

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

### Project title: Synthesis of new fluorescent dyes based on amides

#### 1.1. Project goals

The goal of the project is to synthesize new class of fluorescent dyes based on amides as a substrate. The aza-BF<sub>2</sub> compounds<sup>1,2</sup> will be synthesized starting from relatively simple heterocyclic amines and their reactions with suitable acids or their derivatives to yield amides and finally, in the next step, the aza-BF<sub>2</sub> fluorescent dyes. The properties of resulting fluorophores are going to be modified by placement of the nitrogen atom in the heterocyclic part of molecule. The same nitrogen atom will be used as a basic centre to interact with halogen bonding donor.<sup>3</sup> In this way, the solid samples will be obtained with, preferably, phosphorescent properties. In parallel, the dyes will be studied in solution with the use of various solvents to influence their emissive properties (solvatochromic behaviour<sup>4</sup>). For more information please refer to: <https://sites.google.com/view/bosmialowski>

#### 1.2. Outline

The project begins with the synthesis of the substrates. These will be selected from the plethora of the amino-heterocycles available from commercial sources. The organic synthesis of the amides will be guided in order to a) obtain substrates for next steps of research, b) investigate the properties of amides in the light of their intermolecular interactions in solution and in solid. Reaching mentioned two goals will give a basis to consider the best way in guiding the whole project, and to design new molecules that may be used in another fields of science as, for example, material science. The spectral measurements of the photophysical properties of molecules will be a basis to extent their palette in the light of substituent effect or the extension of the conjugation path to tune their properties.

#### 1.3. Work plan

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

1. The synthesis of amides and final dyes.
2. Their purification and structure confirmation at every step of the synthetic path.
3. Studies of their physicochemical properties including
  - a. absorption,
  - b. fluorescence,
  - c. sensitivity to the polarity of the medium (solvent),
4. Optimization of the molecular structure based on previous results.

#### 1.4. Literature

- (1) Grabarz, A. M.; Laurent, A. D.; Jedrzejewska, B.; Zakrzewska, A.; Jacquemin, D.; Ośmiałowski, B. The Influence of the  $\pi$ -Conjugated Spacer on Photophysical Properties of Difluoroboranyl Derivatives Derived from Amides Carrying a Donor Group. *J. Org. Chem.* **2016**, *81* (6), 2280–2292. <https://doi.org/10.1021/acs.joc.5b02691>.
- (2) Jędrzejewska, B.; Zakrzewska, A.; Mlostoń, G.; Budzák, Š.; Mroczyńska, K.; Grabarz, A. M.; Kaczorowska, M. A.; Jacquemin, D.; Ośmiałowski, B. Synthesis and Photophysical Properties of Novel Donor–Acceptor N-(Pyridin-2-Yl)-Substituted Benzo(Thio)Amides and Their Difluoroboranyl Derivatives. *J. Phys. Chem. A* **2016**, *120* (24), 4116–4123. <https://doi.org/10.1021/acs.jpca.6b04004>.
- (3) Dziuk, B.; Osmialowski, B.; Zarychta, B.; Ejsmont, K. 2-Methyl-N-(Pyrazin-2-Yl)Propanamide-1,2,4,5-Tetrafluoro-3,6-Diiodobenzene (2/1). *IUCrData* **2016**, *1* (9), x161466. <https://doi.org/doi:10.1107/S2414314616014668>.

- (4) Jędrzejewska, B.; Grabarz, A.; Bartkowiak, W.; Ośmiałowski, B. Spectral and Physicochemical Properties of Difluoroboranyls Containing N,N-Dimethylamino Group Studied by Solvatochromic Methods. *Spectrochim. Acta A* **2018**, *199*, 86–95. <https://doi.org/10.1016/j.saa.2018.03.048>.

### **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