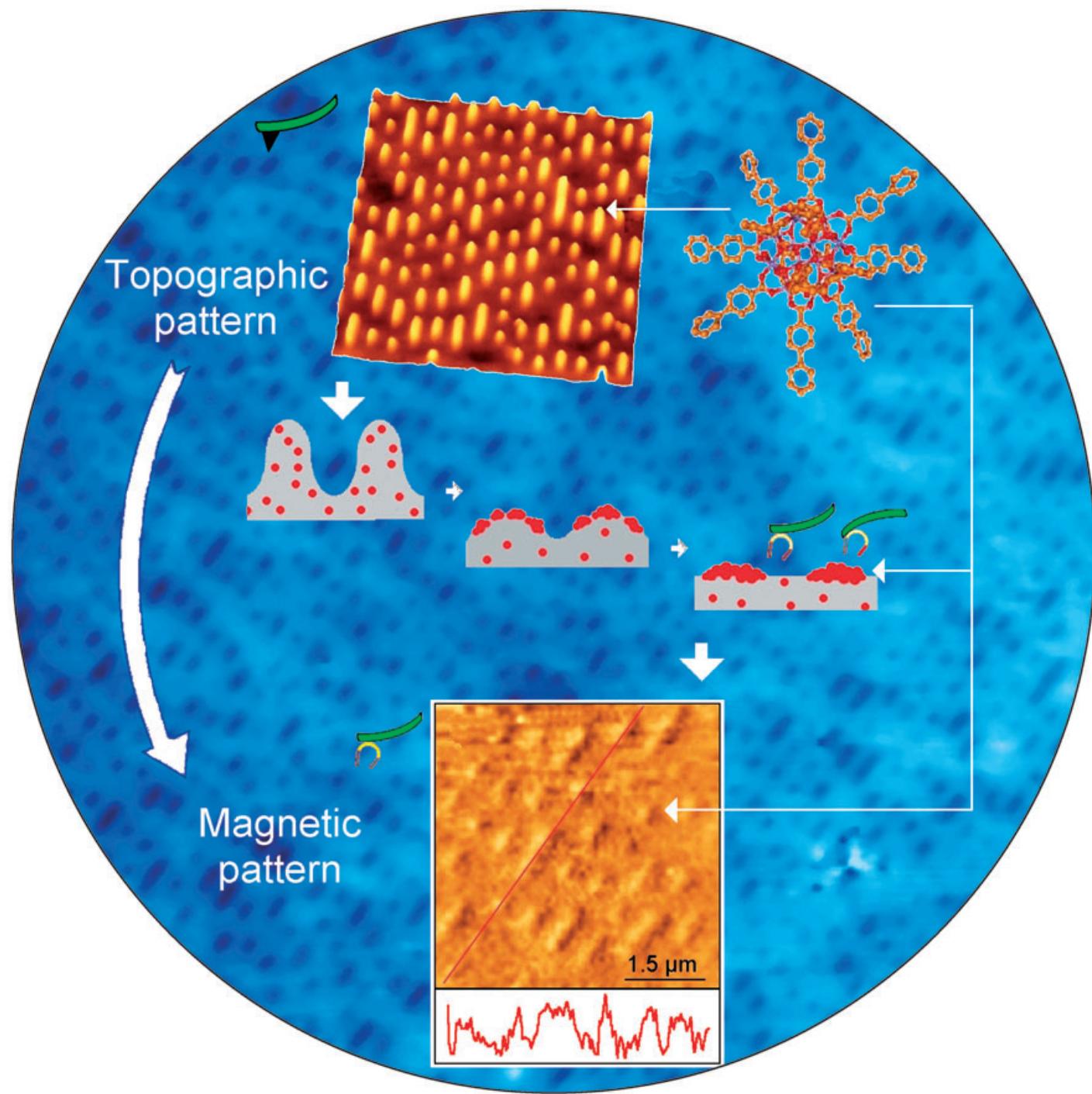


# Communications



A molecule-based magnetic material with a paramagnetic response at room temperature has been used to fabricate patterns of magnetic bits on a polycarbonate surface. This system can be used effectively as a permanent information-storage medium with magnetic readout. For more information see the Communication by J. Veciana, F. Biscarini, and co-workers on the following pages.

## Magnetic Information Storage on Polymers by Using Patterned Single-Molecule Magnets<sup>\*\*</sup>

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Nanosscopic magnetic materials are of increasing interest because of their potential use for ultrahigh-density information storage, quantum computing, sensing, and biomedical applications.<sup>[1–3]</sup> Herein we demonstrate that, while working in the paramagnetic regime, it is possible to encode and read out information from domains of Mn<sub>12</sub> molecules patterned on a polymer surface across a large area. The patterns are fabricated by molding a dispersion of Mn<sub>12</sub> molecules in a polycarbonate matrix on a structured master, then exposing the polymer replica to the vapor of an organic solvent. The protrusions of the replica surface disappear upon exposure to the solvent, and the Mn<sub>12</sub> molecules concentrate on the surface at the positions of the original protrusions. The distribution of Mn<sub>12</sub> molecules at the polymer surface gives rise to a magnetic contrast, which can be imaged by magnetic force microscopy. Information can be transferred from a recorded digital video disk (DVD), functioning as the master, to a magnetically readable flexible medium.

The search for increasingly small, lighter, and cheaper nanoscopic magnetic materials faces the challenge of overcoming anomalies such as dipolar interactions, matrix effects, domain wall rearrangements, and percolation effects, which degrade the observable magnetic properties. Thus, there is a worldwide effort aimed at developing new and enhanced nanostructured magnetic materials. An emerging family that is being explored is molecule-based magnets, because they possess several attractive attributes: 1) they have homogeneous and precisely defined sizes; 2) their chemical and topological structure can be tailored by chemical design; 3) they are soluble in common solvents and hence can be easily processed for applications; and 4) they can be consid-

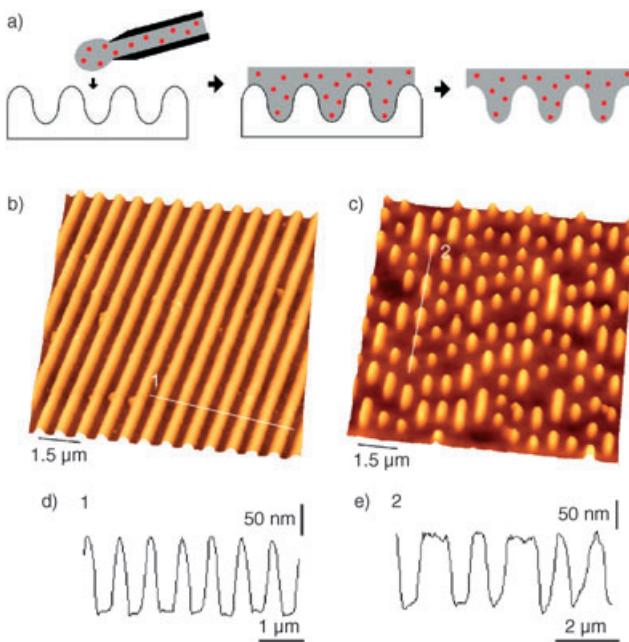
ered as the ultimate limit for storing high densities of information data.<sup>[4]</sup> Mn<sub>12</sub> clusters have a large-spin ground state with appreciable magnetic anisotropy, which results in a barrier for the spin reversal.<sup>[5–8]</sup> As a consequence, interesting magnetic properties such as out-of-phase ac magnetic susceptibility signals and stepwise magnetization hysteresis loops, caused by individual molecules rather than by long-range orderings, are observed below the blocking temperature ( $T_B$ ).<sup>[9]</sup> However, if a truly molecular magnetic device is to be achieved, addressing properly oriented individual magnetic molecules or their aggregates, as well as increasing their critical temperatures of such molecule-based materials, are required. The first successful attempts toward the development of functional molecule-based magnetic devices focused on the deposition and addressing of Mn<sub>12</sub> clusters on different surfaces. Mn<sub>12</sub> clusters have been organized into multilayered films by the Langmuir–Blodgett technique or self-assembly on functionalized surfaces.<sup>[10]</sup> Deposition of isolated or small aggregates of such molecules onto a polycarbonate surface<sup>[11]</sup> and the self-assembly of thiol-substituted Mn<sub>12</sub> clusters on thin Au films<sup>[12]</sup> have also been achieved. Nevertheless, no control of the position and distance between Mn<sub>12</sub> molecules was attained in either case. Recently, we used a stamp-assisted self-organization method to successfully pattern Mn<sub>12</sub> molecules into 50-nm-diameter dots with a characteristic length scale less than 200 nm,<sup>[13]</sup> which demonstrates the possibility of addressing organized clusters on the surface of a silicon wafer.

Herein, we report a reliable and simple methodology to pattern magnetic Mn<sub>12</sub> molecules on a polycarbonate (PC) film, and show that it is possible to map (read) the patterned domains on the film surface while working in the paramagnetic regime. We used the complex [Mn<sub>12</sub>O<sub>12</sub>(O<sub>2</sub>CC<sub>12</sub>H<sub>9</sub>)<sub>16</sub>(H<sub>2</sub>O)<sub>4</sub>] (**1**), whose synthesis has been previously described.<sup>[14]</sup> Frequency-dependent out-of-phase ac signals and hysteresis in the magnetization versus external field are seen for solid samples of complex **1**, which indicates that this complex behaves as a single-molecule magnet with a  $T_B$  value of 4–6 K and as a paramagnet at higher temperatures.<sup>[14]</sup> A consistent magnetic behavior is observed for the same complex dispersed in thin films of polycarbonate.<sup>[11]</sup> In the work described herein, the films are prepared by casting a solution of complex **1** and polycarbonate in CH<sub>2</sub>Cl<sub>2</sub> onto a blank DVD support that acts as a structured master (Figure 1a).<sup>[15]</sup> On the basis of the similarity of the conditions used in the process reported in ref. [11], we infer that the magnetic behavior of complex **1** should remain unchanged.

Once the solvent is evaporated, the replica is removed from the master, which results in a stable, flexible, and transparent film of a solid solution of complex **1** in polycarbonate. The film surface, imaged by atomic force microscopy (AFM), exhibits an inverted pattern with respect to the DVD master, with parallel lines 300-nm wide and 120-nm deep and a periodicity between grooves of 740 nm (Figure 1b). A representative topographical profile along line 1 in Figure 1b is shown in Figure 1d. In a second step, the film is exposed to a saturated atmosphere of CH<sub>2</sub>Cl<sub>2</sub> vapor that swells the film and solvates the polymer chains, thus decreasing the glass transition temperature of the polymer below

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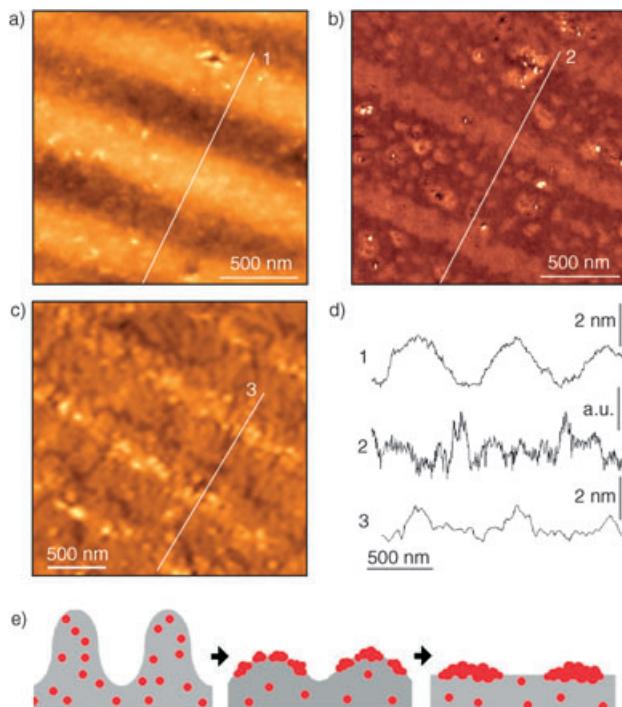
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**Figure 1.** a) Schematic representation of the experimental process followed to obtain a DVD replica made of a solid solution of Mn<sub>12</sub> complex and PC. b) AFM image of a Mn<sub>12</sub>-PC replica exhibiting a sequence of grooves replicating the blank DVD master. The distance between grooves is 740 nm and their depth and width are 120 and 300 nm, respectively. c) AFM image of a Mn<sub>12</sub>-PC replica of a recorded DVD, which exhibits a structured sequence of bits of information as protrusions. One bit corresponds to a protrusion 300 nm wide, 400 nm long, and 120 nm high. d) Topographical line profile along the white line 1 drawn in (b). e) Topographical line profile along the white line 2 drawn in (c).

room temperature. Under these conditions, the structured film surface experiences a smoothening driven by the minimization of the surface tension, which leads to the progressive deletion of the topographic reliefs. The time needed for a complete smoothening depends on experimental parameters such as solvent nature, temperature, and initial surface roughness.

Topographic AFM images of the molded replica after exposure to CH<sub>2</sub>Cl<sub>2</sub> vapor for 120 and 180 s are shown in Figure 2. The protrusions decrease from 120 nm (root-mean-square (rms) roughness 56 nm) to less than 5 nm after solvent exposure for 120 s (Figure 2a and first profile in Figure 2d), and by more than 99% (rms roughness < 1 nm) after 180 s (Figure 2c and third profile in Figure 2d). An extensive film rupture occurs by nucleation and growth of nanosized pores upon longer exposure times (not shown). Interestingly, the corresponding AFM phase-contrast images show that the Mn<sub>12</sub> clusters concentrate preferentially in the regions where the protrusions were originally formed, while they are absent from the grooves (Figure 2b and second profile in Figure 2d). This evidence shows that the lateral (in-plane) diffusion of Mn<sub>12</sub> clusters, which were initially dissolved in the polymer solid solution, is marginal during the smoothening process. Other concurrent mechanisms may be linked to convective or diffusive mass transport toward the sharper protrusions,

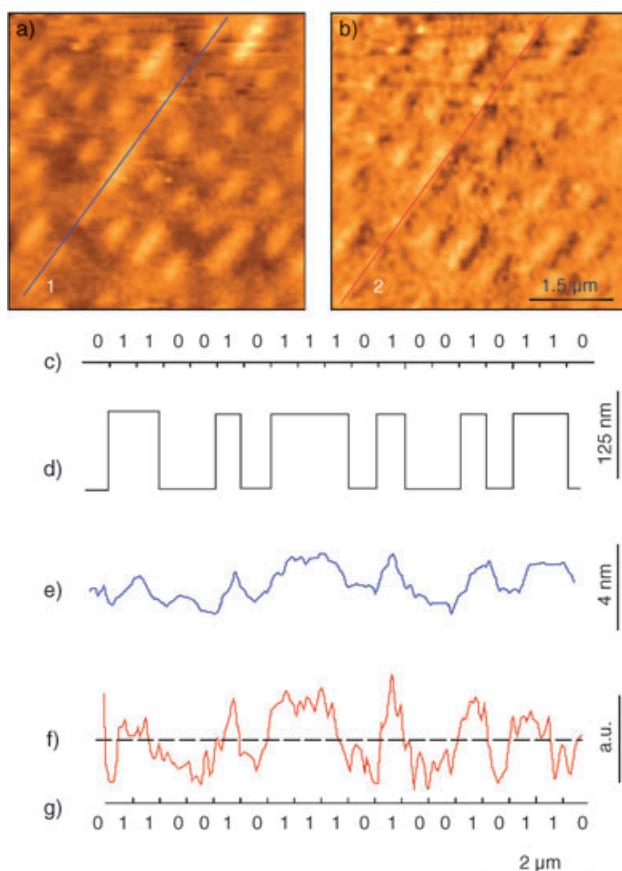


**Figure 2.** a) AFM topography image of a molded film of Mn<sub>12</sub>-PC, as in Figure 1b, after treatment with CH<sub>2</sub>Cl<sub>2</sub> solvent vapor for 120 s. The height of the protrusions has decreased by more than 96% compared to its original value of 120 nm. b) AFM phase-contrast image of the replica surface depicted in (a) showing the inhomogeneous distribution of the Mn<sub>12</sub> solute at the surface. Darker areas are solute-rich regions. c) AFM image of the film after treatment with CH<sub>2</sub>Cl<sub>2</sub> vapor for 180 s. d) Profiles along the white lines shown in the topographic (lines 1 and 3) and phase-contrast (line 2) images. e) Schematic representation of the smoothening and Mn<sub>12</sub> aggregation processes occurring during the CH<sub>2</sub>Cl<sub>2</sub> solvent vapor treatment.

driven by a faster solvent evaporation rate at the loci with smaller curvature.<sup>[16]</sup>

These results encouraged us to further advance this approach by focusing on Mn<sub>12</sub> molecular clusters patterned into domains with controlled shapes and positions on the polymer surface, since these domains of Mn<sub>12</sub> molecules can be used as magnetic bits. With this aim, we molded a Mn<sub>12</sub>-PC film replica of a recorded DVD. AFM imaging of the replica surface reveals an ordered array of 120-nm-thick protrusions of variable length ranging from 380 to 1500 nm, aligned along lines (tracks) with an intertrack distance of 740 nm (Figure 1c). A representative topographical profile along a sector (line 2 in Figure 1c) is shown in Figure 1e.

The Mn<sub>12</sub>-PC replica was then exposed to CH<sub>2</sub>Cl<sub>2</sub> vapor, and the process was interrupted just before the rupture of the film surface took place. At this stage, the original protrusions that replicate the topographic indentations of the coded DVD have almost disappeared (topographic rms roughness is < 1 nm), as is apparent from Figure 3a and 3e. The local magnetic response of the surface film was investigated by magnetic force microscopy (MFM), which revealed the formation of a spatially distributed magnetic pattern that closely follows the original topographic indentations of the recorded DVD (Figure 3b). Again, the preferential concen-



**Figure 3.** a) AFM topography image of a DVD replica after solvent exposure (rms roughness is 1 nm). b) Magnetic mapping of (a) with MFM. The image (phase shift during second pass) was acquired by a two-pass mode using a cobalt-coated magnetic tip. The lift height was 30 nm. c) Sequence of bits that is represented by the topographic sequence along the track marked by line 1 in (a). d) Idealized representation of the corresponding topographical line profile of the track in the replica before exposure to solvent. e) Topographical line profile of the track after exposure to solvent. f) Magnetic contrast along line 2 in (b). The mean signal line (----) is a guide to the eye. g) Sequence of magnetic bits extracted from (f), which shows a perfect correspondence with the original sequence in (c).

tration of  $Mn_{12}$  clusters corresponding to the protrusions of the polymer film surface occurs as previously described. Each sequence of magnetic domains, composed of aggregates of  $Mn_{12}$  molecules, represents magnetically readable information that, overall, replicates the information that was originally accessible by optical readout in the DVD. The magnetic response of the domains of  $Mn_{12}$  molecules, which are paramagnetic at room temperature, to MFM can be ascribed to the strong magnetic contrast with the diamagnetic polymeric surroundings. Similar magnetic responses have been previously observed for other paramagnetic organic molecules on diamagnetic surfaces.<sup>[11,17]</sup> Figure 3d is an idealized representation of the topographical profile of the replica along the track marked by line 1 in Figure 3a before exposure to solvent. The corresponding logic sequence of bits for an optical readout is shown in Figure 3c. Figure 3f shows the line profile of the magnetic force along the same track with a signal-to-noise ratio of 2:1, which makes it possible to resolve

the sequence of magnetic bits represented in Figure 3g (line 2 in Figure 3b). The sequence of magnetic bits perfectly reproduces the original sequence of optical DVD bits.

In summary, we have developed a simple process that is able to fabricate patterns of magnetic bits on a polymer surface, on the basis of a molecule-based magnetic material with a paramagnetic response at room temperature. We demonstrated that this system can be effectively used as a permanent information storage medium with magnetic read-out. The patterning process can be scaled down to smaller length scales and higher densities by improving the resolution of the master, or by patterning the solute/polymer mixture by using a higher-resolution fabrication technique, for example, nanoimprint lithography. This technique may lead to the fabrication of magnetic  $Mn_{12}$  domains with features a few tens of nanometers in size,<sup>[18]</sup> which corresponds to a few molecular diameters (end-to-end distance is 4 nm). Finally, the patterning and addressing of molecular materials across multiple length scales is one of the most important issues in nanotechnology. Extension of this work could lead to the development of next-generation storage media based on a variety of molecular responses,<sup>[19]</sup> for example: charge storage; conformational, orientational, or positional shifting; phase transitions or reorganization; and optical anisotropy changes and fluorescence switching.

## Experimental Section

Sample preparation: Pellets of poly(bisphenol A carbonate) (PC) with  $Mn_{12}$  single-molecule magnets (4% by weight) was dissolved in  $CH_2Cl_2$ , and the solution was cast on a master. The DVD masters were covered with a 100-nm-thick Au film. Circular samples of 1 cm diameter and 20 μm thickness were fabricated.

AFM/MFM measurements: AFM/MFM was carried out in air in intermittent-contact mode for imaging. For MFM measurements, cobalt-coated tips (MDT, Moscow, Russia) were used with the instrument operated in a two-pass mode: in the first pass the topography was measured in intermittent-contact mode; in the second pass the cantilever was lifted to a selected height with respect to the topography line, and the phase shift was measured as the tip followed the stored topography line. The magnetic signal was resolved as phase shift during the second pass. The magnetic contrast was comparable to that of MFM images reported earlier.<sup>[11,17]</sup> The typical lift height was 30 nm which, when compared to sample roughness (<1 nm), was sufficient to avoid topographic artifacts in the magnetic signal. Imaging samples using a nonmagnetic tip did not yield any contrast in the second-pass mode, and neither did a magnetic tip on samples made of polycarbonate alone.

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- [1] D. D. Awschalom, J. M. Kikkawa, *Phys. Today* **1999**, *52*, 33–38.
- [2] H. Ohno, D. Chiba, F. Matsukura, T. Omiya, E. Abe, T. Dietl, Y. Ohno, K. Ohtani, *Nature* **2000**, *408*, 944–946.
- [3] R. L. Edelstein, C. R. Tamashiro, P. E. Sheehan, M. M. Miller, D. R. Baselt, L. J. Whitman, R. J. Colton, *Biosens. Bioelectron.* **2000**, *14*, 805–813.
- [4] J. S. Miller, A. J. Epstein, *MRS Bull.* **2000**, *11*, 21–28.

- [5] D. Ruiz-Molina, G. Christou, D. N. Hendrickson, *Mol. Cryst. Liq. Cryst.* **2000**, *343*, 17–27.
- [6] R. Sessoli, D. Gatteschi, A. Caneschi, M. A. Novak, *Nature* **1993**, *365*, 141–143.
- [7] J. R. Friedman, M. P. Sarachick, J. Tejada, R. Ziolo, *Phys. Rev. Lett.* **1996**, *76*, 3830–3833.
- [8] J. M. Hernandez, X. X. Zhang, F. Luis, J. Bartolomé, J. Tejada, R. Ziolo, *Europhys. Lett.* **1996**, *35*, 301–306.
- [9] D. Gatteschi, R. Sessoli, *Angew. Chem.* **2003**, *115*, 278–309; *Angew. Chem. Int. Ed.* **2003**, *42*, 268–297.
- [10] a) M. Clemente-León, H. Soyer, E. Coronado, C. Mingotaud, C. J. Gómez-García, P. Delhaes, *Angew. Chem.* **1998**, *110*, 3053–3056; *Angew. Chem. Int. Ed.* **1998**, *37*, 2842–2845; b) G. C. Condorelli, A. Motta, I. L. Fragala, F. Giannazzo, V. Rainieri, A. Caneschi, D. Gatteschi, *Angew. Chem.* **2004**, *116*, 4173–4176; *Angew. Chem. Int. Ed.* **2004**, *43*, 4081–4084; c) a) N. Abdi, J. P. Bucher, P. Rabu, O. Toulemonde, M. Drillon, P. Gerbier, *Jnl. Appl. Phys.* **2004**, *95*, 7345–7347; d) J. S. Steckel, N. S. Persky, C. R. Martinez, C. L. Barnes, E. A. Fry, J. Kulkarni, J. D. Burgess, R. B. Pacheco, S. L. Stoll, *Nano Lett.* **2004**, *4*, 399–402; correction: S. L. Stoll, *Nano Lett.* **2004**, *4*, 1167.
- [11] D. Ruiz-Molina, M. Mas-Torrent, J. Gómez, A. I. Balana, N. Domingo, J. Tejada, M. T. Martínez, C. Rovira, J. Veciana, *Adv. Mater.* **2003**, *15*, 42–45.
- [12] A. Cornia, A. C. Fabretti, M. Pacchioni, L. Zobbi, D. Bonacchi, A. Caneschi, D. Gatteschi, R. Biagi, U. Del Pennino, V. De Renzi, L. Gurevich, H. S. J. Van der Zant, *Angew. Chem.* **2003**, *115*, 1683–1686; *Angew. Chem. Int. Ed.* **2003**, *42*, 1645–1648.
- [13] M. Cavallini, F. Biscarini, J. Gómez-Segura, D. Ruiz, J. Veciana, *Nano Lett.* **2003**, *3*, 1527–1530.
- [14] D. Ruiz-Molina, P. Gerbier, E. Rumberger, D. B. Amabilino, I. A. Guzei, K. Folting, J. C. Huffman, A. Rheingold, G. Christou, J. Veciana, D. N. Hendrickson, *J. Mater. Chem.* **2002**, *12*, 1152–1161.
- [15] Y. Xia, E. Kim, X.-M. Zhao, J. A. Rogers, M. Prentiss, G. M. Whitesides, *Science* **1996**, *273*, 347–349.
- [16] R. D. Deegan, O. Bakajin, T. F. Dupont, G. Huber, S. R. Nagel, T. A. Witten, *Nature* **1997**, *389*, 827–829.
- [17] H. Nishide, T. Ozawa, M. Miyasaka, E. Tsuchida, *J. Am. Chem. Soc.* **2001**, *123*, 5942–5946.
- [18] M. D. Austin, S. Y. Chou, *Appl. Phys. Lett.* **2002**, *81*, 4431–4433.
- [19] M. Cavallini, F. Biscarini, S. Léon, F. Zerbetto, G. Bottari, D. A. Leigh, *Science* **2003**, *299*, 531–531.