



NMP3-CT-2004-001561

RADSAS

RATIONAL DESIGN AND CHARACTERIZATION OF
SUPRAMOLECULAR ARCHITECTURES ON SURFACES

Specific Targeted Research Project

Priority 3 - NMP

Final Activity Report

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Project coordinator: Dr. Roman Fasel
Empa – Swiss Federal Laboratories
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Final Version

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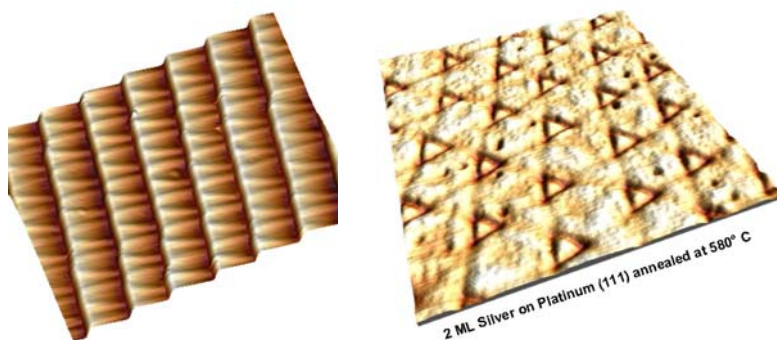
EXECUTIVE SUMMARY

Nanoscale science has experienced a tremendous growth in importance over recent years. The main focus of current research is on understanding, utilising and eventually applying the enormous richness of phenomena on this scale. However, looking closely at the present situation, we still encounter a substantial bottleneck in our attempts at building nanoscale devices. It is not sufficient to show that nanoscale assembly is feasible on the laboratory level, but it also has to be shown that massively parallel fabrication of nano-devices on an industrial scale is feasible. Here, chemical methods of bottom-up construction become important, because only with these methods are the growth processes of complicated systems fast enough for an efficient production procedure. In this sense, the concept of bottom-up construction using methods of chemical synthesis becomes important, because only using these concepts the growth of complex systems is fast enough and provides sufficient quantity to allow an efficient production procedure.

The RADSAS project aimed at developing efficient strategies for parallel, two-dimensional molecular self-assembly on surfaces, which is considered an indispensable prerequisite for the technical realisation of supramolecular design and engineering. RADSAS combined the specific knowledge existing in surface science with the most advanced methods of chemical synthesis to obtain supramolecular structures with unique electronic and transport properties, tailored to reflect the desired behaviour in a wide range of technical applications.

The central aspect of our approach was to introduce site selectivity not only in the molecular building blocks but also in the interaction with the substrate surface. This was accomplished by fabricating surfaces with well defined nucleation sites for the subsequent molecular self-assembly process. Such templates with a regular array of nucleation centres were realised by two-dimensional strain relief and dislocation networks obtained by deposition of one or two monolayers of a metal on a single-crystalline substrate with a different lattice constant - such as Ag/Pt(111) - and by vicinal Au(111) surfaces exhibiting a rectangular superlattice of steps and discommensuration lines.

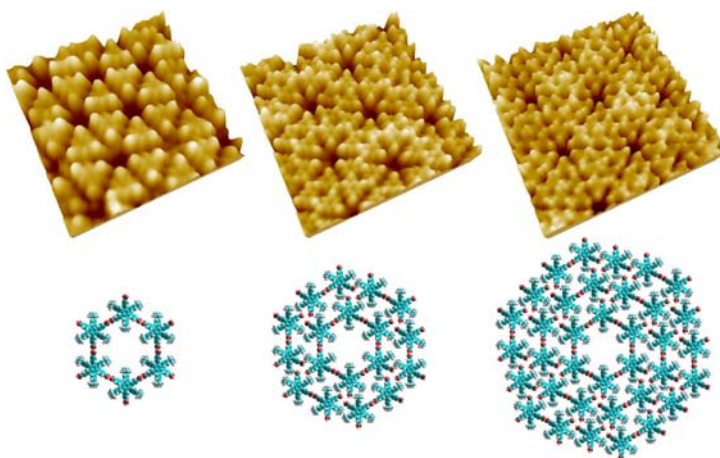
These template surfaces were thoroughly investigated with respect to their site-selectivity upon



Three-dimensional representations of scanning tunneling microscopy images of the Au(11,12,12) (left) and Ag/Pt(111) (right) template surfaces.

molecular adsorption. We could show that both Ag/Pt(111) and Au(11,12,12) template surfaces could successfully be used for the site-specific anchoring of molecular building blocks. Furthermore, the intended directional guiding of (supra-)molecular self-assembly by the nanostructured template surfaces could be demonstrated. Using specifically functionalised entities, we successfully fabricated binary supramolecular wires and ribbons exhibiting unidirectionality and an extremely regular wire-to-wire distance. Using the concepts developed in the project, the successful fabrication of a whole series of supramolecular architectures could be demonstrated.

Last but not least, the processes involved in the self-assembly and the properties of the resulting supramolecular structures were studied using a wide range of experimental as well as theoretical methods. The success of the RADSAS project is largely based on a truly multidisciplinary approach, bringing together researchers in physical surface science, chemical synthesis and theoretical modelling.



Family of two-dimensional honeycomb networks fabricated by self-assembly of 1,3,5-trikis(4'-carboxylphenyl)-2,4,6-trikis(4'-tert-butylphenyl)-benzene on Au(111). The molecule was specifically designed with respect to an optimized assembly into two-dimensional hydrogen-bonded honeycomb networks.



Max-Planck-Institut für Polymerforschung
Max Planck Institute for Polymer Research



THE UNIVERSITY
of LIVERPOOL

Coordinator contact details:

Dr. Roman Fasel

nanotech@surfaces Laboratory

Swiss Federal Laboratories for

Materials Testing and Research (EMPA)

Überlandstrasse 129

CH - 8600 Dübendorf

Switzerland

Project homepage: <http://www.radsas.ch>



Tel. +41 1 823 4348

Fax +41 1 823 4034

Email roman.fasel@empa.ch

RADSAS FINAL ACTIVITY REPORT

“Nanostructured template surfaces and specific endgroup functionalities for the guided self-assembly of supramolecular architectures”

New opportunities for the future fabrication of nanoscale devices will critically depend on the controlled fabrication of surface-supported functional supramolecular structures. A promising strategy is to guide the molecular self-assembly by a combination of specific molecular functionalisation and anisotropic molecule-substrate interactions.

Ultimate-resolution lithographic methods do not reach feature size on the molecular level yet. This limitation can be overcome by self-assembly techniques on surfaces. The controllable fabrication of highly ordered homogeneous self-assembled nanostructures, however, remains a difficult challenge. In the RADSAS project, we have developed an effective strategy to fabricate long-range ordered arrays of supramolecular structures, which relies on

- (i) the use of nanostructured template surfaces exhibiting preferential adsorption sites, and
- (ii) the tailoring of intermolecular interactions by an appropriate choice of molecular building blocks with suitable and complementary end-group functionalities.

In principle, the combination of these approaches allows for the controlled self-assembly of a variety of supramolecular architectures. Here we present a brief summary of the main project achievements, and give a number of illustrative examples.

First, we present the self-assembly of two molecular systems on the vicinal Au(11,12,12) surface to illustrate the consequences of the application of one or both of the above mentioned approaches elaborated within the RADSAS project.

In the first example, fullerene C₆₀ molecules are adsorbed on the Au(11,12,12) template surface. The Au(11,12,12) surface exhibits a rectangular superlattice of 5.8 nm x 7.2 nm periodicity due to its large extended double periodicity: uniformly spaced terraces, separated by straight monatomic steps, and periodic truncated “V” shape discommensuration lines separating face centered cubic (fcc) and hexagonal close-packed (hcp) stacking areas (Fig. 1A).

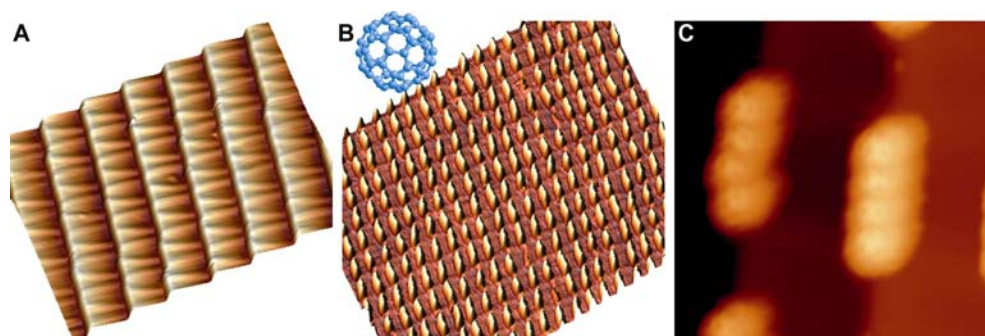


Figure 1

A) STM image of the Au(11,12,12) template surface showing a regular pattern of straight steps and discommensuration lines on a 50 x 50 nm² length scale. B) Formation of a highly regular 2D superlattice of C₆₀ nanochains on the Au(11,12,12) template surface (100 x 100 nm²). C) Location of C₆₀ nanochains on fcc stacking domains at the lower step edges (12 x 12 nm²).

Because of the chemical inertness of C_{60} , we only expect an influence of the inhomogeneous template surface on the self-assembly at room temperature (RT). At a coverage of 0.1 monolayer (ML) and at RT, a two-dimensional (2D) long-range ordered superlattice of molecular nanochains is observed (Fig. 1B). The electron-rich regions near the lower step edges preferentially accommodate the fullerene molecules, which are known to be electron acceptors, leading to the formation of arrays of C_{60} chains that perfectly replicate the periodicity of the gold template surface (Fig. 1C). Such site-selective molecular anchoring is definitely not restricted to C_{60} on Au(11,12,12), but we have demonstrated it for other molecules and other nanostructured template surfaces.

In the second example, the molecular self-assembly is guided not only by the interaction with the substrate surface, but also by specific interactions between the molecular building blocks 1,4-bis-(4,6-diamino-1,3,5-triazine)-benzene (BDATB) (Fig. 2A) and perylene tetra-carboxylic di-imide (PTCDI) (Fig. 2B). PTCDI exhibits on both opposite sides a -CO-NH-CO- (imide) sequence with a NH hydrogen-bond (H-bond) donor (D) and two CO H-bond acceptors (A), giving rise to an A-D-A sequence. BDATB was synthesized in order to provide interaction selectivity by means of complementary end-groups functionalities, NH-N-NH, on opposite sides of the molecules, which correspond to a D-A-D sequence.

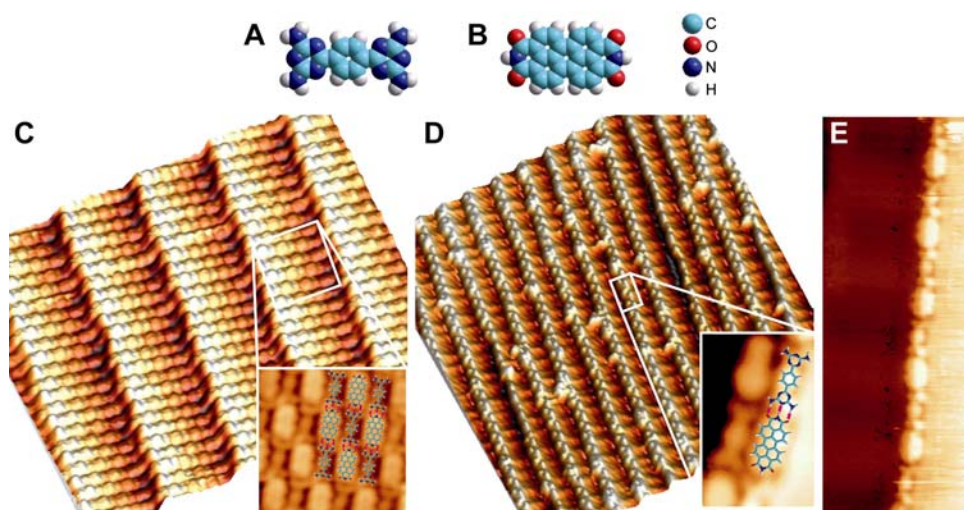


Figure 2

BDATB (A) and PTCDI (B) bicomponent supramolecular organization on Au(11,12,12): STM images of binary supramolecular ribbons (C, $3 \times 3 \text{ nm}^2$), double-row heteromolecular wires (D, $7 \times 7 \text{ nm}^2$), and a single-row wire (E, $5.6 \times 1.5 \text{ nm}^2$).

The STM image of Fig. 2C shows the highly ordered heterocomplex superlattice resulting from a deposition slightly below 1 ML of PTCDI (50%) and BDATB (50%). Formation of the anticipated 3-fold H-bonding pattern, as presented in the superimposed model, determines the directionality of the bicomponent system. In addition, the regular array of steps on the Au(11,12,12) template surface plays an important role in imprinting the unidirectionality of the bicomponent supramolecular structure, which is not observed on a Au(111) surface [2]. A lowering of the surface coverage leads to double-row (Fig. 2D) and single-row bimolecular wires (Fig. 2E). In both cases, the resulting superlattice exhibits an almost constant wire-to-wire separation over extended surface areas. In contrast to the case of C_{60} on Au(11,12,12), there is no apparent preference for either PTCDI or BDATB locating at fcc or hcp stacking areas, indicating a predominance of intermolecular interactions with respect to the influence of the substrate reconstruction. The bicomponent PTCDI-BDATB on Au(11,12,12) system clearly shows that the formation of specific 1D nanostructures and

their long-range growth can be controlled by a rational design of complementary building blocks for 1D multitopic H-bonding and the choice of an appropriate template surface.

Another template surface fabricated and investigated in great detail during the RADSAS project is the 2 ML Ag/Pt(111) trigonal network (Fig. 3). Due to its high spatial adsorption selectivity it represent an excellent template for site-selective molecular adsorption. Complementary molecular building blocks with specific endgroup functionalities were synthesised for the supramolecular network formation on this template surface. From the many substances synthesised and investigated, excellent results were obtained using the hydrogen bond interaction of the carboxylic-diimide functionality with the diamino-triazazine group.

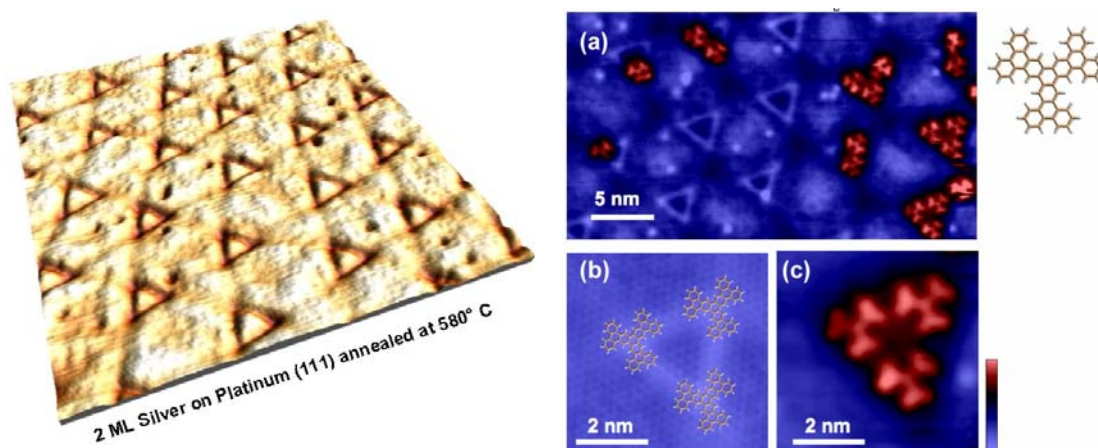


Figure 3

Left: The trigonal network template surface obtained by deposition of 2 ML of Ag on Pt(111) and subsequent annealing to 580 °C.

Right: Hexabenzotriphenylene (HTR) adsorbed on the Ag/Pt(111) template surface. (a) Large-scale STM image showing the preferential adsorption in the hcp_1 regions of the strain-relief pattern. (b) Atomically resolved small-scale image of hcp_1 region with proposed adsorption location and orientation for HTR. (c) Small-scale image of three HTR molecules adsorbed in the hcp_1 region.

The targeted template-directed two-dimensional supramolecular networks on the 2 ML Ag/Pt(111) template surface were achieved using binary and ternary mixtures of PTCDI, diDAT-180° and diDAT-120° molecules, as exemplified in Fig. 4. Self-assembly of the diDAT-120° and the PTCDI molecules on the Ag/Pt(111) template surface results in the formation of the anticipated interconnected two-dimensional network (Fig. 4A). Although the network is not fully regular and the relation with the template substrate periodicity is not directly obvious from the STM images, a FFT transform and autocorrelation analysis clearly shows that the supramolecular network is imprinted by the template structure. The autocorrelation analysis highlights the hexagonal topology of the network structure with a lattice parameter of 7 nm and the orientation of the trigonal pattern of the Ag/Pt template. Furthermore, the network structure is correlated over at least 5 unit cells, which demonstrates the strong relation to the substrate structure. The voids in the molecular network correspond to the fcc sites of the Ag/Pt template structure, which agrees with the observation of low adsorption selectivity in these regions.

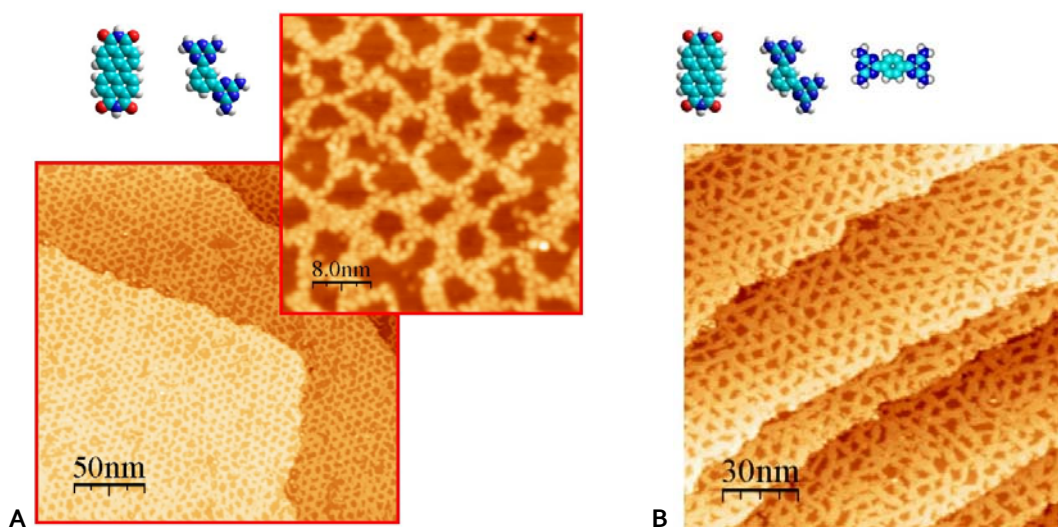


Figure 4

Fabrication of binary and ternary supramolecular networks on the Ag/Pt template surface. A) STM images of the binary supramolecular network formed by PTCDI and diDAT-120°. B) The ternary network resulting from the self-assembly of PTCDI, diDAT-120° and diDAT-180°.

Codeposition of the three molecular building blocks PTCDI, diDAT-120° and diDAT-180° finally results in the formation of a ternary supramolecular network, with molecular ribbons that are shorter than in the case of the binary system and with bifurcations leading to an almost fully interconnected two-dimensional supramolecular system, with rather straight and well ordered strands as shown in Fig. 4B. FFT and autocorrelation analysis again reveal the guidance of the supramolecular network formation by the trigonal pattern of the template surface.

The achievement of the ambitious goals of the RADSAS project relied on a close collaboration between all project partners, and thus between researchers in physical surface science, chemical synthesis and theoretical modelling. Only in this strongly interdisciplinary approach could the processes involved in the self-assembly and the properties of the resulting supramolecular structures be studied using a wide range of experimental as well as theoretical methods. We are proud of the success of the RADSAS project, which has clearly highlighted the potential of a combination of nanostructured template surfaces and appropriately functionalized molecular building blocks for the controlled self-assembly of specific supramolecular architectures on surfaces.

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PROJECT PARTNERS



Swiss Federal Laboratories for Materials Testing and Research

Dübendorf & Thun, Switzerland

Principal Investigators: Dr. Roman Fasel (Dübendorf), Dr. Oliver Gröning (Thun)

Max-Planck-Institut für Polymerforschung

Max Planck Institute for Polymer Research



Max-Planck Institute for Polymer Research

Mainz, Germany

Principal Investigator: Prof. Dr. Klaus Müllen



THE UNIVERSITY
of LIVERPOOL

Surface Science Research Centre

The University of Liverpool, UK

Principal Investigator: Prof. Dr. Werner A. Hofer

Coordinator contact details

Dr. Roman Fasel

nanotech@surfaces Laboratory

Swiss Federal Laboratories for

Materials Testing and Research (EMPA)

Überlandstrasse 129

CH - 8600 Dübendorf

Switzerland

Tel. +41 1 823 4348

Fax +41 1 823 4034

Email roman.fasel@empa.ch