WILHELM UND ELSE HERAEUS-STIFTUNG

663. WE-Heraeus-Seminar

Dynamics and Structure Formation of Organic Molecules on Dielectric Surfaces

February 25 - 28, 2018
at the Physikzentrum Bad Honnef/Germany

Introduction

The Wilhelm und Else Heraeus-Stiftung is a private foundation which supports research and education in science, especially in physics. A major activity is the organization of seminars. By German physicists the foundation is recognized as the most important private funding institution in their fields. Some activities of the foundation are carried out in cooperation with the German Physical Society (Deutsche Physikalische Gesellschaft).

Aims and scope of the 663. WE-Heraeus-Seminar:

In this seminar, we will address fundamental aspects of dynamics and structure formation of organic molecules on dielectric surfaces. Dynamics and structure formation of organic molecules on dielectric surfaces play an important role in many fundamental processes both in nature as well as industrial applications. For example, the interaction of organic molecules with inorganic materials is central in biomineralization as well as for understanding reactivity of solid-liquid interfaces in geochemistry. Within industry, applications range from surface functionalization to emerging field such as molecular electronics.

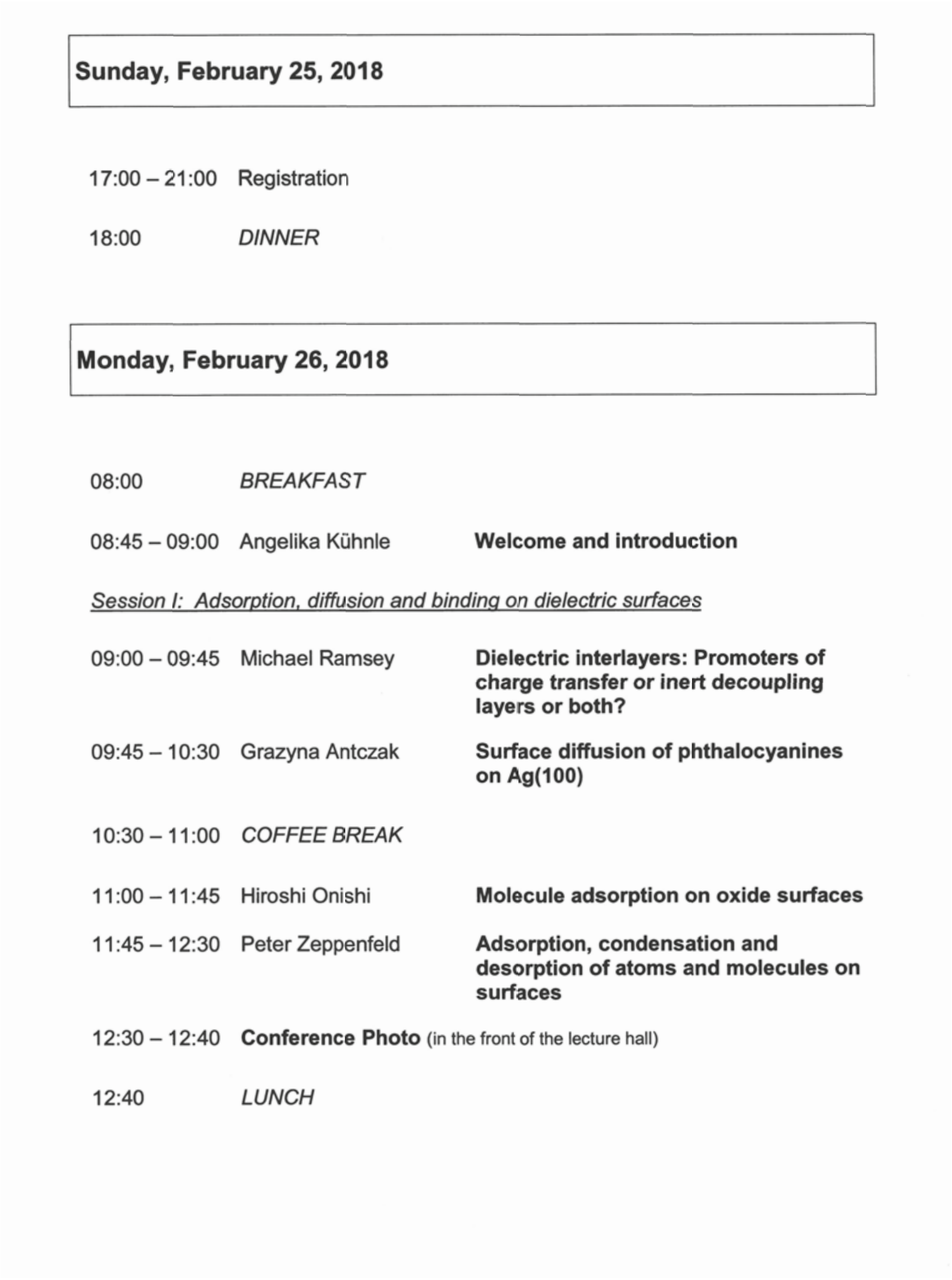
In all these areas, inert and electrically insulating surfaces are in the focus of interest. Many aspects of adsorption, diffusion and structure formation of organic molecules have been intensively studied on metal surfaces. Comparatively little is known about these processes on surfaces of dielectric materials. This is partly due to the fact that dielectric surfaces are difficult to investigate with classical surface science techniques that generally require electrically conducting materials. Only recently, both experimental and theoretical techniques have been developed to also tackle the challenging questions related to molecular dynamics and structure formation on dielectric surfaces. Moreover, the fundamentally different binding and diffusion of organic molecules on dielectric as compared to metal surfaces open up the possibility to explore new physical phenomena in molecular structure formation on dielectric surfaces.

Scientific Organizers:

Prof. Angelika Kühnle	Universität Bielefeld, Germany Physikalische Chemie I E-mail: angelika.kuehnle@uni-bielefeld.de
Prof. Moritz Sokolowski	Universität Bonn, Germany Institut für Physikalische und Theoretische Chemie E-mail : sokolowski@pc.uni-bonn.de

Program

Program



Sunday, February 25, 2018

17:00 – 21:00	Registration	
18:00	*DINNER*	

Monday, February 26, 2018

08:00	*BREAKFAST*	
08:45 – 09:00	Angelika Kühnle	**Welcome and introduction**

Session I: Adsorption, diffusion and binding on dielectric surfaces

09:00 – 09:45	Michael Ramsey	**Dielectric interlayers: Promoters of charge transfer or inert decoupling layers or both?**
09:45 – 10:30	Grazyna Antczak	**Surface diffusion of phthalocyanines on Ag(100)**
10:30 – 11:00	*COFFEE BREAK*	
11:00 – 11:45	Hiroshi Onishi	**Molecule adsorption on oxide surfaces**
11:45 – 12:30	Peter Zeppenfeld	**Adsorption, condensation and desorption of atoms and molecules on surfaces**
12:30 – 12:40	**Conference Photo** (in the front of the lecture hall)	
12:40	*LUNCH*	

Program

Monday, February 26, 2018

14:00 – 14:45	Wolf-Gero Schmidt	**Understanding adsorbate structure formation and on-surface reactions from theoretical spectroscopy**
14:45 – 15:30	Oliver Hofmann	**Hybrid bands and localized orbitals: The role of hybridization for charge localization at interfaces**
15:30 – 16:00	*COFFEE BREAK*	
16:00 – 17:30	**Poster flash presentation and poster session**	
17:30 – 17:45	Stefan Jorda	**About the Wilhelm and Else Heraeus Foundation**
18:30	*WE-HERAEUS DINNER* *(social event with cold & warm buffet with complimentary drinks)*	
20:30	**Poster Award**	

Program

Tuesday, February 27, 2018

08:00	*BREAKFAST*	
09:00 – 09:45	Andrea Floris	**Reactions mechanisms and molecular diffusion on insulating surfaces**
09:45 – 10:30	Michael Rohlfing	**Structure and spectra of organic molecules on chemically inert surfaces from first principles**
10:30 – 11:00	*COFFEE BREAK*	

Session II: Aggregation and structure formation

11:00 – 11:45	Sabine Maier	**Structure formation in molecular self-assemblies on a bulk insulator**
11:45 – 12:30	Francesca Moresco	**Dynamics and manipulation of supramolecular assemblies**
12:30	*LUNCH*	

Program

Tuesday, February 27, 2018

14:00 – 14:45	Leonhard Grill	**On-surface synthesis of molecular nanostructures and their decoupling from a metallic surface**
14:45 – 15:30	Maike Stöhr	**Surface-supported molecular nanostructures: from supramolecular assemblies to on-surface reactions**
15:30 – 16:00	*COFFEE BREAK*	
16:00 – 16:45	Philipp Maaß	**Multicomponent cluster growth and second-layer induced island shaping**
16:45 – 17:30	Adam Foster	**Computational approaches to study molecular structure on insulating surfaces**
18:30	*DINNER*	

Session III: Surface science and society

20:15	Philip Moriarty	**Scratching the surface: Communicating science in a post-truth age**

Program

Wednesday, February 28, 2018

08:00	*BREAKFAST*	

Session IV: Advanced experimental techniques

09:00 – 09:45	Christian Loppacher	**Controlling the growth and morphology of self-assembled films and polymers on ionic substrates**
09:45 – 10:30	Philipp Rahe	**Kelvin probe force microscopy on insulator surfaces**
10:30 – 11:00	*COFFEE BREAK*	
11:00 – 11:45	Alexander Gerlach	**Organic molecules adsorbed on ZnO studied with the X-ray standing wave technique**
11:45 – 12:30	Torsten Fritz	**Optical *in situ* spectroscopy of molecular films**
12:30 – 13:00	Moritz Sokolowski	**Closing remarks**
13:00	*LUNCH*	

End of the seminar and departure

NO DINNER for participants leaving on Thursday morning

Posters

Posters

1	Simon Aeschlimann	**Bishop diffusion involving a chiral flip**
2	Hazem Aldahhak	**PTCDA molecules on terraces and at steps sites of the KCl and NaCl Surfaces**
3	Wojciech Belza	**Growth of ultra-thin *para*-hexaphenyl layers on atomically-flat $TiO_2(110)$ surfaces**
4	Christian Braun	**Influence of adsorbates on the structural and electrical properties of atomic wires**
5	Christine Brülke	**Chemical and electronic decoupling of organic molecules by a monolayer of hexagonal boron nitride**
6	Mirunalini Devarajulu	**Tuning the self-assembly of carboxyl-substituted triphenylaminederivatives on bulk NaCl(001) and KBr(001)**
7	Shadi Fatayer	**Reorganization energy of single molecules on an insulating film measured by atomic force microscopy**
8	Michael Gottfried	**Reactions of organic molecules on oxide surfaces**
9	Niklas Humberg	**One-dimensional molecular chains of Quinacridone on Ag(100) and Cu(111): STM- and SPA-LEED investigations**
10	Philipp Hurdax	**Charge transfer and molecular level alignment on dielectric interlayers on metals**
11	Simon Jaekel	**Reversible and efficient photo-switching of azobenzene derivatives on an insulator surface**
12	Bianca Jennewein	**Portlandite crystallization**

Posters

13	Markus Kratzer	**Growth of small organic molecules on ultrathin hexagonal born nitride**
14	Ina Krieger	**Surface crystallography of large organic molecules on metal and insulator surfaces by LEED-IV using Fourier coefficients**
15	Christian Kumpf	**Towards functionalization of graphene: In situ study of the nucleation of copper-phtalocyanine on graphene**
16	Linda Laflör	**Comparing bulk with thin film dielectric: Ferrocene Dicarboxylic Acid on CaF_2 (111) surfaces**
17	Jia Liu	**Self-assembly of cyano-substituted porphyrin-derivatives on bulk MgO(0001)**
18	Alexander Mehler	**Vibrational progression in both frontier orbitals of a single hydrocarbon molecule on graphene**
19	Agata Sabik	**Structural and electronic properties of CoPc and $F_{16}CuPc$ on Ag(100)**
20	Maximilian Schaal	**Thickness-dependent photoelectron spectroscopy study of 1,2:8,9-dibenzopentacene (trans-DBPen) on Au(111)**
21	Christoph Schiel	**Modeling of molecular stripe formation on insulating surfaces**
22	Lukas Schüller	**Formation of metal-organic coordination networks on a bulk insulator surface**
23	Sebastian Seibert	**Ethanol and water: Probing the solvation structure at the graphite–liquid interface**
24	Hagen Söngen	**Solvation layers at solid-liquid interfaces: Attraction or confinement?**

Posters

25	Shadi Sorayya	**Self-assembly and on-surface reaction of bromo-substituted decacyclene on Ag(111)**
26	Sergey Subach	**Dependence of the adsorption height of graphene-like adsorbates on their dimensionality**
27	Maximilian Vogtland	**Generic repulsion in molecular self-assembly on a bulk insulator: Influence on striped structures formed on calcite (10.4)**
28	Dominik Wrana	**Controllable formation of molecular nanostructures on TiO_2(110): from nanoneedles to dendritic islands**
29	Shengkai Xue	**Atom-scale imaging of TiO_2(110) surface in water by FM-AFM**
30	Xiaosheng Yang	**Oxygen-triggered electronic and structural decoupling at the PTCDA/Cu(100) interface**

Abstracts of Talks

(in chronlogical order)

Dielectric interlayers: Promoters of charge transfer or inert decoupling layers or both?

Michael G. Ramsey

[1]Karl-Franzens Universität Graz, Graz, Austria
E-mail: michael.ramsey@uni-graz.at

Recently we have shown that thin dielectric layers can actively promote charge transfer from the underlying metal substrate to molecules adsorbed on them [1]. Here a comprehensive analysis of the phenomenon of charge transfer promoted by a dielectric interlayers will be attempted. With scanning tunneling microscopy and valence band photoemission tomography, supported by density functional calculations, we are able to unambiguously identify the orbitals involved and quantify the degree of charge transfer. Our experimental approach allows a direct access to the individual factors governing the energy level alignment and charge transfer processes for molecular adsorbates on dielectrics. Here the role of the work function, electron affinity, polarizability and dielectric thickness, is explored. Questions addressed will include: how is the work function catastrophe avoided, when and how is Fermi level alignment achieved and why has the phenomena not been observed in the past?

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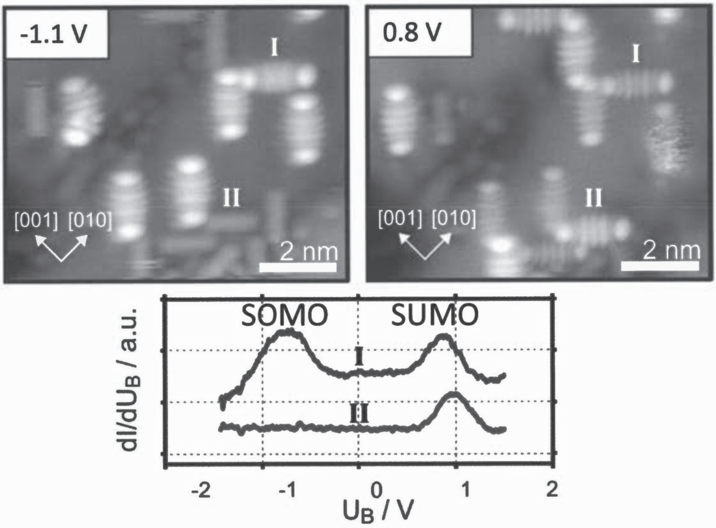

Surface diffusion of phthalocyanines on Ag(100)

G. Antczak[1], **W. Kamiński**[1], **A. Sabik**[1], **K. Morgenstern**[3]

[1] *Institute of Experimental Physics, University of Wrocław, Wrocław, Poland*
[3] *Chair for Physical Chemistry I, Ruhr-Universität Bochum, Bochum, Germany*
e-mail:antczak@ifd.uni.wroc.pl

We explored the adsorption of phthalocyanines (Pc) at low coverages (up to 1 ML). At the temperatures below 30 K the Pcs are immobilized on the silver (100) surface at the timescale of minutes. At temperatures between 40 - 70 K the molecules are mobile and it is possible to track their displacements [1]. Further increase of temperature results in observation of molecular diffusive noise in scanning tunneling microscopy (STM) studies [2]. The molecule adsorbed on the terraces are moving much faster than scanning tip. The molecules adsorbed close to the defects are immobilized by defects. The role of defects immobilizing molecules plays also the adatoms, which comes from fluctuating steps [3]. Coexistence of adatoms and Pc cause appearance of metal-organic networks on the surface. The structure of such networks will be discussed.

The mechanism of surface diffusion of quasi-isolated Pc on Ag(100) was investigated in details by combination of low temperature scanning tunneling microscopy (LT-STM) and density functional theory (DFT) study. Investigations were performed at temperature range 43-50 K. The quasi-isolated phthalocyanines, with cobalt atom embedded at the center, were tracked in STM and effective activation energy for their motion of was determined as 0.15 eV [1]. The basic diffusive steps involved in molecular motion and diffusive trajectories were explored by DFT using Vienna simulation package. Various scenarios were considered and the outcome verified against experiment. The most plausible scenario involves the correlation between translational and rotational motion of molecule. The procedure will be discussed in the talk.

[1] G. Antczak *et al.* JACS **137** 14920 (2015)
[2] G. Antczak *et al.* J. Phys. Chem. C. **121** 542 (2017)
[3] G. Antczak *et al.* J. Phys. Chem. C. **119** 1442 (2015)

Molecule adsorption on oxide surfaces

H. Onishi

Department of Chemistry, Kobe University, Rokko-dai, Nada, Kobe, Japan
E-mail: oni@kobe-u.ac.jp

Polyatomic molecules adsorbed on oxide surfaces are different from those on metals or covalent semiconductors. The ionic property of oxides provides the major reason for the different behaviors. Carboxylic acids (RCOOH) on the (110) surface of rutile TiO_2 are described as a typical set of examples in this lecture.

The TiO_2 surfaces were cleaned in an ultra-high vacuum [1], exposed acids vapor and characterized with photoelectron spectroscopy [2] to evidence dissociative adsorption of carboxylate anion ($RCOO^-$) and proton. Scanning tunneling microscopes (STM) revealed topography of individual carboxylate anions [3] and their diffusion on the surface in a time-lapse manner [4]. Thermal [5] or photo-induced [6] carboxylate reactions were further studied in the absence [6] and presence [7] of Pt nanoparticles on the TiO_2 surface. Organic metal complexes for dye-sensitized solar cells anchored via carboxylate groups were characterized with STM [8] and Kelvin probe force microscopy [9] operated in the vacuum. Characterizing molecules at liquid-oxide interfaces is currently demanded. Our recent efforts to visualize TiO_2 [10] and $SrTiO_3$ [11] surfaces in water will finally be mentioned.

References

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Adsorption, condensation and desorption of atoms and molecules on surfaces

Peter Zeppenfeld[1]

[1]*Institute of Experimental Physics, Johannes Kepler University Linz, Austria*
E-mail: peter.zeppenfeld@jku.at

When atoms or molecules are deposited on surfaces, they can form different ordered or disordered phases depending on the delicate balance between (1) the interaction of the adsorbed particles with the substrate (V_{AS}) and (2) the lateral interaction between the adsorbed particles (V_{AA}). The effective lateral interactions between atoms or molecules on surfaces may be substantially weaker than in the corresponding 3D condensed phase and may even become repulsive. Overall attractive lateral interactions may result in a phase transition from an initial 2D lattice gas phase into a 2D condensed phase above a threshold coverage which depends on the substrate temperature. I will give an overview of the basic physical concepts governing the adsorption, condensation and desorption of atoms and molecules on surfaces and how these processes can be studied experimentally. In particular, I will illustrate how adsorption isotherms and temperature programmed desorption (TPD) can yield quantitative information on the adsorption enthalpy of atoms and molecules and provide access to the interaction parameters V_{AS} and V_{AA} [1,2].
While the case of atoms is rather straightforward, the many internal degrees of freedom of molecular adsorbates provide additional complexity but also novel physical phenomena, such as the possibility of an azimuthal reorientation of molecules during the 2D condensation [3,4]. In this context, polarization resolved optical spectroscopy experiments will be reported, which allow a direct correlation of the in-plane reorientation upon 2D solidification of ultrathin molecular layers.

References

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Understanding adsorbate structure formation and on-surface reactions from theoretical spectroscopy

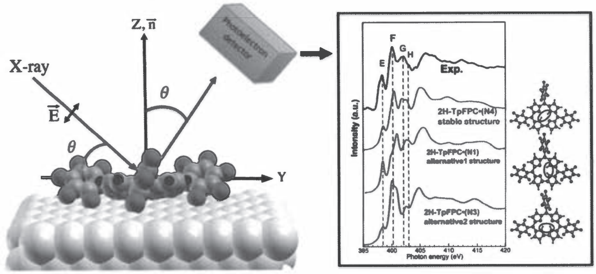
Wolf Gero Schmidt

Lehrstuhl für Theoretische Materialphysik, Universität Paderborn
33095 Paderborn, Germany

W.G.Schmidt@upb.de

Density-functional theory (DFT) based total-energy calculations are extremely helpful in elucidating even complicated bonding configurations of surface adsorbed molecules. Additional insight in intra- and intermolecular interactions can be gained from the comparison of simulated and measured spectroscopic information, e.g., near edge X-ray absorption fine structure (NEXAFS).

This is illustrated in the talk using two examples: (i) The adsorption of PTCDA on terraces and at steps sites of the KCl(100) surface [1-4] and (ii) the identification of on-surface site-selective chemical conversions of free-base corroles adsorbed on Ag(111) [5-7].



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Hybrid Bands and Localized Orbitals: The Role of Hybridization for Charge Localization at Interfaces

O.T. Hofmann[1]

[1]Institute of Solid State Physics, TU Graz, Austria
E-mail: o.hofmann@tugraz.at

At inorganic/organic interfaces, the concept of electrons moving in extended bands meets the notion of localized molecular orbitals. Depending on the strength of the interaction between substrate and adsorbate, charge-transfer across these interfaces takes different guises. When an electron accepting molecule is adsorbed on a weakly reactive metals, density functional theory (DFT) calculations and experimental observation concurrently report the formation of homogenous layers with fractionally filled bands. In contrast, in passivated metals or on dielectric materials, experimental observations indicate that charge localizes spontaneously, yielding an adsorbate layer consisting of both uncharged and integer charged molecules: A situation known as "integer charge transfer" (ICT), for which the detailed mechanism has long remained elusive.

n this contribution, we discuss the experimental and theoretical conditions that must be met in order to observe these two different charge-transfer regions. To that aim, we review the impact of varying hybridization strength on two (not completely) hypothetical systems: On the one hand, we transition from a metal (Cu) to a dielectric material (Cu2O) via gradual "alloying" of the substrate. On the other hand, we alter the doping concentration of a wide bandgap semiconductor (ZnO), to transition between an electric insulator and a metal-like system. For both systems, we discuss the change between the two different charge-transfer regimes and focus on the observables (such as bond length, XPS and UPS spectra, etc.) that would be tell-tale sign of charge (de)localization. Surprisingly, we find that the two regimes are not mutually exclusive, and discuss as case where both band formation (delocalized charge-transfer) and molecular orbitals (coexistence of filled and empty orbitals) are observed at the same time.

References:

Oliver T. Hofmann, Patrick Rinke, Matthias Scheffler, and Georg Heimel, *Integer versus Fractional Charge Transfer at Metal(/Insulator)/Organic Interfaces: Cu(/NaCl)/TCNE*, ACS Nano, 2015, 9 (5), pp 5391–5404

Reactions mechanisms and molecular diffusion on insulating surfaces

A. Floris[1], **C. Paris**[2], **C. Guo**[3], **A. Kühnle**[4], **L. Kantorovitch**[2]

[1]School of Mathematics and Physics, University of Lincoln, Lincoln, UK
[2] Department of Physics, King's College London, London, UK
[3]School of Physics and Technology, Wuhan University, Wuhan, China
[4]Institute of Physical Chemistry, Johannes Gutenberg-University Mainz, Mainz, Germany

E-mail: afloris@lincoln.ac.uk

Ab initio density functional theory is used to characterize several mechanisms of reaction, diffusion and structural transition involving a class of organic molecules (benzoic acid derivatives) as deposited on insulating calcite (10.4) [1-5]. The theoretical investigation is combined with experimental data obtained from non-contact AFM microscopy [3, 5]. In the first part of the contribution, I will illustrate the fundamental principles driving a sequence of molecular transitions on calcite, from molecular deposition to the formation of stable and metastable ordered molecular networks [1, 2]. The quantitative analysis highlights the role of kinetics, as the driving mechanism for the observed specific transition path and, hence, as a possible route to realize molecular structures on surfaces by kinetic control.

The second part is devoted to the analysis of mechanisms of on-surface synthesis on insulators [4, 5]. I will illustrate peculiar dimerization processes [4], revealing a possible role of the insulating substrate as a catalyst, in the total absence of a metallic agent.

The knowledge of reaction and diffusion mechanisms on insulators helps in identifying routes to create ordered molecular patterns (still rather challenging) with technological advantages over structures routinely obtained on metallic surfaces.

References

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Structure and spectra of organic molecules on chemically inert surfaces from first principles

M. Rohlfing[1]

[1]Institut für Festkörpertheorie, Universität Münster, Germany
E-mail: Michael.Rohlfing@wwu.de

Organic molecules on chemically inert surfaces are prototypical adsorption systems. For instance, PTCDA (as single molecules or as commensurate monolayer) on silver or gold is ideally suited for analysing fundamental structural and spectral features. Here we employ a number of first-principles computational approaches (in particular, density-functional theory, DFT, and many-body perturbation theory, MBPT) for a comprehensive understanding of the relationship between the geometric structure and the electronic spectrum. The molecular states can be manipulated in a controlled way when a scanning-tunneling microscope (STM) tip is chemically attached to the PTCDA molecule. By moving the STM tip vertically, the molecule is reversibly peeled off the surface, simultaneously driving the lowest unoccupied molecular orbital (LUMO) from a broad quasiparticle state into a Kondo resonance, as observed in the STM transport spectra. Here we describe this phenomenon by a combination of DFT, MBPT and numerical renormalization group theory. Similar effects occur in gold-decorated molecules on the gold (111) surface without STM manipulation.

References

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Structure formation in molecular self-assemblies on a bulk insulator

S. Maier

[1]*Department of Physics, Friedrich-Alexander University Erlangen-Nürnberg, Germany*
E-mail: sabine.maier@fau.de

A major challenge in realizing single molecular electronic devices is to mechanically stabilize and electrically decouple molecules at and from a surface. However, molecules on insulating surfaces often suffer from a weak, unspecific molecule-surface interaction, which can facilitate diffusion and the assembly of disordered aggregates. Controlling the structure formation of molecular structures on bulk-insulating surfaces requires us to understand the interplay of the underlying intermolecular and molecule-surface interactions.

Here, a systematic study on the adsorption and self-assembly of bridged-triphenylamines is presented on bulk insulators and metals using non-contact atomic force microscopy and scanning tunneling microscopy, respectively, in ultra-high vacuum in combination with density functional theory. [1,2] First, I will discuss how well-ordered 1D, 2D, or 3D assemblies of triphenylamine derivatives on KBr(001) are obtained by tuning the intermolecular interactions, which is realized by carefully selecting the molecular functional groups. We found that triphenylamines with bulky side groups adopt a flat-lying adsorption geometry that yields extended two-dimensional molecular layers exhibiting long-range order. In contrast, planar triphenylamine molecules favor a nearly upright adsorption geometry stabilized by intermolecular π-π interactions.

In a second part, the influence of the molecule-surface interaction on the structure formation of the molecular self-assemblies will be discussed. 1D and 2D molecular self-assemblies on alkali halide surfaces and metal oxide surfaces will be compared.

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Dynamics and Manipulation of Supramolecular Assemblies

Francesca Moresco

Center for Advancing Electronics Dresden and Institute for Materials Science,
TU Dresden, 01069 Dresden, Germany
E-mail: francesca.moresco@tu-dresden.de

For the development of novel functional materials, it is of fundamental importance to study the formation of molecular assemblies molecule by molecule with high spatial precision. In this talk, recent experiments are reviewed, where small supramolecular assemblies are investigated by scanning tunnelling microscopy (STM) at low temperature on the Au(111) surface, discussing the application of the presented results to dielectric substrates.

We will present hydrogen-bonded nanostructures that can be precisely positioned by voltage pulses applied by the STM tip [1]. Such nanostructures can generate work by moving the load of a single atom [2]. Secondly, we will show surface coordination nanostructures based on cyanosexiphenyl molecules that can be controllably tuned and assembled [3].

In the second part of the talk, we will discuss the on-surface synthesis of acene chains up to the length of decacene [4] obtained by on surface reduction. The on-surface generated anthracene and tetracene molecules form self-assembled structures, which are strongly influenced by the on-surface reaction [5]. In particular, the acene molecules maintain the same structure of the epoxyacenes precursors also after the reduction reaction, highlighting the importance of the cleaved oxygen in the assembly formation.

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On-surface synthesis of molecular nanostructures and their decoupling from a metallic surface

Leonhard Grill

Department of Physical Chemistry, University of Graz, Austria
E-mail: leonhard.grill@uni-graz.at

Covalent linking of individual molecules directly on a surface, the so-called on-surface synthesis [1], has developed rapidly in the last years since it represents a reliable strategy to grow functional molecular nanostructures in a controlled fashion [2]. While this bottom-up growth has been successfully used to link molecular building blocks on metallic surfaces in the last years, decoupling from a conducting substrate is important in view of molecular electronics.

In this presentation, various examples will be presented how such a decoupling can be achieved, studying molecular nanostructures and assemblies by scanning probe microscopy that allows imaging and manipulation of the molecules. First, by deposition onto an insulating calcite surface where supramolecular assemblies of weakly interacting azobenzene derivatives reveal very efficient photo-switching, much faster than on metallic surfaces and similar to solution [3]. In order to use the advantages of scanning tunneling microscopy, ultrathin NaCl films on a metallic surface can be used to decouple molecular nanostructures from the substrate if suitable preparation protocols are used [4]. Charge transport channels through the molecular wires and the insulating film can be compared directly. Finally, individual molecules can be lifted off a metallic surface with the microscope tip. In this way, different charge transport channels through the molecular nanostructures can be measured, which is impossible upon planar adsorption on the metallic surface [5].

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Surface-supported molecular nanostructures: from supramolecular assemblies to on-surface reactions

Meike Stöhr

Zernike Institute for Advanced Materials, University of Groningen, The Netherlands
E-mail: name@mymail.cy

The interest in studying organic nanostructures on surfaces emerges from their prospective usage as nanoscale functional materials in applications ranging from electronics to spintronics and catalysis. By making use of molecular recognition processes based on non-covalent interactions, well-ordered 1D and 2D molecular structures can be formed on surfaces. Understanding the interplay of the underlying intermolecular and molecule-substrate interactions, and processes on the atomic and molecular scale is the key for being able to deliberately tune the functional properties of organic nanostructures. However, since the intermolecular interactions for such structures can be rather weak, on-surface covalent coupling has emerged as a viable alternative for obtaining structures with improved stability and conductivity.

In my presentation I will focus on the one side on the influence of the substrate on molecular self-assembly. For this purpose, we studied the adsorption of the same molecule (1,3,5-benzenetribenzoic acid = BTB) on Cu(111), Au(111) and graphene/Cu(111) [1] and observed a decreasing molecule-substrate interaction (when keeping the order of the substrates). In particular, for Au(111) we observed a modification of the electronic surface properties based on the confinement of the Au surface state in the pores of the molecular BTB network. Due to leaky confinement, the states confined in the BTB pores can couple what results in the formation of an artificial 2D band structure. On the other side, I will show two examples where we made use of Ullmann-type coupling for the formation of covalently coupled molecular structures. For a biphenyl derivative functionalized with an alkenyl gem-dibromide we observed the formation of cumulene units [2]. Moreover, a hydrogen dosing treatment employed during the on-surface reaction was proven successful for the removal of the halogen atoms which are split off during the reaction and which often stay chemisorbed on the surface [3].

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Multicomponent cluster growth and second-layer induced island shaping

Philipp Maass

Department of Physics, University of Osnabrück, Barbarastr. 7, 49076 Osnabrück, Germany
E-mail: maass@uos.de

Understanding and control of cluster growth on solid surfaces is a subject of intensive research to develop nanomaterials with new physical properties. Of particular interest is the self-organized structure formation by deposition of atoms and molecules on surfaces, where the interplay of diffusion, nucleation, aggregation, segregation and superlattice ordering yields a rich variety of growth phenomena [1] The resulting structures are often frozen-in non-equilibrium structures with properties distinctly different from the equilibrium bulk phases. Driven by perspectives of molecular electronics and organic photovoltaics. a goal of vital importance is to exploit the complexity of molecular building blocks provided by organic chemistry for generating an even richer spectrum of surface structures [2-4]. A theoretical challenge in this area is to clarify how far concepts based on single atom surface kinetics remain valid, or require modification, when dealing with the larger sizes, potential non-spherical shapes, and internal degrees of freedom of molecules. Against this background I will discuss recent advancements in the theory of nucleation and kinetic growth, with a focus on multi-component cluster growth [5,6| and second-layer induced island shaping [7].

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Computational approaches to study molecular structure on insulating surfaces

Adam S. Foster

Department of Applied Physics, Aalto University, Finland

E-mail: adam.foster@aalto.fi

Many ideas in next generation technology are predicated on atomic and molecular control of surfaces and interfaces. A natural route to providing this level of control is to design the interface directly using molecular building blocks via self-assembly. The molecular design process can either offer functionality directly, as in lubrication or electronics, or act as a template for the adsorption of the active atoms or molecules. Current challenges lie particularly in applying this approach on insulating surfaces, where the electronic properties of the system are conveniently decoupled from the supporting template.

Using a combination of modelling approaches in partnership with Scanning Probe Microscopy experiments, in this work we consider several examples where the interface has been designed by the controlled assembly of molecular layers. We first introduce the computational tools at the heart of our methodology, and discuss the challenges when simulating complex assembly processes and comparing to experiment. We then compare the adsorption and reaction mechanisms on a benchmark insulator system [1], and also contrast to processes on conducting surfaces [2]. Finally, we build upon this to consider new insights offered by modern machine learning simulation approaches.

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Scratching the surface: Communicating science in a post-truth age

Philip Moriarty

[1]*School of Physics and Astronomy, University of Nottingham, UK*
E-mail: philip.moriarty@nottingham.ac.uk

> *There is a cult of ignorance in the United States, and there always has been. The strain of anti-intellectualism has been a constant thread winding its way through our political and cultural life, nurtured by the false notion that democracy means that "my ignorance is just as good as your knowledge".*
>
> Isaac Asimov (1920 – 1992)

Tom Nichols opens Chapter 1 of *The Death of Expertise,* his persuasive and powerful polemic on the "campaign against established knowledge", with the Asimov quote above [1,2]. Although Asimov and Nichols rightly address the key issue, they both are being just a little too parochial in targeting our American cousins alone. The "post-truth"/"post-fact" cult of ignorance is a global, not a national, phenomenon. And for scientists, that's a deeply uncomfortable realization.

Academics, researchers, and teachers tend to believe that just about any problem can be fixed with a little more education: all we need to do is connect with an audience and explain -- the data will speak for itself. But this is hopelessly and dangerously naïve. Acceptance of the evidence for climate change, for example, is riven with issues related to ideology and political bias. No amount of evidence is enough to convince some audiences. After all, there are thriving flat-Earth, homeopathy, and quantum life coaching communities out there...

Universities increasingly encourage their staff and students to engage as much as possible without realizing that the general public sometimes doesn't want to hear what we have to say [3]. I will discuss the issues surrounding online communication and public engagement in this expert-averse environment.

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Controlling the Growth and Morphology of Self-Assembled Films and Polymers on Ionic Substrates

F. Para[1], F. Bocquet[1], L. Nony[1] , and Christian Loppacher[1];
M. Féron[2], and F. Cherioux[2];
M. B. Watkins[4], D. Z. Gao[5], F. Federici Canova[5], D. Gaberle[3], and A. L. Shluger[3].

[1] *Aix-Marseille Université, CNRS, IM2NP UMR 7334, 13397 Marseille, France;*
[2] *Institut FEMTO-ST, Univ. Bourgogne Franche-Comté, CNRS, France;*
[3] *Department of Physics and Astronomy, University College London, UK;*
[4] *School of Mathematics and Physics, University of Lincoln, UK*
[5] *Nanolayers Research Computing LTD, 15 Southgrove Road, Sheffield, UK.*

E-mail: Christian.Loppacher@im2np.fr

Achieving control over formation of molecular films on insulating substrates is important for designing novel functional materials and devices. Our recent work focused first on the identification of the main factors which governing successful control of molecular self-assembly on insulating surfaces. By depositing specially designed organic molecules with interchangeable functional groups and variable-size aromatic bodies on various alkali-halide substrates we gained control over the formation of highly ordered 2D and quasi 1D domains, but we were also able to form 2D gas phases which slowly dewet to form 3D crystallites.

Density functional theory calculations and atomistic molecular dynamics calculations were used to understand the qualitative difference in growth modes for two different molecules and to determine the role played by entropy loss in the morphology and growth modes of self-assembled films.

The achieved knowledge on growth mechanisms of organic thin-films was second used to fabricate desired precursor structures which could then subsequently be polymerized. We present an example where a UV-induced polymerization was used in order to create micrometer long polymer fibres.

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Kelvin Probe Force Microscopy on Insulator Surfaces

P. Rahe

Fachbereich Physik, Universität Osnabrück, Germany
E-mail: prahe@uos.de

The physical interpretation of Kelvin Probe Force Microscopy (KPFM) data critically depends on the experimental conditions, and is especially influenced by the tip and sample materials. Consequently, a number of models have been presented, relating the KPFM signal for example to work function differences [1], charge distributions [2-4], the electrostatic surface potential [5], or the electric field normal component [6].

The starting point for a consistent interpretation of KPFM data is the calculation of the total electrostatic energy for the investigated tip-sample system. Second, an evaluation of the experimental KPFM observable with respect to the externally applied bias voltage reveals the contributions to the KPFM signal. For a tip-sample system exclusively formed by metals, a KPFM signal that can be related to the work function difference between the tip and sample metals is found [1].

In this lecture, the KPFM signal generation on insulator surfaces will be discussed. First, an electrostatic model describing a tip-sample system with a dielectric sample and a point charge distribution will be introduced [7] and the total electrostatic energy calculated [7,8]. This electrostatic model represents the important case of atoms or molecules deposited on insulator surfaces [9], and especially enables the KPFM data interpretation for charged species [2-4]. Second, the theory allows to identify a *weight function for charges* [8,10], which weights the contribution of each point charge depending on its position and experimental parameters. With this analysis, a detailed investigation of the influencing parameters in KPFM experiments is possible.

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Organic molecules adsorbed on ZnO studied with the X-ray standing wave technique

Dr. Alexander Gerlach

Universität Tübingen, Institut für Angewandte Physik, Germany
alexander.gerlach@uni-tuebingen.de

Optical *in situ* spectroscopy of molecular films

T. Fritz
Friedrich-Schiller-Universität Jena, Institut für Festkörperphysik, Helmholtzweg 5,
07743 Jena, Germany
E-mail: torsten.fritz@uni-jena.de

Organic molecular beam epitaxy (OMBE) is the method of choice for producing highly ordered samples. It offers many advantages, such as controlled growth of epitaxial layers with well-defined layer thickness. *In situ* Differential Reflection Spectroscopy (DRS) [1] has been applied to measure the optical characteristics of those films and interfaces. This technique, with its unsurpassed sensitivity down to an effective coverage of less than 0.1 monolayers of aromatic molecules, can be applied during the deposition of the molecules to monitor the film growth in real time.

I will first discuss the details of the measurement principle. The second part of the talk will be devoted to the special optical properties of ultrathin films of archetypal organic semiconductors to illustrate the versatility of DRS. I will also cover the effect of potassium doping on the optical spectra and will elaborate on the strong relation between physical film structure and optical spectra of organic thin films.

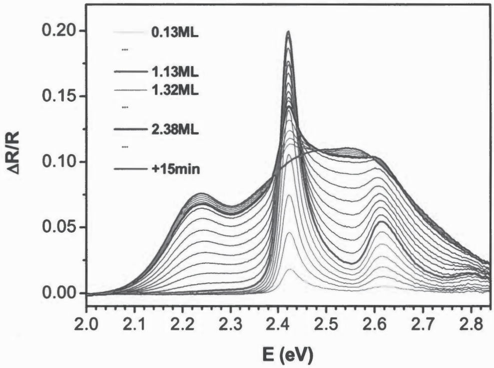

Fig. 1. DRS-spectrum of 1 ML PTCDA on KCl(001). Deposition of more than 1 ML renders the layer structure instable.
Recrystallization into the bulk structure drastically changes the optical spectra from monomer-like towards bulk-like [2].

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Abstracts of Posters

(in alphabetical order)

Bishop Diffusion Involving a Chiral Flip

S. Aeschlimann,[1,2] **F. Kling,**[1] **A. Saal,**[1] **C. Paris,**[3] **A. Floris,**[3] **L. Kantorovich,**[3] **R. Bechstein,**[1] **and A. Kühnle**[1]

[1]Institute of Physical Chemistry, Johannes Gutenberg-University Mainz,
Duesbergweg 10 - 14, 55099 Mainz, Germany
[2]Graduate School Materials Science in Mainz, Staudingerweg 9, 55128 Mainz, Germany
[3]Departement of Physics, King's College London, London WC2R 2LS, United Kingdom
E-mail: siaeschl@uni-mainz.de

Molecular surface diffusion is one of the most fundamental process in nature with far-reaching impact on a wide range of fields including, *e.g.*, catalysis, sensing and surface functionalization [1,2]. So far, molecular surface diffusion studies have mainly been limited to high-symmetry surfaces possessing rotational symmetry. Here, using the low-symmetry (10.4) surface of calcite, we present a novel molecular diffusion mechanism that can be described by the bishop move in chess (see Fig. 1), meaning that only half of the existing lattice sites are accessible for an individual molecular species. Interestingly, due to the only existing symmetry operation of the surface, a glide reflection symmetry, this bishop movement is inevitably associated with a flip in the chiral adsorption footprint of the molecular species towards the surface. Our work demonstrates the pivotal influence of the surface symmetry on the detailed diffusion mechanism, including the adsorption chirality.

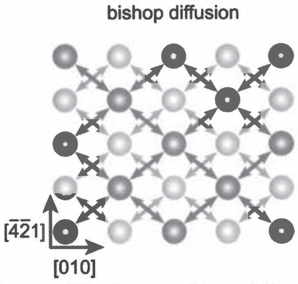

Figure 1: Illustration of bishop diffusion on the calcite (10.4) surface. Performing chess bishop movements, only half of the possible adsorption positions (marked with blue and red spheres, respectively) are accessible.

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PTCDA molecules on Terraces and at Steps Sites of the KCl and NaCl Surfaces

Hazem Aldahhak, Eva Rauls, Wolf Gero Schmidt

Lehrstuhl für Theoretische Physik, Universität Paderborn, Paderborn, Germany

E-mail: aldahhak@mail.uni-paderborn.de

The adsorption of PTCDA ($C_{24}H_8O_6$) on metal substrates has for a long time been used as model system for understanding molecular self-assembly. Ionic crystals as substrate provide the additional possibility to study the molecular properties with little perturbation by substrate screening or strong substrate-adsorbate bonds. Here, we present density-functional theory calculations on the adsorption and the adsorbate-substrate interactions between PTCDA and planar as well as stepped NaCl or KCl surfaces. The adsorption is dominated by van-der-Waals and electrostatic forces. This leads to a site-specific adsorption of the molecule on the surface, resulting in commensurate long-range ordered structures. The influence of the substrate and bonding mechanism on the molecular electronic structure is investigated in detail and compared with the experimental data available. The calculated translational and rotational diffusion barriers in conjugation with the energetic most favorable adsorption on the plane surface and at step edges demonstrate the on-surface aggregation kinetics. Our calculations for the formation energies of different kinds of step edge defects show that the formation of the adsorption sites subsequent to molecular adsorption is more favorable process.[1-3]

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Growth of ultra-thin *para*-hexaphenyl layers on atomically-flat $TiO_2(110)$ surfaces

W. Belza[1], **K. Szajna**[1], **D. Wrana**[1], **K. Cieslik**[1], **M. Kratzer**[2],
C. Teichert[2], **F. Krok**[1]

[1]*Marian Smoluchowski Institute of Physics, Jagiellonian University, Krakow, Poland*
[2]*Institute of Physics, Montanuniversität Leoben, Leoben, Austria*
E-mail: w.belza@doctoral.uj.edu.pl

The growing interest in molecular electronics and its technological applications encourages search for best suitable molecule-substrate systems. In particular, for films composed of rod-like molecules (like oligo-phenylenes), the molecular orientation with respect to the substrate surface is crucial.

We report on the investigation of the nucleation process of *para*-hexaphenyl (6P) molecules, consisting of six interlinked phenyl rings, deposited on flat $TiO_2(110)$ surfaces. Monolayer and sub-monolayer films of 6P (from 0,25 ML to 1,5 ML) were prepared by use of organic molecular beam epitaxy at RT. The surface morphology of the developed molecular structures were investigated *in situ* by means of non-contact atomic force microscopy (ncAFM), scanning tunneling microscopy (STM) and *ex situ* by tapping-mode AFM and electron microscopy (SEM). Additionally, for the surface reconstruction examination, we used a Low Energy Electron Diffraction technique.

It has been found that the submonolayer deposition of 6P on flat $TiO_2(110)$ resulted in the formation of molecular nanowires and a wetting layer (WL) consisting of lying molecules. The molecularly-resolved imaging proved that the WL is a well-ordered straight striped structure of molecular rows (*Figure 1a*). Within the rows the 6P molecules are aligned side-by-side with the average distance of 0,65 nm corresponding to the distance of atomic rows of substrate surface (*Figure 1c*). This wetting layer is a kinetically unstable structure and the molecular stripes rearrange, at the timescale depending on the substrate surface quality, to form a structure following the shape of the $TiO_2(110)$ terrace edges. Finally, an air-exposure of the sample induces a decomposition of the wetting layer and molecular clusters formation.

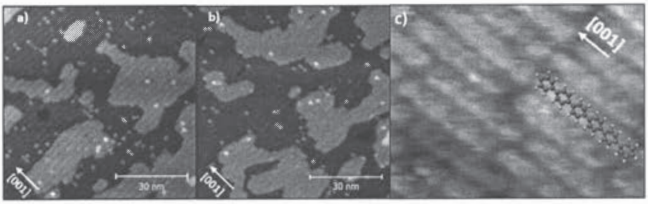

Figure 1. STM images of the wetting layer consisting of side-by-side aligned 6P molecules (U = 1,7 V; I = 50 pA): a) 80x80 nm^2 few hours after 6P deposition; b) 80x80 nm^2 1 day after 6P deposition; c) molecularly resolved STM

Influence of adsorbates on the structural and electrical properties of atomic wires

C. Braun[1] and **W.G. Schmidt**[1]

[1]Lehrstuhl für Theoretische Physik, Universität Paderborn, Paderborn, Germany
E-mail: christian.braun@uni-paderborn.de

In recent years, one-dimensional systems have increasingly come into focus due to their interesting electronic properties including, inter alia, Peierls instabilities and Luttinger liquid behavior. The interplay with the supporting substrate as well as with adsorbates is crucial for understanding the peculiarities of these systems. Promising realizations of quasi-one-dimensional systems are, among others, self-assembled gold nanowires on vicinal Si(111) surfaces.
In this work, the influence of oxygen adsorption upon electrical conductivity on Si(553)-Au and Si(557)-Au was investigated. In the experiment, it was shown that for both systems the electrical conductivity is altered differently by oxygen adsorption.
Modeling of the adsorption process by density functional theory shows that the ad- and rest atoms on Si(557)-Au provide energetically favored adsorption sites, which predominantly alter the transport along the wire direction. [1]

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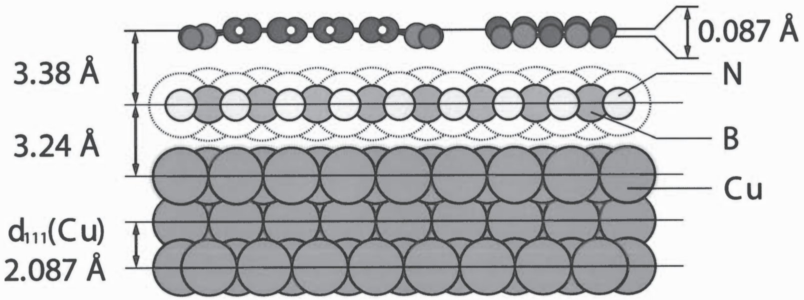
Chemical and electronic decoupling of organic molecules by a monolayer of hexagonal boron nitride

C. Brülke[1], **T. Heepenstrick**[1], **I. Krieger**[1], **X. Yang**[2,3], **S. Weiss**[2,3], **F. Bocquet**[2,3], **F. S. Tautz**[2,3], **S. Soubatch**[2,3] **and M. Sokolowski**[1]

[1]Universität Bonn, Institut für Physikalische und Theoretische Chemie, Wegelerstr. 12, 53115 Bonn, Germany
[2]Forschungszentrum Jülich, Peter Grünberg Institut (PGI-3), 52425 Jülich, Germany
[3]Jülich Aachen Research Alliance (JARA), Fundamentals of Future Information Technology, 52425 Jülich, Germany
E-mail: bruelke@pc.uni-bonn.de

Hexagonal boron nitride (hBN) is a widely studied material due to its similarity to graphene and its properties as a wide band-gap insulator. We report on the ability of one monolayer hBN to electronically and chemically decouple one monolayer of PTCDA from the Cu(111) surface. Using spot profile analysis low energy electron diffraction (SPA-LEED) and scanning tunneling microscopy (STM) we find a big similarity of the PTCDA monolayer to the (102) plane of the bulk crystal. Investigations via photoelectron spectroscopy (XPS and UPS) show electronic decoupling of the molecules from Cu(111) by the hBN monolayer. The HOMO of the monolayer is located at -2.5 eV below E_F, in accordance with previous findings for multilayers of PTCDA. Normal incidence standing wave experiments (NIXSW) reveal that the vertical binding distance of PTCDA to the hBN layer is very large (3.38 Å) and that the out-of-plane distortion of the molecule is very minute (< 0.1 Å). This points to a weak physisorptive bonding in contrast to the chemisorptive bonding found for PTCDA on Cu(111).



Side view of a PTCDA molecule along the long and short molecular axes on one monolayer hexagonal boron nitride on Cu(111). The vertical distances within the molecule are enlarged by a factor of four in order to better see the minute downwards shift of the anhydride groups. Van der Waals spheres for the hBN layer are indicated.

Tuning the self-assembly of carboxyl-substituted triphenylaminederivatives on bulk NaCl(001) and KBr(001)

Mirunalini Devarajulu[1] , Jia Liu[1] , Min-Ken Li[1] , Christian Steiner[1] , Bettina Gliemann[2] , Yi Liu[1] , Tuan Anh Pham[1] , Milan Kivala[2] ,
[1]Department of Physics, University of ErlangenNürnberg, Erlangen, Germany
[2] Department of Chemistry and Pharmacy, FAU Erlangen-Nürnberg, Erlangen, Germany

E-mail: mirunalini.devarajulu@fau.de

While most molecular self-assemblies so far have been studied on metallic substrates, comparatively little is known about molecular self-assemblies on insulating surfaces. One reason is the weak and often unspecific molecule-substrate interaction on bulk insulating surfaces. Therefore, the structure of the self-assemblies is challenging to predict. Here, we present a study on the self-assembly of a carboxyl-substituted dimethylmethylene-bridged triphenylamine derivative [1] on bulk NaCl(001) and KBr(001) by non-contact AFM at low temperature. The intermolecular hydrogen bonding contributes to the formation of 2D monolayers on NaCl(001) and KBr(001). We observed structurally different self-assemblies of the carboxylsubstituted triphenylamine derivative on NaCl(001) and KBr(001), respectively, due to a significant change in lattice mismatch [2]. The surface templating effect and binding motifs will be discussed in detail.

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Reorganization energy of single molecules on an insulating film measured by atomic force microscopy

S. Fatayer[1], B. Schuler[1], W. Steurer[1], I. Scivetti[2], J. Repp[3], L. Gross[1], M. Persson[2] and G. Meyer[1]

[1]IBM Research - Zurich, 8803 Rüschlikon, Switzerland
[2]Department of Chemistry, University of Liverpool, L693BX Liverpool, United Kingdom
[3]Institute of Experimental and Applied Physics, University of Regensburg, 93053 Regensburg, Germany

e-mail: sfa at zurich.ibm.com

Charge state investigations of single adsorbates on ultrathin insulating films has revealed fundamental charging properties. For example, charge state determination and control has been demonstrated on bilayer NaCl for adatoms (1) and molecules (2,3) and the charge distribution within a molecule was mapped (4).

However, multilayered insulating films are necessary to efficiently confine charges on top of a surface – requiring better understanding of adsorbate charging on thicker films (5,6).

Here, we present a novel approach based on single-electron detection to perform tunneling spectroscopy measurements of a molecule on an insulator. Then, we gain insight of charging processes by quantifying a fundamental property of the system, the reorganization energy.

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Reactions of organic molecules on oxide surfaces

Q.T. Fan[1], S.R. Kachel[1], C.C. Wang[2], J.F. Zhu[2], J.I. Martínez[3], J.A. Martín-Gago[3], M. Schmid[1] and J.M. Gottfried[1]

[1]Fachbereich Chemie, Philipps-Universität Marburg, Marburg, Germany
[2]University of Science and Technology of China, Hefei, P.R. China
[3]Institute of Material Science of Madrid (ICMM-CSIC), Madrid, Spain
E-mail: michael.gottfried@chemie.uni-marburg.de

On-surface coordination-chemical reactions such as the direct metalation of tetrapyrroles have been studied in detail on metal surfaces [1]. These reactions are typically performed under solvent-free conditions in ultrahigh vacuum (UHV) by reaction of the organic molecules with coadsorbed or substrate metal atoms. In contrast to this widely studied subject, analogous reactions on oxide surfaces were not investigated prior to our work. Using XPS and STM, we have shown that nickel tetraphenylporphyrin (NiTPP) can be synthesized in-situ on a $TiO_2(110)$-1×1 surface from vapor-deposited Ni atoms and free-base tetraphenylporphyrin (2HTPP). If Ni is deposited onto (sub)monolayer 2HTPP on TiO_2, the reaction proceeds already at room temperature, while elevated temperatures are required when Ni is deposited first. The reaction from 2HTPP to NiTPP is accompanied by changes of the molecular conformation from saddle-shaped to a four-fold symmetry. Similar reactions occur at the $TiO_2(110)$-1×2 surface, but the NiTPP yield depends on which reactant is deposited first. The metalation from 2HTPP to NiTPP is accompanied by changes of the molecular configuration from a tilted two-lobed feature extending along the [001] direction to a four-lobed feature with two diagonal phenyl groups oriented along the [001] direction. The two phenyl rings oriented along the [001] direction appear darker in the STM images, because they are bent downwards into the troughs. When NiTPP is adsorbed on the cross-linked (CL) sites, the four phenyl lobes appear more uniform. This is confirmed by DFT-based STM simulations. Increasing the amount of Ni leads to higher degrees of metalation. The maximum values observed in this work are 85% with a 3-fold Ni excess and 49% with 1:1 Ni/2HTPP ratio for 2HTPP reacting with post- and pre-deposited Ni, respectively, after annealing to 550 K [2]. These studies show that the adsorbate-substrate interactions between Ni and/or 2HTPP and different substrates strongly influence the metalation process of 2HTPP. It thus contributes to a better understanding of the direct on-surface metalation of porphyrins and of surface-confined coordination reactions in general.

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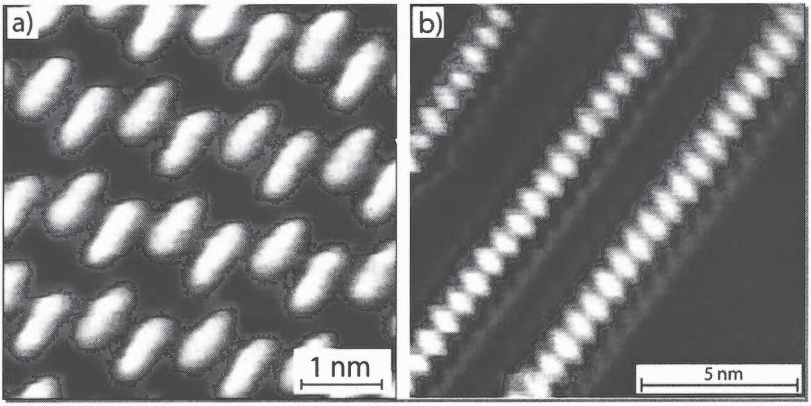
One-dimensional molecular chains of Quinacridone on Ag(100) and Cu(111): STM- and SPA-LEED-investigations

N. Humberg, A. Eslam and M. Sokolowski

Institut für Physikalische und Theoretische Chemie der Universität Bonn
E-mail: humberg@pc.uni-bonn.de

We report a structural analysis of Quinacridone (QA) on Ag(100) and Cu(111) by scanning tunneling microscopy (STM) and spot profile analysis low energy electron diffraction (SPA-LEED). On Ag(100) QA grows at room temperature in parallel homochiral one-dimensional chains, forming a metastable structure. Within these chains the molecules are closely packed and linked via hydrogen bonds. The distance between two neighboring chains varies with coverage. After annealing to 500 K a commensurate heterochiral structure is formed. It consists of homochiral dimers forming periodically idented chains. An oblique unit cell with cell parameters $a = (14.3 \pm 0.2)$ Å, $b = (16.9 \pm 0.2)$ Å and $\alpha = (112 \pm 0.5)$ ° was found.
SPA-LEED patterns of QA on Cu(111) suggest the presence of more disorder. The observed spots smear out, creating a highly symmetric diffraction pattern containing many lines with varying intensities.



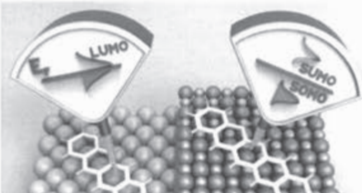
STM-Images of QA on the Ag(100)-surface. a) Structure after annealing. $U_{Bias} = -1.5$ V, $I = 0.25$ nA, $T = 300$ K. b) Metastable structure before annealing. $U_{Bias} = -1.5$ V, $I = 0.25$ nA, $T = 300$ K.

Charge Transfer and Molecular Level Alignment on Dielectric Interlayers on Metals

Philipp Hurdax,[1] **Michael Hollerer**,[1] **Daniel Lüftner**,[1] **Thomas Ules**,[1] **Sergey Soubatch**,[2,3] **F. Stefan Tautz**,[2,3] **Georg Koller**,[1] **Peter Puschnig**,[1] **Martin Sterrer**,[1,]* **Michael G. Ramsey**[1]

[1] *Institute of Physics, University of Graz, 8010 Graz, Austria*
[2] *Peter Grünberg Institut (PGI-3), Forschungszentrum Jülich, 52425 Jülich, Germany*
[3] *Jülich Aachen Research Alliance (JARA), Fundamentals of Future Information Technology, 52425 Jülich, Germany.*

It is becoming accepted that ultrathin dielectric layers on metals are not merely passive decoupling layers, but can actively influence orbital energy level alignment and charge transfer at interfaces. As such, they can be important in applications ranging from catalysis to organic electronics. However, the details at the molecular level are still under debate. Here, we present a comprehensive analysis of the phenomenon of charge transfer promoted by a dielectric interlayer with a comparative study of pentacene adsorbed on Ag(001) with and without an ultrathin MgO interlayer. Using scanning tunneling microscopy and photoemission tomography supported by density functional theory we are able to unambiguously identify the orbitals involved and quantify the degree of charge transfer in both cases. Fractional charge transfer occurs for pentacene adsorbed on Ag(001), while the presence of the ultrathin MgO interlayer promotes integer charge transfer with the LUMO transforming into a singly occupied (SOMO) and singly unoccupied (SUMO) state separated by a large gap around the Fermi energy. We show that by controlling the work function of the dielectric layer we can control the number of charged molecules in the monolayer.



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Reversible and Efficient Photo-Switching of Azobenzene Derivatives on an Insulator Surface

Simon Jaekel[1], **Antje Richter**[2], **Robert Lindner**[2], **Christophe Nacci**[1], **Angelika Kühnle**[2], **Stefan Hecht**[3] **and Leonhard Grill**[1]

[1]*Department of Physical Chemistry, University of Graz, Austria*
[2]*Institute for Physical Chemistry, Johannes-Gutenberg University Mainz, Germany*
[3]*Department of Chemistry, Humboldt-University Berlin, Germany*
E-mail: simon.jaekel@uni-graz.at

Studying single molecular switches is of interest for a better understanding of fundamental physical and chemical processes, but also in view of their possible use in molecular nanotechnology [1].

A prototypical conformational switch is azobenzene, which changes between trans and cis isomers at the central N=N bond upon an external stimulus, showing efficient photochemical activation. In the past years, various studies have shown that adsorption on metal substrates strongly influences the switching properties [2,3], especially for activation by light [4].

Here, we report non-contact atomic force microscopy (nc-AFM) results on the first switching of individual azobenzene molecules on an insulating calcite surface. Unlike on metallic surfaces, *cis* isomers appear on the surface already directly after preparation, indicating kinetic trapping. Illumination with different light sources show that the molecules retain their efficient photoisomerization properties known from solution. Furthermore, the photoisomerization is shown to be reversible and selective, depending on the excitation wavelength.

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Portlandite crystallization

B. Jennewein[1], R. Bechstein[1], S. Klassen[1] and A. Kühnle[2]

[1]Institut für Physikalische Chemie, Johannes-Gutenberg-Universität Mainz, D-55099 Mainz, Germany
[2]Physical Chemistry I, Universität Bielefeld, D-33615 Bielefeld
E-mail: jennewb2@students.uni-mainz.de

In construction industry, cement still plays an important role as the commonly used building material. One of the main components of the hydrated cement is Portlandite ($Ca(OH)_2$). A first step to obtain insights into the interactions between the cement surface and other substances, such as water or organic molecules, is the investigation of the core components of cement. Portlandite is a hydroxide with a layered structure and serves as a model crystal for research aiming at understanding cement surfaces. My work focuses primarily on the hydration structure at the Portlandite-water interface. As an initial step, synthesizing single crystals is mandatory since they are rarely found in nature and they carbonate rather quickly. On my poster, I present my first results from a counter-diffusion crystallization method, first introduced by Johnston in 1914.

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Growth of small organic molecules on ultrathin hexagonal born nitride

M. Kratzer[1], A. Matković[1], J. Genser[1], G. Lin[1], D. Lüftner[2], Z. Chen[2], O. Siri[3], C. Becker[3], P. Pusching[2] and C. Teichert[1]

[1]Institute of Physics, Montanuniversität Leoben, Leoben, Franz-Josef Str. 18, Austria
[2]Institute of Physics, Karl-Franzens-Universität Graz, NAWI Graz, Universitätsplatz 5, Graz, 8010, Austria
[3]Aix-Marseille Universite, CNRS, CINaM UMR 7325, 13288 Marseille, France
E-mail: markus.kratzer@unileoben.ac.at

The role of ultrathin, two-dimensional (2D) substrates in the development of novel electronic devices is yet to come. Quasi 2D materials can act as optically transparent and mechanically flexible electrodes or dielectrics in organic electronics. Graphene as potential electrode material has been studied to some extend as substrate for organic thin film growth [1-6]. Besides graphene, which is the prototype of a 2D material hexagonal boron nitride (hBN) has come into the focus of research as an ultra-thin dielectric. Here, we present the study of growth morphologies of the non-polar small organic model molecule para-hexaphenyl (6P) [7] as well as of the polar dihydrotetraazaheptacene (DHTA7) on SiO_2/Si supported, exfoliated hBN. The substrates have been prepared by micromechanical exfoliation from hBN powders and subsequent transfer to SiO_2/Si substrates. The organic thin films have been deposited by means of hot wall epitaxy (HWE) in a temperature range between room temperature and 360 K. The resulting morphologies were characterized ex-situ by means of atomic force microscopy (AFM). The main growth features are crystalline needle networks that exhibit clear epitaxial relationships between substrate an organic crystal. Comparison with density functional theory (DFT) calculations reveald a (-629) contact plane between 6P and hBN. This resulted in a splitting of ±~6° of the needle growth directions to the hBN zig-zag orientation. For the acene-like DHTA7, very long needles with a splitting of ±~9.5° with repect to the armchair direction has been found. For these needles, where the polar molecules show a π-π stacking according to DFT calculations first results on the charge spreading under illumination obtained by electrostatic force microscopy are presented.

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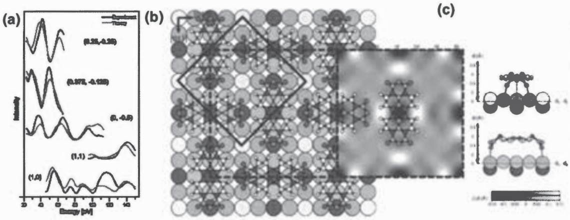
Surface crystallography of large organic molecules on metal and insulator surfaces by LEED-IV using Fourier coefficients

Ina Krieger[1,3], **Georg Held**[2], **Christian Kumpf**[3], and
Moritz Sokolowski[1]

[1]Institut für Physik. und Theo. Chemie, Universität Bonn, 53115 Bonn, Germany
[2]Department of Chemistry, University of Reading and Diamond Light Source, UK
[3]Peter Grünberg Institut (PGI-3), Forschungszentrum Jülich, 52428 Jülich, Germany
E-mail: krieger@pc.uni-bonn.de

We will report on LEED-IV analysis of the large organic molecules PTCDA and NTCDA on the metal and insulator surfaces Ag(100), Ag(111), and KCl(100). Using data from different angles of electron incidence and optimizing the LEED-IV program code we were able to extend the experimental data set and shorten the calculation times required for the complex and large unit cells. Furthermore, the distortion of the PTCDA molecule and the buckling of the Ag surface were described by Fourier coefficients taking into account the symmetry of the system [1]. The idea of this procedure is to suppress unphysical vertical displacements of atoms on a short-wave-length scale by restriction to lower order coefficients.

By this, we obtain good Pendry R-factors, for PTCDA/Ag100 of about 0.23. We were able to derive the vertical distortions of the oxygen atoms in the functional group and the buckling of the Ag surface in rather good agreement with earlier results from DFT and NIXSW studies.



(**a**) Set of experimental (black) and calculated (red) LEED-IV curves for PTCDA/Ag(100) and (**b**) top and (**c**) sectional views of the adsorption geometry of PTCDA/Ag(100) as calculated by LEED-IV. Ag atoms are shown in different shades of blue to indicate the vertical deviation Δd from their position in the relaxed uncovered surface (dashed line, d_0); H atoms are shown in white, O_{carb}/O_{anhyd} in red/blue and the chemically different C atoms are marked by different colors. In the side views, d denotes the vertical adsorption height; the vertical scale is enlarged by a factor of 4 and referenced against the Bragg plane (dashed line, d_B). The primitive unit cell (full lines) and the conventional c(8×8) unit cell (dashed lines) are indicated. The inset in (b) illustrates the modulation of the first Ag layer described by the start parameters of the Fourier coefficients. This is shown for the c(8×8) unit cell.

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Towards functionalization of graphene: In situ study of the nucleation of copper-phtalocyanine on graphene

Daniel Schwarz, Caroline Henneke, Christian Kumpf

Peter Grünberg Institut (PGI-3), Forschungszentrum Jülich, Germany and Jülich
Aachen Research Alliance (JARA) - Fundamentals of Future Information Technology
E-mail: c.kumpf@fz-juelich.de

Molecular films present an elegant way for the uniform functionalization or doping of graphene. Here, we present an in-situ study on the initial growth of copper phthalocyanine (CuPc) on epitaxial graphene on Ir(111). We followed the growth up to a closed monolayer with low energy electron microscopy (LEEM) and selected area electron diffraction (micro-LEED). The molecules coexist on graphene in a disordered phase without long-range order and an ordered crystalline phase. The local topography of the graphene substrate plays an important role in the nucleation process of the crystalline phase.

Fig.1: Growth sequence of CuPc/gr/Ir(111): The first image shows the clean gr/Ir(111) surface in false colors, dark areas corresponding to less, bright to more strongly stressed regions. In the following images CuPc crystallization is first observed on relaxed regions "A", and only subsequently on stressed regions "B".

Graphene flakes on Ir(111) feature regions that are under more tensile stress than others. We observe that the CuPc molecules form ordered domains initially on those graphene regions that are closest to the fully relaxed lattice (see Fig. 1). We attribute this effect to a stronger influence of the underlying Ir(111) substrate for molecules adsorbed on those relaxed regions [1].

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Comparing bulk with thin film dielectric: Ferrocene Dicarboxylic Acid on $CaF_2(111)$ surfaces

L. Laflör[1], F. Schlage[1], M. Reichling[1], P. J. Moriarty[2] and P. Rahe[1,2]
[1]*Universität Osnabrück, Barbarastr.7, Osnabrück, Germany*
[2] *University of Nottingham, University Park, Nottingham, United Kingdom*
E-mail: linda.lafloer@uos.de

It is now established that insulators can facilitate electronic decoupling of adsorbates from conducting environments[1]. While especially thin films of insulating NaCl are widely used for decoupling adsorbed species[2], it has also been suggested that the conductivity through an NaCl bilayer is still dominating the conductivity through conjugated molecules[3]; in this context, thicker insulating layers or bulk insulating material can be required to sustain molecular functionality. To assess the influence of these different environments, it is of great interest to investigate adsorption of functional molecules on thin films and on bulk insulator crystals of the same material and to compare the properties of adsorbed molecules on equivalent surfaces.

In this work we investigate submonolayer coverage of 1,1'-ferrocene dicarboxylic acid (FDCA) molecules deposited on both, $CaF_2(111)$ surfaces of bulk crystals and of thin CaF_2 films on $CaF_1/Si(111)$ under ultra-high vacuum conditions. Ferrocene itself is known for its redox behaviour and is commonly used as a reference in cyclic voltammetry. Accordingly, charge state modification of FDCA deposited on the insulator calcite(104) surface has been presented before[4].

FDCA molecules are investigated at room temperature (RT) on $CaF_2(111)$ surfaces of bulk crystals using non-contact atomic force microscopy (NC-AFM) as well as at room and low temperatures (LT) on CaF_2 thin films. Additionally, scanning tunnelling microscopy (STM) measurements are performed on the thin film samples.

We compare the adsorption characteristics of FDCA on these two surfaces, focusing on geometrical properties. The formation of small FDCA clusters, consisting of typically less than 25 molecules, is observed on bulk crystals as well as on CaF_2 thin films. The clusters are observed to be rather immobile at RT and single FDCA molecules in the clusters can be identified. The identification of both cyclopentadienyl (cp) rings, and consequently the orientation of the molecules on the surface, is possible from NC-AFM measurements at all temperatures.

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Self-assembly of cyano-substituted porphyrin-derivatives on bulk MgO(0001)

M. Devarajulu, M. Li, J. Liu, S. Maier

Department of Physics, Universität Erlangen-Nürnberg, Erlangen, Germany
E-mail: Jia.Liu@fau.de

The realization of molecule-based devices requires functional molecular building blocks integrated on suitable substrates. Due to the strong interaction between molecular building blocks and metal surfaces, most molecular building blocks lost their original functionality on metal surfaces. The week interaction between organic molecular building blocks and bulk insulating surfaces makes it ideal for the fabrication of molecular devices. So organic molecules on insulating surfaces has been attracting more and more attention recently [1]. Here, we present a study on the self-assembly of cyano-substituted porphyrin derivatives on bulk MgO(0001) by non-contact AFM at low temperature.

We observed self-assembly of the cyano-substituted porphyrin-derivatives on MgO(0001). The interaction between intermolecular cyano groups plays an important role in the formation of 2D self-assembly. The detail structure with sub-molecular resolution will be discussed in detail [2].

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Vibrational progression in both frontier orbitals of a single hydrocarbon molecule on graphene

A. Mehler, N. Néel and J. Kröger

Institut für Physik, Technische Universität Ilmenau, Ilmenau, Germany
E-mail: alexander.mehler@tu-ilmenau.de

Vibronic excitations are relevant to molecules that are considered promising building blocks of solar energy conversion or light emitting diodes. In order to probe these genuine molecular properties after adsorption on a surface, appropriate buffer layers are of paramount importance. Here, vibrational progression in both frontier orbitals of an organic electron donor molecule on a graphene-covered metal surface is reported by using scanning tunneling spectroscopy with submolecular resolution. In addition, separated molecules and species embedded in a molecular network exhibit a rigid shift of their entire vibronic spectrum. This work unravels intramolecular changes in the vibronic and electronic structure owing to the efficient reduction of the molecule-metal hybridization by graphene. Financial support by the Deutsche Forschungsgemeinschaft through Grant No. KR 2912/12-1 is acknowledged.

Structural and electronic properties of CoPc and F_{16}CuPc on Ag(100)

A. Sabik, P.-Mazur, F. Gołek and G. Antczak

Institute of Experimental Physics, Department of Physics and Astronomy,
University of Wrocław, Wrocław, Poland
E-mail: agata.sabik@uwr.edu.pl

Metal-phthalocyanines (MPcs) are macrocyclic coordinative organic compounds which exhibit remarkable (opto-)electronic properties. Since that reason MPcs are considered as the active layers in organic electronic devices like organic solar cells or organic field effect transistors [1]. In such devices the organic material is often deposited on the metal electrode. Thus the fundamental studies of metal-organic interfaces lead to better understanding of organic nanotechnology.

Utilizing scanning tunneling microscopy (STM), low energy electron diffraction (LEED) and ultraviolet photoelectron spectroscopy (UPS) we investigate structural and electronic properties of the very first layer of cobalt phthalocyanine (CoPc) as well as prefluorinated copper phthalocyanine (F_{16}CuPc) on the Ag(100) surface.

Both molecules form ordered structures, in monolayer (ML) regime, visible in STM and LEED images. The geometry of the unit cell depends on chemical composition of MPc. CoPc usually arrange in (5x5)R0 structure [2] whereas F_{16}CuPc form commensurate two-domain structure. Finally, we investigate the ordered bimolecular layer which consists of 0.5 ML of CoPc and 0.5 ML of F_{16}CuPc. As it is visible in STM images the layer is compositionally ordered and MPcs create chessboard-like structure on the surface. The obtained images of CoPc and F_{16}CuPc suggest that the charge reorganizations between MPc and Ag(100) vary with the type of molecule.

From UPS investigations we determine wo rk function change of silver substrate induced by adsorption of MPc. 1.0 ML of CoPc decreases Ag(100) work function (*WF*) of about 0.33 eV. The situation is opposite for monolayer of F_{16}CuPc i.e. sample *WF* increases and for 1.0 ML is about 0.12 eV higher than *WF* of Ag(100). In the UP spectra features associated with photoemission from frontier molecular orbitals appear near the Fermi level.

This work has been supported by National Science Center, Poland within the project number 2015/19/N/ST3/01044.

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Thickness-dependent photoelectron spectroscopy study of 1,2:8,9-dibenzopentacene (trans-DBPen) on Au(111)

Maximilian Schaal, Felix Otto, Christian Udhardt, Bernd Schröter, Roman Forker, Torsten Fritz

Institute of Solid State Physics, Friedrich Schiller University Jena, Helmholtzweg 5,
07743 Jena, Germany
E-mail: maximilian.schaal@uni-jena.de

Alkali-metal-doped polycyclic aromatic hydrocarbons received broad attention as potential organic superconductors during the last years. A representative of this class is potassium-doped 1,2:8,9-dibenzopentacene (trans-DBPen) which has a reported transition temperature of 33 K in bulk powder samples [1]. Here we investigate thin films of trans-DBPen on Au(111) by means of thickness-dependent x-ray photoelectron spectroscopy (XPS) and ultraviolet photoelectron spectroscopy (UPS). The XPS results show a thickness-independent line shape and an energy shift by the formation of an interface dipole. The UPS results show an asymmetric broadening of the highest occupied molecular orbital (HOMO) in the monolayer which is attributed to the occurrence of vibronic states. The peak splitting in the bilayer indicates the formation of a dimer structure via π-stacking. Furthermore, we explore the thickness-dependent modification of the binding energy and effective mass of the Shockley surface state of Au(111) by angle-resolved UPS (ARUPS).

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Modeling of molecular stripe formation on insulating surfaces

M. Einax[1,2], C. Schiel[1], R. Bechstein[3], A. Kühnle[3], P. Rahe[1] and P. Maass[1]

[1]Fachbereich Physik, Universität Osnabrück, 49076 Osnabrück, Germany
[2] School of Chemistry, Tel Aviv University, Tel Aviv 69978, Israel
[3]Institut für Physikalische Chemie, Johannes Gutenberg-Universität Mainz, 55099 Mainz, Germany
E-mail: cschiel@uos.de

We discuss theoretical approaches to model molecular stripe formation on dielectric surfaces as observed for racemic heptahelicene-2-carboxylic acid (HCA) molecules and 3-hydroxybenzoic acid (3-HBA) on calcite (104). For the self-assembly of HCA molecules a rate equation approach is developed to explain that HCA wires grow to an effectively limited length. For the self-assembly of the 3-HBA molecules it is argued that adsorption-induced dipolar interactions cause an ordering towards a regular spacing between the molecular stripes. Measured stripe distance distributions show a good agreement with analytical predictions. We present scaling relations for the distance distribution that can be tested experimentally to further substantiate the assumed mechanism of adsorption-induced dipoles.

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Formation of Metal-Organic Coordination Networks on a Bulk Insulator Surface

L. Schüller[1], **M. T. Rahman**[1], **R. Bechstein**[1], **and A. Kühnle**[2]

[1]*Institute of Physical Chemistry, Johannes Gutenberg University Mainz, Duesbergweg 10 - 14, 55099 Mainz, Germany*
[2]*Department of Chemistry, Bielefeld University, Universitätsstraße 25, 33615 Bielefeld, Germany*
E-mail: luschuel@students.uni-mainz.de

Metal-organic coordination networks (MOCNs) are a class of two-dimensional compounds with potentially interesting electronic, magnetic and catalytic properties. [1] A variety of MOCNs have been created on metal surfaces. However, an underlying insulator surface is beneficial for the electronic decoupling of structure and surface. To this end, we demonstrate the self-assembly of organic linker molecules and the formation of MOCN precursor structures in the presence of iron nano-clusters at room temperature.

Our study of biphenyl-4,4'-dicarboxylic acid (BPDCA) in presence of iron on calcite (10.4) unravels two important findings: First, the deposition order plays a vital role in the formation of MOCNs. Second, a strong templating effect of the underlying surface is decisive for the direction, in which the MOCN is more extended. [2] (figure 1)

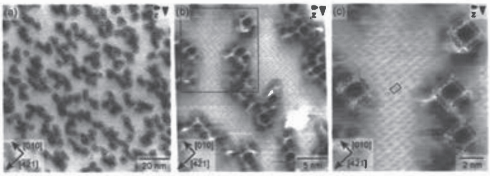

Figure 1: AFM images reveal the formation of MOCN precursor structures formed by BPDCA and iron on the calcite (10.4) surface. [2]

Currently, we vary the size of the linker molecule in order to match the surface unit cell size. Terephtalic acid (TPA), a homologue of BPDCA with one phenyl ring less [3], is examined in presence of iron, as well as 1,1':4',1''-terphenyl-4,4''-dicarboxylic acid (TPDCA), *i.e.*, the homologue of BPDCA with one phenyl ring more. With this work, we explore the formation of an extended MOCN on an application-relevant bulk insulator surface.

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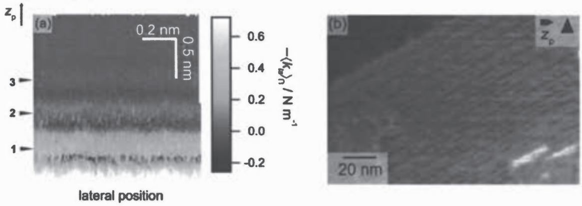
Ethanol and water: Probing the solvation structure at the graphite–liquid interface

S.Seibert,[1*] **H. Söngen,**[1] **H. Jagad,**[2] **S. Klassen,**[1] **R. Bechstein**[1] **and A. Kühnle**[1,3]
[1]*Institute of Physical Chemistry, Johannes Gutenberg-University Mainz, D-55099 Mainz, Germany*
[2]*Department of Metallurgical Engineering and Material Science, Indian Institute of Technology-Bombay, Powai 400076, Mumbai, India*
[3]*Institute of Physical Chemistry, University of Bielefeld, D-33615 Bielefeld, Germany*
**E-mail: sseiber@uni-mainz.de*

Due to the abundance of water and organic molecules in nature, the structure of solid-liquid interfaces is decisive for many environmental processes. An atomistic understanding of the interface is crucial for elucidating fundamental processes such as surface wetting, corrosion and mineral dissolution and growth.

In this study, we investigate the graphite-water and the graphite-ethanol interface with three-dimensional (3D) AFM [1]. A slice through a 3D data set extracted perpendicular to the graphite surface in water (depicting the negative tip-sample force gradient) is shown in the figure (a). Three layers are visible.



Using the solvent-tip-approximation [2], we find that water and ethanol orders in layers above the graphite surface. At the atomic scale we find vertical but no lateral order in both cases. The layered structure at the graphite-water interface can explain due to the attractive graphite-water interaction [3]. Furthermore, sometimes stripes are found to occur on the surface in both liquids. Stripes at the graphite-water interface are shown in figure (b). While these stripes have been observed before by other groups [4, 5], their origin remains unclear so far. We present high-resolution 3D data and discuss them in the view of our current interpretation.

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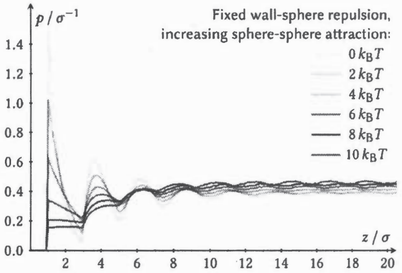
Solvation layers at solid-liquid interfaces: Attraction or confinement?

H. Söngen,[1,6] **L. Zivanovic**,[2] **S. Seibert**,[1] **R. Bechstein**,[1] **P. Spijker**,[2] **H. Onishi**,[5] **A. S. Foster**,[2,3,4] **and A. Kühnle**[1,6]

[1] *Institute of Physical Chemistry, JGU Mainz, Mainz, Germany*
[2] *COMP Centre of Excellence, Department of Applied Physics, Aalto University, Helsinki, Finland*
[3] *Graduate School Materials Science in Mainz, Mainz, Germany*
[4] *Division of Electrical Engineering and Computer Science, Kanazawa University, Kanazawa, Japan*
[5] *Department of Chemistry, Kobe University, Kobe, Japan*
[6] *Physical Chemistry I, Bielefeld University, Bielefeld, Germany*
E-mail: soengen@uni-mainz.de

By using 3D atomic force microscopy, we (and others) observed solvation layers at numerous solid-liquid interfaces, including the calcite-water, dolomite-water and the graphite-water interface.[1-3] In the current study,[4] we discuss two prevalent explanations for the formation of solvation layers: (1) The layered structures are induced by the confinement of the solid surface and (2) layered structures are caused by attractive interactions between the surface and the liquid molecules.

Based on a one-dimensional system of hard spheres we clarify that the confinement of the surface alone (without attractive surface-molecule interactions) can result in the formation of solvation layers. By means of simulation we show that the solvation layers fade when additionally including attractive molecule-molecule interactions (see figure). The layers appear again when including attractive surface-molecule interactions.



With molecular dynamics simulations we show that the confining nature of the graphite surface alone does not explain the solvation layers at the graphite-water interface. We thereby demonstrate that the attractive graphite-water interaction is key for explaining the structure of the graphite-water interface.

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Self-assembly and on-surface reaction of bromo-substituted decacyclene on Ag(111)

S. Menon[1], S. Sorayya[1], J. Tomada[2], K. Amsharov[2] and S. Maier[1]

[1] Department of Physics, FAU Erlangen-Nürnberg, *Germany*
[2] Department of Chemistry and Pharmacy, FAU Erlangen-Nürnberg, Germany
E-mail: Shadi.Sorayya@fau.de

Controlling and understanding the self-assembly of chiral molecules on surfaces is essential for chiral separation and recognition. Here, we report on the self-assembly and reaction of the chiral bromo-substituted decacyclene molecules adsorbed on Ag(111) using high-resolution scanning tunneling microscopy at low temperatures. The steric repulsion between adjacent hydrogen atoms at the peripheral naphthalene units of the decacyclene derivative leads to a twist in the molecular scaffold, and hence several conformers are found upon adsorption on the surface. We observe compact and porous organo-metallic networks upon annealing based on the complex interplay between intermolecular forces and chirality of the constituent molecules. The structural properties of the networks and the chirality will be discussed in detail. Notably, we see a transition from homochiral to heterochiral networks upon annealing.

Dependence of the adsorption height of graphene-like adsorbates on their dimensionality

S. Soubatch[1], S. Weiss[1], X. Yang[1], A. Stein[2], D. Gerbert[2], C. Brülke[3], R. Kremring[3], S. Feldmann[2], A. K. Schenk[4], M. Gille[5], T. Heepenstrick[3], I. Krieger[3], F.C. Bocquet[1], S. Hecht[5], M. Sokolowski[3], P. Tegeder[2] and F. S. Tautz[1]

[1]Forschungszentrum Jülich, Jülich, Germany
[2]Ruprecht-Karls-Universität Heidelberg, Heidelberg, Germany
[3]Universität Bonn, Bonn, Germany
[4]La Trobe University, Melbourne, Australia
[5]Humboldt-Universität zu Berlin, Berlin, Germany

E-mail: s.subach@fz-juelich.de

We measured the adsorption height of various graphene nanoribbons (GNR) on the Cu(111) and the Au(111) surfaces and of graphene and hexagonal boron nitride (hBN) on the Cu(111) surface using the x-ray standing waves technique. We found that both 2 dimensional materials have the height on Cu(111) exceeding the sum of van der Waals radii of the corresponding atoms – copper and carbon or copper and boron/nitrogen, pointing at only weak interactions at the graphene/Cu(111) and hBN/Cu(111) interfaces. Contrary, GNR are found to be physisorbed on Au(111) and chemisorbed on Cu(111), similar to the case of platelet organic molecules. Thus, we observe a strong dependence of the adsorption height on the dimensionality of the adsorbate. In particular, we found that dimensionality overrules the effects of local chemical bonds to the substrate that are formed at edges of the nanoribbons. The latter are responsible for substantial vertical distortions of the GNR.

Generic repulsion in molecular self-assembly on a bulk insulator: Influence on striped structures formed on calcite (10.4)

J. Neff[1], H. Söngen[1], A. Richter[1], M. Vogtland[1], C. Venturini[2], A. Gourdon[2], R. Bechstein[1] and A. Kühnle[3]
[1] *Institute of Physical Chemistry, Johannes Gutenberg-University Mainz,*
Duesbergweg 10-14, 55099 Mainz, Germany
[2] *CNRS, CEMES, Nanoscience Group, BP 94347, 29 Rue J. Marvig, 31005 Toulouse, France*
[3] *Physical Chemistry I, Bielefeld University, Universitätsstraße 25, Room F2-112*
33615 Bielefeld
E-mail: angelika.kuehnle@uni-bielefeld.de

Molecular self-assembly constitutes a convenient ways to create molecular structures at surfaces. In the past, the focus of controlling the structures has been on attractive interactions, while repulsive interactions have been explored only rarely.

Our group has investigated the self-assembly of benzoic acid derivatives with dynamic atomic force microscopy (AFM) at room temperature on calcite (10.4). Here, we focus on those molecules that form striped structures. The obtained next-neighbour stripe distance (*d*) distributions for different molecules differ substantially from what is expected for randomly placed, non-interacting stripes.

The balance between short-range attractive and long-range repulsive forces varies from molecule to molecule: 4-Ethylbenzoic acid (4-EBA) for example also forms islands as indicated by the sharp peak at a stripe distance corresponding to the stripe thickness d_0. In the long-range stripe distance regime, a clear peak is found for all molecules. When excluding kinetic effects during growth, this peak can only be explained by a repulsive mechanism such as, *e.g.*, electrostatic repulsion caused by adsorption induced charge redistribution. This generic repulsion mechanism constitutes an interesting additional option to influence molecular structure formation on surfaces.

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Controllable formation of molecular nanostructures on $TiO_2(110)$: from nanoneedles to dendritic islands

D. Wrana[1], **K. Szajna**[1], **M. Kratzer**[2], **W. Bełza**[1], **B. R. Jany**[1],
C. Teichert[2] **and F. Krok**[1]

[1] *Marian Smoluchowski Institute of Physics, Jagiellonian University, Kraków, Poland*
[2] Institute of Physics, Montanuniversitaet Leoben, Leoben, Austria
E-mail: dominik.wrana@uj.edu.pl

We report on growth of molecular ultrathin films of para-hexaphenyl (6P) on flat rutile titanium dioxide (110) single crystal surfaces. We show the formation of 6P nanostructures can be further tuned either by means of passivation or ion beam irradiation of the substrate surface.

Titanium dioxide as a transparent, wide bandgap semiconductor is widely investigated towards the fabrication of organic light emitting diodes or solar cells. Oxygen rows forming a (1x1) reconstruction make it a perfect anisotropic template for molecular growth, whereas the rod-like structure of *para*-hexaphenyl (6P) molecules induces different optoelectronic properties for various crystallite orientations [1].

Submonolayer deposition of 6P on atomically flat $TiO_2(110)$ (1x1), carried out in UHV at room temperature, results in the formation of tens-of-micrometers long 6P nanoneedles composed of lying molecules and a wetting layer betwixt them. Air passivation of the created molecular structures leaves the nanoneedles unaltered but induces dewetting and subsequent formation of small molecular islands. The present research compromising both ex situ and in situ measurements provides a detailed growth model of all nanostructures [2].

To investigate the influence of ambient air on ultrathin molecular film growth on flat titanium dioxide surfaces, 6P deposition was performed also on air-passivated surfaces. In this case, the formation of dendritic islands, composed of upright standing molecules, is observed. In addition, we have shown that even slight ion beam irradiation of the substrate surface leads to a lying-to-standing orientation transition of the 6P nanostructures.

Rod-like molecules like 6P or pentacene are promising candidates for various optoelectronic devices. The preliminary results from the local-conductivity atomic force microscopy (LC-AFM), confirming the 6P/TiO2 films remarkable electronic properties will be shown.

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Atom-scale imaging of TiO_2(110) surface in water by FM-AFM

Shengkai Xue, **Akira Sasahara, and Hiroshi Onishi**
Department of Chemistry, Kobe University, Rokko-dai 1-1, Nada, Kobe, Japan
E-mail: 154s227s@stu.kobe-u.ac.jp

Titanium dioxide (TiO_2) is widely used in various industrial products including pigments, cosmetics, gas sensors, and photocatalysts. In most cases, TiO_2 shows its performance in aqueous solutions. Hence, in-situ analysis in aqueous solutions would further develop understanding of the useful properties of TiO_2. In this study, the TiO_2 (110) surface was examined in KCl aqueous solution with different pH values (3 – 11) using frequency modulation atomic fore microscopy (FM-AFM) technique.

The topographic image observed at pH 6 is shown in Fig.1 (a). Bright rows extending along the [001] direction were observed. The distance between the rows was 0.67 nm as shown in the A-B cross-section. Protrusions with an interval of 0.28 nm were resolved within the bright rows as shown in C-D cross-section. The dimension of 0.67 nm × 0.28 nm, agrees with that of the unit cell of the TiO_2(110)-(1×1) surface corresponding to a truncation of the bulk crystal. The bright rows were assigned to the rows of the bridging O atoms protruding on the surface. Figure 1(e) shows the distributions of the Δf along the plane perpendicular to the surface. Places where repulsive force applied on the tip are represented bright. The observed checkerboard-like pattern indicates that the aqueous solution was structured according to physically corrugated TiO_2(110) surface.

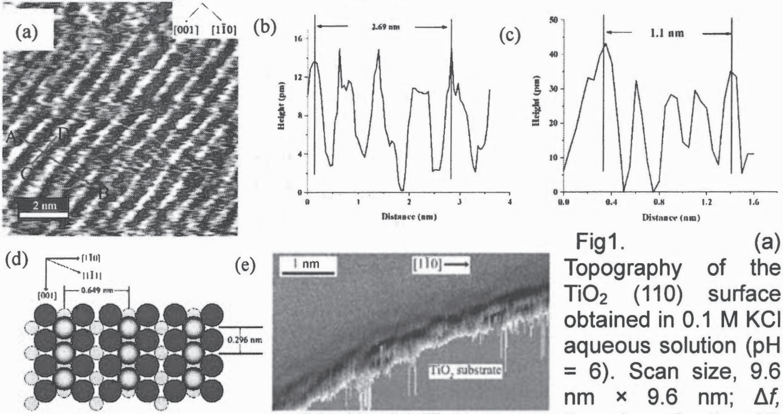

Fig1. (a) Topography of the TiO_2 (110) surface obtained in 0.1 M KCl aqueous solution (pH = 6). Scan size, 9.6 nm × 9.6 nm; Δf, +215 Hz. (b) The cross-section along the line AB in image (a). (c) The cross-section along the line CD in image (a). (d) A model of the TiO_2(110)-(1×1) surface. (e) Two-dimensional Δf distribution across the solution-TiO_2 interface. Scan Size: 3.0 nm × 5.3 nm.

Oxygen-triggered electronic and structural decoupling at the PTCDA/Cu(100) interface

Xiaosheng Yang[1,2], Simon Weiß[1,2], Ina Krieger[3], Timo Heepenstrick[3], Michael Hollerer[4], Philipp Hurdax[4], Daniel Lüftner[4], Peter Puschnig[4], Georg Koller[4], Michael G. Ramsey[4], Moritz Sokolowski[3], F. Stefan Tautz[1,2], Sergey Subach[1,2]

[1]*Peter Grünberg Institut (PGI-3), Forschungszentrum Jülich, 52425 Jülich, Germany*
[2]*Jülich Aachen Research Alliance (JARA), Fundamentals of Future Information Technology, 52425 Jülich, Germany*
[3]*Institut für Physikalische und Theoretische Chemie, Universität Bonn, 53115 Bonn, Germany*
[4]*Institut für Physik, Karl-Franzens-Universität Graz, NAWI Graz, 8010 Graz, Austria*
E-mail: xia.yang@fz-juelich.de

The electronic states and geometric vertical structures of perylene-tetracarboxylic dianhydride (PTCDA) molecule upon an oxygen-reconstructed ($\sqrt{2}$x2$\sqrt{2}$)R45° Cu(100) surface are investigated using angle-resolved photoemission spectroscopy (ARPES) and the normal incidence x-ray standing wave (NIXSW) technique, respectively. The ARPES-based orbital tomography measurement found that, in contrast to PTCDA on intrinsic Cu(100) where strong molecule-substrate interactions are present [1], the oxygen adsorbed on Cu(100) prevents change transfer from metal substrate into the PTCDA molecule. Further, the mechanical separation induced by oxygen is gauged by determining the adsorption height of PTCDA molecules and oxygen atoms on Cu(100) surface. The suppressed charge transfer and the flat geometry of the PTCDA molecule layer with a high adsorption height corroborate that the oxygen simultaneously induces electronic and structural decoupling at the molecule-metal interface.

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