroscopic properties of many complex organic systems. It is rather a new approach that split the changes in the infrared spectrum during the formation of molecular complexes into terms of different physical origins. Personally, I am very impressed with this approach. Continuing, the fourth chapter is devoted to the influence of halogen bonds on the spectroscopic properties of two types of organic fluoroborates in their complexes with perfluorinated fluoro-, bromo-, chloro or iodobenzenes. The first group (A) consists of the $BF(–O)_2$ fragment, which is an electron acceptor and the N,N-dimethylaniline group, in which the dimethylamino group acts as an electron donor. The molecules were designed in such a way that the halogen bond acceptor was remote from the primary electron acceptor involved in intramolecular charge transfer. Their absorption and emission spectra have been well studied. Based on molecular modeling, the following types of systems were obtained and optimized: i) 18 complexes formed as a result of intermolecular interactions of halogen bonds, ii) 12 complexes in stacked systems, stabilized mainly by dispersion interactions, iii) the remaining 6 complexes, which in this group show various intermolecular interactions apart from halogen bonds and π-stacking. They include dyes with a nitrogen atom in position 2 or 3 of the halogen bond acceptor site, interacting with the C_6F_5X molecule. The first group was subjected to in-depth analysis, while the remaining types of complexes were moved to a supplementary chapter. In my opinion, they could have just as easily been included in the main body, given that they were partially covered in the chapter (see p. 38). This is a bit inconsistent. While discussing interaction energies on page 35, I found a typo in the table enumeration (in should be Table 4.1, not Table 4.6, line 14). The interaction energies are not large and correspond to established trends observed in typical systems with halogen bonds: complexes in which the iodine atom acts as a halogen bond donor show the highest interaction energies, regardless of the specific dye used. The same was also found in the second group of dyes (B) studied in this work. To obtain deeper insight into the energy contribution in the complexes, Variational Perturbation Energy Decomposition Analysis was used for complexes formed by three dyes with different solvents. Importantly, regardless of the specific dye involved in complex formation, the ΔE distribution revealed similar trends, suggesting that the main driving force of intermolecular interactions originates from halogen bonds. It was found that the greatest contribution is made by the exchange-repulsion, destabilizing the complexes, which is balanced by the combined effect of electrostatics and delocalization. I fully agree that dispersion effects play a key role in defining the nature of halogen bonds, so it is important to take electronic correlation into account to accurately calculate the total interaction energy. Next, the PhD student discusses the absorption and emission spectra of three dyes in halogenated fluorobenzene solvents based on calculations of their electronic structure. The trends observed in the calculated absorption spectra for all complexes are consistent with experimental data, and the red shift of the calculated emission wavelengths correlates well with the established halogen bond strength trend (Cl < Br < I). Furthermore, it turns out that the emission wavelength is more sensitive to the action of halogen bonding compared to the absorption wavelength, which explains the differences observed in the measurements. Finally, the stability of the complexes formed by type A molecules was rationalized based on ΔG. The second group of dyes (B) has a dipolar structure involving an N–BF_2–O electron-accepting group and a dimethylamino electron-donor group. They were designed to include a halogen bond acceptor positioned near the BF_2 acceptor in the charge transfer pathway. Their complexes with C_6F_5X (where X=F, Br, Cl, I) were analyzed using the same methodology to analyze their stability and to characterize and rationalize their photophysical properties. All analyzes are very important and were done professionally, which I really appreciate. It is worth noting that the initial analyzes were enriched with ^{1}HNMR and ^{15}NNMR spectroscopy, which revealed a variety of possible interactions. Three types of complexes were obtained using molecular modeling: where B dyes and halogen bond donors interacted with each other i) through halogen bonds in heterocyclic nitrogen (12 complexes), ii) through halogen bonds in imine nitrogen (10 complexes) or iii) through π-stacking (15 complexes). The first two have been fully analyzed again. Their relative stabilities are comparable across different B series, while considerations based on the partition energy lead to similar conclusions as in the case of complexes formed by type A molecules. As could be expected, complexes with C_6F_5I are characterized by the highest stability. There is no doubt that the degree of conjugation in the dye and the position of the halogen bond acceptor(s) play a significant role in the relationship between halogen bond strength and photophysical properties. The fifth chapter is devoted to the decomposition of changes in IR spectra caused by halogen bonding. In my opinion, this is a very important part of the work because it develops and implements a theoretical approach that allows interpreting changes in the infrared spectrum during the formation of a molecular complex in terms of different physical origins. It is based on the relationship between the analytical expression of nuclear relaxation polarizability and the infrared intensity. A direct relationship was established between changes in both properties for a specific vibrational mode caused by an intermolecular interaction. The variational-perturbation energy decomposition scheme (VP-EDS) was used to decompose the intermolecular interaction energy and infrared intensity changes after complex formation into terms of different physical origins. This approach increases the interpretative power of IR spectra. However, I do have a comment regarding Figure 5.5. All correlations are fine, but in my opinion they are biased due to the clustering of data points representing different contributions (electrostatics, exchange, induction, dispersion) to the interaction energy. The correlations shown in Figure 5.6 are more reliable, but they involve energy contributions from different complexes (I mean two different halogen bond donors). I have some doubts about this and expect this point to be discussed during the public defense. At the end of the chapter, the PhD student pulls a rabbit out of the hat. IRS-DA analysis of two model systems with halogen bonds: HCN:BrF and HCN:IF and three model complexes of hydrogen bonds HCN:HCL, HCN:HNC and HCN:HCN are mentioned. This is a very interesting point that indicates some perspectives, but also possible limitations of this approach. I would be very grateful some more information could be provided. The doctoral thesis work was prepared with a high level of proficiency, both in terms of editing and graphics. The dissertation is written in very concise way, although it well balances the literature review and highly impressive novel theoretical work. My two minor comments concern the lack of an abstract in Polish (a Spanish or Catalan version would also suit well) and abbreviations. Although the list is almost complete, I found a few missing, like ZPA, CIS, IRS-DA, FF. The analyses, including the literature review, although detailed, are described in an excellent, concise, scientific language. In my opinion, this is a fully professional monograph. I highly appreciate the way the results are presented - all figures, graphs, and tables were prepared with great care. It is worth noting that the essential part has been published in three scientific articles: i) *Journal of Organic Chemistry* [**2022**, *87*, 15159], ii) *Physical Chemistry Chemical Physics* [**2023**, *25*, 11658] and iii) *Physical Chemistry Chemical Physics* [**2023**, *25*, 20173]. In all of them, the PhD student is the first author. It is worth emphasizing that these journals are among the best and in the publishing years they took first quarters in Organic Chemistry or in Physics, Atomic, Molecular & Chemical, respectively. Importantly, Mr. Alejandro Iglesias Reguant was also the author of three other articles published in *Dyes and Pigments* [**2022**, *204*, 110434], *Journal of Molecular Liquids* [**2022**, *363*, 119869] and *Molecules* [**2023**, *28*, 1101]. I also found another his contribution (*Physical Chemistry Chemical Physics* [**2020**, *22*, 4225]) and I wonder why it was not disclosed by him. This high publication mark is impressive and proves his activity, high level of research, but also dedication to science. Reading his doctoral thesis was a real intellectual pleasure for me. To sum up: I am fully convinced that Alejandro Iglesias Reguant's doctoral dissertation contains important elements of scientific novelty. The PhD student defined the research problem well, planned it well and performed quite excellent research. His commitment to work is particularly impressive.

The doctoral thesis by Mr. Alejandro Iglesias Reguant easily meets all formal conditions of the current act on the Academic Degrees and Titles of Republic of Poland. Therefore, it is with great pleasure that I recommend to the Scientific Council of the Chemistry Discipline of the Nicolaus Copernicus University in Toruń that he be admitted to the next stages of the doctoral process. Due to the very high scientific value of the dissertation, the wide scope of research, its complexity and the mature, also very significant scientific achievements of the doctoral student presented in his works, published in excellent journals, I strongly recommend that the Council award a distinction for this dissertation.

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