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On-Surface Synthesis of Carbon-Based Scaffolds and Nanomaterials Using Terminal Alkynes

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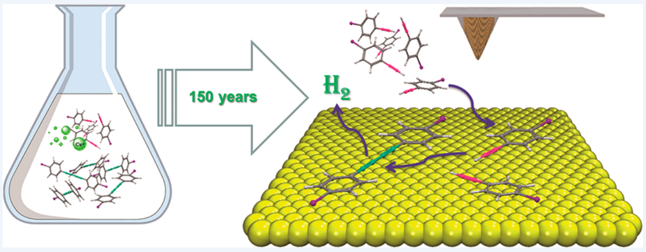

CONSPECTUS: The covalent linking of acetylene compounds is an important synthetic tool to control carbon−carbon bond formation and has been extensively studied for more than a century. Notably, Glaser coupling and subsequently developed refined procedures present an important route for the fabrication of distinct carbon-based scaffolds incorporating units with both sp^2- and sp-hybridizations, such as carbyne chains, or two-dimensional (2D) graphyne or graphdiyne networks. However, the realization of the envisioned regular low-dimensional compounds and nanoarchitectures poses formidable challenges when following conventional synthesis protocols in solution, which we briefly overview. Now, recent developments in on-surface synthesis establish novel means for the construction of tailored covalent nanostructures under ultrahigh vacuum conditions. Here we focus on the exploration of pathways utilizing interfacial synthesis with terminal alkynes toward the atomically precise fabrication of low-dimensional carbon-rich scaffolds and nanomaterials. We review direct, molecular-level investigations, mainly relying on scanning probe microscopy, providing atomistic insights into thermally activated reaction schemes, their special pathways and products. Using custom-made molecular units, the employed homocoupling, cyclotrimerization, cycloaddition, and radical cyclization processes indeed yield distinct compounds, extended oligomers or 2D networks. Detailed insights into surface interactions such as bonding sites or conformational adaptation, and specific reaction mechanisms, including hierarchic pathways, were gained by sophisticated density functional theory calculations, complemented by X-ray spectroscopy measurements. For the fabrication of regular nanostructures and architectures, it is moreover imperative to cope with spurious side reactions, frequently resulting in chemical diversity. Accordingly, we highlight measures for increasing chemo- and regioselectivity by smart precursor design, substrate templating, and external stimuli. The ensuing preorganization of functional groups and control of side reactions increases product yields markedly. Finally, the electronic band structures of selected cases of novel low-dimensional hydrocarbon materials accessible with the monomers employed to date are discussed with a specific focus on their differences to theoretically established graphyne- and graphdiyne-related scaffolds. The presented methodology and gained insights herald further advancements in the field, heading toward novel molecular compounds, low-dimensional nanostructures, and coherently reticulated polymeric layers, eventually presenting well-defined arrangements with specific carbon−carbon bond sequencing and electronic characteristics. The functional properties of these or other foreseeable scaffolds and architectures bear significant prospects for a wide range of applications, for example, in nanoelectronics, photonics, or carbon-based technologies.

■ INTRODUCTION

The development and understanding of carbonaceous compounds and carbon allotropes are topics of major interest for science and technology. Notably zero-, one- and two-dimensional species and architectures are currently explored to generate advanced materials for multiple application fields, including nanoelectronics, molecular separation and storage, nanomechanics, optoelectronics, or energy storage and conversion. An important aspect therein is the control of sp^2-hybridized ring and sp-hybridized chain motifs that can be combined to afford multitudinous scaffolds.[1,2] The most obvious two-dimensional (2D) materials contrivable from this combination are the allotropes known as graphyne[3] (GY) and

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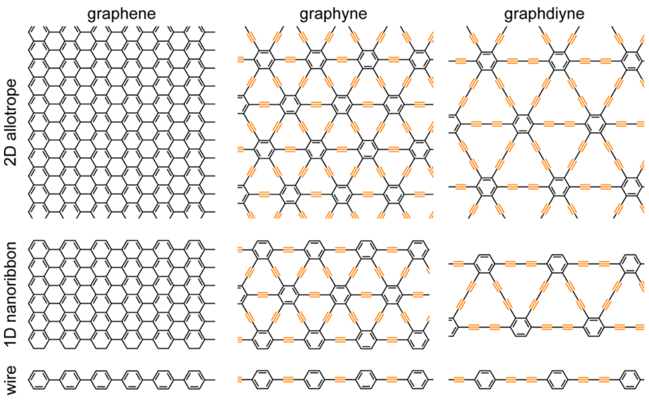
graphdiyne[4] (GDY), depicted in Scheme 1, which are considered promising alternatives for graphene.[5] The crystalline carbon sheets can also be regarded as ideal 2D polymers or covalent organic frameworks, which represent a topical domain in synthetic chemistry,[6] though their fabrication faces great challenges.[7] Moreover, various one-dimensional (1D) counterparts, such as nanoribbons or nanotubes, are achievable from the GY/GDY-related hydrocarbon materials (cf. Scheme 1), expanding the scope of carbyne, ideally being an infinite chain of exclusively sp-hybridized carbon. Also these systems are of high current interest, and substantial efforts were dedicated to their theoretical investigation, albeit limited achievements exist regarding their realization.[5,8] Sophisticated solution-chemistry protocols allow the controlled synthesis of short polymeric strands or patches. However, with increasing oligomer size, undesired side groups, interfering with the targeted material properties, are necessary to provide the required solubility. Additionally, the three-dimensional (3D) character inherent to the polymerization process in solution frequently counteracts the formation of regular low-dimensional structures. Overall, the synthesis of attractive atomically defined carbon-rich materials of the GY/GDY family with conventional methods faces severe obstacles calling for innovative approaches.

The emerging research domain of on-surface covalent synthesis bears promise to tackle this challenge.[9,10] Pioneering work initially demonstrated the bottom-up construction of nanoarchitectures under ultrahigh vacuum (UHV) conditions using the covalent linking of custom-designed molecular building blocks by Ullmann-type coupling.[11] Regarding fullerenes and nanographenes, protocols based on cyclodehydrogenation provided convincing results,[10] which moreover could be successfully combined with dehalogenation reactions to fabricate nanoribbons.[12] Importantly, with the conductance of synthesis procedures at well-defined surfaces, the systems are amenable to investigations with sophisticated tools of interface and nanoscale science. Exquisite insight into the adsorption geometries and the chemical states of precursors, intermediates, and products is notably obtained with scanning probe microscopy in conjunction with high-resolution X-ray spectroscopy.[13] The interpretation of experimental findings and their deeper understanding strongly benefit from complementary computational modeling, where density functional theory (DFT) is the method of choice.[14]

Scheme 1. Overview of Selected 2D Carbon Allotropes and Related Nanomaterials, Emphasizing the Combination of sp^2 (Black) and sp (Orange) Hybridized Carbon Species



In this Account, we survey recent achievements regarding on-surface synthesis of compounds and nanoarchitectures from terminal alkyne precursors on single crystal metal surfaces (Figure 1) and the pertinent potential for fabricating functional nanomaterials. We focus on structure-resolving scanning tunneling microscopy (STM) and atomic force microscopy (AFM), allowing one to characterize both educts and products at the single-molecule level. The most frequently employed reaction in the field of on-surface synthesis relies on thermally activated aryl dehalogenation followed by C−C bond formation leaving halogens as byproducts.[9−12,15,16] In contrast, the reactions highlighted herein generate simply excess hydrogen, which renders them especially suitable for the chemically more sensitive GY/GDY-related scaffolds. Particular emphasis is put on the differences in the coupling mechanism between solution and surface-confined conditions, and strategies to increase control over unwanted side reactions.

■ COUPLING SCHEMES IN SOLUTION

About 150 years ago, Carl Glaser observed that air oxidation of Cu(I)phenyl acetylide led to 1,4-diphenyl-buta-1,3-diyne via dimerization (Scheme 2).[17] Although the initial method involved the isolation of the potentially explosive copper acetylene intermediate, this new C(sp)−C(sp) bond forming reaction has attracted widespread attention in synthetic chemistry.

Numerous versions of the original procedure were developed, differing mainly in the type and amount of used oxidants. Notably, Eglinton and Galbraith demonstrated in 1956 that stoichiometric amounts of cupric salts in methanolic pyridine made the process homogeneous and faster (cf. Scheme 2, Eglinton procedure).[18] A further modification was introduced in 1962 by Hay with catalytic amounts of *N*,*N*,*N*′*N*′-tetramethylethylenediamine (TMEDA) as solubilizing ligand for copper(I) halides in the presence of O_2 (Scheme 2, Glaser−Hay procedure).[19] As the copper−TMEDA complex is soluble in a wide range of solvents, this protocol is more versatile.

In recent years, great progress has been made in this field. Several metal catalytic systems for C(sp)−C(sp) coupling exist.[20] Among them, palladium-catalyzed terminal alkyne dimerization, through oxidative homocoupling, turned to be a useful approach to the synthesis of symmetrical 1,3-diynes (Scheme 2, right).[21] Recent investigations indicate that this reaction might be accomplished in the absence of intentionally added stoichiometric oxidants (to reoxidize Pd(0) to Pd(II)) or with excess of PPh_3, which inhibits alkyne dimerization to enynes *E*,*Z* through head-to-head or head-to-tail coupling

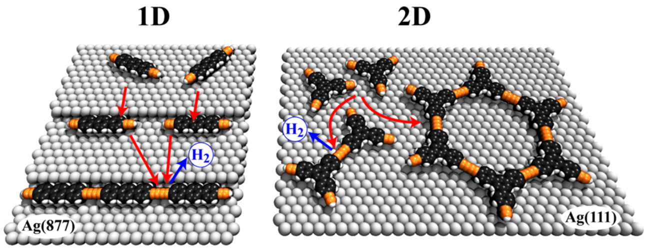
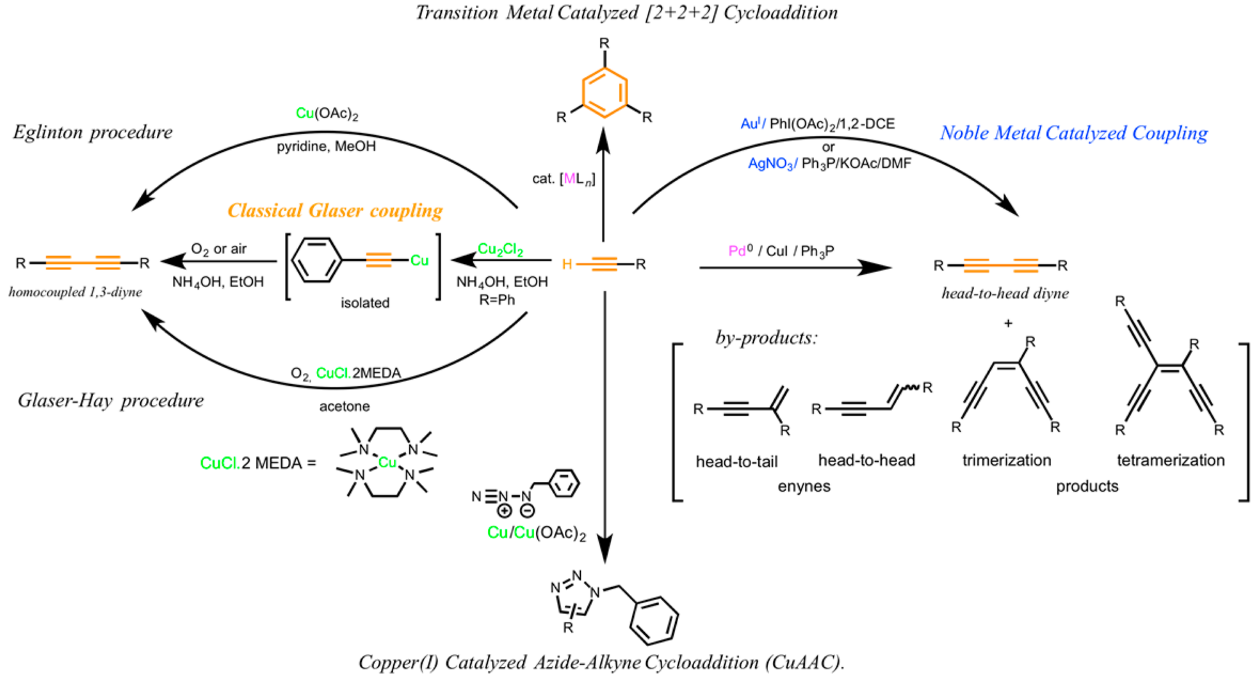
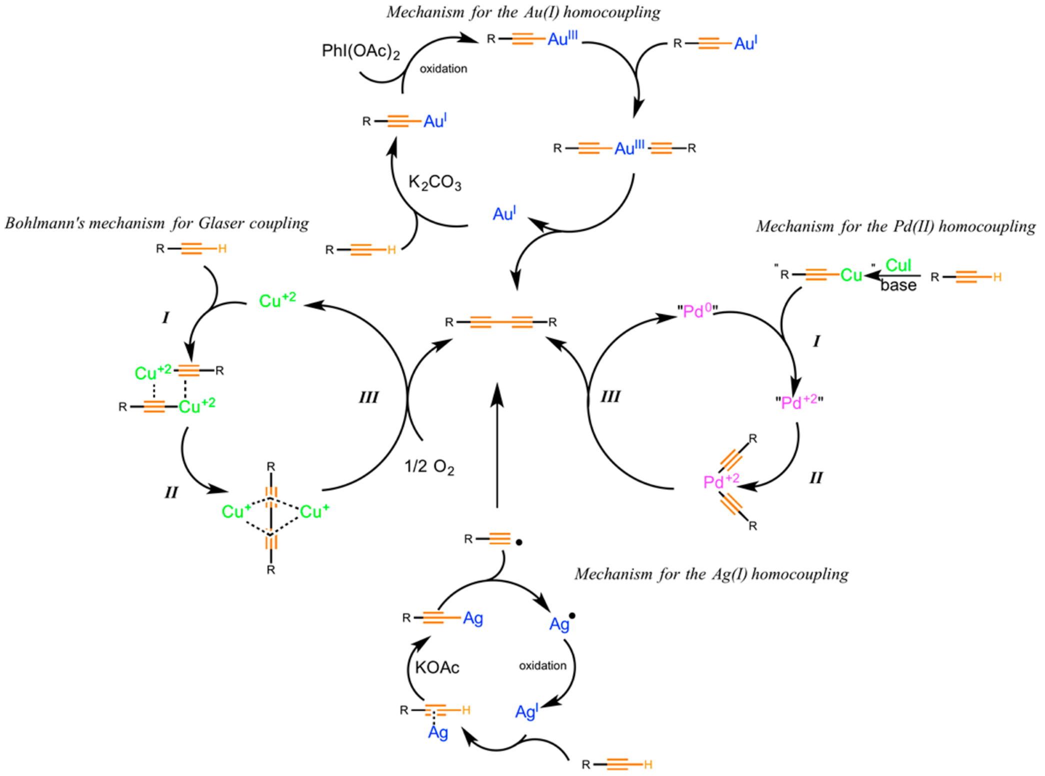


Figure 1. Well-defined surfaces represent versatile platforms to realize novel compounds of the graphyne and graphdiyne family incorporating sp^2 (black) and sp (orange) hybridized carbon atoms from rationally designed precursors.

Scheme 2. Overview of Important Coupling Reactions Involving Terminal Alkynes Showing the Classical Oxidative Glaser Coupling (Left), Cyclotrimerization (Top), Azide–Alkyne Cycloaddition (Bottom), Noble Metal Catalyzed Homocoupling (Right Top), and Homocoupling-Related By-Products (Right Bottom)



Scheme 3. Mechanisms of the Various Terminal Alkyne Dimerization Reactions



(Scheme 2, right bottom).[22] Alternative homocoupling procedures based on noble metal catalytic systems (Scheme 2, right top) are rare and have been developed only recently.

Beyond homocoupling of terminal alkynes, transition metal catalyzed [2 + 2 + 2] cyclization is a well-known process[23] (Scheme 2, top) that has found applications in the synthesis of substituted benzene derivatives. Furthermore, terminal alkynes readily undergo the copper(I)-catalyzed 1,3-dipolar cycloaddition with organic azides to afford 1,4-regioisomers of 1,2,3-triazoles as sole products (Scheme 2, bottom).[24] This reaction is termed the copper(I)-catalyzed azide–alkyne cycloaddition (CuAAC). It can be performed using commercial

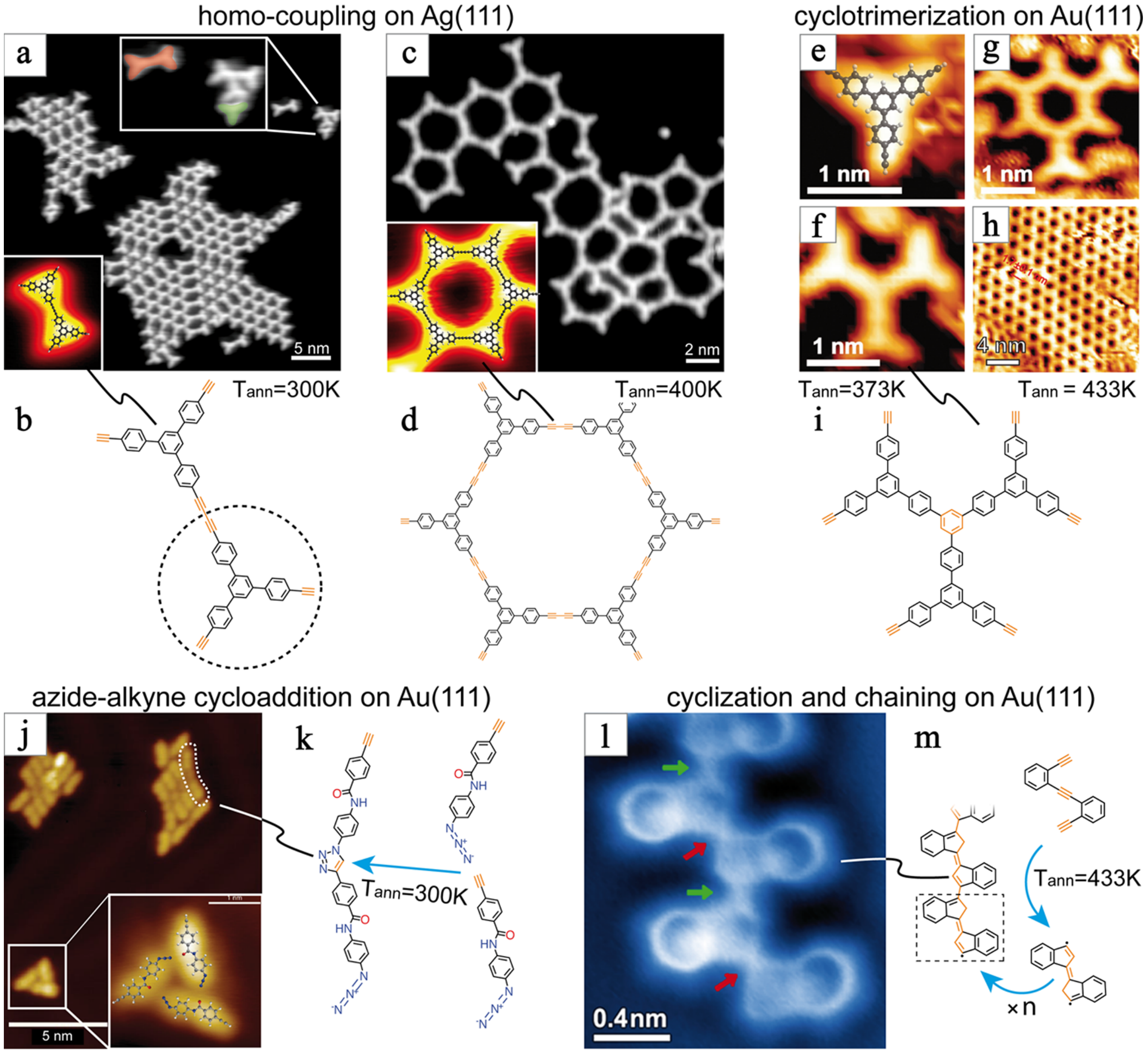


Figure 2. Covalent compounds and networks fabricated by on-surface synthesis with terminal alkynes. (a−d) Homocoupling and hierarchic reaction pathway with ExtTEB on Ag(111), where annealing at 300 (400) K induces covalent dimer (network) formation. (e−i) Cyclotrimerization of ExtTEB on Au(111) starting at $T \approx 370$ K (f,i) and yielding small regular domains $T \approx 430$ K (h). (j,k) Huisgen 3 + 2 dipolar cycloaddition on Au(111). (l,m) Radical cyclization and chaining of enediyne precursors evidenced by nc-AFM, discriminating bridging double bonds (green arrows) from cyclopentene linkages (red arrows) of reaction products. Panels (a) and (c) adapted with permission from ref 32. Copyright 2012 Macmillan Publishers Limited. Panels (e)−(h) adapted with permission from ref 35. Copyright 2014 The Royal Society of Chemistry. Panel (j) reprinted with permission from ref 37. Copyright 2013 American Chemical Society. Panel (l) reprinted with permission from ref 38. Copyright 2014 American Chemical Society.

sources of copper(I) such as cuprous bromide or iodide, but works much better when using a mixture of copper(II) (e.g., copper(II) sulfate) and a reducing agent (e.g., sodium ascorbate) to produce Cu(I) in situ.

The mechanism of the classic Glaser coupling is intricate and not fully understood, albeit it is known that the reaction depends strongly on experimental conditions. An initial proposal involving a radical mechanism was refuted, and the most widely accepted pathway was suggested in 1964 by Bohlmann et al.[25] invoking a dinuclear copper(II) acetylide complex collapsing to the product (Scheme 3). Many of the mechanisms published later[22] involve a similar dicopper(II) complex, although the formation and subsequent collapse are different.

The proposed mechanism for the Pd(II)-catalyzed homocoupling reaction includes three steps (Scheme 3, right): (1) the formation of the alkynylcuprate by base-assisted deprotonation of alkyne in the presence of CuI; (2) subsequent transmetalation with Pd(II) giving a dialkynylpalladium(II) species; (3) final reductive elimination generates Pd(0) and 1,3-diyne.

Compared to the copper and palladium catalysis, other transition-metal mediated homocoupling reactions for the synthesis of 1,3-diynes are limited. Recent examples were

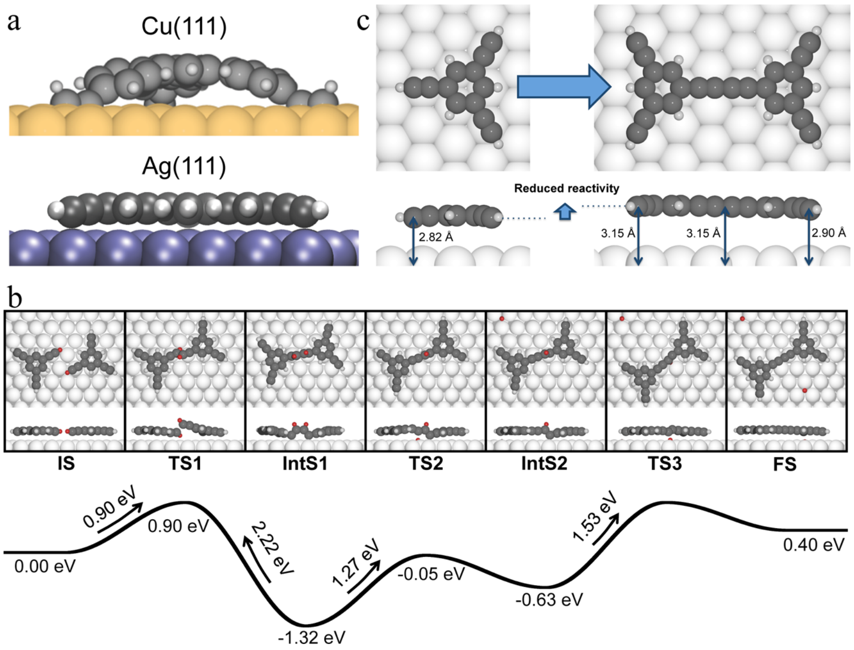


Figure 3. (a) Calculated surface bonding of ExtTEB on Cu(111) vs Ag(111) revealing markedly different conformational adaptations. Reprinted in part with permission from ref 42. Copyright 2015 American Chemical Society. (b) Mechanism of the homocoupling between terminal alkynes exemplified with TEB on Ag(111), showing a simplified picture with initial state (IS), final state (FS), as well as relevant transition (TS) and intermediate states (IntS), and the corresponding energy profile. The hydrogen atoms that are being split off from the formed dimer are rendered in red for clarity. Reprinted with permission from ref 43. Copyright 2014 American Chemical Society. (c) Epitaxy constraints for the dimer result in reduced reactivity as compared to the monomer.

developed for the gold-catalyzed oxidative dimerization of propargylic acetates or nonactivated arenes.[26] Besides the activation of π-systems proposed, gold can also potentially promote oxidative coupling involving gold(I)/gold(III) cycles (Scheme 3, top).[27,28] The reaction of Ph_3PAuCl with acetylene affords alkynyl-gold(I), which is then oxidized to a Au^{III} species. This transmetalation leads to the diethynyl-gold(III) intermediate, which undergoes reductive elimination to give 1,3-diyne and regenerate the Au^{I} catalyst.

Although silver acetylides can be readily prepared and isolated as precipitate, and their chemistry has a long record,[29,30] relatively few silver catalytic systems have been employed and almost only as cocatalyst in the Pd/Ag cross-coupling transformations. Studies on the homocoupling of alkynes with silver salts are scarce. Notably, a silver nitrate-catalyzed homocoupling reaction of alkynes in *N*,*N*-dimethylformamide using triphenylphosphine has been employed as an efficient protocol to afford various 1,3-diyne products from the corresponding aromatic or aliphatic alkynes.[31] The catalytic circle is initiated by formation of π-complex intermediates between silver ions and alkynes, which are deprotonated by KOAc treatment to generate alkynyl silver intermediates (Scheme 3, bottom). In contrast to the mechanisms of Cu-, Pd-, and Au-catalyzed homocouplings, the C−Ag bond undergoes homolysis to generate an alkynyl radical. The homocoupling product appears after quenching of two radicals, which can be terminated by addition of radical scavengers such as hydroquinone or 2,6-di-*tert*-butylphenol, suggesting that the reactions proceed via a radical mechanism. Subsequently Ag(I) is regenerated in situ with oxidation to complete the catalytic cycle.[31]

■ INVESTIGATING ON-SURFACE REACTIONS

A clear-cut demonstration for on-surface synthesized covalent nanostructures from the coupling of terminal alkynes was achieved in 2012.[32] The findings of Zhang et al. include STM data of tritopic precursors (notably 1,3,5-triethynyl-benzene (TEB) and 1,3,5-tris(4-ethynylphenyl)benzene (ExtTEB)) that following evaporation onto Ag(111) self-assemble at low temperatures.[33] Thermal treatment of the organic layers induces highly selective homocoupling, resulting in covalent dimers (see Figure 2a,b for ExtTEB). Upon increasing the temperature, reticulated covalent networks evolve, locally including hexagonal pores (Figure 2c,d). Long-range order, however, is missing in the hydrocarbon scaffold, which is attributed to the formation kinetics involving flexible monomers generating pentagons and heptagons,[34] or the interference of spurious side reactions.

Surprizingly, on the Au(111) surface, the same precursor is engaged in cyclotrimerization reactions[35] that lead to the expression of regular domains on the 20 nm scale after annealing (Figure 2e−i). The results suggest that by changing the chemical nature of the substrate, the preferred coupling type of the terminal alkynes can be steered. It has to be noted, however, that geometrical constraints are expected to also have significant influence on the reaction pathway and a thorough evaluation of potential coverage-dependent reaction preferences is still missing on either of the two substrates.

Related to the 2 + 2 + 2 trimerization of the previous case, also a 3 + 2 cycloaddition was observed under on-surface conditions (Figure 2j) when terminal alkynes interact with azide moieties to carry out the Huisgen click reaction (Figure 2k) either on Cu(111)[36] or on Au(111).[37] Even though these first reports demonstrate the principal feasibility of the reaction, extended structures have not yet been achieved.

Moreover, sophisticated oligomeric chains can be constructed on Au(111) by radical cyclization of enediyne precursors featuring not only terminal, but also internal, alkyne moieties with the appropriate intramolecular positioning (Figure 2m).[38] The isoelectronic formation of two five-membered carbon rings connected by a double bond is nicely evidenced by the noncontact AFM data in Figure 2l. More extended covalent chains have been obtained with the same reaction type with a monomer featuring only internal alkynes.[39]

Finally, it is worth mentioning that the cross-coupling of terminal alkynes with aryl or alkenyl halogenides, understood as surface-confined versions of Sonogashira-like couplings,[40] appears as a potential approach. Even though a first demonstration of the feasibility of such reactions at surfaces under UHV was reported,[41] related protocols for creating covalent scaffolds have not been developed yet.

EXAMINATION OF REACTION PATHWAYS BY COMPUTATIONAL MODELING

Experimental studies have provided great insight into the rich and delicate chemistry of terminal alkynes on metal surfaces. However, due to short-lived transition and intermediate states, insights regarding reaction mechanisms remained limited. This has motivated theoretical investigations using DFT calculations. There have been two independent reports of the reaction mechanism of the homocoupling reaction between terminal alkynes, approaching the problem at the DFT level and assessing reaction paths within the framework of transition state theory. The common main message is that the reaction is initiated by covalent bonding between two end groups, followed by twofold dehydrogenation of the generated intermediate. The intermediate is stabilized by chemisorption to the metal surface, and the hydrogen abstraction processes may be associated with a homolytic mechanism, although this classification is somewhat ambiguous. Notably, the electron exchange with the metal is unparalleled in solution protocols, where ionic species are involved in the mechanism, and an initial deprotonation, which is a heterolytic bond cleavage, mediates the ensuing coupling.

To exemplify the mechanisms of the homocoupling reaction, we characterized the surface bonding of TEB and ExtTEB species, introduced above, on Cu(111) and Ag(111) and examined their coupling behavior. The calculated and experimentally confirmed surface geometries[42] depicted in Figure 3a reveal a bent adsorption geometry on copper as compared to rather flat binding on silver, which effect markedly influences the reactivity.

Figure 3b shows a slightly simplified picture of the overall reaction sequence for the experimentally found dimerization of TEB on Ag(111).[43] Initially, a coupling between two molecules occurs (IS to IntS1), with a barrier of 0.90 eV (TS1). The same barrier was found for ethynyl-benzene on Ag(111), and a slightly lower one (0.79 eV) on Au(111).[44] Upon bond formation, the resulting dimer is in a rather stable intermediate state (IntS1), where the affected carbon atoms are anchored to subjacent Ag surface atoms. To proceed, one needs to break these two carbon−silver bonds and simultaneously release two hydrogen atoms. This is accomplished in a two-barrier pathway, associated respectively with H-abstraction and scission of a carbon−silver bond (IntS1 to IntS2 and IntS2 to FS). The dehydrogenation steps are endothermic, but are considered to be irreversible as the hydrogen atoms are known to desorb associatively as H_2 from Ag(111) at $T < 200$ K.[45]

The hydrogen abstraction, required for finalizing the homocoupling (in Figure 3), implies barriers of 1.27 and 1.53 eV which must be overcome to split off the first and second hydrogen atom, respectively. In particular, the second barrier seems substantial considering the mild conditions employed. However, the experimental evidence for the dehydrogenation steps is pertinent, and it is a question of *how*, rather than *if*, they interfere. One possibility is a potentially overestimated stability of intermediate states by the employed density functionals. Furthermore, the calculations report the potential energy landscape at 0 K, and inclusion of temperature effects, in terms of vibrational enthalpy and entropy, indeed have a reducing effect on the dehydrogenation barrier.[43] An important aspect might be that the system does not relax and thermally equilibrates in the intermediate states, and that part of the energy gained in the highly exothermic coupling is transferred into dehydrogenation. This scenario is not accounted for by transition state theory, and is reminiscent of so-called hot adsorbates that can form following dissociative adsorption processes.[46,47] The DFT modeling furthermore provides a rationale for the hierarchic character of the coupling reaction, which is ascribed to the modified surface interaction of dimeric intermediates. Because the symmetric and optimized monomer adsorption geometry cannot be retained (Figure 3c), dimerized species reside higher above the surface and slightly larger barriers apply for coupling reactions with the second or third alkyne moiety.[32]

An alternative path to initiate the homocoupling would be straightforward alkyne dehydrogenation. With TEB on Ag(111), this process has a barrier of 1.8 eV, that is, twice the energy to induce a coupling reaction.[43] A similar barrier was found for dehydrogenation of ethynyl-benzene on Ag(111), while it is slightly reduced to 1.64 eV on Au(111).[44] Notably, the activation energies for coupling two dehydrogenated ethynyl-benzene molecules exceed by roughly 0.3 eV the respective barriers to couple two intact molecules on either Ag(111) or Au(111).[44] In other words, even if dehydrogenated interfacial species were generated, these will couple less effectively to each other than intact molecules. This is most probably a consequence of the strong molecule−surface interaction for the dehydrogenated monomeric species, and is in conjunction with experimental studies of Ext-TEB on Cu(111), for which the dehydrogenation of the terminal alkyne is observed already at room temperature, but the coupling between the molecules is inhibited.[42]

As a final note, the deposition of the Ext-TEB molecule, on Au(111) instead of Ag(111), triggers a cyclotrimerization reaction rather than the homocoupling.[35] It is fascinating how the subtle substrate change from Ag(111) to Au(111) induces such a fundamental difference for the preferred reaction pathway. Nevertheless, due to the rather limited theoretical insights into the pertaining mechanisms, the underlying reasons are difficult to judge. So far, the cyclotrimerization of Au(111) was only modeled regarding benzene formation from three acetylene molecules, and the analysis indicates a two-step process.[48] However, the initial step of the cyclotrimerization does not differ from that of the homocoupling reaction for such a small model system, as the two carbon atoms of the molecule are indistinguishable. A comparison between the two reactions for a more representative molecule would therefore be of great interest.

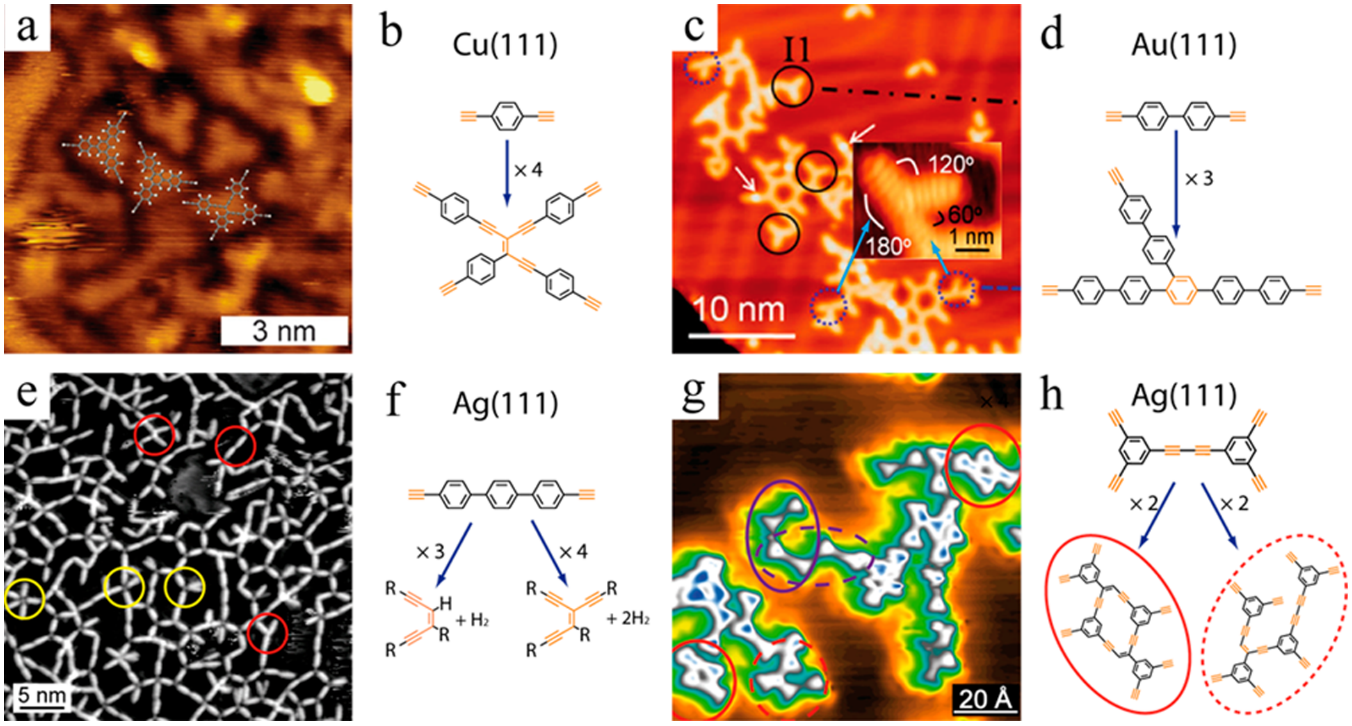


Figure 4. Limited control over possible side reactions resulting in chemical diversity. A broad range of structures results from polymerizing terminal alkynes (a) on Cu(111), (c) on Au(111), and (e) on Ag(111) when employing linear ditopic monomers with (b) one, (d) two, and (f) three phenylene units. (g) Irregular oligomerization of a presynthesized dimeric species (h) on Ag(111) with schemes of specific structural motifs. Panel (a) adapted with permission from ref 50. Copyright 2013 The Royal Society of Chemistry. Panel (c) reprinted with permission from ref 48. Copyright 2014 American Chemical Society. Panel (e) reprinted with permission from ref 51. Copyright 2014 American Chemical Society. Adapted with permission from ref 53. Copyright 2013 Wiley-VCH Verlag GmbH & Co. KGaA.

■ SIDE REACTIONS AND THEIR CONTROL VIA TEMPLATING OR EXTERNAL STIMULI

The irreversibility of covalent reactions frequently obstructs error-correction mechanisms operational during the formation of supramolecular architectures,[49] inhibiting thus the formation of regular one- or two-dimensional scaffolds. Distinctively separated reaction pathways for desired and unwanted coupling mechanisms are advantageous for achieving a targeted structure. In this respect, the rich chemistry related to the carbon triple bonds is detrimental. For example, terminal alkynes on Cu(111)[50] take part in various reactions simultaneously as evidenced by the structural diversity in Figure 4a. Aside homocoupling and cyclotrimerization, the twofold symmetric ditopic monomer undergoes irregular cross-linking of up to four reactive groups (Figure 4b). On Au(111),[48] STM visualizes branching coupling schemes of various geometries (Figure 4c) with a similar linear precursor (extended by one phenylene unit), evidencing that cyclotrimerization can lead not only to threefold symmetric nodes, but also to Y-shaped structures (see Figure 4d). On Ag(111),[51] similar reticulated networks were observed (Figure 4e) when employing the triphenylene precursor derivate (Figure 4f). Again, the hydrocarbon scaffold contains various coupling motifs connecting between two up to five molecules (highlighted red and yellow), the majority of which can be explained by the various previously addressed covalent bonding schemes. A minority of the nodes appearing darker than the backbone, but with a central dot (yellow), are conspicuously different from the usually more protruding covalent connections and could reflect the presence of Ag-acetylides. A very recent investigation of surface reactions of 2,5-diethynyl-1,4-bis-(phenylethynyl)-benzene indeed demonstrated that on the more open (110) and (100) faces of silver the formation of organometallic wires is possible through a Ag-bisacetylide linking motif.[52]

By employing a twofold symmetric precursor featuring an internal butadiyne moiety (Figure 4h), essentially a dimerized TEB derivative, a further study[53] revealed insights not accessible with TEB monomers. After thermally triggering coupling reactions on Ag(111) (Figure 4g), the analysis of the reaction products (red circles) notably reveals the propensity of butadiyne bridges toward cross-coupling with further terminal alkynes. Naturally, such processes represent severe obstacles for the fabrication of regular 2D porous networks and efficient means to suppress such unwanted coupling need to be developed in the future.

For developing sophisticated mechanisms to control side reactions, a thorough understanding of the various undesired coupling pathways is required. Indeed, Gao et al.[54] successfully utilized a monomer featuring alkane side chains steering the assembly of preorganized layers on Au(111) wherein the reactive sites are closely positioned (Figure 5a). Upon the coupling affords well-defined, 1D polymers, as identified by STM (Figure 5b). These results indicate that the side chains act as steric protection groups geometrically shielding the butadiyne bridges and thereby significantly increasing the homocoupling yield. Similar supramolecular prearrangement of the monomers was employed to control alkyne homocoupling on graphite as evidenced by solid–liquid STM.[55]

A different approach toward improved control over on-surface synthesis protocols is provided by templating, that is, using specific interfaces guiding the positioning of educts in a

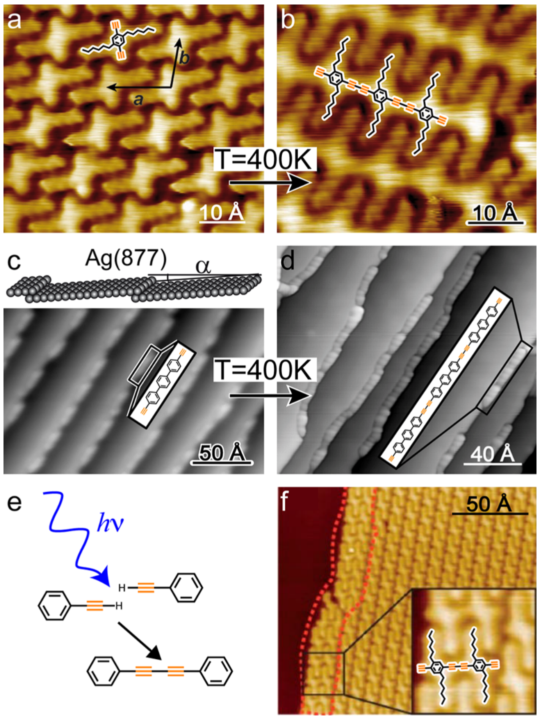


Figure 5. (a) Regular self-assembled domain of a monomer with alkane side chains (highlighted). (b) Well-defined 1D chains locally prevail upon alkyne coupling. (c) Sketch of the ideal Ag(877) surface structure and step-edge alignment of separated linear ditopic precursors (depicted in Figure 4f). (d) Extended graphdiyne nanowires evolve after the directed homocoupling. (e) Principle of photostimulated reaction and (f) its realization employing a preassembled layer on Ag(111) where UV-irradiation induces dimerization at the boundary of the molecular domains. Panels (a) and (b) adapted with permission from ref 54. Copyright 2013 Wiley-VCH Verlag GmbH & Co. KGaA. Panels (c) and (d) reprinted with permission from ref 51. Copyright 2014 American Chemical Society. Panels (e) adapted and (f) reprinted with permission from ref 60. Copyright 2014 American Chemical Society.

favorable fashion.[16,56−58] Indeed, the vicinal Ag(877) surface (Figure 5c) proved helpful for regular alignment of linear ditopic terminal alkyne precursors (imaged as bright sticks) along step-edges similar to earlier work on gold.[59] Moreover, the lateral attachment to the steps enables control over the reaction pathway and effectively suppresses side reactions as evidenced by the formation of 1D extended graphdiyne nanowires (Figure 5d) after annealing to 400 K.[51]

Another promising approach toward the formation of regular nanomaterials relies on the stimulation of the homocoupling reaction via ultraviolet light (Figure 5e). A crucial aspect thereby is whether such mechanisms can be effective when the reactive moieties are in direct contact with the metallic substrates. Recent work[60] demonstrating the light-induced oligomerization on Ag(111) (Figure 5f) and Au(111) reveals that this approach provides access to alkyne-based covalent products. Although the achievements are currently limited to short oligomers, the result highlight that photochemistry is a useful tool to steer on-surface synthesis.

■ ELECTRONIC PROPERTIES

The electronic band structures of the classic, 6-fold symmetric allotropes GY and GDY and their various hydrocarbon low-dimensional relatives were intensely investigated theoretically.[5,8] However, with the monomers and coupling schemes presented here, a different set of regular materials becomes reachable, as exemplified by two prototypical examples. Figure 6a depicts the structure of 1,3,5-graphdiyne (1,3,5-GDY) that would follow from perfect 2D polymerization by homocoupling from TEB (cf. Figure 3). In comparison to GDY in the unit cell of the sixfold symmetric relative, one C_6-ring and three butadiyne bridges are missing. Accordingly, in reciprocal space (Figure 6b), the irreducible area of the unit cell is smaller. The consequences include a large band gap (∼2.4 eV from DFT; see ref 51, methods), a more complex band structure, and the presence of nondispersing states producing a high density of states at specific energies (−7.4, −6.8, −5.8, −3.5, −2.2, and −2.1 eV) from which extraordinary optical characteristics can be expected.

As an example for a 1D scaffold, we discuss the ideal case of extended GDY nanowires formed by vicinal surface templating[51] (Figure 6d). The regular polymeric strand consisting of three consecutive phenylene units connected by a butadiyne moiety represents a direct band gap semiconductor exhibiting a mixture of nondispersing states and dispersing bands similar to phenylene-ethynylene chains.[61] In contrast to the latter, however, the highest valence and lowest conduction band express a more cosine-like shape and a gap opening with respect to the next lower and higher band, respectively (double arrows in Figure 6f). Thereby, the gap depends on the interphenylene ring twist-angles as can be seen from the comparison of the planar and the twisted conformations. With these characteristics, Ext-GDY nanowires appear ideally suited for nonlinear electron transport phenomena related to Bloch oscillations[62] in novel materials differing significantly from semiconductor superlattices.

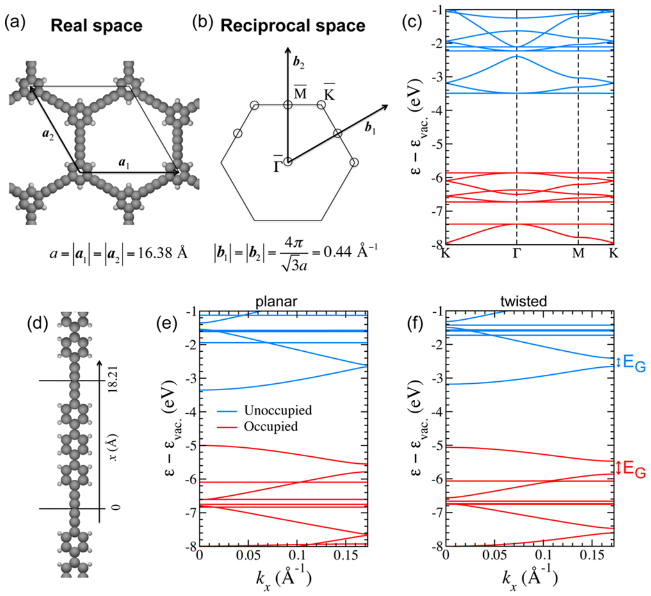


Figure 6. (a) Structure of 1,3,5 graphdiyne with unit cell. (b) The unit cell in reciprocal space. (c) Band structure of 1,3,5 graphdiyne. (d) Structure of the repeating unit of the extended graphdiyne nanowire and corresponding band structures for (e) planar geometry of all phenylene units and (f) with the central phenylene ring rotated by 32°.

FUTURE PERSPECTIVES

The construction of covalent architectures and novel carbon-based nanomaterials by on-surface synthesis using custom-designed precursor molecules featuring terminal alkynes is a powerful approach, but still in its infancy. The successful demonstrations of the various possible pathways opens exciting avenues toward atom-precise, functional organic scaffolds mixing sp- and sp^2-hybridized carbon. Before long-range ordered, high-quality samples of mesoscopic size can be achieved, more effort needs to be invested in the understanding and control of coupling mechanisms and spurious side reactions. However, given the successful demonstration of templated or otherwise steered reactions, we are confident that coupling of terminal alkynes will emerge to an important contribution for the fabrication of advanced covalent architectures, suitable for nanotechnological devices with tunable functional properties.

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Notes

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Jonas Björk received his Ph.D. 2010 from the University of Liverpool. He has been working at Linköping University since then, and is currently an Assistant Professor in theoretical chemistry. His research interests include computational studies of molecules adsorbed on surfaces, particularly focusing on the description of the on-surface reactions relevant for the formation of covalent nanostructures.

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