Usage Report for Fiscal Year 2019

Project Title:

Exploring on-surface photo-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. Photochemical-induced covalent-bonding creation reaction (defined as “photo-synthesis” here) is highly limited on surface under ultrahigh vacuum (UHV) conditions in comparison with thermal-driven synthesis and is expected to have an increasingly broad prospect as is in conventional solution chemistry. By combination of scanning tunneling microscopy/spectroscopy (STM/STS) and theoretical calculations, my research has been mainly focusing on exploration of on-surface photo-synthesis under 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 combination of STM/STS observations and theoretical calculations. The calculations were performed in the framework of density functional theory (DFT) by using the Vienna ab initio simulation package (VASP). The projector-augmented wave method was used to describe the interaction 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 for the models. The simulated STM images were obtained by the Hive program 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 typically ≤ 0.03 eV/Å.

３. Result

In FY2019, I have been mainly studying the following two systems: (1) on-surface cycloaddition reaction; and (2) on-surface self-assembly of one tripod molecule by combination of STM and DFT calculations.

(1) **On-surface metal-mediated dehalogenative cycloaddition reaction** [Zhang C., Kazuma E. and Kim Y. Angew. Chem. Int. Ed., 2019, 58, 17736-17744.]

Dehalogenative cycloaddition reaction is a powerful strategy to generate new ring scaffolds with π-conjugated features on a surface, and thus holds great promise toward atomically precise electronic devices or nanomaterials. The ortho-dihalo substitution provides a good strategy to realize cycloaddition. However, the limited understanding of intermediate states involved hinders mechanistic exploration for further precise design and optimization of reaction products.

In this study, we clarified a metal-mediated dehalogenative cycloaddition reaction pathway by visualizing the step-by-step evolution of stable local minima (competing surface-stabilized radicals and organometallic intermediates) toward cycloaddition products from STM observation in real space (Fig. 1). We chose the 2,3,6,7,10,11-hexabromotriphenylene (HBTP) molecule as the molecular precursor with threefold ortho-dibromo substitution for possible dehalogenative cycloaddition into two dimensions on Ag(111).

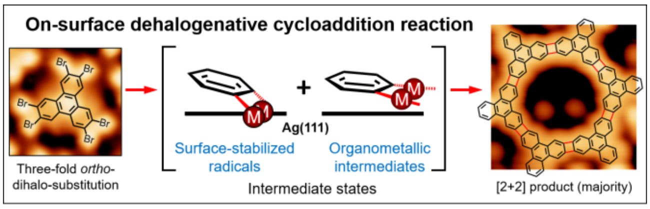

Fig. 1 Schematic illustration of the metal-mediated dehalogenative cycloaddition reaction pathway of HBTP molecule on Ag(111).

Based on the experimental observations, we further calculated the adsorption configurations of the molecular precursor, intermediate states, final covalent-bonded nanostructures and the corresponding self-assembled structures on Ag(111). One typical intermediate state, that is, the organometallic network structure, is shown in Fig. 2. We also revealed the primary intermolecular interactions involved in these structures. Direct comparisons of the DFT-simulated STM images and the STM data have been gained to further confirm the rationality of hypothesis. Fig. 2 indicates nice agreement between the experimental and theoretical results.

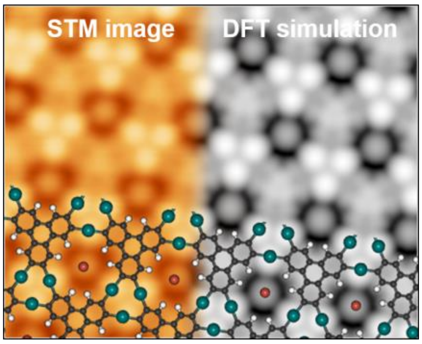

Fig. 2 Submolecularly resolved STM image of the organometallic network (as one typical intermediate state) partially superimposed with the corresponding DFT simulation (the gray part) and structural model on Ag(111).

Finally, at higher temperature 2D covalent networks are formed after several competing intermediate states. Four elementary components, i.e., dominant di-TP, also cis-BTP and trans-BTP, and one minor tris-TP, are found to be involved in the covalent networks (Fig. 3). The corresponding chemical structures and STM morphologies are displayed in Fig. 3a,b. The well-resolved phenyl rings indicate direct correlations between them and also different connection modes. This assignment is further evidenced by DFT-simulated STM images (Fig. 3c) based on the corresponding models on Ag(111) (Fig. 3d) with good consistence in dimension and topography. Besides, the ability in the nice interpretation of long-range polymers based on the elementary components further provides solid evidence to support the assignment of different bonding modes.

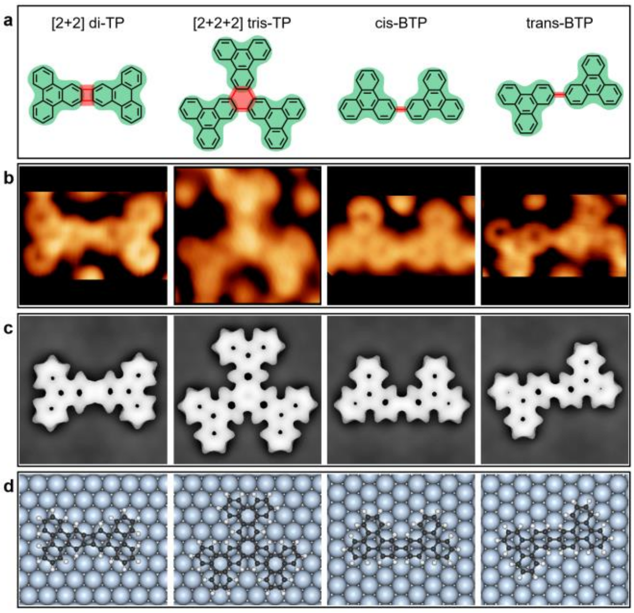

Fig. 3 Four elementary components involved in the formed covalent networks by cycloaddition. (a) Chemical structures of four elementary components (with contours). (b) Submolecularly resolved STM images. (c) Corresponding STM simulations and (d) DFT-optimized structural models on Ag(111).

On the basis of the structural models, the CI-NEB has been used to find the transition states, and subsequently, the possible reaction pathways with the corresponding reaction barriers have been discovered from the point of theoretical calculations (Fig. 4). Based on both experimental and theoretical indications, the underlying mechanisms of the on-surface dehalogenative cycloaddition reaction process have been revealed to provide an atomic-scale understanding of the overall reaction process.

As shown in Fig. 4, we revealed that the first process can be divided into three primary steps：Ⅰ. HBTP to debr-HBTP；Ⅱ. debr-HBTP to organometallic dimer (one side step：Ⅱ’. debr-HBTP to debr2-HBTP)；Ⅲ. organometallic dimer to trimer. Fig. 4a shows the simplified energy diagram of the process (starting from HBTP, through debr-HBTP, and subsequently organometallic dimer and debr2-HBTP, toward organometallic trimer), in which the energy barriers of each process are provided along the reaction pathways. The typical reaction pathways involved and the corresponding structural models of the local minima (i.e., initial states (IS) and final states (FS)) and transition states (TS) are displayed in Fig. 4b-e.

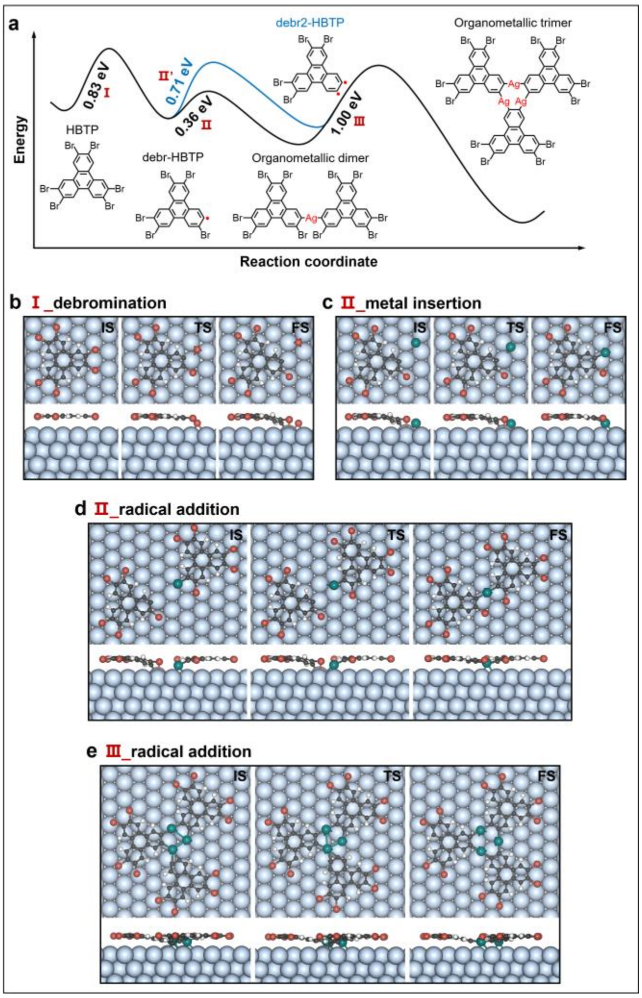

Fig. 4 DFT-calculated reaction pathways from intact HBTP toward formation of organometallic trimer on Ag(111). (a) Simplified energy diagram of the process. (b)-(e) Selected typical reaction pathways and the corresponding structural models of the local minima. (b) Debromination of HBTP to form debr-HBTP. (c) Metal insertion to debr-HBTP to form debr-HBTP+Ag. (d) Radical addition of debr-HBTP and debr-HBTP+Ag to form organometallic dimer. (e) Radical addition of debr2-dimer+2Ag and debr2-HBTP to form organometallic trimer.

As the final process, 2D organometallic networks convert to the dominant di-TP and very limited tris-TP units via formal [2+2] and [2+2+2] cycloadditions (cf. Fig. 3). Endothermic metal elimination process and exothermic cycloaddition process among unstable surface-stabilized radicals has further been revealed from the DFT calculations.

Here, from our stepwise annealing strategy and STM observations, only stable local minima (HBTP, debr-HBTP, dominant organometallic dimer and minor debr2-HBTP, 2D organometallic network and cycloaddition products) exist, which imply the metal-mediated dehalogenative cycloaddition pathway. The substrate here both stabilizes the dehalogenated radicals and provides adatoms to form stable organometallic intermediates. From the theoretical perspective, the incorporation of adatom results in the increased stability and decreased diffusion barrier for further meeting other radicals, which also favors the evolution to organometallic intermediates over the competing radicals. A key insight is the clarification of essential incorporation of metal substrate and adatoms in the evolution process, which determines the selection between competing radicals and organometallic intermediates and can be generalized to other halogen-based on-surface reactions.

(2) **Self-assembly of one three-dimensional tripod molecule** [Chaunchaiyakul S., Zhang C., Imada H., Kazuma E., Ishiwari F., Shoji Y., Fukushima T. and Kim Y. J. Phys. Chem. C, 2019, 123, 31272-31278.]

Upright orientation of a molecular adsorbate is one of the most practical keys for controlling surface functionalities by using self-assembled monolayers. However, lateral interactions between the upright molecules become more complex than planar molecules since they are not confined in a single plane. In this work, we studied the self-assembly of TMMT molecule on Ag(111) (cf. Fig. 5) and explored the intermolecular interactions in forming the structures.

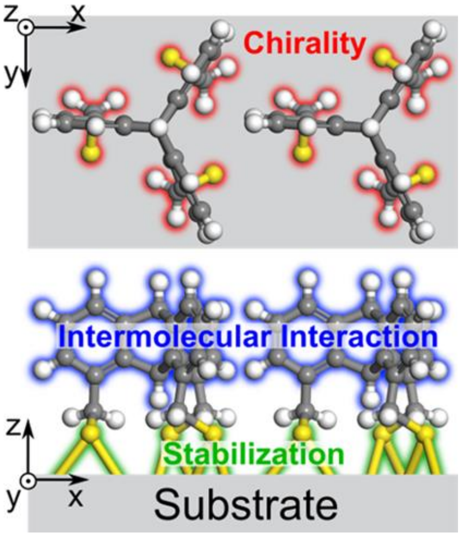

Fig. 5 Schematic illustration of one self-assembled structure of 1,8,13-tris(mercaptomethyl)-triptycenes (TMMT) molecule on Ag(111).

Through combined analysis of experimental and theoretical results of individual TMMTs, we verified their upright orientation on Ag(111). They form four TMMT chiral stereoisomers on surface upon adsorption. The four isomers self-assembled into four types of enantiopure and two types of racemic domains. To explain the main interactions involved, we performed further DFT calculations, which show a weak C-H···π intermolecular interaction between the triptycene units and a strong S-Ag molecule-substrate interaction.

Our results provide a fundamental insight into the formation of upright-oriented molecular assemblies in which the stabilizing forces are not confined two-dimensionally. We reveal that the S atoms, methylene groups, and the triptycene unit of the TMMT molecules play different roles in the self-assembly process. Such fundamental understanding is of important consideration in the design of precursor molecules to achieve precisely aligned functional surfaces and therefore to establish three-dimensional molecular architectures.

4． Conclusion

In FY2019, I have been trying to combine the theoretical calculations with STM/STS experiments to examine a variety of molecular behaviors and reaction pathways towards target nanostructures on the metal surfaces. Such kinds of study made a good combination of real-space observation and theoretical prediction to provide fundamental understandings into the underlying mechanisms in the on-surface reaction/self-assembly processes on the surfaces.

(1) We established the stepwise metal-mediated cycloaddition pathway on Ag(111), along with the competition between radicals and organometallic intermediates. Our results provide the experimental and theoretical understandings into the on-surface dehalogenative cycloaddition reaction and further halogen-based syntheses, which should be significant for the precise design and optimization of n-membered carbocyclic or heterocyclic architectures.

(2) Our theoretical and experimental study of the tripod molecule shows the advantage of three-dimensional precursors with a rigid molecular framework: the capability of adding multiple functional groups to a single molecule. This provides high flexibility in tuning lateral interactions, surface functionalities, and molecule-substrate interactions of self-assembled monolayers. It also makes the triptycene tripod a practically promising platform in the exploration of bio-engineering, molecule-based electronics, and organic energy conversion devices based on interfacial functionalization.

5． Schedule and prospect for the future

In FY2020, I plan to further deeply explore some other topics related to the on-surface photo-induced 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 system for the FY2020 to finish the current project. Hopefully, one paper will be published in the FY2020.

Usage Report for Fiscal Year 2019

Fiscal Year 2019 List of Publications Resulting from the Use of the supercomputer

[Paper accepted by a journal]

1. Zhang C., Kazuma E. and Kim Y.: Atomic-scale visualization of the stepwise metal-mediated dehalogenative cycloaddition reaction pathways: competition between radicals and organometallic intermediates. Angew. Chem. Int. Ed., 2019, 58, 17736-17744.

2. Chaunchaiyakul S., Zhang C., Imada H., Kazuma E., Ishiwari F., Shoji Y., Fukushima T. and Kim Y.: Self-assembly growth of an upright molecular precursor with a rigid framework. J. Phys. Chem. C, 2019, 123, 31272-31278.

[Oral presentation]

1. Zhang C., Kazuma E. and Kim Y.: “Atomic-Scale Visualization of the Stepwise Metal-Mediated Dehalogenative Cycloaddition Reaction Pathways” 第13回 表面･界面スペクトロスコピー, Tokyo, Japan, 2019, December 6-7.