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

Project title: New zinc and copper compounds, their characterization and application for obtaining new materials with fluorescent properties obtained by wet methods

1.1. Project goals

- synthesis of ligands (for example) Schiff bases with different donor atoms e.g. N, O, S,
- modification of ligands with variable substituents and groups with increasing steric and electronic effects to tune charge transfer processes and then metal-to-ligand charge-transfer in complexes,
- synthesis of copper and zinc complexes,
- carrying out the structural characterization of the synthesized compounds and studies on their physicochemical, optical, magnetic, and nonlinear properties
- development and optimization of the deposition conditions of thin layers by wet coating methods, e.g. spin- and dip-coating technique
- studies of relationships between the structure and morphology of the produced materials and their optical properties

1.2. Outline

Thin light emitting films are widely implemented in the form of OLED displays in a broad diversity of products: TV, smartphones or satellite navigation systems. New materials can improve their key parameters, for instance high luminescence, thin designs; they can also provide new unique characteristics of the above mentioned devices. In this context, Cu(II) and Zn(II) complexes with Schiff bases revealing luminescent abilities and potential applications in organic light emitting diodes, magnetic and nonlinear properties constitute a very interesting class of compounds. Additionally, it is commonly known that structures of many organic dyes are complex and their synthesis may be complicated. So, the use of metal coordination compounds seems attractive, as they are photostable and relatively easy to prepare, provided the ligand design and synthesis can be optimized.

At the same time, it may be expected that a small change in the ligand structure will significantly influence the structural, electronic and photonic properties of the compounds. In this context, the study will be focused on the development and evaluation of the physicochemical properties of new ligands, complexes, and thin materials. One of the goals of the proposed project will be to plan the synthesis of new multinuclear ligands including N, O, S donor atoms and their Zn, Cu complexes with fluorescence, magnetic (in the case of complexes), and nonlinear properties of the ligands and complexes. Moreover, the studies on the effect of changing the ligands chromophore systems on the optical properties of the complexes and the ability to synthesize compounds presenting strictly planned optical properties will be a very important part of this research. Thus, apart from the issues related to the synthesis, structural and spectroscopic characterization of the new group of compounds synthesized, the studies on their optical and magnetic properties, and also evaluation of their nonlinear properties, will be of significant importance.

Consequently, the selected group of luminescent compounds will be used in wet coating methods: spin- and dip-coating techniques to give new organic-inorganic materials containing zinc or copper compounds.
Moreover, the chromophore light absorption or luminescence emission properties of the new compounds and hybrid materials will be studied and correlated with the structural features of the chromophore system.
The scope of the project includes performing tasks combining the fields of coordination chemistry, solution and solid-state spectroscopic analysis, new thin materials fabrication and surface analysis. The results will allow the selection of coordination complexes and compounds whose properties will enable obtaining the desired fluorescence hybrid materials and optimizing the application process.
The results obtained within the project will create the basis for the development of new generation materials for optical and magnetic applications.
This PhD project will be conducted in close cooperation with the dr Roman Viter from Institute of Atomic Physics and Spectroscopy University of Latvia in Riga, the research group from the Faculty of Chemistry, University of Wroclaw, EngD Łukasz Skowroński from UTP University of Science and Technology in Bydgoszcz in the field of magnetic characteristic of the isolated compounds, optical studies of the compounds and thin materials and study of the relationships between the structure and morphology of the produced materials and their optical properties. Additionally, the nonlinear characteristics of the obtained compounds will be studied with collaboration with dr hab. Beata Derkowska Zielińska prof. NCU, Faculty of Physics, Astronomy and Informatics, NCU in Torun.

1.3. Work plan

a) synthesis of new ligands with broad spectrum of donor atoms e.g. N-, N,N-, N,O-, or N,S,O-, and substituents with different steric hindrance and different donor-acceptor properties: Br^-, OCH_3,
b) synthesis of new zinc and copper complexes with isolated ligands,
c) structural characteristic of the obtained compounds in the solid state and in a solution by spectroscopic method such as NMR, IR, UV-VIS (D. Chem., NCU Torun, IAPS. University of Latvia), CD (A.M. University Poznań).
d) studies on the fluorescence properties of the compounds in a solution and the solid state-correlation of the molecular structure with photophysical and nonlinear properties of the compounds in the solution and in the solid state.
e) application of the new compounds in the wet coating techniques (spin and dip coating) in order to obtain thin materials
f) characterization of the new materials by SEM/EDX, AFM, TEM, Raman spectroscopy. Studies of the optical properties of materials by Uv-Vis spectroscopy, ellipsometry and fluorescence measurements.

1.4. Literature

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2. Y. Sikdar, R. Modak, D. Bose, S. Banerjee, D. Bieńko, W. Zierkiewicz, A. Bieńko, K. Das Saha, S. Goswami, *Dalton Trans*. **2015**, 44, 8876-8888.
3. M. Barwiolek, E. Szlyk, A. Kozakiewicz, T. Muziol, A. Bieńko, J. Jezierska, *Dalton Trans*. **2018**,

47, 13902-13912.
4. M. Barwiolek, E. Szlyk, A. Berg, A. Wojtczak, T. Muziol and J. Jezierska, Dalton Trans., **2014**, 43, 9924.
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6. A.N. Gusev, M.A. Kiskin, E.V. Braga, M. Chapran, G. Wiosna-Salyga, G.V. Baryshnikov, V.A. Minaeva, B.F. Minaev, K. Ivaniuk, P. Stakhira, H. Ågren, W. Linert, *J. Phys. Chem. C*, **2019**, 123, 11850−11859.
7. A. Schinabeck, J. Chen, L. Kang, T.Teng, H.H. H. Homeier, A. F. Suleymanova, M. Z. Shafikov, R. Yu, C.-Z. Lu, H. Yersin, *Chem. Mater*. **2019**, 31, 4392-4404.
8. L. Gustavo T.A. Duarte, J.C. Germino, R.A. Mendes, J.F. Berbigier, M.M. Faleirosa, F.S. Rodembuschb, T.D.Z. Atvars, *Dyes and Pigments,* **2019**, 171, 107671-1076.
9. B. Derkowska-Zielinska, M. Barwiolek, C. Cassagne, G. Boudebs, *Optics & Laser Technology*, **2020**, 124 105968.

1.5. Required initial knowledge and skills of the PhD candidate

- Analytical thinking
- Mastering fundamental knowledge of coordination chemistry and crystallization processes
  - Willingness to learn and experiment
  - Understanding of organic synthesis and purification methods
  - Ability to work in the laboratory (synthesis and basic spectral measurements)
  - Interest in interdisciplinary science fields covering nanotechnologies, chemistry and physics

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

- Acquiring knowledge of magnetic and optical properties of compounds,
- Ability to determine crystallographic structures,
- Designing and formulating hypotheses on the basis of independent experimentation
- Evaluation of protocols of others
- Ability to design and conduct experiments