Usage Report for Fiscal Year 2024

Project Title:

Exploring on-surface molecular synthesis under ultrahigh vacuum conditions

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１. Background and purpose of the project, relationship of the project with other projects

On-surface synthesis has been demonstrated as a promising bottom-up strategy to construct robust covalent nanostructures with desired patterns and efficient charge transport. By a combination of scanning tunneling microscopy/spectroscopy (STM/STS) and density functional theory (DFT) calculations, my research has been mainly focusing on exploration of on-surface molecular synthesis under ultrahigh vacuum (UHV) conditions both experimentally and theoretically. The ultimate goal of this project is to gain deep understandings of the chemical and physical properties of adsorbates on the surface and unravel the underlying reaction mechanisms with the help of theoretical calculations.

２. Specific usage status of the system and calculation method

I have been investigating the relevant molecular systems on metal surfaces by the combination of STM observations and theoretical calculations. Most of the calculations were performed in the DFT framework using the Vienna ab initio simulation package (VASP). The projector-augmented wave method was used to describe the interactions between ions and electrons. The Perdew−Burke−Ernzerhof generalized gradient approximation exchange-correlation functional was employed, and van der Waals interactions were included using the dispersion-corrected DFT-D3 method of Grimme. The atomic structures were relaxed using the conjugate gradient algorithm scheme as implemented in the VASP code until the forces on all unconstrained atoms were ≤ 0.03 eV/Å. Plane waves were used as a basis set with an energy cutoff of 400 eV. Simulated STM images were obtained based on the Tersoff−Hamann method. The climbing-image nudged elastic band (CI-NEB) was applied to locate the transition states, and the transition paths were optimized until the forces acting on the path were ≤ 0.03 eV/Å.

３. Result

In FY2024, I have systematically studied on-surface molecular assembly and reaction and mainly focused on the controllable regulation of non-covalent and covalent interactions between molecules. Research has been conducted on the exploration of on-surface coupling reactions and mechanisms based on the regulation of extrinsic components, thereby revealing a series of assembly and reaction mechanisms.

(1) Revelation of the mechanism of on-surface dehalogenative coupling reactions on Au(111) [ACS Nano 2024, 18, 14640–14649]

Precisely controlling reaction selectivity to generate desired products is one of the ultimate goals of chemists, which requires fundamental understandings of reaction mechanisms and key influencing factors at the atomic level. Molecule-substrate systems under ultra-high vacuum conditions provide an ideal playground for atomic-scale visualization of reaction intermediate states and products using the advanced scanning probe microscopy to further elucidate reaction mechanisms. Enormous efforts have been devoted primarily to the exploration of the respective properties of the molecular precursors and the underlying substrates, while the subtle interfacial properties between them, e.g. molecular adsorption behavior, have only recently received attention as essential factors. However, the influence of molecular chemisorption direction on reaction selectivity, which is directly related to the molecular diffusion step and is thus non-negligible in on-surface reactions, remains elusive so far.

In our study, we report the influence of molecular chemisorption direction on the selectivity of a dehalogenative coupling reaction between polymerization and cyclization on Au(111) (Figure 1). Such reaction selectivity was experimentally achieved based on different deposition and annealing strategies and evidenced at the submolecular level by scanning tunneling microscopy imaging. Furthermore, the chemisorption direction of a reactive intermediate was theoretically revealed to be the key to the corresponding diffusion steps and thus determining the reaction selectivity by density functional theory calculations.

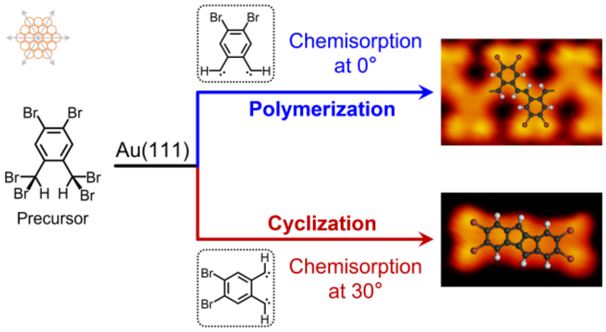

Figure 1. Schematic illustration showing the influence of molecular chemisorption direction on the reaction selectivity of dehalogenative coupling on Au(111).

Our results highlight the significant role of molecular chemisorption directions played in the on-surface reactions and syntheses, especially reevaluating the influence of an unfavorable chemisorption direction and state in reaction pathways and products. More importantly, it provides new fundamental insights into the regulation of reaction selectivity by exploiting some subtle interfacial parameters in the on-surface reactions, which facilitates the precise control of reaction selectivity to fabricate the desired nanostructures.

(2) Development of a novel halogen separation strategy for on-surface dehalogenative reactions on Au(111) [ACS Nano 2024, 18, 9082–9091]

On-surface dehalogenative reaction is significant for atomically precise synthesis of various carbon-based functional nanostructures. Despite the pre-designed and well-controlled reaction manner, it has long been suffering from its main byproduct (halogen, shortened as X) which often impedes the formation of extended nanostructures and property characterization, as well as high C–X activation temperatures, especially on relatively inert Au(111). With an ultimate goal of facilitating the dehalogenative reactions, tremendous efforts have been devoted to either eliminating dissociated halogens or to reducing reaction barriers, mainly through precursor design, halogen-to-halide conversion, and introduction of extrinsic metal atoms, which usually require harsh reaction conditions and lead to other byproducts instead. Therefore, it remains a great challenge to both eliminate the negative impacts of halogens and to facilitate C–Br activation under mild conditions.

In our study, we report a novel halogen separation strategy by introducing extrinsic sodium (Na) into dehalogenative reactions on Au(111), which not only effectively isolates the intermolecular halogens, but also facilitates the intramolecular C–Br activation under mild conditions (Figure 2). By a combination of high-resolution scanning tunneling microscopy imaging and density functional theory calculations, the formation of sodium halides (NaX) from halogens in the separation processes and the reduction in reaction temperatures and barriers have been revealed both experimentally and theoretically, demonstrating the versatility of Na as an effective “cleaner” and “dehalogenator” of surface halogens.

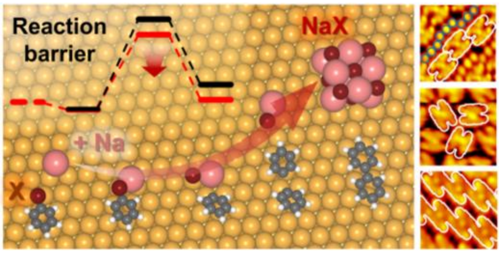

Figure 2. Schematic illustration showing the separation of halogen atoms by sodium from dehalogenative reactions on Au(111).

This “halogen separation strategy” should be significant for dehalogenation-based programmed structure construction and accurate property characterization.

(3) Regulation of reaction products of C–H activation on Ag(111) [ACS Nano 2024, 18, 31478–31484]

Dynamic chemistry, which spans both supramolecular and covalent chemistry, endows nanostructures with promising properties such as structural diversity and self-healing. Fundamental understanding of the dynamic evolution and directional regulation of equilibria, especially at the atomic and submolecular scale in real space, is invaluable for their applications in chemistry and materials science. On-surface chemistry allows the fine determination and control of the intermolecular interactions involved, both non-covalent and covalent, thus enabling the controlled regulation, precise fabrication and, more importantly, direct visualization of nanostructures. Appealed by the robustness of covalent bonds compared to non-covalent ones, tremendous endeavors have been devoted to exploiting dynamic covalent chemistry to synthesize molecular nanostructures and to visualize dynamic processes at solid/liquid interfaces under ambient conditions, which are generally responsive to internal factors. However, directing dynamics of covalent nanostructures, e.g., the typical ring-chain equilibria, on surface by an extrinsic intermolecular interaction remains elusive and challenging, and should bridge the gap between supramolecular and covalent chemistry.

In our study, we have successfully directed the ring-chain equilibrium of covalent organometallic (OM) structures on surface at room temperature by regulating intermolecular electrostatic interactions (Figure 3). This is, to our knowledge, the first time to achieve on-surface dynamic covalent chemistry under ultrahigh vacuum conditions.

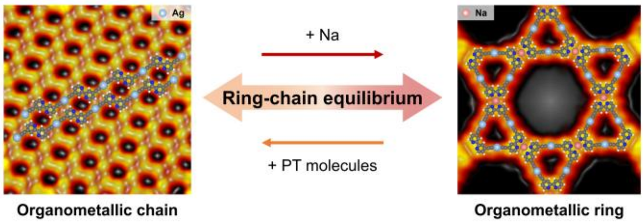

Figure 3. Directing organometallic ring–chain equilibrium by electrostatic interactions on Ag(111).

We select a molecular precursor, 4,4’-diethynyl-2,2’-bipyridine, consisting of two terminal alkynyl groups (for the construction of C_{sp}–Ag–C_{sp} OM bonds) and a bipyridyl moiety (as the potential site for interacting with extrinsic Na). On the basis of dynamic C_{sp}–Ag–C_{sp} OM bonds, by introducing Na or PT molecules to subtly regulate intermolecular electrostatic interactions, we have controllably realized the ring-chain interconversion between covalent trans OM chains and cis OM rings on Ag(111).

To further unravel the mechanism for the dynamic evolution processes and to reveal the role of Na, DFT calculations were performed, as displayed in Figure 4. As shown in the upper panel, for a single DEBPy molecule, the trans-conformation (IS) is energetically more stable than the cis-one (FS) on Ag(111), by 0.28 eV, consistent with the experimental observation. Such a trans-to-cis isomerization has an energy barrier of ~0.68 eV and is endothermic, indicating that the trans-to-cis isomerization is thermodynamically unfavorable.

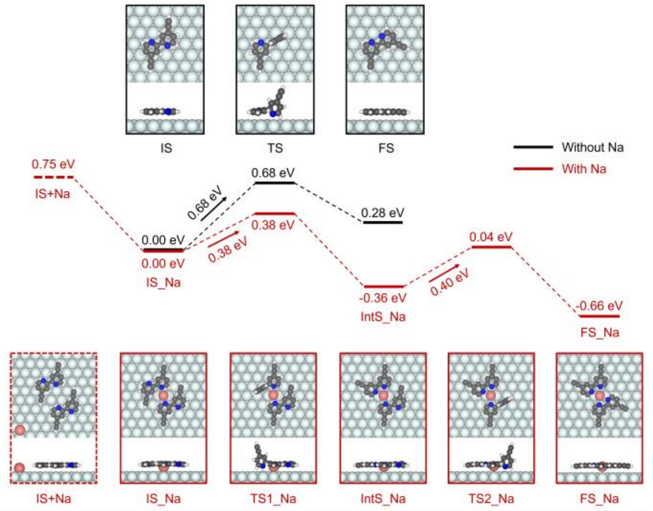

Figure 4. DFT-calculated reaction pathways for the cis-trans interconversion of a DEBPy molecule and a Na-interlinked dimer on Ag(111) without and with the assistance of Na (upper and lower panels), respectively. The structural models of the initial states (IS, IS_Na), transition states (TS, TS_Na), intermediate state (IntS_Na) and final states (FS, FS_Na) are presented, and their energies are provided with respect to those of the corresponding IS. C: gray; H: white; N: navy blue; Na: pink; Ag substrate: light blue.

By contrast, by adding a Na atom to the molecular system with two trans-DEBPy molecules (as shown in the lower panel), the Na atom initially interacts with two opposite N sites of the trans-molecules via 2-fold Na···N electrostatic interactions, forming the Na-interlinked trans-dimer (IS_Na), which is energetically more favorable than the situation without any interactions (IS+Na), by 0.75 eV. Subsequently, with the assistance of the Na atom, the trans-dimer underwent a two-step trans-to-cis isomerization, with energy barriers of ~0.38 eV and ~0.40 eV, respectively, forming the energetically more stable metal–organic cis-dimer via 4-fold Na···N electrostatic interactions. Thus, in the presence of Na, the trans-to-cis isomerization is converted from endothermic to exothermic, which explains the chain-to-ring conversion at RT. Notably, after the addition of PT molecules, the competitive preference of PT to interact with Na over cis-DEBPy results in the removal of Na and allows the reverse cis-to-trans isomerization accompanied by the ring-to-chain conversion.

Our findings unravel the dynamic mechanism of covalent polymers governed by weak intermolecular interactions at the submolecular level, which should integrate both the adaptability of supramolecular chemistry and the robustness of covalent bonding, and offer great opportunities for the fabrication of self-healing polymeric nanostructures.

(4) Control of the selectivity of reaction products by transmetalation on Ag(111) [J. Phys. Chem. Lett. 2024, 15, 11862–11868]

On-surface synthesis has shown great promise in the bottom-up construction of covalent bonding (predominantly C–C bonds) between molecular building blocks with atomic precision, high robustness and efficient electron transfer for potential applications in molecular electronics. To improve the reaction selectivity, metal-organic interactions provided by integrated metals have been generally exploited to provide pre-assembly with molecular components, which exhibit high reversibility, anchor specific molecular conformations, and further allow the precise construction of target nanostructures. Accordingly, various metal atoms have been incorporated into molecular systems on metal substrates, ranging from intrinsic to extrinsic atoms, and more recently, to their cooperative effects, resulting in distinct covalent nanostructures. However, the competitive interactions between intrinsic and extrinsic adatoms and their roles in the formation of different covalent nanostructures remain elusive.

In our study, we have successfully controlled the selectivity of covalent reaction products between isomerically specific trans-chains and cis-rings by transmetalation from intrinsic Ag adatoms to extrinsic Na atoms on a Ag(111) substrate (Figure 5). By a combination of high-resolution scanning tunneling microscopy imaging and density functional theory calculations, the Ag-stabilized organometallic (OM) networks and Na-stabilized OM Kagome structures were constructed in response to the presence of intrinsic Ag adatoms and the addition of extrinsic Na atoms, respectively, leading to the formation of covalent trans-chains and cis-rings with high selectivity as reaction products after the release of metal atoms. Moreover, direct transmetalation of these metal-organic intermediates was also achieved via competitive interactions, which eventually led to the conversion to cis-rings, where the electrostatic interactions provided by extrinsic Na atoms were crucial for the selectivity in reaction products.

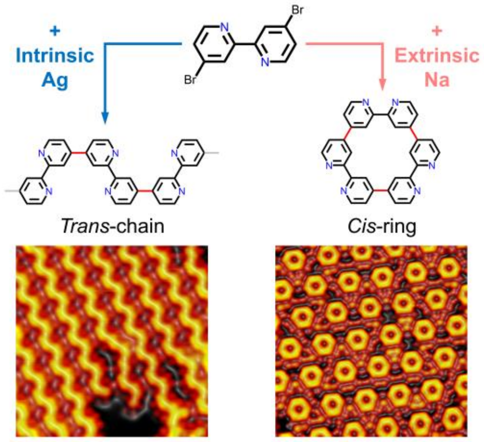

Figure 5. Control of the selectivity of reaction products by transmetalation on Ag(111).

Our results directly visualize the competitive interactions between intrinsic and extrinsic metal atoms in real space and demonstrate their influences on the selectivity of reaction products, which should broaden the regulatory strategies for on-surface synthesis that shed light on the controllable and selective synthesis of target covalent nanostructures.

4. Conclusion

In conclusion, I have corroborated both experimentally and theoretically a series of on-surface molecular reactions and their reaction mechanisms on metal surfaces. Firstly, I have revealed new mechanisms for on-surface reactions, which elucidate the influence of molecular chemisorption direction on reaction selectivity (including reaction products and pathways). Secondly, a new strategy has been proposed for the development of on-surface reaction strategies, which utilizes extrinsic components to assist in the separation of surface halogens and to prepare low-dimensional carbon-based nanostructures. At the same time, the target reaction products have been selectively synthesized and regulated.

5. Schedule and prospect for the future

In FY2025, I plan to further deeply explore some other topics related to the on-surface molecular synthesis from the following prospects: (1) adsorption configurations; (2) molecule-molecule interactions and molecule-substrate interactions; (3) electronic and magnetic properties; (4) possible reaction pathways.

Additionally, I would like to continue using the Hokusai system for the FY2025.

Usage Report for Fiscal Year 2024

Fiscal Year 2024 List of Publications Resulting from the Use of the supercomputer

[Paper accepted by a journal]

1. Zewei Yi, Zhaoyu Zhang, Yuan Guo, Yuhong Gao, Rujia Hou, Chi Zhang*, Yousoo Kim*, Wei Xu*. “Revealing the Influence of Molecular Chemisorption Direction on the Reaction Selectivity of Dehalogenative Coupling on Au(111): Polymerization versus Cyclization” *ACS Nano* **2024**, 18, 22, 14640–14649 (May, 2024).
2. Zhaoyu Zhang, Yuhong Gao, Zewei Yi, Chi Zhang*, Wei Xu*. “Separation of Halogen Atoms by Sodium from Dehalogenative Reactions on a Au(111) Surface” *ACS Nano* **2024**, 18, 12, 9082–9091 (March, 2024).
3. Rujia Hou, Yuhong Gao, Yuan Guo, Chi Zhang*, Wei Xu*. “Directing Organometallic Ring–Chain Equilibrium by Electrostatic Interactions” *ACS Nano* **2024**, 18, 45, 31478–31484 (October 30, 2024).
4. Lei Xu, Chengjie Zhang, Rujia Hou, Yuhong Gao, Zhaoyu Zhang, Zewei Yi, Chi Zhang*, Wei Xu*. “Controlling the Selectivity of Reaction Products by Transmetalation on a Ag(111) Substrate” *J. Phys. Chem. Lett.* **2024**, 15, 47, 11862–11868 (November 20, 2024).

[Oral presentation]

1. Chi Zhang*, Zhaoyu Zhang, Zewei Yi, Yuhong Gao, Rujia Hou, Wei Xu. “Steering on-surface reactions using extrinsic components and mechanistic study”, the 15th International Conference on Atomically Controlled Surfaces, Interfaces and Nanostructures (ACSIN-15), May 10-13, 2024, Su Zhou, China.