On-Surfaces Synthesis on Insulating Substrates

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Abstract On-surface synthesis has attracted great attention in recent years due to its promising potential for creating functional structures on surfaces. An important aspect of on-surface synthesis is the capability to arrive at covalently linked thermally stable structures that offer the possibility for application even in harsh environments outside ultra-high vacuum conditions. Additionally, covalent linking allows for fabricating conjugated structures with superior electron transport properties. Especially, the latter is of tremendous interest when considering future applications in the field of molecular electronics. Having molecular electronics applications in mind explains the need for decoupling of the electronic structure of the molecular network from the underlying support surface. Thus, it is highly interesting to transfer on-surface synthesis strategies from metallic to insulating surfaces. Albeit, insulating surfaces pose several challenges for on-surface synthesis. First, many prototypical insulating support materials interact only weakly with organic molecules. This weak binding frequently results in molecule desorption rather than reaction activation when thermally initiating the reaction. Second, it is known that metals act as catalyst for several reactions that have been performed successfully on metallic surfaces. A simple transfer of these reactions to insulating surfaces in the absence of metal atoms is, therefore, questionable and requires different reaction pathways to be considered. In this chapter, we review the current state-of-the-art in on-surface synthesis on electrically insulating substrates carried out in ultra-high vacuum. Proof-of-principle reactions are discussed with an emphasis on strategies to overcome challenges related to the weak molecule-surface binding often present on insulating surfaces, e.g., by means of photochemical activation. Site-specific and sequential reactions are presented as a promising way for enhancing control and structural complexity of on-surface synthesis on insulating support materials. Finally, the influence of the substrate is shown to induce directionality in on-surface synthesis by favoring specific surface directions.

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1 Introduction

Despite being a relatively young field of research, on-surface synthesis has attracted tremendous interest in the past decade. Impressive progress has been made from one of the first proof-of-principle experiments carried out in 2007 [1] to hierarchical synthesis in a sequential and site-specific manner [2]. Compared to self-assembled structures, molecular networks created by on-surface synthesis provide higher stability, which is of importance when considering applications in a harsh environment outside ultra-high vacuum (UHV). From a synthesis point of view, novel reaction pathways might be possible on the surface due to the confinement of the educts to the two-dimensional surface plane. Moreover, the absence of solvent might enable reactions that are difficult in solution due to low solubility of the reaction product [3]. A further aspect is providing structures that can be incorporated into future molecular electronic devices, such as molecular wires and switches. Here, it is of special interest to create covalently coupled structures that are conjugated and, thus, exhibit high electron transport capabilities.

When discussing molecular electronic applications, however, it is mandatory to decouple the electronic structure of the molecular network from the underlying substrate. Thus, metal surfaces are largely incompatible with molecular electronic applications. Attempts to electronically decouple the molecular structure from the support while still working with metallic substrates have been made to maintain the experimental accessibility of the system by scanning tunneling microscopy (STM). One approach is using so-called "Lander" molecules [4], featuring spacer groups that can act as legs to separate the conjugated core form the surface. Another approach is evaporating a thin insulating film on a metal support [5]. However, both strategies bear sever limitations in terms of materials flexibility. Thus, from an application point of view and for enlarging the materials basis for on-surface synthesis, it is highly desirable to transfer the concept from metallic to bulk insulating substrates.

Bulk insulators, however, have rarely been studied in the context of on-surface synthesis. This is mainly due to experimental restrictions, as insulating surfaces are more difficult to investigate. In particular, STM as a powerful tool for real-space imaging [6] cannot be used as it requires electrically conducting substrates. But also when considering the physico-chemical mechanisms of on-surface synthesis, insulating surfaces pose significant challenges as compared to metal substrates. A major obstacle is the comparatively weak molecule–surface interaction on insulating substrates, which frequently leads to desorption rather than reaction initiation upon annealing. This is why alternative routes for reaction initiation, e.g., by photochemical means are of particular importance for insulating substrates. Moreover, the classical Ullmann reaction that has often been exploited for on-surface covalent linking, which is known to be catalyzed by the presence of copper (or other metal) atoms [1]. These facts readily illustrate that a transfer of on-surface synthesis strategies to nonmetallic systems might not be straightforward. Indeed, only few examples of on-surface synthesis reactions have been presented on an insulating surface so far. An important tool toward investigating such systems is the scanning force microscope operated in the noncontact mode, as this technique allows for direct imaging in UHV with atomic or molecular resolution [7].

Here, we review the current state-of-the-art of on-surface synthesis on insulating surfaces carried out in UHV. First, the specific situation arising from the use of insulating surfaces is briefly discussed. We commence the presentation of experimental results by briefly introducing early studies that have been performed on thin insulating films to maintain the experimental accessibility by STM and other electron-based surface characterization methods. After that, the first proof-of-principle reaction carried out on the surface of a bulk insulator is presented, which has been performed with a benzoic acid derivative on calcite(104). The flexibility of this system has been demonstrated by varying the number and position of the reactive sites. We show the possibility to extend this approach for performing sequential and site-specific reaction to enhance structural control. Photochemical initiation of an on-surface synthesis reaction has been demonstrated using C_{60} molecules on calcite(104). With this system, we also address the option of guiding the on-surface reaction by the underlying substrate, thereby gaining further control over the resulting structures. Finally, the current status is concluded and an outlook discussing future trends is given.

2 Specific Situation on Insulating Substrates

Many studies have addressed on-surface synthesis reaction on metallic substrates. However, only little is known about on-surface synthesis on insulating substrates. A main hurdle when investigating insulating surfaces arises from the comparably poor experimental accessibility of insulating substrates. Standard surface science methods such as STM, photoelectron emission spectroscopy (PES) or low-energy electron diffraction (LEED) rely on electrically conducting materials, thus, they usually cannot be applied to nonconducting surfaces. Only since the advent of scanning force microscopy, this experimental limitation has been partially overcome [7]. Substantial improvements of noncontact atomic force microscopy (NC-AFM) have now developed this technique from an emerging method into a standard routine for direct-space imaging of surfaces with atomic resolution.

However, besides this technical aspect, on-surface synthesis on insulating substrates also pose specific challenges arising from the comparably weak and typically unknown interaction of the educt molecules with the supporting substrate. In fact, compared to metal surfaces, the interaction of organic molecules with electrically insulating surfaces is rather poorly understood. In part, this is a consequence of the limited experimental accessibility discussed above. Besides this technical issue, however, the limited understanding also arises from the fact that the class of insulating materials is much more heterogeneous than the class of metals. The class of insulators spans a wide range from covalently linked crystals such as diamond or titanium dioxide, ionic crystals like sodium chloride or calcium fluoride to van der

Waals bonded molecular crystals. Thus, general statements regarding the interaction of organic molecules with "an insulating surface" are difficult to make.

For prototypical insulating surfaces studied so far, namely KBr(001), $CaF_2(111)$, and NaCl(001), the interaction with organic molecules has been found to be comparatively weak. This statement includes both, the binding energy of the molecules towards the surfaces as well as the diffusion barrier on the surface [8–13]. However, precise values of binding energies and diffusion barriers are generally lacking, except for a few examples [12, 14]. The weak interaction hinders molecular self-assembly on these surfaces, and in most cases it prevents on-surface synthesis reaction to be performed as annealing would lead to desorption instead of reaction initiation. Thus, a prerequisite effort is to explore means to enhance the molecule–surface interaction [15]. Several strategies have been followed in this context, including modification of the surface by electron irradiation [16] and equipping the molecules with specific anchor groups [12, 17]. Besides these modifications, it is also important to consider the reactivity of the surface by comparing the surface energies [18]. In this context, the natural cleavage plane of calcite, calcite(104), has taken a special role. It exhibits a surface energy of approximately 600 mJ/m^2, which is not as high as those of typical metals (e.g., Au (111) with more than 1000 mJ/m^2), but still considerably higher than those of the prototypical insulator surfaces discussed above (e.g., KBr(001) having a surface energy of around 140 mJ/m^2). The high surface energy is synonymous to a reactive surface, which can be understood from the fact that calcite(104) provides several binding sites for electrostatic anchoring as well as hydrogen bonding.

An alternative approach to induce on-surface reactions without risking desorption of the educts from the surface is using other stimuli rather than thermal annealing. This is why photochemical initiation is of special interest when discussion on-surface synthesis on insulating substrates. In principle, photochemical initiation can be used to induce a reaction without heating the educts on the surface. Thus, it can be speculated that problems associated with desorption can be substantially reduced by photochemical initiation.

In addition to the weak interaction, non-metallic surfaces pose another challenge. For many reactions initiated so far on surfaces, the metallic substrate is known to act as a catalyst. The most prominent reaction studied so far is the Ullmann reaction, which is catalyzed by the presence of copper (or, generally speaking any other metal with *d* electrons available) atoms. For this reason, it remains questionable, how on-surface reactions relying on the presence of metal atoms can be transferred to insulating surfaces.

3 Reactions on Thin Insulating Films

For maintaining the accessibility by standard surface science characterization methods such as STM, experiments have been carried out on a thin insulator film supported by a metallic substrate. One example has been the synthesis of a two-dimensional polymeric network of Fe phthalocyanine obtained from the stoichiometric co-deposition of iron and the tetracyanobenzene precursor [19]. These educts have been deposited onto an Ag(100) surface that has been partially covered with monatomic NaCl islands. Due to the weak interaction of the molecules with the thin insulating film, the educts have been observed to preferentially adsorb on the free metal areas. Thus, it has appeared necessary to first cover the metallic parts of the surface with molecules before growth could be obtained on the insulating film. A highly ordered, monodomain network has been achieved on the NaCl islands, again illustrating the high molecular mobility on the insulating surface (see Fig. 1a).

The formation of a molecular wire connecting both metallic and insulating parts on a surface has been demonstrated by the synthesis of poly (9,9-dimethylfluorene) on an Au(111) surface exhibiting NaCl islands [20]. In this work, the wire synthesis has been taken part on the metallic areas of the surface with the NaCl islands repelling the molecular wires. Above a critical NaCl coverage, however, the wires have been observed to rise to the top of the NaCl islands due to space limitations (see Fig. 1b). Scanning tunneling spectroscopy data have been collected at various positions of the wire. The latter data have demonstrated that three NaCl layers appeared insufficient for decoupling of the electronic structure of the wire from the underlying metal support; illustrating that thicker layers are needed for a more efficient decoupling.

From these investigations, the above-mentioned weak molecule–surface interaction in case of an insulating surface becomes apparent, indicating that strategies for molecule–surface anchoring are mandatory for on-surface synthesis on insulating surfaces. Moreover, thin films have been shown to fail when asking for efficient electronic decoupling from the metallic support.

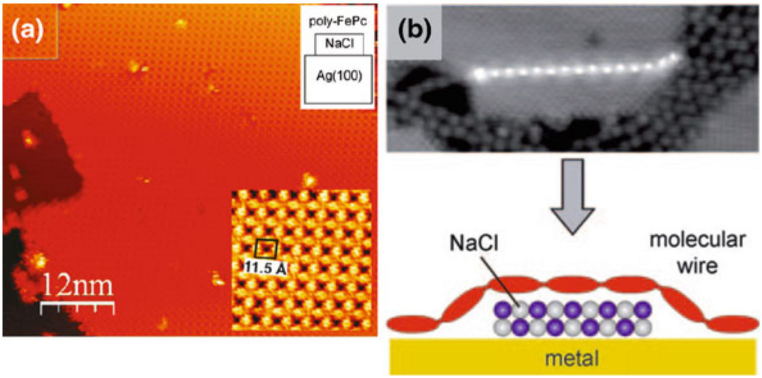


Fig. 1 **a** Two-dimensional network of Fe phthalocyanine on an NaCl island on Ag(100). Reproduced with permission from Abel et al. [19]. **b** Molecular wire of poly(9,9-dimethylfluorene) on an NaCl island on Au(111). Reproduced with permission from Bombis et al. [20]

4 Current State-of-the-Art on Bulk Insulators

In the following section, we review the current state-of-the-art in on-surface synthesis on the surface of a bulk insulator. The first proof-of-principle of an on-surface reaction carried out on an insulating substrate is presented in Sect. 4.1. Varying both number and position of the reactive sites at the molecular building blocks provides a reliable way for controlling the success of the reaction [21]. Based on these results, enhanced reaction control has been achieved by site-specific and sequential reaction initiation [22], which constitutes a promising means for fabricating more complex structures (see Sect. 4.2). Finally, results demonstrating photochemical initiation are reviewed in Sect. 4.3. These results provide a route to overcome problems with desorption of weakly bonded molecules. Moreover, the direction of the oligomerization has been shown to be governed by the underlying substrate, providing an interesting possibility for further structural control by substrate-guided reactions.

Calcite, the most stable modification of calcium carbonate, has been used in the investigations presented here. Calcite has a band gap of 6.0 eV [23], i.e., it constitutes an electrically insulating material. Calcite can be easily cleaved in UHV [24], resulting in the formation of the energetically most favorable (104) cleavage plane (see Fig. 2a). Moreover, as discussed above, calcite(104) has a high surface energy compared to many other insulating surfaces, indicating an increased molecule–surface interaction. This increased interaction is, indeed, observed for many molecules [25].

The molecules that have been used in the studies presented here are shown in Fig. 2b. These include 4-iodobenzoid acid (4-IBA), biphenyl-4,4′-dicarboxylic acid (BPDCA), 2,5-diiodobenzoic acid (DIBA), 3,5-diiodosalicylic acid (DISA), 2-(4-bromophenyl)-6-(4-chlorophenyl)pyridine-4-carboxylic acid (BPCPPCA) as well as C_{60}.

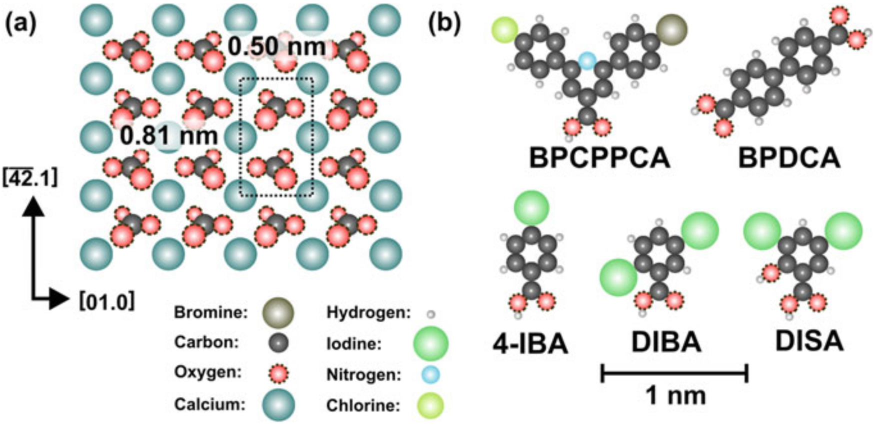


Fig. 2 **a** Calcite crystal structure and **b** molecules studied in this chapter (drawn to scale)

4.1 Proof-of-Principle on a Bulk Insulating Surface

As a first proof-of-principle study, the reaction of several organic molecules has been tested on calcite(104). Among many molecules that have been tested, only few turned out to provide sufficient anchoring towards the surface to initiate the linking reaction by thermal means. Surprisingly, the comparably simple benzoic acid derivatives have been found to be among the successful molecules. The carboxylic acid functionality provides an anchor towards the surface, while the benzene core can be equipped with reactive species. In the simplest case, iodobenzoic acid can be studied. Upon annealing, the iodine atom is cleaved from the molecule, creating reactive radicals on the surface. These radicals diffuse on the surface until they meet another radical to react with.

An important aspect to consider is the deprotonation of the acid group. Depending on the pK_A value of the investigated benzoic acid derivative, the molecules might deprotonate upon annealing before the reaction is initiated. Based on the large number of carboxylic acid molecules deposited onto calcite(104) in UHV [21, 26, 27], a rough estimate can be given regarding the deprotonation state at room temperature. Although the deprotonation surely depends on many other aspects than the pK_A value alone (e.g., the substrate surface and the specific binding geometry), the benzoic acids presented here have been found to obey the following trend. At a pK_A value around 3, the molecule has been observed to deprotonate at room temperature, giving the possibility to follow this transition directly by NC-AFM [27]. Molecules with a pK_A value smaller than 3 are already deprotonated at room temperature, while molecules with a pK_A value larger than 3 require an additional annealing step to induce deprotonation. The latter is of importance when performing on-surface synthesis, as two annealing steps can be required for molecules with a pK_A value larger than 3: In the first step, the molecules become deprotonated, which changes the molecular arrangement on the surface but which is not associated with a covalent linking. Only upon further annealing in the second step, the molecules become dehalogenated and form radicals that can link on the surface. This two-step process has, indeed, been observed for 4-IBA on calcite(104), in agreement with a pK_A value of 4.02 [26].

As shown in Fig. 3, 4-IBA can be covalently linked on calcite(104) using thermal activation. When deposited onto calcite(104) held at room temperature, the molecules are found to be highly mobile, indicating the small diffusion barrier discussed above. As a consequence of the high mobility, molecules are only observed on the surface when confined, e.g., in surface troughs (see Fig. 3a). The situation is changed drastically when annealing the surface to 520 K. This change is ascribed to a deprotonation step. Now, negatively charged molecules exist on the surface, which interact much stronger with the ionic calcite surface than the neutral molecules before annealing. Consequently, a molecular wetting layer is formed with the molecules standing upright and anchoring towards the surface calcium cations (Fig. 3b) [26]. A second annealing step is required for inducing a further structural change. Upon annealing the substrate to 580 K, a molecular structure is found that can be explained by covalently linked dimer molecules arranged in a

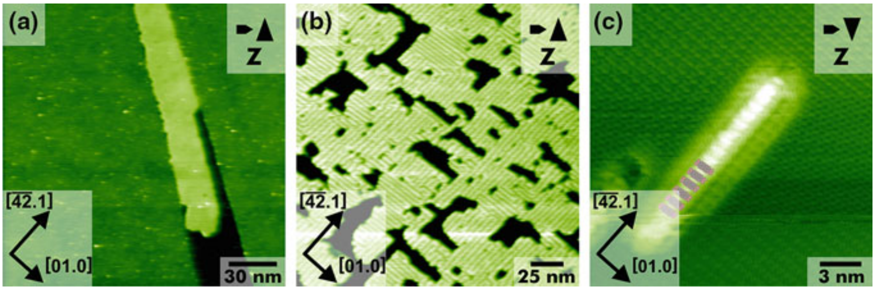


Fig. 3 Proof-of-principle of an on-surface reaction on a bulk insulating substrate [21]. **a** Upon deposition of 4-IBA onto calcite(104) held at room temperature, molecules are only visible when confined into troughs. **b** Moderate annealing to 520 K results in deprotonation and the formation of an extended wetting layer [26]. **c** Upon annealing to 580 K, 4-IBA forms covalently linked molecular dimers on the surface. These dimers resemble their protonated counterparts, which can be obtained from direct deposition of the dimer species, BPDCA [25]

side-by-side fashion (Fig. 3c). This assignment is corroborated by the size of the observed features and by comparing the structure with the appearance of the molecules obtained when directly depositing the reacted species, namely BPDCA [25]. While direct deposition of BPDCA results in two different structures, only the side-by-side structure is obtained for reacted 4-IBA. This can be readily understood from the fact that the reacted 4-IBA is deprotonated, while directly deposited BPDCA is not. Therefore, BPDCA can form a hydrogen-bonded structure with the molecules arranging in a head-to-tail fashion.

To further prove the reaction shown for 4-IBA, the number and the position of the iodine atoms can be changed. When changing the number of the iodine atoms to two in positions 2 and 5 as in DIBA, extended molecular rows are expected on the surface upon covalent linkage. As shown in Fig. 4a, DIBA forms a wetting island upon deposition onto calcite(104) held at room temperature. This indicates a comparatively strong interaction that has been observed with 4-IBA only after the first annealing step. It can, thus, be speculated that DIBA exists on the surface in the deprotonated state already at room temperature. This assumption is supported by the lower pK_A value of 2.51. Upon annealing to 530 K, the structure is changed completely. Now, rows oriented along the [-4-21] substrate direction are found on the surface (Fig. b). This structure can be understood by a twofold dehalogenation of the molecules and covalent linkage of the resulting radicals. Interestingly, the registry of the calcite(104) surface along the [-4-21] direction appears to support the reaction, as the negatively charged carboxylate groups within the row can be positioned atop a calcium ion (see model in Fig. 4c).

As an additional test for the on-surface reaction, the position of the iodine groups at the benzene core can be changed. For this check, DISA has been used, having iodine atoms at position 3 and 5 [21]. Upon linkage, a zigzag pattern is expected if the molecules arrange in an alternating fashion (in fact, also other structures are

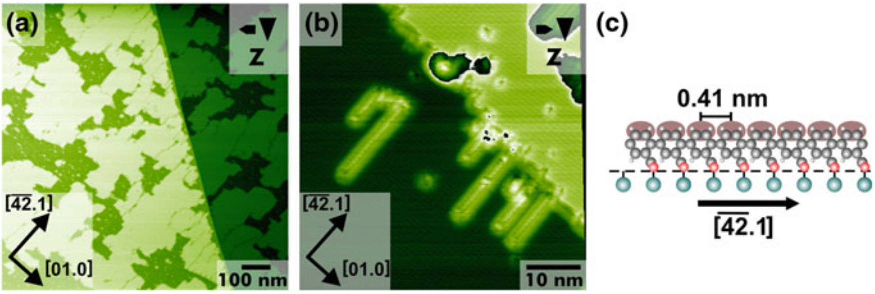


Fig. 4 Changing the number of reactive sites from one to two: DIBA on calcite(104) [21]. **a** Upon deposition of DIBA onto calcite(104) held at room temperature, an extended layer is found on the surface. **b** The structure changes significantly after annealing the surface to 530 K. Now, rows aligned along the [-4-21] substrate direction are formed. **c** Model of the conjugated row on the surface with the negatively charged carboxylate groups anchoring toward the calcite calcium ions

expected for a non-alternating linkage). Again, when depositing this molecule onto calcite(104) held at room temperature, an extended wetting layer is formed as shown in Fig. 5a. In the case of DISA, a perfect (1 × 1) overlayer is obtained, which can be understood by anchoring of the negatively charged carboxylate groups towards the surface calcium ions. This assignment is in agreement with a pK_A of 2.07. A structural change is induced by annealing the surface to 580 K. Now, a structure with reduced height is observed, indicating that the molecules are now lying flat on the surface (Fig. 5b). Among the various patterns observed, also a distinct zigzag structure can be identified. The superposition of the expected zigzag structure illustrates the excellent size match of the obtained structure (see Fig. 5c).

The observed direct response of the resulting structures to the monomer building blocks provides a clear indication for the successful covalent linkage of the molecules. As further evidence, the required temperature can be studied depending

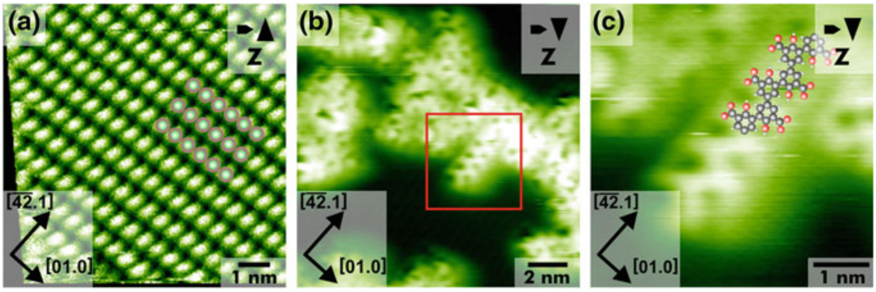


Fig. 5 Changing the position of the reactive sites [21]: DISA on calcite(104). **a** Upon deposition of DISA onto calcite(104) held at room temperature, a (1 × 1) overlayer is formed. **b** After annealing the surface to 580 K, another structure with reduced height is observed. **c** Among the structures seen, also a zigzag pattern is found, which precisely matches the structure expected when having an alternating arrangement of the DISA units within a covalently linked row

on the involved halogen atom. Depending on the halogen-phenyl bond strength, the temperature to induce radical formation is likely to increase when changing the halogen in the order iodine, bromine, chlorine, with the respective bond energies 268, 336 and 399 kJ/mol. This has been tested for the pair DIBA and 2,5-dichlorobenzoic acid. While DIBA has been shown to react at a temperature of 530 K, a temperature of 565 K was needed for radical formation of DCBA on calcite(104). Thus, although the details of the cleavage mechanism remain unclear, the energy required to induce the reaction follows a rather straightforward trend, again corroborating the interpretation of a dehalogenation and covalent linkage reaction.

This discussion directly points to another open question, namely the role of the calcite surface for the dehalogenation step. As mentioned above, the presence of copper is required as a catalyst for the well-known Ullmann reaction. As no metal has been available in the presented studies, another mechanism has to be at play. A possible explanation is a bond weakening of the phenyl-iodine bond upon adsorption of the carboxylate onto the calcite surface. Elucidating the details of the reaction mechanism will, however, require a close interplay of the experimental results with theoretical calculations.

4.2 Site-Specific and Sequential Reaction

A key goal of on-surface synthesis is providing tailor-made molecular networks on surfaces with precise control over structure and functionality. This goal requires enhancing the reaction control, e.g., from a simple one-step process as described above to a two-step reaction with site-specific linkage. This approach has been followed on a metallic surface [2] by using a molecule that has been equipped with both, bromine and iodine substituents. It has been shown that iodine can be cleaved off first, providing site-specific reaction sites that are available for the first-step linking. Only after a second annealing step to slightly higher temperatures, the bromine atoms are removed, making these reaction sites available in the second linking step. Inspired by these results, a similar approach has been taken on calcite(104). A molecule, namely BPCPPCA, has been chosen that provides both, two different halide substituents as well as a carboxylic acid anchor group (see Fig. 2b).

Upon deposition of BPCPPCA onto calcite(104) held at room temperature, molecular islands are observed on the surface as shown in Fig. 6a. These islands exhibit a mirror symmetry axis along the [-4-21] substrate direction. This mirror symmetry can be readily understood by the fact that the molecules form a (2 × 4) superstructure on the surface, which can be arranged in two mirror-symmetric ways on the surface. The islands changes drastically upon a first annealing step at 570 K. Now, row-like features are found on the surface (Fig. b). These rows are aligned along two distinct surface directions, forming an opening angle of about 48°. Considering the molecular structure allows for speculating about the structural details of the rows. A moderate annealing step is expected to exclusively cleave off

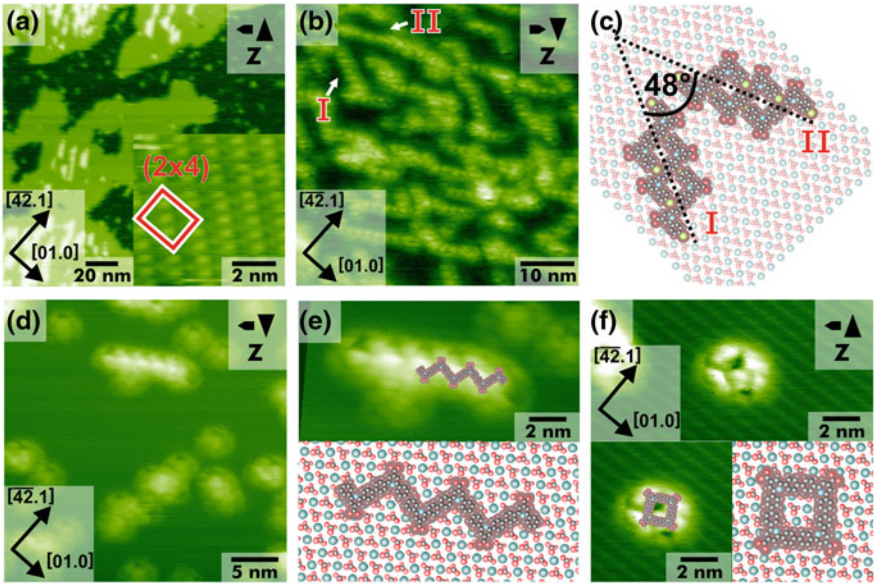
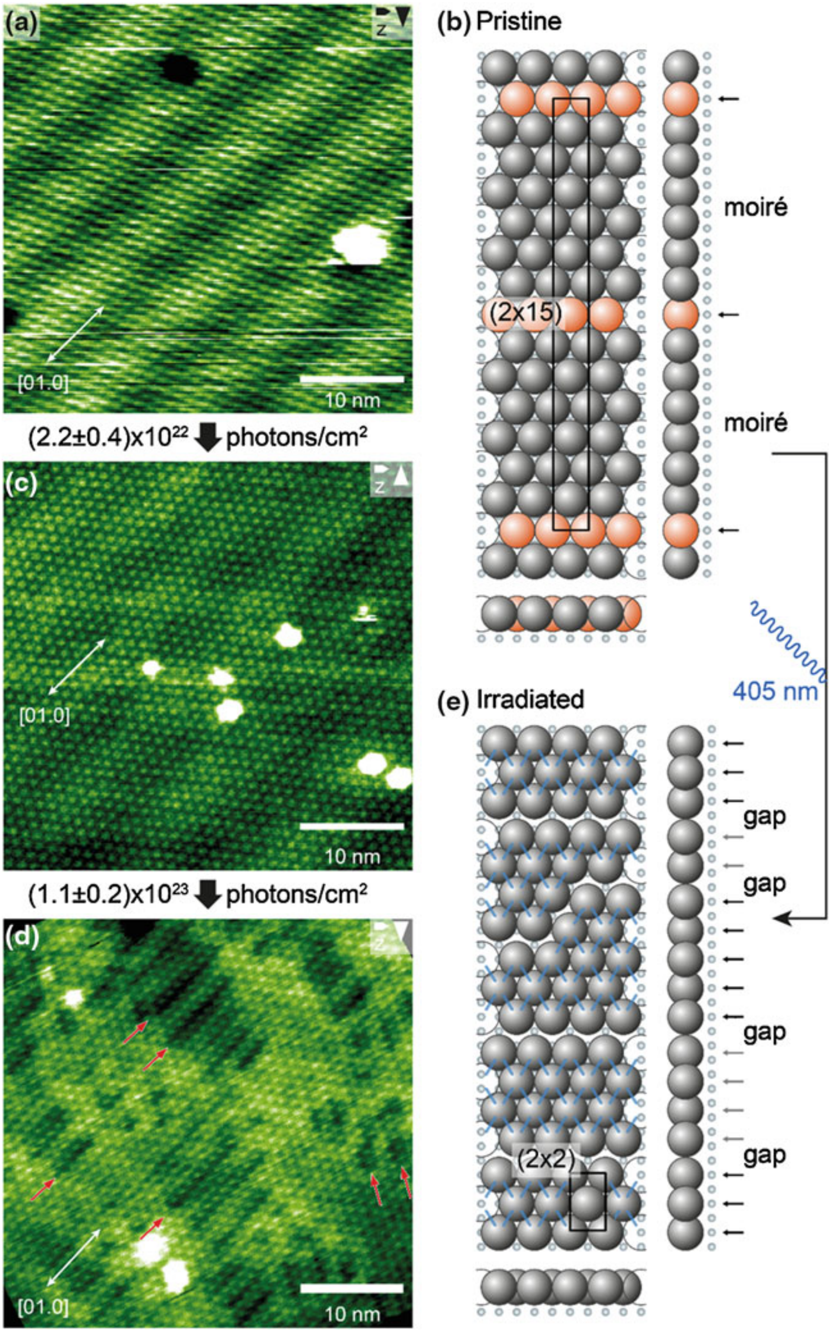


Fig. 6 Site-specific and sequential on-surface reaction on calcite(104) [22]. **a** Upon deposition of BPCPPCA onto calcite(104) held at room temperature, molecular islands with a mirror symmetry axis along [-4-21] exist on the surface. **b** Moderate annealing to 570 K results in the formation of row-like features, oriented along specific surface directions, i.e., resulting in a well-defined opening angle of 48°. **c** Model for the structural arrangement of the row-like features, illustrating the origin of the characteristic opening angle. **d** Further annealing to 610 K induces a second structural change. Now, zigzag chains and ring-like structures are present on the surface. **e** Zoom and structural model of the zigzag chain. **f** Zoom and structural model of a ring structure

the bromine atoms. This results in the formation of molecular dimers either with an "S" or "U" shape. The intermolecular interaction is larger when S-shaped molecules arrange side-by-side. If we now further assume that the carboxylate groups should be positioned atop a surface calcium ion, only two distinct directions are reasonable, as shown in the model in Fig. 6c. These two directions include an opening angle of 48°, precisely as observed in the experiment.

A further structural change is induced when annealing the substrate to 610 K. Upon this second annealing step, the chlorine atoms are expected to dissociate from the dimers, allowing for coupling of the dimers into larger molecular structures. Depending on the conformation of the dimers (S or U-shaped), either zigzag chains (coupling of S-shaped dimers) or ring structures (coupling of two U-shaped dimers) should be formed on the surface. Indeed, two types of structures exist on the surface after the second annealing step as shown in Fig. 6d. Among them, it is possible to identify zigzag chains, as shown in the zoom in Fig. 6e. Superimposing a model of the expected chains demonstrates a perfect size match of the observed periodicity along the chain with the repeat distance of the zigzag structure. Moreover, a specific direction of the chains with respect to the underlying substrate is expected from the


(a)
z
[01.0]
10 nm
(2.2±0.4)x10^{22} photons/cm^2
(c)
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(d)
z
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10 nm
(b) Pristine
moiré
(2x15)
moiré
405 nm
(e) Irradiated
gap
gap
gap
gap
(2x2)

◀ **Fig. 7** Photochemical initiation of an on-surface reaction on a bulk insulator surface [28]. **a** Upon deposition of C_{60} onto calcite(104), elongated islands are formed that show a distinct moiré pattern [18]. **b** The moiré pattern can be readily explained by the different lattice mismatch in the two surface directions as shown in the model. **c** Irradiation with a total of about 10^{22} photons results in an alteration of the structure. The moiré pattern becomes aperiodic. **d** Upon further irradiation with a total of 10^{23} photons, the moiré pattern is vanished. Gaps are formed in the molecular film, which can be understood by considering the molecular model (**e**)

fact that the carboxylate groups of the chain should be placed atop surface calcium ions. One specific direction allows for optimizing this carboxylate–calcium interaction, which is the one drawn in the model in Fig. 6e. This direction is precisely what is observed experimentally, giving further evidence for the proposed model. Besides the chains, also roundish features are revealed on the surface as shown in Fig. 6f. These features can be understood by covalent coupling of two U-shaped dimers. Again, the superimposed model fits in size with the observed ring-like structures. For this structure, it is not possible to optimize the position of all four carboxylate groups within the ring atop a surface calcium ion. The different adsorption positions might be the reason for the somewhat asymmetric appearance of the ring structures. This example demonstrates the feasibility to transfer the strategy of sequential and site-specific reactions to a bulk insulator surface, namely calcite(104).

4.3 Photochemical Initiation

In the above examples, the reaction was initiated by annealing the substrate to a specific temperature, thereby inducing homolytic bond cleavage at the phenyl-halide bond. Although this approach is straightforward experimentally, it bears a severe drawback, which arises from the comparatively weak molecule–surface interaction.

For many molecule–surface systems studied, annealing of the substrate with the aim to initiate the linking reaction only resulted in desorption of the educt molecules from the surface. Thus, it appears mandatory to explore other means of reaction initiation. In this context, photochemical linking is an obvious strategy to decouple reaction initiation from desorption [28–30].

As a straightforward example, C_{60} molecules were chosen, which are known to polymerize in a [2 + 2] cycloaddition when irradiated with light [28]. Upon deposition of C_{60} onto calcite(104) held at room temperature, elongated islands are found on the surface [18]. These islands are formed by C_{60} molecules that arrange in a hexagonal pattern as shown in Fig. 7a. Considering the C_{60}–C_{60} distance in bulk C_{60} of 1.02 nm readily shows that the molecular repeat distance fits nicely to the twofold substrate periodicity of 0.50 nm along the [010] direction. This is why one close-packed direction of the hexagonal molecular layer is aligned along the [010] substrate direction. For the other substrate direction, however, the substrate periodicity of 0.81 nm does not fit to the periodicity of the molecular film of 1.02 nm · sin (60°) = 0.88 nm. Consequently, a moiré pattern is formed, which is readily observed as a height modulation in the image shown in Fig. 7a. A model for the pristine molecular layer is given in Fig. 7b, showing the molecular (2 × 15) superstructure. Molecules that adopt the same adsorption positions (except for a rotation of the underlying carbonate groups) are marked by arrows, directly reflecting the observed moiré pattern. When irradiating the surface covered with molecules with light (405 nm laser diode), the structure changes considerably. Upon a first irradiation step, the moiré pattern starts to degrade and becomes aperiodic as shown in Fig. 7c [28]. Further irradiation results in vanishing of the moiré pattern and the appearance of gaps between the molecules, as marked by the arrows in Fig. 7d. Interestingly, the majority of these gaps are aligned along the [010] direction. Both observations, the vanishing of the moiré pattern as well as the formation of gaps aligned along the [010] direction, can be explained by a simple model in a straightforward manner. As no lattice mismatch exists along the [010] direction, there is no driving force for a linking reaction along this direction. However, linking along the other close-packed row directions of the molecular film, as indicated by the short lines in the model in Fig. e results in a reduction of the molecule–molecule distance along the [-4-21] substrate direction. Interestingly, when C_{60} trimers are formed, the molecule–molecule distance of 0.92 nm [31] projected to the [-4-21] direction becomes 0.80 nm. Thus, upon covalent coupling of the C_{60} molecules along this direction, the lattice mismatch can be lifted, explaining the vanishing of the moiré pattern. As a consequence of the linking along these specific directions, the molecules move closer only in [-4-21] direction, thereby creating a gap that opens along the [010] direction (see Fig. 7e).

These results show that photochemical initiation is possible on a bulk insulator surface. Moreover, the studied system of C_{60} on calcite(104) illustrates how the underlying substrate can be exploited deliberately for guiding the reaction in a specific direction. This constitutes a promising strategy for increasing the structural control in addition to the sequential approach presented above.

5 Summary and Outlook

In recent years, on-surface synthesis has attracted considerable attention due to the impressive potential of this strategy for fabricating novel functional structures at surfaces. This is especially true for the field of future molecular electronics, where tailor-made molecular structures such as wires and switches are needed for constructing functional devices. Having these applications in mind requires strategies to decouple the electronic structure of the molecular network from the underlying substrate. Consequently, electrically insulating rather than metallic substrates are highly interesting for these applications. Compared to metallic substrates, however, little is known about on-surfaces synthesis principles on bulk insulating surfaces. A simple transfer of on-surface synthesis strategies developed on metallic surfaces towards insulating substrates has been demonstrated to be difficult. This is due to the comparably weak molecule–surface interaction present on many insulating surfaces studied so far. Thus, on-surface synthesis on insulating substrates requires to carefully consider the molecule–surface interaction of the system of interest. For the systems studied so far, it has been shown that choosing educt molecules with dedicated anchor functionality appears to be essential for avoiding desorption upon thermal activation of the on-surface reaction. While this need can be partially met by choosing standard educt molecules, the impressive variability of organic synthesis will surely boost the success of on-surface synthesis by providing tailored molecules with dedicated anchor functionalities and reaction sites. Moreover, reaction mechanisms usually requiring the presence of metal atoms, e.g., the Ullmann reaction, need to be reconsidered for transferring these principles to insulating substrates. So far, little is known about the details of on-surface reactions on insulating substrates, clearly asking for theoretical efforts to elucidate the individual reaction steps.

A major effort of future research will be dedicated to increasing the library of available reaction types by exploring suitable educt molecules. Various means of reaction initiation need to be tested as well as co-deposition of two or more educt molecules. Moreover, it will be mandatory to further increase structural control by extending and combining control strategies such as sequential or substrate-guided reactions.

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