2-D Self-assembly of the bis(phthalocyaninato)terbium(III) single-molecule magnet studied by scanning tunnelling microscopy

Jordi Gómez-Segura,[a] Ismael Díez-Pérez,[b] Naoto Ishikawa,[c] Motohiro Nakano,[d] Jaume Veciana[a] and Daniel Ruiz-Molina*[a]

Received (in Cambridge, UK) 3rd May 2006, Accepted 2nd June 2006
First published as an Advance Article on the web 15th June 2006
DOI: 10.1039/b606276h

The presence of alkoxyl chains on the single-molecule magnet [$(Pc')_2Tb^{III}$] and its planar character favour its 2-D self-assembly on HOPG with the molecular plane parallel to the graphite surface, enabling us to control and/or predict the orientation of the preferential magnetization axis on the surface.

Single-molecule magnets (SMMs) are molecular materials with interesting magnetic properties characteristic of nanodomain particles. The combination of a large-spin ground state and high axial magnetic anisotropy results in a barrier for the spin reversal, and therefore, in the observation of slow magnetization relaxation rates, such as out-of-phase ac magnetic susceptibility signals and stepwise magnetization hysteresis loops, attributable to individual molecules rather than long-range ordering.[1] Their advantages are considerable, among them, nanoscale dimensions, monodispersivity, high processability and low cost. Therefore, SMMs are potential candidates for high-density information storage devices[2] and quantum computing applications.[3] However, although SMMs stimulate the realization of a prospective molecular computational device, control over their complex and sophisticated properties still remains a challenge to be circumvented. For instance, a very low blocking temperature, above which SMMs behave as superparamagnets, has limited their practical utilization to date. Moreover, the development of new methodologies to properly address these SMM molecules on a surface is essential. Indeed, the experimental efforts so far reported in this direction are based on large-metal complexes with a dodecamanganese core, the well-known Mn_{12} family. For instance, the preparation of Langmuir–Blodgett[4] or polymeric films,[5] thiol-modified Mn_{12},[6] functionalized Au(111)[7] or Si(100)[8] surfaces and photolithography on Si/SiO_2 surfaces[9] have been reported. However, even though excellent results have been obtained, a main limitation that needs to be addressed is the difficulty in obtaining isolated molecules[10] and/or the need to use different lithographic techniques to obtain molecular ordered arrays.[11] Even more difficult is to orient such anisotropic SMMs with respect to the surfaces.

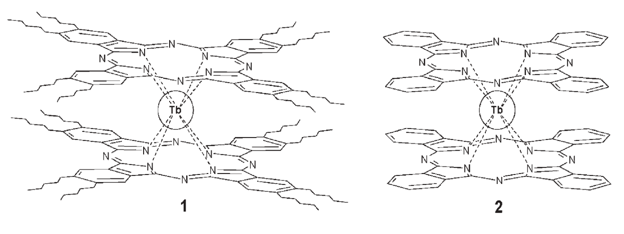
Here, in a further step to expand the range of SMMs explored for deposition on a surface, we report the 2-D self-assembly of the single-molecule magnet [$(Pc')_2Tb^{III}$] (Pc′ = octa(butoxy)-substituted phthalocyaninato ligand) (**1**) (Scheme 1) on highly oriented pyrolytic graphite (HOPG) and its characterization by scanning tunnelling microscopy (STM).

The advantages of complex **1** over the well-known and studied Mn_{12} family are twofold. First, previous work has shown that long-chain alkane substituted phthalocyanines can be ultimately immobilized on substrate surfaces to yield self-organized two-dimensional assemblies of monodispersed molecules, without any lithographic technique.[12] Second, the blocking temperature (T_B) of complex **1** has been rated to be one of the highest T_B so far reported for an SMM (36–50 K).[13] Such T_B are much higher than those for most of the SMMs so far reported, for instance the Mn_{12} family (*ca.* 4–6 K), a fact that may facilitate its development in future molecular-based devices.

A drop of a toluene solution (HPLC grade, Aldrich Inc.) of complex **1** (2×10^{-4} g/cm^3), heated to 55 °C in advance, was cast onto a freshly cleaved HOPG surface and was left to dry at room temperature. Immediately afterwards, large-scale STM images[14] of complex **1** under ambient conditions were obtained over three independent surface areas; similar results were obtained in all cases. Reproducibility between different casting experiments was also satisfactorily checked for freshly prepared samples.

As can be seen in Fig. 1A, complex **1** forms large different regions of molecular arrays with domains that extend from 10 nm up to a hundred nm in some cases. Moreover, Fig. 1B displays an example of an expanded molecular domain, where the phthalocyanine molecules are shown as bright spots whereas the shaded zigzag lines interconnecting the bright regions correspond to the long alkyl substituents that interdigitate between them.

The Fourier Transform analysis of different large scale images shows that the high-contrast phthalocyaninatoterbium cores are arranged into a 4-fold packing with a nearly perfect cubic symmetry. The periodicity within the domains is 2 nm, which equals the average peak-to-peak distance between the centres of phthalocyaninato cores. Angles between domains were also evaluated from the large scale fields, obtaining a value of 30 ± 5 degrees



Scheme 1

---

[a] *Institut de Ciència de Materials de Barcelona (CSIC), Campus UAB, Cerdanyola 08193, Spain. E-mail: dani@icmab.es*
[b] *Laboratory of Bioelectrochemistry and Nanotechnologies (CREBEC), Department of Physical Chemistry, Barcelona 08028, Spain*
[c] *Department of Applied Chemistry, Faculty of Science and Engineering, Chuo University, Bunkyo-ku, Tokyo 112-8551, Japan*
[d] *Department of Applied Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka 575-0871, Japan*

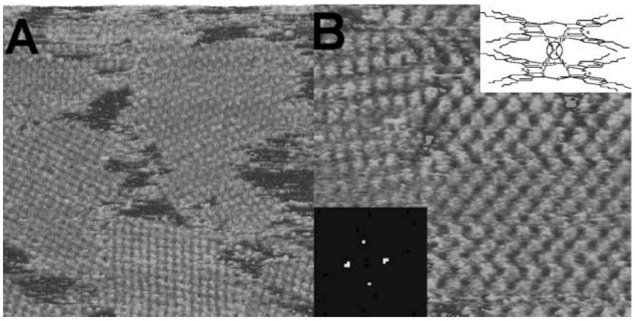


Fig. 1 (A) 75 × 75 nm^2 STM image of various domains presenting a 2-fold symmetry package. (B) 20 × 20 nm magnification of one of the areas. The inset corresponds to the Fourier Transform from the larger scale fields. Tunnelling conditions: bias of 500 mV and 50 pA of setpoint current.

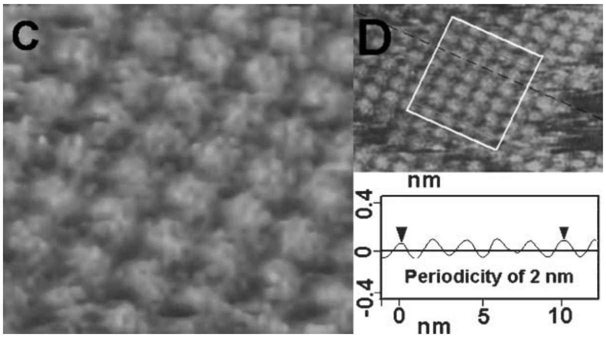


Fig. 2 (C) High-resolution STM image of 8 × 8 nm scan area, where the phthalocyanine molecules can be clearly differentiated as bright spots. (D) Average section of the molecular layer. Tunnelling conditions: sample bias of 500 mV and 50 pA of setpoint current. Z scale is 0.4 nm. Molecular diffusion on the substrate plane, thermally induced or promoted by the STM tip, disturbed the obtaining of higher resolution images.

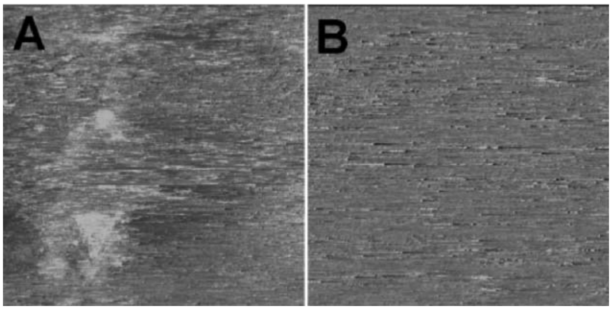


Fig. 3 Large scale 500 × 500 nm^2 STM image of the formed large aggregates after sample ageing (A). 80 × 80 nm^2 detail showing no existence of ordered domains (B). Sample bias of 500 mV and 50 pA of setpoint current. Z scale of 0.4 nm.

or multiple, which is in agreement with the symmetry of the HOPG substrate underneath. These facts suggest a molecular film growth following the main (or the maximum package) HOPG crystallographic directions. Finally, the average height of the molecular layer was approximately 0.3 nm, which is consistent with that previously reported for other phthalocyanine molecules. This fact indicates that the phthalocyanine molecules are adsorbed with their molecular plane parallel to the graphite surface.[12] This fact enables us to control and/or predict for the first time the orientation of the preferential magnetization axis of the SMM perpendicular to the surface (see Fig. 2).

To assess the stability of the self-assembled domains shown in Fig. 1, different STM images over the same region were obtained at different intervals of time. The STM images obtained after one day show that the assembled monolayer completely rolls off to form thermodynamically stabilized solid deposits and aggregates, randomly distributed all over the surface. Such a tendency may be explained by: i) whereas the closely assembled molecular domains will substantially enhance their adsorption stability, the lack of molecules in empty domains will favour diffusion processes in all directions of the HOPG basal plane and ii) although the use of alkyl chains facilitates the interplay of both intermolecular and adsorbate–substrate interactions resulting in the formation of the self-assembled monolayer, the use of a short C_4 alkyl chain is not enough to ensure a proper stability of the monolayer towards thermally induced rearrangements. For instance, for a related peripherally alkylated phthalocyanine, the use of longer C_8 alkane chains seems to strongly enhance the substrate adsorption; they are interdigitated with a separation distance of approximately 2.6 nm between adjacent cores on HOPG.[11]

Then, to give more insight into the origin of such instability, the same experiments were repeated with the SMM complex **2**, which lacks the presence of any alkyl chain. Interestingly, the drop casting of a toluene solution of complex **2** (2×10^{-4} g/cm^3) onto a freshly cleaved HOPG surface and its subsequent study by STM revealed a lack of molecular ordered domains, as confirmed by successive experiments. Indeed, rather than the self-assembled molecular domains initially found for **1**, complex **2** leads to the instantaneous formation of molecular aggregates randomly distributed on the surface. This fact confirms that although thermal diffusion processes may have an influence on the stability of the self-assembled molecular domains found for **1**, the use of alkyl chains that facilitate the interplay of both intermolecular and/or adsorbate–substrate interactions plays a critical role in the organization and stabilization processes (see Fig. 3).

Finally, magnetic force microscopy (MFM) experiments were performed for freshly prepared samples of complex **1**. MFM has already been shown to be a valuable technique to detect the local magnetic field gradient of molecular aggregates on diamagnetic surfaces. Indeed, in such cases, the magnetic response at room temperature is ascribed to the magnetic contrast between the paramagnetic behaviour of the Mn_{12} domains with the diamagnetic surroundings of the HOPG or polycarbonate matrix. However, in the present work, MFM experiments did not reveal any magnetic contrast. This fact could be tentatively attributed to two main reasons. First, the thermal instability of the self-assembled monolayer of complex **1** disturbs the observation of the magnetic signal. And second, and most likely, the low magnetic response of the self-assembled monolayer of complex **1**. Indeed, whereas the observation of magnetic contrast for SMMs deposited on surfaces has been achieved for large molecular aggregates at room temperature, which ensures a proper magnetic contrast, the self-assembled monolayer made of individual molecules of complex **1** does not give enough magnetic contrast.

In conclusion, the double-decker terbium(III) octa-alkoxyl-substituted phthalocyaninato SMM **1** has been shown to be an excellent candidate for deposition on inert HOPG. First, the presence of alkoxyl chains favours its 2-D self-assembly on the surface without the need for supplementary lithographic techniques. Second, clear observation of individual molecules is achieved, a fact that may facilitate their manipulation or analysis. And finally, the adsorption of the phthalocyanine molecules with their molecular plane parallel to the graphite surface enables us to control and/or predict the orientation of the preferential magnetization axis on the surface. However, before any molecular device is envisaged, further research must be undertaken, one of the first steps being the synthesis of new double-decker complexes with longer alkyl chains that ensure improved thermal stabilities.

This work was supported by the NoE MAGMANet (contract NMP3-CT-2005-515767), a Marie Curie RTN Network (contract QUEMOLNA, number MRTN-CT-2003-504880), the MAT2003-04699 project from the DGI (Spain), and a Grant-in-aid for Scientific Research from the Ministry of Education, Science, Sports and Culture of Japan. We thank the Scientific Technical Services of the University of Barcelona for the use of facilities.

Notes and references

1 (*a*) G. Christou, D. Gatteschi, D. N. Hendrickson and R. Sessoli, *MRS Bull.*, 2000, **25**, 66; (*b*) D. Gatteschi and R. Sessoli, *Angew. Chem., Int. Ed.*, 2003, **42**, 268.

2 L. Krusin-Elbaum, T. Shibauchi, B. Argyle, L. Gignac and D. Weller, *Nature*, 2001, **410**, 444–446.

3 E. M. Chudnovsky and J. Tejada, *Macroscopic Quantum Tunneling of the Magnetic Moment*; Cambridge University Press: Cambridge, 1998.

4 M. Clemente-León, H. Soyer, E. Coronado, C. Mingotaud, C. J. Gómez-García and P. Delhaès, *Angew. Chem., Int. Ed.*, 1998, **37**, 2842–2845.

5 D. Ruiz-Molina, M. Mas-Torrent, J. Gómez, A. I. Balana, N. Domingo, J. Tejada, M. T. Martínez, C. Rovira and J. Veciana, *Adv. Mater.*, 2003, **15**, 42.

6 A. Cornia, A. C. Fabretti, M. Pacchioni, L. Zobbi, D. Bonacchi, A. Caneschi, R. Biagi, U. Del Pennino, V. De Renzi, L. Gurevich and H. S. J. Van der Zant, *Angew. Chem., Int. Ed.*, 2003, **42**, 1645.

7 (*a*) A. Naitabdi, J. P. Bucher, Ph. Gerbier, P. Rabu and M. Drillon, *Adv. Mater.*, 2005, **17**, 1612; (*b*) E. Coronado, A. Forment-Aliaga, F. M. Romero, V. Corradini, R. Biagi, V. De Renzi, A. Gambardella and U. del Pennino, *Inorg. Chem.*, 2005, **44**, 7693.

8 J. S. Steckel, N. S. Persky, C. R. Martinez, C. L. Barnes, E. A. Fry, J. Kulkarni, J. D. Burgess, R. B. Pacheco and S. L. Stoll, *Nano Lett.*, 2004, **4**, 399.

9 K. Kim, D. M. Seo, J. Means, V. Meenakshi, W. Teizer, H. Zhao and K. R. Dunbar, *Appl. Phys. Lett.*, 2004, **85**, 3872.

10 L. Zobbi, M. Mannini, M. Pacchioni, G. Chastanet, D. Bonacchi, C. Zanardi, R. Biagi, U. del Pennino, D. Gatteschi, A. Cornia and R. Sessoli, *Chem. Commun.*, 2005, 1640.

11 (*a*) M. Cavallini, F. Biscarini, J. Gómez-Segura, D. Ruiz-Molina and J. Veciana, *Nano Lett.*, 2003, **3**, 1527–1530; (*b*) M. Cavallini, J. Gómez-Segura, D. Ruiz-Molina, M. Massi, C. Albonetti, C. Rovira, J. Veciana and F. Biscarini, *Angew. Chem., Int. Ed.*, 2005, **44**, 888–892; (*c*) M. Mannini, D. Bonacchi, L. Zobbi, F. M. Piras, E. A. Speets, A. Caneschi, A. Cornia, A. Magnani, B. J. Ravoo, D. N. Reinhoudt, R. Sessoli and D. Gatteschi, *Nano Lett.*, 2005, **5**, 1435.

12 (*a*) X. Qiu, C. Wang, Q. Zeng, B. Xu, S. Yin, H. Wang, S. Xu and C. J. Bai, *J. Am. Chem. Soc.*, 2000, **122**, 5550–5556; (*b*) Y. Liu, S. Lei, S. Yin, S. Xu, Q. Zheng, Q. Zeng, C. Wang, L. Wan and C. Bai, *J. Phys. Chem. B*, 2002, **106**, 12569–12574.

13 (*a*) N. Ishikawa, M. Sugita, N. Tanaka, T. Ishikawa, S. Koshihara and Y. Kaizu, *Inorg. Chem.*, 2004, **43**, 5498–5500; (*b*) N. Ishikawa, M. Sugita, T. Ishikawa, S. Koshihara and Y. Kaizu, *J. Phys. Chem.*, 2004, **108**, 11265–11271; (*c*) N. Ishikawa, M. Sugita and W. Wernsdorfer, *J. Am. Chem. Soc.*, 2005, **127**, 3650–3651; (*d*) N. Ishikawa, M. Sugita and W. Wernsdorfer, *Angew. Chem., Int. Ed.*, 2005, **44**, 2931.

14 STM studies were performed at room temperature by using a Molecular Imaging (Phoenix, AZ, USA) microscope head controlled by Nanoscope IIIa (Digital Instruments Veeco Metrology Group, Sta. Barbara, California, USA) electronics. Mechanically cut Pt/Ir 80 : 20 tips were employed.