

Multiple length scale patterning of single-molecule magnets

*Massimiliano Cavallini¹, Fabio Biscarini*¹, Jordi Gomez-Segura², Daniel Ruiz², Jaume Veciana²*

1 CNR- Istituto per lo Studio dei Materiali Nanostrutturati, Sez. di Bologna, Via P. Gobetti 101, I-40129
Bologna, Italy

2 CSIC-Institut de Ciència de Materials de Barcelona, Campus Universitari de Bellaterra, 08193-
Cerdanyola, Spain

AUTHOR EMAIL ADDRESS: f.biscarini@ism.bo.cnr.it

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CNR – Istituto per lo Studio dei Materiali Nanostrutturati (ISMN) Sez. Bologna.

Via P. Gobetti 101, I-40129 Bologna Italy.

Tel. ++39-051-6398523; Fax. ++39-051-6398540

ABSTRACT

Control of materials at multiple length scales is one of the most compelling issues in nanotechnology research nowadays. Here we demonstrate that arrays of nanometer-sized aggregates, each made of a few hundreds of single-molecular magnets, derived from Mn_{12} complexes, can be patterned on large areas by self-organisation assisted by stamps on a surface in a de-wetting regime. The large length scale is imposed by the motif of the stamp protrusions, while the smaller length scales, viz. 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, since repulsive, as opposed to specific, interactions are required. Our result hints to the possibility of a sustainable patterning of single molecular magnets for ultra-high density magnetic storage.

KEYWORDS. Patterning, single-molecule magnets, dewetting.

BRIEFS (WORD Style “BH_Briefs”). If you are submitting your paper to a journal that requires a brief, provide a one-sentence synopsis for inclusion in the Table of Contents.

MANUSCRIPT TEXT

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 storage (3) and for quantum computing applications (4), provided their T_B 's can be increased to reasonable values and the molecules can be organized into addressable domains. With this aim, it has been demonstrated the possibility to deposit isolated SMM's, derived from Mn_{12} complexes, or very small aggregates of such molecules, onto a polycarbonate surface (5). Very recently, self-assembly of thiol-substituted Mn_{12} complexes have been achieved on Au thin films (6). In either cases, no control of position and distance was shown, and despite the latter method is amenable for contact printing, it may be desirable to pattern SMM's onto a variety of surfaces and not being restricted to gold thin films. The use of microcontact printing and capillary filling to pattern the deposition of ferrofluid on a surface with feature of microns was reported (7).

Fabrication of ordered patterns of Mn_{12} SMM is a crucial step to realize memory elements based on these materials. For instance, new systematic studies that allow us to fabricate ordered patterns of SMM's, either isolated or aggregated, onto surfaces where each molecule or molecular aggregate can be used as a bit of information, are highly required. Since Mn_{12} SMM is 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 else by magnetic scanning probes (5).

Here we demonstrate patterning of aggregates of Mn_{12} SMM's with size- and distance control at multiple length scales, ranging from tens nm to mm. We use a convergent approach based on a stamp-assisted deposition of molecules from a solution together with de-wetting phenomena arising from competing interactions between the molecules and the substrate. Such approach, that is suitable for a number of soluble materials (8) and non-wettable substrates, can be in principle pushed down to the limit

where single molecular magnets are patterned into ordered arrays, being this process ultimately limited only by coarsening of the individual molecules.

The complex used in this work is $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CC}_{12}\text{H}_9)_{16}(\text{H}_2\text{O})_4]$ (**1**), whose synthesis has been previously described (9).

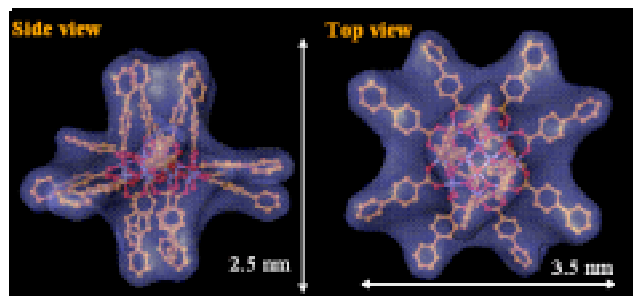


Figure 1. Molecular structure of Mn_{12} complex **1**. Side- and top-view of the molecular structure of complex **1** obtained by molecular modeling. Connolly surfaces around the molecule show the van der Waals shape and volume.

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-like shaped Mn_{12} core stabilized by an outer shell of sixteen biphenyl 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 regime (11) 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 partial wetting regime, correlations arise because of intertwined nucleation and ripening, the latter being 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, that can develop via two possible mechanisms: i) nucleation and growth of holes (16) 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 wetting/dewetting phenomena over a large area in order to control multi-scale organization of complex **1**, from nanometer- sized aggregates of a few molecules to arrays with sub-micrometer or nanometer length scales.

Solution casting is not suitable for multi-scale patterning over a large area, because surface defects pin the receding fluid front and induce non-equilibrium flow of material (19). Since 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.

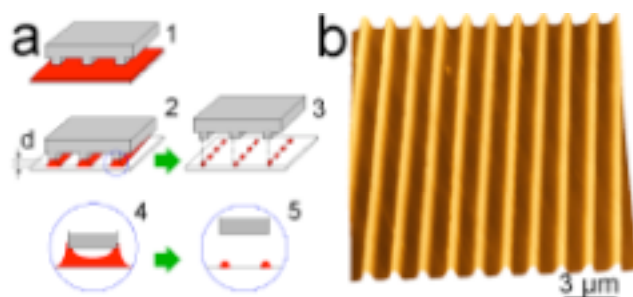


Figure 2. Schematic representation of stamp-assisted deposition. **(a)** (1) The stamp is placed in contact with a layer of solution spread on the substrate; (2) as solvent evaporates, onset of capillary forces pins the solution to the protrusions. Since evaporation rate is faster in the thinner parts, 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 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 nano-droplets are obtained by dewetting of the material deposited upon the regime (4). **(b)** AFM images of the stamp, used in this experiments. It consists of parallel lines 500 nm wide and distant 1.5 μm apart.

The protrusions of the stamp effectively 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 imposes the large area spatial modulation to the solution, and hence to the deposited solute. Accidental defects on the surface become statistically irrelevant, being the stamp features considerably denser and their effect modulated through the choice of solvent and the chemical nature of the surface of the stamp. As the result, the process of droplet formation is confined under the stamp protrusions, and the smaller length scales, viz. droplet size and inter-droplet distances, will depend on the initial concentration of the solution and the volume under the protrusions, that depends ultimately on the distance between the stamp and the substrate. A remarkable outcome of our approach with respect to a printing technique with intimate contact between stamp and substrate is the possibility to down-scale the size of the printed features with respect 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 process FIG. 2a(5). In the case of an extremely dilute solution is possible to obtain ultra-narrow split features, because of the pinning at the sharper edges of the protrusions. In this regime, deposited structures as small as tens nm wide can be obtained using protrusions that are a few hundreds nm wide but with sharper edges. An AFM image of the stamp used is shown in Figure 2b.

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

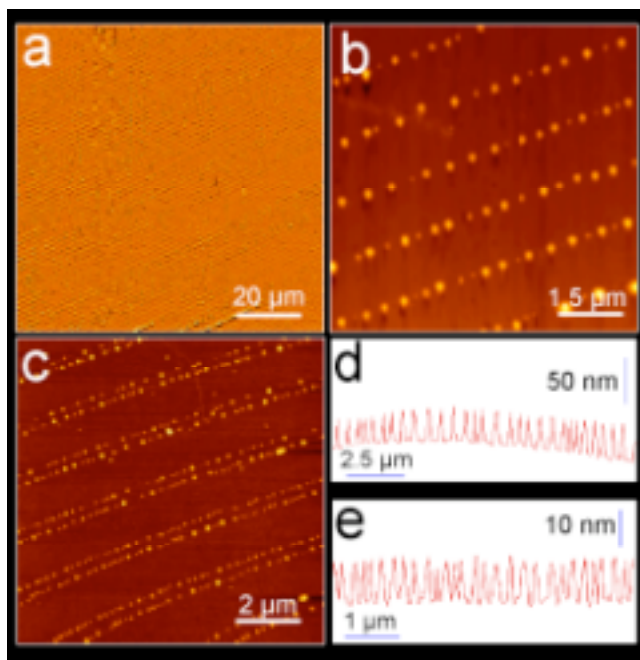


Figure 3 (a) AFM image (error signal) of patterns of **1** fabricated on a large area ($100 \times 100 \mu\text{m}^2$). (b) Image of printed features using a diluted solution; (c) Image of printed features using a very diluted solution; Typical line profile along a line obtained using (d) a diluted solution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

The used substrates was native silicon oxide onto Si(100), obtained by etching silicon wafer into a 10% HF solution for 2 minutes, then rinsed in ultra pure distilled water, and let into humid air (relative humidity 55%) to re-oxidise for 24 hrs.

In Figure 3a, it is shown that patterning is effective across at least $100 \times 100 \mu\text{m}^2$ area, the assessment of the latter 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. Upon a closer magnification (see 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 $441 \pm 138 \text{ nm}$ (Fig. 3d). The remarkable result is that the arrays of complex **1** droplets using a featureless stamp with a much larger size. By using a more dilute solution (Fig. 3c) we obtain split strings of droplets, whose apparent lateral FWHM is $70 \pm 15 \text{ nm}$, their height is $8 \pm 2 \text{ nm}$, while the spacing is $200 \pm 42 \text{ nm}$. Considering that complex **1** can be approximated to an oblate ellipsoid, whose Van der Waals axes are 2.5 and 3.5 nm respectively, we estimate that each aggregate consists of 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 with the hydrophilic surface and the surface energy is the driving force for the film rupture.

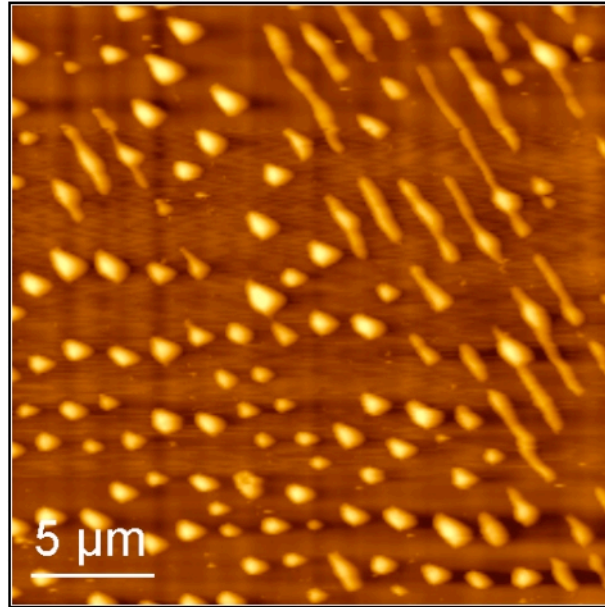


Figure 4. AFM image of printed Mn_{12} SMM on Si(100) with native SiO_x . The stamp was removed a few seconds before the end of process. It is apparent the formation of lines of materials, and how these are rupturing into droplets to give rise to aggregates.

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

The remarkable feature of this approach is that the spatial correlations at smaller length scales are introduced by the dewetting phenomena and not by the stamp. Thus, there is no need of stamps with very fine features to define the individual positions and size of the nanostructures. The technological advantage

consists in the ability to pattern at length scales much smaller than those of the features present in the stamp.

In Figure 5 the same experiment was performed onto a hydrophobic substrate, viz. silicon oxide primed from hexamethyl disloxane (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 into monolayer stripes, 3 ± 1 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-two monolayer stripes of finite size that are amenable for STM experiments.

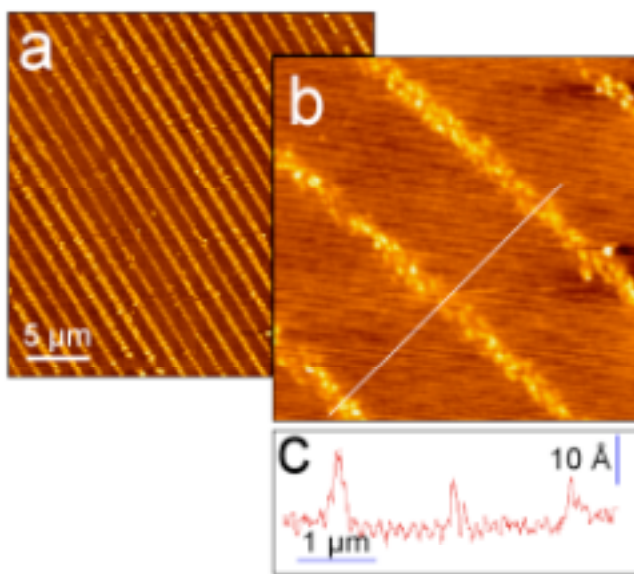


Figure 5 (a), AFM image of printed Mn₁₂ SMM thin film using diluted solution on hydrophobic surface (HMDS); (b), Zoom of (a), the width of printed features is 200 nm and the thick is just one molecule. (c), Topological line profile along the white line.

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 a 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 scale due to the interplay of growth phenomena of the nanostructures. It is therefore a genuine bottom – up patterning at the smaller length scales, where it

exploits competing interactions between adsorbate and the substrate. These can be tuned by design and a proper functionalisation of the outer ligands of Mn_{12} 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 organised into addressable memory elements at ultra-high density.

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