Cite this: Chem. Commun., 2011, 47, 11501-11503

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COMMUNICATION

Matrix-dependent cooperativity in spin crossover Fe(pyrazine)Pt(CN)₄ nanoparticles[†]

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Received 22nd July 2011, Accepted 9th September 2011 DOI: 10.1039/c1cc14463d

Anisotropic nanoparticles of the Fe(pyrazine)Pt(CN)₄ network were prepared embedded in various matrices that revealed to have a dramatic effect on the cooperative spin crossover phenomena. By a judicious choice of the nature of the matrix and the control of interparticle distances, a hysteresis of 15 K was achieved close to room temperature for such nano-objects.

Spin crossover (SCO) systems are among the most fascinating materials in the field of molecular magnetism because they may show hysteresis at room temperature conferring a memory effect to the material. The switching between the high spin and the low spin states may be triggered by different external stimuli such as light, temperature, pressure, magnetic field, etc...¹ This opens the possibility for many useful applications as it has already been suggested and recently demonstrated.² One challenge in this area concerns the integration of SCO objects into nanoscopic devices for miniaturization issues, which implies the preparation and the investigation of the behaviour of nanosized objects. Such objects have been prepared very recently mainly for the triazole and the Hofmann-like clathrate families.^{3-5,7} Size effect has been evidenced in one system⁵ and hysteresis has been observed for sub-10 nm nanoparticles in other two systems.4

In this communication, we demonstrate that the environment of the nanoparticles may play a crucial role in the crossover process and that the cooperativity may be tuned by the matrix surrounding the nanoparticles within the nanocomposite. A hysteresis loop with an aperture of 15 K is evidenced for anisotropic ($10 \times 10 \times 5 \text{ nm}^3$) nanoparticles (NPs) of the Fe(pz)Pt(CN)₄ network when coated with a thin shell of SiO₂, while softer matrices destroy the cooperativity.

The Fe(pz)Pt(CN)₄ nanoparticles were synthesized according to the previously reported method (see ESI[†]).⁵ Transmission Electronic Microscopy (TEM) imaging performed on the nanoparticles in microemulsion (after step 1, see ESI[†]) shows mainly square-like particles (10×10 nm) as well as some rectangular ones that may be due to different relative orientations of the platelet-like particles as against the observation direction (Fig. 1, top left). To assess the exact shape and morphology of the particles, an electron tomography study was performed in TEM mode. A section of the reconstructed volume is plotted (Fig. 1, bottom right and S1, ESI⁺), it shows anisotropic nanoparticles, with in-plane widths L of 10×10 nm and a thickness h of 5 nm (mean L/h ratio slightly inferior to 2, see ESI[†]). This provides an estimation of the average number of atoms of 800 Fe atoms (and 800 atoms of Pt) included in a $10 \times 10 \times 5$ nm³ particle, with a high proportion of 55% Fe atoms located at the surface.

Preliminary studies of the environment effect on the SCO behaviour were evidenced on the particles coated with the AOT (bis(2-ethylhexyl) sulfosuccinate) surfactant. Progressively removing the organic matter by successive washing led to a complete change in the magnetic behaviour (Fig. S2, ESI†).



Fig. 1 TEM image and distribution of 10 nm NPs after step 1 (top), TEM image of **1** dispersed in chloroform (bottom left) and slices redrawn from the reconstructed volume in the XZ direction (bottom right).

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[†] Electronic supplementary information (ESI) available: Experimental section, tomography study, IR data, XRPD data, additional SQUID measurements. See DOI: 10.1039/c1cc14463d



Scheme 1 Calix8, $R = C_8 H_{17}$.

However, when all the organic matter was removed, X-Ray Powder Diffraction (XRPD) showed an increase in the mean size of the objects, indicating a partial connection between the nanoparticles (Fig. S3, ESI†). To avoid the coalescence and investigate the environment effect on the well defined original 10 nm nanoparticles, two coating agents were used: (i) a calixarene based ligand bearing 8 pyridine functions 1 (calix8 = $C_{192}H_{264}N_8O_{16}S_8$, Scheme 1 and ESI† for the synthetic procedure) that may replace the peripheral pyrazine or water molecules and thus avoid coalescence, (ii) the inorganic polymer silica with thin 2 and thick 3 SiO₂ shells.

For 1, TEM imaging of the microemulsion shows relatively monodispersed objects with a size of 10.5 ± 1.8 nm (Fig. 1, top). After addition of calix8 (step 2), the powder is washed with acetone and water several times in order to remove excess surfactant as confirmed by the IR analysis (Fig. S4, ESI[†]). The XRPD diagram is consistent with 10 nm objects within the nanocomposite as expected (Fig. S5, ESI[†]). Elemental Electron Dispersive Spectroscopy X-ray (EDS) analysis performed on 1 gives the following unit formula $FePt(CN)_4(C_4H_4N_2)_{0.4}$. $(H_2O)_{0.5}$ · $(C_{192}H_{264}N_8O_{16}S_8)_{0.07}$ (see Experimental section). This leads to a mean value of 0.56 pyridine/Fe(II), which corresponds to a full coverage of the 55% surface iron sites by calix8 that replace pyrazine on the particles' surface. Nanocomposite 1 is thus made of 10 nm NPs coated by a thin layer of calix8 that has a thickness of around 2 nm. The average distance between the nano-objects is thus around 4 nm. This organic shell prevents the NPs from coalescence and leads to dispersible particles. Indeed, 1 can be dispersed again in CHCl₃; the TEM image (Fig. 1, bottom left) confirms the size and the integrity of the nanoparticles.

The preparation of the silica-coated NPs 2 and 3 was carried out by slightly modifying already published procedures (see ESI[†]).⁶ An average size of 14 nm (14.0 \pm 2.4 nm) was determined for 2 by TEM imaging on the NPs after the silica shell formation prior to their isolation from the microemulsion (Fig. S6, ESI[†]). After recovering, the XRPD diagram confirms the integrity of the clathrate nanocrystals when coated by SiO₂ (Fig. S7, ESI[†]). The presence of the SiO₂ shell was first confirmed by EDS analysis; a Si: Fe: Pt ratio of 6:1:1 was found. A dispersion of the NPs in MeOH allowed imaging the SiO₂ coated NPs by Scanning Transmission Electronic Microscopy in dark field mode (HAADF-STEM) and their composition was probed by Electron Energy Loss Spectroscopy (EELS). Fig. 2 shows a typical profile of one of the largest particles; it reveals that Fe is present on a width of 11-13 nm that corresponds to the Fe(pz)Pt(CN)₄ cores, surrounded by a shell of around 2 nm of silica, leading to an overall size close to 17 nm. Most of the



Fig. 2 STEM image of NPs of **2** after dispersion in methanol (top) and EELS map of one particle showing the presence of Si and Fe in the particle's core (left and right).

particles are isolated and, when present in aggregates, are separated by the thin silica shell (Fig. S8, ESI[†]). For sample **3**, the thicker silica shell can be observed in the TEM images as a mean size of 18.4 ± 3.4 nm is observed in the microemulsion (Fig. S9, ESI[†]). The XRPD diagram still gives a size of 10 nm for the core and the silica shell is estimated to be around 4.5 nm (Fig. S7, ESI[†]), leading to an average separation of 9 nm between the nano-objects within the composite, while this separation is less than 5 nm for **2**. The infra-red spectrum (Fig. S10, ESI[†]) and EDS analysis (Si: Fe: Pt = 60:1:1 for **3**) confirm the much larger amount of silica formed for **3** compared to **2**.

Magnetic studies, performed using a SQUID susceptometer on all three compounds, were repeated in several batches for each one. A strict protocol was applied consisting of heating the sample at 130 °C for 1 hour within the SQUID in order to remove solvent molecules that may have an influence on the magnetic behaviour. The cooling rate was 0.5 K min⁻¹ for all samples. For **3** (thick SiO₂ shell) a gradual transition with the $T_{\rm C}$ close to 220 K is observed; the residual Fe(II) high spin (HS) fraction was found to be around 50% at T = 50 K (Fig. 3). In the case of more concentrated samples **1** and **2**, a steeper transition occurs at higher temperature (around 260 K), and a smaller HS Fe(II) residual fraction remains (30% for both at T = 50 K). In all cases, the decrease of the hysteresis width and the transition temperature is observed together with an increase of the residual HS fraction. It was always observed



Fig. 3 $\chi T = f(T)$ for 1(green), 2 (black) and 3 (red).

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upon increasing the average distance between the nanoparticles within the composite independently from the nature of the coating agent. Indeed, diluting the NPs in the organic polymer polyvinylpyrrolidone (PVP) leads to a magnetic behaviour very close to that of **3** (Fig. S11, ESI†).

The main result that highlights the role of the matrix is the presence of a large hysteresis of 15 K for 2 where the particles are coated with a thin silica shell, while only a very small aperture of 2 K occurs for 1 (the calix-covered particles) and no hysteresis is observed for the diluted composites whether in silica or in PVP. This is consistent with results reported on particles of related 2D networks embedded in PVP.⁷

These results demonstrate that the relative separation between the NPs plays a major role for the cooperativity. The diluted compounds (3 and the PVP coated particles) have weak cooperativity and the amount of the residual HS Fe(II) fraction corresponds to the percentage of Fe(II) ions present on the particles surface. While for the concentrated ones (1 and 2), the cooperativity is stronger. However, the degree of cooperativity depends not only on the average distance between the objects but on the nature of the matrix also. When the particles are coated with the organic ligand (calix8) that imposes a distance between the particles of around 4 nm, only a weak hysteresis is present while for the SiO2 coated NPs a hysteresis of 15 K occurs despite a separation of 5 nm. The observed results lead to the conclusion that the key-point of the magnetic behaviour stems from a conjugated effect of the nature of the matrix and the average distance between the nanoparticles within the nanocomposites. The nature of the interface plays a minor role since compounds 2 and 3 are made of nanoparticles coated with SiO2 and have a completely different magnetic behaviour, while 3 and the PVP nanocomposite have the same magnetic behaviour.

These conclusions may be rationalized by considering the ability of the matrix to transmit the elastic vibrations due to the switching of each nanoparticle from LS to HS. The propagation of the phonons via elastic interactions is invoked in many models to explain the cooperativity of the SCO phenomena, and parameterized in molecular complexes by an empirical interaction parameter Γ .⁸ In the Spiering model, Γ is related to the bulk modulus of the crystal that quantifies the compressibility of the crystal and the ability to transmit the vibrations.⁹ For the case of the embedded nanoparticles, cooperativity is due to the transmission within the nanocomposite of the elastic forces between the single nanoparticles through the matrix. The less compressible the matrix (high bulk modulus) the better the propagation of the vibrations is and the larger the hysteresis is. For a defined matrix (samples 2 and 3), the shorter the distance the better the propagation of the elastic interactions is.

This communication highlights the crucial influence of the matrix surrounding the particles that propagates elastic interactions: a "compressible" matrix leads to a lower cooperativity of the SCO phenomena in the present case, while more rigid media, such as silica, restores the hysteresis loop due to a stronger cooperativity. In a first stage, this may be understood as the variation, through the mechanical/elastic properties of the matrix surrounding the SCO nanoparticles, of the long range elastic interactions which, as we know, are mainly attributed to the electron-phonon couplings within the crystal network. These experimental results thus open new perspectives in the area of spin crossover nanomaterials where cooperativity can be triggered and/or tuned by changing, for instance, the mechanical properties of the media surrounding the nano-objects.

The authors gratefully acknowledge for their financial support from the Higher Education Commission of Pakistan, the French Ministry of Research (ANR grant contract number JCJC N° ANR-08-JCJC-0085-01) and the METSA network. We thank the Centre Commun de Microscopie Electronique d'Orsay for the instrumentation and Dr Gabor Molnar for fruitful discussion.

Notes and references

- P. Gutlich and A. Hauser, Coord. Chem. Rev., 1990, 97, 1–22; J. Krober, E. Codjovi, O. Kahn, F. Groliere and C. Jay, J. Am. Chem. Soc., 1993, 115, 9810–9811; A. Hauser, J. Jeftic, H. Romstedt, R. Hinek and H. Spiering, Coord. Chem. Rev., 1999, 192, 471–491; V. Niel, J. M. Martinez-Agudo, M. C. Munoz, A. B. Gaspar and J. A. Real, Inorg. Chem., 2001, 40, 3838; A. Bousseksou, G. Molnar, L. Salmon and W. Nicolazzi, Chem. Soc. Rev., 2011, 40, 3313–3335; S. Bonhommeau, T. Guillon, L. M. L. Daku, P. Demont, J. S. Costa, J. F. Letard, G. Molnar and A. Bousseksou, Angew. Chem., Int. Ed., 2006, 45, 1625–1629; S. Bonhommeau, G. Molnar, A. Galet, A. Zwick, J. A. Real, J. J. McGarvey and A. Bousseksou, Angew. Chem., Int. Ed., 2005, 44, 4069–4073.
- O. Kahn and J. P. Launay, *Chemtronics*, 1988, **3**, 140; O. Kahn and C. J. Martinez, *Science*, 1998, **279**, 44–48; L. Salmon, G. Molnar, D. Zitouni, C. Quintero, C. Bergaud, J. C. Micheau and A. Bousseksou, *J. Mater. Chem.*, 2010, **20**, 5499–5503.
- 3 S. Cobo, G. Molnar, J. A. Real and A. Bousseksou, Angew. Chem., Int. Ed., 2006, 45, 5786-5789; G. Molnar, S. Cobo, J. A. Real, F. Carcenac, E. Daran, C. Vieu and A. Bousseksou, Adv. Mater., 2007, 19, 2163-2167; T. Forestier, S. Mornet, N. Daro, T. Nishihara, S. Mouri, K. Tanaka, O. Fouche, E. Freysz and J. F. Letard, Chem. Commun., 2008, 4327-4329; T. Forestier, A. Kaiba, S. Pechev, D. Denux, P. Guionneau, C. Etrillard, N. Daro, E. Freysz and J. F. Letard, Chem.-Eur. J., 2009, 15, 6122-6130; J. R. Galan-Mascaros, E. Coronado, A. Forment-Aliaga, M. Monrabal-Capilla, E. Pinilla-Cienfuegos and M. Ceolin, Inorg. Chem., 2010, 49, 5706-5714; A. Tissot, J. F. Bardeau, E. Riviere, F. Brisset and M. L. Boillot, Dalton Trans., 2010, 39(33), 7806-7812; C. Faulmann, J. Chahine, I. Malfant, D. de Caro, B. Cormary and L. Valade, Dalton Trans., 2011, 40(11), 2480; J. M. Herrera, S. T.-P. Titos-Padilla, S. X. W. Chen, J. J. Delgado and E. Colacio, Angew. Chem., Int. Ed., 2011, 50, 3290.
- 4 E. Coronado, J. R. Galan-Mascaros, M. Monrabal-Capilla, J. Garcia-Martinez and P. Pardo-Ibanez, *Adv. Mater.*, 2007, 19, 1359–1361; J. Larionova, L. Salmon, Y. Guari, A. Tokarev, K. Molvinger, G. Molnar and A. Bousseksou, *Angew. Chem., Int. Ed.*, 2008, 47, 8236–8240.
- 5 F. Volatron, L. Catala, E. Riviere, A. Gloter, O. Stephan and T. Mallah, *Inorg. Chem.*, 2008, 47, 6584–6586; A. B. Gaspar, I. Boldog, V. Martinez, P. Pardo-Ibanez, V. Ksenofontov, A. Bhattacharjee, P. Gutlich and J. A. Real, *Angew. Chem., Int. Ed.*, 2008, 47, 6433.
- 6 F. J. Arriagada and K. Osseoasare, *Adv. Chem. Ser.*, 1994, 234, 113–128; F. J. Arriagada and K. Osseoasare, *J. Colloid Interface Sci.*, 1995, 170, 8–17.
- 7 A. B. Gaspar, V. Martinez, I. Boldog, V. Ksenofontov, A. Bhattacharjee, P. Gutlich and J. A. Real, *Chem. Mater.*, 2010, 22, 4271–4281.
- 8 C. P. Slitcher and H. G. Drickamer, J. Chem. Phys., 1972, 56, 2142-2148.
- 9 V. Ksenofontov, H. Spiering, A. Schreiner, G. Levchenko, H. A. Goodwin and P. Gutlich, *J. Phys. Chem. Solids*, 1999, **60**, 393–399; H. Spiering, T. Kohlhaas, N. Romstedt, A. Hauser, C. Bruns-Yilmaz, J. Kusz and P. Gutlich, *Coord. Chem. Rev.*, 1999, **192**, 629–647.