Adsorption and Self-Assembly of the 2,3,5,6-Tetra(2′-pyridyl)pyrazine Nonplanar Molecule on a Au(111) Surface

Xiaohui Li, Bin Li, Yongfei Ji, Jing Zhang, Aidi Zhao, and Bing Wang*

Hefei National Laboratory for Physical Sciences at the Microscale, and Synergetic Innovation Center of Quantum Information & Quantum Physics, University of Science and Technology of China, Hefei, Anhui 230026, China

ABSTRACT: We report our investigation of adsorption and self-assembly of a nonplanar molecule 2,3,5,6-tetra(2′-pyridyl)-pyrazine (TPPZ) on a Au(111) surface using ultrahigh vacuum low-temperature scanning tunneling microscopy joint with density functional theory (DFT) calculations. We find that the nonplanar TPPZ molecules exhibit various adsorption configurations depending on the coverage of molecules. The molecules mainly adsorb at step edges with a flat-lying configuration at low coverages and gather into chiral trimers almost equidistantly separated from each other in the fcc domains accompanied by diffusive molecules in the hcp domains of the herringbone reconstructed Au(111) surface at a coverage of about 0.2 monolayer (ML) and then form two dominant types of ordered domains, i.e., stripe-like (S-phase) and honeycomb-like (H-phase) superstructures, which may reflect the chiral separation characteristics at a coverage of about 1 ML. In the trimers and ordered domains, the adsorption configurations of molecules become declining or almost erect, i.e., an “edge-on” configuration, quite different from the flat-lying configuration at low coverages. After annealing to 380 K the S-phase transfers to the H-phase, and the H-phase may persist after annealing up to 410 K, which can be attributed to the existence of C−H···N hydrogen bonds between the TPPZ molecules with the same chirality. Our observations can be energetically interpreted by considering the interplay of molecule–substrate interaction and intermolecular interaction including van der Waals interaction and hydrogen bonds on the basis of the DFT calculations, where the hydrogen bonds should be a key factor for the formation of the stable ordered H-phase with chiral separation.

I. INTRODUCTION

Supramolecular self-assemblies have been intensely investigated for decades due to their promising potential applications.1−7 They usually occur via noncovalent interactions, including hydrogen bond,8,9 van der Waals (vdW) interactions,8 electrostatic interactions or weak donor−acceptor interactions,10,11 dipole–dipole interactions,12 π−π stacking,13,14 etc. Final architectures of the assemblies depend on the intermolecular and molecule–substrate interactions, as well as the elegant structures of the molecules as building blocks. The subtle balance between the intermolecular interaction and the molecule–substrate interaction may cause various variations of the self-assembled structures.15,16−19 Many factors, such as different types of substrates, coverage of molecules, growth temperature, solvent molecule, and external stimuli, may significantly affect the structures and properties of the assemblies.20,21,22−24 In the cases of nonplanar molecules, the situation may become much more complicated25,26 because the nonplanar molecules have many possible adsorption configurations on the surface and intermolecular interacting configurations, so that small changes of internal and external factors are possible to bring significant variations of the self-assembled structures and related assembly mechanism. For instance, the isomer pairs of nonplanar 6-nitrospiropyran (SP6) and 8-nitrospiropyran (SP8) molecules are just different at the connecting position of the NO2 group; however, such structural difference significantly affects the patterns of their assemblies.27,28 More noticeably, with variation of coverage the nonplanar molecules can often adjust their adsorption conformation on the substrate due to the enhanced intermolecular interaction, and the resulting self-assembled structures may also be changed with good flexibility.16,19,27 On the other hand, many studies have been devoted to role and control of chirality in synthetic supramolecular self-assembly on the surface20−24 because of fundamental interest in surface chirality and its potential applications such as chiral specific sensors, enantiomeric separation, and asymmetric heterogeneous catalysis. Different from the planar molecules that are achiral or prochiral in the gas phase and possess chiral characteristics only after their adsorption and/or self-assemblies on the surface,33 the nonplanar molecules often have intrinsic chirality irrespective of their adsorption, so they should be important in the synthesis and control of chiral supramolecular self-assembly.34 It is challenging to unveil and understand

Received: December 12, 2015
Revised: February 27, 2016
Published: March 3, 2016
complicated interplay between various factors, especially intermolecular interaction, molecule–substrate interaction, and molecular chirality in the self-assembly process of the nonplanar molecule, where the theoretical simulation based on the first-principles calculation may play an important role.\textsuperscript{19}

2,3,5,6-Tetra(2'-pyridyl)pyrazine (TPPZ) is a nonplanar molecule, composed of four pyridine rings bonding through the C–C σ bond to a central pyrazine ring.\textsuperscript{56,57} Low-energy conformations of TPPZ were predicted to have each pyridine ring twisted from coplanarity with the pyrazine by roughly 50°, and then there are 14 conformations of TPPZ that lie in local energy minima.\textsuperscript{56,57} All of these conformers have the same basic shape but differ in the relative positions of the four pyridine nitrogen atoms. Quantum mechanical calculations indicated that among these low-energy conformations of TPPZ the 4$_{\text{NNNN}}$ conformation is more energetically stable than other competitors.\textsuperscript{56,57} Belonging to the D$_2$ point group, the TPPZ molecule with 4$_{\text{NNNN}}$ conformation has three rotation axes $C_3$(i) (i = x, y, and z) (see Figure 1a) and also has chiral character, with enantiomers (denoted as R-TPPZ and L-TPPZ) shown in Figure 1a and 1b. The difference between two enantiomers can be viewed from the twisting of four pyridine rings and the positions of N atoms relative to the pyrazine plane. The TPPZ molecules were used as bis(tridentate) bridging ligands between identical or different metal centers because of their ability to form a plethora of coordination modes with metallic centers\textsuperscript{18–47} and applications in fuel cells,\textsuperscript{48,49} molecular sensors,\textsuperscript{50} photodynamic therapy,\textsuperscript{51} and molecule-based magnets.\textsuperscript{52} Our previous study of supramolecular self-assembly of the 2,4,6-tris(2-pyridyl)-1,3,5-triazine (TPTZ) molecule showed that it can form enantiomorphous domains composed of rhombic supercells with varied periods at various coverages of molecules.\textsuperscript{53} The TPTZ is a planar molecule because it has only three pyridine rings without twisting aroused by steric hindrance. In spite of the similar groups the TPPZ molecule is nonplanar with intrinsic chirality as discussed above, making it different from the planar molecules,\textsuperscript{5,53} and is expected to possess more complicated adsorption configurations on the surface and intermolecular interacting configurations along with stronger chiral characteristics. So it is interesting to examine and understand the behaviors of supramolecular self-assembly of the nonplanar TPPZ molecule.

In this paper, we investigate the adsorption and self-assembly behaviors of the TPPZ molecules on the Au(111) surface by combining scanning tunneling microscopy (STM) experiment with density functional theory (DFT) calculation. The TPPZ molecules and their assemblies exhibit various patterns with the variation of molecular coverages. It is observed that the TPPZ molecules are adsorbed on the Au(111) surface in a flat-lying adsorption configuration of single molecules at a very low coverage and in “edge-on” stacking configuration to form trimers, stripe-like or honeycomb-like superstructures with the suggested chiral characteristics at higher coverages due to local crowding or hydrogen bond interaction. The DFT calculation can provide in-depth understanding of these adsorption and assembly phenomena in terms of interplays between the molecule–substrate and intermolecular interactions.

II. EXPERIMENTAL DETAILS AND THEORETICAL CALCULATIONS

Our experiments were carried out in a homemade ultrahigh vacuum low-temperature STM with a base pressure less than 3 $\times$ 10$^{-8}$ Pa. The Au(111) films were prepared by evaporating Au film onto mica in vacuum. The surface of the Au(111) film was cleaned by repeated cycles of Ar$^+$ sputtering (1000 eV) and annealing to 573 K for 30 min before it was used for molecule deposition. The TPPZ molecules (97%, from Aldrich) were degassed at 380 K with a Knudsen-cell type evaporator in vacuum for about 12 h to exile impurities prior to deposition. Subsequently our experimental samples were obtained by sublimation of the TPPZ molecules at 370 K, while the Au(111) substrate was kept at room temperature. After deposition, the sample was transferred into a cryostat of the microscope and cooled to 120 K. All the STM images were obtained at 120 K with the constant-current mode using an electrochemically etched tungsten tip.

Our DFT calculations were carried out using a DMOL$^3$\textsuperscript{54–56} package in generalized gradient approximation (GGA) with Perdew–Burke–Ernzerhof (PBE)\textsuperscript{57} functional and density functional semicore pseudopotential.\textsuperscript{58} The basis set consists of double numerical atomic orbits augmented by polarization functions. Since the pure GGA functional often fails to describe the systems involving weak interactions such as the adsorption of π-conjugated molecules on metal surfaces and packing between these molecules, we considered long-range dispersion forces in a semiempirical way following the scheme proposed by Tkatchenko and Scheffler (TS)\textsuperscript{59} which has been implemented in the DMOL3 code\textsuperscript{54–56}. In the structural optimizations, the atomic relaxations were performed until the total energies are converged to be smaller than 1.0 $\times$ 10$^{-5}$ Hartree and the forces on the unfixed atoms are smaller than 1.0 $\times$ 10$^{-3}$ Hartree/Å. The STM images were simulated by a Tersoff–Hamann formula\textsuperscript{60,61} The detailed models used to simulate the experimental systems and their related k-point setting for Brillouin-zone integrations have been given in each part of the discussion for the different structures.

III. RESULTS AND DISCUSSION

At very low TPPZ coverage of less than about 0.1 monolayer (ML), it is found that the TPPZ molecules are preferentially adsorbed at the step edge of the Au(111) surface, leaving terraces almost empty, as shown by the STM image in Figure
Here, 1 ML is defined to be a molecule density of about 0.85 nm\(^{-2}\), corresponding to the densest self-assembly of the TPPZ molecular monolayer obtained in our experiment, which will be introduced later. It seems that at this coverage the adsorbed TPPZ molecules almost aggregate into one-dimensional wire structure in some regions along the step edge. The high-resolution STM image (Figure 2b) containing three adjacent TPPZ molecules along the step edge shows moderate intermolecular distance and that singly adsorbed TPPZ molecules occur as a dumbbell-like pattern. In our DFT calculation, we adopt an (8 × 8) supercell of a Au(111) periodic three-layer slab model with a TPPZ molecule on one side of the slab to simulate the adsorption system of a single TPPZ on the Au substrate, and a vacuum layer of about 15.0 Å in the direction perpendicular to the Au slab surface is used to avoid the interaction between the neighboring slabs. The experimental value of bulk Au–Au distance of 2.885 Å is adopted. In the initial configuration for the optimization, the molecule is put with its symmetry center at four typical adsorption sites on the Au(111) substrate, top site, hcp site, fcc site, and bridge site, and the molecular C\(_2\)(x) axis (see Figure 1a) is set to be along the \langle 11\overline{2} \rangle or \langle 1\overline{1}0 \rangle direction (denoted by “1” and “2”) of the Au(111) surface. So there are totally nine possible adsorption configurations being named Xm (X = Top, Hcp, Fcc, and Bri; m = 1, 2), in which two possible bridge site adsorption configurations with C\(_2\)(x) axis along the \langle 11\overline{2} \rangle direction are named Bri1a and Bri1b. In each case, the Brillouin-zone integration is performed only at \Gamma-point. Our calculation shows that among various possible adsorption configurations the most energetically preferred one is Fcc1 (see Figure 2c) of which the structural model is shown in Figure 2d, with the corresponding adsorption energy of −239.4 kJ/mol. In
this adsorption configuration, the TPPZ molecule has conformation close to 4\_\text{NNNN} and its center lies at the fcc site with the direction of the C\_\text{x} axis being close to the (1\_12) direction of the Au(1\_11) surface. Other adsorption configurations have the adsorption energies generally smaller than it by an energy difference ranging from several kJ/mol to beyond 40 kJ/mol. It is noticeable that four configurations, Top1, Hcp1, Fcc1, and Brilb, with the same orientation of the C\_\text{x} axis close to the (1\_12) direction have larger adsorption energies compared to other configurations. Our simulated STM image with constant-current mode is presented in Figure 2e, from which one could find that our theoretical simulation can reproduce the dumbbell-like pattern of the experimental STM image in Figure 2b, so the TPPZ molecule is indeed flat-lying on the Au(1\_11) substrate with four pyridine rings having similar distances from the substrate surface. It is also noted that in our simulated STM image there exists a small difference between the patterns corresponding to the adjacent pyridine rings, which is not resolved in our experimental image. This also results in that we cannot resolve the chirality of a single TPTZ molecule. Actually, the adsorptions of a single R-TPPZ molecule (used in the calculation above) and L-TPPZ molecule are equivalent because the Au(1\_11) surface has mirror image symmetry along the (1\_12) direction which can transform the R-TPPZ to L-TPPZ. Our further analyses based on the DFT calculation show that the STM image at +1.2 V sample bias is mainly contributed by the hybridization states between the lowest unoccupied molecular orbital (LUMO) of TPTZ and Au substrate states, and the pattern of TPTZ in the STM image basically corresponds to the molecular appearance. We have also performed some additional simulations taking the effect of the step edge into account. Since the step edge of the Au(1\_11) surface may exist along various directions, a (4 × 10) centered rectangular supercell of a Au(1\_11) periodic three-layer slab model with an Au adlayer and a TPPZ molecule on one side of the slab is used to simulate the adsorption system of single TPTZ at the (1\_12) step edge of the Au substrate. We consider three possible cases of the molecular adsorption: on the lower Au layer, across the step edge, and on the upper Au layer (adlayer) (see upper panel in Figure 2f). The optimized geometries of the TPTZ molecule and the simulated STM images (lower panel in Figure 2f) are basically consistent with those on the Au terrace.

When the coverage of TPTZ is increased to about 0.2 ML, the molecules can gather into trimers, and the formed TPTZ trimers are located in fcc domains of herringbone reconstruction of Au(1\_11) surface, as shown in Figure 3a and 3b. There exist diffusive molecules in hcp domains, as reflected by the very fuzzy feature along the hcp domains (Figure 3b). The stability in the fcc domains and mobility in the hcp domains of TPTZ molecule could be ascribed to stronger binding energy of the molecule in the fcc domain compared to that in the hcp domain and influence of bias-induced electronic field on the molecular diffusion, as suggested in previous studies of other molecules on the Au(1\_11) surface.\textsuperscript{15,62} The TPTZ trimers in the fcc domains almost equidistantly separate from each other by about 3 nm at 0.2 ML (Figure 3b). One can see that the TPTZ trimers in the fcc domains can be classified into four types as denoted by A1, A2, B1, and B2 in Figure 3b. The B1 (B2) type trimer is actually equivalent to the A1 (A2) type trimer due to a 180° rotation transformation relationship between them. Moreover, it is noted that the TPTZ trimers adsorbed in the fcc domains have chiral characters: A1 (B1) has the contrary arrangement of three TPTZ molecules to that of A2 (B2), suggesting that they are enantiomers. Figure 3c shows the high-resolution STM images of the two TPTZ dimers which appear as Δ and Δ' in Figure 3b, and they belong to A2 and A1 type, respectively. One can find that each TPTZ molecule of the trimers shows dumbbell-like shape, but its intensity distribution and aspect ratio are obviously different from the ones in Figure 2b, and its length is also smaller than the latter. It is also noted that every dumbbell pattern of TPTZ molecule arises from the (1\_12) direction of the Au(1\_11) substrate. Here we assume that the TPTZ molecules in the trimers adopt a different conformation from that of the individually adsorbed molecule in Figure 2. A model of the TPTZ trimer is proposed as follows (Figure 3d): the three TPTZ molecules are packed spirally, and the single molecule becomes slanted so that the axis C\_\text{x} is inclined to the surface. In this special configuration, two pyridine rings as indicated by circles in the top view of the upper panel in Figure 3d are evidently more close to the STM tip than the other two in the same molecule, and then the former two pyridine rings are expected to dominate the molecular pattern in the STM image. The observed chirality of the TPTZ trimers originates from the adsorption of TPTZ molecule with 4\_\text{NNNN} conformation and their packing arrangement on the substrate, similar to that observed in the case of rubrene on Cu(1\_11).\textsuperscript{63} Because the oversize unit cell for a slab model of a TPTZ trimer adsorbed on the Au(1\_11) surface will bring unbearable computing cost for us, we only adopt a cluster model consisting of three molecules without substrate in our DFT simulation to examine

Figure 3. (a) Large-scale STM image (scale bar = 20 nm) of adsorbed TPTZ on Au(1\_11) at coverage of 0.2 ML (imaging conditions: 2.0 V and 0.2 nA). (b) STM image (scale bar = 3 nm) showing four types of trimer structure of TPTZ: A1, A2, B1, and B2 (imaging conditions: 2.0 V and 0.2 nA). (c) Higher-resolution images showing chiral structures of two enantiomers of TPTZ trimer which appear as Δ and Δ' in (b). (d) Top view (left) and side view (right) of two possible trimer structures: T\_A\_L (upper panel), T\_A\_R (lower panel). Green circles denote the position of dumbbell-like pattern. (e) Simulated STM image (constant-current mode, +2.0 V sample bias, and isodensity of 1.83 × 10\^\text{-}\_\text{4} Å\^\text{-}\_\text{3}) corresponding to two trimer structures T\_A\_L (upper panel) and T\_A\_R (lower panel).
the intermolecular interaction in a trimer. The Brillouin-zone integration is also performed only at the Γ-point. Figure 3d displays two optimized trimer structures in which all molecules adopt 4NNNN conformation, and these two trimer structures, i.e., A2-type trimer consisting of three pure L-TPPZ molecules (denoted as T_A2(L)) and A1-type trimer consisting of three pure R-TPPZ molecules (denoted as T_A1(R)), are actually equivalent configurations with specific symmetric transformations if the substrate is not considered. The simulated STM images (Figure 3e) are basically consistent with the experimental observations (Figure 3c), although some subtle details in the simulated pattern are not resolved in the experiment. On the basis of our DFT calculation, the intermolecular interaction energy per molecule is about $-66.9 \text{ kJ/mol}$ obtained by $E = (E_{\text{total}} - 3E_{\text{free-TPPZ}})/3$ (where $E_{\text{total}}$ is the calculated total energy of a trimer and $E_{\text{free-TPPZ}}$ is the energy of a free TPTZ molecule in the gas phase). In this case the vdW-type interaction due to the molecular packing and π−π stacking interaction (indicated by rectangle in the side view of upper panel in Figure 3d) have important contributions to the formation of a TPPZ trimer. We have also simulated the A2-type trimer consisting of three pure R-TPPZ molecules (denoted as T_A2(R)) and A1-type trimer consisting of three pure L-TPPZ molecules (denoted as T_A1(L)), but their corresponding STM images (not shown) are different from the experimental patterns.

When the coverage of TPPZ is further increased to about one monolayer, the TPPZ molecules are observed to assemble into ordered superstructures. Figure 4 shows an STM image of the assembly at about 1 ML, in which there are two typical superstructures, one with stripe-like and the other with honeycomb-like patterns, denoted as S- and H-phases, respectively. The molecule densities of these two phases are similar: about 0.85 molecule/nm² for S-phase and about 0.82 molecule/nm² for H-phase. The herringbone reconstruction of the underlying Au(111) surface can still be observed as a small unperturbed height modulation of the ordered overlayer, and it is even kept across different TPPZ superstructures, which is due to the weak interactions between the TPPZ molecules and the Au(111) surface, as observed in the cases of other molecules with similar structures before.\cite{66,67}

In such cases, the intermolecular interactions are expected to play a dominant role to determine the structure of molecular assembly, though the substrate may modulate the structure to some extent.\cite{8,9}

After annealing to 380 K, the H-phase is dominant domains, and the S-phase rarely appears on the Au(111) surface, which may be ascribed to the transition from the S-phase to the H-phase due to partial desorption of molecules from the S-phase domains. The H-phase may persist after annealing up to 410 K. The S-phase is actually composed of several assembly structures with similar molecular packing configurations but varied alignment directions of molecular patterns. Figure 5a presents a large-scale STM image of a typical structure of the S-phase. It is found that except the image contrast modulation in the direction indicated by line “D1”, which originates from the underlying Au(111) herringbone reconstruction, there exists another contrast modulation in another direction indicated by line “D2”. One period of the latter contrast modulation consists of four brighter molecules and two dimmer ones, but it is not regular for all regions (see the upper right corner in Figure 5a).

The latter contrast modulation may be attributed to the lack of commensurability between the unit cells of the stripe-like superstructure and the Au(111) surface and its induced different molecular adsorption structures on the substrate.\cite{65,68,69}
These two kinds of image contrast modulations jointly produce the observed Moiré-like pattern of this S-phase. By closer inspection of this structure in Figure 5b, we can see that all of the molecules have the same dumbbell-like patterns with the only difference due to the contrast modulations as described above. Figure 5c gives the line profiles of the cutline in Figure 5b, from which we can get the length of two unit vectors $|a_1| = 1.30$ nm and $|a_2| = 0.94$ nm, and the angle $\alpha$ between $a_1$ and $a_2$ is $106^\circ \pm 2^\circ$ without distinctive registry with the substrate. The unit vector $a_3$ is along the direction indicated by line “D1” in Figure 5a. The related simulation is performed with a periodic model consisting of one TPPZ molecule and adopting the experimentally measured unit vectors, and the Au substrate is yet not included. We adopt a $3 \times 4 \times 1$ Monkhorst–Pack k-point grid, which is verified to ensure convergence of our results. Our deduced molecular packing model using the R-TPPZ for this stripe-like superstructure is shown in Figure 5d. The simulation finds that in this superstructure the adsorption configuration of the TPPZ molecule is different obviously from those in individually adsorbed molecules and the trimers: the molecules are slanted due to the close-packing repulsions between them so that the axis $C_z(y)$ is inclined to the surface. The simulated STM image with constant-current mode is shown in Figure 5e. It is found that two pyridine rings in the TPPZ molecule (marked with circles in the three upper unit cells of Figure 5d) dominate the molecular pattern, indicating that in this case the dumbbell-like pattern observed in the experiment actually corresponds to these two pyridine rings. Our calculation shows that the intermolecular interaction energy per molecule of the stripe-like superstructure is $\sim 49.3$ kJ/mol obtained by $E = E_{S_{\text{total}}} - E_{\text{free}-\text{TPPZ}}$ (where $E_{S_{\text{total}}}$ is the calculated total energy of a unit cell of the stripe-like superstructure).

It is noted that in our deduced packing model of the stripe-like superstructure the molecules are of R-TPPZ. In fact, we even try to use L-TPPZ to construct the packing model of the same unit cell in a similar way, and in the optimized configuration (not shown) two pyridine rings dominating its STM image are lined up along the direction deviating from the experimental one. On the other hand, a mirror transformation of mirror plane vertical to the substrate surface of our experimental one. On the other hand, a mirror transformation. The line profiles in Figures 6b and 6c show the periods of 0.94 nm along the molecular rows and 1.30 nm for the adjacent molecular rows. The angle between the A-type and B-type rows is measured to be $148^\circ \pm 5^\circ$, which just corresponds to the angle $\alpha$ between $a_1$ and $a_2$ in Figure 5, given as $180^\circ - 148^\circ /2 = 106^\circ$. So these parameters are the same as those of the stripe-like superstructure in Figure 5. The assembly of pure B-type rows is actually the typical stripe-like superstructure consisting of R-TPPZ shown in Figure 5, denoted as S(R), whereas in the A-type rows the molecules are of L-TPPZ, and their assembly is denoted as S(L). Similarly, there is no distinctive registry with the Au(111) substrate. Figure 6d presents a packing model of two adjacent TPPZ molecular assemblies S(R) and S(L). This suggested spontaneous chiral separation should be related to lower symmetry of the TPPZ molecule. It is noted that at the domain boundary of S(R) and S(L) there may exist steric hindrances between the mirror-symmetrical pyridine rings of two enantiomers according to the packing model. In fact, one can find contrast variations of the molecular patterns at the domain boundary, suggesting that the two adjacent enantiomers may be forced to appreciably change the orientations of their pyridine rings to decrease the steric hindrances. The contrast variations of the molecular patterns are also observed in the internal regions of S(R) and S(L) domains without distinctive ordering, showing that in this hybrid superstructure of two enantiomer rows there exist lots of small and irregular variations of adsorption configurations (especially heights and orientations of the pyridine rings) of TPPZ molecules on the Au surface.

As mentioned above, the S-phase is metastable. Our simulations show that the interaction between the TPPZ molecules and the substrate is not strong enough, and the intermolecular interaction in the S-phase is of weak vdW type, resulting in less stable and more flexible stripe-like assemblies of TPPZ molecules observed in our experiment. Furthermore, the large number of possible noncovalent interactions might result in the coexistence of different metastable supramolecular assemblies with similar energies, so in the S-phase there exist several types of stripe-like superstructures, although among them the one shown in Figure 5 and Figure 6 is commonly observed, as discussed above.
The H-phase, which is stable even when annealing to 410 K, has only one type of honeycomb-like superstructure. As shown in Figure 7a, this superstructure is yet incommensurate with the Au(111) substrate lattice, and we find that the angle between the lattice vector of the TPPZ superstructure and the \([11\overline{2}]\) direction of the Au substrate varies in the range of 0°−14° with a random distribution for different molecular assembly domains. One may also find that there exist two domains located in the left and upper right regions of Figure 7a, labeled as domain I and II, respectively. As shown by the magnified image of domain I in Figure 7b, the lattice unit vectors (from pore to pore) are measured as \(|b_1| = |b_2| = 2.06 \pm 0.04\) nm where the angle \(\beta\) between \(b_1\) and \(b_2\) is 120° ± 3°, and each unit cell contains two trimers consisting of six bright protrusions. The unit cells of the two domains are shown in Figure 7c. It is seen that they are actually mirror images of each other in the assembly plane, with contrary arrangements of TPPZ molecules, suggesting characteristics of enantiomers. It is interesting that there are some short chains around the irregular honeycomb-like superstructure in the lower right region of Figure 7a, and each chain is also composed of six bright protrusions (marked with dashed lines in Figure 7a).

According to the symmetry of this honeycomb-like superstructure, we deduce its molecular packing model, as shown in Figure 7d, where the unit cell includes three pure R-TPPZ molecules for domain I. Such an assembly is denoted as H(R). In the unit cell, the allowed area per molecule is smaller than the estimated footprint of a fully flattened molecule. Therefore, we adopt an almost erect adsorption configuration with the axis \(C_2(y)\) perpendicular to the surface, i.e., an “edge-on” configuration for the TPPZ molecules on the Au(111) surface, which is supported by the volume exclusion requirement of the TPPZ molecules themselves. The simulation is performed with a periodic model consisting of three pure R-TPPZ molecules and adopting the experimentally measured unit vectors, and a 2 × 2 Monkhorst-Pack k-point grid is used. In the lower-left unit cell of Figure 7d, the pyridine rings with higher \(z\)-averaged coordinates, i.e., closer to the STM tip, are marked with circles. They are expected to contribute to the honeycomb-like pattern. The simulated STM constant-current image of \((2 \times 2)\) unit cells of the honeycomb-like superstructure is presented in Figure 7e.
Figure 7e. One can see that the pattern corresponding to every pyridine ring actually consists of two spots, different from the single spot shown in the magnified experimental image (Figure 7b). Our further examination finds that this two-spot pattern is related to a nodal plane of LUMO wave function of the TPPZ molecule. This difference between the experimental observation and theoretical simulation may be mainly ascribed to two factors. One is due to the neglects of the Au substrate and related orbital hybridization between the molecule and substrate in our simulation, and the other is due to the \(d_{z^2}\)-derived states with one nodal plane perpendicular to the molecular assembly surface of the W tip, which was thought to have non-negligible contributions to the tunneling current and STM image in many cases.68–70 The \(d_{z^2}\)-derived states may bring strong current at the position corresponding to the nodal plane of TPPZ LUMO via local orbital symmetry matching.71

We have also replaced three R-TPPZ with L-TPPZ molecules in the stacking model shown by Figure 7d; however, the simulated image could not match the observed images for domain I. Instead, we can obtain the simulated image that matches with domain II by adopting the L-TPPZ stacking model as shown in Figure 7f [denoted as H(L)], which is consistent with their enantiomeric character. The calculated intermolecular interaction energy per unit cell for both H(R) and H(L) assemblies is \(-145.4\) kJ/mol obtained by \(E = E_{H\text{total}} - 3E_{\text{free-TPPZ}}\) (where \(E_{H\text{total}}\) is the calculated total energy of a unit cell of the honeycomb-like superstructure). We have also tried using mixtures of L-TPPZ and R-TPPZ molecules in a unit cell. The calculated intermolecular interaction energy per unit cell is higher than the stacking with pure R-TPPZ (or L-TPPZ) by about \(22.4\) kJ/mol. This difference is attributed to the formation of C–H···N hydrogen bonds between the pure R-TPPZ (or L-TPPZ) molecules but a weakened or even no hydrogen bond between the R-TPPZ and the L-TPPZ molecules in their mixture. As shown in Figure 7g, each molecule can form four C–H···N hydrogen bonds with the adjacent molecules in H(R) [or in H(L)]. It is suggested that the formation of the hydrogen bonds plays a key role for the higher stability of the superstructure, similar to the role of the C–H···N hydrogen bonds in the close-packed assembly of pure enantiomers of the 2,4,6-tris(2-pyridyl)-1,3,5-triazine molecule.8

From our experimental and simulated results discussed above, it is obviously seen that the four pyridine rings have different contrasts in the STM images of various molecular conformations. In the case of individually adsorbed molecules, the dumbbell-like pattern (Figure 8a) mainly reflects the contributions of paired pyridine rings at both sides of the central pyrazine ring because of the flat-lying orientation of molecules with the axes \(C_{2}(x)\) and \(C_{2}(y)\) almost parallel to the surface. However, in the case of trimers the dumbbell-like patterns are relatively thinner and shorter (Figure 8b), and it is suggested that the paired pyridine rings at one side of the central pyrazine ring dominate this pattern since the molecular axis \(C_{2}(x)\) is inclined to the surface. In contrast, in the cases of S- and H-phases in the ordered domains, the patterns corresponding to the single molecules in the STM images are also relatively thinner but have almost the same length as the case of individually adsorbed molecules (Figures 8c and 8d). These patterns are mainly contributed by single pyridine rings at both sides of the pyrazine ring because the molecular axis \(C_{2}(y)\) is no longer parallel to the surface in the S- and H-phases. In the latter three cases, only two pyridine rings dominate the STM image, which is ascribed to the almost “edge-on” configuration of the molecules, i.e., the slanted molecular orientation different from the flat-flying configuration. This change can be also shown by variations of height (or \(z\)-coordinate) differences between four pyridine rings. The slanted molecular orientation in the S-phase results in the two pyridine rings with a higher averaged height from the \(xy\)-plane (representing the Au(111) surface in our simulation) than the other two rings by about 2.24 Å (see the side view in Figure 5d). In comparison, the height difference between four pyridine rings is just about 0.88 Å in the case of individually adsorbed molecules. In the cases of the H-phase and trimers, this difference is even increased to 4.96 and 5.24 Å, respectively, according to our simulations. Joint with the DFT calculations and image simulations, we may thus well identify the molecular configurations observed in the STM images.

The behaviors of molecular adsorption and assembly on the substrate surface are controlled jointly by thermodynamic and kinetic factors. The former drives the molecules to assemble on surfaces into the energetically most stable structures, and the latter makes the molecules diffuse and interact at surfaces.73 Energetically, the difference between the intermolecular interaction energy and the adsorption energy of a molecule on the substrate may also provide some hints to understand the behaviors of the assemblies at different coverages. As given in Figure 2c, the adsorption energies of an individual TPPZ molecule on the Au(111) surface in various adsorption configurations are in range from \(-190\) to \(-240\) kJ/mol. Among them, the energy minima indicate that the four adsorption configurations, i.e., Top1, Hcp1, Fcc1, and Bri1b, should be preferred for the individually adsorbed molecules, while the energy difference among them is very small (in the range of 2.3–12.0 kJ/mol). At an increased coverage of 0.2 ML, the intermolecular interaction interplays with the interaction between the molecule and the substrate, forming stable trimers. In this case, the intermolecular interaction energy is about \(-66.9\) kJ/mol per molecule, which is larger than the energy differences among the preferred adsorption configurations of individual molecules, and the adsorption configuration turns to be slanted; however, the fact that every molecular pattern orients along (112) directions of the Au(111) substrate implies the subtle role of the molecule–substrate interaction in this
case. At this coverage both the nearly periodic array of trimers and the fact that there is no larger molecular assembly structure beyond the trimer suggest the existence of long-range repulsive interaction between the molecules, although in the interior of the trimer the short-range attractive interaction between the molecules dominates. This repulsive intermolecular interaction has been suggested to be caused by the charge accumulation in the adsorbed molecules due to electron donation into the metal substrate. Our Mulliken charge analysis gives about 0.2 electron transfer from one TPPZ molecule to the Au substrate, which is consistent with the above suggestion.

At coverage of about 1 ML, the short-range attractive intermolecular interaction and the steric hindrance play the dominant roles. The incommensurate configurations in the ordered assemblies, i.e., close-packed oblique S-phase and honeycomb-like H-phase, may well support this suggestion. The calculated intermolecular interaction energy is \(-49.3\) and \(-48.5\) kJ/mol (\(-145.4\) kJ/mol in a unit cell) per molecule, or \(-41.9\) and \(-39.6\) kJ/mol-nm\(^{-2}\) in interaction energy density, for the S-phase and H-phase, respectively, which are quite comparable in both of these two phases. We have also compared the intermolecular interaction energies in the two phases using another popular semiempirical way following the scheme proposed by Grimme. Due to the lack of parameters for the Au atom in the DMOL3 code, this scheme is not applicable for the calculation of the molecule–substrate interaction. The Grimme scheme calculations give \(-22.9\) kJ/mol per molecule of the intermolecular interaction energy (\(-19.5\) kJ/mol-nm\(^{-2}\)) for the S-phase and \(-24.3\) kJ/mol per molecule of the intermolecular interaction energy (\(-19.8\) kJ/mol-nm\(^{-2}\)) for the H-phase, giving more consistent calculated results with the experiment than the TS schemes. It was shown that both TS and Grimme schemes yield larger mean absolute relative errors for the vdW interaction than those for the hydrogen bond interaction. In our case, the S-phase is dominated by the vdW interaction, and the H-phase has stronger hydrogen bond interaction; so, the accurate comparison between the intermolecular interaction energies of these two phases based on the TS and Grimme schemes needs to be further evaluated.

We here further discuss the role of the molecular chirality on the adsorption and assembled structures of TPPZ on the Au(111) surface. In the case of individually adsorbed molecules at very low coverage, the molecular chirality of TPPZ has no obvious influence on the adsorption configuration. The mirror symmetry transformation will transform the L-TTPZ/Au(111) adsorption system into R-TTPZ/Au(111), so the two enantiomers of TPPZ have equivalent adsorption configurations at the same adsorption site. For the trimers at low coverage and S-phase at almost one monolayer coverage, the molecule–substrate interaction becomes weak, and the packing volume exclusion dominates the formation of superstructure. We suppose that the enhanced packing volume exclusion results in chiral characteristics and even chiral separation of TPPZ in the trimers and S-phase, although the chiral separation is mainly deduced by our simulation. The chirality-related assembly of the S-phase originates from the vdW interaction, so it is not stable enough. The stability of the H-phase could benefit from the formation of hydrogen bonds in the stacking of pure R-TTPZ (or L-TTPZ) molecules, where the molecular chirality plays an important factor in changing the interaction. Our theoretical analysis shows that the hydrogen bonds can be weakened or even eliminated in the stacking of the different chiral molecules. Therefore, the chiral separation could also lead to the thermodynamically stable assembly in the H-phase.

CONCLUSIONS

In summary, we accomplished a low-temperature (120 K) STM experimental and DFT theoretical study of adsorption and self-assembly of the nonplanar TPPZ molecule on the Au(111) surface from a single molecule to about one monolayer. Coverage dependence indicates that the molecules are adsorbed in a flat-lying orientation at very low coverage to maximize the interaction between the molecule and the Au(111) surface, while they will be adsorbed in an “edge-on” orientation at increased coverage due to local crowding and intermolecular interaction. At very low coverage the TPPZ molecule prefers to be adsorbed at the step edges, consistent with our DFT calculations. When the coverage is increased, the molecules gather into chiral trimers almost equidistantly separated from each other in the fcc domain of the Au herringbone reconstruction substrate, due to a balance between the long-range repulsive and short-range attractive interactions. When the coverage reaches about one monolayer, the TPPZ molecules form two types of ordered self-assembled structures, i.e., S-phase with stripe-like superstructure and H-phase with honeycomb-like superstructure. Both the S-phase and the H-phase have enantiomorphous domains, suggesting the chiral separation characteristics. After annealing to 380 K, the H-phase is dominant domains, and the S-phase rarely appears on the Au(111) surface, which may be ascribed to the transition from the S-phase to the H-phase due to partial desorption of molecules from the S-phase domains. The H-phase may persist after annealing up to 410 K, which is supposed to benefit from the existence of C–H–N hydrogen bonds between the TPPZ molecules with the same chirality.

AUTHOR INFORMATION

Corresponding Authors
*E-mail: libin@mail.ustc.edu.cn.
*E-mail: bwang@ustc.edu.cn.

Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was financially supported by the National Key Basic Research Program (grants 2011CB921400), the "Strategic Priority Research Program" of the Chinese Academy of Sciences (grant XDB01020100), and the National Natural Science Foundation of China (grants 91321309, 21421063, and 21273210).

REFERENCES


