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Magnetic Bistability of Individual Single-Molecule Magnets Grafted on Single-Wall Carbon Nanotubes**

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Magnetic bistability has already been observed and widely investigated for magnetic complexes called single-molecule magnets (SMMs).[1–3] This behavior, observed at the level of a crystal, is due to specific molecular properties, that is, the presence of a high-spin ground state and an easy axis of magnetization for the individual molecules assembled within the crystal. For the design of information storage devices based on single magnetic molecules (albeit at very low temperatures), one major challenge is to confirm the presence of magnetic bistability at the level of individual molecules. The first studies focused on archetypal Mn_{12} SMMs. Unfortunately, because of the relatively weak stability of this family of compounds and the very high sensitivity of the orientation of the easy axis of magnetization towards the environment, no magnetic hysteresis was observed when the molecules were anchored on surfaces.[4] Chemical stability and particularly robustness against deformation are necessary to maintain the magnetic bistability in isolated SMMs, especially when the molecules are electronically coupled to a surface. Very recently, using X-ray magnetic circular dichroism and focusing on a tetranuclear Fe^{III} complex (Fe_4) grafted on gold, Sessoli and co-workers gave the first evidence of the presence of a magnetic hysteresis loop associated with isolated molecules.[5] Another important issue is the investigation of the synergy between electron transport and the magnetic properties of the SMMs, which may eventually be exploited for addressing individual molecules.[6–8] Assembling SMMs on carbon nanotubes (CNTs) is one of the most promising strategies to realize such synergy. One of us and his group studied the grafting of a compound of the Fe_4 family on CNTs, but no magnetic characterization of these devices has been reported.[9]

Herein, we report the noncovalent grafting of a polyoxometalate (POM) SMM of the formula $Na_6((CH_3)_4N)_4[Fe_4(H_2O)_2(FeW_9O_{34})_2]\cdot 45\,H_2O$[10] ($Fe_6$-POM; Figure 1, right) on single-wall carbon nanotubes (SWNTs). We demonstrate that the individual molecules maintain their chemical integrity and still present magnetic bistability when assembled on the surface of the nanotubes.

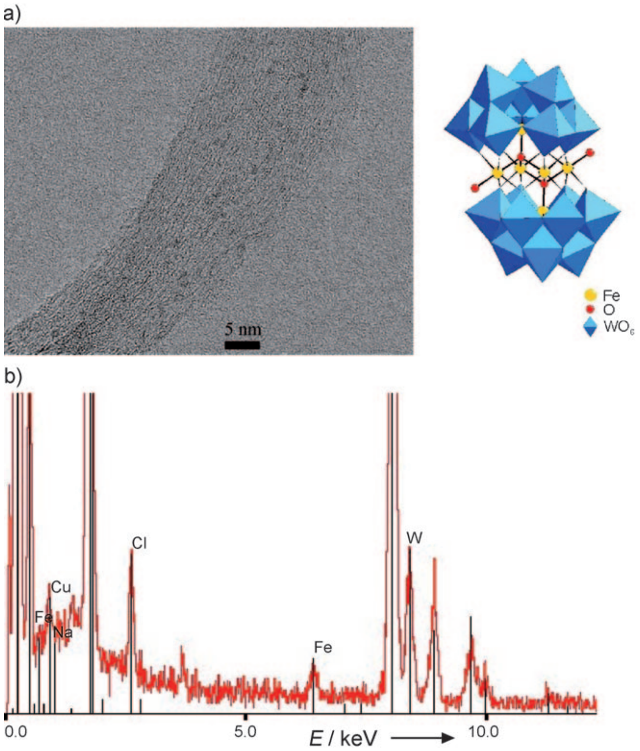

Figure 1. a) HRTEM image of bundles of nanotubes decorated by Fe_6-POM and view of the structure of the polyoxoanion $[Fe_4(H_2O)_2(FeW_9O_{34})_2]^{10-}$; b) the EDX spectrum of the Fe_6@NT system. The red curve is the experimental spectrum; the black lines show the energy of each band of the spectrum.

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The pristine SWNTs were purified using a procedure derived from that reported by Chiang et al.,[11,12] and the grafting of POM molecules was simply achieved by sonication of a suspension of the nanotubes in a dichloroacetic acid buffer containing the Fe_6-POM (see the Supporting Information). To ensure the efficiency of the grafting process and to check the integrity of the complex, we used complementary and independent characterization techniques.

High-resolution transmission electron microscopy (HRTEM) imaging of Fe_6-POM grafted on SWNTs (Fe_6@NT) shows the presence of bundles of nanotubes decorated by dark spots that have the size expected (1.6 × 1 nm) for the individual Fe_6-POM molecules (Figure 1a and Figure S1 in the Supporting Information), and no assemblies with larger sizes were detected. The energy-dispersive X-ray (EDX) spectroscopy studies confirm the presence of tungsten and iron, as expected for the POM complex (Figure 1b).

The Raman and the surface-enhanced Raman spectroscopy (SERS) studies were performed on the Fe_6-POM complex and on a Fe_6@NT sample at two excitation wavelengths (514.5 and 488.0 nm). Characteristic bands of the POM molecules in the 800–1000 cm^{-1} region were found for Fe_6@NT, supporting the EDX results on the success of the grafting process and suggesting that the integrity of the molecules is retained (Figures S3–S5 in the Supporting Information). Typical bands of the SWNTs observed in the 200–230 cm^{-1} region (radial breathing mode) are consistent with nanotubes of 1 to 1.2 nm in diameter, as expected (Figure S4 in the Supporting Information). At the excitation wavelength of 488.0 nm, the intensity ratio between the D (disorder-induced) and G (tangential) modes of the nanotubes observed at 1344 and 1590 cm^{-1}, respectively, is equal to 0.013 (Figure S4 in the Supporting Information), attesting to the excellent quality of the nanotubes after the grafting procedure.[13,14]

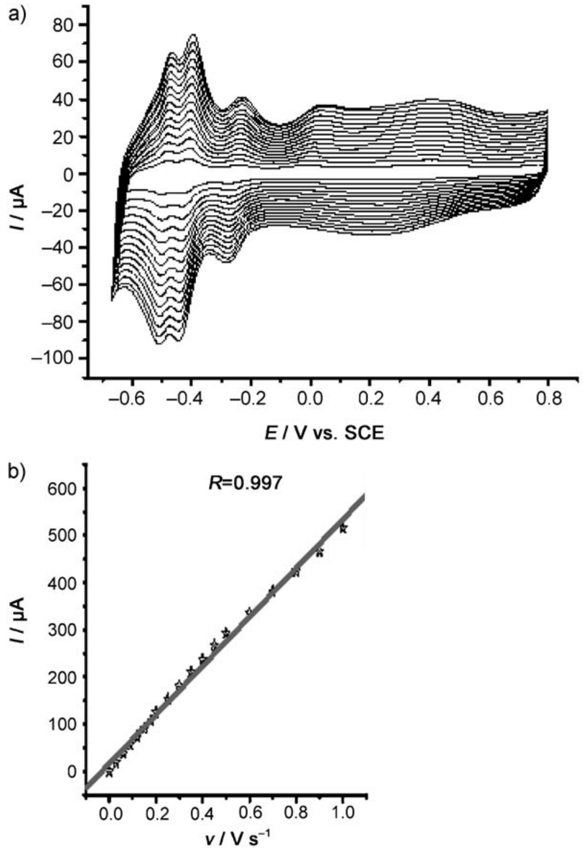

Figure 2. Cyclic voltammograms and peak-current intensity variations for Fe_6@NT in a pH 1 medium (0.5 M Li_2SO_4/H_2SO_4). a) Voltammograms as a function of scan rate (from 0.02 to 0.160 $V s^{-1}$). SCE = saturated calomel electrode. b) Peak-current intensity variations of the second tungsten reduction wave as a function of the scan rate.

Electrochemistry may give valuable information on the chemical stability of the Fe_6@NT system. Figure 2a displays a representative set of cyclic voltammograms for Fe_6@NT. The background curves with the unmodified SWNTs show none of the waves of Figure 2a. The last two waves located at negative potentials arise from the redox behavior of tungsten centers within the grafted Fe_6-POM. The three other waves located at more positive potentials feature the multistep reductions and reoxidations of iron centers, in complete agreement with previous cyclic voltammetry observations of the Fe_6-POM in solution.[10] Such stepwise reductions constitute fingerprints of iron centers within iron-sandwich-type POMs.[15] Both the small anodic-to-cathodic peak potential separation for the waves and the linear variation of the peak current with the scan rate (shown for one tungsten wave, Figure 2b) testify that Fe_6-POM is grafted on the SWNTs.[16] Perfect reproducibility of the voltammogram during prolonged potential cycling confirms that the electrode is durable (Figure S6 in the Supporting Information). Finally, a comparison between SWNT and the carbon black pigment vulcan XC72 as supports indicates better electrochemical kinetics for SWNTs (Figure S7 in the Supporting Information), as expected.[17] All these observations together (see also the Supporting Information) converge to support the successful grafting of Fe_6-POM on SWNTs, the absence of any (nano)-crystallized POMs within the sample, which is consistent with the grafting procedure, and more importantly the integrity and the stability of the resulting material.

The magnetization versus $\mu_0 H/T$ plots (where H is the applied magnetic field and T the temperature) at $T = 2$, 3, 4, and 6 K for Fe_6@NT were found to be practically superimposable with those of the pure complex (Figure S8 in the Supporting Information), showing that the complex maintains its magnetic anisotropy behavior even when scattered on the surface of the nanotubes. This finding is consistent with our hypothesis that the tungsten oxide matrix chelating the Fe_6 moiety prevents extensive deformation of the coordination sphere of the magnetic ions and thus precludes a dramatic change in the anisotropy behavior when the molecules are not assembled within the crystal. Micro-SQUID studies were then carried out on Fe_6@NT and on a Fe_6-POM powder sample and compared to the results with the single crystal, for which SMM behavior was already confirmed (Figure S9 in the Supporting Information).[10] A hysteresis loop with smooth steps (instead of the sharp ones for the single crystal) was observed for a powdered sample of the pure Fe_6-POM compound, as expected for molecules with different orientations and thus a distribution of the magnetization relaxation

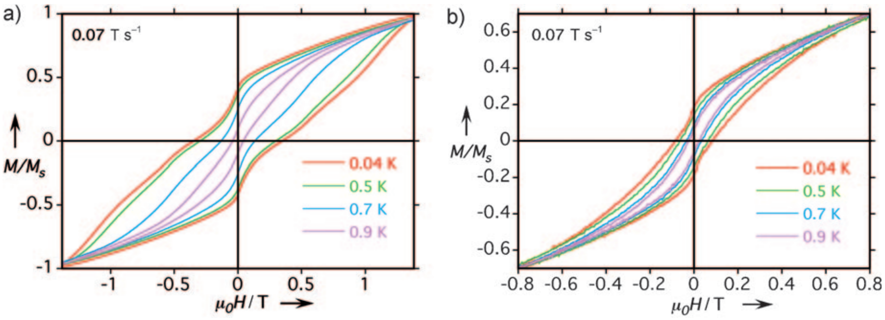

Figure 3. Hysteresis loops at different temperatures for a) the pure Fe_6-POM powder sample and b) the isolated molecules grafted on SWNTs.

time (Figure 3a). Evidence of the slow relaxation of the magnetization of the individual Fe_6-POM molecules is given by the hysteresis loop observed for the Fe_6@NT sample (Figure 3b).[18] It is worth noting that for the isolated molecules, a decrease of the remnant magnetization of approximately 50% occurs relative to the powder sample. Moreover, the coercive field decreases from 3500 Oe for the powder to 900 Oe (at $T = 0.04$ K) for the individual molecules. Such changes may be due to the presence of interactions between the molecules in the powder sample that are absent when the molecules are isolated. The presence of appreciable remnant magnetization and coercive field ($H_C = 660$ and 900 Oe at 0.5 and 0.04 K, respectively) attests to the bistability and thus the presence of a memory effect for the individual molecules. The SMM behavior of the complexes is further confirmed by the dependence of the width of the hysteresis loop on the sweep rate of the applied magnetic field measured at $T = 0.04$ K (Figure S10 in the Supporting Information).

We have thus demonstrated that the noncovalent grafting of an SMM complex on SWNTs does not alter the integrity of the molecules, as evidenced by the different complementary techniques. The crucial result is that the individual molecules present a slow relaxation of the magnetization, leading to magnetic bistability at the level of single molecules and thus enabling the design of single-molecule memory devices. Beyond this important result, the combination of SMMs and SWNTs may open new perspectives in the field of molecular spintronics, where it may become possible to investigate the synergy between electron transport and magnetism at the molecular level.[19]

Experimental Section

Synthesis: The single-wall carbon nanotubes (SWNTs) were synthesized by the so-called HiPco process and purchased as the first purified grade from Carbon Inc. (Houston, Texas). The declared average diameter is 1.1 nm, and the indicated carbon content in the pristine material is 87%. We prepared a 2 mM Fe_6-POM solution in 10^{-2} M dichloroacetic acid buffer (pH 2). We added SWNTs (1 mg) to Fe_6 solution (7.5 mL) and sonicated it for 20 h in an ice-water bath (VWR ultrasonic cleaning device USC 600D at 130 W and 45 kHz). The use of an ice-water bath allowed us to avoid important damage of the SWNTs (see the Raman spectra in the Supporting Information). We filtered the resulting inky suspension on polycarbonate membranes with pores of 200 nm in diameter to remove free Fe_6-POM, and immediately afterwards we redissolved the nanotubes separated on the filter in MilliQ water (7.5 mL). The resulting suspension was dark grey; it shows slow sedimentation with time but it is immediately redispersed by gentle agitation.

Physical measurements: The high-resolution transmission electron microscopy (HRTEM) images were recorded using a JEOL JEM 2011 apparatus (acceleration voltage 200 kV) equipped with a CCD Gatan camera (Orius). The Cu and Cl peaks in the EDX spectrum are due to the grid and solvent molecules, respectively. We recorded the Raman and the surface-enhanced Raman spectroscopy (SERS) spectra using a Jobin–Yvon T64000 Triple Spectrometer Microraman. The spot size is 1–2 μm depending on the objective used. We used, as excitation wavelength, the lines at 514.5 and 488.0 nm from an Ar–Kr laser. The magnetization studies were performed using a Quantum Design SQUID magnetometer and a home-made micro-SQUID device.

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[1] R. Sessoli, D. Gatteschi, A. Caneschi, M. A. Novak, *Nature* **1993**, *365*, 141.
[2] R. Sessoli, H. L. Tsai, A. R. Schake, S. Y. Wang, J. B. Vincent, K. Folting, D. Gatteschi, G. Christou, D. N. Hendrickson, *J. Am. Chem. Soc.* **1993**, *115*, 1804.
[3] D. Gatteschi, R. Sessoli, *Angew. Chem.* **2003**, *115*, 278; *Angew. Chem. Int. Ed.* **2003**, *42*, 268.
[4] M. Mannini, P. Sainctavit, R. Sessoli, C. C. D. Moulin, F. Pineider, M. A. Arrio, A. Cornia, D. Gatteschi, *Chem. Eur. J.* **2008**, *14*, 7530.
[5] M. Mannini, F. Pineider, P. Sainctavit, C. Danieli, E. Otero, C. Sciancalepore, A. M. Talarico, M. A. Arrio, A. Cornia, D. Gatteschi, R. Sessoli, *Nat. Mater.* **2009**, *8*, 194.
[6] G. H. Kim, T. S. Kim, *Phys. Rev. Lett.* **2004**, *92*, 137203.
[7] H. B. Heersche, Z. de Groot, J. A. Folk, H. S. J. van der Zant, C. Romeike, M. R. Wegewijs, L. Zobbi, D. Barreca, E. Tondello, A. Cornia, *Phys. Rev. Lett.* **2006**, *96*, 206801.
[8] L. Bogani, W. Wernsdorfer, *Nat. Mater.* **2008**, *7*, 179.
[9] L. Bogani, C. Danieli, E. Biavardi, N. Bendiab, A. L. Barra, E. Dalcanale, W. Wernsdorfer, A. Cornia, *Angew. Chem.* **2009**, *121*, 760; *Angew. Chem. Int. Ed.* **2009**, *48*, 746.
[10] J.-D. Compain, P. Mialane, A. Dolbecq, I. M. Mbomekalle, J. Marrot, F. Sécheresse, E. Rivière, G. Rogez, W. Wernsdorfer, *Angew. Chem.* **2009**, *121*, 3123–3127; *Angew. Chem. Int. Ed.* **2009**, *48*, 3077–3081.
[11] I. W. Chiang, B. E. Brinson, A. Y. Huang, P. A. Willis, M. J. Bronikowski, J. L. Margrave, R. E. Smalley, R. H. Hauge, *J. Phys. Chem. B* **2001**, *105*, 8297.
[12] G. Charron, S. Mazerat, M. Erdogan, A. Gloter, A. Filoramo, J. Cambedouzou, P. Launois, E. Rivière, W. Wernsdorfer, J.-P. Bourgoin, T. Mallah, *New J. Chem.* **2009**, DOI: 10.1039/b900373h.
[13] M. S. Dresselhaus, G. Dresselhaus, A. Jorio, *J. Phys. Chem. C* **2007**, *111*, 17887.
[14] M. S. Dresselhaus, G. Dresselhaus, R. Saito, A. Jorio, *Phys. Rep.* **2005**, *409*, 47.

[15] B. Keita, L. Nadjo, *Electrochemistry of Isopoly and Heteropoly Oxometalates Encyclopedia of Electrochemistry*, *Vol. 7* (Eds.: A. J. Bard, M. Stratmann), Wiley-VCH, Weinheim, **2006**, pp. 607–700.

[16] E. Laviron in *Electroanalytical Chemistry*, *Vol. 12* (Ed.: A. J. Bard), Marcel Dekker, New York, **1983**, pp. 53–157.

[17] A. T. Masheter, P. Abiman, G. G. Wildgoose, E. Wong, L. Xiao, N. V. Rees, R. Taylor, G. A. Attard, R. Baron, A. Crossley, J. H. Jones, R. G. Compton, *J. Mater. Chem.* **2007**, *17*, 2616.

[18] No magnetic signal was observed for the bare nanotubes studied by micro-SQUID under the same conditions as for the grafted sample.

[19] L. Bogani, W. Wernsdorfer, *Inorg. Chim. Acta* **2008**, *361*, 3807.