

Collaborative CSC (China) - Bordeaux University (France)

Doctoral School of the Chemical Sciences (ED n°40)

PhD topic proposed by Corine Mathonière (Professor), corine.mathoniere@u-bordeaux.fr

Research team: « Molecular Materials & Magnetism » at Centre de Recherche Paul Pascal (CRPP, Pessac); <https://m3.crpp.cnrs.fr/>

Title: Molecule-based Magnets with high Curie Temperatures.

The quest for high performance magnetic materials is essential to respond to the market demand in information storage as well as in many other domains. Despite their extensive technological use, the current magnets experience several drawbacks, such as high energy consuming fabrication and limited access to key elements. This has led to a sustained effort towards identifying new molecule-based magnetic materials that possess all the features associated with the traditional magnets but benefit from the advantages of molecular chemistry. For instance, molecule-based magnets can be synthesized in mild conditions and their solubility in organic solvents allows for the tuning and post-synthetic modification of their physical properties.

The M₃ group at the CRPP has recently demonstrated that the post-modification of a 2D coordination “polymer” Cr(pyrazine)₂Cl₂ (Figure 1) with reducing agents has led to a new material with very exciting properties. The initial compound shows a

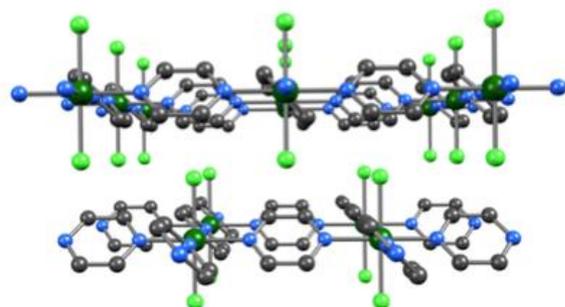


Figure. Perspective view of a 2D structure of Cr(pyrazine)₂Cl₂ prepared recently in our team. This compound is a highly conductive magnet ([Nature Chemistry 2018, 10, 1056](#)). Colour code: dark green, Cr; light green, Cl; blue, N; dark grey, C. H atoms have been omitted for clarity.

ferrimagnetic order at 55 K ([Nature Chemistry 2018, 10, 1056](#)), whereas the post-modified material is a magnet below 510 K, well above the room temperature ([Science, 2020, 370, 587](#)). The huge increase of the ordering temperature is explained by the generation of radicals on pyrazine ligands in the 2D network. As a continuation of the work done in the Cr(pyrazine)₂Cl₂ system, this PhD project will be devoted to the design and synthesis of new high-T_c magnets designed by the post-reduction of other known 2D systems M(pyrazine)₂X₂, M being a 3d metal ion and X = I, Br anions or O-based ligands.

The objectives of the PhD project are to make new high performance molecule-based magnets. Two strategies will be studied: (i) the first is to create bridges in their radical form between the magnetic centers by spontaneous electron transfer between metal ion and bridging ligand, (ii) the second is to create radical bridges by post-synthetic modification. In both approaches, the magnetic interaction through radical ligands will be significantly increased and may lead to magnetic orders.

The first part of the project will consist in preparing and characterizing coordination polymers or extended networks using redox-active ligands or by association of metal ion / ligand pairs for which spontaneous electron transfer takes place. A second part

will be devoted to post-synthetic reduction for synthesized systems which do not have free radical ligands. Finally in the last part of the thesis the study of magnetic properties will be carried out.

Personal qualifications and skills for the applicants:

Good knowledge of coordination chemistry. Experience with preparative coordination and/or solid-state inorganic chemistry is mandatory. Experience with X-ray crystallography is an advantage. Fluency and clarity in spoken as well as written English are essential.

Short CV of Prof. Corine Mathonière: Corine Mathonière, born in 1968 in Montluçon (France), received her education in Chemistry at the University of Paris XI, France. Her Ph.D. work was devoted to the optical properties of molecular-based magnetic materials under the supervision of Prof. O. Kahn (in 1993). After a post-doctoral stay in the group of Prof. P. Day (Royal Institution of Great Britain, Londres), she joined in 1994 the University of Bordeaux 1 as associate professor, then in 2010 was promoted professor. In 2010, she got a junior position of 5 years at the Institut Universitaire de France. Since 1994, Dr. C. Mathonière has developed at the Institut de Chimie de la Matière Condensée de Bordeaux (CNRS) research activities in “Switchable Molecules and Materials molecular” group interested in the synthesis and physical studies of switchable molecular materials. In her research field, she has published 145 articles with 6400 citations and has an *h* index of 44 (November 2020). During her career, Dr. C. Mathonière has trained 5 postdocs, 12 PhD students (1 not yet finished), 8 Master students, and 18 Undergraduate students.

History of contacts of Corine Mathonière with Chinese institutions:

- Collaborations with 2 Chinese research groups, with 6 joined publications since 2010:

Prof. D. Li, Central China Normal University, Wuhan, (4 joined publications).

Prof. X. Bao, Nanjing University of Science and Technology, Nanjing (2 joined publications).

- 3 invitations in China: 2019: the University of Nanjing University of Science and Technology, Nanjing University; 2010: Nanjing University; Peking University.