

Collaborative CSC (China) - Bordeaux University (France)

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

PhD topic proposed by Rodolphe Clérac (CNRS Research director), rodolphe.clerac@u-bordeaux.fr

Research team: «Molecular Materials & Magnetism» (M3 team) at Centre de Recherche Paul Pascal (CRPP, Pessac); <https://m3.crpp.cnrs.fr/>

Title: New conducting Molecular-based magnets.

Molecular materials offer, by virtue of their synthetic routes, a synthetic flexibility which allows fine adjustment of their physical properties. This flexibility makes it possible to generate functional materials, having one property, for example a magnetic order, or several properties, for example a magnetic order and a conductive state.

The M₃ group of CRPP recently demonstrated that the 2D coordination polymer Cr(pyrazine)₂Cl₂ exhibits a magnetic order at 55 K and a conductive state (Figure 1, **Nature Chemistry** 2018, 10, 1056). These two properties are linked to the presence of reduced pyrazines in the material. When this material is treated with a reducing agent, a new material with formula of Cr(pyrazine^{•-})₂(LiCl)_{0.7} is formed and shows a magnetic order below 510 K, well above room temperature (**Science** 2020, 370, 587). The drastic increase in the Curie temperature is explained by the transformation of all the bridging ligands into radicals.

As an extension of the work carried out on the Cr(pyrazine)₂Cl₂ system, this PhD project will be devoted to the design and synthesis of new conductive magnets (**Nat. Commun.** 2022, 12, 5766) by producing reductions on other known 2D systems of formula M(pyrazine)₂X₂ M, being a 3d metal ion and X anions I⁻, Br⁻ or oxygen-based ligands. The redox activity will be provided by the metal center or the bridging ligand, or both. Our goals are to strengthen the magnetic interactions between paramagnetic units as well as the electronic delocalization, in order to design and prepare new conducting magnets based on molecular building blocks.

The first part of the project will consist in preparing and characterizing coordination polymers or extended networks using neutral or reduced pyrazine, or by combining 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 present radical ligands. Finally, in the last part of the thesis, the detailed study of magnetic and electrical properties will be carried out in order to identify the structure-property relationships.

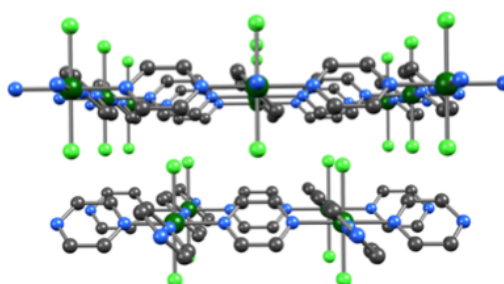


Figure 1. Perspective view of a 2D structure of Cr(pyrazine)₂Cl₂ prepared recently in our team. This compound is a highly conductive magnet (Nat. Chem. 2018, 10, 1056). Colour code: dark green, Cr; light green, Cl; blue, N; dark grey, C. H atoms have been omitted for clarity.

Personal qualifications and skills for the applicants:

The applicant will need to hold a Master degree in Chemistry before starting this PhD. 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 Dr. Rodolphe Clérac: Rodolphe Clérac, born in 1971 in Versailles (France), received his education in Physical-Chemistry at the University of Bordeaux 1, France. His Ph.D. work was devoted to the physical properties of molecular antiferromagnetic materials under the supervision of Prof. C. Coulon (in 1997). After short post-doctoral stay in the group of Prof. O. Kahn (ICMCB, Bordeaux), he joined in 1998 Prof. K. R. Dunbar's group at Michigan State University (East Lansing, Michigan, USA) and worked on the magnetic properties of coordination chemistry based materials. In 1999, he moved with Prof. K. R. Dunbar's group to Texas A&M University (College Station, Texas, USA) where he collaborated with Prof. F.A. Cotton on the magnetic properties of metal-metal bonded complexes. He joined the University of Bordeaux 1 in 2000, as associate professor, then in 2008 became full CNRS researcher and in 2013 was promoted CNRS Research Director. He was elected in 2019 at the European Academy of Sciences and in 2020 at the Academia Europaea, became in 2014 a distinguished fellow of the French Chemical Society and received various awards including the CNRS Silver Medal in 2021, the RSC/SCF Lectureship award in Chemical Sciences in 2022, the France-Berkeley Fund Award in 2017 and the National Chinese Award of the "1000 Talents Program" in 2014. Since 2000, Dr. R. Clérac has developed at the Centre de Recherche Paul Pascal (CNRS) a research group on "molecular materials & magnetism" interested in the synthesis and physical studies of molecular materials (that is currently composed of 1 Assistant Professor, 1 Professor, 4 CNRS researchers, 1 Assistant Engineer, 1 Technician, 4 Post-docs, 10 PhD students). The main subjects currently developed in his group deal with (i) macroconjugated polyaromatic molecules, (ii) molecule-based magnets, (iii) paramagnetic metal-metal bonded complexes, and (iv) magnetic and/or electro-active solutions and liquid-crystals. In this research field, he has published ca. 530 articles with more than 26000 citations and has an *h* factor of 84 (September 2023). During his career, Dr. R. Clérac has trained 35 postdocs, 30 PhD students, 26 Master students, 53 visiting PhD students and postdocs (for short training period) and 26 undergraduate students. Importantly Dr. R. Clérac has also developed a scientific network of active collaborations across the globe with currently 80 research teams in 27 different countries, including 11 research teams in China.