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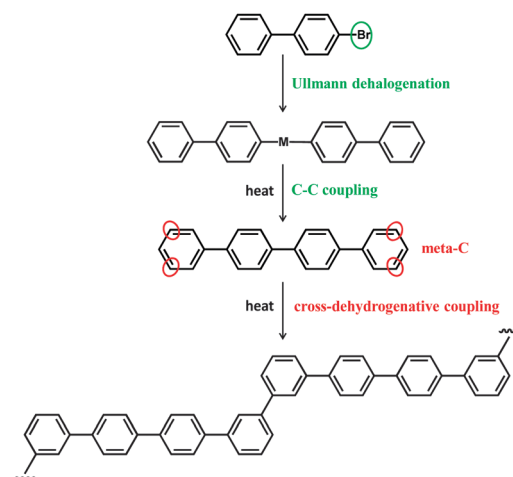
# Formation of polyphenyl chains through hierarchical reactions: Ullmann coupling followed by cross-dehydrogenative coupling†

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From an interplay of UHV-STM imaging and DFT calculations, we have illustrated on-surface formation of polyphenyl chains through a hierarchical reaction pathway involving two different kinds of reactions (Ullmann coupling and cross-dehydrogenative coupling), which will provide a deeper understanding of on-surface chemical reactions and an alternative and efficient strategy to fabricate desired surface molecular nanostructures.

One urgent pursuit of the continuously developing nanoscience and nanotechnology is to achieve robust nanostructures by using the bottom-up strategy. Construction of covalently interlinked molecular nanostructures with relatively high thermal stability<sup>1</sup> and efficient intermolecular charge transport<sup>2,3</sup> has been demonstrated to be a promising method for further applications within the field of nanotechnology, *e.g.* molecular nanoelectronics and nanospintronics. Recently, several typical chemical reactions have been extensively employed and successfully introduced from solution to various metal surfaces within the surface science community, such as Ullmann coupling,<sup>4–18</sup> Bergman cyclization,<sup>19,20</sup> Glaser coupling,<sup>21,22</sup> and click reaction.<sup>23</sup> Furthermore, it has also been demonstrated that specific metal substrates may facilitate some unexpected reactions which can hardly take place in solution, such as surface-catalyzed cyclodehydrogenation,<sup>24</sup> C–C coupling of alkane molecules<sup>25</sup> and intermolecular cross-dehydrogenative coupling.<sup>26</sup> However, to our knowledge, on-surface fabrication of nanostructures has been mainly through one-step reactions<sup>19–29</sup> or one kind of reaction in a hierarchical manner.<sup>5,14</sup> Thus, it would be of utmost interest to explore the feasibility of inducing on-surface hierarchical reactions involving different kinds of chemical reactions<sup>6</sup> with distinct characteristics such as reaction temperatures and/or appropriate reactive sites, which is particularly crucial for delicate fabrication of more sophisticated surface nanostructures.

In this work, we choose the 4-bromobiphenyl (shortened as BBP) molecule as the precursor which contains one halogen atom (*i.e.* Br) capable of introducing Ullmann coupling, and the *meta*-carbon sites (*cf.* Scheme 1) that can undergo cross-dehydrogenative coupling *via* C–H activation.<sup>26</sup> It is known that the Ullmann dehalogenation can take place at relatively low temperatures (typically between 170 K and 240 K) on the copper surface,<sup>7–13</sup> and the subsequent cross-dehydrogenative coupling would take place at higher temperatures ( $\sim 500$  K),<sup>26</sup> which allows us to explore the possible hierarchical reactions on the surface under ultrahigh vacuum (UHV) conditions. From the interplay of high-resolution scanning tunneling microscopy (STM) imaging and density functional theory (DFT) calculations, we have demonstrated that on a Cu(110) surface the BBP molecules dehalogenate and form the corresponding organometallic intermediate at RT. Subsequent thermal treatment ( $\sim 465$  K) releases the linking metal atoms and consequently the quaterphenyl (shortened as (Ph)<sub>4</sub>) molecules are formed as the product of Ullmann coupling.



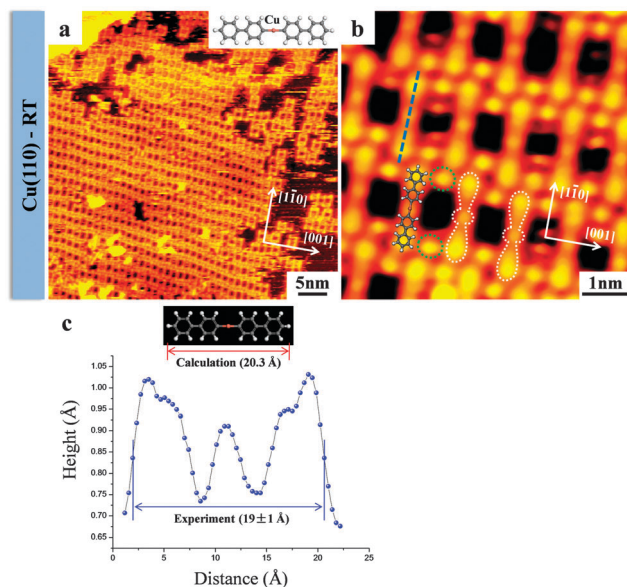
**Scheme 1** Schematic illustration of the reaction path of forming polyphenyl chains via hierarchical chemical reactions (*i.e.* Ullmann dehalogenation and C–C coupling and subsequent cross-dehydrogenative coupling). M denotes a metal atom.

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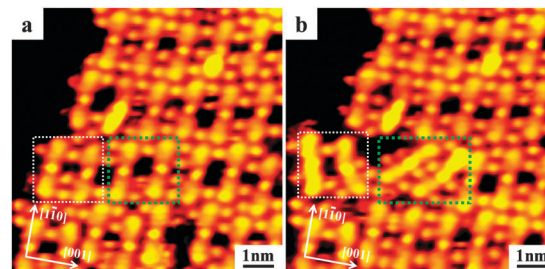
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As expected, still interestingly, further thermal treatment at even higher temperatures ( $\sim 500$  K) results in the formation of covalently bound polyphenyl chains based on  $(\text{Ph})_4$  molecules *via* cross-dehydrogenative coupling. We have, thus, demonstrated the feasibility of fabrication of covalently interlinked nanostructures through on-surface hierarchical chemical reactions as outlined in Scheme 1. These findings will help us to gain deeper insight into the fundamental understanding of on-surface chemical reactions, and may present an alternative and efficient strategy to fabricate more sophisticated surface molecular nanostructures with further applications in molecular nanoelectronics and so on.

Deposition of BBP molecules on Cu(110) held at RT leads to the formation of ordered networks composed of rod-like structures surrounded with bright dots as shown in Fig. 1a and b. Close inspection enables us to identify that the rod-like structures tend to mainly array along the  $[1\bar{1}0]$  direction of the substrate, and each one is imaged as two lobes and a bright protrusion in the center, which is attributed to the biphenyl groups and the Cu atom,<sup>7–13</sup> respectively. Similar structures have been widely reported and proved to be organometallic intermediates<sup>7–13</sup> in the Ullmann coupling process. In addition, the isolated bright dots (indicated by the green ovals in Fig. 1b) are attributed to the detached Br atoms as also found in the previous studies.<sup>7–13</sup> Moreover, the length of the  $(\text{Ph})_2\text{-Cu-(Ph)}_2$  intermediate is measured to be  $19 \pm 1$  Å from the line-scan profile as illustrated in Fig. 1c,



**Fig. 1** Formation of an organometallic intermediate on Cu(110). (a) The large-scale STM image showing the formation of a porous network composed of  $(\text{Ph})_2\text{-Cu-(Ph)}_2$  intermediates and detached Br atoms after deposition of BBP molecules on Cu(110) held at RT. The upper right inset showing the chemical structure of the formed  $(\text{Ph})_2\text{-Cu-(Ph)}_2$  organometallic intermediate where C is gray, H is white and Cu is brown. (b) The close-up STM image showing the details of the organometallic intermediate with the scaled gas-phase optimized structural model superimposed. The green ovals indicate the detached Br atoms, and the white contours indicate the organometallic intermediates. Scanning conditions:  $I_t = 1.10$  nA,  $V_t = -1500$  mV. (c) The line-scan profile along the blue dashed line in (b). The upper panel showing the gas-phase optimized structural model of the  $(\text{Ph})_2\text{-Cu-(Ph)}_2$  intermediate.



**Fig. 2** Lateral STM manipulation on the organometallic intermediates on Cu(110). The white rectangles and green rectangles in (a) and (b) highlight the twist of the C-Cu bond and the local translation before and after manipulation, respectively.

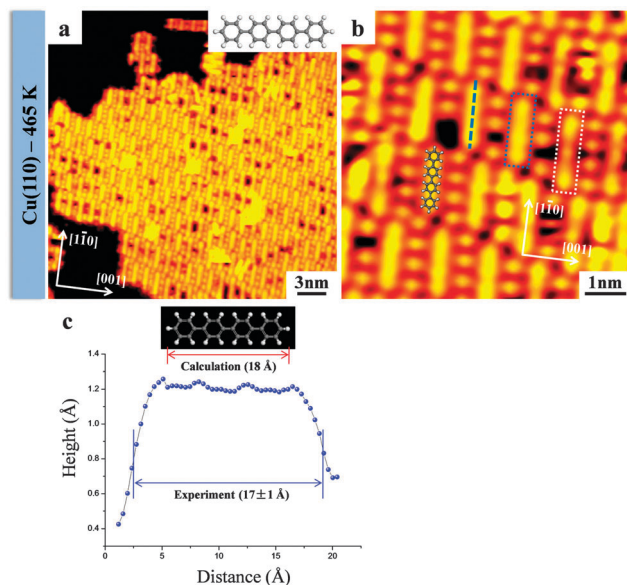
which is in accordance with the theoretical value (20.3 Å). The scaled theoretical model is also superimposed on an individual intermediate where good agreement is achieved. Thus, deposition of the BBP molecule on Cu(110) held at RT results in the C-Br bond dissociation and the formation of an organometallic intermediate.

To test the robustness of the formed organometallic intermediate, we have performed lateral STM manipulations as shown in Fig. 2. After disturbed by the STM tip (parameters:  $I_t = 5.10$  nA,  $V_t = -20$  mV), the  $(\text{Ph})_2\text{-Cu-(Ph)}_2$  intermediates either change the initial morphology with the C-Cu bond twisted or translate with a different molecular orientation as indicated by white rectangles and green rectangles, respectively, which indicates the relative robustness of C-Cu bonding and the flexibility of the C-Cu-C bond.

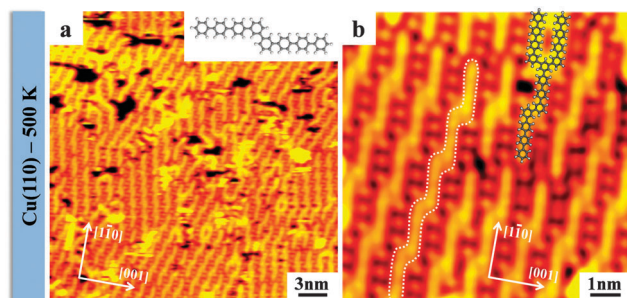
Subsequent annealing of the Cu(110) sample to 465 K results in the formation of a similar close-packed nanostructure with rod-like molecules still arraying along the  $[1\bar{1}0]$  direction of the substrate (Fig. 3a). From the close-up STM image (Fig. 3b), we can clearly distinguish two different kinds of rod-like features coexisting on the surface. Besides some remaining  $(\text{Ph})_2\text{-Cu-(Ph)}_2$  intermediates (one of them is indicated by the white rectangle), the newly formed shorter rods with uniform intramolecular brightness are also found (one of them is indicated by the blue rectangle), which are naturally attributed to the  $(\text{Ph})_4$  molecules based on the Ullmann C-C coupling scenario. The length of the formed  $(\text{Ph})_4$  molecule is measured to be  $17 \pm 1$  Å from the line-scan profile as illustrated in Fig. 3c, which is in accordance with the theoretical result (18 Å), and also well matches the dimensions and morphology of the  $(\text{Ph})_4$  molecule on Cu(110) reported in the previous work.<sup>26</sup> The scaled gas-phase optimized model is also superimposed on the STM image and good agreement is achieved. It is noticed that in this structure more bright dots surrounding the  $(\text{Ph})_4$  and  $(\text{Ph})_2\text{-Cu-(Ph)}_2$  are found, which should be attributed to the released Cu atoms besides the Br atoms. Also note that the  $(\text{Ph})_2\text{-Cu-(Ph)}_2$  intermediates coexist with  $(\text{Ph})_4$  molecules in a wide temperature window ranging from 440 K to 470 K, and higher temperatures lead to the additional reactions which will be discussed below. Thus, annealing the Cu(110) sample to  $\sim 465$  K results in the C-Cu bond dissociation and the formation of the  $(\text{Ph})_4$  product from Ullmann coupling.

Further annealing the Cu(110) sample to 500 K, as expected, still interestingly, we find the formation of separated molecular





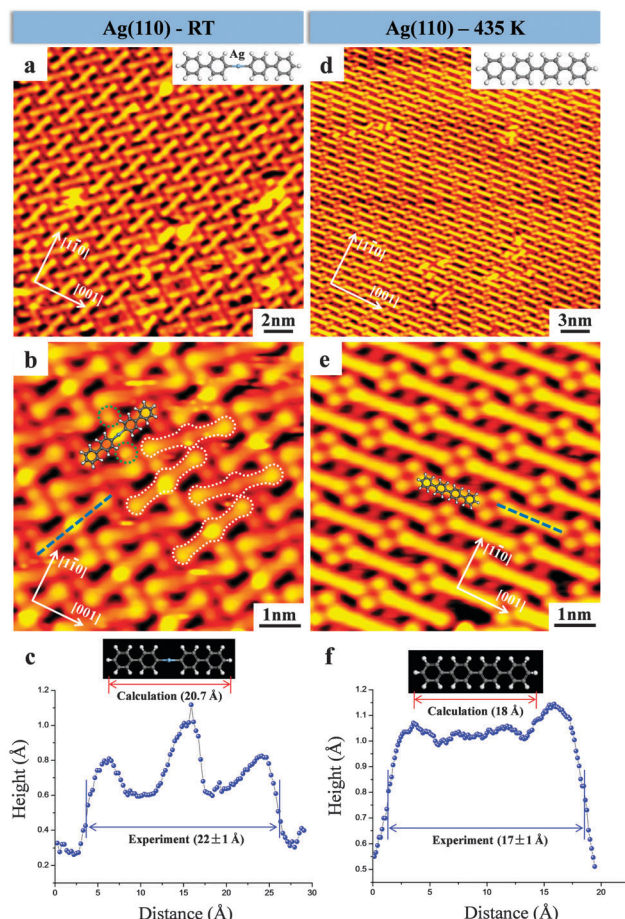
**Fig. 3** Formation of the  $(\text{Ph})_4$  molecule after subsequent thermal treatment on Cu(110). (a) The large-scale STM image showing the formation of a close-packed structure composed of the newly formed  $(\text{Ph})_4$  molecules and the remaining  $(\text{Ph})_2\text{-Cu-(Ph)}_2$  intermediates after annealing the Cu(110) sample to  $\sim 465$  K. The upper right inset showing the chemical structure of  $(\text{Ph})_4$ . (b) The close-up STM image showing the details of the  $(\text{Ph})_4$  molecule with the scaled gas-phase optimized structural model superimposed. The blue and white rectangles indicate  $(\text{Ph})_4$  and  $(\text{Ph})_2\text{-Cu-(Ph)}_2$ , respectively. Scanning conditions:  $I_t = 0.89$  nA,  $V_t = -1200$  mV. (c) The line-scan profile along the blue dashed line in (b). The upper panel showing the gas-phase optimized structural model of  $(\text{Ph})_4$ .



**Fig. 4** Formation of polyphenyl chains on Cu(110) after further thermal treatment at a higher temperature. (a) The large-scale STM image showing the formation of polyphenyl chains after further annealing the Cu(110) sample to 500 K. The upper right inset showing the chemical structure of a simplified polyphenyl chain. (b) The close-up STM image showing the details of the chain structures with the structural model superimposed. The white contour depicts a polyphenyl chain. Scanning conditions:  $I_t = 1.20$  nA,  $V_t = -2000$  mV.

chains (Fig. 4a). The close-up STM image (Fig. 4b) shows the details of the chain structures (one of them is indicated by the white contour) in which we identify that the dimensions and morphology of each unit and the covalent C–C interlinking are identical and also consistent with that of the  $(\text{Ph})_4$  molecule and each unit binds to each other in a shoulder-to-shoulder mode with the same characteristics of polyphenyl chains formed by  $(\text{Ph})_4$  on Cu(110) reported previously.<sup>26</sup> The comparison of the

theoretical models of direct C–C coupling and C–Cu–C interlinking indicates a good agreement between the direct C–C coupling and the experimental lateral offset of the polyphenyl chain (Fig. S1, ESI†). Similar previous studies on cross-dehydrogenative coupling on metal surfaces in UHV have also been reported.<sup>25,29</sup> Also note that the activation temperature in this step ( $\sim 500$  K) is exactly when cross-dehydrogenative coupling of  $(\text{Ph})_4$  on Cu(110) takes place.<sup>26</sup> Thus we believe that the chains shown in Fig. 4a and b are the target polyphenyl chains resulting from  $(\text{Ph})_4$  molecules (the products of the cross-dehydrogenative coupling *via* C–H activation at the *meta*-C sites as reported in our previous work<sup>26</sup>). Note that due to the coexistence of Br atoms in between, the polyphenyl



**Fig. 5** Formation of the  $(\text{Ph})_2\text{-Ag-(Ph)}_2$  organometallic intermediate and the  $(\text{Ph})_4$  molecule on Ag(110). (a) and (d) The large-scale STM images showing the formation of close-packed nanostructures composed of  $(\text{Ph})_2\text{-Ag-(Ph)}_2$  intermediates after deposition of BBP molecules on Ag(110) held at RT and  $(\text{Ph})_4$  molecules after further annealing the sample to  $\sim 435$  K, respectively. The upper right insets showing the chemical structures of the formed  $(\text{Ph})_2\text{-Ag-(Ph)}_2$  intermediate and the  $(\text{Ph})_4$  molecule, respectively, where C is gray, H is white and Ag is azure. (b) and (e) The close-up STM images showing the details of the  $(\text{Ph})_2\text{-Ag-(Ph)}_2$  intermediates and  $(\text{Ph})_4$  molecules with the scaled gas-phase optimized structural models superimposed, respectively. The green ovals in (b) indicate the detached Br atoms, and the white contours indicate the organometallic intermediates. Scanning conditions:  $I_t = 1.00$  nA,  $V_t = -1300$  mV. (c) and (f) The line-scan profiles along the blue dashed lines in (b) and (e), respectively. The upper panels showing the gas-phase optimized structural models of the  $(\text{Ph})_2\text{-Ag-(Ph)}_2$  intermediate and the  $(\text{Ph})_4$  molecule, respectively.

chains tend to be quasilinear and have fewer branches in comparison with that of direct cross-dehydrogenative coupling of  $(\text{Ph})_4$ .<sup>26</sup> The model of chain and branch structures is also superimposed on the STM image. Further annealing the polyphenyl chains on Cu(110) to 525 K results in the disordered chains with Br atoms surrounded as shown in Fig. S2 (ESI†).

To extend the studied system we have also investigated the behaviors of the BBP molecule on a Ag(110) surface. Similar to the situation on Cu(110), deposition of BBP molecules on Ag(110) held at RT results in the formation of  $(\text{Ph})_2\text{-Ag-(Ph)}_2$  organometallic intermediates surrounded by detached Br atoms (Fig. 5a and b), which is also consistent with previous studies on a silver surface.<sup>14–18</sup> On Ag(110) the  $(\text{Ph})_2\text{-Ag-(Ph)}_2$  intermediates array in different directions as shown in Fig. 5a. Annealing the sample to  $\sim 435$  K leads to the formation of  $(\text{Ph})_4$  molecules completely which mainly array along the [001] direction of the substrate with Br atoms surrounded (Fig. 5d and e). The scaled gas-phase optimized structural models of  $(\text{Ph})_2\text{-Ag-(Ph)}_2$  and  $(\text{Ph})_4$  are superimposed on the close-up STM images with good agreement, respectively. The lengths of the  $(\text{Ph})_2\text{-Ag-(Ph)}_2$  intermediate and the  $(\text{Ph})_4$  molecule are measured to be  $22 \pm 1$  Å and  $17 \pm 1$  Å from the line-scan profiles as illustrated in Fig. 5c and f, which are in accordance with the theoretical values of 20.7 Å and 18 Å, respectively. Further annealing the sample to the temperature window ranging from 500 K to 525 K, however, does not result in the formation of ordered polyphenylchains as found on Cu(110), and instead some disordered short chains are formed (Fig. S3, ESI†). In the disordered chain structures, each unit links to another one with smooth and identical junctions and a specific angle which may be attributed to a certain reaction. From that we conclude that the final step of the hierarchical reaction (*i.e.* cross-dehydrogenative coupling *via* C–H activation at the *meta*-C sites) can only be realized on Cu(110) and not on Ag(110). As we know the orientation of the formed  $(\text{Ph})_4$  molecules on Cu(110) (*i.e.* along the [110] direction) and the corresponding registry with respect to the substrate facilitate the cross-dehydrogenative coupling at the *meta*-C sites.<sup>26</sup> With respect to the case on Ag(110): (1) the formed  $(\text{Ph})_4$  molecules have a different molecular orientation (*i.e.* along the [001] direction) and thus different registry with respect to the substrate; (2) the detached Br atoms are distributed in-between the two terminals of the  $(\text{Ph})_4$  molecules, which may hamper the C–H activation at the *meta*-C sites; (3) the intrinsically different chemical nature of the surface compared with Cu(110).

In conclusion, from an interplay of UHV-STM imaging and DFT calculations, we have illustrated on-surface formation of polyphenyl chains through a hierarchical reaction pathway involving two different kinds of reactions, that is, Ullmann coupling and cross-dehydrogenative coupling. The studied system may not only serve as a simple and practical route for multifold fabrication of surface molecular nanostructures, but also provide the possibility of exploring more sophisticated on-surface chemical reactions.

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