Low-temperature scanning tunneling microscopy study of double-decker DyPc$_2$ on Pb Surface

Yang He,$^a$ Yajie Zhang,$^a$ I-Po Hong,$^b$ Fang Cheng,$^a$ Xiong Zhou,$^a$ Qian Shen,$^a$
Jianlong Li,$^a$ Yongfeng Wang,$^{*a,b}$ Jianzhuang Jiang$^c$ and Kai Wu$^a$*

Low-temperature scanning tunneling microscopy (STM), scanning tunneling spectroscopy and dI/dV mapping techniques have been applied to study double-decker DyPc$_2$ molecules on Pb(111) films grown on silicon wafers. The DyPc$_2$ molecules firstly self-assemble into a monolayer where two neighbouring molecules form an azimuthal angle of 6°. Scattered DyPc$_2$ molecules in the second layer can be stabilized on top of the first self-assembled monolayer, adopting a co-axial alignment with the underlying molecules. With the reference to the new layer assembled by Pc molecules generated by the cracking of DyPc$_2$ molecules on the substrate at or above room temperature, the molecular configuration can be directly deduced from STM imaging. The two Pc ligands in the same double-decker molecule rotate 45° with respect to each other. The dI/dV mapping of the individual DyPc$_2$ molecules in the second layer shows that they can appear as either four-lobed or eight-lobed features in the STM images depending on the bias voltage employed.

Introduction

Because of their important properties, lanthanoid-phthalocyaninate molecules have been intensely studied since the 1980s.$^{1-8}$ These decker-like lanthanide coordination compounds represent a novel family of single molecule magnets (SMMs).$^{9-22}$ Magnetic measurements of their powder or crystal samples have confirmed their potential to operate as ‘bits’ for future miniature information storage devices because of their slow magnetic relaxations.$^{9-20,23-25}$ Unlike the SMMs based on multi-nuclear transition metal ion compounds, the lanthanide deckers behave like a ‘magnet’ because of their 4f electrons sandwiched in the ligand field. In multi-nuclear transition metal compounds such as Fe$_8$, Mn$_{12}$ and so on, the magnetic anisotropy originates from the ion–ion magnetic interactions. Many double-, triple- and quadruple-decker lanthanoid-phthalocyaninate molecules have been studied using magnetic susceptibility measurements, nuclear magnetic resonance, electron spin resonance and theoretical calculations. Recently, Yamashita et al.$^{21-24}$ showed that the ferromagnetic dipolar interaction of the symmetric spin system containing two Tb ions in one molecule of crystalline triple-decker Tb$_2$(obPc)$_3$(Pc is phthalocyanine) gave rise to a new magnetic relaxation process, offering an opportunity to tune its quantum properties.

The construction of memory units with SMMs relies on ion–ion or molecule–molecule organization at the molecular scale, which depends on the ability to control individual SMM molecules on surfaces. Scanning tunneling microscopy (STM) has been widely used to study SMMs on single crystal surfaces because of its capabilities of atomic resolution, tip manipulation and tunneling conductance measurement. In 2006, Ishikawa et al.$^{21}$ first reported a room-temperature STM study on the organization of TbPc$_2$ molecules on highly oriented pyrolytic graphite. Afterwards, double-decker lanthanoid-phthalocyaninate molecules on Cu$_{11}$ and Au$_{11}$ were examined with STM under ultrahigh vacuum and low temperature conditions. Because of the planar or pseudo-planar conformation of the aromatic ligand on the outskirts of the metal surfaces, bis(phthalocyaninato)lanthanide molecules were scrutinized with STM to investigate their molecular orbitals, molecular configurations and spin states. Interestingly, both SMM and non-SMM deckers such as CePPT$_2$ and Ce$_2$PPT$_3$ (PPT is tetraphe- nylporphyrin) can be manipulated by the STM tip to rotate the upper ligand, Pc or PPT, like a ‘molecular rotor’ around the molecular axis perpendicular to the ligand planes.$^{30,31}$

Such a family of molecules becomes more and more appealing for scientists to explore with STM their electron spin and possible magnetism, which still remain elusive. This type of study typically involves an isolated molecule or a self-assembled monolayer (SAM) on the surface. Molecules in the monolayer normally form an assembling structure determined by the balance of the molecule–molecule and molecule–substrate
interactions. TbPc$_2$ and YPc$_2$ are reported to form SAMs on Au(111). However, each DyPc$_2$ molecule cracks by losing a Pc ligand upon thermal deposition on the same surface, as reported by Zhang et al. A couple of the SMM-assembled monolayers have been studied to date. The molecular configuration of the decker molecules in the monolayer is a subject of considerable debate because their lower Pc ligand is buried underneath, and only the upper Pc ligand can be directly observed. Their configurations could be drastically different from those in the molecular crystals, and may seriously affect their properties including electron spin. For example, the Kondo effect may be quenched upon direct contact with metal substrates so that it is difficult to explore their electron spin state with STM. In such a situation, isolated decker molecules sitting on the first monolayer are required so that the first monolayer acts as a buffer layer.

In this work, we sublimated intact or cracked DyPc$_2$ molecules onto a Pb film grown on a silicon wafer. We observed a coaxial stacking mode of the second layer double-decker DyPc$_2$ molecules on the underlying ones in the first layer, which is quite different from the stacking mode in its molecular crystal. Via the $\pi-\pi$ stacking mode, the lower Pc ligand of the DyPc$_2$ molecule in the second layer well matched the upper Pc ligand of the underlying molecule in the first layer. The two Pc ligands in the same double-decker DyPc$_2$ molecule rotate by 45° against each other around the molecular axis perpendicular to the Pc planes in both the first and second layers on the Pb substrate.

### Results and discussion

The prepared Pb film is about 4–5 nm in thickness and tens of nm to 100 nm in size. Its exposed surface is (111), as shown by the inset in Fig. 1a. The DyPc$_2$ SAM is balanced by the molecule–molecule and molecule–substrate interactions via van der Waals forces and possesses a pseudo-square molecular lattice (Fig. 1a). Each DyPc$_2$ molecule appears to be eight-lobed, in agreement with previous reports for LnPc$_2$ (Ln is Tb, Y). According to density functional theory (DFT) calculations in the literature, the density of state of the double-decker lanthanoid-phthalocyanine molecules appears to be in four groups of paired lobes when viewed from the top. For these sandwiched molecules adsorbed on metal surfaces, only the upper Pc ligand can be probed by STM. It is assumed that the lower and upper Pc ligands in the same molecule form an azimuthal angle of ~45° with respect to each other based on the crystal data and calculations by Yamashita et al. The line profile (Fig. 1b) shows that each DyPc$_2$ layer in the STM image is about 0.30 nm in apparent height with the exception of the height step of about 0.10 nm, which is assigned to the Pc layer formed by the cracking of the DyPc$_2$ molecule during its thermal sublimation. This will be further discussed later in this paper.

The DyPc$_2$ SAM on Pb looks like a ‘chessboard’ (Fig. 2a). The unit cell is a square with the parameters: $a = b = 2.0$ nm, $\theta = 90°$. Normally, there are two types of molecular orientation in the double-decker SAM, forming an azimuthal angle in the STM image. For example, the upper Pc ligand in the TbPc$_2$ molecule rotates azimuthally by about 15° with respect to its nearest neighbouring counterpart on Au(111). On Pb, however, the corresponding azimuthal angle is ~6° (Fig. 2b). This implies that the assembling structure of the double-decker DyPc$_2$ molecules depends on the substrate. However, it is also possible that during assembly, the upper Pc does not form an angle of 45° against the lower one in the same molecule, which then makes the difference in the azimuthal angle between both Pc ligands. Thus, the two Pc ligands in the same double-decker molecule could rotate against each other by different angles because of their confinement in the SAM. Because the lower Pcs are invisible in the STM images, it is difficult to determine the

### Experimental

All experiments were carried out on a Unisoku low-temperature STM with a base pressure of $<1 \times 10^{-10}$ Torr. The STM can be cooled with liquid N$_2$ or He down to 77 K or 4.3 K, respectively. A heavily doped Si(111)-7×7 wafer (n-type with a resistivity of 0.001–0.005 Ω cm) was cleaned by cycles of flashing up to 1473 K. Pb was deposited onto the cleaned Si wafer at 473–573 K from a homemade Ta boat while the substrate was kept at room temperature (RT). After deposition, the sample was annealed at RT for 1–2 hours. The Pb surface structure was checked with STM at 4.3 K. All STM experiments were performed by using W tips obtained by electrochemical corrosion in a 1 mol L$^{-1}$ NaOH solution. The DyPc$_2$ source (K-cell with a shutter, Unisoku) was heated to 383 K for sublimation while the substrate was cooled by liquid N$_2$. Specifically, the substrate was quickly transferred from the liquid-He temperature zone to the upper chamber at RT for molecular sublimation (about 1 min) and subsequent annealing (about 2 min), during which the substrate temperature was increasing. The substrate was then swiftly transferred back to the STM chamber. The STM temperature, monitored by a diode near its tip, initially increased to 18 K and then fell to 4.3 K at which point both the STM and scanning tunneling spectroscopy (STS) measurements were carried out. Such a procedure was shown to be very efficient in preparing SAMs on Pb films. It also has the advantage of preparing scattered DyPc$_2$ molecules on the SAM so that the molecular configuration can be studied in detail.

![Fig. 1](image.png)

Fig. 1  a) STM image of the DyPc$_2$ SAM with scattered DyPc$_2$ molecules on top. $V_{bias} = -0.99$ V, $I_{feedback} = 22$ pA. Inset: atomic lattice structure of the Pb(111) film on a Si(111)-7×7 wafer. (b) Line profile along the black dashed line in (a). Different height steps represent the existence of the cracked Pc layer, the 1$^{st}$ layer of DyPc$_2$ SAM and the scattered DyPc$_2$ molecule in the 2$^{nd}$ layer, as indicated in the figure.
In the literature, studies normally assume that the upper Pc rotates by 45°C14 against the lower Pc in the same double-decker molecule.9–20 Without direct experimental evidence, this assumption may be risky. Later on, we will clarify this issue using the recorded STM images.

In our experiments, the double-decker DyPc2 molecules in the second layer sit sparsely on top of the initial DyPc2 SAM (Fig. 1). The DyPc2 molecules in the second layer also show the eight-lobed protrusion feature (Fig. 3). Interestingly, these scattered DyPc2 molecules share the C4 axis with the packed ones in the SAM, as shown by Fig. 3. If one assumes that both Pc ligands in the same DyPc molecule form an azimuthal angle of 45°, one would then deduce that the lower Pc ligand of the DyPc2 molecule in the second layer adopts a perfect π–π stacking mode with the upper Pc ligand of the DyPc2 molecule in the SAM (Fig. 3b). This stacking mode is quite distinct from that in the DyPc2 molecular crystal, where the LnPc2 molecules in different layers combine with each other in an edge-to-plane configuration with their molecular axes approximately perpendicular to each other.22 A similar co-axial stacking mode between the double decker LuPc2 molecules in neighbouring layers on the Ag(111) surface has been reported by Toader et al.23

When the DyPc2 molecules are sublimated onto the Pb substrate at RT or higher temperatures, a new unusual molecular layer appears (Fig. 4). The new molecular layer remains adjacent to the SAM and directly contacts the metal substrate.

**Fig. 2** (a) STM image of the DyPc2 SAM on Pb(111) showing the “chessboard” pattern. Vbias = −0.80 V, Ifeedback = 19 pA. The white square indicates the unit cell: a = b = 2.0 nm, θ = 90°. The filled circles (dark green) and squares (light purple) mark the neighbouring DyPc2 molecules with different orientations. (b) Zoomed-in STM image of two neighbouring DyPc2 molecules forming an azimuthal angle of 6°. The two groups of whole numbers from 1 through 8 indicate the eight lobes of these two DyPc2 molecules. (c) Schematic molecular model for the STM image in (a), showing the orientations of neighbouring DyPc2 molecules (dark green circle and light purple square) in the SAM. The unit cell is marked by the black square.

**Fig. 3** (a) STM image of an individual DyPc2 molecule on top of the first DyPc2 SAM. Black lines indicate the co-axial alignment of the top DyPc2 molecule with the underlying one in the SAM. The white and yellow crosses indicate that the top Pc ligand (white cross) of the DyPc2 molecule in the second layer forms an angle of 45° with respect to its counterpart in the SAM (yellow cross). Vbias = −0.90 V, Ifeedback = 39 pA. (b) Molecular model showing the co-axial alignment of two DyPc2 molecules in different layers. The dashed line indicates that the contacting Pc ligands (brown and blue) of these two DyPc2 molecules stick together via the π–π stacking mode.

**Fig. 4** (a) STM image showing the appearance of a new layer (in light blue) in addition to the DyPc2 SAM (purple) and scattered DyPc2 molecules (yellow) on top. Vbias = −1.0 V, Ifeedback = 19 pA. (b) Quasi-three-dimensional STM image of the same area as that in (a). (c) Line profile along the dashed lines in (a) and (b) showing the heights of the new Pc layer, the DyPc2 SAM and the scattered DyPc2 molecules, as indicated in the figure.
(Fig. 4a). Its quasi-three-dimensional image is given in Fig. 4b. The new layer is about 0.10 nm in height according to the line profile given in Fig. 4c. This height is less than half that of the DyPc2 SAM.

The molecular shape in the new layer (Fig. 4a) appears the same as that in the SAM (Fig. 1a) with the same square-like molecule lattice structure and unit cell parameters. This new layer could be either a Pc or DyPc layer generated by the cracking of the double-decker DyPc2 molecules on the heated Pb substrate during thermal sublimation.

The central protrusion of the molecule in the new layer is dark, as can be clearly seen in Fig. 5a. This could stem from either Pc molecules lying flat on the substrate or DyPc molecules with their Dy atoms remaining underneath the Pc molecules in direct contact with the Pb substrate. Zhang et al. previously suggested that DyPc was adsorbed on the Au surface with the Dy atom in direct contact with the substrate. They reported a height of about 0.16 nm for the DyPc molecule. In our case, however, the height of the new layer is only 0.10 nm (Fig. 4c). Therefore, we assign the new layer to the assembly of the Pcs rather than the DyPcs.

With the new Pc layer as a reference, we now have the opportunity to directly deduce the molecular configuration of the double-decker DyPc2 molecules in the SAM. As shown in Fig. 5b and c, the upper Pc ligand in the double-decker DyPc2 molecule in the SAM rotates by 45° with respect to the Pc molecules in the new layer (Fig. 5d). Since it seamlessly connects to the SAM, the new Pc layer simply follows the assembly pattern of the lower Pc ligands in the SAM of the double-decker DyPc2 molecules. Therefore, the upper and lower Pc ligands of the double-decker DyPc2 molecule in the SAM must rotate by 45° against each other.

In previous reports, double-decker DyPc2 molecules on various metal surfaces appeared to be either four-lobed or eight-lobed in STM images, depending on the scanning parameters. This can be somewhat misleading in the determination of molecular morphology based solely upon STM imaging. To verify the morphology, we performed both topological imaging and dI/dV mapping of an individual DyPc2 molecule in the second layer (Fig. 6). The topological image shows an eight-lobed feature (Fig. 6a) with a dim central protrusion at a sample bias voltage of −1.0 V. This means that the STM tip is sensing the highest occupied molecular orbital (HOMO), which is in agreement with the DFT-calculated HOMO of the DyPc2 molecule in free space (Fig. 6b). This lobed feature of the molecule in STM imaging can change with the bias voltage.

The STS results at a constant feedback current of 44 pA are shown in Fig. 6c. Four spectroscopic features positioned at −0.51, 0.77, 1.75 and 1.92 V can be clearly observed. They agree with the energy levels near the Fermi level for a DyPc2 molecule weakly adsorbed on a metal substrate. In constant height mode, the dI/dV mappings of the DyPc2 molecule at the four distinct bias voltages marked in the STS curve in Fig. 6c are given in Fig. 6d–g. At large positive bias voltages such as 1.92 and 1.75 V, the double-decker DyPc2 molecule appears four-lobed. At a bias voltage of 0.77 V, one can barely recognize the eight-lobed feature. However, at a bias voltage of −0.51 V or below, the sharp eight-lobed feature of the molecule can be clearly identified (Fig. 6g and 2b).

**Conclusions**

In summary, intact double-decker DyPc2 molecules have been successfully sublimated onto a Pb(111) film grown at temperatures below 77 K. Proper annealing of the substrate led to the DyPc2 SAM, which possessed a quasi-square-like molecule lattice structure on Pb. Two neighbouring DyPc2 molecules in the SAM formed an azimuthal angle of 6°, which is different from the angle on other metal surfaces. Scattered DyPc2 molecules existed on top of the SAM and adopted a co-axial alignment with their underlying molecules. The contacting DyPc2 molecules in neighbouring layers packed in a π–π stacking mode between the two contacting Pc ligands, different from the packing mode in its molecular crystal. When the Pb substrate was kept at RT or above, some DyPc2 molecules would crack into...
Pc and DyPc fragments. The assembled Pc molecules seamlessly connected to the DyPc2 SAM and followed the assembly pattern of the lower Pc ligand in the SAM. This offered us the opportunity to directly determine the molecular configuration of the DyPc2 molecule in the SAM assembled on a Pb substrate. The two Pc ligands in the same DyPc2 molecule adopted an azimuthal angle of 45°. $dI/dV$ mapping of the individual DyPc2 molecule sitting on top of the SAM showed that it could appear four-lobed or eight-lobed in its STM image, depending on the bias voltage employed. At a bias voltage below $-0.51$ V, the eight-lobed feature of the double-decker DyPc2 molecule could be clearly seen. The DyPc2/Pb system may serve as a useful model to study its electron spin state and Kondo effect on metal surfaces, further advancing our understanding of SMM properties. Such a study is underway in our laboratory.

Acknowledgements

This work was jointly supported by National Natural Science Foundation of China (51121091, 21133001, 21261130090, 51121091, 21228301) and Ministry of Science and Technology (2013CB933400, 2011CB808702), China.

Notes and references