

ASOMEA - IX

9th Workshop on Advanced Spectroscopy of Organic Materials for Electronic Applications

October 23 (Tuesday) - 26 (Friday), 2018
Schluchsee, Germany



Program and Abstracts

ASOMEA-IX

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The series of biannual ASOMEA-workshops began in 2001 as a meeting of Swedish and Japanese scientists working with spectroscopic techniques and theoretical modeling for a better understanding of organic electronic materials and related interfaces. In 2016 the scope of the workshop was widened to include the German community and the intention to focus on organic materials at advanced stages, in situ/operando techniques, and time-resolved spectroscopy to name just a few.

The size and focus of the meeting will support a lively and intimate atmosphere with discussions on the overall progress and development of spectroscopic methods in particular.

Scientific Topics

- Spectroscopy of Molecular Liquids, Solids and Interfaces
- UV and X-ray Photoelectron Spectroscopies/Microscopies
- X-ray Absorption and Emission Spectroscopies
- Time-resolved/Multi-colored Spectroscopies
- Ambient Pressure/Operando Spectroscopies
- and more

Organizers

Prof. Dr. Ulrich Höfer
SFB 1083, Philipps-Universität Marburg
D-35032 Marburg

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SFB 951, Humboldt-Universität zu Berlin
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International Program Committee

Satoshi Kera, Institute for Molecular Science, Japan

Joachim Schnadt, Lund University, Sweden

Stacey Sörensen, Lund University, Sweden

Petra Teger, Universität Heidelberg, Germany

Jun Yoshinobu, University of Tokyo, Japan

Meeting History

2016	Okazaki, Japan
2014	Lund, Sweden
2011	Ishikawa, Japan
2009	Krusenberg Herrgard, Uppsala, Sweden
2007	Chiba, Japan
2005	Vadstena, Sweden
2003	Shonan Village, Tokyo, Japan
2001	Orenas Castle, Glumslöv, Sweden

Financial Support

Funded through the Deutsche Forschungsgemeinschaft (DFG) via Collaborative Research Centers SFB 1083 "Structure and Dynamics of Internal Interfaces" and SFB 951 "Hybrid Inorganic/Organic Systems for Opto-Electronics" (HIOS).

Additional support provided by the "Japan Society for the Promotion of Science" (JSPS).



Scientific Program

Timetable

	Tuesday, 23.10.	Wednesday, 24.10.	Thursday, 25.10.	Friday, 26.10.
07:00-08:55		Breakfast	Breakfast	Breakfast
08:55-09:00		Welcome		
09:00-10:00		Session 1 (Höfer) Kera Broch Cocchi	Session 5 (Tegeder) Lyu Blumstengel Gottfried	Session 9 (Rensmo) Tautz Tegeder T. Yamada
10:00-11:00		Coffee Break	Coffee Break	Coffee Break
11:00-12:00		Session 2 (Nakayama) Harada Ozawa Stadtmüller	Session 6 (Cocchi) Draxl Pucci Jakob	Session 10 (Koch) Rossi Shibuta Duhm
12:00-13:00				Closing
13:00-14:00		Lunch Break	Lunch Break	Lunch Break
14:00-15:00				
15:00-16:00		Session 3 (Ozawa) Fahlman Rensmo Akaike	Session 7 (Shibuta) Y. Yamada Witte Yoshida	Excursion
16:00-17:00		Coffee Break		
17:00-18:00		Session 4 (Duhm) Nakayama Dürr Peisert	Coffee Break	
18:00-19:00	Registration	Poster Preparation		
19:00-20:00	Reception & Dinner	Dinner		
20:00-21:00		Poster Session	Session 8 (Broch) Yoshinobu Casu Ueno	
21:00-21:30			Conference Dinner	

Wednesday, 24.10.2018

08:55 – 09:00 Welcome Address

Session 1 **Chair: Ulrich Höfer, Uni Marburg**

09:00 – 09:35 **Satoshi Kera, NIMS-IMS, Okazaki**
Evolution of electron localization upon assembling the molecules on the surface

09:35 – 10:10 **Katharina Broch, Uni Tübingen**
The impact of charge transfer states on the photophysics of acenes

10:10 – 10:30 **Caterina Cocchi, HU Berlin**
Collective behavior in the optical excitations of push-pull chromophores and their J-aggregate

Coffee Break

Session 2 **Chair: Yasuo Nakayama, Tokyo Univ. of Science**

11:00 – 11:35 **Yoshihisa Harada, Tokyo Univ.**
RIXS for hydrogen bond of liquid water at interfaces

11:35 – 12:10 **Kenichi Ozawa, Tokyo Inst. of Technol.**
Transient photoexcited state at p/n heterojunction in organic photovoltaics: A time-resolved soft X-ray photoelectron spectroscopy study

12:10 – 12:30 **Benjamin Stadtmüller, Uni Kaiserslautern**
Photoemission tomography of fullerenes on surfaces

Lunch Break

Wednesday, 24.10.2018 (continued)

Session 3 **Chair: Kenichi Ozawa, Tokyo Inst. of Technology**

14:30 – 15:05 **Mats Fahlman, Linköping Univ.**
Ternary organic bulk heterojunction solar cells

15:05 – 15:40 **Håkan Rensmo, Uppsala Univ.**
Understanding hybrid solar cell interfaces using photoelectron spectroscopy

15:40 – 16:00 **Kouki Akaike, Tokyo Univ. of Science**
Effects of molecular orientation of fullerene derivative on device performance of bilayer solar cell

Coffee Break

Session 4 **Chair: Steffen Duhm, Soochow Univ., Suzhou**

16:30 – 17:05 **Yasuo Nakayama, Tokyo Univ. of Science**
Structural and electronic characterization of well-defined molecular interfaces

17:05 – 17:40 **Michael Dürr, Uni Gießen**
Reaction dynamics of organic molecules on Si(001) – a route towards controlled organic functionalization of silicon surfaces

17:40 – 18:00 **Heiko Peisert, Uni Tübingen**
Electronic structure and interface properties of FePc and FePcF16 on metal substrates

18:00 – 18:15 Break for preparation of Poster Session

Dinner

19:30 – 21:30 **Poster Session**

Thursday, 25.10.2018

Session 5 Chair: Petra Tegeder, Uni Heidelberg

09:00 – 09:35 **Jiong Lyu, Nat. Univ. Singapore**
Recent STM studies of single molecule and defect in gated 2D material devices

09:35 – 10:10 **Sylke Blumstengel, HU Berlin**
Fingerprint of charge redistribution at hybrid inorganic/organic interfaces revealed by differential reflectance spectroscopy

10:10 – 10:30 **Michael Gottfried, Uni Marburg**
Molecular Topology and Metal Organic Interactions

Coffee Break

Session 6 Chair: Caterina Cocchi, HU Berlin

11:00 – 11:35 **Claudia Draxl, HU Berlin**
Theoretical spectroscopy at hybrid interfaces

11:35 – 12:10 **Annemarie Pucchi, Uni Heidelberg**
Infrared analytics of functional layers for organic electronics

12:10 – 12:30 **Peter Jakob, Uni Marburg**
Electron-vibron coupling at molecule-metal interfaces

Lunch Break

Thursday, 25.10.2018 (continued)

Session 7 Chair: Christian Kumpf, FZ Jülich

- 15:00 – 15:35 **Yoichi Yamada, Tsukuba Univ.**
Exploring the structure-property relationships of the well-ordered organic films
- 15:35 – 16:10 **Gregor Witte, Uni Marburg**
Optoelectronic properties of crystalline organic thin films and heterostructures
- 16:10 – 16:30 **Hiroyuki Yoshida, Chiba Univ.**
The evolution of intermolecular energy bands of occupied and unoccupied molecular states in organic thin film

Coffee Break

Session 8 Chair: Katharina Broch, Uni Tübingen

- 17:00 – 17:35 **Jun Yoshinobu, Tokyo Univ.**
Gas exposure effects on monolayer pentacene FET studied by using non-invasive GaIn probes
- 17:35 – 17:55 **Benedetta Casu, Uni Tübingen**
Nanoscale studies of organic radicals: interface, and spinterface
- 17:55 – 18:10 **Nobuo Ueno, Chiba Univ.**
Introduction to JSPS and its international programs

Conference Dinner

Friday, 26.10.2018

Session 9 **Chair: Håkan Rensmo, Uppsala Univ.**

09:00 – 09:35 **Stefan Tautz, FZ Jülich**
Dispersive states at molecule-metal interfaces

09:35 – 10:10 **Petra Tegeder, Uni Heidelberg**
Formation of occupied and unoccupied hybrid bands at interfaces between metals and organic molecules

10:10 – 10:30 **Takashi Yamada, Osaka Univ.**
Unoccupied electronic states and excited dimer formation at the perylene/graphite interface

Coffee Break

Session 10 **Chair: Norbert Koch, HU Berlin**

11:00 – 11:35 **Mariana Rossi, FHI Berlin**
Critical interplay of atomic structure and level alignment in organic/inorganic interfaces

11:35 – 12:10 **Masahiro Shibuta, Keio Inst.**
Spectroscopy and imaging of photocarriers in organic functional films probed by two-photon photoemission

12:10 – 12:30 **Steffen Duhm, Soochow Univ., Suzhou**
Organic-inorganic energy-level alignment: From academic interfaces to devices

Closing Remarks

Lunch Break

Oral Abstracts Wednesday

Evolution of electron localization upon assembling the molecules on the surface

Satoshi Kera

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Functional organic molecule (FOM) has recently attracted considerable attention both on fundamental research and device applications because of peculiar properties not found in inorganics and small molecules. However the mechanisms and its origin of various device characteristics are still under controversial. Scientific mysteries would be raised because people have believed that electronic structure of FOM would be conserved as in an isolated molecule for solid state due to weak van der Waals interaction. To reveal characteristics of FOM the key investigation would be on precise experiments on the electronic structure at various interfaces, including organic-organic and organic-inorganic (metal/semiconductor) contacts.

High-resolution angle-resolved photoelectron spectroscopy of organic monolayer and bilayer films of perfluoropentacene (PFP) prepared on Ag(111) and graphite substrates are performed to reveal the impact of weak electronic interaction and strong electron-phonon coupling on the molecular orbital states. By comparing two weakly interacting interfaces, we confirm the localization of wave-function spread of each state at the physisorbed interface and shed light on the character of an electron cloud in functional molecular materials. Recent results taken by the momentum microscopy which allows to find a global view of an electron cloud in very short experimental time will be shown to discuss.

The impact of charge-transfer states on the photophysics of acenes

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Charge transfer between a donor and an acceptor is a key parameter for device performance of organic solar cells and constitutes the prototypical scenario for the study of charge-transfer states. However, during the last decade, the formation of a charge-transfer state after optical excitation of *neat* thin films has gained increasing attention due to its strong impact on their photophysics [1]. Effects such as the sign and magnitude of the Davydov-splitting can only be correctly calculated if a significant mixture of charge transfer and Frenkel exciton states are taken into account [1]. Furthermore, charge-transfer states mediate complex photophysical processes, such as the conversion of an excited singlet state into two triplet states on neighbouring molecules. Therefore, the understanding of the impact of these states on photophysical processes is one way towards a tailoring of photophysical properties of organic semiconductors.

The talk will focus on the photophysics of pentacene in blends with molecules of different acceptor strength [2,3], studied using transient absorption spectroscopy and time-resolved photoluminescence spectroscopy. In strongly-interacting blends, the photophysics of the charge-transfer state between the compounds and its dependence on the mixing ratio will be discussed [2]. In the second part of the talk, an alternative approach to tailoring intermolecular interactions will be suggested by introducing spacer molecules in mixed thin films via coevaporation. Using the Davydov-splitting as convenient metric, it will be demonstrated that the charge-transfer character of the lowest electronic excitation can be modified in these blends. Finally, it will be discussed how such a modification affects the time scales of photophysical phenomena [3].

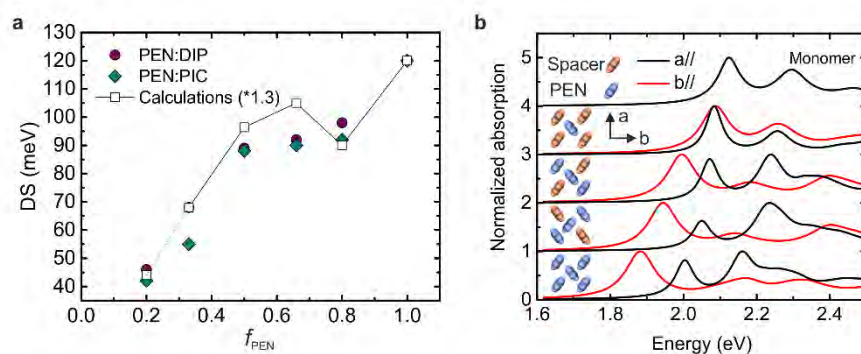


Fig. 1 Davydov-splitting in pentacene:spacer molecule blends as a metric of charge-transfer character [3].

- [1] D. Beljonne *et al.*, Phys. Rev. Lett., 110, 226402 (2013).
- [2] K. Broch *et al.*, Phys. stat. sol. (RRL), 8, 1700064 (2017).
- [3] K. Broch *et al.*, Nat. Commun., 9, 954, (2018).

Collective behavior in the optical excitations of push-pull chromophores and their J-aggregate

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Within a first-principles study based on density-functional theory and many-body perturbation theory (GW approximation and Bethe-Salpeter equation), we investigate the optical excitations of a J-aggregate formed by the $C_{24}H_{19}F_4N$ push-pull chromophore, which is known for its enhanced nonlinear optical properties [1]. We focus on the so-called J-band, the sharp absorption peak dominating the spectral onset of the aggregate, which is red-shifted by a few hundred meV compared to the first bright excitation in isolated molecule. We demonstrate the collective nature of the excitations forming the J-band by analyzing their character in terms of dipole distribution and spatial extension. In this context, we discuss the role of molecular packing, which plays an important role in the optical properties of this J-aggregate [2]. Our results shed light on the microscopic mechanisms leading to the formation of the characteristic absorption peak in J-aggregates and offer new perspectives for understanding the nature of collective excitations in molecular materials [3].

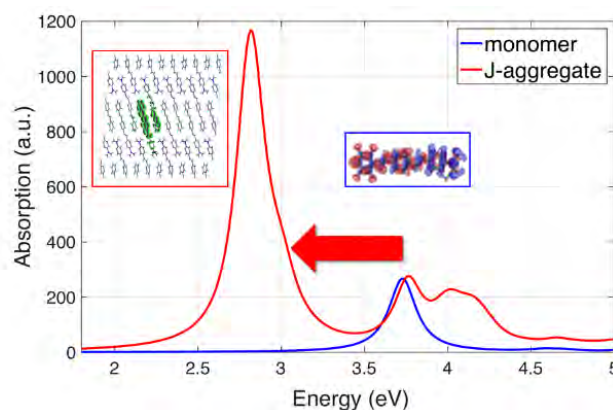


Fig. 1 Optical spectrum of molecule and J-aggregate computed from MBPT.

The red-shift of the J-band is highlighted and the exciton (transition) density of the first peak is shown for the aggregate (monomer) in the inset.

[1] C. Botta *et al.*, J. Mater. Chem. C 2, 5275 (2014).

[2] M. Guerrini *et al.*, submitted (2018).

[3] M. Guerrini *et al.*, in preparation (2018).

RIXS for hydrogen bond of liquid water at interfaces

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X-ray absorption (XAS) and emission (XES) spectroscopy of liquid water are one of the cutting-edge techniques to determine the local hydrogen bond network of liquid water through observation of the valence electronic structure.[1-3] An XES study of liquid water at an interface gives us a good opportunity to explore isolated or highly ordered water molecules than expected in bulk liquid water. In this paper, XES studies on such “unique” water molecules are presented; an isolated extreme is water in a less hydrogen bonded network of acetonitrile. The other extreme is water encapsulated in a polymer.[4] Poly(2-(methacryloyloxy)ethyl trimethylammonium chloride) (PMTAC) brushes,[5] which represent high-density polymer chains, are well suited for investigating the interaction between water and polymers as well as confinement of water by these polymer brushes. The apparent relationship between each XAS/XES spectral profile and a specific hydrogen bond configuration characterized by its strength and local symmetry is demonstrated through these extreme cases. The results indicated that the confined water has tetrahedrally coordinated hydrogen bonds with a uniform distortion like high pressure ice, which should be naturally connected to control the antifouling and lubricating functions of polyelectrolyte brushes. Based on the knowledge of the interpretation of XES spectra of liquid water we further studied water in the close vicinity of biocompatible polymer Poly(2-methoxyethyl acrylate) (PMEA). [6] The result will be discussed in terms of the role of interfacial water.

- [1] T. Fransson *et al.*, Chem. Rev. 116, 7551 (2016).
- [2] S. Myneni *et al.*, J. Phys. Condens. Matter 14, L213 (2002).
- [3] T. Tokushima *et al.*, Chem. Phys. Lett. 460, 387 (2008).
- [4] K. Yamazoe *et al.*, Langmuir 33, 3954 (2017).
- [5] M. Kobayashi *et al.*, Langmuir 28, 7212 (2012).
- [6] M.Tanaka *et al.*, Biomaterials 21, 1471 (2000).

Transient photoexcited state at p/n heterojunction in organic photovoltaics: A time-resolved soft X-ray photoelectron spectroscopy study

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A ubiquitous light-harvesting system paves the way to a zero-emission sustainable society. Organic photovoltaics is a leading solution for such a system as an inexpensive renewable energy source so that great efforts have been devoted to the enhancement of light-electricity conversion efficiency. In the photovoltaics, the conversion efficiency is directly linked to exciton quenching and an electron-hole recombination at the heterojunction in the p-type and n-type organic semiconductor layers. Thus, it is important to establish atomistic picture of the photoexcited carrier behavior at the p/n junction. In our study, transient photoexcited states of phthalocyanine (Pc), fullerene (C_{60}) at a Pc/C_{60} heterojunction fabricated on TiO_2 (Fig. 1) have been examined by time-resolved soft X-ray photoelectron spectroscopy (TRXPS) utilizing a laser-pump/synchrotron-radiation-probe technique, which was conducted at BL07LUS of SPring-8.

One of great advantages of TRXPS is that time-evolution of excited states are traceable individually for each component. In our case, for example, transient photoexcited states of C_{60} and Pc were determined separately by analyzing the chemical shift of C 1s core-level spectra (Fig. 1). Such information cannot be accessible by techniques such as transient UV-vis absorption/emission spectroscopy and laser-pump/laser-probe photoelectron spectroscopy, by which dynamics of the excited carriers are directly examined. TRXPS is more suitable to study carrier dynamics in the complex system like an organic solar cell that is composed of several components. In the presentation, more details of the experimental result will be presented and discussed.

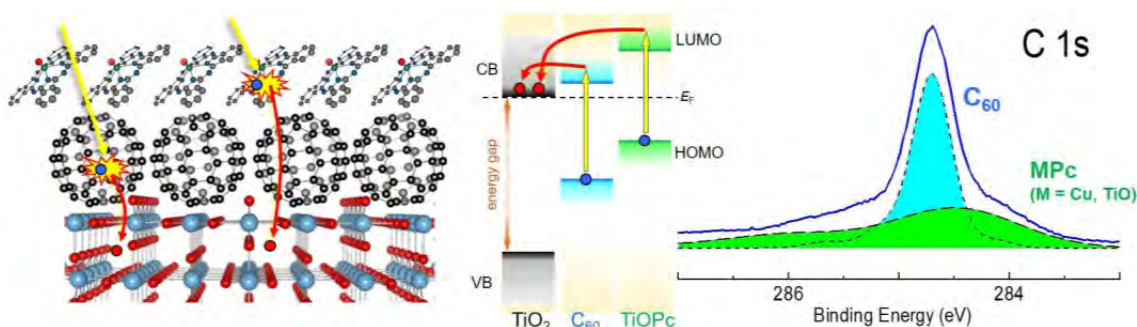


Fig. 1 A schematic drawing of the $Pc/C_{60}/TiO_2$ junction (left) and its energy diagram (center).

A C 1s XPS spectrum which is deconvoluted into the C_{60} and Pc components (right).

The TRXPS measurements were conducted under the approval of the Synchrotron Radiation Research Organization, The University of Tokyo (Proposal Nos. 2016B7503, 2017A7533). Supports from Iwao Matsuda and Susumu Yamamoto (Univ. Tokyo) are greatly appreciated.

Photoemission tomography of fullerenes on surfaces

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One of the great challenge for molecular-based electronics is the design of metal-organic interfaces with dedicated functionalities. In this regard, the combination of angle resolved photoemission spectroscopy (ARPES) with photoemission tomography (PT) has emerged as powerful tool to study and understand the fundamental phenomena of these interfaces. The PT approach allows one to assign spectroscopic ARPES features to the emitting molecular orbital and to reveal modifications of the molecular wave functions caused by the interactions at the interface. In this way, PT provides a unique view onto the interfacial electronic properties and the interactions at the metal-organic interface. So far, however, PT has mainly been limited to planar 2D molecules on surfaces.

Here, we will demonstrate that the PT framework can also be applied to three dimensional molecules. As prototypical systems, we have chosen the fullerene molecules C_{60} and $Sc_3N@C_{80}$. For a C_{60} film on Ag(111), the ARPES signal of the two highest occupied molecular orbitals (HOMOs) reveals a strong band dispersion while the lower lying orbitals appear as well-defined emission maxima in momentum space, see Fig. 1. The emission pattern of all molecular features can be well described in the framework of PT. Accordingly, we can assign the strongly dispersing bands to the HOMO and HOMO-1 bands while the well-defined emission maxima are due to σ -orbitals of C_{60} . A similarly good agreement between the experiment and the PT simulation is found for the fullerene $Sc_3N@C_{80}$.

In this way, our comprehensive investigation of thin films of fullerene molecules clearly underlines the potential of photoemission tomography to describe the momentum revolved photoemission yield of three dimensional molecules on surfaces.

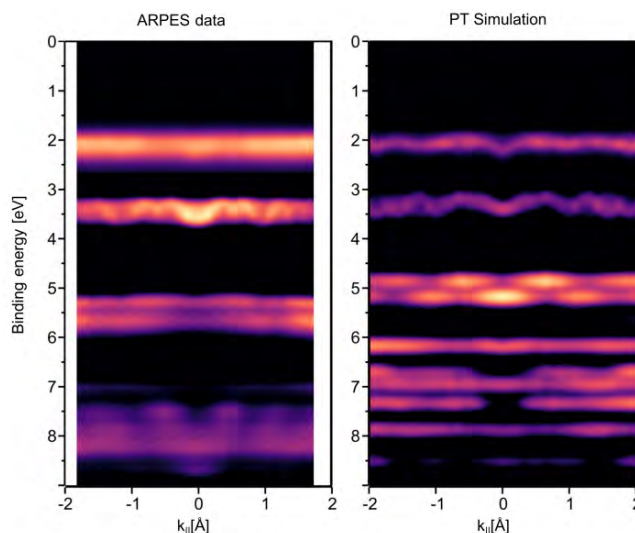


Fig. 1 ARPES data and corresponding PT simulation for a thin film (10ML) of C_{60} on Ag(111) ($E_{ph}=35\text{eV}$, $T_{\text{Sample}}=50\text{K}$).

Ternary organic bulk heterojunction solar cells

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One of the most important tasks during design and fabrication of organic electronic devices is to determine the energy levels of the organic materials and understand the energy level alignment at the interfaces. We use electronic structure measurements of neat polymer films and their interfaces combined with modeling to design ternary organic bulk heterojunction solar cells featuring minimum voltage loss [1] and demonstrate for the first time that open circuit voltage can be enhanced in ternary solar cells compared to the reference binary ones while also enhancing the power conversion efficiency [2]. The key design concept is to select interface combinations that enhance dissociation of the donor and acceptor excitons and to suppress bimolecular and trap-assistant recombination [1,2, 3].

Ultraviolet Photoelectron Spectroscopy (UPS), Inverse Photoemission Spectroscopy (IPES), and cyclic voltammetry (CV) typically are employed to obtain the oxidation/reduction energies of the donor and acceptor materials used in organic photovoltaics (OPV). CV is particularly popular as it is comparatively cheap and can obtain both oxidation and reduction energies, unlike UPS and IPES. The values obtained differ between the techniques, but a linear relationship is typically found, though the slope and intercept of this relation varies significantly between studies and types of organic materials [4-7]. We study a series of typical OPV materials and find a linear relationship of slope 1 between CV oxidation potentials and UPS ionization potentials, but the precision in the CV-derived IP values are not sufficient, however, to enable precise design of energy level alignment at heterojunctions [8].

- [1] C. Wang *et al*, Adv. Energy Mater., 6, 1700390 (2017).
- [2] C. Wang *et al*, Nano Energy, 37, 24 (2017).
- [3] Q. Bao *et al*, Adv. Funct. Mater. 24, 6309 (2014).
- [4] B.W. D'Andrade *et al*, Org. Electron. 6, 11 (2005).
- [5] P.I. Djurovich *et al*, Org. Electron. 10, 515 (2009).
- [6] J. Sworakowski *et al*, Org. Electron. 33, 300 (2016).
- [7] J. Sworakowski *et al*, Org. Electron. 48, 46 (2017).
- [8] C. Wang *et al*, Sol. RRL DOI: 10.1002/solr.201800122.

Understanding hybrid solar cell interfaces using photoelectron spectroscopy

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Partly building on the developments of dye-sensitized solar cells, the last couple of years have witnessed a new development of hybrid perovskite materials used in optoelectronic applications such as solar cells [1,2]. Starting with materials such as $\text{CH}_3\text{NH}_3\text{PbI}_3$ there are now record-breaking cells containing a large variety of cations and anions such as Cs^+ , Rb^+ , formamidinium as well as Br^- , I^- . The efficiency of the conversion process in these systems is largely dependent on the properties of the interfacial region including material organisation, character of the energy levels as well as on energy matching between the different materials. Insight into such material properties is therefore crucial in order to understand and optimize the function. Photoelectron spectroscopy is an ideal tool for non-destructive chemical and electronic characterization of such interfaces and our group is in the forefront of developing such x-ray based spectroscopy techniques and implementing them to investigations on energy materials. Specifically, the presentation will show how to implement new opportunities in photoelectron spectroscopy for the understanding of the interface structure and energy matching in solar cell materials and how conditions (humidity, light and voltage) can effect the structure. [3-5]

- [1] S.D. Stranks, H.J. Snaith, *Nat Nanotechnol* 10, 391 (2015).
- [2] NREL Best Research-Cell Efficiencies. www.nrel.gov/pv/assets/images/efficiency_chart.jpg.
- [3] B. Philippe *et al.*, *Chem Mater.* 27(5):1720, (2015).
- [4] U.B. Cappel *et al.*, *Phys Chem Chem Phys* 18, 21921, (2016).
- [5] U.B. Cappel *et al.*, *Acs Appl Mater Inter.* 9, 34970 (2017).

Effects of molecular orientation of fullerene derivative on device performance of bilayer solar cell

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The orientation of the molecular semiconductors at the donor/acceptor interface is critical for the carrier generation and recombination in organic photovoltaics (OPVs). To provide interface design rule for efficient OPVs, the impact of the orientation of not only donor but also acceptor on fundamental property and device performance has to be investigated. In this study, we demonstrate the orientational change of [6,6]-phenyl-C₆₁-butyric acid methyl ester [PC₆₁BM, inset in Fig. 1(a)] upon crystallization, employing metastable atom electron spectroscopy (MAES) that can probe the outermost electron density. As shown in Fig. 1(a), The MAES spectrum of amorphous (*a*-) PC₆₁BM shows the enhanced signal in the region I, where the π -orbitals of C₆₀ backbone are contributed. In contrast, the spectrum of crystalline (*c*-) PC₆₁BM shows the enhanced photoemission in the region II, where the π -orbitals of the side chain distribute. The results suggest the surface exposure of the side chain outside the *c*-PC₆₁BM film, which was speculated by Zhong *et al* [1]. Based on this finding, we fabricated the direct contact of the C₆₀ backbone with standing molecules of sexithiophene (6T) and indirect contact through the side chain. Characterizing the bilayer OPVs reveals the higher open circuit voltage (V_{OC}) for *c*-PC₆₁BM/6T device [Fig. 1(b)] owing to the increased energy of the charge transfer states and reduced carrier recombination at the D/A interface.

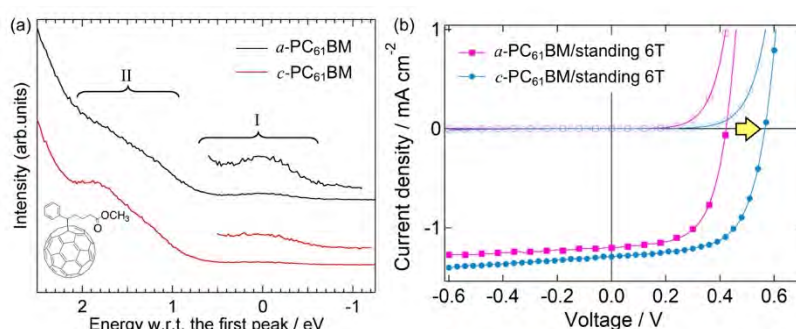


Fig. 1 (a) MAES spectra of *a*- and *c*-PC₆₁BM films. The energy ranges I and II correspond to the photoemission from the π -orbitals of C₆₀ backbone and side chains, respectively. (b) Current density-voltage curves of the bilayer-OPVs comprising *a*- or *c*-PC₆₁BM/standing 6T heterostructures.

[1] Y. Zhong *et al.*, Adv. Energy Mater. 4, 1301332 (2014).

Structural and electronic characterization of well-defined molecular interfaces

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Functionalities of organic electronic devices arise from molecular interfaces in most cases. Therefore, understanding of structural and electronic properties at the molecular contacts is crucial for progress in science and technology in this field. Practical interfaces in the devices themselves are unlikely to be ideal targets for pursuing molecular-scale phenomena at the contacts due to their complex and heterogeneous natures. In contrast, a paradigm of the surface science, that is examination into well-defined interfaces built on single crystal surfaces of one material, may open a route for approaching clear understanding of the interfacial phenomena driving the organic electronic devices, even though such ideal interfaces may be oversimplified for directly modeling the devices themselves. In this contribution, recent advancement in structural and electronic characterization of well-defined interfaces formed on organic semiconductor single crystal surfaces (Fig. 1) achieved by surface science methodologies, such as grazing incidence X-ray diffraction [1-4] and photoelectron spectroscopy [5,6], is discussed.

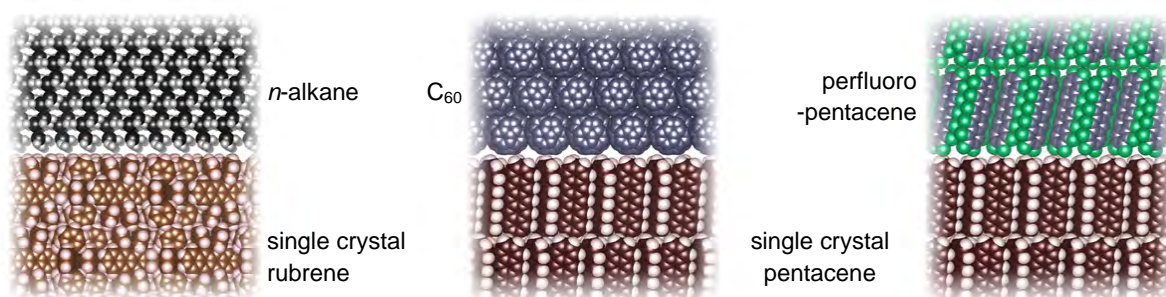


Fig. 1 Schematic drawings of the topical well-defined molecular interfaces.

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- [2] R. Tsuruta *et al.*, J. Cryst. Growth, 468, 770 (2017).
- [3] Y. Nakayama *et al.*, Adv. Mater. Interf. 5, 1800084 (2018).
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- [5] Y. Nakayama *et al.*, Org. Electron. 14, 1825 (2013).
- [6] M. Yamamoto *et al.*, e-J. Surf. Sci. Nanotechnol. 13, 59 (2015).

Reaction dynamics of organic molecules on Si(001) – a route towards controlled organic functionalization of silicon surfaces*

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The adsorption of organic molecules on silicon has been the subject of intense research due to the potential applications of organic functionalization of silicon surfaces in semiconductor technology. The high reactivity of the silicon dangling bonds towards almost all organic functional groups, however, presents a major hindrance for the first basic reaction step of such a functionalization, i.e., chemoselective attachment of bifunctional organic molecules on the pristine silicon surface. Due to this high reactivity, the final adsorption products typically consist of a mixture of molecules adsorbed via different functional groups. For the preparation of well-ordered organic layers on silicon, it is thus important to learn how to control the reactions of the single functional groups.

Using various spectroscopic techniques, such as XPS, UPS, and nonlinear optics, in combination with scanning tunneling microscopy and molecular beam techniques, we investigated in detail the reaction mechanisms, kinetics, and dynamics of different functional groups on Si(001). We make use of these results in order to control the respective reactions by either changing the localized electronic surface states or the molecules' very properties. Electronic excitation and hyperthermal energy distributions of the incoming molecules are investigated as further means of control.

Our main strategy for the controlled functionalization of Si(001) is then based on functionalized cyclooctynes as cyclooctyne's strained triple bond is associated with a direct adsorption channel on the Si(001) surface, in contrast to almost all other organic molecules, which adsorb via weakly bound intermediates [1]. As a consequence, cyclooctyne derivatives with different functional side groups react on Si(001) selectively via the strained cyclooctyne triple bond while leaving the side groups intact (Fig. 1). This second functional group is then used for the covalent attachment of further organic reagents on the road to well-defined molecular architectures on Si(001).

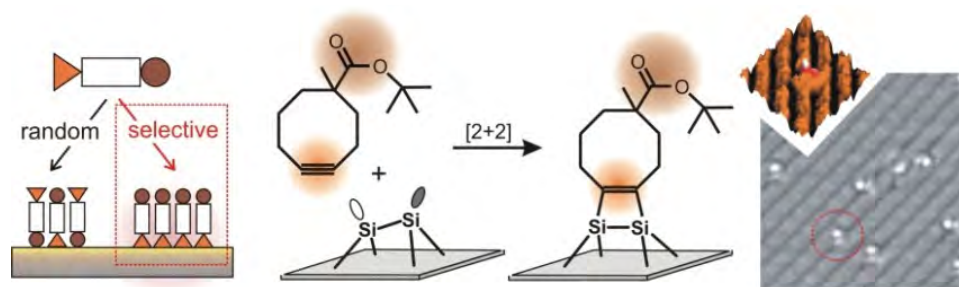


Fig. 1: Bifunctional cyclooctynes react selectively via the strained triple bond of cyclooctyne.

* work performed within SFB 1083 and GRK 1782

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Electronic structure and interface properties of FePc and FePcF₁₆ on metal substrates

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The interfacial electronic structure of iron phthalocyanine (FePc) and perfluorinated iron phthalocyanine (FePcF₁₆) is investigated by photoexcited electron spectroscopies: Photoemission (XPS and UPS) and X-ray absorption spectroscopy (XAS or NEXAFS). The strength and nature of the interaction at the interface depend distinctly on the substrate. As example, a strong interaction of the central metal atom of both phthalocyanines occurs on Ag(111), where the formed interface states close to the Fermi level are determined by the interaction between Fe 3d states and substrate related states.[1, 2] On the other hand, also the macrocycle and the nitrogen atom is involved in the interaction.

Valuable information about the electronic structure of the iron ion is obtained from XAS. A drastic change of the XAS peak shape is observed for thicker FePcF₁₆ films on both Ag(111) and Cu(111), although the molecular orientation is very similar to coverages of few monolayers. Since in both cases the film thickness is distinctly beyond the monolayer regime, interface interactions can be ruled out as a possible origin of this behavior. Rather, the different XAS peak shapes seem to indicate that the multiplicity depend on the detailed arrangement of the FePcF₁₆ molecules.[3] The large flexibility of the ground state of Fe in FePcF₁₆ could be of high interest for spintronic applications.

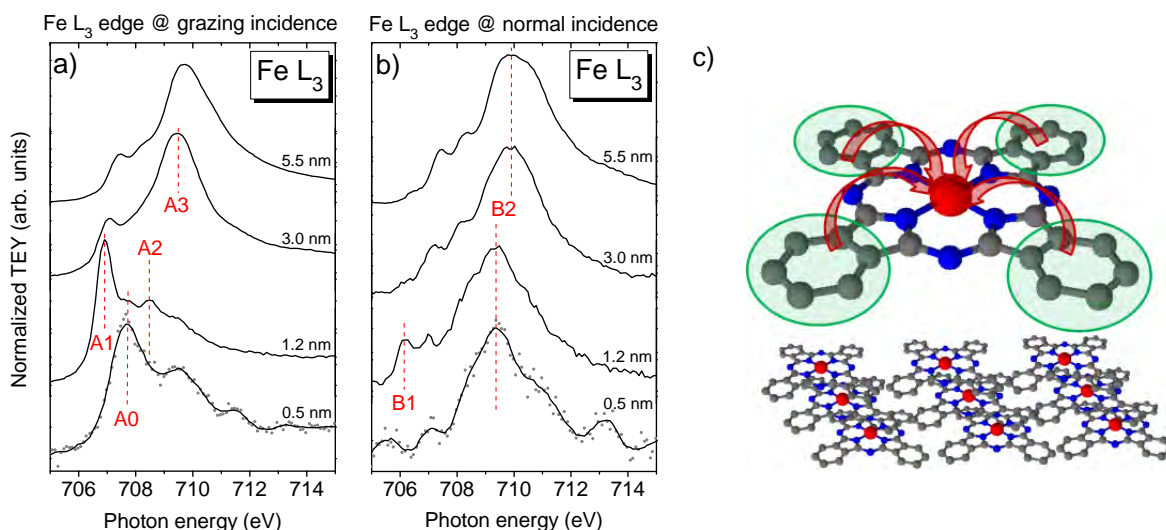


Fig. 1 FePcF₁₆ on Cu(111): XAS spectra of Fe L edge at a) grazing and b) normal incidence.

The feature A0 can be understood by a hybridization of Fe and substrate related orbitals, whereas the increasing complexity at higher coverages point to a change of the spin multiplicity. c) Illustration of the change of the electronic structure of the Fe ion as a consequence of the different arrangement of the molecules.

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Oral Abstracts Thursday

Recent STM studies of single molecule and defect in gated 2D material devices

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The ability to modify the electronic properties of 2D materials via charge-donating or charge-accepting molecules creates new opportunities for fabricating hybrid devices at the nanoscale. In this talk, I will first discuss about new experiments that involve the exploration of individual and self-assembled molecules adsorbed onto the surface of a back-gated graphene device. The back-gated graphene device substrate is unique for single-molecule surface investigations in that it can be electrostatically gated, thus changing and manipulating the charge-state of the supported molecules. Understanding the charge transfer and the resulting electronic structure at molecule/2D materials interface is essential for tuning the electronic and magnetic characteristics of such hybrid devices. I will also talk about a recent demonstration of a giant Stark effect in few-layer black phosphorus (BP) via electrostatic gating. Using LT-STM, we observed that a monotonic reduction of the bandgap of few layer BP occurs after the injected electrons compensate the existing defect-induced holes. We also employed LT-STM to probe the charge state of shallow acceptors in black phosphorus together with an aim to understand the spatial structures of bound hole states near individual acceptors. Our findings open up the new avenue for the investigation into charge transport through single dopants in gated BP nanodevices.

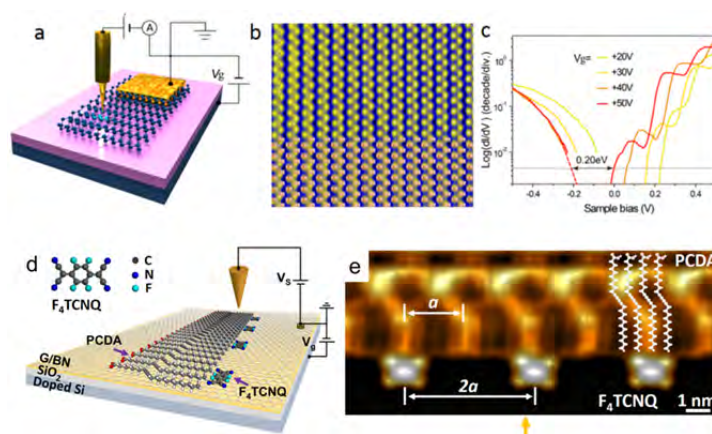


Fig. 1 (a) A back-gated few-layer BP device (b-c) STM imaging and spectroscopy of a gated BP device (d-e) Edge-templated synthesis of F_4TCNQ molecular arrays on a gated graphene FET device.

- [1] S. Wickenburg *et al.*, Nature Comm. 7, 13553 (2016).
- [2] Z.Z. Qiu *et al.*, Nano Letters 17 (11), 6935 (2017).
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- [4] Y.P. Liu *et al.*, Nature Nanotechn. (2018).

Fingerprint of charge redistribution at hybrid inorganic/organic interfaces revealed by differential reflectance spectroscopy

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Hybrid structures combining conjugated organic molecules and inorganic semiconductors allow to merge the better of two worlds. To achieve optoelectronic functionality exceeding that of the individual constituent, both the electronic and optical properties of the hybrid interface must meet certain requirements. Charge redistribution occurring upon deposition of conjugated organic molecules on semiconductor surfaces modulates the electrostatic potential at the hybrid interface. This effect has been exploited to tune the interfacial energy levels. It can be expected that charge redistribution also profoundly affects the optical properties of the hybrid interface. This talk will show that differential reflectance (DR) spectroscopy allows tracking of those changes as a function of the molecular coverage starting from the submonolayer regime [1]. The spectra are recorded in real time and *in situ* during the deposition of the molecules. At the example of various ZnO/organic interfaces it will be shown that the electric field associated with the modulation of the electrostatic potential causes a strong modification of the excitonic absorption of the semiconductor surface. Modelling of the DR spectra considering a Wannier-Mott exciton in an electric field yields the magnitude of the field strength. Consequently, the charge-transfer induced modification of the electrostatic potential and the related changes in the optical spectra are obtained simultaneously. The findings provide insight into the subtle interplay between optical and electronic properties. The consequences on the effectiveness of excitonic coupling across such hybrid interfaces will be discussed.

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Molecular Topology and Metal-Organic Interactions

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Interfaces between π -conjugated organic semiconductors and metal electrodes play a crucial role in the performance of organic (opto)electronic devices. Rational strategies for the improvement of these devices therefore require a detailed understanding of the chemical, electronic and geometric interface structure. In this contribution, we show that the interaction of aromatic molecules with metals depends on the topology of their π -electron systems. This is demonstrated for the isomers azulene, which has a non-alternant π -system with a 5-7 ring structure, and naphthalene, which has an alternant π -system with a 6-6 ring structure. We found that azulene interacts much more strongly with a Cu(111) surface, where its adsorption energy is 1.8 eV, compared to 1.0 eV for naphthalene. The different bond strengths are reflected in the adsorption heights, which are 2.30 Å for azulene and 3.04 Å for naphthalene, as measured by NIXSW. Related differences were observed in the electronic structure of the two interfaces. Substantial transfer of negative charge from the metal to the molecule occurs only for azulene, but not for naphthalene. The observed differences in the molecule/metal bond are related to the π -electronic structure. Azulene has a low-lying LUMO, which is close to the Fermi energy of copper and thus hybridizes with its electronic states, as is shown by photoemission, NEXAFS, and STM data in combination with DFT-based theoretical analysis. Similar trends were observed for other metal surfaces such as Ag(111) and Pt(111). Our results indicate that the electronic properties of metal/organic interfaces can be adjusted through modifications of the π -topology of the organic semiconductor.

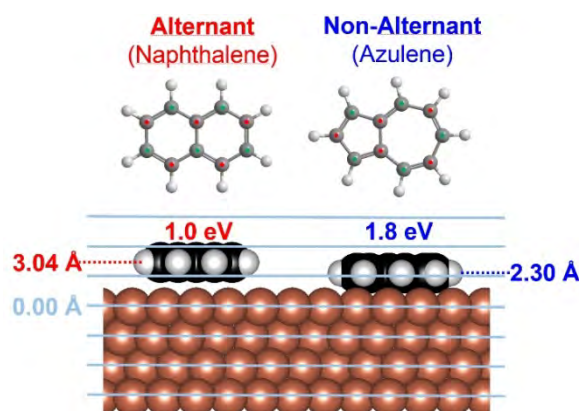


Fig. 1 Alternant (naphthalene) and non-alternant (azulene) π -electron systems on a copper (111) surface. The numbers indicate the respective experimental adsorption heights and adsorption energies.

Theoretical spectroscopy at hybrid interfaces

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From a theory point of view, the *ab initio* description of organic materials and, in particular, their interfaces to inorganic counterparts remains an exciting though challenging issue. Only having proper theoretical concepts and numerical tools in hand which consistently capture the features of molecular materials, from single molecules to hybrid interfaces, allows for getting insight into the leading excitation processes. As many-body effects play a dominant role forefront methodology, that is capable of reliably predicting the electronic structure and optical excitations, is a must.

Selected examples, among them pyridine and poly(*para*-phenylene) on ZnO will show how many-body perturbation theory combined with density-functional theory can be used to explore, control, and predict level alignment and band gaps as well as light-matter interaction at hybrid interfaces, and how simple models and lower-level theory can fail.

Infrared analytics of functional layers for organic electronics

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Infrared (IR) spectroscopy is a powerful non-destructive tool with extreme chemical and structural sensitivity. IR spectra reveal absorption lines from all those specific vibrations of molecules or optical phonons that can couple to the incident photons. IR spectroscopy is also sensitive to low-energetic electronic excitations of plasmonic or polaronic nature in nanostructures of finite size. Nowadays modern IR techniques provide the photometric sensitivity to detect intensity changes down to 10^{-4} , so analytics of monolayers and interfaces is possible if referencing is done carefully. The examples presented in the talk will be the optical phonons and phonon polaritons of ultrathin oxide layers (used to modify electrode surfaces), the IR characterization of the conductivity of gold [1] and ITO layers [2], the IR polaron in doped polymers (*e.g.* [3]), and the charge transfer between organic and inorganic materials as for example CBP/MoO₃ (*e.g.* [4]) and TAPP-Br (molecules produced by L. Gade's team, see [5]) on the ordered Si(553)-1x2-Au surface [6].

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- [6] F. Hötzel *et al.*, J. Phys. Chem. C 121, 8120 (2017).

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Electron-vibron coupling at molecule-metal interfaces

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Dynamical charge transfer processes at interfaces in general proceed on the timescale of a few fs or even below. Due to their high relevance in various technical devices and research areas related to photovoltaic and optoelectronic excitations it is highly desirable to achieve a profound understanding of such processes and to identify relevant parameters that control the timescale and efficiency of this charge transfer.

Experimental studies on electron transfer between two weakly coupled electronic systems often suffer from the fact that pump/probe excitation schemes or photoemission spectroscopy in general involves electronically excited systems. Adoption of the derived dynamical properties to the neutral ground state species (or the-like) must then remain ambiguous. In the present study excitation of vibrational modes has been employed to study electron transfer dynamics for ground-state configurations of molecular adsorbates. Even though this approach comprises a non-ground state situation as well (vibrational excitation), deviation from thereof remains minor as compared to electronic excitations associated with one or two-photon photoemission spectroscopy.

By means of analyzing line shapes of vibrational modes subject to interfacial dynamical charge transfer (IDCT) [1, 2] we are able to accurately and reliably characterize the electron transfer dynamics between adsorbed molecules and a metal substrate. Thereby, the vibrational mode frequency acts as an accurate internal clock to quantify the relevant time scale of these processes. It is invoked that the non-adiabaticity of the electron-vibron coupling is correlated with the coupling of a molecular orbital at ϵ_F to substrate electronic levels and that the relevant time scales are reflected in the width of this molecular orbital which is directly linked to fluctuations in the occupancy of this molecular orbital.

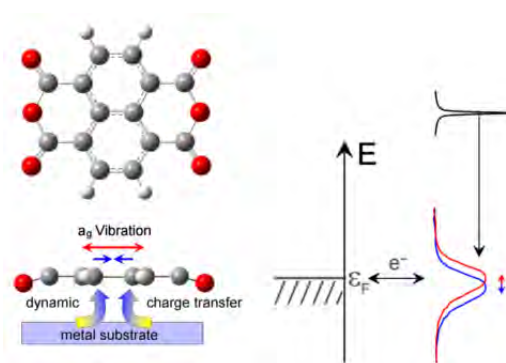


Fig. 1 Scheme describing interfacial dynamical charge transfer between NTCDA and a metal substrate, induced by the excitation of a totally symmetric molecular vibration.

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Exploring the structure-property relationships of the well-ordered organic films

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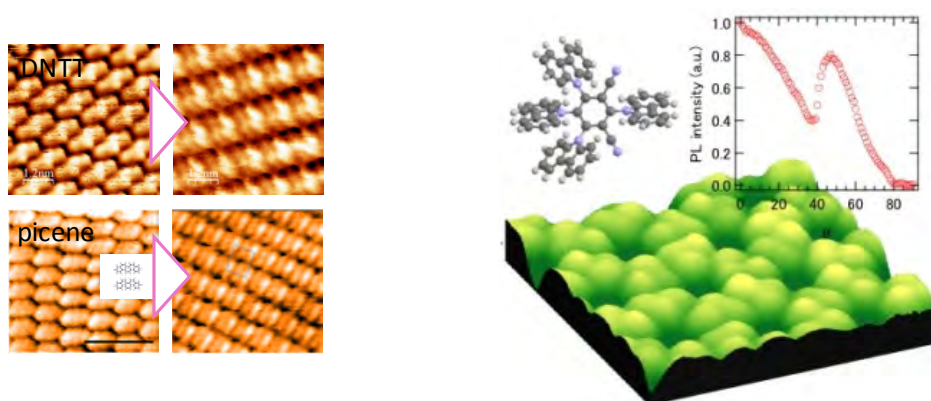
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Since organic materials show significant structure-property relationships, their macroscopic properties should be discussed based on the measurements of well-ordered system. Much progresses in this viewpoint has been made through the single crystalline systems, establishing the understanding of the device properties based on the electron theory. Films, on the other hand, have been still difficult target due to enhanced imperfections, despite their high importance.

We have been investigating the structure-property relationships of the organic film systems using the well-defined systems, based on the molecular-scale structural determination by means of the scanning tunneling microscopy at room temperature. Here, we discuss the recent topics in two well-ordered film systems, (i) Organic semiconductors with enhanced intermolecular force, and (ii) Ordered OLED films.

(i) In the case of the organic semiconductors with enhanced intermolecular interaction such as picene, 6-phenacene and DNTT, phase transition of the monolayer, from face-on to bulk-like configuration, was observed on flat metal surfaces such as Au(111) and Ag(111) (Fig.1[1]). Upon the phase transition, the splitting of HOMO was seen, suggesting the formation of the dispersed HOMO band. The bulk-like, corrugated monolayer can also work as a template for multilayers, resulting in well aligned crystalline islands with huge domain sizes larger than 100 μm .

(ii) Even the case of the complicated OLED molecules such as 4CzIPN which has attracted much attention for exhibiting the thermally-activated delayed fluorescence (TADF), well ordered films were possible and their electronic and optical properties were determined [2]. Fig.2 shows the ordered monolayer of 4CzIPN on the Ag(111) surface, showing a sparse packing. Photoemission spectra of this sparse monolayer can be well fitted by the DFT calculations of DOS of the monomer, suggesting the isolated nature of the molecules. The 4CzIPN films on the glass substrate showed well defined TADF with strong angular dependence reflecting significant ordering in the film.



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Optoelectronic properties of crystalline organic thin films and hetero-structures

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Despite the recent success of optoelectronic organic devices, the fundamental understanding of the involved photo-physical processes is still incomplete. This is mainly due to the complex microstructure of blends utilized in customary devices that hampers precise microscopic interface studies. Polycyclic aromatic molecules such as oligoacenes are versatile building blocks which form crystalline films and can also be modified chemically, e.g. by fluorination which turns the p-type pentacene (PEN) into the n-type perfluoropentacene (PFP). Although the preparation of organic single crystals is frequently not possible, poly-crystalline films with large crystalline domains, predetermined molecular orientation and even of specific polymorphs can be prepared by tuning the growth kinetics and employing template effects. Using spatially resolved micro-spectroscopy allows to characterize in detail the optical properties of the various crystalline phases [1]. For the case of PEN films the exciton energies of the various polymorphs reveal small but characteristic temperature dependent shifts that reflect a notable strain at the interface due to the different thermal expansion coefficient of the organic films and the inorganic support [2]. For the case of PFP, heteroepitaxial crystalline films can be grown onto alkali halide substrates which render polarization and directional resolved optical measurements on individual crystalline molecular domains possible. Based on time- and polarization-resolved pump-probe experiments, this allows studying correlations between molecular packing motifs and singlet-exciton fission processes [3]. Furthermore, structural and optical properties of molecular acceptor/donor hetero-systems are discussed at the examples of PEN/PFP. Using the concept of templated film growth, this affords the realization of hetero-stacks with well-defined molecular interfaces either in standing or lying molecular orientation [4] and thus allow to explore the energetics and dynamics of charge transfer excitons at structurally well-defined interfaces [5].

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- [3] K. Kolata *et al.*, *ACS Nano* 8, 7377 (2014).
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The evolution of intermolecular energy bands of occupied and unoccupied molecular states in organic thin films

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The hole and electron transports in organic semiconductors occur through the intermolecular overlap of the highest occupied molecular orbitals (HOMOs) and lowest unoccupied molecular orbitals (LUMOs), respectively. The orbital overlap results in the splitting of energy levels which evolve into the energy band structure in an infinite system. A measure of the overlap is the transfer integral t . So far, only the splitting in molecular physical dimers [1] and the HOMO band dispersion [2] were observed because preparing physical oligomers beyond the dimers is not easy with organic molecules. Further, no such observations were reported for the LUMO due to the lack of suitable techniques.

In this work, physical oligomers with a controlled number of constituent molecules were realized by tin-phthalocyanine (SnPc) films on graphite grown layer-by-layer in one-dimensional columns. The observation of the splitting of the LUMO became feasible by our new technique, low energy inverse photoelectron spectroscopies (LEIPS) [3,4]. The observed spectral line shapes for both HOMO and LUMO from dimer to pentamer are well-reproduced by the calculated energy splittings based on the Hückel approximation. We determined the transfer integrals for the HOMO as (100 ± 10) meV and for the LUMO as (128 ± 10) meV [5].

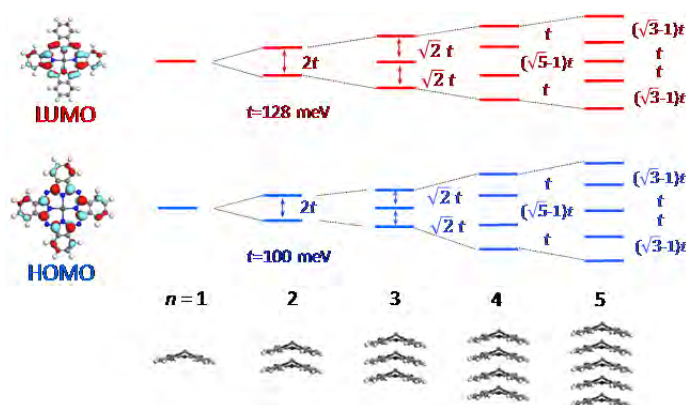


Fig. 1 HOMO and LUMO splittings of SnPc physical oligomers.

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Gas exposure effects on monolayer pentacene FET studied by using non-invasive GaIn probes

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The interactions of gaseous molecules with organic field effect transistors (OFETs) play a crucial role in the electronic transport property. Chemical interactions including oxidization are a serious issue for degradation of long-term stability of organic devices. Physical adsorption can also modify electronic states of OFETs. Gaseous molecules may diffuse into OFET film through defect sites such as grain boundaries, resulting in a change in the film structure and/or the formation of a gap state.

Recently, we have developed the non-invasive liquid-metal GaIn four-probe measurement method for the FET properties of organic monolayer and thin films [1, 2]. In OFET devices, probe-organic contact resistance affects device characteristics even in four-probe measurement because a change in contact resistance at the source probe induces a change in channel potential, resulting in different local carrier density. To overcome this problem, we introduced a feedback circuit between a source probe and a channel voltage probe to keep the channel potential constant [3].

In this presentation, we report that the electrical transport property of monolayer pentacene is highly sensitive to a small amount of exposure to O₂, N₂ and Ar gases using independently-driven four GaIn probes [2]. Liquid metal GaIn probes have been used as non-invasive conductivity electrodes for monolayer OFET films in a vacuum chamber. We carried out the fabrication of monolayer pentacene and the four-probe measurement without exposure to atmospheric air. Four GaIn probes were used *in situ* to measure conductivity in the channel separately from the overall characteristics including contact resistance at the electrode probes [3].

The results show that oxygen exposure of 1 L (10⁻⁶ Torr s) reduces mobility to 8% of the original value in the monolayer film, and the reduction is irreversible, i.e., mobility does not recover its original value after the evacuation. Furthermore, chemically inert gases of nitrogen and argon also reduce the mobility. Therefore, physisorption of gaseous molecules must be involved in this exposure effects. Taking these findings together with the results of photoelectron spectroscopy and atomic force microscopy measurements [2], we propose that the reduction is attributed to the physisorption of atoms/molecules at grain boundaries formed by the coalescence of monolayer islands.

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Nanoscale studies of organic radicals: interface, and spinterface

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Our technological development was made possible also due to the discovery and synthesis of new materials with characteristics at the nanoscale that are designed for specific purposes. This “on purpose” approach, joined to the development of preparation and growth methods, has led to use thin films rather than bulk materials in devices. For several decades thin films, surfaces and interfaces have been intensively investigated. Indeed, device performances rely on the optimized match of thin films of different nature, such as organic/inorganic semiconductors and metals for contacts.

Surprisingly, in comparison, little attention has been devoted to the deposition of organic radicals on a substrate. This might be due to the fact these materials are considered not stable enough for evaporation. In this work, we demonstrate that it is possible to evaporate and deposit organic radicals onto well-defined surfaces under controlled conditions, without degradation.

Using soft X-ray spectroscopies, performed also at synchrotrons, we investigate thin film processes, surfaces and interfaces at the nanoscale, when organic radicals are deposited on metal and metal oxide surfaces. We suggest how to design organic radicals bearing in mind the thermodynamic factors that govern thin film stability, with the purpose of obtaining not only a chemically stable radical, but also stable thin films. We investigate the thermal and air stability of the deposited films, and we explore the influence of the surface/radical chemical bond and the role of surface defects on the magnetic moment at the interface. We find that organic radicals are physisorbed and keep their magnetic moment on inert and passivated surfaces, while defective sites such as oxygen vacancies or presence of OH groups lead to chemisorption of the organic radicals on the surface with quenching of their magnetic moment.

Our work shows that the use of X-ray based techniques represents a powerful approach to reveal the mechanisms governing complex interfaces, such as radical/metal and radical/metal-oxide where it is important to describe both charge and spin behavior (spinterfaces). A deep understanding of stable radical/inorganic spinterfaces may open the way to use radicals in solid state devices, or as quantum bits with dedicated configurations, as proposed for other molecular quantum bits, and in spin-based electronics.

[1] M.B. Casu, Acc. Chem. Res. 51, 753 (2018).

Introduction to JSPS and its international programs

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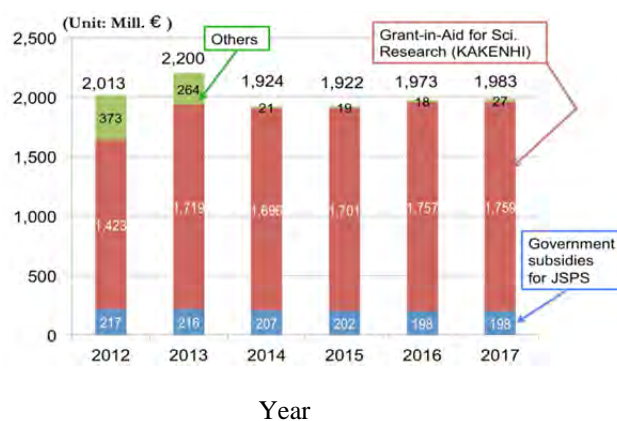
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In this workshop I will briefly introduce *Japan Society for the Promotion of Science* (JSPS) and its international programs for Japan-over sea countries research collaboration. JSPS was established in 1932. Through open competitive research grants and research fellowships for all research fields, now JSPS is recognized as the largest funding agency with the longest history in Japan.

JSPS's three main supports are

- (1) Grant to research projects: Grant-in-Aid, well known as “KAKENHI”, with €1,000,000,000/80,000 projects)
- (2) Fellowships: 6,000 Japanese pre-/post-docs, for researchers at Japanese Institutions, regardless of their nationality.
- (3) International programs:
 - (i) International scholarships from research students, postdocs to established researchers
 - (ii) Bi-lateral programs
 - (iii) Core-to-core program (multi-lateral program).

There are other programs for creating diverse world-level knowledge and enhancing education and research functions of universities etc. The JSPS budget and its transition are shown in the figure. International collaborations are also supported through KAKENHI to researchers in Japan as well as through the international programs (3).



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<JSPS-Stockholm: <http://www.jsps-sto.com>>

<JSPS-Tokyo: <http://www.jsps.go.jp>>

Oral Abstracts Friday

Dispersive states at molecule-metal interfaces

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When molecules adsorb on metal surfaces, their localized states interact with the extended states of the metal. In special circumstances, this can result in molecule-derived states acquiring a k -space dispersion. Such cases are of considerable interest, because they indicate a strong lateral interaction between molecules.

While the measurement of the dispersion as such is standard in angle-resolved photoelectron spectroscopy, the unambiguous identification of a dispersing state as being of molecular origin requires additional information on the corresponding wave functions. As I will illustrate with the help of two examples, this information can come from either photoelectron tomography (PT) or from scanning tunneling spectroscopy/microscopy (STS/STM), both of them adapted for the specific task of addressing dispersing states.

The first example is PTCDA/Cu(100). Here we apply an extension of PT beyond the plane wave approximation that is able to deal with dispersing states. We show that the interaction and hybridization of the lowest unoccupied molecular orbital with substrate states leads to its occupation and the formation of a strongly dispersing intermolecular band (1.1 eV band width) [1].

The second example is the well-known PTCDA/Ag(111) interface state. Here we revisit the question of whether this state is just the up-shifted Shockley surface state of the bare Ag(111) surface, or whether this state has some intrinsic molecular component in its wave function. To study this question, we introduce a new variant of STS, so-called Feature-Detection STS (FD-STs). Our results suggest that the presently accepted model for the metal-molecule interface state at PTCDA/Ag(111) and similar interfaces is incomplete [2].

[1] D. Lüftner *et al.*, Phys. Rev. B 96, 125402 (2017).

[2] A. Sabitova *et al.*, submitted.

Formation of occupied and unoccupied hybrid bands at interfaces between metals and organic molecules

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Efficient charge transport in organic semiconductors and sufficient charge injection at their interfaces with electrodes is crucial for the performance of organic molecule-based electronic devices. Band formation fosters effective transport properties and can be found in organic single crystals of large π -stacking aromatic molecules. However, at molecule/metal interfaces hybrid band formation and band dispersion is a rarely observed phenomenon. Using angle-resolved two-photon photoemission (see Fig. 1) supported by density functional theory calculations we demonstrate such band formation for three different molecule/metal systems in the energy region of occupied as well as unoccupied electronic states. In all cases, strong adsorbate/substrate interactions result in formation of interface states due to hybridization between localized molecular states and delocalized metal bands (sp- or d-bands). These interface states exhibit significant dispersions. Our study reveals that hybridization in combination with an extended well-ordered adsorption structure of the π -conjugated organic molecules is a striking concept to receive and experimentally observe band formation at molecule/metal interfaces.

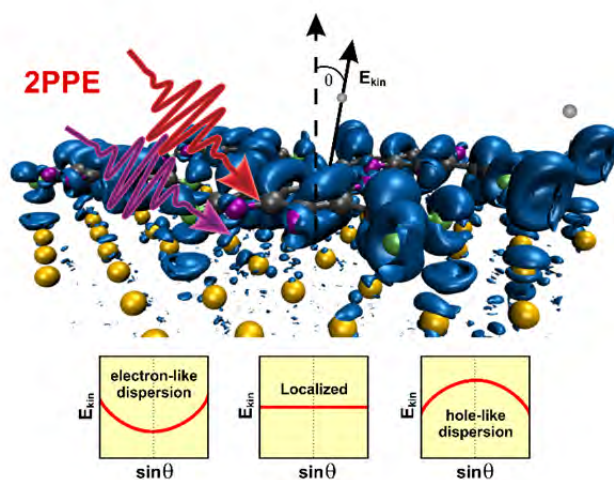


Fig.1 Angle-resolved two-photon photoemission is utilized to gain information about the dispersion (*viz.* electron localization/delocalization) of electronic states at organic molecule/metal interfaces.

Unoccupied electronic states and excited dimer formation at the perylene/graphite interface

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Perylene (see Fig.1) and its derivatives have attracted widespread interest with regard to applications in various electronic devices. In this study, perylene monolayer films on a graphite substrate have been investigated by a combination of two-photon photoemission (2PPE) spectroscopy, low energy electron diffraction (LEED), scanning tunneling microscopy (STM), and photoluminescence spectroscopy.

When the graphite substrate was covered with a monolayer perylene film, visible light emission was observed in response to incident laser light used for 2PPE. Fig. 1 shows photographs taken during the 2PPE experiments, in which green-yellowish and orange light emissions were observed for room temperature (RT) and low temperature (LT, 90K) samples, respectively. At low temperature, visible light with a wavelength at around 630 nm was observed. The overall spectral features are very similar to those reported for perylene α crystals [1], and the origin of the 630 nm peak can be ascribed to the photon emission from an excited state of a molecular dimer (that is, an excimer). Actually, dimerized pairs consisting of single molecular protrusions are seen in the STM image in Fig. 1. The mechanism for the photon emission was examined by acquiring the photon-energy dependent 2PPE spectra of a 1 ML perylene film (Fig. 2). At 90 K, the strong peak “EXCIMER” appeared +1.05 eV above the Fermi level (E_F). Therefore, we propose that the photon emission in Fig. 1 results from transition between the EXCIMER and HOMO levels. To date, visible photon emission from ultrathin 2 ML (or thicker) films has been reported for perylene [2] and its derivatives [3]. The difference between the present data and that obtained from previous studies is that luminescence quenching by the substrate is suppressed on the graphite substrate used in the work reported herein, due to the reduced substrate-molecule interaction as compared to that with a metallic substrate [2,3]. Instead, intermolecular interactions contributed strongly to the formation of a bulk-like structure, as evidenced by the generation of a dimerized configuration having an α crystal-like structure. At room temperature, the strong EXCIMER peak changed to an unoccupied feature with tail component toward higher energy side, and this resulted in the broadened luminescence spectrum in Fig. 1.

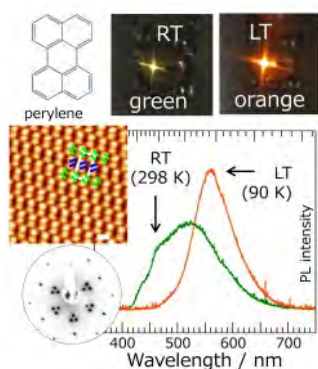
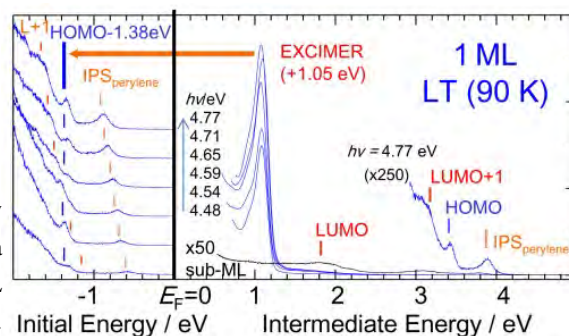


Fig. 1 Photoluminescence from the perylene 1 ML film. Excited at a photon energy of 4.77 eV.

Fig. 2 Photon energy dependent 2PPE spectra of perylene 1 ML acquired at 90 K.



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Critical interplay of atomic structure and level alignment in organic/inorganic interfaces

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The versatile tunability of hybrid inorganic/organic materials makes them promising candidates for more efficient photovoltaic and electronic devices. One aspect that hinders advances in this field is the lack of knowledge or understanding about how the electronic and atomic degrees of freedom cooperate or compete in the final, desired, interface properties. Here we show how work function changes and level alignments are modulated by the structure of the organic components in model hybrid systems comprising strong electron acceptor molecules and acenes, both adsorbed on H/Si(111). We can explain the geometry adsorption preferences quantitatively through the competition between molecule-molecule and molecule-surface interactions. Furthermore, we show that temperature induces large fluctuations in the interface dipole and that for certain systems, the consideration of large commensurate cells is necessary for a quantitative description of level alignment.

Spectroscopy and imaging of photocarriers in organic functional films probed by two-photon photoemission

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Understanding of carrier dynamics at organic functional films is essentially important for further achievement of organic electronics. We have employed two-photon photoemission (2PPE) spectroscopy for the organic films deposited on several substrates, which can sensitively detect the photoexcited electron in the molecular unoccupied states (e.g. the lowest unoccupied molecular orbitals (LUMOs)) with high energy and time resolutions.

In case of C_{60} fullerene thin films deposited on an inert HOPG graphite substrate, photocarrier electrons in LUMO and LUMO+1 are clearly resolved with intense signals (Fig. 1(a)) exhibiting the decay dynamics with a fs-ps regime [1]. In contrast, C_{60} deposited on a metal Au(111) substrate shows broader 2PPE spectral features due to a strong organic-metal interaction [2]. Furthermore, it has also been demonstrated that the energies of LUMOs (as well as HOMOs) of C_{60} can be designed by chemical modification of depositing an alkanethiolate self-assembled monolayer on an interface [3].

In addition, the 2PPE spectroscopy can be extended to 2PPE electron microscopy (2P-PEEM) to detect spatially resolved photocarrier dynamics. Figs. 1(b) and 1(c) compare the standard (one-photon) and 2P-PEEM for 0.2 monolayer C_{60} /HOPG, showing the successful imaging of the photocarrier electrons generated in the C_{60} nanostructured islands [4].

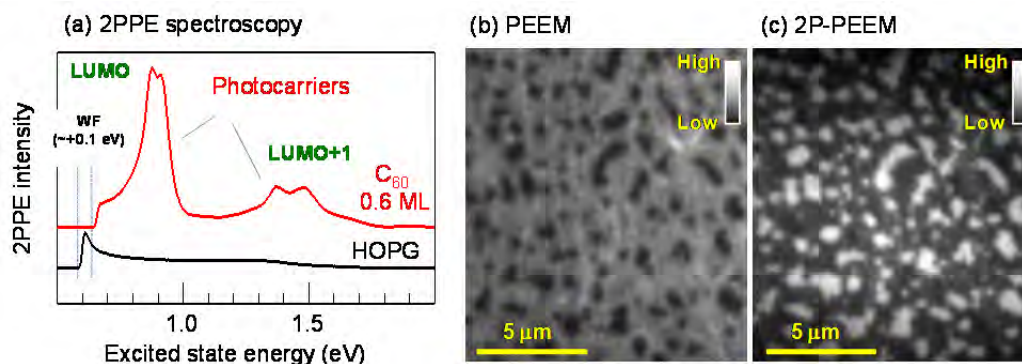


Fig. 1 (a) 2PPE spectra for 0.6 monolayer (ML) C_{60} film on HOPG, (b) standard (one-photon) photoelectron emission microscopy (PEEM) for 0.2 ML C_{60} /HOPG, and (c) 2P-PEEM for the same area of (b) [4]. Photocarriers occupying LUMOs in the C_{60} islands are imaged in 2P-PEEM.

- [1] M. Shibuta *et al.*, Sci. Rep. 6, 35853 (2016).
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Organic-inorganic energy-level alignment: From academic interfaces to devices

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Contact formation at organic-inorganic interfaces is of utmost importance for the performance of organic electronic devices. Organic-metal interfaces serve as well-defined model systems and interface energetics and chemical reactions are accessed by ultraviolet- and X-ray photoelectron spectroscopy (UPS and XPS) [1]. Metal work functions -and thus the energy-level alignment to subsequently deposited organic layers- can be tuned by strongly coupled molecular monolayers [2]. However, molecular diffusion can counteract this effect and we developed UPS and XPS-based indicators to predict the actual arrangement of organic heterostructures on metal substrates [3]. The work function of transition metal oxides can be controlled by oxygen vacancies and by careful preparation the work function of VO₂ can reach up to 6.7 eV [4]. Likewise, the properties of organic-inorganic perovskite thin films depend critically on the preparation conditions and we show how beneficial energy-alignment for photovoltaic applications can be achieved for both, solution processed and vacuum-sublimed perovskite films [5]. Moreover, deposition of MoO_x on hybrid perovskite leads to p-n junctions induced by local electronic doping [6]. In a similar way, an inversion layer can be induced in n-Si and consequently a dopant-free p-n junction is formed [7].

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- [6] Q.-D. Ou *et al.*, Adv. Mater. 30, 1705792 (2018).
- [7] T. Sun *et al.*, Phys. Status Solidi RRL, 11, 1700107 (2017).

Poster Abstracts

Poster Session, Wednesday, 24.10.2018

- 1 Rachana Acharya, MPI Stuttgart**
Alkyl- and fluoroalkyl-phosphonic acid self-assembled monolayer hybrid dielectrics for organic transistors
- 2 Mohsen Ajdari, Uni Heidelberg**
High resolution electron energy loss spectroscopy of N-heteropolycycles on metal surfaces
- 3 Kenichi Aoyama, Tokyo Univ. of Science**
Characterizing chemical and electronic structure of graphitic carbon nitride with photoelectron spectroscopy
- 4 Axel Belser, Uni Tübingen**
Interaction channels between perfluorinated iron phthalocyanine and Cu(111)
- 5 James Borchert, MPI Stuttgart**
Organic TFTs with low contact resistance
- 6 Giulio d'Acunto, Lund Univ.**
ALD of HfO₂ on SiO₂: Identification of surface species by ambient pressure XPS and IR spectroscopy
- 7 Michael Geiger, MPI Stuttgart**
Quantitative analysis of the density of trap states in organic semiconductors by electrical transport measurements on low-voltage thin-film transistors
- 8 Katharina Greulich, Uni Tübingen**
Interface properties of FePcF₁₆ on MoS₂
- 9 Jan Hagenlocher, Uni Tübingen**
Influence of structural defects on the energy level alignment in planar pentacene-perfluoropentacene heterojunctions
- 10 Sebastian Hammon, Uni Bayreuth**
Simulating the pump-probe photoemission process from organic semiconductors in real-time
- 11 Martin Hantusch, IFW Dresden**
Photoelectron spectroscopy of F₆TCNNQ-polycyclic hydrocarbon interfaces
- 12 Philipp Hurdax, Uni Graz, Austria**
Charge transfer and molecular level alignment on dielectric interlayers on metals

- 13 **Masato Iwasawa, Tsukuba Univ.**
Thermal stability of the surfaces of organic single crystals under UHV
- 14 **Hiroyuki Ichikawa, Chiba Univ.**
Interface dipole of the bulk-heterojunction of organic solar cell
- 15 **Svenja Janke, Duke Univ., NC/USA**
Level alignment prediction of hybrid inorganic-organic systems: Tetracene and pentacene on H/Si(111)
- 16 **Tobias Junghöfer, Uni Tübingen**
Organic radical films investigated by X-ray-based spectroscopies
- 17 **Reimer Karstens, Uni Tübingen**
Iron-phthalocyanine on rutile: Main interaction channel oxygen vacancies at the surfaces
- 18 **Benedikt Klein, Uni Marburg**
Molecular topology and surface chemical bond: Alternant vs. non-alternant aromatic molecules
- 19 **Michael Kothe, Uni Marburg**
Evolution of TiOPc-films on Ag(111): Bilayer stacking enables ultra-smooth layers
- 20 **Christian Kumpf, FZ Jülich**
Two-dimensional growth of dendritic islands: NTCDa on Cu(001) studied in real time
- 21 **Christian Kumpf, FZ Jülich**
Steering the growth of multiple ordered hetero-molecular phases by utilizing intermolecular repulsion
- 22 **Alexander Lerch, Uni Marburg**
Time-resolved spectroscopy of electron transfer processes at metal/organic interfaces
- 23 **Xianjie Liu, Linköping Univ.**
Energetic degradation of organometal halide perovskite films upon oxygen, water and illumination
- 24 **Ahmed Mansour, HU Berlin**
Investigating the electronic structure and chemical interactions in doped poly(3-hexylthiophene) with the Lewis acid dopant tris(pentafluorophenyl)borane
- 25 **Matthias Meissner, NIMS-IMS, Okazaki**
Orbital tomography of a strong hole-vibration coupling molecule
- 26 **Christian Metzger, Uni Würzburg**
Orbital imaging of the non-planar molecules

- 27 Andreas Opitz, HU Berlin**
Exciton binding energy of organic materials: Valence vs. core excitation
- 28 Maryline Ralaïarisoa, HU Berlin**
Influence of water, oxygen, and air exposure on the electronic structure of methyl ammonium lead mixed iodide-chloride $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ perovskite films
- 29 Foqia Rehman, Lund Univ.**
Monitoring of atomic layer deposition by synchrotron-based ambient pressure XPS: Towards millisecond time resolution
- 30 Haruki Sato, Chiba Univ.**
Development of angle-resolved low energy inverse photoelectron spectroscopy apparatus
- 31 Thorsten Schultz, HU Berlin**
Importance of homogeneous substrates for ionization potential determination by ultraviolet photoelectron spectroscopy
- 32 Mathias Schwendt, Uni Graz**
Photoemission tomography for π -extended peri-xanthenoxanthene on Cu(111)
- 33 Kohei Shimizu, Chiba Univ.**
"Shallow states" of organic films observed by hv-dependent high-sensitivity photoemission
- 34 Vipilan Sivanesan, Uni Heidelberg**
Exciton dynamics in pentacene-perfluoropentacene heterostructures
- 35 Serguei Soubatch, FZ Jülich**
Dependence of the adsorption height of graphenelike adsorbates on their dimensionality
- 36 Stefan Tautz, FZ Jülich**
Nanoscale engineering with molecules at surfaces
- 37 Ryohei Tsuruta, Tokyo Univ. of Science**
Epitaxial growth of the organic pn heterojunctions
- 38 Yuki Uemura, Chiba Univ.**
Impact of the molecular quadrupole moment in the molecularly mixed film of organic semiconductors

- 39 Ryota Usui, Chiba Univ.**
Enhancement of signal intensity for the inverse photoelectron spectroscopy by the surface plasmon resonance of the Ag nanoparticles
- 40 Ana Valencia, HU Berlin**
Electronic and optical properties of oligothiophene/F4TCNQ charge-transfer complexes: The role of donor conjugation length
- 41 Qiankun Wang, HU Berlin**
Switching the surface electronic properties of polar ZnO crystals with photochromic pyridine-dihydropyrene molecular layers
- 42 Rongbin Wang, HU Berlin**
Solution-processing vs. vacuum-sublimation: Impact on the electronic structure of methylammonium lead iodide perovskite thin films
- 43 Berthold Wegner, HZB & HU Berlin**
Predicting ion pair formation yield in molecular electrical doping from redox-potentials
- 44 Xiaomin Xu, HU Berlin**
Microstructure and elastic constants of transition metal dichalcogenide monolayers from friction and shear force microscopy
- 45 Jin-Peng Yang, Yangzhou Univ.**
Band dispersion of $\text{CH}_3\text{NH}_3\text{PbI}_3$ single crystal
- 46 Xiaosheng Yang, FZ Jülich**
Identifying molecular orbitals and on-surface reaction products with photoemission tomography
- 47 Koki Yoshida, Tokyo Univ. of Science**
Structural and electronic characterization on organic semiconductor homojunctions
- 48 Fengshuo Zu, HU Berlin**
Band structure of $\text{CH}_3\text{NH}_3\text{PbI}_3$ and $\text{CH}_3\text{NH}_3\text{PbBr}_3$ perovskite single crystals from angle-resolved photoelectron spectroscopy

Alkyl- and fluoroalkyl-phosphonic acid self-assembled monolayer hybrid dielectrics for organic transistors

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Hybrid gate dielectrics composed of a thin metal oxide and an organic self-assembled monolayer (SAM) are useful for low-voltage organic thin-film transistors (TFTs) by providing a large dielectric capacitance while minimizing gate leakage and improving overall TFT performance. We have fabricated and characterized organic TFTs with gate dielectrics composed of a plasma-grown AlO_x layer and a solution-processed phosphonic acid (PA) SAM, in which the terminal group and the alkyl chain length of the molecule forming the SAM were varied. Two different terminal groups, namely alkyl and fluoroalkyl groups, and a chain length ranging from 6 to 18 carbon atoms for the alkyl and 6 to 14 carbon atoms (in steps of 2 carbon atoms) for the fluoroalkyl PA molecules were used to form the SAMs. Optimum TFT characteristics are found for the medium chain length molecules in both alkyl and fluoroalkyl-phosphonic acid SAMs, which could potentially be due to maximum ordering and packing density in the SAMs. We explore the possibility of verifying these results with various spectroscopic measurements.

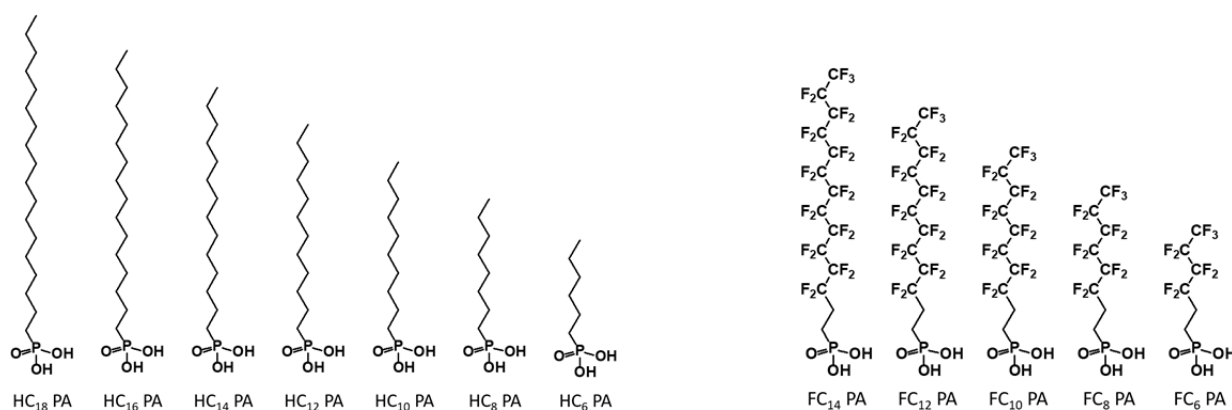


Fig.1 Alkyl- and fluoroalkyl-phosphonic acid molecules

High resolution electron energy loss spectroscopy of N-Heteropolycycles on metal surfaces

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Understanding the adsorption and electronic properties of organic molecules on inorganic substrates provides important insights into the charge transport properties at organic/inorganic interface, which is crucial in determining the performance of electronic devices based on organic semiconductors. High resolution electron energy loss spectroscopy (HREELS) is a powerful tool for investigating both the adsorption geometry via vibrational excitations and electronic properties of the molecules by utilizing electrons with sufficient energy to excite electronic transitions. We successfully employed HREELS to investigate the adsorption and electronic properties of several tetraazaperopyrene (TAPP) derivatives as a function of coverage on Au(111). TAPPs belong to N-Heteropolycyclic aromatic compounds that are promising candidates for n-channel semiconductors which are of great interest especially for field effect transistors [1, 2]. We found that TAPPs without bulky substituents adopt a planar geometry with respect to the substrate in both the monolayer (ML) and thin films (up to 10 ML). Contrary, in their crystal structure the molecules are tilted up to 35° between the molecular planes in neighboring stacks. This adsorption behavior is attributed to the ability of the plane Au(111) surface in adsorbing the planar molecules in a flat adsorption geometry to maximize the substrate/adsorbate interactions and thereby the binding energy. This substrate-induced strictly planar growth, results in the formation of a "flat" monolayer, on which additional molecules also adsorb in a planar fashion.

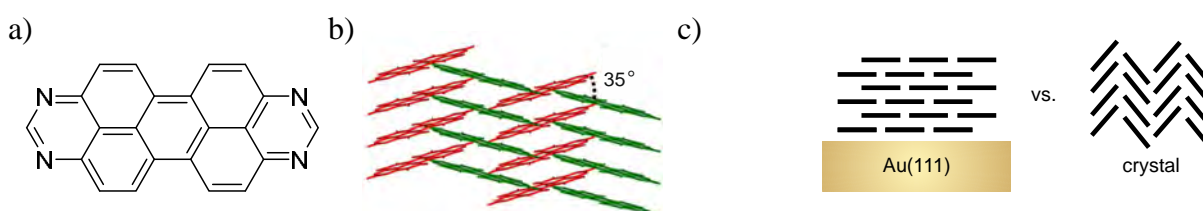


Fig. 1 a) Schematic of TAPP molecule; b) Crystal structure of TAPP;
c) Geometry of TAPP on Au(111) in comparison to its crystal structure [2].

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Characterizing chemical and electronic structure of graphitic carbon nitride with photoelectron spectroscopy

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Graphitic carbon nitride [g-CN, Fig. 1(a)] has attracted enormous interests since it is found that g-CN exhibits the photocatalytic activity under the irradiation of visible light, such as hydrogen evolution via water splitting [1]. g-CN was believed to be g-C₃N₄, where the two dimensional covalent sheets of melem, the repeating unit of g-CN [Fig. 1(a)], are formed. However, the recent structural investigations revealed that g-CN is the linear polymer of melem, melon [Fig. 1(a)] [2–4]. Nevertheless, the interpretation of X-ray photoelectron spectra of g-CN appears to be incomprehensive in previous literature. Moreover, the electronic structure near the energy gap, which is indeed important for understanding the photocatalytic reaction, has not been investigated.

In this work, by utilizing the g-CN and melem films, we reappraised the N 1s X-ray photoelectron spectra of g-CN and identified g-CN as melon [Fig. 1(b)]. The analysis with ultraviolet photoelectron spectroscopy and inverse photoemission spectroscopy revealed the energy levels preferable to water splitting. Theoretical calculations suggest that, along the polymer chain, only the LUMO exhibits the energy dispersion, whereas both the energy dispersions of the HOMO and LUMO are present along π -stacking [5].

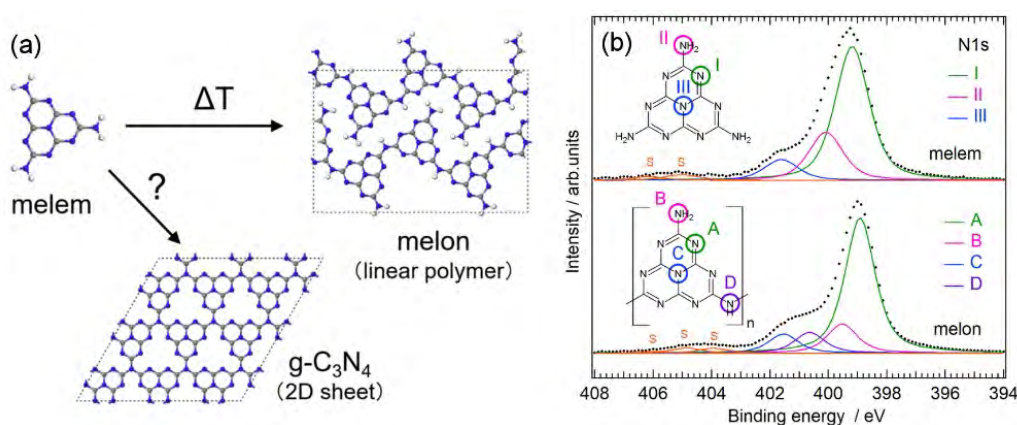


Fig. 1 (a) Process of thermal polycondensation of melem (gray, blue and white balls represent carbon, nitrogen and hydrogen, respectively). (b) XPS N1s spectra of melem (top) and melon films (bottom). Black dots are the measured spectra after subtracting Shirley backgrounds. The peaks labeled S at higher binding energy might be attributed to shake-up satellites.

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Interaction channels between perfluorinated iron phthalocyanine and Cu(111)

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The initial growth and interfacial electronic structure of perfluorinated iron phthalocyanine (FePcF_{16}) on Cu(111) has been studied using X-ray photoelectron spectroscopy (XPS) and polarization dependent X-ray absorption spectroscopy (XAS). The planar molecules are oriented preferred flat lying on the substrate surface during the growth of the first layers while the tilt angle is increased in thicker films. A clear interaction at the interface is observed, involving both the central metal ion and the macrocycle. At monolayer coverages, the Fe2p spectrum shows an interface signal at 707.1 eV, while the C-N component of the C1s spectrum is distinctly shifted with respect to the thicker films. Also the nitrogen atom is involved in the interaction, best visible in the π^* resonance of N K edge spectra recorded from molecules at the interface. [1]

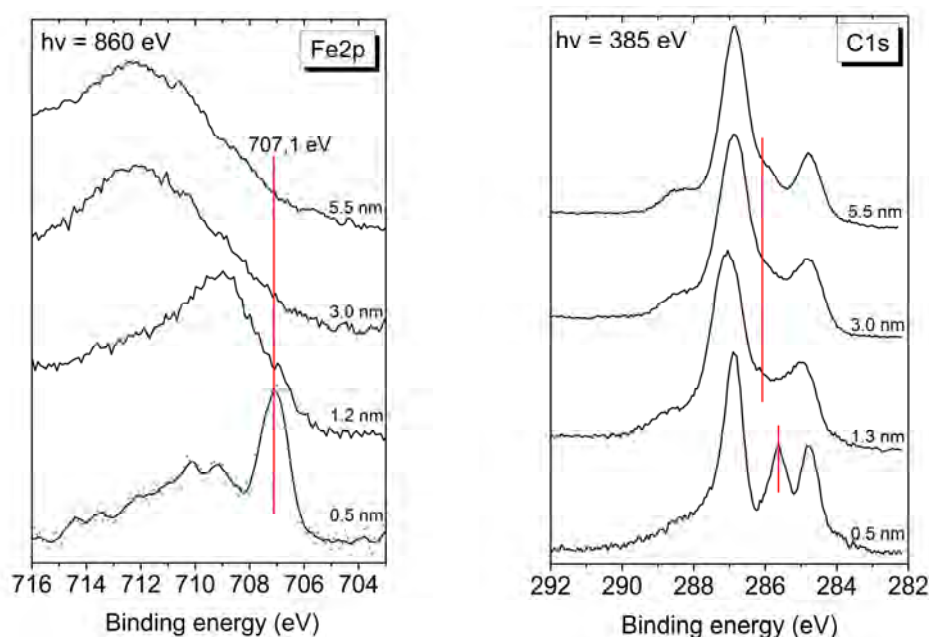


Fig. 1 X-ray photoemission spectra of the Fe2p (left) and C1s (right) core levels. Both the central metal atom and the macrocycle take part in the interaction at the interface.

[1] A. Belser *et al.*, *physica solidi status b*, submitted.

Organic TFTs with low contact resistance

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The performance of organic thin-film transistors (TFTs) can depend significantly on the device architecture. Organic TFTs fabricated in the bottom-gate, bottom-contact (BC) architecture often suffer from larger contact resistances than otherwise similar top-contact (TC) TFTs due to poor morphology of the organic semiconductor layer on the contact-metal surface and lack of a gate-field-induced charge density above the contacts, both of which limit the area for charge exchange [1]. To combat these issues, the surface of the bottom-contacts can be modified with a molecular monolayer, e.g. pentafluorobenzenethiol (PFBT), to increase the work function and improve the semiconductor morphology on the metal surfaces [1,2]. Interestingly, recent simulations [3] predict that with a sufficiently thin gate dielectric and sufficiently small injection barrier, the contact resistance of BC TFTs will be as small as (and even smaller than) that of TC TFTs. Therefore, we fabricated BC and TC TFTs using 2,9-diphenyl-dinaphtho[2,3-b:2',3'-f]-thieno[3,2-b]thiophene (DPh-DNTT) [4] with various gate dielectric thicknesses and analyzed the contact resistances. The results confirm that BC TFTs can indeed have smaller contact resistances than TC TFTs when (1) a sufficiently thin gate dielectric is used and (2) the bottom-contacts are treated with PFBT. We show optimized BC TFTs fabricated on flexible PEN substrates with a record-low contact resistance of 29 Ωcm , along with large on/off current ratio (10^9), large effective carrier mobility (4.7 cm^2/Vs), steep subthreshold slope (62 mV/decade) and very short signal propagation delay (138 ns per stage at a supply voltage of 3.7 V, measured using 11-stage ring oscillators).

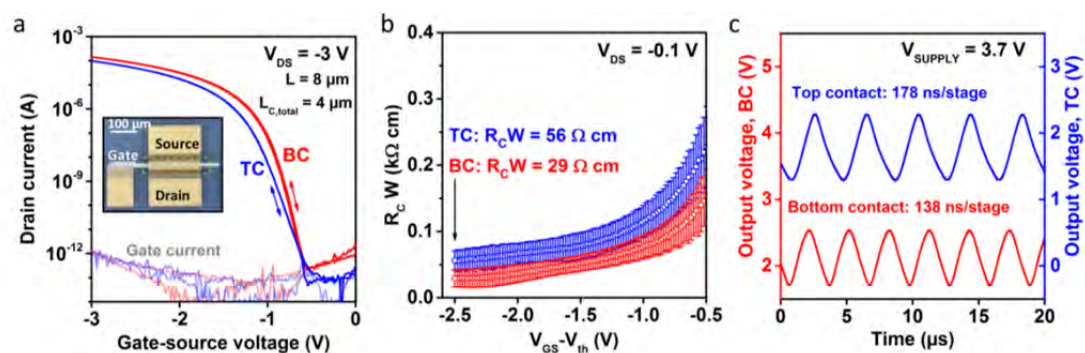


Fig. 1 Comparison of top-contact and bottom-contact DPh-DNTT TFTs: (a) transfer characteristics (b) contact resistance (c) signal propagation delay measured on 11-stage unipolar ring oscillators.

- [1] D.J. Gundlach *et al.*, J. Appl. Phys. 100, 024509 (2006).
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ALD of HfO₂ on SiO₂: Identification of surface species by ambient pressure XPS and IR spectroscopy

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Atomic layer deposition (ALD) is a powerful technique for the deposition of thin film materials with atomic scale precision. Ideal ALD schemes, which always rely on the assumption of a self-limiting nature of the growth, provide guidelines to understand how the ALD growth proceeds and which structures are produced. However, in most case, the detailed surface chemistry of the ALD process is not fully understood, as a result of side reactions, possible non-self-limiting nature of the growth, influence of surface defects and gas phase reactions [1]. In our work, we explore possibilities to gain an exact knowledge of the surface chemistry of the ALD process from the application of *in situ* and *operando* methods, which allow the investigation of surfaces during the reaction.

The ALD of HfO₂ on a native oxide-covered Si(111) surface as well as on an anatase TiO₂(101) surface from tetrakis(dimethylamido)hafnium (TDMAHf) and H₂O was studied using ambient pressure x-ray photoelectron spectroscopy (APXPS) and *in situ* fourier transform infrared spectroscopy (FTIR) with second time resolution. The ALD was carried out at temperatures in between 200 and 280°C, and the surfaced species during the process were investigated. The FTIR data show that the adsorption and reactions of TDMAHf and H₂O on the native oxide-covered Si(111) surface is self-limiting at this temperature (Fig. 1 a). All spectra used have been referenced to the previous spectrum. Operando APXPS at high temporal resolution illustrates the evolution of the C 1s, N 1s and Hf 4f core levels (cf. Fig 2). From these, Hf-amido adsorbates as well as methyl methyleneimine surface species were identified. Our study illuminates the potential of surface sensitive *in situ* and *operando* methods to gain a detailed understanding of the ALD surface process during growth.

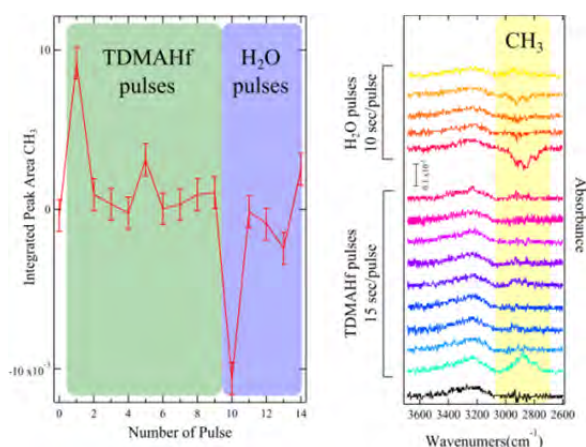


Fig.1 a) Integrated peak area vs number of pulses for the CH₃ stretching modes (2650-3050 cm⁻¹). b) FTIR differential absorbance spectra for ALD of HfO₂ on SiO₂/Si(111).

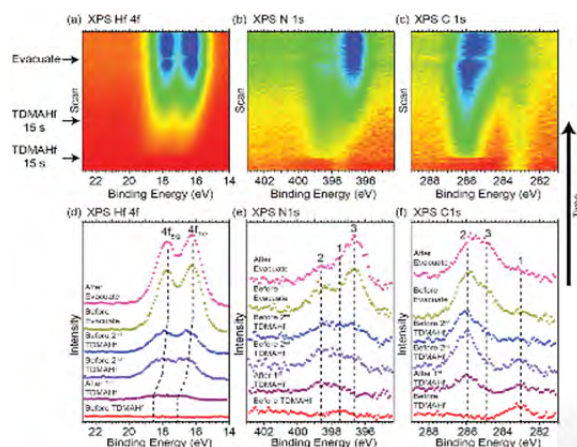


Fig.2 XPS analysis of the first half cycle of HfO₂ ALD on SiO₂/Si(111).

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Quantitative analysis of the density of trap states in organic semiconductors by electrical transport measurements on low-voltage thin-film transistors

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The electrical characteristics of thin-film transistors (TFTs) based on disordered semiconductors are greatly influenced by the density and energetic distribution of localized electronic states in the energy gap of the semiconductor. In the 1980s, Michael Grünewald *et al.* developed a method to convert a measured transfer curve of a field-effect transistor to the underlying density-of-trap-states (trap DOS) function.¹ The Grünewald method has been employed with great success, however, in all previous publications, a critical simplification was made, whereby the potential drop across the semiconductor layer was ignored.²⁻⁴ For high-voltage TFTs, in which the applied gate-source voltage drops almost entirely across the gate dielectric, this simplification is indeed justified. However, for TFTs employed in real applications, low-voltage operation is a critical prerequisite, in which case the above-mentioned simplification is no longer valid. Therefore, we have explored an extension of the Grünewald method by performing the derivation without this simplification. Our results confirm the validity of the original Grünewald method for high-voltage TFTs, but also the need for the extended Grünewald method for low-voltage TFTs. Furthermore, we used this method to investigate the correlation between the surface roughness of the gate dielectric and the trap DOS of the organic semiconductor, and the implications of the surface roughness for the TFT performance.

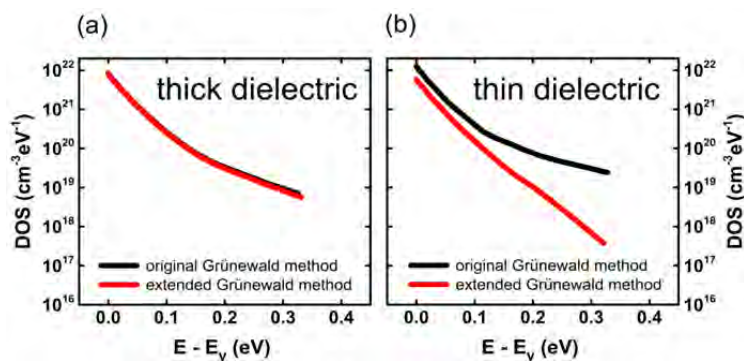


Fig. 1 Density of trap states as a function of energy above the transport level. (a) For the TFT with the high operating voltage the results show that the original Grünewald method is indeed valid. (b) For the TFT with the low operating voltage the trap DOS functions obtained with and without the simplification deviate substantially.

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Interface properties of FePcF₁₆ on MoS₂

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The recently increasing research efforts devoted to layered transition metal dichalcogenides (TMDCs) derives from their novel electronic and magnetic properties. As example, in MoS₂, the size of the bandgap and their nature (indirect to a direct) depends on the number of trilayers.^[1] Moreover, even in the bulk material, MoS₂ shows regions of high spin-polarization.^[2] Electronic properties of TMDC surfaces might be tuned by the adsorption of molecules. On the other hand, electronic and magnetic properties of transition metal phthalocyanines (TMPcs) can be tuned over a wide range. Thus, TMDC/TMPc heterostructures may exhibit novel electronic properties, which could be of high interest for efficient and flexible electronics and spintronics.

We studied interface properties of FePcF₁₆ on a MoS₂ single crystal using photoemission, x-ray absorption (XAS) and scanning tunneling microscopy (STM). Band structure measurements before and after FePcF₁₆ deposition were carried out using the ARTOF analyzer at the PM4 beamline at HZB Berlin (Figure 1). Because of the very high electron transmission (300 times higher compared to hemispherical analyzers) a very limited photon flux, radiation damage of organic molecules can be avoided.^[3] Our results indicate that uniform large-area heterostructures can be prepared. The spin state of FePcF₁₆ in films of about 1 nm is comparable to thick films of FePc on single crystalline substrates but different to thick films of FePcF₁₆ on Ag(111) and Cu(111).^[4] Generally, a weak interaction was observed between FePcF₁₆ and MoS₂.

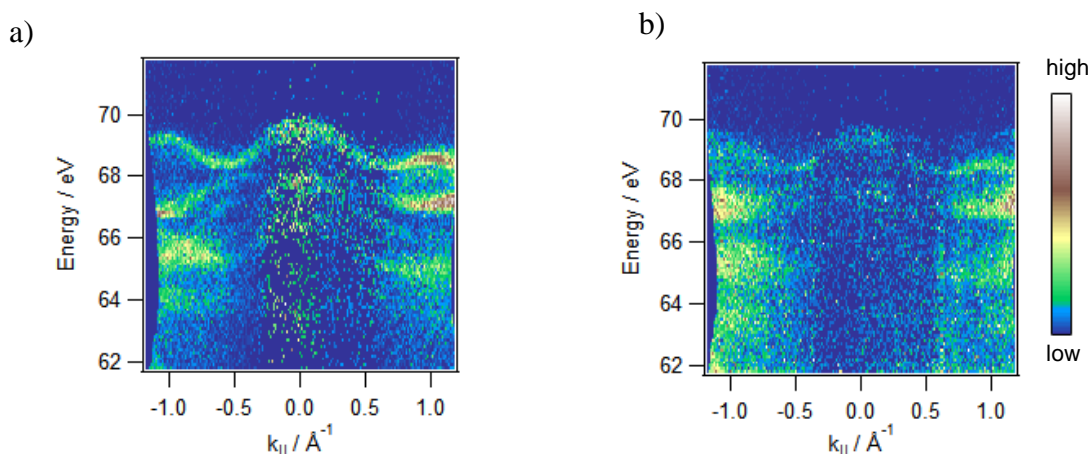


Fig. 2 ARPES band map along the K-Γ-M high symmetry line of a) MoS₂ and b) a thin layer of FePcF₁₆ on MoS₂. Upon adsorption of FePcF₁₆, the band structure of the substrate is attenuated, but still visible.

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Influence of structural defects on the energy level alignment in planar pentacene-perfluoropentacene heterojunctions

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We studied the Energy Level Alignment in planar Pentacene-Perfluoropentacene Heterostructures grown on a native silicon substrate using high-resolution Ultraviolet Photoelectron Spectroscopy (UPS). The films were grown at different substrate temperatures to introduce structural defects which were further studied analyzed by surface x-ray scattering techniques [1]. We found a connection between the magnitude of the interface dipole and the size of the crystallites within the film. We explain this behavior with the film quality dependent arising of gap states which are responsible for the number of transferred charges [2].

[1] K. Yonezawa *et al.*, Adv. Mater. Interfaces 1.5, 1400004 (2014).

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Simulating the pump-probe photoemission process from organic semiconductors in real-time

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Simulating the pump-probe photoemission process in real-time, we apply a first principles time-dependent density functional theory (TDDFT) approach. Within this theoretical framework we are able to calculate (angle-resolved) photoemission directly as a time-dependent process. Firstly, applying our pump-probe method to the one-electron hydrogen system, we are able to verify our TDDFT approach within this transparent test scenario. Secondly, following this successful test, we present first angle-resolved photoemission spectroscopy (ARPES) results (cp. Fig. 1) for the real-time pump-probe simulation of the organic benchmark molecule perylene-3,4,9,10-tetracarboxylic dianhydride (PTCDA).

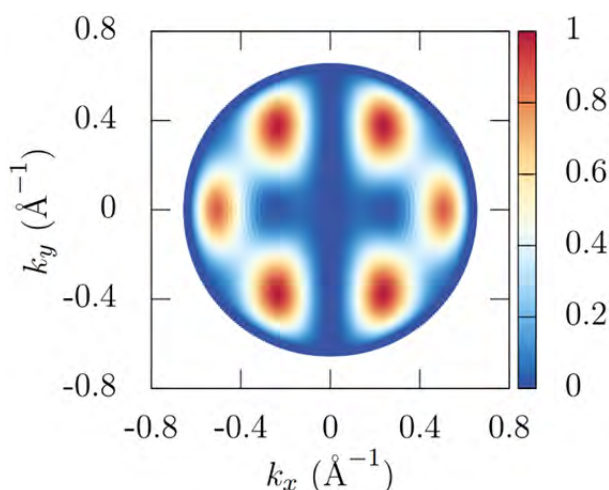


Fig. 1 ARPES intensity momentum map obtained from the real-time simulation of the pump-probe process for PTCDA: Photoemission was recorded after a first pulse with an energy of 2.1 eV, followed by a second pulse with an energy of 6.0 eV and a delay of 10 fs.

Photoelectron spectroscopy of F₆TCNNQ-polycyclic hydrocarbon interfaces

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The doping of polycyclic hydrocarbons, e.g. pentacene, with hexafluorotetracyanonaphthoquinodimethane (F₆TCNNQ) offers the opportunity for new organic electrical devices [1]. While doping affects the bulk system, examining the physical processes at the interfaces of organic semiconductors in more detail is also in the focus of recent research in order to enhance the performance of organic electrical devices. Our work investigates the charge transfer across these interfaces.

We present results for thin film systems consisting of pentacene or di-benz-pentacene (DBP) and F₆TCNNQ, deposited in a multi-step process and analysed after each deposition step by photoelectron spectroscopy. Significant changes are observed in the valence, the nitrogen and the carbon core levels. The intensity ratio of the characteristic F₆TCNNQ-C1s-peaks (286.3 eV; 287.2 eV), as shown in Figure 1, is varying with the layer thickness which indicates a reduction of the electron acceptor in the interface area. The subtraction of the pristine spectra of F₆TCNNQ and of the polycyclic hydrocarbon from the hetero-junction spectrum reveals two clear peaks (285.3 eV; 286.5 eV) which correspond to F₆TCNNQ⁻-ions [2]. Hence, the changes in the photoelectron spectra are directly correlated with the charge transfer processes across the interface.

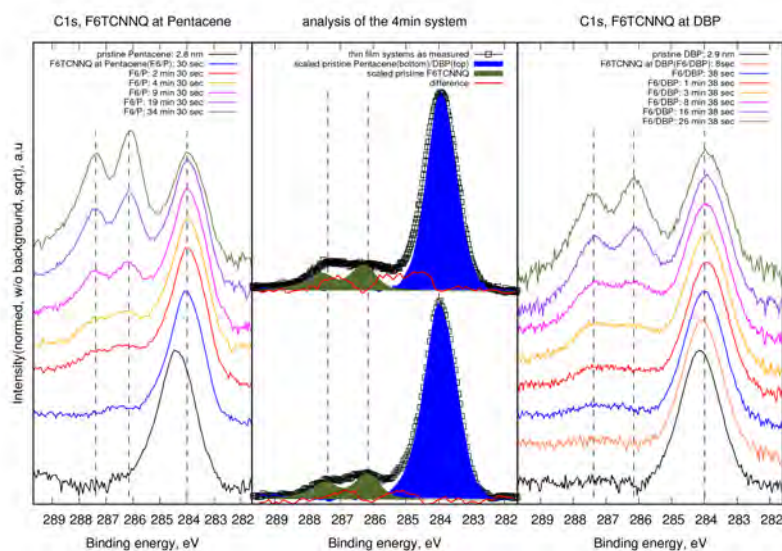


Fig. 1 C1s-core levels of F₆TCNNQ/pentacene and F₆TCNNQ/DBP systems with various deposition times (same rates) and an analysis of two similar systems.

- [1] B. Lüssem *et al.*, Nature Comm., 4, 2775 (2013).
- [2] D. Waas *et al.*, physica status solidi c, submitted (2018).

Charge transfer and molecular level alignment on dielectric interlayers on metals

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Sergey Soubatch^{2,3}, F. Stefan Tautz^{2,3}, Georg Koller¹, Peter Puschnig¹,
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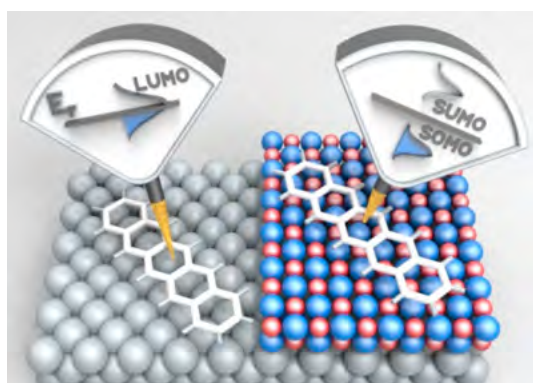
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It is becoming accepted that ultrathin dielectric layers on metals are not merely passive decoupling layers, but can actively influence orbital energy level alignment and charge transfer at interfaces. As such, they can be important in applications 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(100) 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(100), 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.



[1] M. Hollerer *et al.*, ACS Nano 11, 6252 (2017).

Interface dipole of the bulk-heterojunction of organic solar cell

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In order to improve the power conversion efficiency (PCE) of the organic solar cell (OSC), great efforts have been made to reduce the energy loss and increase the open circuit voltage (V_{OC}). For this purpose, the energy of each step of the OSC process is indispensable. Although the energies of the exciton and charge-transfer (CT) state has been precisely determined, the energy of the separated free holes and electrons state (CS state) are only ambiguously evaluated using the ultraviolet photoelectron spectroscopy (UPS) and optical gap, or the oxidation/reduction potentials of individual materials. Further, the interface dipole between the donor (D) and acceptor (A) layers are often ignored. The recent OSC with low-energy loss shows small difference in energy between the CT and CS states, even the CT states is lower than the CS states. To explain the charge separation from the lower CT to higher CS states, the entropy gain is proposed [1].

In this study, we demonstrated a procedure to determine the energy of the CS states and applied it to the bulk-heterojunction of the low-energy loss OSC, PNOz4T and PCBM [2]. At first, we precisely determined ionization energy (IE) and electron affinity (EA) of each material using ultraviolet photoelectron spectroscopy (UPS) and low energy inverse photo-electron spectroscopy (LEIPS) [3], respectively. Then the interface dipole between the D and A layers Δ was estimated from the shift of the core levels using X-ray photoelectron spectroscopy (XPS). Unfortunately, the core level shift was not able to be directly determined because all the elements in the PCBM molecule (C, N, O, H) are common in PNOz4T. We applied the classical least squares to the angle-resolved XPS data to decompose the C1s spectra (Fig. 1) to determine Δ . Based on the values of Δ , IE, and EA, we obtained the energy level diagram (Fig. 2).

The energy of the CS state was found to be 1.33 eV which is lower than that of the CT states, 1.52 eV [2]. As a result, the transition from the CT state to the CS state can proceed without considering the entropy [1].

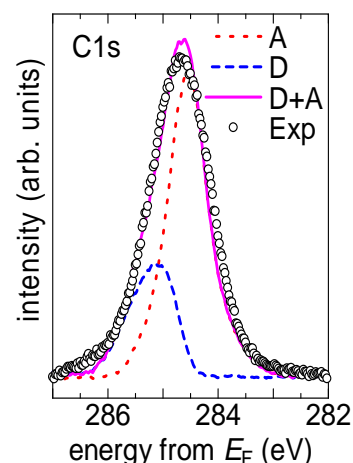


Fig. 1 Decomposed XPS spectrum of PNOz4T (D) and PCBM (A).

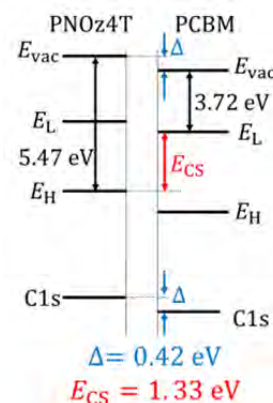


Fig. 2 Energy level diagram.

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Thermal stability of the surfaces of organic single crystals under UHV

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The organic single crystals (OSCs) have been widely utilized due to its high crystallinity and resulting charge mobility. Although the electronic structure of the OSCs have been gradually clarified, the surface/interface properties of OSCs that directly impact on the device performance are yet to be provided. Recent reports have revealed that the electronic properties of OSCs can be significantly affected by the microscopic surface features such as steps.

In order to obtain the more insight into the cleanliness and stability of the surface of OSCs, especially that in UHV condition, we fabricated single crystals with well-known organic semiconductors, such as Pentacene, Rubrene, Tetracene, Perylene, and TCNQ, and investigated their surface under UHV condition.

The surfaces of the single crystals used in this work had inert and clean step-terrace structure at RT in the air. The surfaces of Pentacene and Rubrene-SC were stable even in UHV at RT (Fig.1(a)). However, the surface molecules desorped from both terraces and step edges at 45°C/UHV, resulting in the layer-by-layer removal.

By contrast, the surface structures of Tetracene, Perylene, and TCNQ-SC cannot be maintained at UHV, as shown in Fig.2 (b). The surface flatness of these crystals were gradually lost under UHV on account of the desorption and the cohesion. The surface roughness was more than 30 nm and original step-terrace structure was not observed after 24h under UHV. On the other hand, the roughening of the surface of TCNQ-SC was suppressed at low temperature of -160°C.

These findings indicate that the surface stability show no obvious relation with the molecular weight or the melting point of OSCs. Therefore, we have to pay particular attention to the surface conditions when utilizing OSCs under vacuum.

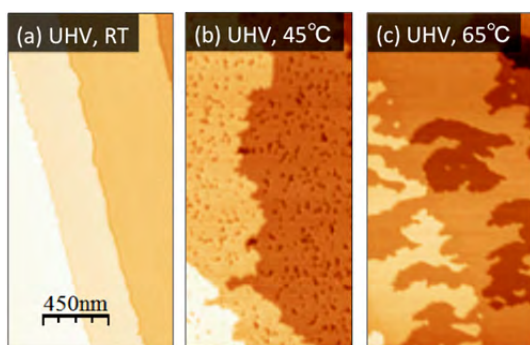


Fig.1 AFM images of Pentacene-SC

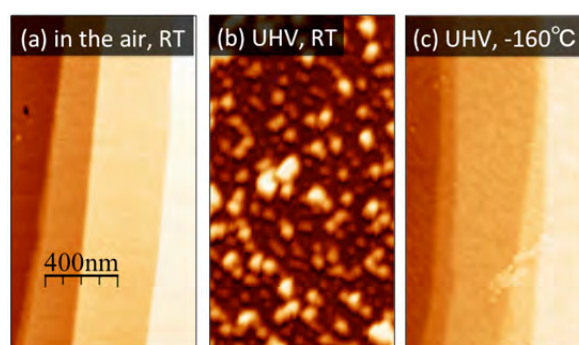


Fig.2 AFM images of TCNQ-SC

Level alignment prediction of hybrid inorganic-organic systems: Tetracene and pentacene on H/Si(111)

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Hybrid organic inorganic systems allow to combine the properties of organic and inorganic substances at the nanoscale and hence open up a wide area for construction of new materials with tunable properties. The position of carrier levels and their alignment determine electronic properties of semiconductor interfaces. In the present work, we address the fundamental question of electronic level alignment from first principles at the level of hybrid functionals within all electron, full potential density functional theory (FHI-aims [1]) for two paradigmatic organic-inorganic semiconductor interfaces, the singlet fission materials tetracene and pentacene on H/Si(111). We investigate the structure of either interface in the low-coverage and in the monolayer regimes and demonstrate that a large coincidence cell between the organic film and inorganic substrate, comprising up to ~1200 atoms, is necessary to describe the correct level alignment quantitatively. We find that a type-I heterojunction is formed in the low-coverage regime, while a type-II heterojunction is predicted in the monolayer regime that allows a potential charge separation between organic and inorganic components.

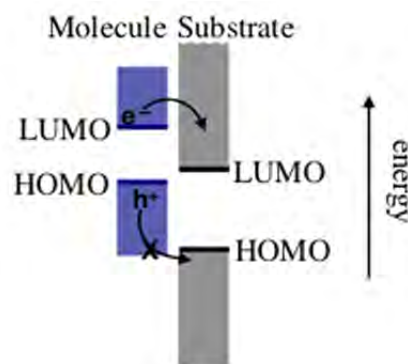


Fig. 3 Schematic energy level alignment of the frontier orbitals of a pentacene monolayer film (blue) on H/Si(111) (grey) calculated with HSE06 for a unit cell with ~1000 atoms. Electrons can transfer from the monolayer to the substrate while holes remain on the monolayer, allowing a potential charge separation.

[1] V. Blum *et al.*, *Comp. Phys. Comm.* **180**, 2175, (2009).

Organic radical films investigated by X-ray-based spectroscopies

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Organic radicals are fascinating materials because of their unique properties, which make them suitable for a variety of possible applications. Their synthesis may be challenging and big efforts have focused on chemical stability. However, introducing a new material in electronics surely requires chemically stable molecules but also stable thin films in view of their use in devices.

In this work we present the results obtained evaporating thin films of stable purely organic radicals. The films were investigated by using a multi-technique approach. We have investigated electronic structure, paramagnetic character, and stability of the obtained films under ultra high vacuum (UHV) and ambient conditions, by X-ray photoelectron spectroscopy, X-ray absorption spectroscopy, atomic force microscopy, and electron paramagnetic resonance spectroscopy [1-4].

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- [4] T. Junghöfer *et al.*, in preparation.

Iron-phthalocyanine on rutile: Main interaction channel oxygen vacancies at the surfaces

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Previous results in the literature show different interaction strength for phthalocyanines on TiO_2 (rutile) obviously depending on the crystal orientation, preparation conditions and phthalocyanine's metal center. [1, 2]

We studied iron phthalocyanine (FePc) and iron hexadecafluoro-phthalocyanine (FePcF_{16}) on the rutile (100) and (110) crystal surfaces using photoemission and X-ray absorption spectroscopy (XAS). Almost no interaction was observed, if the rutile is prepared with few defects (few sputtering and annealing cycles at moderate conditions) and the annealing takes place at an oxygen partial pressure of 1×10^{-6} mbar (especially the shape of the N1s PES spectra is similar to TMPcs on non-interacting oxide surfaces [3]).

If some and especially the last annealing steps are done without oxygen, FePcF_{16} show strong interaction involving the iron metal center and the nitrogen, which is clearly visible by a component at higher binding energy in the N1s photoelectron spectrum (Fig. 1).

We conclude that the interaction of investigated phthalocyanines is considerably influenced by oxygen vacancies at the rutile surface, which can be controlled by the preparation conditions.

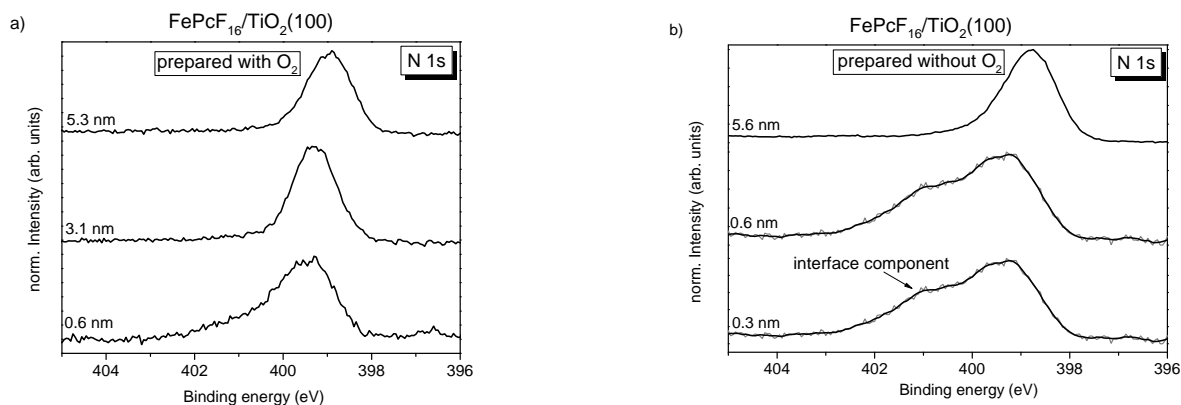


Fig. 1 FePcF_{16} on rutile (100): N1s PES spectra of a) rutile prepared with few defects and O_2 while the annealing; measured with $E_{\text{exc}} = 650$ eV and b) rutile prepared with many defects and no O_2 while the last annealing; measured with $E_{\text{exc}} = 1486.6$ eV.

- [1] P. Palmgren *et al.*, J. Phys. Chem. C 112, 5972 (2008).
- [2] S. Sinha *et al.*, J. Phys. Chem. C 121, 3365 (2017).
- [3] M. Glaser *et al.*, J. Phys. Chem. C 119, 27569 (2015).

Molecular topology and surface chemical bond: Alternant vs. non-alternant aromatic molecules

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In organic light-emitting diodes and related organic-electronic devices, molecular organic semiconductors are typically contacted by metal electrodes. The resulting metal/organic interfaces have a large impact on the performance of these devices, which makes the understanding of their chemical, electronic and geometric structure indispensable for the further rational development of organic electronics. Accordingly, model metal/organic interfaces with aromatic molecules have been a major research topic during the past decade. Up to now, the focus has been almost exclusively on aromatic systems with alternant topology such as pentacene, which have a uniform charge distribution and highly delocalized frontier orbitals. In contrast, aromatic systems with non-alternant topology have non-uniform charge distributions, which can result in considerable in-plane dipole moments, and more localized frontier orbitals. They also violate the Coulson-Rushbrooke pairing theorem and thus have shifted valence levels compared to the isomers with alternant topology. In this contribution, we present the first systematic studies of a non-alternant aromatic molecule on the (111) surfaces of Ag and Cu. In particular, we focus on naphthalene, which has as an alternant topology, and its non-alternant counterpart azulene. On the basis of extensive NEXAFS, PES, TPD, nc-AFM, STM and NIXSW studies, we show that the non-alternant topology results in much stronger interaction with metal surfaces, especially in the case of Cu(111), and that the interaction is more localized. Complementary periodic DFT calculations provide detailed insight into the surface chemical bond and charge redistribution between surface and molecule. A major part of the localized interaction is the donation of electron density into the molecular LUMO. This leads in turn to considerable in-plane and out-of-plane deformations of the adsorbed non-alternant species, while the alternant molecule remains largely undeformed.

Evolution of TiOPc-films on Ag(111): Bilayer stacking enables ultra-smooth layers

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The chemical and thermal robustness of titanyl-phthalocyanine (TiOPc) in combination with its high optical absorption favours its application as photoconductor or chromophore for light-harvesting in organic photovoltaic applications [1]. Beside such device application there is a large interest in the controlled fabrication of smooth molecular spacer layers of controlled thickness in order to prepare molecular hetero-structures. While many π -conjugated materials form highly ordered mono- and bilayer films on metallic (single crystalline) substrates, the films exhibit a notable roughness upon increasing film thickness [2]. Here, we demonstrate that TiOPc forms extremely smooth films on Ag(111), not only in the mono- and bilayer regime [3-5] but also for thicker films exceeding a thickness of 10nm. Combining various analytical techniques including atomic force and scanning tunnelling microscopy (AFM, STM), with X-ray photoelectron spectroscopy (XPS), near-edge X-ray absorption fine structure spectroscopy (NEXAFS) and X-ray diffraction (XRD), we show that for substrate temperatures below 450 K TiOPc forms molecularly smooth films with a rather small overall film roughness. The detailed analysis shows that the films are stabilized by the characteristic molecular bilayers of alternatingly (up and down) oriented titanyl units. Finally, we show that even the thick films are epitaxially oriented with respect to the azimuth direction of the supporting Ag(111) surface.

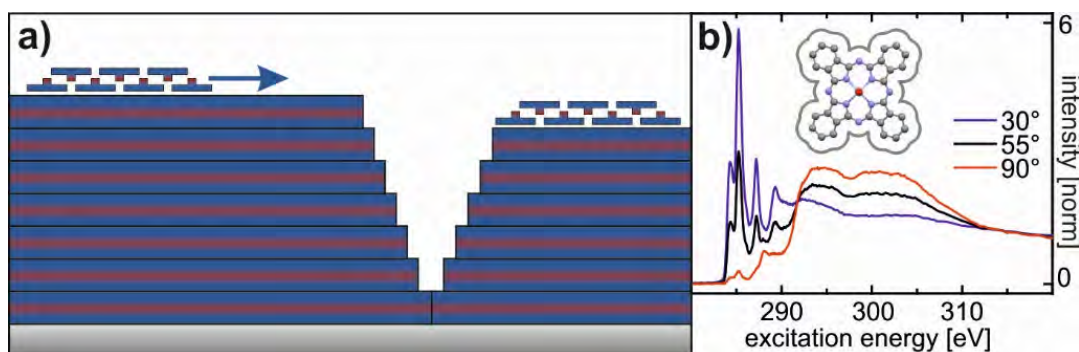


Fig. 1 a) Schematic drawing of the TiOPc multilayer growth mode on Ag(111).

b) NEXAFS data of 10nm TiOPc on Ag(111)

- [1] K. Xiao *et al.*, Appl. Phys. A 77, 367 (2003).
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Two-dimensional growth of dendritic islands: NTCDA on Cu(001) studied in real time

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Real time growth studies of thin films are very rare in the literature, which is quite surprising since they enable an otherwise unrivalled level of control in the growth process of (e.g.) organic thin films and adsorbate systems. In this context, we report a LEEM-based growth study of NTCDA on Cu(001). Figure 1 summarizes the very surprising growth results for this system:

In bright-field LEEM, no contrast but only a decreasing overall intensity is found with increasing coverage (Fig. 1a), while at the same time LEED clearly indicates an ordered structure already at ~ 0.3 ML (b). Dark-field LEEM, however, shows a very clear contrast between two rotational domains at 0.4 ML. Most remarkably, it appears as if the domains were occupying the entire surface already at the small coverage of 0.4 ML and were not growing in size upon further deposition (Fig. 1c).

We explain this surprising finding with fractal structures, formed due to a strongly preferred one-dimensional growth mode at small coverages. This growth mode leads to a long-range ordered network of thin molecular chains spanning over the entire surface already at small coverages. Later in the growth process, voids in this network structure are incrementally filled. This dendritic growth model is supported by energetic arguments based on pair-potential calculations that can explain the preferred growth of one-dimensional structures.

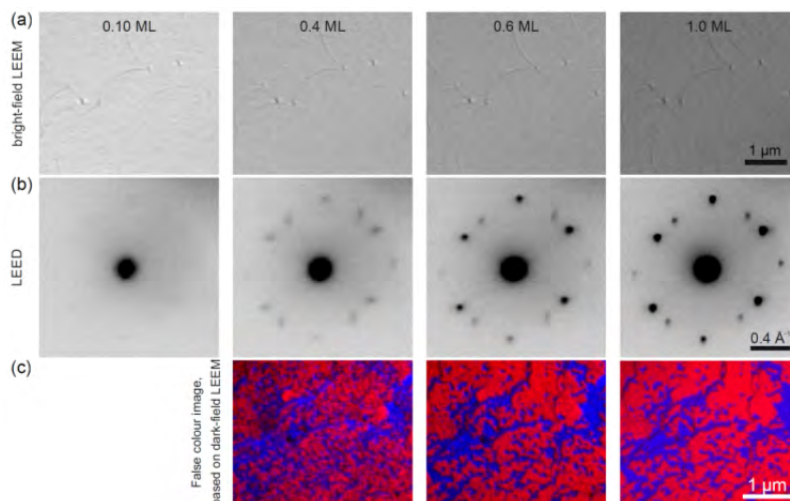


Fig. 1 NTCDA/Cu(001): (a) BF-LEEM, (b) LEED and (c) DF-LEEM images (false-color images of the two rotational domains) at different coverages. While in BF-LEEM no contrast is visible in the entire sub-monolayer regime, the LEED images indicate a well ordered structure arising at ~ 0.3 ML. DF-LEEM also shows the formation of ordered domains covering the entire surface already at 0.4 ML coverage.

Steering the growth of multiple ordered hetero-molecular phases by utilizing intermolecular repulsion

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In characterizing interfaces between organic semiconductors and metals, the formation of molecular blends (i.e., heteromolecular layers containing two types of molecules, usually charge donors and acceptors) is of great interest. In this context, we report a novel thermodynamic phase diagram found for molecular blends formed by PTCDA and CuPc in submonolayers on Ag(111) [1]. Our comprehensive LEEM study identifies five crystalline phases with different stoichiometries. Large eutectic regions exist in the phase diagram, caused by the opposite intermolecular interaction of its components – repulsive for CuPc, attractive for PTCDA. We find that the repulsive species forms a two-dimensional lattice gas, the density of which determines the stability of all other crystalline phases. The existence of critical gas-phase densities is the basis for understanding the constant-volume phase diagram. We anticipate the general validity of this type of phase diagram for binary systems containing 2D gas phases, and emphasize that the density of the gas phase allows engineering of the interface structure.

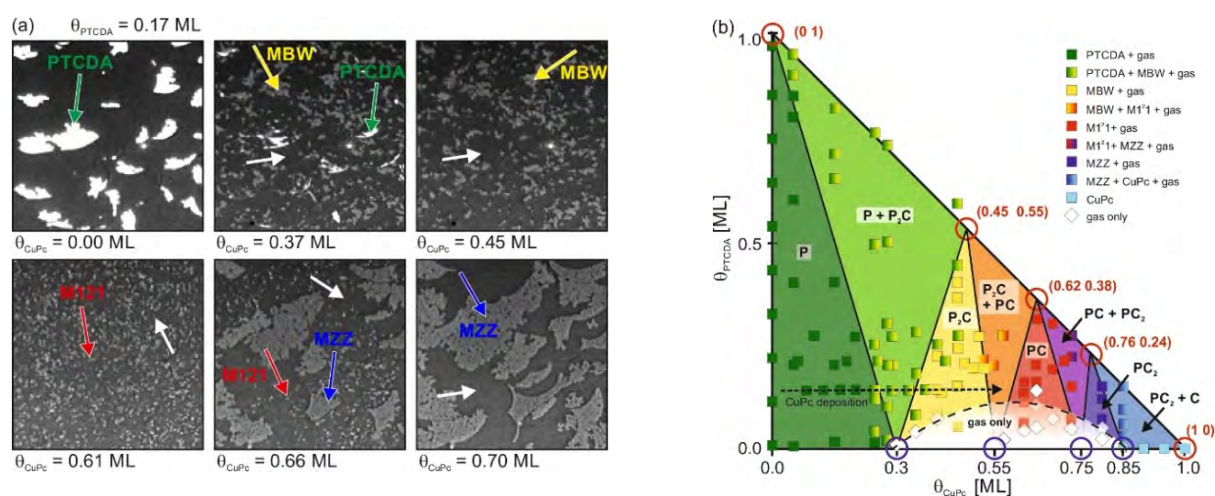


Fig. 1 (a) Bright-field LEEM images recorded during a binary deposition experiment: Initially, 0.17 ML PTCDA form compact islands (upper left image). The following LEEM images were recorded during subsequent deposition of 0.7 ML CuPc. The PTCDA islands (green) are sequentially transformed into MBW (yellow), M121 (red) and MZZ islands (blue), according to the stoichiometry sequence. (b) Corresponding phase diagram for the submonolayer regime: Data points and colored areas mark the regimes of pure and eutectic phases as obtained from experiment and thermodynamic model, respectively. The path of the experiment shown in (a) is indicated by a dotted black arrow. The model is based on more than 20 LEEM experiments with different initial coverages. Abbr.: P = PTCDA, C = CuPc; Sequence and stoichiometry of the phases: PTCDA (P) – MBW (P₂C) – M121 (PC) – MZZ (PC₂) – CuPc (C).

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Time-resolved spectroscopy of electron transfer processes at metal/organic interfaces

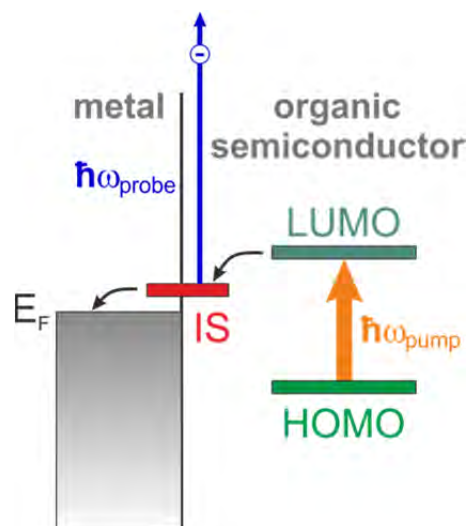
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Interfaces between ordered organic thin films on single-crystal metals constitute well-defined model systems for electrical contacts of organic semiconductor devices. Time-resolved two-photon photoemission (2PPE), a method that combines femtosecond laser pump-probe techniques with photoelectron spectroscopy, can provide detailed microscopic information about electron transfer processes at such model contacts. Specific emphasis of this talk will be on the role of interface-specific electronic states for the charge transfer [1-8].

Experiments with organic bilayer systems, such as CuPc/PTCDA/Ag(111) or PCTDA/TiOPc/Ag(111), unambiguously show that normally unoccupied interface states (IS) can be optically excited from the metal side as well as from the LUMO of the second and even third organic monolayer. Transfer times of electrons from the LUMO into the IS and from the IS to the metal range from 20 to 100 fs. These values indicate that the IS wave function has good overlap with both, the delocalized electron system of the metal and the relevant molecular orbitals. Interface states located between the Fermi level of the metal and the molecular LUMOs are thus able to mediate the charge transfer. The results show that not only the molecular level alignment at the interface, but also the properties of interface-specific electronic states play an important role for the efficiency of organic/metal contacts.



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Work performed in the framework of the Collaborative Research Centre "Structure and Dynamics of Internal Interfaces" (SFB 1083).

Energetic degradation of organometal halide perovskite films upon oxygen, water and illumination

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Due to their large absorption coefficients, tunable band gaps, long carrier diffusion lengths, ambipolar charge transports and low defect concentrations, hybrid organic-inorganic perovskite semiconductors have attracted tremendous attention upon the perspective applications on optoelectronics [1]. Organometal halide perovskites, as a promising photovoltaics materials, have reached a power conversion efficiency over 22% [2] surpassing that of dye-sensitized and organic photovoltaics within a very short timescale. However, the long-term stability remains a major challenge for their commercialization. Understanding the influence from water, oxygen, light illumination and heating upon organometal halide perovskites themselves will be significantly helpful to shed light on their degradation mechanism and to realize a better performance of the corresponding photovoltaic devices.

Here, we present our recent spectroscopic studies of energetic degradation of organometal halide perovskite films by in-situ oxygen, water, and light exposure in a controlled manner [3-4]. We found that oxygen molecules induce an upwards shift of the vacuum level of the perovskite films from formation of an oxygen-induced surface dipole. However, water vapor downshifts the vacuum level significantly, meanwhile, edge of the valence band maximum increases simultaneously, as results, the ionization potential of the perovskite films is kept unchanged.

On light illumination on cationic compositional engineered organometal perovskites, i.e., $\text{MAPb}(\text{I}_{0.83}\text{Br}_{0.17})_3$, $\text{FA}_{0.83}\text{MA}_{0.17}\text{Pb}(\text{I}_{0.83}\text{Br}_{0.17})_3$ and $\text{Cs}_{0.1}(\text{FA}_{0.83}\text{MA}_{0.17})_{0.9}\text{Pb}(\text{I}_{0.83}\text{Br}_{0.17})_3$, all undergo severe degradation under white light illumination in ultrahigh vacuum (UHV) environment, but the degradation rate in the mixed cation perovskites is significantly lower [4]. From the change of their atomic contents and vibration mode with illumination, we attribute this to the defect-induced trap states that trigger the strong coupling between the photo-excited carriers and the crystal lattice. Our results support UHV environment remarkably accelerates the degradation from illumination, and the mixed cations can suppress the photoinduced degradation. Moreover, the applied UHV environment could be an accelerated test method to estimate the photostability of the perovskites.

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Investigating the electronic structure and chemical interactions in doped poly(3-hexylthiophene) with the Lewis acid dopant tris(pentafluorophenyl)borane

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Tris(pentafluorophenyl)-borane (BCF) has been introduced as a strong Lewis acid dopant for organic semiconductors (OSC). The doping mechanism is proposed to be due to the formation Lewis acid-base adducts, in which lone pair electrons transfer from the OSC to the boron atom of the dopant.[1] More recently, BCF has been demonstrated as a p-dopant to P3HT resulting in improved electrical conductivity which has been ascribed to integer charge transfer. [2]

In this contribution, we investigate the electronic and chemical changes in BCF doped P3HT using photoemission spectroscopy, aiming to improve the current understanding of the underlying mechanism of Lewis acid doping of OSC. Ultraviolet photoemission spectroscopy (UPS) is used to probe the changes to the valence band of P3HT upon doping and monitor the changes in the work function of the film. As a result of p-doping, the work function of P3HT increases by ~ 0.7 eV as the occupied states shift towards the Fermi level. We employ X-ray photoelectron spectroscopy (XPS) to investigate the core levels of P3HT and monitor the dopant concentration and chemical changes resulting from interacting with BCF. Deconvolution of the S 2p core levels (Fig. 1) shows an increase of sulfur in a positively charged environment as compared to neutral sulfur. However, this increase is larger than the measured dopant ratio, and scales by different factors with dopant ratio pointing towards a change in the delocalization length of the polaron as the amount of dopant in the film changes. In addition, we provide an overall picture of the changes in the energy of both valence and core levels with doping.

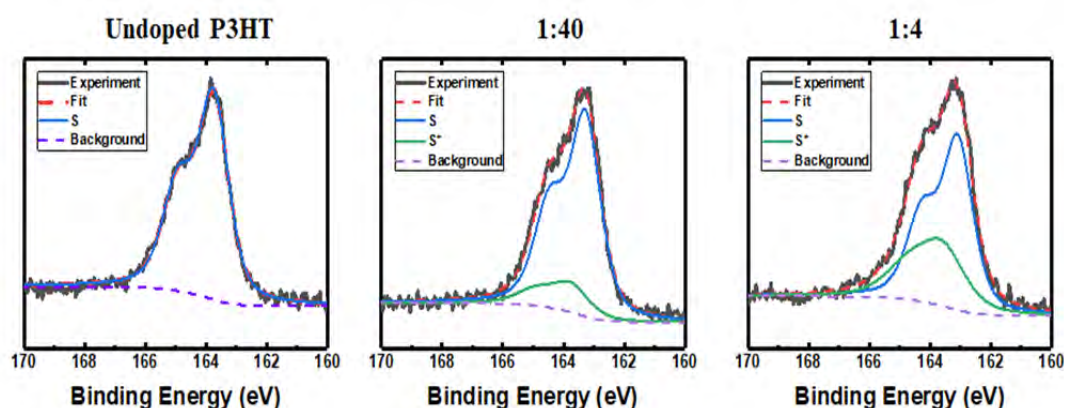


Fig. 1 S 2p core level measured from XPS

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Orbital tomography of a strong hole-vibration coupling molecule

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Photoemission experiments on organic semiconductors have been carried out for many years now. Yet, improvements in experimental technologies and simulation techniques open up new possibilities to study photoemission processes at the interface between organic molecules and substrates that were hardly accessible before.

Here, we present the experimental and computational characterization of the perfluoro-pentacene (PFP)/Ag(111) interface, using the k-space resolving PEEM (photoemission electron microscope) of the NanoESCA beamline at Elettra, Italy, in combination with a structural characterization by low-energy electron diffraction (LEED) and photoemission simulations based on an independent atomic center approximation for final state [1]. This allows us to discuss the effects of the strong hole-vibration coupling of PFP [2] on the photoemission maps and electronic interaction within molecular monolayers and bilayers, respectively.

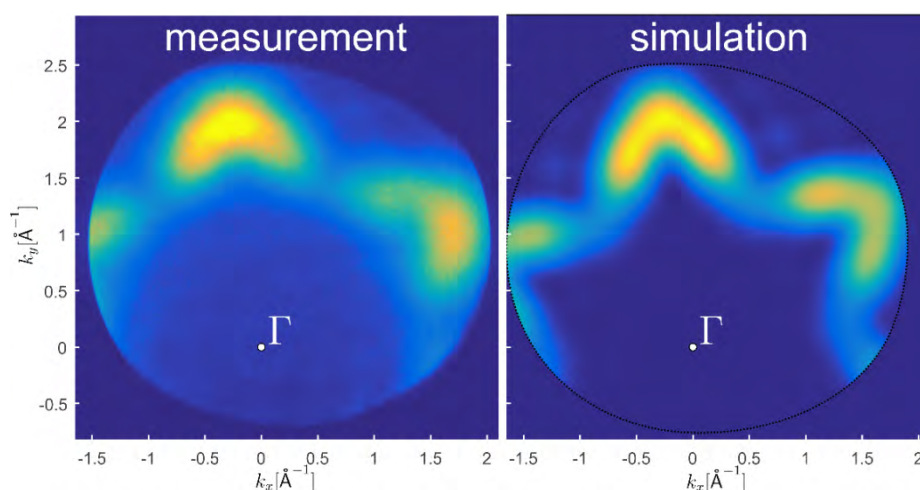


Fig. 1 Comparison between the photoemission maps of a PFP monolayer on Ag(111), as obtained experimentally (left) at 76 K with p-polarized photons ($h\nu = 30$ eV) and by simulation (right).

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Orbital imaging of the non-planar molecules

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We present experimental and simulated data on the photoemission intensity of buckminsterfullerene C_{60} within an evaporated molecular thin film utilizing ARPES measurements combined with the theoretical calculation of the full interface and simulations of the entire photoemission process. The experimental data was acquired by a photoemission electron microscope in Fourier-space imaging mode (kPEEM) which enables the efficient detection of photoelectrons emitted into the entire hemisphere above the sample [1]. The symmetry of the recorded photoemission intensity demonstrates the molecules adsorb with a single alignment and do not rotate on the silver substrate at room temperature. We perform simulations of the photoemission matrix elements within a framework of independent atomic centers (IAC), where the final states is assembled from composite contributions of the individual atoms within the molecule [2],[3]. The comparison between theory and experiment enables the determination of the adsorption geometry and orientation of the C_{60} molecules in agreement with DFT-based structure relaxation of the full interface. Additionally, we characterize the hybridization of the partially occupied LUMO, whose degeneracy is lifted due to symmetry breaking upon adsorption.

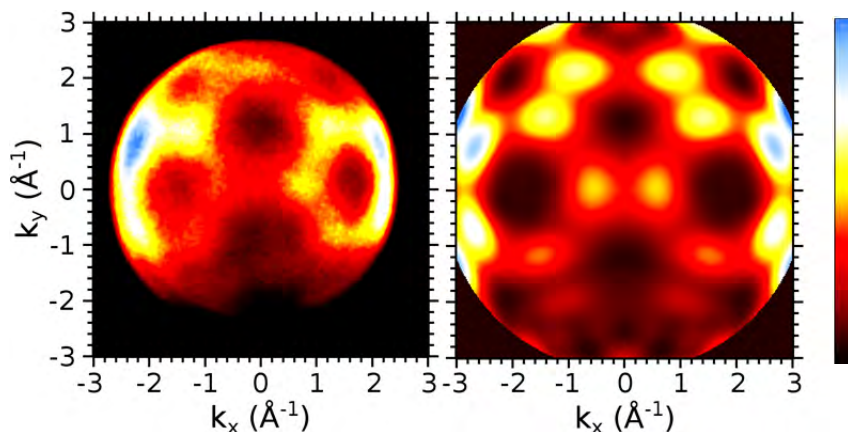


Fig. 1 Experimental (a) and simulated (b) angular photoemission intensity distribution from the degenerate HOMO of buckminsterfullerene C_{60} at a photon energy of 40 eV.

Note that the intensity is cut beyond the detector plate in the experiment.

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Exciton binding energy of organic materials: Valence vs. core excitation

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Organic semiconductors are well known as materials with high exciton binding energy (EBE). This energy can be considered as the difference between the electronic gap (sometimes referred to as charge transport gap) and the excitation energy [1]. In recent years, substantial efforts have been made to determine the EBE of valence excitations and to relate it to fundamental processes in devices, particularly the exciton dissociation in photovoltaic cells [2]. Core excitations, in turn, are widely used for fine structure spectroscopy of organic materials [3] and more recently also from *ab-initio* theory perspective [4].

In this contribution, the EBE is investigated for pristine organic semiconductors with valence (HOMO-LUMO transition) and core excitations (C1s-LUMO transition). We compare these transition energies determined from absorption related measurements with the transport gaps obtained from measurements by direct and inverse photoelectron spectroscopy. The experimental results are compared to first-principles calculations of the x-ray absorption spectra through the solution of the Bethe-Salpeter equation, including a relativistic treatment of the core states [5].

While the EBEs measured for valence excitations of α -sexithiophene and diindenoperylene are in the range of several hundred meV, the EBEs for core excitations are higher than one eV and therefore significantly higher than the value for valence excitations. This comparison shows that the EBE for core excitations is strongly increased and related to the core-hole localization and the poor screening of the electron-hole interaction through intermediate charges as also shown by theoretical investigations of comparable molecular materials [4,6].

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Influence of water, oxygen, and air exposure on the electronic structure of methyl ammonium lead mixed iodide-chloride $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ perovskite films

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During the last few years the class of organic-inorganic perovskite materials has attracted much attention from the photovoltaic community, particularly due to their application in high-efficiency solar cells. However, the rapid progresses in terms of attainable high efficiencies with these materials contrast with stability and reproducibility issues that still represent a serious obstacle for their reliable long-term application. One central aspect related to these stability issues is the effect of environmental conditions that can affect the properties of the perovskite. To gain a better understanding of the processes underlying the effect of environmental conditions, we investigated the surface electronic properties of solution-processed $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ perovskite thin films upon exposure to water, oxygen, and air – as experienced during typical device fabrication and operation conditions.

By means of photoelectron spectroscopy (PES), we characterized perovskite films that were kept in inert-gas (nitrogen) atmosphere of a glove-box or UHV and that exhibit a pronounced n-type surface character mostly due to Pb-related defects [1], where the Fermi-level is closer to the conduction band edge than to the valence band edge. Upon exposure to water vapor, the pronounced n-type surface character was accentuated. This change is mostly reversible after mild heating or drying in UHV. Importantly, a water partial pressure as low as 10^{-6} mbar, as encountered in inert-gas glove boxes and in high vacuum, already decreases the work function, likely due to physisorbed water. Pure oxygen exposure leads to a shift of the Fermi-level towards a mid-gap position, i.e., the surface became significantly less n-type, while the ionization energy (IE) remains unchanged. Comparably, the exposure to ambient air results in a shift of the Fermi-level towards mid-gap position by 0.6 eV, which implies the prevailing effect of oxygen upon that of water in air. Such variations of the electronic structure of perovskite film surfaces will affect the energy-level alignment at the subsequently formed interface between the perovskite and typical charge transport materials on top.

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Monitoring of atomic layer deposition by synchrotron-based ambient pressure XPS: Towards millisecond time resolution

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Atomic layer deposition (ALD) is a thin film deposition technique for depositing uniform and conformal layers on complex three-dimensional topographies. ALD is highly used in different fields of technology, e.g. in microelectronics for metal-oxide semiconductor field effect transistors, in the formation of catalyst materials and in solar cell technology. The understanding of the atomic and molecular surface processes underlying the ALD growth are, however, far from complete, which implies difficulties in further advancing the technology. A thorough investigation for the identification and role of surface species, surfaces defects, impurities and vapour phase reactions is therefore very much needed [1].

Here we have applied ambient pressure x-ray photoelectron spectroscopy (APXPS) to study the ALD growth of metal oxides on the clean native oxide-covered surfaces with different time resolution. APXPS has the advantage that it can be carried out during thin film growth, i.e. under *operando* conditions. Our investigation focuses on the dynamic nature of the ALD process, and it is for the first time that APXPS has been applied to this subject with millisecond time resolution. This is illustrated in Fig. 1, which shows APXP spectra taken during the ALD of HfO₂ on an InAs(100) surface at different time resolution. It is possible to in detail follow the evolution the core levels during ALD.

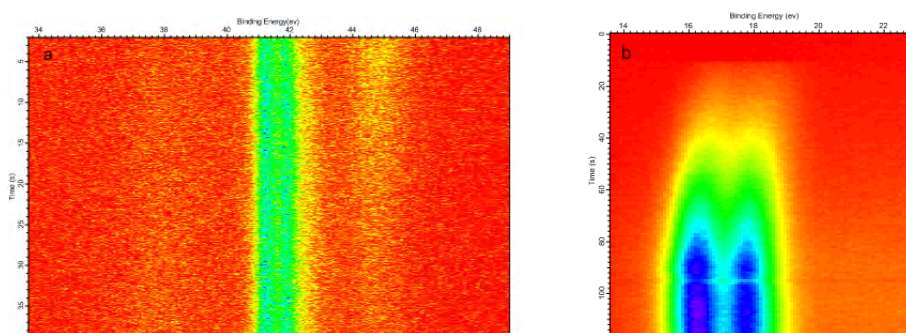


Fig. 1 (a) As 3d spectra taken during the exposure of a native oxide-covered InAs(100) surface during exposure to TDMAT at 10^{-2} mbar. In total 1200 spectra were taken in around 70 s. (b) Hf 4f spectra taken in the same kind of experiment, measured at 0.07 Hz frequency.

[1] F. Zaera, Coord. Chem. Rev. **257**, 3177 (2013).

Development of angle-resolved low energy inverse photoelectron spectroscopy apparatus

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Band dispersions of the occupied and unoccupied states of metals and semiconductors are indispensable information for understanding the charge transport mechanism of the holes and electrons, respectively. The angle-resolved photoelectron spectroscopy is frequently used as a standard technique for the occupied states. On the other hand, the unoccupied states of metals and inorganic semiconductors has been reported by angle-resolved inverse photoelectron spectroscopy (ARIPES).¹ However, the band dispersion of the unoccupied states of the organic semiconductors has not been observed owing to sample damage due to the electron bombardment and the low energy resolution of 0.5 eV comparable to the bandwidth of molecular solids.

In 2012, we developed low energy inverse photoelectron spectroscopy (LEIPS) making it possible to measure the unoccupied states of organic semiconductors without damaging the sample while maintaining high resolution.² In this study, we have developed the angle-resolved LEIPS apparatus aiming at the measurements of the band dispersion of the unoccupied states of the organic semiconductors. However, to focus the low energy electron beam with kinetic energy between 2 and 5 eV was difficult. To overcome this problem, we developed an optimized electron source and thoroughly shielded the stray magnetic and electric fields which enabled us to make the angle-resolved measurement.

Fig. 1 shows the spectra of the unoccupied states of graphite measured by this apparatus. The image potential state was observed at the energy between 3 and 4 eV. The peak energy shifted as the angle of incident electron changed. The relation is consistent with the free-electron nature of the image potential state and the effective mass is calculated to be 0.99 ± 0.10 excellent agreement with the previous value measured by two-photon photoelectron spectroscopy.³

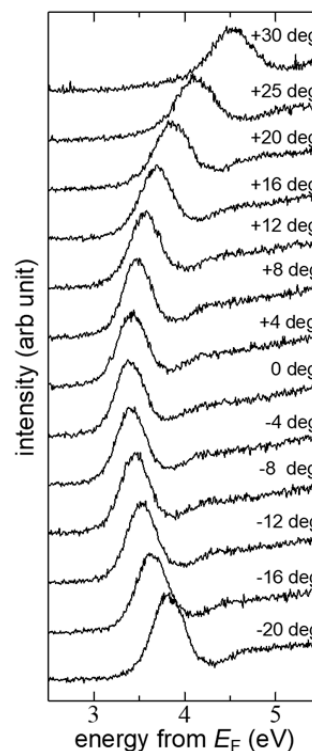


Fig.1 AR-LEIPS spectra of graphite surface

- [1] I. Schäfer *et al.*, Phys. Rev. B 35, 7663 (1987).
- [2] H. Yoshida, Chem. Phys. Lett. 539-540, 180 (2012).
- [3] H. Yoshida, J. Electron Spectrosc. Relat. Phenom. 204, 116 (2015).
- [4] K.Takahashi *et al.*, Phys.Rev. B 85, 075325 (2012).

Importance of homogeneous substrates for ionization potential determination by ultraviolet photoelectron spectroscopy

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Ultraviolet photoemission spectroscopy (UPS) is probably the most widely used technique nowadays to determine the ionization energy (IE) of materials, especially for newly synthesized molecules. Usually these are evaporated onto a substrate and then measured by UPS. For homogeneous substrates the determination of IE from the measured UPS data is straight forward. However, if the used substrate is heterogeneous (intentionally or unintentionally) the conventional method to determine IE yields wrong results and a more elaborated data evaluation is necessary. In an earlier work we demonstrated the effect of a heterogeneous surface on the work function determination by UPS [1]. In this work we now demonstrate the pitfalls of using heterogeneous substrates to determine the IE of molecules by means of well-controlled model systems and show how a more in depth data analysis can still yield correct results.

[1] T. Schultz *et al.*, Adv. Mater. Interfaces 4, 1700324 (2017).

Photoemission tomography for π -extended peri-xanthenoxanthene on Cu(111)

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Organic molecules on metal surfaces often form ordered overlayer structures that are ideally suited for angle-resolved ultraviolet photoelectron spectroscopy (ARUPS) studies. On the theoretical side much information on these systems can be gained by assuming a plane wave for the final state and modelling the initial state within density functional theory (DFT). This approach is called Photoemission Tomography, and here we report a new application of these method for a π -extended peri-xanthenoxanthene (PXX) derivative adsorbed on Cu(111).

The adsorption geometry is determined via DFT calculations and subsequently used for the calculation of momentum maps within the plane wave approximation for the final state. The results of this simulation are compared to experiment. This allows us to assign molecular orbitals to the observed emission features (see Fig. 1 for an example) and to study the charge transfer between the molecule and the substrate.

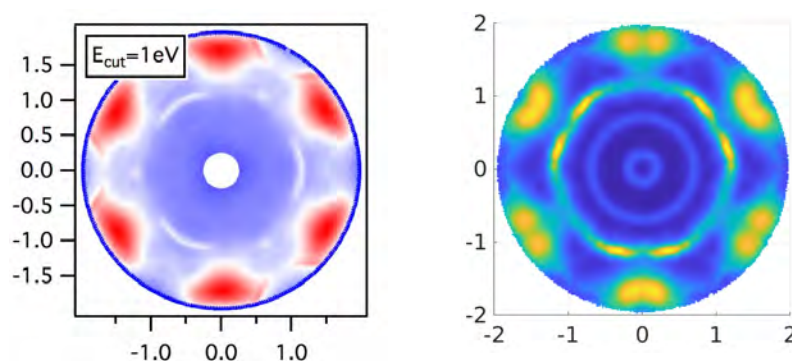


Fig. 1 Experimental momentum map (left) compared to simulated HOMO momentum map (right).

"Shallow states" of organic films observed by $h\nu$ -dependent high-sensitivity photoemission

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In organic electronics, gap states as well as HOMO and LUMO have considerable impact on the performance of devices. Therefore, direct and precise measurement of gap states is integral for further understanding of device physics. For that purpose, we have developed a new variation of ultraviolet photoemission spectroscopy (UPS), $h\nu$ -dependent high-sensitivity UPS ($h\nu$ -HS-UPS) [1-4]. In this method, a series of UPS measurements with various incident photon energies $h\nu$ are performed. Then, the spectra are combined by overlapping spectral parts with similar line shapes between adjacent $h\nu$, which removes the effect of photoionization cross section. In the case of UPS with a single $h\nu$, a wide dynamic range and a strict suppression of ghost signals are required to measure small DOS precisely. In contrast, our method only requires a dynamic range of a two-order magnitude for connecting the adjacent spectra and thus the ghost signals can be excluded. We have applied this method to various organic materials including small molecules and polymers.

By using this technique, not only we successfully acquired a wide range of DOS [1,2] but also we frequently observed "shallow states" above the Fermi level, indicating that excess electrons are in the organic film. The origins of excess electrons can be classified into three types. i) excess electrons are in localized states, so-called trap states. We observed trap states extended to just 2.98 eV below the vacuum level in an alkane (C₄₄H₉₀) film. ii) excess electrons are in LUMO, forming anions. A film of Alq₃ with positive polarization charge on the film surface was found to accumulate anions at the surface, hence anion states were clearly observed [3]. This result proposes $h\nu$ -HS-UPS as a novel method to observe LUMO and carrier states. iii) excess electrons are in LUMO under the attractive potential of holes, forming excitons. In the case of CBP, a shallow peak was observed at the energy where the triplet exciton is expected. The ability to observe DOS of excitonic states will help the understanding on the charge transfer process in optoelectronic devices.

In conclusion, $h\nu$ -HS-UPS succeeded to detect various type of shallow states as mentioned above. The detailed information of these shallow states would facilitate the understanding on the physics of organic devices.

- [1] T. Sato *et al.*, Appl. Phys. Express 10, 011602 (2017).
- [2] T. Sato *et al.*, Appl. Phys. Lett. 110, 111102 (2017).
- [3] H. Kinjo *et al.*, Appl. Phys. Express 9, 021601 (2016).
- [4] K. Shimizu *et al.*, MRS Advances 2, 2261 (2017).

Exciton dynamics in pentacene-perfluoropentacene heterostructures

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Understanding the ultrafast electronically excited state dynamics in organic semiconductors after optical excitation is crucial for the optimization of organic optoelectronic devices. Moreover, the knowledge of the morphology and energetics at donor-acceptor interfaces is important for efficient charge separation in organic solar cells [1, 2]. Thereby, charge transfer (CT) states play a decisive role. To analyse the ultrafast processes at the interface more precisely, both well-defined structures of the samples and a very high time resolution in the experiment are required. In this work we investigated thin films of pentacene (PEN), perfluoropentacene (PFP), and various heterostructures of PEN and PFP by means of femtosecond time-resolved second harmonic generation (TR-SHG). For the donor/acceptor configurations, depending on the molecular orientations at the interface and the excitation energies, the dynamics of charge transfer states were investigated.

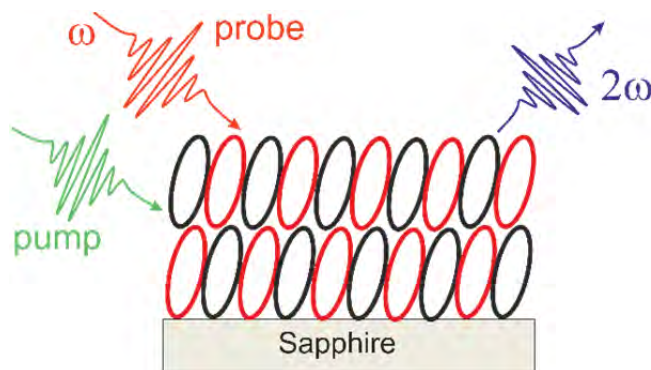


Fig. 1 Schematics of TR-SHG at PEN/PFP heterostructure.

- [1] K. Broch *et al.*, Phys. Status Solidi RRL, 1700064 (2017)
- [1] A. Rinn *et al.*, ACS Appl. Mater. Interfaces, 9, 42020–42028 (2017)

Dependence of the adsorption height of graphenelike adsorbates on their dimensionality

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M. Sokolowski⁴, P. Tegeder², S. Soubatch¹, and F. S. Tautz¹

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Comparing the adsorption heights of various graphene nanoribbons on Cu(111) and Au(111) surfaces to those of graphene and π -conjugated planar organic molecules using the x-ray standing waves technique, we observe that two-dimensional graphene adsorbs much further away from the surface than both one-dimensional graphene nanoribbons and π -conjugated planar molecules—which represent zero-dimensional graphene flakes. We show that this is a direct consequence of the adsorbates' dimensionality [1]. Our results provide insights into the interplay of Pauli repulsion, pushback effect, and chemical interaction for graphenelike adsorbates of any dimensionality on metal surfaces.

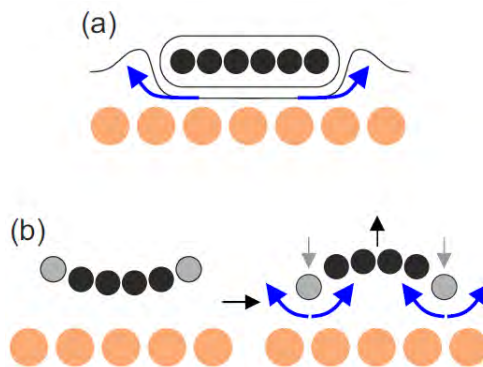


Fig. 1 Charge redistributions at the nanoribbon/metal interface. (a) Schematic illustration of the spill-out charge redistribution (blue arrows) for adsorption of planar molecules and graphene nanoribbons. (b) Schematic illustration of the annealing-induced change of the (3,1)-GNR/Cu(111) geometry.

[1] S. Weiß *et al.*, Phys. Rev. B, 98, 075410 (2018).

Nanoscale engineering with molecules at surfaces

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The study of molecular adsorption at surfaces has long been a focus of surface science. With increasing molecular complexity, new properties and phenomena emerge, and the design of functional single-molecule devices becomes possible. We present recent examples from our research that illustrate the intriguing physics of complex molecules at surfaces.

First, we demonstrate the emergence of a topologically protected quantum critical point in a spin-carrying molecular structure [1, 2]. Among many others, this example may serve as motivation to develop a methodology for crafting molecular “designer structures”. Next, we report our recent advances towards such a methodology [3-6]. Finally, we show that even relatively simple designer structures show intriguing functionalities, including quantum dot behaviour [7], electrostatic potential sensing [8], and coherent single-electron field emission [9].

- [1] T. Esat *et al.*, Phys. Rev. B 91, 144415 (2015).
- [2] T. Esat *et al.*, Nature Physics 12, 867 (2016).
- [3] P. Leinen *et al.*, Beilstein J Nanotechnol. 5, 1926 (2014).
- [4] C. Wagner *et al.*, Nat. Comm. 5, 5568 (2014).
- [5] P. Leinen *et al.*, Beilstein J of Nanotechnol. 6, 2148 (2015).
- [6] C. Wagner *et al.*, Perspectives of Molecular Manipulation and Fabrication. *In* Molecular Architectonics, Advances in Atom and Single Molecule Machines (Ed. T. Ogawa), Springer 2017.
- [7] R. Temirov *et al.*, Phys. Rev. Lett. 120, 206801 (2018).
- [8] C. Wagner *et al.*, Phys. Rev. Lett. 115, 026101 (2015).
- [9] T. Esat *et al.*, Nature 558, 573 (2018).

Epitaxial growth of the organic pn heterojunctions

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Tomoyuki Koganezawa³, Yasuo Nakayama¹**

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Organic electronics is attracting attention as next generation semiconductor electronic devices. Functionalities of most semiconductor devices are originated from charge carrier exchange at p-n junctions. The p-n junctions in the organic electronic devices such as organic photovoltaics are heterojunctions constituted with donor (p-type) and acceptor (n-type) molecules, and thus designing of the molecular contacts is important for improving the device performance. However, detailed mechanisms how the molecules form the donor-acceptor interfaces have not yet been understood thoroughly. Our group has unveiled the crystallographic structures of well-defined organic semiconductor interfaces between epitaxial overlayers of fullerene (C_{60}), an n-type molecule, on single crystal substrates of pentacene (Pn), a p-type organic semiconductor, which provides hints for understanding formation mechanisms of the molecular contacts [1-3]. In this work, we investigated evolution of epitaxial overlayers of C_{60} on single crystal surfaces of a variety organic semiconductors, e.g. rubrene, tetracene, and perylene, by means of grazing incidence X-ray diffraction (GIXD) and atomic force microscopy (AFM).

The C_{60} overlayers of 20 nm-thick were grown by vacuum deposition on the organic single crystal substrates prepared by a physical vapor transport method. GIXD measurements were conducted at BL19B2 or BL46XU, Spring-8.

Two-dimensional GIXD results showed that C_{60} grows in the face-centered cubic (fcc) phase in the (111)-orientation on the rubrene single crystals (Rub-SCs) and the fcc- C_{60} {220} diffraction spots appeared at every 30° of the in-plane azimuthal angle of the sample. This means that the fcc- C_{60} crystallites were not randomly oriented but grew epitaxially on Rub-SC, while their lattice orientations were not unique but there were two nonequivalent crystal domains rotating their in-plane lattice directions by 90° each other, as shown in Fig. 1. This result is contrasting to the previous case of C_{60} on Pn-SC exhibiting the single domain growth [1]. High-resolution GIXD spot profiles revealed that the in-plane mean crystallite size of the epitaxial C_{60} overlayers extended as elevating temperature during the growth. Interestingly, equivalent or rather greater mean crystallite sizes were obtained for the C_{60} /Rub-SC cases in comparison to C_{60} /Pn-SC, despite crystal domains of inequivalent orientations coexisted for the former heterojunction. Interface structures of C_{60} on tetracene and perylene single crystals are also discussed in this presentation.

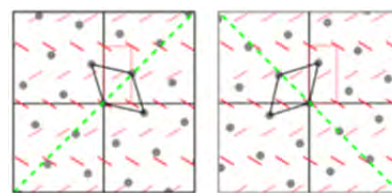


Fig. 1 Schematic drawings indicating lattice orientations of C_{60} (circles) on the surface of Rub-SC (bars).

- [1] Y. Nakayama *et al.*, ACS Appl. Mater. Interf. 8, 13499 (2016).
- [2] R. Tsuruta *et al.*, J. Cryst. Growth 468, 770 (2017).
- [3] Y. Nakayama *et al.*, Adv. Mater. Interf. 5, 1800084 (2018).

Impact of the molecular quadrupole moment in the molecularly mixed film of organic semiconductors

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Recently, it has been reported that the electronic level of thin films of organic semiconductors can be tuned continuously by changing the mixing ratio of the two constituent molecules having quadrupoles with opposite direction [1]. Based on the results from the ultraviolet photoelectron spectroscopy (UPS) experiment and the density functional theory (DFT) calculation, they concluded that the electrostatic effect which can be approximated by the interaction between the cation generated by UPS process and the molecular quadrupole moments plays a central role.

Recently, we demonstrated that the electrostatic energy can be obtained solely from the experimental data [2] by UPS and low energy inverse photoelectron spectroscopy (LEIPS) [3]. In this study, this method is applied to a mixed film of copper phthalocyanine (CuPc) and its fluorinated compound (F_{16} CuPc) with different mixing ratio of molecules to elucidate the mechanism of the continuous change of the energy levels.

The gray circles in Fig.1 represent the combined UPS and LEIPS spectra. The peak of the mixed films can be decomposed into the spectral components of the CuPc and F_{16} CuPc shown by dashed and dotted lines in Fig. 1, respectively. The HOMO and LUMO levels shift rigidly with the molecular ratio without changing the bandgap suggesting that the continuous shift is originate from the electrostatic energy. The electrostatic and electronic polarization energies were evaluated quantitatively from the results.

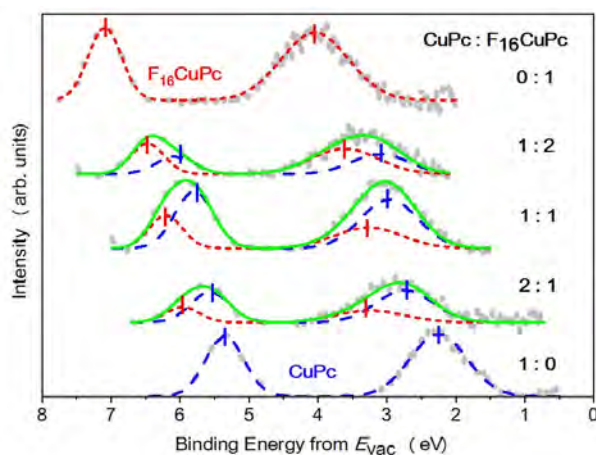


Fig. 1 UPS(left) and LEIPS(right) spectra of the CuPc and F_{16} CuPc co-deposited films.

- [1] M. Schwarze *et al.*, *Science*, **352**, 1446 (2016).
- [2] K. Yamada *et al.*, *Phys. Rev. B*, **97**, 245206 (2018).
- [3] H. Yoshida, *Chem. Phys. Lett.* **539-540**, 180 (2012).

Enhancement of signal intensity for the inverse photoelectron spectroscopy by the surface plasmon resonance of the Ag nanoparticles

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The most direct and thorough information about the unoccupied states can be obtained by inverse photoelectron spectroscopy (IPES), which can be regarded as the time-inversion process of photoelectron spectroscopy (PES). However, the cross section of the IPES process is 5 orders of magnitude smaller than that of PES [1], which impedes the wide use of IPES. In this study, the intensity of the IPES signal is enhanced by SPR. This was, however, impossible because the photon energy involved in conventional IPES exceeds 9 eV and is much higher than the SPR energy of existing materials. In 2012, we developed low-energy IPES (LEIPS) [2]. The energies of detected photons are less than 5 eV, which can be matched with the SPR energy.

Figure 1 shows the setup of LEIPS of the SPR. As the SPR media, we adopted Ag nanoparticles which were prepared by vacuum deposition or electrodeposition with voltage-step method [3]. We observed as much as the 3-fold enhancement of LEIPS signal of Ag nanoparticles. Then an organic semiconductor, copper phthalocyanine (CuPc), was deposited on the Ag nanoparticles. The signal intensity was also enhanced by a factor of 5 (Fig. 2). The wavelength dependence of the LEIPS intensities is similar to the extinction spectra confirming that the signal enhancements are indeed caused by the SPR of Ag nanoparticles.

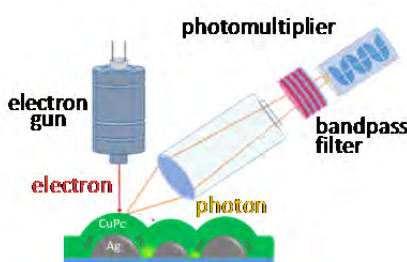


Fig.1 Experimental setup of LEIPS

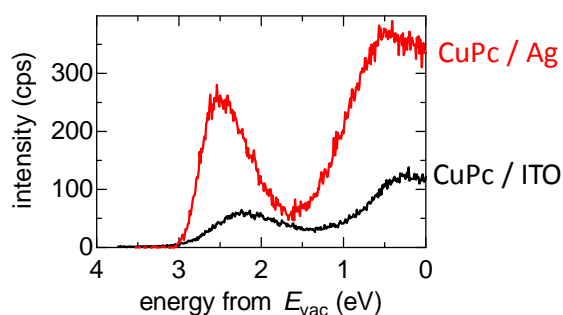


Fig.2 LEIPS spectra of 20-nm thick CuPc film with and without the Ag nanoparticles.

- [1] J. Pendry, Phys. Rev. Lett. 45, 1356 (1980).
- [2] H. Yoshida, Chem. Phys. Lett. 539-540, 180 (2012).
- [3] A. Tsuboi, Adv. Mater. 25, 3197 (2013).

Electronic and optical properties of oligothiophene/F4TCNQ charge-transfer complexes: The role of donor conjugation length

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Doping in organic semiconductors remains a debated issue. Open questions concern the interaction mechanisms between donors and acceptors, and also the role of the conjugation length that can influence the charge transfer (CT) process [1]. To address this issue, we investigate electronic properties and optical excitations of a series of oligothiophene (nT) molecules doped by the strong acceptor F4TCNQ. In the framework of density-functional theory (DFT), and many-body perturbation theory, including the G0W0 approximation and the Bethe-Salpeter equation, we consider CT complexes formed by four different oligomers with increasing length (4T, 6T, 8T and 10T). Based on the level alignment obtained from DFT adopting the CAM-B3LYP hybrid functional [2] we find that the HOMO and the LUMO have CT character in all complexes. On the other hand, occupied and virtual states above and below them are strongly dependent on the nT length. The optical spectra reflect the electronic structure. For all systems, the first bright excitation is dominated by the HOMO-LUMO transition. At increasing donor length, higher-energy peaks exhibit different character, which again points to conjugation-length dependence. The rationale offered by our results contributes to clarify the excitation processes in organic donor/acceptor complexes.

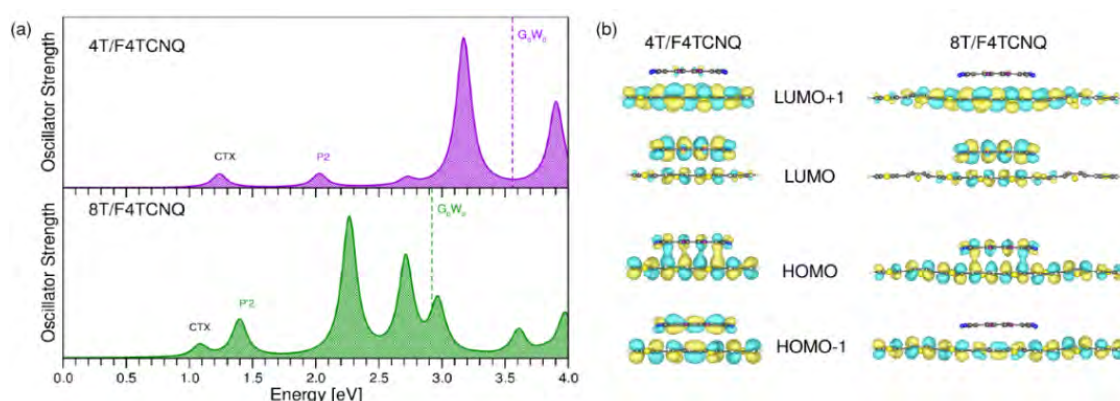


Fig. 4 (a) UV-vis spectra of 4T/F4TCNQ and 8T/F4TCNQ charge transfer complexes. Results from BSE calculations, and the electronic G0W0 energy band gap is indicated by dashed lines. (b) Selected molecular orbitals of both complexes.

- [1] H. Mendez *et al.*, Nat. Comms. 6, 8560 (2015).
- [2] T. Yanai *et al.*, Chem. Phys. Lett. 393, 51 (2004).

Switching the surface electronic properties of polar ZnO crystals with photochromic pyridine-dihydropyrene molecular layers

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Photoswitchable materials are attracting increasing interests for the development of multifunctional devices. A dynamic, light induced control of the electronic energy levels with such materials is a feasible pathway for realizing optoelectronic devices with multifunctional properties in terms of the control of charge transfer and injection. Here, we demonstrate that electronic properties of polar ZnO surfaces can be reversibly modulated with a layer of photoswitches, i.e., pyridine-dihydropyrene (Py-DHP). This is due to the switching between the two Py-DHP isomers (each with different conjugation) induced by illumination with green light and proper heat treatment. Using photoemission spectroscopy and density functional theory (DFT) modelling, we show that the photochromic ring closure/opening reactions result in different valence electronic features of Py-DHP, leading to a reversible shift of the frontier occupied orbitals by 0.7 eV with respect to Fermi level. This accordingly modulates the energy injection barriers at the ZnO/Py-DHP interface. Moreover, upon switching, we observe an increase of the ionization potential for Py-DHP multilayers compared to that of Py-DHP monolayer. We attribute this observation to different molecular orientations existing between the monolayer and multilayer films. Our findings provide a pathway to tuning the interface energy level alignments dynamically through a simple external stimulus, which can in the future be employed in multifunctional optoelectronic devices.

Solution-processing vs. vacuum-sublimation: Impact on the electronic structure of methyammonium lead iodide perovskite thin films

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$\text{CH}_3\text{NH}_3\text{PbI}_3$ thin films were fabricated using several representative synthesis methods that frequently occur in reported literatures, which include spin-coating, [1] evaporation [2] and a combination of the two.[3] We found that the surface morphology, composition and grain size of the films are highly dependent on how the PbI_2 and $\text{CH}_3\text{NH}_3\text{I}$ precursors are mixed, even when the same stoichiometric ratio is used. X-ray photoelectron spectroscopy (XPS) reveals that amount of CH_3^+ -type defect, which is produced by $\text{CH}_3\text{NH}_3\text{I}$ dissociation, is sensitive to both the physical state of $\text{CH}_3\text{NH}_3\text{I}$ and the order of mixing sequence. The variation of the $\text{CH}_3\text{NH}_3^+:\text{CH}_3^+$ ratio (Fig. 1) also affects the valence band and work function of the corresponding films, as revealed by ultraviolet photoelectron spectroscopy (UPS). The charge transport property of these films are further evaluated by examining the energy level alignment between the perovskite film and a model hole transport layer, N,N'-di(1-naphthyl)-N,N'-diphenylbenzidine (NPB). We find that $\text{CH}_3\text{NH}_3^+:\text{CH}_3^+$ ratio (Fig. 1) shows correlation with the offsets between the valence band maximum of perovskite film (VBM) and the highest occupied molecular orbital (HOMO) of NPB as well, and the energy-level alignment with the dual-source, co-evaporated $\text{CH}_3\text{NH}_3\text{PbI}_3$ film is most suitable for efficient hole transport. [4]

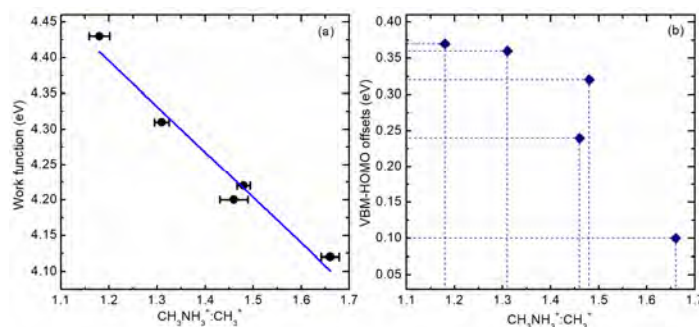


Fig. 1 Plot of (a) work function and (b) VBM (perovskite)-HOMO (NPB) offsets as a function of concentration ratio between CH_3NH_3^+ and CH_3^+ as measured by XPS.

- [1] R.B. Wang *et al.*, ACS Appl. Mater. Interfaces 9, 7859 (2017).
- [2] L. Liu *et al.*, Appl. Phys. Lett. 107, 061904 (2015).
- [3] F. Fu *et al.*, Phys. Status Solidi A 212, 2708 (2015).
- [4] R.B. Wang *et al.*, 2018, submitted.

Predicting ion pair formation yield in molecular electrical doping from redox-potentials

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Electrical molecular doping of organic semiconductors with strong molecular donors and acceptors is a key technological component to control the charge carrier density and Fermi level of the organic semiconductor host. Its efficiency relies on identifying appropriate dopants that are capable of ionizing the semiconductor molecules with a high yield, thereby creating mobile charges. We explore the suitability of two different material parameters to predict ion pair formation in such systems: i) redox-potentials measured by cyclic voltammetry in solution and ii) ionization energy (IE) / electron affinity (EA) measured on individual material thin films by ultraviolet / inverse photoelectron spectroscopy for different sets of semiconductor-dopant combinations using structurally similar molecules. The ion pair formation efficiency of these material combination sets is qualitatively and quantitatively studied by use of optical absorption spectroscopy performed on both solutions and solid thin films. While commonly IE/EA values are employed to guide the selection of molecular dopants for organic hosts, our study provides strong indications that redox-potentials are better suited to identify matching material pairs than IE/EA values. This is ascribed to the strongly film-structure dependent IE/EA values of molecular assemblies on and above the meso-scale, whereas the relevant molecular length scale dopant-semiconductor interaction appears to be better captured by cyclic voltammetry measurements.

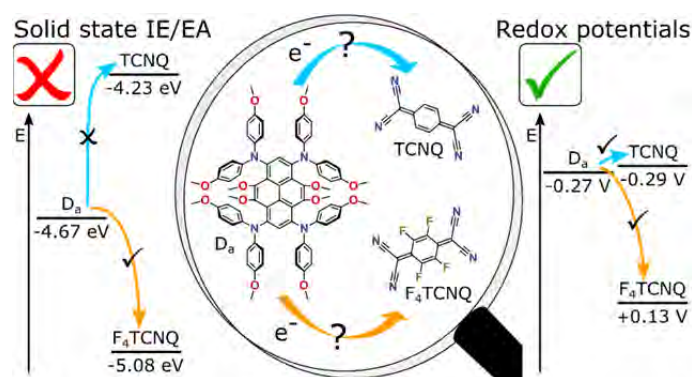


Fig. 1 Comparison of solid state ionization energies / electron affinities and redox-potentials for the prediction of possible charge transfer between host and dopant molecules.

Microstructure and elastic constants of transition metal dichalcogenide monolayers from friction and shear force microscopy

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Optical and electrical properties of two-dimensional transition metal dichalcogenides (TMDCs) grown by chemical vapor deposition (CVD) are strongly determined by their microstructure [1,2]. Consequently, the visualization of spatial structural variations is of paramount importance for future applications [3,4]. Here we demonstrate how grain boundaries, crystal orientation, and strain fields can unambiguously be identified with combined lateral force microscopy (LFM) and transverse shear microscopy (TSM) for CVD-grown tungsten disulfide (WS₂) monolayers, on length scales that are relevant for optoelectronic applications. Further, angle-dependent TSM measurements enable us to acquire the fourth-order elastic constants of monolayer WS₂ experimentally. Our results facilitate high-throughput and nondestructive microstructure visualization of monolayer TMDCs, insights into their elastic properties, thus providing an accessible tool to support the development of advanced optoelectronic devices based on such two-dimensional semiconductors [5].

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Band dispersion of $\text{CH}_3\text{NH}_3\text{PbI}_3$ single crystal

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Solar cells incorporating organic-inorganic perovskites, especially methylammonium lead iodide ($\text{CH}_3\text{NH}_3\text{PbI}_3$), have shown remarkable performances and therefore attracted wide interest recently. For understanding the origin of the high performance, the effective charge carrier masses of $\text{CH}_3\text{NH}_3\text{PbI}_3$ are critical. However, direct experimental data on its electronic band structure, which determines the effective mass, is yet to be provided. In this poster, we will present the electronic structure of self-grown $\text{CH}_3\text{NH}_3\text{PbI}_3$ single crystals studied by using angle-resolved photoelectron spectroscopy on cleaved crystal surfaces after characterizing the surface structure by low-energy electron diffraction. Sharp diffraction patterns agree well with the cubic structure previously determined by X-ray diffraction and confirm a good sample quality. Moreover, a clear band dispersion of the top valence band was observed along different high-symmetry directions, Γ -X and Γ -M directions, of the cubic structure in consistence with theoretical calculations. Based on these values, the effective hole mass was then estimated to be $0.24 (\pm 0.10) m_0$ at the M point and $0.35 (\pm 0.15) m_0$ at the X point, which are significantly lower than in organic semiconductors. Further, we expect an only slightly larger value at the R point by considering the theoretical band structure. Our results reveal the physical origin of the high performance of solar cells incorporating perovskite materials compared to pure organic semiconductors.

Identifying molecular orbitals and on-surface reaction products with photoemission tomography

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Photoemission tomography [1] allows to directly correlate the momentum maps of photoemission intensity measured by angle-resolved photoemission spectroscopy (ARPES) and particular electronic states of organic molecules via the plane wave final state approximation. This simple correlation makes ARPES a quantitative tool for assigning molecular orbitals, 3D orbital imaging, determining the structure of molecule layer, and quantifying the charge transfer between metal substrate and organic adsorbate, and so on [2–5].

In this contribution we report two recent examples of this method. First, the electronic states and geometric vertical structures of perylene-tetracarboxylic dianhydride (PTCDA) molecule on an oxygen-reconstructed ($\sqrt{2}\times\sqrt{2}$)R45° Cu(100) surface are investigated. With photoemission tomography measurement we found that, in contrast to PTCDA on intrinsic Cu(100) where strong molecule-substrate interaction is present [6], the oxygen adsorbed on Cu(100) prevents charge transfer from metal substrate into the PTCDA molecule. The simultaneous electronic and structural decoupling at the molecule-metal interface is further corroborated by X-ray standing wave measurement and DFT calculation [7].

Second, photoemission tomography was used to investigate the thermally induced chemical reaction of dibromo-bianthracene (DBBA) molecule deposited on Cu(110) [8]. We could clearly identify the cyclodehydrogenation product of DBBA upon post-deposition annealing as bisanthene molecules using orbital imaging. Moreover, the exact chemical state of bisanthene can be defined comparing the measured momentum maps and the ones predicted by DFT for different possible adsorption configurations.

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Structural and electronic characterization on organic semiconductor homojunctions

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In order to develop organic electronic devices, it is necessary to establish fundamental physical properties of organic semiconductors. Single crystalline molecular semiconductor materials are good benchmarks for exploration into basic aspects of the materials as well as for indicating one promising direction to overcome mobility drawbacks of general organic semiconductor devices. Meanwhile, regulation of electric properties of organic semiconductor materials through controlled doping has long been an important challenge in the organic electronics field. Whereas tuning of energy level alignments at molecular-molecular and molecular-electrode heterojunctions through doping at the interfaces has already been established as an essential technology of the organic electronics, researches for regulating charge carrier properties of the organic semiconductor materials themselves through doping into crystalline molecular semiconductors, like the cases of Si, are quite limited. Recently, successful doping into single crystal rubrene ($C_{42}H_{28}$) based on homoepitaxy of single crystalline rubrene thin films was reported [1]. In this study, we investigated structural and electronic characterization on homojunctions of two prototypical organic semiconductor materials, rubrene and pentacene ($C_{22}H_{14}$), formed on the single crystal surface of each molecule.

Two-dimensional grazing incidence X-ray diffraction (2D-GIXD) data on the homojunction samples of rubrene revealed substantially identical patterns to those of bare rubrene single crystal samples, as shown in Fig. 1, corroborating excellent crystallinity of the homoepitaxial rubrene thin films grown on the single crystal rubrene [1]. In contrast, an existence of so-called “thin-film phase” pentacene (Pn-TF) on the single crystal pentacene (Pn-SC) was detected in diffraction patterns of pentacene homojunctions (Fig. 2). Electronic structures of these homojunction samples are also presented in this contribution.

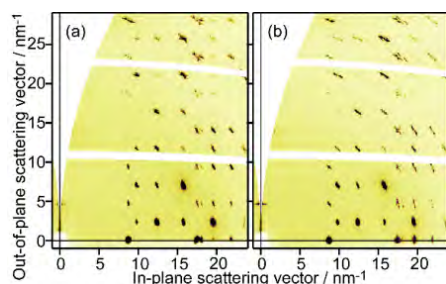


Fig. 1 2D-GIXD patterns of (a) single crystal rubrene and (b) homoepitaxial rubrene samples.

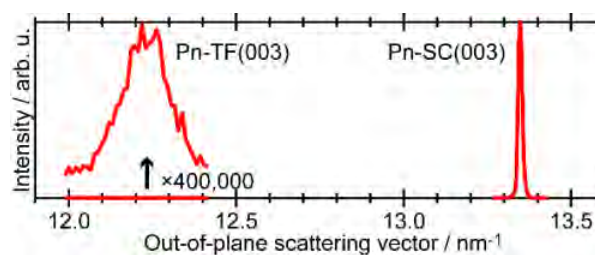


Fig. 2 Out-of-plane diffraction profiles of a pentacene homojunction sample.

Band structure of $\text{CH}_3\text{NH}_3\text{PbI}_3$ and $\text{CH}_3\text{NH}_3\text{PbBr}_3$ perovskite single crystals from angle-resolved photoelectron spectroscopy

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Photovoltaic devices based on halide perovskites with outstanding optoelectronic properties have exhibited tremendous progress in performance.^[1] To understand the origin of these properties comprehensively, detailed knowledge on the underlying electronic band structure is required. Here, we present complementary results from low-energy electron diffraction (LEED), angle-resolved photoelectron spectroscopy (ARPES), and density functional theory (DFT) calculations for $\text{CH}_3\text{NH}_3\text{PbBr}_3$ and $\text{CH}_3\text{NH}_3\text{PbI}_3$ single crystals. For both, sharp LEED patterns corresponding to the (001) surfaces of $\text{CH}_3\text{NH}_3\text{PbBr}_3$ and $\text{CH}_3\text{NH}_3\text{PbI}_3$ were observed together with well-resolved, dispersive valence band (VB) features. Noteworthy, the LEED patterns of $\text{CH}_3\text{NH}_3\text{PbI}_3$ reveal a coexistence of the cubic and tetragonal phase at the sample surface already at room temperature. From ARPES, we determined a bandwidth of ~ 1.0 eV and of ~ 1.3 eV along the X - R direction in $\text{CH}_3\text{NH}_3\text{PbI}_3$ and $\text{CH}_3\text{NH}_3\text{PbBr}_3$ single crystals, respectively. In good agreement with results from DFT calculations, the hole effective-mass, m_h^* , with values as small as $0.18 m_0$ ($\text{CH}_3\text{NH}_3\text{PbI}_3$) and $0.25 m_0$ ($\text{CH}_3\text{NH}_3\text{PbBr}_3$) were found. Furthermore, the fundamental differences between linear and logarithmic methods in determining the VB onset are discussed and addressed. These findings substantially enhance our understanding of the intrinsic optoelectronic properties of halide perovskites.

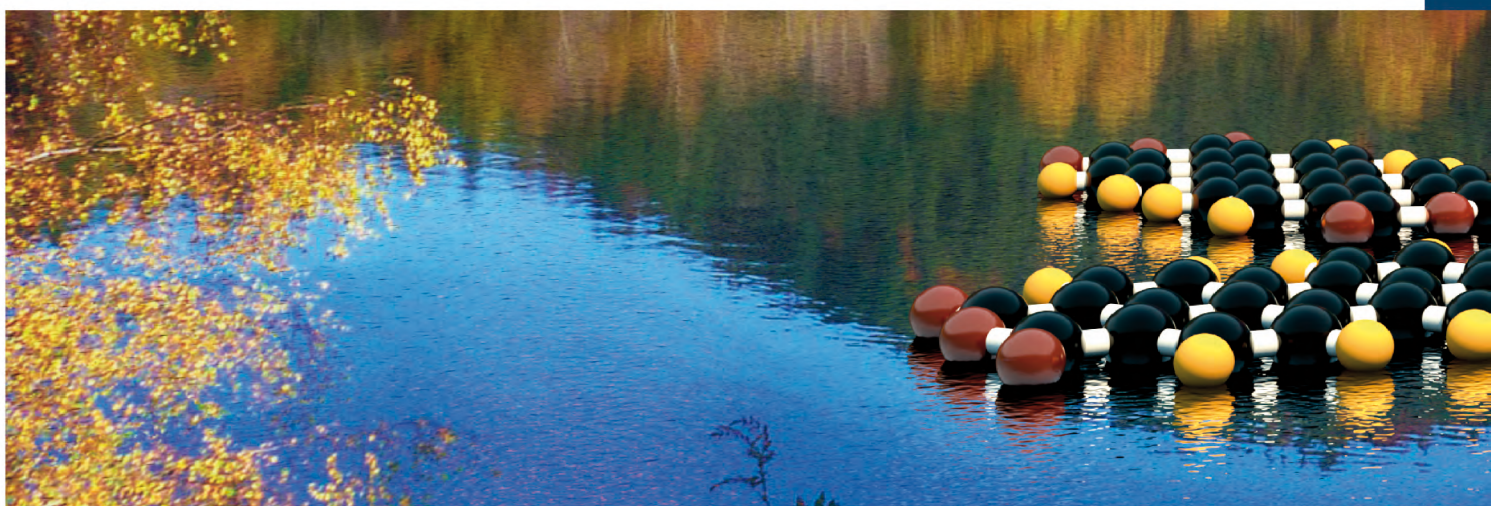
[1] J. Berry *et al.*, Adv. Mater. 27, 5102 (2015).

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