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▶ To cite this version:

Antje Kutz, Md Taibur Rahman, Ville Haapasilta, Chiara Venturini, Ralf Bechstein, et al.. Impact of the reaction pathway on the final product in on-surface synthesis. Physical Chemistry Chemical Physics, 2020, 22 (11), pp.6109-6114. 10.1039/C9CP06044H . hal-02932080

HAL Id: hal-02932080

https://hal.science/hal-02932080

Submitted on 9 Sep 2020

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Impact of the reaction pathway on the final product in on-surface synthesis

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ABSTRACT

On-surface synthesis provides a very promising strategy for creating stable functional structures on surfaces. In the past, classical reactions known from solution synthesis have been successfully transferred onto a surface. Due to the presence of the surface, on-surface synthesis provides the potential of directing the reaction pathway in a manner that might not be accessible in classical solution synthesis. In this work, we present evidence for an acetylene polymerization from a terminal alkyne monomer deposited onto calcite (10.4). Strikingly, although the dimer forms on the surface as well, we find no indication for diacetylene polymerization. This is in sharp contrast to what is observed when directly depositing the dimers on the surface. The different pathways are linked to the specific arrangement of the dimers on the surface. When forming stripes along the [-4-21] direction, the diacetylene polymerization is prohibited, while when arranged in stripes aligned along the [010] direction, the dimers can undergo diacetylene polymerization. Our work thus constitutes a demonstration for controlling the specific reaction pathway in on-surface synthesis by the presence of the surface.

1. Introduction

On-surface synthesis has emerged as a promising approach for the fabrication of functional molecular structures on surfaces.¹⁻⁴ Performed in ultrahigh vacuum (UHV), on-surface synthesis provides the option to create products that might not be accessible in classical solution synthesis due to, e.g., the poor solubility⁵ or high reactivity of the product.⁴ An impressive example for the latter is the synthesis of long acenes,⁶ which are instable under ambient conditions. While nonacene is the largest acene that has been synthesized so far,⁷ the synthesis of decacene has been shown by on-surface reduction on a Au(111) surface.⁸ In another work, triangulene has been synthesized,⁹ a molecule which was predicted in 1953,¹⁰ but never isolated in its unsubstituted form due to its reactivity.

On-surface polymerization¹¹ of conductive chains is of particular interest for molecular electronics applications as it offers the possibility to create electrical contacts for linking mesoscopic objects with nanoscopic functional units. ¹²⁻¹⁷ In this context, an elegant example has been presented already in 2001, where the tip of a scanning tunneling microscope has been used to initiate a diacetylene polymerization on a graphite surface. ^{18, 19} However, molecular electronics applications require electrically insulating substrates to decouple the electronic structure of the molecules from the underlying support surface. Recently, we have shown that a diacetylene polymerization can also be induced on the (10.4) surface of calcite, which is a bulk insulator. ²⁰ In the latter study, the dimer formed by homo-coupling of a terminal alkyne has been used as a precursor. Upon deposition onto the surface, the precursors adopt a specific adsorption geometry with a spatially well-defined arrangement. Such geometrical constraints provide the key when aiming for controlling the reaction by surface templating. ²¹ Given that a specific relative orientation and distance is required for initiating the reaction, ^{22, 23} the arrangement of the

precursors on the surface offers a handle for controlling the reaction pathway. Ideally, different reaction pathways should be selectable depending on the specific adsorption configuration. So far, a clear demonstration for reaction selectivity based on surface templating is, however, lacking.

In the present work, we use a terminal alkyne precursor, namely 3-ethynylbenzoic acid (3-EBA, see Fig. 1a), for on-surface synthesis on calcite (10.4) (Fig. 1b). Terminal alkynes are known to undergo Glaser coupling, ²⁴ and the corresponding reaction has been proven to be possible also on metal surfaces. ²⁵⁻²⁹ We have recently presented the proof of principle that this reaction can also be performed on calcite (10.4).³⁰ Besides homo-coupling, the precursor used here also has the potential to undergo an acetylene polymerization. ^{15, 31-37} On-surface acetylene polymerization has been shown on Au(111),³⁷ however, not on a bulk insulator as yet. Here, we provide experimental evidence for on-surface acetylene polymerization using 3-EBA as a precursor. Upon annealing to 550 K, we obtain acetylene polymer chains with lengths of up to 80 nm as deduced from our dynamic atomic force microscopy (AFM) images. Interestingly, although the dimer forms as well, we find no evidence for diacetylene polymerization. This is surprising as diacetylene polymerization is induced when annealing the directly deposited dimer on the surface. The specificity of this reaction pathway can be understood by the different arrangement of the dimers in the two cases: when formed in an on-surface reaction, the dimers form stripes along the [-4-21] direction. When directly deposited, the dimers form stripes along the [010] direction. In these different arrangements, the alignment of the dimers with respect to each other is different, explaining why diacetylene polymerization is possible in one but not the other arrangement.

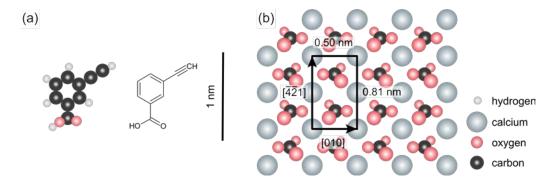


Figure 1. Model of (a) the 3-ethynylbenzoic acid (3-EBA) molecule and (b) the calcite (10.4) surface. The scale bar applies to both models. The calcite (10.4) surface has a rectangular unit cell with dimensions of (0.50×0.81) nm², consisting of two carbonate ions and two calcium ions.

2. Methods

Experimental Part

The calcite crystals used in these experiments were purchased from Korth Kristalle GmbH (Altenholz, Germany). The samples were degassed *in situ* at 700 K for 2 hours prior to cleavage to remove air-borne contaminations. Afterwards, the cleaved crystals were annealed at 650 K for 1 hour to reduce surface charges.

The 3-EBA molecules were purchased from Sigma Aldrich (Germany) or synthesized by us following established procedures³⁸⁻⁴³ Further information on the molecule synthesis can be found in the ESI. The 3-EBA molecules were sublimated *in situ* from a home-built Knudsen cell. For sublimation, the maximum temperature of the cell was about 310 K. During deposition, the chamber pressure remained below $2 \cdot 10^{-10}$ mbar. The molecules were deposited onto a sample kept at room temperature.

All experiments were carried out with a VT AFM 25 atomic force microscope (ScientaOmicron, Taunusstein, Germany) under UHV conditions (base pressure typically better than 4·10⁻¹¹ mbar).

All AFM images presented in this work were captured at room temperature. Therefore, all annealed samples were cooled down to room temperature prior to imaging. The system is equipped with an external lock-in amplifier HF2LI (Zurich Instruments AG, Switzerland) to control the phase shift, amplitude and excitation of the oscillation. We used n-doped silicon cantilevers purchased from NanoWorld (Neuchâtel, Switzerland) with an eigen frequency of around 300 kHz (type PPPNCH). Prior to the measurements, all cantilevers were treated by sputtering with Ar⁺ at 2 keV for 10 minutes to remove possible oxide layers as well as other contaminations.

All images shown here are either topography (z_p) or excitation frequency (v_{exc}) images. The fast and slow scan directions are indicated in the upper right corner in each image. The images are displayed such that under normal imaging conditions (*i.e.*, without contrast inversion⁴⁴) bright colors corresponds to high attractive interactions while dark colors correspond to less attractive or repulsive interactions.

Simulations

All the density functional theory (DFT) computations were performed using the CP2k program suite. ⁴² We used the PBE functional ⁴³ augmented with the D3 dispersion correction scheme ⁴⁴ in all computations, both in the structural optimization calculations (T = 0 K) and in the first-principles molecular dynamics (FPMD) simulations. The electronic structure was solved using the Gaussian Plane Wave Method. ⁴⁵ The valence electrons were expanded in terms of molecularly optimized double-zeta basis functions, ⁴⁷ whereas the core electronic states were approximated with GTH pseudopotentials. ⁴⁶ The electronic density was modelled using a plane wave basis with an energy cutoff of 500 Ry. The FPMD simulations were used to explore suitable bonding patterns and to test the stability of the found structures after optimization calculations. The FPMD

simulations were run for few thousand steps with a 0.5 fs timestep using velocity rescaling thermostat⁴⁵ set to a target temperature of 560 K.

3. Results and Discussion

At first, we investigated the adsorption of 3-ethynylbenzoic acid (3-EBA) on calcite (10.4). More specifically, we performed density-functional theory (DFT) calculations to study the binding geometry of 3-EBA on calcite (10.4). A top and side view of the adsorption geometry is given in Figs. 2a and b, showing a flat-lying molecule. The main axis of the molecule is oriented along the [-4-21] direction with the ring being positioned on a calcium row. The carboxylic acid group binds to the surface via a characteristic binding motif:⁴⁶ the negatively charged carbonyl oxygen is on top of the positively charged surface calcium, while the hydrogen points to the protruding oxygen atom of the surface carbonate group. The adsorbed molecule exhibits a formation energy of -1.5 eV (with a negative energy being favorable to formation), indicating that the molecule should stick on the surface at room temperature. While this is the most stable configuration we found, there are several other possibilities involving the rotation of the molecule's OH-group within 0.4 eV of the ground state. This flexibility likely explains the high mobility of the monomers on the surface despite the strong adsorption, as at room temperature the molecule will rapidly sample through all these configurations offering paths to translational motion.

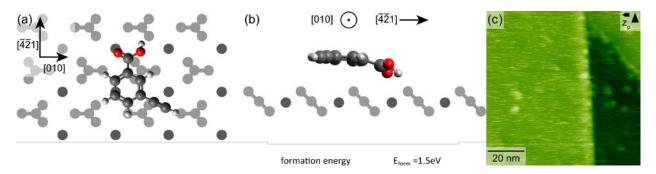


Figure 2. Optimized geometry of an isolated 3-EBA molecule on the calcite (10.4) surface in (a) top view and (b) side view. (c) AFM topography image of an as-deposited calcite (10.4) sample. Two step edges are seen in the image. The terraces are covered by streaky features, indicating mobile species on the surface at room temperature.

To get experimental insights, we sublimated 3-EBA molecules at 310 K for 5 min in front of a freshly cleaved calcite (10.4) surface held at room temperature under UHV conditions and investigated the surface by dynamic AFM at room temperature. In Fig. 2c, a representative AFM image is shown. Two terraces are seen in the image, separated by a step edge. The terraces are decorated by streaky features, which we assign to mobile molecules. No ordered structures are observed at room temperature. From these images, we conclude that the molecules are adsorbed on the calcite (10.4) surface at room temperature, confirming the DFT results presented above. The image indicates that the molecules are highly mobile at room temperature, forming a two-dimensional gas of moving molecules. These are promising conditions for an on-surface reaction.

Next, we present the results of a heating series performed with the sample discussed previously. After heating the molecule-covered sample at 400 K for 1 hour, dot-like bright structures emerged (see Fig. 3a). The streaky features observed on the as-deposited sample were still present, indicative of mobile molecules. When increasing the heating temperature to 450 K for 1 hour, the streaky features nearly vanished. Most importantly, stripe-like structures were formed along the [-4-21] direction (see Fig 3b). Upon heating at 550 K for 1 hour, these stripe-liked structures appeared longer in length (more than 20 nm in Fig. 3c). We could increase the

stripe length up to 80 nm upon dosing more monomers and annealing for longer times (see ESI Fig. S1). The streaky features have completely vanished and only few dot-like clusters remained after heating at 550 K.

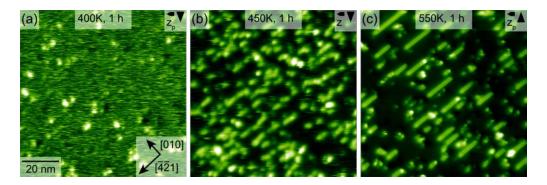


Figure 3. Examples from a heating series of a molecule-covered sample. Each annealing step lasted for 1 hour. (a) Heating to 400 K led to the formation of some bright dots, while (b) heating to 450 K resulted in a reduction of the streaky features and the appearance of stripe-like structures, oriented in the [-4-21] direction. Further heating to (c) 550 K yielded in longer stripes and the disappearance of the streaky features.

To investigate the inner structure of the emerging stripes, we performed high-resolution imaging of a stripe-covered area. As can be seen in Fig. 4a, two different stripe-like structures exist, which are both aligned along the [-4-21] direction. As will be argued in the following, these two structures are assigned to (1) polyacetylene chains and (2) side-by-side aligned dimers.

The majority of the stripes (marked by the red box in Fig. 4) show a periodicity of 0.4 nm along the [-4-21] direction, corresponding to the calcium-calcium distance in this direction (see Fig. 4b-c). Terminal alkynes are known to react *via* an acetylene polymerization.³¹ To investigate whether the stripes formed here indeed constitute acetylene polymers, we again performed DFT calculations. We compared the formation energy of the polymer on the surface with the equivalent number of monomers, *i.e.*, isolated 3-EBA molecules, maintaining compatible atom numbers in both energy evaluations. We found that the acetylene polymer chain has a formation energy, which

is 1.1 eV per molecule lower than the energy of isolated 3-EBA molecules on calcite (10.4). This calculation suggests that an acetylene polymer on the surface should be more favorable than the unreacted monomers. Moreover, the calculated *cis-transoidal* polymer structure fits excellently to the observed stripe structure, as demonstrated in Fig. 4d. With these results, we conclude that an acetylene polymerization can be achieved *via* the deposition of the monomer precursor, 3-EBA, onto calcite (10.4).⁴⁷

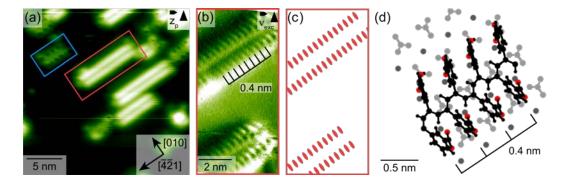


Figure 4. Molecular structure obtained upon heating the sample for 1 h to 550 K. (a) Two different kind of stripes can be seen along the [-4-21] direction, marked by red and blue boxes, respectively. (b) The stripe marked by the red box in (a) is shown in a frequency shift image, revealing the periodicity of 0.4 nm. (c) Sketch illustrating the inner structure of the stripes. (d) Acetylene polymer structure as obtained from DFT, including the calcite (10.4) surface to illustrate the excellent match in size and pattern.

In principle, the 3-EBA monomer used here also has the possibility to undergo dimerization.²⁵ When depositing this dimer directly onto calcite (10.4), we have previously shown that it undergoes diacetylene polymerization.²⁰ This leads to the interesting question as to why there is no indication of diacetylene polymerization upon deposition of the 3-EBA monomer. Does no dimer form? For this, we return to the second structure formed, which is marked by the blue box in Fig. 4a.

In these stripes, dark dots at the periphery of the stripes are observed, which exhibit a periodicity of 0.8 nm along the [-4-21] direction, which corresponds to the unit cell dimension in this direction

(see Fig. 5(a-b)). To obtain further insights into this structure, we compare these stripes with the previously reported arrangement of the dimer molecules when directly deposited onto calcite (10.4).²⁰ When directly deposited onto calcite (10.4), the dimers form islands composed of rows running along the [010] direction. However, a second island structure is found that was reported in our previous work,²⁰ composed of rows oriented along the [-4-21] direction (see Fig. 5c). These rows exhibit a periodicity of 0.8 nm along the row direction and do, indeed, resemble the second stripes observed here. When an image of the second stripe structure is superimposed onto the island, the excellent fit in dimensions becomes evident (see Fig. 5d), indicating that the second stripe structure found here is composed of side-by-side arranged dimers resulting in rows oriented in the [-4-21] direction.

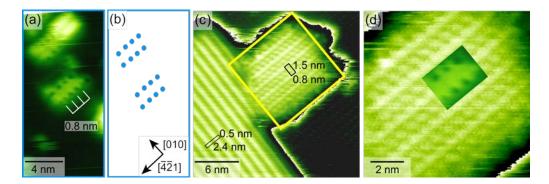


Figure 5. (a) Zoom-in AFM image of second structure formed upon heating the 3-EBA monomer deposited on calcite (10.4) surface, exhibiting the periodicity of 0.8 nm. (b) Sketch illustrating the inner structure of the stripes. (c) Structure observed after direct deposition of the dimer. The yellow box highlights an island composed of stripes oriented along the [-4-21] direction. (d) An area from (a) is superimposed onto the island shown in image (c).

In summary, the two different reaction products observed here are assigned to (1) polyacetylene chains and (2) side-by-side aligned dimers. The latter finding is surprising because it shows that the monomer indeed undergoes homo-coupling and forms dimers, however, no further reaction

towards diacetylene polymers is observed (see Fig. 6). This result demonstrates that a different pathway is taken when the monomer is deposited and only forms dimers on the surface as compared to depositing the dimer directly. In both cases, dimers are present on the surface and arrange side-by-side to form stripes, however, when depositing the dimers directly, the stripes are predominantly aligned along the [010] direction with a periodicity of 0.5 nm along the stripe. ²⁰ In this arrangement, the dimer spacing is in the reported range required for diacetylene polymerization of 0.47 to 0.52 nm and also the angle of the molecular axis with respect to stripe matches the angle of 45°, which has been mentioned in literature. ²³ In contrast to the situation observed after depositing the dimers directly, when the dimers are only formed on the surface, the stripes are aligned along the [-4-21] direction. Here, the periodicity along the stripe is 0.8 nm, which is significantly larger than what has been reported for diacetylene polymerization. ²³ In this case, the dimers do not further react to diacetylene polymers. This comparison demonstrates that, even that the same molecule is present on the surface in both cases, the specific reaction conditions governs the reaction pathway that is taken.

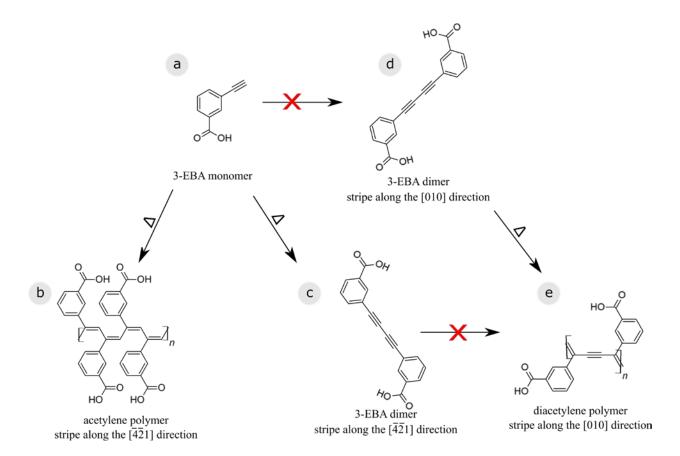


Figure 6. Overview of the reaction pathways of the 3-EBA monomer (a) on calcite (10.4). Upon annealing, acetylene polymerization can be induced (b). The monomer can also form homo-coupled dimers. These dimers align side-by-side and form rows along the [-4-21] direction (c). Interestingly, in this arrangement, the dimers do not react further. When directly depositing the dimers, rows arranged in the [010] direction form (d). Only in this arrangement, the dimers undergo diacetylene polymerization (e).

Conclusion

In conclusion, by the interplay of dynamic AFM experiments and DFT computations we present evidence for an acetylene polymerization carried out on a bulk insulator surface. The terminal alkyne precursor molecule, 3-EBA, used in this work forms a two-dimensional gas of mobile molecules on the surface when deposited at room temperature on calcite (10.4). Heating the sample

at 550 K results in the formation of stripes along the [-4-21] direction, which match excellently

match with cis-transoidal acetylene polymer chains. This assignment is further corroborated by

the DFT calculations, revealing that the acetylene polymerization is associated with an energy gain

of 1.1 eV per acetylene unit formed. Moreover, another type of stripe oriented along the [-4-21]

direction can be found that is identical to a structure formed upon direct deposition of the dimer.

Therefore, we assign these stripes to an arrangement of side-by-side aligned dimers.

Most interestingly, we find no evidence for a further reaction of the latter dimers to form a

diacetylene polymer. This is in sharp contrast to what has been found previously when directly

depositing the dimers. Thus, our result demonstrates that the constraint given by the specific

reaction pathway can effectively control the final product: When the dimer is deposited directly,

the diacetylene polymerization is induced. In sharp contrast, when the dimer is only formed in an

on-surface reaction from the monomer precursor, the diacetylene polymerization is effectively

prohibited. Our work provides a clear example of how the specific reaction pathway in on-surface

synthesis affects the final product.

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Conflicts of interest

The authors declare no conflicts of interest.

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ACKNOWLEDGMENT

We gratefully acknowledge financial support from the EU through grant PAMS (seventh framework program GA 610446). Computing resources from the Aalto Science-IT project and CSC IT Center for Science, Finland, are gratefully acknowledged. This work was furthermore supported by the Academy of Finland through its Centres of Excellence Programme 2015–2017 under project number 284621, as well as project 314877. A.S.F. was supported by the World Premier International Research Center Initiative (WPI), MEXT, Japan.

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- See the ESI for a detailed discussion of other reasonable reaction pathways, in which we provide arguments for discarding all other obvious reaction products.

Electronic Supplementary Information to

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Synthesis of methyl 3-iodobenzoate¹

To a round-bottomed flask were added 3-iodobenzoic acid (2 g, 8.06 mmol), some drops of conc. H₂SO₄ and MeOH (50 mL). The solution was heated under reflux overnight, then it was diluted with diethyl ether and washed with H₂O, a saturated solution of NaHCO₃ and brine. The organic phase was dried over MgSO₄ and evaporated under vacuum. The product **7** (1.473 g) is a white solid and was obtained with a yield of 69. 71 %.

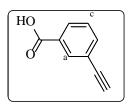
¹**H-NMR** (300 MHz, CDCl₃): δ _H 8.38 (1H, s, Ar-H_a), 8.02-7.99 (1H, m, Ar-H), 7.90-7.87 (1H, m, Ar-H), 7.19 (1H, t, J = 7.8 Hz, Ar-H_c), 3.92 (3H, s, -OCH₃).

Synthesis of methyl 3-ethynylbenzoate²⁻⁴

Methyl 3-iodobenzoate (1 g, 3.8 mmol), CuI (29 mg, $1.52*10^{-1}$ mmol), Pd(PPh₃)₂Cl₂ (53 mg, $7.55*10^{-1}$ mmol) were dissolved in degassed THF(10 mL) in a Schlenk flask. Then trimethylsilylacetylene (0.81 mL), NEt₃ (1.06 mL) were added and degassed again for some minutes. The solution was stirred at room temperature under argon atmosphere. After 3h (when the entire starting compound had reacted) were added TBAF in THF solution (7.65 mL) and some molecular sieves (3Å). The reaction was stirred under air atmosphere and at room temperature overnight. The mixture was then filtered on Celite, washing with Et₂O. The residue was then purified by column chromatography (SiO₂, EtOAc/ hex 0.5 : 9.5) to afford the product (0.392 g, 64.13 %).

¹**H NMR** (300 MHz, CDCl₃) δ_H 8.16 (1H, s, Ar- H_a), 8.03-8.00 (1H, m, Ar-H), 7.68-7.64 (1H, m, Ar-H), 7.41 (1H, t, J = 7.8 Hz, Ar- H_c), 3.92 (3H, s, -OC H_3), 3.12 (1H, s, -CH).

Synthesis of 3-ethynylbenzoic acid^{5, 6,7}



Methyl 3-ethynylbenzoate (91 mg, 5.68*10⁻¹ mmol) was dissolved in MeOH (1.5 mL) under stirring and then a solution of LiOH (16 mg, 6.68*10⁻¹ mmol) in H₂O (1.5 mL) was added to the mixture. The reaction was stirred overnight. Then the solvent was removed *in vacuum*, then HCl 3M was added drop by drop until precipitate at pH 8; then adjusted at pH 2~3 and extracted with EtOAc. The organic phase was washed with brine and dried over an. MgSO₄; removing of the solvent *in vacuum* afforded the target compound (0.045 g, 54.20 %).

¹**H-NMR** (300 MHz, CDCl₃) δ_H 8.23 (1H, s, Ar- H_a), 8.10-8.06 (1H, m, Ar-H), 7.74-7.71 (1H, m, Ar-H), 7.46 (1H, t, J = 7.8 Hz, Ar- H_c), 3.14 (1H, s, -CH).

Additional Image of Reaction Product

We have done the mentioned experiment more than 10 times and investigated a total area of more than 50,000 nm² on several calcite (10.4) surfaces. A further representative image is given below.

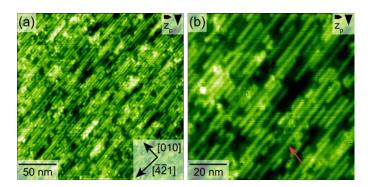


Figure S1. AFM images of stripe-like structures formed by 3-EBA on calcite (10.4) upon heating at 550 K for 10 hours (a). (b) Zoom into the image given in (a), the red arrow indicates a stripe, which has a length of approx. 80 nm.

Discussion of Reasonable other Reaction Products

To elucidate the nature of the majority stripes formed after annealing, we here discuss the possible reaction pathways the precursor 3-EBA can undergo (Fig. S2).

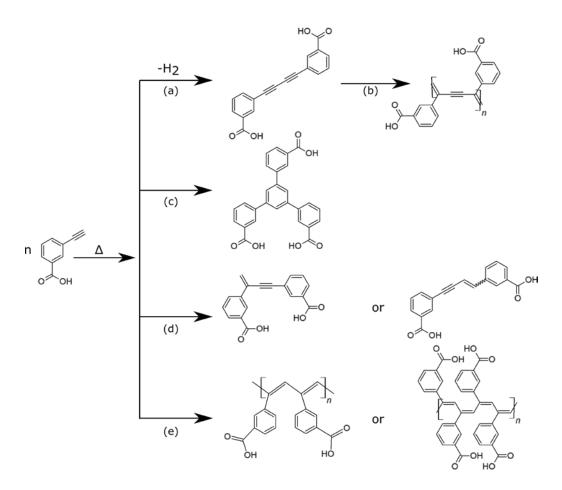


Figure S2. (a) Overview of reaction pathways based on terminal alkynes, namely (a) homocoupling of terminal alkynes with possible subsequent (b) diacetylene polymerization, (c) alkyne cyclotrimerization, (d) alkyne dimerization and (e) acetylene polymerization.

Firstly, the 3-EBA monomers can form straight dimers (Fig. S2a), which are known to subsequently undergo a diacetylene polymerization reaction (Fig. S2b). Secondly, the 3-EBA monomers can undergo a cyclo-trimerization reaction (Fig. S2c) or dimerization reactions that would result in non-straight dimers (Fig. S2d). Finally, terminal alkynes are known to react *via* an

acetylene polymerization (Fig. S2e). Next, we discuss the nature of the majority stripes observed here upon annealing of 3-EBA on the basis of these reaction pathways. As detailed in the main text, the majority stripes are oriented along the [-4-21] direction and show a periodicity of 0.4 nm along this direction.

We discard option S2a, as we can directly compare with the outcome of our previous study:⁸ Previously reported AFM images of the straight dimer molecules (3,3'-(1,3-butadiyne-1,4diyl)bisbenzoic acid, 3-BBA) directly deposited onto calcite (10.4) revealed islands composed of rows running along the [010] direction. As our stripes are aligned perpendicular to the [010] direction, we discard this structure. However, in the previous work, we have observed that 3-BBA molecules can form a second island structure that is composed of rows oriented along the [-4-21] direction (see Fig. 5c in the main text). These rows, however, exhibit a periodicity of 0.8 nm along the row direction, which does not match the 0.4 nm periodicity found here for the stripes. From these experimental evidences, we conclude that the stripes are not composed of the straight dimers (ruling out the option shown in Fig. S2a). Moreover, we performed DFT calculations to further corroborate this experimental conclusion. To this end, we investigated whether the stripes could be formed 3-BBA molecules arranged side-by-side. Our DFT calculations revealed that it is energetically unfavorable for 3-BBA to be arranged side-by-side along the [-4-21] direction with a periodicity of 0.4 nm, giving further evidence for the conclusion that the stripes are not formed by side-by-side arranged molecular dimers.

As has been shown previously, the dimers can further react via a diacetylene polymerization (Fig. S2b).⁸ The diacetylene polymer chain revealed a periodicity of 0.5 nm along the [010] direction on the calcite (10.4) surface. The comparison of the stripes observed here with this

diacetylene polymer chain discards the option of the type A stripes being formed from diacetylene polymers, as these two structures do not agree in orientation nor in periodicity.

Moreover, all non-straight and cyclic structures can be excluded, as the stripes observed here are linear. Thus, we additionally discard the options shown in Figs. S2c and S2d.

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