

Manganese-nitronyl nitroxide radical frameworks as switchable materials and ferrimagnets

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Coordination chemistry of nitronyl nitroxide free radicals has played a major role in the development of molecular-based magnetic materials.^[1] Even today, the metal-nitroxide bond remains a singular source of very diverse and original magnetic systems based on d-p or f-p hetero-spin frameworks.^[2-3] Thus, with nitronyl nitroxide (NIT) wearing imidazole groups (ImHR), we synthesized lamellar compounds $\{[\text{Mn}_2(\text{NITImR})_3]\text{X}\}_n$, in which positively charged 2D manganese-radical coordination polymers alternate with layers of anions X^- (fig. 1).

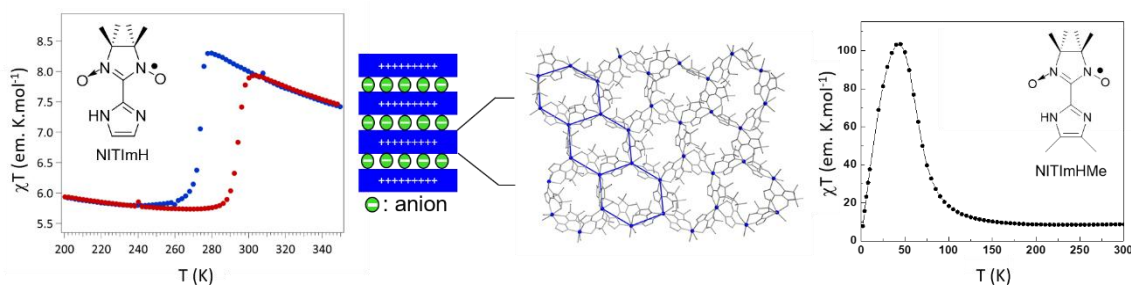


Figure 1: χT vs T for $\{[\text{Mn}_2(\text{NITIm})_3]\text{ClO}_4\}_n$ and $\{[\text{Mn}_2(\text{NITImMe})_3]\text{ClO}_4\}_n$, and X-ray structure

Compounds with imidazole (NITImH) as substituent and BF_4^- , ClO_4^- and PF_6^- anions, exhibit a thermo-induced valence tautomerism (VT) by electron transfer between manganese ions and radicals.^[4] The transition is reversible with hysteresis in the room temperature domain, which make these systems attractive as novel switchable materials (fig.1). Nevertheless, when adding substituents on the imidazole moiety of the radical (NITImHR; R= methyl or chloride) we lose the valence tautomerism and compounds behave as ferrimagnets (fig. 1), with T_C at 50 K.

During this lecture we will show how magnetic properties of these systems may be tuned either by anions, substituents on radical or by pressure, and how this may be related to interaction and cooperativity between layers of Mn(II)-radical polymers.

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