

## New Approaches for Single-Chain Magnets and Related Magnetically Correlated Materials

In order to reveal new theories or new techniques for capturing magnetic dynamics or spin transition in metal-complex-based compounds, we focused here on two types of magnetic compounds, (I) a family of alternating chain compounds composed of  $\text{Mn}^{\text{III}}$  salen-type complexes and TCNQ derivatives ( $\text{salen}^{2-} = \text{N,N}'\text{-ethylenebis(salicylideneimine)}$ ; TCNQ = tetracyano-p-quinodimethane), which is a target for Single-Chain Magnets with a strong correlation beyond the Ising limit, and (II) a family of cyano-bridged  $\text{Co}^{\text{II}}\text{-Fe}^{\text{III}}$  dinuclear compounds that occur an electron transfer at around 100 K to be a  $\text{Co}^{\text{III}}\text{-Fe}^{\text{II}}$  oxidation state at lower temperatures with accompanying a spin transition between high spin at the high temperature region and low spin at low temperature region in different structural space groups, respectively.

The researches on "molecular quantum magnets" that exhibit slow relaxation of the magnetization such as Single-Molecule Magnets (SMMs) have been carried out energetically in the wide fields of chemistry and physics since the beginning of 1990s, and some applications for nanotechnology have been tried in recent years. In this class of materials, one-dimensional materials named Single-Chain Magnets (SCMs) are unique because slow dynamics of their magnetization is closely related to short-range correlations between anisotropic spin units (such as Ising-type spins) along the chain. Clérac and Miyasaka discovered this magnetic property for the first time in a ferromagnetically coupled Ising-like spin chain and they named this class of material as "Single-Chain Magnet" [1]. In comparison to SMMs, SCMs possess an additional degree of freedom than the magnetic anisotropy  $D$  of the chain spin unit ( $D$  defined by:  $H = DS_z^2$ ): the exchange intra-chain coupling  $J$  (defined by:  $H = -2J\sum S_i \cdot S_{i+1}$ ) [2]. This parameter is a real advantage as it can be controlled by an external stimuli, for example by light irradiation, and thus, the SCM behavior could be finely tuned. In addition, we revealed that the SCM behavior might also be affected by a third degree of freedom, i.e. the inter-chain antiferromagnetic interactions  $J'$  [3,4]. Thus, we realize that intra-chain and inter-chain exchange couplings are more flexible and tunable parameters in this type of magnetic materials compared to the magnetic anisotropy, and this type of one-dimensional systems appears to be a good platform to observe boundaries between quantum and bulk (continuum) regimes. Furthermore, recently, we revealed that the SCM behavior is observed not only in the Ising limit with  $|D/J| \gg 4/3$ , but also in other limits like  $|D/J| \leq 4/3$  in the case where  $J$  is relatively large [5,6]. In such systems, the understanding of the domain walls is a key to understand their dynamic behavior. These results indicate that such one-dimensional magnetic materials can potentially be modulated at the molecular level

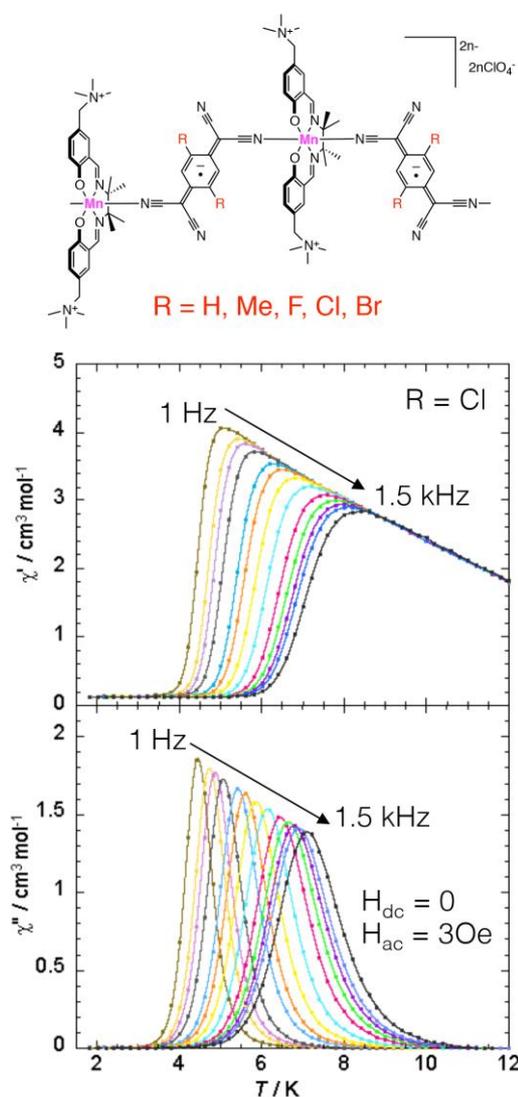


Fig. 1 A schematic representation of the target compounds in the project (I), which are SCM chains composed of  $\text{Mn}^{\text{III}}$  salen-type complexes and TCNQ derivatives, and the temperature dependence of ac susceptibilities ( $\chi'$ : in-phase;  $\chi''$ : out-of-phase) for the  $\text{R} = \text{Cl}$  compound.

by multiple degrees of freedom giving the opportunity of design the next generation of magnets.

Here, we, in particular, focused on two target materials: (I) SCMs with strong correlations in  $|D/J| < 4/3$ , and (II) heterometal compounds that occur a temperature-dependent inter-metal electron transfer. The latter target is not for SCM, but providing a new spin-switching system useful even for SCM works in future.

In the work on the target material (I), we designed a family of alternating chain compounds composed of  $Mn^{III}$  salen-type complexes (salen<sup>2-</sup> = N,N'-ethylenebis(salicylideneimine)) and TCNQ derivatives (TCNQ = tetracyano-p-quinodimethane; TCNQR<sub>x</sub> = TCNQF<sub>2</sub>, TCNQCl<sub>2</sub>, TCNQBr<sub>2</sub>, TCNQMe<sub>2</sub> as already synthesized for the original TCNQ unit (Fig. 1) [5]. These compounds have similar chain forms, but provide different exchange coupling constants, even though all are adopted in the relation of the  $|D/J| < 4/3$ . All compounds exhibited similar spin dynamics behavior as SCMs (Fig. 1) [5], but not followed in the theory of Glauber dynamics for  $|D/J| >> 4/3$ . Thus, this dynamics behavior could be due to the motion of domain wall, which should be explained using a different theory from the Glauber dynamics [7].

In the work on the target material (II), the French team of Dr. R. Clérac (CRPP, CNRS, France) and Prof. C. Mathoniere (Université Bordeaux I/ICMCB, France) prepared materials of cyano-bridged  $Co^{II}$ - $Fe^{III}$  dinuclear compounds

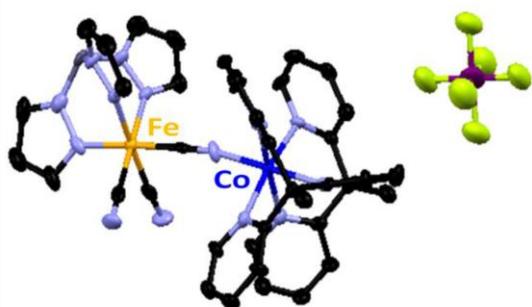


Fig. 2 Structure of cyano-bridged  $Fe^{III}$ - $Co^{II}$  dimer,  $[(Tp)Fe^{III}(CN)_3Co^{II}(PY5Me_2)]PF_6 \cdot 2DMF$ , where the counter anion  $PF_6^-$  can be replaced by  $AsF_6^-$ .

with different counter anions (Fig. 2). This family of paramagnetic compounds exhibited temperature-dependent inter-metal electron transfer to cause a  $Co^{III}$ - $Fe^{II}$  low spin system that was diamagnetic. Interestingly, this transition involved a structural modification changing its space group from Pnma for the high temperature region (paramagnetic) to  $P2_12_12_1$  for the low temperature region (diamagnetic) in the orthorhombic system. Thus, this transition was confirmed by temperature dependence of magnetic properties, which occur a spin transition from a paramagnetic state with  $S = 3/2$  to a diamagnetic state at the transition temperature, and structures measured at higher/lower temperatures than the transition temperature. Furthermore, the measurement of the permittivity of compounds in a pellet sample captured the transition in detail. These data proved that the electron transfer followed by a high spin/low spin transition simultaneously occurred with a reversible structural transition.

### References

- [1] R. Clérac, H. Miyasaka, M. Yamashita and C. Coulon, *J. Am. Chem. Soc.* 124, 12837 (2002).
- [2] C. Coulon, H. Miyasaka and R. Clérac, *Struct. Bond.* 122, 163 (2006).
- [3] C. Coulon, R. Clérac, W. Wernsdorfer, T. Colin and H. Miyasaka, *Phys. Rev. Lett.* 102, 167204 (2009).
- [4] H. Miyasaka, K. Takayama, A. Saitoh, S. Furukawa, M. Yamashita and R. Clérac, *Chem. Eur. J.* 16, 3656 (2010).
- [5] H. Miyasaka, T. Madanbashi, K. Sugimoto, Y. Nakazawa, W. Wernsdorfer, K. Sugiura, M. Yamashita, C. Coulon and R. Clérac, *Chem. Eur. J.* 12, 7028 (2006).
- [6] H. Miyasaka, T. Madanbashi, A. Saitoh, N. Motokawa, R. Ishikawa, M. Yamashita, S. Bahr, W. Wernsdorfer and R. Clérac, *Chem. Eur. J.* 18, 3942 (2012).
- [7] O. V. Billoni, V. Pianet, D. Pescia and A. Vindigni, *Phys. Rev. B* 84, 064415 (2011).