On-surface structural and electronic properties of spontaneously formed Tb$_2$Pc$_3$ single molecule magnets†

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The single molecule magnet (SMM) bis(phthalocyaninato)terbium(III) (TbPc$_2$) has received significant and increasing attention as an exemplar system for realizing molecule-based spin electronics. Attaining higher nuclearity via multi-decker TbPc systems has remained an outstanding challenge, as known examples of Tb$_2$Pc$_3$ systems are only those containing Pc rings with substituents (e.g. alky1, alkoxy). Here we report on the spontaneous formation of Tb$_2$Pc$_3$ species from TbPc$_2$ precursors via sublimation in ultrahigh vacuum (UHV) onto an Ag(111) surface. The presence of Tb$_2$Pc$_3$ molecules on the surface are inspected using scanning probe microscopy with submolecular resolution supported by density functional theory (DFT) calculations and additional chemical analysis. We observe the selective presence of a Kondo resonance (30 K) in the Tb$_2$Pc$_3$ species, that we attribute to differences in the orientation of the internal molecular ligands. Formation of triple-decker complexes offers new possibilities to study and control magnetic interactions not accessible with standard TbPc$_2$ molecules.

1. Introduction

Single-molecule magnets (SMMs) are metal complexes which act as magnetic domains at the single-molecule level:1–3 the nanosize dimensions and quantum nature of SMM systems brings to light several properties that link macroscopic phenomena with the quantum world, such as the emergence of staircase hysteretic behaviour in the magnetisation, quantum phase interference, and temperature independent relaxation processes. SMMs are synthesised by coordinating spin active transition-metal ions (d, f-block) with a variety of ligands. Formation of triple-decker complexes offers new possibilities to study and control magnetic interactions not accessible with standard TbPc$_2$ molecules.

Together via exchange interactions and give rise to systems with high spin multiplicity, and large (as well as negative) zero field splitting with dominant uniaxial magnetic anisotropy.

In particular, the bis(phthalocyaninato) terbium(III) (TbPc$_2$) molecule, stands out in recent years for being extensively investigated. Structurally, the TbPc$_2$ molecule adopts a $D_{4d}$ symmetry and a square anti-prismatic terbium coordination geometry. The complex can be synthesised in the anionic form [TbPc-2]$^-$ and in the uncharged (neutral) form [TbPc$_2$]. These very promising SMM candidates exhibit particularly high energy barriers for magnetisation reversal ($U_{\text{eff}} = 410–641 \text{ cm}^{-1}$) and blocking temperatures ($T_B > 1.7 \text{ K}$); properties that are not quenched even when the molecule is subjected to dimensionally constrained environments (e.g. following surface deposition).5

Further improvements in these properties are expected through increasing the molecule nuclearity by creating a multi-decker TbPc$_3$ system.5,6 It has been previously shown that in pristine Tb$_2$Pc$_3$ the dominant interaction of the lanthanide magnetic moments is dipolar in nature, with only a small contribution from exchange.5,7 However, the importance to study in more depth the electronic/magnetic properties of Tb$_2$Pc$_3$ molecules vs. TbPc$_2$ molecules relies on the fact that the former have two sets of 4f spin active centres that act singly as SMM units,5,8 together with the presence of deloca-

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lised π-electrons on the Pc rings. Such structural and magneto/electronic organisation offers the opportunity for deepening our understanding of basic physical principles, namely how the coupling between lanthanide cations is susceptible to alteration following molecular interaction with magnetic and/or non-magnetic substrates.

These efforts have been hampered by the insolubility of unsubstituted phthalocyanine rings. Only a few multi-decker lanthanide complexes are known today in literature, and mostly comprise of species making use of substituted Pc-rings (e.g. with OEt, OBu, alkyl, alkoxyl chains) to increase solubility. It has been previously suggested that at elevated temperatures, TbPc2 molecules may decompose and form Tb3Pc4 and Tb2Pc3 under certain conditions. However, solid proof of the existence of Tb2Pc3 has been missing so far.

Even in their present state, these key features may promote the technological implementation of the system in real-world devices. In particular, measurements utilizing radio-frequency and magnetic field excitations in TbPc2 point towards the potential use of this molecule for reading the nuclear spin state information of the Tb atom through the coupled electronic states of the metal ion and the ligands.

One prevalent and widely studied phenomena on TbPc2 molecules is the selective and controllable presence of a zero-bias Kondo resonance in the dI/dV spectra, localized to the Pc ligand lobes. The location and strength of the Kondo resonance has been attributed to charge transfer between the substrate and the TbPc2 molecules. The Kondo phenomenon is observed in all studies conducted on the monolayer TbPc2 on Au(111) but not on the Ag(111) substrate. Nevertheless, in the case of the higher apparent height (i.e. brighter) molecules, on Au(111) the Kondo effect is quenched, but is present on Ag(111). In Ara et al. in particular, the brighter molecules are considered as a second layer of TbPc2 molecules. Additionally, the Kondo state can be quenched by physical rotation of the top Pc ligand, and has also been shown to be influenced by the ligand neighborhood. Spin resolved measurements demonstrate the importance of understanding exactly how interaction between the substrate and molecule, e.g., charge transfer, influences the orbital occupancy and resulting electronic properties of the molecules.

Here we report measurements of TbPc2 molecules thermally evaporated in ultrahigh vacuum (UHV) on a single crystal Ag(111) surface and subsequently studied via scanning tunneling (STM) and non-contact atomic force microscopies (nc-AFM). Submolecular spatial AFM resolution achieved with a CO-terminated probe allows us to identify the presence of well ordered, self-assembled islands composed of both TbPc2 and Tb3Pc4 molecules. The unexpected presence of Tb3Pc4 molecules is further supported by manipulation experiments and confirmed by chemical analysis of the molecules collected after the UHV experiments. From these observations we can infer an alternating rotational configuration of the triple Pc ligand stack, which can rationalise the appearance of the Kondo resonance observed on Tb2Pc3 molecules. The experimental evidence is supported by total energy density functional theory (DFT) calculations.

2. Results

After deposition of TbPc2 molecules on the Ag(111) surface held at room temperature (for details see Methods), we observed in STM large areas (>150 × 400 nm) of densely packed molecules surrounded by clean Ag(111), as shown in Fig. 1(a). The molecular layer grows between surface step edges and we clearly observe two different apparent height contrasts within the molecular layer using STM imaging. Detailed inspection of the edge of an island as shown in Fig. 1(b), reveals two distinct molecular contrasts, dark and bright, which correspond to different apparent heights of molecules. Differences in height have been previously observed in STM measurements for TbPc2 absorbed on Au(111) and Ag(111) surfaces and additional species with higher apparent height were attributed to a second layer of TbPc2 molecules.

However, apparent topography measured in STM on the same region may change substantially at different tip-sample biases. Indeed, bias-dependent line profiles, presented in Fig. 2(a), show significant deviation in the apparent STM height between the two different species, making reliable measurement of the height impossible using this method. For certain bias voltages, the higher apparent height molecules are...
roughly double that of the lower apparent height molecules relative to the Ag(111) surface, which is likely why they have previously been identified as a second layer of TbPc₂ molecules.29,32

STM and AFM height determination
To overcome this deficiency in STM height determination, we examined the apparent heights in the nc-AFM mode using a CO-terminated tip. The presence of an inert CO molecule on the metallic tip apex significantly reduces the chemical reactivity of the probe, which allows us to reach the frequency shift minima without variation of tip structure. This measurement has been previously demonstrated to be an accurate way to determine the heights of molecules absorbed on surfaces.43 The frequency shift was recorded as a function of tip–sample distance on the two different molecular regions and Ag(111) surface, as shown in Fig. 2(b). By identifying the frequency shift minimum on the three regions (dark, bright molecules and bare Ag(111) surface), we obtained the height of the two different molecular regions to be 0.62 nm and 0.92 nm with respect to the Ag(111) surface. Systematic error in these values due to energetic contributions beyond the dominant Pauli repulsion have been previously shown to be on the order of pm, far below the height difference we observe here.43,44 In contrast with the apparent height from STM, these measurements show that the higher molecules are not twice as high as their lower counterparts. On the other hand, the two AFM determined heights match well with the distances between the upper Pc ligand of TbPc₂ and Tb₂Pc₃, with respect to the Ag(111) surface as obtained from the total energy DFT simulations, shown in Fig. 2(c). This finding strongly suggests that the higher and lower molecules in STM represent Tb₂Pc₃ and TbPc₂ molecules, respectively.

Molecular manipulation of Tb₂Pc₃
We performed manipulation experiments of the bright molecules, the results of which further reinforce the identification of Tb₂Pc₃ on Ag(111). Fig. 3 shows a sequence of molecular manipulations performed by moving the tip in constant height laterally into the side of different bright molecules, with the direction of tip motion indicated by the arrows. The two tones of bright molecules are likely due to the presence or absence of the Kondo effect discussed later in the manuscript. We expected lateral manipulations to move what we initially supposed to be second layer TbPc₂ molecules. Instead, for the lateral manipulations in Fig. 3(a)–(c), the bright molecule was completely removed from the area (e.g., absorbed to the tip), leaving a hole down to the substrate. The removal of the molecules in Fig. 3(b) and (c) created a channel that was required for the successful lateral movement of the higher molecule, shown in Fig. 3(d). We interpret these observations as evidence that the species with higher apparent height in STM are chemically discrete units, consistent with our identification of them as Tb₂Pc₃.
**Ex situ chemical analysis**

To gain more evidence of the formation of the Tb₂Pc₃ molecules, we performed *ex situ* chemical analysis of the molecules before and after several thermal cycles of evaporation in UHV onto the Ag(111) surface. High-resolution mass spectrometry (time-of-flight tandem mass spectrometer, Q-TOF) for residual material remaining in the crucible after the UHV experiments, confirms the presence of both the TbPc₂ and Tb₂Pc₃ species (ESI† [TbPc₂] with 1183.2 m/z and [Tb₂Pc₃] with 1855.3 m/z) as well as the presence of increasing signatures attributable to half-decker Tb molecules [TbPc]⁺ (see the ESI, Fig. S6–S11†). From these observations we conclude that thermal decomposition in the UHV chamber appears to promote a temperature-induced structural rearrangement of the TbPc₂ molecules, like what has been shown earlier,⁹ following a reaction pathway tentatively highlighted by the following scheme:

\[
4\text{TbPc}_2(\Delta T, \Delta t) \rightarrow \text{Tb}_2\text{Pc}_3 + \text{TbPc}_2 + \text{TbPc} + 2\text{Pc},
\]

where \(\Delta T\) and \(\Delta t\) represent the annealing temperature and time, respectively.

To further test the impact of the annealing temperature and time in promoting the structural rearrangement of TbPc₂ molecules, we screened the pristine material after the annealing process at three different temperatures (700 K, 675 K, 650 K) and short annealing time (\(t = 10\) min). The \(T\) and \(t\) variables chosen for the screening were substantially smaller than that used here to promote the significant formation of Tb₂Pc₃ (annealing temperature \(T = 850\) K, annealing time \(t = 60\) min). Furthermore, we compare how formation of Tb₂Pc₃ is driven at high annealing temperature at various times, after 60 min and 30 min of annealing in vacuum. Analysis of the mass spectra of the recovered material from the UHV crucible for the experiments performed at low temperatures and short times are given in detail in the ESI (Fig. S12† annealing temperature 700 K, \(t = 10\) min). Fig. S15 and S16† show the results obtained for the annealing temperature 850 K, and time \(t = 30\) min experiment. In the low temperature and short annealing time scenarios, a barely detectable signature of the Tb₂Pc₃ specie is observed, together with barely detectable signals ascribable to decomposed/fragmented TbPc₂ molecules (range below 1000 m/z). Moreover, the mass spectra analysis for the material subjected to high temperature annealing under different annealing time indicates that formation of Tb₂Pc₃ is enhanced when longer times are employed (compare Fig. S9, \(t = 60\) min to Fig. S16,† \(t = 30\) min) and such process is accompanied by an increased presence of fragmented Pc ring/decomposed TbPc₂ molecules; thus, while the low-temperature experiments indicate that high annealing temperatures of the pristine TbPc₂ molecules inside the UHV chamber is a prerequisite for getting Tb₂Pc₃ formation, the annealing time is an equally important variable impacting the kinetics of the process, because it appears that longer times, together with high temperatures, favour both formation of substantial amounts of Tb₂Pc₃ but also substantial formation of TbPc molecules (half decker), as previously shown in the reaction scheme depicted above (compare Fig. S9–S16 in the ESI,† where the absence of the TbPc peak at 703.1 m/z can be noted in the latter).

**Structural model**

We performed detailed measurements and analysis of the arrangement of TbPc₂ and Tb₂Pc₃ assemblies on the Ag(111) surface. The nc-AFM technique provides unprecedented spatial resolution of molecular assemblies superior to standard STM imaging.⁴² In particular, the technique allows us to precisely measure the internal orientation of molecules forming the on-surface assembly.

Fig. 4 shows the multiple-height registration of the TbPc₂ relative to the Tb₂Pc₃ deduced from analysis of a single high-resolution AFM image of two domains of TbPc₂ and Tb₂Pc₃ molecules. We have directly measured the position and rotational orientation of the topmost Pc in both the double- and triple-decker species with respect to the Ag(111) lattice (more data shown in the ESI, Fig. S1 and S2†). We inferred the adsorption geometry of the bottom Pc ligand (black, from the atomic registration, and an equidistant ligand spacing due to steric repulsion, consistent with prior observations.⁴⁵ For the TbPc₂ molecules, we can directly add the topmost ligand from the experimental observations, with an alternating 30°/45° pattern relative to the bottom Pc (dark blue/red in Fig. 4b). For the Tb₂Pc₃, we infer that the middle Pc conforms to the alternating 30°/45° pattern of the topmost TbPc₂, and then add the topmost Pc, with a ±5° rotation relative to the bottom Pc (light blue/red).

From these observations, we can identify a two-molecule unit cell commensurate with the Ag(111) lattice (shown in ESI Fig. S2†). Unfortunately, such a big unit cell makes total energy DFT simulations computationally intractable. We per-
formed calculations in a smaller unit cell including only one TbPc$_2$ or Tb$_2$Pc$_3$ species, respectively. This means that the mutual orientation cannot be directly compared to the experimental evidence. According to the total energy DFT simulations the TbPc$_2$ or Tb$_2$Pc$_3$ molecules are stabilised on the Ag(111) surface by an attractive van der Waals interaction and charge transfer between the molecular species and metallic substrate. In both cases, we observed substantial planarization of the Pc ligands with respect to the optimal gas phase configuration (see inset in Fig. 2(c)), as a consequence of the attractive van der Waals interaction with the metallic substrate. The planar structure of the Pc ligands facilitates sub-molecular resolution measurements. Indeed, the calculated AFM images are consistent with the experimental data (see ESI Fig. S5†).

Molecular charge transfer

We extended the nc-AFM measurements to look for differences between the two observed rotational configurations, specifically a detailed examination of the charge distribution across molecule/surface interface and within each molecule. To analyze the charge transfer, we carried out Kelvin probe force microscopy (KPFM) measurements on the two species of molecules as well as the bare Ag(111) (see ESI Fig. S4†). Differences in the capacitive term and local contact potential difference were observed between the three regions. We found the magnitudes of these parameters to be strongly dependent on the tip geometry and tip–sample distance, but the overall trend between Tb$_2$Pc$_3$, TbPc$_2$ molecules and the Ag surface remained very similar. We observed differences in the contact potential difference $V_{CPD}$ between the molecule regions and the bare Ag(111), indicating that there is charge transfer occurring from the substrate towards the molecules, which is also accompanied by charge transfer between domains of Tb$_2$Pc$_3$, TbPc$_2$ molecules. The charge transfer from the surface towards molecules is further supported by total energy DFT calculations of single Tb$_2$Pc$_3$ and Tb$_3$Pc$_3$ molecules deposited on Ag(111) surface, as shown on Fig. 5. These models correspond to the 45° relative rotation, red molecules in Fig. 4(c). Namely, the DFT calculations indicates an extensive depletion of the electron density in surface area (see blue color iso densities shown on Fig. 5) under the molecule. On the other hand, we observe substantial charge redistribution in lower Pc and on Tb atom. This we attribute to molecular orbital reordering upon deposition on the Ag(111) surface. Our simulations predict that upon surface deposition the eight f-electrons of Tb still remain lined up with a total spin $S = 3$ and a total orbital momentum $L = 3$. In the next section, we will show that the charge transfer plays an important role in the appearance of the Kondo effect.

Unfortunately, we do not observe differences on submolecular level between adjacent Tb$_2$Pc$_3$ molecules in the KPFM data. Nevertheless this level of spatial resolution for KPFM is likely limited by mesoscopic tip effects. In principle, we can improve it with an intentional CO-tip functionalization. But to obtain high spatial resolution, we have to operate the probe in close distances and large biases, which gives rise to spurious artefacts in the KPFM measurements.46

Because of the limited spatial KPFM resolution we pursued a different approach to address differences in the internal charge distribution within molecules. Molecular backbones are typically represented by sharp edges caused by lateral bending of the CO-tip. Modification of the internal charge distribution within the molecule modifies the Coulombic interaction experienced by CO-tip. This in turn modifies the position of sharp edges providing information about the variation of the charge distribution.47 We applied this methodology to this system to see if we could correlate the structural and electronic differences we observed in the sub-molecular AFM contrast. Fig. 6(a) and (b) are images of the same group of four Tb$_2$Pc$_3$ molecules, taken in standard STM with a metallic tip (Fig. 6a), and nc-AFM at constant height with a CO-functionalized probe (Fig. 6b). The top Pc ligand model is superimposed on Fig. 6(c) and (d) to guide the eye. The upper left- and right-hand molecules in Fig. 6(b) were imaged in greater detail, shown in Fig. 6(f) and (e) respectively. By filtering and registering these two images to one another, slightly different distortions in the benzene rings can be identified, as shown in Fig. 6(g). Namely, we observe a systematic elongation of benzene rings corresponding to red molecules (two lower Pc ligands are rotated by 45° with respect to each other, see Fig. 4c). Similar geometric distortions have been attributed to charge transfer effects, owing to the combination of Pauli repulsion, van der Waals and coulombic interaction of the CO-tip with the sample.47–50 Therefore, we attribute these differences in lateral distortion of benzene rings to different charge distributions in adjacent Tb$_2$Pc$_3$ molecules. Unfortunately, due to the lack of submolecular resolution of the internal part of the molecules, a direct comparison of the electrostatic potential between two Tb$_2$Pc$_3$ molecules with different internal orientations of Pc ligands cannot be accomplished.
It is noteworthy that very similar alternating distortions were also observed in adjacent TbPc2 molecules with different internal rotations of Pc ligands. This indicates that the different rotations of lower and upper Pc ligands modifies the hybridization with the central Tb atoms and consequently modifies the charge distribution within the molecule.

Electronic structure of TbPc2 and Tb2Pc3

Upon identifying the two distinct geometries of TbPc2 or Tb2Pc3 in the surface assembly, we characterized their respective electronic properties. We carried out scanning tunneling spectroscopic (STS) measurements of the electronic structure, which show qualitative differences between distinctly oriented molecules of each species. Averaged STS spectra acquired on the ligand ring of two adjacent Tb2Pc3 and TbPc2 molecules are plotted on Fig. 7(e) and (f), respectively. We clearly observe distinct positions of the highest occupied/lowest unoccupied molecular orbital (HOMO/LUMO) resonances for Tb2Pc3 and TbPc2 molecules, which are spatially localized on the ligand. In the case of TbPc2 molecules HOMO resonances are located ~0.2 eV lower in energy than those of Tb2Pc3. We can also identify that the width of the HOMO peaks are directly linked to the internal rotation of Pc ligands, see Fig. 7(c). The lowest unoccupied states are spatially localized on Pc ligands similarly to the HOMO orbitals, as seen from spatial STS maps of two adjacent TbPc2 with alternating relative Pc orientations at $V_{\text{bias}} = 130$ mV shown in Fig. 7(c) and (d), respectively.

The most significant observation from these data is the presence of the zero bias peak in the STS spectra only on one type of Tb2Pc3, namely Tb2Pc3. We can also identify that the width of the HOMO peaks are directly linked to the internal rotation of Pc ligands, see Fig. 7(c). The lowest unoccupied states are spatially localized on Pc ligands similarly to the HOMO orbitals, as seen from spatial STS maps of two adjacent TbPc2 with alternating relative Pc orientations at $V_{\text{bias}} = 130$ mV shown in Fig. 7(c) and (d), respectively.

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analysis, we can assign the presence of the Kondo signature to the molecules overlaid with the light red model shown in Fig. 4(b), corresponding to the middle ligand having a 45° rotation relative to the bottom.

To estimate the Kondo temperature $T_K$ of the Tb$_2$Pc$_3$ molecule showing the Kondo effect, we fit selected spectra using the Frota expression for the Kondo resonance:\(^{51,52}\)

$$\rho(\varepsilon) = \text{Im} \left[ -i \sqrt{\frac{i F}{i F + \varepsilon}} \right],$$

with an additional linear background offset, where $\varepsilon$ is the energy and $i F$ is proportional to the half width at half maximum. The Kondo temperature $T_K$ can be calculated from $i F$ as follows:\(^{52,53}\) $i F = 1.455 k_B T_K$, where $k_B$ is the Boltzmann constant. These fits indicate a temperature of approximately 30 K (±5 K), consistent with prior measurements.\(^{29}\) The Kondo temperature $T_K$ has been averaged for several spectra acquired on different lobes of the upper Pc ligand, in positions indicated by red points in Fig. 8(b). There can be only one Kondo temperature for a given molecular state. We attribute the minor spatial variation of the Kondo resonance to experimental errors stemming from changes in the tip–sample distance due to thermal drift. We intentionally selected spectra in the central part of the ligand to minimise sensitivity to this error. The estimated Kondo temperature is far above the experimental temperature $T_{exp} = 5$ K, which indicates that the system is in the strongly coupled Kondo regime.

Next, we analyze the Kondo effect in detail to gain further insight regarding its selective appearance on only the Tb$_2$Pc$_3$ molecules with the middle ligand rotated by 45° with respect to the bottom ligand. The presence of the Kondo resonance is intimately connected to the interaction of singly occupied magnetic impurity states with a bath of non magnetic electrons, typically located in a metallic substrate. This interaction leads to an effective screening of the spin of the localized state, which is manifested by presence of a sharp resonance in the spectral function at the Fermi level.\(^{54}\) The width of the Kondo resonance $\Gamma$ is proportional to the Kondo temperature $T_K$, which defines the relevant energy scale $k_B \Gamma$ of the Kondo effect. The Kondo temperature is determined by several factors, such as the position of the singly occupied state $\varepsilon_i$ with respect to the Fermi level, its hybridisation with the substrate $\Delta$ and on-site Coulomb interaction $U$:\(^{54}\)

$$\Gamma = k_B T_K \approx \sqrt{2 \Delta \pi} \exp \left[ -\frac{\pi}{2 \Delta} \left( \frac{1}{\varepsilon_i} + \frac{1}{\varepsilon + U} \right)^{-1} \right].$$

Another parameter that plays an important role in the quantitative analysis of the Kondo problem is an average occupancy number $n_i$ of the impurity state $\varepsilon_i$.\(^{54}\) In our case, it is represented by the highest occupied molecular level. It has been demonstrated that the Kondo regime is typically established within an occupancy range of $0.8 < n_i < 1.2$ having approximately one unpaired electron in the highest occupied molecular level.\(^{55}\) In the gas phase this is an integer number, but this is not necessarily the case upon deposition on a metallic surface due to additional interaction with the substrate. Indeed, we already established that both KPFM measurements and DFT calculations show charge transfer towards the molecule accompanied by additional charge transfer between domains of TbPc$_2$ and Tb$_2$Pc$_3$. The high resolution AFM images reveal internal charge redistribution of the electrostatic field within molecules and the position of the HOMO with respect to the Fermi level induced by internal rotation of the Pc ligands.

We can estimate the occupancy $n_i$ of the HOMO orbital of Tb$_2$Pc$_3$ molecules showing the Kondo resonance from analysis of the STS spectra using the well known Fano formula:\(^{56}\)

$$\rho(E) = \rho_0 + \frac{(q + \varepsilon)^2}{1 + \varepsilon^2},$$

with an additional linear offset term, where $\varepsilon$ is the normalized energy:

$$\varepsilon = \frac{E - E_K}{\Gamma_{exp}}.$$
line, Fig. 8d). We correct the $\Gamma$ width parameter for thermal broadening:25

$$\Gamma = 2\sqrt{(\pi k_B T)^2 + 2(k_B T K)^2}$$

where we take $T = 5$ K as the temperature of the microscope ($k_B$ is the Boltzmann constant). The corrected value $\Gamma = 4.3$ meV gives the Kondo temperature $T_K = 50$ K. This value is a little bit higher than the value obtained by the Frota fit. Finally, the occupation number $n_i$ of the HOMO orbital can be deduced from the corrected $\Gamma$ using the following expression:54

$$E_K = \Gamma \tan \left( \frac{\pi}{2} (1 - n_i) \right).$$

We obtained the average occupation $n_i = 0.9$, which fits into the predicted range of occupancies where the Kondo effects may appear. We can check the consistency of this fit, by using the corrected value of $\Gamma = 4.3$ meV and solving eqn (2) subject to the additional constraint that $n_i = -\frac{\varepsilon_i}{U} + \frac{1}{2}$. With this constraint, we obtained numerically optimised values for the Coulomb repulsion $U = 1.2$ eV; $\varepsilon_i = -480$ meV, the distance of the HOMO below the Fermi level; and $\Delta = 106$ meV, the width of the HOMO orbital. However, the excitation signal used for our measurements is large in comparison to the observed Kondo resonance, so these fit values have to be interpreted with considerable caution. That said, they reasonably match those from the experiment, which can be estimated from the STS spectra of the Tb$_2$Pc$_3$ molecule with Kondo resonance shown on Fig. 7(e): $U \sim 1.1$ eV, $\varepsilon_i \sim -550$ meV, and $\Delta \sim 150$ meV. In contrast, for the non-Kondo HOMO orbital (light blue, 7e) we estimate $\varepsilon_i \sim -650$ meV, and for TbPc$_2$ $\varepsilon_i \sim -950$ meV.

Based on the experimental evidence showing correlation between the position of HOMO orbitals with respect to the Fermi level and appearance of the Kondo resonance, we attribute the appearance of Kondo resonances to two factors: (i) the charge transfer from the surface to molecules and between different domains of TbPc$_3$ and TbPc$_2$ molecules, and (ii) the internal rotation of Pc ligands, further modifying the internal charge redistribution within molecules and importantly modifying the position of the highest occupied molecular resonance. Based on these observations, we propose the following scenario to rationalize the presence/absence of Kondo resonances in Tb$_2$Pc$_3$ and TbPc$_2$ molecules.

In the case of Tb$_2$Pc$_3$ molecules, it has been shown that the Kondo resonance observed on TbPc$_2$ molecules on Au(111) surface is related to the presence of an unpaired electron in the $\pi$-orbital of the upper Pc ligand, as discussed by Komeda et al.11 However, in the case of the Ag(111) surface, the presence of a semi-occupied molecular orbital (SOMO) is suppressed by additional charge transfer upon deposition of the molecule on a metallic surface. This changes the occupancy of the HOMO and shifts its energy far from the Fermi level, and consequently the Kondo effect is quenched.

The situation is slightly different in the case of Tb$_2$Pc$_3$ molecules, where the three Pc$^{2-}$ ligands accumulate a total charge of $-6$, which is fully compensated by charge $+6$ provided from the two Tb$^{3+}$. However, this neutrality is broken upon additional charge transfer towards the molecule after adsorption onto the surface, giving rise to the presence of an unpaired electron in the upper Pc ligand. In the case of the Tb$_2$Pc$_3$, the presence of the Kondo resonance is further modulated by the internal rotation of the Pc ligand following the scenario proposed by Komeda et al.11 Namely, the rotation of the Pc ligands changes the hybridization of the HOMO orbital, which shifts downwards its energy and increases its width. In principle, this effect increases the orbital occupancy of the HOMO level and reduces the effective exchange interaction between the localized electron in the HOMO and the bath of electrons. Consequently, the Kondo resonance disappears.

3. Conclusions

In summary, we have employed nc-AFM based techniques to identify our multiple height system as a mixture of TbPc$_2$ and Tb$_2$Pc$_3$ molecules, subsequently confirmed with separate chemical analysis. We established a structural model of the mixed Tb$_2$Pc$_3$ and TbPc$_2$ monolayer relative to the underlying Ag(111) surface using high-resolution AFM imaging. Spectroscopic measurements show the selective presence of a Kondo peak in the top ligand of alternating Tb$_2$Pc$_3$ species. High-resolution imaging of molecules exhibiting and lacking the Kondo peak show geometric distortions in the Pc ligand structure that we attribute to structural and charge environment differences. We use these structural measurements to model and simulate the charge transfer between the substrate in the various configurations: these quantitative differences are correlated with the qualitative appearance of the Kondo electronic signature. These data provide a comprehensive portrait for understanding the roles of structure and charge transfer in controlling the Kondo signature, and points to their utility in evaluating future candidate SMMs for use in surface based devices.

4. Methods

Experimental

Synthesis is accomplished by direct cyclization of the ring precursor (1,2-dicyanobenzene) at high temperatures in the presence of a metal salt (e.g. Tb(acac)$_3$), 1,8-diazabicyclo(5.4.0) undec-7-ene (DBU) and high boiling solvents (e.g. pentanol, hexanol).9,55 The measurements described here were performed using commercial, ultrahigh vacuum (UHV) low-temperature microscopes with combined STM/nc-AFM capabilities (Specs-JT Kolibri: $f$ ~ 1 MHz, $Q$ ~ 120k, $K$ ~ 540 kN m$^{-1}$, 50 pm amplitude and Createc-qPlus: $f_0$ ~ 30 kHz, $Q$ ~ 17k, $K$ ~ 1.8 kN m$^{-1}$, 50 pm amplitude). The Ag(111) single crystal (Mateck) was prepared by repeated Ar sputtering/annealing cycles. The TbPc$_2$ molecules were degassed in vacuum by repeated cycling to the evaporation temperature, 850 K. Coversages were obtained with a 15 min deposition in ambient pressure of $5 \times 10^{-8}$ mbar (base pressure $1 \times 10^{-10}$ mbar) with the Ag(111)
surface at 300 K (line-of-sight distance 30 cm), before subsequent insertion into the low-temperature microscope (5 K). CO was dosed onto the surface (pressure $8 \times 10^{-8}$ mbar, 15 seconds) after the sample temperature was <10 K, for subsequent tip functionalization. STS point spectra and maps were acquired using the lock-in measurement technique, with an AC signal (~1 kHz) amplitude 5 mV (point/grid spectroscopies) or 15 mV (STS maps) added to the tip–sample junction. The presence of additional Tb$_2$Pc$_3$ molecules in the precursor TbPc$_2$ molecule batch that was annealed in UHV for the experiments was subsequently confirmed with matrix-assisted laser desorption/ionization (MALDI) spectroscopy (spectra shown in the ESI†).

**Computational**

The optimized structures of TbPc$_2$ and Tb$_2$Pc$_3$ molecules on Ag(111) were calculated by the FHI-AIMS program package$^{60}$ based on ab initio density functional theory (DFT). We used exchange correlation functional PBE + $U$ with $U = 5$ eV for f-electrons of Tb and van der Waals interaction was approximated by the Tkatchenko-Scheffler dispersion correction method.$^{63}$ The AFM images were calculated with Probe Particle code.$^{48,64}$ We used the following parameters of the flexible probe-particle tip model: the effective atomic radius $R_e = 0.24$ nm$^{-1}$ and effective atomic radius $R_e = 1.661$ Å. We added a quadrupole-like charge distribution at the tip apex to simulate the CO-tip for all the AFM simulations$^{50}$ (quadrupole charge of $-0.05 \times 0.712$ eÅ$^2$).

**Author contributions**

P. J, M. S, J. H and A. C devised the experiments. J. H and A. C made the samples and did the measurements. B. T, T. C and M. M aided the UHV experiments. G. Z synthesized the molecules. G. Z and B. P performed the chemical analysis. P. M and P. J did the theoretical calculations. J. H, A. C, and P. J analyzed the data and composed the manuscript. All authors discussed the results and commented on the manuscript.

**Conflicts of interest**

There are no conflicts to declare.

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