ADVANCED MATERIALS
www.advmat.de

On-Surface Synthesis of Carbon Nanostructures

Qiang Sun, Renyuan Zhang, Jun Qiu, Rui Liu, and Wei Xu*

Novel carbon nanomaterials have aroused significant interest owing to their prospects in various technological applications. The recently developed on-surface synthesis strategy provides a route toward atomically precise fabrication of nanostructures, which paves the way to functional molecular nanostructures in a controlled fashion. A plethora of low-dimensional nanostructures, challenging to traditional solution chemistry, have been recently fabricated. Within the last few decades, an increasing interest and flourishing studies on the fabrication of novel low-dimensional carbon nanostructures using on-surface synthesis strategies have been witnessed. In particular, carbon materials, including fullerene, carbon nanotubes, and graphene nanoribbons, are synthesized with atomic precision by such bottom-up methods. Herein, starting from the basic concepts and progress made in the field of on-surface synthesis, the recent developments of atomically precise fabrication of low-dimensional carbon nanostructures are reviewed.

1. Introduction

From the life and organic chemistry, we know how unique the binding properties of carbon element are. Those properties are rooted in its ability to form linear (sp^1), planar (sp^2), or tetragonal (sp^3) bond configurations. Its unique properties have spanned an incredibly rich structural phase diagram of pure carbon nanomaterials due to the sp^2 bond configuration. Over the course of the last 30 years, a continuous series of discoveries and scientific breakthroughs (e.g., fullerenes, multi- and single-walled carbon nanotubes (CNTs), isolation of graphene, synthesis of porous graphene, and graphene nanoribbons (GNRs)) have made many of those materials envisioned in this carbon structure diagram physically available.[1–3]

Recently, on-surface synthesis has emerged as a promising approach to construct novel nanostructures, which are still of significant challenge to traditional solution-based chemistry. Special interest is paid to low-dimensional carbon nanostructures, owing to the successive discoveries of carbon allotropes, including fullerene, carbon nanotubes, and graphene. Furthermore, their properties have been proved to be promising in numerous scientific and industrial applications.[4–8]

Formation of nanostructures through on-surface chemical reactions is particularly attractive because of its following characteristics: (i) it allows the formation of covalently interlinked nanostructures, which possess high thermal and chemical stability with respect to noncovalent self-assembled nanostructures; (ii) the reduced degree of freedom of molecular precursors on surfaces (i.e., confinement effect) as well as the interactions between molecular precursors and surfaces may favor some specific molecular adsorption configurations, resulting in unexpected chemical reactions and formation of nanostructures, which could hardly obtained by conventional solution chemistry; (iii) it prohibits the influence of solvents and other contaminants under the well-controlled ultrahigh vacuum (UHV) conditions; (iv) it allows the synthesis of macromolecules or nanostructures with high molecular weight that could not be synthesized in solutions due to the solubility issues; and (v) it is feasible to be in situ characterized by surface sensitive techniques, e.g., scanning tunneling microscopy (STM), noncontact atomic force microscopy (nc-AFM), and X-ray photoelectron spectroscopy (XPS), which allows us to get both the structural and chemical information with high resolution.

Here, we will summarize the recent work regarding on-surface synthesis of atomically precise low-dimensional carbon nanostructures, including graphene-derived porous graphene, graphene nanoribbons, and single chirality carbon nanotubes, as well as the emerging carbon nanostructures with acetylenic scaffolding and organometallic carbon chains (i.e., metalated carbyne).

2. On-Surface Synthesis of 0D Carbon Nanostructures

One of the most famous 0D carbon nanomaterials is fullerene, which represents a family of cage molecules with a variety of sizes and shapes. The C_{60} molecule has gained most attention because of its superconducting property, along with high mechanical and thermal resistance.[9] Despite numerous research efforts devoted in this field, the controllable synthesis of the fullerenes with reliable yield and purity still remains as a great challenge.

On-surface synthesis involving dehydrogenation and cyclization of planar molecular precursors has proved to be a promising choice. Otero et al. have designed two nearly planar polycyclic aromatic hydrocarbons, $C_{60}H_{30}$ and its analogue $C_{57}H_{33}N_3$.[10]

Dr. Q. Sun, Prof. R. Zhang, Prof. J. Qiu, Prof. R. Liu, Prof. W. Xu
Key Laboratory for Advanced Civil Engineering
Materials (Ministry of Education)
College of Materials Science and Engineering
Tongji University
Shanghai 201804, P. R. China
E-mail: xuwei@tongji.edu.cn

The ORCID identification number(s) for the author(s) of this article can be found under https://doi.org/10.1002/adma.201705630.

DOI: 10.1002/adma.201705630

As shown in **Figure 1**a, they found that after the deposition and thermal heating of the molecular precursor on Pt(111) surface, the molecular precursors dehydrogenated, performed a surface catalyzed cyclodehydrogenation process and eventually formed the corresponding fullerene and triazafullerene molecules on the Pt(111) surface. Surprisingly, the efficiency of this cyclodehydrogenation process is almost 100% along with no indication of desorption of the molecules on the surface suggesting that all of molecular precursors are transformed into fullerenes. In the lower panel of Figure 1a, it shows the STM image after deposition of $C_{57}H_{33}N_3$ on a platinum (111) surface. The size and topology of the STM image, with three wings characterizing the molecular shape, confirm that the molecules do not fragment but retain their planar structure upon adsorption. Upon annealing the sample at 750 K, a surface reaction takes place and the triangular molecules transform into round molecules with an apparent height of about 0.38 nm and a diameter of 1.5 nm, in analogy to the STM appearance of a commercial C_{60} adsorbed on a platinum surface. Moreover, further evidence for the thermally induced cyclization of $C_{57}H_{33}N_3$ is provided by XPS spectra. Here, the strong covalent interaction between the precursor molecules and the platinum surface are considered to play a key role in this reaction. To further test the catalytic effect of the Pt(111) surface, they have also performed similar experiments on a relatively inert Au(111) surface, which contrarily did not exhibit the same reaction.

This surface-catalyzed cyclodehydrogenation method could also be applied to the synthesis of other cage molecules. The synthesis of fullerenes with higher molecular weight than the most familiar C_{60} and C_{70} remains a challenge because of the low yield of the evaporation technique and the complicated purification issues. Amsharov et al. used the surface-catalyzed cyclodehydrogenation of planar precursors on Pt(111) to achieve the synthesis of C_{84}.[11] They demonstrated that this reaction is quite efficient and controllable. Moreover, they have designed a modified $C_{60}H_{30}$ isomer, which finally formed an open-cage structure, highlighting the importance of the precursor design. In addition, Abdurakhmanova et al. found that two molecular precursors $C_{54}H_{24}$ and $C_{60}H_{30}$ could yield (9, 0) zigzag and (6, 6) armchair carbon nanotube end caps using the surface-assisted cyclodehydrogenation on the Rh(111) surface.[12] Here, the choice of the surface is also critical in determining the on-surface reaction. The different interactions between the molecules and substrates could rule the competitive reaction pathways, that is, cyclodehydrogenation versus dehydrogenative polymerization. Pinardi et al. reported that the aromatic precursors tend to carry out intramolecular cyclodehydrogenation on Pt(111), while intermolecular dehydrogenative polymerization dominates on Au(111), Cu(110), or Cu(111) surface.[13]

Wei Xu received his Ph.D. degree in surface physical chemistry from Aarhus University, Denmark, in 2008. Following this, he was a postdoctoral fellow at the Interdisciplinary Nanoscience Center (iNANO), Aarhus University, Denmark, and at the Departments of Chemistry and Physics, Penn State University, USA. Currently, he is a Professor at Tongji University, P. R. China, where he has been since 2009. His main research interests include molecular self-assembly and reaction on surfaces, and novel carbon nanostructures like graphyne/graphdiyne and carbyne.

Nanographenes or graphene quantum dots (GQDs) have attracted widespread attention due to their potentials in the field of molecular electronics. However, the atomically precise fabrication of nanographenes has still remained as a challenge. Surface-assisted cyclodehydrogenation provides a synthetic route to the fabrication of tailored nanographenes from polyphenylene precursors. As shown in Figure 1b, Treier et al. designed a polyphenylene precursor, a kind of nanographene, that could be thermally induced by intramolecular cyclodehydrogenation following several intermediate steps.[14] They have also observed two intermediates stabilized on the surface by high-resolution STM images, yielding unprecedented

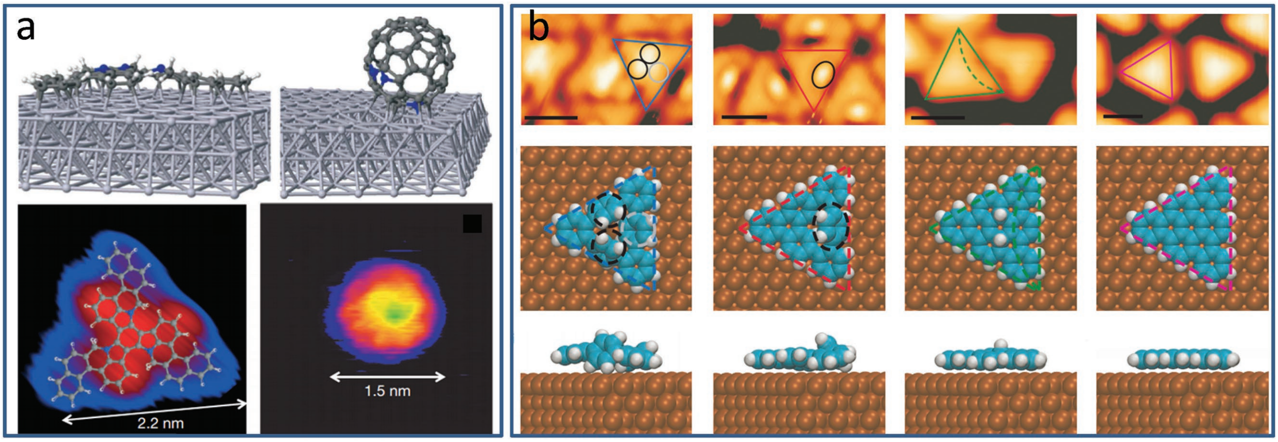

Figure 1. On-surface synthesis of 0D carbon nanostructures. a) The $C_{57}N_3$ triazafullerene formed after the cyclodehydrogenation process on Pt(111). Adapted with permission.[10] Copyright 2008, Nature Publishing Group. b) The atomically precise fabrication of tailored nanographenes by dehydrogenative intramolecular aryl–aryl coupling reaction. Adapted with permission.[14] Copyright 2011, Nature Publishing Group.

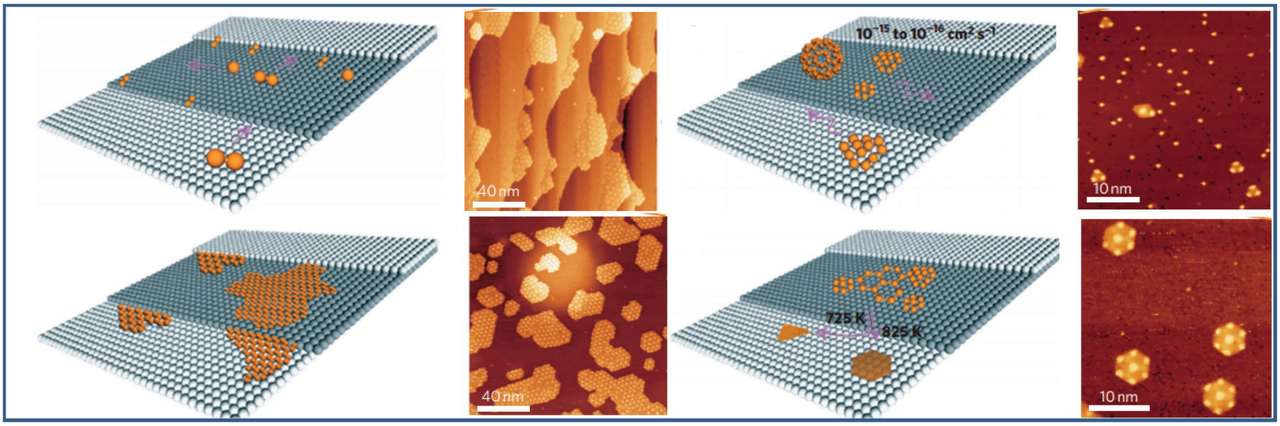

Figure 2. Geometrically well-defined graphene quantum dots are synthesized on a ruthenium surface using C_{60} molecules as precursors. Adapted with permission.[18] Copyright 2011, Nature Publishing Group.

insight into a dehydrogenative intramolecular aryl–aryl coupling reaction. Moreover, they derived a reaction mechanism for the complete dehydrogenation that is catalytically activated and enhanced by the adsorbate–substrate interaction. In light of the fact that polyphenylenes have higher solubility and lower thermal evaporation temperatures than their dehydrogenated nanographene counterparts, this on-surface method suggests a promising strategy for the controllable formation of nanographenes with atomic precision. In line with the aforementioned study, several studies have shown the formation of different planar polyaromatic hydrocarbons by surface-assisted intramolecular dehydrogenation reactions even on an inert Au(111) surface.[15,16] In addition to the intramolecular C—C coupling, Fan et al. have constructed a hyperbenzene from a designed V-shaped aromatic bromide by the intermolecular C—C coupling.[17]

It is noteworthy that Lu et al. have demonstrated that the formation of geometrically well-defined GQDs is feasible from C_{60} molecules on Ru(0001) surface.[18] As shown in **Figure 2**, they have synthesized a series of atomically defined GQDs by metal-catalyzed cage-opening of C_{60} molecules. By a combination of STM imaging and density functional theory (DFT) calculations, they suggest that the strong C_{60}–Ru interaction induces the formation of surface vacancies followed by a subsequent embedding of C_{60} molecules in the surface. The fragmentation of the embedded molecules at elevated temperatures then produced carbon clusters that undergo diffusion and aggregation to form graphene quantum dots. They have also compared the formed carbon nanostructures produced by C_{60} and C_2H_4. The limited mobility of the carbon clusters derived from C_{60} restricts the formation of nanographene with larger size in comparison with those from C_2H_4 carbon sources. From a comparison with the formation of fullerenes from different planar polyaromatic hydrocarbons, these observations further suggest the interconvertibility between graphene and fullerenes, and underline the role of surfaces in on-surface chemistry.

In 1990, Eigler and Schweizer pioneered atomic manipulations by deliberately placing atoms using STM tip in an atomically precise fashion.[19] Later on, seminal work of molecular reactions triggered by STM manipulation have been reported.[20] STM manipulation provides a highly controllable and powerful toolkit for on-surface synthesis of molecules or nanostructures, even for those of extreme reactivity. Triangulene, the smallest triplet-ground-state polybenzenoid, has been an enigmatic molecule ever since it was first hypothesized, due to the stability issue. Pavliček et al. have shown the on-surface generation of the unsubstituted triangulene by a combined STM and AFM manipulation.[21] As shown in **Figure 3**a, triangulene was successfully formed by the voltage pulse from the tip to dehydrogenate molecular precursors. STM measurements combined with DFT calculations further confirmed that the triangulene keeps its free-molecule properties on the surface. Interestingly, the triangulene could be stabilized and adsorbed on three different materials including two insulating surfaces (NaCl, Xe) and also on a metal (Cu) surface. Using the same method, other kinds of ployaromatic hydrocarbons could also be formed on surfaces. As indicated in Figure 3b, Krüger et al. present the on-surface reduction of diepoxytetracenes to form tetracene on Cu(111) by STM tip-induced manipulation.[22] They have also found that thermal activations could yield the formation of tetracenes as well. The identification of the products is unambiguously demonstrated by means of nc-AFM with single chemical bond resolution. Another example is the formation of a “olympicene” radical.[23]

Notably, acenes which belong to a family of polycyclic aromatic hydrocarbons formed by linearly fused benzene rings have received increasing attention recently. However, the synthesis of acenes becomes incrementally challenging as the length of the molecule increases due to their instabilities and high activities. Krüger et al. have synthesized an unprecedented decacene through the on-surface reduction of tetraepoxy decacene precursors on Au(111).[24] Almost at the same time, Urgel et al. have formed an Au-directed heptacene organometallic complexes on Au(111) using an α-diketone-protected heptacene precursor.[25] They have observed individual heptacene species on the surface as well. Meanwhile, Zuzak et al. have accomplished the on-surface formation of nonacene by dehydrogenation of an air-stable partially saturated precursor.[26]

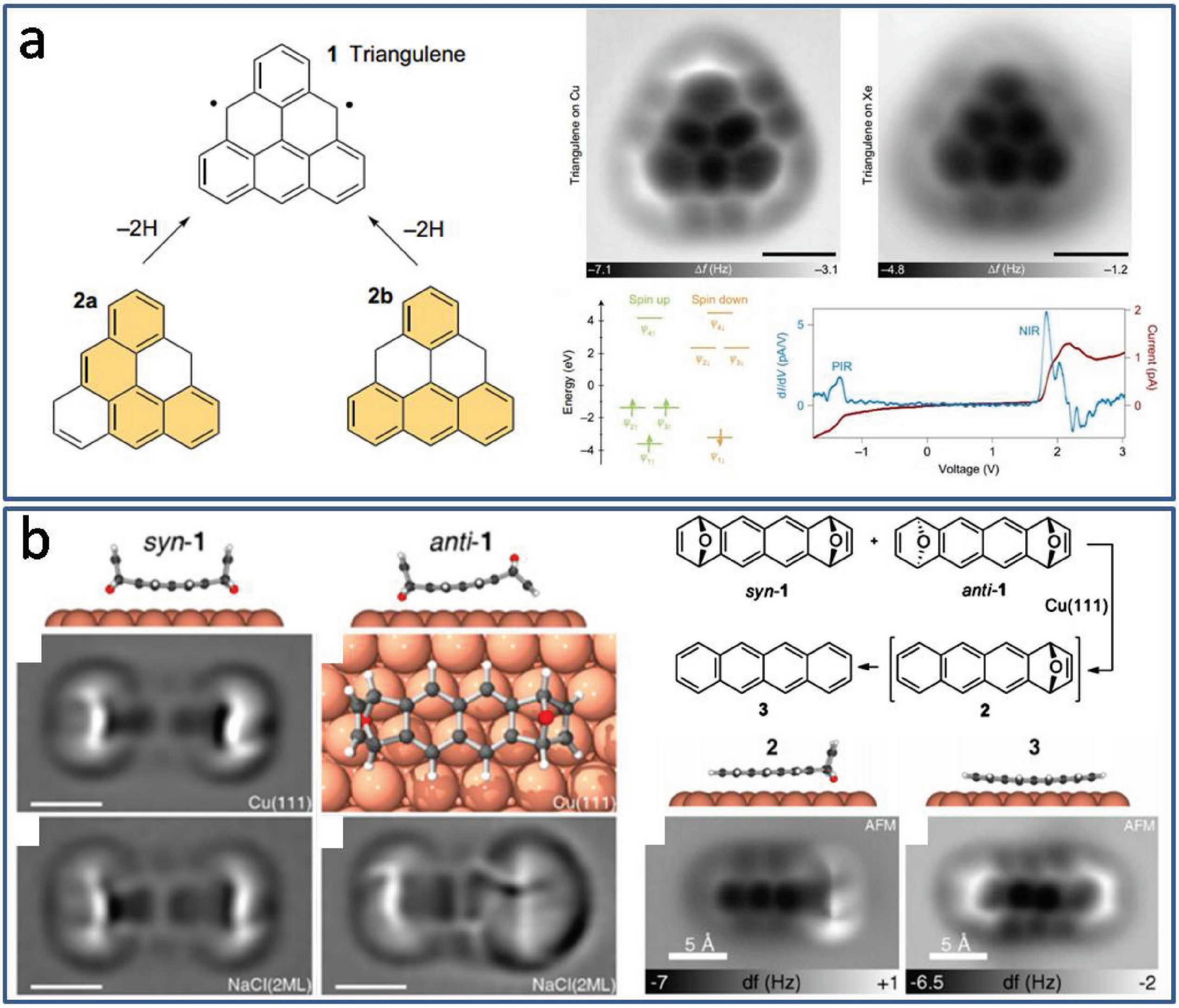

Figure 3. a) Generation of triangulene by STM tip manipulations. AFM images of triangulene and its energy-level scheme and scanning tunneling spectroscopy. Adapted with permission.[21] Copyright 2011, Nature Publishing Group. b) On-surface reduction of diepoxytetracenes to form genuine tetracene on Cu(111). Adapted with permission.[22] Copyright 2016, American Chemical Society.

3. On-Surface Synthesis of 1D Carbon Nanostructures

GNRs are considered to be promising candidates for further electronics since their bandgaps are sufficiently large for practical applications as digital electronics.[27] More importantly, the molecular structures of GNR including its topology, edge structure, width, and even atomic defects would have significant influences on its transport properties.[28] Meanwhile, a desirable control of their atomic structures still remains as a great challenge. Consequently, the rapid advancement of on-surface synthesis of specifically designed molecular precursors provides a promising route toward atomically precise graphene nanoribbons.

As illustrated in **Figure 4**a, Cai et al. first designed and reported a bottom-up method for the fabrication of atomically precise graphene nanoribbons.[29] After thermal sublimation of 10,10′-dibromo-9,9′-bianthryl precursor monomers onto a solid surface, the molecules are activated by removal of their halogen substituents, yielding biradical species. After the first thermal activation step, the biradical species diffuse across the surface and undergo radical addition reactions to form linear polymer chains. Then, the molecular chains are further annealed to induce a surface-assisted cyclodehydrogenation, and transform to the targeted GNRs with atomic precision.

This recipe has been widely utilized to synthesize GNRs supported on surfaces ever since the seminal work. We have summarized different kinds of GNRs formed by the bottom-up method as shown in **Table 1**. Substantial efforts have been devoted to the formation of GNRs with armchair edges including widths (N) of three (i.e., poly-p-phenylene), five, six, seven, nine, thirteen, fourteen, fifteen, and twenty-one carbon atoms. The main idea lies in a delicate choice of the precursors as the trigger of dehalogenative reaction followed by

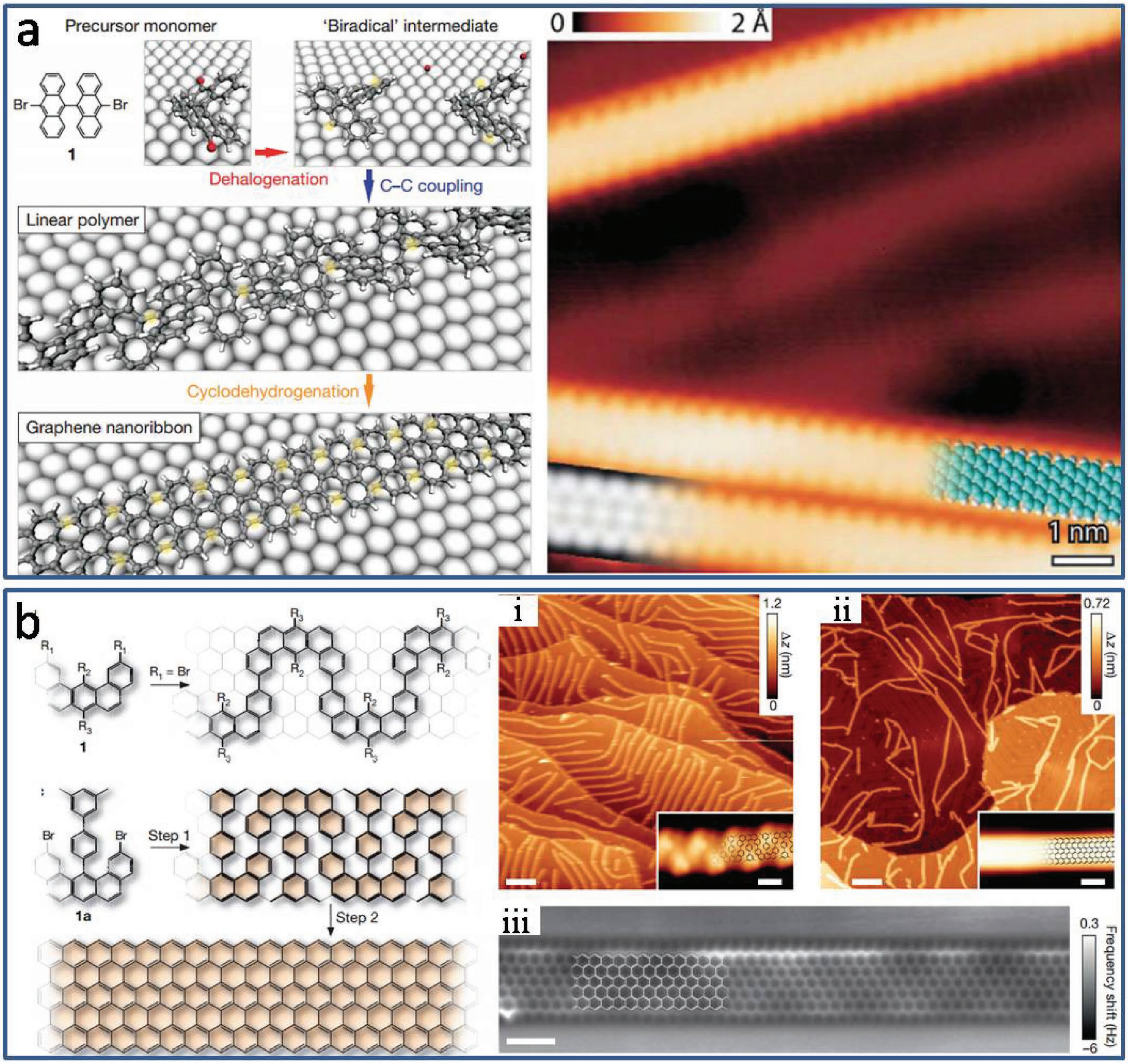

Figure 4. On-surface synthesis of armchair and zigzag graphene nanoribbons. a) Steps for surface-supported GNR synthesis and the STM image of the 7-AGNR on Au(111). Adapted with permission.[29] Copyright 2010, Nature Publishing Group. b) Synthetic strategy to GNRs with zigzag edges. STM images showing products of surface assisted C–C coupling and cyclodehydrogenation of the precursors, respectively. AFM image confirms the formation of the 6-ZGNRs. Adapted with permission.[50] Copyright 2016, Nature Publishing Group.

C–C coupling. It is more challenging to grow GNRs with a larger width due to the limitation of the size of the precursors aroused by their evaporation issues. It has also been demonstrated that N of 6, 14 and 21 could be fabricated via cross-dehydrogenative coupling of prealigned GNRs,[37,42] which sheds light on fabricating GNRs with larger widths. However, the crosslink processes are not easy to control, and GNRs of different width or GNRs not fully completed would exist on surfaces simultaneously. In addition, monomer design also provides routes towards the substitutional "doping" of GNR by replacing carbon atoms with heteroatoms, such as boron, sulfur, or nitrogen.[44–47] Remarkably, GNRs with zigzag edges are expected to have spin-polarized electronic edge states, which would be promising for spintronics. Recently, Ruffieux et al. described the bottom-up synthesis of GNRs with zigzag edge through the surface assisted polymerization and cyclodehydrogenation of specifically designed precursors (as shown in Figure 4b).[50]

In addition to the aforementioned GNRs, others with exotic edge structures or atomic structures within the chains could also be formed by selecting specially designed precursors. For instance, chevron type, chiral (3,1) and acene type GNRs are formed on surfaces (see ref. in Table 1). It is noteworthy that graphene-like nanoribbons with periodically embedded

Table 1. A summary of GNRs formed by on-surface synthesis strategies.

	Armchair			Zigzag	
Type	Substrate	Refs.	Type	Substrate	Refs.
N = 3	Cu(110), Cu(111), Ag(111), Au(111), Au(110)	[30–33]	6-ZGNR	Au(111)	[50]
N = 5	Au(111), Cu (111)	[34–36]		**Cove-edged**	
N = 6	Au(111)	[37]	Bischrysene based	Au(111)	[51]
N = 7	Au(111), Au(110), etc.	[29,38,39]		**Chevron**	
N = 9	Au(111)	[40]	Tetraphenyl triphenylene	Au(111), Ag(111)	[29]
N = 13	Au(111)	[41]	Nitrogen doped	Au(111)	[52,53]
N = 14	Au(111)	[42]	Fluorenone and chevron	Au(111)	[54]
N = 15	Au(111)	[43]		**Others**	
N = 21	Au(111)	[42]	Chiral (3,1)	Cu(111)	[55–57]
Boron-doped *N* = 7	Au(111)	[44–46]	4- and 8-membered ring	Au(111)	[58]
Sulfur-doped *N* = 7	Au(111)	[47]	Acene type	Au(111)	[59]
Edge-fluorinated *N* = 7	Au(111)	[48]	5/7-GNR	Au(111)	[60]
Edge-CN *N* = 7	Au(111)	[49]	7/14-GNR	Au(111)	[61,62]

four- and eight-membered rings have been synthesized via surface-assisted dehalogenation and cyclodehydrogenation of 1,6,7,12-tetrabromo-3,4,9,10-perylene-tetracarboxylic-dianhydride.[58] Graphene nanoribbon consisting of segments with alternating widths has been formed on the surface as well.[60–62]

The controlled synthesis of monodisperse "single-chirality" single-walled carbon nanotubes (SWCNTs) remains as a significant challenge as well, which hampers their extraordinary properties for numerous technological applications. As shown in **Figure 5**, Sanchez-Valencia et al. designed a bottom-up strategy toward the synthesis of single-chirality and essentially defect-free SWCNTs with lengths up to a few hundred nanometers.[63] First, a singly capped ultrashort (6,6) SWCNT seed was formed via surface-catalyzed cyclodehydrogenation of the designed precursor $C_{96}H_{54}$ on Pt(111). Then, the targeted nanotube was elongated by exposing to a carbon feedstock gas such as ethylene or ethanol at temperatures between 670 and 770 K. The formation of (6,6) SWCNT was identified by the high-resolution STM image, and Raman spectroscopy was used to determine its orientation as well as single chirality assessment.

The incorporation of acetylenic scaffoldings or sp-hybridized carbon provides an important route to fabricate novel carbon nanostructures/nanomaterials, which are predicted with extraordinary physicochemical properties. The most straightforward ideas represent the introduction of precursors with alkynyl groups. Recently, Sun et al. have fabricated an organometallic wire ($[-\mathrm{Cu}-\mathrm{C}-\mathrm{C}-]_n$) (i.e., metalated carbyne) by dehydrogenative of ethyne molecules and coupling with copper atoms on a Cu(110) surface under ultrahigh-vacuum

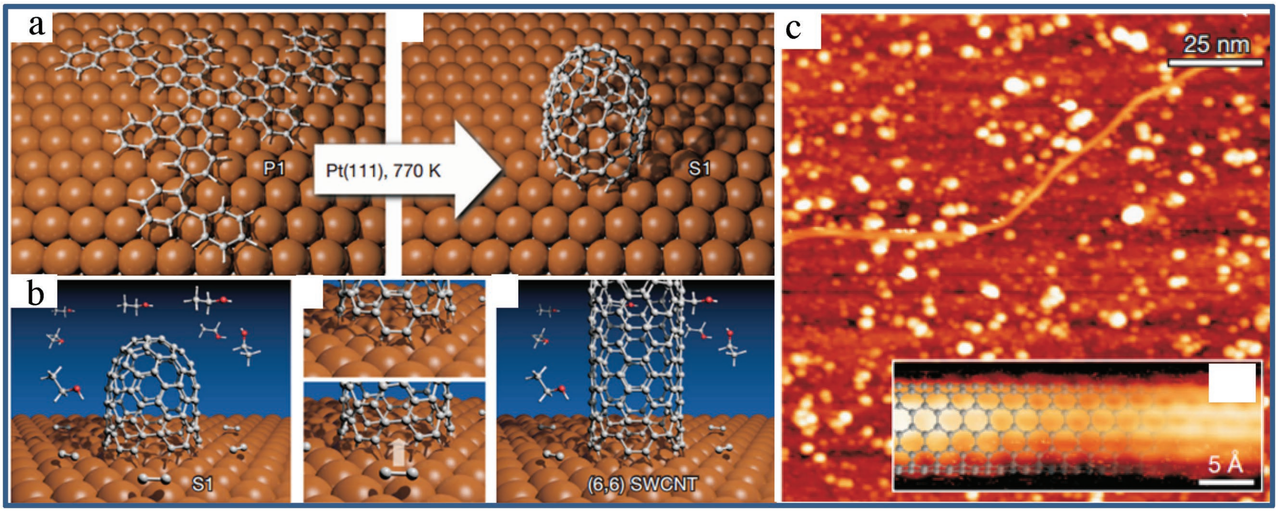

Figure 5. a,b) Synthetic route to single-walled carbon nanotubes, which is achieved by the formation of (6,6) SWCNT seeds followed by nanotube epitaxial elongation. c) The STM image identifies the (6,6) SWCNT. Adapted with permission.[63] Copyright 2014, Nature Publishing Group.

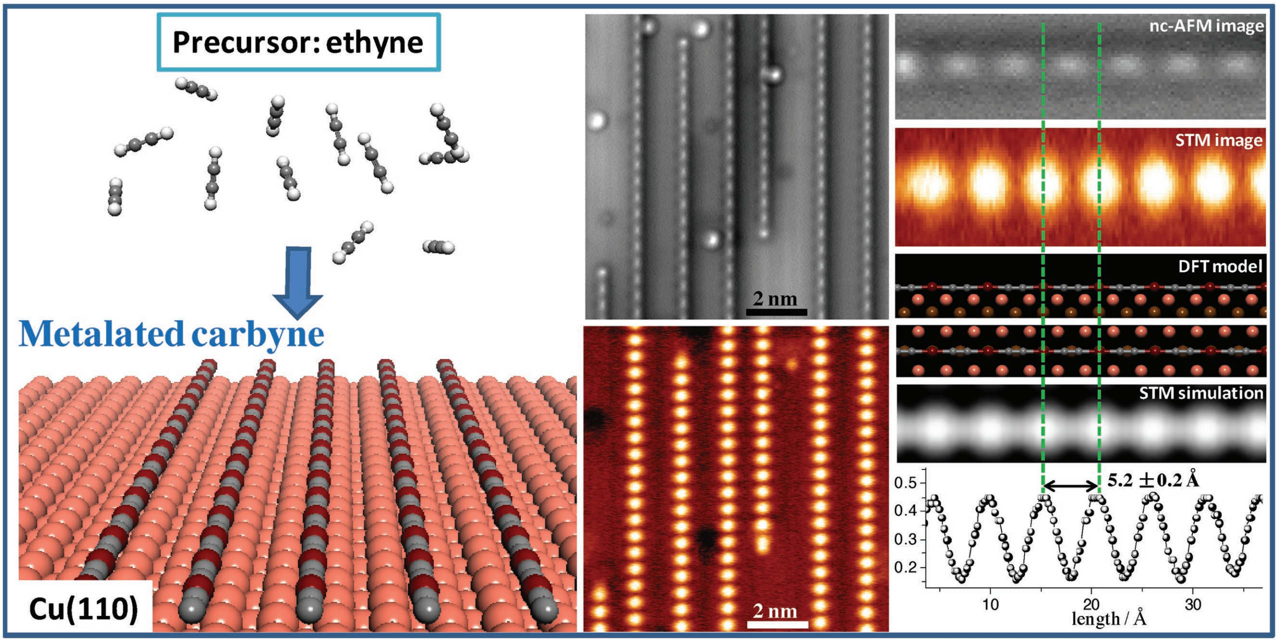

Figure 6. On-surface synthesis of organometallic carbon chains by dehydrogenative coupling of ethyne molecules and copper atoms on a Cu(110) surface. Adapted with permission.[64] Copyright 2016, American Chemical Society.

conditions (see **Figure 6**).[64] The chains grew along the anisotropic substrate and were found to extend to the submicron scale (with the longest ones up to ≈120 nm). Meanwhile, the same group formed a 1D molecular wire with acetylenic scaffoldings, as well as a C—Au—C organometallic chain (see **Figure 7**a).[65] Herein, they have designed the molecular precursors with terminal alkynyl bromide, and introduced the dehalogenative homocoupling reactions on the surface. This strategy

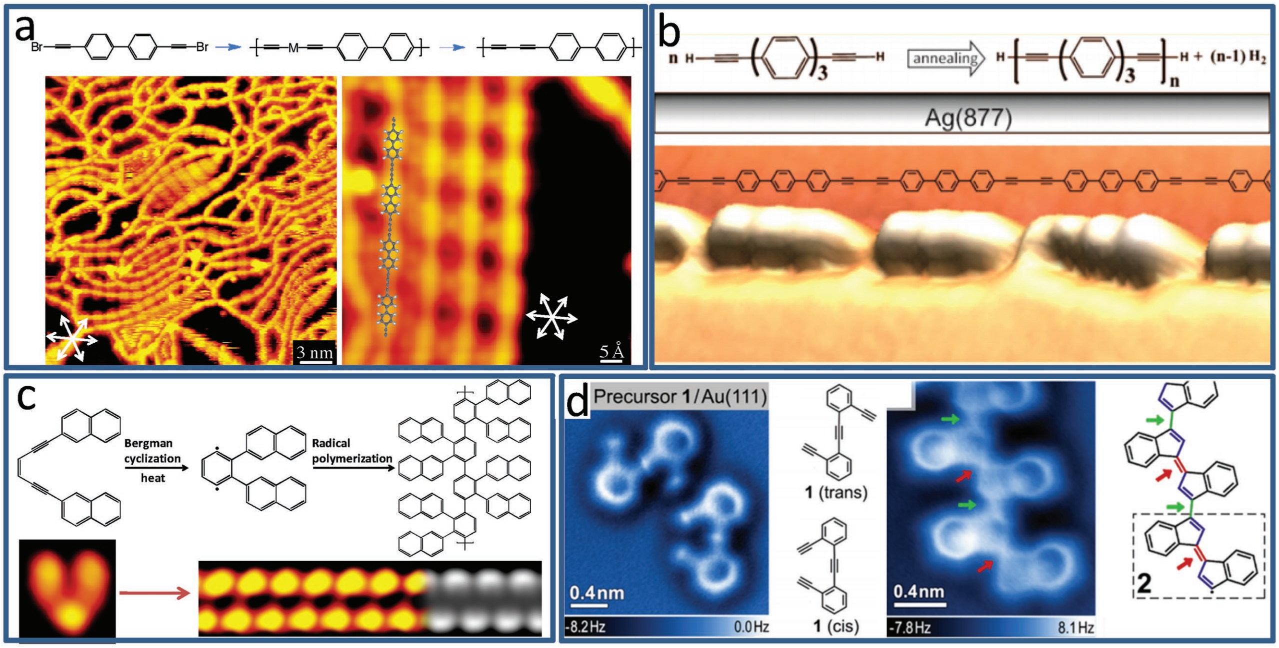

Figure 7. a) Molecular chains with acetylenic scaffoldings formed via dehalogenative homocoupling of terminal alkynyl bromides. Adapted with permission.[65] Copyright 2016, American Chemical Society. b) Molecular wire grown by the homocoupling of terminal alkyne along the step-edges of the Ag(877) vicinal surface. Adapted with permission.[67] Copyright 2014, American Chemical Society. c) On-surface formation of 1D polyphenylene chains through Bergman cyclization followed by radical polymerization on Cu(110). Adapted with permission.[69] Copyright 2013, American Chemical Society. d) A polyacetylene-type molecular chain was obtained through cooperative thermal enediyne cyclization followed by a step-growth polymerization. Adapted with permission.[70] Copyright 2014, American Chemical Society.

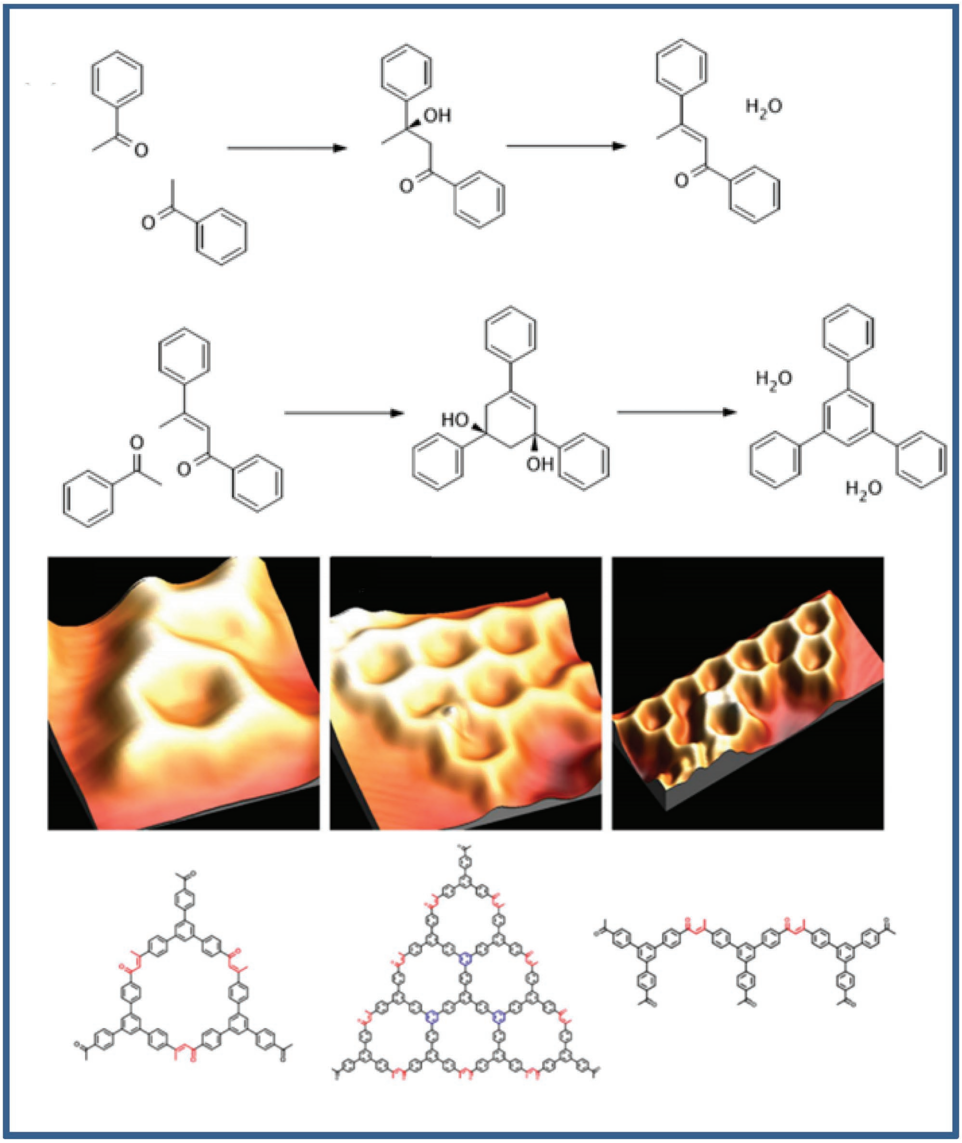

Figure 8. 2D conjugated covalent networks formed via dimerization and cyclotrimerization of acetyls on surfaces. Adapted with permission.[78] Copyright 2015, American Chemical Society.

surpasses the previously applied method of dehydrogenative homocoupling of terminal alkyne in producing less byproducts.[66] In this respect, Cirera et al. improved the chemoselectivity of the linking process with terminal alkyne by aligning molecules along the step edges of the Ag(877) vicinal surface (see Figure 7b).[67] Liu et al. explored the influences of the lattice plane of Ag surfaces in the reaction of terminal alkyne.[68] Beyond that, enediyne groups have also been used to construct molecular chains on surfaces. As shown in Figure 7c, Sun et al. constructed 1D polyphenylene chains through Bergman cyclization followed by radical polymerization on Cu(110).[69] While, a polyacetylene derivative was obtained through cooperative thermal enediyne cyclizations (see Figure 7d).[70] Besides, a plethora of 1D molecular chains have been formed on surfaces, mainly through the dehydrogenative C—C coupling reactions[71,72] or dehalogenative C—C coupling reactions.[73,74]

4. On-Surface Synthesis of 2D Carbon Nanostructures

2D covalent organic nanostructures are promising materials for future nanotechnological applications owing to their novel and adjustable electronic properties. On-surface synthesis has provided an unprecedented route toward the formation of an abundance of atomically precise surface nanostructures with highly chemical and mechanical stability. In this respect, seminal works as well as the most widely used surface reactions so far are Ullmann coupling of aryl halides on surfaces.[75–77] In this section, we review the recent progress in on-surface formation of 2D carbon nanostructures, with special focuses on non-Ullmann type reactions.

Besides Ullmann-type reactions on surfaces, other types of reaction have also been explored to construct 2D conjugated

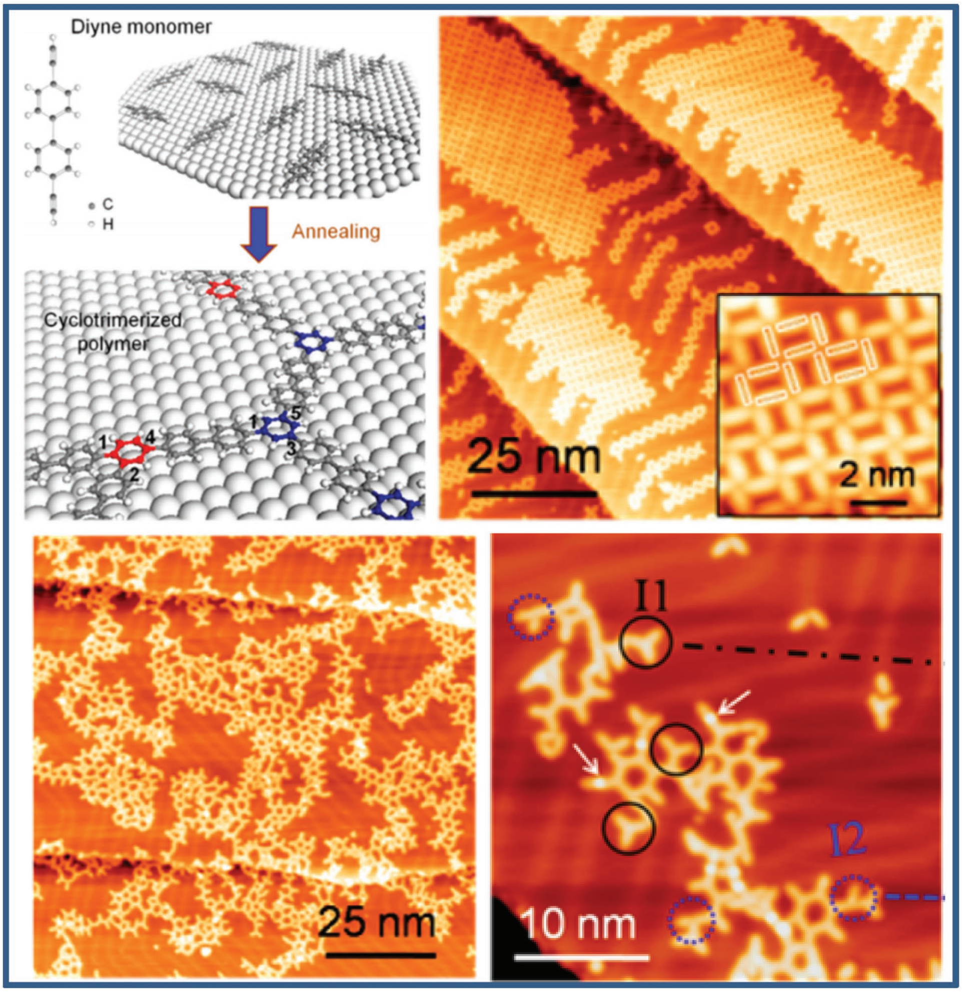

Figure 9. 2D conjugated networks formed by cyclotrimerization of alkynes. STM images at different annealing temperatures. Adapted with permission.[79] Copyright 2014, American Chemical Society.

polymers. As illustrated in **Figure 8**, Yang et al. have shown that 2D covalent networks were formed by forming an additional phenyl ring through cyclotrimerization of acetyls on a Ag(111) surface.[78] STM has been applied to study the reaction pathways and the products. With the aid of DFT calculations and XPS, they have further explored the underlying reaction mechanisms and identified the rate-limiting steps of the reaction as well as the side products. In line with the cyclotrimerization of acetyls, Zhou et al. have investigated the cyclotrimerization of alkynes.[79] A diyne monomer 4,4′-diethynyl-1,1′-biphenyl was designed, which has a two alkynyl groups terminated at the end of a diphenyl backbone (see **Figure 9**). After annealing the molecule-covered sample, the diyne molecules are polymerized, generating networks with branch and hexagonal structures presented by STM imaging. Very soon after their work, Liu et al. have studied the same reaction on the surface. In this case, they chose an aryl alkynes 1,3,5-tris-(4-ethynylphenyl)benzene with tri-topic functional groups. It turned out that the cyclotrimerization of this molecule proceeded with a higher selectivity, and resulted in 2D polyphenylene nanostructures exhibiting a honeycomb topology.[80]

Although a lot of works have been devoted in developing different surface reactions with the aim of constructing 2D nanomaterials, the long-range ordering of formed structures is still a challenge. The kinetic irreversibility of the formed structures usually leads to defects. As shown in **Figure 10**a, Eichhorn et al. have investigated the influences of different kinetic reaction parameters on the morphology and defects density of covalent networks obtained by Ullmann coupling on Au(111) using an iodine- and bromine-functionalized aromatic precursor.[81] The structural quality of the covalent networks was evaluated for different parameters including surface temperatures, heating rates, and deposition rates by statistical analysis of STM data. In addition, it is also noteworthy that Sun et al. have fabricated a graphdiyne-like structure as well as the corresponding C—Au—C organometallic porous structures by dehalogenative homocoupling of terminal alkynyl bromide on the Au(111) surface (see Figure 10b).[65] This strategy exhibits a better yield with respect to the formation of diyne moieties in comparison with the homocoupling of terminal alkynes.[82]

The direct C—H bond activation of aromatic groups represents an alternative route toward the C—C coupling reactions.

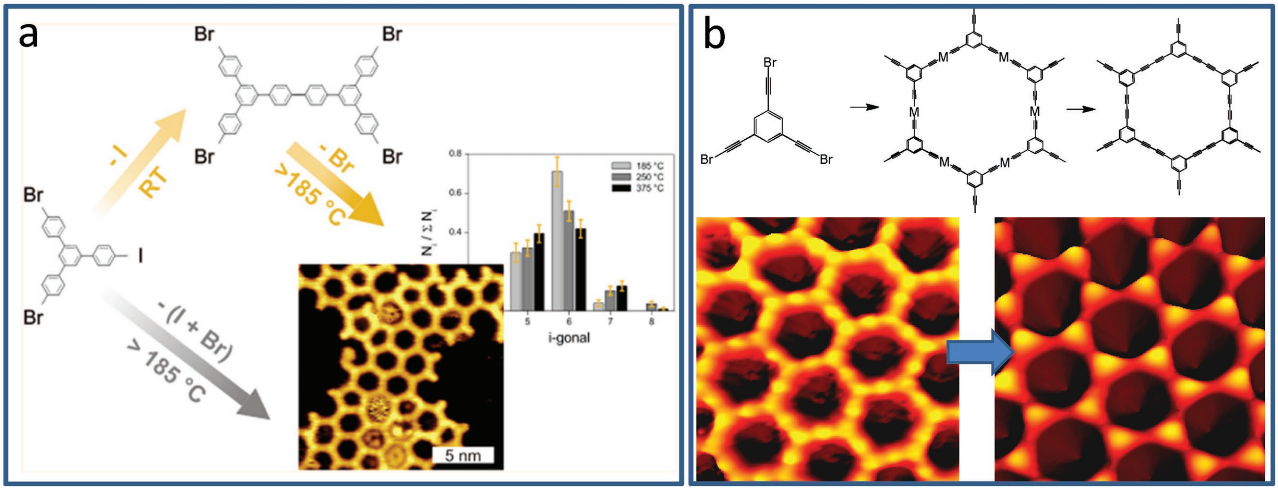

Figure 10. a) The influence of kinetic parameters on the morphology and quality of covalent networks are studied. Adapted with permission.[81] Copyright 2014, American Chemical Society. b) Molecular network with acetylenic scaffoldings formed via dehalogenative homocoupling of terminal alkynyl bromides. Adapted with permission.[65] Copyright 2016, American Chemical Society.

Sun et al. obtained a 2D polymer structure formed through direct C—H activation followed by an aryl–aryl coupling of a metalphthalocyanine.[83] By the introduction of hydroxyl directing groups to the precursors, Li et al. achieved selective ortho–ortho coupling on metal surfaces. A porous polyphenylene network is formed through the diselective ortho C—H bond activation on the Au(111) surface.[84]

5. Outlooks and Perspectives

We have reviewed a series of recently reported on-surface synthesis studies, which demonstrate the increasing interest toward the synthesis of novel low-dimensional carbon nanostructures with atomic precision. Especially, those carbon allotropes including carbyne and graphyne, which are proposed but yet to be synthesized, have aroused great attention from the surface science community. Although breakthroughs or advances have been achieved on the formation of novel carbon nanostructures by the on-surface synthesis method, a lot of questions and problems are yet to be addressed. For instance, the yield of this method is far below practical applications or mass production, which require their productions in macroscopic quantities. The reaction mechanisms are still not fully understood, although comprehensive experiments combined with DFT calculations have been performed. Moreover, the practical use or transfer of these carbon nanostructures from metal surfaces to other substrates, which are more technologically relevant still faces substantial challenges.

Acknowledgements

Q.S. and R.Z. contributed equally to this work. The authors acknowledge financial support from the National Natural Science Foundation of China (21473123, 21622307, 51641306, 51602221), Shanghai Municipal Natural Science Foundation (16ZR1438400, 17ZR1432200) and Key Basic Research Project of Shanghai (13JC1405300, 16JC1403300).

Conflict of Interest

The authors declare no conflict of interest.

Keywords

atomic precision, carbon nanostructures, graphene nanoribbons, low-dimensional materials, on-surface synthesis

Received: September 28, 2017
Revised: November 21, 2017

---

[1] V. Singh, D. Joung, L. Zhai, S. Das, S. I. Khondaker, S. Seal, *Prog. Mater. Sci.* **2011**, *56*, 1178.
[2] D. Jariwala, V. K. Sangwan, L. J. Lauhon, T. J. Marks, M. C. Hersam, *Chem. Soc. Rev.* **2013**, *42*, 2824.
[3] M. J. Allen, V. C. Tung, R. B. Kaner, *Chem. Rev.* **2009**, *110*, 132.
[4] A. Hirsch, *Nat. Mater.* **2010**, *9*, 868.
[5] Q. Fan, J. M. Gottfried, J. Zhu, *Acc. Chem. Res.* **2015**, *48*, 2484.
[6] F. Klappenberger, Y. Q. Zhang, J. Bjork, S. Klyatskaya, M. Ruben, J. V. Barth, *Acc. Chem. Res.* **2015**, *48*, 2140.
[7] G. Franc, A. Gourdon, *Phys. Chem. Chem. Phys.* **2011**, *13*, 14283.
[8] P. A. Held, H. Fuchs, A. Studer, *Chem. Euro. J.* **2017**, *23*, 5874.
[9] *Fullerenes: Chemistry, Physics, and Technology*, (Eds.: K. M. Kadish, R. S. Ruoff), Wiley-VCH, Weinheim, Germany **2000**.
[10] G. Otero, G. Biddau, C. Sánchez-Sánchez, R. Caillard, M. F. López, C. Rogero, F. J. Palomares, N. Cabello, M. A. Basanta, J. Ortega, J. Méndez, A. M. Echavarren, R. Pérez, B. Gómez-Lor, J. A. Martín-Gago, *Nature* **2008**, *454*, 865.
[11] K. Amsharov, N. Abdurakhmanova, S. Stepanow, S. Rauschenbach, M. Jansen, K. Kern, *Angew. Chem.* **2010**, *122*, 9582.
[12] N. Abdurakhmanova, A. Mueller, S. Stepanow, S. Rauschenbach, M. Jansen, K. Kern, K. Y. Amsharov, *Carbon* **2015**, *84*, 444.
[13] L. Pinardi, G. Otero-Irurueta, I. Palacio, J. I. Martinez, C. SanchezSanchez, M. Tello, C. Rogero, A. Cossaro, A. Preobrajenski, B. Gomez-Lor, A. Jancarik, I. G. Stara, I. Stary, M. F. Lopez, J. Mendez, J. A. Martin-Gago, *ACS Nano* **2013**, *7*, 3676.

[14] M. Treier, C. A. Pignedoli, T. Laino, R. Rieger, K. Müllen, D. Passerone, R. Fasel, *Nat. Chem.* **2011**, *3*, 61.
[15] P. H. Jacobse, A. van den Hoogenband, M. E. Moret, R. J. Klein Gebbink, I. Swart, *Angew. Chem.* **2016**, *128*, 13246.
[16] C. Rogers, C. Chen, Z. Pedramrazi, A. A. Omrani, H. Z. Tsai, H. S. Jung, S. Lin, M. F. Crommie, F. R. Fischer, *Angew. Chem., Int. Ed.* **2015**, *54*, 15143.
[17] Q. Fan, C. Wang, Y. Han, J. Zhu, W. Hieringer, J. Kuttner, G. Hilt, J. M. Gottfried, *Angew. Chem., Int. Ed.* **2013**, *52*, 4668.
[18] J. Lu, P. S. E. Yeo, C. K. Gan, P. Wu, K. P. Loh, *Nat. Nanotechnol.* **2011**, *6*, 247.
[19] D. M. Eigler, E. K. Schweizer, *Nature* **1990**, *344*, 524.
[20] S.-W. Hla, L. Bartels, G. Meyer, K.-H. Rieder, *Phys. Rev. Lett.* **2000**, *85*, 2777.
[21] N. Pavliček, A. Mistry, Z. Majzik, N. Moll, G. Meyer, D. J. Fox, L. Gross, *Nat. Nanotechnol.* **2017**, *12*, 308.
[22] J. Krüger, N. Pavliček, J. M. Alonso, D. Pérez, E. Guitián, T. Lehmann, G. Cuniberti, A. Groudon, G. Meyer, L. Gross, F. Moresco, D. Peña, *ACS Nano* **2016**, *10*, 4538.
[23] A. Mistry, B. Moreton, B. Schuler, F. Mohn, G. Meyer, L. Gross, A. Williams, P. Scott, G. Costantini, D. J. Fox, *Chem. - Eur. J.* **2015**, *21*, 2011.
[24] J. Krüger, F. Garcia, F. Eisenhut, D. Skidin, J. M. Alonso, E. Guitian, D. Perez, G. Cuniberti, F. Moresco, D. Peña, *Angew. Chem., Int. Ed.* **2017**, *56*, 11945.
[25] J. I. Urgel, H. Hayashi, M. Di Giovannantonio, C. A. Pignedoli, S. Mishra, O. Deniz, M. Yamashita, T. Dienel, P. Ruffieux, H. Yamada, R. Fasel, *J. Am. Chem. Soc.* **2017**, *139*, 11658.
[26] R. Zuzak, R. Dorel, M. Krawiec, B. Such, M. Kolmer, M. Szymonski, A. M. Echavarren, S. Godlewski, *ACS Nano* **2017**, *11*, 9321.
[27] L. Talirz, P. Ruffieux, R. Fasel, *Adv. Mater.* **2016**, *28*, 6222.
[28] T. Wassmann, A. P. Seitsonen, A. M. Saitta, M. Lazzeri, F. Mauri, *Phys. Rev. Lett.* **2008**, *101*, 096402.
[29] J. Cai, P. Ruffieux, R. Jaafar, M. Bieri, T. Braun, S. Blankenburg, M. Muoth, A. P. Seitsonen, M. Saleh, X. Feng, K. Mgllen, R. Fasel, *Nature* **2010**, *466*, 470.
[30] J. A. Lipton-Duffin, O. Ivasenko, D. F. Perepichka, F. Rosei, *Small* **2009**, *5*, 592.
[31] W. Wang, X. Shi, S. Wang, M. A. Van Hove, N. Lin, *J. Am. Chem. Soc.* **2011**, *133*, 13264.
[32] X. Zhou, F. Bebensee, Q. Shen, R. Bebensee, F. Cheng, Y. He, H. Su, W. Chen, G. Xu, F. Besenbacher, T. R. Linderoth, K. Wu, *Mater. Chem. Front.* **2017**, *1*, 119.
[33] K. J. Shi, D. W. Yuan, C. X. Wang, C. H. Shu, D. Y. Li, Z. L. Shi, X. Y. Wu, P. N. Liu, *Org. Lett.* **2016**, *18*, 1282.
[34] H. Zhang, H. Lin, K. Sun, L. Chen, Y. Zagranyarski, N. Aghdassi, S. Li, Q. Duhm, D. Zhong, Y. Li, K. Mullen, H. Fuchs, L. Chi, *J. Am. Chem. Soc.* **2015**, *137*, 4022.
[35] A. Kimouche, M. M. Ervasti, R. Drost, S. Halonen, A. Harju, P. M. Joensuu, J. Sainio, P. Liljeroth, *Nat. Commun.* **2015**, *6*, 10177.
[36] K. Sun, P. Ji, H. Zhang, K. Niu, L. Li, A. Chen, Q. Li, K. Mullen, L. Chi, *Faraday Discuss.* **2017**, *204*, 297.
[37] A. Basagni, F. Sedona, C. A. Pignedoli, M. Cattelan, L. Nicolas, M. Casarin, M. Sambi, *J. Am. Chem. Soc.* **2015**, *137*, 1802.
[38] M. Koch, F. Ample, C. Joachim, L. Grill, *Nat. Nanotechnol.* **2012**, *7*, 713.
[39] A. Batra, D. Cvetko, G. Kladnik, O. Adak, C. Cardoso, A. Ferretti, D. Prezzi, E. Molinari, A. Morgante, L. Venkataraman, *Chem. Sci.* **2014**, *5*, 4419.
[40] L. Talirz, H. Söde, T. Dumslaff, S. Y. Wang, J. R. Sanchez-Valencia, J. Liu, P. Shinde, C. A. Pignedoli, L. B. Liang, V. Meunier, N. C. Plumb, M. Shi, X. L. Feng, A. Narita, K. Müllen, R. Fasel, P. Ruffieux, *ACS Nano* **2017**, *11*, 1380.
[41] Y. C. Chen, D. G. De Oteyza, Z. Pedramrazi, C. Chen, F. R. Fischer, M. F. Crommie, *ACS Nano* **2013**, *7*, 6123.
[42] H. Huang, D. Wei, J. Sun, S. L. Wong, Y. P. Feng, A. H. C. Neto, A. T. S. Wee, *Sci. Rep.* **2012**, *2*, 983.
[43] N. Abdurakhmanova, N. Amsharov, S. Stepanow, M. Jansen, K. Kern, K. Amsharov, *Carbon* **2014**, *77*, 1187.
[44] E. Carbonell-Sanroma, P. Brandimarte, R. Balog, M. Corso, S. Kawai, A. Garcia-Lekue, S. Saito, S. Yamaguchi, E. Meyer, D. Sanchez-Portal, J. I. Pascual, *Nano Lett.* **2017**, *17*, 50.
[45] S. Kawai, S. Saito, S. Osumi, S. Yamaguchi, A. S. Foster, P. Spijker, E. Meyer, *Nat. Commun.* **2015**, *6*, 2098.
[46] R. R. Cloke, T. Marangoni, G. D. Nguyen, T. Joshi, D. J. Rizzo, C. Bronner, T. Cao, S. G. Louie, M. F. Crommie, F. R. Fischer, *J. Am. Chem. Soc.* **2015**, *137*, 8872.
[47] G. D. Nguyen, F. M. Tom, T. Cao, Z. Pedramrazi, C. Chen, D. J. Rizzo, T. Joshi, C. Bronner, Y. C. Chen, M. Favaro, S. G. Louie, F. R. Fischer, M. F. Crommie, *J. Phys. Chem. C* **2016**, *120*, 2684.
[48] H. Hayashi, J. Yamaguchi, H. Jippo, R. Hayashi, N. Aratani, M. Ohfuchi, S. Sato, H. Yamada, *ACS Nano* **2017**, *11*, 6204.
[49] E. Carbonell-Sanroma, J. Hieulle, M. Vilas-Varela, P. Brandimarte, M. Iraola, A. Barragan, J. Li, M. Abadia, M. Corso, D. Sanchez-Portal, D. Peña, J. I. Pascual, *ACS Nano* **2017**, *11*, 7355.
[50] P. Ruffieux, S. Wang, B. Yang, C. Sanchez-Sanchez, J. Liu, T. Dienel, L. Talirz, P. Shinde, C. A. Pignedoli, D. Passerone, T. Dumslaff, X. Feng, K. Mullen, R. Fasel, *Nature* **2016**, *531*, 489.
[51] J. Liu, B.-W. Li, Y.-Z. Tan, A. Giannakopoulos, C. Sanchez-Sanchez, D. Beljonne, P. Ruffieux, R. Fasel, X. Feng, K. Müllen, *J. Am. Chem. Soc.* **2015**, *137*, 6097.
[52] Y. Zhang, Y. Zhang, G. Li, J. Lu, X. Lin, S. Du, R. Berger, X. Feng, K. Müllen, H.-J. Gao, *Appl. Phys. Lett.* **2014**, *105*, 023101.
[53] J. Cai, C. A. Pignedoli, L. Talirz, P. Ruffieux, H. Söde, L. Liang, V. Meunier, R. Berger, R. Li, X. Feng, K. Müllen, R. Fasel, *Nat. Nanotechnol.* **2014**, *9*, 896.
[54] G. D. Nguyen, H. Z. Tsai, A. A. Omrani, T. Marangoni, M. Wu, D. J. Rizzo, G. F. Rodgers, R. R. Cloke, R. A. Durr, Y. Sakai, F. Liou, A. S. Aikawa, J. R. Chelikowsky, S. G. Louie, F. R. Fischer, M. F. Crommie, *Nat. Nanotechnol.* **2017**, *12*, 1077.
[55] C. Sánchez-Sánchez, T. Dienel, O. Deniz, P. Ruffieux, R. Berger, X. Feng, K. Müllen, R. Fasel, *ACS Nano* **2016**, *10*, 8006.
[56] P. Han, K. Akagi, F. Federici Canova, H. Mutoh, S. Shiraki, K. Iwaya, P. S. Weiss, N. Asao, T. Hitosugi, *ACS Nano* **2014**, *8*, 9181.
[57] F. Schulz, P. H. Jacobse, F. F. Canova, J. van der Lit, D. Z. Gao, A. van den Hoogenband, P. Han, R. J. M. Klein Gebbink, M. -E. Moret, P. M. Joensuu, I. Swart, P. Liljeroth, *J. Phys. Chem. C* **2017**, *121*, 2896.
[58] M. Liu, M. Liu, L. She, Z. Zha, J. Pan, S. Li, T. Li, Y. He, Z. Cai, J. Wang, Y. Zheng, X. Qiu, D. Zhong, *Nat. Commun.* **2017**, *8*, 14924.
[59] H. Sakaguchi, S. Song, T. Kojima, T. Nakae, *Nat. Chem.* **2017**, *9*, 57.
[60] P. H. Jacobse, A. Kimouche, T. Gebraad, M. M. Ervasti, J. M. Thijssen, P. Liljeroth, I. Swart, *Nat. Commun.* **2017**, *8*, 119.
[61] S. Wang, N. Kharche, E. Costa Girão, X. Feng, K. Müllen, V. Meunier, R. Fasel, P. Ruffieux, *Nano Lett.* **2017**, *17*, 4277.
[62] C. Ma, L. Liang, Z. Xiao, A. A. Puretzky, K. Hong, W. Lu, V. Meunier, J. Bernholc, A. P. Li, *Nano Lett.* **2017**, *17*, 6241.
[63] J. R. Sanchez-Valencia, T. Dienel, O. Groning, I. Shorubalko, A. Mueller, M. Jansen, K. Amsharov, P. Ruffieux, R. Fasel, *Nature* **2014**, *512*, 61.
[64] Q. Sun, L. Cai, S. Wang, R. Widmer, H. Ju, J. Zhu, L. Li, Y. He, P. Ruffieux, R. Fasel, W. Xu, *J. Am. Chem. Soc.* **2016**, *138*, 1106.
[65] Q. Sun, L. Cai, H. Ma, C. Yuan, W. Xu, *ACS Nano* **2016**, *10*, 7023.
[66] H. Y. Gao, H. Wagner, D. Zhong, J. H. Franke, A. Studer, H. Fuchs, *Angew. Chem., Int. Ed.* **2013**, *52*, 4024.

[67] B. Cirera, Y. Q. Zhang, J. Bjork, S. Klyatskaya, Z. Chen, M. Ruben, J. V. Barth, F. Klappenberger, *Nano Lett.* **2014**, *14*, 189.

[68] J. Liu, Q. Chen, L. Xiao, J. Shang, X. Zhou, Y. Zhang, Y. Wang, X. Shao, J. Li, W. Chen, G. Q. Xu, H. Tang, D. Zhao, K. Wu, *ACS Nano* **2015**, *9*, 6305.

[69] Q. Sun, C. Zhang, Z. Li, H. Kong, Q. Tan, A. Hu, W. Xu, *J. Am. Chem. Soc.* **2013**, *135*, 8448.

[70] Riss, S. Wickenburg, P. Gorman, L. Z. Tan, H.-Z. Tsai, D. G. de Oteyza, Y.-C. Chen, A. J. Bradley, M. M. Ugeda, G. Etkin, S. G. Louie, F. R. Fischer, M. F. Crommie, *Nano Lett.* **2014**, *14*, 2251.

[71] D. Zhong, J. Franke, S. K. Podiyanachari, T. Blamker, H. Zhang, G. Kehr, G. Erker, H. Fuchs, L. Chi, *Science* **2011**, *334*, 213.

[72] Q. Sun, C. Zhang, H. Kong, Q. Tan, W. Xu, *Chem. Commun.* **2014**, *50*, 11825.

[73] J. Liu, T. Dienel, J. Liu, O. Groening, J. Cai, X. Feng, K. Müllen, P. Ruffieux, R. Fasel, *J. Phys. Chem. C* **2016**, *120*, 17588.

[74] C. Bombis, F. Ample, L. Lafferentz, H. Yu, S. Hecht, C. Joachim, L. Grill, *Angew. Chem., Int. Ed.* **2009**, *48*, 9966.

[75] M. Bieri, M. Treier, J. Cai, K. Aït-Mansour, P. Ruffieux, O. Gröning, P. Gröning, M. Kastler, R. Rieger, X. Feng, K. Müllen, R. Fasel, *Chem. Commun.* **2009**, 6919.

[76] R. Gutzler, H. Walch, G. Eder, S. Kloft, W. M. Heckl, M. Lackinger, *Chem. Commun.* **2009**, 4456.

[77] L. Grill, M. Dyer, L. Lafferentz, M. Persson, M. V. Peters, S. Hecht, *Nat. Nanotechnol.* **2007**, *2*, 687.

[78] B. Yang, J. Björk, H. P. Lin, X. Q. Zhang, H. M. Zhang, Y. Y. Li, J. Fan, Q. Li, L. F. Chi, *J. Am. Chem. Soc.* **2015**, *137*, 4904.

[79] H. Zhou, J. Liu, S. Du, L. Zhang, G. Li, Y. Zhang, B. Z. Tang, H. J. Gao, *J. Am. Chem. Soc.* **2014**, *136*, 5567.

[80] J. Liu, P. Ruffieux, X. Feng, K. Müllen, R. Fasel, *Chem. Commun.* **2014**, *50*, 11200.

[81] J. Eichhorn, D. Nieckarz, O. Ochs, D. Samanta, M. Schmittel, P. J. Szabelski, M. Lackinger, *ACS Nano* **2014**, *8*, 7880.

[82] Y. Q. Zhang, N. Kepcija, M. Kleinschrodt, K. Diller, S. Fischer, A. C. Papageorgiou, F. Allegretti, J. Bjork, S. Klyatskaya, F. Klappenberger, M. Ruben, J. V. Barth, *Nat. Commun.* **2012**, *3*, 1286.

[83] Q. Sun, C. Zhang, L. Cai, L. Xie, Q. Tan, W. Xu, *Chem. Commun.* **2015**, *51*, 2836.

[84] Q. Li, B. Yang, H. Lin, N. Aghdassi, K. Miao, J. Zhang, H. Zhang, Y. Li, S. Duhm, J. Fan, L. Chi, *J. Am. Chem. Soc.* **2016**, *138*, 2809.