1. OPIS PROJEKTU DOKTOSKIEGO (4000 znaków max., łącznie z celami i planem pracy)

Project title:

Searching for new boron-containing charge-transfer materials for applications in nonlinear optics

1.1. Project goals

The aim of the proposed PhD project is to search a new class of boron-containing charge-transfer materials with high nonlinear optical properties allowing for their effective practical application in nonlinear optical devices. The specific goals include:

- Designing boron-containing charge-transfer materials with the desired optical properties by computational chemistry;
- Selection of most effective two-photon absorbers exhibiting the desired properties and their further optimization for applications in nonlinear optical devices;
- Production of thin layers of newly synthesized boron-containing charge-transfer materials with the spin-coating method;
- Precise characteristics of the photophysical properties of the obtained species with the determination of the best promising materials
- Examination of optical properties of new boron-containing charge-transfer materials;
- Quantum-chemical study of the observed optical phenomena in the condensed phase;
- Study of the nonlinear optical properties of new boron-containing charge-transfer materials.

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 boron-containing charge-transfer materials with the desired nonlinear optical properties by computational chemistry;
2) Study of optical properties of selected charge-transfer materials;
3) Study of nonlinear optical properties of selected charge-transfer materials;
4) 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 experience in experimental optics, communicative English written and spoken, programming skills highly appreciated, ability of working both independently and in the team, eager to take on challenges, motivation to conduct scientific research.

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

The project will benefit from three groups of tools: theoretical calculations 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 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. This doctorate will be interdisciplinary.