# Research project for Master degree

**Field:**
Supramolecular Chemistry

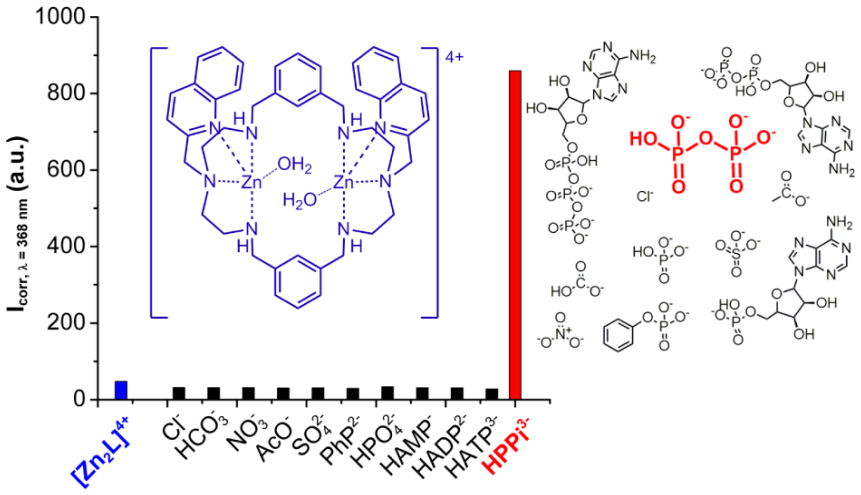
**Title:**
**Development of metal-based fluorescent sensors for the detection of phosphorylated anions**

**Workplace:**
Coordination and Supramolecular Chemistry Laboratory, ITQB NOVA, Oeiras, Portugal.

**Duration of the work:**
As required by the student's Master degree plan.

**Supervisors:**
Dr. Luís M. P. Lima (llima@itqb.unl.pt); Prof. Rita Delgado (delgado@itqb.unl.pt)

**Background:**
Anions play very important roles in areas such as biology, medicine, catalysis and the environment, thus motivating great interest in the development of compounds capable of selectively recognizing and sensing anionic substrates. For many applications anion sensors should work in aqueous medium, which remains a challenge due to the high free energies of hydration of most anions. A very successful strategy for anion sensing in water uses metal complexes bearing one or two vacant coordination positions available for binding the anion of interest. Among a number of metal cations, zinc(II) is one of the most commonly employed, especially for anions of biological importance such as phosphorylated ones and when the detection method is based on fluorescence emission.[1]




We are interested in developing fluorescent metal-based sensors based on zinc(II) complexes appended with fluorophores suitable for UV and mainly visible emission. The desired complexes should be obtained from small polyamine ligands possessing three or four donor atoms and selectively functionalized with an appropriate fluorophore such as quinoline or coumarine groups. We have recently described a dinuclear zinc(II) complex capable of selectively sensing pyrophosphate among a range of phosphorylated and other anions (see example in the Figure),[2] and we now aim to develop smaller ligands for mononuclear zinc(II) complexes instead.


1. H. T. Ngo, X. Liu and K. A. Jolliffe, *Chem. Soc. Rev.* **2012**, *41*, 4928–4965.
2. L. M. Mesquita, V. André, C. V. Esteves, T. Palmeira, M. N. Berberan-Santos, P Mateus, and R. Delgado, *Inorg. Chem.* **2016**, *55*, 2212–2219.

**Objectives:**

- Synthesis of a new organic ligand for complexation of zinc(II) and functionalized with a suitable fluorophore
- Study of the properties of the zinc(II) complexes of the synthesized ligand in the recognition and sensing of phosphorylated anions

**Work plan:**

An organic ligand suitable for complexation of zinc(II) with two vacant coordination positions will be rationally designed. Synthesis and isolation of the ligand will be performed by suitable organic chemistry reactions and techniques, and its structure will be characterized by NMR spectroscopy. The zinc(II) complexation properties of the ligand will be studied mainly by UV-vis absorption and fluorescence spectroscopic titrations in buffered aqueous solution. The formation constant for the complex will be determined as well as the association constants for the complex interaction with a range of phosphorylated anions such as phosphate, phenylphosphate, pyrophosphate, ADP, ATP, etc. Anion binding may possibly be studied also by NMR spectroscopy while taking advantage of the $^{31}P$ resonances of the anions. The complex will be subjected to crystallization attempts in the absence and in presence of the different anions to allow for determining possible solid state structures by X-ray diffraction.