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

**Project title:** Synthesis, structural studies and fluorescent properties of pincer complexes based on acridine

### 1.1. Project goals

The aim of the project is the preparation of acridine-based ligands and their coordination into pincer complexes. Their applicability as a sensor will be assessed by detailed fluorescence studies, which will be preceded by detailed structural analysis, including studies of the electron structure. The potential application in the material and membrane science of complexes as enhancers is also foreseen. It is aimed to leverage acridine-based compounds to enhance membrane transport and separation, fostering innovative designs, sensor integration, and selective ion or molecule transport.

### 1.2. Outline

Acridines are a group of compounds that are extensively studied because of their anticancer activity, application as sensors, and as catalysts in different organic reactions. Acridine is a scaffold for versatile modifications with thoroughly selected substituents in different positions or with ring dearomatization. It is known as a hardly coordinating ligand but often forms a salt occurring as a cation. Modification in 4 and 5 positions with substituents bearing donor atoms allows for metal coordination. In such a system, it forms a pincer complex with predefined stereochemistry. Such coordination compounds are also known as catalysts in many reactions which cannot be catalyzed by other pincer complexes. This class of compounds with a central nitrogen atom also involved in coordination allows for the preparation of chemosensors, whose properties are related to the acridine conjugated ring system and chelating properties possible due to properly selected substituents in the 4 and 5 positions. Acridine core structure assures very good fluorescence characterization, namely, high quantum yield, large Stokes shift, and long fluorescence lifetime. Additional substituents affect not only the coordination mode but can also tailor fluorescence properties. Acridine-based sensors are often studied because of their ability to interact with biological molecules, e.g. DNA. They are less often used for the detection of metals because current acridine-based dyes reveal some drawbacks, e.g., the fluorescence often is not significantly increased. Sensor molecules should be switched between two states (on/off strategy or significant change of fluorescence in the presence of the analyte). It can be achieved via intramolecular charge transfer, metal-ligand charge transfer, and photoinduced electron transfer.

The proposed project starts with the preparation of 4,5-substituted acridines via the synthesis of 4,5-bis(*N,N*-di(2-hydroxyethyl)iminomethyl (BHIA), which in subsequent steps can be converted into the designed ligands. In the final step, such a ligand will be coordinated. Detailed structural studies are predicted because currently, the number of such structures, especially complexes, is relatively limited. Hence, such studies provide deeper insight into metal cation-ligand interactions. Moreover, structural studies are crucial in the design of sensors based on a supramolecular approach related to host-guest chemistry, providing information about molecular recognition. This strategy allows for the rational design of next-generation chemosensors based on the acridine moiety.

### 1.3. Work plan

1. Synthesis of ligands being substituted acridine analogues (mainly 4,5-substituted) and their characterization using e.g. elemental analysis, IR ad Ramans spectroscopy, NMR and XRD.

2. Synthesis of complexes with such ligands and selected metals (3d transition metals and lanthanides) and its characterization using e.g. elemental analysis, thermal analysis, IR ad Ramans spectroscopy, NMR and XRD.
3. Determination of the electronic structure of the obtained compounds via theoretical calculations and XAS measurements (in XANES and EXAFS regions).
4. Fluorescence measurements – general characterization and assessment of the prepared system as a sensor due to spectral changes observed upon binding or coordination of the analyte.

### 1.4. **Literature** *(max. 10 listed, as a suggestion for a PhD candidate)*


1. Andreas Schmidt, Ming Liu. Recent Advances in the Chemistry of Acridines. Advances in Heterocyclic Chemistry, 2015, **115**, 287-353.
2. Mehdi Pordel, Hanieh Gheibi, Ayda Sharif. Recent Advances in the Synthesis and Optical Applications of Acridinebased Hybrid Fluorescent Dyes. *Journal of Fluorescence*, 2024, https://doi.org/10.1007/s10895-024-04001-3
3. A. Visscher, S. Bachmann, C. Schnegelsberg, T. Teuteberg, R. A. Mata, D. Stalke. Highly selective and sensitive fluorescence detection of $Zn^{2+}$ and $Cd^{2+}$ ions by using an acridine sensor. *Dalton Trans*., 2016, **45**, 5689-5699.
4. Chenxing Guo, Adam C. Sedgwick, Takehiro Hirao, Jonathan L. Sessler. Supramolecular fluorescent sensors: An historical overview and update. *Coordination Chemistry Reviews*, 2021, **427**, 213560.
5. John Marques Dos Santos, et al. The Golden Age of Thermally Activated Delayed Fluorescence Materials: Design and Exploitation, 2024, **124**, 13571-14110


### 1.5. **Required initial knowledge and skills of the PhD candidate**

- basic knowledge in crystallography
- basic knowledge in organic and coordination chemistry
- critical thinking
- hard-working person and eager to learn
- a person working in a team

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

- managing the work in the laboratory
- solving scientific problems
- performing advanced organic syntheses and preparing complexes
- carrying out diffraction experiments
- experimental data presentation as papers published in peer-reviewed journals and at conferences in oral and written form