Magnetic Bistability on Molecular Scale : Single-Molecule Magnet

Lu Xu Literature Seminar November 29th, 2012

In 1980, Lis[1] reported the synthesis and structure of $Mn_{12}O_{12}(MeCO_2)_{16}(H_2O)_4$ (Mn_{12}Ac), a compound containing an unprecedented dodecanuclear cluster with disc-shaped geometry (Figure 1). Several years later, magnetization data for this compound collected indicates a spin ground state S = 10, which is subjected to large negative zero-field splitting. This results in an energy barrier U_{eff} separating the two lowest energy levels of M_s = -10 and M_s = +10. As a consequence of the energy barrier intrinsic to its ground state, the magnetization of Mn_{12}Ac can be pinned along one direction, and then relaxes only slowly at very low temperature[2, 3]. This class of multinuclear metal cluster that shows stable magnetization of purely molecular origin is called Single-molecule Magnet (SMM)[4, 5]. The slow relaxation is also observed by hysteresis experienced when magnetization is measured in a magnetic field sweep: on lowering the magnetic field again after reaching the maximum magnetization the magnetization remains at high levels and it requires a reversed field to bring magnetization back to zero (Figure 2). Steps can be observed at regular intervals in hysteresis loop, which correspond to an increase in the rate of change in magnetization when there is an energy coincidence of the levels on the opposite parts of the double-well potential. This phenomenon is called quantum tunneling[6].

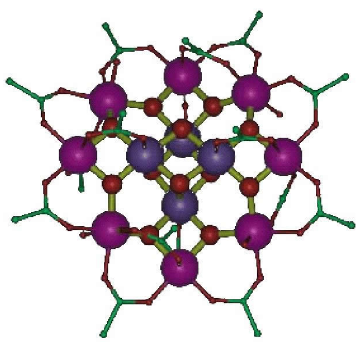

Figure 1 Structure of Mn_{12} cluster

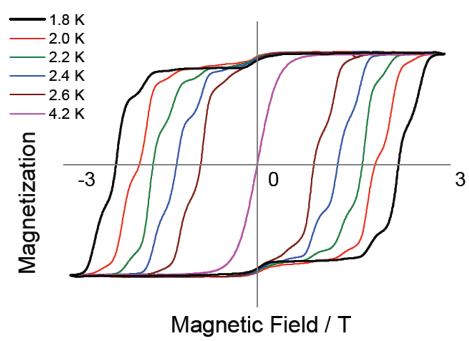

Figure 2 Typical hysteresis loop of SMM

The discovery that individual molecules can function as magnets provides a new "bottom-up" approach to nanoscale magnetic materials. Since the synthesis of the remarkable magnetic properties of Mn_{12} cluster, much effort has been devoted to searching other examples of molecules exhibiting such behavior, including Cu, Fe, Cr or even bimetal clusters[7,8,9]. The preparation of multinuclear metal complexes with large spin ground states and large negative zero-field splitting is a formidable challenge to synthetic chemists. In contrast to the predictive synthetic principles of organic chemistry, it is very difficult to synthesize SMMs in a traditional manner. Nevertheless, chemists have explored various classes of SMMs aside from the previously well studied Mn_{12} cluster. By manipulating the bridging group and periphery ligand, it is possible to change molecule symmetry and modify exchange interaction between metal ions, which strongly impact the number of spin ground state and zero-field splitting[10].

In recent work, Christou and coworkers[11] reported a giant $\{Mn_{84}\}$ SMM, which had a 4.2 nm diameter torus structure (Figure 3). It exhibited both magnetization hysteresis and quantum tunneling effect, and crystallized as supramolecular nanotubes. It is the largest SMM that has been synthesized up to date. The record for highest anisotropy barrier for SMM is $Mn_6O_2(Et\text{-}sao)_6(O_2CPh(Me)_2)_2(EtOH)_6$, with U_{eff} = 86.4 K and blocking temperature 4.5 K[12]. In the attempt to anchor single-molecule magnets on conducting surface, Forment-Aliaga and coworkers[13] deposited $[Mn_{12}O_{12}(bet)_{16}(EtOH)_4](PF_6)_{14}\cdot 4CH_3CN\cdot H_2O$ (Mn_{12}bet) on previously functionalized gold surfaces (Figure 4). Results showed that while their electronic properties were retained after depositing, the magnetization of Mn_{12}bet molecules is perturbed with respect to the pristine molecules. In an alternative strategy, Slageren and coworkers[14] successfully encapsulated Mn_{12}Ac in carbon nanotubes, yielding a new type of hybrid nanostructure that combines all the key SMM properties of guest molecules with functional properties of the host nanotube. The non-covalent interactions, which are responsible for efficient transport and encapsulation of the guest molecules into nanotubes, allow the molecules to stay mobile within the nanotube and align along the applied magnetic field.

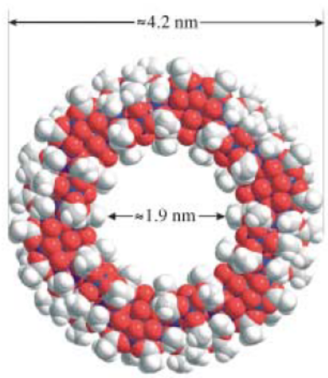

Figure 3 Giant $\{Mn_{84}\}$ cluster

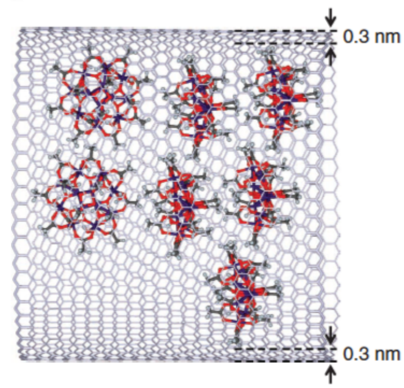

Figure 4 Mn_{12}Ac in carbon nanotube

Several applications for SMMs have been envisioned. One of the most obvious among them is their potential use as magnetic data storage media. An individual molecule is capable of storing a single bit of binary information as direction of its magnetization. This could lead to surface storage densities as high as 200,000 Gbits/in^2, approximately three orders of magnitude greater than can be achieved with current magnetic alloy film technology. Thus, the use of monolayers of SMMs as a storage media could one day lead to extremely high density data storage device. SMMS have also been considered promising candidate for molecular spintronics[15]. Spintronic systems exploit the fact that the electron current is composed of spin-up and spin-down carriers, which carry information encoded in their spin state and interact differently with magnetic materials. Molecular spin-transistor and molecular spin valves are two examples of incorporating SMMs into spintronic devices[16, 17].

In conclusion, the field of SMM is growing very fast since the discovery of first SMM, people are exploiting new families of SMMs in the pursuit of high anisotropy barrier and high blocking temperature, as well as trying to anchor SMMs on substrate and demonstrate nanoscale spintronic devices. The novel quantum tunneling effect that is intrinsic to SMMs is also drawing the attention of many theoretical physicists[18]. SMMs combine the classical macroscale properties of a magnet to the quantum properties of a nanoscale entity, which makes it one of the most appealing research focuses in various fields of science and technology.

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