

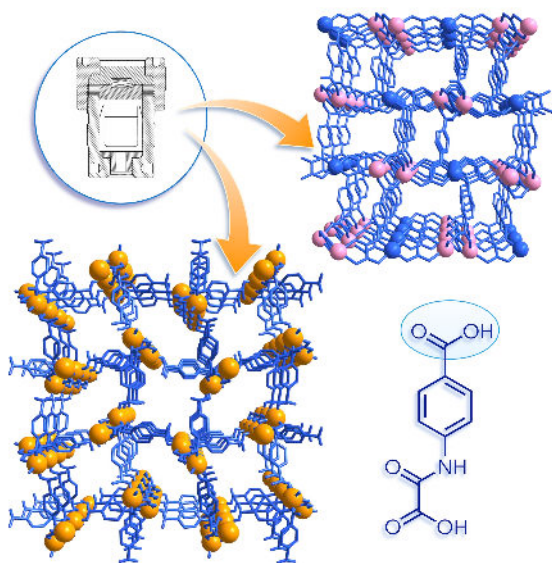
Reactivity of oxamate ligands in solvothermal and microwave synthetic conditions: preparing MOFs for molecule sensing or ion mobility.

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Oxamate ligands contribute in many coordination chemistry fields. They are the source of numerous molecular materials with an impressive range of applications and properties: water remediation, sieving, sensing, catalysis or magnetism.¹⁻⁴ The search for novel forms of oxamate ligands and the exploration of the coordination architectures it is possible to attain are inherently related to these successes and stress the importance of investigative synthetic work. Particularly, oxamate ligands have successfully led to the design and preparation of porous magnets.⁵⁻⁷ The unique ability of these ligands to permit the preparation of metal-organic frameworks (MOFs) that behave as permanent magnets relies on the implementation of both spin topology and spin polarisation when preparing heterobimetallic compounds.⁸ Historically, phenyloxamate ligands have been largely studied for these reasons, yet less than a dozen structural morphologies have been identified over the past 30 years.⁹ Almost all arise from bench, aqueous media reactions, and show poor to moderate thermal stability. More recently, the use of multi-polydentate amino-acid-based oxamate ligands has offered numerous new MOF morphologies with remarkable properties.¹⁰



This has motivated us to investigate multi-polydentate ligands where the phenyloxamate scaffold is augmented with hydroxo or carboxylato coordinating groups. The study of their reactivity with 3d metal ions (Cu(II), Co(II) et Mn(II)) has successfully led to new structural morphologies and we have also demonstrated that solvothermal synthetic conditions are advantageous in the crystallisation process.¹¹⁻¹⁴

With prior design of the ligands and of the metal ions complexes starting materials, we aim in the course of this project to extend our synthetic approach and orient the preparation of our networks towards two important fields of study in MOF chemistry: ion mobility and molecule sensing.

While molecule separation by MOFs relies on their porosity (i.e. size and reactivity of the pores), molecule sensing combines porosity with a physicochemical response from the framework. Obtaining porous networks is thus paramount, and two major obstacles have been identified in our study of oxamate-based MOFs: (i) the formation of charged networks where the alkylammonium or alkaline counter-cations originating from the synthesis block the channels, preventing the occurrence of porosity, and (ii) the weak to moderate stability of the oxamate ligands in harsh solvothermal conditions, which are necessary to try and form the networks from metal ions basic salts and in the absence of the afore-mentioned counter-cations.

To tackle these structural issues and prepare neutral networks, we will tune the starting materials' charge and investigate the association of di- and tri-valent 3d metal ions, and the use of pyridino-oxamate ligands in solvothermal conditions. We will also develop microwave synthetic conditions to increase the reactivity of our ligands, while preventing their degradation.

To procure the network a physicochemical response appropriate to the detection of molecule, two strategies will be used, both involving a magnetic response. The first strategy will be based on the preparation of magnets, implementing spin topology and spin polarisation in Cu(II)/Co(II), Cu(II)/Mn(II/III) and Cu(II)/Fe(II/III) heterobimetallic compounds. Here, we seek detection through the variation of the magnetic order temperature or nature.^{15–17} The second strategy will focus on the formation of switchable networks with the introduction of Fe(II/III) spin crossover (SCO) centres in the framework. Indeed, SCO centres are extremely sensitive to their environment, and even the weakest modifications can be detected.^{18,19}

Finally, our charged networks will be evaluated on their ionic conduction properties (protons, alkaline and multivalent ions) within the frame of a pre-existing collaboration (PHENIX lab in Sorbonne Université, D. Dambournet). More specifically, we target intercalation materials for applications in battery. This study will benefit from the ERMES group expertise in paramagnetic NMR, and its use to monitor the electronic state and the local structure of the material during the different steps of the intercalation process.

This project includes: bench organic and inorganic synthesis for the preparation of the starting materials; coordination chemistry in solvothermal and microwave conditions for the preparation of the networks; solution and solid-state NMR, solution and solid-state UV-Vis, FT-IR, powder X-ray diffraction, single-crystal X-ray diffraction, thermodiffraction, TGA, and SQUID magnetometry for the characterisation of the compounds and the study of their properties.

We are seeking a highly motivated student with a keen interest in developing skills both in synthetic coordination chemistry and multi-technique physicochemical characterisations. Candidates should hold or be about to obtain a master's degree in chemistry or materials science.

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Deadline for application: May 12th 2023. Guidelines:

<http://www.ed406.upmc.fr/fr/contrats-doctoraux/depot-des-candidatures.html>

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