SUPPORTING INFORMATION

for

Integration and measurement of single molecule magnets on μ-SQUID sensors by dip pen nanolithography: the role of interphases

by

S1. Contact angle evolution with solvent mixture content

![Figure S1. Series of optical images of 3 μl droplets deposited on Si/SiO2 substrates for binary mixtures of solvents made of (a) DMF; (b) DMF + 10 % v/v glycerol; (c) DMF + 20 % v/v glycerol; and (d) DMF + 24 % v/v glycerol.]

S2. Attenuated total reflectance-Fourier transform infrared (ATR-IR) analysis of the stability of Mn12bz molecules in the binary mixture DMF:glycerol

After multiple trials, the ration of the binary mixture DMF:glycerol for the DPN experiments was fixed. Best results were obtained by adding a 5-10 % v/v of glycerol to a solution of Mn12bz in DMF. To test the stability of the molecular compound in such mixture, attenuated total reflectance-Fourier transform infrared (ATR-FTIR) experiments of a solution of the Mn12bz (20 mg·mL⁻¹) in DMF containing a 5 % v/v of glycerol were performed. The background signal of the solvents was subtracted from the IR spectrum since the bands coming from the mixture of solvents almost completely hindered the peaks of the compound. In this way, the main characteristic peaks of the Mn12bz were slightly distinguished in the resulting spectrum (Figure S2).

![Figure S2. IR spectrum of the Mn12bz crystal (bottom) and the Mn12bz in a mixture of DMF and 5 % v/v of glycerol, after subtracting background signal from the mixture of solvents (top).]
S3. X-Ray Photoelectron Spectroscopy (XPS) of spin-coated Mn$_{12}$bz in the binary mixture DMF:glycerol

Sample was prepared by spin coating of a 10 mg/ml Mn12bz solution in a DMF/glycerol (95/5) mixture on a Si/SiO$_2$ substrate.

![XPS spectrum recorded for the spin-coated Mn$_{12}$bz in the binary mixture DMF:glycerol. The line overlapping the experimental data points correspond to the best fit in curve components, which are represented underneath.](image)

Figure S3 shows the Mn 2p core level double peak of the spin-coated Mn$_{12}$bz in the binary mixture DMF:glycerol. The spin-orbit splitting generates two peaks for Mn$_{12}$ derivatives: the highest it is attributed to 2p$_{3/2}$ and the lowest to 2p$_{1/2}$, being the difference in binding energy of 11.7 eV.\(^\text{1}\) This clearly shows that the Mn is oxidized. The line shape can be decomposed in three different peaks, labelled A-C. The best fit is shown as a continuous line with a very satisfactory overlap of the experimental data points.

The main experimental peaks are centered at 641.6 eV and 642.7 eV of binding energy corresponding to Mn$^{3+}$ (A) and Mn$^{4+}$ (B), respectively. The area ratio between both peaks (A/B) and the intensity ratio are 1.8 and 2.1, which is in agreement with the stoichiometry of 8 atoms of Mn$^{3+}$ and 4 atoms of Mn$^{4+}$ in the molecular core. Peak C, centered at 645.7 eV, could be tentatively related to Mn$^{2+}$ and be assigned to manganese carbonate,\(^\text{2}\) and/or the interaction of several groups with fragments of the molecule.\(^\text{3}\)

XPS experiments have confirmed that neither the binding energies nor the chemical state of the Mn atoms in the magnetic core are altered, and hence the cluster integrity.

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S4. Fabrication of large patterns fabricated for grazing incidence X-ray diffraction (GI-XRD) characterization

Figure S4. Optical microscopy images of (a) simultaneous patterning of Mn₁₂bz on Si/SiO₂ by using the twelve MP tips of the cantilever array, (b) magnification view of a section of the pattern were slight differences between arrays fabricated with different tips can be observed and (c) large pattern fabricated by repeating 3-4 times coating and writing steps. Variation in bright between arrays indicate different degrees of drying of the arrays as well as slight differences in dot size. The line mark used as reference for localize the array can be observed.

Figure S5. GIXRD patterns of bulk and structured samples fabricated on Si/SiO₂ substrates by DPN process. A solution of Mn₁₂bz (10 mg mL⁻¹) in DMF and 5 % v/v of glycerol was used as ink for the preparation of both samples.

S6. Additional characterization of the arrays by energy dispersive X-ray spectroscopy (EDX)

Along with the HR-TEM study, additional information regarding to the elemental composition of the arrays was obtained by inspecting the sample using energy dispersive X-ray spectroscopy (EDX) microanalysis. The array was fabricated by DPN process on a carbon-coated TEM grid by using as ink a solution of Mn₁₂bz (10 mg mL⁻¹) in DMF and 5 % v/v of glycerol. In these experiments, different X-ray spectra were collected by focusing the electron beam of the EDX equipped TEM on different dots of the arrays. In the spectra pattern, the presence of Mn element inside each one of the dots was clearly confirmed by the
presence of the corresponding peak. Interestingly, these results emerge as a clear evidence of the presence of Mn$_{12}$bz molecules inside the structures generated by the AFM tip.

**Figure S6.** EDX spectrum showing the Mn peaks of an area of the dot nanostructure shown in inset image.

S7. Estimation of the number of Mn$_{12}$bz molecules deposited in samples DPN-1 and DPN-2.

For both samples, the number of the molecular entities deposited with the tip is estimated based on geometrical considerations. AFM analysis of depositions fabricated exactly under the same experimental conditions followed for Sample-3 and Sample-4 but on top of Si/SiO$_2$ substrates provide information about the dimensions of such deposits. These dimensions are then used for the estimation.

DPN1 consists in a structured sample made of 1320 identical dots 249 ± 9 nm in diameter and 7 ± 1 nm height (as measured in a replica fabricated on Si/SiO$_2$). The area of a dot is 48695.5 nm$^2$. The disk-like Mn$_{12}$bz molecule (2.1 × 1.2 nm) can self-organize on the surface into two different orientations or a combination of both. Both orientations are considered in order to study the two limit situations.

When the molecules are all oriented with their axial positions perpendicular to the surface, the surface area occupied is ~3.5 nm$^2$. Considering the densest packing of identical circles organized in a plane (hexagonal packing arrangement), with a packing density of 0.9069, the maximum number of molecules that can be organized in a monolayer of one of the dots is around 1·10$^4$. Additionally, since the average height of the dot is 7 nm and considering the 1 nm contribution of solvents, we can assume that up to 5 layers of molecules can be organized inside each dot. Then, the estimated number of molecules inside each one of the dots is 6·10$^4$.

Finally, since inside the coil a number of 1320 identical dots were fabricated, the total amount of molecules that can be in the sensor is up to 8·10$^7$.

Alternatively, when the molecules are all oriented with their axial positions parallel to the surface, the surface area occupied is ~2.5 nm$^2$. According to this, the maximum number of molecules that can be organized in a monolayer of one of the dots is 2·10$^4$. Additionally, since the average height of the dot is 7 and considering the 1 nm contribution of solvents, we can assume that up to 3 layers of molecules can be organized inside each dot. Then, the estimated number of molecules inside each one of the dots is 5·10$^4$. Considering the 1320 identical dots fabricated inside the coil, the total amount of molecules that can be integrated in the sensor is up to 7·10$^7$.
From this study, the average of the two values calculated allow to estimate that an order of $8 \cdot 10^7$ molecules were integrated in the pickup coil for DPN1.

DPN2 consists in a thin-film that completely covers the coil of 27 µm internal diameter. The circular area of the deposit is 572.5 µm$^2$ (corresponding to circular pattern 27 µm in diameter) and ~ 7 nm in height. Herein, the two orientations of the molecules are also considered.

In the first case, all molecules organize with their axial positions perpendicular to the surface. Considering the surface area occupied by a molecule in this orientation is ~ 3.5 nm$^2$ and the packing density of 0.9069, the maximum number of molecules that can be organized in a monolayer of the thin-film is $1.7 \cdot 10^8$. Additionally, since the average height measured for the thin-film is 7 nm and the solvent background is up to 1 nm, we can assume that up to 5 layers of molecules can be organized inside the film. Therefore, the estimated number of molecules that form the thin-film is up to $8.3 \cdot 10^8$.

In the second case, all molecules organize with their axial positions parallel to the surface. The area occupied by a molecule in this orientation is ~ 2.5 nm$^2$. According to this, the maximum number of molecules that can be organized in a monolayer of the thin-film is $2.1 \cdot 10^8$. Similarly, we can estimate that up to 3 layers of molecules in this orientation can be organized inside the film. Therefore, the estimated number of molecules that form the film is up to $6.2 \cdot 10^8$.

From this study, the average of the two values calculated allow to estimate that an order of $7.2 \cdot 10^8$ molecules was integrated in the pickup coil for DPN2.

S8. Magnetic susceptibility measurements on sample DPN2.