



Stereospecific on-Surface Cyclodehydrogenation of Bishelicenes: Preservation of Handedness from Helical to Planar Chirality

Bahaaeddin Irziqat, Aleksandra Cebrat, Miloš Baljžović, Kévin Martin, Manfred Parschau, Narcis Avarvari, Karl-heinz Ernst, Karl-Heinz Ernst, Lawrence Scott, Angelika Kühnle, et al.

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Stereospecific On-Surface Cyclodehydrogenation of Bishelicenes: Preservation of Handedness from Helical to Planar Chirality --Manuscript Draft--

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| Opposed Reviewers: | |
| Abstract: | The on-surface dehydrogenation of bispentahelicene on a gold(111) surface has been studied by means of scanning tunneling microscopy. Deposition of 2,2'-Bispentahelicene onto a gold surface in ultrahigh vacuum leads exclusively to formation of the homochiral (M,M)- and (P,P)- diastereomers. Thermally induced |

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| | cyclodehydrogenation proceeds then enantiospecifically into planar coronacorone that breaks mirror symmetry due to surface confinement. Upon cooling, the coronacorone enantiomers crystallize into a two-dimensional conglomerate of homochiral domains. |
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Transfer of manuscript to Chemistry - A European Journal

Sehr geehrter Herr Dr. Ross

Uploaded please find the revised manuscript entitled "*Stereospecific On-Surface Cyclodehydrogenation of Bishelicenes: Preservation of Handedness from Helical to Planar Chirality*", authored by Bahaaeddin Irziqat, Aleksandra Cebat, Miloš Baljžović, Kévin Martin, Manfred Parschau, Narcis Avarvari, and Karl-Heinz Ernst.

The paper has been transferred from Angewandte Chemie to Chemistry - A European Journal. Our point-by-point reply to the reviewers' comments are listed below in this cover letter. For your convenience, we have uploaded an annotated version of the manuscript that highlights all changes made.

Our manuscript reports the stereospecific transmission of handedness from helical chirality to planar chirality of a prochiral planar molecule which is truly chiral due to surface confinement. Such process is unique as it has been only reported previously for a Diels-Alder reaction of helicenes on surfaces but not for pure cyclodehydration of helicenes. Hence, the manuscript goes certainly beyond our recent Chemistry - A European Journal paper dealing with formation of nanographenes.

Yours sincerely

Prof. Dr. Karl-Heinz Ernst

Distinguished Senior Researcher – Empa
Professor at the Department of Chemistry, University of Zurich

Response to reviewer's comments:

First, we like to thank all reviewers for their fruitful comments which have been considered carefully. Below please find our replies and the details of actions taken in regard of the comments and suggestions.

COMMENTS TO AUTHOR:

Reviewer 1: The authors present a concise study of stereospecific on-surface synthesis. Chiral helicene molecules are deposited onto a gold(111) surface. STM images are taken before and after reaction (initiated by heating to 670 K.) The chirality of the molecules is preserved upon dehydrogenation: The products are achiral, but remain chiral due to confinement onto the surface. This study adds an interesting aspect to the on-surface synthesis literature.

My major criticism concerns Figure 2c. This STM image is used to argue that heterochiral rows are formed. Even though I believe the authors are right with this assignment, I cannot deduce this myself from the given image. To me, bright features are seen, which do not disclose the chirality. The situation is different in Figure 2a, where the less bright part around the bright features reveal the chirality in a convincing manner. Thus, this halo is in fact required to discern the chirality. In Figure 2c, I cannot see the halo - thus I do not think this image is sufficient to support the assignment made. I think it is in the interest of the authors to provide a more convincing argument.

Author reply: We are pretty sure that we can deduct handedness from the STM images and provide now better evidence for our assignment, but also modified our statements.

Action taken: The following changes related to this comment have been made:

- (page 2, column 1, 2nd paragraph below Figure 1) Instead the earlier statement "A closer look onto submolecular contrast of straight zigzag rows reveals that these are of heterochiral composition with both enantiomers alternating in a row (Fig. 2c).", we state now: "Judged by the faint contrast near the bright protrusions, both enantiomers are found in this semi-ordered van-der-Waals-assembly (Figure S2)".
- We included a new figure (Figure S2) into the Supporting Information in which the halos are clearly observed and described. In particular at the terminal ends of the zigzag rows the handedness can be deducted. The figure caption of Figure S2 explains the analysis of absolute handedness. Figure S2 also shows that at close packed monolayer coverage both enantiomers are present in a single domain.
- We changed/deleted annotations within Figures 2c and 2d in order to better explain where the contrast allows assignment of handedness and where not.
- Figure caption Figure 2: Instead "(c) STM image (10 nm × 10 nm, U = -2.5 V, I = 20 pA, T = 50 K) of a zigzag chain segment, in part superimposed with stick models of both bis[5]H enantiomers. A straight zigzag chain shows alternation of enantiomers." It reads now: "(c) STM image (10 nm × 10 nm, U = -2.5 V, I = 20 pA, T = 50 K) of a zigzag chain segment, in part superimposed with bis[5]H molecular stick models. Circular arrows indicate the clockwise (blue) and counterclockwise (red) intermolecular helical descent deduced from STM contrast.

Reviewer 1:

Secondly, I wonder why the as-deposited molecules form a racemat with both enantiomers in the unit cell while the reacted species segregate into enantiopure domains. A zero-order answer would of course be that the interaction of the respective molecules is optimized in these two cases. However, I could imagine that this aspect deserves a little more attention.

Author reply: As the helicenes have no polar groups, it has to be van-der-Waals interaction, which is maximized by maximal overlap of parts of the molecular helixes. In case of the planar coronocoronene the edge-on-overlap is minute. Our force field modelling favors the homochiral dimer

by 0.72 kcal/mol. The homochiral arrangement, however, is rather due to the possibility of denser lateral packing and therefore due to maximizing the interaction with the surface.

Action taken: We state now:

- (page 2, column 1, 2nd paragraph below Figure 1): “In order to allow for maximal van-der-Waals-contact, the unit cell contains both enantiomers and along the molecular lattice vectors enantiomers alternate (Figure S3).”
- (page 2, last paragraph): “In contrast to bis[5]H dimers, force-field modelling of surface-confined dimers of 2 shows a small preference for homochiral interactions (Figure S7). However, such conglomerate aggregation is rather due to the denser packing in case of homochiral domains, thus resulting in an overall larger molecule-surface interaction.”
- The new Figure S7 compares heterochiral and homochiral coronocoronene dimers.

Reviewer 2: In this manuscript, the authors investigated on-surface dehydrogenation of bispentahelicene on a gold(111) surface by means of scanning tunneling microscopy. It is shown that thermally induced cyclodehydrogenation proceeds indeed stereospecifically, and then enantiospecifically into planar coronocoronene due to surface confinement.

The manuscript presents an idea of chiral separation, which is interesting itself. While, the results shown in the manuscript lacks novelty since cyclodehydrogenation process has been well investigated in the field, and self-assembly of the planar coronocoronene into homochiral islands is not surprising either.

Author reply: That homochiral aggregation for planar prochiral entities occurs is certainly not imperative. There are numerous studies in which prochiral molecules do not form conglomerates but racemic 2D lattices. For planar prochiral species forming racemate lattices see for example: *Angew. Chem., Int. Ed.* 2000, 39, 792–795. / *J. Am. Chem. Soc.* 2005, 127, 10101–10106. / *J. Am. Chem. Soc.* 2010, 132, 10440–10444 / *Nano Lett.* 2008, 8, 4162–4167. (Nonplanar prochiral species form even more frequently racemic lattices.)

With regard to novelty, we disagree with the reviewer. Our study reports that a small single molecule undergoes stereospecific conversion from helical to planar chirality. Enantiospecific helical to prochiral entity conversion has been previously only once observed in a Diels-Alder on-surface reaction (Ref. 17 of MS) but not by pure dehydrogenation only.

Reviewer 2: The driving force of formation of homochiral islands is not discussed, where DFT calculations are mandatory.

Author reply: We have performed force field calculations and stated that these prefer heterochiral recognition for helicenes and homochiral recognition for the planar coronocoronene. We disagree that DFT is mandatory. In an earlier study we have shown that force field-based modelling leads to identical results for intermolecular recognition of helicenes as obtained with DFT (see *ACS Nano* 2017, 11, 865-871). In the case of planar coronocoronene, we disagree with the reviewer that DFT calculations would be able to successfully describe the weak intermolecular edge-to-edge interactions.

Action taken: We state now:

- (page 2, last paragraph): “In contrast to bis[5]H dimers, force-field modelling of surface-confined dimers of 2 show a small preference for homochiral interactions (Figure S7). However, such conglomerate aggregation is rather due to the denser packing in case of homochiral domains, thus resulting in an overall larger molecule surface interaction.”
- The new Figure S7 compares heterochiral and homochiral coronocoronene dimers.

Reviewer 2: I do not think the results presented here deserved to be published in *Angew. Chem. Int. Ed.* Before resubmission elsewhere the following questions could be considered:

1) As shown in Fig. 2b, with increasing coverage, the molecules assemble into the partly ordered chain. However, the periphery of 2,2'-bispentahelicene molecule are only hydrogen atoms, so what's the driving force for the molecules to interact with each other in the chain?

Author reply: As the helicenes have no polar groups, it has to be van-der-Waals interaction, which is maximized by maximal overlap of parts of the molecular helixes.

Action taken: We state now:

- (page 2, column 1, 2nd paragraph below Figure 1): “Judged by the faint contrast near the bright protrusions, both enantiomers are found in this semi-ordered van-der-Waals-assembly (Figure S2)”.
- And for the monolayer structure: (page 2, column 1, 2nd paragraph below Figure 1): “In order to allow for maximal van-der-Waals-contact, the unit cell contains both enantiomers and along the molecular lattice vectors enantiomers alternate (Figure S3).”

2) The contrast of straight zigzag rows in Fig. 2c and full monolayer coverage structure in Fig. 2d are not clear enough to recognize the chirality of 2,2'-bispentahelicene. The submolecular resolution imaging with a CO-modified tip (similar to Fig. 3e and f) could provide more convincing results.

Author reply: Submolecular resolution with a CO-modified tip works for planar molecules when repulsive forces can become large. For helicenes with their flexibility a clear deduction of handedness is hardly possible.

Action taken: The following changes related to this comment have been made:

- (page 2, column 1, 2nd paragraph below Figure 1) Instead the earlier statement “A closer look onto submolecular contrast of straight zigzag rows reveals that these are of heterochiral composition with both enantiomers alternating in a row (Fig. 2c).”, we state now: “Judged by the faint contrast near the bright protrusions, both enantiomers are found in this semi-ordered van-der-Waals-assembly (Figure S2)”.
- We included a new figure (Figure S2) into the Supporting Information in which the halos are clearly observed and described. In particular at the terminal ends of the zigzag rows the handedness can be deduced. The figure caption of Figure S2 explains the analysis of absolute handedness. Figure S2 also shows that at close packed monolayer coverage both enantiomers are present in a single domain.
- We changed/deleted annotations within Figures 2c and 2d in order to better explain where the contrast allows assignment of handedness.
- Figure caption Figure 2: Instead “(c) STM image (10 nm × 10 nm, U = −2.5 V, I = 20 pA, T = 50 K) of a zigzag chain segment, in part superimposed with stick models of both bis[5]H enantiomers. A straight zigzag chain shows alternation of enantiomers.” It reads now: “(c) STM image (10 nm × 10 nm, U = −2.5 V, I = 20 pA, T = 50 K) of a zigzag chain segment, in part superimposed with bis[5]H molecular stick models. Circular arrows indicate the clockwise (blue) and counterclockwise (red) intermolecular helical descent deduced from STM contrast.

3) The authors state that after complete planarization, as achieved after thermal treatment at 670 K, the scenario of homochiral domains and conglomerate aggregation is attributed to the preference for homochiral interactions. However, there is no theoretically calculated data in the manuscript. A more detailed mechanism analysis of such a process should be provided.

Action taken: We state now:

- (page 2, last paragraph): “In contrast to bis[5]H dimers, force-field modelling of surface-confined dimers of 2 show a small preference for homochiral interactions (Figure S7). However, such conglomerate aggregation is rather due to the denser packing in case of homochiral domains, thus resulting in an overall larger molecule surface interaction.”
- The new Figure S7 compares heterochiral and homochiral coronocoronene dimers, its figure caption states now the difference in interaction energies for hetero- and homochiral dimers.

Reviewer 3: This study reports the deposition of helicene derivatives on a Au(111) surface and their transformation upon thermal treatment into a planar coronene species. The focus is on the chirality and the self-assembly of the precursor and product molecules. The measurements are mainly done by scanning tunneling microscopy at low temperatures, partially using a functionalized CO tip to enhance the contrast, supported by force field calculations. The data is well presented and the manuscript is written in a clear fashion, nevertheless I see limited substance and novelty and

therefore do not recommend publication in *Angewandte Chemie*. The first step in the on-surface process is the self-assembly of the bis[5]H molecules, which form a racemate at full coverage (the assignment is not clear - see below). By sample heating, cyclodehydrogenation is induced that leads to more planar structures. The chirality of the precursor molecules is preserved during this process, which is obvious from their chemical structure (and visible in scheme 1). Cyclodehydrogenation itself is not novel and has been reported for many molecules, it is nowadays rather straightforward to see such an effect on a gold surface. It is also clear that such a process proceeds stereospecifically. As a consequence of this chemical transformation, homochiral islands appear. Such an effect, a consequence from the specific shape and adsorption configuration of the molecules, has been seen for many molecules in the past - so also there I do not see sufficient conceptual novelty and rather a new molecule that shows such an effect.

Author reply: Stereospecific conversion from helical chirality to planar chirality has been reported only once before in a different chemical reaction (Ref. 17 of MS).

That homochiral aggregation for planar prochiral entities occurs is also not guaranteed. There are many studies in which prochiral molecules do not form conglomerates but racemic 2D lattices. For planar prochiral species forming racemate lattices see for example: *Angew. Chem., Int. Ed.* 2000, 39, 792–795. / *J. Am. Chem. Soc.* 2005, 127, 10101–10106. / *J. Am. Chem. Soc.* 2010, 132, 10440–10444 / *Nano Lett.* 2008, 8, 4162–4167. (Nonplanar prochiral species form even more frequently racemic lattices.)

Additional points:

(1) While Fig.2a shows the chirality of the individual molecules very clearly, I cannot see the claimed molecular chiralities in Fig.2c and d. Despite being a key argument of the manuscript (for instance the alternation of enantiomers in Fig.2c that I cannot see), this assignment is not very convincing. A much better presentation is required.

Author reply: We provide now better evidence for our assignment and modified our statements.

Action taken: The following changes related to this comment have been made:

- (page 2, column 1, 2nd paragraph below Figure 1) Instead the earlier statement “A closer look onto submolecular contrast of straight zigzag rows reveals that these are of heterochiral composition with both enantiomers alternating in a row (Fig. 2c).”, we state now: “Judged by the faint contrast near the bright protrusions, both enantiomers are found in this semi-ordered van-der-Waals-assembly (Figure S2)”.
- We included a new figure (Figure S2) into the Supporting Information in which the halos are clearly observed and described. In particular at the terminal ends of the zigzag rows the handedness can be deduced. The figure caption of Figure S2 explains the analysis of absolute handedness. Figure S2 also shows that at close packed monolayer coverage both enantiomers are present in a single domain.
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(2) Why did the authors use different sample temperatures (7 K and 50 K)? Their reasons would be of interest to the reader.

Author reply: In order to confirm homochiral aggregation we decided to perform CO-modified STM tip studies. CO molecule pick-up requires much lower temperatures than the 50 K of our VT-STM apparatus.

Action taken: We state now (page 2, 2nd-last paragraph): “Confirmation of this scenario required submolecular resolution, which was achieved by STM studies at 7 K with a carbon monoxide modified STM tip. (Figure 3e,f).”

(3) On page 2, the authors write "...it shows strong preference to be incorporated into homochiral domains of 2 (Fig. 3d)". The meaning of this sentence is not clear. Where should the molecules adsorb in a full monolayer - if not in the homochiral domains?

Author reply: We specify now what was meant.

Action taken: We state now (page 2, 2nd-last paragraph): "...and it shows strong preference to be incorporated into homochiral domains of completely planarized product with identical handedness “

(4) As a side comment, I was surprised by the acknowledgment for the SNSF for "continuous support". I suppose that they financed part of this research, either via equipment or by people - if so, this could be specified.

Author reply: Helicene – surface research has been supported by SNSF since 1996.

Action taken: We state now: “KHE gratefully acknowledges support provided by Swiss National Science Foundation (grant 182082) and the”

COMMUNICATION

Stereospecific On-Surface Cyclodehydrogenation of Bishelicenes: Preservation of Handedness from Helical to Planar Chirality

Bahaaeddin Irzizat,⁺ Aleksandra Cebrat,⁺ Miloš Baljžović, Kévin Martin, Manfred Parschau, Narcis Avarvari, and Karl-Heinz Ernst*

In memory of Richard Ernst

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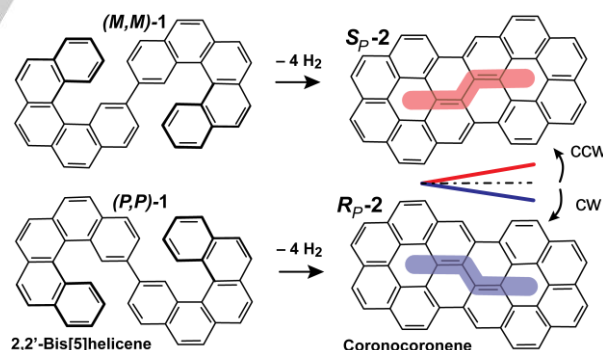
Supporting information for this article is given via a link at the end of the document.

Abstract: The on-surface dehydrogenation of bispentahelicene on a gold(111) surface has been studied by means of scanning tunneling microscopy. Deposition of 2,2'-Bispentahelicene onto a gold surface in ultrahigh vacuum leads exclusively to formation of the homochiral (*M,M*)- and (*P,P*)-diastereomers. Thermally induced cyclodehydrogenation proceeds then enantiospecifically into planar coronocoronene that breaks mirror symmetry due to surface confinement. Upon cooling, the coronocoronene enantiomers crystallize into a two-dimensional conglomerate of homochiral domains.

Cyclodehydrogenation of sterically overcrowded precursor molecules into planar polycyclic aromatic hydrocarbons (PAH) is an important step to all-carbon nanostructures, such as nanographenes.^[1-4] For that matter, on-surface chemistry has become an important approach towards new functional interfaces that are hardly available by solution chemistry.^[5-7] For example, graphene nanoribbons, carbon nanotubes and nanographenes have been synthesized after deposition of aromatic precursors followed by thermally induced dehydrogenation and C-C coupling.^[8-12]

Due to surface alignment and two-dimensional (2D) packing of precursors, C-C coupling reactions can proceed highly stereospecifically.^[13] For helically shaped aromatic hydrocarbons, so-called helicenes, diastereoselectivity has been reported for on-surface Ullmann coupling into bishelicenes.^[14,15] Bisheptahelicene or dibenzoheptahelicene, for example, can be

planarized thermally on surfaces by Diels-Alder cycloaddition followed by cyclodehydrogenation.^[17,18]



Scheme 1. Stereospecific cyclodehydrogenation of bisheptahelicene into coronocoronene. Due to surface confinement the product is chiral. (*M,M*)- and (*P,P*)-2,2'-bis[5]H enantiomers turn into *S_P*- and *R_P*-enantiomers, respectively. *S_P* stands for going intramolecularly from one coronene center to the other if one has to turn left, while for *R_P* one has to turn right.

Here, it is shown that the hitherto unknown 2,2'-bispentahelicene ($C_{44}H_{26}$, bis[5]H) undergoes cyclodehydrogenation such that the sense of helicity is converted specifically into planar chirality (Scheme 1). At first, the self-assembly of bis[5]H on a gold(111) surface has been investigated by means of scanning tunneling microscopy (STM), supported by force field calculations and time-

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of-flight secondary ion mass spectrometry (ToF-SIMS). After deposition of bis[5]H onto Au(111), only (*M,M*)- and (*P,P*)-bis[5]H enantiomers are observed on the surface. This finding is attributed to substantial steric overcrowding of a potential surface-confined (*M,P*)-isomer in combination with low inversion barriers of the pentahelicene subunits (Figure 1). As the distal ends of both enantiomers spiral up away from the center, C-C coupling and dehydrogenation leads to planar corononene (**2**) enantiomers, which aggregate upon cooling into homochiral domains, *i.e.*, into a 2D conglomerate.

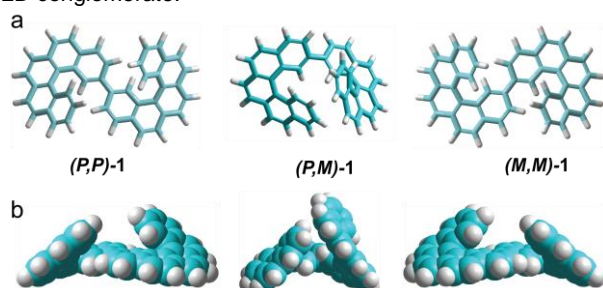


Figure 1. Diastereomers of bis[5]H. a) Stick models of the (*P,P*)- and (*M,M*)-enantiomers and the (*M,P*)-meso form. b) Full-space models of the diastereomers.

Details of experimental and computational methods as well as chemical synthesis of racemic bis[5]H, involving a homo-coupling of 2-Br-[5]H, are presented in the **Supporting Information**. Briefly, the molecules have been sublimated in ultrahigh vacuum onto the gold surface held at room temperature. STM investigation has been performed after cooling the sample to 50 K and to 7 K. Dehydrogenation has been induced by stepwise annealing to 400 °C.

Figure 2 shows STM images of bis[5]H on Au(111). At low coverage the handedness of single molecules is clearly deduced by bright protrusions (Figure 2a). As these are the upper (distal) ends of the spirals, spiraling downward in a counterclockwise fashion (red circular arrow) marks (*M*)-helicity and spiraling downward in a clockwise fashion (blue circular arrow) marks (*P*)-helicity. Modelled electron density grayscale maps of unoccupied states of the two enantiomers fully relaxed on the surface (Figure S1) support the assignment (Figure 2a, insets). With increasing coverage, the molecules assemble into partly ordered motifs, aligned by the Au(111) surface structure (Figure 2b,c). That is, chains form along the hcp/fcc superstructure of the reconstructed surface.^[19] Judged by the faint contrast near the bright protrusions, both enantiomers are found in this semi-ordered van-der-Waals-assembly. (Figure S2). At full monolayer coverage a 2D racemate crystal is formed (Figure 2d). In order to allow for maximal van-der-Waals-contact, the unit cell contains both enantiomers and along the molecular lattice vectors enantiomers alternate (Figure S3). Force-field model calculations performed for bis[5]H dimers on the surface also show a small preference for heterochiral recognition (Figure S4).

Thermal treatment at 620 K and 670 K leads to almost complete and fully complete planarization of bis[5]H into **2**, respectively. Dehydrogenation occurs at eight C atoms and four new C-C bonds are formed between C atoms 1 and 14, 1' and 14', 3 and 13', as well as between 3' and 13 of the bis[5]H molecule

(Figure S5). Such chemistry is supported by ToF-SIMS, showing the loss of 8 H-atoms (Figure S6).

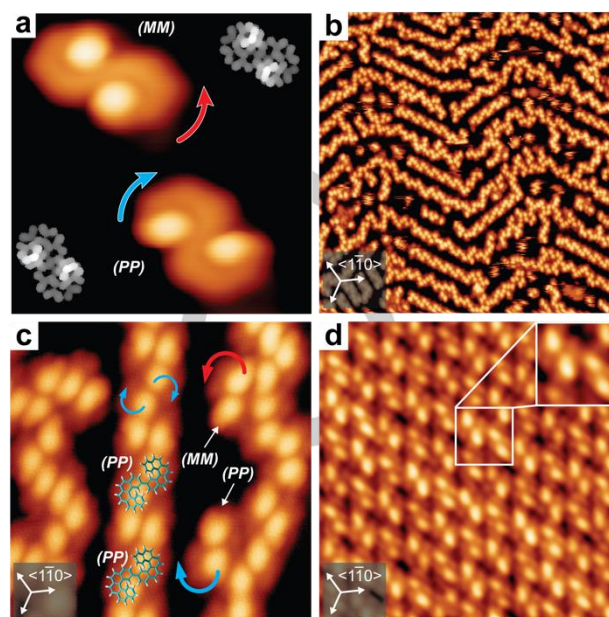


Figure 2. Self-assembly of racemic bis[5]H on Au(111). (a) High-resolution STM image (4 nm × 4 nm, U = 400 mV, I = 120 pA, T = 7 K) showing individual (*M,M*)- and (*P,P*)-bis[5]H enantiomers. Circular colored arrows indicate the sense of helicity spiraling downward. The insets present grayscale unoccupied orbital density maps. (b) STM image (60 nm × 60 nm, U = −2.5 V, I = 20 pA, T = 50 K) at submonolayer coverage showing in part zigzag chains, oriented along the herringbone reconstruction of the Au(111) surface. (c) STM image (10 nm × 10 nm, U = −2.5 V, I = 20 pA, T = 50 K) of a zigzag chain segment, in part superimposed with bis[5]H molecular stick models. Circular arrows indicate the clockwise (blue) and counterclockwise (red) intermolecular helical descent deduced from STM contrast. (d) STM image (15 nm × 15 nm, U = −2.5 V, I = 25 pA, T = 50 K) of the monolayer saturation coverage structure. The inset (3 nm × 3 nm) is a magnified cut-out and shows different contrast for adjacent molecules. See Figure S2 for STM pattern analysis. Triple white arrows mark the orientation of the (111) surface.

Figure 3 shows STM images of the planarization products. After treatment at 620 K, there are a few molecules that still show a bright protrusion on one side (Figure 3a). These are entities in which only one helicene subunit has been cyclodehydrogenated (Fig. 3b,c). As the planar product is chiral in its adsorbate state, aspects of chirality also apply to its self-assembly. The absolute handedness of semi-planarized product is easily determined, and it shows strong preference to be incorporated into homochiral domains of completely planarized product with identical handedness (Figure 3d). After complete planarization, as achieved after thermal treatment at 670 K (or bis[5] deposition at that temperature) conglomerate aggregation into homochiral domains of **2** was observed. Confirmation of this scenario required submolecular resolution, which was achieved by STM studies at 7 K with a carbon monoxide modified STM tip. (Figure 3e,f).

In contrast to bis[5]H dimers, force-field modelling of surface-confined dimers of **2** shows a small preference for homochiral interactions (Figure S7). However, such conglomerate aggregation is rather due to the denser packing in case of homochiral domains, thus resulting in an overall larger molecule-surface interaction. As the molecular mobility at 670 K is high, homochiral recognition occurs upon cooling at lower

temperatures. Enantiomeric conversion can be safely excluded because the large contact area between molecule and surface causes strong binding. Based on previous density functional theory (DFT) studies,^[20,21] the binding energy of **2** to Au(111) is estimated to be between 4.42 eV and 5.63 eV.

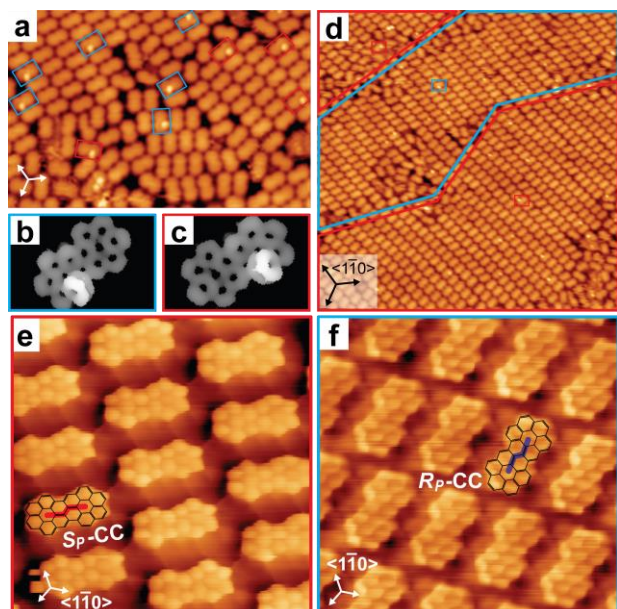


Figure 3. Selective formation of coronacorone via thermally induced cyclodehydrogenation of bis-[5]H on Au(111). (a) STM image (22 nm × 15 nm, U = 1.0 V, I = 20 pA, T = 50 K) revealing the coexistence of mostly planar species and semi-planarized species highlighted by red and blue rectangles after annealing to 620 K. (b,c) Unoccupied states density maps of the opposite-handed semi-planarized products show only one bright helical subunit per molecule. (d) STM image (40 nm × 40 nm, U = 1.2 V, I = 20 pA, T = 50 K) showing the predominant presence of self-assembled domains of completely planar molecules. The semi-planarized molecules suggest the presence of a 2D conglomerate. Homochiral domains are indicated by red and blue edging. (e,f) High-resolution STM images (5 nm × 5 nm, U = 70 mV, I = 1.44 nA, T = 7 K; and 5 nm × 5 nm, U = 50 mV, I = 1.12 nA, T = 7 K) acquired after annealing to 670 K. At this stage, the planarization is complete and a conglomerate of homochiral domains of S_p-2 (e) and R_p-2 (f) is formed.

Each enantiomer converts exclusively to a specific product. (*M,M*)-bis[5]H gives S_p-2 and (*P,P*)-bis[5]H leads to R_p-2, meaning that on-surface cyclodehydrogenation proceeds indeed stereospecifically. Enantiomerization of the [5]H subunits is expected to occur even on the surface at these temperatures, but a potentially forming *meso*-(*M,P*) form cannot undergo complete dehydrogenation. Once the dehydrogenation starts on one side of the molecule, the chirality of the product is fixed, thus explaining the stereospecificity. Semi-planarized product can only lead to opposite handed completely planarized product if it flips over on the surface. Again, such process is highly unlikely due to the strong interaction of planar polyaromatic hydrocarbons with the surface.

The last step of on-surface synthesis of graphene nanoribbons (GNR) includes also cyclodehydrogenation.^[22–24] Starting with polyanthrylene polymers, annealing to 600 K causes partial cyclodehydrogenation, and annealing at 670 K causes formation of planar ribbons. The mechanism of the cyclodehydrogenation into GNR has previously been studied by means of DFT.^[20,25] Transferring the conclusions of that study to the bis[5]H cyclodehydrogenation leads to the following reaction

mechanism (Figure S8): i) Due to temperature induced vibrations of the molecular frame and van der Waals interactions, the distal end of one helix gets closer to the proximal part, enabling C–C bond formation between C atoms 1 and 14 as well between 3' and 13. ii) The hydrogen atoms at the proximal part of the helix are then catalytically detached by the surface. iii) The upper hydrogen atoms at C13 and C14 are transferred by a 1,3 shift to rim carbon atoms, forming an intermediate CH₂ group from which iv) the lower hydrogen atoms are also catalytically detached. Alternatively, thermally allowed 1,5-H shifts or the involvement of gold adatoms, both not considered in the DFT evaluations, could be involved here. Because a semi-dehydrogenated species with only one helix planarized is observed as intermediate, the first C–C bond formation must have the highest barrier with the following steps easier to complete. The fact that hydrogen at sterically overcrowded positions is most reactive is also supported by catalytic oxidation of respective polyaromatic hydrocarbons.^[25]

In summary, adsorption of bis[5]H leads exclusively to formation of (*M,M*)- and (*P,P*)-enantiomers on Au(111), whereas a *meso*-(*M,P*) form is not observed on the surface. At full monolayer coverage aggregation into a 2D racemate crystal occurs. Thermally induced cyclodehydrogenation proceeds stereospecifically to planar coronacorone, which is chiral due to surface confinement. The product assembles then into a conglomerate of enantiopure domains. Such reaction is a special example of topochemistry in which the alignment of reactant by the surface supports enantiospecific conversion.

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Keywords: chirality • STM • on-surface chemistry • helicenes • polyaromatic hydrocarbons

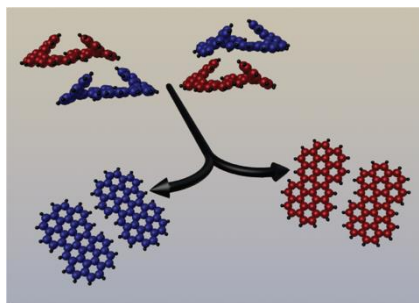
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COMMUNICATION

Chirality

Entry for the Table of Contents



Flattening helices but still keeping the handedness. On-surface cyclodehydrogenation of bishelicene enantiomers leads stereospecifically to chiral planar polyaromatic hydrocarbons followed by their homochiral aggregation into a two-dimensional conglomerate.

