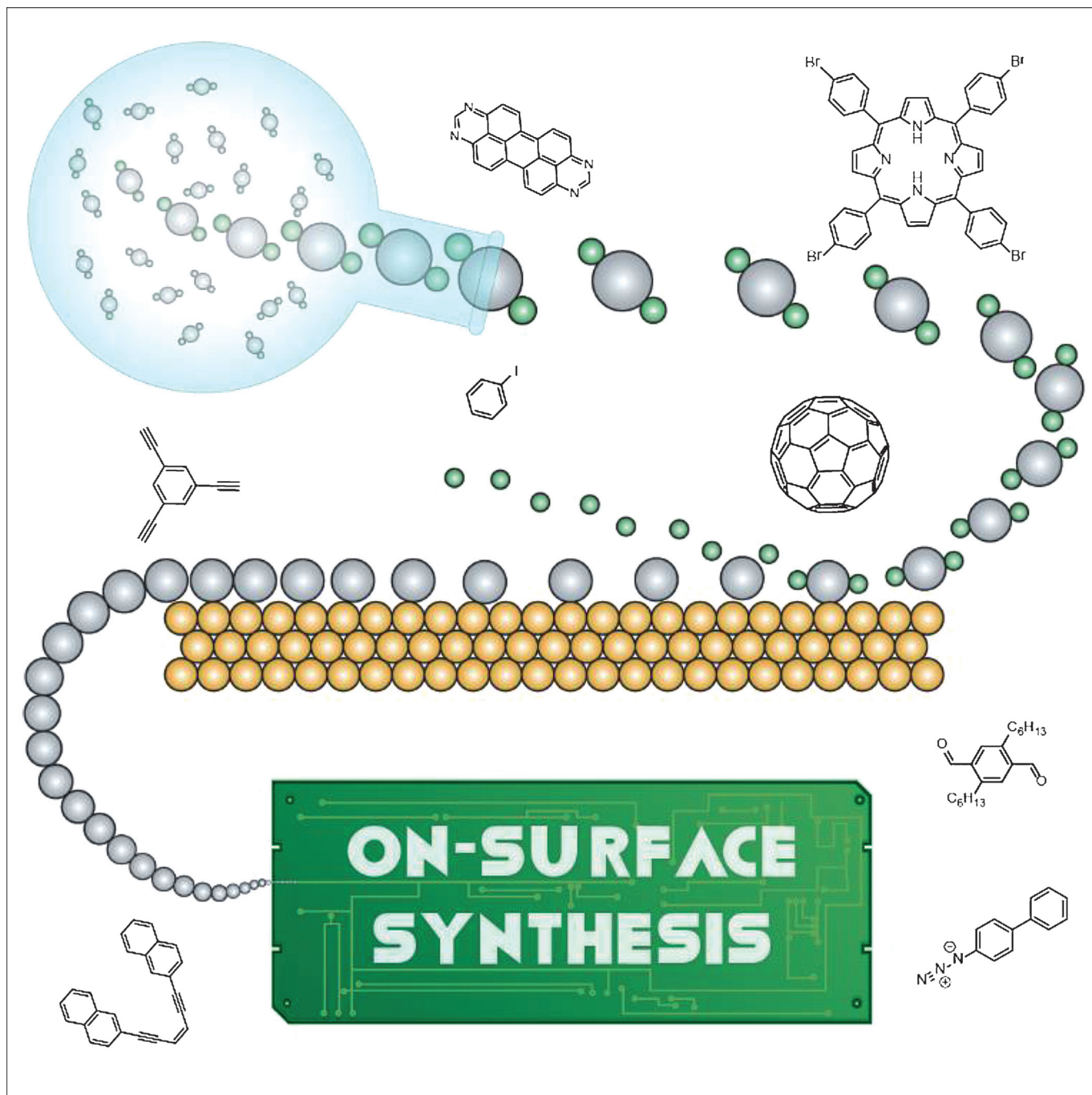


VIP **On-Surface Reactions**

Robert Lindner<sup>[a, b]</sup> and Angelika Kühnle<sup>\*[a]</sup>



On-surface synthesis constitutes a rapidly growing field of research due to its promising application for creating stable molecular structures on surfaces. While self-assembled structures rely on reversible interactions, on-surface synthesis provides the potential for creating long-term stable structures with well-controlled properties, for example superior electron transport for future molecular electronic devices. On-surface synthesis holds the promise for preparing insoluble compounds that cannot be produced in solution. Another highly exciting

aspect of on-surface synthesis is the chance to discover new reaction pathways due to the two-dimensional confinement of the reaction educts. In this review, we discuss the current state-of-the-art and classify the reactions that have been successfully performed so far. Special emphasis is put on electrically insulating surfaces, as these substrates pose particular challenges for on-surface synthesis while at the same time bearing high potential for future use, for example, in molecular electronics.

## 1. Introduction

In recent years, on-surface chemical reactions have proven to be a highly versatile tool for the creation of stable molecular structures.<sup>[1–7]</sup> As compared to molecular self-assembly, which relies on reversible intermolecular interactions, on-surface synthesis provides the opportunity to create stable molecular structures by the formation of covalent bonds. Performing the reactions directly on the surface bears a great potential for surface functionalization and the creation of functional devices, for example, in the field of molecular electronics. On-surface reactions can be realized without solvents under ultra-high vacuum conditions, which allows for utmost control over the purity of products. Moreover, on-surface synthesis offers the possibility to prepare compounds that cannot be synthesized in solution due to solubility issues. Most importantly, the confinement of the reaction to two dimensions gives access to entirely new reaction pathways, such as stabilizing specific conformers. For the investigation of these reactions, scanning probe techniques are a most valuable tool, since they allow for directly imaging the precursors and their resulting products with sub-molecular resolution in real space.

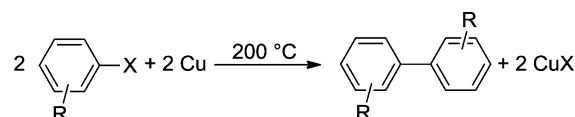
In this review, we give an overview of the advances and the current state-of-the-art in this highly active field of research. Because on-surface reactions have also been explored under ambient conditions<sup>[4]</sup> and at the solid–liquid interface,<sup>[8]</sup> we focus on reactions performed under ultra-high (UHV) vacuum conditions. Also, we limit this review to reactions resulting in covalent bonds, thus, we omit, for example, the wide field of coordination bonds.<sup>[9]</sup> Starting from proof-of-principle studies at the beginning of this millennium, the further development of these pivotal reactions is discussed. Furthermore, concepts improving reaction control, structural complexity and stoichiometry are presented. Finally, first successful approaches towards on-surface synthesis on insulating substrates are shown.

[a] R. Lindner, Prof. Dr. A. Kühnle  
Institute for Physical Chemistry  
Johannes-Gutenberg University  
Duesbergweg 10-14, 55128 Mainz (Germany)  
E-mail: kuehnle@uni-mainz.de

[b] R. Lindner  
Graduate School of Excellence: "Materials Science in Mainz"  
Staudinger Weg 9, 55128 Mainz (Germany)

## 2. Early Studies

Among the very first examples for the on-surface creation of covalent bonds between molecules is the well-known Ullmann coupling. The classical Ullmann synthesis has first been described in 1904<sup>[10]</sup> and allows for the selective formation of carbon–carbon bonds between two aryls, by a Cu-mediated activation of aryl halides, such as chlorobenzene (see



Scheme 1. Cu-mediated Ullmann-coupling between two Aryl halides.

Scheme 1). On a surface, this has been demonstrated with scanning tunneling microscopy for the first time by Hla et al. in 2000.<sup>[11]</sup> In that work, they adsorbed iodobenzene on a Cu(111) surface held at 20 K. By applying a voltage pulse with the tip of a scanning tunneling microscope (STM), the carbon–iodine bond could be cleaved. Subsequently, two closely lying phenyl radicals were brought into proximity of each other by lateral manipulation, again using the STM tip. With a further voltage pulse, the two phenyl radicals were covalently linked to form a biphenyl molecule. The successful linkage was demonstrated indirectly by manipulation of the newly formed molecule that was moved as an entity. Another prominent example for on-surface synthesis using an STM tip to initiate the reaction is the polymerization of diacetylenes. Aono et al. have been able to initiate the polymerization of 10-12-nonacosadiynoic acid, adsorbed on a graphite surface, into a polydiacetylene nanowire. Interestingly, the start of the reaction could be precisely controlled by applying a voltage pulse with an STM tip, while the reaction direction was governed by the underlying substrate, resulting in unidirectional rows.<sup>[12]</sup>

Despite the impressive nature of these experimental achievements, reaction initiation by the tip of an STM appears unlikely to be adopted for the creation of extended nanostructures, because of its serial concept.

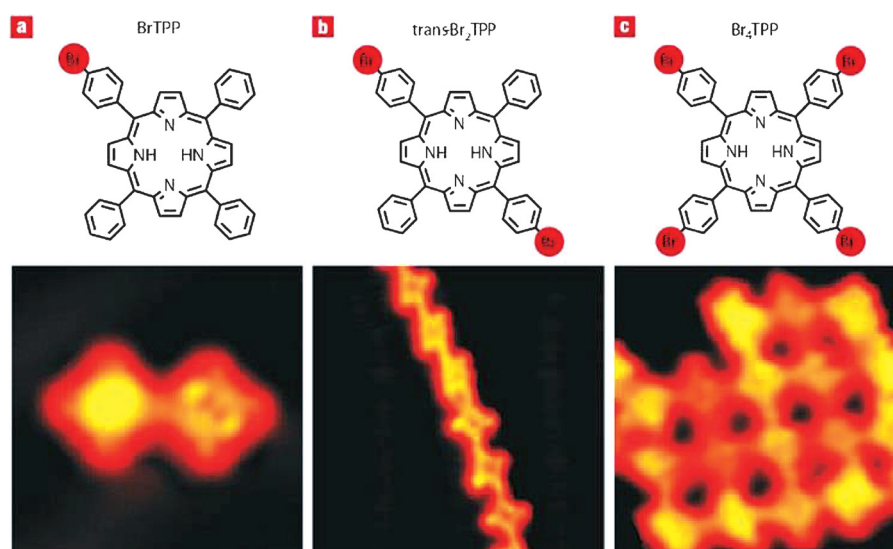
## 3. On-Surface Synthesis on Metal Surfaces

Soon after the demonstration of an on-surface reaction initiated with the tip of an STM, other means to initiate a reaction

have been explored to enable a parallel approach. Since on-surface reactions can be classified as a new kind of reaction type, well-established reaction concepts and reaction procedures have to be thoroughly adapted to fit the new environment on the surface. Although it can be challenging to transfer existing synthesis concepts to surfaces, numerous synthetic protocols have already been transferred and adapted to match the specific conditions of on-surface synthesis.

### 3.1. Further Studies on the Ullmann Coupling

A most promising parallel approach has been published by Grill et al. in 2007.<sup>[13]</sup> After adsorbing porphyrins with a varying number of bromine substituents on a Au(111) surface, they



**Figure 1.** Ullmann coupling of substituted porphyrins with control over the dimensionality. By using different building blocks with (a) one, (b) two or (c) four Br substituents, dimers, one-dimensional lines or two-dimensional networks are formed (see STM images below). Adapted from Ref. [13].

Robert Lindner studied chemistry at Stuttgart University (Germany) and changed to Johannes Gutenberg University, Mainz (Germany), after his undergraduate studies. For his Master thesis he joined the group of Angelika Kühnle working on "Photopolymerization of C<sub>60</sub> on Calcite". Hereafter, he continued to work on his Ph.D. in the group of Angelika Kühnle on molecular self-assembly and on-surface synthesis.



Angelika Kühnle studied physics at the Free University Berlin (Germany). After finishing her Master's thesis, she joined the group of Flemming Besenbacher at Aarhus University (Denmark), where she did her Ph.D. on "Molecular Self-Assembly and Chiral Recognition: Biologically Relevant Molecules on Metal Surfaces". She then joined the polymer research labs at the chemical company BASF SE in Ludwigshafen (Germany). In 2005 she was awarded an Emmy Noether Grant of the German Research Foundation (DFG). In 2009 she was appointed as a full professor at the Institute for Physical Chemistry at Mainz University. Her research interest focuses on exploring fundamental processes at insulating surfaces for understanding molecular self-assembly and on-surface synthesis.



have been able to deliberately steer the dimensionality of the reaction product. By annealing the gold substrate to 400 K, thermal homolysis of the carbon–bromine bond has been induced and a phenyl radical has been created. During diffusion on the surface, the highly reactive radicals recombined and formed dimers, linear chains or extended networks (see Figure 1). Based on the same strategy, other examples exist in the literature. Lipton-Duffin et al. have demonstrated the coupling of diiodobenzene on Cu(110).<sup>[14]</sup> By using the two isomers 1,4-diiodobenzene and 1,3-diiodobenzene, they were able to create poly(*para*-phenylene) lines and poly(*meta*-phenylene) zigzag rows, respectively. Additionally, the reaction of 1,3-diiodobenzene allowed for the formation of sexiphenylene macrocycles. A similar approach has been used by Fan et al. By enlarging the reactant by two *meta*-positioned phenyl rings, that is, changing from 1,4-dihalobenzene to 4,4'-dihalo-*m*-terphenyl, they were able to synthesize hexagonally arranged hyperbenzene macrocycles on a Cu(111) surface.<sup>[15]</sup> Similarly, the synthesis of poly(3,4-ethylenedioxythiophene) by polymerization of 2,5-diiodo-3,4-ethylenedioxythiophene on Cu(110) has been shown.<sup>[16]</sup> Further examples for Ullmann-like on-surface syntheses have been shown on Cu,<sup>[17–20]</sup> Ag,<sup>[20–26]</sup> Au,<sup>[19,26–34]</sup> CaCO<sub>3</sub>,<sup>[35–37]</sup> NaCl@Au,<sup>[38]</sup> h-BN@Ni,<sup>[39]</sup> sapphire,<sup>[40]</sup> and graphene@Ni.<sup>[39]</sup>

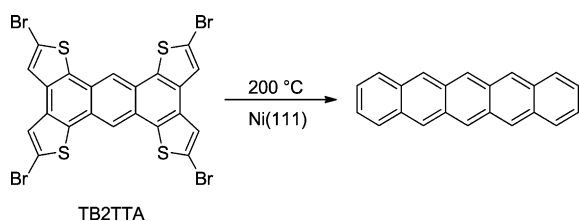
The reactivity of the surface is highly dependent on the crystal facet used and on the type of metal. Saywell et al. have used a stepped Au(10,7,7) surface to polymerize dibromoterfluorene. By simple statistics they have shown that the reaction most likely takes place at the step edges.<sup>[41]</sup> In a comprehensive study comparing various surfaces, Gutzler et al. have shown that the Ullmann coupling crucially depends on the underlying substrate.<sup>[42]</sup> Thermal annealing of monolayers of 1,3,5-tris(4-bromophenyl)benzene on graphite(001), Cu(111) and Ag(110) has clearly shown that the homolytic cleaving of the C–Br bonds does not take place on graphite, since the

molecules desorb before they are able to react. On metals, however, the split-off Br atoms are chemisorbed to the surface and, in consequence, stabilized. Thus, it is crucial to carefully consider the influence of the substrate on the surface reaction. In this context, metal substrates provide the great advantage that they are catalytically active and typically possess a rather high surface energy.<sup>[43–45]</sup>

### 3.2. Further Parallel Approaches

In the interest of enlarging the set of synthetic tools for the creation of covalent structures directly on the surface, additional chemical reactions have already been successfully converted into on-surface synthesis concepts. These are discussed in the following.

As stated in the introduction, the confinement of reactions to two dimensions enables the possibility of new reaction pathways. This has been shown for the conversion of the four-fold brominated anthratetrathiophene TB2TTA (see Scheme 2).<sup>[46]</sup> By deposition of the molecule onto Ni(111) and



**Scheme 2.** Conversion of TB2TTA to Pentacene on a Ni(111) surface, via a novel reaction pathway.

subsequent annealing to 200 °C, they have been able to convert the molecule into single pentacene molecules. They have proposed a reaction mechanism, proceeding via a dehalogenation, followed by a desulfurization reaction. Hereby a highly reactive, unsaturated carbon species is produced, which undergoes a dehydrogenation reaction to form pentacene.

C–H bonds are known to be rather inert, especially when considering long alkyl chains. A possibility for activating this bond is the use of aromatic groups or methyl groups added to an aromatic core. Very recently Wiengarten et al. have demonstrated the creation of homocoupled porphine arrays. The activation of the C–H bonds situated directly at the aromatic ring allowed for the creation of up to three C–C bonds between neighboring molecules.<sup>[47]</sup> Due to the desorption of molecules upon post-deposition annealing, they deposited the molecules directly on a surface, held at elevated temperatures. By performing the reaction at different sample temperatures, they were able to increase the yield of coupled porphine from 70% at 533 K, to 99% at 613 K.

In't Veld et al. have shown an oligomerization of tetra(mesityl)porphyrin.<sup>[48]</sup> This reaction is facilitated by the fact that the radicals formed when cleaving off one hydrogen atom are comparatively stable. This stabilization is due to the aromatic core of the mesityl groups, which stabilizes radicals by delocalization. Hence, the recombination of the two created radicals is

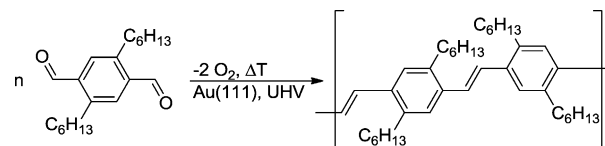
hindered and the porphyrin radicals exist long enough to find a suitable reaction partner. Thus, simple annealing of these precursors on a Cu(110) held at 420–470 K has been shown to be sufficient to form covalently linked oligomers.

The C–H activation of linear alkanes has been shown by Zhong et al.<sup>[49]</sup> Deposition of di(eicosyl)benzene (DEB) on a Au(110) surface constrained the molecules into one dimension. Subsequent annealing to 420 K has yielded the corresponding polymer, namely poly(DEB). Calculations have shown that the Au(110) surface lowers the C–H activation energy from  $E_a > 4$  eV to  $E_a \approx 1$  eV. This work impressively demonstrates that even a rather simple and especially unreactive molecule, if treated correctly, can undergo an on-surface reaction and result in stable surface structures.

A very special approach to create fullerene hemispheres has been shown by Rim et al.<sup>[50]</sup> Using hexabenzocoronene as a precursor adsorbed on a Ru(0001) surface, relatively mild annealing to 380 K was shown to initiate multiple cyclodehydrogenation reactions, as was corroborated by H<sub>2</sub> temperature-programmed desorption (TPD) spectra. Additional STM images revealed the conversion of hexabenzocoronene into fullerene hemispheres. This concept has been further explored by Otero et al.<sup>[51]</sup> They deposited C<sub>60</sub>H<sub>30</sub> and C<sub>57</sub>H<sub>33</sub>N<sub>3</sub> onto a Pt(111) surface. Upon annealing the substrate to 750 K they were able to transform the first compound into C<sub>60</sub> fullerenes and the second compound into a triazafullerene, respectively. Based on the same strategy, Amsharov et al. have been able to synthesize a higher fullerene, that is, C<sub>84</sub>, on a Pt(111) surface.<sup>[52]</sup>

A unique decarboxylation reaction has been shown by Gao et al.<sup>[53]</sup> The deposition and subsequent annealing of naphthalene-dicarboxylic acid on both, Ag(111) and Cu(111), at first resulted in a deprotonation due to the coordination between the carboxylate and the metal. In a second step CO<sub>2</sub> was cleaved off, yielding a one-dimensional chain of naphthalene biradicals linked by metal atoms. As a last step, the biradicals recombined in order to form polynaphthalene wires.

All of the aforementioned reactions, however, rely on the activation of either C–H bonds or C–X bonds, both being single bonds. Diaz Arado et al. have demonstrated the use of aldehyde groups in a McMurry-type<sup>[55]</sup> reductive coupling reaction for the direct synthesis of vinylene groups (Scheme 3). In order



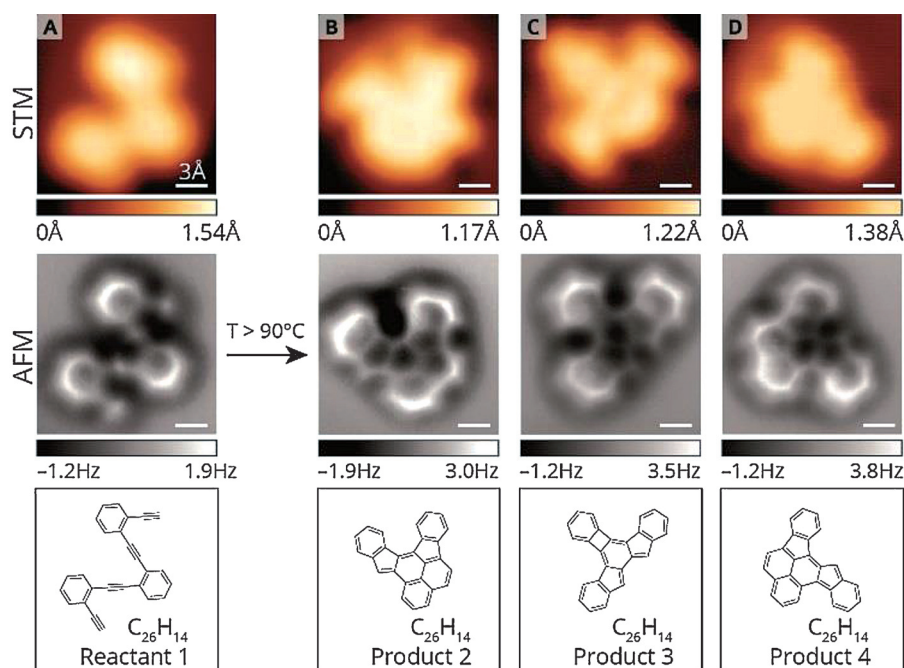
**Scheme 3.** McMurry-type reductive coupling of aldehydes. Adapted from Ref. [54].

to circumvent the desorption of the molecules, before the reaction has taken place, they have followed the strategy of depositing the molecules directly onto the Au(111) substrate kept at 250 °C.

A non-reductive approach to create double bonds has been presented by Matena et al. Upon deposition of 1,3,8,10-tetra-

azaperopyrene on a Cu(111) surface, the molecule readily tautomerized into an intermediate N-heterocyclic carbene (NHC). Subsequently, the NHCs recombined to form regular oriented oligomer chains.<sup>[56,57]</sup>

One of the most studied cycloaromatization reactions is the Bergman cyclization.<sup>[59]</sup> By heating of an enediyne, a highly reactive *para*-benzyne radical is formed, which yields a benzene ring if supplied with hydrogen atoms from a donor. This reaction has been shown in a very special way by García de Oteyza et al.<sup>[58]</sup> As can be seen in Figure 2, heating of the ethynyl-substituted phenyl rings on a Ag(100) surface has initiated an intramolecular Bergman cyclization, yielding three isomeric products. Furthermore, they were able to assign all isomers by submolecularly resolved nc-AFM images. The Bergman cyclization has also been used for creating polyphenylene nano-

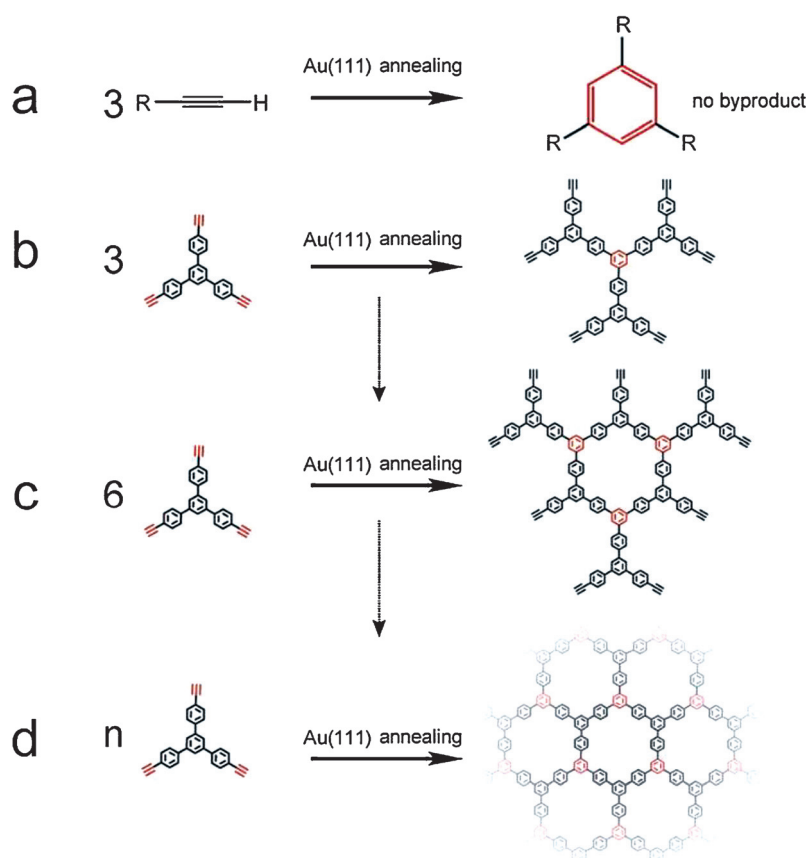


**Figure 2.** Bergman cyclization on Ag(100). Upon thermal annealing, the precursor (A) reacts and forms the three isomers (B–D). Adapted from Ref. [58].

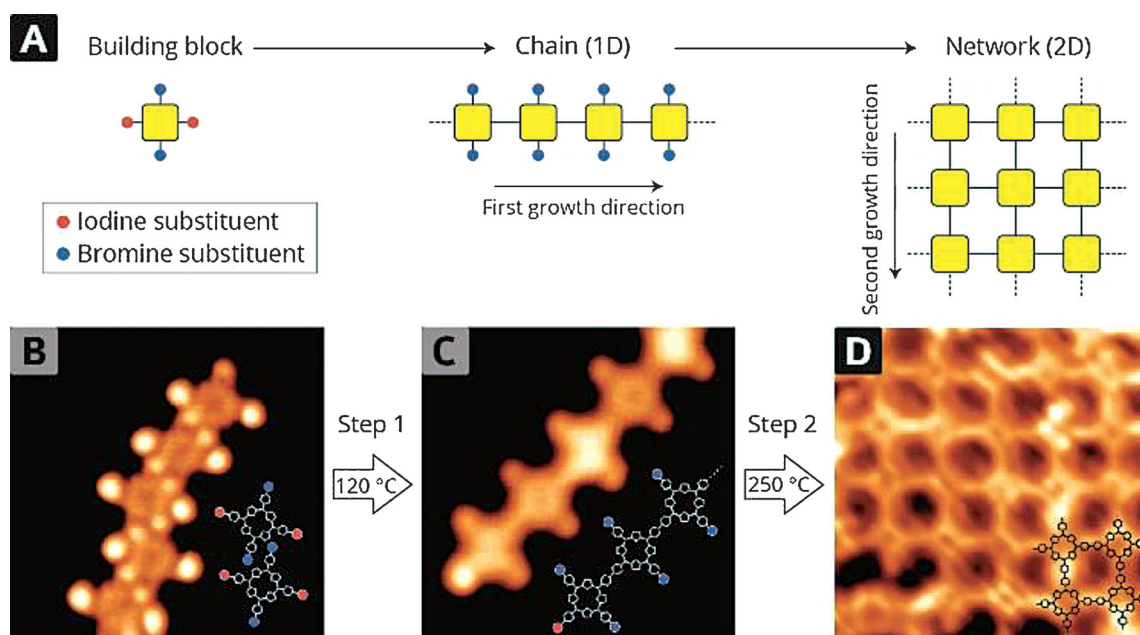
wires. For this purpose, Sun et al. deposited 1,6-di-2-naphthylhex-3-ene-1,5-diyne onto a Cu(110) surface.<sup>[60]</sup> Instead of saturating the intermediate *para*-benzyne diradicals with hydrogen, the highly reactive molecules have recombined to yield the respective polyphenylene chains. Since alkynes bear a triple bond, they allow for synthesizing aromatic molecules via cycloaddition. This has been shown recently by Liu et al. on Au(111).<sup>[61]</sup> As shown in Scheme 4, the stepwise reaction of triethynyl benzene yielded a two-dimensional polyphenylene network, with a pore size of 1.7 nm.

Besides being highly active precursors, as just shown, alkyne groups bear the potential for the creation of rigid and linear nano-wires, due to the *sp* hybridization of the carbon atoms. In order to covalently link these alkyne groups, chemists have used Glaser-type coupling reactions based on Cu catalysis for the last 150 years.<sup>[62]</sup> Very recent-

ly, this reaction has been transferred to surfaces by Zhang et al.<sup>[63]</sup> Unlike the Ullmann coupling previously discussed, the



**Scheme 4.** Cyclotrimerization of triethynyl benzene to form a 2D network. Adapted from Ref. [61].



**Figure 3.** (A) Two-step activation mechanism of the Ullmann coupling using iodine and bromine substituents; The pristine molecules (B) form linear chains after a first heating step (C), which react further to a two-dimensional network (D); Adapted from Ref. [28].

subsequent annealing of the adsorbed molecules resulted in desorption of 1,3,5-triethynylbenzene molecules, leaving only the bare Ag(111) sample surface. However, by deposition onto the Ag(111) surface, held at 330 K, they were able to induce dimerization and oligomerization. After this first reaction step, the surface could be annealed to 370 K, inducing a further oligomerization of the molecules. The on-surface coupling of alkynes has also been shown on Cu,<sup>[64]</sup> Ag,<sup>[65,66]</sup> as well as by photochemical activation with visible light.<sup>[67]</sup>

As discussed for the Ullmann coupling, the substrate has a crucial influence on the reaction. In two comparative studies, Gao et al. have found that on the Ag(111) surface the desired linear coupling product of a bisethynylbenzene was formed with a yield of 64%.<sup>[68,69]</sup> On Au(111) the yield of the linear product was only 25%, with the main product molecules with alkene functionalities. Additionally, they observed a similar trend for the Glaser coupling on Cu(111).<sup>[53]</sup>

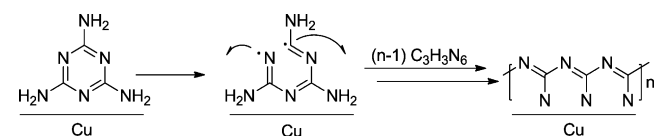
### 3.3. Sequential Activation

In order to gain more control over the reaction, a sequential reaction process has been explored as a highly promising approach for hierarchical covalent linkage. Making use of the differences in bonding strength in halogen-carbon bonds, Grill et al. have been able to steer the degree of polymerization.<sup>[28]</sup> By exchanging two of the iodine atoms in tetrakis(4-iodophenyl)-porphyrin by bromine atoms, they could exclusively cleave off the iodine atoms in a first annealing step. After the subsequent formation of a one-dimensional polymer chain, cleaving of the carbon-bromine bonds was initiated by a second annealing step. By following this route, they could crosslink the linear polymer chains, obtained in the first annealing step, re-

sulting in an extended two-dimensional network structure with improved degree of order (see Figure 3).

A remarkable example has been shown by combining the Ullmann coupling with a subsequent Scholl reaction.<sup>[70]</sup> The latter is a coupling reaction between two arene compounds by the loss of hydrogen (cyclodehydrogenation). Cai et al. deposited 10,10'-dibromo-9,9'-bianthryl on a Au(111) surface.<sup>[26]</sup> At first, the Ullmann coupling was initiated, by annealing of the substrate to 470 K. Hereby, the bianthryl units formed a linear polymer chain. After a consecutive second annealing step at 670 K, a linear graphene nanoribbon was obtained via the aforementioned Scholl reaction. Furthermore, depending on the employed precursor, they were able to precisely choose between zigzag and armchair graphene nanoribbons. Recently, this has been shown via a photopolymerization approach on HOPG.<sup>[71]</sup>

Lin et al. have shown the ring-opening polymerization of melamine on Cu(111) (see Scheme 5).<sup>[72]</sup> By annealing, they observed two phase changes. At room temperature the pristine



**Scheme 5.** Ring-opening polymerization of melamine on Cu(111). Adapted from Ref. [72].

melamine molecules self-assembled in an upright standing configuration. Upon heating to 420 K, the domains reoriented into linear chains. Further annealing to 570 K resulted in the formation of a two-dimensional covalent network.

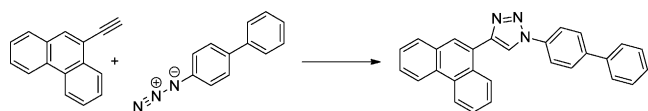
### 3.4. Reactions Involving Two Reactants

Since it is often not possible or feasible to incorporate all groups necessary for a reaction in a single molecule, reactions involving two reactants have been explored. Such reactions also bear the potential that reaction initiation might occur without the need of annealing, simply by codeposition of the two educt species. Among the first approaches, the condensation reaction of an aldehyde and an amine yielding a Schiff base has been shown by Weigelt et al. on a Au(111) surface.<sup>[73]</sup> In this work, no annealing was needed to induce this reaction, simply the presence of the two molecules at the surface was sufficient. By taking the next logical step and using bi- and tri-functional molecules, they, consequently, were able to form a polyimine network on the same surface.<sup>[74,75]</sup> More recently, this reaction has been shown on HOPG in combination with supramolecular ordering.<sup>[76]</sup> Similar reactions have been the condensation of primary amines to tertiary amines,<sup>[77]</sup> the formation of a polyimide<sup>[78,79]</sup> and the polycondensation using boronic acids<sup>[80–83]</sup> and with co-sublimated hydroxy-functionalized molecules.<sup>[84,85]</sup> The condensation of boronic acids has also been initiated by e-beam irradiation.<sup>[86]</sup> Furthermore, the condensation between highly reactive acyl chlorides with amines on Ag(111) has shown to yield the respective polyamides.<sup>[87–89]</sup>

Despite being highly valuable synthetic tools, by introducing numerous reactive groups into polymers, condensation reactions bear one drawback for on-surface synthesis, namely the formation of byproducts. The condensation product, for example water or even hydrochloric acid, contaminates the surface and can lead to side reactions or other undesired effects. Thus, addition reactions, which yield no byproducts per definition, have been investigated for on-surface synthesis.

As an example for an addition reaction, melamine, an aromatic triamine, has been studied by Jensen et al.<sup>[90]</sup> This molecule readily reacts with 1,4-phenylene diisocyanate on a Au(111) surface to form polyurea networks. Mild annealing has shown to further accelerate the polymerization by disrupting the close-packed melamine domains.

The well-known Huisgen 1,3-dipolar cycloaddition is a very versatile method for the creation of 1,4-substituted triazoles in standard organic chemistry (see Scheme 6).<sup>[92]</sup> Here, an alkyne



**Scheme 6.** Huisgen 1,3-dipolar cycloaddition between 9-ethynylphenanthrene and 4-azidobiphenyl. Adapted from Ref. [91].

and an azide undergo a Cu-catalyzed cyclization in an atom-economic reaction. Because of the high yields and the inherent atom economy, it falls under Sharpless' definition of "click" chemistry.<sup>[93]</sup> Bebensee et al. have been the first to transfer this reaction to a Cu(111) surface.<sup>[91]</sup> By cosublimation of 9-ethynylphenanthrene and 4-azidobiphenyl, it was found that these

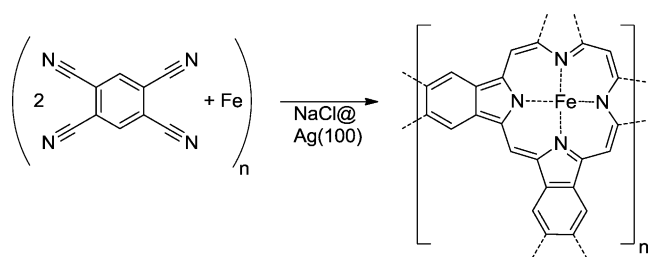
two compounds react already at room temperature to yield the corresponding triazole. Similarly, Diaz Arado et al. have shown an oligomerization approach on Au(111), where the azide and the alkyne were present in the same molecule.<sup>[94]</sup> Furthermore, the formal [2+2] cycloaddition between an alkyne-substituted porphyrin and 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ) has been shown by Fesser et al.<sup>[95]</sup> Table 1 provides an overview of successfully conducted on-surface reactions carried out in an ultra-high vacuum.

**Table 1.** Overview of successfully conducted on-surface reactions carried out in ultra-high vacuum.

Reaction name	Stimulus	Substrate and reference
Ullmann coupling	$\Delta T$	Cu, <sup>[11,14–20,42]</sup> Ag, <sup>[20–26,42]</sup> Au, <sup>[13,19,26–34,41,81]</sup> CaCO <sub>3</sub> , <sup>[35–37]</sup> HOPG, <sup>[42]</sup> NaCl@Au, <sup>[38]</sup> h-BN@Ni <sup>[39]</sup> graphene@Ni <sup>[39]</sup>
Ullmann coupling	$h\nu$	Sapphire, <sup>[40]</sup> HOPG <sup>[71]</sup>
Glaser coupling	$\Delta T$	Cu, <sup>[64,68,69]</sup> Ag, <sup>[53,63,65,66,68,69]</sup> Au, <sup>[68,69]</sup>
Glaser coupling	$h\nu$	Cu, <sup>[53]</sup> Ag, <sup>[53]</sup> Au <sup>[53]</sup>
Bergman cyclization	$\Delta T$	Cu, <sup>[60]</sup> Ag <sup>[58]</sup>
Huisgen cycloaddition	$\Delta T$	Cu, <sup>[91]</sup> Au <sup>[94]</sup>
Scholl reaction	$\Delta T$	Ag, <sup>[48,26,47]</sup> Au, <sup>[26,49]</sup> Pt, <sup>[51,52]</sup> Ru, <sup>[50]</sup> HOPG <sup>[71]</sup>
Ring-opening polymerization	$\Delta T$	Cu <sup>[72]</sup>
NHC oligomerization	$\Delta T$	Cu <sup>[56,57]</sup>
Condensation reaction	$\Delta T$	Cu, <sup>[80,83]</sup> Ag, <sup>[84,80,82,85,87–89]</sup> Au <sup>[73–75,77–81]</sup>
Condensation reaction	$\Delta T$	Ag <sup>[86]</sup>
Carbonyl-analogue addition	$\Delta T$	Au, <sup>[90]</sup> Ag, <sup>[96]</sup> NaCl@Ag <sup>[96]</sup>
McMurry reaction	$\Delta T$	Au <sup>[54]</sup>
[2+2+2] cycloaddition	$\Delta T$	Au <sup>[61]</sup>
[2+2] cycloaddition	$\Delta T$	Au <sup>[95]</sup>
[2+2] cycloaddition	$h\nu$	CaCO <sub>3</sub> <sup>[97]</sup>
Decarboxylative polymerization	$\Delta T$	Cu, <sup>[67]</sup> Ag <sup>[67]</sup>
Desulfurization + recyclization	$\Delta T$	Ni <sup>[46]</sup>

## 4. Reactions on Insulating Substrates

As discussed above, metal surfaces exhibit several advantages for on-surface synthesis. First, organic precursor molecules typically anchor firmly to metal surface, permitting the use of annealing as a straightforward reaction initiation. Second, metal surfaces have been shown to promote the on-surface reaction by acting as a catalyst.<sup>[42]</sup> Extending the possible substrates to electrically non-conducting surfaces is, however, of fundamental interest to provide maximum flexibility for future applications. Most importantly, when considering on-surface synthesis for molecular electronics applications, the molecular electronic structure needs to be decoupled from the underlying substrate, which is not the case when using metallic substrates. Hence, exploring reactions on thin insulating films and, especially, bulk insulators is of utmost importance. First reactions on thin insulating films, supported by a metallic substrate, have been realized by Abel et al.<sup>[96]</sup> By using a standard route for the synthesis of metallophthalocyanines (see Scheme 7), they have been able to synthesize two-dimensional networks.

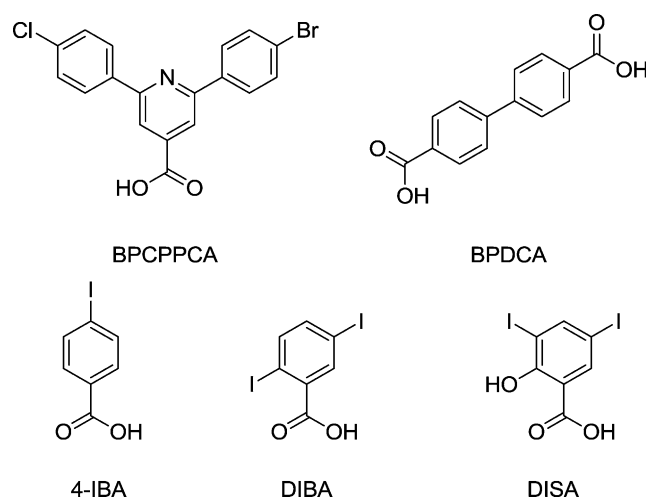


**Scheme 7.** Reaction Scheme for the on-surface synthesis of a two-dimensional phthalocyanine network. Adapted from Ref. [96].

By depositing 1,2,4,5-tetracyanobenzene and Fe in a ratio of 2:1, the phthalocyanine network was formed spontaneously at room temperature on a Ag(100) surface. Although the surface was partially covered with NaCl islands in advance, the educts favored adsorbing on the metal due to a higher molecule–substrate interaction. Only after the metallic parts were covered with molecules, did the molecules form a two-dimensional network on the NaCl islands, again illustrating the typically weak molecule–surface interaction in the case of nonmetallic surfaces. The basic reaction for the phthalocyanine synthesis is, like the Huisgen cycloaddition, atom-economic, and, thus, no contaminations are produced on the surface. The real value of this synthesis is the potentially exchangeable metal atom, which allows the networks to be adapted to specific requirements. The drawback, however, of these thin insulating films is that the molecules are not fully electronically decoupled from the substrate. This is evident from the ability to perform scanning tunneling spectroscopy on top of such islands.<sup>[38]</sup> Thus, it is mandatory to extend the materials' base of the supporting surface to the heterogeneous class of bulk insulators. For these substrates, specific anchoring strategies have to be developed to compensate for the lower surface energy of the substrate. The interaction between the molecule and the substrate can be increased by introducing specific side groups in the molecules, by matching the molecule dimensions with the substrate periodicity and by increasing the number of functional groups.<sup>[98]</sup>

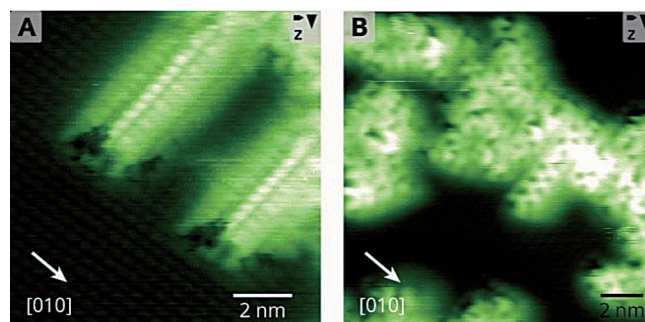
As a first example of an on-surface reaction on a bulk insulator substrate, Kittelmann et al. have explored Ullmann-type coupling on  $\text{CaCO}_3$  (104), calcite. On  $\text{CaCO}_3$ , carboxylic acid groups have proven to be valuable functional groups in order to anchor the molecules to the surface (see also Scheme 8).<sup>[36,98]</sup> Thus, for a simple proof-of-principle 4-iodobenzoic acid (4-IBA) was chosen. This compound possesses a carboxylic acid group for anchoring to the surface, and a thermally cleavable carbon-iodine bond. Upon adsorption of 4-IBA on  $\text{CaCO}_3$  and subsequent annealing above 520 K, molecular species were obtained that fit in size with the expected reaction product, namely 4,4'-biphenyldicarboxylic acid (BPDCA). This on-surface reaction step has been further corroborated by separate deposition of ex-situ synthesized BPDCA.<sup>[35]</sup> In order to obtain linear polymers, two reactive groups have to be present in the *para* position.

Consequently, 2,5-diiodobenzoic acid has been studied on  $\text{CaCO}_3$ . After deposition and subsequent annealing of the sub-



**Scheme 8.** Molecules used for on-surface synthesis on insulators.

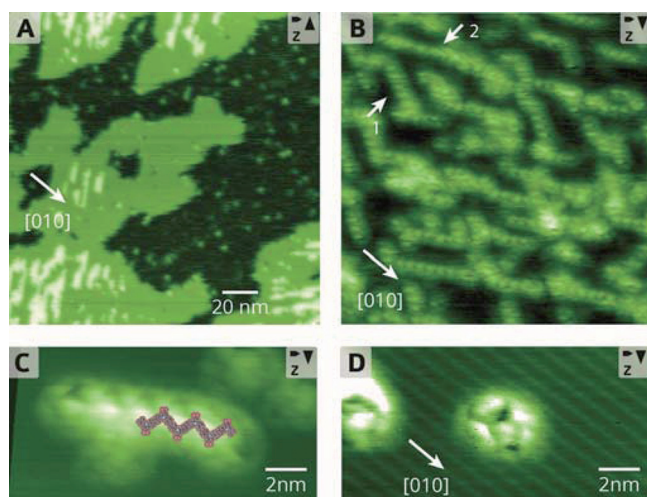
strate above 530 K one-dimensional molecular rows were revealed, aligned perpendicularly to the [010] substrate direction (Figure 4A). Accordingly, when adsorbing 3,5-diiodosalicylic acid onto the same surface, a zigzag pattern can be observed after thermal annealing (Figure 4B). Thus, even the shape of the reaction product could be controlled by varying the positions of the reactive sites.



**Figure 4.** Thermally initiated Ullmann-type coupling of (A) diiodobenzoic acid and (B) diiodosalicylic acid. Adapted from Ref. [35].

Inspired by the sequential activation strategy first demonstrated by Grill et al.,<sup>[28]</sup> Kittelmann et al. have extended the above reaction route by using a benzoic acid derivative with two different halogen atoms, namely 2-(4-bromophenyl)-6-(4-chlorophenyl)pyridine-4-carboxylic acid (BPCPPCA). This precursor has been chosen as it bears the potential for a site-specific, two-step reaction on the bulk insulator calcite.<sup>[37]</sup> After deposition of BPCPPCA, molecular islands with a (2×4) superstructure were observed on the surface (Figure 5A). This structure is changed drastically after a first annealing step to 570 K. Now, the molecules formed row-like structures, presumably induced by the cleaving of the C–Br bonds (Figure 5B). A second qualitative change was induced by annealing the substrate to 610 K (Figure 5C). This change is explained by homolysis of the C–Cl





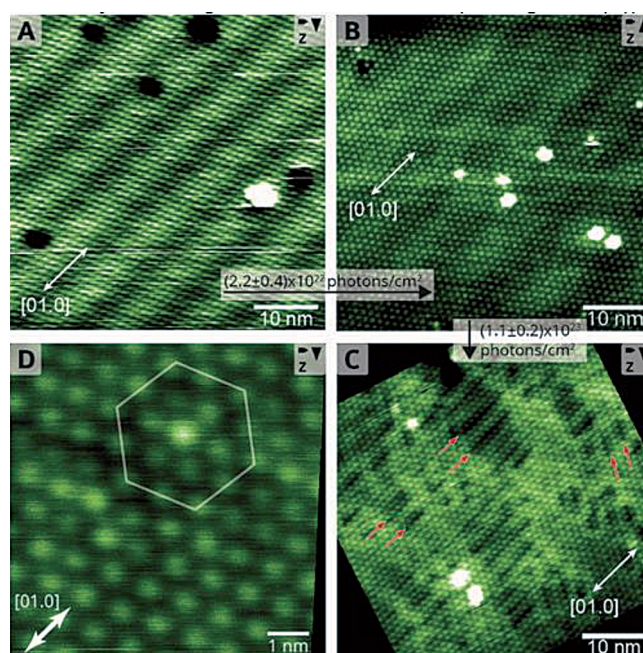
**Figure 5.** Site-specific and sequential on-surface reaction on the (104) surface of calcite.<sup>[37]</sup> (A) Islands of BPCPPCA deposited onto calcite(104). (B) After a first annealing step to 570 K rows along specific surface directions are observed. (C) After a second annealing step at 610 K, zigzag chains are observed on the surface. (D) Additionally, ring-like structures can be observed.

bonds, allowing for the formation of extended zigzag and closed-ring structures (Figure 5D).

The abovementioned examples on calcite all rely on the thermal initiation of an Ullmann-type of reaction. This raises the fundamental question as to why the reaction could be initiated even in the absence of a metal catalyst. A definite answer to this question is lacking at present, but it appears possible that the strong anchoring of the molecule towards the calcite surface weakens the C–X bond and, thus, favors homolytic cleavage of this bond.

From a fundamental point of view, it is most desirable to explore other means of reaction initiation than thermal activation. This is especially true for insulating surfaces to reduce the risk of desorption upon reaction initiation. But also for decoupling the deposition from the initiation step, it is highly important to explore photochemical initiation as activation step for on-surface synthesis.

The first example of photochemical initiation on a bulk insulator has been the [2+2] cycloaddition of C<sub>60</sub> molecules on calcite(104).<sup>[97]</sup> Here, the pristine molecules arranged in a hexagonal pattern. Due to a mismatch with the underlying calcite substrate, a moiré pattern was observed (Figure 6A).<sup>[43]</sup> Upon irradiation with a 405 nm laser, the moiré pattern first became irregular (Figure 6B). Finally, domains separated by dark lines were visible (Figure 6C). This change in the moiré pattern has been ascribed to C<sub>60</sub>–C<sub>60</sub> covalent linking, which changes the C<sub>60</sub>–C<sub>60</sub> distance and thus crucially affects the moiré pattern. The reaction was further confirmed by a direct observation of the shortening in the intermolecular distances (Figure 6D). The orientation of the domains has been explained by the mismatch with the underlying substrate. This mismatch constitutes the driving force for the reaction, which, consequently, is highly favored along a specific substrate direction. Thus, this



**Figure 6.** A monolayer of C<sub>60</sub> on calcite (10.4) before and after irradiation. (A) The pristine film shows a moiré pattern. After irradiation the moiré pattern becomes aperiodic (B) and eventually vanished (C). Instead, domains separated by dark lines (red arrows) are observed (D) A close-up reveals the change in distance between individual C<sub>60</sub> molecules (white hexagon). Adapted from Ref. [97].

study has demonstrated the potential to even control the reaction direction by the underlying substrate lattice.

## 5. Conclusions and Outlook

On-surface synthesis shows great promise for creating functional molecular structures at surfaces. When compared to self-assembly, on-surface synthesis outperforms it in terms of structural stability and specific materials properties such as electron transport. Moreover, this emerging concept allows for preparing compounds that might not be accessible by a classical, solution-based approach due to poor solubility of the involved species. As a most exciting perspective, the two-dimensional confinement of the educt molecules on the surface can be deliberately employed for stabilizing transient structures, which offers the potential to explore entirely new reaction pathways. Fully exploiting the benefits of on-surfaces synthesis will require detailed insight into the chemical nature of the molecule–surface interaction and the specific adsorption geometry. Scanning probe microscopy techniques performed in ultra-high vacuum have proven to provide the most detailed real-space information, which has greatly advanced this rapidly growing field of research.

## Acknowledgements

*Stimulating discussions with Ralf Bechstein and Antje Richter are gratefully acknowledged. We thank the European Commission for*

financial support through the European Project PAMS (seventh framework program GA 610446). R.L. is a recipient of a fellowship through the Excellence Initiative (DFG/GSC 266).

**Keywords:** molecular electronics · molecular structure formation · scanning probe microscopy · two-dimensional confinement · ultrahigh vacuum

- [1] A. Gourdon, *Angew. Chem. Int. Ed.* **2008**, *47*, 6950–6953; *Angew. Chem.* **2008**, *120*, 7056–7059.
- [2] G. Franc, A. Gourdon, *Phys. Chem. Chem. Phys.* **2011**, *13*, 14283–14292.
- [3] L. Bartels, *Nat. Chem.* **2010**, *2*, 87–95.
- [4] J. Sakamoto, J. van Heijst, O. Lukin, A. D. Schlüter, *Angew. Chem. Int. Ed.* **2009**, *48*, 1030–1069; *Angew. Chem.* **2009**, *121*, 1048–1089.
- [5] D. F. Perepichka, F. Rosei, *Science* **2009**, *323*, 216–217.
- [6] X. Zhang, Q. Zeng, C. Wang, *Nanoscale* **2013**, *5*, 8269–8287.
- [7] N. R. Champness, *Nat. Nanotechnol.* **2007**, *2*, 671–672.
- [8] J. A. A. W. Elemans, S. Lei, S. De Feyter, *Angew. Chem. Int. Ed.* **2009**, *48*, 7298–7333; *Angew. Chem.* **2009**, *121*, 7434–7469.
- [9] J. V. Barth, *Surf. Sci.* **2009**, *603*, 1533–1541.
- [10] F. Ullmann, *Justus Liebigs Ann. Chem.* **1904**, *332*, 38–81.
- [11] S. Hla, L. Bartels, G. Meyer, K. Rieder, *Phys. Rev. Lett.* **2000**, *85*, 2777–2780.
- [12] Y. Okawa, M. Aono, *Nature* **2001**, *409*, 683–684.
- [13] L. Grill, M. Dyer, L. Lafferentz, M. Persson, M. V. Peters, S. Hecht, *Nat. Nanotechnol.* **2007**, *2*, 687–691.
- [14] J. A. Lipton-Duffin, O. Ivashenko, D. F. Perepichka, F. Rosei, *Small* **2009**, *5*, 592–597.
- [15] Q. Fan, C. Wang, Y. Han, J. Zhu, W. Heringer, J. Kuttner, G. Hilt, J. M. Gottfried, *Angew. Chem. Int. Ed.* **2013**, *52*, 4668–4672; *Angew. Chem.* **2013**, *125*, 4766–4770.
- [16] J. A. Lipton-Duffin, J. A. Miwa, M. Kondratenko, F. Cicoira, B. G. Sumpter, V. Meunier, D. F. Perepichka, F. Rosei, *Proc. Natl. Acad. Sci. USA* **2010**, *107*, 11200–11204.
- [17] M. Xi, B. E. Bent, *Surf. Sci. Lett.* **1992**, *278*, A69–A70.
- [18] M. Di Giovannantonio, M. El Garah, J. Lipton-Duffin, V. Meunier, L. Cardenas, Y. F. Revurat, A. Cossaro, A. Verdini, D. F. Perepichka, F. Rosei, G. Contini, *ACS Nano* **2013**, *7*, 8190–8198.
- [19] M. Koch, M. Gille, A. Viertel, S. Hecht, L. Grill, *Surf. Sci.* **2014**, *627*, 70–74.
- [20] R. Gutzler, L. Cardenas, J. Lipton-Duffin, M. El Garah, L. E. Dinca, C. E. Szakacs, C. Fu, M. Gallagher, M. Vondráček, M. Rybachuk, D. F. Perepichka, F. Rosei, *Nanoscale* **2014**, *6*, 2660–2668.
- [21] M. Bieri, M. Treier, J. Cai, K. Ait-Mansour, P. Ruffieux, O. Gröning, P. Gröning, M. Kastler, R. Rieger, X. Feng, K. Müllen, R. Fasel, *Chem. Commun.* **2009**, 6919–6921.
- [22] M. Bieri, S. Blankenburg, M. Kivala, C. A. Pignedoli, P. Ruffieux, K. Müllen, R. Fasel, *Chem. Commun.* **2011**, *47*, 10239–10241.
- [23] S. Schlögl, T. Sirtl, J. Eichhorn, W. M. Heckl, M. Lackinger, *Chem. Commun.* **2011**, *47*, 12355.
- [24] J. Eichhorn, T. Strunskus, A. Rastgoo-Lahrood, D. Samanta, M. Schmittel, M. Lackinger, *Chem. Commun.* **2014**, *50*, 7680–7682.
- [25] F. Schlütter, F. Rossel, M. Kivala, V. Enkelmann, J. P. Gisselbrecht, P. Ruffieux, R. Fasel, K. Müllen, *J. Am. Chem. Soc.* **2013**, *135*, 4550–4557.
- [26] J. Cai, P. Ruffieux, R. Jaafar, M. Bieri, T. Braun, S. Blankenburg, M. Muoth, A. P. Seitsonen, M. Saleh, X. Feng, K. Müllen, R. Fasel, *Nature* **2010**, *466*, 470–473.
- [27] L. Smykalla, P. Shukryna, M. Korb, H. Lang, M. Hietschold, *Nanoscale* **2015**, *7*, 4234–4241.
- [28] L. Lafferentz, V. Eberhardt, C. Dri, C. Africh, G. Comelli, F. Esch, S. Hecht, L. Grill, *Nat. Chem.* **2012**, *4*, 215–220.
- [29] T. Lin, G. Kuang, X. S. Shang, P. N. Liu, N. Lin, *Chem. Commun.* **2014**, *50*, 15327–15329.
- [30] J. Eichhorn, D. Niecarz, O. Ochs, D. Samanta, M. Schmittel, P. J. Szabelski, M. Lackinger, *ACS Nano* **2014**, *8*, 7880–7889.
- [31] L. Massimi, O. Ourdjini, L. Lafferentz, M. Koch, L. Grill, E. Cavaliere, L. Gavioli, C. Cardoso, D. Prezzi, E. Molinari, A. Ferretti, C. Mariani, M. G. Betti, *J. Phys. Chem. C* **2015**, *119*, 2427–2437.
- [32] S. Schlögl, W. M. Heckl, M. Lackinger, *Surf. Sci.* **2012**, *606*, 999–1004.
- [33] T. Lin, X. S. Shang, J. Adisoejoso, P. N. Liu, N. Lin, *J. Am. Chem. Soc.* **2013**, *135*, 3576–3582.
- [34] J. Adisoejoso, T. Lin, X. S. Shang, K. J. Shi, A. Gupta, P. N. Liu, N. Lin, *Chem. Eur. J.* **2014**, *20*, 4111–4116.
- [35] M. Kittelmann, P. Rahe, M. Nimrich, C. M. Hauke, A. Gourdon, A. Kühnle, A. Ku, *ACS Nano* **2011**, *5*, 8420–8425.
- [36] M. Kittelmann, M. Nimrich, J. L. Neff, P. Rahe, W. Greñ, X. Bouju, A. Gourdon, A. Kühnle, *J. Phys. Chem. C* **2013**, *117*, 23868–23874.
- [37] M. Kittelmann, M. Nimrich, R. Lindner, A. Gourdon, A. Kühnle, *ACS Nano* **2013**, *7*, 5614–5620.
- [38] C. Bombis, F. Ample, L. Lafferentz, H. Yu, S. Hecht, C. Joachim, L. Grill, *Angew. Chem. Int. Ed.* **2009**, *48*, 9966–9970; *Angew. Chem.* **2009**, *121*, 10151–10155.
- [39] C. Morchutt, J. Björk, S. Krotzky, R. Gutzler, K. Kern, *Chem. Commun.* **2015**, *51*, 2440–2443.
- [40] D. Sloan, Y. Sun, H. Ihm, J. M. White, *J. Phys. Chem. B* **1998**, *102*, 6825–6830.
- [41] A. Saywell, J. Schwarz, S. Hecht, L. Grill, *Angew. Chem. Int. Ed.* **2012**, *51*, 5096–5100; *Angew. Chem.* **2012**, *124*, 5186–5190.
- [42] R. Gutzler, H. Walch, G. Eder, S. Kloft, W. M. Heckl, M. Lackinger, *Chem. Commun.* **2009**, 4456–4458.
- [43] P. Rahe, R. Lindner, M. Kittelmann, M. Nimrich, A. Kühnle, *Phys. Chem. Chem. Phys.* **2012**, *14*, 6544–6548.
- [44] K. F. Wojciechowski, *Surf. Sci.* **1999**, *437*, 285–288.
- [45] L. Vitos, A. V. Ruban, H. L. Skriver, J. Kollár, *Surf. Sci.* **1998**, *411*, 186–202.
- [46] L. E. Dinca, C. Fu, J. M. MacLeod, J. Lipton-Duffin, J. L. Brusso, C. E. Szakacs, D. Ma, D. F. Perepichka, F. Rosei, *ACS Nano* **2013**, *7*, 1652–1657.
- [47] A. Wiengarten, K. Seufert, W. Auwärter, D. Eciija, K. Diller, F. Allegretti, F. Bischoff, S. Fischer, D. a. Duncan, A. C. Papageorgiou, F. Klappenberger, R. G. Acres, T. H. Ngo, J. V. Barth, *J. Am. Chem. Soc.* **2014**, *136*, 9346–9354.
- [48] M. In't Veld, P. Iavicoli, S. Haq, D. B. Amabilino, R. Raval, *Chem. Commun.* **2008**, 1536–1538.
- [49] D. Zhong, J.-H. Franke, S. K. Podiyanchari, T. Blömker, H. Zhang, G. Kehr, G. Erker, H. Fuchs, L. Chi, *Science* **2011**, *334*, 213–216.
- [50] K. T. Rim, M. Sijaj, S. Xiao, M. Myers, V. D. Carpentier, L. Liu, C. Su, M. L. Steigerwald, M. S. Hybertsen, P. H. McBreen, G. W. Flynn, C. Nuckolls, *Angew. Chem. Int. Ed.* **2007**, *46*, 7891–7895; *Angew. Chem.* **2007**, *119*, 8037–8041.
- [51] 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. Mendez, A. M. Echavarren, R. Perez, B. Gomez-Lor, J. A. Martin-Gago, *Nature* **2008**, *454*, 865–868.
- [52] K. Amsharov, N. Abdurakhmanova, S. Stepanow, S. Rauschenbach, M. Jansen, K. Kern, *Angew. Chem. Int. Ed.* **2010**, *49*, 9392–9396; *Angew. Chem.* **2010**, *122*, 9582–9586.
- [53] H.-Y. Y. Gao, D. Zhong, H. Mönig, H. Wagner, P.-A. Held, A. Timmer, A. Studer, H. Fuchs, *J. Phys. Chem. C* **2014**, *118*, 6272–6277.
- [54] O. D. Arado, H. Mönig, J.-H. Franke, A. Timmer, P.-A. Held, A. Studer, H. Fuchs, *Chem. Commun.* **2015**, *4*, 1166–1169.
- [55] J. E. McMurry, M. P. Fleming, *J. Am. Chem. Soc.* **1974**, *96*, 4708–4709.
- [56] M. Matena, T. Riehm, M. Stöhr, T. A. Jung, L. H. Gade, *Angew. Chem. Int. Ed.* **2008**, *47*, 2414–2417; *Angew. Chem.* **2008**, *120*, 2448–2451.
- [57] M. Matena, M. Stöhr, T. Riehm, J. Björk, S. Martens, M. S. Dyer, M. Persson, J. Lobo-Checa, K. Müller, M. Enache, H. Wadepohl, J. Zegenhagen, T. A. Jung, L. H. Gade, *Chemistry* **2010**, *16*, 2079–2091.
- [58] D. García de Oteyza, P. Gorman, Y.-C. Chen, S. Wickenburg, A. Riss, D. J. Mowbray, G. Etkin, Z. Pedramrazi, H.-Z. Tsai, A. Rubio, M. F. Crommie, F. R. Fischer, *Science* **2013**, *340*, 1434–1437.
- [59] R. R. Jones, R. G. Bergman, *J. Am. Chem. Soc.* **1972**, *94*, 660–661.
- [60] Q. Sun, C. Zhang, Z. Li, H. Kong, Q. Tan, A. Hu, W. Xu, *J. Am. Chem. Soc.* **2013**, *135*, 8448–8451.
- [61] J. Liu, P. Ruffieux, X. Feng, K. Müllen, R. Fasel, *Chem. Commun.* **2014**, *50*, 11200–11203.
- [62] C. Glaser, *Ber. Dtsch. Chem. Ges.* **1869**, *2*, 422–424.
- [63] Y.-Q. Zhang, N. Kepčija, M. Kleinschrodt, K. Diller, S. Fischer, A. C. Papageorgiou, F. Allegretti, J. Björk, S. Klyatskaya, F. Klappenberger, M. Ruben, J. V. Barth, *Nat. Commun.* **2012**, *3*, 1286.
- [64] J. Eichhorn, W. M. Heckl, M. Lackinger, *Chem. Commun.* **2013**, *49*, 2900–2902.

- [65] B. Cirera, Y. Q. Zhang, S. Klyatskaya, M. Ruben, F. Klappenberger, J. V. Barth, *ChemCatChem* **2013**, *5*, 3281–3288.
- [66] B. Cirera, Y. Q. Zhang, J. Björk, S. Klyatskaya, Z. Chen, M. Ruben, J. V. Barth, F. Klappenberger, *Nano Lett.* **2014**, *14*, 1891–1897.
- [67] H.-Y. Y. Gao, P. A. Held, M. Knor, C. Mück-Lichtenfeld, J. Neugebauer, A. Studer, H. Fuchs, *J. Am. Chem. Soc.* **2014**, *136*, 9658–9663.
- [68] H.-Y. Y. Gao, H. Wagner, D. Zhong, J.-H. Franke, A. Studer, H. Fuchs, *Angew. Chem. Int. Ed.* **2013**, *52*, 4024–4028; *Angew. Chem.* **2013**, *125*, 4116–4120.
- [69] H.-Y. Y. Gao, J.-H. H. Franke, H. Wagner, D. Zhong, P.-A. A. Held, A. Studer, H. Fuchs, *J. Phys. Chem. C* **2013**, *117*, 18595–18602.
- [70] R. Scholl, C. Seer, R. Weitzenböck, *Ber. Dtsch. Chem. Ges.* **1910**, *43*, 2202.
- [71] C.-A. Palma, K. Diller, R. Berger, A. Welle, J. Björk, J. L. Cabellos, D. J. Mowbray, A. C. Papageorgiou, N. P. Ivleva, S. Matich, E. Margapoti, R. Niessner, B. Menges, J. Reichert, X. Feng, H. J. Raeder, F. Klappenberger, A. Rubio, K. Müllen, J. V. Barth, *J. Am. Chem. Soc.* **2014**, *136*, 4651–4658.
- [72] Y. P. Lin, O. Ourdjini, L. Giovanelli, S. Clair, T. Faury, Y. Ksari, J. M. Themlin, L. Porte, M. Abel, *J. Phys. Chem. C* **2013**, *117*, 9895–9902.
- [73] S. Weigelt, C. Busse, C. Bombis, M. M. Knudsen, K. V. Gothelf, T. Strunskus, C. Wöll, M. Dahlbom, B. Hammer, E. Lægsgaard, F. Besenbacher, T. R. Linderoth, *Angew. Chem. Int. Ed.* **2007**, *46*, 9227–9230; *Angew. Chem.* **2007**, *119*, 9387–9390.
- [74] S. Weigelt, C. Bombis, C. Busse, M. M. Knudsen, K. V. Gothelf, E. Lægsgaard, F. Besenbacher, T. R. Linderoth, *ACS Nano* **2008**, *2*, 651–660.
- [75] S. Weigelt, C. Busse, C. Bombis, M. M. Knudsen, K. V. Gothelf, E. Lægsgaard, F. Besenbacher, T. R. Linderoth, *Angew. Chem. Int. Ed.* **2008**, *47*, 4406–4410; *Angew. Chem.* **2008**, *120*, 4478–4482.
- [76] Y. Li, J. Wan, K. Deng, X. Han, S. Lei, Y. Yang, Q. Zheng, Q. Zeng, C. Wang, *J. Phys. Chem. C* **2011**, *115*, 6540–6544.
- [77] S. Weigelt, J. Schnadt, A. K. Tuxen, F. Masini, C. Bombis, C. Busse, C. Isvoranu, E. Ataman, E. Lægsgaard, F. Besenbacher, T. R. Linderoth, *J. Am. Chem. Soc.* **2008**, *130*, 5388–5389.
- [78] M. Treier, R. Fasel, N. R. Champness, S. Argent, N. V. Richardson, *Phys. Chem. Chem. Phys.* **2009**, *11*, 1209–1214.
- [79] M. Treier, N. V. Richardson, R. Fasel, *J. Am. Chem. Soc.* **2008**, *130*, 14054–14055.
- [80] S. Clair, M. Abel, L. Porte, *Chem. Commun.* **2014**, *50*, 9627–9635.
- [81] T. Faury, S. Clair, M. Abel, F. Dumur, D. Gigmes, L. Porte, *J. Phys. Chem. C* **2012**, *116*, 4819–4823.
- [82] T. Faury, F. Dumur, S. Clair, M. Abel, L. Porte, D. Gigmes, *CrystEngComm* **2013**, *15*, 2067.
- [83] O. Ourdjini, R. Pawlak, M. Abel, S. Clair, L. Chen, N. Bergeon, M. Sassi, V. Oison, J.-M. Debierre, R. Coratger, L. Porte, *Phys. Rev. B* **2011**, *84*, 125421.
- [84] N. A. A. Zwaneveld, R. Pawlak, M. Abel, D. Catalin, D. Gigmes, D. Bertin, L. Porte, *J. Am. Chem. Soc.* **2008**, *130*, 6678–6679.
- [85] R. Coratger, B. Calmettes, M. Abel, L. Porte, *Surf. Sci.* **2011**, *605*, 831–837.
- [86] S. Clair, O. Ourdjini, M. Abel, L. Porte, *Chem. Commun.* **2011**, *47*, 8028–8030.
- [87] C. H. Schmitz, J. Ikonov, M. Sokolowski, *J. Phys. Chem. C* **2009**, *113*, 11984–11987.
- [88] C. H. Schmitz, J. Ikonov, M. Sokolowski, *J. Phys. Chem. C* **2011**, *115*, 7270–7278.
- [89] C. Schmitz, M. Schmid, *J. Phys. Chem. C* **2011**, *115*, 18186–18194.
- [90] S. Jensen, H. Früchtel, C. J. Baddeley, *J. Am. Chem. Soc.* **2009**, *131*, 16706–16713.
- [91] F. Bebensee, C. Bombis, S.-R. Vadapoo, J. R. Cramer, F. Besenbacher, K. V. Gothelf, T. R. Linderoth, *J. Am. Chem. Soc.* **2013**, *135*, 2136–2139.
- [92] R. Huisgen, *Proc. Chem. Soc.* **1961**, *17*, 357–396.
- [93] H. C. Kolb, M. G. Finn, K. B. Sharpless, *Angew. Chem. Int. Ed.* **2001**, *40*, 2004–2021; *Angew. Chem.* **2001**, *113*, 2056–2075.
- [94] O. Díaz Arado, H. Mönig, H. Wagner, J.-H. H. Franke, G. Langewisch, P. A. Held, A. Studer, H. Fuchs, *ACS Nano* **2013**, *7*, 8509–8515.
- [95] P. Fesser, C. Iacovita, C. Wäckerlin, S. Vijayaraghavan, N. Ballav, K. Howes, J.-P. Gisselbrecht, M. Crobu, C. Boudon, M. Stöhr, T. A. Jung, F. Diederich, *Chemistry* **2011**, *17*, 5246–5250.
- [96] M. Abel, S. Clair, O. Ourdjini, M. Mossoyan, L. Porte, *J. Am. Chem. Soc.* **2011**, *133*, 1203–1205.
- [97] R. Lindner, P. Rahe, M. Kittelmann, A. Gourdon, R. Bechstein, A. Kühnle, *Angew. Chem. Int. Ed.* **2014**, *53*, 7952–7955; *Angew. Chem.* **2014**, *126*, 8087–8090.
- [98] P. Rahe, M. Kittelmann, J. L. Neff, M. Nimmrich, M. Reichling, P. Maass, A. Kühnle, *Adv. Mater.* **2013**, *25*, 3948–3956.

---

Received: February 26, 2015

Published online on May 12, 2015