

Electronic Structure of Surface-supported Bis(phthalocyaninato) terbium(III) Single Molecular Magnets

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ABSTRACT

The electronic structure of isolated bis(phthalocyaninato) terbium(III) molecules, a novel single-molecular-magnet (SMM), supported on the Cu(111) surface has been characterized by density functional theory and scanning tunneling spectroscopy. These studies reveal that the interaction with the metal surface preserves both the molecular structure and the large spin magnetic moment of the metal center. The 4f electron states are not perturbed by the adsorption while a strong molecular/metal interaction can induce the suppression of the minor spin contribution delocalized over the molecular ligands. The calculations show that the inherent spin magnetic moment of the molecule is only weakly affected by the interaction with the surface and suggest that the SMM character might be preserved.

The miniaturization of information storage devices drives the search for new nanoscale magnetic materials. Single molecular magnets (SMMs) formed by metal-organic complexes are very promising candidates as their large spin ground-state and large magnetic anisotropy are characteristics of each isolated molecule.¹ Moreover, these systems provide a natural playground to explore magnetism at the nanoscale. Their future technological applications, such as quantum computing and high-density magnetic storage devices, are presently hampered by the difficulty of adsorbing SMMs onto surfaces and, quite importantly, by the lack of understanding on whether their magnetic properties are modified upon adsorption. In particular, the nonapplicability of conventional techniques, which allow an in-vacuum deposition, has so far hindered the systematic study of individual molecular magnets on surfaces. Solution-based deposition techniques including drop casting,^{2,3} Langmuir–Blodgett,⁴ microcontact printing,⁵ covalent Au–S attaching,⁶ and surface functionalization⁷ have been successfully used to transfer molecules to surfaces but the magnetic properties of the adsorbed

molecules have so far not been demonstrated.³ This has tentatively been assigned to an induced local disorder caused by the used deposition techniques or by the coupling to the surface.⁸

In this letter, we describe the structural, magnetic and electronic properties of a surface-supported SMM by combining scanning tunneling microscopy (STM) and spectroscopy (STS) with numerical simulations based on density functional theory (DFT). Topographic images and conductance maps of isolated SMM (namely bis(phthalocyaninato) terbium(III)) achieved at several energies confirm that the molecular structure is unchanged by the interaction with the surface. The Tb-4f electron states, which are responsible for the large magnetic moment of the molecular magnet, are little affected by molecular adsorption on the metal surface. Thus, it can be expected that the SMM character of the surface supported bis(phthalocyaninato) terbium(III) (abbreviated by TbPc2) molecules is preserved.

TbPc2 molecules represent the first example of mononuclear metal complexes behaving as SMMs (i.e., showing large magnetic anisotropy, slow relaxation of the magnetic moment and quantum tunneling of magnetization).^{9,10} Each TbPc2 molecule consists of a terbium ion located between two phthalocyanine (Pc) ligands (Figure 1a). The Pc ligands are rotated with respect to each other by 45° around their normal axis so that the Tb ion is 8-fold coordinated with

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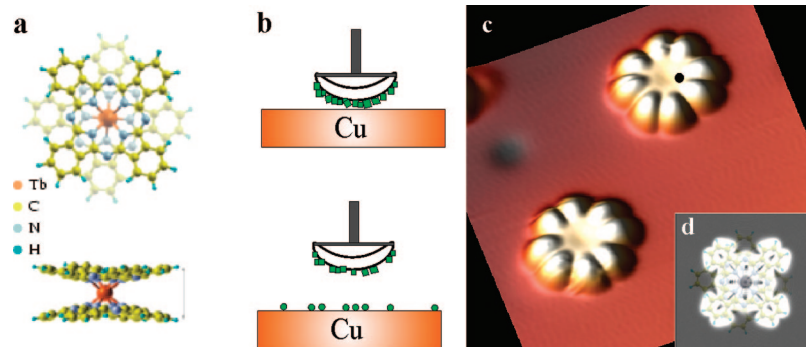


Figure 1. (a) Structure of the TbPc₂ molecule. (b) Scheme of the dry-imprinting technique (see text). (c) Constant current topograph of two isolated TbPc₂ molecules supported by the Cu(111) surface (image size, 7 nm × 7 nm; tunneling conditions, −0.8 eV, 0.7nA); the black dot indicates the position where the dI/dV spectrum in Figure 2 was obtained. (d) Simulated STM image of an isolated TbPc₂ molecule.

the N atoms (see Figure 1a). Because of this molecular structure, TbPc₂ differs fundamentally from any single plane Pc molecules which do not show any single molecular magnet character. The molecules have been synthesized according to the protocol described by de Cian et al.¹¹ which has been adapted to the use of microwave techniques. The molecules have been deposited on the surface in ultrahigh vacuum (UHV) conditions using a dry imprint technique. Specifically, a soft applicator, formed by a fiberglass bundle coated with a fine-grained powder of the TbPc₂ crystals, was brought in gentle contact with the copper surface (Figure 1b) previously cleaned by cycles of Ar-sputtering and annealing. This leads to direct deposition of single molecules as well as molecular clusters on the Cu(111) surface.

A representative STM topograph of TbPc₂ molecules adsorbed on the Cu(111) surface, achieved in UHV at a temperature of 10 K, is reported in Figure 1c. The two molecules are rotated with respect to each other by 45°. This rotation is not compatible with the hexagonal symmetry of the support, thus suggesting that the adsorption site and configuration are not determined by the substrate symmetry. Each molecule presents 8 molecular lobes in a 4-fold symmetry with an apparent height of about 3 Å. The specific structure of the molecule in the topographic image closely resembles the 4-fold symmetry observed in single-plane Pc¹² supported by metal surfaces. Moreover, the micrograph is in very good agreement with the simulated STM image calculated for an unsupported TbPc₂ and projected onto a plane parallel to the Pc ligands (Figure 1d, calculation details are given below). These findings indicate that the TbPc₂ molecule adsorbs on one Pc molecular plane in a flat lying configuration on the Cu(111) surface. The observed molecular structure and the adsorption configuration, showing isolated molecules, persists upon annealing up to 550 K and does not lead to the formation of ordered structures. Although the comparison between measured and calculated topographic STM images demonstrates that the molecular structure is preserved, a strong interaction with the substrate might compromise the molecular magnetic properties.¹³ In order to clarify this point and to elucidate the nature of the molecular bond to the substrate, the electronic properties of the SMM complex adsorbed on the copper substrate have been studied in detail. Figure 2a displays the dI/dV spectrum

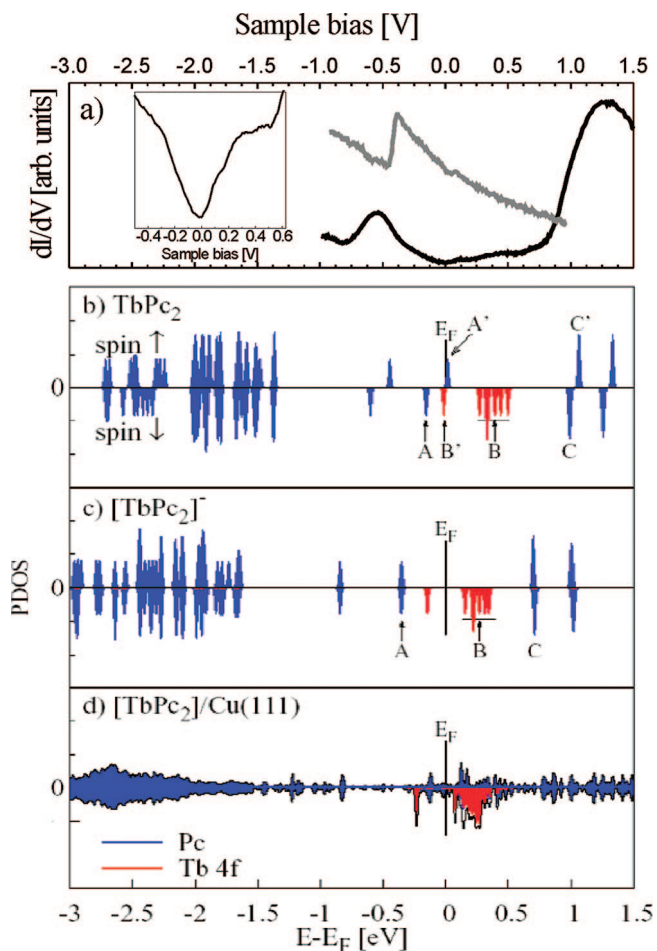


Figure 2. Density of states of TbPc₂ molecule. (a) Experimental dI/dV spectrum for the surface-supported molecule measured at the dot position in Figure 1c. The spectrum achieved on the clean Cu substrate (gray line). In inset, the dI/dV spectrum achieved on the molecule has been replotted to better visualize the low energy range. (b) Calculated spin-resolved electron DOS for the unsupported neutral TbPc₂ and (c) charged [TbPc₂][−] molecule (d) as well as molecular projected DOS (PDOS) for the artificial model Cu/TbPc₂ system (see text). Black vertical lines mark the Fermi levels (E_F) while red (gray) and blue (dark gray) areas represent the Tb-4f and Pc PDOS, respectively. Spin up (↑) and down (↓) states are plotted separately above and below the thin horizontal zero line.

measured on the TbPc₂ molecule. The spectrum is characterized by two major peaks (centered at −0.55 and 1.2 eV). At

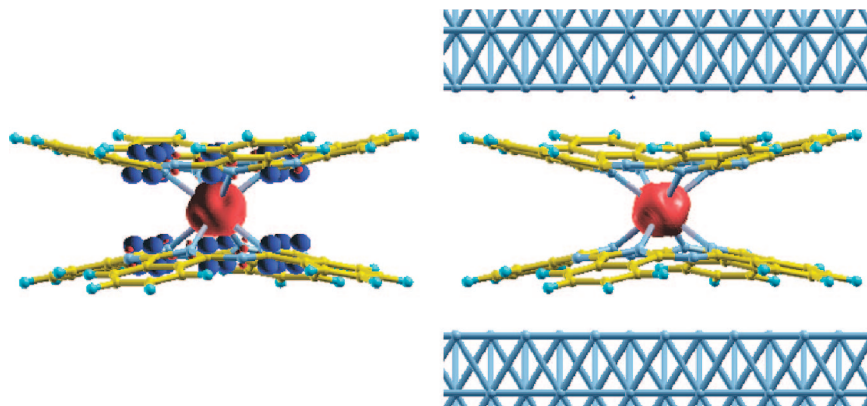


Figure 3. Calculated spin densities for the neutral TbPc2 molecule unsupported (left) and interacting with two Cu(111) surfaces (right). Red and blue areas represent the spin system localized on the Tb ion and delocalized over the two Pc ligands, respectively.

intermediate energies, peaks of weaker intensity can be observed (inset). For comparison, also the dI/dV spectrum achieved on the clean copper surface is shown in the figure. The energy position of the peaks in the dI/dV spectrum allows us to assign them to electronic structure of the molecules and to exclude contributions from the substrate.^{14,15}

First-principles calculations have been performed to gain insight into these spectroscopic features. Here, we do not aim at a precise *ab initio* characterization of the adsorption and electronic structures of the complete system formed by the TbPc2 supported by a metal surface. Achieving this goal would be computationally too demanding and the quality of this prediction would be affected by several limitations of the approximations used to represent the energy functionals. Our goal is to give a qualitative picture of the physical properties of the supported TbPc2 molecules through their electronic and magnetic characterization. This will be performed considering the unsupported neutral molecules and including stepwise modifications as a function of the molecular charge state and of the interaction strength with a model Cu(111) metal surface.

The calculations were based on DFT with the Perdew–Burke–Ernzerhof generalized gradient-corrected approximation for the exchange and correlation functional.¹⁶ Atomic cores were represented by ultrasoft pseudopotentials,¹⁷ while the wave functions and the Fourier representation of the charge density were described with a plane-wave basis set limited by kinetic energy cutoffs up to 40 and 400 Ry, respectively. All calculations were spin polarized and performed with the PWscf code of the Quantum-ESPRESSO distribution.^{18,19}

The spin-resolved electronic states corresponding to the self-consistent solution for the neutral form of the unsupported TbPc2 are displayed in Figure 2b. Red and blue areas represent the contribution to the electronic states of the Pc molecular orbitals of Tb-4f atomic states, respectively. The Löwdin charge population analysis shows that 2.6 electrons are transferred from the metal center to the Pc ligands (1 and 1.6 from the f and s channels, respectively) so that, with respect to the Tb atomic $6s^2 4f^9$ valence configuration, the metal center is predicted to have an ionic charge of $2.6+$. The corresponding calculated spin magnetic moment for the

Tb ion is $5.9 \mu_B$, so that as far as the magnetic properties are concerned, the Pc-complexed Tb ion is a very good approximation for an isolated Tb^{3+} ion having a magnetic moment of $6 \mu_B$ and a total angular momentum of $J = 6$. Remarkably, the charge transferred from the Tb ion to the ligands is not sufficient to saturate them, since each Pc plane requires 2 electrons to be saturated. As a result, the ligands of the TbPc2 complex form an open shell system. The corresponding unpaired electron, whose energy is labeled as “A” in Figure 2b, has π -character and is delocalized over both ligands, in agreement with previous experimental and theoretical analysis on closely related systems.^{20–22} The unpaired unoccupied ligand state (“A”) and the filled Tb-4f state (“B”) have almost the same energy, but their hybridization is prevented by their different spatial location on the molecule. The neutral unsupported TbPc2 molecule has therefore two spin systems that are displayed by the calculated spin density shown in Figure 3: One (shown in red) is strongly localized on the metal center, arises from the 4f states, carries a magnetic moment of $5.9 \mu_B$, and in the limit of an isolated Tb^{3+} ion would have $J = 6$; the other (shown in blue) is delocalized over the two Pc ligands, is determined by the unpaired π electron, and is defined by $S = 1/2$.

In the charged system, indicated by $[TbPc2]^-$, the additional electron delocalized on the molecular ligand occupies the lowest unoccupied molecular orbital (LUMO) of the neutral unsupported TbPc2 (see A’ and A in Figure 2b,c). This saturates the ligands and suppress their spin polarization. Despite the strong variation in the electronic structure resulting from the saturation of the ligands state, the magnetic properties of the SMM as determined by the localized Tb 4f states are remarkably stable (compare the red areas in Figure 2).

The decoupling between the two spin systems is fundamental also to preserve the SMM properties of surface-supported TbPc2 molecules. In the following, we will demonstrate that the SMM behavior of the TbPc2 molecule could be preserved upon adsorption on the Cu(111) surface, even in the extreme case of strong metal-molecular interaction leading to bond formation.

To support this conclusion, we devised a model system that admittedly does not represent the true metal-molecule interface but instead provides us with an extreme case where the interaction between metal and molecular magnet is maximized. In this model system, the molecule is located symmetrically between two Cu(111) surface planes (modeled by 3 Cu layers) at a distance of 2.0 Å (Figure 3). This closely corresponds to the situation of such a molecule in a break junction experiment, and that is of direct relevance for applications in molecular electronics. The calculated projected density of states (PDOS) of the ligands (Figure 2d) obtained by projecting the wave functions on atomic states, clearly shows a strong hybridization between the ligand molecular orbitals (states A and C in particular) and the electron states of the metal surface. This hybridization completely suppresses the delocalized ligand spin system but preserves the large magnetic moment of the Tb ion ($5.8 \mu_B$) as in the unsupported molecules. The spin system localized on the Tb center is therefore unaffected by the presence of the surfaces. This is evident by comparing the spin densities of the neutral isolated and the TbPc2 molecule interacting with the metal surfaces as shown in Figure 3.

This analysis allows us to conclude that the SMM properties of TbPc2 deriving from the Tb ion are preserved even in the presence of an artificially strong molecular interaction with the metal surfaces. Given the flat lying adsorption configuration determined by the STM images, the easy axis of magnetization can be depicted to be orthogonal to the Pc planes (and thus to the surface) as in the case of free-standing molecules.²³ It is worth noting that in the present experimental study, the TbPc2 molecule being adsorbed on one surface represents an intermediate case between the two theoretically studied situations. In the experimental case, the surface-molecular interaction is therefore intrinsically weaker than the one simulated by the model system described above.

The relevant states, labeled as A, B, and C in Figure 2, can be visualized better and identified in energy-resolved conductance maps. These maps are achieved by recording the dI/dV signal at different positions and show the DOS resolved in space at constant energy.²⁴ As in the topography, the higher electron density at a chosen energy is displayed in lighter color. The experimental images of the surface supported TbPc2 molecule are shown in the upper panels of Figure 4 and are directly compared with the corresponding charge density calculated for the unsupported molecule, are displayed in the lower panels of the Figure.

Both the experimental and theoretical maps reflect a pronounced spatial variation of electron densities across the molecule with distinctive features at characteristic energies. The dI/dV maps display the same trend as a function of increasing energy. They show four pairs of lobes well delocalized over the π -molecular orbitals of the Pc ligands at -0.8 eV (A), a weak cross-like feature centered on the Tb atom and developing along the Tb–N bonds at 0.4 eV (B), and again four pairs of lobes delocalized over the PC ligand at 0.8 eV (C). This substantiates the presence of

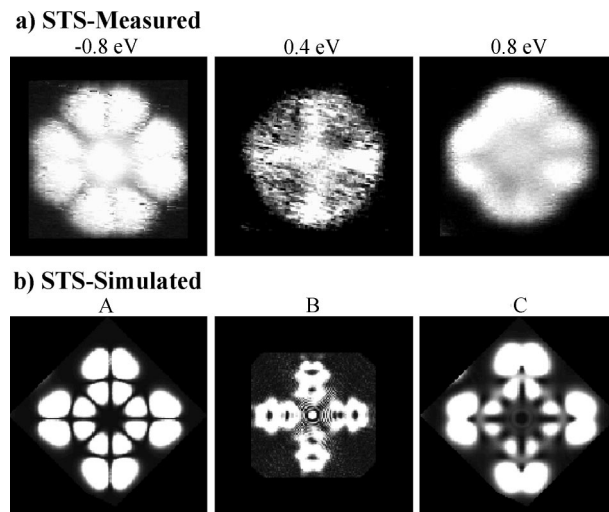


Figure 4. Energy resolved conductance maps of the $[\text{TbPc2}]^-$ molecule at energies corresponding to the electron states labeled by A, B, and C in Figure 2. (a) Experimentally measured and (b) calculated energy-resolved charge densities.

electron states highly localized on the metal center and appearing as peaks with minor intensity at intermediate energies in Figure 2a.

Even by considering the well-known shortcomings of the approximation used in DFT calculations (in particular in the highest occupied molecular orbital (HOMO)–LUMO gap of the ligands, and in the position and splitting of the Tb-f states), the experimental differential conductance dI/dV spectrum measured on the surface-supported molecule is very similar to the calculated electron states for the unsupported molecules (Figure 2). This comparison allows us to assign the two major peaks (A and C) to occupied and unoccupied ligand orbitals, and the minor structure in between them (B) to the spin-polarized Tb states. The presence of the same spectral and spatial electronic features in calculated gas-phase and in the measured surface-supported molecules further substantiate the conclusion that, besides the eventual suppression of the ligand spin due to strong metal-molecule hybridization, the inherent molecular electronic structure is preserved. TbPc2 can therefore be considered as an ideal system for future spin-polarized characterization of the magnetic properties of surface supported SMMs. Our results indicates that the SMM properties are preserved upon adsorption on surfaces and in metal gap structures which are relevant for molecular applications.

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