Surface Chemistry

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# Polymerization of Polyanthrylene on a Titanium Dioxide (011)-(2 × 1) Surface**

*Marek Kolmer, Amir A. Ahmad Zebari, Jakub S. Prauzner-Bechcicki,* Witold Piskorz, Filip Zasada, Szymon Godlewski, Bartosz Such, Zbigniew Sojka, and Marek Szymonski*

One of the most challenging promises of nanotechnology is an ultimate level of control in fabrication of nanoscale structures, machines, and devices. Fine positioning of single atoms demonstrated by Eigler and Schweizer,[1] or precise control over Ullmann reaction on Cu surface reported by Hla and co-workers,[2] are excellent examples of achievable mastery in the field of scanning tip-induced processes. However, if larger one-dimensional and two-dimensional nanostructures are targeted, the tip-induced methods are not the most favorable: they would require tremendous amount of time for accomplishment. Thus, taking an advantage of self-assembly and thermal triggering is a very encouraging strategy among others in delivering the highest possible precision and efficiency in fabrication of large nanostructures.[3] It has been envisaged that functionalizing individual molecular precursors (building blocks) with precisely chosen linking sites should allow for future bottom-up construction of miscellaneous molecular devices.[3d,4] Accordingly, many research groups have recently reported successful direct on-surface formation of covalently bonded molecular structures with use of various thermally triggered chemical reactions on metallic surfaces.[3b–d,4,5] These reports refer to formation of a wide range of structures, spanning from simple dimers to longer oligomers, or even two-dimensional molecular networks. Yet, to the best of our knowledge, the on-surface fabrication of covalently bonded molecular structures accomplished on semiconducting surfaces has not been reported.

An approach that offers direct formation of complex molecular structures in a predefined form on a desired substrate surface, by itself, is a very attractive idea from a technological point of view. A possibility to merge, in a bottom-up fashion, a substrate possessing chosen bulk and surface properties (for example, appropriate band gap, catalytic reactivity, and so on) with specifically designed large molecular architectures (for example, networks with pores of uniform size and preferred shape) is a key advantage of the discussed method. Understanding the on-surface processes leading to the formation of such molecular objects will advance many technological branches, such as nano-electronics, gas- and bio-sensing, solar cells, and many others.

Herein, we present the on-surface polymerization on a semiconducting metal oxide surface, namely $TiO_2$. Molecular precursors 10,10′-dibromo-9,9′-bianthryl (DBBA, see Figure 1 A, commercially available from St-Jean Photochemicals Inc.), are deposited on a (011) face of the rutile titania (Figure 1 C) using a standard Knudsen cell. The polymerization is thermally activated, either through post- or during-deposition annealing. Formation of extended polyanthrylenes

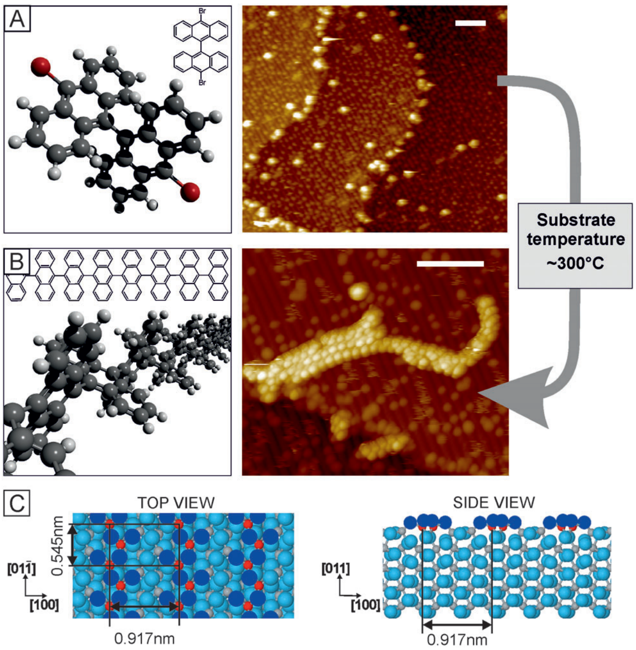

*Figure 1.* On-surface polymerization of DBBA molecules on a $TiO_2$ surface. Models and STM images (white scale bars: 5 nm) of A) DBBA monomers and B) polyanthrylenes. STM images: small bright dots on the zigzag rows are ascribed to surface hydroxyl groups.[9] C) Model of the $TiO_2$(011)-(2×1) surface, top and side views. Oxygen atoms are marked blue (dark blue is reserved for the two-fold coordinated oxygen atoms forming the characteristic double zigzag rows, running along the [01$\bar{1}$] crystallographic direction of the surface).[10] Titanium atoms are marked gray; five-fold coordinated titanium atoms are shown in red.

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[*] M. Kolmer, A. A. Ahmad Zebari, Dr. J. S. Prauzner-Bechcicki, Dr. S. Godlewski, Dr. B. Such, Prof. M. Szymonski
Centre for Nanometer-Scale Science and Advanced Materials, NANOSAM, Faculty of Physics, Astronomy and Applied Computer Science, Jagiellonian University
Reymonta 4, 30-059 Krakow (Poland)
E-mail: jakub.prauzner-bechcicki@uj.edu.pl
Dr. W. Piskorz, Dr. F. Zasada, Prof. Z. Sojka
Faculty of Chemistry, Jagiellonian University
Ingardena 3, 30-060 Krakow (Poland)

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(see Figure 1 B) from DBBA molecules directly on the Au(111) surface has been reported quite recently.[5b,6]

Oligomer formation requires substantial mobility of the adsorbed precursors. It has been shown for several molecular species studied on the (011) face of rutile that the admolecules are mobile enough to form different 1D or 2D weakly bonded structures,[7] including formation of non-covalently bonded PTCDA molecular wires.[8] The interaction of the polyaromatic core of PTCDA with the underlying substrate forces a planar adsorption geometry and does not impede the mobility of the admolecules. Thus, we anticipate rather high mobility of the DBBA molecules on the (011) face of rutile.

As expected, DBBA molecules deposited at low coverage on the substrate kept at room temperature are so mobile that stable scanning tunneling microscopy (STM) imaging conditions at room temperature (RT) are hardly achievable. Imaging at liquid nitrogen temperature (LNT) allows to resolve single molecules distributed on terraces and attached to step-edges (Figure 1 A). There is no trace of polymeric species on the surface, suggesting that the deposited precursors still possess their halogen substituents. The polymerization reaction is triggered thermally. We annealed the sample with the molecules at 300 °C. As a result, we observed randomly distributed, short oligomers. Further annealing at the same temperature does not result in formation of more ordered or more extended structures.

Better conditions for efficient polymerization into longer chains were achieved when molecules are deposited on the substrate kept at 270 °C. During deposition we kept a low molecular flux; that is, the temperature of the evaporator was set to 135 °C to assure a submonolayer coverage and disallow a dissociation reaction in the evaporator. Monomers, dimers, and longer oligomers are obtained (Figure 2). Analysis of the STM images reveals an excellent agreement in appearance of the polymer chains between our data and the results reported for the Au(111) substrate.[5b] Namely, along the chains there are observed protrusions appearing alternately on both sides with a periodicity of 0.86 nm, which is in line with previous observations for the DBBA polymers on the Au(111) surface, and with the periodicity of the bianthryl core,[5b] 0.86 nm and 0.85 nm, respectively (Figure 2). The width of the polyanthrylenes expected from their structural model is about 1 nm, and as it can be inferred by comparison with the substrate periodicity (the distance between the surface reconstruction rows is about 0.92 nm; see the model in Figure 1), it is the value observed in the presented data.

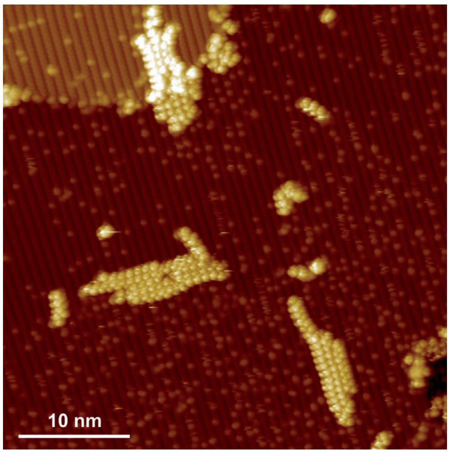

***Figure 2.*** DBBA molecules deposited on the $TiO_2$(011) surface kept at 270 °C; STM imaging at LNT (10 pA, +2 V). 50 nm × 50 nm.

Interestingly, when molecular precursors are deposited at low coverage, longer polyanthrylenes are often observed in bunches rather than as single, long entities (Figure 2, and Figure 3 A). As the main building block of the oligomer is the bianthryl core, it is expected that oligomers in a bunch interact through the van der Waals or π-interactions. In line with such conjecture, we observed the bunches with molecular chains mostly laying parallel to each other. The interaction between oligomers is of non-covalent character, and therefore it is much weaker than the coupling that connects bianthryl monomers. Applying a tip-induced manipulation allows the oligomers to be disentangled from a bunch, as demonstrated by two subsequent STM scans (Figure 3). As predicted for oligomers, the polyanthrylene chains survive such harsh scanning conditions, in contrast to the bunches of chains. Our result is similar to that reported by Grill et al.[3d] In their work, porphyrin dimers were obtained by deposition of porphyrin molecules with a single Br substituent on the Au(111) surface and subsequent annealing. The heating triggered the C−Br bond cleavage, diffusion of the organic fragments, and their recombination into dimers. Eventually, the resulting porphyrin dimers were found to form clusters. Intact dimers can be easily separated from these clusters by the lateral manipulation with the STM tip. In this way, it is demonstrated that two porphyrin molecules in the dimer are bonded by a strong covalent bond in comparison to rather weak non-covalent bonds binding the clusters.[3d]

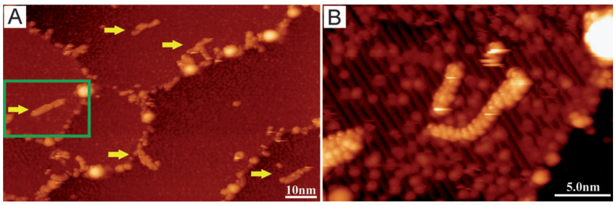

***Figure 3.*** STM images of DBBA oligomers assembled on $TiO_2$(011) (imaging at LNT, 10 pA, +2 V) (A) 100 nm × 60 nm (scale bar 10 nm), longer oligomers and bunches of oligomers (marked by yellow, horizontal arrows); (B) 25 nm × 17.5 nm (scale bar 5.0 nm), enlargement of the region marked with the green rectangle in (A), showing a disentangled bunch of polymers as a result of a tip-induced manipulation obtained by 100 pA constant current scanning conditions.

As reported by Cai et al.,[5b] further annealing of the polyanthrylene chains on the Au(111) surface to 400 °C leads to a cyclodehydrogenation reaction and formation of a fully aromatic system, that is, graphene nanoribbons. To test if such a reaction is feasible on the surface of titanium dioxide we decided to anneal the sample covered with oligomers. To promote formation of longer oligomers, we increased the coverage (three times longer deposition) and substrate temperature during the deposition to 350 °C. The resulting unordered network of long molecular chains is so stable that it was possible to achieve good imaging conditions in RT STM (not shown). After further annealing of the sample at 400 °C and 450 °C (for 30 minutes at each temperature), the molecular network remained practically intact. It is concluded that up to 450 °C the cyclodehydrogenation reaction is not initialized on the $TiO_2$(011)-(2 × 1) surface. Additionally, it is evident that the obtained polyanthrylenes are quite robust to thermal treatment. The question whether the cyclodehydrogenation reaction leading to planarization and thus to formation of graphene nanoribbons could be thermally triggered at higher temperatures on the $TiO_2$(011) surface remains unanswered, and is subjected for further, on-going research.

Our experimental findings are corroborated with density functional theory (DFT) modeling of the DBBA monomer and dimer adsorbed on the $TiO_2$(011)-(2 × 1) surface. We used the Vienna ab initio simulations package (VASP).[11] For reliable description of the electronic structure of rutile titanium dioxide we employed projector augmented plane wave (PAW)[12] method for description of the electron-ion interactions, and PW91 GGA exchange-correlation functional, as parameterized by Perdew and Wang.[13] Additionally, to account for dispersion forces that play important role in the adsorption of policyclic molecules on the surface of rutile,[14] we used the semi-empirical Grimme extension[15] of the DFT method (DFT-D). The GGA/DFT-D calculations revealed a weak adsorption energy (0.11 eV per molecule) of DBBA that is dominated by the dispersion term (0.08 eV per molecule). It results from the molecule–substrate attractive interactions (−1.09 eV) counterbalanced by the admolecule deformation (+0.98 eV). Owing to the presence of the bianthryl core in the DBBA molecule (see Figure 1), the adsorption geometry is governed by tendency to keep each anthryl as parallel to the substrate as possible. In contrast, the short C−C bond, connecting the anthryl moieties in the bianthryl core, does not let the molecule to arrive at flat geometry. Consequently, although the adsorbed molecule preserves its 90° dihedral angle between the anthryl planes, one of them is significantly deformed owing to the interaction with the protruding surface ions, thereby partly losing its aromatic character. As a result, the C−Br bond in the adsorbed DBBA is elongated ($\Delta d_{\text{C-Br}} = 0.09$ Å) and weakened ($\Delta BO$(Mayer) = −0.16). In the optimized geometry, the hydrogen atoms closest to the surface are 1.8 Å above the topmost ions of the substrate; additionally, the bromine atoms are 4.95 Å above the topmost ions. These results strongly suggest that no chemical interaction is expected between the molecule and the substrate. Translations along and across the zigzag rows, and rotation with respect to the surface normal, change the adsorption energy only by 2–5 %. Such observations are in line with the fact that the direction-independent dispersion forces dominate the surface–molecule interactions and suggest that the monomers should be able to diffuse on the surface. Applying the same calculation for a dimer adsorbed on the (011) face gives coherent result: the dimer adsorption energy is nearly twice the monomer, namely 0.21 eV per molecule. Finally, simulations of STM images were performed as topographs of the constant local density of states within the Tersoff–Hamann theory[16] with additional Gaussian blurring to include tip broadening effects. As can be seen in Figure 4, there is an excellent agreement between the calculated and the measured images.

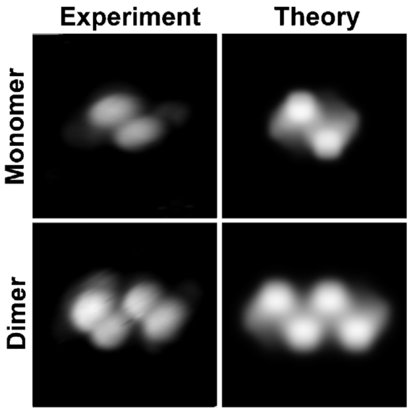

*Figure 4.* Comparison between experimental and theoretical STM images of DBBA monomer and dimer. Left column: in the experimental images the contrast is set to expose the molecules. The right panel: simulated images with Gaussian blurring mimicking the tip broadening of experimental images. (Both experiment and theory: 3 nm × 3 nm, 2 pA, +2 V).

For metallic surfaces and molecular precursors containing halogen atoms at linking sites, the on-surface polymerization reaction has been described as a two-step process:[3d] 1) selective thermal C-X (X = I, Br) bond cleavage, resulting in radical/ion formation, followed by 2) radical/ion recombination, resulting in formation of oligomers. At increased substrate temperatures, there are several processes that could take place simultaneously and compete with each other, that is, cleavage of the C−X bond, diffusion of molecular precursors and radicals/ions, recombination of the radicals/ions, and desorption of smaller molecular species. Proper balance between these processes results in formation of long oligomers.[5f]

Replacing the metal surface with titanium dioxide changes the reaction environment drastically, and thus it is rather unlikely that the on-surface polymerization will necessarily follow the same pathway. In the case of titanium dioxide surfaces, the most important issue is their distinct chemical nature and the related properties. Among several possible routes of C−C bond formation explored by DFT screening, a concerted process of early C−C bond formation accompanied by late C−Br bond cleavage and a multistep proton assisted coupling exhibited the lowest activation barriers (below 1.95 eV). The latter, being energetically most preferred and specific for oxides, is featured by proton transfer from surface hydroxyl groups to DBBA admolecules (1.39 eV), the rather easy migration of this species on the aromatic framework (0.65–1.13 eV), and preferred attachment to the Br-bearing carbon atom. The resultant rehybridization and substantial weakening of the C−Br bond facilitates the carbon–carbon bond formation and release of $Br_2$ byproduct, which only requires 0.82 eV. Certainly, an exact mechanism of oligomer formation on the titanium dioxide surface is definitely not resolved yet. Reaction details of the proposed scenario and analysis of other possible variants are the subject of on-going research.

In conclusion, we have demonstrated the feasibility of thermally triggered, on-surface polymerization on the $TiO_2$-(011)-$(2\times 1)$ surface. Experimental observations were corroborated by DFT calculations and simulation of the STM images. In a broader context, the method of covalent assembly of organic building blocks on surfaces is shown to be applicable for semiconducting, photonic, or photocatalytic materials. It is expected that the reaction mechanism of DBBA polymerization on metal oxide surfaces is different from that reported for metals. Regardless of the differences in the pathways leading to covalently bonded molecular nanostructures, the discussed thermally driven on-surface polymerization appears as more universal and very promising method for constructing miscellaneous molecular devices on substrates with a suitable band gap.

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