Self-organization of Mn_{12} single-molecule magnets into ring structures induced by breath-figures as templates

Jordi Gómez-Segura,[a] Olga Kazakova,[b] Julia Davies,[b] Patrick Josephs-Franks,[b] Jaume Veciana[a] and Daniel Ruiz-Molina*[a]

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Cooling evaporation of a CH_2Cl_2 solution of Mn_{12} clusters on highly oriented pyrolitic graphite (HOPG) initiates the formation of water droplets that act as templates for the formation of self-assembled molecular magnetic rings.

Single-molecule magnets (SMMs) exhibit large spin ground states with large magnetoanisotropy, resulting in an energy barrier for spin reversal. As a consequence, each molecule exhibits slow magnetization relaxation rates and interesting magnetic properties that are characteristic for nanoscale magnetic particles, such as out-of-phase ac magnetic susceptibility signals and stepwise magnetization hysteresis loops.[1] Therefore, SMMs represent an exciting breakthrough towards the realisation of ultimate high-density information storage devices and quantum computing applications.[2] However, if a truly molecular computational device based on SMMs is to be achieved, new systematic studies that allow us to obtain spatially and geometrically controlled patterns of SMMs on a given surface are essential. One of the first steps in this direction was the organization of these molecules within multilayered Langmuir–Blodgett films.[3] Since then, other approaches such as self-assembly of a thiol modified Mn_{12} complex;[4] grafting on Au(111)[5] or Si(100)[6] surfaces; and photolithography on Si/SiO_2 surfaces[7] have been reported. In our group, we have also been strongly involved in the development of new methodologies to address individual Mn_{12} molecules, both on the surface of polycarbonate thin-films by a soft lithographic technique and for the multiple length scale patterning of Mn_{12} molecules over different surfaces (HOPG and Si/SiO_2).[8]

Here, in a further step to expand the range of methodologies explored for the deposition of functional molecular materials on a surface, we report a new valuable and simple route based on the condensation of water droplets on a cold surface that act as a template for the self-organization of Mn_{12} molecules into magnetic rings. Such a methodology, based on the well-known breath-figures phenomenon,[9] has already been successfully used to generate 2D or 3D ordered macroporous materials based on polymeric systems[10] but not for ordering molecules on surfaces.

The molecule of choice was the Mn_{12} complex $[Mn_{12}O_{12}(O_2CR)_{16}(H_2O)_x]$ comprising aromatic biphenyl moieties ($R = C_6H_4C_6H_5$) (**1**).†[11] In addition to being well studied, this molecule exhibits a considerable thermal and chemical stability,[12] large volume and a hydrophobic outer shell that is expected to favour molecular self-assembly through π···π interactions between the phenyl groups. Initially, a solution of **1** in a highly volatile organic solvent (CH_2Cl_2) was cast onto freshly cleaved HOPG wafers under a moist atmosphere. Imaging of the surface by atomic force microscopy (AFM) after solvent evaporation reveals the formation of uniform ring-shaped deposits of Mn_{12} randomly distributed all over the surface. A topographic image and the corresponding height profile are shown in the top section of Fig. 1. The image shows several ring-shaped structures located on the HOPG surface, a pattern that was confirmed after additional measurements were made in at least three different well-separated 50 × 50 μm^2 sites. In each of the images, rings appear to be relatively uniform in size, with an experimental averaged height that ranges from 119 to 135 nm, averaged diameters ranging from 4.2 to 4.6 μm and a ring-thickness at half height of approximately 140 nm.

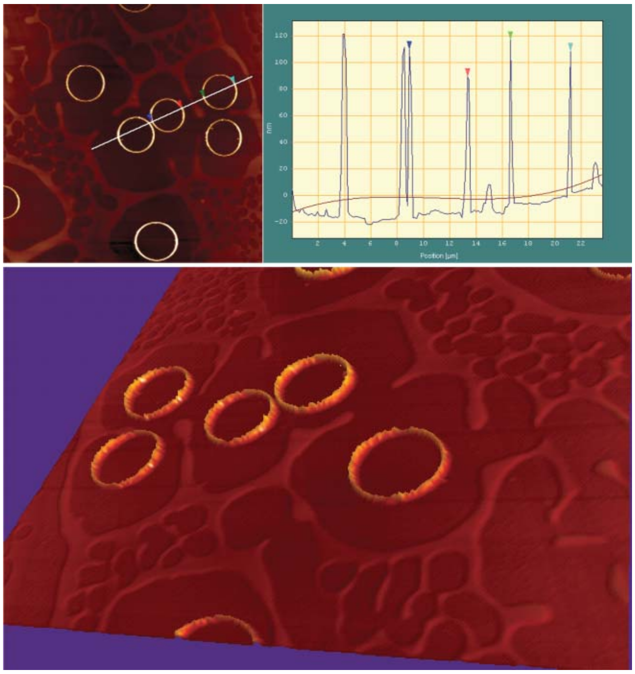

Fig. 1 Drop-casting on HOPG from a CH_2Cl_2 solution of **1** exposed to a moist atmosphere. AFM top-view topographic image (top left). Height profile (top right) across lined-up rings indicated in the top-view topographic image and the corresponding 3D image (bottom). Scan size is 35 μm.

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[a] *Institut de Ciència de Materials de Barcelona (CSIC), Campus Universitari, 08193 Bellaterra, Catalonia, Spain.*
E-mail: dani@icmab.es; Fax: +34 93 580 57 29; Tel: +34 93 580 18 53
[b] *National Physical Laboratory (NPL), Hampton Road, Teddington, Middlesex, UK TW11 0LW. Fax: +44 20 8614 0563;*
Tel: +44 20 8943 6654

The self-assembly of cobalt nanoparticles into rings has already been reported by Wei *et al.*[13] In such work, bracelet self-assembly in solution has been attributed to the existence of magnetic dipolar interactions and evaporation-driven flow on wetted surfaces. In the case of Mn_{12} single-molecule magnets, a feasible interpretation for the formation of the rings is shown in Fig. 2. Drop casting of a solution of complex **1** in CH_2Cl_2 results in an initially continuous thin-film. Subsequently, along the course of the evaporative cooling, water droplets condense from the moist atmosphere onto the film surface, according to the well-known breath-figures mechanism (step a). The water droplets locally cap the liquid film surface and the solvent is only allowed to evaporate in between the droplets, driven by convective motion (step b), as previously observed in polymeric matrixes.[10] In the later stages of solvent evaporation, the continuous thin-film undergoes fragmentation as ascribed to characteristic dewetting phenomena,[14] although the spherical cap water droplets remain unaltered on the surface of the HOPG. As a consequence, the residual solution is strategically confined to the constrained regions at the periphery of each droplet (step c).[15] During completion of the evaporation process, solute molecules accumulate to form solid deposits of Mn_{12} that recall the droplet perimeter (steps d and e). The formation of such rings is most likely favoured by self-assembly through $\pi\cdots\pi$ interactions between the phenyl groups and by the existence of dipolar interactions between molecules, although also in a small degree due to their paramagnetic character at room temperature. The regions immediately surrounding the rings are depleted in Mn_{12} deposits because of a rapid radial shrinkage to the droplet edges, although a residual thin-film of Mn_{12} molecules remains on the surface along the film fragmentation path, showing the characteristic morphology of the dewetting patterns (see bottom of Fig. 1).[14]

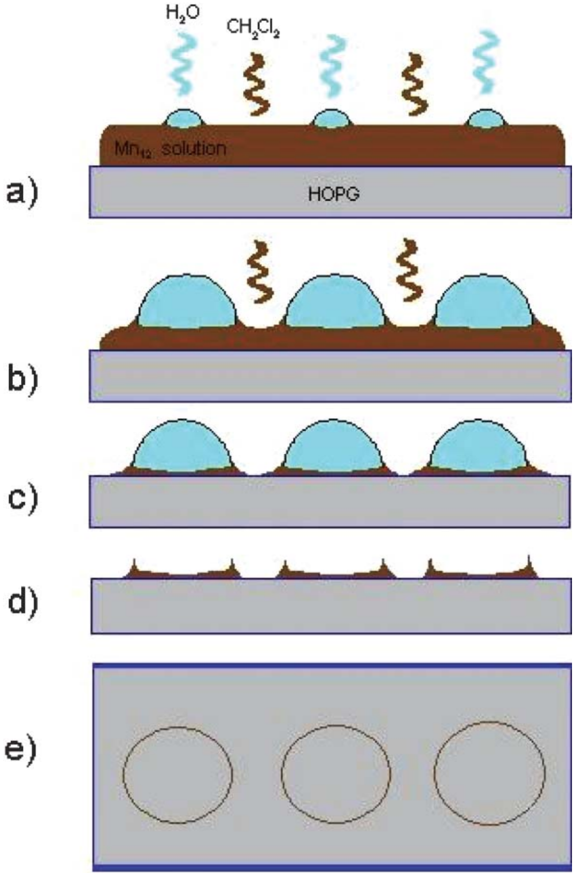

Fig. 2 Schematic stepwise representation of the solvent evaporation process. Evaporative cooling causes water droplets to condense on the surface of the thin solvent film. The edges of the water droplets pin the solution and a solid deposit of Mn_{12} is formed in the location of the concave capillary bridge.

To give more insight into the mechanism shown in Fig. 2, the same experiments were repeated on a hydrophilic Si/SiO_2‡ surface. As shown in Fig. 3, imaging of the surface by AFM after solvent evaporation reveals this time the lack of regular ring patterns in at least three different well-separated 50 × 50 μm^2 sites. On the contrary, the observation of an inhomogeneous distribution of amorphous features has been attributed to the enhanced hydrophilicity of the native silicon oxide compared with HOPG. The wetting characteristics of the water molecules imply a decrease in the droplet flatness ratio (*i.e.*, the ratio of droplet height to radius). Therefore, more extended wetting areas are prone to disruption giving rise to a distribution of dispersed features. There is, however, the potential to extend this work to more hydrophilic substrates with technological relevance, such as SiO_2, using appropriate surface modification methods to form a hydrophobic surface.

Finally, to assign the rings shown in Fig. 1 to Mn_{12} molecules rather than any solvent impurity, further characterization of the Mn_{12} rings was performed using magnetic force microscopy (MFM). MFM uses a magnetic tip that allows the combination of topographic imaging of an object with the mapping of a local distribution of magnetic moments.

A first scan was acquired at a height intimately close to the sample surface (about 3–5 nm), where the short-range van der Waals force is active, such that the obtained image is predominantly topographic. A similar pattern to that shown in Fig. 1, with a poorer resolution due to the use of a thicker Co-coated tip, was observed (see Fig. 4). Subsequently, the tip was retracted to a selected lift scan height in the range 50–300 nm, where magnetic interactions become apparent at the expense of topographic effects. In all the distance ranges, the phase shift (MFM image) of the cantilever oscillations reveals changes in the resonant frequency

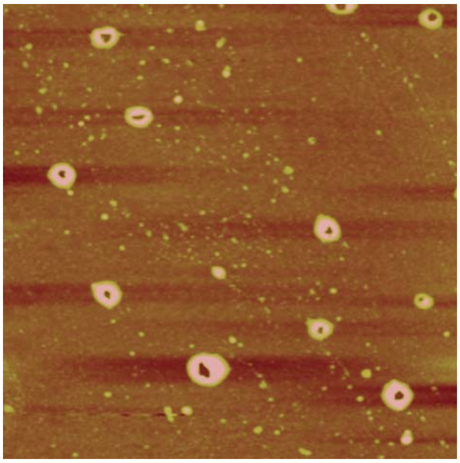

Fig. 3 Drop-casting onto a hydrophilic Si/SiO_2 wafer from a CH_2Cl_2 solution of **1** exposed to a moist atmosphere. Scan size is 10 μm.

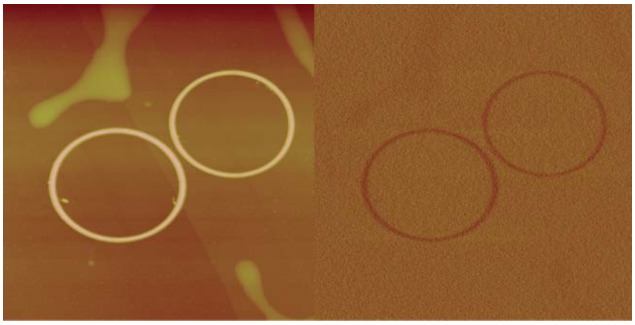

Fig. 4 MFM images of Mn_{12} rings of **1** on HOPG: topography (left) and the corresponding phase-contrast image at 300-nm lift height (right). Scan size is 12 μm.

induced by magnetic interaction between the tip and the sample at the position of the rings previously found by topographic imaging. For instance, Fig. 4 shows the spatial variation of magnetic forces obtained with a Co-coated tip at 300 nm, at which height the interatomic van der Waals force is suppressed and only long-range magnetic forces persist.

The MFM image shown in Fig. 4 was obtained at room temperature, where Mn_{12} clusters are paramagnetic without a preferential ordering of their magnetic moments. Nevertheless, application of a near magnetic field (*i.e.*, the field induced by the magnetic tip, which to some extent can be considered as a magnetic dipole) is likely to magnetize the individual molecules even at room temperature. Moreover, even though small, the collection of the magnetic moments of the molecules is enough to generate a magnetic contrast with the diamagnetic surrounding, detectable even at room temperature.[16] As a consequence, the magnetic moments of all molecules become observable by MFM. This fact was confirmed when a non-magnetic Si tip was used, under similar experimental conditions.§ In this case, all traces of rings on the phase-lag image due to topographic effects decrease progressively until the scan height reaches approximately 50 nm, when they disappear completely.

In summary, breath-figures have been used as a template method to arrange Mn_{12} SMMs into reproducible and uniform magnetic ring-shaped self-assemblies. Moreover, breath-figures are a well-known phenomenon that is prone to form ordered arrays with controlled sizes under specific experimental conditions.[17] With this aim, we are currently exploring the feasibility to achieve spatially controlled patterns of self-assembled rings on surfaces not only of Mn_{12} but also of several other functional molecular systems. Studies in order to understand the influence of experimental parameters on the size of magnetic ring-shaped self-assemblies are also underway.[18]

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Notes and references

† The synthesis of **1**, $[Mn_{12}O_{12}(O_2CC_6H_4C_6H_5)_{16}(H_2O)_4]$, has been described elsewhere.[11] A CH_2Cl_2 solution of **1** (10^{-4} g cm^{-3}) was cast onto freshly cleaved HOPG (Agar Scientific) or Si/SiO_2 in a moist atmosphere (relative humidity 65%).

‡ A Si(100) wafer was chemically etched with a 10% HF solution for 2 min and rinsed in ultrapure distilled water. Reoxidation was carried out in a moist atmosphere (relative humidity 55%) for 24 h.

§ AFM/MFM measurements were performed using a commercial atomic force microscope MultiMode operating in air at room temperature. The AFM images were acquired in tapping mode using phosphorus or antimony (n) doped Si tips (spring constant = 40 N m^{-1}, resonant frequency = 300 kHz). For MFM measurements, Co/Cr-coated tips were used operating in the lift mode (spring constant = 2.8 N m^{-1}, resonant frequency = 75 kHz).

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