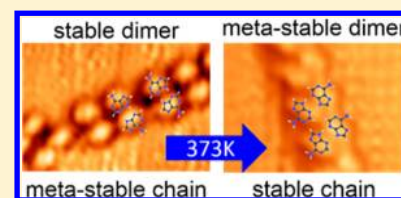


# Thermally Controlled Adenine Dimer Chain Rotation on Cu(110): The Critical Role of van der Waals Interactions

Yu Yang Zhang,<sup>†,‡</sup> Ye-Liang Wang,<sup>‡</sup> Lei Meng,<sup>‡,§</sup> Sheng Bai Zhang,<sup>\*,†</sup> and Hong-Jun Gao<sup>\*,‡</sup><sup>†</sup>Department of Physics, Applied Physics & Astronomy, Rensselaer Polytechnic Institute, Troy, New York 12180, United States<sup>‡</sup>Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China<sup>§</sup>College of Science, Minzu University of China, Beijing 100081, China

**ABSTRACT:** The theory of adenine dimer chain assembly on Cu(110) surface is controversial, due in large to the lack of an adequate description of the van der Waals (vdW) interactions. Here, we show by a combined first-principles calculation and experiment that the role of the vdW interactions is to tilt the energy balance at different levels of chain hierarchy. We find that the stable chains are made of metastable dimers, whereas the metastable chains, close in energy to the stable ones, are made of stable dimers. As such, at room temperature deposition, adenine dimers exist primarily in their stable form. This leads to the formation of metastable chains. By annealing at elevated temperature, however, more dimers can exist in the metastable form. This leads to the nucleation of the stable chains at a different orientation. The thermally controlled chain rotation is expected to be of general importance to the understanding of amino acids assembly and functionalization at the most elemental level.



## INTRODUCTION

Van der Waals (vdW) interactions are ubiquitous, and their importance in biological structures and related systems cannot be overstated. The assessment of vdW interactions requires a fundamental understanding of their contributions at the single molecule level<sup>1,2</sup> but, even more importantly, at the pattern assembly level.<sup>3,4</sup> Biomolecules such as DNA base and peptides on solid surfaces have been widely used to investigate vdW interactions and self-assembly patterns.<sup>5–12</sup> Among them, adenine on copper has drawn much attention as a prototypical system.<sup>13–23</sup> Adenine (C<sub>5</sub>N<sub>5</sub>H<sub>5</sub>) is an important nucleobase molecule that combines a five-membered ring, a six-membered ring, and an amino functional group. It is widely reported that adenine molecules prefer to form a chainlike structure on Cu(110) surface.<sup>14–16</sup> A stable chain with (±1, 2) orientations with respect to the substrate has been confirmed by scanning tunneling microscopy (STM) and low-energy electron diffraction (LEED) experiments.<sup>15</sup> Theoretically, however, how to reliably simulate the vdW interaction in such systems remains unanswered. The widely used exchange correlation functionals (Exc), such as the local density approximation (LDA) and generalized gradient approximation (GGA), in the density functional theory (DFT) either misrepresent or neglect the vdW interaction. In the reported PBE calculation,<sup>19,20</sup> the binding energy of an adenine dimer on Cu(110) surface is 0.55 eV/molecule, whereas that of an isolated adenine is 0.56 eV/molecule. The small negative energy difference (0.55 – 0.56 = –0.01 eV) suggests that adenine molecules have little chance to form dimers. In contrast, experiments have revealed that adenine only adsorbs as dimer or dimer chains,<sup>14,15</sup> not as isolated molecules.

In recent years, various corrections have been applied to standard DFT to describe vdW interactions efficiently. This

includes GGA with interatomic correction (e.g., PBE-D<sup>24</sup> and DFT-vdW<sup>25</sup>) and DFT plus local atomic potential (e.g., DFT-LAP<sup>26</sup>). First-principles vdW density functionals (e.g., vdW-DF<sup>27</sup> and vdW-DF2<sup>28</sup>) have also been attempted. Progress has been made. For example, it has been shown that unless vdW interaction is explicitly included,<sup>4</sup> water molecules would not wet Cu(110) and Ru(0001) surfaces, in contradiction with experiment. vdW interactions are also important for the binding energy and distance of benzene molecules on metal surfaces<sup>2</sup> and for the lattice constant of molecular crystals.<sup>29</sup> Because of the intrinsic lack of dispersion interaction in PBE functional, the PBE results can be used as a reference to assess the effects of vdW interactions.

In this paper, we combine quantum mechanical calculations based on density functional theory with experiment to unveil the role of vdW interaction on the self-assembly of adenine dimer chains on Cu(110). It reveals that adenine molecules form primarily two different types of dimer chains with characteristically different orientations. The previously reported dimer chains along the (±1, 2) directions are made of metastable dimers, rather than stable dimers. This happens because such an arrangement can maximize the vdW interactions between adjacent dimers. The theory further predicts the existence of a metastable dimer chain along the (±4, 1) directions made of stable dimers. Experiments are carried out in searching for the predicted metastable structure. It reveals that the metastable chains form at room temperature (RT). As the formation of the stable chains requires rotation of the dimers, only upon annealing at or above 373 K, the

**Received:** December 4, 2013

**Revised:** February 25, 2014

**Published:** March 6, 2014

metastable dimer chains transform into the stable chains. The switch in the chain orientation may be viewed as an elementary function that the system may utilize.<sup>30</sup>

## METHOD

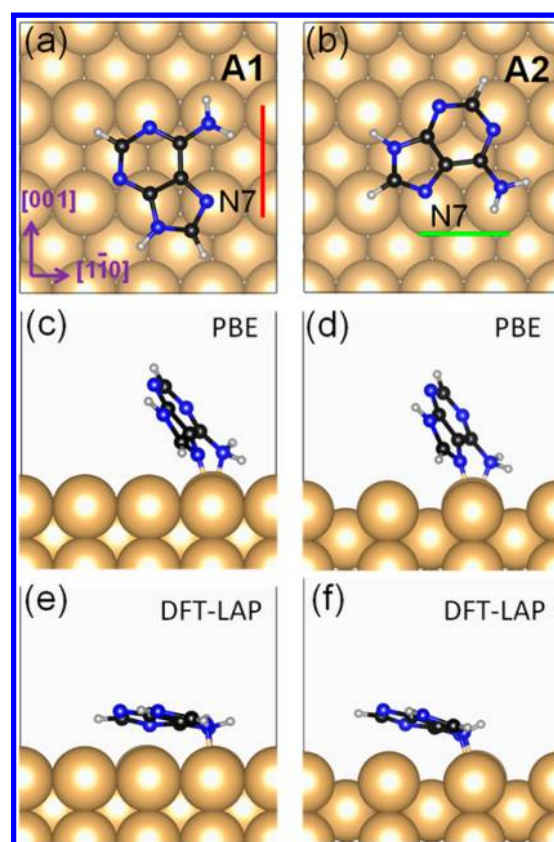
We employ a recently developed method known as the DFT-LAP approach.<sup>26</sup> It includes the vdW interaction without significant extra computational cost beyond standard DFT and has been tested in various systems.<sup>26,29,31</sup> Vanderbilt-type ultrasoft pseudopotentials<sup>32</sup> are used. We use four-layer copper atoms to model the substrate. The top two layers of the substrate and the adenine molecules are fully relaxed. The size of the supercell is determined on a case-by-case basis. The slabs are separated by more than 20 Å vacuum. The electronic wave functions were expanded in plane waves with a kinetic energy cutoff of 400 eV. Gaussian smearing with a 0.01 eV smearing width is used, and k-sampling is determined by the size of the supercell. Binding energies are tested to converge to within 0.01 eV. We also perform calculations using two other popular vdW-based methods, i.e., PBE-D<sup>24</sup> and vdW-DF2.<sup>28</sup>

The experiments are performed in an ultrahigh vacuum (UHV) system with a base pressure of  $2 \times 10^{-10}$  mbar, which provides controlled conditions for the sample preparation and characterization.<sup>33,34</sup> The Cu(110) single crystal is cleaned by repeated cycles of Ar<sup>+</sup> sputtering (700 eV) and subsequent annealing at 850 K. Commercially available adenine (Aldrich, 98% purity) in powder form is outgassed in a Knudsen-cell type evaporator and then deposited onto the Cu(110) surface held at RT. The temperature of the cell is kept at 420 K, as measured by a thermocouple contacted with the cell. The sample is then transferred from the preparation chamber to the STM chamber, which comprises a variable-temperature STM apparatus. STM measurements are carried out with an electrochemically etched tungsten tip. The sample is returned to the preparation chamber for annealing treatment at 373 K for 15 min. STM images are then taken. All STM measurements are performed at 300 K in the constant current mode.

## RESULTS AND DISCUSSION

**Isolated Adenine Molecules.** For isolated adenine molecule adsorbed on the Cu(110) surface, there exist two lower-energy configurations, A1 and A2, whose top views are given in Figures 1a and 1b, respectively. Figures 1c and 1d show the side views of A1 and A2 according to PBE; Figures 1e and 1f show the corresponding DFT-LAP results. Compare Figures 1c and 1d with Figures 1e and 1f, it is clear that *the primary role of vdW interactions is to flatten the adenine molecules against the Cu(110) surface.* When comparing the results of DFT-LAP with those of PBE, we find that vdW interactions increase the binding energy significantly (see Table 1) by drastically reducing the average distance between adenine molecule and Cu substrate. The tilt angle  $\theta$  between adenine and substrate may be used to characterize the average distance (see Table 2). Without vdW interactions (i.e., PBE),  $\theta$  is 50° for A1 and 60° for A2. With vdW interactions (i.e., DFT-LAP), however,  $\theta$  is reduced to only 10° for A1 and only 15° for A2.

We can qualitatively understand the larger  $\theta$  in PBE than in DFT-LAP by considering the physisorption of a benzene ring on Cu(110) for which experimental results are available. Here, PBE gives a negligible binding energy of 0.02 eV, which is significantly smaller than experiment, 0.53 eV. Accordingly, the PBE binding distance of 4.2 Å is also significantly larger than



**Figure 1.** Two low-energy adsorption configurations of isolated adenine molecule on Cu(110) surface. (a), (c), and (e) are for configuration A1, whereas (b), (d), and (f) are for configuration A2. (a) and (b) are top view. (c) to (f) are side view. Black, blue, and gray balls are carbon, nitrogen, and hydrogen atoms, respectively, whereas yellow balls are copper atoms. Surface lattice vectors are 2.56 Å along  $[1-10]$  and 3.62 Å along  $[001]$ . A  $p(4 \times 3)$  supercell is used in the calculation.

**Table 1.** Calculated Binding Energy (in eV) per Molecule for Adenine on Cu(110)<sup>a</sup>

		PBE	DFT-LAP	PBE-D	vdW-DF2
isolated adenine	A1	0.72	<b>1.30</b>	1.67	<b>0.86</b>
	A2	<b>0.75</b>	1.21	1.63	<b>0.86</b>
adenine dimer	D1	1.44	3.03	3.74	2.30
	D2	<b>1.51</b>	<b>3.06</b>	<b>3.86</b>	<b>2.34</b>
dimer chain	C1	1.45	<b>3.10</b>	<b>3.79</b>	<b>2.36</b>
	C2	<b>1.51</b>	3.07	3.77	2.34

<sup>a</sup>Lower energy states are indicated by bold.

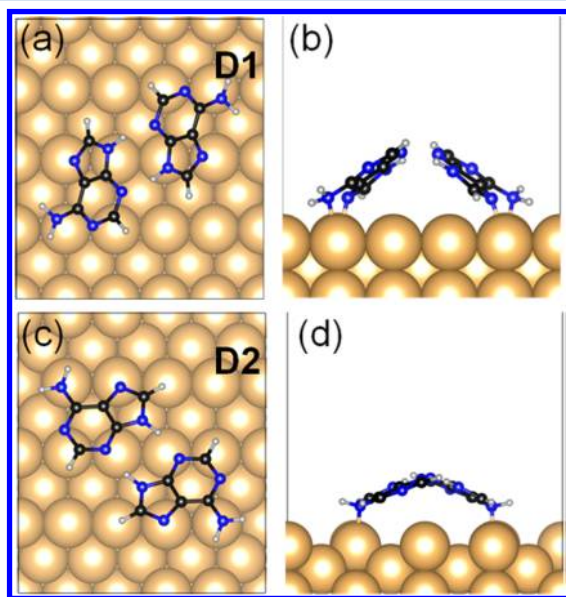
**Table 2.** Adenine Angle  $\theta$  (in deg) with Respect to the Substrate

		PBE	DFT-LAP
isolated adenine	A1	50	10
	A2	60	15
adenine dimer	D1	30	30
	D2	30	25

experiment of 3.0 Å. The same can be expected for a physisorbed five-membered ring. The adenine is, however, not purely physisorbed but is chemisorbed by the nitrogen atom, N7 in Figure 1a, plus its chemisorbed amine group on the surface. To increase the separation of the physisorbed rings

from the substrate, the adenine molecule is forced to adopt a larger tilt angle, although unphysically. The same is true for other vdW systems, such as TBA/Ag(100)<sup>35</sup> and CoPc/Cu(111).<sup>36</sup>

**Adenine Dimers.** Starting with A1 and A2, and taking into account various possible hydrogen-bonding configurations, we find that there are only two possible low-energy dimer structures on Cu(110), i.e., D1 and D2. Figures 2a and 2b



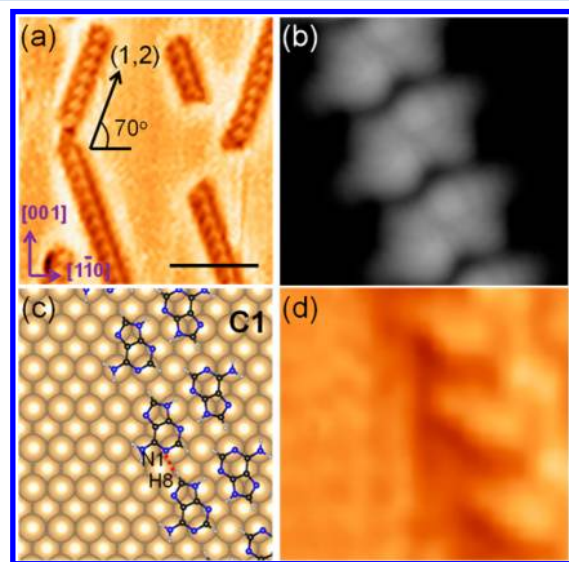
**Figure 2.** Two low-energy adsorbed adenine dimer structures on Cu(110) surface. (a) and (c) are top views, whereas (b) and (d) are side views.

show the DFT-LAP results for D1 in top and side view, whereas Figures 2c and 2d show the results for D2. In both cases, the two adenine molecules in the same dimer have identical  $\theta$ . Upon dimerization, the  $\theta$  difference between DFT-LAP and PBE vanishes for D1, and  $25 - 30 = -5^\circ$  for D2. Hence, in both cases,  $\theta$  has changed considerably with respect to isolated adenine. While the angle change optimizes hydrogen-bonding strength, it comes with an energy penalty by weakening the adenine binding to the substrate. One may write the total binding of the adenine as that with the substrate and that with neighboring adenine. PBE is expected to overestimate the repulsion between adenine and substrate. It is also expected to underestimate the hydrogen bonding between adenine pair. The calculated PBE binding energy for D1 is 1.44 eV, which is twice the binding energy of isolated adenine, 0.72 eV. Hence, PBE predicts no adenine dimerization on Cu(110), in contradiction with experiment. In contrast, the DFT-LAP binding energy for D1 is 3.03 eV, whereas the binding energy of isolated adenine is 1.30 eV. There is therefore a net gain of  $3.03 - 2 \times 1.30 = 0.43$  eV. Without the substrate, the binding between the two adenine molecules would be 0.9 eV. Hence, the energy penalty due to  $\theta$  change in DFT-LAP is estimated to be  $0.9 - 0.43 = 0.47$  eV for D1.

In the DFT-LAP calculation, isolated A1 is more stable than isolated A2; after their dimerization, however, D2 (consisting of an A2–A2 dimer) becomes more stable than D1 (consisting of an A1–A1 dimer). This may be qualitatively understood: in the  $2A1 \rightarrow D1$  process,  $\theta$  changes by  $20^\circ$  from  $10^\circ$  to  $30^\circ$ . In the  $2A2 \rightarrow D2$  process, however,  $\theta$  changes by only  $10^\circ$  from  $15^\circ$

to  $25^\circ$ . The smaller angle change is expected to cause less energy penalty, making the D2 dimer more stable than the D1 dimer.

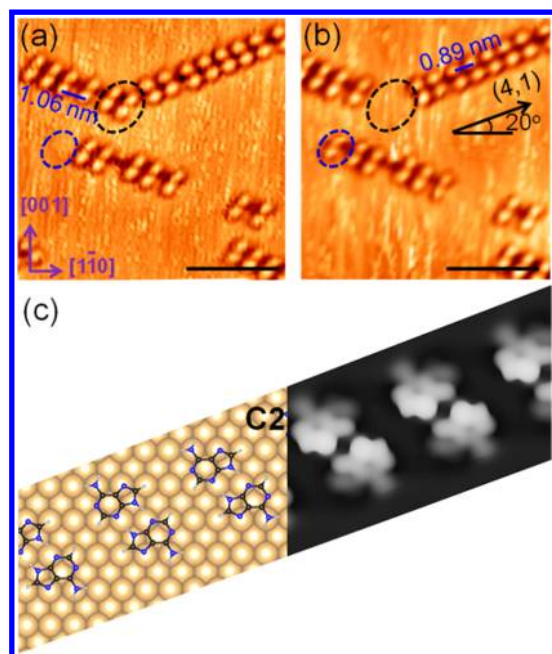
**Adenine Dimer Chains.** According to literature, adenine adsorbs on Cu(110) as chains of dimers<sup>14,15</sup> whose chain structure has been calculated previously using DFT.<sup>17,19,20</sup> Our STM experiment also reveals the chain structure, labeled C1 in Figure 3, along the  $(\pm 1, 2)$  directions. Our DFT-LAP



**Figure 3.** Stable adenine C1 chains on Cu(110) surface. (a) is a large-scale STM image, taken at  $U = -0.1$  V and  $I = 0.06$  nA. Here, the black-line scale bar is 5 nm. (b) is a simulated STM image at  $U = -0.1$  V, along with a magnified experimental image. (c) shows the calculated atomic structure for C1. (d), taken at  $U = -0.1$  V and  $I = 0.10$  nA, for comparison.

calculation, however, suggests that these stable dimer chains consist of metastable dimers D1 in Figure 2a, rather than the stable dimers D2 in Figure 2c. Within a C1 chain, the distance between two adjacent dimers is 0.72 nm. Compared with an isolated dimer D1, the binding energy per dimer in the C1 chain has increased from 3.03 to 3.10 eV. The simulated STM images at  $-0.1$  V in Figure 3b show agreement with experiment in Figure 3d.

The results in Figure 3 raise an important question: if the stable dimer chains are made of metastable dimers, what has happened to the stable dimers? Our experiment reveals that after the deposition of adenine molecules on Cu(110) at RT a different dimer chain (labeled C2 in Figure 4) emerges. The C2 chain is along the  $(\pm 4, 1)$  directions, instead of the  $(\pm 1, 2)$  directions for C1. Here, the distance between two adjacent dimers can vary considerably from 0.89 to 1.06 nm. A large density of kinks is also observed. In addition, dimers inside a C2 chain can move. Figures 4a and 4b show two consecutive images taken for the same area. Two dimers, indicated by the larger black circle, have moved away during the time elapsed. One of them has added on to a nearby chain, indicated by the smaller blue circle. These observations are consistent with DFT-LAP calculation in which the dimer binding energy is only 0.01 eV per dimer. Figure 4c shows the atomic structure of C2 chain and the corresponding simulated STM image. We observe the transition from the metastable C2 chain to the stable C1 chain after annealing at 373 K.



**Figure 4.** Metastable adenine C2 dimer chains on Cu(110) surface. (a) and (b) show time-lapsed STM images ( $U = -0.1$  V and  $I = 0.04$  nA). Here, the black-line scale bar is 5 nm. (c) shows the calculated atomic structure for C2 (left) and the simulated image (right).

One may argue that the above experimental observations support a stronger binding energy for C2 than what has been predicted by DFT-LAP. While this is certainly possible, we would like to point out that although the C2 chain has relatively weak binding energy among its D2 dimers, isolated D2 dimers are stable and hence abundant during sample preparation at RT. In contrast, the formation of the stable C1 chain is kinetically hindered at this temperature due to the lack of its parent (metastable) D1 dimers. During annealing at elevated temperature, however, more D2 are promoted to D1. This appears to be a necessary step for the nucleation and formation of the C1 chains thereafter. One may also wonder if the chain direction can be reversed, for example, by disrupting the hydrogen bonds between N1–H8 in Figure 3c via a weak electromagnetic wave excitation or a tiny local current injection. Although being most elementary, such a tunability points to an important direction to build up functions out of amino acid groups.

At present, how to accurately calculate vdW interactions for complex systems like the current one is still controversial. Nevertheless, Table 1 shows that three vdW schemes, DFT-LAP, PBE-D, and vdW-DF2, yield identical conclusions, except for the formation of the metastable C2 chain from the D2 dimer. On this account, only the DFT-LAP results qualitatively agree with experiment.

## CONCLUSIONS

In summary, DFT-LAP calculation predicts the possible existence of a second (and metastable) adenine chain on the Cu(110) surface, which is subsequently identified by experiment. The application of the accurate vdW scheme, namely, DFT-LAP, further points to an important fact that the stable adenine chain is made of metastable dimers, whereas a close-in-energy metastable adenine chain is made of the stable dimers. Because of this, the adenine chain directions are temperature

controlled as revealed by experiment. By comparing the results between PBE and DFT-LAP, the critical role of the vdW interactions also becomes evident: PBE predicts stable D2 and C2. There is therefore never a chain rotation around the axis perpendicular to the Cu(110) surface.

## AUTHOR INFORMATION

### Corresponding Authors

\*E-mail zhangs9@rpi.edu (S.B.Z).

\*E-mail hjgao@iphy.ac.cn (H.J.G).

### Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

We acknowledge Karl-Heinz Ernst for fruitful discussions. Work at RPI was supported by US DOE Office of Basic Energy Sciences (Grant DE-SC0002623). Work in China was supported by MOST (Nos. 2013CBA01600 and 2011CB932700), NSFC (Nos. 61222112 and 11334006), and the Chinese Academy of Sciences. The supercomputer time was provided by the XSEDE Science Gateways program and the Computational Center for Nanotechnology Innovations (CCNI) at Rensselaer Polytechnic Institute (RPI).

## REFERENCES

- Aradhya, S. V.; Frei, M.; Hybertsen, M. S.; Venkataraman, L. Van der Waals Interactions at Metal/Organic Interfaces at the Single-Molecule level. *Nat. Mater.* **2012**, *11*, 872–876.
- Liu, W.; Carrasco, J.; Santra, B.; Michaelides, A.; Scheffler, M.; Tkatchenko, A. Benzene Adsorbed on Metals: Concerted Effect of Covalency and van der Waals Bonding. *Phys. Rev. B* **2012**, *86*, 245405.
- Li, G.; Cooper, V. R.; Cho, J.-H.; Du, S.; Gao, H.-J.; Zhang, Z. Self-Assembly of Molecular Wires on H-terminated Si(100) Surfaces Driven by London Dispersion Forces. *Phys. Rev. B* **2011**, *84*, 241406.
- Carrasco, J.; Santra, B.; Klimeš, J.; Michaelides, A. To Wet or Not to Wet? Dispersion Forces Tip the Balance for Water/Ice on Metals. *Phys. Rev. Lett.* **2011**, *106*, 026101.
- Otero, R.; Lukas, M.; Kelly, R. E. A.; Xu, W.; Lægsgaard, E.; Stensgaard, I.; Kantorovich, L. N.; Besenbacher, F. Elementary Structural Motifs in a Random Network of Cytosine Adsorbed on a Gold(111). *Surf. Sci.* **2008**, *319*, 312–315.
- Kelly, R. E. A.; et al. An Investigation into the Interactions Between Self-Assembled Adenine Molecules and a Au(111) Surface. *Small* **2008**, *4*, 1494–1500.
- Lingenfelder, M.; Tomba, G.; Costantini, G.; Colombi Ciacchi, L.; De Vita, A.; Kern, K. Tracking the Chiral Recognition of Adsorbed Dipeptides at the Single-Molecule Level. *Angew. Chem., Int. Ed.* **2007**, *46*, 4492–4495.
- Wang, Y.; Lingenfelder, M.; Classen, T.; Costantini, G.; Kern, K. Ordering of Dipeptide Chains on Cu Surfaces through 2D Cocrystallization. *J. Am. Chem. Soc.* **2007**, *129*, 15742–15743.
- Yang, B.; Wang, Y.; Li, G.; Cun, H.; Ma, Y.; Du, S.; Xu, M.; Song, Y.; Gao, H. J. Influence of Deoxyribose Group on Self-Assembly of Thymidine on Au(111). *J. Phys. Chem. C* **2009**, *113*, 17590–17594.
- Gao, H. J.; Gao, L. Scanning Tunneling Microscopy of Functional Nanostructures on Solid Surfaces: Manipulation, Self-Assembly, and Applications. *Prog. Surf. Sci.* **2010**, *85*, 28–91.
- Papageorgiou, A. C.; Fischer, S.; Reichert, J.; Diller, K.; Blobner, F.; Klappenberger, F.; Allegretti, F.; Seitsonen, A. P.; Barth, J. V. Chemical Transformations Drive Complex Self-Assembly of Uracil on Close-Packed Coinage Metal Surfaces. *ACS Nano* **2012**, *6*, 2477–2486.
- Bogdan, D.; Morari, C. Electronic Properties of DNA Nucleosides Adsorbed on a Au(100) Surface. *J. Phys. Chem. C* **2012**, *116*, 7351–7359.

- (13) Yamada, T.; Shirasaka, K.; Takano, A.; Kawai, M. Adsorption of Cytosine, Thymine, Guanine and Adenine on Cu(110) Studied by Infrared Reflection Absorption Spectroscopy. *Surf. Sci.* **2004**, *561*, 233–247.
- (14) Chen, Q.; Richardson, N. V. Enantiomeric Interactions between Nucleic Acid Bases and Amino Acids on Solid Surfaces. *Nat. Mater.* **2003**, *2*, 324–328.
- (15) Chen, Q.; Daniel, J. F.; Richardson, N. V. Self-Assembly of Adenine on Cu(110) Surfaces. *Langmuir* **2002**, *18*, 3219–3225.
- (16) Blankenburg, S.; Schmidt, W. G. Long-Range Chiral Recognition due to Substrate Locking and Substrate-Adsorbate Charge Transfer. *Phys. Rev. Lett.* **2007**, *99*, 196107.
- (17) Feyer, V.; Plekan, O.; Prince, K. C.; Šutara, F.; Skála, T.; Cháb, V.; Matolin, V.; Stenuit, G.; Umari, P. Bonding at the Organic/Metal Interface: Adenine to Cu(110). *Phys. Rev. B* **2009**, *79*, 155432.
- (18) Preuss, M.; Schmidt, W. G.; Bechstedt, F. Coulombic Amino Group-Metal Bonding: Adsorption of Adenine on Cu(110). *Phys. Rev. Lett.* **2005**, *94*, 236102.
- (19) Preuss, M.; Bechstedt, F. Self-Assembly of Adenine-Dimer Chains on Cu(110): Driving Forces from First-Principles Calculations. *Surf. Sci.* **2008**, *602*, 1643–1649.
- (20) Rauls, E.; Blankenburg, S.; Schmidt, W. G. DFT Calculations of Adenine Adsorption on Coin Metal (110) Surfaces. *Surf. Sci.* **2008**, *602*, 2170–2174.
- (21) McNutt, A.; Haq, S.; Raval, R. RAIRS Investigations on the Orientation and Intermolecular Interactions of Adenine on Cu(110). *Surf. Sci.* **2003**, *531*, 131–144.
- (22) Furukawa, M.; Yamada, T.; Katano, S.; Kawai, M.; Ogasawara, H.; Nilsson, A. Geometrical Characterization of Adenine and Guanine on Cu(110) by NEXAFS, XPS, and DFT Calculation. *Surf. Sci.* **2007**, *601*, 5433–5440.
- (23) Bogdan, D.; Morari, C. Effect of van der Waals Interaction on the Geometric and Electronic Properties of DNA Nucleosides Adsorbed on Cu(111) Surface: A DFT Study. *J. Phys. Chem. A* **2013**, *117*, 4669–4678.
- (24) Grimme, S. Semiempirical GGA-Type Density Functional Constructed with a Long-Range Dispersion Correction. *J. Comput. Chem.* **2006**, *27*, 1787–1799.
- (25) Tkatchenko, A.; Scheffler, M. Accurate Molecular van der Waals Interactions from Ground-State Electron Density and Free-Atom Reference Data. *Phys. Rev. Lett.* **2009**, *102*, 073005.
- (26) Sun, Y. Y.; Kim, Y.-H.; Lee, K.; Zhang, S. B. Accurate and Efficient Calculation of van der Waals Interactions within Density Functional Theory by Local Atomic Potential Approach. *J. Chem. Phys.* **2008**, *129*, 154102.
- (27) Dion, M.; Rydberg, H.; Schröder, E.; Langreth, D. C.; Lundqvist, B. I. Van der Waals Density Functional for General Geometries. *Phys. Rev. Lett.* **2004**, *92*, 246401.
- (28) Lee, K.; Murray, É. D.; Kong, L.; Lundqvist, B. I.; Langreth, D. C. Higher-Accuracy van der Waals Density Functional. *Phys. Rev. B* **2010**, *82*, 081101.
- (29) Xie, W.; Sun, Y. Y.; Zhang, S. B.; Northrup, J. E. Structure and Sources of Disorder in Poly(3-Hexylthiophene) Crystals Investigated by Density Functional Calculations with van der Waals Interactions. *Phys. Rev. B* **2011**, *83*, 184117.
- (30) For instance, if the chain were conductive, it would allow thermally switching electrical conduction between the ( $\pm 1$ , 2) and ( $\pm 4$ , 1) directions.
- (31) Zheng, Z.; Zhao, J.; Sun, Y.; Zhang, S. Structures and Lattice Energies of Molecular Crystals Using Density Functional Theory: Assessment of a Local Atomic Potential Approach. *Chem. Phys. Lett.* **2012**, *550*, 94–98.
- (32) Vanderbilt, D. Soft Self-Consistent Pseudopotentials in a Generalized Eigenvalue Formalism. *Phys. Rev. B* **1990**, *41*, 7892.
- (33) Wang, Y. L.; Gao, H. J.; Guo, H. M.; Wang, S.; Pantelides, S. T. Bonding Configurations and Collective Patterns of Ge Atoms Adsorbed on Si(111)-(7 × 7). *Phys. Rev. Lett.* **2005**, *94*, 106101.
- (34) Wang, Y. L.; Gao, H. J.; Guo, H. M.; Liu, H. W.; Batyrev, I. G.; McMahon, W. E.; Zhang, S. B. Tip Size Effect on the Appearance of a STM Image for Complex Surfaces: Theory Versus Experiment for Si(111)-(7 × 7). *Phys. Rev. B* **2004**, *70*, 073312.
- (35) Li, G.; Tamblyn, I.; Cooper, V. R.; Gao, H.-J.; Neaton, J. B. Molecular Adsorption on Metal Surfaces with van der Waals Density Functionals. *Phys. Rev. B* **2012**, *85*, 121409.
- (36) Cuadrado, R.; Cerdá, J. I.; Wang, Y.; Xin, G.; Berndt, R.; Tang, H. CoPc Adsorption on Cu(111): Origin of the C4 to C2 Symmetry Reduction. *J. Chem. Phys.* **2010**, *133*, 154701.