



**SFB 1083**

Structure and Dynamics  
of Internal Interfaces

## **Winter School 2017**

Schloss Rauischholzhausen  
January 17th – 18th, 2017



Foto: Schloss Rauischholzhausen

## **Scientific Program**





**Tuesday, January 17<sup>th</sup>, 2017**

**Welcome**

08:45 – 09:00      **Ulrich Höfer, Malte Zugermeier, Marcel Reutzel**  
*Opening Remarks*

**Session I** (Chair: Malte Zugermeier)

09:00 – 10:00      **Alexey Chernikov**  
***Tutorial** – Exciton physics of semiconducting 2D materials*

10:00 – 11:00      **Katrin Siefermann**  
***Tutorial** - Ultrafast photoemission electron microscopy in materials science*

11:00 – 11:30      Coffee Break

**Session II** (Chair: Andreas Namgalies)

11:30 – 12:30      **Matteo Gatti**  
***Tutorial** - Exciton band structure in two-dimensional materials*

12:30 – 13:00      **Katrin Siefermann**  
***Scientific** - Ultrafast photoemission electron microscopy in materials science*

13:00 – 14:00      Lunch Break

**Session III** (Chair: Paul Nikodemiak)

14:00 – 14:20      **Philipp Hofmann**  
***A8** - Synthesis of Novel Pentacene Derivatives and Cyclooctynes for the Study of Internal Interfaces*

14:20 – 14:40      **Josua Pecher**  
***A6** - Using computational chemistry to predict the elementary steps of growing organic/silicon interfaces*

**Tuesday, January 17<sup>th</sup>, 2017**

- 14:40 – 15:00      **Eike Dornsiepen**  
*A9 - Functional Binary and Ternary Organotin Sulfide Clusters*
- 15:00 – 15:20      **Eduard Baal**  
*A7 - Design of model systems for the investigation of inter- and intramolecular charge transfer processes*
- 15:20 – 15:40      Coffee Break
- Session IV** (Chair: Andre Rinn)
- 15:40 – 16:00      **Maria Weseloh**  
*B7 - Interface-Dominated Semiconductor Laser Structures*
- 16:00 – 16:20      **Katharina Gries**  
*A5 - TEM analysis of buried interfaces in inorganic and organic heterostructures*
- 16:20 – 16:40      **Sebastian Gies**  
*B1 - Optical Spectroscopy of Type-II Excitons in (Ga,In)As/GaAs/Ga(As,Sb) Heterostructures*
- 16:40 – 17:00      **Jonas Zimmermann**  
*B5 - Second-harmonic imaging microscopy: a newly developed experimental setup for time-resolved studies on 2-dimensional heterostructures*
- 17:00 – 17:20      **Osmo Vänskä**  
*B4 - Dynamics of charge-transfer excitons*
- 18:00 – 19:00      Dinner
- 19:30                Get-Together

Wednesday, January 18<sup>th</sup>, 2017

07:30 – 08:30 Breakfast and Check Out

**Session V** (Chair: Sebastian Thussing)

09:00 – 10:00 **Christian Papp**  
***Tutorial** - In-situ Studies of the Reactivity of Model Catalysts: Surface Chemistry from flat surfaces to nanoparticles*

10:00 – 10:30 **Matteo Gatti**  
***Scientific** - Exciton band structure in two-dimensional materials*

10:30 – 11:00 Coffee Break

**Session VI** (Chair: Christian Länger)

11:00 – 12:00 **Ellen Backus**  
***Tutorial** - Towards understanding the mechanism of water splitting on TiO<sub>2</sub>*

12:00 – 12:30 **Alexey Chernikov**  
***Scientific** – Exciton physics of semiconducting 2D materials*

12:30 – 13:30 Lunch

**Session VII** (Chair: Marcel Reutzel)

13:30 – 14:00 **Christian Papp**  
***Scientific** - In-situ Studies of the Reactivity of Model Catalysts: Surface Chemistry from flat surfaces to nanoparticles*

14:00 – 14:30 **Ellen Backus**  
***Scientific** - Towards understanding the mechanism of water splitting on TiO<sub>2</sub>*

14:30 – 14:50 **Henning Döscher**  
***A1** - GaP-interlayer formation on epitaxial GaAs(100) surfaces in MOVPE ambient*

Wednesday, January 18<sup>th</sup>, 2017



- 14:50 – 15:10      **Christian Lammers**  
*B3 - The rise and fall of charge transfer excitons - coherent and incoherent dynamics*
- 15:10 – 15:30      **Andrea Karthäuser**  
*A2 - Unexpected Interface Dewetting of “Stable” DNTT Thin Films*
- 15:30 – 15:50      **Malte Zugermeier**  
*A4- From Metal-Organic Interfaces Towards More Complex Interphase Systems*
- 15:50 – 16:10      Coffee

**Session VIII** (Chair: Andreas Beyer)

- 16:10 – 16:30      **Markus Franke**  
*A12- Adsorption height determination of molecular layers on crystalline substrates using the Normal Incidence X-ray Standing Waves Technique*
- 16:30 – 16:50      **Sebastian Flade**  
*A3- Ultrathin organic films on surfaces*
- 16:50 – 17:10      **Anna-Katharina Hansmann**  
*B8 - Quantum chemistry for molecular vibrational and electronic transitions at organic interfaces*
- 17:10 – 17:30      **Alexander Lerch**  
*B6 - Probing interface mediated charge transfer on metal/organic systems via two-photon photoemission*
- 17:30 – 17:50      **Andre Rinn**  
*B2 - Dynamics of inter- and intramolecular charge transfer*
- 18:00                  Departure





# Exciton physics of semiconducting 2D materials

Alexey Chernikov

<sup>1</sup> *Department of Physics, University of Regensburg, Germany*

Since the discovery of graphene, a single sheet of carbon atoms, research focused on two-dimensional (2D) van der Waals materials evolved rapidly due the availability of atomically thin, thermally stable crystals with intriguing physical properties. The 2D materials naturally inherit major traits associated with systems of reduced dimensionality: strongly enhanced interactions, efficient light-matter coupling, and sensitivity to the environment. In particular, the considerable strength of the Coulomb forces, i.e., electrical attraction and repulsion between the charge carriers, introduces a rich variety of many-body phenomena. It leads to the emergence of atom-like electron-hole quasi-particles, such as excitons, trions, and biexcitons, with unusually high binding energies and efficient light absorption.

In this talk, I will focus on the physics of excitons in atomically-thin semiconducting transition-metal dichalcogenides (TMDCs), largely determining the optical response of these ultra-thin layers. The observation of exciton binding energies on the order of many 100's of meV and the marked deviation of the electron-hole attraction from the conventional Coulomb law will be discussed. The results reflect both strong carrier confinement and the distinctive nature of the dielectric screening in atomically thin systems. I will further describe how the Coulomb effects in TMDCs can be externally tuned either by electrical and optical injection of charge carriers or through the engineering of the dielectric environment in heterostructures.

# Ultrafast photoemission electron microscopy in materials science

Andreas Neff<sup>1</sup>, Falk Niefind<sup>1</sup>, Katrin R. Siefermann<sup>1</sup>

<sup>1</sup> *Leibniz Institute of Surface Modification (IOM), Leipzig, Germany*

Numerous technical applications are based on the interaction of functional materials with light: sensors, photovoltaics, photocatalysts etc. Many of these functional materials are complex. In particular, they are not homogeneous on the nanoscale. For example, they comprise a mix of crystalline and amorphous domains, or a mix of organic and inorganic materials (nanocomposites). Because of this complexity, it is not well understood how the exact nanoscale structure correlates with (photo)-physical properties of such functional materials. Understanding this correlation is crucial for rational design and optimized performance of the materials, but remains a major challenge for experiment and theory.

We address this challenge with a novel microscopic approach in which we combine a femtosecond laser system with a photoemission-electron microscope (PEEM) (Figure 1). In my talk I will present how this microscopic approach allows us to image morphology of organic semiconductor films with a lateral resolution of  $< 100$  nm. The images reveal amorphous and crystalline domains of the sample, as well as the orientation of polymer chains in crystalline domains. A clear dependence of the nanoscale morphology on the processing of the organic semiconductor film is observable and correlates with device performance.

In addition, performing PEEM experiments with femtosecond laser pulses enables us to image ultrafast photo induced dynamics. The results are “real-time movies” of excited state dynamics - currently with a lateral resolution of 100 nm and a temporal resolution of 150 fs. In experiments on P3HT (Poly(3-hexylthiophen-2,5-diyl)) films we find that the lifetime of photoexcited states depends on the degree of order of polymer chains. Accordingly, we detect different lifetimes for amorphous and crystalline domains on the sample. These findings are consistent with a model which assumes different concentrations of trap states for crystalline and amorphous domains.

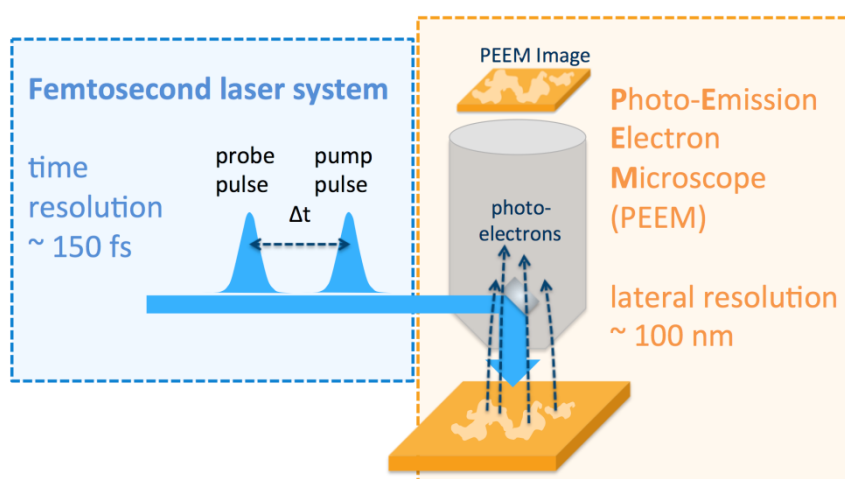


Fig. 1 Femtosecond time resolved photoemission-electron microscopy (fs-PEEM).

# Exciton band structure in two-dimensional materials

**Matteo Gatti**

<sup>1</sup> *LSI, Ecole Polytechnique, CNRS, Palaiseau (France)*

<sup>2</sup> *European Theoretical Spectroscopy Facility (ETSF)*

<sup>3</sup> *Synchrotron SOLEIL, Gif-sur-Yvette (France)*

The response of materials to electromagnetic fields is determined by electronic excitations that are strongly influenced by electron-hole (e-h) interactions. The e-h attraction leads to the formation of excitons, which are a fundamental aspect in the functionality of many optoelectronic devices, as excitons can propagate in materials carrying excitation energy that can be transformed and exploited by different means.

Nowadays, the ab initio solution of Bethe-Salpeter equation (BSE) represents the state-of-the-art method to obtain spectra in excellent agreement with experiments in a large variety of materials, to perform accurate analysis, and to successfully predict experimental results [1].

In the first part of the presentation, I will introduce the main concepts of many-body Green's function theory, the GW approximation and the BSE. In the second part, I will discuss the use of the BSE to study exciton band structures of 2D materials [2].

[1] R. M. Martin, L. Reining, D. M. Ceperley, *Interacting Electrons: Theory and Computational Approaches* (Cambridge University Press 2016)

[2] P. Cudazzo, L. Sponza, Ch. Giorgetti, L. Reining, F. Sottile, and M. Gatti, “Exciton band structure in two-dimensional materials”, *Phys. Rev. Lett.* **116**, 066803 (2016).

# Synthesis of Novel Pentacene Derivatives and Cyclooctynes for the Study of Internal Interfaces

**P. Hofmann<sup>1</sup>, P. Nikodemiak<sup>1</sup>**

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SFB-Project A8

Semiconductor /organic internal interfaces are an important issue for different applications such as OPVs.<sup>[1]</sup> To obtain a detailed understanding of the structure and dynamics at internal interfaces two different systems were investigated: Substituted Pentacenes (**A**) and cyclooctyne derivatives as precursors for film preparation of a well-defined thickness (**B**).

The performance of pentacenes and *N*-heteroacenes in thin-film devices is determined by their solid-state packing motifs which can be influenced by introducing a permanent dipole moment.<sup>[2]</sup> We report the synthetic progress towards self-complementary compounds, comprising electron-rich and electron-poor moieties such as **1** and **2** and of *N*-heteroacenes (like **3**) with exceptionally high *N*-content which are potential n-type semiconducting materials.<sup>[3]</sup>

Structurally well-defined interfaces are accessible via a layer-by-layer approach using compounds with different functionalities. Suitable building blocks for a layer construction are the cyclooctynes (**4** and **5**) as well as the linker molecule **6**.<sup>[4, 5]</sup>

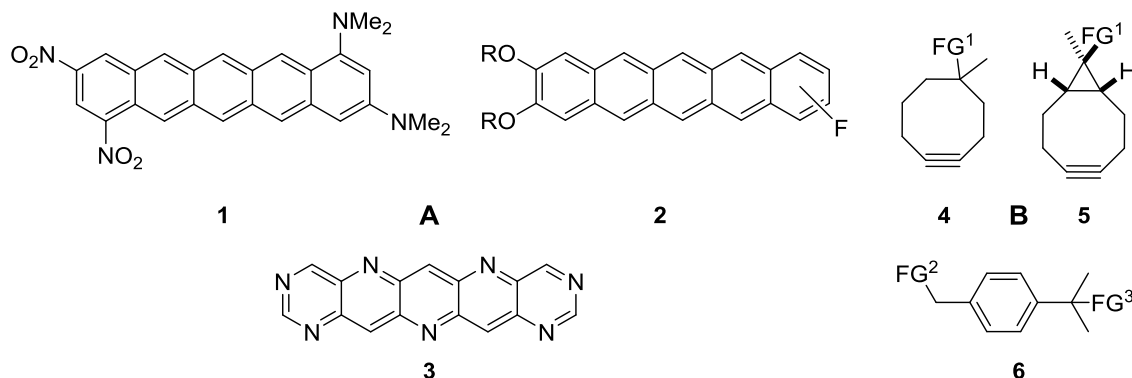


Fig. 1: Substituted pentacenes and cyclooctyne derivatives.

[1] R. Zhou, M. P. Srinivasan, *J. Colloid. Interf. Sci.* **2013**, 392, 158-166.

[2] J. Schwaben, N. Münster, M. Klues, T. Breuer, P. Hofmann, K. Harms, G. Witte, U. Koert, *Chem. Eur. J.* **2015**, 21, 13758.

[3] M. Winkler, K. N. Houk, *J. Am. Chem. Soc.* **2007**, 129, 1805-1815.

[4] M. Reutzel, N. Münster, M. Lipponer, C. Länger, U. Koert, M. Dürr, *J. Phys. Chem. C* **2016**, 120, 26284.

[5] N. Münster, P. Nikodemiak, U. Koert, *Org. Lett.* **2016**, 18, 4296-4299.

# Using computational chemistry to predict the elementary steps of growing organic/silicon interfaces

**Josua Pecher, Ralf Tonner**

*Department of Chemistry, Philipps-Universität Marburg, Germany  
SFB-Project A6*

The creation of organic/semiconductor interfaces is important in extending the application range of semiconductors and in the development of new materials and devices. A possible approach for this is represented by the following four elementary steps: (1) Adsorption of single molecules on the bare silicon surface, (2) growth of an ordered monolayer, (3) covalent attachment of the second layer and (4) properties of the interface. Cyclooctyne is a promising candidate for this approach, as it has been shown to bind strongly to the Si(001) surface and form dense and ordered structures.<sup>[1]</sup> Since covalent attachment of a second layer is only possible if another functional group is present, the adsorption behaviour of bifunctional cyclooctynes has to be investigated. Experimental studies have shown an ether derivative to bind chemoselectively to the surface,<sup>[2]</sup> while other derivatives, e.g. with an alkyne side group, might allow for easily performable click chemistry reactions in the third step. We calculated the adsorption dynamics and reactivity of cyclooctyne<sup>[3]</sup> and two derivatives using density functional theory in order to be able to understand and predict how selectivity is influenced by the presence of certain side groups. Furthermore, computational studies on steps 2 to 4 yield important insights into the origins of experimentally observed behavior and the transferability of chemical and physical concepts onto the complex field of interface growth.<sup>[4]</sup>

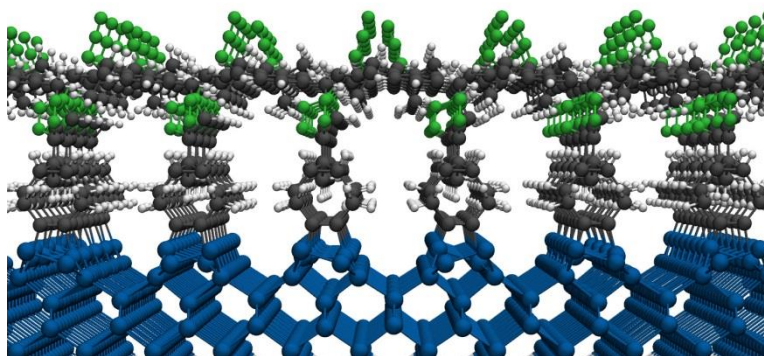


Fig. 1 Exemplary structure of a possible organic/silicon interface grown using a cyclooctyne derivative.

[1] G. Mette, M. Dürr, R. Bartholomäus, U. Koert, U. Höfer, *Chem. Phys. Lett.* **2013**, 556, 70.

[2] M. Reutzel, N. Münster, M. A. Lipponer, C. Länger, U. Höfer, U. Koert, M. Dürr, *J. Phys. Chem. C* **2016**, 120, 26284.

[3] J. Pecher, R. Tonner, *submitted*.

[4] J. Pecher, S. Schmidt, R. Tonner, *in preparation*.

# Functional Binary and Ternary Organotin Sulfide Clusters

Eike Dornsiepen, Eugenie Geringer, Niklas Rinn and Stefanie Dehnen

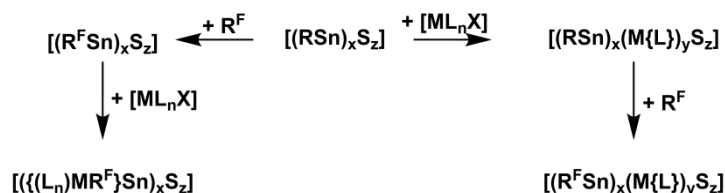
Department of Chemistry, Philipps-Universität Marburg, Germany

SFB-Project A9

The last few decades have afforded a large variety of tetrelchalcogenide clusters featuring organic ligands.<sup>[1]</sup> These can be assembled as core-shell-shell clusters with an inorganic core based on a semiconductor-derived composition, surrounded by an organic ligand sphere, which itself is the basis for a second shell comprising transition metal complexes. For this project, clusters featuring chelating ligands have been prepared, which can capture transition metal ions. Another approach consists in the attachment of metallocenes to the clusters and the investigation of their electrochemical properties.<sup>[2]</sup>

The reaction of functional binary clusters with hetero- and polyaromatic systems of complementary reactivity has resulted in a series of new clusters that potentially enable deposition on surfaces or carbon nanotubes.<sup>[3]</sup>

Another route addresses reactions of binary organotin chalcogenide clusters with coinage metal complexes to access ternary clusters that allow for fine tuning of the physical properties of the inorganic core. In this fashion, a variety of ternary clusters showing unprecedented structural motifs has been prepared whose optoelectronic properties are currently under investigation.<sup>[4]</sup>



Scheme 1: Access to binary and ternary organotin sulfide clusters with functional organic ligands (R = organic moiety, R<sup>F</sup> = functional organic ligand, M = transition metal, L = ligand, X = anion).

- [1] a) H. Berwe, A. Haas, *Chem. Ber.* **1987**, 120, 1175-1182; b) L. Nicole, C. Laberty-Robert, L. Rozes, C. Sanchez, *Nanoscale* **2014**, 6, 6267-6292; c) Z. Hassanzadeh Fard, C. Müller, T. Harmening, R. Pöttgen, S. Dehnen, *Angew. Chem.* **2009**, 121, 4507-4511; d) J. P. Eußner, B. E. K. Barth, E. Leusmann, Z. You, N. Rinn, S. Dehnen, *Chem. Eur. J.* **2013**, 19, 13792, 13802.
- [2] E. Leusmann, M. Wagner, N. W. Rosemann, S. Chatterjee, S. Dehnen, *Inorg Chem.* **2014**, 53, 4228-4233.
- [3] E. Leusmann, F. Schneck, S. Dehnen, *Organometallics* **2015**, 34, 3264-327.
- [4] J. P. Eußner, S. Dehnen, *Chem. Commun.* **2014**, 50, 11385-11388.

# Design of model systems for the investigation of inter- and intramolecular charge transfer processes

**Eduard Baal<sup>1</sup>, Malcolm Bartlett<sup>1</sup>, Robin C. Döring<sup>2</sup>, Michael Kothe<sup>3</sup>, Gregor Witte<sup>3</sup>, Sangam Chatterjee<sup>2</sup>, Jörg Sundermeyer<sup>1</sup>**

<sup>1</sup> Department of Chemistry, Philipps-Universität Marburg, Germany, SFB Project A7

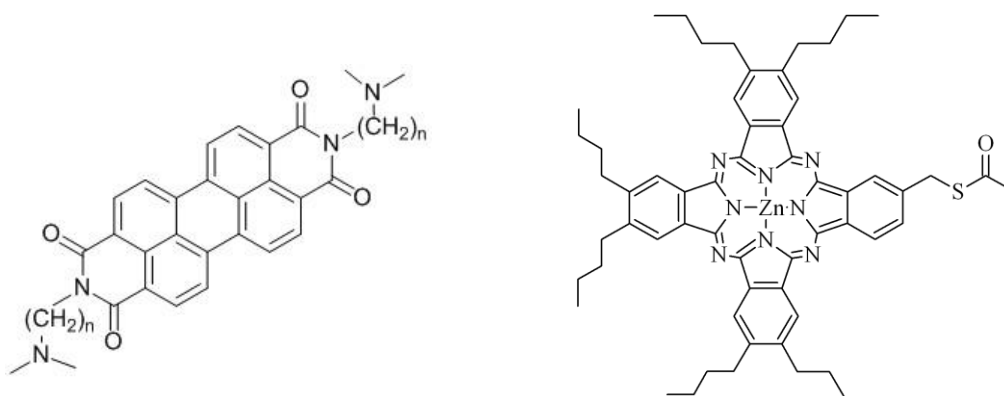
<sup>2</sup> Department of Physics, Philipps-Universität Marburg, Germany, SFB Project B2

<sup>3</sup> Department of Physics, Philipps-Universität Marburg, Germany, SFB Project A2

Project A7 is focusing on the design of new model compounds for the investigation of inter- and intramolecular charge transfer processes. Such new compounds are mainly obtained by the tailoring of their electronic properties and the introduction of new anchoring moieties. In this talk, two molecule classes are presented.

Perylene dihydrazides (PDH), a new class of donor-acceptor perylene diimides, was synthesized and fully characterized. The incorporation of an extremely short spacer unit and additional alkyl chains of varying lengths between the donor and the acceptor allowed us a systematical investigation of the intramolecular charge transfer across internal interfaces. Protonation and methylation of PDHs provided us with a second control path of intramolecular processes.

A novel unsymmetrical zinc phthalocyanine (Pc) possessing a single thioacetyl group has been synthesized for the purpose of forming ordered monolayers on Au substrates. The ZnPc has been synthesized via a multi-step, convergent synthesis of different dinitrile precursors, and purification of the target complex was achieved using a combination of extraction and chromatographic techniques. The design of the complex allows for solubility in common, low boiling solvents without significantly hindering packing effects and for orientational flexibility of the molecules once attached to the Au substrate.



**Fig. 1.** Chemical structures of the investigated series of perylene imides (left) and a novel unsymmetrical Pc bearing a thioacetyl group.

# Interface-Dominated Semiconductor Laser Structures

**Christian Berger, Maria J. Weseloh**

*Department of Physics, Philipps-Universität Marburg, Germany  
SFB-Project B7*

Laser emitting at long wavelengths are needed in different areas of application, for example in telecommunication. Unfortunately, laser systems operating at these wavelengths suffer from significant Auger-losses.

Auger-losses can to a great extent be reduced by employing a W-Laser design. For this purpose, two wide band-gap semiconductor materials are combined. The recombination occurs across internal interfaces, since electrons and holes are confined in spatially separated layers.

In this project, we microscopically design W-Laser heterostructures and predict their luminescence and gain properties. We analyze the laser optical properties for different characteristic features of the internal interface between the heterostructure layers. Furthermore, by comparison of our calculations with the experimentally measured optical properties, we determine the design of experimentally grown laser heterostructures with high accuracy.

In the new funding period, it is also planned to develop and apply a microscopic simulation for the short-pulse generation of W-Lasers in mode-locking configurations. For this purpose, VECSELs with W-arrangement of the quantum-well will be used together with the appropriate SESAMs.



# TEM analysis of buried interfaces in inorganic and organic heterostructures

Rocío Félix<sup>1</sup>, Han Han<sup>1</sup>, Katharina I. Gries<sup>1</sup>, Andreas Beyer<sup>1</sup>, Tobias Breuer<sup>1</sup>, Gregor Witte<sup>1</sup>,  
Wolfgang Stolz<sup>1</sup>, Kerstin Volz<sup>1</sup>

<sup>1</sup> *Department of Physics, Philipps-Universität Marburg, Germany  
SFB-Project A5*

For the investigation of heterostructures and buried interfaces therein transmission electron microscopy (TEM) is an extremely useful tool since it allows the analysis of structures at a local scale. Within the framework of project A5 two material classes were analyzed: inorganic as well as organic semiconductors.

Depending on the kind of material different TEM related techniques were applied:

- Z-contrast imaging in scanning TEM (STEM) mode permits the evaluation of an interface in inorganic semiconductors at atomic resolution. Comparison of experimentally obtained data with simulation provides information on the degree of composition intermixture in the interface region.

The inorganic heterostructures analyzed in project A5 are mainly GaP/Si and (Ga,In)P/GaAs. It was shown that the first system intrinsically exhibits a structured, pyramidal interface, which consists of “charge neutral” facets (Fig.1 a) and b)). The second one has an interface structure that strongly depends on the growth conditions (like temperature, GaP-rich interlayers and growth interruption times).

- Since organic semiconductors can be very electron beam sensitive, fast TEM techniques are required to receive the desired data. Electron diffraction, which fulfills this requirement, can be used to achieve quick information on the crystallographic structure of samples on a very small scale.

As organic semiconducting materials the molecules pentacene (PEN) and perfluoro-pentacene (PFP) were selected and grown pure or as a mixture on different substrates like graphene (Fig. 1 c)), SiO<sub>2</sub> and KCl. Via electron diffraction the relative orientation between organic layers and substrate as well as between the organic compounds itself were evaluated.

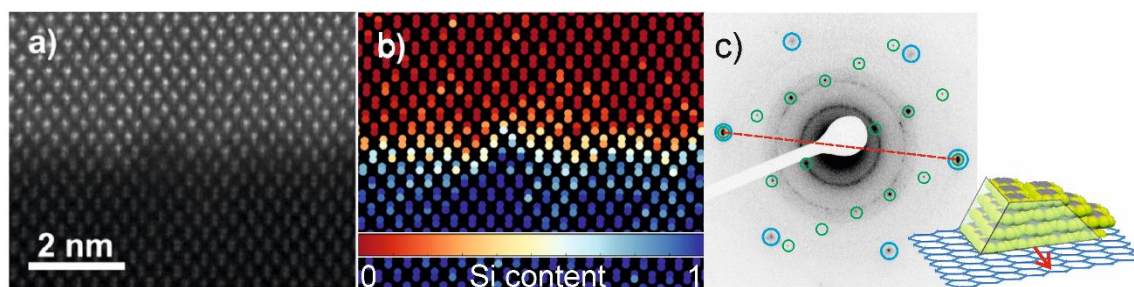


Fig. 1 a) and b) STEM Z-contrast image of a GaP/Si interface and its quantitative evaluation of the Si content [1]. c)

Electron diffraction pattern of PFP (green) on graphene (blue). The inset shows the orientation of a PFP island on graphene [2].

[1] A. Beyer et al., Chem. Mater. **28**, 3265-3275 (2016)

[2] R. Félix et al., Cryst. Growth Des., accepted (2016), <http://dx.doi.org/10.1021/acs.cgd.6b01117>

# Optical Spectroscopy of Type-II Excitons in (Ga,In)As/GaAs/Ga(As,Sb) Heterostructures

**Sebastian Gies<sup>1</sup>, Benjamin Holz<sup>1</sup>, Maria J. Weseloh<sup>1</sup>, Christian Fuchs<sup>1</sup>, Wolfgang Stolz<sup>1</sup>, Jörg Hader<sup>2,3</sup>, Jerome V. Moloney<sup>2,3</sup>, Stephan W. Koch<sup>1</sup>, and Wolfram Heimbrodt<sup>1</sup>**

<sup>1</sup> *Department of Physics and Material Sciences Center, Philipps-Universität Marburg, Germany, SFB-Project B1,A1,B4*

<sup>2</sup> *Nonlinear Control Strategies Inc, 7040 N. Montecatina Dr., Tucson, AZ 85704, USA*

<sup>3</sup> *College of Optical Sciences, University of Arizona, Tucson, AZ 85721, USA*

We investigated a series of (Ga,In)As/GaAs/Ga(As,Sb) type-II multi-quantum well heterostructures (MQWH) by experimental and theoretical (project B4(SW Koch/Kira)) means. The samples were grown by project A1(Stolz) using metal-organic vapor-phase epitaxy and consist of a (Ga,In)As-QW confining the electrons and a Ga(As,Sb)-QW (hole confinement) to form a type-II structure. The charge-carrier confining well are separated by an internal GaAs layer of varying thickness between  $d = 0$  nm and 4.8 nm.

The investigation was done using cw- and time-resolved (TR) photoluminescence spectroscopy (PL) at temperatures between 10 K and RT as well as power-dependent PL. At RT one can clearly see the type-II PL as the lowest transition and the type-I Ga(As,Sb) at slightly higher energies (see figure 1). The temperature-dependent PL reveals an interesting behavior. With decreasing temperature the Ga(As,Sb) transition vanishes and the (Ga,In)As PL appears. This can be understood considering the following. At low temperatures, the phonon-assisted hole tunneling (which is slower than the electron tunneling) cannot take place efficiently and the (Ga,In)As-QW is visible. With increasing temperature the hole tunneling becomes better and the (Ga,In)As emission vanishes. At the same time the Ga(As,Sb) CB is thermally populated and the Ga(As,Sb) emission occurs. Furthermore, by conjunction of experiment and theory, it was possible to determine the hetero-offset of the GaAs/Ga(As,Sb)-interface (5.5%) with very high precision, and it was found that the (Ga,In)As-CB edge and the Ga(As,Sb)-VB edge increase their energetic separation with decreasing temperature. Furthermore, the time-resolved measurements revealed a mono-exponential decay of the type-II luminescence for  $T > 70$  K. Below this the relaxation processes in the QWs and the hole-tunneling play an important role. A triple-exponential decay behavior was found. After an initial, fast decay the type-II PL is fed and increases before the type-II decay with lifetimes of approx. 70 ns takes place.

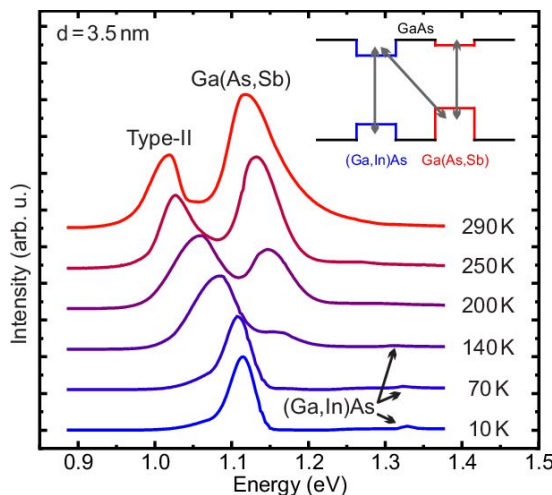


Fig. 1: Temperature-dependent PL spectra of the sample with  $d = 3.5$  nm normalized to the type-II emission. The band edges of the MQWH are given in the top right corner.

# Second-harmonic imaging microscopy: a newly developed experimental setup for time-resolved studies on 2-dimensional heterostructures

**Jonas Zimmermann, Gerson Mette, Ulrich Höfer**

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Van-der-Waals coupled 2D materials span the whole range from metallic over semiconducting up to isolating materials and their combination leads to fascinating opportunities for designing stacked heterostructures. The huge variety of possibilities calls for experimental methods which can effectively probe the structure as well as the electron dynamics of these heterostructures.

Here, we present first results of our new experimental setup for time-resolved studies on interfaces between 2D heterostructures. Our SHG microscopy technique allows us to quantify the crystal structure via polarization dependent measurements and gives us access to the electron dynamics via time-resolved pump-probe measurements. We demonstrate the capabilities of our setup with measurements done on CVD grown  $\text{MoS}_2/\text{WS}_2$  flakes. The spatial resolution of the experiment is diffraction limited to about  $2\mu\text{m}$ . The relative orientation of several crystal domains can be determined with an error of a few degrees. Because the setup is designed to exclude any dispersion afflicted components, high temporal resolution by the use of ultra-short laser pulses in a pump-probe measurement is achieved. This combination of high temporal and spatial resolution can be applied to 2D heterostructures to study the effects of relative crystal orientation on time-dependent charge transfer processes between different materials.

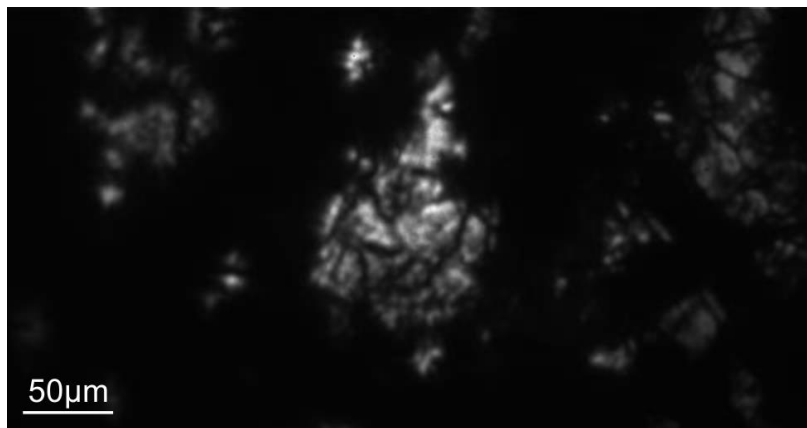


Fig. 1 SHG microscopy image of a CVD grown  $\text{WS}_2$  flake. Clearly visible are the domain boundaries between different crystal orientations.

# Dynamics of charge-transfer excitons

**O. Vänskä<sup>1</sup>, M. P. Ljungberg<sup>1,2</sup>, P. Springer<sup>1</sup>, M. Weseloh<sup>1</sup>, P. Koval<sup>2</sup>,  
D. Sánchez-Portal<sup>2,3</sup>, S. W. Koch<sup>1</sup>, M. Kira<sup>1,4</sup>**

<sup>1</sup> *Department of Physics and Material Sciences Center,*

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*B4/GP1*

A charge-transfer exciton (CTX) is a bound electron-hole pair where the electron and hole reside on the opposite sides of an internal interface of a system. The operational principles of many devices, like solar cells, have been found to be dependent on the properties of CTXs. Although CTXs have been intensively studied, many of their features are poorly known.

In our work, we use microscopic modelling for the dynamics of charge-transfer states in inorganic semiconductor heterostructures as well as at organic-inorganic interfaces. In particular, we study the optical absorption, photoluminescence and THz response. Additionally, we investigate possibilities of coherent-control schemes of selective quasiparticles transport through internal interfaces and model formation of CTXs.

To describe the dynamics of CTXs in complex system, like at the organic-inorganic interfaces, we present a hybrid cluster-expansion and density-functional-theory approach [1]. We use this approach to model absorption in bulk TiO<sub>2</sub> [1]. As a model organic-inorganic interface, we use a monolayer of pentacene on top of TiO<sub>2</sub>. We find [2] that this system has a highly polarization-dependent absorption spectrum that originates from charge-transfer states.

In inorganic structures, we demonstrate a coherent-control scheme for a transport of either correlated or uncorrelated electrons through interface [3]. The respective transport protocols are highly efficient and selective. On this basis, we introduce an additional transport protocol where only correlations are transported between neighboring quantum wells.

[1] O. Vänskä, M. P. Ljungberg, P. Springer, D. Sánchez-Portal, M. Kira, and S. W. Koch, *J. Opt. Soc. Am. B* 33, C123 (2016).

[2] M. P. Ljungberg, O. Vänskä, P. Koval, S. W. Koch, M. Kira, and D. Sánchez-Portal, arXiv:1610.01789 (2016).

[3] O. Vänskä, I. Tittonen, S. W. Koch, and M. Kira, *Phys. Rev. Lett.* 114, 116802 (2015).

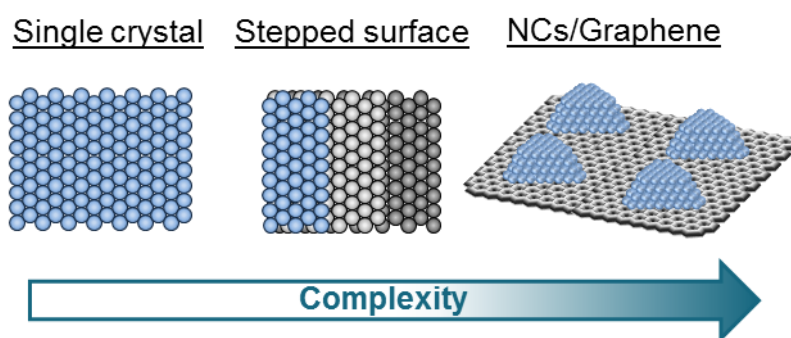
# In-situ Studies of the Reactivity of Model Catalysts: Surface Chemistry from flat surfaces to nanoparticles

Christian Papp

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The increasing complexity from surface science to real catalysis leads to the “materials gap”. To close this gap, studies of adsorption and reaction experiments on graphene-supported nanoparticles under *in situ* conditions were conducted with the particular aim to point out similarities and differences of results from “traditional” single crystal studies and the more complex, more realistic nanoparticles. It is shown that the use of a quantitative spectroscopy allows for gaining a detailed insight even to these complex systems, thereby facilitating a further step into bridging the materials gap from fundamental science to applied sciences. The use of graphene as a substrate gives intriguing new possibilities, as the template effect of graphene can lead to a very narrow size distribution, while graphene itself is chemically innocent, thereby making side processes such as spill over and reverse spill over less likely.

The systems discussed range from extremely well studied systems such as the adsorption and reaction of CO on a Pt(111) surface, going to stepped surfaces and finally to nanocluster arrays supported on a graphene support. Also the important chemistry of sulphur, being a strong catalyst poison, on such systems will be discussed. While the adsorption behavior on nanoclusters is strongly reminiscent of the adsorption on stepped surfaces, a strong increase in the reactivity of nanoparticles systems is found.



The figure illustrates the increasing complexity of different model systems.

1. K. Gotterbarm, F. Späth, U. Bauer, C. Bronnbauer, H.-P. Steinrück, C. Papp, ACS Catalysis, 5 (2015) 2397
2. K. Gotterbarm, F. Späth, U. Bauer, H.-P. Steinrück, C. Papp, Topics in Catalysis, 58 (2015) 573.

# Towards understanding the mechanism of water splitting on TiO<sub>2</sub>

Saman Hosseinpour, Simon J. Schlegel, Shumei Sun, Ellen H.G. Backus

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Finding a clean and renewable energy source to replace fossil fuels has attracted much attention, the past few decades, as a requirement for the sustainable development of societies. Direct hydrogen generation on TiO<sub>2</sub> by photocatalytic dissociation of water using sunlight was already proposed more than 40 years ago. However, despite extensive work in this area, the fundamentals of the process remain ill-understood, mainly due to the lack of a proper tool to specifically explore the interface between water and TiO<sub>2</sub>. Sum frequency generation spectroscopy (SFG), is an inherently surface sensitive tool, allowing the study of the water-TiO<sub>2</sub> interface. In a sum frequency generation process a visible and an infrared laser beam are combined at the interface and the vibrational spectrum of solely the molecules at the interface can be obtained. In this way we can specifically study the water molecules at the TiO<sub>2</sub> surface. As a first step in understanding the water splitting reaction, we studied the binding of water to the substrate. We present data on water in contact with various types of TiO<sub>2</sub> substrates. From the intensity and frequency of the SFG signal we extract information about the binding of water to the TiO<sub>2</sub>. Moreover, we show first time-resolved SFG data after excitation of the TiO<sub>2</sub> with an UV pump pulse which mimics the sun light. Preliminary data show that the surface charge changes on ultrafast timescales upon excitation resulting in reorientation of the water molecules. These UV-pump SFG-probe data illustrate the first steps towards following the photo-induced dissociation of water at the TiO<sub>2</sub> interface in real-time.

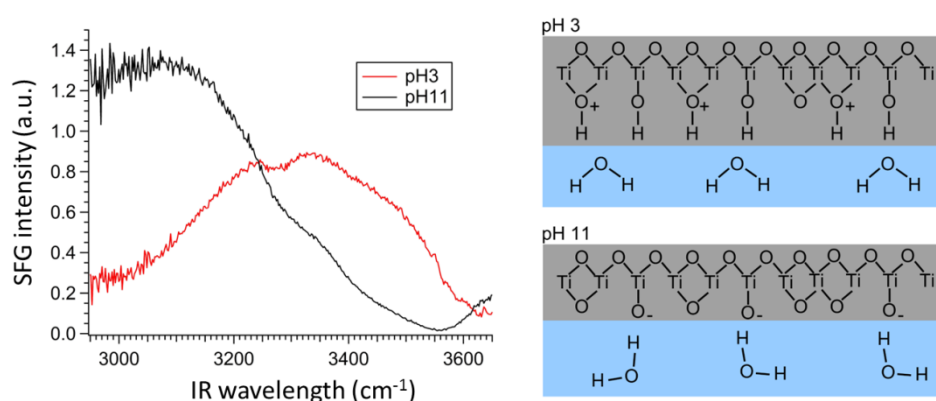


Fig. 1 SFG spectra of water at low and high pH in contact with amorphous TiO<sub>2</sub> (left) and sketches of the water structure at the interface at low and high pH (right).

# GaP-interlayer formation on epitaxial GaAs(100) surfaces in MOVPE ambient

**Henning Döscher<sup>1</sup>, Philip Hens<sup>1</sup>, Andreas Beyer<sup>1</sup>, Leander Tapfer<sup>2</sup>, Kerstin Volz<sup>1</sup>, and Wolfgang Stolz<sup>1</sup>**

<sup>1</sup> *Department of Physics & Materials Science Center, Philipps-Universität Marburg, Germany*

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*SFB-Project A1*

Thinnest gallium phosphide (GaP) layers embedded in GaAs-based epitaxial films may passivate surface states and surface recombination [1], act as effective diffusion barriers (for dopants etc.) protecting crucial layers integral to the function of complex device structures or may influence the interface formation in heterostructures. Ideal interlayers might consist of just a singular monolayer (ML) of the embedded material abruptly confined within the host matrix, but in practice these interlayers will smear out with the host material. This disorder is driven by a multitude of fundamental and practical factors limiting the sharpness of epitaxial III-V hetero-interfaces such as (a) roughness of the growth surface, (b) vertical extent of the present surface reconstruction, (c) finite exchange rate of process and precursor gases, (d) background ambient of the growth environment, and (e) thermal inter-diffusion. We investigate preparation strategies for different GaAs(100) surface reconstructions and their stability in MOVPE ambient with respect to the formation of sharp functional hetero interfaces and interlayers.

Periodical deposition of thinnest GaP-interlayers embedded in a GaAs matrix enabled effective layer thickness and the actual ternary composition analysis by high-resolution X-ray diffraction (HR-XRD) and scanning transmission electron microscopy (STEM). *In situ* reflection anisotropy spectroscopy (RAS) [2] monitored the GaAs surface reconstruction preceding the GaP interlayer deposition and provided important insight for sharper interface preparation strategies. In effect, we obtain ternary Ga(AsP) interlayers with peak concentrations way below unity P-content, extending over several ML instead. In particular, the c(4x4) GaAs standard growth surface terminates with two ML of As [3] usually maintained by an explicit overpressure in the gas phase at elevated temperature. Better preconditions to embed sharp interlayers of another group V species such as P might be obtained by a growth interruption also avoiding any group-V-stabilization. Our *in situ* results indicate that obtaining explicitly Ga-rich surface reconstructions requires thermal annealing at significantly higher temperature to induce the required removal of As from the surface. We also investigated an alternative preparation approach by a group III prepulse and observed the formation of Ga-rich surface reconstruction and its subsequent decay to a more As-rich configuration in absence of As precursor flow – indicating significant As<sub>4</sub> supply from the MOVPE ambient.

## References:

- [1] R. Beaudry et al., Journal of Applied Physics 87 (2000) 7838.
- [2] P. Weightman et al., Reports of Progress in Physics 68 (2005) 1251.
- [3] A. Ohtake, Surface Science Reports 63 (2008) 295.



# The rise and fall of charge transfer excitons - coherent and incoherent dynamics

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*SFB-Project B3*

Charge transport through semiconductor interfaces takes place on ultrashort timescales and affects the characteristics of transistors and optoelectronic devices, e.g. semiconductor lasers and LEDs. Therefore, further understanding of fundamental phenomena like the one of charge transfer excitons is desirable.

Here, we demonstrate the coherent as well as incoherent dynamics of spatially indirect charge transfer excitons in a type II multi double quantum wells by means of THz and four wave mixing spectroscopy over several orders of magnitude from femto- to nanoseconds.

Our THz measurements show the formation of charge transfer excitons on a timescale of hundreds of picoseconds after optical excitation and their recombination in several nanoseconds by probing resonant internal quantum transitions of excitons (1s-np), as Fig. 1 shows. These findings are complemented by four wave mixing in order to resolve the coherent dynamics of indirect excitons. In particular, quantum beats between direct and indirect excitonic resonances as well as dephasing dynamics are measured here.

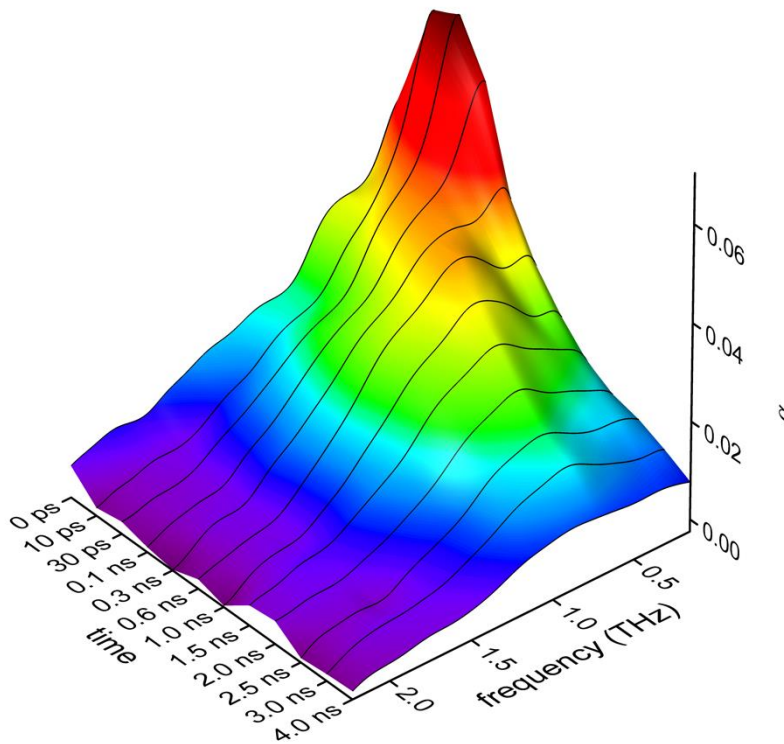


Fig. 1 THz absorption for various temporal delays after optical excitation. For early times, an unbound electron-hole plasma dominates the absorption dynamics. After 0.3 ns a distinct 1s-2p resonance at 0.7 THz marks the formation of charge transfer excitons. Later on, this signal decays due to radiative recombination.



# Unexpected Interface Dewetting of “Stable” DNTT Thin Films

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The internal interfaces in organic heterolayers are of key importance for several organic electronic applications. For example, these interfaces are decisive for the separation of excitons in photovoltaic devices. Furthermore, the interfaces between OSC films and inorganic substrates determine the injection barriers for charge carriers.

Well-defined model systems of both interface types are prepared and studied in project A2. These heterosystems are morphologically and structurally characterized by atomic force microscopy (AFM) and X-ray diffraction (XRD), followed by studies of their respective molecular orientation and chemical properties by XPS and NEXAFS.

In this subproject the structure of the novel high performance organic semiconductor dinaphthothienothiophene (DNTT,  $C_{22}H_{12}S_2$ ) is studied. DNTT is of great interest due to its high charge carrier mobility [1], which exceeds the values of the well-known system pentacene. Prototypical organic field effect transistors have in particular revealed a temporal stability of DNTT-based transistors [2]. However, observing the morphology of thin DNTT films over time, we monitored a dewetting of these films, also on device-relevant substrates. Depending on the film thickness, even a complete break of the DNTT films could be observed, which will strongly degrade the system's conductivity.

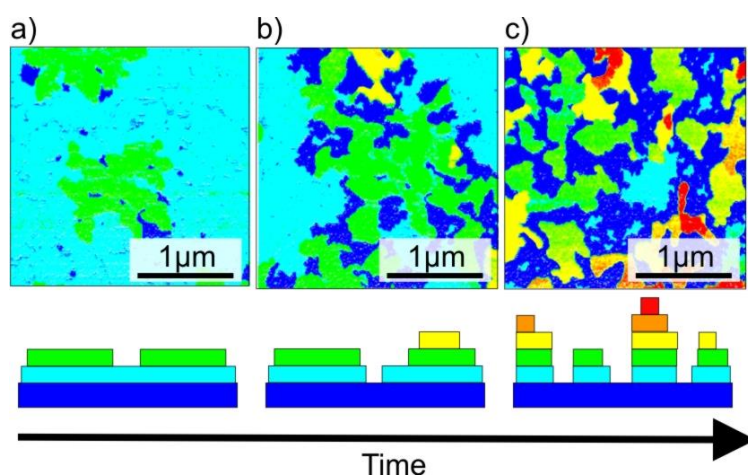


Fig. 1: AFM micrographs of a 2 nm thick DNTT thin-film on SiO<sub>2</sub> after (a) 10 min, (b) 2 h and (c) 15 h, showing a dewetting over time. Below: Corresponding height sketch.

[1] Yamamoto, T.; Takimiya, K. *J. Am. Chem. Soc.* **2007**, 129, 2224.

[2] Zschieschang, U.; Ante, F.; Kälbein, D.; Yamamoto, T.; Takimiya, K.; Kuwabara, H.; Ikeda, M.; Sekitani, T.; Someya, T.; Blochwitz-Nimoth, J.; Klauk, H. *Org. Electron.* **2013**, 14, 1516.

# From Metal-Organic Interfaces Towards More Complex Interphase Systems

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*SFB-Project A4*

Metal-organic interfaces are an important field in surface science and a highly topical system in organic electronics or catalytical applications, which gain more and more interest in our modern world. For years different organic model systems on metal single crystal surfaces were studied and a fundamental understanding of the processes inherent in the formation of these metal-organic interfaces and the reactions on these surfaces was established. However, many important properties of real-world devices are not sufficiently reflected by these idealized model systems. This “material gap” has to be addressed to make the knowledge gained from model systems useful for the improvement of real devices. We will show how this can be achieved by systemically moving from idealized models towards more complicated systems.

Surface functionalization for catalytical applications can be achieved with planar metal complexes. Oxidation state tuning is a possibility to increase the control over the chemical and electronic properties of these metal complexes. This is possible by the attachment of axial ligands on the metal center. However, to avoid competition between these ligands with the reactants for the axial coordination site, a more suitable solution is the modification of the planar ligand. In contrast to porphyrins, corroles on Ag(111) oxidize metal atoms to their +III state in a surface-confined coordination reaction. We studied monolayers and multilayers of an octa-alkyl corrole and their reaction with different d-block metals by XPS, UPS, NEXAFS and STM.

As an example for a more complex metal-organic interphase layer, the reaction of cobalt with bulk tetraphenylporphyrin will be discussed. Depth profiling of the chemical composition of this buried interface system was performed by means of Hard X-ray Photoelectron Spectroscopy. A genetic optimization routine revealed the concentration profile of the cobalt-tetraphenylporphyrin interphase layer.<sup>[1]</sup>

Furthermore, an overview of the arsenal of methods which are used in our group within the SFB 1083 will be given.

- [1] M. Chen, H. Zhou, B. P. Klein, M. Zugermeier, C. K. Krug, H.-J. Drescher, M. Gorgoi, M. Schmid and J. M. Gottfried, *Phys. Chem. Chem. Phys.* **2016**, DOI: 10.1039/C6CP05894A.

# Adsorption height determination of molecular layers on crystalline substrates using the Normal Incidence X-ray Standing Waves Technique

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SFB-Project A12*

One important aspect when investigating molecular layers or 2D materials on a substrate is the understanding of the interaction across the interface, i.e., between the adsorbate layer and the underlying substrate. From a structural point of view, the bonding distance is the most important parameter. Therefore, it is crucial to precisely determine the adsorption heights of the atomic species in the adsorbate layer on the substrate. The Normal Incident X-ray Standing Wave (NIXSW) technique is maybe the only technique with sufficient precision ( $\Delta z < 0.05 \text{ \AA}$ ) to obtain these parameters. It is performed at a synchrotron radiation source and based on X-ray Photoelectron Spectroscopy (XPS) making it chemically sensitive. It therefore allows to determine the adsorption heights of all atomic species that can be distinguish in XPS core level spectra.

We will introduce the NIXSW technique and show a number of typical examples that are relevant for the research field of the SFB 1083.

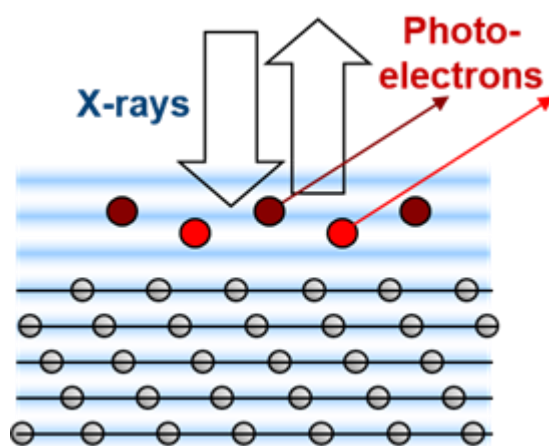


Fig. 1 Principle of the NIXSW technique.

# Ultrathin organic films on surfaces

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*SFB-Project A3*

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Fourier Transform Infrared Reflection Absorption Spectroscopy (FT-IRAS) is a versatile method helping us to characterize ultrathin molecular layers on surfaces and thereby obtain a thorough understanding of its properties. Specifically, we are able to trace structural phase transformations induced by thermal annealing as well as by changing the coverage or thickness of the grown films. Organic molecules display characteristic vibrational modes which allow an easy discrimination and tracking of individual organic molecular species within heterostructures. Molecular desorption and temperature induced dissociation processes are monitored using Temperature Programmed Desorption (TPD). Spot Profile Analysis Low-Energy Electron Diffraction (SPA-LEED) measurements provide information regarding the long range order of the topmost adsorbate layers.

Using these methods we investigate heterolayer structures consisting of various phthalocyanine complexes (CuPc, TiOPc, SnPc), PTCDA, pentacene and fullerenes, grown on Ag(111) and Graphene/Ru(0001) substrates. The combination of the aforementioned methods provides us a comprehensive picture of various phenomena such as thermal stability, structural properties (molecular orientation), interlayer exchange within heterostructures and interfacial dynamical charge transfer.

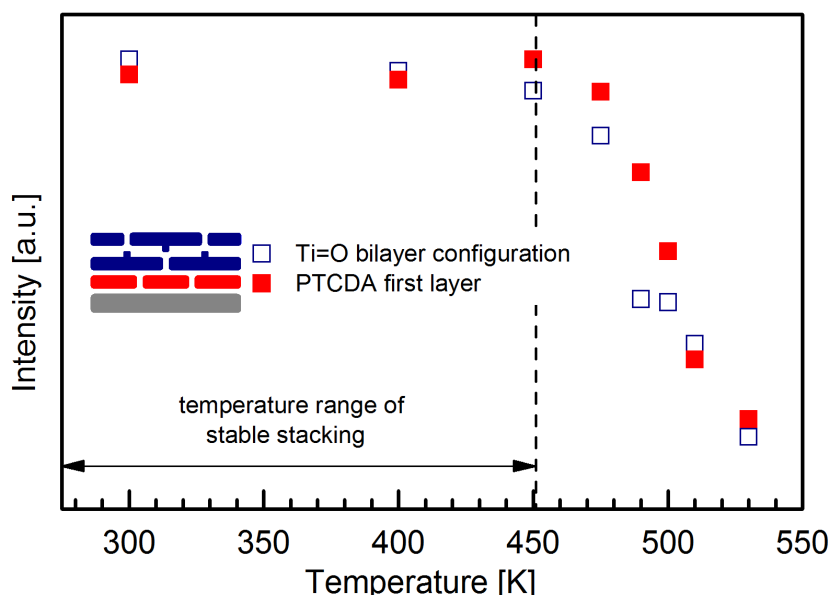


Fig. 1 Thermal evolution of the stacked TiOPc bilayer, grown on top of PTCDA/Ag(111). The intensities of the characteristic vibrational modes of (i) the PTCDA monolayer and (ii) the TiOPc bilayer are plotted as a function of annealing temperature.

# Quantum chemistry for molecular vibrational and electronic transitions at organic interfaces

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The ultimate goal of this project is to obtain a detailed understanding of vibronically excited states of organic molecules at internal interfaces to identify general features and major processes that determine the nature and behaviour of these states, with the long-term vision to use this insight subsequently to design internal interfaces with desired properties. An outline of the different steps to achieve that goal, which were considered until now is given in the following. As a first step, we focused on the model system of pentacene and its perfluoro derivative. A wealth of studies, both experimentally and theoretically, focused on these molecules with extended conjugated  $\pi$ -systems, especially on the non-fluorinated derivatives. That fact qualifies it to be an appropriate test system for the methodological protocol and compare our own calculations with experiments and previous theoretical investigation, due to the size of the system we were initially limited to DFT calculations. Calculations on a high computational level ( $G_0W_0$ , CC2) were first tested for a smaller test systems consisting of ethylene and perfluoro ethylene.

To obtain quick access to the important parameters for charge transfer and singlet fission processes, we decided to focus first on the description of the involved monomers. Important molecular parameters for the charge transfer are the singlet excitation energies of the involved monomers, as well as their ionization energy and electron affinity. The charge transfer gap can be used to estimate the likeliness of a direct charge transfer process. Important molecular parameters for the singlet fission are the singlet and triplet excitation energies of the involved monomers. It is well known that the whole process is favoured only if it is isoergic or only slightly exoergic.

To include the interaction between the molecules which are relevant for the charge transfer and singlet fission processes, dimers are considered as a minimal object to describe the charge transfer and singlet fission processes more accurately. Furthermore, the possibilities of different methods describing the surrounding crystal must be kept in mind.

Finally, first solid state calculations were started with periodic boundary conditions. Therefor we are again limited to DFT calculations. Additionally, dispersion corrections were included in the calculations. The unit cells of pentacene and perfluoropentacene, as well as a mixed unit cell containing both molecules were optimized in the  $\pi$ -stacked and the herringbone arrangement. The investigation and comparison of the band structure can give further insight to estimations of the electronic coupling between the monomers. Additionally, a supercell approach can be used to have a better model for the interface between pentacene and perfluoropentacene crystals.

# Probing interface mediated charge transfer on metal/organic systems via two-photon photoemission

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<sup>1</sup>*Department of Physics, Philipps-Universität Marburg, Germany*

<sup>2</sup>*Centro de Física de Materiales San Sebastian, Spain*

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The charge carrier transport across metal/organic and organic heterointerfaces was investigated by means of time-resolved two-photon photoemission (2PPE). We deposited thin layers of controlled thickness of titanylphthalocyanine (TiOPc), copper(II)phthalocyanine (CuPc) and perylene-3,4,9,10-tetracarboxylic dianhydride (PTCDA) on an Ag(111) substrate as well-defined model systems for organic semiconductor heterolayer interfaces. An optical parametric oscillator (OPO) provided tuneable pump pulses with photon energies ranging from 1.6 to 2.5 eV while at the same time the probe photon energy stays constant.

The Shockley-type interface states of a monolayer of PTCDA/Ag(111) and TiOPc/Ag(111), located 0.6 eV and 0.3 eV above the Fermi level, are usually populated from the metal and show little dependence on excitation energy. For the heterosystems CuPc/PTCDA/Ag(111) and PTCDA/TiOPc/Ag(111) we find a strong resonant enhancement at 1.8 eV and 2.3 eV, respectively. Time-resolved measurements show a delayed filling of the interface states on the time scale of 50 fs for CuPc/PTCDA and 200 fs for PTCDA/TiOPc under these conditions, before the population relaxes by electron-hole-pair decay into the metal. Comparison with a bilayer of pure PTCDA/Ag(111) and TiOPc/Ag(111) reveal that these resonances are the result of a HOMO-LUMO excitation in the second or third layer followed by a fast electron transfer to the interface state. Our results highlight that metal/organic interface states, located between Fermi level and LUMO, directly contribute to charge separation and transfer between metals and organic semiconductors.

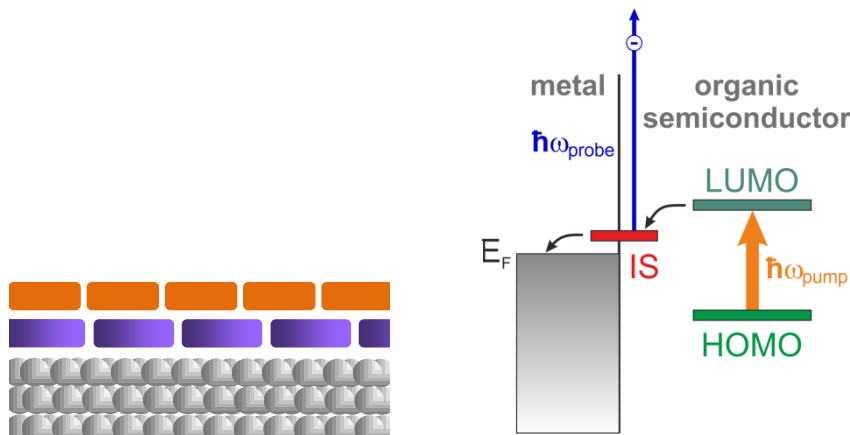


Fig. 1 Schematic illustration of a heterostructure (left) and selective excitation of the organic overlayer followed by charge transfer to the interface state and relaxation into the metal (right).

# Dynamics of inter- and intramolecular charge transfer

**Andre Rinn<sup>1</sup>, Robin C. Döring<sup>1</sup>, Eduard Baal<sup>2</sup>, Tobias Breuer<sup>3</sup>, Gregor Witte<sup>3</sup>, Jörg Sundermeyer<sup>2</sup>, Sangam Chatterjee<sup>1,4</sup>**

<sup>1</sup> Department of Physics, Philipps-Universität Marburg, Germany, Project B2

<sup>2</sup> Department of Chemistry, Philipps-Universität Marburg, Germany, Project A7

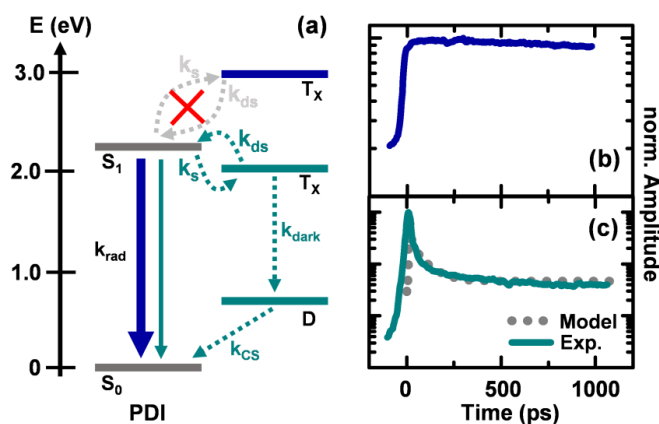
<sup>3</sup> Department of Physics, Philipps-Universität Marburg, Germany, A2

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Project B2 aims to investigate electronic excitations at internal interfaces using all-optical techniques. Most recently, the focus shifted to interfaces on the molecular scale. This includes two aspects: on the one hand, solid-state heterosystems of donor-acceptor molecules and on the other hand intra-molecular interfaces, where donor and acceptor groups are covalently linked in one single molecule. This talk presents a brief overview on this work stressing similarities and differences of the two model systems.

First, the molecular-scale internal interface in specially functionalized perylene diimides (PDIs) is discussed. These molecules consist of a perylene backbone and an attached donor group coupled by alkyl spacers. The length of the spacer is varied for different coupling strength between this molecular donor-acceptor pair. Figure 1 displays the influence of different spacer length on the time-resolved photoluminescence (TRPL) of the perylene core. The dynamics of the luminescence are governed by the potential landscape of singlet and triplet excitons and the resulting inter system crossing (ISC).

The second example deals with the impact of different crystalline packing motifs on the emission spectra and carrier dynamics of pentacene (PEN) and perfluoropentacene (PFP) heterostructures. Both materials can be grown in different packing motifs and molecular alignment by exploiting substrate-mediated templating effects. We compare the optical properties of pristine PEN and PFP thin films of different molecular alignment with their corresponding bilayer heterostructures and intermixed thin-films.



**Fig. 1:** Energy level diagram (a) and TRPL data of exemplary PDI derivatives with a donor group (b) and without a donor group (c) attached to the PDI core and donor group.





## Conference Venue Schloss Rauischholzhausen

Schloss Rauischholzhausen is considered the most attractive estate of Justus-Liebig-Universität Giessen. Conferences, workshops, seminars and festivities are held here on a regular basis. Due to its proximity to Marburg it is also frequently booked for events organized by Philipps-Universität Marburg.

**The property** was first mentioned in a charter book of the monastery of Fulda between 750 and 779 and was initially a fief of the Lords of Eppstein until the Archbishop of Mainz acquired it completely in 1369. From then on the vassals called themselves Lords Rau of Holzhausen, one of the knights on the eastern bank of the Rhine.

The last member of the Rau family served as an officer in the Hessian army. When Hesse-Kassel became part of Prussia he refused to join the Prussian army and sold all his property to the ambassador's delegate, Stumm.



The new owner, Ferdinand Stumm, was a member of a famous family of industrialists. He became imperial ambassador in Madrid and was ennobled by Kaiser Friedrich in 1888. Many famous lords, earls, and dukes were his guests, among others Kaiser Friedrich and the Duke of Hesse.

He resigned as an envoy in 1890 and died in 1925, which left him 35 years to take care of the castle and its park. His eldest son, Ferdinand von Stumm, inherited the castle and sold the complete Holzhausen property in 1937. The castle was bought by the Kerkhoff Foundation in Bad Nauheim and

then leased to the University of Giessen as a site for experiments in agriculture.

The forest was sold to Mr. von Waldhausen, while the castle and the adjacent park were made available to the public. A school was founded in the castle for the training of kindergarten teachers.

After having been confiscated as Nazi property by the Allied forces in 1945, the castle and the park became property of the state of Hesse and were put at the disposal of Justus Liebig University Giessen as a conference centre.

**The castle** of Rauischholzhausen was designed by the architect Carl Schaefer, a student of Gottlieb Ungewitter, in the style of Klein-Potsdam. The construction lasted from 1871 to 1878 and the castle was lavishly decorated. In 1873 the building collapsed, because the foundations had been badly laid. Carl Jonas Mylius and Alfred Friedrich Bluntschli, both students of the architect Semper, were commissioned to redesign the castle according to Schaefer's original concept. In 1875, construction of the roof and the south-east wing was completed. The main building, reminiscent of an English manor house, was finished a year later. In 1878 the half-timbered wing of the building was completed.

When Rau von Holzhausen first lived on the location of today's castle he stayed at the castle mill, which is located at the lower entrance to the park and was built in the 16th century. In today's pond there was a water castle which could be approached through the large portal which still adorns the atrium of the castle. The door frame is decorated by a lion's head with a ring in its mouth and the Ionic columns may be identified as belonging to the Renaissance style.

**The park** is designed in the English style and contains almost three hundred different types of trees. Two creeks run through the park and form several ponds connected by artificial cascading waterfalls. Sculptures including a Lithuanian princess, a female slave, a virgin, and a weary Rambler may be found between groups of trees.

## Participants

### Invited Speakers

Dr. Alexey Chernikov	University of Regensburg
Dr. Katrin Siefermann	Leibniz Institute of Surface Modification, Leipzig
Dr. Matteo Gatti	Ecole Polytechnique, Paris
Dr. Christian Papp	Friedrich-Alexander-Universität Erlangen-Nürnberg
Dr. Ellen Backus	Max Planck Institute of Polymer Research, Mainz

### SFB Members

Eduard Baal	Claudio Krug
Malcolm Bartlett	Jan Kuhnert
Dr. Andreas Beyer	Pirmin Kükelhan
Nicolas Bock	Christian Lammers
Robin Carl Döring	Christian Länger
Eike Dornsiepen	Alexander Lerch
Dr. Henning Döscher	Dr. Gerson Mette
Sebastian Flade	Ingo Meyenburg
Markus Franke	Andreas Namgalies
Eugenie Geringer	Paul Nikodemiak
Sebastian Gies	Josua Pecher
Yvonne Grell	Dr. Marcel Reutzel
Katharina Greulich	Andre Rinn
Dr. Katharina Gries	Niklas Rinn
Maria Hagen	Rocio Felix
Han Han	Luise Rost
Anna-Katharina Hansmann	Lukas Ruppenthal
Dr. Alrun Hauke	Anna Lonny Christa Schiller
Benjamin Heidelmeier	Maik Schöninger
Jan Herritsch	Sebastian Thussing
Philipp Hofmann	Dr. Osmo Vänskä
Stefan Renato Kachel	Frederic Wagner
Andrea Karthäuser	Maria Weseloh
Benedikt Klein	Jonas Zimmermann
Michael Kothe	Malte Zugermeier