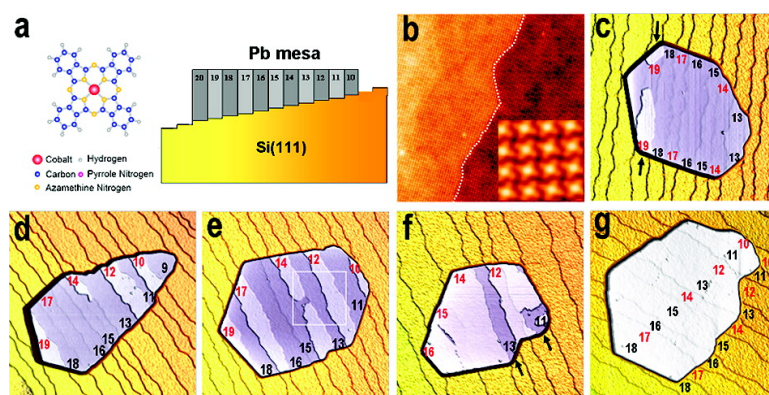


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## Quantum Size Effect Directed Selective Self-Assembling of Cobalt Phthalocyanine on Pb(111) Thin Films

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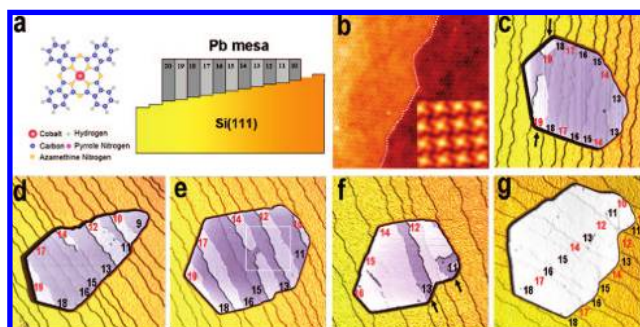
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Magnetic organic molecules, owing to their unprecedented ability of self-assembly of ordered nanostructures on various metals,<sup>1–3</sup> can be utilized to construct magnetic architectures. These well-defined molecular structures are promising and important for the development of emerging molecular spin electronics and for understanding and manipulation of magnetic coupling between molecules and molecule–metal interaction.<sup>4,5</sup> In this regards, quantum size effects (QSE) in a great number of nanostructured materials provide a novel approach to tailor molecule–metal substrate interaction and could be deemed to play an important role in the process of molecular self-assembly.<sup>6</sup> For a two-dimensional (2D) metallic thin film on a semiconductor substrate, such as Pb film on Si, quantized energy levels are formed because of strong electron confinement in the film normal direction by the semiconductor bandgap and vacuum barrier, which could significantly modify electronic structure near the Fermi level and physical properties of the films.<sup>7–10</sup> Very recently, thickness-dependent oscillatory oxygen adsorption and oxidation of the Pb(111) films were observed and it provides a direct evidence on the influence of QSE on surface chemical reactivity.<sup>11</sup> A problem with this study is that it is difficult to identify the chemical nature of oxygen adsorbents. More critically, surface kinetic processes, such as adatom diffusion, could be modified by QSE as well,<sup>9,10</sup> and make the interpretation of the observed thickness-dependent behaviors complicated.

In this Communication, we report an unambiguous evidence for quantum modulation of surface adsorption by using cobalt phthalocyanine (CoPc) as a probing molecule. We show that CoPc molecules can be identified unequivocally by an atomically resolved scanning tunneling microscopy (STM) image of the molecules adsorbed on the Pb(111) thin films. In addition, because of very long diffusion length, the adsorption sequence of the CoPc molecules on the Pb mesas is merely determined by film thickness, which rules out the contribution of a surface kinetic process. This work further provides a technologically feasible way to modulate molecular magnetic coupling by quantum confinement of a nanostructure since its physical size, such as the film thickness, can now be precisely and conveniently controlled with current nanotechnology.

The experiments were performed in an ultrahigh vacuum low temperature STM system with a base pressure of  $2 \times 10^{-10}$  Torr. Commercial Si(111) wafers with a resistivity of  $0.01 \Omega \cdot \text{cm}$  were used as substrate, and the clean Si(111)- $7 \times 7$  surfaces were prepared by flash annealing to  $\sim 1200$  °C while keeping the vacuum better than  $1 \times 10^{-9}$  Torr. Pb (99.999%) was deposited on the Si(111)- $7 \times 7$  surfaces held 200 K from a Knudsen cell at a rate of 0.32 ML/min. After the samples were warmed up to room temperature, wedge-shaped Pb islands (mesas) form,<sup>11</sup> as schematically shown



**Figure 1.** (a) The schematic structure illustrations of both the CoPc molecules and Pb mesas grown on Si(111) substrate. (b) STM image of the CoPc SAM formed on the Pb mesa. The insert is a high resolution image showing the four-lobe structure of CoPc. The dotted white line indicates a buried Si step. (c–g) Sequential STM images showing the morphology evolution of Pb mesa surfaces with increasing CoPc coverage from 0.1 (c) to 1 ML (g). The yellowish background corresponds to the Si substrate; the gray-colored islands are the Pb mesas, while the brightest features the SAMs of CoPc on Pb mesas. The digital number (10, 11, 12 . . .) in all the figures dictates the Pb film thickness of the corresponding region measured in a unit of one atomic monolayer. The red numbers indicate the preferential thickness, and the black numbers indicate the unfavorable thickness by QSE. All images were acquired at a sample bias of 5 V and a tunneling current of 100 pA. Image size: (b) 600 nm  $\times$  600 nm, (c) 800 nm  $\times$  800 nm, (d) 700 nm  $\times$  700 nm, (e) 500 nm  $\times$  500 nm, and (f) 500 nm  $\times$  500 nm.

in Figure 1a. The mesas have a flat-top (111) surface and laterally they can extend over several Si steps at the Pb/Si interface. CoPc molecules (Aldrich Inc.) were deposited from a homemade Ta boat on the substrate held at room-temperature. All STM measurements were performed at 80 K in the constant current mode and by using electrochemically etched polycrystalline W tips.  $dI/dV$  maps, which are proportional to local density of states (DOS), were recorded by adding a modulation voltage (5 mV, 3 kHz) to the specific sample bias ( $-6$  mV) and detecting the signal by a lock-in amplifier.

Figure 1a shows the structure model of CoPc and the schematic drawing of the Pb mesa grown on Si(111)- $7 \times 7$  surface. At room temperature, CoPc molecules form ordered self-assembled monolayer (SAM) on the top of the mesa as shown in Figure 1b. Each molecule is imaged as a uniform four-lobe structure with a protrusion on the center of the cobalt ion due to enhanced density of states in the empty  $3d_{z^2}$  spin–orbital of cobalt (see the insert of Figure 1b),<sup>1,4</sup> in agreement with the molecular structure model in Figure 1a.

The series STM images from Figure 1c to Figure 1g display the morphology evolution of the Pb mesa surfaces with increasing CoPc coverage. In the images, the brightest features on the gray-scaled islands correspond to the SAMs (for their structure detail, see Figure 1b). We can clearly see that there is a distinct thickness-dependent adsorption behavior. At very low coverage (0.1 ML) (Figure 1c),

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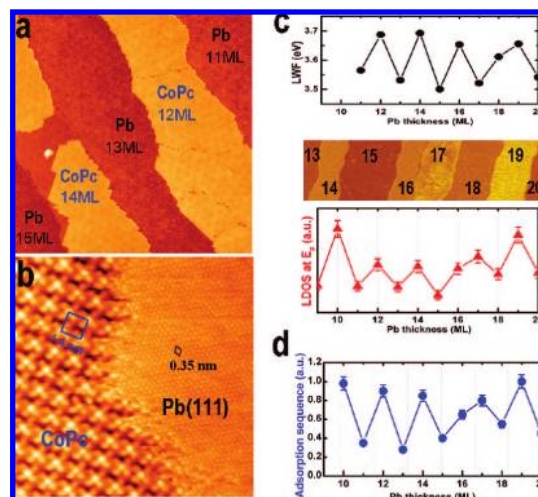
adsorption exclusively takes place at 19 ML, while the rest surface at other thicknesses (from 13 to 18 ML) is completely free of molecules. This suggests that the diffusion barrier of CoPc on the Pb(111) surface is very small, which is essential in promoting the preferential adsorption and in identifying the QSE, compared to the case of oxygen.<sup>11</sup> After the 19 ML terrace is fully covered with molecules, 10 ML will be the next thickness of choice, and then 12 ML, 14 ML (Figure 1d). At 16 ML, the adsorption preference switches to the odd-numbered thickness, 17 ML (Figure 1e). With further increasing coverage, other odd-numbered thicknesses will be sequentially occupied by molecules, in order of 15, 11, 13 ML (Figure 1f). Finally, the whole mesa surface is covered with one monolayer molecules (Figure 1g). In summary, the adsorption is oscillatory with a period of 2 ML; below 16 ML, adsorption on even numbered thickness is preferred, and above 16 ML the preference switches to odd-numbered layers.

The observation documents a transition thickness 16 ML, which is the beating point that can be well-understood under the Sommerfeld–Bohr quantization rule for a metal (Pb) thin film,<sup>12</sup>  $2k(E)Nd_0 + \theta(E) = 2n\pi$ . A consequence of the rule is that for a given electron energy  $E$ , only a certain set of film thicknesses satisfies the formula and is stable. For Pb,  $k_F$  (the Fermi wave-vector) and  $d_0$  (the lattice constant along the film normal direction) are  $0.611 \text{ \AA}^{-1}$  and  $2.86 \text{ \AA}$ , respectively, which will lead to a 1.8 ML oscillation period in the film stability and surface reactivity. Since film thickness is always measured as an integer (in unit of atomic layers), the small difference of 0.2 ML between 1.8 and 2 ML results in a 9 ML beating pattern, which shows up at 16 ML as an odd–even transition thickness in stability and surface reactivity (the next transition will appear at 25 ML, as shown in our previous study<sup>8,11</sup>).

The thickness-dependent oscillating adsorption is better seen in Figure 2a, which is zoomed from Figure 1e, where SAMs are observed on even-numbered thicknesses (12 and 14 ML) while no molecule on the odd-numbered thicknesses (11, 13, and 15 ML). From the undisturbed neighboring Pb(111)- $1 \times 1$  surface (Figure 2b), the SAM can explicitly be identified to have a 4-fold symmetry with a unit cell of  $1.4 \text{ nm} \times 1.4 \text{ nm}$ , and the structure of the molecules is well preserved. The observation demonstrates that neither kinetic process such as diffusion nor interfacial reaction is involved in the oscillating behavior. Hence, the interpretation of data in terms of QSE becomes straightforward.

The correlation between the thickness-dependent adsorption and QSE is dictated in Figures 2c and 2d. The QSE modulates the electronic structure of the films, leading to a thickness-dependent up–down oscillating local work function and local DOS( $E_F$ ), as also demonstrated in our previous studies.<sup>5,8,11</sup> Figure 2d shows the adsorption sequence of CoPc molecules as a function of Pb film thickness. By comparing Figure 2c with Figure 2d, it is immediately evident that there is a clear one-to-one correspondence between the adsorption sequence and QSE-modulated local DOS( $E_F$ ); the higher the local DOS( $E_F$ ) is, the earlier the adsorption takes place.

In conclusion, thickness-selective adsorption of CoPc molecules on quantum confined Pb thin films has been observed, which is used as an unassailable proof for QSE modulated adsorption and



**Figure 2.** (a) STM image zoomed from the marked area in Figure 1e showing the preferential adsorption of CoPc molecules at 12 and 14 ML, and no molecule adsorption at 11, 13, and 15 ML where bare Pb surface can be seen. (b) High resolution STM image ( $15 \text{ nm} \times 15 \text{ nm}$ ) showing the structures of both CoPc molecules and the Pb(111)- $1 \times 1$  surface. The unit cells of the CoPc SAM and the uncovered Pb(111)- $1 \times 1$  surface are indicated by the square and rhombus, respectively. (c) Local work function (upper panel),  $dI/dV$  map (middle panel), and local DOS( $E_F$ ) (lower panel) as a function of film thickness from 10 to 20 ML, measured by using lock-in technique with a bias modulation of 5 mV at 3 kHz. The sample bias was set to  $-6 \text{ mV}$  in the  $dI/dV$  measurement. (d) Measured adsorption sequence of CoPc molecules on Pb(111) films at different thicknesses from 10 to 20 ML.

self-assembly on a metal surface. The ability of regulating surface adsorption by QSE opens a novel avenue to tailor magnetic coupling of various molecules and may find applications in emerging molecule-based spintronics.

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