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Single-Chain Magnets: Their Characteristic Magnetism Closely Correlated with Crystal Structures

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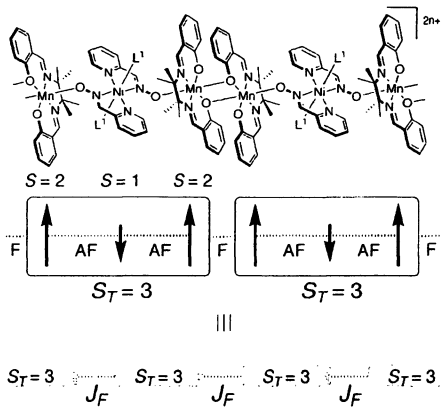
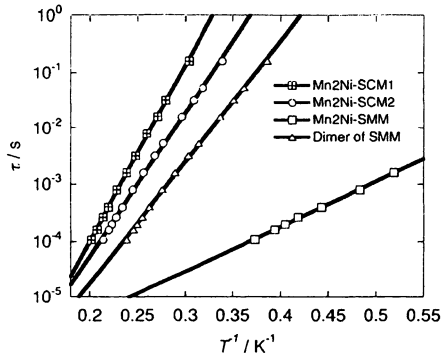
Since the discovery of the first Single-Molecule Magnet (SMM) in the beginning of 1990s, a number of candidates of SMM has been synthesized and investigated on their fundamental phenomena such as slow relaxation of the magnetization, quantum spin tunneling and quantum phase interference.[1] Single-Chain Magnet (SCM), as if it assumes to be chain-formed SMMs, discovered in this centuly[2] has been increasing much attention because of its peculiarity on isolated one-dimensionality and exchange-correlated dynamics in superparamagnetism (i.e., Glauber dynamics[3]). Our synthetic strategy for SCMs is to align Ising-type anisotropic axes of molecular building units in one-dimensional through an exchange mediator as bridging-ligands or another paramagnetic building units. The family of Mn^{III} salen-type compounds acts as a good buiding unit possessing a stromg uni-axial anisotropy defined as an out-of-plane Jahn-Teller axis. Indeed, we revealed SMM behavior in a simple dimer of Mn^{III} ions, $Mn_2(saltmen)_2(ReO_4)_2$, with the energy barrier for reversal of the magnetization 18 K which can be understood by $|D|S^2$.[4] The 1-D connecting of such dimers with Ni^{II} molecular units results in new magnetic systems, i.e., Single-Chain Magnet (SCM); $[Mn_2(saltmen)_2Ni(pao)_2(L^1)_2](A)_2$, which can be assumed to be ferromagnetic Ising-like chain with repeat of S = 3 spin units caused from antiferromagnetically-coupled Mn^{III}-Ni^{II}-Mn^{III} unit connected with a J_F.[5] The energy barrier is ca. 70 K through the series, which can be understood by $(8J + |D|)S^2$ when the correlation length is shorter than finit chain length.[6] The trimer unit of $[Mn^{III}$-Ni^{II}-$Mn^{III}]$ (S = 3) has been also isolated, which has exhibited SMM behavior with the energy barrier of 18 K explained by $|D|S^2$.[7] Structurally-similar chains $[Mn_2(5\text{-}Rsaltmen)_2Ni(pao)_2(bpy)](A)_2$ have been synthesized. However, these chains are no longer described by a simple regular chain with a J_F, but described by J_1 and J_2 (i.e., un-regular chain). The spin relaxation dynamics



of these chain compounds are understood by $n|D|S^2$ with n = 2, because of $J_1 >> J_2 \approx 0$.

Another ferromgnetic system with cyano-bridging has been also designed, which was a SCM with an S = 9/2 spin repeating unit.[8] The heterometallic 1 :1 assembly resulted in various SCM systems as Mn^{III}-Ni^{II} (ferri), Mn^{III}-radical (ferri), Mn^{III}-Fe^{III} (ferro), Mn^{III}-Mn^{III} (ferro), Mn^{III}-Cr^{III} (ferri) etc. Several examples of SCM will be present.



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