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Role of π -Radicals in the Spin Connectivity of Clusters and Networks of Tb Double-Decker Single Molecule Magnets

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(5) Supporting Information

ABSTRACT: When single molecule magnets (SMMs) selfassemble into 2D networks on a surface, they interact *via* the π -electrons of their ligands. This interaction is relevant to the quantum entanglement between molecular qubits, a key issue in quantum computing. Here, we examine the role played by the unpaired radical electron in the top ligand of Tb double-decker SMMs by comparing the spectroscopic features of isolated and 2D assembled entities on surfaces. High-resolution scanning tunneling microscopy (STM) is used to evidence experimentally the Kondo resonance of the



unpaired radical spins in clusters and islands and its quenching due to up-pairing at orbital overlaps. The presence or the absence of the Kondo feature in the dI/dV maps turns out to be a good measure of the lateral interaction between molecules in 2D networks. In a 2D cluster of molecules, the π -orbital lobes that are linked through the orbital overlap show paired-up electron wave function (one singly occupied molecular orbital (SOMO) with spin-up and the other with spin-down) and therefore do not experience the Kondo resonance in the experiment. As a result, small clusters built by STM-assisted manipulation of molecules show alternating Kondo features of quantum mechanical origin, from the monomer to the dimer and the trimer. On the other hand, when the TbPc₂ molecular clusters grow larger and form extended domains, a geometric rearrangement occurs, leading to the quenching of the Kondo signal on one lobe out of two. The even distribution of overlapping (SOMO) lobes on the perimeter of the molecule is induced by the square symmetry of the semi-infinite lattice and clearly distinguishes the lattice from the clusters.

KEYWORDS: π -radicals, single molecule magnets, spin network, Kondo effect, clusters of SMMs, qubit entanglement, scanning tunneling microscopy

Since the magnetic magnets (SMMs), made of metal ions stabilized by appropriate ligands, participate in promising strategies of encoding information in single, all identical, units.¹ The mononuclear bis(phthalocyaninato)lanthanide(III) complexes ($LnPc_2$) have attracted a great deal of interest,² and among them, the TbPc₂ double-decker has been the most investigated mononuclear SMM in recent years. This success is due to its high magnetic anisotropy barrier and slow relaxation time of the magnetization^{3,4} but also to its robustness and evaporability.^{5,6} The growth and self-assembly of these $LnPc_2$ double-deckers on surfaces have therefore been addressed by many authors as this represents a prerequisite for their in-depth study by local techniques such as scanning tunneling microscopy (STM).^{6–22}

The neutral $[\text{TbPc}_2]^0$ complex contains two electronic spin systems: a central J = 6 high-spin (S = 3 and L = 3) with an intrinsic anisotropy arising from the Tb³⁺ 4f-electrons and a $S = 1/2 \pi$ -radical due to a singly occupied highest occupied

molecular orbital (HOMO) that is delocalized over the two Pc ligands. Due to the strong spin-orbit coupling and Pc ligand field, the electronic ground state doublet $J_z = \pm 6$ is isolated from the excited state by a gap of several 100 K.¹⁷ The strong magnetic coupling of the Tb³⁺ electron spin and the radical spin is ascertained from conductance measurements in supra-molecular spin-valve and spin-transistor structures,^{18,19} where the radical is used as a read-out quantum dot. A ferromagnetic exchange interaction of about 300 mT was measured between the magnetic moment carried by the Tb³⁺ ion and the radical spin 1/2.²⁰ In the latter setup, it is the detection of the electronic magnetic moment of the TbPc₂ SMM that allows the electronic read-out of the terbium nuclear spin state, with I = 3/2 through the hyperfine coupling. A recent RF-assisted STS

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Figure 1. (a) STM images I = 60 pA and V = -0.3 V showing the manipulation of TbPc₂ with the tip of the STM. (b) STS above the center and a lobe of a single TbPc₂ molecule adsorbed on Au(111) substrate with a modulation voltage of 10 mV (rms). (c) By decreasing the modulation voltage to 1 mV (rms), it is possible to evidence the zero bias peak shown here as a function of distance from the substrate.

experiment performed at the site of the Pc ligands also yields similar conclusions.²¹ As a result, it was suggested that the coupling between the nuclear spin and the radical through the Tb electronic moment could be exploited in quantum information processing.²⁰

Charge and spin states of the TbPc₂ molecules may be altered upon adsorption on surfaces.^{7–10} A special case, however, is embodied by the monolayer of TbPc₂ molecules adsorbed on Au(111), where the π -radical electron survives the adsorption and populates the top Pc ligand, leading to the experimental observation of a Kondo resonance in the dI/dVspectra above some specific points of the network.^{6,11,12} The absence of Kondo effect on the ligand when the molecule is residing on Cu(111) or on a Co substrate is rationalized by the fact that the electron in the π -orbital pairs-up with an electron transferred from the substrate due to the much stronger molecule substrate interaction.^{7,8} The molecule then bears a negative charge [TbPc₂]⁻.

Despite the work accumulated over the past decade, the effects of the environment on the magnetic properties of SMMs is not well understood. In particular, a large impact of the crystalline environment on their magnetic properties has been emphasized.^{14,15} If these types of molecules are to be used in future spintronics devices, a better understanding of this phenomenon is compulsory. In the present work, special attention is given to the role played by the π -electrons in the coupling of adjacent SMMs in clusters obtained by STMassisted molecular manipulation or in self-assembled 2D islands on surfaces. For this purpose, low-temperature (4.6 K), highresolution scanning tunneling spectroscopy (STS) is used to explore the Kondo resonance of the unpaired radical spins and their quenching due to pairing-up at orbital overlaps. The Kondo origin of the zero bias peak (ZBP) above the ligands of TbPc₂ on Au(111) has been ascertained previously by STS as a function of temperature and external magnetic field¹¹ and makes it an interesting system for this study. In particular, due to the weak interaction with the substrate, no f-electrons are

involved in the Kondo effect contrary to the case of DyPc_2 complexes on $\text{Cu}(100).^{16}$

RESULTS AND DISCUSSION

Isolated Tb Double-Deckers on Au(111). The presence of the two Pc ligands promotes face-on adsorption of the molecules on metal surfaces, thus facilitating the investigation of electronic and magnetic properties by high-resolution STM/ STS. Compact islands of molecules are easily formed by onsurface self-assembly at room temperature.^{6,11} However, before we study the monolayer islands of SMM, the local electronic properties of single isolated molecules on the bare surface must be addressed. For this purpose, single molecules are extracted from a monolayer island by tip manipulation. The molecule is dragged away from a monolayer island and examined at a distance from it, as shown in Figure 1a.

Figure 1b shows the dI/dV spectra recorded above one lobe and above the center of the single molecule at T = 4.5 K. The tip-sample distance was stabilized on a free area of Au(111) before opening the feedback loop. Both show a resonance at -0.45 eV, which is broader on the lobe, whereas an empty state resonance is found at +0.25 eV above the lobe and +0.40 eV above the center. These resonances are also found in assemblies of molecules and will be discussed later; they should not be confused with the HOMO and LUMO (lowest unoccupied molecular orbital) (-0.9 and +0.8 eV) identified in earlier studies of such molecules assembled in domains.¹² Decreasing the modulation voltage amplitude and taking the dI/dV spectra over an interval between -50 and +50 meV above a lobe of the single molecule leads to the spectra shown in Figure 1c. Identical ZBPs in the high-resolution dI/dV spectra are measured above all the eight lobes of the terbium doubledecker molecule (see Figure S1). The peak intensity versus tipsample distance shows a significant decrease in the range from 2 to 4.7 Å, where it is reduced to the noise level (see Figure 1c). This resonance appears only on the lobes of the top ligand and vanishes rapidly when the tip is moved toward the center of the

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Figure 2. Molecular manipulation. The electronic distribution of the top ligand is highlighted in red in order to facilitate the molecular identification during manipulation. (a,b) Molecule number 1 is used as a reference. (c-e) Molecules labeled 1, 2, and 3 are pulled out of the domain as indicated by the green arrows. (f) Molecule 2 is moved toward molecule 1 to form a dimer. (g) Molecule 3 is added to the dimer to form a trimer. (h) Further manipulation on molecule 3 to form a compact trimer. (i) Molecule 4 is inserted into the trimer. (j,k) Extraction and subsequent insertion with a rotation of molecule 4. After this process, the whole island is translated by 0.5 nm as depicted in (k). (l) same domain as in (k) without the superposed phthalocyanine model. The tunneling parameters for the topography are I = 70 pA, V = -0.3 V.

molecule. The shape of the ZBP observed on the isolated molecule (Figure 1c) is similar to previously reported Kondo resonances measured above magnetic mono- and double-decker complexes, $^{6,23-25}$ which are well described by a Fano function: 26

$$\frac{\mathrm{d}I(V)}{\mathrm{d}V} \propto \frac{(\varepsilon+q)^2}{\varepsilon^2+1} \text{ with } \varepsilon = \frac{eV - E_0}{\Gamma}$$

where Γ is the width of the resonance, E_0 the peak position, and q is the ratio of tunneling into the resonance and into the continuum. The fitting of our data leads to the following values: $E_0 = 5.2 \pm 0.1$ meV, q = 3.93, and G = 9.56 meV. Accounting for thermal and modulation voltage broadening²⁷ on G, this leads to a Kondo temperature of $T_{\rm K}$ = 38 K ± 1 K. Contrary to most transition metal phthalocyanines (TMPc) on metal surfaces, where the Kondo resonance is due to 2D surface electron scattering by the magnetic atom, here, it is the unpaired spin of the π -radicals of the Pc ligand that is responsible for the scattering. The lower Kondo temperature compared with the one of TMPc around $T_{\rm K} \approx 200$ K,^{24,25,28,29} along with a higher value of the Fano parameter q, indicates smaller ligand hybridization to the substrate. Furthermore, moving the molecule to different places by atomic manipulation leads to the conclusion that the ZBP of $TbPc_2$ on Au(111) is not site-dependent nor does it depend on the bottom ligand orientation with respect to crystal directions of Au(111) (see

Figure S2). This is quite different from other TMPc systems where the nature of the Kondo resonance might change dramatically as a function of adsorption site.^{24,25}

Molecular Clusters by STM-Based Manipulation. In order to understand the evolution of the spin connectivity, from the single object to the molecular film, step-by-step assembling of clusters by molecular manipulation with the STM tip was performed. The attractive potential between the tip and the SMM is used to manipulate laterally the molecule by the socalled pulling procedure.³⁰ When the tip is moved at a constant height along a predefined path above the surface (feedback loop open), the molecule is dragged on the surface by the tip. If during manipulation, the tip trajectory passes off-center, a rotation of the molecule occurs simultaneously with the translation movement. For the purpose of island construction, both rotation and translation are used to assemble molecules in their close-packed configuration. While manipulation is a powerful tool, it must be emphasized that appropriate tunneling conditions such as a low current and negative bias voltages are necessary to prevent the molecules from being dragged around by the tip during the scanning process.

Molecular clusters are built step-by-step as described in Figure 2. At each step, the structure is analyzed by means of dI/dV spectroscopy. In the following, the red contour of each molecule represents the molecular orbital extension taken from the isolated molecule (Figure 1). Inside each molecule, a model

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of the top Pc is drawn in order to visualize the molecular orientation.

Prior to molecular assembly, four molecules have been extracted one-by-one from a large self-assembled domain, as depicted in Figure 2a-e. It has been verified that all the isolated molecules exhibit the Kondo resonance on each of their eight lobes. The dimer, trimer, and tetramer are then built by STM manipulation. The process of manipulation is further explained in the Methods section. The molecules are moved along a welldefined path until they have reached the optimal moleculemolecule interaction with another molecule on the surface. As an example, the molecule labeled 2 is moved toward molecule labeled 1 to form a dimer, as shown in Figure 2f. After manipulation, the molecules in the dimer are oriented parallel to each other, a configuration that does not appear in extended domains (vide infra). The center-to-center distance between the two molecules is 1.45 nm and makes this dimer configuration particularly stable. Spectroscopic measurements performed above the two molecules do not show any ZBP, which indicates an absence of a Kondo resonance on the dimer.

As shown in Figure 2g, when a third molecule labeled 3 is added to the dimer, molecule 2 spontaneously rotates by 6° to adapt to the presence of both molecules 1 and 3. Again, no Kondo resonance was observed on this molecular chain. In Figure 2h, molecule 3 is further manipulated to form a compact trimer. Again, molecules 1 and 2 adapt their orientation to optimize their interaction with molecule 3. As a result, molecules 1 and 3 form a parallel configuration, whereas 1 and 2 and 2 and 3 are staggered with respect to each other. Interestingly, this compact trimer exhibits a Kondo resonance above the intersection of all three molecules with $T_{\rm K} = 34$ K. No Kondo peak is observed on the other molecular lobes and on the center of the molecule, suggesting that this resonance is created by the interaction of all three molecules.

Next, manipulation consists of the formation of a tetramer, as depicted in Figure 2i, where molecule 4 was moved toward the trimer. It is noteworthy that the insertion of the last molecule does not create any geometrical modification (rotation or translation) of the pre-existing trimer. The resulting tetramer island of Figure 2i does not form a square planar geometry and as such cannot be considered as a fragment of the network (see Figure 5b). It may thus be a result of either a minimum energy configuration or a relative minimum whose origin is the sequential island construction by manipulation. To verify this assertion, molecule 4 was extracted from the tetramer (Figure 2j) and subsequently reinserted with a counterclockwise rotation of 25°, achieving a better match with the former trimer. Pulling harder on molecule number 4 with the STM tip toward the right-hand side produces a displacement of the whole tetramer by 0.5 nm, as shown in Figure 2k. This demonstrates the robustness of the tetramer cluster as pulling on molecule number 4 produces the displacement of the entire cluster with no visible fragmentation and ascertains the idea that the molecule-molecule interaction overcomes the molecule-substrate interaction. In the following, the last TbPc₂ tetramer is therefore considered as the most stable structure on Au(111). A Kondo resonance with $T_{\rm K}$ = 31 K is measured on the tetramer of Figure 2k at the overlap of three lobes. No Kondo resonance is found elsewhere on the cluster.

The lobe matching of the different molecular clusters is summarized in Figure 3. When a dimer is formed, the molecular orbitals of the two ligands strongly overlap; that is, two lobes of the first molecule overlap with the same two lobes



Figure 3. Schematics representation of lobe matching for (a) parallel and staggered dimer, (b) trimer, and (c) tetramer as observed experimentally. Yellow represents the two-lobe overlaps (no Kondo), and red represents the three-lobe overlap showing an experimental Kondo feature. The white circles do not show measurable Kondo signal.

of the second molecule, as shown schematically in Figure 3a. It is found that interactions between molecules in a cluster are such that only two types of molecular building blocks are found corresponding to the parallel and staggered dimer of Figure 3a. The molecule centers are separated from each other by 1.45 nm in the parallel and 1.62 nm in the staggered configuration. This is very different from the self-assembled domains (see next section) were only single-lobe overlaps are observed between neighboring molecule. As a result, in the dimer, a pairing-up of the delocalized electrons leads to a Kondo quenching everywhere above the dimer.

In the compact trimer, the only spot that shows a Kondo resonance is the one consisting of three overlapping lobes in the center of the cluster, as shown in the schematics of Figure 3b by the red spots. This comes about because the three single electron wave functions overlap at this point, yielding a net spin. It is noteworthy that not more than three lobes are allowed to overlap at the same time in a molecular cluster. Therefore, larger 2D clusters can always be regarded as fragments of trimers. Similar to the case of the large selfassembled domains, no Kondo resonance is observed on the lobes at the perimeter of the clusters. The relaxation of the outer lobes probably yields a too low Kondo temperature to be measured experimentally.

When an isolated molecule is dragged toward an already formed 2D cluster, the molecule snaps into the available space at the perimeter of the cluster, simultaneously adjusting its azimuthal angle. The tetramer is thus formed from the trimer in a well-defined manner, as shown schematically in Figure 3c. It involves the same type of orbital overlaps as the trimer (two red spots in Figure 3c) and therefore shows a similar Kondo temperature (*i.e.*, $T_{\rm K} = 31$ K).

Table 1 summarizes our measurements in terms of geometryrelated Kondo temperatures. As will be shown in the next section, the geometrical arrangement of TbPc₂ molecules in self-assembled domains (anticipated in Table 1) are different from those observed in small clusters. One may wonder at Table 1. Molecular Clusters, Specific Locations of Kondo Resonance, Kondo Temperatures Measured at Specific Locations, and STM Images for Each Entity of Tb Double-Decker SMM on the Au(111) Substrate

Cluster	Kondo resonance	т _к (К)	STM image
Monomer	On all 8 lobes	38	
Dimer	No Kondo	N/A	
Trimer (chain)	No Kondo	N/A	Salar Sa
Trimer (compact)	On 3-lobe overlap	34	
Tetramer (compact)	On 3-lobe overlap (2 places)	31	
Domain	On non-overlapping lobes	22	



Figure 4. Electronic density distribution as provided by DFT calculations within a B3LYP scheme at a value of 0.001 e/Å³ for two dimer configurations. (a) Parallel configuration: the Tb–Tb distance is $d(\parallel) = 14.48$ Å. (b) Staggered configuration: the Tb–Tb distance is $d(\perp) = 16.20$ Å. (c) HOMO wave functions of the dimer at values of $\pm 2 \times 10^{-3} 1/Å^{3/2}$ for the parallel configuration. Red = positive, blue = negative amplitude. The white circle shows the place where the orbital overlap is examined. (d) Detail of the merging of electronic density distribution on closest aromatic rings at a value of $1 \times 10^{-3} e/Å^3$. (e) Merging of the SOMO wave functions of the two monomers on the closest aromatic rings (isosurface $\pm 1 \times 10^{-3} 1/Å^{3/2}$). The color code for atoms is H, white; C, gray; N, blue; Tb, red.

which stage the small cluster structure switches to the 2D semiinfinite structure.

A theoretical analysis is necessary to obtain a better understanding of the elementary processes that are at the origin of orbital overlap and Kondo behavior when the clusters are formed. Unfortunately, first-principles calculations involving several molecules of rare earth complexes in contact with a metal surface require a computational effort and resources exceeding our present availability. For this reason, we limited density functional theory (DFT) calculations to the estimation



Figure 5. (a,b) Constant current STM images of TbPc₂ molecular islands grown on Au(111) obtained with I = 70 pA, V = -0.5 V. Corresponding 2D fast Fourier transform of the molecular domain is depicted in the inset of the top right corner of (b); the bar corresponds to 1.3 nm⁻¹. Two lattice vectors are highlighted. $a_{1,2}$ represent the lattice parameters of one molecular type, $b_{1,2}$ those of the next neighbors. Two topographic contrasts are observed for molecules in a domain. The bright ones are labeled A, and the dark ones are labeled B. (c) dI/dV spectroscopy performed at the center of both A-type (red) and B-type (black) molecules. Vertical dotted lines show the correspondence between different peaks. (d) Topography image showing the places where spectroscopy was performed.

of the electronic structure change when a dimer is formed in the absence of any substrate. We first calculated the electronic structure of the monomer. The gap between the highest occupied and the lowest unoccupied level is $E_g(\text{mono}) = 640$ meV and compares well with the experimental value of 760 meV. As expected, the highest occupied level is a singly occupied molecular orbital (SOMO). More information on the monomer can be found in Figure S3. Second, for the dimer calculation, we considered the two geometries observed experimentally: (1) the parallel (||) and (2) the staggered (\perp) configurations (Figure 3a). The molecule centers are separated from each other by 1.45 nm in the parallel and 1.62 nm in the staggered configuration. In the parallel configuration, one molecule is shifted 1.34 nm parallel and 0.59 nm perpendicular with respect to the first one.

The calculated electronic density distributions of Figure 4a,b show that, in both cases, the molecules fit perfectly, one into the other with the usual structure in which the top and the bottom Pc ligands are rotated by 45° with respect to each other. The nesting, however, is more efficient in the parallel configuration, which is reflected in the fact that the parallel configuration is lower in energy by 300 meV and therefore constitutes the ground state. In this respect, see also the video of the 3D electronic density for the dimer in the parallel configuration. This is also by far the most frequent structure observed experimentally for isolated dimers; the staggered structure only appears as a part of larger clusters. The energy gap between the occupied and the unoccupied levels is $E_{g}(||) =$ 260 meV and $E_{\sigma}(\perp) = 120$ meV for the parallel and the staggered geometry, respectively (see Figure S4). The stability of the parallel configuration compared to the staggered one is also reflected in its larger energy gap. Interestingly, the total

wave function of the system in both configurations corresponds now to a singlet HOMO, that is, paired-up electrons. This is in good agreement with the experiment that shows a quenching of the Kondo resonance upon the dimer formation. A similar observation is made on a local basis above the overlap of orbitals (Figure 4d) on close-by aromatic rings. It is important to notice that no chemical bond is formed at this stage. Instead, in Figure 4e, a phase continuity of the wave function is observed across the space between the two monomers (same color means same phase). The positive wave function is represented by the red color and the negative one by the blue color; the latter is also present in the red "tube" between the two molecules, and it is just hidden by the red "envelope". These calculations required 4096 cores on an IBM-Blue Gene Q facility. They are on the verge of what is affordable and cannot be continued on larger clusters for the moment; however, we believe that they convincingly capture the relevant physics of the cluster formation such as stability, SOMO paringup, and the trend of HOMO-LUMO gap.

Self-Assembled Monolayers of Tb Double-Deckers on Au(111). In the following, the same approach is applied to the analysis of molecules assembled in a network. When the TbPc₂ molecules are adsorbed on Au(111) at 300 K, they tend to form islands of various sizes, as depicted in the STM image of Figure 5a. As first pointed out by Komeda *et al.*,¹¹ the STM image of the self-assembled monolayer reveals a checkerboard contrast of molecules (see Figure 5b). Bright and dark molecules (marked A and B, respectively) correspond to TbPc₂ molecules in two different states. A closer examination of the STM images reveals that upon condensation of the 2D phase from the isolated molecules, each molecule shares four of its lobes, out of eight, with adjacent molecules of the network

(along A–B or B–A); the other four lobes out of eight (along A–A or B–B) do not overlap. The even distribution of overlapping lobes on the perimeter of the molecule is induced by the symmetry of the semi-infinite lattice and clearly distinguishes the lattice from the clusters. Unit cell vectors of such compact domain are labeled a_1 and a_2 with the following lattice parameters: $a_1 = a_2 = 2.0 \pm 0.1$ nm. The next neighboring molecules are identified by the vectors b_1 and b_2 where $b_1 = b_2 = 1.42 \pm 0.05$ nm. The angle is $\alpha = 90 \pm 1^\circ$ in both lattices. The latter values are in good agreement with those deduced from earlier studies.^{11,13,23}

The spectra recorded above the center of A- and B-type molecules are shown in Figure 5c; they look quite different from those of the isolated molecules (Figure 1b). The two resonances on either side of the Fermi level are now close together. This tendency of gap reduction upon formation of the cluster units was already emphasized on the basis of the calculation for the dimer in the previous section. Because, in both cases (isolated and self-assembled), the molecules rest on the same Au(111) substrate, it can only result from the lateral interaction among molecules. The difference of A- and B-type molecules in the STS spectra of Figure 5c is materialized by the vertical dotted lines. The two features at -0.9 and +0.8 eV do not shift significantly and are similar to those reported on other metalo-phthalocyanine molecules^{12,13,16,22} and sometimes identified as HOMO and LUMO.¹² The two resonances that are closest to $E_{\rm f}$ are separated by only 150 meV above the Atype molecule and 320 meV above the B-type molecule. Noteworthy is the additional peak in the unoccupied states observed at +620 meV on the B-type molecule, which may well be the distinguishing mark of the dark (B) compared to the bright (A) molecule after self-assembly.

Whereas the above dI/dV measurements demonstrate the presence of two kinds of TbPc₂ molecules inside a monolayer, it is hardly sufficient to conclude on the conformation of individual molecules within the network. For this purpose, more sensitive tunneling conditions ($V \approx 10$ meV and $I \approx 10$ pA) were used in this work to visualize the molecular orbitals of the inner part of the molecules. Figure 6a shows a highresolution STM image of a terbium double-decker monolayer on Au(111). The different orbital distribution in the center of A- and B-type TbPc₂ molecules is now clearly visible, as highlighted in Figure 6b,c. The "external lobes" are simultaneously visible, but due to contrast enhancement, they now appear as large black dots. Notice that inside a given A or B molecule, the inner and outer lobes possess the same phase. These results are consistent with the calculated MO distribution obtained by DFT calculation by Vitali et al.⁷

The angle between the two lines in Figure 6b,c represents the smallest angle between lobes and is found to be equal to 15° . This value is in good agreement with the work of Komeda *et al.*,¹¹ who first postulated a different orientation of A- and B-type molecules based on the observation of four hardly distinguishable lobes of B-type molecules from usual topographic images. Ultimately, the results of Figure 6b,c not only show a different orientation of A- and B-type molecules but also show different contrasts, providing information on the relationship between top and bottom Pc ligand (to be analyzed further). It is clear, for example, that by keeping a 45° azimuthal angle between the top and the bottom ligands (as in the isolated molecule of Figure 1) a forbidden structural overlap leading to steric repulsions would occur. Therefore, the only way to accommodate the bottom ligands is by assuming the Article



Figure 6. High-resolution constant current topography, I = 70 pA and V = -50 mV. Under these conditions, A and B show two different electronic distributions of the central part of the molecules. Magnified images: B-type molecule shows eight distinct spots, and A-type molecules show extended "lobes" leading to cross-like contrasts in the center. Two lines are drawn on both images to highlight the different orientation of the inner lobes of A-and B-type molecules.

same orientation for all of them, similar to monolayer MPc molecules.^{31,32} In this case, two configurations of the TbPc₂ with different azimuthal angle are obtained. The reduction of the apparent height of the B-type molecules by 0.3 Å compared to that of A-type molecules in the STM topography (see Figure 5d) results from the different azimuthal angle as the substrate effect is assumed to be similar in both A- and B-type molecules, due to the negligible top ligand—substrate interaction. The above results, in accordance with earlier ones, ^{12,13} demonstrate that the electronic property of an assembly of molecules can be very different from that of an isolated molecule, as a consequence of the large influence of intermolecular interactions. The lateral bond formation between Co-porphyrin molecules was likely found to change the molecule–substrate separation and thus the Kondo screening of the metal centers.³³

As a result of the decoupling, an interesting correlation was established by Komeda *et al.*¹² between the unpaired π -electron orbital energy and the Kondo resonance in a special situation where some molecules in the monolayer are tilted and consequently show a wide range of energy distribution of the SOMO on all eight lobes of the molecule. This effect has been attributed to a changing interaction of the top ligand with the substrate due to the tilting. We also found similar sharp peaks on specific molecules (in the range from -500 to -200 meV); however, in the present work, we focus on the current situation observed on a large scale in extended domains of molecules where the SOMO is well-defined (does not shift). Our measurements then show that the Kondo resonance only appears on one lobe out of two, namely, those that do not have an overlap with a neighboring molecule.

In the following, we show that the STS measurements provide a deeper insight into the local electronic properties of adsorbed molecules as it ideally allows making links between the spectroscopic features of the condensed 2D phase and those already present in the isolated molecules. Figure 7a shows dI/dV spectra recorded above three areas corresponding to the large color circles in the topography image of Figure 7b. The spectra acquired above the center of an A-type molecule (red)



Figure 7. (a) dI/dV spectroscopy performed above the three areas shown in the topography image in (b), same color code. The inset in (a) shows a close-up of the ZBP spectrum acquired above the non-overlapping lobes between four molecules indicated by a green dot in the topography with a modulation voltage of 1 mV (rms). (c) Schematic representation of the network formed by the overlapping lobes (yellow) of A- and B-type molecules. (d) Unit cell showing four adjacent molecules with the proper orientation inside the network. The bright yellow lobes are as before, common to A and B molecules. The red lobes on the contrary are the "dangling" lobes belonging to either A or B molecules. The bold cross describes the orientation of each molecule, and the red arrows refer to the different chirality of A and B molecules.

and above the overlap of two adjacent double-deckers (blue) are similar, although the spectrum recorded above the overlap exhibits a larger gap of about 300 meV compared to 150 meV above the center. On the other hand, the spectrum acquired above the non-overlapping lobes (green) exhibits an occupied level that is strongly downward shifted to -500 meV, whereas the excited level is upward shifted to +260 meV. As a result, the gap above non-overlapping lobes is 760 meV. It is notable that the spectra acquired above non-overlapping lobes, between four adjacent TbPc₂ molecules (Figure 7a, top spectrum) show the same features at -500 and +260 meV as the spectra observed above the lobes of an isolated single molecule in Figure 1b. Furthermore, a careful study by high-resolution STS shows that the non-overlapping lobes are also those leading to the detection of a ZBP related to a Kondo effect (inset of Figure 4a) with $T_{\rm K} \approx 22$ K. Same measurements above the overlapping lobe (one molecular lobe out of two) do not show any evidence for a Kondo effect. Our findings furthermore demonstrate a clear correlation between the wide-range spectroscopic features (Figure 7a) and the simultaneous appearance of a Kondo resonance. The reoccurring gap, related to the appearance of the Kondo resonance, provides conclusive evidence that the peaks at -500 and +260 meV are due to the single electron occupied SOMO and corresponding unoccupied state.

The Kondo resonance observed above, in monolayer networks, exhibits a Kondo temperature $T_{\rm K} \approx 22$ K lower than that of the isolated TbPc₂ molecule on Au(111), for which $T_{\rm K} \approx 38$ K. Even though the same radical spin is responsible for the Kondo resonance in both cases, this difference refers to a more efficient screening for the isolated molecule. Keeping in

mind that only the spin properties of the top Pc ligands are accessible by STS, there is much to learn from the spatial distribution of the Kondo signal as it is affected by the presence of the neighboring radicals. Radicals have been investigated extensively in the context of molecular magnetism; in particular, the SOMO–SOMO overlap has been recognized to play an important role in the magnetic ordering of crystals made of neutral organic radicals.^{34,35} Here, we discuss further the reason why the Kondo resonance survives the self-assembly on some parts of the molecular network and is quenched otherwise.

STM topography images show unusual extension of the molecular orbitals of $TbPc_2$ double-deckers on Au(111), as can be seen from the superposed atomic skeleton in Figure S2, where the orbitals are significantly bulging out of the molecular framework, way beyond the normal atomic positions, in contrast with the single Pc ligand in direct contact with the surface that does not show this effect. Such a large extension of molecular lobes in STM images is typically found for aromatic molecules that are decoupled from the substrate by some ultrathin insulating layer.³⁶⁻³⁸ The lobes of such Pc radicals are prone to couple with those of neighboring molecules because the intermolecular overlaps of such SOMOs tend to adopt a bonding character. The interpretation of the STM data then becomes straightforward because the lobes in the 2D network that are linked through the orbital overlap show paired-up electron wave function (one SOMO with spin-up and the other with spin-down) and therefore do not experience the Kondo resonance in the experiment. The schematic views in Figure 7c,d show the lobes observed in the STM experiment. Among the eight lobes of each molecule, four of them have an overlap with the neighboring molecules (yellow spots in Figure 7c). For symmetry reasons, the four overlapping lobes lie on the four branches of a cross. Each B-cross is rotated by 15° with respect to the A-cross, which leads to the 2D zigzag network shown in Figure 7c. As shown in Figure 7d, it is the specific bond with the neighboring molecule, every second (yellow) lobe that leads to the reorientation by 30° of B-type molecules with respect to A-type molecules. More precisely, it is the overlap and avoided overlap both together which can be understood in a simple way by noticing the even distribution of paired-up SOMO lobes, similar to VSEPR model for simple molecules.³⁹

On the other hand, our STS measurements show that the four unpaired lobes per molecule (orange dots in Figure 7d) still show a Kondo resonance, even though the screening by the substrate electrons is less efficient. An estimate of the interaction between radicals spins, S = 1/2, is obtained from the magnetic characterization of $[YPc_2]^0$ bulk material (no f-electrons) where an antiferromagnetic radical–radical interaction of about 1 K has been measured.^{40,41} This value is comparable to the exchange interaction between the radical and the Tb electron spin.²⁰ A clear picture thus appears, where a network of Tb electronic moments is mutually coupled through the radicals; this network, in turn, provides an efficient screening for the weakly coupled nuclear spin system.

Finally, the coupling of the SMM through the network indicated in Figure 7d induces a chirality of electronic origin. For symmetry reasons, the overlapping lobes are not the same in A- and B-type molecules; that is, the overlapping lobe is positioned clockwise in A-type, whereas it is positioned counterclockwise in B-type molecules (see Figure 7d), thus forming racemic domains. Here, the electronic nature of the molecule is modified by spin-pairing with the neighboring molecule, and it is different from the chirality induced by the substrate¹⁶ or the one induced by STM tip manipulation.⁹

The geometrical arrangement of TbPc₂ molecules in small clusters is different from those observed in self-assembled domains where only one lobe overlaps with a neighboring molecule. One may answer now the question concerning the stage at which the small cluster structure recovers the 2D semiinfinite structure. At least a sizable number of molecules must have a network environment (four neighboring molecules) and a number in excess of a few tens of molecules are necessary for that, as can be seen in Figure 5a where the checkerboard motif is still perturbed at the edge of small islands. The geometrical and magnetic arrangements of TbPc₂ molecules in this work have been explained exclusively by the stability provided by overlapping orbitals to such an extent that it appears like the main driving force in the assembly process. It is, however, based on arguments that have been developed quite early and used in predicting the geometry of $\pi - \pi$ interaction.⁴²

CONCLUSION

In summary, we have used high-resolution STM to evidence experimentally the spin networking of SMMs. Our analysis is based on the identification of the molecular orbital lobes in the STM images of molecular networks. The Kondo effect was used as a tool to follow the presence of unpaired radical spins on the orbital lobes of the top ligand of a $TbPc_2$ SMM. It is found that the double-decker molecules are linked through long-range orbital overlaps leading to a quenching of the Kondo resonance. The magnetic exchange interactions resulting from the overlapping orbitals lead to a fully connected spin network. Furthermore, it is found that the molecular arrangements of small compact clusters built by STM-assisted molecular manipulation are different from those observed in the extended domains. The symmetry breaking of the finite system (directional interaction) compared to the infinite lattice then leads to more than one orbital overlap between two adjacent molecules. However, the experiment shows that in all cases the structures are made of two types of dimer fragments, parallel and staggered. Our findings prepare a way to detect the lateral interaction among molecules in both self-assembled as well as tip-manipulated molecular assemblies and demonstrate that the Kondo effect is a dedicated tool to follow the spin networking driven by radicals. The "bottom-up" approach adopted here may help in designing and engineering chemically tailored molecules with the desired electronic structure and magnetic behavior.

METHODS

Experimental Details. All sample preparations were carried out in an ultrahigh vacuum (UHV) system with a base pressure of 1×10^{-10} mbar. The single-crystalline Au(111) substrate was cleaned by Ne⁺ sputtering and annealing cycles. The powder of TbPc₂ molecules (synthesized by the Ruben group at the Karlsruhe Institute of Technology) was first degassed *in vacuo* at a temperature slightly below the sublimation temperature for 24 h. Deposition of TbPc₂ occurred at a sublimation temperature of 600 K onto the Au(111) kept at room temperature. Molecule sublimation was performed in a side chamber of the UHV system; during this operation, the pressure was kept below 1×10^{-9} mbar. All STM/STS data were acquired at 4.5 K. STS spectra were measured using a lock-in detection with a modulation between 1 and 10 mV (rms) depending on the features to be resolved.

Molecular manipulation was carried out by means of the "pulling" procedure; that is, the molecule-tip interaction is used to laterally manipulate the molecules by means of an attractive potential. The tip was positioned 4 Å above the surface before the feedback loop is opened. When the tip is moved at constant height above the surface, the molecule is dragged along a well-defined path on the surface. For the purpose of cluster construction, both molecular rotation and translation were used. The tunneling current is monitored as a function of x-y coordinates for a better control of the manipulation process. The building of a molecular cluster is easily performed by separately manipulating a single molecule toward a specific area. In this way, up to four molecules, forming a tetramer, could be successfully assembled. The manipulation was achieved using a bias voltage V = 0.1V and a current I = 4 nA. We considered that the optimal geometry of the cluster was reached when the molecule to be added to the cluster could not be moved further under the same condition. After each manipulation, the obtained structure was investigated by means of dI/ dV spectroscopy.

Computational Methods. We resort to first-principles simulations within the density functional theory⁴³ framework as implemented in the CPMD⁴⁴ code. The Becke exchange⁴⁵ and the Lee-Yang-Parr correlation⁴⁶ functional have been used to describe the exchange and correlation contributions, complemented by the exact exchange⁴⁷ (B3LYP). Core-valence interactions have been described by norm-conserving Troullier-Martins⁴⁸ pseudopotentials (PPs) for N, C, and H, whereas for Tb, we make use of a Goedecker-Teter-Hutter⁴⁹ semicore PP. Valence electron orbitals were represented in a plane wave (PW) basis set with a cutoff energy of 80 Ry. To eliminate the problem of periodically repeated images, typical of standard PW approaches, an isolated cell⁵⁰ with an edge of 47.7 Å was used. A spin-unrestricted approach is adopted in all the simulations, and van der Waals interactions were included according to Grimme's D2 formula.⁵¹ All structures have been fully optimized until residual atomic forces are smaller than 10⁻⁴ Hartree/Bohr.

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Site-dependent Kondo resonance measured on an isolated $TbPc_2$ on Au(111); detailed analysis of adsorption site, molecular conformation, and respective orientation of bottom and top ligands on the Au(111) surface; DFT calculation of monomer and dimer $TbPc_2$ double decker (PDF)

Video of the electronic density distribution (DFT calculation) for the dimer in the parallel configuration (MPG)

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Notes

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