

1. PHD PROJECT DESCRIPTION (4000 characters max., including the aims and work plan)

Project title: Synthesis and spectral studies of fluorescent difluoroborates

1.1. Project goals

The goal of the project is to synthesize new class of fluorescent dyes and test them in order to gain information how much the change of the substituent^{1,2} is able to influence the position of the absorption and fluorescence maximum. In the next step the structure of the charge transfer exhibiting molecules³ is going to be modified as to obtain compounds capable for two-photon absorption.⁴ Selected molecules will be studied in detail experimentally and with the use of theoretical methods and their potential for two-photon excited microscopy purposes will be judged and then optimized.

1.2. Outline

The project begins with the synthesis of the substrates that will be CH or NH acids. With those in hand the next step is to convert their molecules directly into the highly light absorbing compounds. After first experimental results the idea of the research will be judged in the light of its optimal performance. Thus, the following decisions will be made in the light of next steps in the synthesis: a) the use of the proper substituent to make the reaction yield higher, b) choosing the best molecular fragment in the light of its rigidity that should be a warrant of the radiative energy dissipation and c) the use of the proper substituents as to obtain compounds carrying bulky groups which, then could be used for controlling the intermolecular interactions in solid state.

1.3. Work plan

The list below shows main point towards reaching the project goals.

1. The synthesis of dyes.
2. Their purification and structure confirmation.
3. Studies of their physicochemical properties including
 - a. absorption,
 - b. luminescence,
 - c. sensitivity to the polarity of the medium (solvent),
 - d. two-photon absorption studies of the chosen compounds.
4. Optimization of the molecular structure based on previous results.

1.4. Literature

- (1) Zakrzewska, A.; Zaleśny, R.; Kolehmainen, E.; Ośmiałowski, B.; Jędrzejewska, B.; Ågren, H.; Pietrzak, M. Substituent Effects on the Photophysical Properties of Fluorescent 2-Benzoylmethylenequinoline Difluoroboranes: A Combined Experimental and Quantum Chemical Study. *Dye. Pigm.* **2013**, *99* (3), 957–965.
<https://doi.org/10.1016/j.dyepig.2013.08.002>.
- (2) Zakrzewska, A.; Kolehmainen, E.; Valkonen, A.; Haapaniemi, E.; Rissanen, K.; Chełcińska, L.; Ośmiałowski, B. Substituent Effect in 2-Benzoylmethylenequinoline Difluoroborates Exhibiting through-Space Couplings. Multinuclear Magnetic Resonance, X-Ray Diffraction, and Computational Study. *J. Phys. Chem. A* **2013**, *117* (1), 252–256.
<https://doi.org/10.1021/jp311072q>.
- (3) Grabarz, A. M.; Laurent, A. D.; Jędrzejewska, B.; Zakrzewska, A.; Jacquemin, D.; Ośmiałowski, B. The Influence of the π -Conjugated Spacer on Photophysical Properties of

Difluoroboranyls Derived from Amides Carrying a Donor Group. *J. Org. Chem.* **2016**, *81* (6), 2280–2292. <https://doi.org/10.1021/acs.joc.5b02691>.

- (4) Bednarska, J.; Zaleśny, R.; Wielgus, M.; Jędrzejewska, B.; Puttreddy, R.; Rissanen, K.; Bartkowiak, W.; Ågren, H.; Ośmiałowski, B. Two-Photon Absorption of BF₂-Carrying Compounds: Insights from Theory and Experiment. *Phys. Chem. Chem. Phys.* **2017**, *19* (8), 5705–5708. <https://doi.org/10.1039/c7cp00063d>.

1.5. Required initial knowledge and skills of the PhD candidate

A candidate should be familiar with:

- a) organic synthesis and compounds separation/purification
- b) methods to study the photophysical properties of molecules
- c) drawing conclusions based on systematic changes implemented in molecules
- d) being familiar with the current research tools related to database search, office software and more specialized one related to physicochemical characterisation of organic compounds

1.6. Expected development of the PhD candidate's knowledge and skills

It is expected that PhD student will gain the following skills:

- a) synthesis of new fluorescent dyes and methods form their purification
- b) ability to tune the properties in systematic way based on the Hammett substituents constants
- c) ability to design structure of fluorophores in order to obtain compounds capable for sensing
- d) ability to tune the structure of the two-photon absorption active compounds