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COMMUNICATION

On-surface synthesis of planar acenes *via* regioselective aryl-aryl coupling

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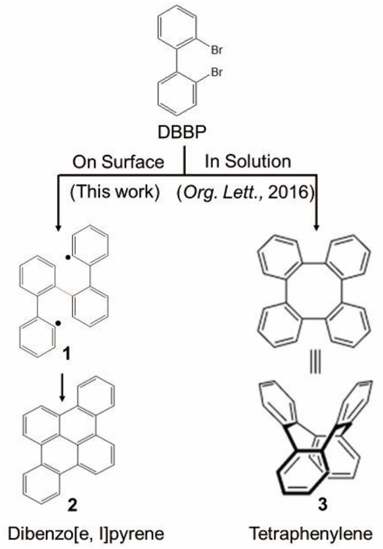
The reaction of 2,2'-Dibromo-Biphenyl on a Ag(111) surface leads to the formation of planar acenes with a high-regioselectivity rather than nonplanar saddle-shaped tetraphenylene as the typical product in solution chemistry. The regioselective aryl-aryl coupling reaction is attributed to the hydrogen repulsion between the reactants on the confined two-dimensional surface.

Polycyclic aromatic hydrocarbons (PAHs) refer to two or more fused aromatic rings without substituents or heteroatoms, which display exotic optical, electronic, and magnetic properties.[1-3] Attracted by their potential to become next-generation functional materials using in organic thin-film transistors, organic photovoltaics, nonlinear optics, spintronics, and energy storage devices, the synthesis of PAHs has become one of the research hotspots for many years.[3-5] Great efforts have been made to synthesize PAHs, and multiple synthetic pathways have been proposed.[6, 7] In particular, an important method to extend polycyclic aromatics is to add C_n fragments to small PAHs through the aromatization of the newly formed C_6 rings *via* C-C coupling.[7] However, the synthesis of PAHs in solution is sometimes hampered by side reactions and tedious separation of mixtures, resulting in low yield of target products.[5, 8-11]

To more efficiently synthesize PAHs, various strategies have been adopted such as transition-metal catalysis,[12-14] and drastic conditions.[6, 7, 10] In addition, the recent developed on-surface chemistry also provides an effective route for engineering shape-specific PAHs.[15-22] Compared with the organic reactions in solution, the two-dimensional (2D) confinement effect of a surface can reduce the molecular degrees of freedom, thus significantly simplifying the reaction pathways and improving the reaction selectivity.[17] Therefore, on-surface synthesis typically facilitates the formation of planar structures, providing an unprecedented opportunity to synthesize planar PAHs. In contrast, the PAHs obtained from in-solution synthesis are often nonplanar in the three-dimensional (3D) reaction environments.[2, 23, 24] For the already known synthesis of PAHs on surfaces, the planarization of products is often assisted by the intramolecular cyclodehydrogenation.[17] Moreover, some PAHs have been synthesized on surfaces *via* intermolecular aryl-aryl coupling subsequent to dehydrogenation[25-27] and dehalogenation.[21, 28] For instance, Fasel *et al.* successfully performed three PAHs *via* intermolecular aryl-aryl coupling of 2,3-dibromotetracene molecules on Ag(111).[21] For the intermolecular coupling, though no direct experimental



Scheme 1 Chemical structure of the precursor 2,2'-Dibromo-Biphenyl (DBBP) and its different dimerization products, the nonplanar saddle-shaped tetraphenylene that was synthesized in solution, and the planar rhombic dibenzo[e,l]pyrene formed on the metal surface in this work.

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evidence until now, it is expected that the 2D confinement of a surface could steer the reaction pathway, leading to the formation of completely different PAHs products with those in solution. This would be valuable for the exploration of novel low-dimensional PAHs which are difficult obtained in solution synthesis.

Herein, we report that the reaction pathways of a precursor molecule are completely different in solution *vs.* on surface. The planar acenes are selectively synthesized *via* intermolecular aryl-aryl coupling on a metal surface, whereas the non-palanar products were obtained, as illustrated in scheme 1. Deposition of 2,2'-Dibromo-Biphenyl (DBBP, synthetic procedure: see Fig. S1) precursor molecules onto the Ag(111) surface at room temperature followed by annealing to 450 K leads to the formation of planar dibenzo[e,l]pyrene (DB[e,l]P) *via* hierarchical intermolecular aryl-aryl coupling and cyclodehydrigenation, in sharp contrast with the nonplanar saddle-shaped tetraphenylene products[29] in solution. It is demonstrated that the reaction mechanisms are different between the solution-based synthesis and the present on-surface synthesis: in the former case, the tetraphenylene is obtained *via* a double Suzuki reaction or double Ullmann reaction,[8, 30, 31] whereas in the latter case the DB[e,l]P is formed by debrominative coupling and the subsequent combination of debrominative and dehydrogenative coupling.[32] The precise regioselective aryl-aryl coupling can be attributed to the surface confinement which reduces the flexibility of the molecules. Our investigation shows that 2D template effect on surface plays a significant role for both intramolecular and intermolecular reactions on surface. Scanning tunnelling microscopy (STM) and synchrotron radiation photoemission spectroscopy (SRPES) reveal the structural evolution of the molecules at an atomic level.

Deposition of DBBP onto the Ag(111) surface at room temperature leads to the formation of highly ordered dimer arrays on the terraces of Ag(111), as revealed by STM image shown in Fig. 1a. The orientation of molecules in each array (marked by green line) is the same, rotating 15° with respect to [1-10] direction of the substrate. These molecules are arranged into a rhombic unit cell, whose parameters are a=b=13±0.4 Å and α=135°. At this temperature, DBBP monomers undergo complete debromination (as confirmed by the XPS results shown in Fig. S2), and two resultant bi-radicals are linked by one Ag atom forming a bow-shaped dimer (Fig. 1b). The bright protrusion of the interstitial silver atoms can be seen more clearly under a higher sample bias (Fig. S3). The bow-shaped dimer has been demonstrated in the previous work[33] to be stabilized by four-fold C-Ag-C bonds, as seen in the corresponding superimposed molecular model (Fig. 2b). In particular, each dimer is symmetrically surrounded by eight relatively dark dots, which refer to the eight peripheral Br adatoms detached from the precursor molecules. This implies that the ordered molecular phase on the surface is stabilized by Br···H-ph hydrogen bonds.

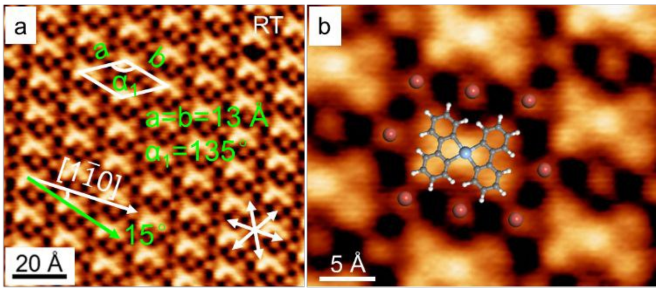

Fig. 1 (a) A large-scale STM image taken after deposition of DBBP onto Ag(111) surface at RT. (b) Zoom-in STM image of (a) superimposed with corresponding molecular model. Tunneling parameters: (a, b) T_t= - 0.18 mA, V_t= - 1.90 V. Color code: Ag, blue; C, grey; H, white; Br, brown.

Further annealing the sample at 450 K results in the disappearance of organometallic (OM) dimer array phase. The Ag(111) surface is populated with ordered planar rhombic molecules (Fig. 2a and 2b). Here, we discuss two possible reaction pathways to obtain a PAH: 1) a double Ullmann coupling reaction would occur and tetraphenylene with eight-membered ring would be constructed (**molecule 3** shown in Scheme 1);[29] 2) a rhombic molecule (**molecule 2** shown in Scheme 1) could be synthesized by debrominative coupling and the subsequent combination of debrominative and dehydrogenative coupling. Because of the planar configuration of final product shown in Fig. 2b the product cannot be tetraphenylene. Thus, we consider to attribute this final product to DB[e,l]P. It is found that the rhombic and planar molecular model of DB[e,l]P match perfectly with the obtained structure. In addition, the measured molecular length (9.9±0.4 Å) and width (7.2±0.4 Å) are in close agreement with widths of the reported counterparts in armchair 9-Graphene nanoribbons (GNRs) (9.67 Å)[34] and zigzag 4-Zigzag GNRs (7.1 Å)[35], respectively. Hence, we propose that the OM dimers undergo the second reaction pathway, generating the final product, DB[e,l]P. On the Ag(111) surface, the three DB[e,l]P molecules within the molecular unit cell have three different orientations. Interestingly, the surrounding Br atoms also orient in three directions (as guided by blue arrows in Fig. 3b), rotating by ~30° with respect to the three high-symmetry directions of Ag(111). Thus, the ordered DB[e,l]P molecular phase should be stabilized

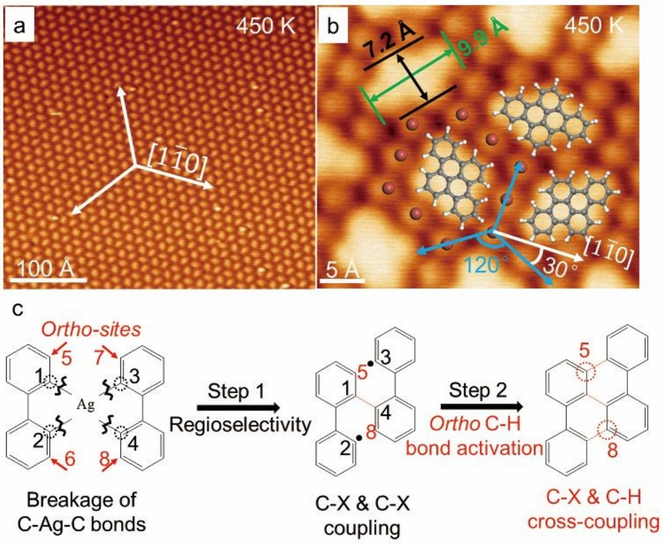

Fig. 2 (a) Overview STM image taken after annealing the sample at 450 K. (b) High-resolution STM image as well as the superimposed with corresponding molecular models. (c) The illustration of the regioselective C-C coupling and *ortho*-sites C-H bond activation. Tunneling parameters: (a) T_t= - 0.15 mA, V_t= - 1.90 V; (b) T_t= - 0.14 mA, V_t= - 2.90 V. Color code: Ag, blue; C, grey; H, white; Br, brown.

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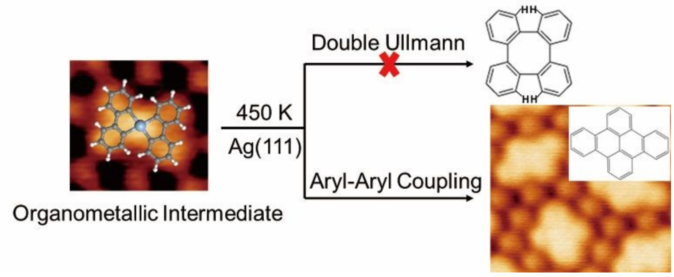
by the Br···H bond interactions. Note that the intensity of C 1s declines obviously from 300 K to 450 K in SRPES, which can be attributed to the partial desorption of molecules (see Fig. S2).

Probing deeply into the reaction process, the most possible mechanism is shown in Fig. 2c. Initially, OM dimers undergo the breakage of four-fold C-Ag-C bonds, forming the two biradicals with four equivalent activated sites (previous C-Br sites), as marked by dashed black circles (number: 1-4). Subsequently, the two diagonal active sites (either 1 and 4 or 2 and 3) undergo regioselective C-C coupling reaction, while another two active sites remain unchanged. Here we take 1 and 4 active sites as example for the Ullmann C-C coupling, shown as step **1** in Fig. 2c. After the C-C coupling at 1 and 4 sites, the two *ortho* C-H bonds (5 and 8 sites) of newly generated C-C bond are activated at elevated temperature (450 K). This is reasonable because the C-H activation below 450 K has already been reported in prior works.[32, 36, 37] Finally, as shown in step **2**, the two new active sites stemming from C-H activation form two C-C covalent bonds with adjacent active sites (two remaining active sites after step 1) to give the final product DB[e,l]P. Note that in step 1 the C-C coupling takes place between two active sites formed by C-Br cleavage, whereas in step **2** the C-C coupling involves the active sites originating from both C-H and C-Br activation (cross-coupling). In addition, the proposed intermediate between OM and product DB[e,l]P is not observed experimentally, suggesting that the cleavage of C-Ag-C in OM is the rate-determining step in the whole reaction steps. This means once the C-Ag-C breakage happens, step **1** and **2** with lower reaction barrier can take place immediately, leading to the formation of the final products in a short time.



Scheme 2. Illustration for synthesis of DB[e,l]P. Instead of the Ullmann coupling, selective aryl-aryl coupling will occurs when the silver atom is released from the organometallic intermediate.

Interestingly, only selective aryl-aryl coupling but no double Ullmann coupling was observed in our experiments after the release of the silver atom from OM intermediate (Scheme 2). This regio-selectivity leads to the high selective formation of DB[e,l]P as the final product. The reason could be ratinalized as follows. After OM dimer undergoes desilverization into two biradicals, the hydrogen repulsion (5 and 7 sites, 6 and 8 sites shown in Fig. 2c) between the two neighbouring monomers is rather strong. It is therefore difficult for these two neighbouring biradicals to approach into an ideal configuration for double Ullmann coupling. Instead, the regioselective C-C coupling between diagonal active sites (step **1** exhibited in Fig. 2c) are favorable due to the weaker steric hindrance. After that C-H activation and cross-coupling occur to complete the formation of the final product DB[e,l]P. The whole reaction process is assisted by the 2D surface confinement which can reduce molecular flexibility and facilitate the planarization of products. In comparison, for the case in solution the molecules have high degree of freedom (flipping, rotating and diffusing), which minimizes the steric hindrance. Thus, the steric hindrance between H atoms of neighbouring biradical monomers is not an issue. Therefore, it is not surprising that the tetraphenylene, which is sterically hindered on surface, dominates in solution. In short, the precise regioselective aryl-aryl coupling can be attributed to the 2D confinement on the surface, which reduces the flexibility of the molecules.

Conclusions

In summary, we demonstrate that reaction pathway of intermolecular C-C coupling of 2,2'-Dibromo-Biphenyl on a Ag(111) surface is different from that in solution. The planar dibenzo[e,l]pyrene is obtained with high selectivity on the Ag(111) surface *via* aryl-aryl coupling rather than nonplanar saddle-shaped tetraphenylene formed *via* double Ullmann coupling. The highly regioselective aryl-aryl coupling can be attributed to the 2D confinement of the surface which brings steric hindrance between monomers. Our study demonstrates that PAHs can be prepared differently from those in solution *via* on-surface synthesis, especially planar molecules.

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Conflicts of interest

There are no conflicts to declare.

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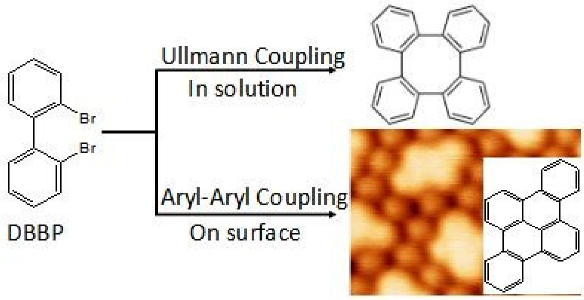

The reaction of 2,2'-Dibromo-Biphenyl (DBBP) on the surface leads to the generation of planar dibenzo[e,l]pyrene, in contrast to the nonplanar saddle-shaped tetraphenylene formed in solution.