Iodine-Induced Structural Transformations of Co-Phthalocyanine on Au(111)

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ABSTRACT: Iodine doping in organic films has been well studied in polymer chemistry, while the role of iodine doping in regulating self-assembled molecular structures on surfaces under ultrahigh vacuum conditions has been little discussed. Herein, we choose iodine (I_2) and cobalt-phthalocyanine (CoPc) molecules as a model system that presents stepwise structural transformation of CoPc self-assembled structures



induced by I_2 doping at different dosages. It is found that iodine atoms prefer to occupy the face-centered cubic regions of the Au(111) herringbone reconstruction at the first step, and the herringbone reconstruction is completely lifted when dosing more and more I_2 until the system reaches a full-monolayer coverage. By regulating the I_2 dosages step by step on a CoPc precovered surface, various I-CoPc structures are obtained. Furthermore, thermal treatment results in the formation of more homogeneous long-range ordered I-CoPc structures.

INTRODUCTION

The field of structural transformation of self-assembled structures has been well studied in varied and innovative directions for on-surface molecular self-assembly.¹⁻³ Organic molecules interacting with various atoms (including metals or halogens) or small molecules have attracted more and more attention, where a variety of complicated multicomponent structures possessing specific properties have been con-structed.^{4–12} Among others, halogen is a common dopant in organic films in polymer chemistry.^{13–17} In recent years, the influence of individual halogen atoms on the formation of organic structures has received particular attention for onsurface chemistry.⁷⁻⁹ For example, bromine atoms can induce phase transition of assembled molecular superstructures via C-Br…Br bonds.⁷ It was also shown that atomic bromine mediated self-assembled networks by C-H…Br bonds.⁸ Recently, as reported by our group,⁹ the iodine atoms are found to be able to induce structural transformation of metal-organic motifs.

On the other hand, controllable construction of selfassembled nanostructures of metallo-phthalocyanine (MPc; M = Fe, Co, Ni, Mn, etc.) on solid surfaces 18-21 has been widely investigated over the past decades owing to its broad range of applications, such as molecular electronics, sensing elements, catalysis, light harvesting, and organic light-emitting diodes.^{22–24} Most previous works were focused on the adsorption of gas molecules (such as CO, 25 NO, 26 NH₃, 27,28 and so on 22,29) binding to the metallic center of MPc molecules as axial ligands, which result in geometric changes and furthermore influence both the electronic and magnetic properties of MPc, while halogen atoms are usually used to decorate the Pc molecules by attaching to either the metal center^{30,31} or the peripheral phenyl rings^{28,32} for the following in situ molecular assemblies or chemical reactions on surfaces.³³ Moreover, Göthelid et al.³⁴ showed that predeposition of iodine as an intermediate layer on

Pt(111) can reduce the interaction between ZnPc molecules and the metal surface. However, to our knowledge, the role of iodine doping in regulating self-assembled structures of MPc molecules on surfaces under ultrahigh vacuum (UHV) conditions has been little discussed. It is therefore of general interest to study the influence of halogen atoms in the selfassembly behaviors of MPc molecules on the surface, which may furthermore help to increase our fundamental understanding of the electronic and magnetic properties of the metal centers.

Herein, we choose iodine (I_2) as the dopant to investigate the interaction between iodine atoms and cobalt-phthalocyanine (CoPc) molecules on the Au(111) surface. From the highresolution scanning tunneling microscopy (STM) imaging, we unravel that (i) iodine atoms prefer to occupy the face-centered cubic (fcc) regions of the herringbone reconstructions surrounded by CoPc molecules at the first step, and the reconstructions are completely lifted when dosing more iodine to a full-monolayer coverage of a multicomponent system in a general scenario; (ii) by stepwise deposition of iodine atoms onto the CoPc precovered surface held at room temperature (RT), different I–CoPc self-assembled structures are observed; (iii) by thermal treatment of the surface, thermodynamically more stable I-CoPc structures are obtained. These findings provide a real-space determination of the interaction between iodine atoms and CoPc molecules on the surface, which would render further characterizations of the electronic and magnetic properties of the metal centers within different I-MPc structures.

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Figure 1. (a) Large-scale STM image of the self-assembled structure of CoPc molecules on Au(111) at RT. (b) Close-up STM image with the structural model superimposed. The substrate lattice direction is indicated by a white arrow, and the unit cell of the structure is indicated by a green contour. H, white; C, gray; N, blue; Co, light blue.



Figure 2. (a) STM image showing low-coverage iodine self-assembled structure on Au(111) at RT. (b) Large-scale and (c) close-up STM images showing the high-coverage iodine self-assembled structure on Au(111) at RT. The inset in (c) shows a line profile along the blue line.

METHODS

All STM experiments were performed in a UHV chamber (base pressure 1×10^{-10} mbar) equipped with a variable-temperature, fast-scanning "Aarhus-type" STM using electrochemically etched W tips purchased from SPECS,^{35,36} a molecular evaporator and an e-beam evaporator, and other standard instrumentations for sample preparations. The Au(111)substrate was prepared by several cycles of 1.5 keV Ar⁺ sputtering followed by annealing at 820 K for 15 min, resulting in clean and flat terraces separated by monatomic steps. The CoPc molecules (purchased from Tokyo Chemical Industry Co., Ltd.) were loaded into a glass crucible in the molecular evaporator. After a thorough degassing, the molecules were deposited onto the Au(111) substrate by thermal sublimation at 570 K, and the sample was thereafter transferred within the UHV chamber to the STM, where measurements were carried out at ~100-150 K. I₂ (purchased from Sigma-Aldrich, purity >99%) was then dosed in situ onto the surface through a leak valve at a pressure of 3×10^{-8} mbar for 1 min. Scanning conditions: $I_t = 0.5-0.8$ nA, $V_t = \sim 1200$ mV. All of the STM images were further smoothed to eliminate noises.

RESULTS AND DISCUSSION

Deposition of CoPc molecules on the clean Au(111) substrate at RT at the coverage of 0.7 monolayer leads to the formation of a highly ordered self-assembled structure (structure I), as shown in Figure 1a.³⁷ The Au(111) herringbone reconstruction is still preserved, indicating the relatively weak interactions between

CoPc molecules and the substrate.^{38,39} From the high-resolution close-up STM image (Figure 1b), we identify that a single CoPc molecule is imaged as a four-lobe pattern with a bright protrusion (i.e., the Co atom) in the center.³⁷ One of the axes of CoPc is along the [011] direction of the substrate, and owing to 3-fold symmetry of the Au(111) surface, three equivalent molecular orientations are observed.^{3,40,41} The self-assembled CoPc structure displays a square unit cell ($a_1 = b_1 = 15$ Å, $\theta_1 = 90^\circ$), as shown in the green contour in Figure 1b. The intermolecular interactions are mainly van der Waals forces.

Exposure of the clean Au(111) sample at RT to the iodine atmosphere at a pressure of 3×10^{-8} mbar for 1 min leads to the perturbation of the herringbone reconstruction, as shown in Figure 2a. As previously shown in the literature, 9,42 I₂ would dissociate into the atomic form and chemisorb on the surface under UHV conditions. Most of iodine atoms resolved in pronounced density of states aggregate in fcc regions of the Au(111) surface, and parts of soliton walls are perturbed. It can also be seen that some iodine clusters are located at the elbow sites. Similar behaviors were also observed for a variety of molecules adsorbed on the Au(111) surface.⁴³ Increasing the iodine dosages to a full-monolayer coverage leads to the formation of an extended close-packed structure with iodine atoms resolved as bright dots, as shown in Figure 2b. The highresolution image (Figure 2c) shows a $\sqrt{3} \times \sqrt{3}$ R30° lattice structure, and the distance between two nearest iodine atoms is ~5 Å (cf. the inset in Figure 2c), which is equal to $\sqrt{3}$ times of the Au(111) lattice constant as reported.^{44,45} In this case, the herringbone reconstruction is completely lifted. The disturb-



Figure 3. STM images showing the process of structural transformations via step-by-step deposition of iodine atoms on the CoPc precovered surface at RT. (a-e) Coexistence of different structures during the transformations. Dashed lines in (a) and (e) indicate domain walls of the Au(111) herringbone reconstruction and the structural boundaries. (f) Structure IV obtained by final dosing of iodine atoms on the sample.

Figure 4. (a-c) Close-up STM images of the I–CoPc structures II, III, and IV, where the unit cells are indicated in the images, respectively. (d-f) Corresponding schematic structural models. H, white; C, gray; N, blue; Co, light blue; I, brown.

ance of the herringbone reconstruction is attributed to the relatively strong interaction between iodine atoms and the surface.

To investigate the interaction between iodine atoms and CoPc molecules, we dose iodine step by step (at a vapor pressure of 3×10^{-8} mbar for 1 min at a low coverage of 0.05 monolayer in each step) on a CoPc precovered surface at RT, and a

Figure 5. Large-scale (a-c) and close-up (d-f) STM images of the I–CoPc structures V, VI, and VII, respectively, obtained by annealing the surface at 420 K. The unit cells are indicated in the images. (g-i) Corresponding schematic structural models. H, white; C, gray; N, blue; Co, light blue; I, brown.

successive process of structural transformations is observed, as shown in Figure 3. Figure 3a shows that the iodine atoms prefer to interact with the CoPc molecules in the fcc regions by forming the I-CoPc structure labeled as structure II (where the selfassembled structure of CoPc is labeled as structure I). By increasing the dosages of iodine, the I-CoPc structures labeled as III and IV within the fcc regions are obtained, as shown in Figure 3b-d, in which the CoPc molecules in hexagonal closedpacked (hcp) regions are still not perturbed (i.e., by keeping as structure I). Deposition of iodine for another 1 min under the same pressure results in the perturbation of the CoPc molecules in hcp regions (after fcc regions are completely occupied) by forming the structure II, as shown in Figure 3e. Finally, the whole surface is covered by I-CoPc structure IV (and meanwhile the herringbone reconstruction is lifted) with iodine doping by one more step, as shown in Figure 3f. The above process indicates that the interaction between iodine atoms and the substrate plays a crucial role in such a structural formation.

The close-up STM images allow us to identify the I–CoPc structural motifs within the structures II, III, and IV, as shown in Figure 4, in which the iodine atoms are imaged as dots embedded among the CoPc molecules. Figure 4a shows that an

iodine atom is located in the center of four CoPc molecules (and the self-assembled CoPc structure is little perturbed), and within the unit cell of $a_2 = b_2 = 15.5$ Å with $\theta_2 = 83^\circ$, the local ratio of CoPc/I is 1:1. From the close-up STM image of structure III (a_3 = 18.5 Å, b_3 = 19.5 Å, and θ_3 = 124°) shown in Figure 4b, it can be noted that three more iodine atoms are embedded into the two sides of CoPc molecules and local ratio of CoPc/I is 1:4. If the dosage of iodine is further increased, the structure IV is formed, as shown in Figure 4c, in which the whole periphery of each CoPc molecule is surrounded by iodine atoms. This structure is composed of two structural motifs, as indicated by green and blue contours in Figure 4c, in which the local ratios of CoPc/I are 1:5 (cf. the green unit cell of $a_4 = 20$ Å, $b_4 = 17.5$ Å, and $\theta_4 =$ 60°) and 1:6.5 (cf. the blue expanded unit cell of $a_5 = 21$ Å, $b_5 =$ 17.5 Å, and $\theta_5 = 64^\circ$), respectively. The similar structural transformation process is also observed in the case of Cotetraphenylporphyrin (CoTpp) rearrangements under NO atmosphere.⁴⁰

To investigate the influence of thermal treatment on the structural transformations of I–CoPc structures, we anneal the samples with different ratios of CoPc/I and obtain a series of homogeneous structures, as shown in Figure 5. After annealing

The Journal of Physical Chemistry C

the structure shown in Figure 3b at 420 K for 10 min, we observe the formation of a more ordered structure (labeled as structure V) with iodine atoms homogeneously distributed at the two sides of CoPc molecules, as shown in Figure 5a. In this case, the herringbone reconstruction is also completely lifted. From the close-up STM image shown in Figure 5d and the structural model in Figure 5g, we identify that the ratio of CoPc/I is 1:3 in this extended I–CoPc structure ($a_6 = 20$ Å, $b_6 = 16$ Å, and $\theta_6 =$ 84°). Further regulating the ratio of CoPc/I when deposited at RT and followed by annealing at 420 K results in other two extended I-CoPc structures. For example, the one shown in Figure 5b is identified as structure VI ($a_7 = 38.5$ Å, $b_7 = 53$ Å, and $\theta_7 = 75^\circ$), in which the ratio of CoPc/I is 1:4.25 as evidenced from the close-up STM image (Figure 5e) and the structural model (Figure 5h). Such a structure is an intermediate state before the iodine atoms completely occupy the available sites around CoPc molecules. When the iodine atoms reach the saturation situation, a homogeneous long-range ordered structure VII after annealing at 420 K is observed, as shown in Figure 5c. The homogeneous array has a unit cell of $a_8 = 20$ Å, b_8 = 17.5 Å with $\theta_8 = 60^\circ$. In this structure, the ratio of CoPc/I is 1:5. The structures V, VI, and VII are thermodynamically more stable than those before annealing, and in these structures, the iodine atoms are more homogeneously distributed, forming long-range ordered I-CoPc structures.

According to the previous literature, it is noted on the basis of the results that desorption of iodine atoms occurs at 523 K on Au(111).⁴⁴ In addition, the CoPc self-assembled structure remains unchanged on Au(111) when further annealed until reaching the C–H activation temperature at 680 K.²¹ Therefore, the annealing temperature 420 K is sufficiently low to safely exclude any possibilities of iodine atoms desorption and C–H activation in CoPc molecules. Moreover, we have performed additional comparative studies after annealing the homogeneous system shown in Figure 5a and found that the structure remained unchanged until 523 K, which can to some extent verify that the desorption energy is even higher. Therefore, thermal treatment triggers the structural transformation, resulting in the thermodynamically most stable structure, rather than the ratio of CoPc/I or the change of molecules.

CONCLUSIONS

In conclusion, on the basis of high-resolution STM images, we have systematically studied the interactions between iodine atoms and CoPc molecules by demonstrating the structural transformations of I-CoPc structures with respect to the ratios and thermal treatments. At low coverages of iodine on a CoPc precovered surface, the iodine atoms prefer to absorb on fcc regions of Au(111) herringbone reconstruction. By increasing iodine dosages step by step, various I-CoPc structures are obtained and the herringbone reconstruction is lifted finally. Thermal treatment can make iodine atoms diffuse more evenly to construct more homogeneous long-range ordered I-CoPc structures. The real-space experimental determination of I-CoPc hybrid structures at the single-molecule level presented in this work would render further characterization of the electronic and magnetic properties of the metal centers in relation to halogen doping, and also, on the other hand, investigation of the fundamental mechanism of transport properties with respect to halogen doping.

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) Pfeiffer, C. R.; Pearce, N.; Champness, N. R. Complexity of Two-Dimensional Self-assembled Arrays at Surfaces. *Chem. Commun.* **2017**, *53*, 11528–11539.

(2) Cai, L.; Sun, Q.; Bao, M.; Ma, H.; Yuan, C.; Xu, W. Competition between Hydrogen Bonds and Coordination Bonds Steered by the Surface Molecular Coverage. *ACS Nano* **2017**, *11*, 3727–3732.

(3) Cheng, Z. H.; Gao, L.; Deng, Z. T.; Jiang, N.; Liu, Q.; Shi, D. X.; Du, S. X.; Guo, H. M.; Gao, H. J. Adsorption Behavior of Iron Phthalocyanine on Au(111) Surface at Submonolayer Coverage. *J. Phys. Chem. C* 2007, *111*, 9240–9244.

(4) Zhang, C.; Wang, L.; Xie, L.; Ding, Y.; Xu, W. On-Surface Dual-Response Structural Transformations of Guanine Molecules and Fe Atoms. *Chem. – Eur. J.* 2017, 23, 2356–2362.

(5) Liu, J.; Lin, T.; Shi, Z.; Xia, F.; Dong, L.; Liu, P. N.; Lin, N. Structural Transformation of Two-Dimensional Metal–Organic Coordination Networks Driven by Intrinsic In-Plane Compression. *J. Am. Chem. Soc.* **2011**, *133*, 18760–18766.

(6) Krull, C.; Robles, R.; Mugarza, A.; Gambardella, P. Site- and Orbital-Dependent Charge Donation and Spin Manipulation in Electron-Doped Metal Phthalocyanines. *Nat. Mater.* **2013**, *12*, 337–343.

(7) Niu, T.; Wu, J.; Ling, F.; Jin, S.; Lu, G.; Zhou, M. Halogen-Adatom Mediated Phase Transition of Two-Dimensional Molecular Self-Assembly on a Metal Surface. *Langmuir* **2018**, *34*, 553–560.

(8) Lu, J.; Bao, D. L.; Dong, H.; Qian, K.; Zhang, S.; Liu, J.; Zhang, Y.; Lin, X.; Du, S. X.; Hu, W.; et al. Construction of Two-Dimensional Chiral Networks through Atomic Bromine on Surfaces. *J. Phys. Chem. Lett.* **2017**, *8*, 326–331.

(9) Xie, L.; Zhang, C.; Ding, Y.; Xu, W. Structural Transformation and Stabilization of Metal-Organic Motifs Induced by Halogen Doping. *Angew. Chem., Int. Ed.* **2017**, *56*, 5077–5081.

(10) Sun, Q.; Zhang, C.; Cai, L.; Tan, Q.; Xu, W. Oxygen-Induced Self-Assembly of Quaterphenyl Molecules on Metal Surfaces. *Chem. Commun.* **2014**, *50*, 12112–12115.

(11) Stadtmüller, B.; Lüftner, D.; Willenbockel, M.; Reinisch, E. M.; Sueyoshi, T.; Koller, G.; Soubatch, S.; Ramsey, M. G.; Puschnig, P.; Tautz, F. S.; et al. Unexpected Interplay of Bonding Height and Energy Level Alignment at Heteromolecular Hybrid Interfaces. *Nat. Commun.* **2014**, *5*, No. 3685.

(12) Liu, J.; Chen, T.; Deng, X.; Wang, D.; Pei, J.; Wan, L. J. Chiral Hierarchical Molecular Nanostructures on Two-Dimensional Surface by Controllable Trinary Self-Assembly. *J. Am. Chem. Soc.* **2011**, *133*, 21010–21015.

(13) Chiang, C. K.; Fincher, C. R.; Park, Y. W.; Heeger, A. J.; Shirakawa, H.; Louis, E. J.; Gau, S. C.; MacDiarmid, A. G. Electrical Conductivity in Doped Polyacetylene. *Phys. Rev. Lett.* **1977**, *39*, 1098– 1101.

The Journal of Physical Chemistry C

(14) Kumar, D.; Sharma, R. C. Advances in Conductive Polymers. *Eur. Polym. J.* **1998**, *34*, 1053–1060.

(15) Hayashi, K.; Shinano, T.; Miyazaki, Y.; Kajitani, T. Fabrication of Iodine-Doped Pentacene Thin Films for Organic Thermoelectric Devices. J. Appl. Phys. **2011**, 109, No. 023712.

(16) Bazaka, K.; Jacob, M. V. Effects of Iodine Doping on Optoelectronic and Chemical Properties of Polyterpenol Thin Films. *Nanomaterials* **2017**, *7*, 11.

(17) Solonenko, D.; Gasiorowski, J.; Apaydin, D.; Oppelt, K.; Nuss, M.; Keawsongsaeng, W.; Salvan, G.; Hingerl, K.; Sariciftci, N. S.; Zahn, D. R. T.; et al. Doping-Induced Polaron Formation and Solid-State Polymerization in Benzoporphyrin–Oligothiophene Conjugated Systems. J. Phys. Chem. C 2017, 121, 24397–24407.

(18) Gottfried, J. M. Surface Chemistry of Porphyrins and Phthalocyanines. *Surf. Sci. Rep.* 2015, *70*, 259–379.

(19) Takada, M.; Tada, H. Low Temperature Scanning Tunneling Microscopy of Phthalocyanine Multilayers on Au(111) Surfaces. *Chem. Phys. Lett.* **2004**, 392, 265–269.

(20) Kröger, J.; Jensen, H.; Néel, N.; Berndt, R. Self-Organization of Cobalt-Phthalocyanine on a Vicinal Gold Surface Revealed by Scanning Tunnelling Microscopy. *Surf. Sci.* **2007**, *601*, 4180–4184.

(21) Sun, Q.; Zhang, C.; Cai, L.; Xie, L.; Tan, Q.; Xu, W. On-Surface Formation of Two-Dimensional Polymer via Direct C-H Activation of Metal Phthalocyanine. *Chem. Commun.* **2015**, *51*, 2836–2839.

(22) Sedona, F.; Di Marino, M.; Forrer, D.; Vittadini, A.; Casarin, M.; Cossaro, A.; Floreano, L.; Verdini, A.; Sambi, M. Tuning the Catalytic Activity of Ag(110)-Supported Fe Phthalocyanine in the Oxygen Reduction Reaction. *Nat. Mater.* **2012**, *11*, 970–977.

(23) Blochwitz, J.; Pfeiffer, M.; Fritz, T.; Leo, K. Low Voltage Organic Light Emitting Diodes Featuring Doped Phthalocyanine as Hole Transport Material. *Appl. Phys. Lett.* **1998**, *73*, 729–731.

(24) Marom, N.; Kronik, L. Density Functional Theory of Transition Metal Phthalocyanines, II: Electronic Structure of MnPc and FePc-Symmetry and Symmetry Breaking. *Appl. Phys. A: Mater. Sci. Process.* **2009**, *95*, 165–172.

(25) Stróżecka, A.; Soriano, M.; Pascual, J. I.; Palacios, J. J. Reversible Change of the Spin State in a Manganese Phthalocyanine by Coordination of CO Molecule. *Phys. Rev. Lett.* **2012**, *109*, No. 147202.

(26) Park, J. H.; Choudhury, P.; Kummel, A. C. NO Adsorption on Copper Phthalocyanine Functionalized Graphite. *J. Phys. Chem. C* **2014**, *118*, 10076–10082.

(27) Isvoranu, C.; Wang, B.; Ataman, E.; Schulte, K.; Knudsen, J.; Andersen, J. N.; Bocquet, M. L.; Schnadt, J. Ammonia Adsorption on Iron Phthalocyanine on Au(111): Influence on Adsorbate-Substrate Coupling and Molecular Spin. J. Chem. Phys. **2011**, 134, No. 114710.

(28) Wäckerlin, C.; Nowakowski, J.; Liu, S. X.; Jaggi, M.; Siewert, D.; Girovsky, J.; Shchyrba, A.; Hählen, T.; Kleibert, A.; Oppeneer, P. M.; et al. Two-Dimensional Supramolecular Electron Spin Arrays. *Adv. Mater.* **2013**, 25, 2404–2408.

(29) Liu, L.; Yang, K.; Jiang, Y.; Song, B.; Xiao, W.; Li, L.; Zhou, H.; Wang, Y.; Du, S.; Ouyang, M.; et al. Reversible Single Spin Control of Individual Magnetic Molecule by Hydrogen Atom Adsorption. *Sci. Rep.* **2013**, *3*, No. 1210.

(30) Li, C.; Wang, Z.; Lu, Y.; Liu, X.; Wang, L. Conformation-Based Signal Transfer and Processing at the Single-Molecule Level. *Nat. Nanotechnol.* **2017**, *12*, 1071–1076.

(31) Hong, I. P.; Li, N.; Zhang, Y. J.; Wang, H.; Song, H. J.; Bai, M. L.; Zhou, X.; Li, J. L.; Gu, G. C.; Zhang, X.; et al. Vacuum Synthesis of Magnetic Aluminum Phthalocyanine on Au(111). *Chem. Commun.* **2016**, *52*, 10338–10341.

(32) Chen, L.; Li, H.; Wee, A. T. S. Nonlocal Chemical Reactivity at Organic-Metal Interfaces. *ACS Nano* **2009**, *3*, 3684–3690.

(33) Grill, L.; Dyer, M.; Lafferentz, L.; Persson, M.; Peters, M. V.; Hecht, S. Nano-Architectures by Covalent Assembly of Molecular Building Blocks. *Nat. Nanotechnol.* **2007**, *2*, 687–691.

(34) Ahmadi, S.; Agnarsson, B.; Bidermane, I.; Wojek, B. M.; Noël, Q.; Sun, C.; Göthelid, M. Site-Dependent Charge Transfer at the Pt(111)-ZnPc Interface and the Effect of Iodine. *J. Chem. Phys.* **2014**, *140*, No. 174702. (35) Besenbacher, F. Scanning Tunnelling Microscopy Studies of Metal Surfaces. *Rep. Prog. Phys.* **1996**, *59*, 1737–1802.

(36) Lægsgaard, E.; Österlund, L.; Thostrup, P.; Rasmussen, P. B.; Stensgaard, I.; Besenbacher, F. A High-Pressure Scanning Tunneling Microscope. *Rev. Sci. Instrum.* **2001**, *72*, 3537–3542.

(37) Chen, L.; Hu, Z.; Zhao, A.; Wang, B.; Luo, Y.; Yang, J.; Hou, J. G. Mechanism for Negative Differential Resistance in Molecular Electronic Devices: Local Orbital Symmetry Matching. *Phys. Rev. Lett.* **2007**, *99*, No. 146803.

(38) Kong, H.; Yang, S.; Gao, H.; Timmer, A.; Hill, J. P.; Arado, O. D.; Mönig, H.; Huang, X.; Tang, Q.; Ji, Q.; et al. Substrate-Mediated C–C and C–H Coupling after Dehalogenation. *J. Am. Chem. Soc.* **2017**, *139*, 3669–3675.

(39) Pham, T. A.; Song, F.; Nguyen, M. T.; Li, Z.; Studener, F.; Stöhr, M. Comparing Ullmann Coupling on Noble Metal Surfaces: On-Surface Polymerization of 1,3,6,8-Tetrabromopyrene on Cu(111) and Au(111). *Chem. – Eur. J.* **2016**, *22*, 5937–5944.

(40) Wang, Y.; Ge, X.; Manzano, C.; Kröger, J.; Berndt, R.; Hofer, W. A.; Tang, H.; Cerda, J. Supramolecular Patterns Controlled by Electron Interference and Direct Intermolecular Interactions. *J. Am. Chem. Soc.* **2009**, *131*, 10400–10402.

(41) Zhao, A. D. Scanning Tunneling Microscopy Study for Detecting and Manipulating Quantum States on the Molecular Scale. Ph.D. Dissertation, University of Science and Technology of China: Hefei, 2006.

(42) Rastgoo-Lahrood, A.; Björk, J.; Lischka, M.; Eichhorn, J.; Kloft, S.; Fritton, M.; Strunskus, T.; Samanta, D.; Schmittel, M.; Heckl, W. M.; et al. Post-Synthetic Decoupling of On-Surface-Synthesized Covalent Nanostructures from Ag(111). *Angew. Chem., Int. Ed.* **2016**, *55*, 7650–7654.

(43) Driver, S. M.; Zhang, T.; King, D. A. Massively Cooperative Adsorbate-Induced Surface Restructuring and Nanocluster Formation. *Angew. Chem., Int. Ed.* **2007**, *46*, 700–703.

(44) Rastgoo-Lahrood, A.; Lischka, M.; Eichhorn, J.; Samanta, D.; Schmittel, M.; Heckl, W. M.; Lackinger, M. Reversible Intercalation of Iodine Monolayers between On-Surface Synthesised Covalent Polyphenylene Networks and Au(111). *Nanoscale* **2017**, *9*, 4995– 5001.

(45) Utsunomiya, T.; Tatsumi, S.; Yokota, Y.; Fukui, K. Potential-Dependent Structures Investigated at the Perchloric Acid Solution/ Iodine Modified Au(111) Interface by Electrochemical Frequency-Modulation Atomic Force Microscopy. *Phys. Chem. Chem. Phys.* **2015**, *17*, 12616–12622.

(46) Buchner, F.; Seufert, K.; Auwärter, W.; Heim, D.; Barth, J. V.; Flechtner, K.; Gottfried, J. M.; Steinrück, H. P.; Marbach, H. NO-Induced Reorganization of Porphyrin Arrays. *ACS Nano* **2009**, *3*, 1789–1794.