

## CPP 3: Organic Electronics and Photovoltaics - Layer Morphology and Molecular Aggregation

Time: Monday 9:30–13:00

Location: C 243

## Invited Talk

CPP 3.1 Mon 9:30 C 243

**Time-resolved in-situ x-ray scattering to resolve structure formation in thin film processing** — ●EVA M. HERZIG — Universität Bayreuth, Physikalisches Institut, Herzog Group - Dynamik und Strukturbildung, 95440 Bayreuth, Germany

The nanomorphology of thin films determines a wide range of physical properties and therefore the performance of functional thin films. Typical examples are found in organic electronics as in organic or hybrid photovoltaics. Understanding the self-assembly processes that occur during the drying of the photoactive film, will allow us to make progress in controlled nanomorphology tuning. We have developed tools to investigate thin film formation processes using synchrotron radiation to resolve structural developments with time [1]. We can control various processing parameters to systematically investigate the influence of these parameters on the final thin film morphology. This allows us, for example, to resolve the temporal evolution of polymer crystallization processes [2]. We complement the structural analysis with time-resolved spectroscopy measurements to gain further understanding on the structure formation processes. In this talk, the influence of the deposition environment is discussed and its role for controlling the thin film morphology and the resulting material properties. - - - [1] S. Pröller et al. "Note: Setup for chemical atmospheric control during in situ grazing incidence X-ray scattering of printed thin films" Rev. Sci. Instrum. 2017, 88(6): 066101. [2] S. Pröller et al. "Following the Morphology Formation In Situ in Printed Active Layers for Organic Solar Cells" Adv. Energy Mater. 2016, 6(1): 1501580.

CPP 3.2 Mon 10:00 C 243

**The impact of morphology and polymer-fullerene miscibility on device stability of organic solar cells** — ●ANDREJ CLASSEN, CHAOHONG ZHANG, YAKUN HE, HEUMUELLER THOMAS, NING LI, JOSE DARIO PEREA, STEFAN LANGNER, and CHRISTOPH BRABEC — FAU Erlangen-Nürnberg, Germany, Erlangen

As organic PV efficiencies regularly exceed 10%, the science of stabilization and lifetime gains importance. Several degradation phenomena in organic solar cells are related to an increase in trap density, and have been studied with respect to their impact on open-circuit voltage and fill factor. The short circuit current may be affected by fullerene dimerization which shows a clear dependence on active layer morphology and can be avoided by using different fullerene derivatives. Interestingly, in several novel high performing polymers, such as PTB7 and PCE11, intrinsic morphological instabilities have been observed. Utilizing different fullerene derivatives, we find that increased solubility of the fullerene within the polymer matrix allows superior device stability, but can reduce the initial device performance. Thus a fine balance between stability and device performance has to be found by tuning the donor-acceptor ratio in those systems. To separate effects from several different degradation mechanisms that usually occur at the same time, we perform tests under controlled environmental conditions to avoid photo-oxidation and distinguish between thermal and light induced degradation by applying a series of temperature steps in the dark.

CPP 3.3 Mon 10:15 C 243

**investigating the degradation of PffBT4T-2OD: PCBM solar cells by in-operando GISAXS/ GIWAXS measurements** — ●DAN YANG<sup>1</sup>, FRANZISKA C. LÖHRER<sup>1</sup>, VOLKER KÖRSTGENS<sup>1</sup>, ARMIN SCHREIBER<sup>1</sup>, SIGRID BERNSTORFF<sup>2</sup>, JILLIAN BURIK<sup>3</sup>, and PETER MÜLLER-BUSCHBAUM<sup>1</sup> — <sup>1</sup>TU München, Physik-Department, LS Funktionelle Materialien, 85748 Garching — <sup>2</sup>Elettra Sincrotrone Trieste, Basovizza, 34149 Trieste, Italy — <sup>3</sup>University of Alberta, Department of Chemistry, Edmonton, Canada

Polymer bulk heterojunction solar cells are showing great potential as a cost-effective alternative to conventional solar cells in near future due to their easily scalable and solution-based manufacturing. The power conversion efficiencies (PCE) of lab-scale devices have already exceeded 13%. Aside from optimizing the initial PCE of solar cells, their long-term stability must be considered as a key role in the organic solar cell (OSCs) development. The degradation of OSCs mainly focuses on the role of oxygen, water and intrinsic degradation of constituent materials. To investigate the degradation behaviour of the donor material in organic solar cells, PffBT4T-2OD: PC71BM solar cells are

probed with in-operando GISAXS and GIWAXS measurements. From the combination of the morphology changes with the J-V performance, the degradation mechanisms can be well understood. This should be very important for optimizing the individual materials to improve the stability of organic solar cells.

CPP 3.4 Mon 10:30 C 243

**Influence of solvent additive 1,8-octanedithiol on P3HT:PCBM solar cells** — WEIJIA WANG<sup>1</sup>, LIN SONG<sup>1</sup>, DAVID MAGERL<sup>1</sup>, DANIEL MOSEGUI GONZALES<sup>1</sup>, VOLKER KÖRSTGENS<sup>1</sup>, MARTINE PHILIPP<sup>1</sup>, JEAN-FRANCOIS MOULIN<sup>2</sup>, and ●PETER MÜLLER-BUSCHBAUM<sup>1</sup> — <sup>1</sup>TU München, Physik-Department, LS Funktionelle Materialien, 85748 Garching — <sup>2</sup>HZG at MLZ, 85747 Garching

Organic solar cells based on poly(3-hexylthiophen-2,5-diyl):phenyl-C60-butyric acid methyl ester (P3HT:PCBM) have developed into a well-controlled model system for studying fundamental questions, although device efficiencies of other blends using low band gap polymers demonstrated significantly higher device efficiencies. We investigate the influence of solvent additive 1,8-octanedithiol (ODT) on polymer crystallinity, surface and inner morphology, and quantitative molecular miscibility of P3HT and PCBM as function of the ODT volume concentration. The crystallinity is probed with absorption spectroscopy and grazing incidence wide angle X-ray scattering. The morphology and miscibility are characterized via AFM and time-of-flight grazing incidence small angle neutron scattering. ODT processing proves to be beneficial for promoting P3HT crystallinity and optimizing the inner morphology in terms of substructures and molecular miscibility, consequently leading to a better photovoltaic performance.

CPP 3.5 Mon 10:45 C 243

**Effect of Side Chain Modification on Crystallization and Crystal Orientation in Thin Films of Poly(3-(6-bromohexyl)thiophene)** — ●OLEKSANDR DOLYNCHUK<sup>1</sup>, PHILIP SCHMÖDE<sup>2</sup>, PAUL M. REICHSTEIN<sup>2</sup>, MATTHIAS FISCHER<sup>1</sup>, MUKUNDAN THELAKKAT<sup>2</sup>, and THOMAS THURN-ALBRECHT<sup>1</sup> — <sup>1</sup>Experimental Polymer Physics, Institute of Physics, Martin Luther University Halle-Wittenberg, Germany — <sup>2</sup>Applied Functional Polymers, Macromolecular Chemistry I, University of Bayreuth, Germany

Semicyrystalline conjugated polymers are of great interest as organic materials for various electronic devices due to a remarkable combination of semiconducting, thermal and mechanical properties, which strongly depend on morphology and orientation of polymer crystals. This work aims a comparative study of crystallization of poly(3-(6-bromohexyl)thiophene) (P3BrHT) and poly(3-hexylthiophene) (P3HT) in bulk and in thin films. Differential scanning calorimetry evidenced a significant decrease of crystallization and melting temperatures and melting enthalpy of P3BrHT as compared to P3HT. Temperature dependent wide-angle XRD revealed a distortion of crystal lattice in bulk P3BrHT and allowed estimating crystallinity in this material that amounted to about 43%. The crystal orientation in ultrathin films of both polymers spin coated on SiO<sub>2</sub>/Si and graphene was explored using grazing incidence XRD. The results indicated stronger face-on crystal orientation with  $\pi$ - $\pi$  stacking normal to both substrates in as-spun P3BrHT than P3HT, whereas melt-crystallized P3BrHT on graphene has only face-on oriented crystals.

## 15 min. break

CPP 3.6 Mon 11:15 C 243

**Studying lamellar-like morphologies of conjugated polymers through a new symmetry-inspired model** — ●CRISTINA GRECO, KURT KREMER, and KOSTAS DAOULAS — Max Planck Institute for Polymer Research, Mainz, Germany

In conjugated polymers, charge transport properties are known to be strongly affected by morphology. An interesting recent observation is that, to achieve high mobilities, perfect lamellar order is not necessary [1]. Here we present a simple model that enables the study of morphologies with partial lamellar order, at device-relevant length scales. Nonbonded interactions responsible for coplanarity in chain orientation and for stacking are described by anisotropic soft potentials constructed on the basis of symmetry considerations. Using polyalkylthiophenes as a test system, we perform Monte Carlo simulations of

chains of various lengths. Lamellar-like morphologies are obtained, either as mono- or polydomains. The type of lamellar order is identified by computing 2D scattering patterns, which can be compared with experimental GIWAXS data. From this analysis, we conclude that our morphologies correspond to a smectic mesophase, which was also reported in experiments [2]. We analyze the organization of chains inside the lamellae and identify in a simple way connectivity pathways between the lamellae. In perspective, atomistic detail can be reintroduced via backmapping, allowing for prediction of charge transport [3]. [1] R. Noriega et al. *Nat. Mater.* 2013, 12, 1038. [2] Z. Wu et al. *Macromolecules* 2010, 43, 4646. [3] P. Gemünden et al. *Macromol. Rapid Commun.* 2015, 36, 1047.

CPP 3.7 Mon 11:30 C 243

**Orientation and Order Bottle Brush Copolymers** — ●ARTHUR MARKUS ANTON<sup>1</sup>, CHRISTIAN DAVID HEINRICH<sup>2</sup>, MUKUNDAN THELAKKAT<sup>2</sup>, and FRIEDRICH KREMER<sup>1</sup> — <sup>1</sup>Peter Debye Institut für Soft Matter Physics, Leipzig University — <sup>2</sup>Macromolecular Chemistry I, University of Bayreuth

Compared to linear polymers bottle brush copolymers provide advantages, such as higher chain mobility or increased persistence length. Concerning this, a protocol on the preparation of brush copolymers containing electronically active poly(3-hexylthiophene) (P3HT) segments in their side chains has recently been published [1]. With rising side chains length highly crystalline materials are obtained; lamellar crystals have been observed *for the first time* in the case of brush copolymers. Moreover, the charge carrier mobility in brushes is comparable to linear P3HT, whereas the brushes' excellent thermal stability gives rise to further applications [1]. To analyze the molecular organization in the P3HT bottle brush films infrared transition moment orientational analysis (IR-TMOA) is employed [2,3]. The spectral absorption is recorded depending on the polarization *and in addition* on the inclination of the sample film relative to the incident light. This enables to determine the spatial orientation and order of particular molecule segments. While linear P3HT exhibits a distinct face on orientation, no macroscopic order is evident in the brush copolymer.

[1] C. D. Heinrich and M. Thelakkat, *J. Chem. Phys. C* 4 (2016) 5370

[2] A. M. Anton, F. Kremer et al., *J. Am. Chem. Soc.* 137 (2015) 6034

[3] A. M. Anton, F. Kremer et al., *Macromolecules* 49 (2016) 1798

CPP 3.8 Mon 11:45 C 243

**Investigating molecules response toward laser illumination during laser directed self-assembly (LDSA)** — ●ANDHIKA ASYUDA<sup>1</sup>, LINUS PITHAN<sup>1,2</sup>, ANTON ZYKOV<sup>1</sup>, ANDREAS OPITZ<sup>1</sup>, and STEFAN KOWARIK<sup>1,3</sup> — <sup>1</sup>Humboldt-Universität zu Berlin, Institut für Physik, Berlin — <sup>2</sup>European Synchrotron Radiation Facility, Experiments Division ID03, Grenoble — <sup>3</sup>Bundesanstalt für Materialforschung und Prüfung, 8.6 Fibre Optic Sensors, Berlin

A growth of tetracene thin film is among intensively studied vapor-deposited molecular film. While tetracene is usually grown as randomly oriented polycrystalline film, Pithan et al [1] demonstrated a way to use laser illumination during thin film growth for aligning the growing crystallites in the film. The key of this approach is choosing a laser wavelength matching 1 of its 2 Davydov components.

An aligned crystalline film is indeed desirable for device realization, such as transistor, due to anisotropic carrier transport in organic semiconductors. However, there is no investigation yet of structural properties of photoaligned film, such as roughness, island surface area, and island density. In this contribution, various growth parameters of a photoaligned tetracene film are discussed, particularly for their influences to film morphology and anisotropy. Recent AFM data consistently show an increase in grain size due to photoalignment, regardless of substrate temperature and molecular flux during the growth.

[1] L. Pithan, et al, *Adv. Mater.* 2017, 29, 1604382

CPP 3.9 Mon 12:00 C 243

**Impact of the excitation spot adjustment in angular resolved photoluminescence experiments** — ●CHRISTIAN HÄNISCH, SIMONE LENK, and SEBASTIAN REINEKE — Dresden Integrated Center for Applied Physics and Photonic Materials (IAPP) and Institute for Applied Physics, TU Dresden, Germany

One of the main pathways of optimizing the performance of organic light-emitting diodes (OLED) is the reduction of optical loss modes by aligning the transition dipole moments (TDM) of the light-emitting molecules parallel to the substrate interface.

Angular resolved photoluminescence spectroscopy is the most promi-

nent experimental technique to determine the anisotropy factor as a measure of the average TDM orientation. Despite the widespread application of this method, a quantitative discussion of the impact of specific setup configurations is - to the best of our knowledge - missing so far. Especially, the accurate positioning and size of the optical excitation spot is very important as well as its distance to the detector.

With help of a numerically solved ray optics model, we show that already small displacements of the excitation spot can lead to remarkable changes in the measured emission spectra. For non-ideal setup configurations, the accuracy of experimental data fits can be drastically improved using the developed corrections.

Hence, this work enables not only to numerically treat unavoidable experimental non-idealities such as displacements caused by the substrate thickness but also helps to quantify and state measurement deviations of the anisotropy factor.

CPP 3.10 Mon 12:15 C 243

**Control of molecular orientation on a single substrate by changing growth parameters leads to switching of thin-film optical properties** — ●GIULIANO DUVA<sup>1</sup>, LINUS PITHAN<sup>2</sup>, ALEXANDER GERLACH<sup>1</sup>, ALEXANDER JANIK<sup>1</sup>, ALEXANDER HINDERHOFER<sup>1</sup>, and FRANK SCHREIBER<sup>1</sup> — <sup>1</sup>Eberhardt Karls Universität Tübingen, Tübingen, Germany — <sup>2</sup>European Synchrotron Research Facility (ESRF), Grenoble, France

The Optical response of many organic semiconductors (OSC) can exhibit anisotropy depending on the average orientation of the molecular components [1]. Diindenoperylene (DIP) is an OSC whose HOMO-LUMO transition dipole moment is parallel to the long molecular axis. Organic Molecular Beam Deposition (OMBD) allows a high degree of control over the thin film structure. Using OMBD, uniaxially ordered DIP films in a standing-up configuration at room temperature are obtained exhibiting a strong optical anisotropy, with the out-of-plane component of the dielectric function being roughly ten times higher than the in-plane component in the visible spectrum [2]. Here we present a method to change the molecular orientation without modifying the substrate or reducing crystal quality. Growth via OMBD followed by annealing allows to obtain ordered, atmosphere-stable films of mostly lying-down DIP exhibiting inverted optical properties compared to films of standing-up DIP. We also discuss a possible mechanism to explain this effect.

[1] A. Hinderhofer et al. *Chem. Phys. Chem.* 13 (2012).

[2] U. Heinemeyer et al. *Phys. Rev. B* 78 (2008).

CPP 3.11 Mon 12:30 C 243

**Elucidating Aggregation Pathways And Structural properties Of Chromophores With The Help Of MD-Simulations** — ●AXEL BOURDICK<sup>1</sup>, MARKUS REICHENBERGER<sup>2</sup>, ANNA KÖHLER<sup>2</sup>, and STEPHAN GEKLE<sup>1</sup> — <sup>1</sup>Biofluid Simulation and Modeling, University of Bayreuth, 95440 Bayreuth (Germany) — <sup>2</sup>Experimental Physics II, University of Bayreuth, 95440 Bayreuth (Germany)

We investigate the aggregation behaviour of the donor-acceptor molecules pDTS(FBTTh2)2 ("T1") and p-SIDT(FBTTh2)2 ("H1") in MTHF solutions. Using optical spectroscopy, we find that T1 forms aggregates in solution while H1 aggregates only when processed as a thin film, but not in solution. Free energy molecular dynamics (MD) simulations based on force-fields derived from quantum-mechanical density functional theory fully reproduce this difference. Interestingly, our simulations reveal that this difference is not due to the lengthy carbon side chains. Instead, it can be traced back to the different molecular symmetry which allows T1 to form an aggregated state in which the central donor units are spatially well separated while a similar configuration is sterically impossible for H1. As a consequence, any aggregation of H1 necessarily involves aggregation of the central donors which requires, as a first step, stripping the central donor of its protective MTHF solvation shell. This unfavorable process leads to a significant kinetic hindrance for aggregation and explain the strongly differing aggregation behavior of T1/H1 in MTHF despite their otherwise similar structure.

CPP 3.12 Mon 12:45 C 243

**H- an J-type electronic coupling in single conjugated polymer aggregates** — ●THERESA EDER<sup>1</sup>, THOMAS STANGL<sup>1</sup>, MAX GMELCH<sup>1</sup>, KLAAS REMMERSSEN<sup>2</sup>, DIRK LAUX<sup>2</sup>, SIGURD HÖGER<sup>2</sup>, JAN VOGELSANG<sup>1</sup>, and JOHN LUPTON<sup>1</sup> — <sup>1</sup>Institut für Experimentelle und Angewandte Physik, Universität Regensburg — <sup>2</sup>Kekulé-Institut für organische Chemie und Biochemie, Universität Bonn

Single-molecule spectroscopy (SMS) has proved to be a useful tool to

further understand light and charge generation in organic semiconductors. However, it is not sufficient to unravel the various coupling processes between single polymer chains which take place in the organic layer of devices like an organic light emitting diode or solar cell. To bridge the gap between those thick layers and single molecules we grow single aggregates which consist of several single polymer chains. Depending on their morphology those aggregates can show distinct types of coupling which can be generally explained using the concept of H- and J-type coupling. Here we show not only that the type of

coupling can be chosen by using modified polymers, but we can also switch reversibly between H- and J-type coupling of one and the same single aggregate by exposing it to solvent vapour. To distinguish between the different types of aggregates we examine them using SMS and extract their characteristic photophysical properties. This experiment contributes to a further understanding of electronic interactions between polymer chains in an aggregate and highlights the simultaneous existence of H- and J-type coupling in well-ordered aggregates [1]. [1] Eder et al., Nature Comm. 8, 1641 (2017)