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2D Self-Assembly and Catalytic Homo-coupling of the Terminal Alkyne 1,4-Bis(3,5-diethynyl-phenyl)butadiyne-1,3 on Ag(111)

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The covalent linking of terminal alkynes is a promising approach for the bottom-up fabrication of novel, carbon-rich or all-carbon materials, which was recently extended towards interfacial architectures. Here we report the synthesis of a novel organic species (1,4-bis(3,5-diethynylphenyl)butadiyne-1,3) and employ it to engineer self-assembled supramolecular layers and covalent networks on the Ag(111) surface. Samples are prepared in-situ under ultra-high vacuum conditions and examined at the molecular level with scanning tunneling microscopy. After evaporating the two-fold symmetric molecule onto the substrate at temperatures below 300 K and subsequent cooling to 5 K we find highly regular supramolecular phases commensurate with the underlying silver surface and stabilized

mainly by weak, non-covalent interactions originating from the terminal ethynyl moieties. Annealing at temperatures between 350 and 500 K triggers catalytic conversions with the pertaining covalent coupling reactions resulting in small aggregates or irregular polymeric networks. Our detailed analysis of the binding motifs demonstrates that two competing reaction pathways dominate the covalent linking processes. The first is the Glaser–Hay-type homo-coupling of two alkyne terminations leading to a linear butadiyne bridge. The second is the connection of a butadiyne group to a laterally attacking terminal alkyne, converting the attacked ethyne to ethene moieties, which presents a major obstacle for the production of regular networks.

Introduction

Novel carbon-based two-dimensional materials such as graphene, graphyne or graphdiyne have attracted enormous interest in the past years due to their outstanding properties.^[11] While graphene seems to have advanced towards technological applications,^[2] the production of high-quality samples of the latter two materials and their derivatives remains largely elusive.^[3] Currently, there is an emerging research domain providing new tools which could help to overcome this problem: the formation of molecular nano-architectures using templated covalent reactions carried out under ultra-high vacuum conditions (UHV) on well-defined metal surfaces.^[4] This approach already proved to be successful for the production of novel or-

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ganic species and various one-dimensional structures with atomic precision,^[5] and of two-dimensional networks.^[6] Moreover, under the on-surface conditions, different reaction pathways and even novel reactions become possible as a result of the influence of a catalytic support.^[7]

Recently, we have introduced the surface-assisted homocoupling of terminal alkynes on a noble metal surface as a new tool for covalent bottom-up construction.^[8] The employed functional moiety represents a highly versatile building block in 3D supramolecular chemistry due to its capability to establish C–H···π hydrogen bonds in which it acts as proton acceptor and donor at the same time.^[9] On noble metal surfaces the ethynyl groups remain decisive for the low-temperature self-assembly of three-fold symmetric 1,3,5-triethynyl-benzene (TEB), as well as its extended derivative 1,3,5-tris-(4-ethynylphenyl)benzene (Ext-TEB).^[10] Upon thermal activation, both species selectively dimerize covalently on the Ag(111) surface at 300 to 330 K while avoiding polymerization.^[8] At higher annealing temperatures (T=400 K), reticulated polymer networks evolve that lack the targeted regularity and porosity.

In the present work we aim at gaining a better understanding of the previously encountered hierarchic reaction pathway and general aspects of homo-coupling reactions using the dimeric reaction intermediate from scratch.^[8] To this end, we synthesized the compound 1,4-bis(3,5-diethynylphenyl)butadiyne-1,3 (1, Scheme 1) and explored its 2D self-assembly and onsurface covalent reactions on the Ag(111) surface with scanning tunneling microscopy (STM). After adsorption and sponta-



Scheme 1. Chemical structure of 1,4-bis(3,5-diethynylphenyl)butadiyne-1,3 (1)—TEB-dimer.

neous ordering at sample temperatures below 300 K, a densepacked and an open-porous supramolecular phase coexist, both featuring intact molecules. At an annealing temperature of 350 K, covalent bonding between the organic constituents sets in, yielding products consisting of two or more molecules. The analysis of the exhibited bonding geometries is more straightforward than in the previous case of the TEB polymerization, where at the reaction onset a mixture of TEB monomers and already reacted TEB dimers was present, complicating the interpretation of the observed motifs. Herein, our findings reveal that the central butadiyne moiety of 1 is often covalently linked to a laterally approaching terminal alkyne. This reaction represents a major obstacle for the production of regular, porous networks using the on-surface homo-coupling reaction of terminal alkynes. These insights are important for the development of refined approaches aiming at the bottom-up construction of novel carbon-based materials beyond graphene with terminal alkynes, for which avoiding this side reaction will increase the quality of the resulting covalently bonded layer or nanostructures.

Results and Discussion

Synthesis

The molecule **1** consists of two 1,3,5-triethynylbenzene species, connected by a single covalent bond resulting in a central butadiyne bridge (Scheme 1).

Scheme 2 shows the synthesis of the TEB-dimer based on a protecting group approach. The key element in the synthesis is the bisprotected triyne **3**. For its preparation we make use of the selective palladium-catalyzed coupling of 1,3,5-tribrombenzene and two terminal alkynes with protecting groups of different polarity at the alkyne moiety, and the site-selective removal of (3-cyanopropyl)-dimethylsilyl group in the presence of triisopropylsilyl (TIPS) groups. [(3-Cyanopropyl)-dimethylsilyl]acetylene (CPDMSA) combines the mild conditions with a high polarity of the hydroxyl containing protecting groups.^[11] It simplifies chromatographic separation after coupling to aromatics with more than one reactive site, thus enabling success-



Scheme 2. Synthesis of 1, conditions: a) $[Pd(PPh_3)_4]$, Cul, Ph₃P, iPr_2NH , 90 °C, 52%; b) K₂CO₃, THF/MeOH, RT, 98%; c) Cul, TMEDA, Et₃N, Acetone, RT, 80%; d) Bu₄NF, THF, RT, 85%.

ful separation of the target compound **2** from the mixture of four products.

A facile and efficient pathway for the copper iodide and ligand *N,N,N',N'*-tetramethylethane-1,2-diamine (TMEDA) promoted homo-coupling reaction of terminal alkyne **3** under ambient temperature and air as an oxidant was used^[12] affording the symmetrical 1,4-disubstituted 1,3-butadiyne **4** in excellent yield. The target compound **1** was synthesized by removal of the tri-isopropylsilyl (TIPS) groups by fluoride-induced desilylation.

Supramolecular assembly at low temperature

The TEB-dimer exhibits a two-fold ($C_{2\nu}$) symmetry with a length of 14.38 Å. Accordingly, single molecules appear in the STM images as two connected triangular protrusions reminiscent of a bow-tie.^[8]

After depositing for 40 min with a low flux onto the cold substrate ($T_s = 200$ K), highly regular organic layer structures cover the entire surface (Figure 1). Two coexisting superstructures are easily distinguishable due to the remarkable difference in their geometries. While in the dense-packed (DP) phase (Figure 1, upper right) all molecules are aligned in the same direction, the open-porous (OP) phase features its constituents in three orientations (Figure 1, bottom left). The absence of a Moiré pattern and the uniformity of the apparent imaging height in both phases suggest that they are commensurate with the underlying silver surface.



Figure 1. Large-scale STM image of 1 self-assembly on Ag(111) showing the dense-packed (upper right) and the open-porous (bottom left) phases coexisting together on the same terrace. Some impurities appear as white protrusions ($U_{\text{bias}} = 1.0 \text{ V}$, $I_t = 0.06 \text{ nA}$).

A large-scale STM image of the OP phase is reproduced in Figure 2a demonstrating the regularity of the superstructure. Due to its invariance under 60° rotations, this is a highly symmetric phase for which no rotational domains exist. The zoomed-in picture (Figure 2b) highlights that three and six molecules enclose triangular (green) and hexagonal (blue) pores, respectively. Considering the center of each molecule, it becomes evident that the network is based on a kagomé lattice, thus featuring a trihexagonal tiling of the surface.^[13] The unit cell is highlighted in red, showing the basis vectors $\bar{a}_{\scriptscriptstyle OP}$ and $b_{\scriptscriptstyle OP}$ and the enclosed angle $heta_{\scriptscriptstyle OP}$. The yellow star in the lower right site of the picture indicates the high-symmetry directions of the underlying Ag(111) surface. As indicated by the dashed red line, the vector \vec{a}_{OP} fits to the direction of the surface primitive vector \vec{u} , which is the [110] direction of the crystal. Additionally, b_{OP} is parallel to the primitive vector \vec{v} , therefore this structure is invariant under 60° rotation.

However, we find two different organizational enantiomorphic arrangements of this phase as illustrated in Figure 3. The designation for clockwise and counterclockwise chirality is given due to the direction of the tilting of the stars, which in Figure 3 a are spinning to the left (counterclockwise) and in



Figure 2. a) STM image of the sample annealed to 300 K after depositing on 200 K substrate leading to the open-porous (OP) phase ($U_{\text{bias}} = 1.05 \text{ V}$, $I_t = 0.12 \text{ nA}$). b) OP details and molecular ordering ($U_{\text{bias}} = 1.05 \text{ V}$, $I_t = 0.12 \text{ nA}$). The yellow star shows the high-symmetry directions of the Ag(111) surface, θ is the angle between \bar{a} and \bar{b} and the red polygon shows the unit cell. Green triangle and blue hexagon show the two types of porous that we find in this phase. c) Model with the TEB dimers located on the substrate. The \bar{a}_{OP} vector is parallel to the primitive vector of Ag(111) \bar{u} and \bar{b}_{OP} is parallel to \bar{v} , which show the commensurate superlattice. δ_{OP} is the rotation angle, highlighted by the green and blue lines.



Figure 3. Different relative positioning of the building blocks of the porous phase results in clockwise b) ($U_{\text{bias}} = -0.5 \text{ V}$, $I_t = 0.06 \text{ nA}$) and counterclockwise a) ($U_{\text{bias}} = 1.05 \text{ V}$, $I_t = 0.12 \text{ nA}$) rotating motifs in two enantiomorphs of the chiral kagomé structure.

Figure 3 b to the right (clockwise). Our data show that there is no preference for one or the other enantiomorph. This is expected since in both assemblies the single molecules obey the same epitaxy with the substrate. In general, we could not observe simultaneously the two orientations on the same terrace, i.e., domain boundaries follow atomic steps.

For quantitative evaluation of the experimental data, topographic data of the same area were recorded with four different slow scan directions and the geometric values of the structures in these images were averaged to minimize the error caused by drift. The measured lengths of the basis vectors and the angles are $\left|\vec{a}\right| = \left|\vec{b}\right| = 23.1 \pm 0.5$ Å and $\theta = 60.4 \pm 0.7^{\circ}$ (Figure 2a).

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Guided by the experimental values, we built the model depicted in Figure 2 c, for which a ball-and-stick representation of the molecules was chosen and where Ag(111) surface atoms were sketched by blue circles. The values of the model are:

$$\left|\vec{a}\right| = \left|\vec{b}\right| = 23.11$$
 Å and $\theta = 60^{\circ}$,

which in terms of the surface primitive vectors can be expressed in matrix form as:

$$\begin{pmatrix} \vec{a}_{OP} \\ \vec{b}_{OP} \end{pmatrix} = \begin{pmatrix} 8 & 0 \\ 0 & 8 \end{pmatrix} \begin{pmatrix} \vec{u} \\ \vec{v} \end{pmatrix}$$

For the positions of the molecules with respect to the substrate, in the model we propose that each molecule occupies the same epitaxial position. In our previous work a DFT calculation of the energetically most favorable adsorption geometry of a single isolated molecule on the Ag(111) surface was presented, indicating preferential alignment along high-symmetry substrate directions for the terminal alkyne groups of an isolated species.^[8] Using this configuration for the model of the network (Figure S1 in the Supporting Information) leads to an unsatisfying reproduction of the STM data as discussed in the Supporting Information. The agreement can be increased by assuming a slight rotation of each molecule around its center by an angle δ , leading to the model displayed in Figure 2c.

Using the mentioned averaging procedure, we could minimize the drift effects in the data and estimate the rotation angle to $\delta_{\text{OP}} = -3.0 \pm 0.1^{\circ}$ for the counterclockwise orientation (Figure 3 a) and $\delta_{\rm OP}\!=\!3.0\pm0.1^\circ$ for the clockwise one (Figure 3 b). After analyzing the distances (blue lines in Figure 2 c) between the terminal hydrogen and the closer triple bond of the acetylene groups (Figure S2 in the Supporting Information), we find that the value is 3.23 ± 0.03 Å fitting to a weak hydrogen-bonding interaction (C–H \cdots π) scheme. Furthermore, we suggest that the proton acceptor ring interaction^[14] between benzene rings and π clouds of nearby ethyne moieties increases the non-covalent binding between the organic units. We conclude that the rotation is a result of increasing intermolecular attraction until the energy losses, due to unfavorable molecule-substrate interaction, pose a limit. Overall, the principles behind the network formation seem to be closely related to the case of the TEB monomers,^[10] as expected due the similarity of the building blocks. Our previous extensive DFT modeling has revealed that the commensurate superstructure of the TEB network and the molecular rotation induced chirality result from a delicate balance between the intermolecular force and molecular substrate interaction,^[10] as generally expected for interfacial supramolecular assemblies.^[15]

The second supramolecular phase constructed from **1** is presented in Figure 4a, in which an overview image shows the geometry of this dense-packed structure in which the molecules form a compact layer as they arrange in a "stretcher bond" brickwork filling the surface plane.

The zoomed-in image (Figure 4b) shows the unit cell (red) and the basis vectors \vec{a}_{DP} and \vec{b}_{DP} , enclosing the angle θ_{DP} The



Figure 4. a) STM images from a sample at 200 K deposition showing the dense-packed phase. A defect of four missing molecules can be observed at the center of the picture (U_{blas} = 80 mV, l_{t} = 66 pA). b) Zoomed-in image with the polygon (red) highlighting the unit cell of this phase, and the star (yellow) showing the three high-symmetry directions of the substrate. This is the left-enantiomorph, highlighted by the green arrow and the blue line along the long molecular axis (U_{blas} = -80 mV, l_{t} = 0.07 nA). c) Model built from the experimental STM data. The basis vectors \bar{a}_{DP} and \bar{b}_{DP} form the angle θ_{DP} and α_{DP} is the angle between \bar{b}_{DP} and $[\bar{1}10]$ direction of the Ag(111) substrate. The rotation angle δ_{DP} is enclosed by blue and green lines.

angle between \bar{b}_{DP} and the surface [$\bar{1}$ 10] direction is denoted as α_{DP} . This lattice appears in three different orientations with respect to the substrate, in agreement with the two-fold symmetric appearance of the organic units and the six-fold symmetry of the substrate when the second layer is not taken into account. Also this phase exhibits chiral properties. With respect to the direction given by the long axis of the molecules, the next entity is displaced to the left. Therefore, this domain is denoted as L-enantiomorph. Consistently, we also found domains of the R-enantiomorph.

The experimental values extracted using the procedure of the four directions scans for \vec{a}_{DP} and \vec{b}_{DP} vectors are 19.8 \pm 0.3 Å and 13.14 \pm 0.13 Å respectively. The estimation of the angles is $\theta_{DP} = 89.8 \pm 1.2^{\circ}$ and $\alpha_{DP} = 70.9 \pm 0.6^{\circ}$.

Figure 4c displays the model built by considering the unit cell of this network to be commensurate with the substrate. While along the \vec{b}_{DP} direction every molecule occupies the same registry, along the \vec{a}_{DP} direction only every second unit has the same adsorption geometry. Thus, the superstructure features higher-order commensurability.

The values proposed for this model are $\vec{a}_{DP} = 20.20$ Å, $b_{DP} = 13.24$ Å, $\alpha_{DP} = 71^{\circ}$, and $\theta_{DP} = 87^{\circ}$. The matrix representation for the superlattice in terms of the primitive vectors is:

$$\begin{pmatrix} \vec{a}_{DP} \\ \vec{b}_{DP} \end{pmatrix} = \begin{pmatrix} 5 & 3 \\ -4 & 5 \end{pmatrix} \begin{pmatrix} \vec{u} \\ \vec{v} \end{pmatrix}$$

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Each terminal alkyne interacts with two neighboring moieties (sky and dark blue lines in Figure 4c) almost in the same direction. The average value for the distance between the *para*hydrogen of the benzene ring and the center of the nearby ethyne is 2.9 Å (sky blue). For the terminal hydrogen of the acetylene and the center of the closer triple bond the value is 2.6 Å (dark blue). Both values are significantly smaller than those in the OP phase, in which each terminal functional group interacts with three neighboring moieties partly in the opposite direction. Thus in the DP phase the intermolecular attraction seems to have more anisotropic character with the major axis pointing approximately along the long molecular axis.

Similar as in the OP phase, also here the molecules exhibit a rotation angle by which they deviate from the preferred absorption geometry (Figure 4c and S3 in the Supporting Information). In this case the deviation is stronger leading to an experimental angle of $\delta_{\rm DP} = 7.7 \pm 1.3^{\circ}$. The analysis of the interatomic distances of the terminal hydrogen of the acetylene groups and the nearest triple bond (Figure S4 in the Supporting Information) matches with the range of the hydrogenbonding (1.5-3 Å). The explanation for the deviation angle is that the molecules tilt clockwise due to the minimization of the distance with both neighbors along the long molecular axis thereby maximizing the molecule-molecule interaction. This is reinforced by a weaker hydrogen-bonding along \bar{a}_{DP} direction. Due to those two interactions, a shear force acts on the molecules resulting in the clockwise rotational displacement (Figure 4c). In the R-enantiomorph the molecules rotate counterclockwise (not shown) to optimize intermolecular forces.

Next we discuss the energetic and kinetic characteristics of the two phases. For this purpose we calculated the density of the unit cell in the models, which are $\rho_{\rm DP}=0.75$ molecules nm⁻² and $\rho_{\rm OP}=0.56$ molecules nm⁻², and analyzed all the data for each sample measuring the area covered by both superstructures. Samples are divided in two different cases: 1) with a high molecular coverage such that all terraces are covered to a high extent, but no second or higher layer growth set in, and 2) with low coverage such that many pristine terraces are occupied at most by small amount of isolated dimers.

At 200 K in case 1), the DP phase is occupying 60% of the covered area leaving 40% for the OP. Following annealing to 300 K, the OP structure increases to 92% indicating dominance of this network at such conditions. Case 2) is totally different, showing only the DP lattice when depositing at 200 K. After the annealing to 300 K, the OP structure is present, but 85% of the organic layer is allocated by the DP phase. We conclude that the energetically preferred arrangement is the OP structure, but its expression can be kinetically hindered. The OP network can only form when during the growth the temperature is high enough to allow a reorientation of all the molecules and the molecular coverage is high enough to facilitate the condensation into the porous structure employing the cyclic binding motifs. On the DP domains, defects like the one shown in Figure 4a are present, which is a further indication

that this phase is indeed not the thermodynamically preferred structure.

Catalytic coupling reactions

After demonstrating the ability of **1** to form long-range ordered supramolecular structures, we tested its usefulness for the construction of covalently bonded networks. Since **1** is the same molecule obtained after the first step of the homo-coupling reaction of TEB monomers,^[8] we expect further insight into the identified hierarchic reaction pathways and notably to shine light on the following two aspects with it. First, how does the absence of TEB monomers during the reaction process influence the resulting final polymeric networks? A minimum of three homo-coupling reactions of **1** is necessary to form a regular hexagon, the basic ingredient for a regular porous network, while for the TEB monomer six reactions are required. Second, what are the obstacles which prevent the formation of more regular sheets up to now?

Figure 5a displays a large-scale topographic image of a sample obtained by evaporating **1** at room temperature and subsequent annealing to 400 K. The molecules have formed a polymerized network with long and irregular strands. Pores are hardly visible, those present are formed by loops of the polymeric chains, but none can be found in a regular pattern. After annealing at 500 K (Figure 5 b), the structural characteristics remain the same demonstrating that once the covalent reaction have progressed to the full extent, the resulting structure is thermally very stable.



Figure 5. a) STM data of a sample annealed to 400 K ($U_{\text{bias}} = -1.0$ V, $I_t = 0.08$ nA) and b) to 500 K ($U_{\text{bias}} = 0.53$ V, $I_t = 0.06$ nA). c) Sample annealed to 420 K using the TEB monomer for the comparison of both molecules ($U_{\text{bias}} = -0.92$ V, $I_t = 0.1$ nA). a) to c) were recorded at 5.5 K. d) STM image recorded at room temperature presenting the stability of the arrangement for a sample annealed to 500 K after a 400 K hot deposition ($U_{\text{bias}} = 2.4$ V, $I_t = 0.26$ nA).

At this stage we tested also direct deposition onto hot substrates with temperatures between 350 and 500 K (not shown). At 350 K, polymerization occurs generating dimers and short oligomers, but larger polymers are hardly formed. For higher temperatures, the resulting regularity and porosity of polymeric films bear quite similar properties to those obtained by annealing.

In order to compare the networks formed from 1 (Figure 5a) with those from the TEB monomer, we prepared a sample with the latter with similar preparation conditions. As discussed in our recent work, the TEB monomers adsorb only transiently to the Ag(111) surface under reaction conditions. Therefore the preparation has been carried out by a hot deposition (330 K), followed by annealing steps to 370 and 420 K (Figure 5c). The structures generated by this process closely resemble those of molecule 1. Therefore, our comparison indicates that starting from the presynthesized dimer has no significant influence on the polymerization process, i.e., the circumvention of the hierarchic pathway does not decisively affect the eventual outcome.

As a final test of the expected structural stability, we measured the covalent networks fabricated from 1 at room temperature. The image presented in Figure 5 d shows a sample obtained by deposing onto a hot substrate at a temperature of 400 K. The similarity with the structures recorded at low temperatures is obvious. The whole network is stably imaged indicating that no mobile parts are present in this reticulated structure. Thus the covalent networks exhibit the expected stability.

With the aim of better understanding the underlying coupling mechanisms, we further investigated the onset of the reaction. We thus prepared a sample by depositing a small amount of **1** onto a hot substrate at 350 K. The result is shown in Figure 6a, in which a small DP-domain of unreacted species can be observed around a screw dislocation (top left), but most of the molecules form small clusters with only few members each. The most frequent cluster type consists of two molecules and is highlighted with the red circles. The magnification in the inset (upper right) indicates that these clusters are reacted molecules covalently-linked to each other.

For a deeper analysis, high-resolution data are presented with a multi-color code in Figure 6b. In this preparation we can also find short polymers with different geometry and accordingly varying chemical configurations. Some of the polymer strands (solid and dashed violet circles in Figure 6b) show a linear connection between the former molecular endgroups. Such a configuration is expected for the on-surface homo-coupling reaction in which a butadiyne bridge is formed from two terminal alkynes.^[8] The geometry of these strands is consistent with the gas phase geometry of the expected products. The schemes of corresponding products are presented in Figure 6 c (solid and dashed violet circles). The gas phase geometries were optimized using the HYPERCHEM software within the AM1 framework.

Obviously, there are structures visible in Figure 6b (highlighted in red) that can only be explained by another covalent reaction mechanism. We suggest that the end of the polymer



Figure 6. a) STM overview image from a 350 K deposition. Although a selfassembled island can be observed, the major part of the sample exhibits irregular aggregates. Red circles mark the prevalent configuration in the right upper corner, occurring at these conditions ($U_{\text{bias}} = 313 \text{ mV}$, $I_t = 0.09 \text{ nA}$). b) High-resolution image showing the initial steps of covalent coupling reactions. Violet encircled connections would lead to a regular polymerized network. Side reactions marked by red circles render the structure formation highly uncontrollable ($U_{\text{bias}} = 313 \text{ mV}$, $I_t = 0.06 \text{ nA}$). c) Geometrically optimized schemes of the most characteristic coupling motifs observable in a) and b).

strand in the lower central part of the image (red dashed circle) can be formed by linking a former central butadiyne group of the forelast molecule to a former terminal alkyne of the last molecule. In this covalent linking process one ethyne moiety, which is constructed from sp-hybridized carbons, of the former butadiyne bridge gets modified to an ethene group with sp² hybridized carbon atoms (Figure 6 c, red solid circle). In this process the hydrogen atom of the attacking alkyne is transferred to the resulting ethene group, thus all the educts are used for building the product. Two of these reactions are necessary to form the two molecule clusters (red solid circles in Figure 6 b and c) mentioned before.

The importance of the latter mechanism is that it proceeds under the same conditions as the homo-coupling reaction. A recent study of the on-surface polymerization of 1,4-diethynylbenzene on Cu(111)^[16] revealed a plethora of different reactions occurring simultaneously on this more reactive support, and we encountered similar obstacles with the TEB and Ext-TEB units on copper surfaces.^[17] For the rational bottom-up construction of novel materials with the on-surface homo-coupling reaction, effective ways must be found to prevent such side reactions. In our initial demonstration of the surface-confined alkyne homo-coupling, we revealed that atomistic details of the catalytic environment provided by the substrate influence the reaction mechanism.^[8] In particular, it became clear that a change in adsorption height due to matching or mismatching epitaxy with the substrate is responsible for initiating or preventing the reaction at a substrate temperature of 330 K. A different approach focusing on the chemistry of the building blocks was employed recently, in which linear alkane chains

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helped to form one-dimensional oligomers through covalent linking of terminal alkynes.^[18] This approach is consistent with our findings, because the side chain prevented the formed butadiyne bridges from being attacked by further terminal alkynes simply by steric hindrance. Since such side groups are often unwanted in the targeted material novel tools must be developed in the future to fully exploit the potential of the onsurface homo-coupling reaction for the controlled construction of novel molecular species, nanostructures or 2D networks.

Conclusions

We synthesized a novel organic building block featuring terminal alkynes and a central butadiyne group and demonstrated its aptitude for building non-covalent architectures and covalent coupling reactions on the Ag(111) surface. The expression of long-range ordered supramolecular phases reflects a delicate balance between molecule-substrate interaction and intermolecular attraction originating mainly from the terminal ethynyl moieties. Annealing at temperatures between 350 and 500 K triggered surface-assisted catalytic conversions with reaction products in the form of covalently-connected, irregular 2D polymers. Using special preparations we identified intermediate binding motifs that allow to pinpoint a competing reaction to the wanted homo-coupling namely an additional alkyne reacting into the butadiyne bridge from the side. Only when such reaction channels are prevented by the careful design of the catalytic environment under which reactions proceed, will it be possible to fully exploit the on-surface homo-coupling reaction for the controlled construction of well-defined novel molecular species, nanostructures or 2D materials.

Experimental Section

Synthesis details

Reactions requiring an inert gas atmosphere were conducted under argon, and the glassware was oven-dried (140 °C). THF was distilled from potassium prior to use. Triethylamine and di-isopropylamine were distilled over CaH₂ and stored under argon. CPDMSA^[19] was synthesized according to published procedures. Commercially available chemicals were used as received. Thin-layer chromatography was performed on aluminum plates precoated with Merck 5735 silica gel 60 F₂₅₄. Column chromatography was performed with Merck silica gel 60 (230-400 mesh). ¹H NMR and ¹³C NMR spectra were recorded on a Bruker DRX 500 spectrometer, chemical shifts are given in ppm, referenced to residual proton resonances of the solvents. The matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectroscopy measurements were carried out on a Synapt G2-S HDMS spectrometry workstation. Elemental analyses of carbon, hydrogen, and nitrogen were carried out in a Vario Micro Cube. IR spectra were measured in KBr pellets on MAGNA FTIR 750, Nicolet.

1,4-Bis(3,5-diethynylphenyl)butadiyne-1,3 (1)

A solution of Bu_4NF in THF (1 M; 0.5 mL, 0.5 mmol) was added to a solution of **4** (2.0 g, 2.16 mmol) in THF (40 mL). The mixture was stirred for 3.5 h at room temperature and then poured into ether

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and water. The organic layer was washed with water and brine and dried over MgSO₄. The solvent was removed in vacuum and the residue was purified by flash chromatography over Celite/SiO₂ with hot benzene following recrystallization from benzene to afford 1 as a white powder (520 mg, 85%). ¹H NMR (CD₂Cl₂): δ = 13.25 (s, 4H, C \equiv CH), 7.64 (t, *J* = 1.15, 2H_{arom}), 7.60 ppm (d, *J* = 1.15, 4H_{arom}); ¹³C NMR (CD₂Cl₂): δ = 74.88, 79.34, 80.31, 81.53, 122.69, 123.59, 136.28, 136.57 ppm; IR (KBr): $\tilde{\nu}$ = 3295 ($\nu_{C \equiv C-H}$, s), 3068, 2876 (ν_{C-H} , w), 2159 cm⁻¹ ($\nu_{C \equiv C}$, vw); HRMS (MALDI-TOF): *m/z*: calcd for C₂₄H₁₀ 298.0782 [*M*⁺]; found: 297.9771 (100%); elemental analysis calcd (%) for C₂₄H₁₀: C, 96.62; H, 3.38; found: C, 96.58; H, 3.92.

4-({3,5-Bis-[(triisopropylsilanyl)-ethynyl]-phenylethynyl}-dimethyl-silanyl)-butyronitrile (2)

1,3,5-Tribrombenzene (3.1 g, 10.0 mmol), [Pd(PPh₃)₄] (120 mg), Cul (60 mg) and triphenyl posphine (120 mg) were dissolved in THF (50 mL) under an argon atmosphere. The solution was heated to 95 °C and CPDMSA (1.7 g, 11.0 mmol) dissolved in THF (5 mL) was added dropwise over 15 min. The mixture was stirred for 0.5 h at this temperature. Then, 2-tri-isopropylsilylacetylene (TIPSA; 5.51 g, 30.0 mmol) was added and the solution stirred at this temperature for 3 h. After cooling to room temperature, diethyl ether and water were added; the organic phase was separated and washed with water, 10%-H₂SO₄, water, and brine. After drying over MgSO₄ and evaporation of the solvent, the crude product was purified by column chromatography on SiO_2 using hexane/CH_2Cl_2 (60:1) as eluent ($R_f = 0.38$) to afford **2** as a white powder (3.05 g, 52%). ¹H NMR (CD₂Cl₂): $\delta = 0.24$ (s, 6H, CH₃), 0.83–0.89 (m, 2H, CH₂), 1.17 (s, 42H, TIPS), 1.80-1.87 (m, 2H, CH₂), 2.46 (t, J=6.99, 2H, CH₂), 7.53–7.54 ppm (m, 3H_{arom}); ¹³C NMR (CD₂Cl₂): δ =0.0, 13.57, 16.17, 20.69, 24.69, 33.89, 94.71, 96.05, 106.40, 107.23, 121.99, 125.70, 126.39, 137.13, 137.24 ppm; IR (KBr): $\tilde{\nu} = 2946$, 2866 (ν_{C-H} , vw), 2165 cm⁻¹ ($\nu_{C=C}$ vw); HRMS (MALDI-TOF): m/z: calcd for C₃₆H₅₇NSi₃: 587.3799 [*M*⁺]; found: 544.1752 (100%); elemental analysis calcd (%) for C₃₆H₅₇NSi₃: C, 73.52; H, 9.77; N, 2.38; Si, 14.33; found: C, 73.55; H, 9.92; N, 2.37.

1-Ethynyl-3,5-bis-[(triisopropylsilanyl)-ethynyl]benzene (3)

K₂CO₃ (4.7 g, 34.2 mmol) was added to a solution of **2** (3.0 g, 6.8 mmol) in THF/methanol (2:1; 25 mL) and the mixture was stirred for overnight at room temperature. Diethyl ether and water were added; the organic phase was separated, washed with water, 10%-H₂SO₄, water, brine and dried over MgSO₄. The crude product was purified by flash chromatography over Celite with hot hexane following recrystallization from hexane to afford **3** as a white powder (2.3 g, 98%). ¹H NMR (CD₂Cl₂): δ =1.15 (s, 42 H, TIPS), 3.18 (s, 1H, C≡CH), 7.55 ppm (s, 3H_{arom}); ¹³C NMR (CD₂Cl₂): δ =11.39, 18.51, 78.33, 81.84, 92.65, 104.98, 120.0, 122.74, 124.27, 135.19 ppm; IR (KBr): $\tilde{\nu}$ =3302 ($\nu_{C≡C-H'}$ w), 2952, 2866 ($\nu_{C-H'}$ s), 2159 cm⁻¹ ($\nu_{C≡C'}$ m); elemental analysis calcd (%) for C₃₀H₄₆Si₂: C, 77.85; H, 10.02; Si, 12.14; found: C, 77.65; H, 9.92.

1,4-Bis(3,5-bis((triisopropylsilyl)ethynyl)phenyl)butadiyne-1,3 (4)

Compound **3** (1.0 g, 2.1 mmol), TMEDA (25.0 mg, 10 mol%), Cul (20.5 mg, 5 mol%) and Et_3N (650 mg, 6.4 mmol) were added to acetone (10 mL) at ambient temperature. The reaction mixture was stirred at RT for 20 h. The progress of the reaction was monitored by TLC. After completion of the reaction, the solvent was removed

under reduced pressure and the crude product obtained was purified by flash chromatography over Celite^{*} following recrystallization from hexane to afford **4** as a white solid (2.2 g, 80%). ¹H NMR (CD₂Cl₂): $\delta = 1.17$ (s, 84H, TIPS), 7.59 (t, J = 1.55, 2H_{arom}), 7.60 ppm (d, J = 1.55, 4H_{arom}); ¹³C NMR (CD₂Cl₂): $\delta = 14.26$, 18.77, 74.64, 80.57, 93.34, 105.05, 122.41, 124.76, 135.75, 135.96 ppm; IR (KBr): $\tilde{\nu} = 2952$, 2878 (ν_{C-H} , vs), 2159 cm⁻¹ ($\nu_{C \equiv C}$, s); elemental analysis calcd (%) for C₆₀H₉₀Si₄: C, 78.02; H, 9.82; Si, 12.16; found: C, 78.05; H, 9.92.

STM measurements

All data shown were obtained with a home-built Besocke beetletype STM scanning at 5.5 K incorporated in a liquid helium bath cryostat or at RT where indicated. The whole system, preparation chamber and STM, were operated under ultra-high vacuum conditions (UHV) with pressures below 2×10^{-10} mbar and is vibration isolated by seven suspension legs. The samples were prepared under the same conditions in the preparation chamber with the deposition performed on the pristine Ag(111) surface, cleaned beforehand by repeated cycles of Ar⁺ sputtering with subsequent annealing to 775 K. The organic molecular beam epitaxy (OMBE) was heated to sublime the molecules at T=390 K onto the substrate held at $T_{\rm s}$. To control the substrate exposure a mass spectrometer was used to monitor the flux. After the preparation the sample was transferred to the STM stage and cooled down till the thermal equilibrium was reached.

For the determination of the structural properties of the phases, the analysis was carried out by averaging the values of images recorded in the four slow scanning directions. To calibrate the measurements, this same method was initially applied to the pristine Ag(111) substrate. All the errors given correspond to the statistical analysis; no systematic errors were taken into account.

Hyperchem

For optimizing the geometries and the models for the TEB dimer, HYPERCHEM's (HYPERCHEM, Hypercube Inc., Gainesville, FL) semi empirical methods applying the AM1 model were used.

Keywords: alkynes · Glaser–Hay-type homo-coupling · heterogeneous catalysis · nanochemistry · oligomerization · self-assembly

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