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

Project title:

New boron-containing charge-transfer dipolar and quasi-quadrupolar materials for applications in nonlinear optics

1.1. Project goals

The aim of the proposed PhD project is to develop a new class of boron-containing photoactive materials for the applications in nonlinear optics. The specific goals include:

- rational design of the potent two-photon absorbing materials of dipolar or quadrupolar character;
- selection of most effective two-photon absorbers exhibiting the desired properties and their further optimization for applications in nonlinear optical devices;
- precise characteristics of the photophysical properties of the obtained species with the determination of the best promising materials;
- determination of the general structure-photooptical property relationship for the investigated class of systems in gas phase and condensed phase with the computational chemistry tools.

1.2. Outline

The strategies of the rational design of promising materials for nonlinear optics, exhibiting large two-photon absorption cross section, desired and tunable excitation wavelength, and preferably high fluorescence quantum yield, include the extension of the π-electron system and introduction of substituents ensuring strong intramolecular charge transfer [1-5]. However, it is known that the extension of the aromatic core of the molecule and introduction of the strong electron-withdrawing or electron-donating substituents can favor the intermolecular interactions such as stacking or hydrogen bonding to solvent, which significantly quench the fluorescence or can diminish the TPA cross section. Therefore, the proper balance of these factors is necessary to be provided. Among the known systems, the growing interest in the field of nonlinear optics can be observed in the difluoroborates family of fluorofores, revealing extremely strong absorption and fluorescence [5]. For these reasons, the subject of the present project involves the boron-containing molecules, which will be optimized with respect to the linear and nonlinear optical properties as well as their solubility or aggregation.

Measurements of nonlinear absorption coefficient and nonlinear refractive index of the proposed materials will be carried out using the newly built Z-scan measurement system. Parallel to the experimental research, advanced quantum-chemical calculations will be carried out, allowing for a more complete understanding of the essence of the basic mechanisms of phenomena occurring in these compounds and determining their nonlinear optical properties. The combination of theoretical and experimental methods will optimize the proposed family of materials in terms of increasing the effectiveness of nonlinear effects.

The result of the PhD project will be to obtain a group of compounds showing: 1. shift of the

absorption spectrum, 2. large cross-sections for two-photon absorption at wavelength of 532 nm, 3. changing of the nonlinear absorption coefficient with increasing intensity of the incident light, 4. change of nonlinear refractive index.

1.3. Work plan

1) Designing charge-transfer dipolar and/or quasi-quadrupolar materials with the desired nonlinear optical properties by computational chemistry;
2) Synthesis of charge-transfer dipolar and/or quasi-quadrupolar systems selected on the basis of preliminary calculations;
3) Study of optical properties of selected charge-transfer dipolar and/or quasi-quadrupolar materials;
4) Study of the nonlinear optical properties of selected charge-transfer dipolar and/or quasi-quadrupolar materials;
5) Quantum-chemical study of the observed optical phenomena in the condensed phase.

1.4. Literature

[1] Z. Chen, et al., Dyes Pigm. 173, 107876, 2020.
[2] T. Enoki, et al., Phys. Chem. Chem. Phys. 19, 3565, 2017.
[3] M. Pawlicki, Angew. Chem. Int. Ed. 48, 3244, 2009.
[4] Z. Sekkat, W. Knoll, (Eds.) Photoreactive Organic Thin Films, Acad. Press - Elsevier Science: Amsterdam, 2002
[5] E.F. Petrusevich, B. Ośmiałowski et al., J. Phys. Chem. A. 125, 2581, 2021.

1.5. Required initial knowledge and skills of the PhD candidate

Master of Physics or Master of Chemistry or related fields of exact and natural sciences.
Basic physics, basic organic chemistry and spectroscopy, basic quantum chemistry or quantum physics, experience in application of computational chemistry packages, communicative English written and spoken, programming skills highly appreciated, ability of working both independently and in the team, eager to take on challenges.

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

The project will benefit from three groups of tools: theoretical calculations, organic synthesis and the photooptical measurements, thus providing a PhD candidate an exceptional strong and complete background for the rational design of nonlinear optical materials from scratch. The candidate will gain the thorough knowledge of theoretical methods for two-photon absorption description, the organic chemistry feeling in design and synthesis of new boron-containing compounds and the comprehensive skills in spectroscopic and nonlinear measurements. Additionally, PhD student will learn the basics of programming and data analysis.
Therefore, development of the PhD student knowledge and skills is expected in the field of optics, nonlinear optics and quantum chemistry as well as synthesis of charge-transfer dipolar and/or quasi-quadrupolar materials. This doctorate will be interdisciplinary.