

Multiple Length Scale Patterning of Single-Molecule Magnets

Massimiliano Cavallini,[†] Fabio Biscarini,^{*,†} Jordi Gomez-Segura,[‡]
Daniel Ruiz,[‡] and Jaume Veciana[‡]

CNR – Istituto per lo Studio dei Materiali Nanostrutturati, Sez. di Bologna,
Via P. Gobetti 101, I-40129 Bologna, Italy, and CSIC – Institut de Ciència de
Materials de Barcelona, Campus Universitari de Bellaterra, 08193 Cerdanyola, Spain

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ABSTRACT

Controlling materials on multiple length scales is one of the most compelling issues in nanotechnology research today. Here we demonstrate that arrays of nanometer-sized aggregates, each made of a few hundred single-molecule magnets derived from Mn_{12} complexes, can be patterned on large areas by self-organization assisted by stamps on a surface in a dewetting regime. The large length scale is imposed by the motif of the stamp protrusions, and the smaller length scales, viz., the size and distance of the molecular aggregates, are controlled by deposition and growth phenomena occurring in a volume confined beneath the protrusions by capillary forces. The method is general to a variety of molecular materials and substrates because repulsive, as opposed to specific, interactions are required. Our result hints at the possibility of sustainable patterning of single-molecule magnets for ultra-high-density magnetic storage and quantum computing.

Single-molecule magnets (SMM) have a large-spin ground state with appreciable magnetic anisotropy, resulting in a barrier for the spin reversal. As a consequence, interesting magnetic properties such as out-of-phase ac magnetic susceptibility signals and stepwise magnetization hysteresis loops due to individual molecules rather than to long-range ordering are observed below the blocking temperature (T_B) where the magnetization relaxation rates are very slow.^{1,2} Such molecules may become materials with a potential impact in ultra-high-density magnetic storage³ and in quantum computing applications,⁴ provided their T_B values can be increased to reasonable values and the molecules can be organized into addressable domains. With this aim, the possible deposition of isolated SMMs derived from Mn_{12} complexes or very small aggregates of such molecules onto a polycarbonate surface⁵ has been demonstrated. Very recently, the self-assembly of thiol-substituted Mn_{12} complexes has been achieved on Au thin films.⁶ In either case, no control of position and distance was shown, and although the latter method is amenable for contact printing, it may be desirable to pattern SMMs onto a variety of surfaces rather than being restricted to gold thin films. The use of micro-contact printing and capillary filling to pattern the deposition of a ferrofluid on a surface with features on the order of micrometers was reported.⁷

The fabrication of ordered patterns of Mn_{12} SMMs is a crucial step in the realization of memory elements based on

these materials. New approaches that allow direct fabrication of ordered patterns of SMMs, either isolated or aggregated, onto surfaces where each molecule or molecular aggregate can be used as a bit of information are required. Because Mn_{12} SMM is a paramagnetic material at room temperature, an ordered pattern of molecular aggregates is technologically more relevant than individually isolated molecules dispersed on a surface in view of developing new storage media. Arrays of domains with a characteristic size and position can indeed be addressed and read differentially by a magnetic head or by magnetic scanning probes.⁵

Here we demonstrate the patterning of aggregates of Mn_{12} SMMs with size and distance control on multiple length scales ranging from tens of nanometers to millimeters. We use a convergent approach based on the stamp-assisted deposition of molecules from a solution together with dewetting phenomena arising from competing interactions between the molecules and the substrate. Such an approach, which is suitable for a number of soluble materials⁸ and nonwettable substrates, can be in principle pushed down to the limit where single-molecule magnets are patterned into ordered arrays, this process ultimately being limited only by the coarsening of the individual molecules.

The complex used in this work is $[Mn_{12}O_{12}(O_2CC_{12}H_9)_{16}(H_2O)_4]$ (**1**), whose synthesis has been previously described.⁹

Figure 1 shows the molecular structure of complex **1**, obtained by the minimization of its structure with a force field method.¹⁰ Complex **1** exhibits a structure with a coin-shaped Mn_{12} core stabilized by an outer shell of 16 biphenyl

* Corresponding author. E-mail: f.biscarini@ism.bo.cnr.it. Tel: ++39-051-6398523. Fax: ++39-051-6398540.

[†] CNR.

[‡] CSIC.

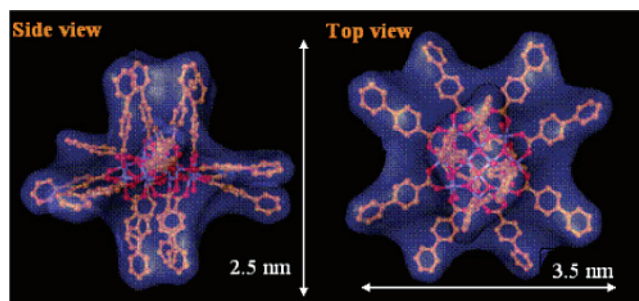


Figure 1. Molecular structure of Mn_{12} complex **1**. Side and top views of the molecular structure of complex **1** obtained by molecular modeling. Connolly surfaces around the molecule show the van der Waals shape and volume.

carboxylate ligands. The ligands make the outer shell hydrophobic, and we expect that the deposition of **1** from a solution onto a hydrophilic surface will result in spherically capped droplets formed by aggregates of molecules. Two possible mechanisms may indeed contribute to this phenomenology: nucleation and growth in a partial wetting regime¹¹ or dewetting of an initially smooth film.¹² Both phenomena have been observed in thin films of molecular materials and are known to yield spontaneously spatial correlations in size and distance upon certain conditions.^{13–15}

In the case of growth in the partial wetting regime, correlations arise because of intertwined nucleation and ripening, the latter being a size/distance-dependent phenomenon that stops as the ripened nuclei have reached the same size at an equilibrium distance.^{13–14}

Dewetting is the rupture of an initially continuous film upon an external perturbation, which can develop via two possible mechanisms: (i) nucleation and growth of holes¹⁶ and (ii) spinodal dewetting.¹⁷ The latter occurs by fluctuations of the film surface with the emergence of a characteristic wavelength that, for a given material, is controlled by the film thickness. The latter is therefore a desirable mechanism, being dependent on a convenient experimental variable.¹⁸

Our strategy is to control the wetting/dewetting phenomena over a large area in order to control the multiscale organization of complex **1** from nanometer-sized aggregates of a few molecules to large arrays with submicrometer or nanometer length scales.

Solution casting is not suitable for multiscale patterning over a large area because surface defects pin the receding fluid front and induce a nonequilibrium flow of material.¹⁹ Because defects are randomly distributed, the result is a spatially inhomogeneous deposition of aggregates. To overcome the problem of defining the positions on the surface where deposition will occur, we assist the deposition of the solute with stamps placed gently on top of the solution layer. The process we developed is schematically described in Figure 2.

The protrusions of the stamp act as pinning sites for the drying solution, and the critical concentration for the solute to start precipitating is reached only in the small volume of solution confined under the protrusion. The stamp imparts the large-area spatial modulation to the solution and hence

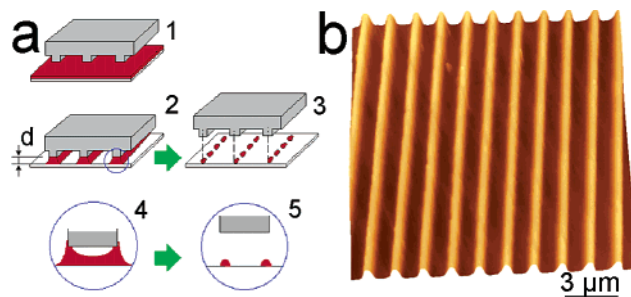


Figure 2. Schematic representation of stamp-assisted deposition. (a) (1) The stamp is placed in contact with a layer of solution spread on the substrate. (2) As the solvent evaporates, the onset of capillary forces pins the solution to the protrusions. Because the evaporation rate is faster in the thinner parts, the receding front between adjacent protrusions leaves dry areas in between. (3) As the critical concentration is reached in the solution confined under the protrusion, Mn_{12} clusters precipitate. The material is deposited according to the positive replica of the stamp; as the deposition is followed by dewetting, arrays of droplets with a characteristic size and distance will form. (4) Dilute solutions yield split structures pinned to the edges of the protrusions. (5) Strings of nanodroplets are obtained by dewetting the material deposited upon the regime (4). (b) AFM images of the stamp used in this experiment. It consists of parallel lines that are 500 nm wide and with 1.5 μm pitch.

to the deposited solute. Accidental defects on the surface become statistically irrelevant because the stamp features are considerably more dense and their effect is modulated through the choice of solvent and the chemical nature of the surface of the stamp. As a result, the process of droplet formation is confined under the stamp protrusions. The smaller length scales, viz., droplet size and interdroplet distances, will depend on the initial concentration of the solution and the volume under the protrusions, which is controlled by the distance between the stamp and the substrate. A remarkable outcome of our approach with respect to a printing technique with intimate contact between the stamp and substrate is the possibility to downsize the printed features with respect to the lateral size of the protrusions.⁸ This is achieved by controlling the distance between the stamp and the substrate and, indirectly, the lateral size of the menisci forming under the protrusions by exploiting the process shown in Figure 2a.⁸ In the case of an extremely dilute solution, it is possible to obtain ultranarrow split features because of the pinning at the sharper edges of the protrusions. In this regime, deposited structures as small as tens of nanometers wide can be obtained by using protrusions that are a few hundred nanometers wide but have sharper edges. An AFM image of the stamp that is used is shown in Figure 2b.

The result of the deposition of a solution of SMM **1**, obtained following the methodology described in Figure 2, is shown in Figure 3.

The substrates that were used were native silicon oxide deposited onto Si(100), obtained by etching a silicon wafer with a 10% HF solution for 2 min and then rinsing it in ultrapure distilled water before reoxidizing it in humid air (relative humidity 55%) for 24 h.

In Figure 3a, it is shown that patterning is effective across at least a $100 \times 100 \mu\text{m}^2$ area, the assessment of the latter

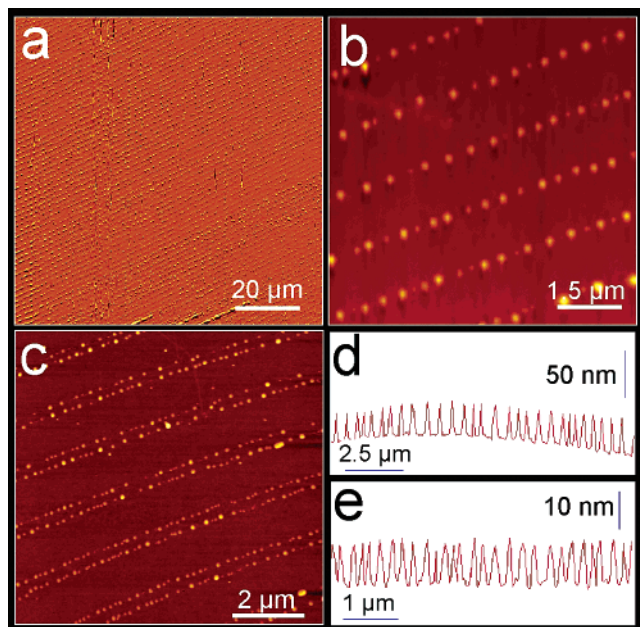


Figure 3. (a) AFM image (error signal) of patterns of **1** fabricated on a large area ($100 \times 100 \mu\text{m}^2$). (b) Image of printed features using a dilute solution. (c) Image of printed features using a very dilute solution. Typical line profile along a line obtained using (d) a dilute solution (corresponding to b) and (e) a very dilute solution (corresponding to c).

being limited by the maximum scan length of the AFM piezoelectric tube. We succeeded in patterning $1 \times 1 \text{ mm}^2$ areas on a laboratory bench. The pattern is made of parallel lines that replicate the periodicity of the stamp. At greater magnification (Figure 3b), the lines appear to consist of droplets aligned along the stretching direction: their average size is $270 \pm 89 \text{ nm}$, and their distance is $441 \pm 138 \text{ nm}$ (Figure 3d). The remarkable result is that the arrays of complex **1** droplets are obtained by using a featureless stamp with a much larger size. By using a more dilute solution (Figure 3c), we obtain split strings of droplets, whose apparent lateral fwhm is $70 \pm 15 \text{ nm}$; their height is $8 \pm 2 \text{ nm}$, and their spacing is $200 \pm 42 \text{ nm}$. Considering that complex **1** can be approximated by an oblate ellipsoid whose van der Waals axes are 2.5 and 3.5 nm, we estimate that each aggregate consists of a few hundred molecules.

The patterning mechanism is a wetting/dewetting transition that occurs after the stamp-assisted deposition of Mn_{12} stripes. The stripes, which have a hydrophobic shell, have no affinity for the hydrophilic surface, and the surface energy is the driving force for the film rupture.

Figure 4 supports the mechanism by the dewetting of initially continuous strips or lines of deposited material, as opposed to nucleation and growth in the partial wetting regime. Here the process of the formation of aggregates was stopped by removing the stamp before completion. The imaged area shows droplets of different sizes that have not completed either their coalescence or fragmentation and lines, not yet dewetted, that are breaking into droplets by bulging and narrowing on a characteristic length scale. We cannot establish details about the specific mechanism of dewetting

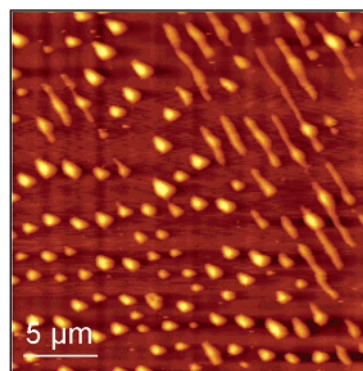


Figure 4. AFM image of a printed Mn_{12} SMM on Si(100) with native silicon oxide. The stamp was removed a few seconds before the end of the process. The formation of lines of materials and how these are rupturing into droplets to give rise to aggregates is apparent.

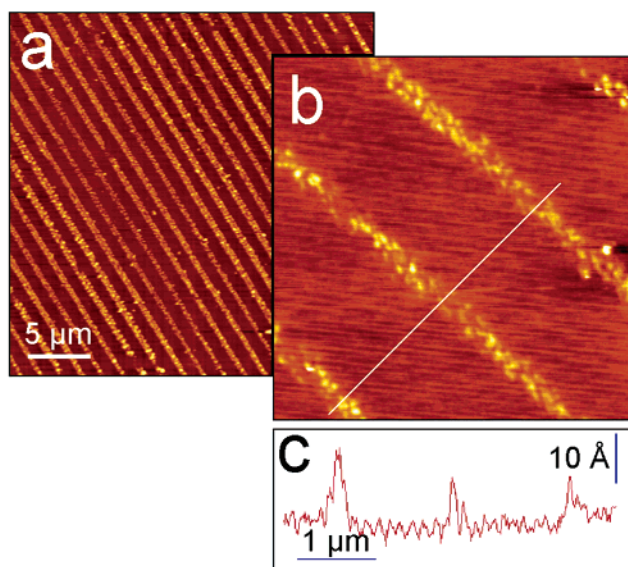


Figure 5. (a) AFM image of a printed Mn_{12} SMM line pattern using a diluted solution on a hydrophobic surface (HMDS). (b) Enlargement of a. The width of the printed features is 200 nm, and the thickness is only one molecule. (c) Topographical line profile along the white line.

because the kinetics of rupture is experimentally difficult to image in real time.

The remarkable feature of this approach is that the spatial correlations on smaller length scales are introduced by the dewetting phenomena and not by the stamp. Thus, there is no need for stamps with very fine features to define the individual positions and sizes of the nanostructures. The technological advantage consists of the ability to pattern on length scales much smaller than those of the features present in the stamp.

In Figure 5, the same experiment was performed on a hydrophobic substrate, viz., silicon oxide primed from hexamethyl disiloxane (HMDS). The silicon oxide surface is terminated with trimethylsilyl groups. Similar results were obtained on highly oriented pyrolytic graphite. In this case, the wettability of the surface by complex **1** molecules results in monolayer stripes, $3 \pm 1 \text{ nm}$ high and less than 200 nm

wide, that replicate the motifs of the protrusions. Thus, by using wetting conditions instead of dewetting, we can deposit one to two monolayer-thick stripes of finite lateral size that are amenable to STM experiments.

In conclusion, the possibility to pattern ordered arrays of nanostructures made of small Mn₁₂ single-molecule magnets has been demonstrated. The approach we devised is based on stamp-assisted deposition from a solution on a substrate in a regime of partial wetting or dewetting. Our method integrates two important features into a convergent approach: (i) a large-area, parallel fabrication due to the use of the stamp and (ii) the capability of introducing multiple length scales because of the interplay of the growth phenomena of the nanostructures. It is therefore a genuine bottom-up patterning on smaller length scales, where it exploits competing interactions between the adsorbate and the substrate. These can be tuned by the design and a proper functionalization of the outer ligands of the Mn₁₂ complex and of the substrate. This is particularly appealing in the case of magnetic molecules, where we could imagine, by suppressing coalescence and ripening phenomena, that single molecules could be organized into addressable memory elements at ultrahigh density.

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