

1. PUBLISHABLE SUMMARY

Project objectives: Molecular based magnetic materials may be ranged in two classes. One class comprises the so call molecule-based magnets (MBM) in which the spin carriers interact in a three-dimensional array in the solid state. They may be organic, organometallic or coordination compounds. While different at the atomic scale, their magnetic behaviour is not different from the traditional magnets. The second class concerns the so called single-molecule magnets (SMM) in which a limited number of metal ions form a giant molecule with a giant magnetic spin. The magnetism is fundamentally different from the traditional magnets and is no more a solid state property. Indeed, these are the giant molecules which behave individually as isolated magnets. SMM have been proved to be relevant for quantum computing but the blocking temperatures below which these phenomena is observed are still very low (<5K) for practical applications.

The proposal was to synthesize chiral Single-Molecule Magnets (SMM) or Single-chain Magnet (SCM) by assembling magnetic “chiral molecular bricks”. The objective was to expand researches on SMM and SCM into new polynuclear compounds with nano-dimension to observe new phenomena due to cooperatives effects between chirality and magnetic properties such as the magneto-chiral effect or the enhancement of the energy barrier due to symmetry breaking.

Work performed since the beginning of the project: The work has first concerned the synthesis of bicomparmental ligands such as *D*-HL1, *L*-HL1, *D*-HL2, *L*-HL2 shown on Figure 1.

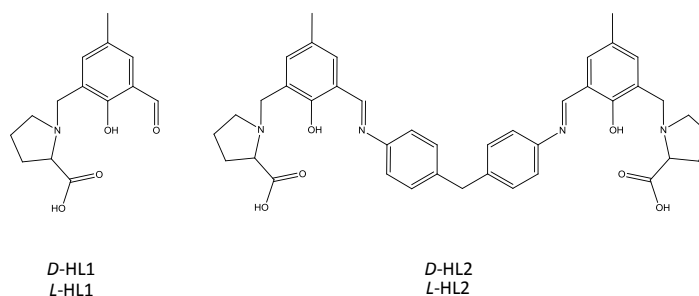


Figure 1. Example of bicomparmental chiral ligands.

Then for the synthesis of coordination compounds we followed a step by step strategy. For example in a first step 3d metals ions were coordinated to the chiral ligand to create a homometallic “Chiral magnetic bricks” as shown on Figure 2.

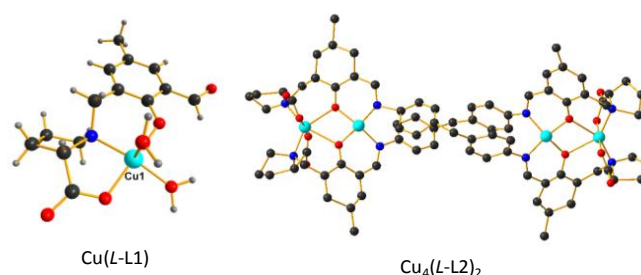


Figure 2. X-ray crystal structure of copper(II) “Chiral magnetic bricks” with ligand L-HL1 and L-HL2.

The second step consisted to assemble these homometallic “Chiral magnetic bricks” with lanthanide(4f) or another 3d metal ions to obtain a heterometallic system. For most compounds we succeeded to grow single crystal from which the crystal structures have been fully characterized. This part of the work has been realized with the collaboration of Assistant Professor G. Pilet and engineer E. Jeanneau from the team of Prof. D Luneau which has its own diffractometer. Dr. G. Novitchi has benefited greatly of training on the X-ray experimental technique. More than 20 crystal structures of chiral compounds have been done during the project comprising:

- Homometallic 1D-polimeric networks with Co (II) or Ni (II);
- Heterometallic 1D-polimeric networks [Dy^{III}₃Cu^{II}];
- Heterospin Co(II)-radical systems;
- Mn(III) hexanuclear cluster.

The studies of the magnetic properties were carried out mainly by Dr. G. Novitchi on a Quantum Design MPMS-XL5 equipped for AC susceptibility measurement in the team of Prof. D. Luneau. For some complexes supplementary measurements have been made on micro SQUID in collaboration with Dr. W. Wernsdorfer at Institut Néel in Grenoble. To better understand the nature of magnetic interaction and impact of chirality on the properties theoretical calculation have been performed in collaboration with the group of Prof. L. Chibotaru (Belgium). The work of Dr G. Novitchi gave rise up to now to 7 publications (1 Chem. Sci., 2 Inorg. Chem., 1 Dalton Trans, 1 Polyhedron, 1Eur. JIC and 1 Appl. Phys A. Mater) and several other are in preparation.

Main achievement: We were able to synthesis both D and L isomer of a heterometallic [Dy^{III}₃Cu^{II}] chain built from an alternation (Figure 3) between trinuclear Dy₃ SMM-building block and chiral copper(II) bis-valinate complex which is here the “chiral magnetic bricks”. Circular dichroism spectroscopy as well as X-rays diffraction studies proved unambiguously the enantiopurity of compound with chirogenese of the chiral environment in Dy₃. We found that the ground state of Dy₃ units in the chain, is characterized by almost perfect toroidal moments According to the calculations, a very strong toroidal magnetization can be induced in single-crystals of these compounds by applying a magnetic field at low temperature. Therefore this compound is multiferroic of T–F type where the applied homogeneous magnetic field can induce toroidal magnetization, and vice versa, and an applied circular magnetic field can induce a homogeneous ferromagnetic moment in the crystal. With the possibility of induced ferrotoroidicity, the [Dy₃Cu] polymer described here represent the first molecular-based material among the inorganic multiferroic crystals known to date. This work done in collaboration with Prof. A. Powell from Karlsruhe Institute of Technology was published as an edge article in Chemical Science (*Chem. Sci.* **2012**, 3, 1169-1176).

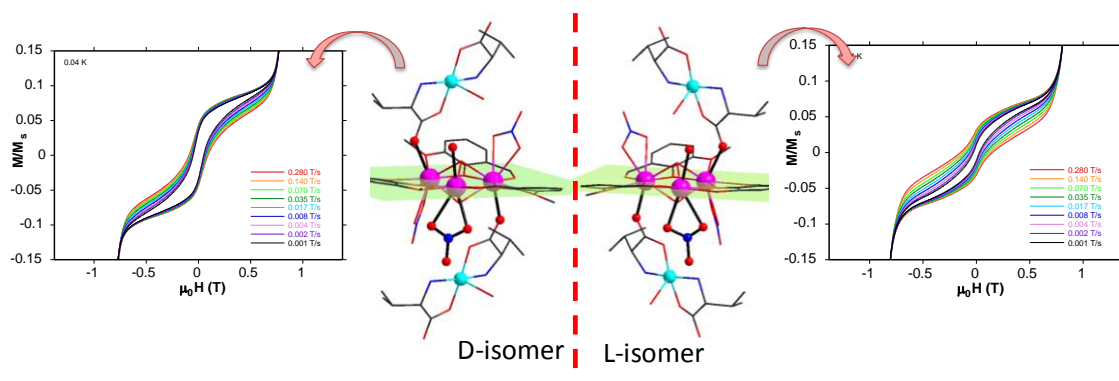


Figure 3. Hysteresis loops for two chiral heterometallic Dy/Cu isomeric networks.

Expected final results and potential impact and use: The societal issues of molecular magnets are numerous. Since its discovery a century ago magnetic recording has revolutionized our life from media to computing. The aim Single-Molecule Magnet is not to replace the existing magnets but to have novel magnetic materials for future applications such as in information storage or process as they have been proved to be relevant for quantum computing. In contrast to traditional magnets they are made in mild conditions and thus they are energy saving and they their environment impact is low. Because they are mainly organic with a small fraction of inorganic metal centers they are well suited for multi-functional purposes. This well exemplified by the [Dy₃Cu] compound obtained by Dr G. Novitchi and reported above as this SMM is also a multiferroic.

In conclusion this major result obtained by Dr. G. Novitchi shows that the objective of the project to synthesis chiral SMM in order to observe new phenomena due to cooperatives effects between chirality and magnetic properties has been fully achieved.