

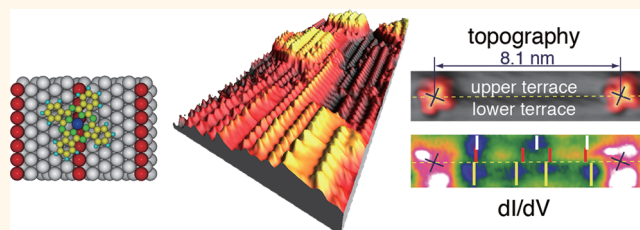
Highly Ordered Cobalt–Phthalocyanine Chains on Fractional Atomic Steps: One-Dimensionality and Electron Hybridization

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ABSTRACT Precisely controlled fabrication of low-dimensional molecular structures with tailored morphologies and electronic properties is at the heart of the nanotechnology research. Especially, the formation of one-dimensional (1D) structures has been strongly desired due to their expected high performance for information processing in electronic/magnetic devices. So far, however, they have been obtained by tough and slow methods such as manipula-



-tion of individual molecules, which are totally unsuited for mass production. Here we show that highly ordered cobalt–phthalocyanine chains can be self-assembled on a metal surface using fractional atomic steps as a template. We also demonstrate that the substrate surface electrons, which can be confined by cobalt–phthalocyanine molecules, can propagate along the step arrays and can hybridize with the molecular orbitals. These findings provide a significant step toward readily realization of 1D charge/spin transport, which can be mediated either directly by the molecules or by the surface electrons.

KEYWORDS: one-dimensional · self-assembling · phthalocyanine · stacking-fault · surface states · quantum well

Establishing the way to control the fabrication of low-dimensional structures is indispensable in realizing highly efficient and functional nanoscale devices. The self-assembly of organic molecules and/or atoms on atomically well-defined surfaces is one of the most promising approaches to a repeatable fabrication of nanostructures.^{1–3} This so-called bottom-up approach aims to guide the assembly of adsorbates into surface structures with controlled shape, size, and location through inherent processes such as adsorption, surface diffusion, and nucleation. So far, a variety of atomic-scale templates, such as reconstructed clean surfaces^{4–16} and regular monatomic (MA) step arrays on vicinal surfaces^{17–27} have been utilized for self-assembly processes. Through this technique, organic molecules form two-dimensional (2D) molecular networks,^{6,7,13} 2D ultrathin films,^{6,9,11,14,15} and quasi-one-dimensional (1D) structures^{6,7,10,12,15,15,25–27} on these surfaces. The morphology of the

adsorbed molecular layer depends on the atomic structure of the substrate, the relation between the intermolecular and molecular–substrate interactions, and the shape of the molecule.

Among the low-dimensional structures, the 1D system has an advantage over the 2D system in terms of the efficiency of charge and/or spin transport,²⁸ since it is restricted along a particular direction (for schematic illustration, see Figure 1a,b). One-dimensionality is also important to enhance the interaction between the molecules and to make the information transfer through them more efficient. For example, an indirect charge/spin intermolecular interaction can be dominated by Friedel or Ruderman–Kittel–Kasuya–Yoshida (RKKY) interactions in the presence of metallic substrate.²⁹ In this case, the interaction strength is proportional to r^{-n} , where r is the intermolecular distance and n is the dimension of the system, thus making the reduction of dimensionality

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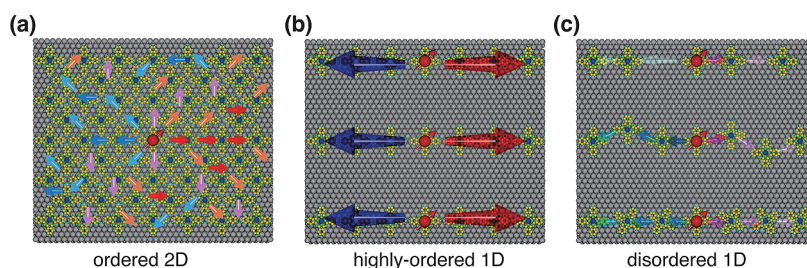


Figure 1. Transport of electric and magnetic information. The way of charges and/or spins propagations in a (a) 2D molecular network, a (b) highly ordered 1D chain and (c) disordered 1D structures. The transport efficiencies of charges and spins are high in panel b but low in panel c because of the disturbance from the disordering.

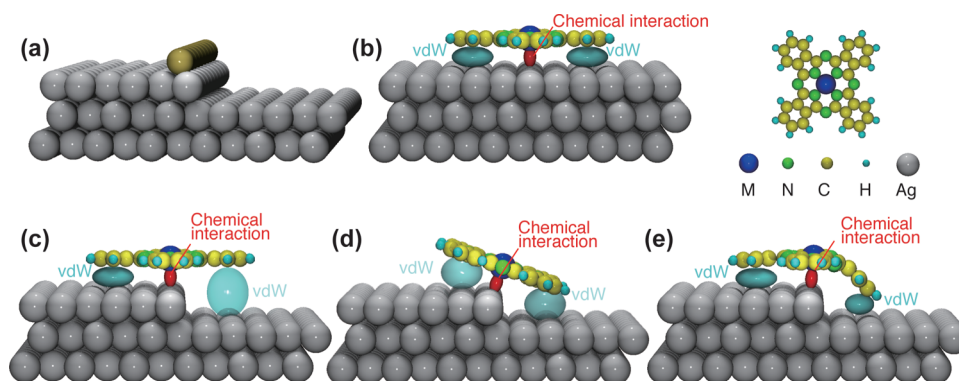


Figure 2. Phthalocyanine molecules adsorption. Schematic illustrations of (a) an 1D atomic chain adsorbed on a MA step, (b) a MPC molecule adsorbed on a flat surface, nondistorted MPC molecules (c) with the molecular plane parallel to the surface and (d) with tilted angle, and (e) a wrapped MPC on a MA stepped surface. The chemical interaction between the MPC molecule and surface atoms is indicated by red and the vdW interaction by light blue. The difference in the light blue tunneling represents the difference in the vdW force.

more favorable.^{30,31} The quality of the 1D structure is also a key factor for the transport efficiency because the presence of disorder apparently disturbs the transport process (Figure 1c).

For adsorbed atoms, MA stepped surfaces lead to the formation of well-ordered straight atomic chains due to their template effect (Figure 2a).^{18,20–23} On the contrary, organic molecules only form either disordered chains^{15,17,24–26} or a quasi-2D structure¹⁹ on MA stepped surfaces. This can be understood as follows by taking a metal–phthalocyanine (MPC) molecule for instance (Figure 2b). In contrast to adatoms interacting locally with the substrate, the adsorption of MPC molecules is more complicated; it involves the chemical bonding at the center metal atom and the van der Waals (vdW) force at the Pc ligands. Figure 2 panels c–e schematically show the adsorption of nondistorted (c,d) and distorted (e) MPC molecules on MA steps. These figures suggest that vdW interaction between the MPC and the surface becomes weaker in the case of panels c and d, and that, in the case of panel e, the MPC would be energetically unstable due to its large distortion. Of these three possibilities, the adsorption geometry of Figure 2d has been reported for Au MA steps.^{25,26} However, MPC molecules can have various rotation angles since the adsorption site of the benzene rings is not determined

because of the weakened vdW force. This also leads to inhomogeneous spacing between neighboring molecules. As a result, the transport of charges and spins through molecular chains will be severely hindered, as shown above in Figure 1c. A quasi-1D molecular chain has been reported to be formed on a 2D molecular sheet covered Ag(111) surface,^{32,33} but the charges and spins would mainly pass through the 2D layer in this case. Thus it is highly desirable to use another form of template to realize highly ordered molecular chains on a substrate with 1D electronic structure.

In this study, we demonstrate the first successful formation of self-assembled highly ordered cobalt-Pc (CoPc) molecular chains on a substrate with 1D electronic structure. This gives a major step toward the realization of one-dimensional charge/spin transport in organic devices.

RESULTS AND DISCUSSION

Formation of 1D CoPc Molecular Chains. To realize highly ordered 1D organic molecular chains, a surface with regular step arrays whose step height is smaller than that of atomic steps is advantageous. This is because the adsorbed molecule can interact with the surface through both chemical bonding and vdW forces while a molecular distortion can be suppressed compared to

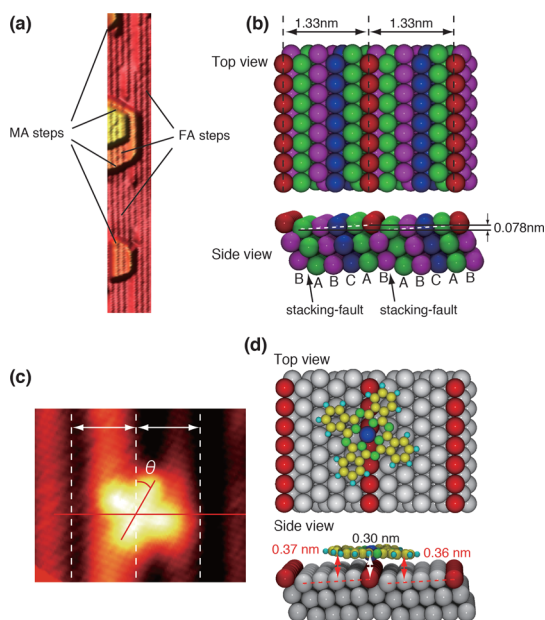


Figure 3. Adsorption site of a cobalt-phthalocyanine molecule: (a) a $70 \text{ nm} \times 10 \text{ nm}$ STM image ($V_{\text{sample}} = +1.5 \text{ V}$ and $I = 20 \text{ pA}$) and (b) schematic illustration of a striped Ag surface; (c) STM image of a CoPc molecule adsorbed on the striped Ag surface ($V_{\text{sample}} = +1.0 \text{ V}$ and $I = 20 \text{ pA}$); (d) top and side views of the optimized computational model of a CoPc molecule adsorbed on the striped surface. The numbers in the side view figure of panel d indicate the height differences between the C atoms of the benzene rings and the surface Ag atoms and that between Co and the step edge Ag atom.

that on MA steps. Ag films grown on $\text{In/Si}(111)-(4 \times 1)^{27}$ satisfy this requirement; they have regular step arrays with a height of 0.078 nm ($1/3$ of the MA height), accompanying $\text{Ag}(111)$ terraces with a width of 1.33 nm (five-atom wide). Figure 3 panels a and b show a scanning tunneling microscopy (STM) image of this surface and a schematic illustration of its atomic structure, respectively. As shown in Figure 3b, fractional atomic (FA) steps are induced by stacking-faults. Their stability has been attributed to the good lattice matching between the striped Ag and $\text{In/Si}(111)-(4 \times 1)$ surfaces and the small stacking-fault energy of Ag.³⁴ In the following, this structure is referred to as a striped Ag surface.

An STM image of a single CoPc molecule adsorbed on the striped Ag surface is shown in Figure 3c. The direction of the Ag stripes and the orientation of the adsorbed CoPc are clearly seen, and the angle between the diagonal axis of CoPc and the stripe direction (θ) is determined to be 30° . By analyzing more than 1250 CoPc molecules, we found that $\sim 82\%$ of the adsorbed molecules have $\theta = \pm 30^\circ$ as shown in Figure 3c, $\sim 7\%$ have $\theta = 0^\circ$, $\sim 10\%$ have $\theta = \pm 45^\circ$, and the remaining $\sim 1\%$ does not belong to any of these angles. Note that the above positive and negative values of θ are equivalent due to the mirror symmetry at the step edge. Furthermore, Figure 3c shows that the center

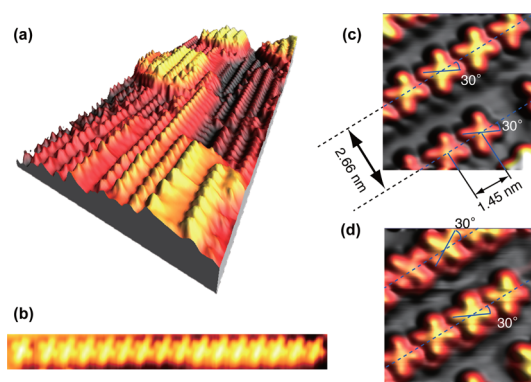


Figure 4. Formation of cobalt-phthalocyanine molecular chains: (a) a $30 \text{ nm} \times 60 \text{ nm}$ STM image of CoPc adsorbed striped Ag surface; (b) the rotation angle is unique in one molecular chain; (c) high-resolution $5 \text{ nm} \times 5 \text{ nm}$ STM images with two CoPc chains with (c) the same molecular orientations and (d) different orientations. All images were taken using $V_{\text{sample}} = +1.0 \text{ V}$ and $I = 20 \text{ pA}$.

of the molecule is located close to the stacking-fault fractional steps indicated by the white dashed lines.

A more detailed adsorption structure has been evaluated by performing density functional theory (DFT) calculations, where the vdW density functional (vdW-DF)³⁵ is adopted to include the vdW interaction between the CoPc molecule and the Ag substrate. Figure 3d shows the top and side views of the optimized $\theta = 30^\circ$ structure of CoPc molecule adsorbed on the striped Ag surface. In this figure, the central Co atom of the molecule is adsorbed on the bridge site of two Ag atoms located at the edge of the upper terrace. As shown in Figure 3d, this rotation angle brings the center of all the four benzene rings of CoPc near the hollow site of the Ag surface, as in the case of the CoPc adsorbed on a flat $\text{Ag}(111)$ surface.³⁶ The side view picture illustrates that the distance between the C atoms of the benzene rings far from the Co atom and the substrate Ag atoms ($\sim 0.37 \text{ nm}$ and $\sim 0.36 \text{ nm}$) and the one between the Co atom and the step edge Ag atom ($\sim 0.30 \text{ nm}$) are almost equal to those for a CoPc on a flat $\text{Ag}(111)$ surface. Consequently, the CoPc molecule is no longer planar and the benzene rings bend slightly toward the surface on a striped Ag. The similarities in the adsorption site and the distance from the surface of the benzene rings support the idea that the vdW force plays an important role for CoPc adsorption on the striped Ag substrate.

Figure 4 displays the STM images of a striped Ag surface covered with a half monolayer of CoPc. As shown in Figure 4a, highly ordered 1D molecular chains, which are aligned along the stripe direction, are formed on the surface. The maximum length of the molecular chains was approximately 25 nm , whose value is comparable with the domain size of the Ag striped structure obtained in the present study. The intermolecular distance within a molecular chain is 1.45 nm (Figure 4c). This value is close to the intermolecular distance of

1.4 nm in a monolayer CoPc film,³⁷ which corresponds to the interval of six Ag atoms at the step. The distance between adjacent molecular chains, 2.66 nm, is twice the length of the terrace width of the striped Ag surface, indicating that CoPc molecules adsorb at every second step edges. This reflects the fact that the lengths of the unit cell of a single crystal CoPc film ($\sim 2 \times 1.5 \text{ nm}^2$ in the case of monoclinic structure³⁸ and $\sim 1.4 \times 1.4 \text{ nm}^2$ in the case of monolayer film³⁷) is larger than the stripe width, although a single CoPc molecule ($\sim 1 \times 1 \text{ nm}^2$) can fit within a single Ag stripe.

The rotation angles of CoPc molecules are identical within one chain (Figure 4b). The unique rotation angle indicates the presence of intermolecular interaction within the molecular chain, which can be either a direct molecular–molecular interaction or an interaction *via* the substrate. In contrast, molecules of adjacent chains can have different rotation angles; they are either identical (Figure 4c) or different (Figure 4d). This indicates that the intermolecular interaction between adjacent chains is much weaker than that within a molecular chain, and therefore that the formed molecular chains have strong 1D characteristics. This should allow an efficient charge/spin transport through the molecules as explained above.

Interaction between CoPc and Surface Electrons. The charge and spin states of molecules can be mediated by the electronic states of the substrate surface. This has been recently demonstrated by fabricating Fe atomic wire on a 2D Cu surface by atom manipulation, where the magnetic states of individual adatoms were observed using spin-polarized STM.³¹ However, the interaction between adatoms was very weak, which required an operation temperature as low as 300 mK. As mentioned above, such interaction would be greatly enhanced for a 1D system, that is, when the substrate electrons propagate in a 1D fashion. The electronic states of the MA stepped surface used in the former studies often show a 2D character,^{25,26} indicating that a MA stepped surface is not a good template for the present purpose. Regarding the striped Ag, a previous experimental study clarified the presence of 1D surface electronic states using the scanning tunneling spectroscopy (STS) technique,³⁹ which may be utilized for the spin/charge transport. However, it is still not clear how molecules interact with these 1D surface states. We therefore performed STS measurements on a striped Ag surface with CoPc molecules.

The uppermost image in Figure 5a shows the topography image of two CoPc molecules adsorbed on the same stripe, and the lower ones are the dI/dV images measured at the same position using sample biases (V_{sample}) between +0.3 and +0.55 V. A high dI/dV signal corresponds to a high local density of states (LDOS) on the surface. The position of the FA steps of the substrate are presented by the horizontal

yellow lines, and the positions of the molecules are indicated by the crosses in both the topography and dI/dV images. The intermolecular distance is 8.1 nm. As shown in the dI/dV images, the intensity at the positions of molecules becomes higher than that of the substrate for $V_{\text{sample}} > +0.4$ V. This indicates that the threshold energy of the lowest unoccupied molecular orbital (LUMO) of CoPc adsorbed on a striped Ag surface is located at an energy ~ 0.4 eV above the Fermi level.

For all energies between +0.325 and +0.550 V, clear differences in the dI/dV intensities are observed between the upper and lower terraces separated by the FA step. In the direction along the stripe, the intensity is almost constant at $V_{\text{sample}} = +0.325$ V and lower, but modulations appear at higher biases. The yellow vertical lines indicate the positions with low intensity at the lower terrace, the red ones are those at the step edge and the white ones are those at the upper terrace. In the right table, n_{lower} , n_{edge} , and n_{upper} denote the number of positions with low intensity at the lower terrace, step edge, and upper terrace, respectively. Figure 5b shows the cross sectional profile of the topography image and those of the dI/dV images measured with V_{sample} from +0.35 to +0.55 V on the lower terrace. The positions with low and high dI/dV intensities (indicated by blue and green colors, respectively) increase in number with increasing V_{sample} (see also the table of Figure 5a). This means that the surface electrons of the striped Ag substrate are quantized between the two CoPc molecules, and that the observed modulations are due to electron standing waves.⁴⁰ Figure 5c shows the topography image of four CoPc molecules adsorbed on the same stripe and its dI/dV image obtained at $V_{\text{sample}} = +0.55$ V. The number of node (low intensity position) increases for a longer intermolecular distance, suggesting the possibility to tune the quantized energies by manipulating the intermolecular distance.

As mentioned above, clearly different dI/dV intensities are observed for the lower and upper terraces of the Ag stripe separated by the FA step. This indicates that the surface electrons are confined within each terrace by the FA steps and cannot cross the step freely. The 1D surface electronic states of a striped Ag substrate agree well with the recent study,³⁹ in which the surface states are described by decoupled 1D states rather than by extended 2D Bloch states. The variation in the node positions in the transverse direction (*i.e.*, the lower and upper terraces and the step edge) may be attributed to different properties of the potential walls, because they are formed by different parts of the molecule (*e.g.*, π -orbitals of the ligands with different C–Ag distance, and d-orbital of the central Co atom).

The quantum confinement of a 1D surface electronic state by the CoPc molecules suggests that this system enables 1D electrostatic and/or magnetic

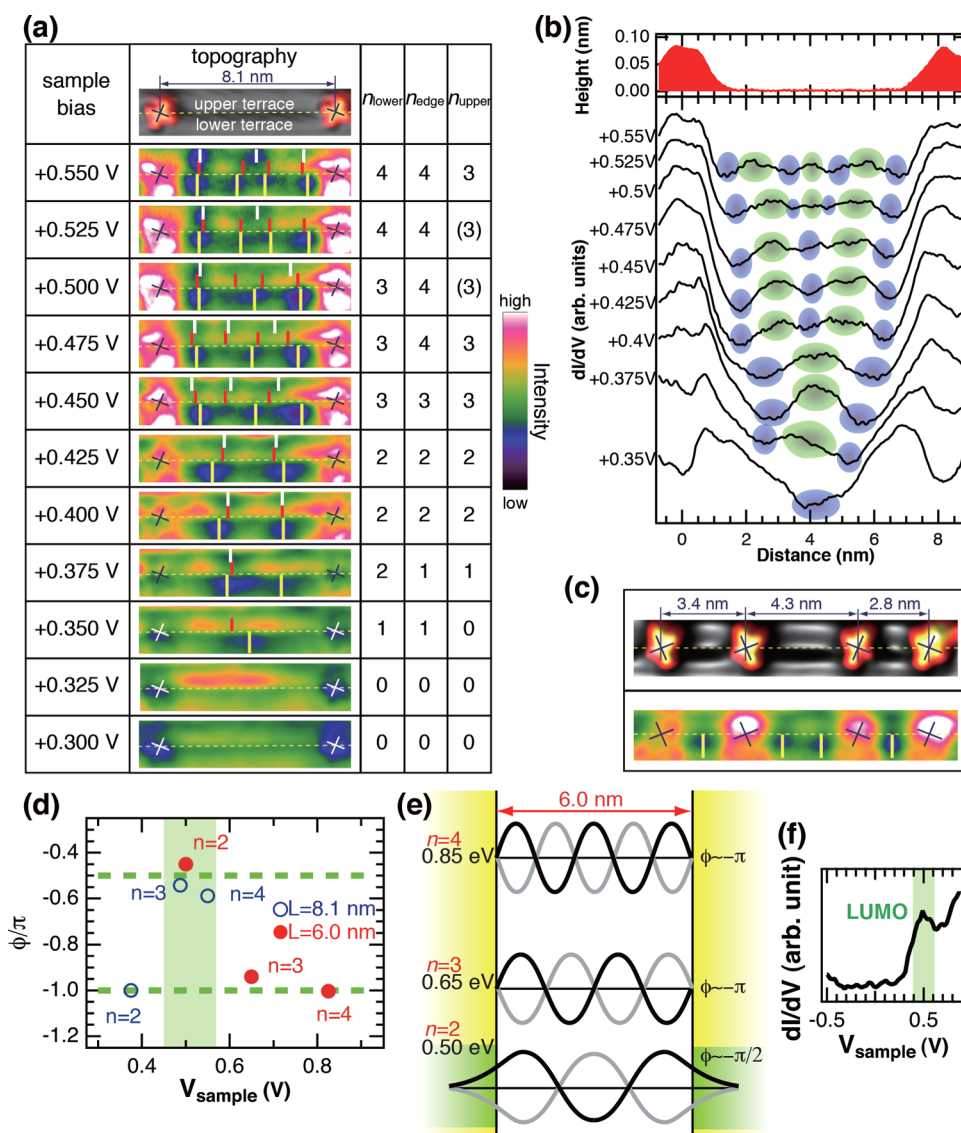


Figure 5. Surface electrons confined by cobalt-phthalocyanine molecules: (a) topography and dI/dV images of CoPc molecules adsorbed in the same stripe with an intermolecular distance of ~ 8.1 nm; (b) height profile obtained from the topography image, and cross sectional profiles of dI/dV images at different V_{sample} on the lower terrace; (c) topography and dI/dV images of CoPc molecules adsorbed with intermolecular distances of ~ 3.4 , ~ 4.3 , and ~ 2.8 nm obtained at $V_{\text{sample}} = +0.55$ eV; (d) phase shifts obtained by analyzing the standing waves at $L = 8.1$ nm and $L = 6.0$ nm using the phase accumulation model. n indicates the number of nodes of the standing wave; (e) schematic illustration of standing waves with different number of node at $L = 6.0$ nm; (f) dI/dV spectrum obtained on top of the benzene ring of a CoPc molecule with $V_{\text{sample}} = 0.5$ V.

intermolecular interactions intermediated by the surface electrons,^{41,42} and may be utilized for 1D charge/spin transport. This ability can be discussed in more details by understanding the interaction between the surface electrons and the molecular potential wall by the so-called phase accumulation model^{43,44} (also referred to as the Bohr-Sommerfeld quantization rule⁴⁵). In this model, the condition for forming a standing wave can be expressed as $\phi + kL = \pi n$, where L is the distance between the two molecules, k is the wavenumber, n is the quantum number (*i.e.*, the number of observed node at the lower terrace) and ϕ is the phase shift on reflection at the potential wall. To obtain the phase shift ϕ , we have analyzed two data sets of standing waves corresponding to $L = 8.1$ nm

and $L = 6.0$ nm. The result shows that (i) $\phi = -\pi$ at $V_{\text{sample}} = 0.375$ V and $V_{\text{sample}} > 0.6$ V, and (ii) $\phi = -\pi/2$ at $V_{\text{sample}} \approx 0.5$ V (Figure 5d). The quantized energy level of each quantum number is determined by the intensity of the quantum well state. That is, the intensity of the quantum well state is maximized at the quantized energy level, such as at $+0.375$ eV for $n = 2$ and $+0.45$ eV for $n = 3$ as shown in Figure 5b. The phase shift $\phi = -\pi$ indicates that the incident and reflected waves exactly cancel each other at the edge of the potential wall as in the case of infinite potential wall; in contrast, $\phi = -\pi/2$ means that the wave function penetrates into the wall (Figure 5e). Within a range of 0.3 V $< V_{\text{sample}} < 1.0$ V, ϕ depends on only V_{sample} and not on the number of node n or the length L . Since $V_{\text{sample}} = 0.5$ V

corresponds to the energy of the LUMO (Figure 5f), the observed phase shift suggests that confined surface electrons with an energy of 0.5 eV interact with the LUMO. Therefore, electrons and spins of the molecule can be mediated through these confined states.

CONCLUSIONS

The present results demonstrate the successful formation of highly ordered 1D molecular chains by using

a FA stepped surface as a substrate. The high degree of order and the interaction between the confined surface electrons and molecular orbital suggest the ability of transferring charges and spins with a high efficiency. Finally, due to the 1D character of the surface electrons, the spin–spin and electron–electron interactions mediated through the substrate should be enhanced. This has an advantage of raising the operation temperature of future information transport devices and makes them realizable.

METHODS

Sample Preparation and STM Measurements. All experiments were performed in an ultrahigh vacuum chamber that is equipped with a LEED, an Auger electron spectroscopy (AES) apparatus, and a STM under a base pressure of $<1 \times 10^{-8}$ Pa. The striped Ag substrate was prepared by first flashing a Si(111) wafer at temperature up to 1520 K to obtain a Si(111)-(7 × 7) clean surface. Then a small amount of In (~1.8 ML) was deposited on the surface followed by sample annealing in the temperature range of 610–630 K for 5 min to obtain a well-developed In/Si(111)-(4 × 1) substrate surface.⁴⁶ After that we cooled down the sample to 110 K and deposited Ag on top of it. A slow annealing to room temperature allowed us to obtain the striped Ag substrate. CoPc, which was carefully outgassed below 450 K for over 1 h prior to evaporation, was deposited on the striped Ag substrate at room temperature. The deposition rate (~0.05 nm/min) was estimated by a quartz microbalance and calibrated by the obtained STM images. STM measurements were performed below 8.6 K.

Density Functional Theory Calculation. All calculations were performed using the QUANTUM ESPRESSO package.⁴⁷ Electron-ion interactions were described by ultrasoft pseudopotentials.⁴⁸ The valence wave functions and augmented charge density were expanded in terms of a plane-wave basis set with cutoff energies of 27 and 270 Ry, respectively. The van der Waals density functional³⁴ was used to express the exchange–correlation energy of interacting electrons. A stripped Ag(111)-(10 × 7) surface was simulated using a repeated-slab model with the three Ag layers and 2 nm–vacuum region. A CoPc molecule was placed above the Ag surface. Brillouin zone sampling was done at the Γ point, and the Fermi surface was treated by the Marzari–Vanderbilt cold-smearing technique⁴⁹ with the smearing parameter of 0.01 Ry (0.136 eV). During the geometry optimization, only the atoms in the bottom Ag layer were fixed, while other atoms were fully relaxed until the remaining force acting on atoms is less than 0.05 Ry/nm. To exclude the artificial dipole electric field imposed on the surface from the periodic image cells in the repeated slab, the scheme of effective screening medium was employed.⁵⁰

Conflict of Interest: The authors declare no competing financial interest.

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Supporting Information Available: Rotation angle distribution of CoPc adsorbed on the striped surface. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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