Surface Chemistry

DOI: 10.1002/anie.200802229

On-Surface Covalent Coupling in Ultrahigh Vacuum

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C—C coupling · carbenes · radical reactions · scanning probe microscopy · surface chemistry

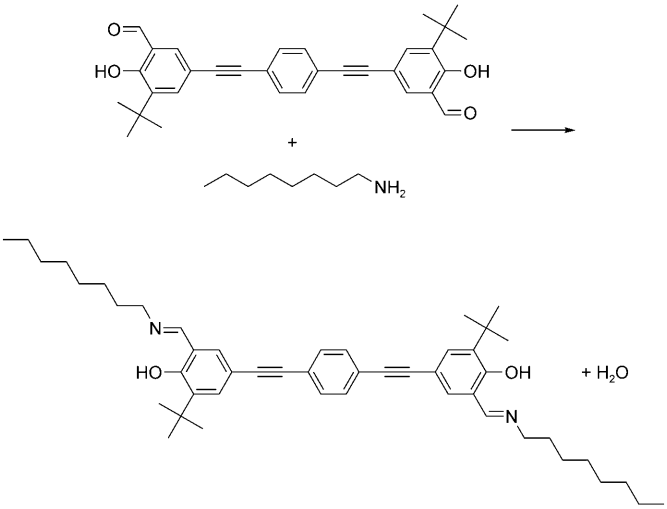
The formation of 2D nanostructures through self-assembly on surfaces is a promising strategy for the fabrication of nanoscale devices by a bottom-up approach.[1] Complex molecular structures held together by weak and reversible van der Waals interactions, hydrogen bonds, and metal complexation[2] have been obtained under ultraclean conditions, namely in an ultrahigh vacuum (UHV). However, such structures are inherently fragile and the intermolecular interactions are weak, which precludes, for example, mechanical stability or intermolecular charge transport. Interconnection of the molecules in a controlled way directly on a surface through robust and irreversible covalent bonding offers a way to overcome these limitations. Such on-surface chemistry under ultraclean conditions potentially presents several advantages over solution synthesis:

a) on-surface and UHV experiments allow a much broader range of reaction temperatures to be used: Sublimation cell or substrate temperatures can be easily controlled from 4 to 600 K without risk of air oxidation or solvent decomposition;
b) the 2D confined geometry could favor some reactions or supramolecular aggregates that are not usually observed. These can arise as a result of entropic or kinetic effects or through interaction with the substrate;
c) it could allow the preparation, from suitable small precursors, of extended 1D or 2D arrays of rigid oligomers or polymers that are impossible to synthesize in solution for solubility reasons;
d) on-surface reactions can be followed by UHV scanning tunneling microscopy (STM). This powerful technique not only allows imaging at the submolecular level, but also very local spectroscopic measurements, tip-induced reactions, and molecular manipulation.

Until recently, such studies were surprisingly rare. A few tip-induced reactions have been demonstrated, such as Ullmann coupling[3] or the polymerization of diynes,[4] but this technique cannot be extended to large arrays of molecules and requires very specific self-assembled molecular structures.[5]

Remarkably, five different examples of the covalent assembly of molecular building blocks on a surface in a UHV have appeared in the past six months. This Highlight summarizes the various aspects of these important results, which have opened up new avenues for the realization of robust functionalized molecular surfaces and arrays for molecular devices and machines.

Linderoth and co-workers[6] were able to form a bisimine by coadsorption of a bis(hydroxybenzaldehyde) and octylamine on a Au(111) surface maintained at room temperature (Scheme 1). The condensation reaction was confirmed by X-ray photoelectron spectroscopy (XPS) and by comparison of the STM images with those of the reaction product obtained from solution and subsequently deposited onto the surface. It is somewhat surprising that this reaction can occur on the surface, because of the complex reaction pathway: in solution the reaction involves the formation of a hemiaminal and an acid-catalyzed dehydration step.



Scheme 1. On-surface formation of an imine.

DFT calculations showed that, in the absence of solvent, the vicinal phenolic group catalyzes the reaction by protonation of the hemiaminal hydroxy group. However, this calculation did not take into account the possible role of the substrate in the reaction pathways: the substrate could also reduce the reaction barrier in the absence of an acidic

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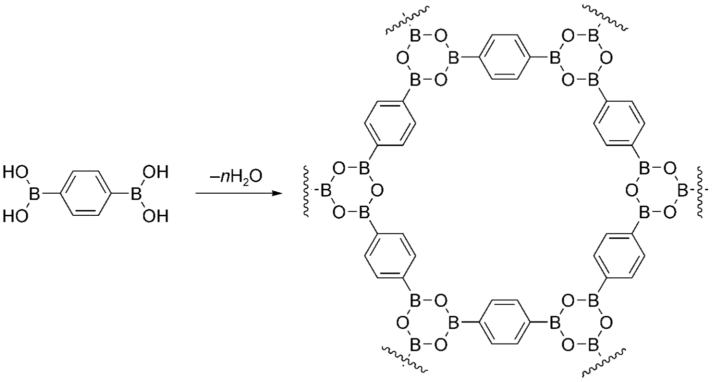


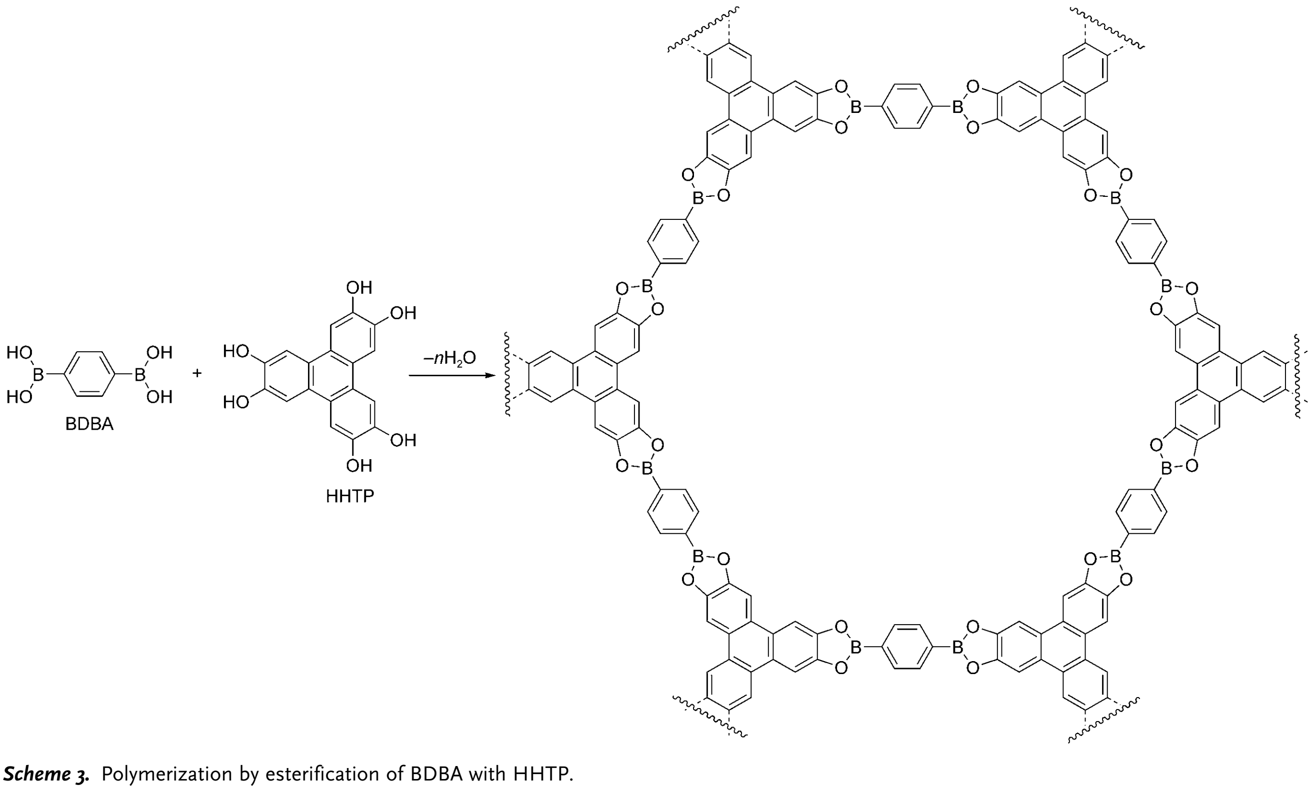
Scheme 2. Polymerization of BDBA by dehydration. The pores have a diameter of about 15 Å.

catalyst. A detailed analysis of the same reaction with a three-spoke trialdehyde was also recently completed.[7] The authors demonstrated that the reaction and self-assembly processes showed pronounced kinetic effects which had important consequences for the final self-assembly of the formed trisimine molecules. In a first step, the trialdehyde was evaporated onto the Au(111) substrate at room temperature. Then, octylamine was dosed on to the substrate, which was maintained either at low temperature (170 K)—resulting in the growth of octylamine multilayers—or at room temperature. After a brief annealing at 300–400 K, the substrates were cooled to 120–170 K for STM imaging. The on-surface reaction at high amine flux and with a cold substrate gave a compact 2D assembly reminiscent of the structure formed by the trialdehyde alone, which suggests a topochemical reaction occurred. In contrast, open porous networks were formed at low amine flux and with a substrate at room temperature. Both of these structures were different from the one obtained by depositing the solution-prepared trisimine. These results demonstrate that on-surface reactions can not only provide new molecules, but can also allow the formation of self-assembled structures not obtainable by standard ex situ synthesis/deposition methods.

More recently, Abel and co-workers described boronate-based reactions, previously known to produce highly ordered covalent 3D networks,[8] on an Ag(111) surface.[9] Intermolecular dehydration of 1,4-benzenediboronic acid (BDBA) was shown to form extended arrays of boroxine (Scheme 2).

It is worth stressing that these porous 2D networks are thermally very stable and not damaged even by annealing at 750 K for 5 minutes. The second reaction they described[9] was the esterification of BDBA by 2,3,6,7,10,11-hexahydroxytriphenylene (HHTP), which yielded networks of polygons that were dominated by hexagons with a pore size of about 29 Å (Scheme 3). This reaction even proceeded at room temperature, thus indicating a low activation barrier—as observed in solution. To inhibit the homopolymerization of BDBA, a monolayer of HHTP was initially deposited, followed by co-deposition of the two molecules. Excess HHTP and liberated water were removed from the surface by annealing. The formation of such extended arrays with large and very stable nanopores will allow further surface functionalization as well as a way to investigate experiments on reactivity in a confined space.

The three reactions described above, imine formation, dehydration of a boronic acid, and esterification, are on-surface versions of reactions that are well known in solution.



Scheme 3. Polymerization by esterification of BDBA with HHTP.

However, the large temperature range tolerated and the presence of a clean, potentially reactive substrate also permits reactions that are not encountered in solution.

The first example of radical covalent coupling of tetraphenylporphyrins (TPPs) was recently reported by Grill et al.[10] Their experiments rely on the thermal dissociation of bromine–carbon(phenyl) bonds to give radical fragments that are prone to dimerization. This activation was done either by annealing a Au(111) substrate that was partially covered with brominated TPP molecules, or during sublimation from a Knudsen cell (above 470 K). The so-obtained mono- or polyradical species diffused on the substrate, even at 150 K, and then reacted with each other to form either 1D or 2D arrays of coupled porphyrins, depending upon the number and positions of the bromine atoms in the precursor porphyrins (Figure 1). The covalent bonding was demonstrated by scanning tunneling spectroscopy data, which showed a broad peak at 3 eV centered around the intermolecular connection, thus clearly showing the presence of the new carbon–carbon bond. Lateral manipulation by STM was used to evaluate the strength of the inter- or intramolecular bonding. In contrast, the same experiment performed with unsubstituted TPP led to fragile islands of molecules only maintained through van der Waals interactions.

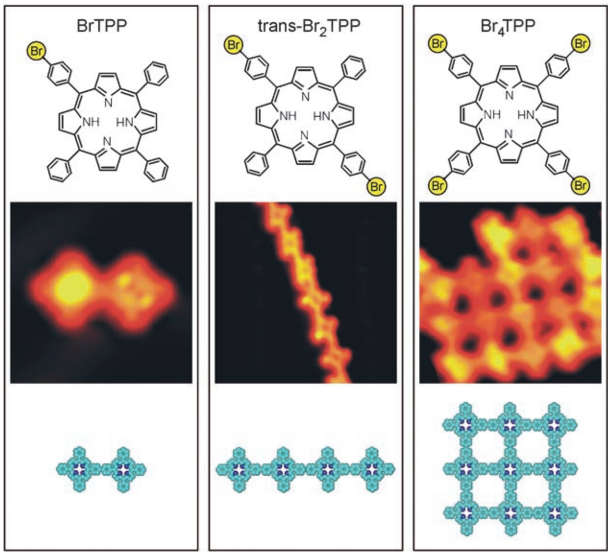


Figure 1. 1D and 2D arrays formed by oligomerization of porphyrin radicals (reprinted with permission from L. Grill).

This experiment shows that even polyradicals can be sublimated, and that these are stable enough, on Au(111), to diffuse and react. Furthermore, it opens up the possibility of controlling the topology of the created structure, since it reflects the chemical structure of the building blocks (Figure 1).

This result is in contrast with the study carried out by Weiss and McCarty[11] on dissociative chemisorption of *para*-diodobenzene on a more reactive Cu(111) surface; this reaction is considered to be the first step in the polymerization of diiodobenzene through a copper-catalyzed Ullmann coupling reaction. In this case, the thermal decomposition of the dihalide on the substrate at room temperature led to lines of protopolymers without intermolecular bonding. No mention was made of any attempt to form C–C bonds by annealing at higher temperature or by using more weakly physisorbed aromatic compounds.

Shortly afterwards, Amabilino, Raval, and co-workers[12] published a surface-assisted radical coupling of tetra(mesityl)porphyrins on a Cu(110) surface. In this case, the porphyrin was sublimated at 150 °C onto the substrate at room temperature. The STM images showed that the molecules were located at individual sites of the metal surface, at distances where they were not in contact. Annealing between 150 and 200 °C resulted in the formation of a new arrangement and the evolution of hydrogen. The majority of molecules then appeared in lines as well as angular and gridlike structures, with intercore distances corresponding to a covalent bond between the mesityl groups of the molecules. The authors proposed a mechanism in which reduction of the methyl groups by the copper surface generates $CH_2^{\bullet}$ radicals, which are then involved in the homocoupling of radicals. It can be expected that this type of reaction would not occur on a more inert substrate such as Au(111).

Even more recently, Jung, Gade, and co-workers[13] demonstrated the thermally induced C–C coupling of N-heterocyclic carbenes on a Cu(111) surface. In a first step, 1,3,8,10-tetraazaperopyrene (TAPP) was sublimated at submonolayer coverage onto a substrate maintained at 150 °C, which led to the formation of a porous network. The authors assigned this 2D packing to a coordination polymer, formed through interaction of the lone pairs of electrons on the nitrogen atoms with the copper atoms. This arrangement was stable up to 190 °C and evolved above 250 °C into 1D chains of covalently coupled molecules (Figure 2).

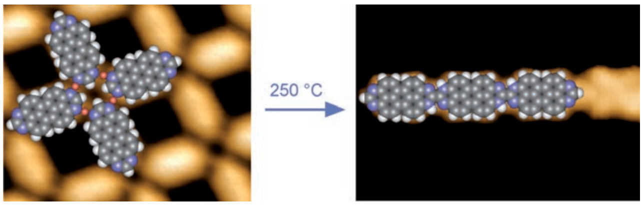


Figure 2. From metal coordination to covalent coupling (reprinted with permission from L. Gade and T. Jung); red Cu, blue N, gray C, white H.

The mechanism of the oligomerization stems from the tautomerization and dimerization of the carbenes of TAPP, a process favored by the polycyclic character of the monomer and which becomes exothermic after trimerization (Scheme 4).

The polymerization yields robust chains with delocalized electrons. Eventually, these chains can interact to form a double-stranded band of oligomers held together through coordination with the copper atoms. This experiment opens the way to the preparation of high-conductance molecular wires, which are impossible to synthesize by standard

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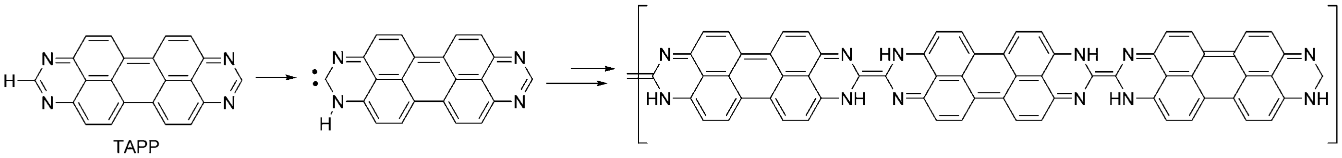

Scheme 4. Tautomerization and polymerization of TAPP.

reactions in solution because of their expected high reactivity and low solubility.

These five studies of on-surface covalent coupling reactions are very important breakthroughs towards the fabrication of stable complex nanostructures on surfaces. Such nanostructures have numerous potential applications in molecular electronics, sensors, surface nanomachines, and catalysis. It is worth stressing the variety of reactions and the different types of activation mechanisms that have been described: formation of an imine, dehydration, and esterification as well as the coupling of radicals and carbenes, thus opening up a new field of research. Further advances will require a detailed analysis of all the parameters that control the reactions: leaving groups, influence of the substrate, diffusion/preorganization of the reactants, activation steps, reaction mechanism, and kinetics. In the longer term, the use of multifunctional precursors will allow sequential reactions on a surface to yield stable complex 2D arrays of molecular subunits.

Published online: August 7, 2008

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