Bottom-Up Fabrication of Two-Dimensional Polymers on Solid Surfaces

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Abstract Two-dimensional polymers are a novel class of future materials that are not purely hypothetical anymore, but have not been realized in full yet. A promising and versatile synthetic approach is the bottom-up fabrication by polymerization of monomers into covalently cross-linked nanostructures on solid surfaces. This chapter introduces the synthetic approach consisting of monomer deposition and activation, and describes a typical characterization scheme by established surface science techniques—high-resolution Scanning Tunneling Microscopy for structures and X-ray Photoelectron Spectroscopy for chemical state. The coupling chemistry is largely predetermined by monomer functionalization and various coupling reactions can be utilized to achieve cross-linking on surfaces. A major aim of this chapter is to compare and discuss the most popular interlinking chemistry and to highlight important implications when classical reactions are transferred from a beaker to a solid surface. The most important distinction is whether coupling proceeds irreversibly and remains kinetically controlled or whether thermodynamical control is possible. Ullmann coupling is a prominent example for an irreversible reaction. Recent achievements with focus on defect formation as well as the occurrence and utility of organometallic intermediates are discussed. Long-range ordered covalent organic frameworks were demonstrated based on boronic acid condensation. In this context, emphasis will be put on the importance of bond reversibility. Moreover, coupling reactions of terminal alkynes are introduced, and both possibilities and limitations are illustrated by referring to recent examples.

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1   Motivation and Aim

Molecular self-assembly has been studied on surfaces for almost three decades now. Although this research could already be considered as a first liaison between surface science and organic chemistry, this relationship grew more intense in 2007–2008 when the two seminal papers by Grill et al. and Porte et al. on Ullmann coupling and boronic acid condensation indicated that solid surfaces may also be an advantageous venue for coupling reactions between comparatively large organic molecules [1, 2]. This had at least two implications: On the one hand, the whole tool-box of microscopic and spectroscopic surface science techniques became available to study the progression, intermediates, and products of chemical reactions. On the other hand, the apparent templating effect of surfaces by confinement of the reacting species in two dimensions has ignited ideas to use "flatlands" for the synthesis of extended 2D networks or ultimately for the fabrication of novel 2D materials. It is intriguing to compare self-assembled monolayers (SAMs) on surfaces with graphene, the most prominent 2D material. As illustrated in Fig. 1, graphene is extremely stable and the strong coupling between its carbon atoms by covalent bonds promotes the ability to conduct electrons, not to mention the unique electronic band structure and the unprecedented charge carrier mobilities. The properties of graphene, however, are mostly predetermined by its unalterable structure, and an atomically precise modification remains extremely challenging. On the other hand, SAMs are structurally and chemically extremely versatile, owing to the diversity and variability of its constituents, the organic molecules. Yet, the typical intermolecular bonds that stabilize these monolayers, i.e. van-der-Waals, hydrogen, or metal coordination bonds, are relatively weak. This not only accounts for the comparatively low chemical, mechanical, and thermal stability of SAMs, but also precludes electronic transport across these structures. This direct comparison naturally sets the goal of getting the best of both worlds—versatility and stability—
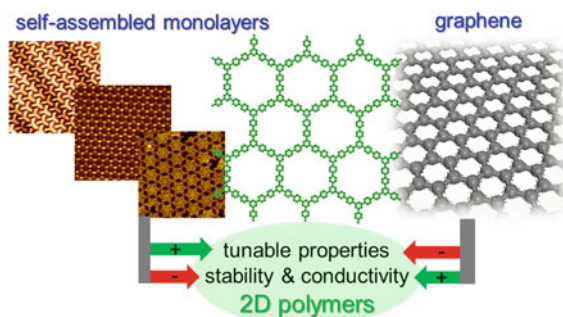

Fig. 1 SAMs versus graphene. Major advantages of SAMs are tunability and versatility which in turn are disadvantages of graphene. On the contrary, high stability and conductivity are application-relevant properties of graphene, but substantial drawbacks of SAMs. Both advantages are united in 2D polymers that bridge these two materials

by upgrading SAMs to two-dimensional (2D) polymers through covalent cross-linking. The terminology of the field has not settled yet, so 2D polymers are not rigorously defined. Distinctions could be made concerning the degree of structural order or the thickness—one atom versus one monomeric unit. Nevertheless, the materials which are the ultimate goal of the subsequently described endeavors would be defined as organic, fully covalently cross-linked networks which are only one atom thick and crystalline, i.e., exhibit long-range order and translational symmetry. The pursued synthetic approach toward 2D polymers is on-surface polymerization, where the coupling reactions are inspired by synthetic organic chemistry and the preparation and characterization tools are provided by surface science.

2 Typical Approach

A scheme of the typical approach for on-surface polymerization experiments is shown in Fig. 2 and comprises three steps: deposition, activation, and characterization. All individual steps can be carried out either under ambient or ultra-high vacuum (UHV) conditions. The benefit of working under ambient conditions is the low experimental effort, but this approach can suffer from limitations, e.g. concerning the usage of more reactive surfaces. Deposition under ambient conditions is typically performed from solution by drop-casting or spin-coating. Albeit relatively straightforward, sample homogeneity can still be a challenge.

Deposition in UHV is typically performed through the vapor phase of the compound. Smaller molecules with sufficiently high vapor pressure at room temperature can just be dosed through a leak valve, for compounds with larger sublimation enthalpies standard deposition sources with heated crucibles (Knudsen
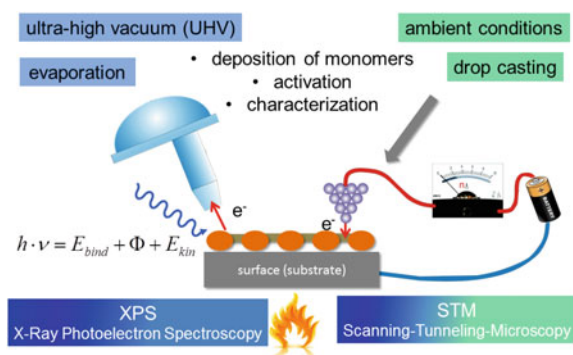

Fig. 2 Illustration of the typical experimental approach consisting of the three steps: deposition, activation, and characterization. Deposition and activation can both be conducted under UHV (*blue*) and ambient (*green*) conditions. Similarly, STM can be carried out in both environments, whereas XPS measurements are restricted to UHV, but are applicable to ex situ prepared samples

cells) are used. Limitations can arise for both deposition methods: solution deposition can be limited by low solubility, especially for larger molecules, whereas the reactivity of a compound can preclude thermal sublimation. Heating the crucible initiates a kinetic competition between sublimation and reaction. Depending on the respective enthalpies or activation barriers, reactions in the crucible can become favored, leading to the formation of larger aggregates that cannot be sublimed anymore.

Thermal annealing is the most common method for activating reactions on surfaces. However, alternative means of activation include irradiation with electrons—globally by an electron gun or locally by an STM tip—or energetic light. Depending on the reactivity of the system, thermal energy at room temperature can already be sufficient; hence, further annealing is not needed. Again external energy input activates two competing processes, i.e., the intended reaction on the surface, but also desorption from the surface. A typical solution to this "desorption problem" is increasing the adsorption energy of the monomers by enlarging the size of the organic backbone or using already preformed dimers, trimers etc. instead of monomers. However, by the same token the temperature required for deposition via sublimation increases. Accordingly, a compromise concerning the monomer size has to be found, where deposition via sublimation is still possible, and thermal activation of the polymerization on the surface is not impaired by desorption. In principle, it is also possible to work with protecting groups for sublimation and subsequent deprotection on the surface or to use more sophisticated deposition techniques for thermally instable compounds as electrospray ionization. It is noteworthy, that the reactivity arises from the specific combination of monomer and surface. This was nicely demonstrated by the example of alkanes on Au(110), where even the combination of relatively inert molecules with a relatively noble surface gave rise to unexpected coupling reactions [3].

For characterization mostly typical surface science techniques are used. Since on-surface polymerization has largely been developed from the self-assembly community, scanning tunneling microscopy (STM) is one of the favorite characterization tools. Molecular resolution can relatively easily be accomplished with widely available instruments, and imaging in real space facilitates a direct structure assessment. Moreover, in many cases, STM derived inter- or intramolecular distances already facilitate unambiguous verification of covalent coupling. In this context, it is particularly important that STM is not restricted to long-range ordered structures, because the covalent networks are in most cases less well-ordered than their supramolecular counterparts and exhibit high defect densities. The basic STM sample requirement of electrical conductivity is so far not a serious limitation, as for many coupling reactions the catalytic activity of metals is indispensable. Nevertheless, insulator surfaces are particularly interesting, especially for electronic transport measurements through the covalent nanostructures. On insulators, not only the reaction mechanisms can be expected to be very different, but also more sophisticated tools as non-contact atomic force microscopy (NC-AFM) become necessary.

Even though formation of new covalent bonds is often concluded from distance measurements in STM images, a complementary, chemically more sensitive characterization can be quite useful. Therefore, X-ray photoelectron spectroscopy (XPS) is ideally suited: Chemical core level shifts can unambiguously prove the proposed reaction or facilitate identification of the chemical state, especially when STM images are inconclusive. Moreover, the global character of XPS efficiently leads to solid statistical conclusions that are cumbersome to derive from local STM data. This is particularly useful for studying the progression of a reaction, e.g. the ratio between reacted and unreacted monomers in dependence of a specific activation protocol. At the moment, alternative spectroscopic techniques are less commonly used, despite their potential to provide additional complementary information. In particular, vibrational spectroscopy can also reveal the formation of new bonds or molecular groups. For instance, ex situ Raman spectroscopy was successfully employed to verify the formation of atomically precise graphene nano-ribbons [4]. Also first steps to access the electronic structure were taken by scanning tunneling spectroscopy and photoelectron spectroscopy experiments [5].

At present, the lack of long-range order in most covalent networks precludes the use of surface-sensitive diffraction techniques as low electron energy diffraction (LEED). Such experiments facilitate a very efficient and reliable structural characterization on a more global scale and would increase the precision of structural data. Furthermore, the epitaxial relation between covalent networks and supporting surface could easily be derived. More sophisticated techniques as Spot-Profile Analysis LEED may even give access to a global characterization of domain sizes. The recent advancements of structural quality will also bring LEED experiments on covalent nanostructures within reach.

3 Coupling Reactions

The volume of organic chemistry textbooks impressively demonstrates the richness and versatility of suitable functional groups and reactions for chemical coupling. A distinction can be made between homo- and crosscoupling, i.e., whether the same or different molecular species react with each other. Crosscouplings are much more versatile, but their implementation in surface chemistry remains challenging. Co-deposition of two different monomers in a stoichiometric ratio may be cumbersome, but is not a principal problem. However, both functional groups involved in crosscoupling are reactive and very often have a pronounced affinity for homocoupling which is difficult to fully suppress. In synthetic organic chemistry, a kinetic competition between different coupling reactions results in a lower yield, but on surfaces it hampers the formation of ordered networks. Nevertheless, first examples such as, for instance, Sonogashira coupling of iodobenzene and phenylacetylene was demonstrated on Au(111) [6]. The art is finding reaction conditions, i.e., surfaces, coverages, temperatures, deposition sequences, etc. that exclusively promote crosscoupling.

A further distinction can be made between reactions that can become reversible under suitable conditions or remain irreversible in any event. Condensation where a smaller molecule is formed and eliminated during the coupling is a prototypical type of possibly reversible reaction. An example is the release of H_2O during the self-condensation (dehydration) of boronic acids or the Schiff base reaction. According to Le Chatelier's principle, increasing the amount of H_2O in the system shifts the chemical equilibrium toward the unreacted starting material. In other words, a water atmosphere induces bond reversibility, and hence promotes error correction which is so far considered a necessity for the growth of long-range ordered structures of any kind. A more detailed description of boronic acid condensation on surfaces is provided in the next section. Ullmann coupling is a prominent example for an irreversibly proceeding coupling reaction on surfaces. The newly formed bonds are kinetically inert and cannot be opened up again under normal reaction conditions. This implies that Ullmann polymerization is kinetically controlled and any type of error correction mechanism is absent. Consequently, the structural quality is significantly lower than for SAMs, or the networks can even be entirely irregular, respectively. The dimensionality of the targeted covalent nanostructure plays an important role here: 1D structures as graphene nano-ribbons or polyphenylene chains do not suffer from high defect densities, because the monomers are just stringed together and this binding motif does not allow for topological defects. 2D networks, however, have many more possibilities to form defects, rendering the growth of long-range ordered structures based on irreversible coupling reactions truly challenging or even impossible.

4 Boronic Acid Condensation

The introduction of covalent organic frameworks (COF)—purely organic crystalline porous materials based on covalently cross-linked organic entities—by Yaghi and co-workers initiated a new and ever growing research direction [7, 8]. COFs are exclusively composed of light elements and exhibit high permanent porosities. This leads to ultralow densities which render these materials particularly promising for mobile gas storage applications. Most COFs exhibit a layered structure comparable to graphite, i.e. covalent bonds within the layers, whereas relatively weak interlayer bonds mediate a defined stacking. The first COFs were obtained by either the self-condensation of 1,4-benzene diboronic acid (BDBA) into COF-1 or the co-condensation with hexahydroxytriphenylene (HHTP) into COF-5 [7]. X-ray powder diffractometry revealed a high degree of crystallinity that was attributed to slightly reversible reaction conditions in the solvothermal synthesis. Apparently, the layered COF structure was inspiring for surface scientists, and Porte et al. were the first to demonstrate boronic acid coupling on Ag(111) [1]. Even though the BDBA monomer is only ditopic, the resulting networks are fully cross-linked in two dimensions. The reason can be understood by means of the reaction scheme for para-diboronic acids in Fig. 3a illustrating the cyclocondensation of three
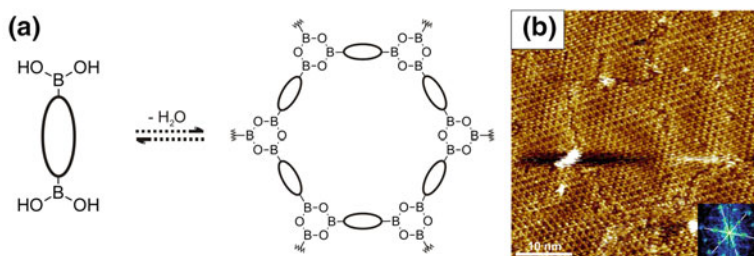
Fig. 3 a Reaction scheme of the self-condensation of para-diboronic acids into 2D COFs. **b** STM image of a 2D COF-1 monolayer synthesized from BDBA on graphite(0001) under reversible reaction conditions. The *inset* shows the corresponding FFT. Reprinted with permission from Refs. [12, 13]. Copyright 2012 and 2011 American Chemical Society

monomers: three boronic acid groups form a B_3O_3 boroxine ring, whereby three water molecules are released. Detailed atomistic simulations of the polymerization on Ag(111) suggest coupling via an intermediate dimer and propose an overall endothermic reaction [9]. The driving force of the boronic acid polycondensation is the entropy gain through the water release. Boronic acid condensation on surfaces was first demonstrated under UHV conditions, where the released water is immediately removed from the system by the vacuum pumps [1]. In the absence of gaseous water, boronic acid condensation proceeds irreversibly, i.e. without the possibility for error correction, resulting in less regular networks with many defects. To improve the networks, Porte et al. systematically studied the dependence between structural quality and reaction parameters, e.g., different metal surfaces, temperatures, and deposition rates [10]. For a meaningful comparison and solid conclusions, a quantitative assessment of the structural quality becomes necessary. For rather irregular networks, a statistical analysis of STM data is most appropriate. An elaborate statistical analysis based on the minimal spanning tree revealed that in UHV the best boronic acid networks could be grown on silver surfaces by working with higher deposition rates [10].

Yet, the key to structural perfection is taking advantage of bond reversibility. For boronic acid condensation this means that the polymerization has to be carried out in a water atmosphere. So far it is not quantitatively known how much water is actually required. From own experiments, we conclude that a water partial pressure in the order of 10^{-6} mbar—the highest bearable in a UHV system—is not sufficient. Consequently, ambient conditions are the best environment to realize reversible reaction conditions. In this synthetic approach, the monomers are typically deposited from solution and the polymerization is activated in a small autoclave or reactor by heating to temperatures of 100–150 °C. The reversibility inducing water can be supplied either by adding pure liquid water or by the thermally activated release of crystal water from hydrates [11]. For instance, blue vitriol ($CuSO_4 \cdot 5H_2O$) reversibly releases part of its crystal water already around 100 °C. A representative STM image of a 2D COF obtained by reversible condensation of BDBA on graphite is depicted in Fig. 3b. One interesting aspect of this approach is

that bond reversibility can be switched on and off at will, just by the presence or absence of water. Even though no in situ microscopic studies of the polymerization are available, it appears reasonable that a slow transition from the fully reversible (non-bonding) to the irreversible regime is an important ingredient for high-quality networks, in order to always remain close to equilibrium. This transition is achieved by reducing the water partial pressure and/or the temperature. Water can be removed by working in an open system or when using $CuSO_4 \cdot 5H_2O$ as a water source, by rehydration at lower temperature.

In bulk COF synthesis, almost infinite structural versatility is achieved by co-condensation of boronic acids with diols. Proof of principle for this co-condensation on surfaces has already been provided with HHTP and BDBA in the seminal UHV work [1]. However, generally applicable protocols of how this crosscoupling on surfaces can yield high-quality networks have so far not been developed. A promising approach to bimolecular covalent networks is deposition of one monomer onto the surface and supplying the other monomer through the vapor phase, as nicely demonstrated for the co-condensation of amines and aldehydes [14]. In case the reactor has to be heated to either activate the reaction or to increase the vapor pressure of the compound in the gas phase, desorption of the compound on the surface has to be prevented by a high adsorption energy. Moreover, it is important to suppress homocoupling on the surface, i.e., by adsorbing a relatively inert compound.

Yet, structural versatility can already be achieved with the self-condensation of para-diboronic acids. For instance, tailoring of pore sizes by varying the length of the organic backbone has been demonstrated with a homologous series of diboronic acids with backbones ranging from phenyl to quaterphenyl [12]. Similarly, pyrene-based 2D COFs indicated possibilities to tune the chemical nature of the organic scaffold. A serious limitation for solution-based approaches, however, arises from the limited solubility of larger molecules. Deposition of larger boronic acids by vacuum sublimation is also not possible, because the relatively high sublimation temperatures required for larger monomers already activate the preferential polymerization in the crucible of the deposition source. Alternative concepts would be using protecting groups for sublimation and subsequent deprotection on the surface [15]. On the other hand, the high reactivity of boronic acids can also be used for the "in-crucible" synthesis of more complex molecules from abundantly available smaller boronic acids as p-bromobenzene boronic acid and 3,5-dibromophenyl boronic acid [16, 17]. Already these smaller boronic acids are too large for thermal sublimation. Accordingly, when heating the crucible, three monomers condensate into the corresponding trimer with a newly formed boroxine ring as threefold symmetry center. These compounds are then sufficiently inert for thermal sublimation.

The reversibility of boronic acid condensation in a water atmosphere is a blessing and a curse. On one hand, it provides the grounds for the synthesis of long-range ordered covalently cross-linked networks that feature the anticipated thermal and mechanical stability. On the other hand, not only the surface-supported 2D COFs but also their bulk counterparts degrade under ambient conditions, due to humidity-induced bond breaking.

Moreover, it is instructive to study the electronic properties of boronic acid-derived COFs. Experimental band structure data are unfortunately not available; however, density functional theory (DFT) simulations for a COF-1 monolayer suggest a semiconducting behavior with a band gap in the order of ~ 3 eV [17]. Apart from the band gap, the dispersion relation is equally important. The 2D COF-1 bands come out essentially flat, indicating localized electrons with high effective mass. The reason for this is the insulating effect of the boroxine rings which effectively decouple the phenyl rings from each other. In other words, any 2D COF synthesized by boronic acid condensation will not be suitable as an electronically active material. It is worth mentioning that nominally π-conjugated networks can be synthesized by condensation reactions, whereby the condensation of amines with aldehydes is a proven example for on-surface polymerization [18].

Based on the combined properties of boronic acid-derived 2D COFs—structural versatility, high mechanical stability, and water solubility—applications where a porous network is required as a template for one processing step, while it should be removed in a subsequent processing step appear most promising.

5   Ullmann Coupling

The enormous interest in highly stable and electronically conjugated networks calls for a coupling chemistry that establishes new C–C bonds. To this end, the surface variant of classical Ullmann coupling as introduced by Grill et al. is highly appropriate [2]. The principal reaction scheme is relatively straightforward: brominated or iodinated precursor molecules are deposited onto a metal surface, typically Cu, Ag, or Au. Upon adsorption, the weakly bonded halogen substituents are split off with the aid of the catalytic properties of the metal surface. DFT simulations propose an activation barrier in the order of 0.5–1.0 eV for the overall exothermic dehalogenation [19]. The energy gain is partly related to the relatively strong adsorption of the spit off halogens. The activation barrier decreases in the order Au > Ag > Cu, i.e., with increasing reactivity of the metal surface, and is for all surfaces studied ~ 0.3 eV lower for iodine than for bromine substituents. This trend appears plausible, considering the differences in carbon–halogen bond strength. However, the bond dissociation energy of C–I is ~ 0.65 eV lower than for C–Br in iodobenzene versus bromobenzene [20], indicating a distinct surface influence. In any case, iodinated precursors are more reactive, and deiodination readily takes place at room temperature (RT) even on less-reactive gold surfaces [21]. On the contrary, the reactivity of the metal surface plays a decisive role for brominated compounds: on copper, debromination already occurs at room temperature, whereas on gold additional heating to ~ 150–200 °C is required [22]. The vast differences in activation temperatures for deiodination versus debromination on gold can be used for a defined sequential coupling by selective activation of iodine and bromine sites [23, 24]. Silver surfaces occupy an interesting intermediate position, where partial debromination is observed at room temperature, whereas full

debromination also requires additional heating [25]. The incomplete debromination on silver cannot simply be explained with a fixed value for the reaction barrier, and detailed studies may shine more light on the actual mechanism of surface-catalyzed dehalogenation.

Dehalogenation results in so called surface-stabilized radicals (SSR), where the dangling bonds of the dehalogenated carbons bind to the underlying metal surface. The further progression of the coupling reaction strongly depends on the metal surface. On Au(111), the generally accepted picture is that the SSR are mobile, diffuse around and form covalent bonds upon encounter. However, the detailed atomistic knowledge of these processes is not very advanced: The nucleation behavior is not well studied, e.g., the role of step-edges for immobilization of monomers. It is also not clear, how fast the coupling step takes place, i.e., whether there are effective entropic or even energetic barriers. Nevertheless, the coupling reaction is kinetically controlled and the irreversibility of newly formed interlinks typically results in irregular networks with high defect densities. In most studies, Ullmann polymerization is carried out under UHV conditions, however, drop-casting of respective solutions onto preheated Au(111) surfaces under ambient conditions has also yielded covalent structures [26, 27].

On the more, reactive Cu and Ag surfaces intrinsic adatoms interfere with the coupling step. Instead of directly establishing covalent bonds, the SSR form intermediate organometallic complexes and networks based on carbon-metal-carbon interlinks [28–30]. Upon further annealing, the metal atoms can be released; whereby the metastable organometallic bonds are irreversibly converted into covalent bonds (see Fig. 4a). For example, room temperature deposition of 1,3,5-tris-(bromophenyl) benzene (TBB) onto Cu(111) results in disordered organometallic networks [30], a typical STM image is depicted in Fig. 4b. The disorder is attributed to the irreversibility of the relatively strong C–Cu bonds. The resulting covalent networks are similarly disordered, suggesting that the initial organometallic arrangement is maintained during the conversion. On Ag(111) partly ordered organometallic networks were observed [31]. This may be viewed as an
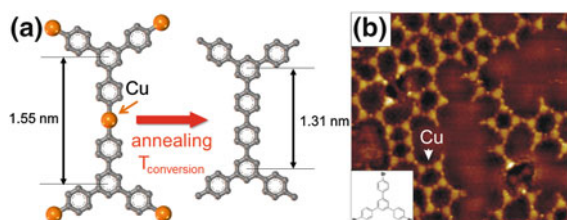

Fig. 4 **a** Structure of an organometallic dimer with triphenylbenzene backbones. Annealing at $T_{conversion}$ triggers the conversion from organometallic to covalent. According to gas-phase DFT calculations the center-to-center distance shrinks from 1.55 to 1.31 nm. **b** STM image acquired after room temperature deposition of TBB (cf. *inset* for structure) onto Cu(111). Fully debrominated molecules are interlinked via organometallic C–Cu–C bridges into networks. The linking copper atoms are imaged as dots between molecules (example marked by *arrow*)

indication for reversibility of the weaker C–Ag bonds, indicating possibilities for error correction. At present, the role of the adatoms for the initial reaction step—the dehalogenation—has not been clarified; however, it appears likely that the under-coordinated, thus more reactive, adatoms also promote halogen cleavage. On Au(111) organometallic networks have only rarely been observed [32]. The differences of the metal surfaces with respect to dehalogenation and organometallic intermediates are summarized in Table 1.

An intriguing question is, whether the structural quality of covalent networks obtained by kinetically controlled coupling reactions can be improved by optimization of reaction parameters (e.g. temperatures, heating or deposition rates) or the preparation sequence (e.g. room temperate deposition and subsequent heating versus deposition at elevated substrate temperature). A detailed comparison requires a quantitative measure of the network quality. Ideal networks based on threefold symmetric, straight connecting precursors as TBB are hexagonal. However, irregular tetragonal, pentagonal, heptagonal, and octagonal pores are commonly observed defects [22]. Consequently, a statistical analysis just by counting the different pore types in a significant number of STM images provides first insights. Yet, even networks that exclusively consist of ideal hexagonal pores can be far from perfect, due to frequently observed branching or vacancies [33]. Therefore, additional statistical indicators as the average number of adjacent pores have to be evaluated. For Ullmann polymerization of 1,3-bis(-bromophenyl)-5-(p-iodophenyl) benzene (BIB, c.f. inset to Fig. 5a) on Au(111), the influence of different reaction parameters on the network quality was studied in detail [24]. This brominated and iodinated precursor was also designed to compare hierarchical versus direct polymerization: room temperature deposition onto Au(111) selectively activates the iodine sites, resulting in covalent and kinetically inert dimers; only further annealing above the debromination threshold ($\sim$175 °C) activates full polymerization; whereas upon high temperature deposition, both iodine and bromine sites become activated, resulting in the direct polymerization into networks. However, no substantial differences could be found for the two different polymerization protocols.

In the following, we focus on the influence of deposition rate and surface temperature for direct polymerization. Figure 5 depicts representative STM images

Table 1 Dehalogenation of brominated versus iodinated precursors and occurrence of organometallic intermediates for different metal surfaces

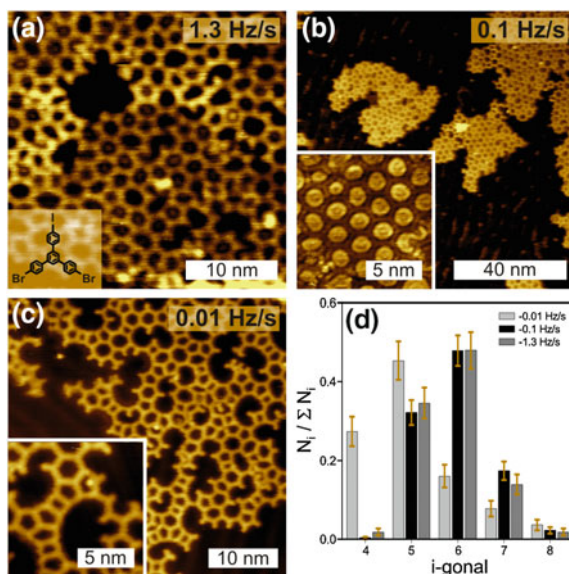| $d^{10}s^1$ metal	Bromine cleavage	Iodine cleavage
Cu(111) organometallic $\rightarrow$ disordered	Full @ RT	Full @ RT
Ag(111) organometallic $\rightarrow$ ordered	Partial @ RT Full @ $\sim$150 °C	Full @ RT
Au(111) *rarely* organometallic intermediates	None @ RT Full @ $\sim$180 °C	Full @ RT

Fig. 5 STM images of covalent networks obtained by deposition of BIB (structure in *inset* to **a**) onto Au(111) held at 250 °C with different deposition rates (indicated in the *upper right* corners as frequency decline rates of a quartz crystal microbalance); **a** "normal" and **b** "slow" deposition with 1.3 and 0.1 Hz/s lead to comparable network quality; **c** whereas networks obtained by "ultraslow" deposition with 0.01 Hz/s exhibit a substantial amount of tetragonal and pentagonal pores, as also apparent from the corresponding pore geometry distribution in (**d**). Reprinted with permission from Ref. [24]. Copyright 2014 American Chemical Society

of covalent networks obtained by deposition of BIB onto Au(111) held at 250 °C with rates spanning over two orders of magnitude. The corresponding pore geometry distributions are summarized in Fig. 5d. Deposition with "normal" and "slow" rates (cf. Fig. 5a and b) leads to comparable distributions, while "ultra-slow" deposition results in a markedly increased number of pentagonal and even tetragonal pores, as also evident from the STM image in Fig. 5c. A comparable series of experiments where the surface temperature was varied while the deposition rate was kept constant revealed an increasing amount of pentagonal pores for increasing surface temperatures.

To develop strategies for improving the network quality, an atomistic understanding of defect formation is useful. Increased numbers of pentagonal pores were experimentally observed for higher surface temperatures or extremely low deposition rates. Both dependencies can consistently be explained by a relatively simple model. During polymerization, a stage occurs where a five-membered open ring which is missing one monomer is not yet closed. As sketched in Fig. 6, two different reaction pathways are conceivable: either the five-membered open ring is closed in a bimolecular reaction into an ideal hexagonal pore by addition of one
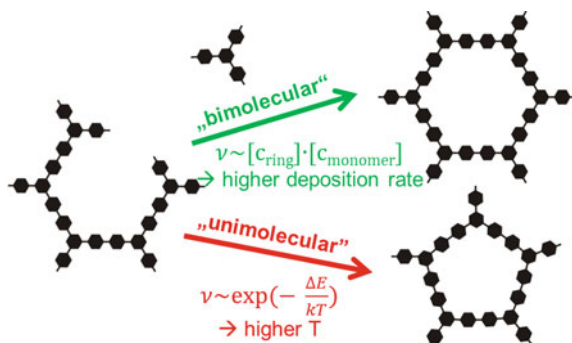
Fig. 6 Illustration of the kinetic competition between the bimolecular reaction (*green*) that yields ideal hexagonal pores versus the unimolecular reaction (*red*) that results in irregular pentagonal pores

more monomer or the five-membered ring becomes an irregular pentagonal pore in an unimolecular ring-closing reaction. The latter process requires bond distortion and is hence associated with an energy barrier. According to chemical kinetics, the bimolecular reaction rate depends on the concentration product of five-membered open rings and available monomers which increases with deposition rate. The unimolecular ring-closing reaction has to overcome an energy barrier, thus the rate becomes enhanced at higher surface temperatures according to an Arrhenius law.

The studies above have indicated possibilities to improve the quality of covalent networks by optimizing reaction parameters. Yet, structural perfection or at least long-range order appears to be beyond this approach. Alternatively, reversibility of organometallic bonds on Ag(111) might bear the potential to yield significantly better networks. The basic idea is taking advantage of a two stage protocol: The first step employs bond reversibility in organometallic networks for equilibration into highly ordered structures. This can be viewed as a self-assembly process. Yet, slightly higher temperatures $T_{\text{equilibration}}$ are required, due to the relative strength of C–Ag bonds as compared to supramolecular interactions. In the second step, these ordered organometallic networks are converted into similarly ordered covalent networks by additional heating at $T_{\text{conversion}}$ that is ideally significantly higher than $T_{\text{equilibration}}$. This scheme is far from being a topochemical reaction, because the conversion is accompanied by a considerable shrinkage of intermolecular distances (cf. Fig. 4a), hence obtaining very large domains might still be difficult. Nevertheless, the proof of concept is illustrated by the STM images in Fig. 7, where (a) was acquired directly after room temperature deposition of BIB onto Ag(111). In the STM contrast of this particular image, the interconnecting Ag atoms appear as clearly recognizable bright features between the fainter molecules. Molecule–molecule distances are in accord with organometallic bonds. The corresponding room temperature C 1s XP spectrum in Fig. 7d exhibits both a shoulder at higher binding energy corresponding to still brominated carbon (C_{Br}) and a shoulder at lower binding energy corresponding to Ag-bound carbon (C_{Ag}). The STM image in

Fig. 7 STM images of BIB on Ag(111) obtained after **a** room temperature deposition **b** annealing at 125 °C, and **c** annealing at 250 °C [25]. **d** C 1s XP spectra acquired directly after room temperature deposition and after annealing to 250 °C. Reproduced with permission from The Royal Society of Chemistry
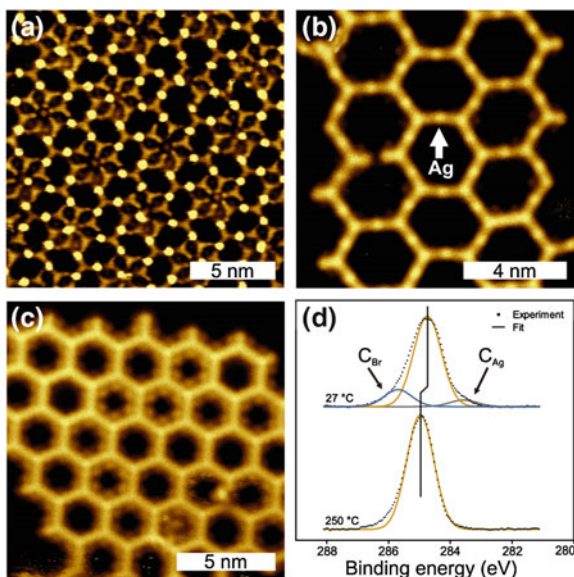

Fig. 7b was obtained after moderate heating at 125 °C for extended periods of time and shows a quite regular porous hexagonal network. The faint dots between interconnected molecules (example marked by the arrow) correspond to still present Ag atoms. A comparison of Fig. 7a and b makes obvious: annealing induced a massive structural reorganization that inevitably required breaking and reforming of C–Ag bonds, thereby proving their reversible nature at slightly elevated temperature. First indications of a conversion to covalent were only observed at higher temperatures of ∼150 °C, whereas a sizable conversion required ∼170 °C. Accordingly, further annealing at 250 °C ultimately results in fully covalent networks. The STM image in Fig. 7c shows a structurally perfect domain obtained via an ordered organometallic intermediate. The annealing was carried out extremely carefully with a low heating rate, in order to stay close to equilibrium structures during the progressive conversion. Both shoulders in the C 1s XPS data have disappeared after annealing, indicating a full conversion of all active sites into C–C bonds (cf. Fig. 7d).

6 Coupling of Terminal Alkynes

A drawback of Ullmann coupling is surface contamination by strongly adsorbing byproducts. The split off halogens chemisorb and in particular iodine can block part of the surface and hamper further polymerization [21]. In this respect, exploring alternative reactions can be rewarding and ethynyl groups appear to be sufficiently reactive for on-surface chemistry, but also sufficiently inert for deposition via

thermal sublimation. The only possible reaction byproduct is H_2 which readily desorbs from the surface. Terminal alkynes were already used for the synthesis of bulk COFs that are porous but not crystalline [34]. A priori different coupling reactions are conceivable: Glaser-Hay coupling, where a new C–C σ-bond is formed and only H_2 is released as a byproduct; cyclo-trimerization—an atom-economic reaction, where three ethynyl groups form a new phenyl ring; but also more complex coupling reaction schemes can occur; In the following, the surface chemistry of 1,4-diethynylbenzene (DEB) on Cu(111) is discussed as an example [35]. After room temperature deposition, STM reveals ordered structures of presumably intact molecules. Thermal annealing induces massive structural changes, leading to disordered structures and filamentous networks, representative STM images are shown in Fig. 8. The structures are imaged with uniform apparent height, suggesting a more or less well-defined coupling. Obtaining these structures is rather insensitive to the precise preparation protocol. Differences were neither observed for different annealing temperatures in the range of 175–350 °C nor for deposition onto a preheated surface. Despite the disorder, reoccurring motifs can be identified, most frequently: threefold-stars as well as larger and shorter dumbbells. The limited possibilities of coupling reactions facilitate identification of the reaction products by overlaying geometry-optimized candidate structures on the STM images (see Fig. 8). Accordingly, all these structures can be derived from DEB using only Glaser-Hay coupling and trimerization, the respective reaction schemes are depicted in Fig. 9: The threefold stars simply result from trimerization of three DEB into 1,3,5-tris(4′-ethynylphenyl)benzene (TEB) molecules. The larger dumbbells originate from a secondary Glaser-Hay coupling of two TEB molecules, whereas the shorter dumbbells form by secondary trimerization of one TEB lobe with two more DEB. However, also more complex reaction products were observed, in accord with bulk COF synthesis.

The lack of a clear preference for a specific coupling reaction among the different possibilities—i.e. the limited regioselectivity—inhibits polymerization into ordered
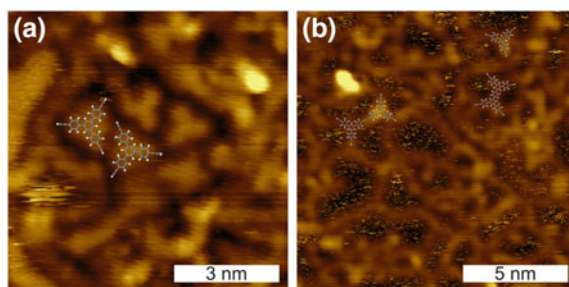

Fig. 8 STM images obtained after the thermally activated polymerization of DEB on Cu(111). Frequently encountered motifs as **a** threefold stars as well as **b** longer and shorter dumbbell are overlaid with optimized geometries of candidate structures. Size and shape consistency aids in the identification of reaction products [35]. Reproduced with permission from The Royal Society of Chemistry
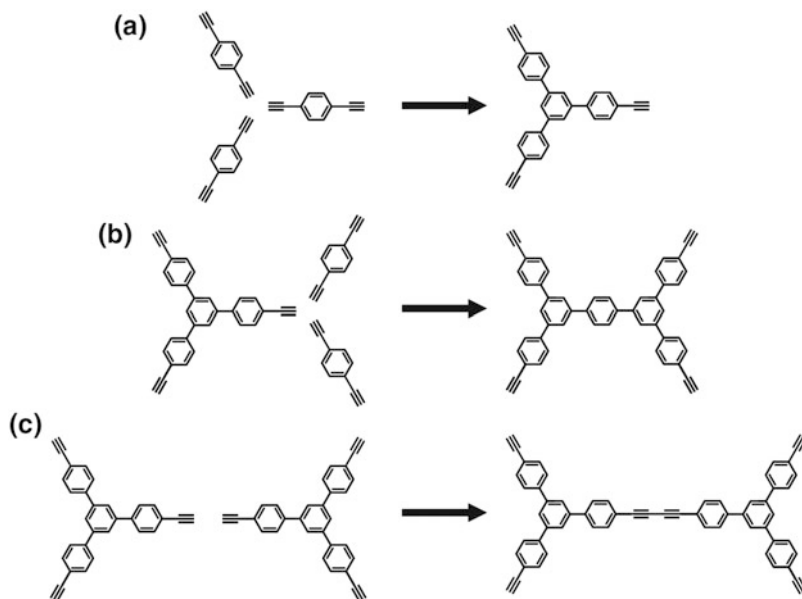
Fig. 9 Schemes of primary and secondary coupling reactions observed for DEB on Cu(111). **a** Threefold stars **b** shorter dumbbells **c** larger dumbbells

networks. Similar observations were already made for the reaction of acetylene—the smallest ethynyl molecule—on copper surfaces. Exclusive trimerization would yield benzene; however, on Cu(111) various alternative reaction products as butadiene and cyclooctatetraene were identified by temperature-programmed desorption experiments [36]. Yet, a significantly higher benzene yield on Cu(100) hints toward possibilities to enhance the regioselectivity by using different crystallographic surface orientations.

Similarly, polymerization of TEB on Ag(111) resulted in covalent, but not very well-ordered networks [37]. Even though a competition between Glaser-Hay coupling and trimerization was similarly observed, irregular, e.g., pentagonal pores are more common defects. The origin of these defects lies in the flexibility of the molecular backbone. The deformation energy associated with irregular pores is not exceedingly high [21], thereby promoting thermally activated defect formation. Moderate annealing of TEB on Ag(111) only leads to dimers, while full polymerization required higher temperatures [37]. A possible origin was proposed on the basis of elaborate DFT calculations: The substrate registry of the covalent dimer is less favorable, resulting in an enlarged molecule–surface distance. This reduces the catalytic effect of the surface, and gives rise to a higher activation barrier for coupling beyond the dimer. Such registry effects might also be important for other surface-catalyzed reactions, as the growing covalent aggregates are less flexible and cannot easily adopt to the surface as supramolecular structures.

A combined STM and DFT study of ethynyl trimerization on Au(111) proposes a reaction mechanism via a dimeric intermediate state and a significantly lower reaction temperature on the surface as compared to solution [38]. Interestingly, on Au(111) a clear preference for trimerization was observed for TEB [39], again indicating possibilities to selectively catalyze a specific coupling reaction by the choice of surface.

Imposing additional geometrical constraints on the adsorbed monomers is an interesting concept to promote regioselectivity. An experimental implementation thereof is working on vicinal surfaces that consist of small terraces of defined width and crystallographic orientation. Confining monomers on smaller terraces can prohibit certain molecular arrangements that are necessary for specific couplings. A proof of principle experiment is the polymerization of ethynyl terminated p-oligophenylenes on Ag(877) [40]. Constraining the 18.8 Å long monomers on the 36.6 Å wide terraces could suppress trimerization and exclusively yielded graphdiyne wires by Glaser-Hay type coupling. Even though this approach is elegant and very appealing, its application is most likely limited to the targeted synthesis of 1D structures.

7 Conclusions and Outlook

On-surface polymerization has already demonstrated its potential as a facile bottom-up approach for the fabrication of novel covalent nanostructures that are synthetically not accessible by any other means. Limited solubility of larger molecules and aggregates is a serious limitation for solution chemistry that does not necessarily apply to surface chemistry. The holy grail of structural perfection has so far only been achieved for polymerization under slightly reversible reaction conditions or for one-dimensional structures that are less prone to defect formation. In principle, bond reversibility is a matter of the ratio bond energy to thermal energy, i.e., kT. However, the limited thermal stability of organic molecules precludes extremely high temperatures that have helped to improve the structural quality of bottom-up fabricated graphene. The currently best covalent 2D networks are synthesized by condensation reactions. Yet, alternative coupling reactions might be desirable in terms of chemical stability or electron mobility.

Long-range order is not a strict requirement for any type of application. However, crystallinity promotes evolution of a defined band structure for electronic applications, but is also very advantageous for simulations. Similarly, membrane applications, e.g. for gas separation, become much more powerful through atomically precise pores. Long-range order is difficult to achieve for several reasons: one reason is the kinetically driven and irreversible formation of topological defects as, for instance, irregular pentagonal or heptagonal pores in hexagonal networks. Competing coupling reactions can be a further problem. Obviously, this is a severe issue for crosscoupling, but is, for instance, similarly crucial for homocouplings of chemically versatile ethynyls. Even though it is hard to imagine strategies to

completely avoid defects during kinetically controlled growth, a detailed study of defect formation is worthwhile. An atomistic understanding of defect formation is the first step toward a systematic development of strategies to avoid or at least minimize defects.

On surfaces, Ullmann coupling is the best studied and most applied polymerization reaction. It works reliably on metals, in a sense that the topology of ideal networks is predefined by the halogen substitution pattern of the precursor molecule. Since unwanted side-reactions do not occur for Ullmann coupling, topological defects remain the most severe issue. These defects are associated with bond distortion; consequently, energy is required for their formation. A promising concept would thus be the development of low-temperature polymerization schemes to suppress thermally activated defect formation.

The most appealing property of covalent nanostructures is the prospect of charge transport [41]. A requirement for meaningful experiments in this direction is working on insulating surfaces, which means either in situ synthesis or subsequent transfer. In the common Ullmann approach, the metal surface is needed to initiate the coupling by dehalogenation. However, first experiments on calcite surfaces have shown that Ullmann coupling on bulk insulator surfaces is feasible [42]. In this particular case, carboxylic acid groups were used as anchors to prevent desorption during heating until sufficiently high temperatures for the dehalogenation have been reached. Yet, other strategies are similarly conceivable. Since adatoms may play a so far unrevealed role for the dehalogenation, hybrid metal–insulator approaches, where metal atoms are deposited onto an insulator, might also be worthwhile pursuing. Alternatively, transfer procedures as template stripping have been further developed for graphene research, but might be similarly applicable to covalent organic nanostructures.

Organic chemistry is extremely diverse, thus an obvious strategy is to further explore different coupling reactions on surfaces. Boronic acid condensation and ethynyl polymerization was inspired from bulk COF synthesis. In this respect, the ionothermal synthesis of carbonitride COFs by nitrile trimerization appears particularly rewarding, as there are no known side-reactions and byproducts in this atom-economic reaction [43]. However, the harsh reaction conditions at temperatures of 400 °C in liquid $ZnCl_2$ may already indicate a low reactivity, and it remains to be explored if nitrile trimerization on surfaces is possible at all. Even though for a limited number of couplings, the potential energy landscape of a presumed reaction pathway has been simulated by DFT [33, 37, 44], on-surface chemistry remains far from being predictable. In many cases, the intuition even of most experienced organic synthetic chemists fails to predict whether and how a particular reaction proceeds on a specific surface. Many examples have proven that the geometric templating effect in combination with the chemically active role of the surface and/or the interplay with adatoms can totally alter reaction geometries and barriers or even mechanisms.

In summary, the current approach is mostly empiric. This can be cumbersome not only due to the inherent slowness of UHV experiments, but also due to the almost infinite parameter space. A reaction that does not work on one surface might

readily proceed on another surface. Nevertheless, the increasing number of joint surface scientists and organic chemists' teams will inevitably generate a wealth of interesting, insightful, and surprising results as well as novel organic nanostructures, and even maybe the perfect 2D polymer.

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