ABSTRACT: We investigated the structural and electronic/spin configurations of a film of the Co tetrakis(1,2,5-thiadiazole) porphyrazine (CoTTDPz) molecule adsorbed on the Au(111) surface by a scanning tunneling microscope (STM). CoTTDPz has a structure similar to that of the Co phthalocyanine molecule, but the benzene ring of the isoindole of the phthalocyanine molecule is replaced by the pentagon moiety of 1,2,5-thiadiazoles that has an S atom at the apex. We find an ordered molecular lattice with a threefold symmetry where a nearest-neighbor distance of 1.30 nm was measured, which is significantly smaller than that observed for the metal Pc molecule. The unit cell of the lattice contains two molecules that are rotated by 60° relative to each other. With the configuration achieved by this rotation, the neighboring molecules can form a stronger interaction through bonding between the S atom at the apex of one molecule and the N atom of the other (the N atom that is bridging the thiadiazoles). The strong interaction between the molecule and the substrate appears in the spin state examined by the detection of the Kondo resonance, which is formed by the screening of an isolated spin by the conduction electron. Even though the existence of the spin was confirmed for the bulk and thick films of this molecule, no Kondo features are detected for the molecules in the first, second, and third layers of the films. However, the isolated molecule in the third layer showed an intriguing combination of the Kondo feature and an inelastic excitation feature caused by a spin-flip process.

INTRODUCTION

Due to the wide applications of organic molecules to the electronics devices, the control of the interface between the molecule and the metal surface attracts attentions. Especially, the understanding of the film growth at the initial stage has fundamental importance over the final properties of the organic devices, which has been studied energetically in recent decades. Among such studies, metallo-phthalocyanines (MPcs) and their derivatives are the most well-studied molecules due to not only their thermal stability but also tunable electronic properties and adsorption configurations with the change of the metal atom at the center. In addition, several double-decker Pc molecules possess an intriguing property of the single-molecule magnets (SMMs), which makes them good candidates for advanced quantum computing materials. Despite such importance, most of the works for the control of molecule–molecule and molecule–substrate interaction are restricted to the cases governed by their weak interactions including the van der Waals forces.

In the control of such interactions, the property of the outer perimeter of the molecule (or the ligand) plays a critical role. In that sense, the modification of the perimeter of the MPC family molecules might be able to tune the molecular interaction with the surroundings, while the molecule keeps the intriguing properties of the MPcs. Stuzhin and their co-workers synthesized metallo-tetrakis(1,2,5-thiadiazole) porphyrazines (MTTDPz),11,12 in which the benzene ring in the Pc ligand is replaced with the reactive moiety of 1,2,5-thiadiazoles, which has an S atom at the apex. This S atom interacts with the N atom of the neighbor molecule, which is bridging the thiadiazoles.13,14 Our previous works on vanadyl tetrakis(thiadiazole) porphyrazine (VOTTDPz) show that the substituted ligands give a large effect on the stacking and the magnetic properties.15

In this article, we report a low-temperature scanning tunneling microscope (LT-STM) study of cobalt TTDPz (CoTTDPz) molecule adsorbed on the Au(111) surface. The chemical structure of CoTTDPz is shown in Figure 1a. We performed STM and scanning tunneling spectroscopy (STS) experiments to characterize the bonding configuration and
Figure 1. (a,b) STM image of film I; (a) occupied state image (10 × 10 nm², −0.8 V, 100 pA) and (b) unoccupied state image (14 × 14 nm², 0.5 V, 100 pA); white arrow refers to the [110] direction of Au(111). α and β are unit vectors of the nonreconstructed Au(111). (c) Schematic model of the unit cell and molecule rotation. (d) Molecules adsorbed near the Au step edge; red arrows refer to raised lobes. (e) dI/dV on the isolated molecule. Red, green, and blue curves are obtained at the bare Au, the molecule center, and the ligand, respectively. Tip positions in corresponding colors are shown in the image. I = 0.4 nA, V = 0.2 V, Vrms = 20 mV for red and green, and Vrms = 10 mV for blue. (f) dI/dV on the molecule in film I. I = 0.1 nA, V = 0.5 V, and Vrms = 10 mV.

The electronic properties of CoTTDPz. In addition, we examine the spin property of the molecule by detecting the Kondo resonance near the Fermi level, which is caused by the screening of the spin of the molecule by the conduction electrons.

### RESULTS AND DISCUSSION

We start with the description of the first layer of the CoTTDPz film on Au(111), which we call as phase I hereafter. We show the topographic image of the phase I film in Figure 1a,b obtained with the occupied and unoccupied states, respectively. As can be seen in the inner structure of the molecule in both images, the molecule shows a symmetric four-lobe shape, indicating flat-lying adsorption on Au(111). This configuration can also be seen in the first layer of MPc and VOTTDPPz films on Au(111). Herringbone of Au(111) under phase I can be clearly distinguished in a large-scale image (not shown here), indicating that molecules do not change the conventional 22 × √3 reconstruction of Au(111).

The molecular lattice of phase I can be described using the unit cell shown as a green parallelogram in Figure 1b. The unit cell can be constructed by two vectors a₁ and a₂. It contains two molecules that are not equivalent because the azimuthal angles of them are rotated by ~60° relative to each other. Thus, we can define “row” of the molecules along which the molecules have an identical azimuthal rotation angle and the molecules in the next row are rotated by 60°. The unit cell can be expressed with the unit vectors a₁ and a₂, whose lengths are 1.30 and 2.60 nm, respectively, and are rotated by 60° relative to each other. They are commensurate with Au(111) and can be expressed by unit vectors of the nonreconstructed Au(111) surface (here called α and β) as follows:

\[
\begin{align*}
(a_1) &= (4.5 \ 0 \ 9) \\
(a_2) &= (0 \ 0 \ 0)
\end{align*}
\]

The model is illustrated in Figure 1c.

The lattice shows a significant difference from the molecular lattice reported for the film of the MPc molecules formed on Au(111). When the coverage was close to the monolayer, they often show the quasi-square lattices that were reported for the CoPc, VO-Pc, FePc, and H₂Pc molecules. The pseudo-square unit cell can be expressed as follows:

\[
\begin{align*}
(a_1) &= (5 \ 0 \ 6) \\
(a_2) &= (0 \ 0 \ 5)
\end{align*}
\]

The reported nearest-neighbor distances (nnd) of the Pc molecules for these cases are close to 5 times of the nnd of the Au(111) surface, which corresponds to 1.44 nm. Thus, the nnd of 1.30 nm observed for the CoTTDPz molecule in this experiment is significantly shorter than those reported for MPc and H₂Pc cases.

It is intriguing to notice that the topographic image shows a large change when the polarity of the tunneling bias voltage is reversed. Although the molecule appears as the cross with almost equal heights at the center and the perimeters in the unoccupied state image of Figure 1b, the central part of the molecule is much enhanced in the occupied state image in Figure 1a. This phenomenon is attributed to the shift of Co d orbital in vacuum becomes fully occupied due to charge transfer and shows an enhanced signal when occupied states are imaged by negative bias.

The difference in the adsorption configuration of CoTTDPz from the MPc molecules can also be found in other features. Figure 1d shows molecules adsorbed near the step edge. It has been discussed that the molecule adsorbed at the step edge tends to have a canted bonding configuration; that is, a part of the molecule is bonded on the upper terrace and the other is bonded on the lower terrace of a step edge. Zhao and co-workers showed that, for the CoPc molecule adsorbed on the Au(111) surface, more than 75% of CoPc molecules at the step edge have one or two lobes anchoring on the higher terrace. However, for the current system of the CoTTDPz molecule on Au(111), only ~30% of the molecules were confirmed to have the tilted configuration (the raised lobes are marked by red arrows in the figure). We speculate that a strong lateral thiadiazole–Au bonding is the underlying mechanism for the suppressed appearance of the tilted configuration.

STS (dI/dV) spectra measured for the isolated molecule and the molecule in the phase I film are illustrated in Figure 1e,f.
respectively, and we show the spectra obtained both at the center and the ligand positions in both panels. The condition of the STM tip was checked by confirming the surface state of the bare part of the Au(111) surface before taking the molecular spectra, which is shown by the plot in red.

For the spectrum of the isolated molecule shown in Figure 1e, we identify the features at \( \sim -0.36 \) V (blue curve) and \( \sim -0.54 \) V (green curve) together with a common feature at \( \sim 0.13 \) V. In addition, a weak feature can be identified at \( \sim +0.65 \) V on the ligand position.

It is interesting to notice that we can find the corresponding features in the spectra obtained for an isolated CoPc adsorbed on Cu(100) if we ignore the shift of the bonding energy. However, the STS obtained for the CoPc molecule adsorbed on Au(111) is much different and has no corresponding features. Moreover, there appeared a feature near the Fermi level for the former case, which is missing for the latter. This feature is interpreted as the adsorption-induced states (AISs) formed by the hybridization of the electronic states of the substrate and the molecule. It is well known that the Cu(100) substrate has a stronger bonding with the CoPc molecule than Au(111) does, which is supposed to be the origin of differences in the STS of the two.

We can find the AIS at 0.13 V in the spectrum of Figure 1e. Combined with the similarity in the STS features, we consider that the electronic structure of the CoTTDPz molecule on Au(111) is similar to that of CoPc on Cu(111) rather than that on Au(111), which is due to the strong bonding of the CoTTDPz molecule with the Au(111) substrate with the presence of reactive species of S and N atoms.

The spectra shown in Figure 1f are obtained for the molecule in the lattice of the phase I film. The green curve shows a similar shape to the corresponding one in Figure 1e, but the peak position is shifted to \( -0.31 \) V in (f) from \( -0.56 \) V in (e). We also see another new peak at \(-0.53\) V in (f). The differences are derived from the formation of the molecule–molecule interactions.

After the completion of the first monolayer, the second layer was formed with subsequent deposition of the molecule of the CoTTDPz molecule, in which two types of adsorption configurations labeled phases IIa and IIb were observed.

We first examine the bonding configuration of phase IIa. Figure 2a shows the topographic image of phase IIa of the second layer. Unlike the symmetric four-lobe feature observed in phase I, a single lobe out of four lobes is highlighted in an asymmetric manner. This is illustrated in the magnified image in the inset of Figure 2a, where the enhanced lobes are marked by blue dots. To demonstrate that this was not caused by the tip effect, we show the area where both phases I and IIa are visible in Figure 2b. In this image, while four lobes appear with an equivalent contrast in phase I, one particular lobe possesses a heightened contrast in phase IIa.

When the polarity of the tunneling bias was reversed, this asymmetric height distribution among the ligand is enhanced. We show the change of the topographic image with the reversal of the bias-voltage polarity in Figure 2c in which the upper half corresponds to the unoccupied state, while the lower corresponds to the occupied one. In the occupied state image of phase I shown in Figure 1a, the central part of the molecule is highlighted. Similarly in the lower half of Figure 2c, we see that the central parts of the molecules marked by red dots are bright. However, the bright spot is seen not only at the center but also at one of the lobes that are marked by blue dots. By comparing the unoccupied and occupied state images of the molecule, we can identify the relation between the molecule structure and the height distribution. The result is schematically shown by superimposing the skeleton of the molecule on the topographic image. The structure and contrast distribution can be summarized as follows: (1) the molecules in the neighboring rows have different azimuthal rotation angles as in phase I and (2) one of the four lobes is highlighted whose position appears in an alternative manner in the neighboring row.

We show the temporal model for this film with a top view in Figure 2d and with a cross-sectional view in Figure 2e. We consider that the asymmetric height distribution among the four lobes is deduced from the canted bonding of the molecule, as indicated in Figure 2e. The direction of the tilt is identical among the rows that are twisted if compared with the one of the neighboring rows.

The stacking of the second layer on the first layer is depicted in the model of Figure 2f. We found that the unit cell of phase IIa is skewed from that of phase I (the length from 1.30 \( \times \) 2.60 to 1.22 \( \times \) 2.77 nm\(^2\) and the angle from 60 to 64\(^\circ\)). The structural change from phase I to IIa should be related to the
relaxation of the film structure due to the decreased interaction with the substrate.

The tilt angle of the molecule can be roughly estimated by considering the height difference of the two lobes along the canted direction, measured as 0.18 nm, and the size of the molecule of 1.30 nm. This yields $\arcsin(0.18/1.3) \approx 8^\circ$ for the estimated tilt angle from the flat-lying configuration. A similar tilted configuration was reported for MPc. For the CoPc molecule, they found a tilted stacking in the second layer in which the tilt angle has been estimated as $3^\circ$.\textsuperscript{16} The authors claim that the canted configuration observed in the second and higher layers is due to the polymorphs of the crystal of the MPc molecules. We can find a case where a further canted bonding configuration in the second layer of the FePc molecule film grown on Au(111), in which the inclination has been claimed to be about $40^\circ$.\textsuperscript{21} In the estimation of the angle, the authors observed an isolated FePc molecule in the second layer since the height difference between the lobes can be measured more precisely for the isolated molecule compared to the case for the molecule in the film.

Figure 2f illustrates $dI/dV$ spectra measured on the lobe of the molecule of phase IIb; two sharp features are observed at $-1.0$ and $0.7$ V together with weak features at 0.77 and 1.1 V. The sharp peaks in the occupied state are obviously corresponding to the features of highest occupied molecular orbital (HOMO) and HOMO-1 observed in Figure 1f, which are remarkably enhanced and the shift to the lower energy after partially decoupled from the Au substrate due to the presence of the first layer. We also see that the weak features in the unoccupied state in Figure 1f shift to higher energy without a large change in their intensity. However, these features develop into a strong peak as lowest unoccupied molecular orbital (LUMO) at 0.79 V in the spectrum obtained on the center of the molecule (Figure 2g), while HOMO and HOMO-1 are depressed with a little change in energy position. We measured spectra on the nonhighlighted lobes of the molecule in the phase II film, which was similar to those obtained on the center of the molecule in the same film.

Next, we discuss another phase of the second layer labeled IIb. Figure 3a displays the surface area where two phases of II and IIb coexist. These two types of the second layers were formed on different domains of the first layer of phase I and not found next to each other. The height difference between the layers of phase IIb and phase I is $\sim 230$ pm, which was higher than that between II and I.

The lattice and the azimuthal angle of the molecule can be observed in the magnified image of Figure 3b. For an eye guide, the molecular model is superimposed on the topographic image by a simplified cross representing the two symmetry lines of the molecule.

We should note that, unlike the cases of phases I and IIb, the molecules are directing to a single direction and the alternative rotational angle between the neighboring molecules is no more observed. The unit cell is defined by $c_1$ and $c_2$, which have the sizes of 1.23 and 1.43 nm, respectively, with an angle of 63$^\circ$, in which $c_1$ is rotated $\sim 10^\circ$ from the [110] direction of the Au lattice. Thus, the unit vector of $c_2$ is almost half in the length if compared with $a_2$ due to the absence of the azimuthal rotation. Similar structures can be seen in the previous works for CoPc/Cu(111),\textsuperscript{5,6} SnPc/NaCl,\textsuperscript{7} and FePc/Ag(111).\textsuperscript{28}

If we assume a flat-lying bonding configuration with the lattice parameters and rotation angles given above, the molecule alignment is like the model illustrated in Figure 3c.

In this configuration, the overlap of the S atoms is expected at the site marked by the blue and white circles in Figure 3b, which causes a large steric repulsion. One way to avoid this repulsion is to tilt the molecules, which increases the vertical gap between sulfur atoms, as illustrated in Figure 3d. In Figure 3b, only two lobes out of the four lobes can be clearly seen and the others are almost invisible, the former of which is marked by blue dots and the latter by white dots in Figure 3b. The contrast variation indicates that the molecule is tilted where the blue lobes are lifted and the white lobes are closer to the substrate. To estimate the tilt angle quantitatively, we like to observe an isolated molecule as discussed for the FePc molecule in the previous paragraph.

For this purpose, we employ the third layer grown on the second layer of phase IIb. We consider that the bright molecules observed in Figure 3b are the isolated molecules of the initial stage of the third layer. The bright molecule is observed at the on-top site of phase IIb, and the intramolecular...
structure looks similar to that of the second layer. However, there is an intriguing difference in the electronic states in the $dI/dV$ spectra obtained at the lower molecule (second layer) and at the higher molecule (third layer), which are shown in Figure 3e,f, respectively. The features corresponding to HOMO-1, HOMO, LUMO, and LUMO + 1 are observed at the energies of $-1.30$, $-0.81$, $0.71$, and $1.1$ V for the second layer molecule in Figure 3e and at $-1.23$, $-0.99$, $0.41$, and $0.79$ V for the third layer in Figure 3f, respectively. In the latter case, the energy separation between the occupied states becomes smaller and the intensive HOMO-1 peak is remarkably weakened, as shown on the left side of Figure 3f. On the other hand, the energy gap between LUMO and LUMO + 1 has an almost constant value of $0.38$ V for both the second and third layers but the peak position is shifted toward the Fermi level for the third-layer molecule.

The evidence that the bright features in Figure 3b correspond to the third-layer molecule can be obtained by comparing the STS spectrum obtained on each of them. As shown in Figure 3b, STS on the third-layer molecule is almost identical to that of the bright molecules shown in Figure 3f. In addition, the height of this film from the IIb phase is $0.23$ nm, the same as that observed for the bright molecules from phase IIb. These features support that the bright spots in Figure 3b are the molecules in the third layer.

The molecular lattice in Figure 3g is identical to that of phase IIb except the appearance of pairing of the two rows of molecules and a gap between the pairs. Combined with the observation that the third-layer molecule is found at the on-top site on the film of phase IIb, we consider that the molecules in phase IIb and in the third layer have a similar bonding configuration. Following the method shown for the FePc on Au(111),27 we can calculate the most accurate tilt angle from the X-ray crystallography. Thus, we focus on the bright molecule in the image of Figure 3b, which is the isolated molecule in the third layer. We can estimate the tilt angle from the height difference between the two lobes, which indicates a height difference of $250$ pm and an angle of $11^\circ$. The tilt angle is large enough to make an enough space to avoid the steric repulsion between the blue and white parts of Figure 3b.

Now, we discuss the magnetic property of the CoTTDPz molecule on Au(111). The magnetic properties of the molecule in the bulk and thick film were reported by our group,5,14 the results show a weak antiferromagnetic and paramagnetic ordering, respectively, and the spin is located on the Co atom at the center.

We examine the STS spectrum near the Fermi level for the isolated CoTTDPz molecule on Au(111) surface shown in Figure 4a. Although we expect that the spins are at the center of the molecule, the obtained spectrum illustrated in Figure 4b shows no Kondo resonance. The absence of the Kondo feature suggests that the molecule spin is quenched due to a molecule–substrate interaction.

A similar case has been investigated for the CoPc molecule. The CoPc molecule has a spin of $S = 1/2$ in vacuum,29 which is located in the $d_z^2$ orbital. Zhao et al. examined the Kondo state of CoPc adsorbed on Au(111). No Kondo feature is observed for the CoPc deposited on the Au(111) surface.30 Nonmagnetic Co$^{2+}$ for the nondistorted CoPc molecule adsorbed on Au(111) was confirmed by other experimental24 and theoretical31–33 studies. In these reports, the disappearance of the spin is explained by the filling of the $d_z^2$ state as a result of charge transfer from the substrate.

For the molecule in the multilayer film, it is expected that the molecule–substrate interaction is weakened by the presence of the underlying film, which makes the spin return to the Co atom. Stepanow et al. examined X-ray absorption spectroscopy (XAS) and X-ray magnetic circular dichroism (XMCD) for the same system.32 They showed that three-dimensional (3d) magnetic moment exists in the $dz^2$ state for the multilayer film of CoPc. Chen and co-workers demonstrated the Kondo resonance for the CoPc molecule in the second layer.35

Although we expected a similar behavior for the CoTTDPz molecule on Au(111), the $dI/dV$ spectra near the Fermi level obtained at the molecules of phase IIb, IIa, and III did not show any feature of the Kondo resonance. The absence of the Kondo resonance indicates that the quenching of the Co spin by charge transfer is active on phase III.

Nevertheless, we detected the Kondo resonance at the isolated molecules in the third layer on phase IIb. We show the topographic image of such molecules in Figure 4c together with the obtained Kondo peaks in Figure 4d, where the colored circles in Figure 4c indicate the positions where the spectra plotted with the same color in Figure 4d were obtained. At the ligand position of the isolated molecule adsorbed at the edge of the film of phase IIb (dark-blue circle), we obtained a sharp Kondo peak, whose width is $7.6$ mV. On the other hand, the lobe at the green position provides a wider peak with a width of $24$ mV. In addition, we see a characteristic dip at the Fermi level. For the right-hand molecule, the lobe marked by the red circle shows a peak with a further wide peak width.

Nagaoka et al. introduced a formula for the temperature dependence of the Kondo peak width, $I(T)$
\[ \Gamma(T) = 2\sqrt{(\pi k_B T)^2 + 2(k_B T)^2} \]

where \( \Gamma \) is the width of the Kondo peak, \( k_B \) is the Boltzmann constant, and \( T_K \) is the Kondo temperature. The fitting of the dark-blue plot of Figure 4d yields \( T_K = 31 \) K, while the green curve gives \( T_K = 98 \) K for the Kondo part of the deconvoluted peak.

It is well established that \( T_K \) is strongly affected by the distance between the spin and substrate; the stronger the interaction, the higher the Kondo temperature.\(^\text{25,34,35}\) In our case, the dark-blue lobe of the left molecule in Figure 4c was at the perimeter of II\( b \) and fuzzy in the image. Since molecules in II\( a \) were tilted, the target was most likely separated from the layer of phase II\( b \), which induces a weak coupling with the substrate followed by the recovery of the spin to the Co atom.

On the other hand, the green lobe is attached to the layer of phase II\( a \), whose schematic model is shown in Figure 4f. The higher \( T_K \) observed for the green curve reveals this difference.

In addition, the green plot of Figure 4e has a sharp dip at the Fermi level, a ladder-type change of the conductance at the symmetric positions around the Fermi level forming a dip feature near the Fermi level. The dip feature in the \( dI/dV \) plot at the Fermi level was observed in the conductance plot for the atom/molecule on the insulating layer or in the multilayer film; examples of the former can be seen for the system of Mn atom on Al\(_2\)O\(_3\)/NiAl,\(^\text{30}\) FePc molecule on the Cu\((111)(2 \times 1)\rangle-O\) surface,\(^\text{25}\) and the ones for the latter are the organic radical molecule (C\(_{24}\)H\(_{23}\)O\(_2\)N\(_4\)) on Au\((111),\(^\text{38}\) the TbPc\(_2\) molecule of the multiple layer on Ag\((111),\(^\text{39}\) and CoPc on Pb.\(^\text{33}\) For the former two cases, the conversion of the Kondo peak in the \( dI/dV \) spectrum to dips is a characteristic of the inelastic process. The origin of the dips is attributed to the inelastic spin-flip process in which the tunneling electron excites spin states appearing as inelastic components in the \( dI/dV \) spectrum. The experiment on the CoPc molecule was executed in its multilayer film (third to fifth layer) grown on the lead surface at the sample temperature at 0.4 K and with a magnetic field of 11 T. The inelastic feature appeared at \(-18\) meV. The energy is much higher than that expected for the excitation of the 1/2 spin. Instead, it is considerably due to a collective spin excitation of the chain of \(-Co-N-Co-\). This chain is formed in the surface-normal direction by the stacking of multiple CoPc layers where the Co atom is located at the on-top position of the N atom of the inner circle. The collective spin excitation of this antiferromagnetic chain forms the IE feature.

We consider that the green curve is composed of the Kondo peak and the IETS dip. The dip has a width of \(-6\) meV, which is much larger than that expected from the spin excitation of the 1/2 spin in the magnetic field of 3 T. Similar to the CoPc case mentioned above, we should consider the chain formation for the CoTTDPz molecule in the surface-normal direction, and larger energy is needed for the spin-flip due to the collective spin excitation.

The \( dI/dV \) spectrum obtained at the red point of Figure 4c shows a broad feature corresponding to \( T_K \) of \(-165\) K, which suggests a stronger bonding with the substrate than that obtained at the edge of the islands.

**SUMMARY**

In summary, we investigated the structure and electronic/spin configuration of the film of the Co tetrakis(1,2,5-thiadiazole) porphyrazines (CoTTDPz) molecule adsorbed on the Au\((111)\) surface. CoTTDPz has a similar structure to the Co phthalocyanine molecule except that its perimeter is terminated with S and N atoms instead of C–H. The active nature of the S and N atoms compared to that of the C–H species should form enhanced molecule–substrate and molecule–molecule interactions. We investigate their effect on the structural and electronic properties.

In the first layer, we find an ordered molecular lattice with a threefold symmetry where a nearest-neighbor distance of 1.30 nm was measured, which is significantly shorter than that observed for the metal Pc molecule. The unit cell of the lattice contains two molecules that are rotated by 60\(^\circ\) relative to each other. The azimuthal rotation is considerably due to the stronger interaction between the S atom at the apex of the ligand and the N atom in the inner ring. By this rotation, a compact lattice can be realized compared to MPc molecules on the Au\((111)\) surface.

In the second layer, we found two types of bonding configurations. The first one, phase II\( a \), shows a similar structure to that of the first layer. However, the molecules are tilted from the flat-lying configuration and the tilting direction alternatively changes neighboring molecules. The other phase of the second layer, phase II\( b \), shows the absence of the azimuthal rotation between neighboring molecules. Instead, they show a higher tilted angle to avoid steric repulsion. Apparent stronger interaction between the molecule and the substrate can be seen in the STS, including the finding of the adsorbate-induced state near the Fermi level that was observed previously for CoPc on the Cu\((111)\) surface, in agreement for the weak interaction case on Au\((111)\).

In addition, the STS spectra observed in the second and third layers show a significant change, indicating that the effect of the substrate is not completely shielded in the second layer. In both phases II\( a \) and II\( b \), the Co d state arises a sharp peak as LUMO at around 0.8 V, but the HOMO peak from the molecule ligand is much stronger in II\( a \); this result is reproducible, and the source of the enhancement remains a mystery. The HOMO features are weakened in the third layer (both protrusion and film), while a LUMO + 1 peak arises at the position that is 0.4 V higher than LUMO; this peak is more likely due to the vibrational mode on the molecule, as reported before.\(^\text{27}\) The strong interaction between the molecule and the substrate also appears in the spin state examined by the detection of the Kondo state. Even though the existence of the spin was confirmed for the bulk and thick films of this molecule, no Kondo features are detected for the molecules in the first, second, and third layers except for the isolated molecule in the third layer.

**EXPERIMENTAL SECTION**

Experiments were carried out using a Unisoku LT-STM operated at \(-4.7\) K with a base pressure of \(-10^{-9}\) Pa. The Au\((111)\) substrate was prepared by repeated cycles of Ar\(^+\) sputtering and annealing in ultrahigh-vacuum (UHV) conditions. The CoTTDPz molecule was deposited onto the Au substrate held at room temperature by heating a Ta boat. The STS measurement was carried out using the lock-in amp technique in which modulation voltage, \( V_{rms} \), was superimposed on the tunneling voltage.

**AUTHOR INFORMATION**

**Corresponding Author**

Tadahiro Komeda – Institute of Multidisciplinary Research for Advanced Materials (IMRAM, Tagen), Tohoku University,
Yu Wang — Department of Chemistry, Graduate School of Science and Institute of Multidisciplinary Research for Advanced Materials (IMRAM, Tagen), Tohoku University, Sendai 980-8578, Japan; orcid.org/0000-0003-2342-8184; Email: tadahiro.komeda.a1@tohoku.ac.jp

Jie Hou — Department of Chemistry, Graduate School of Science and Institute of Multidisciplinary Research for Advanced Materials (IMRAM, Tagen), Tohoku University, Sendai 980-8578, Japan

Keitaro Eguchi — Department of Chemistry & Research Center for Materials Science, Nagoya University, Nagoya 464-8602, Japan; orcid.org/0000-0001-8405-4900

Chihiro Nanjo — Department of Chemistry & Research Center for Materials Science, Nagoya University, Nagoya 464-8602, Japan

Tsuyoshi Takaoka — Department of Chemistry, Graduate School of Science and Institute of Multidisciplinary Research for Advanced Materials (IMRAM, Tagen), Tohoku University, Sendai 980-8578, Japan

Yasuyuki Saino — Department of Chemistry, Graduate School of Science and Institute of Multidisciplinary Research for Advanced Materials (IMRAM, Tagen), Tohoku University, Sendai 980-8578, Japan

Kunio Awaga — Department of Chemistry & Research Center for Materials Science, Nagoya University, Nagoya 464-8602, Japan; orcid.org/0000-0002-2193-0747

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.9b04453

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This study was supported in part by the Grant-in-Aid for Scientific Research (S) (No. 19H05621) (Tadahiro Komeda). The authors acknowledge the financial support by the Center for Spintronics Research Network (CSRN).

REFERENCES

1. Akkerman, H.-B.; Blom, P. W. M.; de Leeuw, D. M.; de Boer, B. Towards molecular electronics with large-area molecular junctions. Nature 2006, 441, 69–72.
2. Dodabalapur, A. Organic light emitting diodes. Solid State Commun. 1997, 102, 259–267.
3. Forrest, S. R. The path to ubiquitous and low-cost organic electronic appliances on plastic. Nature 2004, 428, 911–918.
4. Horowitz, G. Organic thin film transistors: From theory to real devices. J. Mater. Res. 2004, 19, 1946–1962.
5. Barth, J. V. Molecular architeconic on metal surfaces. Annu. Rev. Phys. Chem. 2007, 58, 375–407.
6. He, Y.; Kroger, J.; Wang, Y. F. Organic Multilayer Films Studied by Scanning Tunneling Microscopy. ChemPhysChem 2017, 18, 429–450.
7. Awärter, W.; Ecija, D.; Klappenberger, F.; Barth, J. V. Porphyrins at interfaces. Nat. Chem. 2015, 7, 105–120.
8. Gottfried, J. M. Surface chemistry of porphyrins and phthalocyanines. Surf. Sci. Rep. 2015, 70, 259–379.
9. Huang, Z. C.; Zhang, Y. J.; Yang, H.; Song, H. J.; Cen, Y.; Kai, W. A chemist’s overview of surface electron spins. Chem. Soc. Rev. 2017, 46, 1955–1976.
10. Komeda, T. Spins of adsorbed molecules investigated by the detection of Kondo resonance. Surf. Sci. 2014, 630, 343–355.
11. Bauer, E. M.; Cardarilli, D.; Ercolani, C.; Stuzhin, P. A.; Russo, U. Tetraakis(thiadiazole)porphyrinates. 2. Metal complexes with Mn(I), Fe(II), Co(II), Ni(II), and Zn(II). Inorg. Chem. 1999, 38, 6114–6120.
12. Stuzhin, P. A.; Bauer, E. M.; Ercolani, C. Tetrakis(thiadiazole)-porphyrinates. I. Syntheses and properties of tetrakis(thiadiazole)porphyrin and its magnesium and copper derivatives. Inorg. Chem. 1998, 37, 1533–1539.
13. Suzuki, Y.; Fujimori, M.; Yoshikawa, H.; Awaga, K. Packing motifs and magento-structural correlations in crystal structures of metallo-tetraakis(1,2,5-thiadiazole)porphyrine series, MTTPDps (M = H-2, Fe, Co, Ni, Cu, Zn). Chem. - Eur. J. 2004, 10, 5158–5164.
14. Eguchi, K.; Nanjo, C.; Awaga, K.; Tseng, H. H.; Robashik, P.; Heutz, S. Highly-oriented molecular arrangements and enhanced magnetic interactions in thin films of CoTTDP using PTCDAs templates. Phys. Chem. Chem. Phys. 2016, 18, 17360–17365.
15. Hou, J.; Wang, Y.; Eguchi, K.; Nanjo, C.; Takaoka, T.; Sainoo, Y.; Awaga, K.; Komeda, T. Inter-molecule interaction for magnetic property of vanadyl tetakis (thiadiazole) phthalocyanine film on Au(111). Appl. Surf. Sci. 2018, 440, 16–19.
16. Takada, M.; Tada, H. Low temperature scanning tunneling microscopy of phthalocyanine multilayers on Au(111) surfaces. Chem. Phys. Lett. 2004, 392, 265–269.
17. Lu, X.; Hips, K. W.; Wang, X. D.; Mazur, U. Scanning Tunneling Microscopy of Metal Phthalocyanines: d7 and d9 Cases. J. Am. Chem. Soc. 1996, 118, 7197–7202.
18. Barlow, D. E.; Hips, K. W. Scanning Tunneling Microscopy and Spectroscopy Study of Vanadyl Phthalocyanine on Au(111): The Effect of Oxygen Binding and Orbital Mediated Tunneling on the Apparent Correlation. J. Phys. Chem. B 2000, 104, 5993–6000.
19. Barlow, D.; Scudiero, L.; Hips, K. W. Scanning Tunneling Microscopy of 1, 2, and 3 Layers of Electroactive Compounds. Ultramicroscopy 2003, 97, 47.
20. Lu, X.; Hips, K. W. Scanning Tunneling Microscopy of Metal Phthalocyanines: d6 and d8 Cases. J. Phys. Chem. B 1997, 101, 5391–5396.
21. Cheng, Z. H.; Gao, L.; Deng, Z. T.; Liu, Q.; Jiang, N.; Lin, X.; He, X. B.; Du, S. X.; Gao, H. J. Epitaxial Growth of Iron Phthalocyanine at the Initial Stage on Au(111) Surface. J. Phys. Chem. C 2007, 111, 2656–2660.
22. Komeda, T.; Ishikii, H.; Liu, J. Metal-free phthalocyanine (H2Pc) molecule adsorbed on the Au(111) surface: formation of a wide domain along a single lattice direction. Sci. Technol. Adv. Mater. 2010, 11, No. 054602.
23. Cuadrado, R.; Cerda, J. I.; Wang, Y. F.; Xin, G.; Berndt, R.; Tang, H. CoPc adsorption on Cu(111): Origin of the C4 to C2 symmetry reduction. J. Chem. Phys. 2010, 133, No. 154701.
24. Heinrich, B. W.; Iacovita, C.; Brumme, T.; Choi, D.-J.; Limot, L.; Rastel, M. V.; Hofer, W. A.; Kurtos, J.; Bucher, J.-P. Direct Observation of the Tunneling Channels of a Chemisorbed Molecule. J. Phys. Chem. Lett. 2010, 1, 1517–1523.
25. Zhao, A. D.; Hu, Z. P.; Wang, B.; Xiao, X. D.; Hou, J. G. Kondo effect in single cobalt phthalocyanine molecules adsorbed on Au(111) monoatomic steps. J. Chem. Phys. 2008, 128, No. 234705.
26. Takada, M.; Tada, H. Scanning tunneling microscopy and spectroscopy of phthalocyanine molecules on metal surfaces. Jpn. J. Appl. Phys. 2005, 44, 5332–5335.
27. Wang, Y. F.; Kroger, J.; Berndt, R.; Tang, H. Molecular Nanocrystals on Ultrathin NaCl Films on Au(111). J. Am. Chem. Soc. 2010, 132, 12546–12547.
28. Gopakumar, T. G.; Brumme, T.; Kroger, J.; Toher, C.; Cumberti, G.; Berndt, R. Coverage-Driven Electronic Decoupling of Fe-Phthalocyanine from a Ag(111) Substrate. J. Phys. Chem. C 2011, 115, 12173–12179.
29. Reynolds, P. A.; Figgis, B. N. Metal phthalocyanine ground states: covalence and ab initio calculation of spin and charge densities. Inorg. Chem. 1991, 30, 2294–2300.
30. Zhao, A. D.; Li, Q. X.; Chen, L.; Xiang, H. J.; Wang, W. H.; Pan, S.; Wang, B.; Xioa, X. D.; Yang, J. L.; Hou, J. G.; Zhu, Q. S.
Controlling the Kondo effect of an adsorbed magnetic ion through its chemical bonding. *Science* **2005**, *309*, 1542−1544.

(31) Hu, Z.; Li, B.; Zhao, A.; Yang, J.; Hou, J. G. Electronic and Magnetic Properties of Metal Phthalocyanines on Au(111) Surface: A First-Principles Study. *J. Phys. Chem. C* **2008**, *112*, 13650−13655.

(32) Stepanow, S.; Miedema, P. S.; Mugarza, A.; Ceballos, G.; Moras, P.; Cezar, J. C.; Carbone, C.; de Groot, F. M. F.; Gambardella, P. Mixed-valence behavior and strong correlation effects of metal phthalocyanines adsorbed on metals. *Phys. Rev. B* **2011**, *83*, No. 220401.

(33) Chen, X.; Fu, Y. S.; Ji, S. H.; Zhang, T.; Cheng, P.; Ma, X. C.; Zou, X. L.; Duan, W. H.; Jia, J. F.; Xue, Q. K. Probing superexchange interaction in molecular magnets by spin-flip spectroscopy and microscopy. *Phys. Rev. Lett.* **2008**, *101*, No. 197208.

(34) Nagaoka, K.; Jamneala, T.; Grobis, M.; Crommie, M. F. Temperature dependence of a single Kondo impurity. *Phys. Rev. Lett.* **2002**, *88*, No. 077205.

(35) Komeda, T.; Ishiki, H.; Liu, J.; Katoh, K.; Shirakata, M.; Breedlove, B. K.; Yamashita, M. Variation of Kondo Peak Observed in the Assembly of Heteroleptic 2,3-Naphthalocyaninato Phthalocyaninato Tb(III) Double-Decker Complex on Au(111). *Ac Nano* **2013**, *7*, 1092−1099.

(36) Heinrich, A. J.; Gupta, J. A.; Lutz, C. P.; Eigler, D. M. Single-atom spin-flip spectroscopy. *Science* **2004**, *306*, 466−469.

(37) Tsukahara, N.; Noto, K. I.; Ohara, M.; Shiraki, S.; Takagi, N.; Takata, Y.; Miyawaki, J.; Taguchi, M.; Chaimani, A.; Shin, S.; Kawai, M. Adsorption-Induced Switching of Magnetic Anisotropy in a Single Iron(II) Phthalocyanine Molecule on an Oxidized Cu(110) Surface. *Phys. Rev. Lett.* **2009**, *102*, No. 167203.

(38) Zhang, Y. H.; Kahle, S.; Herden, T.; Stroh, C.; Mayor, M.; Schlickum, U.; Ternes, M.; Wahl, P.; Kern, K. Temperature and magnetic field dependence of a Kondo system in the weak coupling regime. *Nat. Commun.* **2013**, *4*, No. 2110.

(39) Ara, F.; Qi, Z. K.; Hou, J.; Komeda, T.; Katoh, K.; Yamashita, M. A scanning tunneling microscopy study of the electronic and spin states of bis(phthalocyaninato)terbium(III) (TbPc2) molecules on Ag(111). *Dalton Trans.* **2016**, *45*, 16644−16652.