Spontaneous separation of on-surface synthesized tris-helicenes into two-dimensional homochiral domains†

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The on-surface Ullmann coupling of 2,3-dibromo[4]helicene molecules is studied on Au(111) and Cu(111) surfaces. bis-helicene and tris-helicene are identified with scanning tunnelling microscopy and X-ray photoelectron spectroscopy as reaction products. The produced star-shaped tris-helicenes self-assemble on Au(111) spontaneously into large homochiral domains.

Although 170 years have passed since Pasteur's seminal experiment of conglomerate crystallization,¹ it is still not understood at all why and under which conditions chiral compounds aggregate into homochiral or racemate crystals.² Better insight into these complicated processes has been gained from the self-assembly of chiral molecules on single-crystal surfaces.^{3,4} In particular the molecular self-assembly of helical aromatic hydrocarbons, so-called helicenes, on surfaces has received significant attention.^{5,6} Surfaces functionalized with helicenes are also of interest for chiroptical electronic devices⁷ or for electron-spin filtering.⁸ While self-assembled layers facilitate studying interesting phenomena,^{9–12} covalently linked chiral modified materials would be much more robust and therefore better suited for applications.

So far, the Ullmann reaction¹³ has been the most successful approach for creating carbon-carbon bonds between adsorbed molecules.^{14–20} In most of the previously reported work a single C–C bond is created between monosubstituted organohalides. However, C–C coupling between molecules substituted with two halogens in close vicinity, *i.e.* in *ortho*- or *peri*-position is also possible. The coupling of two *ortho*-substituted molecules^{21,22} leads usually to the formation of a 4-membered ring.²³ Interestingly, the synthesis of 'cyclobutadiene-linked' compounds has been rather challenging in solution,^{24,25} in contrast to on-surface chemistry where 4-membered rings seem to be not as rare.^{21–23} Notably, coupling of two *peri*-

substituted molecules leads to the formation of a 6-membered ring.²⁶ Also polymers containing 4- and 8-membered rings after additional dehydrogenation have been reported.²⁷ Finally, condensation of three *ortho*-dibrominated molecules to a 6-membered ring has been achieved.²² Here, the on-surface condensation of 2,3-dibromo[4]helicene²⁸ (diBr[4]H)§ by means of Ullman coupling on Au(111) and Cu(111) surfaces is reported (Figure 1). As products the dimeric bisphenantro[2,3;2',3'-b,h]biphenylene (bis[4]H) and the trimeric trisphenantro[3,4;3',4';3'',4''-b,h,n]triphenylene (tris[4]H) are identified.† The stereochemical analysis of diastereoisomers formed on the surface is performed by scanning tunnelling microscopy (STM).

Figure 1. Ullmann coupling of 2,3-dibromo[4]helicene (a) on Au(111) to (b, c) tris- and (d, e) bis[4]helicenes. (b-e) STM images compared with extended Hückel simulations allow for the identification of the reaction products. (b) In *star*-tris[4]H the sense of helicity of all three helicene subunits is identical, either clockwise (*P*) or counter-clockwise (*M*). Only the (*M,M,M*)-enantiomer is shown. (c) In *anchor*-tris[4]H one of the three helicene subunits is aligned with opposite sense from the other two. (d, e) Bis-helicenes exist as *syn*- and *anti*-isomers.

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The samples were prepared in ultra-high vacuum by Ar⁺ ion sputtering, annealing and thermal sublimation of the molecules. For detailed methods and imaging parameters see ESI[†] and Table S1 therein. The molecular layers were analysed by *in-situ* STM and X-ray photoelectron spectroscopy (XPS).

The molecules were identified by comparing STM images with extended Hückel theory (EHT) simulations performed on molecular structures relaxed on four-layer metal slabs using molecular mechanics. By comparison with STM contrast it is possible to identify if the helicenes spiral away or towards the surface.²⁹

STM images of single reaction products obtained after inducing the Ullmann coupling by annealing to 573 K on Au(111) are shown in Figure 1. Note that, consistent with literature,³⁰ Ullmann coupling occurs after annealing to 423 K, but the herein shown intramolecular resolution was achieved on a sample prepared at 573 K. Schemes of diBr[4]H and of the reaction products are also shown. Coupling of two and three molecules results in formation of bis- and tris-helicenes, respectively. The bis-helicenes exist as *syn*- and *anti*-stereoisomers (Figure 1d,e). The tris-helicenes form isomers in which all three helicene subunits have the same handedness (*star*-tris[4]H, Figure 1b) and isomers where one helicene has opposite sense of helicity with respect to the others (*anchor*-tris[4]H, Figure 1c). In the *star*-tris[4]H all distal helicene ends

spiral up, identifying them as (*P,P,P*)- and (*M,M,M*)-enantiomers. These configurations are favoured by better areal contact to the substrate, maximizing van der Waals (vdW) interaction. The structures of the *anchor*-tris[4]H imply significant repulsion between two of the three helicene subunits. Therefore, one of the helicene ends spirals towards the surface and two spiral away from it, which actually creates a pseudo [9]helicene subunit. In the *syn*- and *anti*-bis[4]H both helicene subunits spiral up, as in the case of 2,2'-bis[4]helicene on Cu(100).²⁹

After annealing diBr[4]H on Au(111) to 473 K, self-assembled domains of *star*-tris[4]H are observed (Figure 2). In a single domain all molecules have the same handedness. Domains with molecules of opposite handedness coexist on the same sample (Figure 2a). Therefore, the on-surface synthesized *star*-tris[4]H enantiomers spontaneously separate into homochiral domains. Small protrusions identified as Br atoms are imaged next to the self-assembled *star*-tris[4]H. Similar halogen-mediated self-assembly has been reported previously for other molecules at noble metal substrates.^{31,32} Remarkably, the unit cell of the self-assembled domains contains 7 Br ad-atoms and one *star*-tris[4]H (Figure 2c). This implies mass transport of 1 Br atom per *star*-tris[4]H to allow the formation of the self-assembled domains.

Figure 2 STM images showing the self-assembly and spontaneous enantiomer separation of chiral *star*-tris[4]H. (a) Large scale image showing self-assembled domains of (*P*)-*star*-tris[4]H and (*M*)-*star*-tris[4]H. (b, c) STM images at larger magnification of the self-assembled domain of (*P*)-*star*-tris[4]H. (a, b) A significant part of the sample is covered with a disordered layer, containing *anchor*-tris[4]H, *syn*- and *anti*-bis[4]H, impurities and malformed molecules. Images a) and b) were flattened by subtraction of a smoothed version of them to allow for good contrast of different terraces.

Interestingly, spontaneous separation of enantiomers occurs despite the presence of large disordered areas consisting of a mixture of *anchor*-tris[4]H, *syn*- and *anti*-bis[4]H. Moreover, other, odd appearing molecules identified as impurities or non-specific coupling products are found. They amount to 16% of the helicene subunits (Table S2, ESI[†]). Based on the abundance of impurities on Cu(111) (Table S2, ESI[†]), around 3% of the deposited molecules are not intact diBr[4]H. The higher abundance of irregular products on Au(111) could suggest that to some extent non-specific coupling and modifications, such as dehydrogenation, C–H activation or isomerization, may

occur on Au(111) during annealing. However, most molecules are intact and can be identified as one of the 4 species discussed in Figure 1. The statistical analysis (Table S3, ESI[†]) is further limited by the fact that the self-assembled domains of *star*-tris[4]H are very large, making it difficult to quantify the relative fraction of these isomers. About 10 to 30% of the surface is covered with self-assembled domains of tris[4]H. Among the identified four species (*syn*- and *anti*-bis[4]H, *star*- and *anchor*-tris[4]H), about half of them are bis[4]H. Also, about half of the bis[4]H are *syn*-isomers, in accordance with the outcome expected for statistical coupling. Interestingly,

more than half of the tris[4]H are *star*-isomers. Even if the self-assembled *star*-tris[4]H are not counted, still 40% of the tris[4]H in the disordered areas are *star*-tris[4]H. Purely statistical coupling should lead to 75% *anchor*-tris[4]H and 25% *star*-tris[4]H and can therefore be excluded. C 1s XPS (Figure S1, ESI[†]) shows that desorption of *anchor*-tris[4]H cannot account for non-statistical coupling. Thus, the favoured formation of *star*-tris[4]H means that even at the high temperature during Ullmann coupling the steric repulsion in the *anchor*-tris[4]H is substantial and causes a preference for *star*-tris[4]H because of better steric accessibility under reaction conditions.

The STM study is complemented by Br 3p and C 1s XPS (Figure 3). Consistent with the literature,³⁰ the shift of the Br 3p_{3/2} XPS peak of 1 monolayer (ML) diBr[4]H on Au(111) to lower binding energy confirms C–Br bond scission after annealing to 463 K (Figure 3a). Furthermore, the C 1s signal has a symmetric line-shape after annealing (Figure 3b), suggesting the absence of C–Br and C–Au bonds. C 1s spectra overlaid for direct comparison are presented in Figure S1 (ESI[†]).

Figure 3. X-ray photoelectron spectroscopy of 1 ML diBr[4]H adsorbed on Au(111) (a,b) and on Cu(111) (c,d). (a) On Au(111), the shift of the Br 3p_{3/2} signal from 183.6 eV to 181.4 eV after annealing to 463 K shows that the C–Br bond is broken. (b) The disappearance of the C 1s shoulder around 285 eV after annealing also indicates dissociation of the C–Br bonds. The symmetric line shape (centred at 284.0 eV) after annealing indicates that only C–C and C–H are present. (c) On Cu(111), the shift of Br 3p_{3/2} to lower binding energies occurs between 106 K and 356 K, showing the dissociation of the C–Br bond in this temperature range. (d) The C 1s spectrum obtained at 106 K exhibits a shoulder at higher binding energy due to the intact C–Br bonds. After annealing to 356 K, a shoulder at lower binding energies (284.0 eV) is observed, indicating the presence of organometallic C–Cu bonds. After annealing to 463 K a symmetric line shape is observed, indicating C–C coupling. The spectral weight of the fitted shoulders was fixed to 12.5%, consistent with 2 Br per molecule.

If Cu(111) is used as a substrate, Br 3p XP spectra show that C–Br bond breaking occurs between 106 K and 356 K (Figure 3c). Facile C–Br bond breaking has also been reported for other molecules on Cu substrates.^{29,30,33} The C 1s XP spectra obtained

on a sample prepared on Cu(111) at 356 K are asymmetric due to a shoulder at lower binding energy. Such low C 1s binding energy is an indication of organometallic carbon bonds.^{34–36} However, annealing to 463 K (Figure 3d) leads to a symmetric C 1s signal. This is a strong indication for the absence of C–Cu or C–Br bonds and that C–C coupling has occurred. Note that all signals in the Br 3p and C 1s XP spectra are shifted to lower binding energies on Au(111) with respect to Cu(111) due to the comparably stronger screening of the core-hole on Au.³⁷

Figure 4. STM images showing the reaction products obtained on Cu(111) after annealing to different temperatures. (a) Organometallic Cu-tris[4]H and Cu-tetra[4]H after annealing to 353 K. They are compared with extended Hückel simulations in the insets. Note that the simulations fail to reproduce the contrast on the coordinated Cu atoms. (b) Organic species after annealing to 443 K. Virtually only *syn*- and *anti*-bis[4]H exist, only very few tris[4]H are found.

Figure 4a displays STM data obtained after annealing of diBr[4] on Cu(111) to 356 K. Tetrameric and trimeric structures are found (Table S4, ESI[†]). The appearance of these structures can be modelled with EHT as organometallic Cu-tris[4]H and Cu-tetra[4]H. The simulations, however, fail to reproduce the contrast on the metal atoms in the centres. Both Cu-tris[4]H and Cu-tetra[4]H complexes exist as different stereoisomers (not shown). Overlaid EHT simulations are displayed in Figure S2 (ESI[†]). In contrast, after annealing to 463 K, *i.e.* above the threshold temperature for C–C coupling on Cu substrates,³⁰ dimeric molecules are imaged (Figure 4b). They are identified as *syn*- and *anti*-bis[4]H. Interestingly, tris[4]H are only rarely observed (5% abundance, Table S5, ESI[†]). Such preference for formation of bis[4]H on Cu(111) and the above-mentioned

preferred formation of tris[4]H on Au(111) can be rationalized by the reactivity of Cu with respect to Au and by the mobility of adsorbates on these substrates. The higher reactivity of Cu combined with the lower mobility of adsorbates on it has been found to favour kinetically-preferred products,¹⁶ i.e. the first possibility for bond formation is realized with a higher probability. In the present work, the possibilities are the formation of bis[4]H and tris[4]H, corresponding to coupling of two and three molecules. Therefore, the higher reactivity of Cu and the lower mobility on it leads to a higher probability for C–C bond formation and to preferred formation of bis[4]H. Conversely, the lower probability for C–C bond formation on Au and the higher mobility on it allows for a higher yield of tris[4]H. It is anticipated that the ratio between bis- and tris[4]H can be also tuned by the molecular coverage, the sublimation rate and the annealing temperature if the deposition is performed on a hot substrate.³⁸ However, such studies are beyond the scope of this communication.

In conclusion, Ullmann coupling of *ortho*-substituted 2,3-dibromo-[4]helicenes on Au(111) leads to both tris[4]helicene (6-membered ring) and bis[4]helicene (4-membered ring). Different stereoisomers are observed. Unless sterically hindered, e.g. in *anchor*-tris[4]H, the helicene ends point away from the surface. The star-shaped enantiomers of *star*-tris[4]H spontaneously resolve into self-assembled domains with Br atoms located in-between the molecules. Due to the comparably higher reactivity of Cu(111) virtually only bis[4]H are produced by Ullmann coupling on this surface.

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Conflicts of interest

There are no conflicts to declare.

Notes and references

- #bis[4]H refers here to bisphenantro[2,3;2',3'-b,h]biphenylene and is distinct from 2-2'-bis[4]helicene reported in ref. 29.
- §The synthesis of 2,3-dibromo[4]helicene is reported in ref. 28
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