Magnetically induced optical bi-stability of the molecular nanomagnet $Mn_{12}O_{12}(OOCMe)_{16}(H_2O)_4$ in an organic glass

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The magnetic hysteresis of the mixed-valence manganese cluster, $Mn_{12}O_{12}(OOCMe)_{16}(H_2O)_4$, ($Mn_{12}$),[1] a molecular superparamagnet,[2] can be optically detected in a dilute, frozen organic glass below the blocking temperature of 3.8 K by magnetic circular dichroism spectroscopy.

The manganese ions of Mn_{12} form a mixed valence cluster of overall tetragonal symmetry S_4, with four inner manganese(IV) ions each of spin $S = 3/2$, surrounded by eight manganese(III) ions of spin $S = 2$ (Fig. 1). Exchange interactions within the cluster result in a total cluster spin of $S = 10$. Anisotropy of uniaxial symmetry, due to the cluster crystalline field, separates the spins into a ladder of energy levels with $M_S = \pm 10$ being lowest in energy, about 60 K below the highest level with $M_S = 0$.[3,4] Thus the spins encounter a thermal barrier to re-orientation at ultra-low temperature and relaxation between sublevels $+S$ and $-S$ is extremely slow.[5,6] Consequently, at low temperatures, hysteresis is observed in the susceptibility as the magnetic field is cycled. Remarkably, hysteresis loops observed with single crystals of Mn_{12}, oriented with the unique molecular axis (Z) parallel to an applied field, show distinct stepped features at magnetic fields where the energies of different collective spin states of the manganese cluster coincide. This is interpreted as quantum mechanical tunnelling (QMT) of the electron spins through the thermal barrier.[5,6]

Although the absorption spectrum between 400 and 850 nm of an optically clear, organic glass of Mn_{12} is almost featureless, the magnetic circular dichroism (MCD) spectrum[7] shows a series of broad bands of positive and negative signs, Fig. 1. At 1.7 K after application of a polarising field of ±5 T a circular dichroism signal remains at zero magnetic field with an intensity of 30% of the signal at magnetic saturation. The sign of this signal depends on the direction of the polarising magnetic field. Hence the MCD signal reports the previous magnetic history of the sample.

Measurement of the magnetic field dependence of the MCD intensity at a given wavelength at a temperatures below and above the blocking temperature of 3.8 K (Fig. 2) shows a marked hysteresis on cycling the field at 1.7 K but no hysteresis at 4.2 K. It is, at first sight, surprising that significant polarisation remains at zero field since there is no molecular orientation in the glass.

In the case of Mn_{12} the optical selection rules for the cluster electronic states are $\Delta S = 0$ and $\Delta L = +1$ or -1 for the absorption of right or left circularly polarised light. It is expected that, in the wavelength region 400–800 nm, single-ion intra-d shell transitions will be present, arising from $^5E_g \rightarrow {}^5T_{2g}$ of Mn^{III} and $^4A_{2g} \rightarrow {}^4T_{1g}$ and $^4T_{2g}$ of Mn^{IV}, under O_h, although the possibility of oxide to Mn^{IV} charge transfer transitions cannot be excluded.[8,9] Exchange coupling of the Mn^{III} and Mn^{IV} imparts an overall cluster spin to these states. The orbital moments of the excited states dictate the selection rule $\Delta L = \pm 1$. Optical transitions arising from the ground-state spin manifolds $M_S = -S$ and $M_s = +S$ give rise to oppositely circularly polarised transitions whose intensity depends on the population differences between the $\pm S$ levels. Absorption of circularly polarised light requires that the optical transitions being excited have non-zero electric dipole components perpendicular to one another and to the applied field.[10] Hence Mn_{12} cluster subpopulations with particular orientations will be selectively detected if either the Zeeman splitting is highly

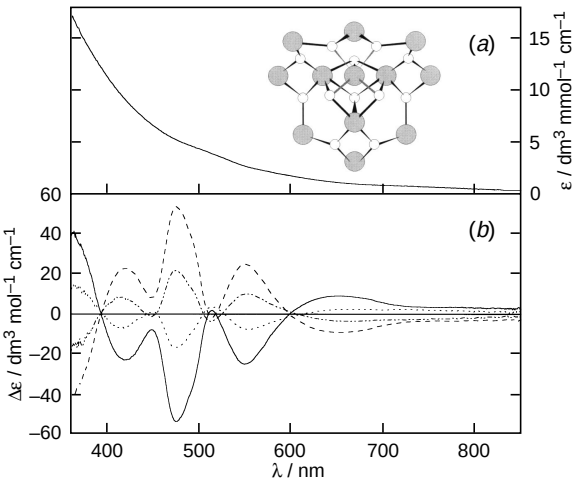

Fig. 1 (*a*) Absorption spectrum of Mn_{12} at room temperature; (*b*) MCD spectra of Mn_{12} in a frozen organic glass (dmf–MeCN) at 1.70 K and magnetic fields of 5 T (——) followed by reduction of field to zero (·····) and then application of a field of − 5 T (– – –) followed by zero field (–·–·–). MCD spectra are measured as the differential absorption of left and right circularly polarised light, ($\Delta\varepsilon = \varepsilon_L - \varepsilon_R$), by applying a uniform magnetic field parallel to the direction of the light beam.[7]

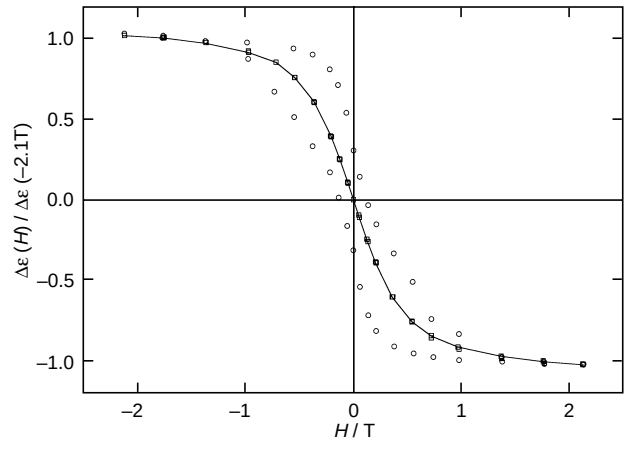

Fig. 2 MCD magnetisation measured between −2.1 and +2.1 T at 474 nm and at temperatures of (□) 4.2. and (○) 1.70 K of a frozen glass of Mn_{12}: upper line, field swept from −2.1 to +2.1 T; lower line, field swept from +2.1 to −2.1 T. Each point was determined by changing the magnetic field to a new value in steps of 0.1–0.2 T and allowing the MCD signal to become static, a period of 20–30 s. No further change in the MCD signal was observed over a period of several minutes. The solid line is the simulated curve for a multi-step Orbach process with orientational averaging.

anisotropic or the optical transitions are strongly polarised. The field dependences of the MCD intensities, at temperatures above the blocking temperature, are sensitive to the linear polarisation of optical transitions, that is, whether they are polarised *XY* and *XZ* (or *YZ*).[11] The MCD magnetisation at 550 nm can be fit well to the case of a purely *XY* polarised transition whereas that of 475 nm component corresponds to an equal mixture of *XY* and *XZ* (or *YZ*) polarisation (data not shown). Thus MCD hysteresis can be detected *via* an optical transition which has mixed polarisation presumably because of the high *g*-value anisotropy, $g_{//} = 40$, $g_{\perp} = 0$, within the $M_S = \pm 10$ pair of ground levels.

Attempts have been made to simulate the MCD and susceptibility hysteresis curves using a model in which relaxation takes place between two potential wells *via* a multi-step Orbach process. In this model the system is excited from one spin level to the next, until it reaches the top of the anisotropy barrier, followed by decay to the bottom of the other well.[12] A phonon density distribution curve was used resulting in a single-parameter model giving a simulation of the effective rate which depends only on the spin–lattice relaxation rate. The simulation reproduces the overall form of the susceptibility curves, including the fields at which the polarisation falls to zero at three different temperatures, and the MCD curves at 4.2 K (Fig. 2). However, it fails to account adequately for the MCD hysteresis seen at 1.7 K. This is probably due to the importance of QMT effects at lower temperatures.[5,6,13–16]

In conclusion, we have shown that the MCD spectra of Mn_{12} allow ground-state hysteresis effects to be measured even in randomly oriented molecular arrays. The MCD method offers a rapid method of surveying molecular paramagnets with potentially interesting properties. The shape of the curves suggests the need to include quantum tunnelling effects before the MCD hysteresis behaviour can be fully understood. But the feature of most significance reported here is that the resultant solutions are optically bi-stable and the effects can be induced or erased by application of a magnetic field. These properties suggest means of storing information in molecular magnetic devices with potential applications as quantum computers. Optical methods of addressing such molecules have the advantage of sensitivity and high speed combined with narrow band widths.

A. J. T. thanks the EPSRC/BBSRC for support of this work.

Footnote and References

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Received in Bath, UK, 30th May 1997; 7/03839I