

Controlling the Selectivity of Reaction Products by Transmetalation on a Ag(111) Substrate

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ABSTRACT: On-	surface synthesis has shown o	rreat promise in the precise bottom-up	Br
preparation of mo	lecular nanostructures. Apart f	From the direct $C-C$ coupling reaction	Intrinsic Extrinsi

preparation of molecular nanostructures. Apart from the direct C–C coupling reaction pathway, an alternative strategy is to exploit the metal–organic interactions provided by integrated metals for preassembly, which exhibit high reversibility and can anchor specific conformations of molecular precursors, thus allowing the precise construction of nanostructures with improved reaction selectivity. Previous studies have mainly been devoted to the construction of target reaction products through the incorporation of metal atoms, ranging from intrinsic to extrinsic atoms on metal substrates and, more recently, to their cooperative effects. However, the formation of different covalent nanostructures by competitive interactions between intrinsic and extrinsic adatoms remains elusive. Herein, we controlled the selectivity of covalent reaction products from isomerically specific *trans*-chains to *cis*-rings, resulting from the transmetalation of intrinsic Ag adatoms to extrinsic Na atoms on a Ag(111) substrate. Our results exhibit the competitive interactions between



intrinsic and extrinsic metal atoms in real space and demonstrate their influence 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.

n-surface synthesis, as a prevailing interdisciplinary field, has shown great promise in establishing covalent bonds between molecular building blocks and fabricating molecular nanoarchitectures on surfaces in a bottom-up way. $^{\rm 1-4}$ A direct way to construct covalent bonds between molecular precursors is to exploit covalent reactions (e.g., the well-known Ullmanntype coupling^{4–8} and series of C–C coupling reactions^{9–12}), whereas the irreversibility of such covalent nature and undesirable reaction pathways usually inhibit defect healing and lead to poor reaction selectivity.¹³ Based on the preassembly of molecular precursors, including the template effect provided by metal-organic interactions,¹³⁻¹⁵ an alternative strategy has been proposed by first forming metal-organic structures and then annealing to release metals to obtain the final covalent products. Compared to covalent C-C bonds, metal-organic interactions exhibit reversibility and higher flexibility, allowing defect healing and the formation of extended molecular nanostructures.¹⁶ In particular, the integrated metals can anchor specific conformations of molecular precursors and direct their assembly and even reactions,^{13,17–19} further allowing the precise construction of nanostructures with improved reaction selectivity. So far, enormous efforts have been devoted to the construction of target reaction products based on the integration of metal atoms forming metal-organic intermediates. The intrinsic adatoms usually result in various covalent nanostructures according to different types of substrates,¹⁷ while the introduction of extrinsic adatoms (e.g., Fe, Cu, Na, Gd) can

further provide distinct products from those obtained in the absence of these adatoms.^{13–15,18,19} More recently, it has been shown that some specific nanostructures are formed based on the cooperative effects of intrinsic and extrinsic atoms.^{13,18} However, to the best of our knowledge, the formation of different covalent nanostructures by the competitive interactions between intrinsic and extrinsic adatoms remains elusive, which would be crucial for the fundamental understanding of the role of transmetalation in reaction selectivity. It is therefore of general interest to directly visualize the influences of intrinsic and extrinsic adatoms on the selectivity of reaction products and to compare their transmetalation processes, which should be inspiring for the selective synthesis of target covalent nanoarchitectures on the surface.

In this study, the selectivity of covalent reaction products from isomerically specific *trans*-chains to *cis*-rings was successfully controlled by transmetalation from intrinsic Ag adatoms to extrinsic Na atoms on a Ag(111) substrate. The selected molecular precursor, 4,4'-dibromo-2,2'-bipyridine (abbreviated as DBBPy, cf. Scheme 1), contained a bipyridyl

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"Reaction pathways of DBBPy molecules on Ag(111) in response to the presence of intrinsic Ag adatoms and the addition of extrinsic Na atoms, respectively, involving two different metal–organic intermediates and covalent products (i.e., *trans*-chains and *cis*-rings) with high selectivity, and their transmetalation process. C: gray; H: white; N: blue; Br: red; Ag adatom: sky-blue; Na: pink.

moiety for interacting with metal atoms,^{13,19,20} providing the possibility to anchor the specific cis-conformation of DBBPybased molecular components. The Ag adatoms on the Ag (111) substrate and Na atoms were applied as intrinsic and extrinsic metal sources, respectively. Through a combination of high-resolution scanning tunneling microscopy (STM) imaging and density functional theory (DFT) calculations, Agstabilized organometallic (OM) networks and Na-stabilized OM Kagome structures were constructed in response to the presence of Ag adatoms and the addition of 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 by introducing Na atoms into the Ag-stabilized OM networks through competitive interactions, which eventually led to conversion to cis-rings. In addition, the electrostatic interactions between extrinsic Na atoms and cis-bipyridyl moieties in all molecular forms were shown to be crucial for the selective construction of the cis-rings. Our results exhibit the competitive interactions between intrinsic and extrinsic metal atoms in real space and demonstrate their influence on the selectivity of reaction products, which should shed light on the controllable and selective synthesis of covalent nanostructures on surface.

After the deposition of DBBPy molecules on Ag(111) held at ~250 K, a close-packed self-assembled structure formed (Figure 1a), which consisted entirely of Z-shaped molecules with adjacent molecules alternating in a "head-to-body" arrangement (Figure 1b). Each Z-shaped molecule has two bright protrusions at both ends linked by a darker rod and is attributed to the *trans*-DBBPy molecule based on both the morphology and the relative stability compared to that of the *cis*-form. DFT calculations were further performed on an individual *trans*-DBBPy molecule absorbed on Ag(111), and the energetically most favorable model is shown in Figure 1c, adopting a flat-lying configuration. Based on the DFToptimized model, the STM simulation was implemented and is shown in the upper part of Figure 1d. The *trans*-DBBPy has a Z-shaped morphology consistent with that shown in the STM images. In addition, a *cis*-DBBPy molecule absorbed on Ag(111) was also simulated, showing a C-shaped morphology instead (the lower panel of Figure 1d).

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Interestingly, upon annealing the above sample to \sim 500 K, a triangular network structure gradually formed (Figure S1), and the regular network structure is shown in Figure 1e. The closeup high-resolution STM image (Figure 1f) further shows that the network is constructed by hexagonal trimers, trapezoidal monomers and round dots, where the hexagonal trimers are connected to each other via trapezoidal monomers (as indicated by the corresponding blue silhouettes, respectively). It is worth noting that the trapezoidal monomers resemble the C-shaped cis-DBBPy molecule instead of the Z-shaped transform. This thus indicated that trans-to-cis isomerization occurred, forming cis-DBBPy-based molecular components due to the interaction between Ag adatoms and N atoms in line with the previous report.²¹ Moreover, given that the cleavage of the C-Br bond and the formation of the C-Ag OM bond can take place in such a temperature range, 2^{1-24} it is reasonable to propose that Br atoms were detached from cis-DBBPy molecules, with the remaining moieties bonded to Ag adatoms. Accordingly, each trapezoidal monomer consists of one dehalogenated *cis*-DBBPy molecule and two Ag adatoms, and each hexagonal trimer is composed of three dehalogenated cis-DBBPy molecules and three Ag adatoms. In addition, dark dots located in the cavities of the network are attributed to detached Br atoms. Subsequently, DFT calculations were carried out with the optimized network structure shown in Figure 1g and further superimposed on the STM image (Figure 1f) with good agreement. The DFT model also clearly reveals that there are two interaction modes between Ag and N atoms, i.e., one Ag adatom coordinates with four N sites on two opposite bipyridyl moieties, while the other Ag adatom directly binds to a debrominated molecular moiety (forming a trapezoidal monomer) and simultaneously coordinates with two N sites on an adjacent bipyridyl moiety, consistent with the work by Xiong et al.²¹

Then the sample was further annealed at ~540 K, and the regular triangular network transformed into islands of closepacked chain structures (Figure 1h). The close-up STM image shows that the chain structures appear predominantly in an armchair shape, while others appear in a zigzag shape, as indicated by the white dotted rectangle (Figure 1i). In addition, the surrounding dark dots between chains are attributed to detached Br atoms, while Ag adatoms were released and diffused back to the underlying surface. Notably, the structure of such armchair-shaped chains can be distinguished from the ends of the chains, as typically indicated by the white arrows in Figure 1i, where the terminal and penultimate molecular units have an included angle of 60°, suggesting a composition of debrominated trans-DBBPy molecular components connected via C-C bonds in a cislike manner. The DFT-optimized model was also superimposed on Figure 1i to guide the eye. Besides, the zigzagshaped chains are attributed to debrominated trans-DBBPy molecular components connected via C-C bonds in a translike connecting manner. Two sequential STM images recorded



Figure 1. Formation of *trans*-chains in the presence of intrinsic Ag adatoms through Ag-stabilized OM intermediate structures on Ag(111). (a) Large-scale and (b) close-up STM images (superimposed with the structural models of *trans*-DBBPy) showing the formation of a close-packed self-assembled structure after the deposition of DBBPy molecules at ~250 K. (c) DFT-optimized structural model of *trans*-DBBPy on Ag(111) and (d) STM simulations of *trans*-DBBPy (upper panel) and *cis*-DBBPy (lower panel). (e) Large-scale and (f) close-up STM images of Ag-stabilized triangular OM structures (superimposed with the DFT-optimized model) obtained after annealing at ~500 K. (g) DFT-optimized structural model of the triangular network on Ag(111). (h) and (i) STM images of *trans*-chains obtained after annealing at ~540 K. The ends of the chains are indicated by the white arrows, and the zigzag-shaped chain part is highlighted by the white rectangle. (j) Sequential STM images recorded in the same region showing conformational changes of *trans*-chains during scanning at RT (left) and corresponding schematic models (right). Scanning conditions: V = -1.2 V, I = 0.5-0.7 nA. The close-packed directions of Ag(111) are indicated by the white arrows. Ag substrate: light blue; Ag adatom: sky-blue; C: gray; H: white; N: blue.

in the same region during scanning at RT further capture the *in situ* conversion in real space, with the corresponding structural models displayed on the right (Figure 1j), directly illustrating the conformational change by flipping around the C–C bond²⁵ (highlighted in red). Interestingly, the interaction between intrinsic Ag adatoms and N sites on bipyridyl moieties can anchor the molecular conformation, leading to the formation of *cis*-form-based OM intermediates. Nevertheless, due to the dissociation of C–Ag–C bonds and the release of Ag adatoms back to the Ag(111) substrate with increasing temperature, ^{21,26,27} covalent *trans*-chains (which are generally energetically more favorable²⁸) were formed with high selectivity instead of *cis*-rings. Therefore, the intrinsic Ag adatoms fail to anchor the covalent *cis*-structures at higher temperatures.

Next, extrinsic Na atoms were introduced into the molecular system for direct comparison to the situation with intrinsic Ag adatoms. After the deposition of DBBPy molecules on Ag(111) held at ~250 K (Figure 2a), Na atoms were further dosed at RT, followed by annealing at ~500 K. Interestingly, the self-assembled *trans*-DBBPy structure transformed to a

regular Kagome network structure (Figure 2b). From the close-up STM image (Figure 2c), it can be identified that the Kagome network is formed by hexagonal trimers (as typically indicated by blue hexagons) that are connected to each other in a "side-to-side" way. It is noteworthy that the morphology of each hexagonal trimer is identical to that shown in Figure 1f at a similar annealing temperature, which is thus attributed to the OM trimer with three debrominated cis-DBBPy moieties and three bright Ag adatoms. The remaining darker protrusions distributed in the cavities are assigned to dissociated Br atoms. Note that the presence of Na atoms is generally not visible according to previous reports, 29,30 whereas they can interact with N sites on pyridyl rings via electrostatic interactions.^{29–32} Accordingly, we proposed that two adjacent hexagonal OM trimers are connected to each other via a central Na atom and performed DFT calculations. The optimized structure is shown in Figure 2d and superimposed on Figure 2c with the corresponding STM simulation (the gray part), presenting nice agreement and supporting the structural assignment. Simultaneously, DFT calculations were also performed on a single OM trimer on Ag(111), and the structural model adopts an almost



Figure 2. Formation of *cis*-rings with the addition of extrinsic Na atoms through the Na-stabilized OM intermediate structures on Ag(111). (a) STM image of close-packed self-assembled *trans*-DBBPy upon deposition at ~250 K. (b) Large-scale and (c) magnified STM images (overlaid with the corresponding DFT-optimized model and STM simulation) showing the formation of a Na-stabilized Kagome network after the introduction of Na at ~300 K, followed by annealing at ~500 K. The individual OM trimers are indicated by blue hexagons. (d) DFT-optimized structural model of the Kagome network on Ag(111). (e) DFT-optimized structural model and (f) corresponding STM simulation of a single OM trimer on Ag(111). (g) Large-scale and (h) zoomed-in STM images of *cis*-rings obtained after annealing at ~510 K, overlaid with the DFT-optimized models. The *cis*-rings are indicated by green hexagons, and triangular clusters are indicated by white dotted triangles. (i) DFT-optimized structural model and (j) corresponding STM simulation of a covalent *cis*-ring on Ag(111). (k) Line profiles along the red and blue lines (AB and CD) depicted in (h). Scanning conditions: V = -1.2 V, I = 0.6 nA. The close-packed directions of Ag(111) are indicated by the white arrows in (a). Ag substrate: light blue; Ag adatom: sky-blue; C: gray; H: white; N:blue; Na: pink.

flat-lying configuration (Figure 2e), with the connecting Ag adatoms appearing as bright protrusions in the STM simulation (Figure 2f).

Subsequently, the above sample was annealed at ~510 K, resulting in the formation of hexagonal rings (Figure 2g). The magnified STM image (Figure 2h) shows that hexagonal rings (typically indicated by green hexagons) are evenly distributed on the sample and separated by a large number of dark dots, with some bright dots. Notably, certain sides of the hexagonal rings are interconnected by a triangular cluster consisting of three bright dots as indicated by white dotted triangles, which will be analyzed in detail in the following content. Obviously, the hexagonal rings indicated in green (Figure 2h) exhibit a uniform contrast in morphology and are discernibly smaller compared to those indicated in blue shown in Figure 2c, corresponding to the absence of Ag adatoms. Consequently, these smaller hexagonal rings are assigned to covalent trimers that are converted from OM trimers by the release of Ag adatoms. Moreover, the lengths of the six sides of such covalent hexagons are alternating. Line profiles along the long

side (i.e., the red line AB) and the short side (i.e., the blue line CD) depicted in Figure 2h are displayed in Figure 2k, and the lengths were measured to be 9.16 ± 0.10 and 7.20 ± 0.15 Å, respectively. From the DFT-optimized structural model (Figure 2i), a planar configuration can be observed, with the lengths of the long and short sides (indicated by the red and blue arrows) calculated to be 9.18 and 7.17 Å, respectively, consistent with the experimental observations. The STM simulation further reproduced the morphology (Figure 2j), confirming the formation of covalent *cis*-rings.

Therefore, the electrostatic interaction between extrinsic Na and N sites on bipyridyl moieties effectively anchors the specific *cis*-conformation of DBBPy-based molecular components to form OM trimers, followed by the release of Ag adatoms while maintaining the *cis*-conformation to form covalent *cis*-rings. In particular, due to the extrinsic source of Na atoms and the relative stability of the whole molecular system, Na atoms tend to interact with *cis*-bipyridyl moieties (via 4-fold Na…N electrostatic interactions) rather than diffuse alone²⁹ or interact with *trans*-bipyridyl moieties (via 2-fold

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Na…N interactions) (more details in Figure S2), resulting in the stabilized *cis*-conformation even after Ag adatoms are released to construct *cis*-rings. In contrast, the situation is quite different for intrinsic Ag adatoms, which would be released at high temperatures and diffuse back to the underlying Ag(111) substrate, leading to the disanchored molecular components and further selection of the *trans*-conformation due to its higher stability to form *trans*-chains instead. Accordingly, this different behavior of intrinsic Ag adatoms and extrinsic Na atoms contributes to the different conformational preferences and reaction pathways.

To explore the competitive interactions between extrinsic Na atoms and intrinsic Ag adatoms and to directly visualize the influence of transmetalation, extrinsic Na atoms were gradually introduced into the triangular OM network (phase I) obtained by annealing the DBBPy-precovered Ag(111) sample at \sim 500 K (Figure 3a). After subsequent annealing at ~500 K, a stepwise transmetalation process between intrinsic Ag adatoms and extrinsic Na atoms was captured, and the coexistence of phase I and Na-involved Kagome networks (phase II) was initially achieved until complete transformation into phase II with additional Na (Figure S3). When Na atoms were further dosed onto the above sample followed by annealing at \sim 500 K, another triangular network (phase III) appeared with the coexistence of phase II separated by a white dotted line (Figure 3b). Such a direct transmetalation process experimentally indicated the competitive interactions between these OM intermediate structures. Notably, the transmetalation processes on the surface reported in previous studies are either intramolecular (e.g., in the metalloporphyrins systems^{33,34}) or intermolecular (e.g., metal substitution in metal-organic frameworks^{16,35}) metal exchanges with the same molecular backbones or structures. In our case, the transmetalation process from intrinsic Ag to extrinsic Na is accompanied not only by the metal substitution but also by the structural transformation, showing a more complex process with the embedding of two types of metals.

With increasing Na dosage followed by annealing at \sim 500 K, triangular phase III became dominant (Figure 3c). The closeup STM image (Figure 3d) shows that OM trimers (indicated by blue hexagons) are regularly distributed and connected to each other by a triangular cluster consisting of three bright dots (indicated by white dotted triangles, identical to those shown in Figure 2h). Similar bright dots surrounded by molecules were also reported in previous works and referred to isolated salt (i.e., NaX, X stands for halogen).^{36,37} It is also noteworthy that these clusters of bright dots emerged after dosing more Na atoms, while dissociated Br atoms were widely distributed on the sample (surrounding the molecular structures). Thus, these bright dots are naturally assigned to isolated NaBr (the tentative model of phase III is shown in Figure S4), while the darker dots existing in the cavities are attributed to extra Br atoms. Moreover, from the relative positions of OM trimers to triangular salt clusters, it is easy to find that the triangular salt clusters face the long sides of OM trimers (i.e., with a bipyridyl moiety in the middle), which can be rationalized by the potential electrostatic interactions between them.

After further annealing the sample at \sim 510 K, covalent *cis*rings were also formed as expected (Figure 3e) and were isolated by a large number of dots with different contrasts. Triangular clusters of three bright dots coexisted (as those shown in phase III), and their relative positions to the *cis*-rings are consistent with those shown in Figure 3f, also indicating



Figure 3. Transmetalation process from intrinsic Ag adatoms to extrinsic Na atoms in response to the dosage of Na with the formation of cis-rings on Ag(111). (a) STM image of Ag-stabilized OM triangular structures (phase I) obtained after the deposition of DBBPy and annealing at ~500 K. (b) Coexistence of a Na-stabilized OM Kagome structure (phase II) and another OM structure (phase III) after the introduction of more Na followed by annealing at ~500 K. (c) Large-scale and (d) close-up STM images of phase III obtained after further introduction of Na followed by annealing at ~500 K. OM trimers and bright triangular clusters are indicated by blue hexagons and white dotted triangles, respectively. (e and f) Formation of cisrings after annealing the former sample at ~510 K. Cis-rings and bright triangular clusters are indicated by green hexagons and white dotted triangles, respectively. Scanning conditions: V = -1.2 V, I =0.6 nA. The close-packed directions of Ag(111) are indicated by the white arrows. Ag substrate: light blue; Ag adatom: sky-blue; C: gray; H: white; N: blue; Na: pink.

the formation of isolated NaBr.^{37,38} Therefore, the conversion of isomerically specific products from *trans*-chains to *cis*-rings was achieved with high selectivity by both the initial addition of Na and direct transmetalation from Ag to Na, indicating the competitive interactions provided by Na atoms in the whole process.

In conclusion, we have successfully controlled the selectivity of covalent reaction products (i.e., isomerically specific *trans*chains and *cis*-rings) by transmetalation from intrinsic Ag adatoms to extrinsic Na atoms on Ag(111). By combining STM imaging and DFT calculations, direct transmetalation of the metal—organic intermediate structures was also visualized by introducing additional Na atoms into the Ag-stabilized OM networks, forming *cis*-rings via competitive interactions. Our results display the competitive interactions between intrinsic and extrinsic metal atoms at the submolecular level in real space and their decisive roles in the reaction selectivity, which should broaden the regulatory strategies for on-surface synthesis that shed light on the controllable and selective synthesis of target covalent nanostructures.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpclett.4c03040.

Additional experimental methods, supplementary STM images of the gradual formation of Ag-stabilized OM structures, DFT calculations of total energies of simplified *trans*-chains and *cis*-rings with one Na, STM images of the transmetalation process from intrinsic Ag adatoms to extrinsic Na atoms (PDF)

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Notes

The authors declare no competing financial interest.

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