POSITIONING OF SINGLE-MOLECULE MAGNETS ONTO SIO$_2$ NANOPATTERNS WITH SUB-50 NM ACCURACY

S. Tatay, E. Coronado, A.Forment-Aliaga, F.M. Romero, R. V. Martínez, F. García, R. Garcia*
Instituto de Ciencia Molecular (ICMol), Universidad de Valencia, Edificio institutos de Paterna, Paterna (Spain)
sergio.tatay@uv.es

High-spin molecules with a significant magnetic anisotropy has prompted the interest in dodecanuclear manganese complexes of general formula $[Mn_{12}O_{12}(RCOO)_{12}(H_2O)_{12}]$. Potential applications of Mn_{12} single-molecule magnets (SMM) as bits for information storage or 'qbits' for quantum computation require methods for nanoscale controlled position and/or manipulation of those molecules. In the search of suitable procedures to deposit SMM onto different approaches has been used.[1-7] However, currently none of those methods allow positioning one or just a few single-molecule magnets into a predetermined nanoscale region of the surface.

Local oxidation nanolithography (LON) is a scanning probe nanolithography that allows the fabrication of templates as well as a variety of electronic, optical and mechanical nanoscale devices. It is based on the spatial confinement of the oxidation reaction within a water meniscus formed between a nanometer-size protrusion, usually, although not exclusively, the tip of an atomic force microscope (AFM) and the sample surface.[8]

Our contribution to the implementation of SMM onto different substrates is based on the electrostatic interactions between a positively-charged Mn_{12} derivative and the surface of interest. With this aim, we have synthesized Mn_{12} complexes with appended cationic tetralkylammonium groups.[9] Here we report a process for the transfer of $Mn_{12}O_{12}(bet)_{16}(EtOH)_4][(PF_6)]_{14}$ (Mn_{12}-betaine) from a macroscopic liquid solution into a predetermined nanoscale region of a silicon surface. The method allows the fabrication of nanostructures made of Mn_{12}-betaine on a silicon oxide template while the rest of the macroscopic surface remains free of molecules. Local oxidation is used to fabricate silicon oxide nanopatterns, either dots or stripes, over a Si(100) surface coated with a 3-amino-propyltriethoxylsilane SAM. Their width ranges from 30 to 500 nm while the length can be modified from a few nanometers up to several micrometers. Nanoscale direct assembly arises from a combination of three factors: (i) the strength of the attractive electrostatic interactions between the molecules and the local oxides, (ii) the weak repulsive interaction between the molecules and the unpatterned surface and (iii) the size of the nanopattern.

References:

[1] J. Means, V.; Meenakshi, R. V. A. Srivastava, W. Teizer, A. A. Kolomenskii, H. A. Schuessler, H. Zhao, K. R. Dunbar, *J. Magn. Magn. Mater.* **248** (2004) 215.
[2] M. Cavallini, F. Biscarini, J. Gomez-Segura, D. Ruiz, J. Veciana, *Nano Lett.* **3** (2003) 1527.
[3] D. Ruiz-Molina, M. Mas-Torrent, J. Gómez, A. I. Balana, N. Domingo, J. Tejada, M. T. Martínez, C. Rovira, J. Veciana, *Adv. Mater.* **15** (2003) 42.
[4] (a) 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.* **4** (2004) 399. (b) A. Nait Abdi, J. P. Bucher,

P. Rabu, O. Toulemonde, M. Drillon, P. Gerbier, *J. Appl. Phys.* **95** (2004) 7345. (c) G. G. Condorelli, A. Motta, I. L. Fragalà, F. Giannazzo, V. Raineri, A. Caneschi, D. Gatteschi, *Angew. Chem. Int. Ed.* **43** (2004) 4081.
[5] A. Naitabdi, J. P. Bucher, P. Gerbier, P. Rabu, M. Drillon, *Adv. Mater.* **17** (2005) 1612.
[6] 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. Int. Ed.* **42** (2003) 1645.
[7] M. Mannini, D. Bonacchi, L. Zobbi, F. M. Piras, E. A. Speets, A. Caneschi, A. Cornia, A. Magnani, B. Jan Ravoo, D. N. Reinhoudt, R. Sessoli, D. Gatteschi, *Nano Lett.* **5** (2005) 1435.
[8]. (a) M. Tello, R. Garcia, *Appl. Phys. Lett.* **79** (2001) 424. (b) Instrumentation and nanopatterning process are similar to the one described below but using water menisci.
M. Tello, R. Garcia, J.A. Martín-Gago, N. F. Martinez, M.S. Martin-Gonzalez, L. Aballe, A. Baranov, L. Gregoratti, *Adv. Mater.* **17** (2005) 1480.
[9] (a) E. Coronado, M. Feliz, A. Forment-Aliaga, C. J. Gómez-García, R. Llusar, F. M. Romero, *Inorg. Chem.* **40** (2001) 6084. (b) A. Forment-Aliaga, E. Coronado, M. Feliz, A. Gaita-Ariño, R. Llusar, F. M. Romero, *Inorg. Chem.* **42** (2003) 8019. (c) E. Coronado, A. Forment-Aliaga, A. Gaita-Ariño, C. Giménez-Saiz, F. M. Romero, W. Wernsdorfer, *Angew. Chem. Int. Ed.* **43** (2004) 6152.

Figure 1: Patterns fabricated by Local Oxidation Nanolithography before and after deposition of Mn_{12}-betaine. (a) AFM image of two parallel stripes. (b) Cross-section along the line shown in (a). (c) Topographic image of the pattern shown in Fig. 2a after deposition of Mn_{12}-betaine. The molecules appear as white dots in the image. (d) Topographic image of a local oxide dot of 80 nm in diameter. (e) The phase image reveals the presence of Mn12-betaine forming a nanoscale ring around the dot. The phase shift image reveals the different mechanical properties between the molecules and the dot.