Single-molecule magnet behaviour in metal–organic nanospheres generated by simple precipitation of $Mn_{12}O_{12}$ clusters†

Inhar Imaz,[a] Fernando Luis,[b] Chiara Carbonera,[b] Daniel Ruiz-Molina[c] and Daniel Maspoch*[a]

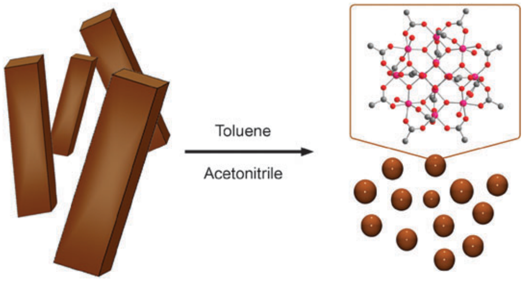
Received (in Cambridge) 17th October 2007, Accepted 11th December 2007
First published as an Advance Article on the web 21st January 2008
DOI: 10.1039/b716071b

Metal–organic sub-50 nm spherical particles that exhibit single-molecule magnet behaviour have been fabricated by direct precipitation of $Mn_{12}O_{12}$ clusters in a mixture of acetonitrile and toluene.

Micro- and nanoparticles have evolved into a powerful family of materials for many applications ranging from data storage, catalysis, photonics, electronics, lithography and microlenses to biosensors.[1] Therefore, widespread attention has been paid to new strategies for fabricating particles with novel compositions and properties. Metal–organic solids are hybrid materials created by the association of metal ions and organic ligands, which have recently shown a wide range of promising properties in gas sorption, sensing, catalysis, ion exchange, magnetism, optics, *etc.*[2] Because of the vast range of properties, one of the current objectives is the synthesis of nanoscale metal–organic materials (NMOMs).[3] To date, there are at least two possible routes to fabricating NMOMs. One involves the use of microemulsion techniques, which have already enabled the synthesis of Prussian blue- and triazol-based magnetic nanoparticles, and Gd(III) nanorods that can be used as multimodal contrast enhancing agents.[3–8] The second is based on precipitation processes.[9–13] For example, nanoparticles of neutral metal–salen complexes have been fabricated by using compressed antisolvent technology with supercritical carbon dioxide as the precipitant.[9] More recently, a method consisting of both coordination polymerization and precipitation in a poor solvent has allowed the synthesis of colloidal amorphous particles from infinite coordination polymers that show interesting optical properties and ion-exchange capabilities.[10,11] We have been inspired by the latter route to show that one can use a simple precipitation process to obtain functional nanoparticles from pre-synthesized magnetic metal–organic clusters.

Manganese oxide clusters of general formula $[Mn_{12}O_{12}(RCOO)_{16}(H_2O)_4]$ (Mn_{12}; R = alkyl, aryl) present a remarkable single-molecule magnet behaviour. These complexes present a large spin ground state together with a strong uniaxial anisotropy, resulting in an energy barrier for spin reversal. Therefore, Mn_{12} clusters can be considered as magnetic units of a sharply defined size that may offer new possibilities for high-density information storage molecular devices, spintronic systems and quantum-computing applications.[14] However, before these applications can be realized, micro- and nano-sized Mn_{12}-based systems, either in the form of structured surfaces or particles, must be fabricated. To date, while Mn_{12} clusters have been structured on surfaces[15–18] or synthesized in the form of sub-micron crystals,[19–21] less work has been reported on the obtaining of nanosized particles. The synthesis of Mn_{12}-based nanoparticles would be important, for example, to determine how the magnetic properties are modified in the transition from the macroscopic to the nanoscopic world, *i.e.*, size, crystallinity and dimensionality effects. In this communication, we report the fabrication of sub-50 nm Mn_{12}-based spheres that show SMM behaviour by a direct precipitation process. A series of solvents, such as hexane, chloroform, dimethylformamide, acetonitrile, toluene and dichoromethane, and respective solvent mixtures were systematically studied to determine the optimum conditions for nanoparticle formation. Under the studied conditions, Mn_{12}-based nanospheres were only obtained when an acetonitrile solution of crystalline Mn_{12} clusters were mixed with an antisolvent such as toluene (Scheme 1).

In a typical experiment, a macroscopic crystalline sample of $[Mn_{12}O_{12}(CH_3COO)_{16}(H_2O)_4]\cdot 2CH_3COOH\cdot 4H_2O$ (Mn_{12}-Ac, Fig. 1a) was dissolved into acetonitrile, and the resulting solution was added to an aliquot of toluene under vigorous stirring at room temperature (see ESI†). The mixture was then stirred for 1 h. A gradual opacity indicative of precipitation was observed. The resulting precipitate was collected by centrifugation, washed several times with acetonitrile and toluene, and finally dispersed in toluene. The final brown



Scheme 1

---

[a] *Institut Català de Nanotecnologia, Campus Universitari, 08193 Bellaterra, Catalonia, Spain. E-mail: daniel.maspoch.icn@uab.es; Fax: +34 93 581 4411; Tel: +34 93 581 4299*
[b] *Instituto de Ciencia de Materiales de Aragón, CSIC-Universidad de Zaragoza, 50009 Zaragoza, , Spain*
[c] *Centre d'Investigació en Nanociència i Nanotecnologia, Campus Universitari, 08193 Bellaterra, Catalonia, Spain*

† Electronic supplementary information (ESI) available: Detailed experimental data, EELS, IR, DLS and additional TEM and FE-SEM images of Mn_{12}-based nanoparticles. See DOI: 10.1039/b716071b

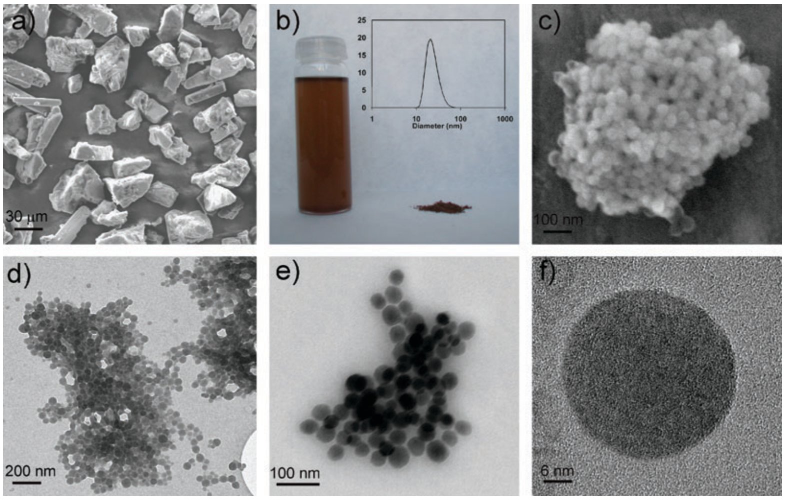


Fig. 1 (a) SEM image of polycrystalline Mn_{12}–Ac sample obtained by classical diffusion process. (b) Brown colloidal suspension in toluene (left) and powder (right) of Mn_{12}-based nanospheres. (c) FE-SEM image of separated nanoparticles. (d) low-magnification TEM and (e,f) higher magnification TEM images of spherical Mn_{12}-based particles. The inset in (b) shows the DLS measurement performed on the suspension showing a mean particle size of 24 ± 8 nm.

colloid showed a remarkable stability since preliminar aggregation traces only appeared after three weeks (Fig. 1b, left).

Fig. 1c shows a field emission scanning electron microscopy (FE-SEM) image of the collected precipitate, which reveals the generation of large amounts of stable nanosized particles with an average diameter of 30 ± 7 nm. The particle size was further studied by dynamic light scattering (DLS) characterization (inset of Fig. 1b). The DLS measurement performed on the suspension shows a mean particle size of 24 ± 8 nm, which is in good agreement with FE-SEM studies. We further examined the colloidal solution by high resolution TEM. Low and high magnification TEM images confirm that such nanoparticles are amorphous and spherical in shape (Fig. 1d–f).

Although the amorphous nature of nanoparticles hinders their structural analysis, additional evidences confirm the presence of Mn_{12}–Ac units. The electron energy-loss spectroscopy (EELS) spectra performed on single colloidal spheres reveal that every sphere contains manganese, oxygen and carbon (see Fig. 1s of ESI†). Also, the chemical composition of such particles determined by elemental analysis agrees with the presence of $[Mn_{12}O_{12}(CH_3COO)_{16}(H_2O)_4]$ clusters.† The IR spectrum reveals typical low frequency bands in the 500–750 cm^{-1} range (520, 561, 647, and 710 cm^{-1}) corresponding to Mn–O stretches, and evidences the presence of the $Mn_{12}O_{12}$ units.[16] In addition, the bands situated in the 1400–1700 cm^{-1} range reflect the carboxylate group vibrations.

Further evidence that the cluster preserves its structural integrity and its physical properties is given by magnetic measurements. To ascertain the presence and stability of nanoparticles, all magnetic measurements were performed on a sample that was analyzed by FE-SEM before and after these measurements were made. AC susceptibility data of Mn_{12}-based particles are plotted in Fig. 2. The data show the frequency-dependent behaviour typical of single-molecule magnets (SMMs), with a blocking of the real-part χ' accompanied by the onset of a non-zero imaginary component χ''. The equilibrium susceptibility, measured above the blocking temperature for each frequency, is well fitted by the Curie–Weiss law (solid line in Fig. 2). The fit gives $g = 2.04$ for $S = 10$, which are compatible with clusters having the same ground state as crystalline Mn_{12} compounds. Another important point deduced from these data is the absence of any magnetic impurity in the sample.

A further detailed analysis of these measurements reveals that the magnetic properties of such nanospheres do significantly change with respect to the bulk polycrystalline material. It is evident that a large fraction of fast-relaxing molecules (of the order of 40%), which are absent in the original crystalline material, are present in the nanoparticles.[22] In addition, the magnetic relaxation time of the majority, or the slow relaxing species, turns out to be about 3.5 times shorter than what is found in the polycrystalline Mn_{12}–Ac compound (see the inset of Fig. 2 where data for both materials are compared). Such variations are not unexpected, since the spin reversal strongly

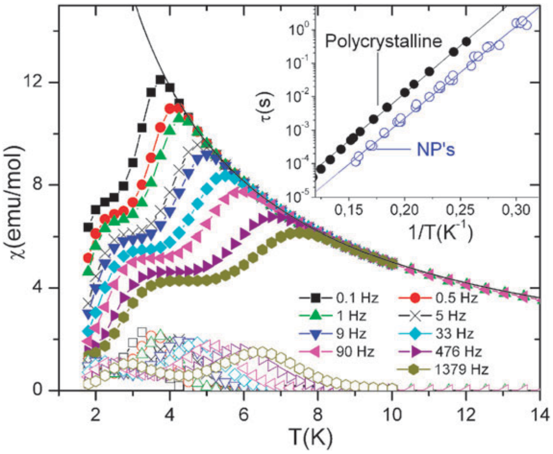


Fig. 2 AC magnetic susceptibility measurements as a function of temperature at different frequencies ($H_{DC} = 0$). The χ'' curves (open symbols) are closest to the temperature axis. (Inset: relaxation time (τ) of the nanoparticles (NP's) and of bulk crystalline Mn_{12}–Ac *vs.* $1/T$. Solid lines are least-square fits to the Arrhenius equation).

depends on parameters such as quantum tunnelling probabilities,[23] spin–phonon couplings,[24] and dipole–dipole interactions[25] between molecular spins, all of which can be affected by the crystallographic symmetry or by the increase of the surface-to-volume ratio. In recent times there has been increasing evidence showing that extrinsic perturbations, like lattice defects[26] or disorder in the position of interstitial molecules,[27] play a crucial role in determining the mechanism of quantum tunnelling of Mn_{12}–Ac spins. Our nanoparticles offer a well defined situation to investigate such phenomena.

As is shown in Fig. 2, the relaxation time follows the Arrhenius law with an activation energy $U = 63(1)$ K, which is close to the value $U = 65(1)$ K measured for the bulk material.[14,28] This fact indicates that the magnetic anisotropy of the $Mn_{12}O_{12}$ core is approximately preserved in the particles, though with a difference of 3(1)%. This indicates a slightly faster tunneling in the nanoparticle system. Moreover the short value found for the pre-factor $\tau_0 \sim 7(1) \times 10^{-9}$ s, which is nearly four times shorter for the nanoparticles than for the bulk material, reflects a strong interaction of the molecular spins with the vibrations of the lattice. This effect might result from the amorphous character of the particles, which increases the density of available vibrations with respect to an ordered solid. These results show that parameters that control how long the magnetic memory of a SMM lasts and how fast decoherence sets in (τ_0 controls the loss of quantum coherence caused by phonons) can be modified by structural changes.

In summary, we have demonstrated a versatile precipitation approach for structurating pre-synthesized functional Mn_{12} units in the form of sub-50 nm particles that preserve SMM behaviour with significant differences compared to the crystalline Mn_{12}–Ac material. Both, the methodology for the preparation of such nanospheres and the study of their differential magnetic properties, have obvious implications for the design of future applications of these molecular bits, which often require depositing them onto surfaces or processing them in diverse chemical forms.[29]

This work was supported by projects MAT2006-13765-C02 and Nanomateria-DGA. D.M. thanks the Ministerio de Ciencia y Tecnología for a RyC contract. Funding from the European Network of Excellence MAGMANet is also acknowledged. The authors thank the Servei de Microscopia of the UAB, Serveis Cientifico-Tècnics of the UB, and the Laboratori de Nanotecnologia de MATGAS.

Notes and references

1 (*a*) A. T. Bell, *Science*, 2003, **299**, 1688; (*b*) M. J. Bruchez, M. Moronne, P. Gin, S. Weiss and A. P. Alivisatos, *Science*, 1998, **281**, 2031; (*c*) T. A. Taton, C. A. Mirkin and R. L. Letsinger, *Science*, 2000, **289**, 1757; (*d*) J. Wang, M. S. Gudksen, X. Duan, Y. Cui and C. M. Lieber, *Science*, 2001, **293**, 1455; (*e*) M.-H. Wu and G. M. Whitesides, *Appl. Phys. Lett.*, 2001, **78** 2273; (*f*) J. Ramos, A. Millan and F. Palacio, *Polymer*, 2000 **41**, 8461.

2 (*a*) M. Eddaoudi, D. B. Moler, H. Li, B. Chen, T. M. Reineke, M. O'Keeffe and O. M. Yaghi, *Acc. Chem. Res.*, 2001, **34**, 319; (*b*) C. Janiak, *Dalton Trans*, 2003, 2781; (*c*) S. Kitagawa, R. Kitaura and S.-i. Noro, *Angew. Chem., Int. Ed.*, 2004, **43**, 2334; (*d*) D. Maspoch, D. Ruiz-Molina and J. Veciana, *Chem. Soc. Rev.*, 2007, **36**, 770.

3 W. J. Rieter, K. M. L. Taylor, H. An, W. Lin and W. Lin, *J. Am. Chem. Soc.*, 2006, **128**, 9024.

4 S. Vaucher, M. Li and S. Mann, *Angew. Chem., Int. Ed.*, 2000, **39**, 1793.

5 S. Vaucher, J. Fielden, M. Li, E. Dujardin and S. Mann, *Nano Lett.*, 2002, **2**, 225.

6 D. Brinzei, L. Catala, C. Mathonière, W. Wernsdorfer, A. Gloter, O. Stephan and T. Mallah, *J. Am. Chem. Soc.*, 2007, **129** 3778.

7 Y. Guari and J. Larionova, *Chem. Commun.*, 2006, 2613.

8 E. Coronado, J. R. Galán-Mascarós, M. Monrabal-Capilla, J. García-Martínez and P. Pardo-Ibáñez, *Adv. Mater.*, 2007, **19**, 1359.

9 C. A. Johnson, S. Sharma, B. Subramaniam and A. S. Borovik, *J. Am. Chem. Soc.*, 2005, **127**, 9698.

10 (*a*) M. Oh and C. A. Mirkin, *Nature*, 2005, **438**, 651; (*b*) M. Oh and C. A. Mirkin, *Angew. Chem., Int. Ed.*, 2006, **45**, 5492.

11 Y.-M. Jeon, H. Heo and C. A. Mirkin, *J. Am. Chem. Soc.*, 2007, **129**, 7480.

12 X. Sun, S. Dong and E. Wang, *J. Am. Chem. Soc.*, 2005, **127**, 13102.

13 H. Maeda, M. Hasegawa, T. Hashimoto, T. Kakimoto, S. Nishio and T. Nakanishi, *J. Am. Chem. Soc.*, 2006, **128**, 10024.

14 (*a*) G. Christou, D. Gatteschi, D. N. Hendrickson and R. Sessoli, *MRS Bull.*, 2000, **25**, 66; (*b*) D. Gatteschi and R. Sessoli, *Angew. Chem., Int. Ed.*, 2003, **42**, 268; (*c*) R. Sessoli, D. Gatteschi, A. Caneschi and M. A. Novak, *Nature*, 1993, **365**, 141; (*d*) D. Ruiz-Molina, G. Christou and D. N. Hendrickson, *Mol. Cryst. Liq. Cryst.*, 2000, **343**, 335.

15 S. Willemin, G. Arrachart, L. Lecren, J. Larionova, T. Coradin, R. Clérac, T. Mallah, C. Guérin and M. Sanchez, *New J. Chem.*, 2003, **27**, 1533.

16 J. Gómez-Segura, J. Veciana and D. Ruiz-Molina, *Chem. Commun.*, 2007, 3699, and references therein.

17 G. G. Condorelli, A. Motta, I. L. Fragalà, F. Giannazzo, V. Raineri, A. Caneschi and D. Gatteschi, *Angew. Chem., Int. Ed.*, 2004, **43**, 4081.

18 A. Naitabdi, J.-P. Bucher, P. Gerbier, P. Rabu and M. Drillon, *Adv. Mater.*, 2005, **17**, 1612.

19 D. Seo, W. Teizer, H. Zhao and K. R. Dunbar, *J. Magn. Magn. Mater.*, 2007, **312**, 205.

20 M. Muntó, J. Gómez-Segura, J. Campo, M. Nakano, N. Ventosa, D. Ruiz-Molina and J. Veciana, *J. Mater. Chem.*, 2006, **16**, 2612.

21 B. S. Luisi, K. D. Rowland and B. Moulton, *Chem. Commun.*, 2007, 2802.

22 Z. Sun, D. Ruiz, D. N. Hendrickson, N. R. Dilley, M. B. Maple, M. Soler, K. Folting, G. Christou and J. Ribas, *Chem. Commun.*, 1999, 1973.

23 (*a*) J. R. Friedman, M. P. Sarachik, J. Tejada and R. Ziolo, *Phys. Rev. Lett.*, 1996, **76**, 3830; (*b*) J. M. Hernández, X. X. Zhang, F. Luis, J. Bartolomé, J. Tejada and R. Ziolo, *Europhys. Lett.*, 1996, **35**, 301; (*c*) L. Thomas, F. Lionti, R. Ballou, D. Gatteschi, R. Sessoli and B. Barbara, *Nature*, 1996, **383**, 145.

24 (*a*) D. A. Garanin and E. M. Chudnovsky, *Phys. Rev. B*, 1997, **56**, 11102; (*b*) F. Luis, J. Bartolomé and J. F. Fernández, *Phys. Rev. B*, 1998, **57**, 505; (*c*) M. N. Leuenberger and D. Loss, *Europhys. Lett.*, 1999, **46**, 692.

25 (*a*) N. V. Prokof'ev and P. C. E. Stamp, *Phys. Rev. Lett.*, 1998, **80**, 5794; (*b*) J. F. Fernández and J. J. Alonso, *Phys. Rev. Lett.*, 2003, **91**, 047202.

26 (*a*) E. M. Chudnovsky and D. A. Garanin, *Phys. Rev. Lett.*, 2001, **87**, 227205; (*b*) R. Amigó, E. del Barco, Ll. Casas, E. Molins, J. Tejada, I. B. Rutel, B. Mommouton, N. Dalal and J. Brooks, *Phys. Rev. B*, 2002, **65**, 172403.

27 (*a*) A. Cornia, R. Sessoli, L. Sorace, D. Gatteschi, A. L. Barra and C. Daiguebonne, *Phys. Rev. Lett.*, 2002, **89**, 257201; (*b*) E. Del Barco, A. D. Kent, E. M. Rumberger, D. N. Hendrickson and G. Christou, *Phys. Rev. Lett.*, 2003, **91**, 047203; (*c*) S. Hill, R. S. Edwards, S. I. Jones, N. S. Dalal and J. M. North, *Phys. Rev. Lett.*, 2003, **90**, 217204.

28 F. Luis, V. González, A. Millán and J. L. García-Palacios, *Phys. Rev. Lett.*, 2004, **92**, 107201.

29 L. Bogani, L. Cavigli, M. Gurioli, R. L. Novak, M. Mannini, A. Caneschi, F. Pineider, R. Sessoli, M. Clemente-León, E. Coronado, A. Cornia and D. Gatteschi, *Adv. Mater.*, 2007, **19**, 3906.