PHD PROJECT DESCRIPTION

(4000 characters max., including the aims and work plan to de published online)

Project title:

Synthesis, characterization, and application of new macrocyclic imines, including (2+2) and (3+3) types, and their metal complexes as electroluminescent materials for OLEDs

1.1. Project goals

The main goal of the project is the synthesis, characterization, and application of new macrocyclic imines of (2+2) and (3+3) types and their metal complexes as emissive materials in OLED devices.

Specific objectives include:

- design and synthesis of macrocyclic compounds with tailored structures,
- design and synthesis of metal macrocyclic compounds with tailored structures,
- investigation of the influence of steric and electronic substituents on photophysical properties,
- analysis of structure–property relationships,
- fabrication and optimization of OLED devices using the synthesized compounds as emissive layers

1.2.

Outline

Macrocyclic imines, containing azomethine (-C=N-) groups, are versatile compounds with applications in materials chemistry and optoelectronics. Their properties can be tuned by modifying diamine and dialdehyde precursors, enabling control over steric and electronic effects. These factors, together with non-covalent interactions, significantly affect emission behavior. Due to their planar structures and extended π-electron delocalization, macrocycles are promising candidates for OLED emissive layers. OLED performance depends strongly on the emissive material, particularly the HOMO–LUMO gap, which is influenced by molecular structure and intermolecular interactions. Organic Light-Emitting Diodes (OLEDs) represent a cornerstone of the modern optoelectronic industry, offering a transformative approach to display technologies and solid-state lighting. Their widespread adoption is driven by a unique set of physicochemical and operational characteristics, including:

- **Physical Properties:** Ultralight weight and ultrathin profiles.
- **Performance:** Wide viewing angles, rapid response times, and high luminance across a broad color gamut.
- **Economic & Ecological Factors:** Low-cost fabrication potential and a reduced environmental footprint compared to traditional semiconductor technologies. The core of an OLED device is the **Emissive Layer (EML)**, where the radiative recombination of excitons occurs. Currently, the EML utilizes a diverse range of luminescent chemical compounds, which can be categorized into three primary groups:

1. **Purely Organic Compounds:** Often utilized for their high processing flexibility.
2. **Inorganic Materials:** Known for their robustness and thermal stability. In the development of advanced EML materials, **Schiff base ligands** and their coordination complexes with **transition metals** and **lanthanide ions** play a fundamental role. The interest in these systems stems from their:

Complementing the use of macrocyclic imines, benzimidazole derivatives or complexes have emerged as another critical group of compounds. They are characterized by essential structural and optical features that make them ideal candidates for the emissive layer. Their high thermal stability, electron-transporting abilities, and intense fluorescence/phosphorescence make them indispensable in the design of next-generation, high-performance OLED devices.

1.3. Work plan

1. Synthesis

1. preparation of macrocyclic imines (2+2) and (3+3),
2. synthesis of the fluorescence metal compounds
3. optimization of reaction conditions and purification methods.

2. Characterization

1. structural and spectroscopic analysis (NMR, IR, UV-Vis, fluorescence, X-ray),
2. investigation of the substituent and chirality effects.
3. DFT calculation of photophysical properties

3. Photophysical studies

1. emission spectra and quantum efficiency measurements,
2. time-resolved luminescence studies.

4. OLED fabrication

1. preparation of emissive layers (with PVK),
2. construction of devices eg. (ITO/PEDOT:PSS/EML/Al),
3. evaluation of electroluminescent properties.

5. Data analysis

1. correlation of molecular structure with device performance,
2. identification of key factors influencing efficiency.

1.4. Literature (max. 7 listed as a suggestion for a PhD candidate preliminary study)

1. D. Jankowska, T.M. Muzioł, M. Pokładko-Kowar, E. Gondek, P. Popielarski, M. Barwiołek, New Benzimidazole derivatives, spectroscopy characterization and their application as electroluminescent materials, Journal of Molecular Structure 1350 (2026) 144092. https://doi.org/10.1016/j.molstruc.2025.144092.
2. M. Barwiolek, D. Jankowska, A. Kaczmarek-Kędziera, S. Wojtulewski, L. Skowroński, T. Rerek, P. Popielarski, T.M. Muziol, Experimental and Theoretical Studies of the Optical Properties of the Schiff Bases and Their Materials Obtained from o-Phenylenediamine, Molecules 27 (2022) 7396. https://doi.org/10.3390/molecules27217396.
3. Jankowska D., Muzioł T.M., Mandal D., A. Kaczmarek-Kędziera, I. Tepliakova, R.Viter, M. Barwiolek, ZnO-benzimidazole composite for selective detection of Zn^{2+} and Mg^{2+} ions , Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 343(1-29) (2025) 126604. DOI:10.1016/j.saa.2025.126604

4. Jankowska DL, Łakomska I, Muzioł T, Skowronski L, Rerek T, Popielarski P, Barwiołek M. The optical properties of 3 + 3 macrocyclic Schiff base thin material obtained by the Molecular Beam Epitaxy method. Spectroc. Acta Pt. A-Molec. Biomolec. Spectr. 326:1–10 (2025).
5. Barwiołek M, Jankowska D, Kaczmarek-Kędziera A, et al. New dinuclear macrocyclic copper(II) complexes as potentially fluorescent and magnetic materials. *Int. J. Mol. Sci.* 2023;24:1–24. doi:10.3390/ijms24033017
6. A. Alvarez-Quesada, J.E. Báez, J.O.C. Jiménez-Halla, G. Ramos-Ortiz, G. González-García, Difluoroboron Complexes Based on Benzimidazole–Phenolates as Blue Emitters, Inorg. Chem. 63 (2024) 6649–6659. https://doi.org/10.1021/acs.inorgchem.3c04504.
7. S.-J. Lin, Y.-C. Cheng, C.-H. Chen, Y.-Y. Zhang, J.-H. Lee, M. Leung, B.-Y. Lin, T.-L. Chiu, New high-Tg bipolar benzimidazole derivatives in improving the stability of high-efficiency OLEDs, J. Mater. Chem. C 11 (2023) 161–171.

1.5 Required initial knowledge and skills of the PhD candidate

1. basic knowledge of organic, inorganic and physical chemistry,
2. basic knowledge of coordination chemistry,
3. understanding of organic synthesis and reaction mechanisms,
4. knowledge about basic spectroscopic techniques (NMR, UV-Vis, IR),
5. ability to read scientific literature in English.

Additional advantages:

6. experience in materials chemistry or photophysics,
7. knowledge of thin-film techniques or optoelectronic materials characterization (SEM, AFM, TEM analysis)

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

During the project, the PhD candidate will gain:

- advanced skills in organic synthesis and macrocyclic chemistry,
- expertise in spectroscopic and structural characterization,
- knowledge of photophysical processes and optoelectronic materials,
- practical experience in OLED fabrication and testing,
- ability to analyze structure–property relationships,
- experience in scientific writing, publishing, and presenting research results.