

CPP 46: Organic Thin Films II (joint session CPP/DS/HL, organized by DS)

Time: Wednesday 15:00–17:00

Location: CHE 91

CPP 46.1 Wed 15:00 CHE 91

Crystallinity and Degradability of Nano- and Microscaled Biopolymer Thin Films — PREETAM ANBUKARASU¹, DOMINIC SAUVAGEAU¹, and ANASTASIA ELIAS^{1,2} — ¹Chemical and Materials Engineering, University of Alberta, Edmonton, Canada — ²Leibniz-Institut für Polymerforschung Dresden e. V.

Enzymatically-degradable polymer thin films are attractive for biomedical, packaging, micro-electronic and agricultural applications. The stability and degradability of these materials are known to depend on both the parameters under which they are processed, and on the environmental conditions under which degradation occurs. Processing conditions are especially relevant for semi-crystalline polymers, since the degree of crystallinity of a material is an important determinant of its degradability.

In this work, we examine the effect of nano-scale dimensional constraint on the crystallinity and enzymatic degradability of polyhydroxybutyrate (PHB), a biopolymer. The physical properties of solution-cast PHB films of varying thicknesses were examined by atomic force microscopy (AFM, lamella orientation & surface profile) and x-ray diffraction (XRD, crystallinity & crystal anisotropy). The enzymatic degradability was tested using a diffraction grating-based optical sensor. We found that as the thickness of the samples was reduced from 5 μm to less than 100 nm, the crystallinity of the films decreased, while the rate of degradation increased. However, below 100 nm, surprisingly slow degradation rates were observed. This occurs due to the fact that these films are amorphous, inhibiting the binding of the enzymes.

CPP 46.2 Wed 15:15 CHE 91

Determination of the molecular orientation in absorptive organic thin films — CHRISTIAN HÄNISCH, SIMONE LENK, and SEBASTIAN REINEKE — Dresden Integrated Center for Applied Physics and Photonic Materials (IAPP) and Institute for Applied Physics

The overall efficiency of organic light-emitting diodes (OLEDs) is mainly limited by the high refractive index of the organic layers causing a trapping of large portions of the initially emitted light. Using emitter molecules with transition dipole moments parallel to the interface planes of an OLED reduces this loss channel and hence, increases the outcoupling efficiency of the device. The orientation of the molecules' transition dipole moments can be determined by angular resolved photoluminescence spectroscopy.

We investigate the impact of the organic layer's absorption on the determined orientation value by evaluating the emission spectra of single organic layers with thicknesses up to 150 nm. Numerically, these emission layers are represented by a set of radiating electrical dipoles which are homogeneously distributed over the whole layer. To represent the absorption of the excitation light, the single dipoles are weighted by an exponential function according to the Beer-Lambert law.

Using this method, we can show that the orientation parameter of the red phosphorescent emitter Ir(MDQ)₂(acac) doped into NPB is stable over a time range of several months at temperatures between room temperature and 80°C which is only 5% below the glass transition temperature of NPB.

CPP 46.3 Wed 15:30 CHE 91

Interface-Controlled DNTT Thin Films: Growth, Morphology, and Temporal Evolution — ANDREA KARTHÄUSER¹, TOBIAS BREUER¹, HAGEN KLEMM², FRANCESCA GENUZIO², GINA PESCHEL², ALEXANDER FUHRICH², THOMAS SCHMIDT², and GREGOR WITTE¹ — ¹FB Physik, Philipps-Universität Marburg, 35032 Marburg, Germany — ²Abt. Chemische Physik, FHI der MPG, 14195 Berlin, Germany

The high charge carrier mobility and chemical stability of dinaphthothienothiophene (DNTT) render this new organic semiconductor (OSC) especially interesting for organic field effect transistors (OFETs) [1, 2]. Despite such device advances, the structure and morphology of DNTT thin films are so far rather unexplored. On the prototypical substrates SiO₂ and graphene we prove a substrate-mediated control of the molecular orientation by means of NEXAFS and XRD measurements. Furthermore, by using atomic force microscopy (AFM) and photoelectron emission microscopy (PEEM) we analyzed the morphology of DNTT films with variable thicknesses and find a temporal dewetting of these films. This pronounced island formation leads to a breakup of the film which is most efficient for thin films of a few monolayers. Finally we

have extend this study also to device relevant substrates by analyzing DNTT films that were grown on SAM treated dielectrics. Again a distinct dewetting is found, which is expected to affect the long-term performance of DNTT devices and appears surprising in view of the reported long term stability of DNTT-OFETs [2].

[1] Yamamoto, T.; J. Am. Chem. Soc. (2007), 129,224. [2] Zschieschag, U.; Org. Electron. (2013), 14, 1516.

CPP 46.4 Wed 15:45 CHE 91

Direct photo alignment and optical patterning: Controlling molecular thin film growth on the meso-scale — LINUS PITHAN^{1,3}, PAUL BEYER¹, LAURA BOGULA¹, ANTON ZYKOV¹, PETER SCHÄFER¹, JONATHAN RAWLE², CHRIS NICKLIN², ANDREAS OPITZ¹, and STEFAN KOWARIK¹ — ¹Humboldt-Universität zu Berlin, Institut für Physik, Berlin, Germany — ²Diamond Light Source, Didcot, UK — ³ESRF, Grenoble, France

A novel strategy for direct photoalignment of molecular materials using optothermal re-orientation is introduced. We show that it is possible to fabricate anisotropic and photolithographically patterned organic molecular thin films based on light-directed molecular self-assembly (LDSA).[1]

Growing tetracene thin films via LDSA on amorphous silica, we employ 532 nm laser illumination, which matches the lower Davydov absorption band, to induce preferential orientations of molecular crystal grains. Based on grazing incidence X-ray diffraction (GIXD) as well as optical spectroscopy we determine a threshold laser power for azimuthal alignment. The patterning and polarized light emission that is possible with LDSA is important for applications such as polarized organic light emitting diodes or photonic metasurfaces.

[1] L. Pithan et. al. Adv. Mater. doi:10.1002/adma.201604382

CPP 46.5 Wed 16:00 CHE 91

Modern *in situ* real-time X-ray scattering and nucleation theory for an enhanced understanding of molecular self-assembly — ANTON ZYKOV¹, SEBASTIAN BOMMEL^{1,2}, YVES GARMSHAUSEN³, LINUS PITHAN^{1,4}, PAUL BEYER¹, GONZALO SANTORO⁵, STEFAN HECHT³, JÜRGEN P. RABE¹, and STEFAN KOWARIK¹ — ¹Inst. f. Physik, Humboldt-Universität zu Berlin — ²DESY, Hamburg — ³Inst. f. Chemie, Humboldt-Universität zu Berlin — ⁴ESRF, Grenoble, France — ⁵Inst. de Ciencia de Materiales de Madrid, CSIC, Spain

Quantifying nanoscale processes that drive the self-assembly of organic molecules into functional thin films is the prerequisite to understand and steer structure formation. In a study on the growth of PTCDI-C₈ we unravel a remarkable layer-dependent molecular diffusion behaviour from an innovative simultaneous *in situ* acquisition of X-ray reflectivity growth oscillations and diffusively scattered X-rays and the application of state-of-the-art nucleation theory. This allows us to determine nucleation energies, critical cluster sizes and attempt frequencies.[1] These quantities can be strongly influenced when applying chemical tuning to well-known molecules. We showcase this on the example of the growth of 6P and 6PF2. As a result of the fluorination we achieve a significant film smoothing as desired for applications, where an efficient in-plane charge carrier transport is of importance.

[1]A. Zykov et al., J. Chem. Phys. 146, 052803 (2017)

CPP 46.6 Wed 16:15 CHE 91

Modeling of singlet fission in weakly-interacting acene molecules — SHARAREH IZADNIA¹, DAVID W. SCHÖNLEBER², ALEXANDER EISFELD², ALEXANDER RUF¹, AARON C. LAForge¹, and FRANK STIENKEMEIER¹ — ¹Physikalisches Institut, Universität Freiburg, Hermann-Herder-Str. 3, 79104 Freiburg, Germany — ²Max-Planck-Institut für Physik komplexer Systeme, 01187 Dresden

Singlet fission, a process in which a singlet excited state is converted into two triplet states, is a means to circumvent the Shockley-Queisser limit for energy conversion in solar cells. In a recent experiment, singlet fission was observed in a disordered system where organic chromophores are distributed on the surface of a rare gas cluster. Here we give details on the theoretical modeling of singlet fission in this system. Our kinematic model explicitly takes into account the details of the geometrical arrangement of the system as well as the time-dependent populations of the relevant states of each molecule. Using this model, which goes beyond usual mean-field treatment, we study the trends

obtained by singlet fission, exciton-exciton annihilation, and singlet hopping on the experimental observables. Our simulations support the conclusion of the experimental observation that SF is present even at weakly interacting conditions.

CPP 46.7 Wed 16:30 CHE 91

Ultra-robust thin film devices from metal-terpyridine wires — ●FLORIAN VON WROCHEM¹, MARIA ANITA RAMPI², and WOLFGANG WENZEL³ — ¹Materials Science Laboratory, Stuttgart — ²Dipartimento di Chimica, Universita' di Ferrara — ³Institute of Nanotechnology, Karlsruhe Institute of Technology, Germany

Considerable efforts have been undertaken within the past decades to shift organic-based thin-film devices from basic research to the application level. A major hurdle is given by the thermal deposition of the metal electrodes, which remained elusive due to the damage and the electrical shorts experienced by the fragile molecular layers. Here, we show that large area molecular junctions of outstanding electronic properties and robustness can be realized using densely packed molecular wires consisting of FeII-terpyridine complex oligomers, despite a conventional fabrication process involving top electrode evaporation directly on the molecular layer. Surprisingly, these oligomer-based devices are stable for over 2 years under regular current-voltage cycling,

withstanding a wide range of temperatures (150-360 K) and applied voltages (3 V). Electrical studies in conjunction with ab-initio calculations reveal that charge transport (i) occurs via electron (hopping) conduction and is limited by the charge injection through a Shottky barrier (0.72 eV), following Richardson-Schottky injection.

CPP 46.8 Wed 16:45 CHE 91

Superradiance from two dimensional brick-wall aggregates of dye molecules: the role of size and shape for the temperature dependence — ●ALEXANDER EISFELD¹, CHRISTIAN MARQUARDT², and MORITZ SOKOLOWSKI² — ¹MPI-PKS — ²Uni Bonn

Aggregates of interacting molecules can exhibit electronically excited states which are coherently delocalized over many molecules. This can lead to a strong enhancement of the fluorescence decay rate which is referred to as superradiance (SR). To date, the temperature dependence of SR is described by a $1/T$ law. Using an epitaxial dye layer and a Frenkel-exciton based model we provide both experimental and theoretical evidence that significant deviations from the $1/T$ behaviour can occur for brickwall-type aggregates of finite size leading even to a maximum of the SR at finite temperature. This is due to the presence of low energy excitations of weak or zero transition strength.