

Room-temperature selective cyclodehydrogenation on Au(111) via radical addition of open-shell resonance structures

Corresponding Author: Professor Pei-Nian Liu

This file contains all reviewer reports in order by version, followed by all author rebuttals in order by version.

Version 0:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

In their paper, "Room-temperature selective cyclodehydrogenation on Au(111) via radical addition of open-shell resonance structures", Deng-Yuan Li et al. demonstrate a unique and hitherto unexplored pathway for on-surface cyclodehydrogenation. Formation of radicals by homolysis of C-Br bonds is frequently utilized in the on-surface synthesis of nanographenes. Here, Pei-Nian Liu and co-workers show that a delocalized π -radical can migrate to a keto group and lead to intra-molecular cyclodehydrogenation at room-temperature on Au(111). The reaction products are characterized using high-resolution scanning probe techniques that resolve the chemical structure of the molecules. The experimental results are well-supported by density functional theory calculations. Additional DFT calculations are utilized to provide a plausible reaction pathway. The reaction barrier obtained is in excellent agreement with experiments. Suitable control experiments put these results on a solid footing. Overall, this is a highly intriguing manuscript and I strongly recommend its publication in Nature Communication. However, there are certain aspects that must be addressed before publication.

1. The authors claim that the delocalization of the π -radical onto the keto group by way of resonance structures is key to the low-temperature cyclodehydrogenation presented in the paper. This is indeed an under-explored concept, and this paper would be the first to intentionally exploit it. The introduction therefore could emphasize this aspect more. I would encourage the authors to take a more didactic approach. One avenue that they could take is to compare, and contrast, their reaction with the keto-enol tautomerism of solution-chemistry.

2. On line 69-70, the authors suggest that the transient radicals play a role in reaction mechanisms when the difference between the closed-shell and open-shell resonance hybrid structures is small. It would be very instructive if these energies could be obtained for the molecule 1. Moreover, I would expect that, in an open shell configuration, the delocalized unpaired π -electron should have a significant probability density over the oxygen atom, which could be nicely illustrated by plotting the SOMO wave function.

3. A conclusive control experiment that supports the interpretation of the authors is when they deposited the precursor 1 on a cold Au(111) surface. STM imaging of this sample showed non-planar unreacted molecules. This clearly showed that the reaction indeed is occurring on the surface (as opposed to in the crucible while sublimating the precursor). However, there is no description of what 'cold' means. The authors should provide a more careful description of their in-vacuum synthetic protocols.

4. It is surprising that 1 undergoes debromination at temperatures close to or below room temperature. In Ref. 65, 90% of the molecules were debrominated at 400 K, while de-bromination of a gem-dibromide occurred at 500 K in Ref. 66. There is only one previous study; J.I. Urgel et al *Angew.Chem.Int.Ed.* (2020) 59,13281 that showed a two-step debromination, where the first occurred at room temperature. However, the gem-dibromide was installed on a 5-membered ring. Can the authors comment on why they are seeing a debromination at such low temperatures?

5. The authors have provided simulated nc-AFM images of a variety of structures, except those in Fig. 2. Obtaining a simulated nc-AFM image for at least the structures in Fig 2f and 2g is essential. In the experimental images the C-O bond is not resolved. This is to be expected, and AFM simulations can reproduce this effect. In some cases, it also depends on the surface registry of the oxygen with the Au substrate (see for instance: Fig. 4 in A. Berdonces-Layunta et al., *ACS Nano* (2021) 15, 3, 5610 and Fig. 3 in A. Kinikar et al., *ACS Nanosci. Au* (2024) 4, 2, 128)

6. Because many of the structures are not exactly planar, interpretation of nc-AFM images can be tricky. Using a Laplace filter can enhance the contrast of 'bonds' versus the background. The authors should consider showing Laplace filtered images in the SI so that the structures become more apparent.

7. In Fig. 4 I-n, the assignment of the structure to the experimental data is not satisfactory. I also question the need for these data in the main text. The authors can either find a structure that better reproduces the experimental nc-AFM image or move this specific dataset into the SI and leave the structure unassigned. The only conclusion that can be drawn from the nc-AFM image (Fig. 4m) is that it is a non-planar structure.

8. Based on the difficulty of correctly identifying the chemical structures based on nc-AFM and the mismatch between the experiments and simulations in Fig. 4, the results obtained by the authors do not fully support the statement on lines 264-265. I would recommend the authors to motivate the reaction mechanism on purely chemical grounds without referring to the identification of the intermediates by nc-AFM (which is not convincing). The DFT calculation results are already in excellent agreement with the observed reaction dynamics. The results shown in Fig. 4 can then be presented after discussing the reaction mechanism in the SI.

9. It is very hard to follow the reaction proposed based on Fig. 5. The authors should add a chemical schematic (showing only the relevant portion of the molecules) to the figure. It would also be beneficial if instead of showing the model of the entire molecule, only the relevant portion was zoomed in and represented. The top-view and side view can be relegated to the SI.

10. Some minor comments: The use of amplified to mean magnified in the context of STM images is non-standard. References 44-48 on line 61 have brackets. The phrase "the planar monomer products are significantly less" on line 152 is incomplete.

Reviewer #2

(Remarks to the Author)

I co-reviewed this manuscript with one of the reviewers who provided the listed reports. This is part of the Nature Communications initiative to facilitate training in peer review and to provide appropriate recognition for Early Career Researchers who co-review manuscripts.

Reviewer #3

(Remarks to the Author)

In the manuscript Li et al. describe an interesting approach for the room temperature cyclodehydrogenation driven by radical formed in the resonance structures. The study fits into the quickly developing area of on-surface chemistry. However, I regret that the authors present the approach only on a single example forming a molecule, which does not seem to exhibit any interesting properties or be of broad interest in general. While the purpose of the study is to introduce a new concept for the synthesis of new compounds it seems that a sole example of only one precursor and one substrate is not sufficient to justify the idea as more general. Therefore in order to support publication in Nature Communications I suggest to demonstrate the idea on a different substrate than Au(111) or at least a different example of precursor and target compound to show that the radical addition of open-shell resonance structures might provide a new and more versatile pathway for the synthesis of novel compounds.

Additionally below I attach more detailed comments on the manuscript content:

- Page 5, line 100, the authors refer to [65, 66] showing debrominative C-C coupling, however the reaction was not observed there at RT, but at elevated temperature, do the authors know why here the dimerization occurs at RT?
- Page 5, line 115, the correct version shall rather be: The amplified STM images show that one dimer has a mirror-symmetric structure (Fig. 2d, left) and the other dimer has a centrosymmetric structure (Fig. 2e, left).
- The nc-AFM images are either of low quality or not correctly processed (e.g. Figure 2) therefore the presence of the ring containing oxygen is either barely visible or even impossible to recognize, I suggest improving clarity of the nc-AFM images
- Figure 2f,g – how do the authors recognize CH₃ moieties in the structures? In nc-AFM images the lobe ascribed to the CH₃ moiety is very "weak", in other studies (also cited here refs 67-68) the CH₃ groups exhibiting a 3D structure are usually more pronounced. The STM image also does not show any prominent feature. I am not convinced that the assignment is correct.
- The assignment of the observed in STM features to dimers of AAQ molecules (SI, Fig. 4) is hypothetical, why the anthracene cores appear much brighter? Due to the steric interactions the two parts of the AAQ molecule could not be flat.
- Figure 3, the acquired spatial dI/dV images (Fig. 3b left panels) do not correspond to the simulated ones (Figure 3b right panels), in fact if one compares the data presented for other orbitals in SI (Figure 5) it seems that the experimental data might be much better represented by the mixture of orbitals (e.g. HOMO & HOMO-1, LUMO & LUMO+1). This might be the effect of the interaction with the substrate. I guess that the comparison of the calculated and experimental spectroscopy data is presented to ensure formation of the claimed species, but I think that in the present form (gas phase simulations not matching the experiment) this is not helpful at all.
- The STS single point spectra in Fig. 3 are very smooth, are they averaged?
- Page 9, line 196, the authors say "For a submonolayer of precursor 1 deposited on a cold Au(111) surface..." – what does "cold" exactly mean?
- SI, Figure 6, the assignment of the individual molecules to form self-assemblies is unclear, the additional schemes would be beneficial, additionally all images are presented with different scale-size, which also does not help to recognize the presence of individual species in the assemblies
- SI, Figure 8, the simulated images differ quite significantly from the experimental ones, therefore I find the assignment hypothetical, are the authors sure that the experimental images show debrominated species?
- Figure 4, I am not convinced by the assignment (especially) in Figure 4e,f,g and 4l,m,n, comparison of 4e,f shows significant deviation, whereas in 4m the AFM images is almost featureless and does not correspond to the simulations shown in panel 4n; additionally it seems that the caption of panel o is missing
- Apart from SI Figure S9 the authors do not see and comments on Br atoms, it is known that Br atoms on Au disturb the herringbone pattern, this is not observed here, are the authors sure that the Br atoms are detached from the precursors at

RT? Where are these Br atoms on the surface?

To sum up, I could not recommend publication of the manuscript in Nature Communications in its present form. However, after appropriate revision and extension the manuscript may become publishable in Nature Communications.

Reviewer #4

(Remarks to the Author)

In this paper, Li and coworkers reported a room-temperature cyclization reaction on Au(111) for the formation of oxygen-carbon bonds using the precursor 10-(dibromomethylene)-[1,2'-bianthracen]-9(10H)-one. They demonstrated that the radical addition decreases the cyclodehydrogenation temperature and further improves the chemoselectivity of dehydrogenation. Bond-resolved STM/AFM studies visualized the reaction process, including stepwise debromination to form surface-bound carbenes, C-C coupling of carbenes, and intramolecular radical addition/hydrogen elimination to attain planarization. Moreover, the authors revealed the reaction mechanism with complementary DFT calculations, high chemoselectivity of the cyclodehydrogenation results from the reversibility and different thermodynamics of the radical addition step. Overall, this paper is well-structured and holds potential for publication in Nat. Commun., pending the authors' attention to the raised concerns.

1. The authors claimed the resonance between the cumulene and acetylene, did they observe the cumulene structure? And how do they quantify this resonance process? such as the energy difference between the two structures.
2. Building upon the resonance claim, the authors proposed a reaction process involving the radical shift from C to O atom, but this radical shift process lacks clarity and warrants further explanation. DFT calculations could offer valuable insights into this mechanism.
3. In Figure 4, the authors observed the intermediates featuring radicals within their structure, have they confirmed the presence of the radical feature via STS? In addition, have they also observed any intermediates proposed in Figure 4a during the formation of dimers?
4. Concerning the formation of dimers on the Au surface, what is the yield or ratio of α,α -dimer, β,β -dimer and α,β -dimer?
5. Given that the manuscript presents only one example precursor, it would be beneficial for the authors to comment on the generality of this cyclization reaction. Additionally, they should discuss the potential for further development of this reaction for other intriguing carbon nanostructures, which would enhance the significance and impact of their findings.
6. The caption of Figure 4o is missing, and it appears to duplicate a figure already present in Figure 1c.

Version 1:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

Deng-Yuan Li, Pei-Nian Liu, and their colleagues have done an admirable job in addressing all the reviewers' concerns. The new data obtained is of exceptional quality and satisfactorily addresses the issue of non-planar intermediates from an experimental standpoint. I am convinced this is an important and interesting contribution to the field of on-surface science. While I recognize the need for the prompt publication of this work, the authors have not satisfactorily addressed Reviewer 1 point 2 and Reviewer 4 point 2, regarding the presence of the radical on the oxygen atom.

A crucial part of the story-line is the resonance between the closed-shell and open-shell molecules, supported by the small energy difference between these two configurations (~ 3 meV). However, the authors must also show the delocalized pi radical has significant probability density over the oxygen atom. This is a straightforward calculation, and I am certain the authors already possess this data. Demonstrating the presence of the radical on the oxygen atom would provide visually compelling evidence supporting the proposed mechanism. Conversely, if the radical is not present on the oxygen atom, this would also be highly interesting. The reaction works, and the DFT calculations of the mechanism are in excellent agreement. The mechanism relies on the presence of an unpaired electron on the oxygen atom which makes perfect chemical sense. However, if the radical is not on the oxygen atom, it would imply that we as a community have not understood something foundational. Therefore, no matter what the SOMO orbital map of the open-shell structure shows, it would add to the story.

The work done by the authors in this revision is commendable. I hope they can quickly address the point raised above.

Reviewer #2

(Remarks to the Author)

I co-reviewed this manuscript with one of the reviewers who provided the listed reports. This is part of the Nature Communications initiative to facilitate training in peer review and to provide appropriate recognition for Early Career Researchers who co-review manuscripts.

Reviewer #3

(Remarks to the Author)

I appreciate the effort undertaken by the authors to answer all raised concerns.

I find the replies satisfactory and I also appreciate the additional experiments, especially with a different substrate.

Although the rings with O atoms are in experimental images significantly less visible than in the simulations, I find the overall discussion convincing and therefore I recommend the manuscript for publication in Nature Communications.

Reviewer #4

(Remarks to the Author)

The revised manuscript has addressed my previous comments and suggestions. I have no further major objections.

Version 2:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

The authors have successfully addressed all the comments. I congratulate them on an excellent manuscript.

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Response to reviews' comments

Reviewer #1:

In their paper, "Room-temperature selective cyclodehydrogenation on Au(111) via radical addition of open-shell resonance structures", Deng-Yuan Li et al. demonstrate a unique and hitherto unexplored pathway for on-surface cyclodehydrogenation. Formation of radicals by homolysis of C-Br bonds is frequently utilized in the on-surface synthesis of nanographenes. Here, Pei-Nian Liu and co-workers show that a delocalized π -radical can migrate to a keto group and lead to intra-molecular cyclodehydrogenation at room-temperature on Au(111). The reaction products are characterized using high-resolution scanning probe techniques that resolve the chemical structure of the molecules. The experimental results are well-supported by density functional theory calculations. Additional DFT calculations are utilized to provide a plausible reaction pathway. The reaction barrier obtained is in excellent agreement with experiments. Suitable control experiments put these results on a solid footing. Overall, this is a highly intriguing manuscript and I strongly recommend its publication in Nature Communication. However, there are certain aspects that must be addressed before publication.

Reply: We would like to extend our profound gratitude for your great effort to evaluate our manuscript. Your recognition of the importance of this work is gratifying, and your thoughtful reading and insightful comments and suggestions have helped us significantly improve this manuscript. We have revised our manuscript accordingly. Please see the following point-by-point responses.

1. The authors claim that the delocalization of the π -radical onto the keto group by way of resonance structures is key to the low-temperature cyclodehydrogenation presented in the paper. This is indeed an under-explored concept, and this paper would be the first to intentionally exploit it. The introduction therefore could emphasize this aspect more. I would encourage the authors to take a more didactic approach. One avenue

that they could take is to compare, and contrast, their reaction with the keto-enol tautomerism of solution-chemistry.

Reply: We appreciate the comment and insightful suggestion. In chemistry, resonance is a way of describing bonding in some molecules by combining several resonance structures into a resonance hybrid. The resonance hybrid is an average of the hypothetical resonance structures, which can represent the accurate structure of a molecule. Tautomerism refers to a chemical equilibrium between several structural isomers. For example, keto-enol tautomerism is a chemical transformation between a keto form and an enol form, which involves the transfer of an α -H atom and the reorganization of bonding electrons. Tautomers are different chemical species that are distinguished by their differing atomic arrangements, molecular geometries, and physicochemical and spectroscopic properties. In contrast, resonance hybrid forms are merely alternative Lewis structural descriptions of a single chemical species, whose true structure is a quantum superposition that is essentially an average of the idealized, hypothetical geometries implied by this resonance. Therefore, we have added a brief introduction by comparing resonance and keto-enol tautomerism in the revised manuscript as suggested by the reviewer.

On Page 5, the second paragraph, “Moreover, the radical shift from C to O……” has been revised to “Moreover, the radical shift from C to O through resonance from cyclohexadienone radical to the phenoxyl radical (similar to the keto-enol tautomerism)”.

2. On line 69-70, the authors suggest that the transient radicals play a role in reaction mechanisms when the difference between the closed-shell and open-shell resonance hybrid structures is small. It would be very instructive if these energies could be obtained for the molecule 1. Moreover, I would expect that, in an open shell configuration, the delocalized unpaired π -electron should have a significant probability density over the oxygen atom, which could be nicely illustrated by plotting the SOMO wave function.

Reply: We thank the reviewer's comment and insightful suggestion. Following the review's suggestion, we performed DFT calculations for molecule 1 adsorbed on the Au(111) surface and obtained the most stable adsorption geometry. The results show that the energy of molecule 1 in the closed-shell resonance structure is slightly lower than that in the open-shell resonance structure by 2.6 meV (Fig. R1, left), demonstrating that the ground state of molecule 1 is closed-shell at $T = 0$ K. In addition, according to the theory of resonance, the accurate structure of a molecule is essentially an average of several hypothetical resonance hybrid structures. Compared with 0 K in the calculations, room temperature may increase the proportion of open-shell resonance hybrid structures of molecule 1, promoting the radical addition reaction. Therefore, at room temperature, the formation of the open-shell resonance structure of molecule 1 is transient.

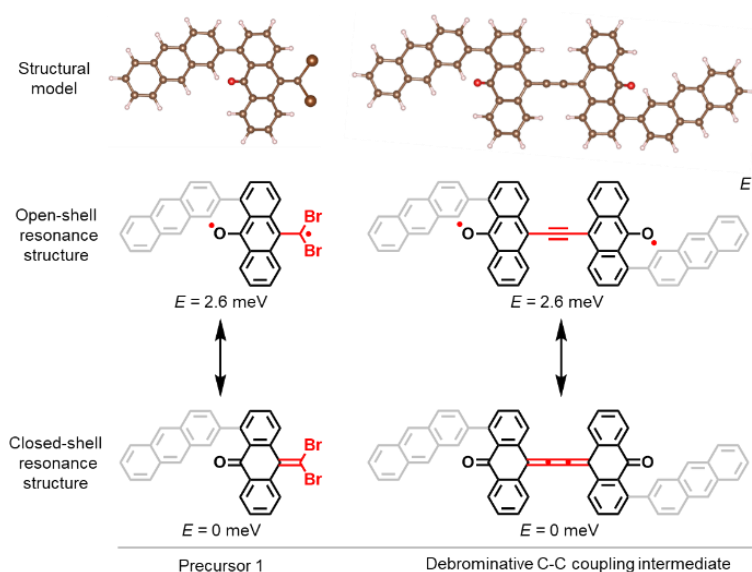


Fig. R1. DFT-calculated relative energies of precursor 1 and debrominative C-C coupling intermediate in the closed-shell or open-shell resonance structures.

In the revised manuscript, the DFT-calculated relative energies of precursor 1 and debrominative C-C coupling intermediate in the closed-shell or open-shell resonance structures have been added to Supplementary Fig 1.

3. A conclusive control experiment that supports the interpretation of the authors is when they deposited the precursor 1 on a cold Au(111) surface. STM imaging of this sample showed non-planar unreacted molecules. This clearly showed that the reaction indeed is occurring on the surface (as opposed to in the crucible while sublimating the precursor). However, there is no description of what 'cold' means. The authors should provide a more careful description of their in-vacuum synthetic protocols.

Reply: Thanks for the comment and suggestion. In the revised manuscript, “The preparation process of the two cold Au(111) samples is as follows: first, the Au(111) substrate is precooled to 5 K; second, the cold Au(111) is quickly transferred to the sample stage maintained at 293 K, and the precursor 1 is deposited on the cold Au(111) surface; finally, the cold Au(111) sample is quickly transferred to the sample stage maintained at 5 K (the whole process takes less than 3 minutes).” has been added to the Methods section.

4. It is surprising that 1 undergoes debromination at temperatures close to or below room temperature. In Ref. 65, 90% of the molecules were debrominated at 400 K, while de-bromination of a gem-dibromide occurred at 500 K in Ref. 66. There is only one previous study; J.I. Urgel et al *Angew.Chem.Int.Ed.* (2020) 59,13281 that showed a two-step debromination, where the first occurred at room temperature. However, the gem-dibromide was installed on a 5-membered ring. Can the authors comment on why they are seeing a debromination at such low temperatures?

Reply: We thank the reviewer's comments. We agree that debromination of gem-dibromide on the Au(111) surface usually occurs at 400-500 K based on the precious literature reports. In our case, the debromination of molecule 1 on Au(111) occurs at a lower temperature, which can be assigned to the transformation from low active dibromomethylene (sp^2 C–Br activation) of closed-shell resonance structures to highly active dibromomethyl radical (similar to sp^3 C–Br activation) of open-shell resonance structures (*Angew. Chem. Int. Ed.* **2022**, 61, e202204123; *Angew. Chem. Int. Ed.* **2018**, 57, 4035; *ACS Nano* **2024**, 18, 14640; *ACS Nano* **2018**, 12, 7959). The driving force of

transformation is the release of molecular strain via aromatization and planarization. The corresponding discussion has also been added to the first paragraph on Page 11.

5. The authors have provided simulated nc-AFM images of a variety of structures, except those in Fig. 2. Obtaining a simulated nc-AFM image for at least the structures in Fig 2f and 2g is essential. In the experimental images the C-O bond is not resolved. This is to be expected, and AFM simulations can reproduce this effect. In some cases, it also depends on the surface registry of the oxygen with the Au substrate (see for instance: Fig. 4 in A. Berdonces-Layunta *et al.*, *ACS Nano* (2021) 15, 3, 5610 and Fig. 3 in A. Kinikar *et al.*, *ACS Nanosci. Au* (2024) 4, 2, 128)

Reply: We thank the reviewer's insightful comment and suggestion. To more clearly confirm the chemical structure of the cyclodehydrogenation products, we further performed nc-AFM imaging and obtained high-quality nc-AFM images that can resolve the C-O bonds (a slightly dark contrast in Fig. R2 and R3) and CH₃ (a bright 3D feature in Fig. R2c, d and R3b, c). The corresponding experimental and simulated nc-AFM images have also been added in Fig. 2 and Supplementary Fig. 3 and 5.

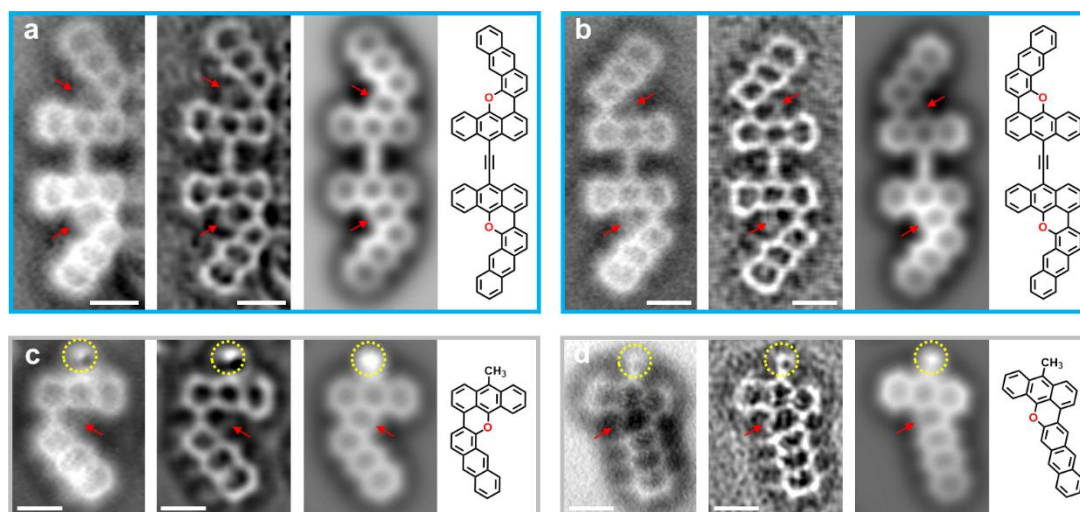


Fig. R2. a,b nc-AFM images of two representative planar dimers formed by the removal of α -H and the corresponding Laplace-filtered nc-AFM images, nc-AFM simulations, and chemical structures. c,d nc-AFM images of two representative planar monomers (c: *cis*-monomer; d: *trans*-monomer) and the corresponding Laplace-filtered nc-AFM images, nc-AFM simulations, and chemical structures. The red arrows and yellow dotted circles indicate O atoms and methyl groups. Scale bars for all images: 0.5 nm.

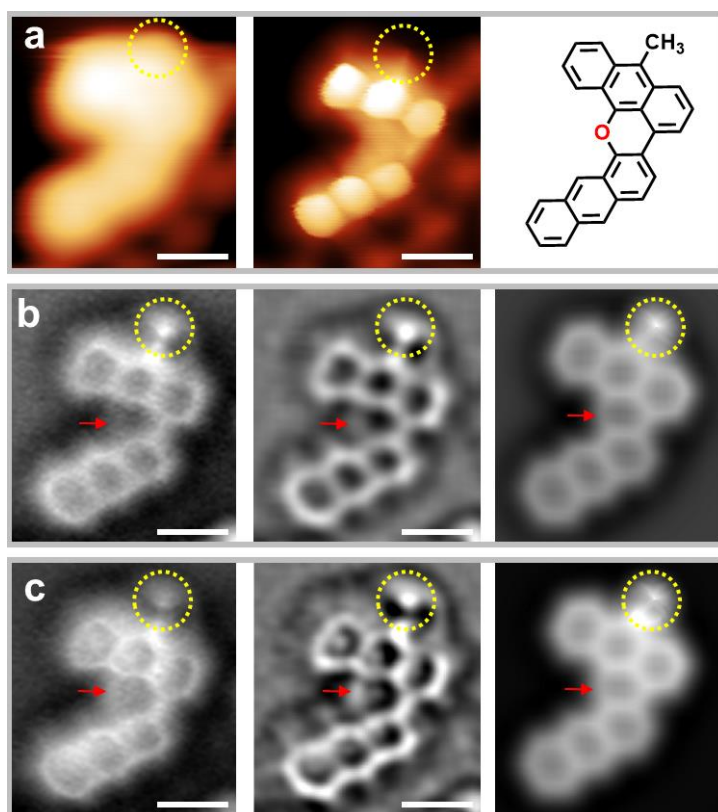


Fig. R3. **a** Zoom-in STM and BR-STM of one planar *cis*-monomer and the corresponding chemical structure. **b,c** nc-AFM images of one planar *cis*-monomer with different tip heights using a flexible CO tip and the corresponding Laplace-filtered nc-AFM images, nc-AFM simulations. The yellow dotted circles and red arrows indicate methyl groups and O atoms. Scale bars for all images: 0.5 nm. Tip height: **b** $z = -68$ pm with respect to STM setpoint of 0.1 V, 50 pA on Au(111). **c** $z = -75$ pm with respect to STM setpoint of 0.1 V, 50 pA on Au(111).

6. Because many of the structures are not exactly planar, interpretation of nc-AFM images can be tricky. Using a Laplace filter can enhance the contrast of 'bonds' versus the background. The authors should consider showing Laplace-filtered images in the SI so that the structures become more apparent.

Reply: We thank the reviewer's suggestion. As shown in Fig. R2-R7, we further performed nc-AFM imaging of nonplanar structures observed in our experiments and obtained high-quality nc-AFM images. The corresponding STM, BR-STM, nc-AFM, and Laplace-filtered nc-AFM images have been added to Fig. 2 and 4 of the revised manuscript and Supplementary Fig. 3, 5, 14-17.

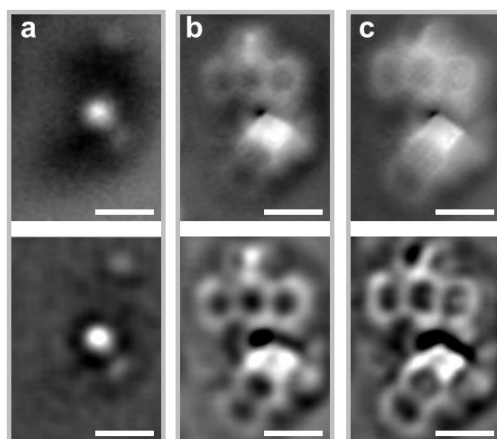


Fig. R4. **a-c** nc-AFM images (above) of an individual nonplanar monomer species I with different tip heights using a flexible CO tip and the corresponding Laplace-filtered nc-AFM images (below). Scale bars for all images: 0.5 nm. Tip heights: Tip height: **a** $z = -18$ pm with respect to STM setpoint of 0.1 V, 100 pA on Au(111). **b** $z = -32$ pm with respect to STM setpoint of 0.1 V, 100 pA on Au(111). **c** $z = -89$ pm with respect to STM setpoint of 0.1 V, 100 pA on Au(111).

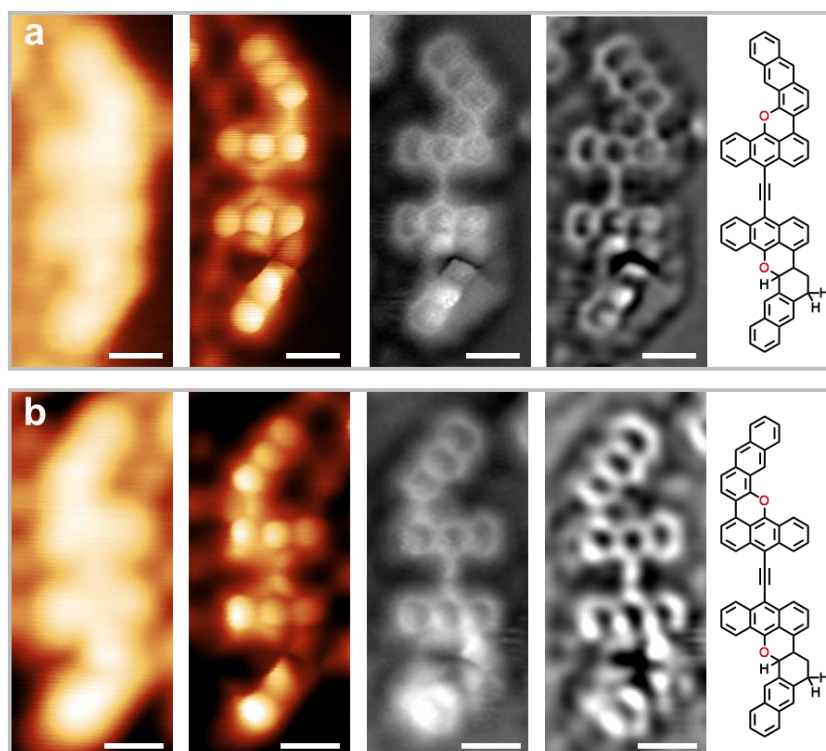


Fig. R5. **a** Zoom-in STM, BR-STM, and nc-AFM images of nonplanar *cis*- α,α -dimer species II with incomplete dehydrogenation on one side and the corresponding Laplace-filtered nc-AFM image and chemical structure. **b** Zoom-in STM, BR-STM, and nc-AFM images of nonplanar *trans*- α,α -dimer species II with incomplete dehydrogenation on one side and the corresponding Laplace-filtered nc-AFM image and chemical structure. Scale bars for all images: 0.5 nm. Scanning parameters: **a** STM: $U = 0.1$ V, $I = 10$ pA. BR-STM: CO tip, constant-height, 10 mV. **b** STM: $U = 0.1$ V, $I = 100$ pA. BR-STM: CO tip, constant-height, 10 mV.

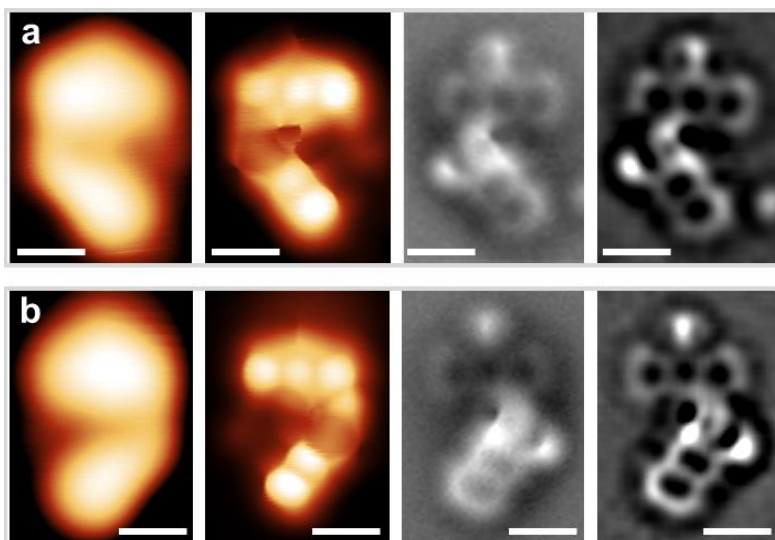


Fig. R6. a,b Zoom-in STM, BR-STM, and nc-AFM images of other nonplanar monomer species and the corresponding Laplace-filtered nc-AFM images. Scale bars for all images: 0.5 nm. Scanning parameters: **a** STM: $U = 0.2$ V, $I = 10$ pA. BR-STM: CO tip, constant-height, 10 mV. **b** STM: $U = 0.5$ V, $I = 10$ pA. BR-STM: CO tip, constant-height, 10 mV.

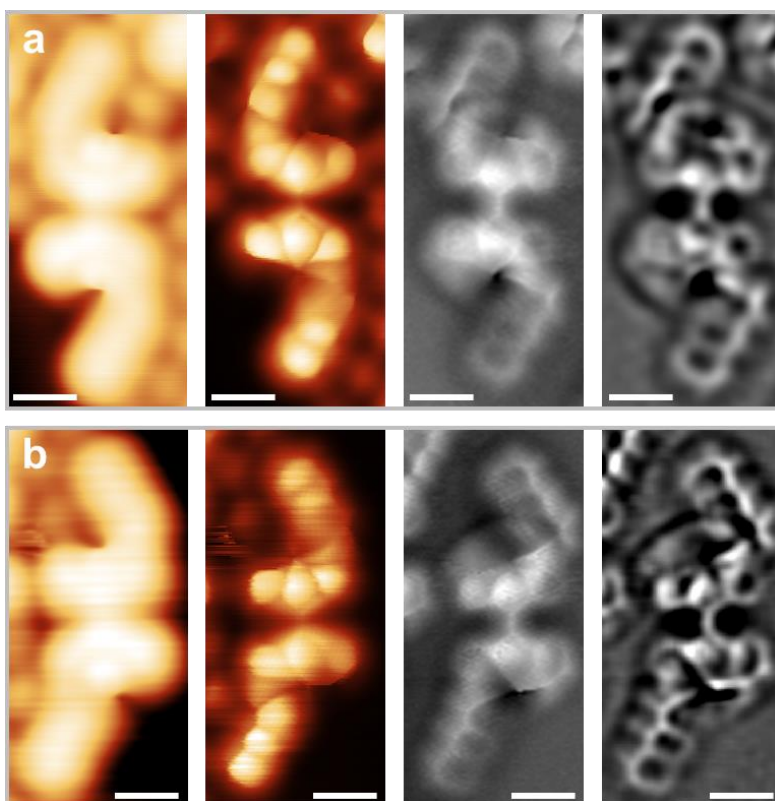


Fig. R7. a,b Zoom-in STM, BR-STM, and nc-AFM images of other nonplanar α,α -dimer and α,β -dimer species and the corresponding Laplace-filtered nc-AFM images. Scale bars for all images: 0.5 nm. Scanning parameters: **a,b** STM: $U = 0.1$ V, $I = 100$ pA. BR-STM: CO tip, constant-height, 10 mV.

7. In Fig. 4 l-n, the assignment of the structure to the experimental data is not satisfactory. I also question the need for these data in the main text. The authors can either find a structure that better reproduces the experimental nc-AFM image or move this specific dataset into the SI and leave the structure unassigned. The only conclusion that can be drawn from the nc-AFM image (Fig. 4m) is that it is a non-planar structure.

Reply: We thank the reviewer's suggestions. We performed the STM and nc-AFM imaging of nonplanar structures observed in our experiments and obtained high-quality images (Fig. R4 and R6). The corresponding discussion has been added to the first paragraph on Page 12 of the revised manuscript. The corresponding data have been added to Fig. 4 and Supplementary Fig. 14 and 15.

8. Based on the difficulty of correctly identifying the chemical structures based on nc-AFM and the mismatch between the experiments and simulations in Fig. 4, the results obtained by the authors do not fully support the statement on lines 264-265. I would recommend the authors to motivate the reaction mechanism on purely chemical grounds without referring to the identification of the intermediates by nc-AFM (which is not convincing). The DFT calculation results are already in excellent agreement with the observed reaction dynamics. The results shown in Fig. 4 can then be presented after discussing the reaction mechanism in the SI.

Reply: Following the reviewer's suggestion, we have revised Fig. 4 in the revised manuscript. In addition, the proposed reaction pathway based on the experimental results and DFT calculations has been added to Supplementary Fig. 23.

9. It is very hard to follow the reaction proposed based on Fig. 5. The authors should add a chemical schematic (showing only the relevant portion of the molecules) to the figure. It would also be beneficial if instead of showing the model of the entire molecule, only the relevant portion was zoomed in and represented. The top-view and side view can be relegated to the SI.

Reply: According to the reviewer's suggestion, we have added chemical structures in DFT-calculated reaction pathways and revised Fig. 5 in the revised manuscript.

10. Some minor comments: The use of amplified to mean magnified in the context of STM images is non-standard. References 44-48 on line 61 have brackets. The phrase "the planar monomer products are significantly less" on line 152 is incomplete.

Reply: We thank the reviewer for the careful reading. We have corrected the non-standard wording and errors in the revised manuscript.

Reviewer #2:

I co-reviewed this manuscript with one of the reviewers who provided the listed reports. This is part of the Nature Communications initiative to facilitate training in peer review and to provide appropriate recognition for Early Career Researchers who co-review manuscripts.

Reply: We appreciate the comments to help to improve our manuscript.

Reviewer #3:

In the manuscript Li et al. describe an interesting approach for the room temperature cyclodehydrogenation driven by radical formed in the resonance structures. The study fits into the quickly developing area of on-surface chemistry. However, I regret that the authors present the approach only on a single example forming a molecule, which does not seem to exhibit any interesting properties or be of broad interest in general. While the purpose of the study is to introduce a new concept for the synthesis of new compounds it seems that a sole example of only one precursor and one substrate is not sufficient to justify the idea as more general. Therefore in order to support publication in Nature Communications I suggest to demonstrate the idea on a different substrate than Au(111) or at least a different example of precursor and target compound to show

that the radical addition of open-shell resonance structures might provide a new and more versatile pathway for the synthesis of novel compounds.

Reply: We appreciate the reviewer's insightful comments and suggestions to help us improve the manuscript. Following the review's suggestion, we have performed the same experiment on the Ag(111) substrate, as shown in Fig. R8. The corresponding discussion and data have also been added to the revised manuscript and Supplementary Fig. 24.

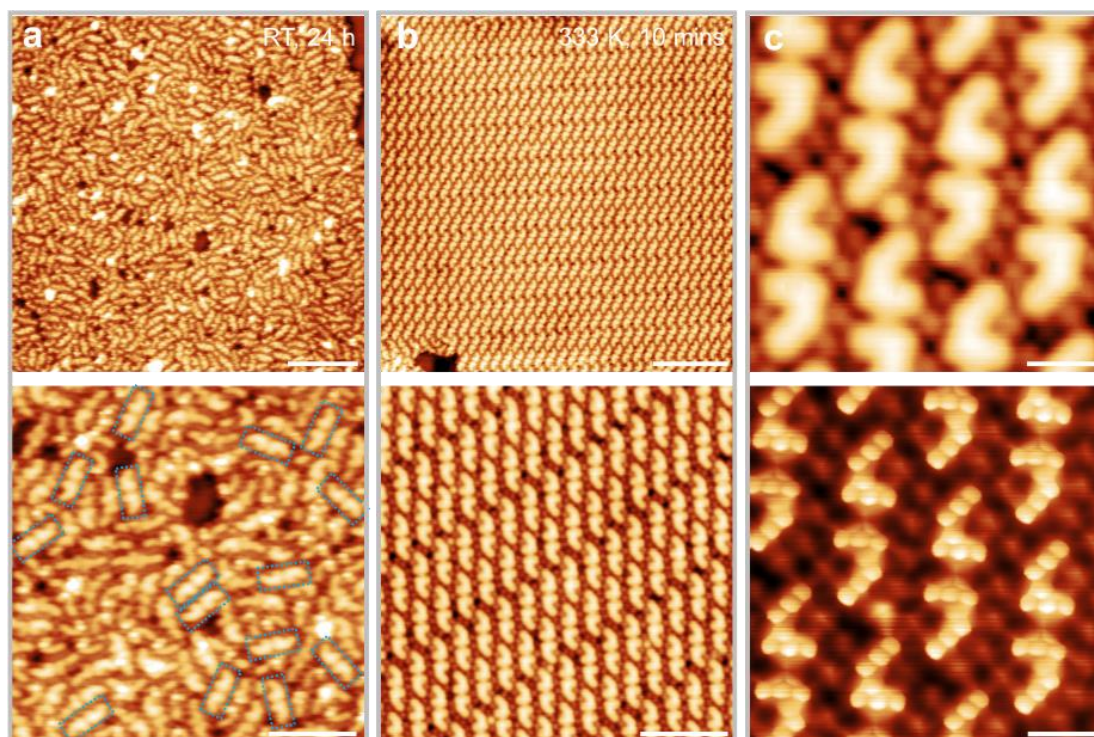


Fig. R8. **a** Large-scale (above) and high-resolution (below) STM images after annealing a Ag(111) sample with precursor **1** at room temperature for 24 h. The blue dotted frames indicate the planar dimer products. **b** Large-scale (above) and high-resolution (below) STM images after annealing a Ag(111) sample with precursor **1** at 333 K for 15 minutes. **c** Zoom-in STM (above:) and BR-STM (below) images of planar dimer products on Ag(111). Scale bars: **a,b** above: 10 nm. below: 5 nm. **c** 1 nm. Scanning parameters: **a** $U = 0.1$ V, $I = 10$ pA. **b** $U = 10$ mV, $I = 10$ pA. **c** above: $U = 10$ V, $I = 10$ pA. below: CO tip, constant height, $U = 10$ mV.

On Page 15, the second paragraph, “To further demonstrate the generality of radical addition of open-shell resonance structures in the on-surface synthesis of novel molecular structures, we performed the same experiments on the Ag(111) substrate. As shown in the supplementary Fig. 24, an irregular molecular island was formed after depositing precursor **1** on the Ag(111) surface held at room temperature for 24 h under

UHV conditions (Supplementary Fig. 24a). High-resolution STM image shows that the irregular molecular islands are mainly composed of a small amount of monomers, a large amount of non-planar and planar dimer products, and bromine atoms, indicating that at room temperature some molecules on Ag(111) undergo a debromination C-C coupling and cyclodehydrogenation cascade reaction similar to that on Au(111). It is noteworthy that the slight difference in the reactivity of the two substrates at room temperature may be due to the different interactions between the reaction intermediates and the metal substrate. When the same sample was further annealed at 333 K for 15 minutes, large-scale regular phases were formed and composed of planar dimers and Br atoms (Supplementary Fig. 24b). High-resolution STM and BR-STM images further confirmed the chemical structure of planar dimer products (Supplementary Fig. 24c). These results demonstrate that the radical addition of the open-shell resonance structures in molecules on Ag(111) is also effective in lowering the reaction temperature of intramolecular cyclodehydrogenation.” has been added.

Additionally below I attach more detailed comments on the manuscript content:

- Page 5, line 100, the authors refer to [65, 66] showing debrominative C-C coupling, however the reaction was not observed there at RT, but at elevated temperature, do the authors know why here the dimerization occurs at RT?

Reply: We thank the reviewer’s comments. Generally, the debromination C-C coupling reaction on the Au(111) surface includes two steps: debromination and C-C coupling, in which debromination is the rate-determining step. Therefore, the debromination reaction is accompanied by C-C coupling. According to the previous reports (*Angew. Chem. Int. Ed.* **2019**, *58*, 6559); *Nat. Nanotechnol.* **2020**, *15*, 437), the debromination of *gem*-dibromide on the Au(111) surface usually occurs at 400-500 K. In our case, the debromination of molecule 1 on Au(111) occurs at a lower temperature, which can be assigned to the transformation from low active dibromomethylene (sp^2 C–Br activation) of closed-shell resonance structures to highly active dibromomethyl radical (similar to sp^3 C–Br activation) of open-shell resonance structures (*Angew. Chem. Int. Ed.* **2022**, *61*, e202204123; *Angew. Chem. Int. Ed.* **2018**, *57*, 4035; *ACS Nano* **2024**, *18*, 14640;

ACS Nano 2018, 12, 7959). The driving force of transformation is the release of molecular strain via aromatization and planarization.

- Page 5, line 115, the correct version shall rather be: *The amplified STM images show that one dimer has a mirror-symmetric structure (Fig. 2d, left) and the other dimer has a centrosymmetric structure (Fig. 2e, left).*

Reply: We thank the reviewer's careful reading. We have revised the corresponding statement in the revised manuscript.

- *The nc-AFM images are either of low quality or not correctly processed (e.g. Figure 2) therefore the presence of the ring containing oxygen is either barely visible or even impossible to recognize, I suggest improving clarity of the nc-AFM images*

Reply: We thank the reviewer's comment and insightful suggestions. To more clearly confirm the chemical structures of the cyclodehydrogenation products, we further performed the nc-AFM imaging and obtained high-quality nc-AFM images that can resolve the C-O bonds (a slightly dark contrast in Fig. R2 and R3) and CH₃ (a bright 3D feature in Fig. R2c, d and R3b, c). The corresponding experimental and simulated nc-AFM images have also been added to Fig. 2, 4 and Supplementary Fig. 3, 5, 14-17.

- *Figure 2f,g – how do the authors recognize CH₃ moieties in the structures? In nc-AFM images the lobe ascribed to the CH₃ moiety is very “weak”, in other studies (also cited here refs 67-68) the CH₃ groups exhibiting a 3D structure are usually more pronounced. The STM image also does not show any prominent feature. I am not convinced that the assignment is correct.*

Reply: We thank the reviewer's comment. To more clearly confirm the chemical structure of the planar monomer products, we further performed the nc-AFM imaging and obtained high-quality nc-AFM images that can resolve the CH₃ (a bright 3D feature in Fig. R2c, d and R3b, c). The corresponding experimental and simulated images have also been added to Fig. 2 and Supplementary Fig. 3 and 5.

- *The assignment of the observed in STM features to dimers of AAQ molecules (SI, Fig. 4) is hypothetical, why the anthracene cores appear much brighter? Due to the steric interactions, the two parts of the AAQ molecule could not be flat.*

Reply: Thanks for the questions. In the STM image of the dimer of AAQ molecules, the brighter anthracene cores might be assigned to the nonplanar structures caused by the steric interactions between the C-H bonds of anthracene and the C=O bond of anthraquinone. In addition, we performed the STM simulation based on DFT-optimized structure models. The results show that the experimental STM image agrees well with the simulated image, demonstrating a suitable assignment. The corresponding data have been added to the Supplementary Fig. 8d.

- *Figure 3, the acquired spatial dI/dV images (Fig. 3b left panels) do not correspond to the simulated ones (Figure 3b right panels), in fact if one compares the data presented for other orbitals in SI (Figure 5) it seems that the experimental data might be much better represented by the mixture of orbitals (e.g. HOMO & HOMO-1, LUMO & LUMO+1). This might be the effect of the interaction with the substrate. I guess that the comparison of the calculated and experimental spectroscopy data is presented to ensure formation of the claimed species, but I think that in the present form (gas phase simulations not matching the experiment) this is not helpful at all.*

Reply: We thank the reviewer's comments and insightful suggestions. We agree that the slight difference between experimental dI/dV maps and DFT simulations in the gas phase is derived from the coupling effect of the Au(111) substrate. For the experimental dI/dV maps at negative voltages in Fig. 3, the local density of states maps of HOMO can well resemble the observed features. For the experimental dI/dV maps at positive voltages in Fig. 3, the local density of states maps of LUMO do not match the observed features well, but the local density of states maps of mixed LUMO containing LUMO and LUMO+1 can match well the observed feature. Therefore, we accepted the reviewer's insightful suggestion.

In the revised manuscript, the local density of states maps of LUMO in Fig. 3 has been changed using the local density of states maps of mixed LUMO containing LUMO

and LUMO+1. The corresponding discussion has also been added to the first paragraph on Page 9.

- *The STS single point spectra in Fig. 3 are very smooth, are they averaged?*

Reply: Thanks for the question. The STS single point spectra in Fig. 3 were obtained by averaging the results of 30 cycles.

- *Page 9, line 196, the authors say “For a submonolayer of precursor 1 deposited on a cold Au(111) surface...” – what does “cold” exactly mean?*

Reply: Thanks for the question. In this sentence “For a submonolayer of precursor 1 deposited on a cold Au(111) surface...”, the “cold” means low temperature (less than 200 K).

To facilitate the understanding of cryogenic sample preparation, we have added a more careful description of the in-vacuum synthetic protocols in the Methods section of the revised manuscript.

- *SI, Figure 6, the assignment of the individual molecules to form self-assemblies is unclear, the additional schemes would be beneficial, additionally all images are presented with different scale-size, which also does not help to recognize the presence of individual species in the assemblies*

Reply: We appreciate the comments. For the self-assemblies formed after depositing molecule 1 on a cold Au(111) surface, we cannot precisely determine the intermolecular interaction of individual molecules by STM imaging due to the intrinsic nonplanar feature. By comparing the constant-current and -height STM images as well as DFT simulations, the adsorption geometries of individual molecules can be well identified.

To better recognize the individual species in the observed self-assemblies, we accepted the review’s advice. All STM images in Supplementary Fig. 10 have been changed to the same scale size and the individual species are also fitted accordingly.

- SI, Figure 8, the simulated images differ quite significantly from the experimental ones, therefore I find the assignment hypothetical, are the authors sure that the experimental images show debrominated species?

Reply: Thanks for the question. To clarify the chemical structure of nonplanar dibrominated species, we further performed the STM imaging and simulations by screening the adsorption configurations based on DFT-optimized structure models. The high-quality STM image of surface-bound carbene intermediate was obtained, which agrees well with the corresponding STM simulation, demonstrating the formation of debrominated species via step-wise debromination. In the revised manuscript, the corresponding STM image and simulation in Fig. 4 and Supplementary Fig. 12 have been changed.

- Figure 4, I am not convinced by the assignment (especially) in Figure 4e,f,g and 4l,m,n, comparison of 4e,f shows significant deviation, whereas in 4m the AFM images is almost featureless and does not correspond to the simulations shown in panel 4n; additionally it seems that the caption of panel o is missing

Reply: We thank the comment. We performed the STM and nc-AFM imaging of nonplanar structures observed in our experiments and obtained high-quality images (Fig. R4 and R6). The corresponding discussion has been added to the first paragraph on Page 12 of the revised manuscript. The corresponding data have been added to Fig. 4 and Supplementary Fig. 14 and 16.

- Apart from SI Figure S9 the authors do not see and comments on Br atoms, it is known that Br atoms on Au disturb the herringbone pattern, this is not observed here, are the authors sure that the Br atoms are detached from the precursors at RT? Where are these Br atoms on the surface?

Reply: We appreciate the insightful comment and question. To confirm the Br atoms on Au(111) surfaces, we performed large-scale STM imaging of Au(111) samples containing different coverage of molecule 1. In the Au(111) sample with low coverage of molecule 1, only a few Br atoms can be observed between the two dimer products

(Fig. R9). In the Au(111) sample with high coverage of molecule 1, Br atoms can assemble with planar dimer products to form molecule islands, as shown in Supplementary Fig. 13. In general, at suitable annealing temperatures, especially higher temperatures, a large number of free bromine atoms can easily disturb the herringbone pattern of Au(111) surface (*Nano Lett.* **2023**, *23*, 148). In our case, we did not observe the herringbone pattern disturbed by the bromine atoms on the Au(111) surface, which can be attributed to the low reaction temperature and only a small number of free bromine atoms, excluding bromine atoms assembled with molecules.

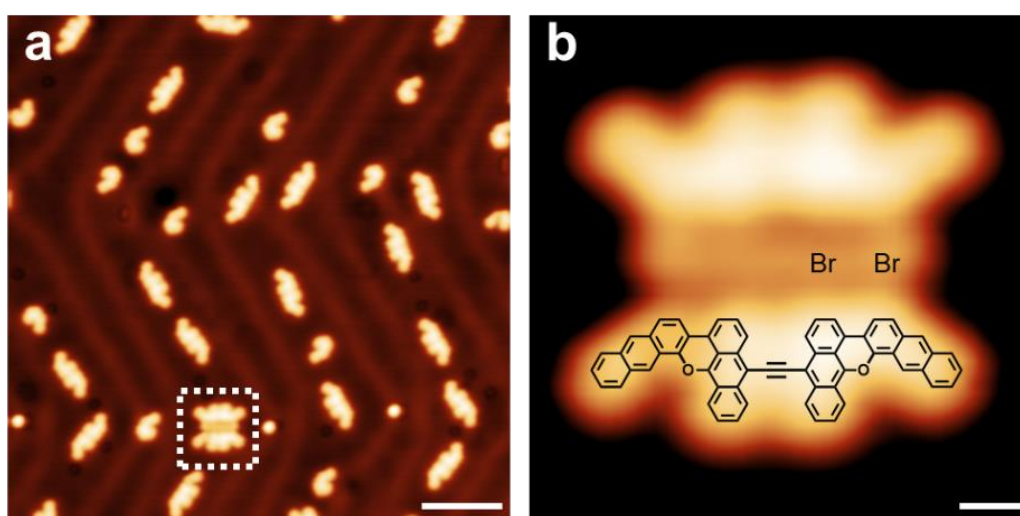


Fig. R9. **a** High-resolution STM image after annealing at room temperature for 12 h. **b** Zoom-in STM image of the assembly of two planar *cis-α,α*-dimers and bromide atoms (white dotted frame). Scale bars: **a** 5 nm. **b** 0.5 nm. Scanning parameters: **a,b** $U = 0.2$ V, $I = 10$ pA.

To sum up, I could not recommend publication of the manuscript in Nature Communications in its present form. However, after appropriate revision and extension the manuscript may become publishable in Nature Communications.

Reply: We appreciate the reviewer's comments and insightful suggestions to help us improve the manuscript. We have revised the manuscript according to your nice suggestions and hope you enjoy reading it, in which we aim to convey these main messages more clearly.

Reviewer #4:

In this paper, Li and coworkers reported a room-temperature cyclization reaction on Au(111) for the formation of oxygen-carbon bonds using the precursor 10-(dibromomethylene)-[1,2'-bianthracen]-9(10H)-one. They demonstrated that the radical addition decreases the cyclodehydrogenation temperature and further improves the chemoselectivity of dehydrogenation. Bond-resolved STM/AFM studies visualized the reaction process, including stepwise debromination to form surface-bound carbenes, C–C coupling of carbenes, and intramolecular radical addition/hydrogen elimination to attain planarization. Moreover, the authors revealed the reaction mechanism with complementary DFT calculations, high chemoselectivity of the cyclodehydrogenation results from the reversibility and different thermodynamics of the radical addition step. Overall, this paper is well-structured and holds potential for publication in Nat. Commun., pending the authors' attention to the raised concerns.

Reply: We are grateful to the reviewer for the encouraging comments, suggestions, and appreciation of our work. We have revised our manuscript accordingly. Please see the following point-by-point responses.

1. The authors claimed the resonance between the cumulene and acetylene, did they observe the cumulene structure? And how do they quantify this resonance process? such as the energy difference between the two structures.

Reply: We thank the reviewer's comments and insightful suggestions. In our experiment, we observed a few nonplanar debromination C-C coupling intermediates during the stepwise annealing (Fig. R5 and R7). However, we did not determine the cumulene or acetylene structures due to the intrinsic nonplanar feature. In addition, we performed the DFT calculations for the nonplanar debromination C-C coupling intermediate adsorbed on the Au(111) surface. The results show that the energy difference between the closed-shell and open-shell resonance structures is only 2.6 meV at $T = 0$ (Fig. R1, right), suggesting a closed-shell ground state. Therefore, the resonance between the cumulene and acetylene at room temperature is transient and difficult to observe.

2. *Building upon the resonance claim, the authors proposed a reaction process involving the radical shift from C to O atom, but this radical shift process lacks clarity and warrants further explanation. DFT calculations could offer valuable insights into this mechanism.*

Reply: Thanks for the suggestion. We performed the DFT calculations for closed-shell and open-shell nonplanar debromination C-C coupling intermediate adsorbed on the Au(111) surface. The results found that the energy of nonplanar debromination C-C coupling intermediate in the closed-shell resonance structure is slightly lower than that in the open-shell resonance structure by 2.6 meV (Fig. R1, right), demonstrating that the ground state of nonplanar debromination C-C coupling intermediate is closed-shell at $T = 0$. In addition, according to the theory of resonance, the accurate structure of a molecule is essentially an average of several hypothetical resonance hybrid structures. Compared with zero degrees in the calculations, room temperature may increase the proportion of open-shell resonance hybrid structures of molecule 1, promoting the radical addition reaction. Therefore, at room temperature, the formation of the open-shell resonance structure is transient, and the corresponding radical shift from C to O atom is also transient.

3. *In Figure 4, the authors observed the intermediates featuring radicals within their structure, have they confirmed the presence of the radical feature via STS? In addition, have they also observed any intermediates proposed in Figure 4a during the formation of dimers?*

Reply: We appreciate the comments. We tried to perform the STS for observed nonplanar reaction intermediates, but we did not observe the radical feature because the closed-shell structure under 5 K is major and the formation of the open-shell structure is transient during the room-temperature cyclodehydrogenation. In addition, a variety of nonplanar dimer intermediates have also been observed during the formation of planar dimers, as shown in Fig. R5 and R7. The corresponding discussion and data have also been added to the revised manuscript and Supplementary Fig. 14 and 16.

4. Concerning the formation of dimers on the Au surface, what is the yield or ratio of α,α -dimer, β,β -dimer and α,β -dimer?

Reply: Thanks for the question. We performed a more detailed statistical analysis by counting the number of dimers with different geometries on the Au(111) surface. The corresponding results have also been added to the revised manuscript.

On Page 7, the first paragraph, “.....(more than 61% α,α -dimers and less than 1% α,β - and β,β -dimers).....” has been added.

5. Given that the manuscript presents only one example precursor, it would be beneficial for the authors to comment on the generality of this cyclization reaction. Additionally, they should discuss the potential for further development of this reaction for other intriguing carbon nanostructures, which would enhance the significance and impact of their findings.

Reply: We thank the reviewer’s comment and suggestion. In this work, the radical addition can lower the cyclodehydrogenation temperature on Au(111), which may be a general method for achieving other on-surface reactions induced by highly active radical species at lower temperatures. Furthermore, the radical addition provides the potential for further development of cyclodehydrogenation reactions on inert insulating surfaces, which will facilitate the on-surface synthesis and exploration of intrinsic electronic properties of other interesting carbon nanostructures.

In the Discussion section of the revised manuscript, “Furthermore, the radical addition of open-shell resonance structures may be applied in developing insulating surface covalent coupling reactions, thereby enabling the direct synthesis and intrinsic properties exploration of novel molecules on insulating surfaces.” has been added.

6. The caption of Figure 4o is missing, and it appears to duplicate a figure already present in Figure 1c.

Reply: We thank the reviewer's careful reading and reminder. Following the review's suggestion, we have removed Fig. 4o to Supplementary Fig. 23 of the revised manuscript.

Response to reviews' comments

Reviewer #1:

Deng-Yuan Li, Pei-Nian Liu, and their colleagues have done an admirable job in addressing all the reviewers' concerns. The new data obtained is of exceptional quality and satisfactorily addresses the issue of non-planar intermediates from an experimental standpoint. I am convinced this is an important and interesting contribution to the field of on-surface science. While I recognize the need for the prompt publication of this work, the authors have not satisfactorily addressed Reviewer 1 point 2 and Reviewer 4 point 2, regarding the presence of the radical on the oxygen atom.

A crucial part of the story-line is the resonance between the closed-shell and open-shell molecules, supported by the small energy difference between these two configurations (~3 meV). However, the authors must also show the delocalized pi radical has significant probability density over the oxygen atom. This is a straightforward calculation, and I am certain the authors already possess this data. Demonstrating the presence of the radical on the oxygen atom would provide visually compelling evidence supporting the proposed mechanism. Conversely, if the radical is not present on the oxygen atom, this would also be highly interesting. The reaction works, and the DFT calculations of the mechanism are in excellent agreement. The mechanism relies on the presence of an unpaired electron on the oxygen atom which makes perfect chemical sense. However, if the radical is not on the oxygen atom, it would imply that we as a community have not understood something foundational. Therefore, no matter what the SOMO orbital map of the open-shell structure shows, it would add to the story.

The work done by the authors in this revision is commendable. I hope they can quickly address the point raised above.

Reply: We thank the reviewer's insightful comments and suggestions to help us improve the manuscript. Following the review's suggestion, we performed DFT calculations for molecule 1 and debrominative C-C coupling intermediate in the open-

shell resonance structures and obtained the spin density distributions. The results show that molecule 1 and debrominative C-C coupling intermediate in the open-shell resonance structures both exhibit a certain spin density distribution on the oxygen atom, demonstrating the presence of the radical on the oxygen atom. In the revised manuscript, the corresponding spin density distributions of molecule 1 and debrominative C-C coupling intermediate in the open-shell resonance structures have been added to Supplementary Fig 1.

Reviewer #2:

I co-reviewed this manuscript with one of the reviewers who provided the listed reports. This is part of the Nature Communications initiative to facilitate training in peer review and to provide appropriate recognition for Early Career Researchers who co-review manuscripts.

Reply: We thank the reviewer for the comments of our work.

Reviewer #3:

I appreciate the effort undertaken by the authors to answer all raised concerns.

I find the replies satisfactory and I also appreciate the additional experiments, especially with a different substrate.

Although the rings with O atoms are in experimental images significantly less visible than in the simulations, I find the overall discussion convincing and therefore I recommend the manuscript for publication in Nature Communications.

Reply: We thank the reviewer for the encouraging comments and appreciation of our work.

Reviewer #4:

The revised manuscript has addressed my previous comments and suggestions. I have no further major objections.

Reply: We thank the reviewer for the appreciation of our work.