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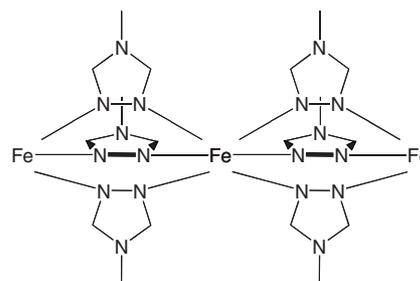
Bistable Spin-Crossover Nanoparticles Showing Magnetic Thermal Hysteresis near Room Temperature**

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Spin-crossover systems^[1–3] are a paradigmatic example of bistable materials. In such materials the magnetic state can be tuned from a low-spin configuration to a low-lying metastable high-spin configuration through external stimuli: thermally, by means of light irradiation, or under pressure.^[4–6] Therefore, they have been postulated as components for a new generation of memory devices,^[7] multifunctional materials,^[8] and other magnetic applications.^[9] In order to reach this goal, this phenomenon needs to occur at temperatures close to room temperature, be easily reversible, and be stable. Most examples of spin-crossover systems known to date that meet these requirements are based on iron complexes.^[10–14]

Some of the most promising candidates come from the $[\text{Fe}(\text{trz})_3]\text{X}_2$ ^[15] family, where trz is a triazole derivative and X is the counter anion. In these compounds, the metal ions are bound by the ligands, giving 1D polymeric structures (Scheme 1) that exhibit a cooperative spin transition from Fe^{II} low spin (LS) to high spin (HS). Both the temperature at which this transition occurs and the existence of hysteresis during the process can be tuned by playing with combinations of different triazole derivatives and anions.^[16] The spin transition is accompanied in these triazole complexes by a significant color change, in addition to the change in the magnetic moment from $S_{\text{LS}} = 0$ to $S_{\text{HS}} = 2$. This color change, usually from deep purple/red to light pink or white, has been used to develop write/read applications.^[7]

The next step towards possible technological applications for these materials will require a big effort regarding their



Scheme 1. Polymeric structure of the $[\text{Fe}(\text{trz})_3]\text{X}_2$ ^[15] family.

processing as suitable components, including miniaturization in the framework of current technologies. Nanoparticles of these materials have been reported,^[17] but the reduced size in this case resulted in suppression of the magnetic hysteresis. The preparation of stable nanoparticles that retain magnetic bistability and hysteresis is an obvious, and key, challenge.

Nanoparticles of $[\text{Fe}(\text{Htrz})_2(\text{trz})](\text{BF}_4)$ have been prepared using the reverse micelle technique (see the Experimental section). Clear deep-purple suspensions of these nanoparticles in *n*-octane are stable for weeks, without the appearance of any cloudiness. In addition, the solid produced by controlled evaporation of the solvent can be suspended again to yield a bright transparent suspension. This suspension does indeed turn light pink when heated up, maintaining this color until it cools down below 70 °C. Both colors, each associated with a different spin state, are stable for a wide range of temperatures (Fig. 1).

The size distribution in these nanoparticle suspensions was investigated by dynamic light scattering using a Malvern Zetasizer instrument. A one-day-old suspension showed a narrow single peak at 11 ± 5 nm (Supporting Information, Fig. S1), with the maximum at 10.9 nm and medium statistical size at 14.6 nm. This indicates that a very narrow size distribution is obtained using this synthetic procedure without further purification.

Transmission electron microscopy (TEM) images (Fig. 2) of droplets from these suspensions, after solvent evaporation, showed a regular distribution of roughly spherical nanoparticles. The average nanoparticle size, estimated by particle counting, was found to be below 20 nm. The assembly of the nanoparticles made this counting difficult. However, this result is in good agreement with data obtained by dynamic light scattering.

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Figure 1. Bistability of a suspension of the title nanoparticles in octane: in the low-spin state (left) and in the high-spin state (right).

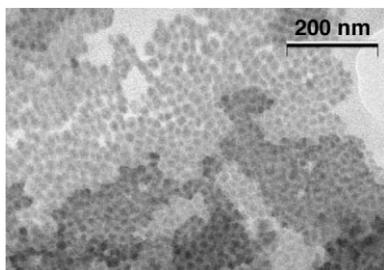


Figure 2. TEM image of as-prepared $[\text{Fe}(\text{Htrz})_2(\text{trz})](\text{BF}_4)$ nanoparticles.

A suspension of as-prepared $[\text{Fe}(\text{Htrz})_2(\text{trz})](\text{BF}_4)$ nanoparticles was dried by removal of the solvent in vacuo, and magnetic measurements were performed on the solid residue. As shown in Figure 3, the spin transition is clearly preserved, and it remains almost identical to that reported for bulk samples. The transition is very abrupt with a well-shaped thermal

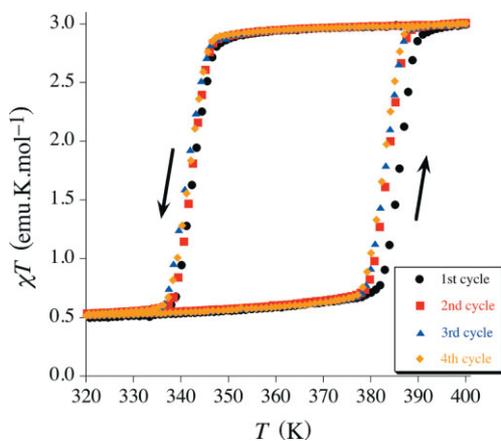


Figure 3. Magnetic thermal hysteresis for as-prepared $[\text{Fe}(\text{Htrz})_2(\text{trz})](\text{BF}_4)$ nanoparticles (magnetic moment represented per mole of Fe).

hysteresis loop of over 40 K. The magnetic moment increases with a $T_c \uparrow$ of 386 K, and when the temperature is lowered $T_c \downarrow$ occurs at 343 K. After successive cycles the heating-up transition moves slightly towards lower temperatures, stabilizing at $T_c \uparrow = 384$ K.^[18] This change is opposite to that observed for bulk samples, where the hysteresis slightly increases after a few cycles.^[19] Another difference in the magnetic properties compared with the material in the bulk is the high relative magnetic moment found at low temperatures. This indicates a higher HS population, which can be estimated as around 20 %, whereas less than 10 % was reported for the bulk. This difference could be attributed to the high surface area of the nanoparticles. Surface Fe atoms will possess a partial coordination, favoring their HS state at all temperatures.

In conclusion, we have demonstrated that the reverse micelle technique can be applied to polymeric spin-crossover systems, such as $[\text{Fe}(\text{Htrz})_2(\text{trz})](\text{BF}_4)$, to control the growth of the crystallites. Small nanoparticles of diameters around 10 nm and narrow size distribution were obtained. It is easy to envision that, by modifying the synthetic procedure, the size and critical temperatures of these nanoparticles can be tuned. On one hand, different ratios of solvent, water, and surfactants will lead to different micelle sizes, which will affect the particle size and, maybe, the magnetic properties. On the other hand, the critical temperatures can be lowered towards room temperature by changing the composition of the nanoparticles. Indeed, on doping the $[\text{Fe}(\text{Htrz})_2(\text{trz})](\text{BF}_4)$ nanoparticles with 20 % Zn^{II} , the thermal reversible hysteresis loop moves to $T_c \uparrow \sim 356$ K and $T_c \downarrow \sim 336$ K (Fig. S3). Complete studies of these two strategies are under way.

The good stability of these nanoparticles in organic solvents also opens the possibility of processing these suspensions as thin films and other nanostructures to be deposited on substrates or embedded/inserted in organic or inorganic matrices. As the bistability is a property of the nanoparticle, it is expected that the resulting materials will retain the spin-crossover phenomenon.

Experimental

$\text{Fe}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ (1 g, 2.96 mmol) was dissolved in water (6 mL), and added to a mixture of sodium dioctyl sulfosuccinate (10 g, 98 %), in 100 mL of octane. After a few minutes of stirring, behenic acid (2 g) was added to this suspension. 1,2,4-*H*-Triazole (0.614 g, 0.0089 mol) was dissolved in ethanol (3 mL), and added to a mixture of sodium dioctyl sulfosuccinate (10 g, 98 %) in 100 mL of octane. The two suspensions were mixed and stirred for 4 h. Afterwards, the mixture was filtered to yield a purple suspension of $[\text{Fe}(\text{Htrz})_2(\text{trz})](\text{BF}_4)$ nanoparticles. The Zn-doped nanoparticles were prepared by the same procedure.

Magnetic measurements were carried out with a Quantum Design (SQUID) magnetometer MPMS-XL-5 with an applied field of 1000 G (0.1 T). Calorimetry measurements were performed with a Mettler Toledo DCS 821e differential scanning calorimeter.

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