SYMPOSIUM EP05

Excitons, Electrons and Ions in Organic Materials
November 26 - November 29, 2018

Symposium Organizers
Rodrigo Noriega, University of Utah
Jonathan Rivnay, Northwestern University
Elizabeth von Hauff, Vrije Universiteit Amsterdam
Ni Zhao, Chinese University of Hong Kong

Symposium Support
The University of Utah, Department of Chemistry

* Invited Paper

SESSION EP05.01: Mixed Ionic-Electronic Conduction—Materials and Characterization
Session Chairs: Paul Meredith and Jonathan Rivnay
Monday Morning, November 26, 2018
Hynes, Level 2, Room 208

8:00 AM *EP05.01.01
Local Structure and Counter-Ion Properties Control Ion Uptake in Organic Electrochemical Transistors David S. Ginger; University of Washington, Seattle, Washington, United States.

Organic electrochemical transistors (OECT) are of interest for applications in biochemical sensing and signal transduction across the biological/digital divide. The excellent performance of conjugated polymers in these applications is due to the ability of the polymer to accommodate ionic countercharge throughout the device volume. The resulting volumetric capacitance which allows for very large modulations of the charge density in the transistor channel and large transconductance values. Combining OECT measurements on different polymers with different counter ions, we study how both polymer morphology and the chemical nature of the counter ions affect ion uptake and coupling between ionic and electronic transport. Furthermore, we use electrochemical strain microscopy (ESM) to probe local swelling resulting from ion uptake, and correlate ion uptake with both polymer structure and the chemical properties of the ions, providing microscopic insight into these processes that lead us to propose new material design rules.

8:30 AM EP05.01.02
Operando X-Ray Scattering Reveals Ion-Induced Structural Changes During Electrochemical Gating of Poly(3-hexylthiophene) Elayne Thomas1, 2, Rodrigo Noriega1, 2, Hidenori Nakayama1, Bhooshan C. Popere3, Rachel Segalman1 and Michael L. Chabinyc1, 2; 1Stratingh Institute for Chemistry, University of Groningen, Groningen, Netherlands; 2Zernike Institute for Advanced Materials, University of Groningen, Groningen, Netherlands.

The semicrystalline nature of most semiconducting polymers complicates the relationship between morphology and electronic conduction. In order to increase their electrical conductivity, charge carriers are introduced into conjugated polymers by extrinsic dopants, usually by introduction from solution or by infiltration from a vapor. In this case, the dopant molecule, now ionized, is the counterion to the charged backbone. There is currently little understanding of how these ions interact with the amorphous and crystalline regions of the semiconductor to achieve the observed large changes in electrical conductivity.

To address the question of how ions interact with these distinct phases, we have explored the evolution in morphology and optoelectronic properties of a conjugated polymer in an organic electrochemical transistor. By using a novel polymeric ionic liquid (PIL) as the gate insulator, we carry out for the first time operando studies capturing the structural evolution in poly(3-hexylthiophene) (P3HT) during electrochemical gating by X-ray scattering. PILs contain one ion covalently bonded to the polymer backbone and one ion that is mobile, which allows for control of counterion diffusion as well as low-voltage device operation. From these experiments, we find that negatively-charged ions from the dielectric first infiltrate the amorphous regions of the semiconductor, and penetrate the crystalline regions at a critical carrier density of 4 × 10^20 cm^-3. Upon infiltration, the crystallites expand by 12% in the alkyl stacking direction and compress by 4% in the σ-σ stacking direction. The stark change in crystal structure of P3HT correlates with a sharp increase in the effective carrier mobility. Complementary UV-visible spectroscopy reveals that holes induced in P3HT first reside in the crystalline regions of the polymer, which verifies that a charge carrier need not be in the same physical domain as its associated counterion. Our results provide a comprehensive view of doping in P3HT which challenges the assumption that trap filling is the sole mechanism to justify the non-linear trend in electrical conductivity with carrier density.

8:45 AM EP05.01.03
Conjugated Polions—Charged Semiconducting Polymers Processed from Protic Solvents Ryan Chiechi1, 2, Lambert Jan Anton Koster2, Nutifafa Doumon2 and Gang Ye1, 2; 1Stratingh Institute for Chemistry, University of Groningen, Groningen, Netherlands; 2Zernike Institute for Advanced Materials, University of Groningen, Groningen, Netherlands.

Semiconducting conjugated polymers have found applications in field-effect transistors, sensors, solar cells, etc. In essentially any application that requires a semiconducting material, the semiconducting material can be replaced with a properly-designed conjugated polymer, endowing a device with the useful properties of polymers such as solution-processing, mechanical compliance, thinness and light weight. However, the solutions from which thin-films of conjugated polymers are cast contain very small amounts of polymer, on the order of tens of milligrams per milliliter. The nonpolar nature of π-conjugated moieties means that high-quality films can only be cast from solvents that are either difficult or impossible to work with at scale.
A one approach to creating conjugated polymers that can be processed from “green” solvents is to decorate them with charged pendant groups to form conjugated polyelectrolytes that can be dissolved in polar, protic solvents like water or methanol. However, designing conjugated polyelectrolytes that are both processable and retain high carrier mobility is challenging because of the disparate physical properties of the backbone and pendant groups. This amphiphilic nature drives the polymer chains to self-assemble such that, in polar solvents, the hydrophobic backbone chains pack together and are shielded by a shell of ionic pendant groups to minimize unfavorable solvent interaction. These protein-like aggregates are carried into the films, leading to poor pi-pi contact. Our approach is to place closed-shell charges into the backbones of conjugated polymers to match the ionic character of the pendant groups such that the backbone is directly solubilized by polar solvents. The resulting conjugated polymers are intrinsic semiconductors; they are not bipolararic and are EPR silent. Their band-gaps can be tuned via common push-pull strategies and they form high-quality films with good carrier mobility from polar, protic solvents. The cations in the backbone are generated from pre-polymers by the loss of methanol under acidic conditions. Thus, we can process high-quality thin-films from wet formic acid, which is non-toxic, non-flammable and is already used industrially at scale.

9:00 AM  *EP05.01.04*  
Polar and Reactive Side Chain Functionalization of Conjugated Polymers for Redox and Bio-Electronic Applications  
John R. Reynolds; Georgia Institute of Technology, Atlanta, Georgia, United States.

Conjugated polymers provide a unique encompassing set of structurally tunable optical, electronic transport, and redox properties that allows their present and potential use in a host of applications which span field effect transistors, light emitting diodes, solar cells and photodetectors, and electrochromism, along with batteries, supercapacitors, and bio-electronics. Processing of these materials is carried out using a variety of solution methods including spin-coating, spray-coating, blade-coating, slot die coating and ink jet printing. The ability to process these polymers from environmentally benign solvents and aqueous solutions is highly advantageous for possibilities in large scale roll-to-roll processing. Maintaining competitive electronic properties while achieving aqueous solubility is difficult for several reasons. 1) Materials with polar functional groups that provide aqueous solubility can be difficult to purify and characterize. 2) Many traditional coupling and polymerization reactions cannot be performed in aqueous solution. 3) Ionic groups, though useful for obtaining aqueous solubility, can lead to a loss of solid-state order as well as a screening of any applied bias. In this lecture, we will address how side chain polarity, from charge neutral ether and ester functionality to ionic functionality, impacts not only processing, but also charge transport, redox switching and optical properties. As an alternative, a multistage side-chain cleavage approach will be presented that allows a functional group to be used for its intended purpose, then removed once the functionality becomes unnecessary. Through the attachment of multistage sidechains, conjugated materials can be synthesized, characterized, and purified in organic solvents, converted to a water-soluble form for aqueous processing, and brought through a final treatment to leave behind the desired electronic material as a solvent-resistant film.

9:30 AM  BREAK

10:00 AM  *EP05.01.05*  
Semiconducting Polymer for Bioelectronics and Field Effect Transistors  
Lain McCulloch; 1Imperial College London, London, United Kingdom; 2King Abdullah University of Science and Technology, Thuwal, Saudi Arabia.

The evolution of organic electronics has now reached the commercial phase, with the recent market introduction of the first prototypes based on organic transistors and organic solar cell modules fabricated from solution. Understanding the impact of both the organic semiconductor design and processing conditions, on both molecular conformation and thin film microstructure has been demonstrated to be essential in achieving the required optical and electrical properties to enable these devices. Polymeric semiconductors offer an attractive combination in terms of appropriate solution rheology for printing processes, mechanical flexibility for rollable processing and applications, but their optical and electrical performance requires further improvement in order to fulfill their potential. Synthesis of conjugated aromatic polymers typically involves carbon coupling polymerisations utilising transition metal catalysts and metal containing monomers. This polymerisation chemistry creates polymers where the aromatic repeat units are linked by single carbon-carbon bonds along the backbone. In order to reduce potential conformational, and subsequently energetic, disorder due to rotation around these single bonds, an aldol condensation reaction was explored, in which a bisisatin monomer reacts with a bisoxindole monomer to create an isoindigo repeat unit that is fully fused along the polymer backbone. This aldol polymerization requires neither metal containing monomers or transition-metal catalysts, opening up new synthetic possibilities for conjugated aromatic polymer design, particularly where both monomers are electron deficient. Polymers with very large electron affinities can be synthesised by this method, resulting in air stable electronic transport, demonstrated in solution processed organic thin film transistors. We present an electrical, optical and morphology characterisation of polymer thin films, illustrating structure-property relationships for this new class of polymers. Organic electrochemical transistors (OEVTs) have been shown to be promising devices for amplification of electrical signals and selective sensing of ions and biologically important molecules in an aqueous environment, and thus have potential to be utilised in bioelectronic applications. The sensitivity, selectivity and intensity of the response of this device is determined by the organic semiconducting polymer employed as the active layer. This work presents the design of new organic semiconducting materials which demonstrate significant improvements in OEVT performance, through operation in accumulation mode, with high transconductance and low operating voltage.

10:30 AM  *EP05.01.06*  
Organic Electrochemical Transistors—Developments on Modelling the Transient Response and on Device Fabrication  
Gregorio C. Faria; Sao Carlos Physics Institute, University of Sao Paolo, Sao Carlos, Brazil.

Organic Electrochemical Transistors (OEVTs) have recently been the focus of great attention due to their ability to support both ionic and electronic conduction and their successful application as highly-sensitive biosensors and neuromorphic devices. In the first part of my talk, I will discuss a universal model for the transient drain current response in OEVTs. Using equivalent circuits and semiconductor charge injection physics, the model is able to reconstruct the drain current in OEVT devices, is applicable to both planar and membrane-functionlized devices, and allows one to extract useful impedances of any system from only a single transient measurement. For the second part of my talk, I will present a general method and accompanying guidelines for fabricating both non-aqueous and aqueous based OEVTs using water-insoluble hydrophilic semiconducting polymers. By taking advantage of the interactions of semiconducting polymers in certain organic solvents and the formation of a stable liquid-liquid interface between such solvents and water, we successfully fabricated OEVTs with high transconductance, ON/OFF ratios of 10^6, and enhancements in stability. Using the model discussed in the first part of the talk, key fundamental properties of both the device and active channel materials were extracted, including volumetric capacitance and intrinsic hole mobility. Finally, the benefits of using liquid-liquid interface OEVTs to measure bacterial membrane disruption will be briefly discussed.

11:00 AM  *EP05.01.07*  
In Situ Methods for Understanding Charge Transport in a Conducting Redox Polymer  
Mia C. Sterby, Rikard Emanuelsson, Maria Strømme and Martin Sjödin; Uppsala University, Uppsala, Sweden.
Organic materials can be used to ensure sustainable electrical energy storage, but since organic molecules are generally insulating conducting additives are commonly used to ensure electrical conductivity throughout the material. A different approach is to use conducting redox polymers (CRPs). CRPs consist of a redox active pendant group, used for its high capacity, attached to a conducting polymer backbone. The CRP presented here is aimed to be used as the positive electrode in a water-based organic battery.

In this work we employ the well-studied conducting polymer poly(3,4-ethylenedioxythiophene) (PEDOT) with a quinone pendant group, a combination that we have proven can work in an all-organic proton battery. Quinones constitute an attractive class of molecules as they possess a high charge storage capacity, show reversible redox chemistry, and are naturally occurring, e.g., in the electron transport chains in respiration and in photosynthesis. The aim of the study is to understand the charge transport properties of the CRP.

The CRP studied is characterized by various in-situ electrochemical methods including conductance, Quartz Crystal Microbalance (QCM), UV-vis and Electron Paramagnetic Resonance (EPR). Based on the results the electron and ion transport during electrochemical redox conversion will be discussed.


11:15 AM *EP05.01.08
Conductive Polymer Electrodes for Biosensors and Energy Conversion Erin L. Ratcliff; University of Arizona, Tucson, Arizona, United States.

Conductive polymer electrodes offer the possibility to control redox properties through synthesis and processing, if critical structure-property relationships are understood. Importantly, these semiconductors demonstrate a hybrid electronic-ionic conduction mechanism, and thus, have unique electrochemical behaviors relative to classical inorganic semiconductor electrodes.

This talk will provide new insights into the mechanism of charge transfer at conductive polymer/liquid interfaces. A mathematical framework will be demonstrated using a modified Marcus-Gerisher model that enables prediction of rate constants from simple film properties. Experimental evaluation of potential-dependent rate constants will be demonstrated. Results will be contextualized in electrochemical devices.

11:45 AM EP05.01.09
Correlation Between Redox, Charge Carrier Transport and Ion Molecular Structure Properties in Ion-Gated PCBM Films Tian Lan1, Francesca Soavi2, Jonathan Sayago3 and Clara Santato4; 1Ecole Polytechnique de Montreal, Montreal, Quebec, Canada; 2 Universita di Bologna, Bologna, Italy; 3Universidad Nacional Autonoma de Mexico, Temixco, Mexico.

The n-type organic semiconductor phenyl-C61-butyric acid methyl ester (PCBM), a soluble fullerene derivative well investigated for organic solar cells and transistors, can undergo several successive reversible, diffusion-controlled, one-electron reduction processes. We exploited such processes to shed light on the correlation between electron transfer properties, ionic and electronic transport as well as device performance in IL-gated transistors. Two ILs were considered, based on bis(trifluoromethylsulfonyl)imide [TFSI] as the anion and 1-ethyl-3-methylimidazolium [EMIM] or 1-butyl-1-methylpyrrolidinium [PYR14] as the cation. The aromatic structure of [EMIM] and its lower steric hindrance with respect to [PYR14] favor a 3D (bulk) electrochemical doping. As opposed to this, for [PYR14] the doping seems to be 2D (surface-confined). If the n-doping of the PCBM is pursued beyond the first electrochemical process, the transistor current vs. gate-source voltage plots in [PYR14][TFSI] feature a maximum that points to the presence of finite windows of high conductivity in IL-gated PCBM transistors.


1:30 PM *EP05.02.01/BM07.02.01
Interacting Ion and Electron Currents Paul Meredith; Swansea University, Swansea, United Kingdom.

Ionic and electronic conduction mechanisms are underpinned by fundamentally different physics [1]. For example, ions diffuse through a conducting matrix via centre of mass transport that can be described by classical processes. Electrons and holes are quantum mechanical entities characterised by delocalisation, tunnelling or hopping. These fundamental differences impose radically different length-and-time-scales on ionic and electronic conduction – and generally speaking the solid-state physics of ions and electrons have remained two very different fields requiring different skill sets [2]. However, bioelectronics, where a central challenge is the transduction between ion and electron currents, is a scientific collision point between the two worlds.

In my talk I will summarise the major differences between ionic and electronic solid state electrical conduction. I will also describe methods that can probe the relevant time-and-length scales in order to identify and disentangle the native signatures of each carrier type [3, 4]. A number of model systems and devices will be exemplified that allow the study of ion and electron conduction processes, and indeed provide a means to test prototypical concepts in transduction and bioelectronic logic interfaces [5, 6].

We have recently developed the organic electrolytic photocapacitor (OEPC), a nanoscale optoelectronic device for eliciting action potentials in neurons. Herein, we cover in detail the physical mechanisms behind the charge generation and dynamics of charging and capacitive coupling in these devices using optoelectronic/electrochemical measurements combined with simulation and modeling. Electrochemical impedance measurements allow corroboration of these models, and reveal the nature of photocapacitive and photofaradaic effects in the devices. Using scanning probe microscopy techniques, we have evaluated the mechanical properties of the nanocrystalline films, finding relatively low Young’s moduli in the range of 500 MPa. In order to take a reductive approach compared with previous measurements of neurons and electrogenic tissues, we have validated the performance of OEPCs using nonexcitable cells, *Xenopus laevis* oocytes. We find rapid membrane potential changes in the range of tens to hundreds of millivolts are induced by OEPC devices, showing extremely effective capacitive coupling and explaining previous findings of action potential generation. The overall result of our work is a fuller physical and mechanistic understanding of this novel device platform, and a roadmap for guiding future development.

### 2:15 PM BM07.02.03

**The Design of Air Stable, Redox Active Conjugated Polymers and Their Applications in Accumulation Mode OECTs**

Alexander Giovannitti\(^1\), Reem Rashid\(^2\), Jenny Nelson\(^1\), Iain McCulloch\(^1\) and Jonathan Rivnay\(^1\),

\(^1\)Imperial College London, London, United Kingdom; \(^2\)Northwestern University, Chicago, Illinois, United States.

Organic electrochemical transistors (OECTs) are receiving a great deal of attention due to the ability to efficiently transduce biological signals. The working principle of OECTs relies on the modulation of the conductivity of an organic semiconductor, which can be modified by applying a potential at the gate electrode and driving electrochemical redox reactions in aqueous solution (doping/de-doping of the organic semiconductor). OECTs can either be operated in accumulation\(^1\) or depletion mode\(^2\) where the operation in accumulation mode has the advantage of lowering the operational voltage and therefore improve the power consumption of the device (device is in an off state rather than an on state when no gate voltage is applied). Recently, high performing OECT materials have been reported based on electron rich alkoxythiophene copolymers which show low oxidation potentials in aqueous electrolytes and enable OECT operation at low voltages.\(^2\)

However, one drawback of these easily oxidizable polymers is that the copolymers can become oxidized by reactions with oxygen from ambient air. This result in the formation of p-doped polymers and superoxide anions (O$_2^-$) where the latter is a reactive radical and might cause harm to biological systems or degrade the organic semiconductor. As a result of this oxidation reaction, a constant gate voltage would need to be applied to keep the material in its neutral state (and the device off).

We will present the development of an air-stable conjugated polymers based on donor-acceptor type copolymer. The copolymer shows reversible redox reaction at potentials below 0.3 V vs Ag/AgCl. When exposed to aqueous ambient conditions, the polymer does not become oxidized. Long-term stability tests were carried out where devices were exposed to ambient conditions for more than 6 months with no sign of degradation. The polymer shows a good stability when charged with up to one hole per repeat unit (polaron) with transconductances in the range of 80 S/cm (at -0.7 V). This work demonstrates the importance of chemical design strategies for the development of accumulation mode OECT materials to mitigate reactions with oxygen in aqueous electrolytes and ambient conditions.


### 2:30 PM BM07.02.04

**Polythiophene Derivatives as Mixed Organic Ionic and Electronic Conductors**

Christine Luscombe, University of Washington, Seattle, Washington, United States.

Mixed organic ionic and electronic conductors are being explored for a wide range of applications, from bioelectronics to neuromorphic computing, artificial muscles and energy storage applications. These materials exploit the simultaneous transport properties of ionic and electronic carriers to enable novel device functions. Recently, polymer semiconductors have received significant amounts of attention because of their flexibility, biological compatibility and ease of fabrication. These materials, particularly thiophene-based polymers such as poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate)(PEDOT:PSS) and related derivatives, have demonstrated significant enhancements in performance in a relatively short amount of time, with transconductance values of PEDOT:PSS transistors surpassing those achieved even with graphene.

Through our NSF Designing Materials to Revolutionize and Engineer our Future (DMREF) award with researchers at Cornell University and the University of Chicago, we have been investigating the synthesis of ethylene-glycol functionalized polythiophenes, their thin film morphology, and their ionic and electronic conductivities, and comparing against theoretical predictions. In this talk, the effect on the density of the ethylene-glycol side chains and their pattern of placement on ionic conductivity will be discussed.

### 3:00 PM BREAK

### 3:30 PM BM07.02.05

**Mixed Conductivity in Conducting Polymer Thin Films**

Sabine Ludwig, University of Stuttgart, Stuttgart, Germany.

This talk will give an overview about our recent activities on electronic and ionic conductivity in conjugated and redox polymer thin films with different molecular architectures. Preparation of films is done either by electropolymerization or solution deposition followed by morphology tuning, e.g. by solvent vapor annealing.\(^1\)

We are particularly interested in three-dimensional architectures based on branched monomers such as terthiophenes (3T) or triphenylamines (TPA). TPA redox moieties are useful to allow for electrochemical or chemical crosslinking of as-deposited films. Both, with TPA redox polymers\(^2\) and with...
polymers which bear TPA as pending redox moieties of linear polythiophenes[3] we could perform successful crosslinking and simultaneous doping of polymer films. The films provide very high stabilities with high electronic conductivities as evidenced by cyclic voltammetry coupled with in-situ conductance measurements and four-point-probe measurements. In the case of 3T we have reported on ionopolymer and copolymer films of 3T and ethylenedioxythiophene which allow polymer-analogous reactions to induce ionic functionalities, thereby creating branched conjugated polyelectrolyte films.[4], [5]

To get a better understanding on mixed conductivity in polymer films, we have recently performed a study on electronic and ionic conductivity of linear conjugated polyelectrolytes by impedance spectroscopy and dc-measurements.[6] The clear dependence of the conductivities as function of humidity and degree of doping will be discussed in the talk in more detail.


4:00 PM *EP05.02.06/BM07.02.06 Soft Electronic and Ionic Neural Interfaces Klas Tybrandt1,2, Dion Khodagholy1, Flurin Stauffer2 and Janos Vörös2; 1Department of Science and Technology, Linköping University, Norrkoping, Sweden; 2Institute for Biomedical Engineering, ETH Zürich, Zurich, Switzerland; 3Department of Electrical Engineering, Columbia University, New York, New York, United States.

Two-way communication between electronics and neural tissue is key for advancing diagnosis and therapies for neurological diseases and disorders, as well as proving detailed information about brain signaling. Establishing such neural interfaces is a major challenge, as the tissue response to implants can have a detrimental effect on the signal quality and functionality of the implant. Also, electrical stimulation is inherently limited in its stimulation of neural tissue, in comparison to the sophisticated chemical signaling processes within biological tissue. Here, I present our efforts in addressing two critical technological aspects for the creation of versatile neural interfaces; the matching of mechanical properties of tissues and electronics, and the development of fast and low-leakage chemical interfaces. Soft electronic biomedical implants have a demanding set of requirements, including biocompatibility, mechanical and electromechanical properties, long-term stability and electrode performance. To meet these requirements, we have developed a high-performance, long-term stable soft and stretchable composite for neural electrodes. Based on this composite, high-density soft electrode grids were developed and implanted onto brain surface of rats. The electrodes provided high-quality recordings during three months of implantation. Next, I will outline our strategy for creating high-speed low-leakage chemical neural interfaces, by discussing the relationship between delivery delay and leakage, and then present an iontronic approach to achieve low leakage and small delay simultaneously.


Neuromorphic computing could address the inherent limitations of conventional silicon technology in dedicated machine learning applications. Recent work on silicon-based asynchronous spiking neural networks and large crossbar-arrays of two-terminal memristive devices has led to the development of promising neuromorphic systems. However, delivering a parallel computation technology, capable of implementing compact and efficient artificial neural networks in hardware, remains a significant challenge. Organic electronic materials offer an attractive alternative to such systems and could provide neuromorphic devices with low-energy switching and excellent tunability, while being biocompatible and relatively inexpensive.

This talk describes state-of-the-art organic neuromorphic devices and provides an overview of the current challenges in the field and attempts to address them[1]. We demonstrate a novel concept based on an organic electrochemical transistor[2] and show how some challenges in the field such as stability, linearity and state retention can be overcome[3].

Furthermore, we investigate chemical doping mechanisms in the active material for improved material functionality and demonstrate that this device can be entirely fabricated on flexible substrates, introducing neuromorphic computing to large-area flexible electronics and opening up possibilities in brain-machine interfacing and adaptive learning of artificial organs.

1 van de Burgt et al. Nature Electronics, 2018
2 van de Burgt et al. Nature Materials, 2017
3 Keene et al. J Phys D, 2018

4:45 PM EP05.02.08/BM07.02.08 Anisotropic Conducting Polymer Films for Bioelectronics Patricia Jastrzebska-Perfec, Georgios Sypopoulos, Jennifer Gelinas and Dion Khodagholy; Columbia University, New York, New York, United States.

Anisotropic conductive films, which consist of electrically conductive particles dispersed in nonconductive media, are increasingly being applied to establish high-density electrical bonds between electronic boards and chips. However, current anisotropic composites utilize metallic particles, often nickel and epoxy-based media, that require high thermocompression energy for bonding. Therefore, they have limited applicability in thin-film, conformable, and plastic-based devices that are used in bioelectronic applications. Furthermore, these materials are not biocompatible, significantly limiting their use in biological systems. We hypothesized that replacing the metallic particles with conducting polymer particles combined with a biocompatible nonconducting matrix would address this limitation. We developed a novel anisotropic conducting polymer (ACP) consisting of poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS) conducting polymer particles dispersed in a matrix of crosslinked chitosan (CS). To determine the permeability of PEDOT:PSS to CS, we characterized the resistances of thin CS-based films sandwiched with PEDOT:PSS and gold pads. We investigated the particle size, structure, density and distribution of pure PEDOT:PSS particles and PEDOT:PSS-coated CS particles. The anisotropy was defined by the ratio of horizontal and vertical impedance between interconnects. We benchmarked the anisotropy of the developed ACPs by geometrically varying an array of gold electrodes. The final ACP, which was created at 70°C with minimal pressure, yielded anisotropy of 10^4-10^6. The ACP was then used to maintain precise connections between a high density conformable implantable neural probe and back-end electronics. It enabled complete chronic in vivo implantation of these electronics with minimal encapsulation layers, highlighting applicability for use in bioelectronic and clinical devices.
Organic field-effect transistors (OFETs) have received considerable attention as essential components of organic electronics, which have the advantage of large-area scalability and processability over inorganic based transistors. However, organic semiconductors (OSCs) in OFETs have relatively low electrical transport properties that need to be improved before realization in commercial applications. In order to improve the electrical transport properties of dopants are commonly introduced to bulk or surfaces of OSC films. In contrast to bulk doping, surface doping (SD) achieved by the addition of dopants to the top of film surfaces can lower the adverse effects on electrical properties seen in bulk doping. Previous SD studies have shown enhancement in device performances but did not clearly investigate the SD mechanism systematically.

The SD efficiency can vary greatly depending on the properties of the OSCs, dopants, and especially the film conditions since the doping effect can be sensitive to the film structure. Therefore, we investigate the SD mechanism through a comparative study of two different OSC materials, small molecule PTCDI-C8 and polymer N2200, doped with two kinds of aminosilanes, and various thicknesses and grain sizes of deposited films to find the optimum SD condition. We characterized the doped films and OFETs by using AFM, Grazing-incidence X-Ray Diffraction, Infrared spectroscopy, electrical measurements, etc.

As a result, higher doping efficiency showed in the doped PTCDI-C8 OFETs than N2200 OFETs due to the difference of intrinsic OSC properties such as its open film morphology. Additionally, the SD efficiency is decreased with increasing thickness and grain size of the OSC films. The more electron donating groups the dopant has, the lower doping concentration is needed to reach the same optimized value. Importantly, we find that there are two doping concentration regimes. In low doping concentrations, the dopants primarily contribute to the increase in mobility. In higher doping concentrations, the dopants also enhance the threshold voltage. Furthermore, the SD process does not adversely affect other OFET properties such as the on-off ratio.

Therefore, our results demonstrate that the properties of OSCs, dopants and particularly the film conditions must be considered in order to maximize the SD efficiency for improved OFET performances.

Metal Organic Frameworks in a Blended Polythiophene Hybrid Film with Surface-Mediated Vertical Phase Separation for the Fabrication of a Highly Sensitive Humidity Sensor Young Jin Jang, Eun Hye Kwon and Yeong Don Park; Energy and Chemical Engineering, Incheon National University, Incheon, Korea (the Republic of).

Demand for portable gas sensors capable of monitoring the atmospheric environment in daily life is growing as air pollution deteriorates. Organic field-effect transistors (OTFTs) are regarded as an ideal flexible platform for creating portable, lightweight, and robust sensor devices. OTFTs are sensitive to physical and chemical stimuli because small interactions between a semiconductor and a target analyte amplify the electrical signal of a transistor device under the field-effect mobility, drain current, and threshold voltage. However, organic transistors inevitably suffer from poor stability and bad electrical properties, resulting in a slow response and recovery of the sensor device. We attempted to address this issue by developing an OTFT-based humidity sensor, in which a humidity-capturing material was inserted into the polymeric semiconductor. In this study, a facile, reliable, fast-response, highly sensitive poly(3-hexylthiophene-2,5-diyli) (P3HT)-based humidity sensor was developed by introducing metal organic frameworks (MOFs), HKUST-1, into the semiconducting layer. HKUST-1 displayed an excellent ability to capture water molecules, thereby generating and attracting charge carriers derived from water molecules present in the active layer. The HKUST-1/P3HT hybrid film showed excellent device sensitivity with an enhanced electrical current and a threshold voltage shift as a function of the relative humidity due to the superior gas capture properties and the porosity of HKUST-1. The surface energy of the substrate altered the distribution and location of HKUST-1 in the active layer, which improved the sensitivity of the hydrophilic surface. A dynamic gas sensing test revealed that the hybrid film displayed a reliable and stable performance with fast response and recovery times. The introduction of MOFs into a conjugated polymer stabilized and sensitized the devices, providing a facile method of improving gas sensor technologies based on organic semiconductors.

Tuning Electrical Properties of Phenanthroimidazole Derivatives to Construct Multifunctional Deep-Blue Electroluminescent Materials Zelin Zhu; City University of Hong Kong, Hong Kong, Hong Kong.

The maturity of longer wavelength emitters (green and red) makes it more urgent to develop high performance deep-blue emitters OLED (organic light-emitting diodes). A blue emitter that can serve as a multifunctional material (e.g. as host for the green and red counterparts) is of high interest in this field.

A comparative study was carried out for pristine vs. degraded organic light emitting diode (OLED) devices regarding their luminescence characteristics using time-resolved electroluminescence (TREL). Notable changes were observed in the temporal form of the TREL curve upon materials degradation, which was found to be due to the trapped charges formed during the OLED operation. The TREL decay time of degraded OLED was found to be longer than that of pristine OLED due to the excitons produced by weakly bound charges trapped in the organic layer that are released by thermal energy even without applying the voltage pulse. On the other hand, the onset time of luminescence was found to be shorter due to the excitons from strongly bound charges that are released by the application of the voltage pulse. We demonstrated that TREL can be effectively used to identify different types of effect and to investigate the luminescence mechanisms of a light-emitting device.

Enhancement of N-Type Organic Field-Effect Transistor Performances Through Surface Doping with Aminosilanes Nara Shin1,2, Jakob Zessin1,2, Min Ho Lee1, Mike Hanbuch1,2 and Stefan C. Mannsfeld1,2; 1TU Dresden, Dresden, Germany; 2Leibniz Institute for Solid State and Materials Research Dresden, Dresden, Germany.

Organic field-effect transistors (OFETs) have received considerable attention as essential components of organic electronics, which have the advantage of large-area scalability and processability over inorganic based transistors. However, organic semiconductors (OSCs) in OFETs have relatively low electrical transport properties that need to be improved before realization in commercial applications. In order to improve the electrical transport properties of dopants are commonly introduced to bulk or surfaces of OSC films. In contrast to bulk doping, surface doping (SD) achieved by the addition of dopants to the top of film surfaces can lower the adverse effects on electrical properties seen in bulk doping. Previous SD studies have shown enhancement in device performances but did not clearly investigate the SD mechanism systematically.

The SD efficiency can vary greatly depending on the properties of the OSCs, dopants, and especially the film conditions since the doping effect can be sensitive to the film structure. Therefore, we investigate the SD mechanism through a comparative study of two different OSC materials, small molecule PTCDI-C8 and polymer N2200, doped with two kinds of aminosilanes, and various thicknesses and grain sizes of deposited films to find the optimum SD condition. We characterized the doped films and OFETs by using AFM, Grazing-incidence X-Ray Diffraction, Infrared spectroscopy, electrical measurements, etc.

As a result, higher doping efficiency showed in the doped PTCDI-C8 OFETs than N2200 OFETs due to the difference of intrinsic OSC properties such as its open film morphology. Additionally, the SD efficiency is decreased with increasing thickness and grain size of the OSC films. The more electron donating groups the dopant has, the lower doping concentration is needed to reach the same optimized value. Importantly, we find that there are two doping concentration regimes. In low doping concentrations, the dopants primarily contribute to the increase in mobility. In higher doping concentrations, the dopants also enhance the threshold voltage. Furthermore, the SD process does not adversely affect other OFET properties such as the on-off ratio. Therefore, our results demonstrate that the properties of OSCs, dopants and particularly the film conditions must be considered in order to maximize the SD efficiency for improved OFET performances.
we introduce a n-type group, TPPO (triphenyl phosphine), to the N1-position of violet-blue fluorophore phenantroimidazole (PI) and successfully develop one deep-blue (TPAPOPPI) and two violet-blue emitters (3-CzPOPPI and CzBPOPPI) for OLEDs (organic light-emitting diodes). With highly twisted linkage, the TPPO group shows negligible influences on their photophysical properties of the new materials and the materials inherit high efficient deep-blue and violet-blue emission of the PI unit and its C2-connected arylamine skeletons. Meanwhile, TPPO group can open a new channel to transport electron. The electron injection and transport abilities of the developed emitters are enhanced. Non-doped devices using the 3-CzPOPPI and the CzBPOPPI emitters exhibit EQE\textsubscript{max} (external quantum efficiency) of 5.08% and 4.42% with CIE (Commission Internationale de l’Eclairage) coordinates (0.156, 0.061) and (0.104, 0.071), respectively. Similar efficiencies and even deeper blue emissions (CIE, > 0.050 for 3-CzPOPPI and 0.044 for CzBPOPPI) were observed in OLEDs with these emitters doped in 4,4’-bis(N-carbazolyl)-1,1’-biphenyl. TPAPOPPI is demonstrated to be a multifunctional deep-blue emitter and presents impressive performances when serving as non-doped (EQE\textsubscript{max} = 6.69%, CIE: (0.152, 0.095)) and doped (EQE\textsubscript{max} = 6.61%, CIE: (0.154, 0.068)) as well as a high-performance host for yellow phosphorescent OLED. By doping a yellow phosphorescent dye (PO-01) into a TPAPOPPI host, a white OLED with a high EQE of 20.3% and a low driving voltage of 3.2 V (at 1,000 cd m\textsuperscript{-2}).

**EP05.03.05**

**Silicon Phthalocyanines—From Recent and Upcoming Publications Will Be Presented**

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Phthalocyanines (Ps) are among the oldest commercial dyes used as industrial pigments and photo-receptors. Their optical properties, stability, and ease of synthesis have made them ideal as active materials for a plethora of optoelectronic applications. [1] Silicon phthalocyanines (SiPs) have two axial bonds originating from the Si atom, which can serve as functionalization sites without affecting the inherent optoelectronic properties of the phthalocyanine macrocycle itself. Therefore, we have used the axial groups as handles to improve solid state engineering and improve charge transport through the thin films.[2,3] We fabricated planar heterojunction organic photovoltaic devices (PHD) by physical vapour deposition and used the SiPc derivatives as both donor and acceptor layers, illustrating the ambipolar behavior of these molecules.[2,3] Through solid state engineering we were able to improve the overall efficiency by ~40% compared to the unsubstituted C2-SiPc. These preliminary OPV devices surpassed performances by similar PHD devices made using typical copper, aluminum and zinc (CuPc, AlPc, and ZnPc).

Similar chemistry produced solution processable SiPc-based ternary additives for P3HT:PcBM bulk heterojunction OPVs with increased photo generation at the interface, which translates to a 20% increase in overall efficiency.[4,5] When replacing PC61BM directly, the SiPc derivatives resulted in devices with similar power conversion efficiency (PCE).[5] Recently we have reported the use of a multifunctional SiPc tertiary additive that not only increase the efficiency of the OPV but also increases the stability by migrating to the interface and crosslinking the P3HT and PC61BM domains.[6] These studies are showing potential for SiPs in OPVs as multifunctional additives which simultaneously enhance device performance and device stability. Finally, we are fabricating high performing n-type organic thin film transistors based on these SiPc derivatives. Processing parameters, such as deposition rate, substrate temperature and surface modification can improve the electron mobility by 2-3 orders of magnitude.[7] Again through SiPc functionalization for targeted solid state engineering we were able to develop high performing n-type SiPc based OTFTs with a mobility of >0.5 cm\textsuperscript{2}V\textsuperscript{-1}s\textsuperscript{-1} - Currently the highest performing n-type Pc based thin film device.[8] Computational studies further demonstrate the potential of these versatile molecules.[9] Results from recent and upcoming publications will be presented.

**References**


**EP05.03.06**

**The Role of Ultrathin Interface Tunneling Layer for Both Carrier Injection and Perfect Charge Confinement to Realize Highly Efficient OLEDs**

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Each interface for organic light emitting diodes (OLEDs) plays a determinant role in the device performances and lifetimes. Thus, there has been lots of interest on interfaces in OLED for the critical insight of the fundamental parameters affecting efficiency as well as operational lifetime. Despite decades of research in interface engineering, OLEDs cannot show their full potential because of the lack of technology to maximize their interfacial stability. In other interest on interfaces in OLED for the critical insight of the fundamental parameters affecting efficiency as well as operational lifetime. Despite decades of research in interface engineering, OLEDs cannot show their full potential because of the lack of technology to maximize their interfacial stability. In other

words, the poor lifetime caused by efficiency reduction resultant from the charge imbalance and a resultant chemical degradation by accumulated charge at their interfaces has still been the most problematic issues for the realization of dominant use of OLEDs in the display as well as lighting applications.

In this study, we have introduced a unique technology to improve the device efficiency as well as stability via interface modification. In other words, when charges are injected into emitting layer (EML) [i.e., from the hole transport layer (HTL) and the electron transport layer (ETL)], charges are accumulated on both interfaces of EML due to the charge injection barrier. From this result, the deterioration of the interface characteristics is known to proceed by such accumulated charges. To minimize this interfacial degradation, the accumulated charges at the interfaces of EML should be reduced. Herein, we propose a new methodology to release the interfacial degradation by inserting ultrathin interface tunneling layer (ITL, ~1 nm) for lowering the effective barrier at the interfaces of EML. Fortunately, ITL could work as an exciton confine layer due to its high triplet energy (T1 > 2.7 eV) so that we could realize highly efficient green phosphorescent OLEDs (PHOLEDs) (EQE: 21.0 %) as well as much longer device lifetime (~ 2.5 times).

**References**


**Acknowledgements**

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Effect of Substituents of thiophene-vinylene-thiophene-Based Conjugated Polymer Donors on the Performance of Fullerene and Non-Fullerene Solar Cells

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Semiconducting polymers consisting of (E)-1,2-di(thiophen-2-yl)ethene (TVT) derivatives and benz[1,2-b:4,5-b']dithiophene with conjugated thiophene side chains (BDTT) were designed and synthesized to investigate the effect of fluorine and cyano groups in the 3-position of the thiophene ring in TVT on the photovoltaic properties. The corresponding PBDDT-TFT, PBDDT-FTVT, and PBDDT-CNTVT copolymers containing TVT, di-fluoro TVT (FTVT), and di-cyano TVT (CNTVT), respectively, demonstrated considerable variations in optical, electrochemical, morphological, and charge transporting properties. PBDDT-FTVT showed suitable frontier orbital energy levels, favorable face-on orientation, and a well-mixed and smooth morphology in the blends with 3,9-bis(2-methylene-(3-{1-[dicyanomethylen(e)-1-iodo]})-5,11,17-tetraakis(4-hexyloxyphenyl)-dithieno[2,3-d:2',3'-d']-s-indaceno[1,2-b:5,6-b']dithiophene (ITIC) and [6,6]-(2-cyanoethyl)-bicyclic acid methyl ester (PCBM). In contrast, PBDDT-CNTVT showed unfavorable frontier orbital energy levels and bimodal orientation in the thin film state, which interrupted efficient charge transport in organic photovoltaic devices. The device fabricated using PBDDT-FTVT exhibited the highest power conversion efficiency (PCE) of up to 6.50% with ITIC and a slightly lower PCE of 6.35% with PCBM.

Effect of Substituents of thiophene-vinylene-thiophene-Based Conjugated Polymer Donors on the Performance of Fullerene and Non-Fullerene Solar Cells

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Suppressing Dark Current in Organic Phototransistors Featuring a MoOx Layer

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We present an OPT with low dark current while maintaining its high responsivity. We were able to suppress the dark current over four orders of magnitude, by using a hole selective layer as the source/drain contact on a n-type semiconductor. The responsivity of our OPT was over 0.2 A/W under illumination of light with the power density of 0.5 mW/cm².

References


Blue-Emitting, Single-Benzene Fluorophore Based on Push-Pull Structure

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Conjugated and rigid structure in organic molecules is essential to exhibit fluorescence. Accordingly, benzene has been widely employed to impart rigidity and extend the conjugation within molecular structure. One or more number of benzene is required to show efficient fluorescence, but many benzene rings
in a molecule give a negative effect such as fluorescence quenching because of pi-pi interaction in the solid state. A single benzene-based fluorescent molecules will be a good candidate, which can be applied usefully in many fields, including bioimaging and optoelectronic devices, because aggregation-caused quenching can be easily prevented. Substituents on the benzene ring can affect the fluorescence property of the molecule. The formation of electronic push-pull system by introduction of electron donating and withdrawing group enables the single-benzene molecule to exhibit high fluorescence. We will discuss a blue emissive single-benzene molecule with push-pull structure which was easily synthesized. Various molecules with different structure were synthesized to investigate the cause of the fluorescence by changing substituents. The results showed that the fluorescence emission was caused by the push-pull system and inter- and intramolecular hydrogen bonding.

EP05.03.13 Synthesis of Polythiophene Derivatives with Oligoisobutylene Side Chains and Their Cross-Linking System Satoshi Miyano and Tomoya Higashihara; Yamagata University, Yonezawa, Japan.

In recent years, polymer semiconductors have received much attention due to their mechanical flexibility and solution-based low-cost processability. However, their durability for stretched stress is not enough for applying to wearable and implantable devices. The low stretchability of polymer semiconductor is due to high crystallinity which hinder the stiff main chain and strong intermolecular interactions. Here, we developed novel polythiophene derivatives, P3IBTs, which contain oligoisobutylene units in their side chains. We expect that several branched points on side chains weaken \( \pi-\pi \) stacking interaction and thereby decrease crystallinity of the polymers. In addition, we tried to develop cross-linked P3IBT to realize the formation of an inherently stretchable polymer semiconductor.

We prepared polythiophene derivatives with diisobutylene side chain (P3IB2T) \( (M_n = 12,000, M_w/M_n = 1.17) \) and triisobutylene side chain (P3IB3T) \( (M_n = 13,000, M_w/M_n = 1.21) \) by Kumada catalyst-transfer polycondensation. Their thermal, optical properties and crystalline nature were also investigated. The melting temperature of P3IB2T was determined by DSC, showing a distinct endothermic peak for \( T_m \) at 130 °C. On the other hand, there are neither endothermic nor exothermic peaks in the DSC curve of P3IB3T. Therefore, this polymer would be more amorphous-like than P3IB2T.

The absorption spectrum of P3IB2T film showed low absorption intensity around 620 nm, indicating weak \( \pi-\pi \) stacking interaction. Moreover, P3IB3T films showed the blue-shifted absorption spectrum compared to P3IB2T ones probably due to larger torsion of main chains affected by triisobutylene side chain. Next, the crystalline nature of the polymer thin films was evaluated by Grazing incidence wide-angle x-ray scattering (GIWAXS). P3IB2T and P3IB3T films showed edge-on orientation, judged from the azimuth plots of \( (200) \) diffraction patterns. Moreover, (010) diffraction patterns were not observed for P3IB2T and P3IB3T films, probably due to less \( \pi-\pi \) stacking interaction by oligoisobutylene side chains.

Finally, we cross-linked P3IB3T to realize the formation of an inherently stretchable polymer semiconductor. 4,4’-Methylenebis(2,6-methyl-2H,4H-[1,2,4]triazine-3,5-diyl)bis(methoxymethyl)phenol) and isopropyl p-toluenesulfonate were used as cross-linker and thermal acid generator, respectively. The cross-linked P3IB3T showed quite lower tensile strength (0.68 MPa) and higher elongation at break (141%) than a poly(3-hexylthiophene) pristine film.

EP05.03.14 Decatacition C\( ^{\circ} \) Nanoconjugates with Light-Harvesting Antenna and Intramolecular Electron-Transfer Processes for Photodynamic Bio-Applications He Yin, Min Wang and Long Y. Chiang; Chemistry, University of Massachusetts Lowell, Lowell, Massachusetts, United States.

Functionalized fullerene derivatives with retaining photophysical characteristics show promising light harvesting ability, and may have potential future for photodynamic bio-applications. We recently reported a nanostructure with a light-harvesting antenna conjugate \( \text{C}_{60}[^{\circ}\text{CPAF}-(\text{MN}^6_{\text{C}})^2]-(\text{I}^-)_{10} \) (LC15), which showed promising light-harvesting ability. Here we report a modified synthetic route to obtain well-characterized new fullerene derivative \( \text{C}_{60}[^{\circ}\text{CPAF}-(\text{MN}^6_{\text{C}})^2]-(\text{I}^-)_{10} \) (LC21) with less steps and higher yield. As \( \text{C}_{60} \) is replaced by more effective \( \text{C}_{70} \) which has broader absorption, the covalent incorporation of a visible light-harvesting antenna moiety CPAF and \( \text{C}_{60} \) provides broad photo-absorption from 300–650 nm. The ability of the electron-rich CPAF antenna to undergo intramolecular photocrossed electron-donation to the \( \text{C}_{60} \) electron-acceptor cage in LC21 allows the dominant of the anionic (C\( ^{\circ} \text{CPAF} \)) radical derived photochemistry alongside with triplet energy transfer-based photochemistry. The anionic (C\( ^{\circ} \text{CPAF} \)) radical can lead to the generation of superoxide radicals, and facile intersystem crossing efficiency from the fullereny singlet excited state \( \text{C}_{70}^{(\text{S})} \rightarrow \text{C}_{70}^{(\text{T})} \) to its long-lived triplet excited state \( \text{C}_{70}^{(\text{T})} \). The efficient production of \( \text{O}_2^{\cdot -} \) in triplet energy-transfer processes. Furthermore, not only increasing hydrophilicity of the conjugate, but incorporation of ten counter iodide anions \( (\text{I}^-) \) to LC21 may also allow the photooxidation of iodide via electron-transfer to either excited fullerene cage \( [\text{C}_{60} \circ \text{CPAF}]^2 \) to \( \text{C}_{70}^{(\text{T})} \) * in aqueous media, leading to further formation of fullerony anion radical intermediate (C\( ^{\circ} \text{CPAF}_\text{a}^{\cdot -} \)). The extinction coefficient (calculated from the corresponding UV-vis spectra of LC21 under both UVA and white light demonstrated promising light-harvesting ability. We synthesized two redox sensitive fluorescein FL) probes for the detection of \( \text{O}_2^{\cdot -} \) and \( \text{O}_2^{\cdot -} \) separately in aqueous PBS solution with high selectivity and specificity. The compound may be used as effective photosensitizer and nano-PDT drug for photoinactivation of pathogens.

EP05.03.15 Eco-Friendly Solution Floating Dip-Coating Method for High Crystalline Polythiophene Film Fun Hye Kwon, Young Jin Jang and Yeong Don Park; Energy and Chemical Engineering, Incheon National University, Incheon, Korea (the Republic of).

In the past decades, organic thin-film transistors based on conjugated polymer films have been intensively studied due to their potential applications in flexible, wearable, and low-cost electronics. Various reliable solution-printing techniques for the fabrication of organic electronics have been developed, and among these solution-processing approaches dip-coating is well known for manufacturing uniform and crystalline polymer thin-film. However dip-coating process spends large amount of polymer solution, recently many studies report bi-phase system which stacks the low density solution onto the high density solvent as a support solvent. Bi-phasic system reduces the amount of polymer solution, but it still uses large amount of organic solvents. In this study we replaced organic solvent with deionized water having high surface tension as a support solvent, and floated polymer solution on deionized water to control the solvent evaporation rate during dip-coating process. The additive solvents and addition methods determined the molecular order, morphology, and charge carrier transport of the resulting dip-coated polymer thin-film. This study confirms that eco-friendly dip-coating system has been developed, and resulting polymer film showed high performance despite the use of deionized water which was known to be fatal to the organic device.

EP05.03.16 Fabrication of Highly Efficient Red-Light-Selective Organic Photodetector Sandwiched Between Transparent Electrodes Tomomi Takagi, Yosuke Horii, Toshikatsu Sakai, Takahisa Shimizu, Hiroshi Ohtake and Satoshi Aihara; NHK Science and Technology Res Labs, Tokyo, Japan.

We are developing a vertically stacked organic image sensor that is overlaid with three organic photoconductive films, each of which is sensitive to only one of the three primary colors (red, green and blue), to realize a compact camera with high picture quality. To fabricate a photodetector with high transparency at wavelengths outside the detection region, a structure with an organic film sandwiched between transparent electrodes is necessary. Sputtering methods are commonly used to form transparent conductive electrodes, such as those made of indium tin oxide (ITO), on an organic film.
However, organic films are easily damaged by the charged particles generated during the sputtering of ITO films, degrading the performance of photodetectors [1]. We previously succeeded in reducing such damage by using electron beam (EB) evaporation to form the ITO electrode on the green-light-selective organic film instead of sputtering as it produces less damage during the ITO deposition [2]. In this study, we fabricated a red-light-selective photodetector sandwiched between transparent electrodes using boron sub-2,3-naphthalocyanine chloride (SubNC) as a photconductive material. The structure of the photodetector was bottom ITO (150 nm thick)/tris(8-hydroxyquinolinato)aluminum (Alq3) (30 nm)/SubNC (100 nm)/2,7-bis(9-carbazolyl)-9,9-spirofluorene (Spiro-2CBP) (30 nm)/top ITO (30 nm). The Spiro-2CBP and Alq3 are electron- and hole-blocking layers, respectively, and were inserted to block electron and hole injection from the electrodes to the photoconductive layer, which would have generated dark current in the photodetector. The top ITO electrode was deposited by EB evaporation. The photodetector showed high external quantum efficiency (EQE) of 80% at a bias voltage and irradiation wavelength of 11.2 V and 630 nm, respectively. However, a dark current of 20 nA/cm² was obtained at 11.2 V, which is relatively high for image sensor applications. Therefore, we introduced a new hole-blocking layer of gallium(III) oxide (Ga2O3) between Alq3 and the bottom ITO electrode because the ionization potential of Ga2O3 (8.1 eV) is higher than the highest occupied molecular orbital (HOMO) level of Alq3 (5.7 eV). The new structure of the photodetector was ITO (150 nm)/Ga2O3 (5 nm)/Alq3 (30 nm)/SubNC (100 nm)/Spiro-2CBP (30 nm)/top ITO (30 nm). The dark current and EQE of the new photodetector was 2 nA/cm² and 76.5% at 16 V, respectively. In consequence, the dark current of the photodetector was successfully reduced by more than one order of magnitude compared with that without the Ga2O3 layer.


EP05.03.17  
Reliable Organo-Compatible Superhydrophobic Protection for Organic Field Effect Transistors Daekyoung Yoo1, Youngrok Kim1, Misook Min1, Geun Ho Ahn2, Der-Hsien Liem3, Jingon Jang3, Hyunhak Jeong3, Younggu Song3, Seungjun Chung3, Ali Jarvey3 and Takhee Lee1; 1Seoul National Univ, Seoul, Korea (the Republic of); 2Korea Institute of Science and Technology, Seoul, Korea (the Republic of); 3University of California, Berkeley, Berkeley, California, United States.

Organic semiconductors have attracted significant interest for realizing next-generation electronics due to their fast, low-cost, and low-temperature processabilities. Nevertheless, it is widely studied that they could be drastically degraded by water-based hindrances. Although some efforts to address this issue by encapsulating with various materials such as parylene, silicone, barrier foil, or a superhydrophobic glass have been reported, novel approaches to introduce an effective protection layer directly on organic components are highly desirable. In this regard, the introduction of a superhydrophobic protection layer onto the organic semiconductor layers can be a promising approach to realize reliable and practical organic semiconductor applications. The materials and processes for the superhydrophobic protection layer formation need to be organo-compatible, so that they do not damage physically or chemically when placed on the organic layers, and thus their electrical characteristics would not be degraded. In this presentation, we report a facile method to deposit an organo-compatible superhydrophobic protection layer on organic semiconductors under ambient conditions. The superhydrophobicity was achieved by simply dipping organic devices in a highly fluorinated solution dispersed with fluoroalkylsilane-coated titanium-dioxide nanoparticles. Furthermore, the uniform protection layer could be deposited using a simple dipping process without any physical damages by optimizing the solvent system to match surface energy with underlying organic semiconductors. The proposed protection layer had good resistance against light-stress, mechanical-stress, and water-based threats. Moreover, protected organic devices exhibited reliable electrical properties even exposed to strong solvents while maintaining self-cleaning properties from extreme water repellency and showing good thermal stability. This study provides a practical solution to enhance the reliability of organic devices in the natural environment.

EP05.03.18  
Near Infrared-to-Blue Photon Upconversion Based on Singlet-to-Triplet Direct Transition Yoichi Sasaki1, Nobuhiko Yanai1, 2 and Nobuo Kimizuka1, 2; 1Department of Chemistry and Biochemistry, Graduate School of Engineering, Kyushu University, Fukuoka, Japan; 2Center for Molecular Systems (CMS), Kyushu University, Fukuoka, Japan.

The efficient use of near-infrared (NIR) light has been much coveted in energy and biological applications. For example, although the NIR light from 700 nm to 900 nm shows good tissue transparency, the photon energy in this region is too weak for important biological applications such as bioimaging, photodynamic therapy, and drug release. The blue light with a wavelength shorter than 500 nm is known to trigger drug release and in vivo photochemical reactions, and therefore it is imperative to produce such higher-energy visible light under NIR excitation. Photon upconversion (UC) is a methodology that converts lower-energy photons into higher-energy photons. Triple-tetra-annihilation based UC (TTA-UC) is especially promising since it works under weak excitation intensity like sunlight. Despite its importance, it has been difficult to obtain NIR (>700 nm) to blue (<500 nm) TTA-UC. This is because the energy loss associated with the intersystem crossing (ISC) of donors limits the use of acceptors with high H1 and S1 energy levels, and consequently the width of the anti-Stokes shift. To maximize the anti-Stokes shift and to achieve the TTA-UC from NIR to blue region, it is essential to develop TTA-UC systems without ISC. Recent efforts have been accordingly devoted to developing new mechanisms that circumvent the energy loss of ISC such as TADF molecules, QDs, perovskites, and heavy metal complexes. These sensitizers, however, tend to show short excited state lifetime (<10 ns), and triple-tetra energy transfer (TTT) from the sensitizers to acceptor molecules is often inefficient. In this work, we demonstrate an efficient NIR (>700 nm)-to-blue (<500 nm) TTA-UC by judicious developments of new Os(II) bis(terpyridine) complexes with singlet-to-triplet (S-T) direct transition. We achieved NIR-to-blue TTA-UC for the first time with a large anti-Stokes shift of 0.97 eV with a good UC efficiency.

EP05.03.19  

Understanding degradation processes in organic solar cells is very important for the development of new materials with improved stability. One of the conventional ways to study the changes induced by the degradation processes is Raman spectroscopy. The main disadvantage of the Raman technique is that the measured signal is an integral over the entire volume of the measured sample. It is especially pronounced when there is an overlap between the Raman spectra over different layers of the solar cells. This is the case when a polyfluorene blend (F8BT:PFB) is the active layer and PEDOT:PSS serves as an electron blocker. To overcome this drawback we use ultra-thin, semi-transparent, layers of gold (4 nm) in between the different layers of the cell. This ultra-thin layer is specifically design to have plasmons around the Raman excitation laser (660 nm). When it is inserted between the ITO and the polyfluorene blend it is the blend signal that is dominated. Using this technique and monitoring the degradation at short-circuit current condition we observed the following. Firstly, the time dependence of the surface enhanced Raman signal is monotonic in contrast with the conventional Raman where it is not. Secondly, we were able to separately analyze the degradation of the different layers. We found out that the main peak of the PEDOT:PSS Raman spectrum shifts to the right and its relative height, with respect to the other peaks, decreases which indicates an increase in the resistance of this layer. We also show that for the blend the main damage is done to the BT unit of the F8BT and that mainly affect electron conduction in the device. We believe that this new approach can
be used to analyze other organic devices and at different excitation using other metals.

**EP05.03.20**

**Solvent-Vapor-Annealed A–D–A-Type Semicrystalline Conjugated Small Molecules for Flexible Ambipolar Field-Effect Transistors**

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Over the past two decades, many types of conjugated polymers or small molecules (SMs) have been synthesized and utilized as semiconducting materials for organic field-effect transistors (OFETs). To realize the high-performance and flexible OFETs, the fabrication process should be efficiently optimized at a low temperature condition and solvent-vapor-annealing (SVA) is a well-known process for controlling the morphology of SM thin films in ambient condition.

In this study, three kinds of acceptor-donor-acceptor (A-D-A) type SM semiconductors were designed and synthesized by introducing different electron-withdrawing endcapping groups of dicyanovinyl (VCN), cyano-hodanidine (RCN) and cyano-indanone (INCN) at both termini, which enables to finely tune the frontier energy levels of semiconducting materials. All the OFETs exhibited ambipolar FET characteristics and SVA treatment changes crystalline structure and FET characteristics of semiconducting films remarkably. The SVA effect depending on the endcapping groups was logically investigated by using a DFT calculation, UV-vis absorption spectroscopy, 2-dimensional grazing incidence x-ray diffraction (2D GIXD), and atomic force microscopy (AFM). The as-coated P3T4-INCN films exhibited the hole mobility of 0.03 cm2V-1s-1 and electron mobility of 0.01 cm2V-1s-1. Finally, the P3T4-INCN OFET performance was significantly enhanced via SVA with chloroform, resulting in the hole mobility of 0.14 cm2V-1s-1 with the good ambipolar charge transport behaviors.

In addition, a flexible OFET array with solvent-vapor-annealed P3T4-INCN was successfully fabricated on the polyethylene naphthalate (PEN) substrate. This OFET device exhibited the hole mobility of 0.15 cm2V-1s-1 and electron mobility of 0.05 cm2V-1s-1, an on-off current ratio of ~102, and excellent mechanical stability even after 300 bending cycles.

**EP05.03.21**

**Nanocomposite of Nickel Oxide Nanoparticles and Polyelectrolyte Oxide as Printable Injection Layer for Organic Solar Cells**

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In the field of organic electronics, rising research attention has been dedicated to the investigation of novel interlayers. A family of materials that has been deserved increasing interest for such purposes is the one of transition metal oxide nanoparticles, which can provide high quality interfaces for both charge injection or extraction. Metal oxide nanoparticles are suitable for solution-processed electronics thanks to many advantages: they can be dissolved in organic solvents and used as printable inks, can be processed at relatively low temperatures and can offer an increased stability compared to conjugated polymers. However, they also present certain technical challenges due to the higher surface to bulk ratio (i.e. surface trap states) or present problems during film formation (i.e. agglomeration). (1) For this reason, various kinds of polymers can be employed to offer a hybrid solution to these issues.

We present here the improvement of the processability of non-stoichiometric nickel oxide (NiOx) nanoparticle ink by blending with high molecular weight polyelectrolyte oxide (PEO). Recently, NiOx has attracted increasing attention as a hole extraction layer in organic and perovskite photovoltaics due to its excellent optical transparency, p-type conductivity and good electron blocking properties. Nonetheless, the fabrication of highly efficient NiOx thin films is challenging due to the low viscosity of the inks or the high sintering temperatures of the precursor approach. Here, we show how PEO can help dispersing the nanoparticles hindering their aggregation after deposition without compromising film functionality. Through Kelvin Probe, Contact Angle measurement, X-ray Photoelectron Spectroscopy and Transmission Electron Microscopy we observe that the presence of PEO is beneficial for a better tunability of the NiOx film thickness and morphology. We also show that such effect on the film formation is observed to be beneficial when the NiOx:PEO blends are applied as a hole extraction layer on OPV devices, improving device performance. Moreover, the inclusion of the polymer in the nanoparticle ink allows, for the first time, the inkjet-printing of the NiOx layer without requiring high temperature post-treatment. (2) Finally, we verified the possible migration of the PEO used in these devices through the bulk heterojunction towards the cathode (3), defining a dual purpose for the polymer: on one hand passive matrix for the nanoparticles as anode, on the other functionalizer of the cathode.

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**EP05.03.22**

**Fast, Efficient Luminescence in Carbene-Cu(I) Complexes and Other Coinage Metals**

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For as long as it has been a subject of study, the luminescence of copper(I) complexes has been plagued by slow, inefficient luminescence. This is a result of two major factors: weak spin-orbit coupling, due to the light metal; and large excited state reorganization energies, associated with a formal oxidation at the d10 metal center in MLCT transitions. While the latter culprit can be mitigated by increasing the steric bulk around the metal, addressing the former is a more challenging endeavor. With this in mind, I will discuss recent work from our lab, where we have prepared carbene-Cu(I) complexes exhibiting fast (k > 107 s-1), efficient (PLQY ~ 100%) phosphorescence, with emission colors tunable over the visible spectrum. These results have allowed us to develop new paradigms for designing Cu(I) complexes, and to expand our understanding down the periodic table to Ag(I) and Au(I) complexes. Specifically, I will highlight newly-isolated Au(I) and Ag(I) complexes with remarkable photophysical properties that underscore their potential for OLED applications.

**EP05.03.23**

**Polar-Functionalized Diisothiophene Polymers as a Platform for Aqueous-Compatible Electrochemical and Bioelectronic Devices**

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There has been increasing interest in developing redox-active polymers capable of electrochemically interfacing with biological systems for sensing and therapeutic applications. As an example, organic electrochemical transistors (OECTs), which have emerged as a highly sensitive in vivo biosensing platform, hinge on bulk transport of aqueous doping ions through conjugated polymer films for stabilizing conducting states and controlling current through the transistor channel. In the pursuit of aqueous-compatible systems, there has been a growing body of work demonstrating how highly polar oligo(ether) side side chains enhance the redox activity and ion transport properties of conjugated polymers for use in OECTs. Herein, we present a family
of dioxothiophene-based polymers functionalized with side chains spanning a range of polarities, including ester, diester, and oligo(ether) analogues, and explore how factors such as solubility, redox potential, ion transport and storage, and conductivity switching depends on the chemical nature of the substituent side chain. These materials exhibit excellent redox stability in physiologically-relevant electrolytes and can be prepared through straightforward direct (hetero)arylration polymerization chemistries. We evaluate the dynamic electrochemical and optical behavior of these polymers, paying special attention to their potential-dependent mixed ionic/electronic transport employing techniques such as electrochemical impedance spectroscopy, and demonstrate their utility in aqueous-based electrochemical devices. Through these studies, we aim to establish important structure-property relationships for exploring the materials design space of side chain polarity for high-performing bio-electrochemical devices.

**EP05.03.24**

**Lactam Containing Two Isomeric Polymers For OPVs with High Open-Circuit Voltages**

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The molecular design of the wide bandgap (WBG) is important for non-fullerene polymer solar cells to obtain simultaneously high power conversion efficiency (PCE) and open circuit voltage ($V_{oc}$). In this study, we developed two isomeric lactam acceptor, thieno[3,2-c]quinoxalin-4(H)-one (TQO) and thieno[3,2-c]isouquinolin-5(H)-one (TIQO), to compare the their optical and electrical properties. The WBG donor-acceptor (D-A) type polymers, PBDT-TQO and PBDT-TIQO, were synthesized using the 4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene (BDT) as electron donor building block and TQO or TIQO as electron accepting building block for fullerene and non-fullerene organic solar cells. PBDT-TQO and PBDT-TIQO showed absorption range below 600 nm and low-lying HOMO energy levels. The appropriate match of the energy levels between donors and acceptors could be applied for fullerenne and non-fullerene OSC. PCEs of the devices based on PC$_{71}$BM achieved 3.02 % for PBDT-TQO:PC$_{71}$BM and 3.92 % for PBDT-TIQO:PC$_{71}$BM, respectively. For better photovoltaic performance, the devices based on polymer:non-fullerene acceptor (ITIC or IT-4F) were fabricated. A PCE of PBDT-TIQO:IT-4F achieved 7.62 %, while the device of PBDT-TIQO:ITIC was afforded PCE of 6.56 % thanks to increase short-circuit current density ($J_{sc}$) and open-circuit voltage ($V_{oc}$).

**EP05.03.25**

**Ion Transport and Reaction Kinetics on the Operation of AC-Driven Electrochemiluminescence Devices**

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Electrochemiluminescence (ECL) is light emission from redox precursors generated through a series of electrochemical processes. This process can be exploited in fabricating a light-emitting device, which is referred to as the electrochemiluminescence device (ECLD). Unlike conventional solid-state light-emitting device, the operation of ECLDs relies on mass transport of the luminophores and electrochemical electron transfer reactions; the oxidative and reductive forms of ECL luminophores have to encounter to form the excited states before emitting light eventually. Herein, we investigate the influence of these dynamic factors on the emission characteristics of AC-voltage driven ECLDs. Benchmark ionic transition metal complex ECL luminophore and ionic liquids are used as the ECL luminophore and the electrolyte materials, respectively, for our model device. The dynamic processes in the ECLD could be simply modeled using i) the Fick’s law to describe the diffusion process near the electrode, ii) the first order reaction of the ECL luminophore at the electrode, and iii) the second order annihilation reaction between the reduced/oxidized luminophores, based on the associated reaction constant and the diffusion constant obtained from separate electrochemical analysis techniques, respectively. The model yielded transient ECL intensity profile of the device over a single switching cycle of an AC electrical input which matched well with experimental results. Moreover, the time-averaged values of the transient profiles matched with the characteristic operational frequency-dependent ECL properties of the device, which initially increase with increasing frequency but then peak and decrease at higher frequencies. Using the model giving well-matching results to the experimental observations, the influence of diffusion and the reaction rates on the performance of an ECLD could be analyzed separately and systematically, which is difficult to carry out from experiment. The fundamental understanding on the operation of this emerging class of light-emitting device platform provides practical guidelines to advance its performances.

References:


**EP05.03.26**

**Dynamics of Charge Distribution and Emission Zone in Sandwich Light-Emitting Electrochemical Cells**

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In contrast to the multiple layers required for a state-of-the-art organic light-emitting diode, light-emitting electrochemical cells (LECs) are usually built from a single emissive layer that contains an electrolyte and is sandwiched between two electrodes. Due to the presence of mobile ions, the single layer can perform all the tasks that take place in an electroluminescence device, i.e. facile electrical charge injection, transport, excitation and radiative recombination. The LEC device concept sounds simple, but in truth it’s not easy at all; despite twenty years of research, resolving the dynamics of the injected electrical charge as well as identifying the zone where light is emitted in sandwich devices present considerable scientific challenges. Here, we study the temporal evolution of organic salt-based LECs and demonstrate that photorabsorption spectroscopy in combination with electrical capacitance measurements enables the determination of the distribution of the injected, uncompensated electronic charge inside these devices. For constant-voltage operating conditions and over a period of hours, the Stark effect signal intensity and the capacitance increase steadily, but to a different extent. We demonstrate that this difference sensitively depends on the position and distribution width of injected mobile charges. Estimates show a substantial spreading over the active layer of the injected charge density with time, screening the electric field behind the charge peak [1]. We also studied how the p- and n-doped regions and the intrinsic (i) emission zone evolve over time [2]. By analysing incident photon-to-current conversion efficiency and angular emission measurements with optical simulations, and correlating the results with capacitance measurements, we were able to obtain a clear picture of the p-i-n situation and the emission zone of cyanine dye LECs. The spectral photocurrent response analysis in [2] was possible because of the high photocurrent response of this type of LEC. Indeed, we recently observed efficient photoinduced charge generation in the bulk of pristine cyanine dye films with internal quantum efficiency exceeding >40% [3]. We report on this unusual behavior because intrinsic photogeneration of charge carriers in organic semiconductors is generally attributed to high energy ionization or exciton dissociation by a strong electric field.

References:

Structural Evaluation of 5,5'-Bis(naphth-2-yl)-2,2'-bithiophene in Organic Field-Effect Transistors with α-Octadecyltrichlorosilane Coated SiO2 Gate Dielectric Andreas E. Lauritzen1,2, Mikael Torkkel1, Oier Bikondoa1,4, Jes Linnet1,5, Luciana Tavares1, Jakob Kjelstrup-Hansen2 and Matti Knaapila1,1
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We report on the structure and morphology of 5,5'-bis(naphth-2-yl)-2,2'-bithiophene (NaT2) films in bottom-contact organic field-effect transistors (OFETs) with octadecyltrichlorosilane (OTS) coated SiO2 gate dielectric, characterized by atomic force microscopy (AFM), grazing-incidence X-ray diffraction (GIXRD) and electrical transport measurements. Three types of devices were investigated with the NaT2 thin-film deposited either on (1) pristine SiO2 (corresponding to higher surface energy, 47 mJ/m2) or on OTS deposited on SiO2 under (2) anhydrous or (3) humid conditions (corresponding to lower surface energies, 20-25 mJ/m2). NaT2 films grown on pristine SiO2 form nearly featureless 3-dimensional islands. NaT2 films grown on OTS/SiO2 deposited under anhydrous conditions form staggered pyramid islands where the interlayer spacing corresponds to the size of the NaT2 unit cell. At the same time, the grain size measured by AFM increases from hundreds of nanometers to micrometers and the crystal size measured by GIXRD from 30 nm to more than 100 nm. NaT2 on OTS/SiO2 deposited under humid conditions also promotes staggered pyramids but with smaller crystals (30 – 80 nm). The NaT2 unit cell parameters in OFETs differ 1 – 2% from those in bulk. Carrier mobilities tend to be higher for NaT2 layers on SiO2. (2 – 3×10^-4 cm^2/Vs) compared to NaT2 on OTS (2×10^-5 – 1×10^-4 cm^2/Vs). An applied voltage does not influence the unit cell parameters when probed by GIXRD in operando.

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Printed and flexible electronics based on soluble conjugated organic molecules have drawn tremendous interest as a new paradigm for the fabrication of large-area and low-cost optoelectronics and electronics applications. Those polymers should be preferably aligned in the perpendicular direction through the active channel of organic field-effect transistors (OFETs). Morphological control and structural ordering of the conjugated polymers via large area printing method is an important issue in order to achieve high performance OFETs and its electronic circuitry. In this study, we report various directional printing methods (off-centered spin-coating, dip-coating, and bar-coating) for preferable arrangement of conjugated polymers, such as high mobility PCDTFTBT and DPPT-TT. Those polymer OFETs showed high charge carrier mobilities as high as 11 cm²V⁻¹s⁻¹ and balanced ambipolar charge transport behavior in the top-gated OFET structure with polymer dielectrics. This remarkable enhancement is mostly attributed to improved arrangement and ordering of polymer chains through the active channel and better uniformity of OFET parameters is also obtained by this large-area printing techniques. Moreover, high-k fluorinated polymer dielectrics significantly contribute to increase high charge carrier density under low voltage conditions. Finally, higher mobilities and well-balanced P-channel and N-channel characteristics in comparison to conventional coating methods was successfully applied to develop complementary-like printed circuits, it is expected to realize high performance flexible and wearable electronic devices via cost-effective simple printing methods.

EP05.03.31
A Sky Blue Thermally Activated Delayed Fluorescence (TADF) Emitter Realizing Efficient White Light Emission Through In Situ Metal Complex Formation
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In this work, we have developed a pyrazine/acridine based thermally activated delayed fluorescence (TADF) emitter named 2,6-bis[4-(9,9-dimethyl-9,10-dihydroacridine)-phenyl]pyrazine (2Ac-PRZ) for organic light-emitting devices (OLEDs). This emitter has a metal coordination ability to form a metal complex via in situ doping of copper iodide (I) (CuI). The neat film of 2Ac-PRZ showed sky blue emission with a peak at 463 nm, and the photoluminescence quantum yield (PLQY) of 17%. On the other hand, when CuI was doped into 2Ac-PRZ layer, the doped layer showed white emission with dual emission peak at 463 nm and 583 nm with PLQY up to 34%. We used this co-deposited layer of 2Ac-PRZ/CuI as an emissive layer (EML) in OLEDs. We fabricated OLEDs with a structure [ITO/ triphenylamine-containing polymer: 4-isopropyl-4′-methyldiphenyl-iodonium tetrakis(pentafluorophenyl)borate (PPBI)] (20 nm)/di-[4-(N,N-ditolyl-amino)-phenyl]cyclohexane (TAPC) (20 nm)/CuI-doped 2Ac-PRZ (20 nm)/ 3,3'',5,5'-tetra(3-pyridyl)-1,1';3',1''-terphenyl (B3PyPB) (50 nm)/LiF (0.5 nm)/Al (100 nm). The device showed white emission with a CIE of (0.41, 0.45), and very high external quantum efficiency of over 10%.

EP05.03.32
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Carrier transport materials such as hole and electron transport materials (HTMs and ETMs) play a key role in determining organic light-emitting device (OLED) performances, such as driving voltage, efficiency and operation lifetime. A representative HTM for OLEDs is α-NPD that exhibits relatively high glass transition temperature ($T_g$) of 100 °C, and moderate hole mobility of 8.8×10⁻⁶ cm²/V·s among reported HTMs. In this work, we developed a novel series of HTMs aiming higher thermal stability and higher hole mobility than those of α-NPD by introducing [1]benzothieno[3,2-b][1]benzophenophene (BTBT) molecules. BTBT is famous in organic field effect transistor (OFET) [1], and has realized excellent hole mobility for OFET applications. A novel HTM containing BTBT showed superior thermal stability with $T_g$ of 155 °C, and good hole transport property in OLEDs. An OLED with a structure of ITO/ 3,3,6,10,11-Hexacyano-1,4,5,8,9,12-hexaazatriphenylene (HATCN)/ novel HTM 9,9′-diphenyl-9H,9′H-3,3′-bicarbazole (BCzPh)/ tris(2-phenylpyridinato)iridium(III) (Ir(ppy)₃)-doped BCzPh/ 3,3''5,5''-tetra(3-pyridyl)-1,1''3',1''-terphenyl(B3PyPB)/ 8-quinolinolato lithium (LiQ)/ Al was fabricated. The device exhibited driving voltage of 3.7 V and EQE of 17% at 1000 cd/m². These performances suggest the potential usefulness of these HTMs for OLEDs.


EP05.03.33
Stable Solution-Processed Small-Molecule Phosphorescent Tandem Organic Light-Emitting Devices
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Recently, solution-processed polymer tandem organic light-emitting devices (OLEDs) comprising multiple light-emitting units connected by carrier generation layers have been reported as a promising way to realize long lifetime solution-processed OLEDs [1, 2]. However, those both with high device efficiency and long lifetime have been reported yet. In this work, we report the development of a stable solution-processed small-molecule phosphorescent tandem OLEDs, in which ten-layers were formed by solution-processing. We newly developed solvent-tolerant small molecule host materials with indolocarbazole, phenylcarbazole, and triazine units for phosphorescent EML. These materials showed high tolerance to methanol solvents. The upperlayer material on the EML is ZnO nanoparticle (NP), and it should be dispersed in methanol. The surface condition of the ZnO NPs was tuned to disperse them in methanol by modifying the conventional synthetic procedure. As a result, we succeeded in fabrication of solution-processed small-molecule orange phosphorescent tandem OLED comprising two light-emitting units. At a nominal luminance of 1000 cd/m², the driving voltages were 5.2 V for the first unit device, 5.1 V for the 2nd unit device, and 10.7 V for the tandem device, respectively. The driving voltage of the tandem device was almost similar to the sum of the 1st and the 2nd unit devices. The external quantum efficiency of the tandem OLED is 1000 cd/m² 25.2% under Lambertian assumption. The device stability of the two kinds of single units and the tandem device were evaluated at a constant current density of 2.5 mA/cm² corresponding to initial nominal luminances of 520 cd/m² for the 1st unit device, 340 cd/m² for the 2nd unit device, and 1240 cd/m² for the tandem device, respectively. The times to 70% of the initial luminances were 75 h for the 1st unit device, 57 h for the 2nd unit device, and 68 h for the tandem device, respectively. Considering much higher luminance of the tandem device than the others, the tandem device obviously showed much longer device lifetime than the others.

References:
Organic field-effect transistors (OFETs) could offer a signal amplification for flexible pressure sensors based on them. However, the achievement of both low-voltage operation and ultra-high sensitivity remains a challenge for OFET-based pressure sensors. In this presentation, novel polyacrylic acid containing composite dielectrics are demonstrated for flexible OFETs and ultra-sensitive pressure sensors with low voltage operation. The OFETs using the composite dielectrics showed remarkably improved electrical performance under a much lower operating voltage of than those with a pristine polyacrylic acid dielectric. The OFETs also reveal excellent flexibility and bending stability during mechanical tests with different bending radii and cycles. Based on the dielectric engineering as well as a device structure innovation, flexible OFET-based pressure sensors with both low-voltage operation and ultra-high sensitivity are further achieved. The resulting sensors deliver a high sensitivity at a low-operating voltage, a rapid response time, and excellent operating stability. These results provide a promising strategy to design and synthesize high-performance flexible dielectrics for OFETs and pressure sensors.

EP05.03.35
Transient Electroluminescence Analysis in Organic Light Emitting Diodes—The Effect of the LiF Thickness in LiF/Ag Cathode
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Time dependence studies in organic light emitting diodes are in the center of many researches due to the increase of interest in these devices for data transfer at high rates via modulation of visible light. In our study we examine the influence of charge injection on the time-dependency of the electroluminescence after driving the OLED from steady state to open circuit condition. In contrast to time-resolve-photoluminescence (TRPL) technique where the excitation is done by optical pulse, in our approach we monitored the temporal evolution of the emission under electrical excitation. The proposed technique combined with steady-state analysis allows us to take into account the interplay of various electronic processes and to investigate not just the excitons dynamics but also the charge dynamics. For this purpose, we fabricated polyfluorene-based OLEDs with LiF/Ag cathodes differing only by the thickness of the LiF layer for controlling the electron injection efficiency. Transient electroluminescence measurements accomplished by using a homemade fast switching driver that design to couple with the high impendence of the OLED and limitations on the maximum current flow in the device. Our driver successfully drives the OLED to open circuit condition in 5ns. Two exponential decays of the EL were observed after the turn-off, an initial fast decay in the time domain of tens of ns followed by a slow decay in the time domain of hundreds of nano-second. These lifetimes are much longer than the lifetime of the singlet excitations that were measured using TRPL (sub-nano to nano seconds). Capacitance – Voltage characteristic was performed due to its sensitivity to the barrier height and built-in potential. We observed changes in the peak position, maximum capacitance and peak shape. We found correlation between these parameters, the charge injection and accumulation and the measured transient EL lifetimes. We discovered that devices with higher charge injection efficiency and lower charge accumulation at the electrodes exhibit longer transient EL lifetimes. In addition, the shape of the peak capacitance that can be associated with the changes of space-charge regions is correlated to the longer transient EL lifetime.

EP05.03.36
Computational Design of Non-Fullerene Acceptors for Organic Solar Cells
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To date, most of the acceptor used in organic solar cells are fullerene or their derivatives. As fullerene exhibit only weak light absorption in the Vis spectral region, practically half of the active material does not contribute to exciton and charge generation, limiting the maximum efficiency of these devices to ca. 12%. The way forward to reach higher solar cell efficiencies is to replace fullerene with strongly-absorbing dye molecules, namely, nonfullerene acceptors (NFAs). However, the systematic design of acceptor molecules with tailored properties has yet to be demonstrated. The difficulty here is that, while fullerene is an electrostatically “inert” molecule, new acceptors typically have strong static quadrupole moments. This complicates the interplay of electrostatic forces at the donor-acceptor interface, making it difficult to predict and design appropriate donor-acceptor combinations. As a result, in order to optimize solar cell efficiency, one has to appropriately balance the individual electrostatic contributions to energy profiles. Exploring the long-range electrostatic interaction at the interface, we demonstrate for a set of recently developed NFAs that the electrostatic bias potential can be directly related to the stabilization (or destabilization) of CT states as well as changes of the photovoltaic gap. Therefore, it is an important quantity to account for when designing non-fullerene acceptors. Furthermore, we compare theoretically-predicted nonfullerene acceptors with experimental data to assess the quality of our approach. We find that the correlation between quadrupole moments, charge separation efficiency, and CT-state energy predicted by our model is experimentally reproduced for several different small molecules and polymer donor / non-fullerene acceptor combinations. This allows us to predict new NFA structures using combinations of readily available molecular building blocks that can potentially reach to even higher performances than currently achieved in state-of-the-art NFA devices.

EP05.03.37
Micropatterning of Organic Electronic Materials Using a Facile Aqueous Photolithographic Process
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Patterning organic semiconductors via traditional solution-based microfabrication techniques is precluded by undesired interactions between processing solvents and the organic material. Herein we show how to easily avoid these problems and introduce a simple lift-off method to pattern organic semiconductors. Positive tone resist is deposited on the substrate, followed by conventional exposure and development. After deposition of the organic semiconductor layer, the remaining photoresist is subjected to a flood exposure, rendering it developable. Lift-off is then performed using the same aqueous developer as before. We find that the aqueous developers do not compromise the integrity of the organic layer or alter its electronic performance. We utilize this technique to pattern four different organic electronic materials: epinolodione, a luminescent semiconductor, p-n photovoltaic bilayers of metal-free phthalocyanine and N,N′-dimethyltetraacarboxylic diimide, and finally the archetypal conducting polymer poly(3,4-ethylenedioxythiophene). The result of our efforts is a facile method making use of well-established techniques that can be added to the toolbox of research and industrial scientists developing organic electronics technology.

EP05.03.38
Stabilization of Organic Solar Cells Using Radical Scavengers and Singlet Oxygen Quenchers
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In contrast to time-resolve-photoluminescence (TRPL) technique where the excitation is done by optical pulse, in our approach we monitored the temporal evolution of the emission under electrical excitation. The proposed technique combined with steady-state analysis allows us to take into account the interplay of various electronic processes and to investigate not just the excitons dynamics but also the charge dynamics. For this purpose, we fabricated polyfluorene-based OLEDs with LiF/Ag cathodes differing only by the thickness of the LiF layer for controlling the electron injection efficiency. Transient electroluminescence measurements accomplished by using a homemade fast switching driver that design to couple with the high impendence of the OLED and limitations on the maximum current flow in the device. Our driver successfully drives the OLED to open circuit condition in 5ns. Two exponential decays of the EL were observed after the turn-off, an initial fast decay in the time domain of tens of ns followed by a slow decay in the time domain of hundreds of nano-second. These lifetimes are much longer than the lifetime of the singlet excitations that were measured using TRPL (sub-nano to nano seconds). Capacitance – Voltage characteristic was performed due to its sensitivity to the barrier height and built-in potential. We observed changes in the peak position, maximum capacitance and peak shape. We found correlation between these parameters, the charge injection and accumulation and the measured transient EL lifetimes. We discovered that devices with higher charge injection efficiency and lower charge accumulation at the electrodes exhibit longer transient EL lifetimes. In addition, the shape of the peak capacitance that can be associated with the changes of space-charge regions is correlated to the longer transient EL lifetime.
interface engineering plays on the figures-of-merits of OLETs is discussed. In particular, the effect of a series of multifunctional electrodes on both the external quantum efficiency (EQE) and the optical power of the corresponding devices is reported.

In multilayer optoelectronic devices it is a major challenge to match interfaces both from chemical and electronic considerations. Herein, we report on the use of phosphonic acid based self-assembled monolayers (SAMs) to adjust the interface between solution-processed nickel oxide (sNiO) hole-contact layers and the donor (F42zPe) in organic solar cells. We provide a detailed analysis of infrared (FTIR) and photoelectron spectroscopy (XPS) that reveals the chemisorption of the molecules. A nominal layer thickness of around one monolayer is found and insight into the chemical composition of the underlying sNiO film and the SAM is given. Additionally, density functional theory (DFT) calculations simulate the possible binding mechanism and configurations. Via the SAM formation, we are able to increase the work function of the sNiO film by up to 0.8 eV and optimize the energy level alignment to the donor. However, in-operando measurements of the solar cells show that this does not necessarily lead to an improvement of the device performance. We propose that the intrinsic charge carrier density and surface states created upon modification play an important role in facilitating efficient charge transport across such an interface.

Highly Conductive and Stretchable Homopolymer Ion Gels by Physical Crosslinking Routes Hye-young Yeo, Young Kyung Jo, Kyoungook Cho and Keun Hyung Lee; Chemistry and Chemical Engineering, Inha University, Incheon, Korea (the Republic of).

Ion gels, ionic liquid based-polymer gel electrolytes, have attracted great research attention recently due to outstanding advantages of high ionic conductivity, large capacitance, flexibility, non-volatility, and high potential stability window. Several methods have been suggested to solidify ionic polymer networks by constructing 3D polymer networks. Herein, we report on the use of phosphonic acid based self-assembled monolayers (SAMs) to adjust the interface between solution-processed nickel oxide (sNiO) hole-contact layers and the donor (F42zPe) in organic solar cells. We provide a detailed analysis of infrared (FTIR) and photoelectron spectroscopy (XPS) that reveals the chemisorption of the molecules. A nominal layer thickness of around one monolayer is found and insight into the chemical composition of the underlying sNiO film and the SAM is given. Additionally, density functional theory (DFT) calculations simulate the possible binding mechanism and configurations. Via the SAM formation, we are able to increase the work function of the sNiO film by up to 0.8 eV and optimize the energy level alignment to the donor. However, in-operando measurements of the solar cells show that this does not necessarily lead to an improvement of the device performance. We propose that the intrinsic charge carrier density and surface states created upon modification play an important role in facilitating efficient charge transport across such an interface.

Modification of Interfaces with Organic Molecules in Optoelectronic Devices Sebastian Hietzschold1,2, Sabina Hillebraud3, Florian Ulrich4, Jakob Bombsch5, Valentina Rohmeier5, Shuangying Ma6, Wenlan Liu6, Andreas Koehn3, Annemarie Pucci3, Wolfgang Kowalsky6, Eric Mankel4,5, Sebastian Beck3,5 and Robert Lovričević1,2

Layered interfaces are of crucial importance in optoelectronic devices. Here, we report on the performance of the resulting devices is enhanced, the presence of ionic species in CPES layers causes complications in the device response due to charge trapping and electric field screening effects. In this sight, the use of conjugated polyaromatics (CPAs) is demonstrated as a new and efficient alternative to CPES. Indeed, the conjugated backbone of CPAs are modified with polar non-ionic side groups, thus avoiding ion-depending drawbacks. By introducing a layer of polyfluorene containing phosphonate groups (PF-EP) underneath the metal electrodes, a clear improvement of the electron injection properties results in a more than twofold increased light-emission (optical power) and a five-times enhanced EQE of p-type OLETs, with superior performance in comparison with the relative CPA-containing devices. Moreover, the great benefit of using a transparent glass substrate allows for a deep investigation of the morphological and photoluminescent characteristics of both CPA- and CPA-buried interlayers within complete multilayered OLETs. Hence, by means of an optical scanning probe technique, the operation mechanisms of the investigated interlayers are elucidated.

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In order to develop high-performance organic electronic materials, it is of great importance to understand charge transport phenomena at molecular level. Here, we report the synthesis as well as the optical and electron-transport properties of a series of discrete alternating donor–acceptor (D-A) oligomers. These molecules are terminated with methyl-thiol anchors for single-molecular conductance measurements using the scanning tunneling microscope-based break-junction (STM-BJ) technique. The electronic properties of the oligomers are further investigated by UV-Vis, Cyclic Voltammetry and Density Function Theory (DFT) calculations to understand the factors affecting conductance. By fitting to the Simmons Model, we find the intra-chain electron transport follows an electron tunneling mechanism whereby the molecule conductance is a function of molecule length. The dependence of oligomers' conductance on potential-bias are also discussed. These findings shed light on the underlying electron transport mechanism in donor-acceptor organic semiconductor materials.

**EP05.03.43**

**Solution-Processable Polymeric Surface Modification with Organic Self-Assembled Layer for Ultraflexable Amplifier Circuits**

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We have developed surface modification process of polymer dielectrics with solution-processable triptycene (Trip) derivatives for high mobility organic thin-film transistors (OTFTs). The surface modification improves the averaged mobility of OTFTs from 0.41 cm²/Vs to 2.23 cm²/Vs. The nested packing of Trip molecules results in the formation of 2D hexagonal arrays, which stack one-dimensionally into a multilayer structure. Due to the unique assembling property, the Trip derivatives can form a highly oriented film on the surface of polymer without any anchoring groups. In this study, we have succeeded in forming 5-μm-thick closely-packed Trip layers on polymer dielectrics using blade coating (BC) known as a simple solution process. In addition, organic operational amplifier have been realized based on the modification technique. Flexible device technologies have been expected for next-generation applications such as flexible bio-medical devices. OTFTs are the potential building blocks because they are intrinsically flexible and are compatible with low-cost printing processes. In this sense, OTFTs with polymer gate dielectrics are a promising structure among various types of OTFTs because of their efficient flexibility and processability. However, one problem is that polymer dielectrics possess a lot of disorders and charge trap sites on the surface. Therefore, it is difficult to form highly-crystalline organic semiconductor films on polymer dielectrics, leading to OTFTs with low mobility. Recently, it has been reported that thermally-evaporated Trip layers are useful for modifying polymer surface to avoid the negative effect of disorders and charge trap sites on the polymer. Here, we report the simple solution process in ambient conditions to form Trip layers. The improvement of mobility of OTFTs is better than that of the Trip layer formed by thermal vacuum evaporation (TVE). We fabricated top-contact bottom-gate OTFTs with hybrid gate dielectrics of Trip/parylene (5 nm/38 nm) on 1.5-μm-thick parylene substrates. We compared two types of Trip as referred to Trip.H and Trip.OMe. First, we formed Trip.OMe layers by using BC and TVE as a reference sample. The OTFTs with Trip.OMe layers formed by TVE and BC showed the averaged mobility of 1.59 and 2.23 cm²/Vs, respectively. These values were much higher than that of OTFTs without Trip.OMe layers (0.41 cm²/Vs). Moreover, the mobility improvement with BC was better than TVE. Secondly, the mobility of OTFTs was degraded to 0.18 cm²/Vs with using Trip.H. Although the structural difference of Trip.H is very small comparing with Trip.OMe, the effect of mobility improvement was largely different. We analyzed the devices with Grazing incident X-ray diffraction and atomic force microscopy. In the presentation, we will reveal the detailed analysis about the structural effect of Trip and demonstrate an organic operational amplifier as a practical application.


**EP05.03.44**

**Wide-Range Tuning and Enhancement of Organic Long Persistent Luminescence Kazuya Jinna,1,2, Ryota Kabe1,3 and Chihaya Adachi1,1,1,2, JIST, ERATO, Adachi Molecular Exciton Engineering Project, c/o OPERA, Kyushu University, Fukuoka, Japan; 3International Institute for Carbon Neutral Energy Research (WPI-ICNER), Kyushu University, Fukuoka, Japan; 4Center for Organic Photonics and Electronics Research (OPERA), Kyushu University, Fukuoka, Japan.

Long persistent luminescence (LPL) materials have applications in glow-in-the-dark paints such as emergency signs and watches. Current highly efficient LPL materials are based on inorganic materials. In contrast, we recently developed a novel LPL emitter composed only of organic molecules (R. Kabe et al., Nature, 550, 384 (2017)). This organic long persistent luminescent (OLPL) system has advantages over inorganic LPL materials of solubility, transparency, and flexibility. The origin of OLPL emission is the charge-transfer transition of an exciplex. The very slow charge recombination of separated carriers results in LPL of over 30 minutes at room temperature. However, exciplexes have been known to possess low photoluminescence quantum yield (ΦPL) and poor color purity. In organic light-emitting diodes (OLEDs) based on exciplexes, these problems were resolved by adding small amounts of emitter dopants into the exciplex-forming matrix (Y. S. Park et al., J. Appl. Phys., 110, 124519 (2011)). The emitter dopants harvest exciplexes generated by either photoexcitation or charge recombination through Förster energy transfer (FRET). After that, the emitter dopants emit light with improved brightness and color purity relative to the exciplex emission.

Here, we apply a similar technique to improve the ΦPL, color purity, and emission duration of OLPL while at the same time tuning the color over a wide range. We adopted the OLPL exciplex system of N,N,N',N'-tetramethylbenzidine (TMB) and 2,8-bis(diphenylphosphoryl)dibenz[b]thiophene (PPT) and five emitter dopants: 2,5,8,11-tetra-tet-butylperylenyl (TBPc) for blue, 9,10-bis(N,N-di-p-tolyl)aminoanthracene (TTPA) for green, 2,8-di-tet-butyl-5,11-bis(4-tet-butylphenyl)-6,12-diphenyltetraene (TBBR) for orange, 4-(dicyanomethylene)-2-methyl-6-phenyl-4H-pyran (DCM) for red, and tetr phenyl dibenzopiperiphene (DBP) for deep red. The LPL spectra of the exciplex matrices with the emitter dopants corresponded to the emission spectra of the emitter dopants, ranging from red to greenish-blue. These results indicate that the LPL emission occurs after FRET from the exciplex to the emitter dopants. Furthermore, warm white emission was achieved by doping with two emitters (TBPc and DBP). In addition to improving ΦPL and color purity because of better emission properties of dopants than exciplexes, some emitter dopants can also trap the separated electrons and inhibit charge recombination, thereby also extending the emission duration. For example, a TBBR-doped film exhibited a ΦPL that is 3.5 times higher than that of the exciplex and the longest LPL duration of 1,415 s. In conclusion, the simple doping of emitters into an exciplex matrix provides an easy method to broadly tune LPL emission and to improve the color purity, ΦPL, and emission duration. This technique will enable the development of a wide range of organic glow-in-the-dark paints.

**EP05.03.45**

**PEDOT:PSS Films in Redox-Active Devices**

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**Wide-Range Tuning and Enhancement of Organic Long Persistent Luminescence**

Kazuya Jinna1,2, Ryota Kabe1,3 and Chihaya Adachi1,1,1,2, JIST, ERATO, Adachi Molecular Exciton Engineering Project, c/o OPERA, Kyushu University, Fukuoka, Japan; 3International Institute for Carbon Neutral Energy Research (WPI-ICNER), Kyushu University, Fukuoka, Japan; 4Center for Organic Photonics and Electronics Research (OPERA), Kyushu University, Fukuoka, Japan.

We present new designs for fast and reversibly switchable redox-active devices using PEDOT:PSS both as a transparent electrode material and an interface film exploiting its capacitive properties. Thin PEDOT:PSS films have been incorporated in window-type purple-to-transmissive electrochromic devices and symmetric electrodes as part of charge storage devices. We reached a conductivity up to 2000 S cm⁻¹ when post-treating PEDOT:PSS films using different (in)organic acids on different substrates, enough to reversibly switch multiple ECPs made in the Reynolds Group depending on the targeted application. We will demonstrate how the device construction, charge-balancing and electrode conductivity have an influence on the device performance focusing on switching speed and capacitive behavior. We combine our device design with a fundamental study of the mixed electron and ion transport processes occurring in the ECP films at the electrodes looking for links to device performance. Using these new device structures, we have developed an easy way to produce both electrochromic and charge storage devices using solution processable polymers and roll-to-roll compatible coating techniques.

EP05.03.46
Bi-Layer Structure Gate Dielectrics for Low-Voltage Operating Organic Field-Effect Transistors and Printable Flash Memory

Moon Jihoon and Kang-Jun Baeg; Wearable Device, Pukyong National University, Busan, Korea (the Republic of).

Solution-processed pi-conjugated organic semiconductors potentially enable to flexible and stretchable opto-electronic applications via large-area, high-throughput, and low-cost graphic arts printing methods. For development of printed and flexible electronics, organic field-effect transistors (OFETs) and non-volatile memory as well as their integrated circuits are key components and they should be operated under low-power condition. Ultra-low power consumption would be a crucial requirement for determine its applicability for wearable and IoT-based consumer products. Gate-dielectric capacitance and its interface with semiconductor active channel is important to reduce the operation voltage. In this study, we develop the optimized top-gate and bi-layer polymeric gate dielectric structure for high performance OFETs and their integrated circuits under low power operation conditions. Although high-k fluorinated polymers such as P(VDF-TrFE-CTFE) and P(VDF-TrFE-CFE) could induce large accumulation of charge carriers at the semiconductor-dielectric interface, those dielectrics adversely affects the performance of N-type OFETs by pushing electrons at the interface and large charge injection barrier due to the high polarity of the C-F bonds. The depletion phenomena could be remarkably improved by incorporation of intermediate polystyrene layer and/or appropriate charge injection layer to facilitate electron injection and efficient accumulation at the interface between the PVDF polymers and organic semiconductors. This approach has enabled high-performance, low-voltage driven OFETs and flexible and printed integrated circuits. Moreover, we also applied the same bi-layer structure for non-volatile OFET memory using chargeable gate dielectric (electret) layers.

EP05.03.47
Fabrication of Conducting Bulk Structures Made of Polyythiophene Derivatives

Anna I. Hofmann, Renee Kroon, Ida Holm, Anja Lund and Christian Muller; Chemistry and Chemical Engineering, Chalmers University of Technology, Göteborg, Sweden.

One of the main assets of plastic electronics is the possibility to process semiconductor polymers from solution, e.g. via printing, which promises cost-efficient production of light-weight and flexible devices. Thus, most conducting polymers are currently studied in the form of thin-films cast from solution. For applications such as organic thermoelectrics, however, conducting bulk structures are highly sought after. Nevertheless, the fabrication of highly conducting bulk structures remains a major challenge in the field of organic electronics. In this talk, we present different strategies for the bulk processing of doped conjugated polymers and for the doping of polymer bulk structures, using various types of acid dopants and counter ions, as well as side chain engineering. We demonstrate that hot-pressing of an acid doped polythiophene derivative yields free standing and flexible films with conductivities of up to 120 S cm⁻¹. This opens up a wide range of new possibilities for the fabrication of electronics, from electrochemical devices to thermoelectric modules.

EP05.03.48
All Printed Electrolyte-Gated Transistors and Inverters by Spray Coating

Kyungeuk Cho1, Young Kyung Jo1, Hye-young Yoo1, Kihyon Hong2 and Keun Hyung Lee1; 1Inha University, Incheon, Korea (the Republic of); 2Chungnam National University, Chungnam, Korea (the Republic of).

Ion gels, consisting of room temperature ionic liquids and a host polymer networks, have attracted great attention as solid electrolyte because they possess excellent advantages of ionic liquids such as ionic mobility, specific capacitance, and chemical and electrochemical stabilities in a solid form. In order to employ ion gels in electronic devices, solution processing methods including aerosol-jet printing, spin coating, and transfer printing have been demonstrated. However, alternative processing strategies are desirable to provide a diversity of process methods and to realize low cost production of printed electronics. In this regard, a spray coating technique was applied to fabricate electrolyte-gated transistors and inverters. Not only the ion gel gate dielectric but all thin film layers including source/drain electrodes, a semiconductor, a gate electrode were sprayed in various substrates for flexible and low cost thin film transistors and inverters. All spray-coated transistors exhibited low operation voltages 1 V, low turn on voltage at around 0 V, and reasonably high on/off current ratio about 10³ because of the high capacitance of the ion gels. Furthermore, all sprayed inverters operating at low voltages were also fabricated based on the ion gel-gated transistors. These results show that the spray printing technique provides a promising and reliable route to fabricate all printed thin-film transistors and other electrochemical electronic devices.

EP05.03.49
Electrical, Thermal and Morphological Properties of Semicrystalline Homopolymer Ion Gels for Solid-State Electrochemical Transistors

Young Kyung Jo1, Hye-young Yoo1, Kyunggeuk Cho1, Kihyon Hong2 and Keun Hyung Lee1; 1Chemistry and Chemical Engineering, Inha University, Incheon, Korea (the Republic of); 2Material Science, Chungnam National University, Daejeon, Korea (the Republic of).

Ionic liquids have been received great attention in electrochemical device application due to their outstanding physicochemical properties such as non-volatility, large ionic conductivity and specific capacitance. To provide mechanical strength to the liquid electrolyte, a structure forming polymer is blended with ionic liquid to make solid polymer electrolytes known as ion gels. In this work, we fabricated physically-crosslinked ion gels by using an aliphatic polyanhydride over the composition 10-50 polymer wt%. The material properties of the resulting ion gels such as surface morphology, thermal stability, mechanical strength, ionic conductivity, and specific capacitance of the resulting ion gels were systematically investigated and the correlation between these parameters was examined. Specifically, fabricated ion gels were thermally stable up to 200 °C, and thus the gels could operate thin-film electrochemical devices such as electrolyte-gated transistors under very high operation temperatures. By using these ion gels as a high capacitance gate dielectric, we could successfully fabricate organic thin-film transistors that operated at low voltage (<1 V) with high on/off current ratio ~10⁵. These results demonstrate that the phase-separation mediated physical ion gels provide a convenient way to fabricate highly conductive and mechanically robust solid polymer electrolytes for various solid-state thin-film devices.

EP05.03.50
Suppressing the Photo-Induced Degradation of Inverted Non-Fullerene Organic Solar Cells

Tim Becker, Tobias Gahlmann, Niklas Koehler, Florian Zimmermann, Fabian Goebelmann, Kai O. Brinkmann and Thomas Riedl; Institute of Electronic Devices, University of Wuppertal, Wuppertal, Germany.
Over the last years the field of organic photovoltaics made tremendous progress due to the development of new acceptor molecules instead of the common fullerene. Beyond the enhancement in efficiency to over 14% [1] an increased thermal stability of the bulk hetero junctions is achieved [2]. However, the stability under continuous operation in the maximum power point (MPP) is rarely reported. The vast majority of publications on non-fullerene active layers are utilizing an inverted device architecture with Zinc Oxide (ZnO) as electron extraction layer (EEL). Previous reports on inverted fullerene-based OPV have indicated photo-induced degradation if ZnO EELs are used. This degradation effect has been associated with a loss of selectivity of the illuminated ZnO and the concomitant onset of parasitic recombination of holes at the ZnO/organic interface [3]. In this work we use MPP-tracking to demonstrate that the photo-induced degradation of inverted fullerene-free devices comprising ZnO EELs is substantially more severe than that previously found in fullerene-based devices. Specifically, the PCE of a PBDB-T:ITIC device drops by 60-70% within 30 min of operation in the MPP, while the corresponding PBDDB-T:PC61BM only drops by < 40% in the same time scale. The degradation effect applies to various non-fullerene acceptors, such as ITIC [4] or IEICO [5]. A comparative study of various ZnO layers (atomic layer deposition, nanoparticles, sol-gel) shows the general validity of this effect for all ZnO-based systems. We evidence that the degradation is associated with the UV spectral components of the solar spectrum, it takes place even under inert conditions and is reversible in darkness. We will show that the ZnO/acceptor interface is crucially important for the severity of the degradation effect. We attribute the strong photo-induced degradation in the non-fullerene cells to the relatively higher HOMO level of e.g. ITIC (5.5 eV) compared to PCBM (6.1 eV).

Thereby, non-fullerene acceptors have a lower ability to block holes therefore and give rise to substantial parasitic recombination at the interface to the illuminated ZnO EEL. Thereby the UV-induced loss of selectivity of ZnO [3] has significantly stronger negative impact in the non-fullerene devices due to increased recombination with extracted electrons. We will show that the use of a C60 monolayer on top of the ZnO EEL dramatically suppresses the photo-induced degradation. These insights will be important for a serious application of high-efficiency non-fullerene OPV.


EP05.03.51
Air-Stable, Balanced Ambipolar Split-Gate Organic Thin-Film Transistors
Hocheon Yoo1, Masahiro Nakano2, Sungmin On1, Han-Koo Lee1, Kazuo Takimya2 and Jae-Joon Kim1; 1Pohang University of Science and Technology, Pohang, Korea (the Republic of); 2RIKEN Center for Emergent Matter Science, Wako, Japan.

Ambipolar organic thin-film transistors (OTFTs) have attracted great interest for the development of more compact circuits. Nonetheless, most previous studies investigating ambipolar organic semiconductors have reported results measured in either high vacuum or nitrogen atmosphere due to a lack of air stability. To develop a systematic design methodology for air-stable ambipolar organic semiconductors, it is necessary to fundamentally study the dependence of the material/device characteristics on the environmental atmosphere. Here, we demonstrate ambipolar OTFTs with balanced p/n characteristics under ambient air using PNDTI-BT-DP. Based on results from XPS, UPS, and electrical characterizations in high vacuum and ambient air, we analyze the underlying mechanisms that account for the well-balanced p/n characteristics of the PNDTI-BT-DP-based OTFTs in ambient air. We further demonstrate the air-stable ambipolar split-gate OTFTs that operate as either a unipolar p- or n-type device based on electrical control. Finally, we report results showing that the device characteristics for both p- or n-type operations were maintained in ambient air for ~120 hours.

EP05.03.52
Highly-Aligned Organic Semiconductor Films via Programmed Bar-Coating for High-Performance Organic Transistors
Seon Baek Lee, Boseok Kang, Seonghyun Kim, Woong Sung and Kilwon Cho; POSTECH, Pohang, Korea (the Republic of).

Organic thin film transistors (OTFTs) have received enormous interest due to their great potential for realizing low-cost, lightweight and flexible electronics that are solution-processed in a large area. Recent researches have mainly been devoted to developing new organic semiconducting materials and novel solution-processing techniques for achieving high performance organic thin film transistors (OTFTs). Spin-coating has been frequently used in a lab scale due to its simplicity, but has fatal drawbacks, such as large amount of material waste, difficulty in scaling up and incompatibility with a conventional roll-to-roll (R2R) system. Several techniques have been developed for the alternative and bar-coating is considered as the promising printing technique for large area uniform coating. Here, we introduced the bar-coating to fabricate highly-aligned small molecule organic semiconductor (2,7-diocetyl[1]benzothieno[3,2-b][1]benzothiophene, CBTBT) films. We fabricated the large-area OTFT arrays which exhibit superior charge carrier mobility with high uniformity and reproducibility. The correlation between process conditions and crystal size was observed, and a crystallization mechanism of bar-coated films was identified. Furthermore, we proposed programmed bar-coating technique and fabricated infinitely continuous highly-crystalline films with high uniformity in large-area.

EP05.03.53
Effects of Inserting an Ionic Liquid in Conjugated Polymer
Beatriz Pesco, Leonardo J. de Siqueira and Laura O. Peres; Federal Univ of Sao Paulo, Diadema, Brazil.

Conjugated polymers are widely studied materials due to their diversity applications. However, its rigidity provides low solubility to the material. One strategy to solve this problem is the insertion flexible groups into the insoluble conjugate material. In this context, the present work presents the synthesis of a block polymer, which is composed of intercalated conjugated and non-conjugated segment, derived from poly(p-phenylene vinylene) (PPV) and poly(ethylene oxide) (PEG), respectively. The material was synthesized and characterized by infrared, UV-Vis and fluorescence. The results showed a better solubility of the block polymer in organic solvent without significant change of its luminescent properties. The ionic liquid (IL) butyltrimethyl ammonium bis(ethylenediamine) acetate was incorporated into the polymer material in proportions of 1:1 and 3:1 (polymer mass ratio/IL). The results obtained by X-ray diffraction show that the polymeric material is crystalline, which is gradually lost/decreased upon the addition of the ionic liquid. It was also observed difference in absorption, emission, DSC and TGA files, showing that there is an interaction between the block polymer material and the ionic liquid, which promoted improvement in the emission intensity and greater thermal stability.

EP05.03.54
Exciton Blocking Layers in Organic Photovoltaic Devices
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Exciton blocking layers are essential for efficient organic photovoltaic device operation, where they serve to block excitons at the anode or cathode contact in order to reduce losses in the cells. At the anode side, excition blocking layers are typically implemented in contact with a hole transporting layer, such as
molybdenum oxide (MoO$_3$), where they prevent recombination at the metal oxide interface$^1$. Exciton blocking layers that also transport electrons have at the same time shown to efficiently reduce losses at the cathode contact.

In this work, the use of different organic interlayers integrated as exciton blocking layers in organic photovoltaic cells is presented. The exciton blocking layers are integrated either between MoO$_3$ hole contact layer and the active organic layer, or as cathode contact layers between ITO and the active organic layer. Besides organic solar cell device development and characterization, the integration of the layers is studied through hole-only and electron-only devices, optical spectroscopy analysis and morphology studies, in combination with complete optical and electrical device modeling. From the characterization and modeling, ideal thicknesses of the organic exciton blocking layers are found, based on a delicate interplay between the exciton blocking properties, the series resistance and the exciton generation profiles in the devices$^1$. Significantly improved device performances are observed in small molecule DBP/C$_{70}$ based organic photovoltaic cells when including specific organic interlayers (one of them being 4P-NPD) in combination with MoO$_3$, due to the added exciton blocking properties at the hole contacts. In addition, we evaluate here the effect of different exciton blocking layers on the performance of solar cells with up-scaled device areas. This is specifically area-dependent performance behavior observed in BCP based cathode contact layers, where BCP based exciton blocking and electron transporting stacks are introduced to improve the performance of up-scaled devices$^2$. The work thus addresses the need and challenge of incorporating exciton blocking layers in organic solar cells, and addresses the issue of device scale-up, which is needed for further implementing these layers in industrially relevant organic solar cells modules.


EP05.03.55
Photo-Conductivity and Self-Assembly of Melanin Thin Films on Patterned SiO$_2$/Si Substrate
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Eumelanin is a biomacromolecule featuring fascinating properties such as broadband optical absorption, metal chelation, photoconduction and hydration-dependent electrical response, this last mainly attributable to protonic transport [1-3]. Because of the limited processability, a model describing the correlation between supramolecular aggregation of eumelanin and fundamental optical and electrical properties does not exist yet.

Eumelanin is synthesized by the oxidative polymerization of (5,6)-dihydroxindole (DHI) and (5,6)-dihydroxyindol-2-carboxylic acid (DHICA) building blocks. Co-existing redox states (hydroquinone, semiquinone, quinone), different polymerization sites and a wide variety of supramolecular arrangements block physicochemical disorder to the material [4].

Using chemically controlled eumelanin is the key to gain insight into the fundamental aspects of its functional properties. Our group is currently studying the mechanism of solid-state polymerization of DHI and DHICA at surfaces, to achieve thin films suitable for structural, optical and electrical characterizations. AFM and FTIR investigations on spin coated samples of DHI and DHICA show that the monomers aggregate, eventually polymerizing in ambient conditions. We performed photoconductivity studies on such samples, obtained from spin coating DHICA on gold-patterned SiO$_2$/Si substrates and on Corning® 87 glass, collecting optical spectra and transient current measurements as a function of relative humidity (%RH). We observed a broad absorption peak at 330 nm, red shifting over time, providing an evidence of solid-state assembly and polymerization, supported by AFM. Nanometer-sized nuclei grew into spherical and rod-shape structures, the size of which is larger for films stored at high %RH with respect to those stored in ambient condition, demonstrating the critical role of H$_2$O in promoting lateral interactions.

Our investigations open the opportunity to demonstrate eumelanin-based organic solar cells and, on the long term, organic solar batteries based on the quinone-semiquinone-hydroquinone redox species, where light harvesting could help to enhance the storage properties of eumelanin.

References

EP05.03.56
Half- and Quarter-Wavelength Resonance in Fabry–Pérot Cavity Based OLEDs
Ekani Dahal$^1$, Benjamin Isenhart$^1$, Karen Cianciulli$^2$, Bin Du$^1$, Olivia Sergiovanni$^1$ and Matthew S. White$^1$; $^1$The University of Vermont, Burlington, Vermont, United States; $^2$Asheville School, Asheville, North Carolina, United States.

Organic light-emitting diodes (OLEDs) have a promising next-generation display and solid-state lighting applications. By forming an optical cavity using the metallic electrodes enclosing the device, we have fabricated various narrow peak emission OLEDs. Varying the thickness of the optical cavity, we observed the interesting change in wavelength peaks. We have used Tris(8–hydroxyquinolinato)aluminium, Alq$_3$, as emissive layer (EL) and added the electron transport layers (ETL) and hole transport layers (HTL) in between the metal electrodes. We observed the optical cavity effect by varying the thickness of the ETL and HTL and keeping the EL fixed. The device with the thinner optical cavity showed a quarter-wavelength resonance as a red wavelength peak whereas increasing the thickness of the cavity shifted the wavelength peak to blue and further increase in the thickness to the green emission peaks as half-wavelength resonance. These narrow-peak emission peaks have full width at half maxima (FWHM) of 10 nm, indicating a cavity finesse of roughly 80 when measuring over +/- 9 degrees with respect to normal.

EP05.03.57
Towards a Better Control of Solution-Processed P-Doped Films—Identifying the Impact of Residual Water in Organic Solvents
Tamara Domschke$^1$, Alexandre Pereira$^2$, Raphael Clerc$^2$ and Alexandre Carella$^2$; $^1$CEA-LITEN, Université Grenoble Alpes, Grenoble, France; $^2$UJM-Saint-Etienne CNRS UMR 5516, Laboratoire Hubert Curien, Université de Lyon, Saint Etienne, France.

Chemical doping allows tuning the electrical and optoelectronic properties of organic semiconductors (OSC) and conductive polymers$^1$. However, chemical doping is often accompanied with physicochemical disorder to the material$^2$.

Doping with organic solvents is widely used for fabrication of OSCs$^3$. Solvent exposure is a key factor in the performance of organic optoelectronic devices, but to date, understanding its impact is still limited. In this work, the use of different organic solvents as solvents for solution-processed organic thin films is studied.$^1$ The impact of residual water in organic solvents during OSC fabrication is analyzed.

First, we report on the strong thickness-dependent conductivity results observed for doped films ranging from 200 nm to 15 nm, where the conductivity decreased from $10^4$ S.cm$^{-1}$ to $10^7$ S.cm$^{-1}$, respectively. Also, a clear bleaching of the doping signature is observed in the UV-vis-NIR absorption spectra although EDX mapping presented an homogeneous distribution of the dopant in the film, for all thicknesses. The stirring conditions of the blend solution are identified as key parameters controlling the doping efficiency in thinner films (lower solution concentration). A similar trend was found for PBDTTT-C doped with the planar electron acceptor 7,7,8,8-tetracyano-2,3,5,6-tetrafluorodiquinodimethane (F4TCNQ).

In a second part, we correlate the decreasing doping efficiency of lower blend concentrations with the residual water present in the processing solvent. Therefore, our study emphasizes the importance of controlling the water molar fraction of the solvent to achieve reproducible electrical and optoelectronic results for doped films, independent of the blend concentration. As a result, the electrical conductivity of PBDTTT-C doped with Motf(tfd-COF)$_3$ increased from $10^4$ S.cm$^{-1}$ to $10^7$ S.cm$^{-1}$ and showed to be reproducible for different blend concentrations.

Finally, we will give insights into the possible mechanism involved in the doping efficiency alteration caused by the presence of residual water in the processing solvent.


EP05.03.58
Design of Conducting-Polymer-Free Highly Flexible Organic Light Emitting Diodes Having Oxide-Based Thin-Film Encapsulation Layers
Hampjung Kim, Jeonghyun Kwon, Cheolgyu Kim, Taek-Soo Kim, Kyung Cheol Choi and Seunghyup Yoo; KAIST, Daejeon, Korea (the Republic of).

Flexible OLEDs require flexible electrodes and thin film encapsulation (TFE) layers. Unfortunately, oxides that limit the flexibility of OLEDs are used to create electrodes and TFE layers that exhibit the best performance. To address this problem, research has been conducted on flexible electrodes and TFE layers that can replace oxides. Nonetheless, oxide-based transparent electrodes such as ITO and ZO are best suited as transparent electrodes for OLEDs due to their high transmittance and electrical conductivity. It is also known that Al2O3 in the oxide-based TFE layer can be formed at a high density and exhibits the best sealing characteristics.

In this study, a very thin PET substrate with a thickness of 6 μm was used to reduce deformation on the device. Among the oxide electrodes, IZO has a lower process temperature than ITO and is suitable for use on heat-sensitive substrates such as PET. And the Al2O3 TFE layer deposited by the ALD process has excellent sealing properties, but the stability against mechanical deformation is very low. In the experiment, the stable folding condition was found by observing the change of sheet resistance and WVTR according to the strain. The results show that the critical strain of Al2O3 is too low to be bent less than 1 mm. However, considering the overall device structure, the Young's modulus of layers including Al2O3 was much higher than that of the substrate; for this reason, even though the thickness was very thin, it greatly influenced the optimal device structure. The neutral plane located at the center of the substrate is displaced due to the effect of the device deposited on the substrate. In general, the thickness of the substrate is very thick, so the influence of the neutral plane is negligible. However, since the effect is too large to be ignored in our case, the exact strain value can only be obtained by locating the actual neutral plane. Results from ANSYS simulation, the position of the neutral plane in the entire device structure is just below the interface between the substrate and the device. Finally, with a bending radius of 740 μm, the strain applied to the outermost Al2O3 is 0.21%, the safety margin identified by the experiment, and the maximum stress value is lower than that of Al2O3, which is known as 379 MPa.

Consequently, an OLED that operates reliably at a bending radius of curvature of less than 1 mm is realized using an transparent conductive oxide electrode and TFE layer, which are known to be prone to crack formation upon bending. The optimal radius of curvature was established by taking into account the influence of the entire device structure and the limiting deformation of the weaker layer and explained why this could be done using a simulation based on a finite-element method (FEM).

EP05.03.59
Effect of Counterion Exchange of Conjugated Polyelectrolytes in Organic Electrochemical Transistors
Brian Khau and Elsa Reichmanis; Georgia Institute of Technology, Atlanta, Georgia, United States.

The palette of mixed ionic-electronic materials for organic electrochemical transistors (OECTs) can be divided into three types: PEDOT-PSS and its derivatives, semiconducting polymers with nonionic polar chains, and conjugated polyelectrolytes (CPEs). To date, the relative amount of literature on CPEs-based OECTs dwindles in comparison to PEDOT-PSS-based devices. We assert that CPEs provide a useful pedagogical system for understanding mechanisms of ionic and electronic transport in OECTs. Through ion-exchange on an anionic polythiophene with a pendant carboxyl group, poly[3-(4-carboxypropyl)]thiophene-2,5-diyl](PCPT), a series of analogues are produced with the same conjugated backbone, only differing in their cations. This procedure clearly elucidates how the choice of counter-ion dictates operation of an accumulation-mode OECT. Firstly, we highlight how these analogues differ in microstructure and phase morphology at various length scales, characterized via optical microscopy and scattering techniques. Secondly, we investigate the photophysical processes of the cast films through ultra-fast spectroscopic methods to understand the effect of counter-ion on charge transport. Lastly, we demonstrate that the counter-ion plays a crucial role in modulating electrolytic ion injection into the polymer film during OECT operation, via cyclic voltammetry and spectroelectrochemistry.

EP05.03.60
Fine-Tuning Polymer Packing and Crystallinity in All-Polymer Solar Cells Through Side-Chain Engineering
Yilei Wu and Zhenan Bao; Stanford Institute, Stanford, California, United States.

Polymer crystallinity and self-assembly behavior play a crucial role in the performance of all-polymer solar cells (a-PSCs). Many aspects of how polymer crystallinity and aggregation influence active-layer morphology and photovoltaic performance, however, remain still elusive. Herein, we report a simple yet effective way to modulate the crystallinity of the well-known naphthalene diimide (NDI) based polymer (N2200), by systematically replacing a certain amount alkyl side-chains with bulky aromatic side-chains. Specifically, we synthesized a series of random polymer with different molar ratio of the two side-chains and found that the crystallinity of these acceptor polymer decreases with increasing amount of bulky aromatic side-chains as evidenced by UV-VIS-NIR absorption and photoluminescence spectroscopy, as well as thermal analysis and grazing incidence x-ray scattering techniques. Importantly,
compared to the reference semicrystalline N2200; preliminary OPV results show that mixing of more amorphous acceptor polymers with an amorphous donor polymer (PTB7-Th) enables all-PSCs with increased PCE, on account of higher short-circuit current density ($J_{sc}$) and fill factor (FF). Our results demonstrate how the polymer crystallinity and packing motives can be systematically tuned by side-chain engineering approach and highlights the importance of polymer structure and morphology on all-PSCs device performance.

**EP05.03.61**

**Electrospun Optical Fibers Composed of a Regenerable Polymer and Approaches for Reducing Their Propagation Losses** Yuya Ishii; Faculty of Fiber Science and Engineering, Kyoto Institute of Technology, Kyoto, Japan.

Polymer micro-/sub-microfibers have unique properties including small diameter, light weight, mechanical flexibility, and large surface-area-to-volume ratio. Because such fibers also have inherent waveguide structures, they are promising as building blocks for small, mechanically flexible optical devices such as waveguides and sensors. In this study, we have fabricated electrospun micro-/sub-microfibers composed of a biodegradable and regenerable polymer and investigated their optical propagation losses. Additionally, versatile approaches for reducing the propagation loss and diameters of the fibers have been demonstrated. An amorphous polymer, poly(DL-lactic acid) (PDLLA), was used as the core material because it exhibits high transparency in the visible range and is both biodegradable and regenerable. Single aligned PDLLA fibers with diameters of approximately 1.7 μm were fabricated with an electrospinning method and the intensity of light transmitted in the fibers was investigated with increasing temperature. The transmission intensity significantly increased after heating over the glass transition temperature ($T_g$) of the fibers, 49.8 °C, which indicated that the propagation loss in the fibers decreased after heating over $T_g$. The propagation loss was investigated before/after heating up to 55 °C because this temperature was above $T_g$ of the PDLLA fibers; in addition, the transmitted light intensity showed the maximum intensity at 55 °C. The propagation loss was significantly reduced after heating. For example, the propagation loss in one of the fibers was reduced from 17 to 8.1 dB cm$^{-1}$ under 532-nm illumination. These results demonstrated that heating of the electrospun PDLLA fibers above $T_g$ significantly reduced the propagation loss in the fibers. An ultraviolet–visible absorption measurement and morphological characterization revealed that the propagation loss reduction was achieved by the reduction of extrinsic excess scattering losses arising from the extrinsic density inhomogeneity in the fibers. The as-electrospun PDLLA fibers were then drawn at 55 ± 2 °C to reduce the extrinsic density inhomogeneity and fluctuations in the fiber diameter. After fivefold drawing, the PDLLA fibers showed significant decreases in their fiber diameters to approximately 0.5 μm and reductions in the root-mean-square roughness for each fiber diameter. The propagation loss in each fiber was significantly decreased after thermal drawing; for example, from 16 to 6.6 dB cm$^{-1}$ at 532 nm. Although a decreased fiber diameter normally increases propagation loss in fibers, the propagation loss after thermal drawing was decreased. This was attributed to the reduced fluctuation in the fiber diameter due to thermally drawing and the decreased extrinsic density inhomogeneity in the fibers due to heating.

**EP05.03.62**

**Structure and Electrical Properties of Metal Ion Doped Polydopamine (PDA)** Haoqi Li, Yao Zhao and Fei Ren; Mechanical Engineering, Temple University, Philadelphia, Pennsylvania, United States.

Polydopamine (PDA) is a bio-inspired polymer that can be synthesized through self-assembly of dopamine monomers under mild conditions. Thermal treatment can convert PDA into a conductive phase, commonly known as carbonized PDA (cPDA). This work studied the effect of three metal ions, i.e. Na+, Mg2+, Cu2+, on the synthesis of PDA and its conversion to cPDA. Both Cu$^{2+}$ and Mg$^{2+}$ could interact with PDA, which influenced the growth of PDA thin film, morphology change of PDA particles upon thermal annealing, and the electrical properties of heat-treated thin films. In contrast, the presence of Na$^+$ ion during the synthesis of PDA did not show any effect. This difference can be explained by the variation of the three ion species to react with PDA through coordination bonding: Cu$^{2+}$ > Mg$^{2+}$ > Na$^+$. In this study, SEM and TEM were used to examine the chemical composition of PDA thin film and particles. EDS and XPS are employed to study the chemical composition. The structure was investigated using electron diffraction and Raman spectroscopy, and the properties were evaluated with respect to the electrical conductivity and thermoelectric Seebeck coefficient. The results from this work provide a potential approach to control the structure and properties of PDA and cPDA materials through metal ion doping.

**EP05.03.63**

**Highly Orthogonal Semiconducting Polymers for Solution Tandem Electronics** Han Wool Park1, Keun-Yeong Choi2, Haejung Hwang1, Boseok Kang1, Joo Sung Kim1, Hyuk Min Kweon1, Je Hyung Koo1, Kilwon Cho1, BongSoo Kim1, Kwon Bum Chung1, Soo-Ki Kwon1, Yun-Hi Kim1, Moon Sung Kang1, Hejin Lee2 and Do Hwan Kim1; 1Hanyang University, Seoul, Korea (the Republic of); 2Soongsil University, Seoul, Korea (the Republic of).

Polymer electronic devices are receiving great attention because semiconducting polymers are soluble in conventional solvents, which results from being inexpensive in the field of electronics. This opportunity, however, serves as a trade-off when one tries to implement these processes in assembling practical electronic devices, since the as-deposited tandem films would be vulnerable to following solution processes. Here, we report a highly orthogonal semiconducting polymer (OSP) that is capable of showing chemical and physical tolerance during multiple solution coating and photolithography processes. We adopted the recently developed sol-gel process to obtain the orthogonality of organic semiconductor against the solvents and chemical coatings. We could prepare self-assembled structures with quasi-3D random or ladder properties. The resulting structure produced film resistant to severe external stimuli. Moreover, the peculiar topology of organometallic gel network containing with molecular pores could be successfully utilized as a template to form an interpenetrating polymer network (IPN) with functional electronic organic units. As a result, we could demonstrate that sub-micron patterning and forming of tandem structures of OSP films can be done readily through conventional photolithography with sequential solution and etching processes, and finally fabricate tandem electronic devices including basic complementary metal-oxide-semiconductor (CMOS) inverters and pixelated polymer light-emitting diodes (PLEDs). Ultimately, the proposed strategy is expected to open up new avenues for the fabrication of optoelectronic devices that require high-resolution tandem processing of polymer semiconductors such as OLED microdisplays, organic CMOS image sensors, and artificial eyes.

**SESSION EP05.04: Bioelectronic Devices**

Session Chairs: Gregorio Faria and Jonathan Rivnay

Tuesday Morning, November 27, 2018

Hynes, Level 2, Room 208

8:00 AM *EP05.04.01
Engineering Conjugated Polymers for Bioelectronics Sahika Inal; King Abdullah University of Science and Technology, Thuwal, Saudi Arabia.

Conducting both ionic and electronic charge carriers, conjugated polymers are impacting on a large variety of biology-related applications as the electronic material interfacing with living systems. A device type that has predominantly utilized these polymers as its active component is the organic electrochemical transistor (OECT) – an electrolyte gated transistor used for ionic-to-electronic signal transduction. In this talk, I will show a comprehensive study on the thin film properties of a series of conjugated polymers and evaluate the concomitant performance of electrolyte gated transistors comprising these polymers. We investigate how systematic chemical modifications impact on the electrochemical activity of the materials, thereof the device operation. I will present two cases where engineering the material is crucial to develop an OECT based sensor for metabolites and transducers for interfacing lipid bilayers. Highlighting the materials properties that enable enhanced mixed conduction, this work provides an understanding of materials-device performance relations for the development of next generation organic electronic sensors.

8:30 AM EP05.04.02
Ion Gated Transistor—A Mixed Ionic-Electronic Transistor Georgios Spyropoulos, Jeremy Savarin, Jennifer Gelinhas and Dion Khodagholy; Columbia University, New York, New York, United States.

As our understanding of the brain’s physiology and pathology progresses, increasingly sophisticated technologies are required to advance discoveries in neuroscience and develop more effective approaches to treat brain disease. To meet this challenge, we propose a novel transistor architecture that provides an efficient interface with biological substrates, especially neural networks, through its channel’s intrinsic ion mobility. Because independent electronic gating can be applied to these transistors, they can be incorporated into integrated circuits, unlike their electrolyte-gated counterparts. The channel consists of a composite film based on highly conductive poly(3,4-ethylendioxythiophene) doped with polystyrene sulfonate (PEDOT:PSS) enriched with D-sorbitol. At the gate electrode, an ion exchange membrane serves as ion conductor. To determine an optimal transistor configuration and material composition, we microfabricated transistor arrays of varying geometrical parameters. In doing so, we were able to extract conductivity, contact resistance, and electrochemical impedance values for all the critical interfaces of various composites. Furthermore, output characteristics and current temporal response of each configuration revealed the key driving physical parameters and provided insight into optimization of the device for various applications. The resulting optimal transistors were tested as electroencephalography (EEG) interface and amplifier circuitry and compared with organic electrochemical transistors and surface electrodes showed promising signal-to-noise ratio and spatio-temporal resolution.

8:45 AM *EP05.04.03
Organic Bioelectronics In Vitro—3D, Biomimetic Devices and Cell Models Roisin Owens; University of Cambridge, Cambridge, United Kingdom.

In vitro models of biological systems are essential for our understanding of biological systems. In many cases where animal models have failed to translate to useful data for human diseases, physiologically relevant in vitro models can bridge the gap. Many difficulties exist in interfacing complex, 3D models with technology adapted for monitoring function. Polymeric electroactive materials and devices can bridge the gap between hard inflexible materials used for physical transducers and soft, compliant biological tissues. An additional advantage of these electronic materials is their flexibility for processing and fabrication in a wide range of formats. In this presentation, I will discuss our recent progress in adapting conducting polymer devices, including simple electrodes and transistors, to integrate with 3D cell models. We go further, by generating 3D electroactive scaffolds capable of hosting and monitoring cells. I will also highlight recent research using biomimetic models of cell membranes interfaced with organic electronic devices for drug discovery.

9:15 AM EP05.04.04
Highly Efficient Organic Photodiodes Operated in Aqueous Electrolytes Achilleas Savvas and Sahika Inal; Biological and Environmental Science and Engineering, King Abdullah University of Science and Technology, Thuwal, Saudi Arabia.

Optical techniques have greatly accelerated advances in modern medicine. Lasers and optical devices are now in wide range use in clinical practice to assess health condition and treat disease.[1] Recently, a new category of light sensitive devices based on organic semiconducting materials has emerged as promising candidates for restoring vision,[2] and recording neuronal activity.[3] In this study, we present an organic photodiode comprised of a solution processed organic semiconductor p-n bilayer junction. Our device, operating in aqueous electrolytes including cell culture media, produces large photocurrents when illuminated with low intensity, broad spectrum light source. We show that in this p-n bilayer junction, which is insulating prior to illumination by light, the photo-generated excitons are rapidly disassociated leading to large photocurrents as well as high ON/OFF ratios in the range of μA/cm² and 10⁶, respectively. These findings together with an in depth electrochemical analysis suggest a highly efficient photo-capacitive phenomenon at the solid/liquid interface. The devices are freestanding, operate without external wires or electrical bias and show a remarkably stable, continuous operation in aqueous media. This is the first demonstration of an easy-to-fabricate, biorganic platform, capable of delivering large photocurrents in aqueous electrolytes with potential for direct photostimulation of living cells.


9:30 AM EP05.04.05
Vapor Deposited Conducting Polymers for Electrochemical Energy Storage Trisha L. Andrew; University of Massachusetts Amherst, Cambridge, Massachusetts, United States.

Lightweight energy storage technologies are integral for powering emerging wearable health monitors and smart garments. Reactive vapor deposition creates films of doped conjugated polymers with tunable mesoporosity, which results in efficient, reversible and thickness-independent ion transport when optimized. Vapor deposited conjugated polymer films are also highly conductive and can act as sole component electrodes with which to fashion pseudocapacitive charge storage devices. Pseudocapacitors comprised of vapor-deposited doped polymer films display higher areal and volumetric capacitances than solution-processed counterparts, to the extent that energy densities comparable to state-of-the-art carbon materials can be obtained with vapor deposited polymer films. Further, since vapor deposition allows for textured and fragile substrates to be nondestructively coated, various textiles and fibers/yarns can be transformed into high-performance, super-deformable, wearable electrodes, electrochemical transistors and pseudocapacitors. Taken together, reactive vapor deposition and off-the-shelf fabrics present a unique combination of processing technique and device substrate with the potential to create lightweight and portable charge storage solutions.
Molecular doping is a crucial tool for controlling the charge carrier concentration in organic semiconductors for a range of optoelectronic devices such as field-effect transistors, solar cells and thermoelectric generators. We show that doping of both p- and n-type conjugated polymers can be enhanced by exchanging the commonly used unpolar side chains with polar side chains. The use of oligo ethylene glycol side chains with a polythiophene, p(g42T-T), is demonstrated to significantly improve the compatibility with common molecular p-dopants such as 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F4TCNQ) and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ).[1] The same is shown for n-doping of a polar naphthalenediimide-alkoxybithiophene demonstrated to significantly improve the compatibility with common molecular p-dopants such as 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F4TCNQ) and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ).[1] The same is shown for n-doping of a polar naphthalenediimide-alkoxybithiophene copolymer p(gNDI-gT2) that also carries oligo ethylene glycol based side chains with the benzimidazole-dimethylbenzamine based n-dopant N DMAU.[2] In both cases a much higher electrical conductivity can be reached using a smaller dopant fraction and hence limited influence on the polymer nanostructure.


10:30 AM EP05.05.02
Stability of Charge Transfer States in Doped P3HT Films
Kristen Watts, Bharati Neelamraju, Erinn Ratcliff and Jeanne Pemberton; University of Arizona, Tucson, Arizona, United States.

Poly-(3-hexyl-) thiophene (P3HT) is frequently viewed as a model system for photonic and electronic devices. The molecule 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F4TCNQ) and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) are well-known p-type dopant for P3HT. The interaction between P3HT and F4TCNQ has been described as an integer charge transfer (ICT) from P3HT to F4TCNQ based on vibrational spectroscopy evidence[1,2], although films are typically significantly thicker than what is used in devices. Recent evidence indicates that the degree of charge transfer is predicated on processing conditions, with demonstration of a partial charge transfer complex (CPX) formed under certain processing conditions, although the exact cause is unclear.[3] To date, the doping state has proven to be challenging to precisely define and control, despite P3HT-F4TCNQ being a model system for doping in organic electronics.

Using state-of-the-art capabilities, we provide new insights into the doping mechanism of P3HT-F4TCNQ system using vibrational spectroscopy and imaging (FTIR spectroscopy and Raman microscopy) of device-relevant films. Our new chemical insights will be discussed in the context of electronic states, with a specific focus on the proposed ICT versus CPX states that are being vigorously discussed in the organic electronics community. Results from additional studies on the effects of temperature and substrate on CPX formation will be presented along with results from GIWAXS, conductivity and AFM studies that demonstrate how the presence of the CPX state impacts important film characteristics such as microstructure, charge transport, and morphology.


10:45 AM EP05.05.03
Spectral Signatures and Spatial Coherence of Bound and Unbound Polarons in P3HT Films—Theory vs Experiment
Raja Ghosh1, Annabel R. Chew2, Jonathan Onorato3, Viktoria Pakhnyuk4, Christine Ruscombe5 and Frank Spano6; 1Temple University, Philadelphia, Pennsylvania, United States; 2Materials Science and Engineering, Stanford University, Stanford, California, United States; 3Materials Science and Engineering, University of Washington, Seattle, Washington, United States; 4Chemistry, University of Washington, Seattle, Washington, United States.

The origin of the mid-IR spectral features for hole absorption in doped and undoped P3HT films is investigated theoretically and experimentally. Using a Holstein-style Hamiltonian[1,2,3,4,5,6,7,8,9,10,11] to treat the prominent vinyl stretching mode, the low-energy peak (A) is found to arise primarily from intrachain transitions, in contrast to the predicitions of the more conventional treatments[12] based self-trapped, mid-gap polarons, where peak A is entirely interchain in origin. Signatures for polaron coherence are identified and used to analyze the molecular weight dependence of the IR spectrum for P3HT doped with F4TCNQ. Generally, the polaron coherence lengths along the chain and stacking axes increase with molecular weight, consistent with similar studies conducted on hole absorption in undoped P3HT. We also show that the spectral changes in bound and unbound polarons corresponds to a polaron coherence number of Ncoh of approximately 4-7 for bound holes and approximately 16-18 for unbound holes.

3. Ghosh, R.; Chew, A. R.; Onorato, J; Pakhnyuk, V; Ruscombe, C K; Salleo, A.; Spano, F. C. Spectral Signatures and Spatial Coherence of Bound and
that impact charge transport and anisotropy. Here, we report on blade coated OFETs from P(NDI2OD-T2) in toluene, an aggregating solvent. We achieved a mobility of 2 cm²/Vs with 10x anisotropy between charge transport parallel and perpendicular to the coating direction, a result on par with previous studies. The authors’ OFETs fabricated using the wire bar and brush coating methods. However, blade coating provides a more idealized processing environment and is usually desired to be suppressed. Here, polystyrene and poly(methyl methacrylate) (PMMA) were used to shift the onset of the drift of the p-dopant molybdenum tris[1-(methoxycarbonyl)-2(trifluoromethyl)phenyl]-2-diethylamino] (P3HT) films to significantly higher applied electrical fields. We investigate the resulting films and devices by means of the suppression of the dopant drift which is attributed to the intercalation of the dopant in the insulator. Both insulators show significantly different film morphologies in the blends potentially affecting the dopant distribution. Whereas polystyrene forms very homogeneous layers with P3HT, PMMA tends to shape large domains which could hinder the intercalation of dopants. This leads to more dopants remaining in the semiconductor and to an earlier onset of the observed drift. In compliance with this the dopant drift in the homogeneous polystyrene blends was found to be stronger suppressed from an onset of less than 1 V/µm in pure P3HT to more than 3 V/µm in the blend. This suppression of dopant drift adds a further interesting point to the list of improvements in organic electronics through the use of semiconductor insulator blends.

Unbound Polaron in P3HT Films: Theory vs Experiment (Just Accepted, Journal of Physical Chemistry C)


11:00 AM EP05.05.04
Suppression of Dopant Drift in Organic Semiconductors via Blending with Insulating Polymers Marc-Michael Barf1,2, Leonard Krupnik2,3, Robert Lovric1,2, and Wolfgang Kowalsky1,2,3, 1TU Braunschweig, Braunschweig, Germany; 2InnovationLab, Heidelberg, Germany; 3Heidelberg University, Heidelberg, Germany.

Blending low cost insulators with semiconducting polymers has shown to enhance performance of electronic devices in multiple cases through morphological changes in the active layer [1,2]. Also doping of organic semiconductors is a common method to improve the efficiency of devices like organic light emitting diodes, organic solar cells or organic field effect transistors. By increasing conductivity or creating space charge regions charge transport within such devices can be enhanced [3-5]. However, due to the electrical fields applied to the devices, dopants can potentially move within them and thereby change their electrical properties [6]. Since stability plays a critical role in device operation, such a drift of dopants can cause major problems and is usually desired to be suppressed.

Polymer aggregation has been proposed to play a critical role in morphological evolution during film drying and in defining long-range structural features amenable to authors’ OFETs fabricated using the wire bar and brush coating methods. However, blade coating provides a more idealized processing environment and is usually desired to be suppressed. Here, polystyrene and poly(methyl methacrylate) (PMMA) were used to shift the onset of the drift of the p-dopant molybdenum tris[1-(methoxycarbonyl)-2(trifluoromethyl)phenyl]-2-diethylamino] (P3HT) films to significantly higher applied electrical fields. We investigate the resulting films and devices by means of the suppression of the dopant drift which is attributed to the intercalation of the dopant in the insulator. Both insulators show significantly different film morphologies in the blends potentially affecting the dopant distribution. Whereas polystyrene forms very homogeneous layers with P3HT, PMMA tends to shape large domains which could hinder the intercalation of dopants. This leads to more dopants remaining in the semiconductor and to an earlier onset of the observed drift. In compliance with this the dopant drift in the homogeneous polystyrene blends was found to be stronger suppressed from an onset of less than 1 V/µm in pure P3HT to more than 3 V/µm in the blend. This suppression of dopant drift adds a further interesting point to the list of improvements in organic electronics through the use of semiconductor insulator blends.

11:15 AM EP05.05.05
Direct Probe of the Nuclear Modes Limiting Charge Mobility in Molecular Semiconductors Adam J. Moule1, Thomas Harrelson1, Varani Dantanarayana1, Correy Koshnick1, Dinqi Nai1, Enrique Gomez2, John Anthony3, Alessandro Troisi4 and Roland Faller1; 1University of California, Davis, California, United States; 2University of California, Davis, California, United States; 3The Pennsylvania State University, State College, Pennsylvania, United States; 4University of Liverpool, Liverpool, United Kingdom.

Organic semiconductors (OSCs) provide the unprecedented ability to tailor properties like electronic band gap, mechanical flexibility, processability, and biocompatibility. Recent theories suggest that low frequency dynamic intra- and intermolecular motions are critical to determining localization of the charge carrier, and thus, control the hole mobility. So far, however, it has not been possible to measure intramolecular motions experimentally and therefore no unequivocal and quantitative link exists between molecular-scale thermal disorder and macroscale hole mobility in OSCs. Here we use inelastic neutron scattering (INS) to probe thermal disorder directly by measuring the high resolution phonon spectrum in six different small molecule OSCs. Because of the virtually perfect agreement between the INS spectra and first principle simulations, we can study the coupling between hole and molecular dynamics starting from the exact knowledge of the nuclear motions in each system. This knowledge is used to generate a set of electron-phonon coupling parameters, which are used to compute hole mobility using transient localization theory. We have discovered that in some high performing materials, an important component of the non-local electron phonon coupling is carried by high frequency phonons, unlike what was previously thought. Once this element is properly taken into account the mobility, calculated from first principles, is in excellent quantitative agreement with macroscopic measurements. The analysis of the results reveal routes to improve charge mobility by engineering phonon and electron-phonon coupling.

11:30 AM EP05.05.06
A Tale of Two Crystals—It was the Best Alignment, It was the Worst Alignment Nils E. Persson, Sebastian Engmann, Subhrangsu Mukherjee, R. J. Kline, Lee Richter and Dean M. DeLongchamp; National Institute of Standards and Technology, Gaithersburg, Maryland, United States.

Significant advancements in molecular design, crystal engineering, and device fabrication have placed solution-processed polymer transistors on a steady path toward commercialization. Central to these efforts is a growing understanding of semiconducting polymers’ process-structure-property relationships. Polymer aggregation has been proposed to play a critical role in morphological evolution during film drying and in defining long-range structural features that impact charge transport and anisotropy. Here, we report on blade coated OFETs from P(NDIO2D-T2) in toluene, an aggregating solvent. We achieved a mobility of 2 cm²/Vs with 10x anisotropy between charge transport parallel and perpendicular to the coating direction, a result on par with previous authors’ OFETs fabricated using the wire bar and brush coating methods. However, blade coating provides a more idealized processing environment amenable to in situ studies, while also serving as a model of production-scale slot die coating. Using simultaneous in situ GIWAXS and split-polarized
UV-Vis reflectance measurements, we tracked the structural evolution of P(NDI2OD-T2) in toluene during blade coating and film drying. At 5 mm/s, results from GIWAXS indicated that crystalline aggregates were present in the wet film shortly after blade passage and well before drying was complete, and furthermore, that these aggregates maintained their orientation relative to the coating direction throughout the drying process. The UV-Vis spectra did not develop strong anisotropy until the final moments of film drying, when polymer backbones aligned parallel to the coating direction. Taken together, these data suggest that aligned crystal nuclei were deposited that seeded further polymer aggregation and alignment throughout the bulk. Films cast at speeds below 0.1 mm/s displayed practically the opposite trend, with backbones aligning overall perpendicular to the coating direction and with a commensurate change in mobility anisotropy. At this process condition, a surface layer of fibrils arranged in a striking periodic wave-like pattern was observed via AFM. We supplement these results with polarized RSoXS, NEXAFS, and ellipsometry to give a near-comprehensive picture of the remarkable structural diversity in thin films of aggregated P(NDI2OD-T2).


11:45 AM EP05.05.07
Excitons and Mobile Carriers in Semiconductor Polymers and Polymer Blends Robert Street; Palo Alto Research Center, Palo Alto, California, United States.

The most obvious features in the optical absorption of semiconducting polymers are excitons, which exhibit disorder-broadened peaks with width 50-100 meV and phonon sidebands arising from electron-phonon interactions. The exciton binding energies are about 0.5 eV. Electronic devices such as solar cells and TFTs, reflect the properties of mobile carriers, either holes or electrons. Carriers in high mobility materials have a relatively small binding energy, often attributable to trapping in band tails. Excitons and mobile carriers are different species with characteristically different properties. For example, despite the fairly narrow exciton absorption bands, band structure calculations find band widths in polymers of order 1 eV. There is no contradiction, since one-electron bands are invariably larger than exciton linewidths and the two are largely unrelated. Band to band transitions are not apparent in polymer optical spectra because the exciton has a large oscillator strength by virtue its localization. A more significant difference between excitons and carriers is in their degree of localization, and one way to observe the difference is in miscible polymer blends. There are several examples where carriers are delocalized such that their wave function extends over several polymers and hence responds to an average alloy composition with an effective band edge that varies smoothly with composition. At the same time the excitons retain the character of the individual polymer because they are more highly localized on a single polymer chain, by virtue of their greater binding energy. Studies of dilute alloys give added information about the carrier delocalization. Modeling of electronic properties needs to recognize the difference. It is common to model the polymer as having narrow Gaussian bands similar in shape to the one-electron bands, and furthermore, that these aggregates maintained their orientation relative to the coating direction throughout the drying process. The UV-Vis spectra did not develop strong anisotropy until the final moments of film drying, when polymer backbones aligned parallel to the coating direction. Taken together, these data suggest that aligned crystal nuclei were deposited that seeded further polymer aggregation and alignment throughout the bulk. Films cast at speeds below 0.1 mm/s displayed practically the opposite trend, with backbones aligning overall perpendicular to the coating direction and with a commensurate change in mobility anisotropy. At this process condition, a surface layer of fibrils arranged in a striking periodic wave-like pattern was observed via AFM. We supplement these results with polarized RSoXS, NEXAFS, and ellipsometry to give a near-comprehensive picture of the remarkable structural diversity in thin films of aggregated P(NDI2OD-T2).

SESSION EP05.06: Local Structure and Electronic Properties
Session Chairs: Alessandro Troisi and Ni Zhao
Tuesday Afternoon, November 27, 2018
Hynes, Level 2, Room 208

1:30 PM *EP05.06.01
Imaging Defects and Electronic Disorder in Organic Semiconductors Daniel Frisbie; University of Minnesota, Minneapolis, Minnesota, United States.

The central thesis of this talk is that many structural defects in crystalline organic semiconductors have surface potential signatures that can be recorded and imaged by scanning Kelvin probe microscopy (SKPM) with sub-100 nm resolution. This allows straightforward visualization of defects that are difficult to detect by other methods. Additionally, we argue that surface potential fluctuations are a direct measure of static electronic disorder, namely band edge variations, that will impact electron and hole transport. Thus, surface potential imaging not only reveals defects in crystalline organic semiconductors but importantly provides a direct link to electronic disorder (e.g., traps, scattering centers) that degrades transport performance. This talk will focus on three illustrative examples based on thin films and single crystals of benchmark organic semiconductors, including one case where we can make a thorough connection between structure, surface potential, and field effect transport. We propose that in many cases the surface potential contrast associated with a given defect arises due to inhomoegeneous strain around the defect. To support this, we further describe the first direct measurements of the strain-surface potential relationship for macroscopic single crystals of rubrene. Overall, we suggest that surface potential measurements are a powerful approach to understanding correlated structural and electronic disorder in soft organic semiconductors.

2:00 PM EP05.06.02
Correlative Imaging of Nanoscale Morphology and Electronic Properties of Organic Semiconductors with Novel Analytical Scanning Electron Microscopy Rasmus Schroeder1,2, Dirk Freixas1, Jakob Wensorsra1, Wen-Shan Zhang2, Jörg Eisele1, Jochen Kammerer1, Martin Pfannmüller1 and Irene Wacker1; 1Centre for Advanced Materials, Heidelberg University, Heidelberg, Germany; 2BioQuant, Heidelberg University Hospital, Heidelberg, Germany; 3Carl Zeiss Microscopy, Oberkochen, Germany.

Analytical electron microscopy (EM) is instrumental for visualizing the nanoscale morphology e.g. of the active layer in organic solar cells [1,2]. At present, transmission EM (TEM) is used, and electron energy loss spectroscopy (EELS) and low energy loss spectroscopic imaging (low-loss ESI) can be applied to generate material contrast in the images. This provides also information about the local electronic properties of the material analyzed: As an example, [2] visualized the mixed material phase in bulk heterojunctions (BHJ) via an increased EELS signal deriving from additional excitabile electronic states in the mixed material phase. One obvious problem with TEM techniques, however, is the relatively high energy carried by the imaging electrons, which produces considerable beam damage especially for organic compounds. In addition, the projection character of the formed image leads always to the question, how the finite thickness of the sample may affect the assignment of different materials and material mixes in the projection image. To overcome the above mentioned TEM problems we have investigated a novel, advanced DELTA-SEM [3], which allows electron spectroscopy of secondary electrons (SEs). When lowering electron energies below e.g. 100 eV landing energy, beam damage seems minimized and at the same time the SE signal derives from a very thin surface layer of the sample.
In first experiments the polymer/fullerene BHJ PTB7/PC60BM was studied. At 50 eV landing energy we recorded SE spectra in analogy to ESI imaging used before. These raw spectra have been analyzed using non-linear statistical algorithms and machine learning. In contrast to [2] we this time used unsupervised machine learning, which excludes any additional personal bias. The resulting segmentations of the spectral BHJ images from both, TEM and novel Delta-SEM, were in excellent agreement with the “three phase model” proposed before.

To better understand the contrast mechanism of spectral imaging with the DELTA-SEM we performed additional experiments using a variety of organic semiconductors. Experiments with halogenated Tetraazaperopyrenes (TAPPs) show distinct differences in SE spectra for non-conductive vs. semi-conductive TAPPs. As described by theory [4,5] the shape of the SE spectra can be directly related to work-function, electron affinity, or bandgap. At present we investigate the possibilities to derive such electronic properties directly from our SE spectroscopic data.

[6] The authors acknowledge funding of the DELTA project by the German Federal Ministry of Education and Research to RRS (FKZ: 13GW0044).

2:15 PM *EP05.06.03

For high-performance semiconductor devices, good ohmic contacts between the electrode and the semiconductor layer are required to enable the maximum current density across the contact. Nominally undoped conjugated polyelectrolytes have employed as charge transport layers in organic devices. They do not have a well-defined workfunction that is sufficiently small or large, nor a sufficiently low electrical resistivity. In this talk, I will discuss the self-compensated doped polymer strategy to overcome some of these challenges. The self-compensated, deliberately charge-doped polymers (polyelectrolytes) can provide the low resistivity and extreme workfunction needed to make true ohmic injection contacts. These doped polymers are generated by a separate charge-carrier doping of conjugated polyelectrolytes and compensation by their covalently bonded counter-ion, which enables the use of strong dopants to access extreme workfunction. This strategy also stabilize film from de-doping and suppress dopant migration. We previously demonstrated solution-processed ohmic contacts using these self-compensated doped polymers for high-performance light-emitting diodes, solar cells, photodiodes and transistors, including ohmic injection of both carrier types into polyfluorene. I will further discuss the role of these counter-ion and also the spectator cations in their solution-processability, bulk and interface morphologies in workfunction manipulation. Yet another similar general strategy is using charge-doped polyelectrolyte monolayer assembly to achieve ohmic contact to semiconductor for field-effect transistors. An undoped polyelectrolyte monolayer is self-assembled and self-aligned to the electrode, sacrificial dopant ions are inserted into this layer, which then dopes the organic semiconductor at the contact. When this occurs, the doped interface is counterbalanced by the undoped conjugated polyelectrolyte monolayer. Polyelectrolyte counter-ion monolayer cannot diffuse, so delta-doping is stabilized at the contact. This delta-doped layer has a well-defined work function at the semiconductor side of contact and sufficiently low tunnel resistance for direct metal injection into semiconductor, overcoming a critical challenges of using undoped polyelectrolytes.


2:45 PM EP05.06.04
Metallic-Type Transport in Polymers—Towards Establishing Structure/Property Interrelationships [2] Hongmo Li1, Andre Zeumault2, David Valverde2, Stephen Barlow2, Yadong Zhang3, Seth R. Marder2, Carlos Silva2 and Natalie Stingelin1; 1School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, Georgia, United States; 2School of Chemistry & Biochemistry, Georgia Institute of Technology, Atlanta, Georgia, United States.

Current organic electronics research aims at exploiting the unique property matrix of “plastic” semiconductors, including their chemical tunability, straightforward processability and mechanical flexibility, to create new applications. While much knowledge has been developed in the synthesis of semiconductor conjugated organic materials, there is still an immense need for establishing broadly applicable design guidelines towards highly conductive macromolecular matter [1,2]. Moreover, the multitude of possibilities for “plastic” semiconductors and dopants to assemble together over different length scales creates a daunting task to establish comprehensive and relevant correlations between structure, processing and properties. We will present here a multidisciplinary approach towards a framework to predict such structure/property interrelations. We will focus on polythiophene derivatives as model systems, including poly[(3-hexylthiophene-2,5-diyi)] (P3HT) and poly[(2,5-bis(3-tetradecylthiophen-2-yl)thieno[3,2-b][1]thiophene)] (PBTBT), [3] and discuss how the spatial arrangement, manipulated through intercalation and co-crystal formation with dopants, affects charge transport. We will conclude with providing a tentative picture of the complex correlation of structure and electronic landscape for the understanding of conducting “plastics” of metallic-type transport.


3:00 PM BREAK
We review the recent process made to develop quantitative models to predict the intrinsic mobility of molecular semiconductors, leading to the recently proposed "map of molecular semiconductors" [Nature Materials, 16, 998, (2017)]. We then discuss the two main avenues for computer aided materials discovery namely (i) the definition of benchmark accurately-resolved chemical systems and (ii) a rapid method to screen hundreds/thousands of compounds (real or hypothetical). A general approach to converge toward a common accepted theoretical model for charge transport in this class of materials is proposed.

4:00 PM EP05.07.02
Impact of Chain Conformation on the Density of States and Charge Transport in Conjugated Polymers Xinruiuan Shi1; Vojtech Nadazdy2, Aleksandr Perevedentsev1, Jarvist Frost1, Xuhua Wang1, Elizabeth von Hauff1, Roderick MacKenzie2 and Jenny Nelson1; 1Department of Physics, Imperial College London, London, United Kingdom; 2Institute of Physics, Slovak Academy of Sciences, Bratislava, Slovakia; 3Department of Materials, ETH Zürich, Zürich, Switzerland; 4Department of Physics and Astronomy, Vrije Universiteit Amsterdam, Amsterdam, Netherlands; 1Faculty of Engineering, University of Nottingham, Nottingham, United Kingdom.

Charge transport in organic semiconductors is characterised by a strong degree of disorder in both the site energy and the electronic coupling between adjacent sites. This disorder arises from variations in the chemical structure and conformation of molecular units, as well as in the weak binding interactions between them. Structural disorder due to molecular conformational freedom is expected to affect the density of states distribution, and hence the optoelectronic properties of the material. However, until now there has been little experimental evidence of the direct relationship between particular conformational defects and observed transport properties.

To this end, we address the chain conformation – hole transport relationship in two model systems. In the case of poly(9,9-diocylfluorene) (PFO), we investigate the impact of introducing a planarised conformer, known as the ‘β-phase’ [1], on vertical-mode hole transport through otherwise glassy PFO layers using a combination of time-resolved, frequency-resolved, and steady-state transport measurements. We demonstrate that β-phase introduces a remarkable ~hundredfold drop in time-of-flight hole mobility ($\mu_h$) at room temperature, while it reduces $\mu_h$ measured from hole-only devices by a factor of less than 5. We also show how the use of high-dynamic-range photocurrent spectroscopy and energy-resolved electrochemical impedance spectroscopy [2] maps out a consistent picture of trap states due to the β-phase content, namely, a sharp sub-gap feature lying ~0.3 eV above the highest occupied molecular orbital of glassy PFO. Using a drift-diffusion model capable of resolving carriers in both time and energy [3], we show how the apparently contradictory transport phenomena obtained via different probes are explained by a single model with the experimentally derived density of states.

We extend our study to a high-mobility indacenodithiophene-based copolymer (IDT–BT) [4] where—in contrast to PFO—the chains favour a planar geometry in the ground state and therefore conformational heterogeneities are less likely to act as traps. We use our results on the two polymer types to consider the limits to charge-carrier mobility through disordered polymeric semiconductors, and design criteria for higher performance materials.


4:15 PM EP05.07.03
Versatile Molecules for Organic Electronics and Photonics John Anthony1, Chad Risko1, Oana D. Jurchescu2, Anthony J. Petty, III1, Alex Ai1 and Hamna Haneef2; 1University of Kentucky, Lexington, Kentucky, United States; 2Wake Forest University, Winston-Salem, North Carolina, United States.

Through combined efforts in theory and synthesis, we have developed ever more detailed understanding of the behavior of organic semiconductors in the solid state. From this knowledge, we have developed modified systems to enhance performance in both electronic and photonic applications. For charge transport, we are addressing issues related to vibrational modes (phonons) that can disrupt electronic coupling in two different ways - by substantially rigidifying the portion of the molecule that attaches solubilizing groups to the core, or by making the core itself more flexible, to better damp these vibrational modes. One of these approaches has already yielded new materials with impressive hole transport properties in transistors. On the photonic front, we have expanded the scope of molecules used in fast singlet fission, improving photostability and allowing attachment of functional groups to better interface with triplet-harvesting materials.

4:30 PM *EP05.07.04
Plastic Semiconductors—How We Can Exploit Blending to Manipulate Functions? Natalie Stingelin; Georgia Institute of Technology, Atlanta, Georgia, United States.

Artifacts made of polymers – “plastics” – are ubiquitous in our daily live, and polymers such as polyethylene, polypropylene or poly(ethylene terephthalate) have developed into multi-billion markets since their discovery some 80 years ago. Surprisingly, however, various, important aspects of these versatile materials are not understood, especially when used in blends. Processing them into useful products, especially of specific and/or multiple functions, is thus often directed by time-consuming, intricate trial-and-error approaches. The complexity result from the difficulty to characterize polymeric systems: they are of high molecular weight; they lack usually heavy atoms leading to low contrast between components; the feature a low stability, e.g. in electron beams, etc. Here we discuss pathways to gain understanding of the role of multiscale structure and phase behavior in determining the final properties and functions of multicomponent polymer blends, including ion and electron/hole transport (i.e. mixed conduction. Starting with systems where reliable processing pathways towards specific features have been advanced, we discuss strategies towards a unifying structure/property picture for multifunctional architectures made of ‘plastics’ that can lead to a knowledge platform towards widely-applicable design rules for smart, plastic artefacts. We use as examples of discoveries in the last decade that addition of large fractions of an insulating bulk ‘plastics’ such as high-density polyethylene does not negatively affect charge transport of electrons or holes and that addition of the commodity polymer poly(ethylene oxide) allows manipulation of the overall aggregate character of the ubiquitous polymeric semiconductor poly(3-hexylthiophene). Similar observations have been made with higher efficiency plastics, such as poly[(5,6-difluoro-2,1,3-benzothiadiazol-4,7-diyl)-alt-(3,3’’’-di(2-octyldodecyl)-2,2’,5’,2’’,5’’’-quaterthiophen-5,5’’’-diyl)] (PCE11). We will show that combining classical polymer science tools with well-established and recently developed, characterization techniques can be used to identify design- and processing criteria for functional polymer blends towards specific functions by unveiling the relevant structural features on all length scales that make specific blends work and give some materials discovery and will permit to start with the creation of a materials database for macromolecular blends.
Unsymmetric Squaraine for Narrow Band Green-Selective Organic Photodiodes

The near-infrared emission and absorption properties of semiconducting donor-acceptor polymers and single-walled carbon nanotubes are highly sensitive to the presence of charge carriers that may be induced electrochemically or by a field-effect. New states, here polaron or trions, with unique optical properties are formed and can be tuned, investigated and even utilized in a range of optoelectronics devices such as electrochromic cells, light-emitting transistors and diodes. Furthermore, the hybridization of light and matter in optical microcavities integrated in these devices and thus the formation of polaritons with low mass enables a new approach towards the manipulation of absorption and emission of carbon-based and solution-processed semiconductors. The controlled electrochemical generation of charged trion-polaritons with low effective mass in purified, monochiral single-walled carbon nanotubes may even lead to cavity-enhanced charge transport. Here, we will discuss several examples of (cavity-integrated) devices that rely on polarons, trions or polaritons.

Organic Polariton Photodiodes with an Extended Responsivity

Exciton-polaritons are hybrid light-matter quasiparticles which are formed when molecules are placed within an optical cavity such that their electronic transition can interact strongly with the vacuum electromagnetic (EM) field. In this regime of interaction, the rate of energy transfer between Frenkel molecular excitons and EM modes is faster than their individual uncoupled decay rates. The polariton dispersion relation is separated into upper (UP) and lower (LP) branches with resonance energies that lie on opposite sides of the bare exciton energy. Over the last decade, polaritons have attracted great interest due to their remarkable light-matter properties and have been exploited for novel device applications such as low-power polariton lasers, polariton optical circuits, quantum devices.

In principle, the efficiency and spectral response of an organic photodiode (OPD) is limited by the photophysical and optoelectronic properties of the active layers. In particular, it has been extremely challenging to develop active layers (typically the donor) which absorb light efficiently at near infrared and infrared wavelengths. Therefore, an attractive novel approach to push the donor absorption to the infrared without requiring the synthesis of new materials is to strongly couple the excitons with vacuum EM field. Especially, in the ultra-strong coupling (USC) regime, the LP absorption can be red-shifted by a significant fraction of the bare exciton energy while still maintaining a large exciton content.

In this work, we demonstrate for the first time polariton OPDs operating in the USC regime. This is achieved in a standard OPD structure consisting of a mixed donor-acceptor heterojunction with Silver (Ag) electrodes that also act as mirrors to form the optical cavity. We study two types of polaritonic OPDs using donor materials that have previously been widely used for organic photovoltaics. A visible absorber, copper (II) phthalocyanine (CuPc), and a near infrared absorber, tin (II) phthalocyanine (SnPc). These devices show narrow responsivity with a very weak angle-dependence. More importantly, they can be tuned to operate in a spectral range outside that of the bare exciton absorption. Remarkably, we show that the responsivity of a polariton OPD can be pushed to near infrared wavelengths, where few organic absorbers are available, with external quantum efficiencies exceeding those of a control OPD. In the presentation, I will also discuss possible polariton modifications to the molecular photophysics beyond the absorption spectrum, e.g. in charge separation and diffusion.

References
Light emitting electrochemical cells (LEECEs) from ionic transition metal complexes (tMCs) offer the potential for high efficiency electroluminescence in a simple, single layer device. However, LEECs typically rely on the use of rare metal complexes. This has limited their cost effectiveness and put constraints on their applicability. With a view to leveraging the efficient emission of these complexes while mitigating costs, we describe here a host/guest LEEC strategy that relies on the use of carbazole-based small molecule organic host molecules and tMC guests. Three positively-charged host molecules were prepared via the coupling of 4-bromophenylbenzimidazole (PBI) with a carbazole (Cz). This has allowed a comparison between hosts bearing methoxy (PBI-CzOMe) and tert-butyl (PBI-CzBu) substituents, as well as an unsubstituted analogue (PBI-CzH). Cyclic voltammetry and UV-visible absorption revealed that all three host materials have large bandgaps characterized by reversible oxidation and irreversible reduction events. Based on electronic structure calculations the host HOMO resides primarily on the carbazole moiety while the LUMO is located primarily on the phenyl-benzimidazolium unit. Photoluminescence analysis of thin film blends of PBI-CzH with tMC guests confirmed that the emission was blue-shifted relative to pristine tMC films, consistent with what was seen in dilute dichloromethane solution. LEEC devices were prepared based on thin films of the pristine hosts, pristine guests, and 90%/10% (w/w) host/guest blends. Among these host/guest blends, LEEC’s based on PBI-CzH displayed the best performance, particularly when an iridium complex was used as the guest. The system in question yielded a luminescence maximum of 624 cd/m² at an external quantum efficiency of 3.80%. This result stands in contrast to what is seen with typical OLED host studies, where tert-butyl substitution of the host generally leads to better performance. To rationalize the present observations, the host materials were subject to single crystal X-ray diffraction analysis. The resulting structures revealed clear head-to-tail interactions in the case of both PBI-CzH and PBI-CzOMe. No such interactions were evident in the case of PBI-CzBu. Furthermore, PBI-CzH showed a relatively smaller spacing between the successive HOMO and successive LUMO levels relative to PBI-CzOMe and PBI-CzBu, a finding consistent with more favorable charge transport and energy transfer. The results presented here can help inform the design and preparation of host materials suitable for use in single layer tMC LEECs.

9:15 AM EP05.08.05
Nano-Alignment in Semiconducting Polymer Films—A Path to Achieve High Current Density and Brightness in Organic Light Emitting Transistors Mojeeb U. Chaudhry1 and Ebinazar Namdas2; 1Department of Engineering, Durham University, Durham, United Kingdom; 2School of Mathematics and Physics, University of Queensland, Brisbane, Queensland, Australia.

The charge carrier mobility in Organic light emitting field effect transistors (OLETs) is a limiting factor in realising high current densities along with a trade-off between brightness and efficiency. In this work we, present a highly ordered semiconducting polymer films by controlling the nanoscale morphology through nanoscale grooved substrates and dip coating deposition. The OLET device fabricate using these ordered films results in high current densities in OLETs. The heterostructure OLETs demonstrate high brightness, exceeding 29,000 cd m⁻² at an EQE of 0.4% for a yellow emitter and 9,600 cd m⁻² at EQE of 0.7% for a blue emitter. These devices outperform the best OLETs reported in literature. These results represent a significant advancement in organic optoelectronics and are an important milestone towards realisation of new applications in displays and electrically pumped lasing.

9:30 AM EP05.08.06
The Role of Higher Order Effects in Rubrene:C60 OLEDs Lee Richter1, Sebastian Engmann1, Adam Barito2, Emily G. Bittle1, Noel C. Giebink2 and David Gundlach1; 1National Institute of Standards and Technology, Gaithersburg, Maryland, United States; 2Department of Electrical Engineering, The Pennsylvania State University, University Park, Pennsylvania, United States.

Singlet-fission (SF) and triplet-triplet-annihilation (TTA) in organic materials at room temperature have recently gained much interest. The increasing focus on SF is due to the promise of increased current density for organic photovoltaics and quantum yields approaching 100% in detector applications, while the interest in TTA is in the promise of organic light emitting diodes (OLEDs) with emission yields beyond the 25% singlet limit and low turn-on voltages. Recent studies have focused on rubrene as possible singlet fission and triplet-triplet annihilation material and devices based on rubrene/C60 bilayers with a luminescence threshold of approximately half the bandgap of rubrene have been reported. Two mechanisms have been proposed as the origin of the early turn-on: (i) Auger assisted energy up-conversion, and (ii) triplet-triplet annihilation at the heterojunction interface. In both cases, the charge dynamics at the heterojunction interface are crucial to the mechanism, yet detailed investigations on these higher order processes are missing. Herein, we systematically alter the rubrene/C60 interface in OLED devices, resulting in either greatly suppressed or enhanced formation of the CT-state and recombination rate. We find that suppressing the CT-formation yields a 3-fold increase in device luminance compared to the prototypical rubrene/C60 device, while maintaining a low turn-on voltage. The increased luminance of devices with a BCP interlayer suggests a reduction in parasitic effects of the CT-state. Quantitative analysis of the modified interface devices suggest that Auger assisted up-conversion and TTA can be ruled out as the origin of the sub-bandgap turn-on. Rather, band-to-band recombination remains the most likely radiative recombination process.

9:45 AM EP05.08.07
Photoluminescence Quantum Yield Simulation Method for Phosphorescent OLED Emitter Materials Inkoo Kim, Won-Joon Son and Youn-Suk Choi; Samsung Electronics, Suwon, Korea (the Republic of).

High-performance organic light-emitting diode (OLED) devices incorporating phosphorescent emitter materials are undoubtedly one of the most promising candidates for next-generation flat panel and mobile displays, because not only of their superior picture quality showing high contrast ratios and wide color gamut, but also of their efficient power consumption. Cyclometallated complexes as phosphorescent dopants disposed within the emissive layer can effectively harvest both singlet and triplet electrodegenerated excitons, leading to internal quantum efficiencies close to 100%. Among many required properties for high performance, photoluminescence quantum yield (PLQY) and radiative lifetime of emitters are the two key photophysical properties of phosphorescent emitters for securing durability and efficiency of the OLED device. The former has been notoriously difficult to simulate computationally as the underlying non-radiative triplet-singlet transition is spin-forbidden and demands the interplay of spin-orbit and non-adiabatic coupling.

In this work, we report a novel formulation for quantitative predictions of PLQY of phosphorescent OLED emitter materials. The present method based on purely first-principle theoretical ground for reliable predictions, incorporating the relativistic and the non-Born-Oppenheimer effects on the same level of generalization in the framework of Fermi’s golden rule using correlation function approach. The accuracy of the present method is assessed and verified by comparing the computed results with the experimental results of various cyclometallated complexes in red-to-green spectral range, respectively, and is substantiated its applicability for the blue-emitters. The results of this work demonstrates that quantitative PLQY predictions of phosphorescent emitters over the entire color range can be delivered solely from quantum chemical calculations, providing additional means of narrowing down the optimal emitters in an a priori fashion in the on-going development of novel phosphorescent emitters for a future OLED device.

10:00 AM BREAK
Photon energy upconversion is a potentially viable strategy for increasing the power conversion efficiency of conventional single junction solar cells. Recently hybrid devices involving colloidal semiconductor quantum dots coupled to molecular chromophores have shown remarkably high upconversion efficiencies, the basic mechanism involves light absorption by the dot, followed by triplet energy transfer to the chromophore with a final step of triplet-triplet annihilation to generate a single, high-energy output photon. Here, we present a holistic approach to simulating the key step of triplet energy transfer. We begin by developing a kinetic model for understanding the transient PL spectra of the devices, which allows us to isolate the triplet transfer rate directly from experimental measurements. Second, we examine the electronic states that participate in the triplet energy transfer step, paying particular attention to surface trap states that likely modulate energy transfer. Finally, we study the dependence of the rate on the ligand shell, showing that unexpected restructuring of the ligand sphere dramatically influences the transfer rate.

11:00 AM EP05.09.02
New Frontiers for Triplet Fusion Upconversion Dan Congreve1, Andrew Pun2 and Luis Campos2; 1Rowland Institute at Harvard, Cambridge, Massachusetts, United States; 2Columbia University, New York, New York, United States.

Upconversion, the process of generating one high energy photon from two low energy ones, holds huge potential across a wide variety of applications. One rapidly emerging process to achieve upconversion is triplet fusion upconversion. This process requires two materials: a sensitizer that absorbs low energy light and transfers it to the triplet state, and an annihilator which can convert two triplets into one high energy singlet, which can then fluoresce. Recent materials efforts has led to rapid improvements in efficiency and spectral range, with infrared-to-visible upconversion reaching as far into the infrared as 1000 nm. These strong materials improvements have now opened up a wide range of applications in which this unique process can be applied.

In this talk, I will demonstrate these material improvements and the new fields we can apply them to. First, we utilize a new series of annihilators to precisely tune the upconverted emission to the wavelength needed for a particular application. By pairing these annihilators with photocatalysts, we can perform photochemistry using only NIR light, where visible or blue light would traditionally be required, opening up new avenues for scale-up and drug delivery. Finally, we show that by precisely engineering a nano-capsule carrier, we can build these materials into a bio-compatible platform, allowing for new discoveries in optogenetics and bio-imaging that are not hampered by the limited light penetration and high power densities of traditional measurement techniques.

11:15 AM EP05.09.03
Long-Lived Triplet Excitons and Radical Ion Pairs in Organic Semiconducting Host–Guest Systems Kyota Kabu1, 2, Naoto Notsuka1, 2, Kenichi Goushi1, 2 and Chihaya Adachi1, 2, 3; 1JST-ERATO ADACHI Molecular Exciton Engineering Project, Fukuoka, Japan; 2OPERA, Kyushu University, Fukuoka, Japan; 3International Institute for Carbon-Neutral Energy Research, Fukuoka, Japan.

Long persistent phosphors are widely commercialized as glow-in-the-dark paints for watches, indicators, emergency lights, and afterglow safety lamps and are being explored for use in in vivo bioimaging since the emission can be observed long after excitation. Some organic aromatics are known to show long-lived emission called phosphorescence originating from a spin-forbidden transition from the triplet excited state to the single ground state at low temperatures. However, long-lived triplet excitons on organic molecules easily deactivate at room temperature because of the presence of thermally activated nonradiative pathways. We demonstrate long-lived phosphorescence, under both optical and electrical excitation, at room temperature resulting from suppression of the nonradiative deactivation of triplet excitons in conventional organic semiconducting host–guest systems. The nonradiative deactivation pathway strongly depends on the triplet energy gap between the guest emitting molecules and the host matrices, and we show that the triplet energy gap required to effectively confine the long-lived triplet excitons (ΔE ≈ 0.5 eV) is much larger than that of conventional host–guest systems for phosphorescent emitters (N. Notsuka et al. Adv. Funct. Mater. 27, 1703902 (2017)). A host–guest system can also produce long-lived emission through sufficient stabilization of the radical ion pair generated between an electron donating molecule and electron accepting molecule. A blend of the strong electron-donating molecule N,N,N',N'-tetramethylbenzidine (TMB), which has a very stable radical cation, and the strong electron-accepting molecule 2,8-bis(diphenylphosphoryl)dibenzo[b,d]thiophene (PPT), which has a high triplet energy and provides a rigid amorphous environment to help suppress nonradiative deactivation, forms excited-state charge-transfer (CT) complexes (exciplexes) upon weak photo-irradiation. Some of the exciplexes separate into radical ion pairs, and the generated radical cation localizes on TMB while the radical anion diffuses through the PBPO host and is stored for long periods. Gradual charge recombination of radical ion pairs in this system produces continuous emission over 1 h at room temperature. This organic long persistent luminescence (OLPL) system is transparent and soluble, and potentially flexible and color tunable, which will open new applications for LPL in large-area and flexible paints, biomarkers, fabrics, and windows (K. Kabe et al. Nature 550, 384–387 (2017)).

11:30 AM EP05.09.04
Flapping Molecule as a Key Structure for Light-Melt Adhesive and Ratiometric Force Probe Shohei Saito; Kyoto University, Kyoto, Japan.

Flapping molecules (FLAP) bearing a fused 8-membered ring at the center have been recently recognized as an emerging class of photoresponsive systems. The FLAP molecules were reported as key structures that show a V-shaped-to-planar conformational change in the lowest singlet excited state (S1), emitting fluorescence with large Stokes shifts. Along this line, we have demonstrated the utilities of FLAP as photofunctional materials such as photoreresponsive liquid crystals, light-melt adhesive, molecular viscosity probes, singlet fission chromophores, and conformationally flexible emitting fluorescence with large Stokes shifts. Along with this line, we have demonstrated the utilities of FLAP as photofunctional materials such as photoresponsive liquid crystals, light-melt adhesive, molecular viscosity probes, singlet fission chromophores, and conformationally flexible emitting fluorescence with large Stokes shifts. Along with this line, we have demonstrated the utilities of FLAP as photofunctional materials such as photoresponsive liquid crystals, light-melt adhesive, molecular viscosity probes, singlet fission chromophores, and conformationally flexible emitting fluorescence with large Stokes shifts. Along with this line, we have demonstrated the utilities of FLAP as photofunctional materials such as photoresponsive liquid crystals, light-melt adhesive, molecular viscosity probes, singlet fission chromophores, and conformationally flexible emitting fluorescence with large Stokes shifts.
A thin film of donor polymer is transferred onto an acceptor thin film. Before the film transfer, ultraviolet photoemission spectroscopy and low-energy inverse photoemission spectroscopy were conducted to obtain the electronic structures of the surface of each film, which gave the information on the electronic structures of the donor/acceptor interface after making the contact. This allows us to investigate the electronic structures near the D/A interface and the way the films are transferred. The results clearly showed that the charge generation becomes more field-dependent as the energetic offsets of the donor and the acceptor decrease. This indicates that the energetic offsets have a large influence on the charge generation efficiency, which appears to oppose to the concept claimed in the recent reports that the charge generation happens through thermalized “cold” charge transfer states. The detailed analysis of this controversial observation will be given in the presentation. In addition, we found the same effects of the energetic structures for non-fullerene acceptors as for the fullerene derivatives except strong light absorption in visible range. Therefore, we concluded that the non-fullerene acceptors are not special in term of the energetic driving force for the charge generation.

2:15 PM EP05.10.03
Thermodynamics of Charge Separation in Organic Solar Cells Samantha Hood1, Adam Gluchowski2, Katherine Gray2 and Ivan Kassal3; 1Imperial College London, Kensington, United Kingdom; 2The University of Queensland, St Lucia, Queensland, Australia; 3The University of Sydney, Sydney, New South Wales, Australia.
Organic solar cells are promising candidates as a renewable energy source due to the possibility of cheap, lightweight and flexible devices. However, due to their disordered structure, charge behaviour in these devices is not well understood, making it difficult to systematically improve device performance. In particular, a vigorous debate surrounds how the positive and negative electric charges overcome their mutual attraction to form an electric current. While charge separation can occur with near-unity efficiency and on a sub-picosecond timescale, the full details of this process remain unclear. In typical models, the Coulomb binding between the electron and the hole can exceed the thermal energy $k_B T$ by an order of magnitude, making it impossible for the charges to separate before recombining [1, 2].

Here, we consider the entropic contribution to charge separation in the presence of disorder and find that even modest amounts of disorder have a decisive effect, reducing the charge-separation barrier to about $k_B T$ or eliminating it altogether [3]. Therefore, the charges are usually not thermodynamically bound at all and could separate spontaneously if the kinetics otherwise allowed it.

We also investigate the role of charge delocalisation on lowering the Coulomb attraction between charges. Delocalisation has been typically thought to lower the barrier to charge separation by effectively allowing the charges to be further apart. We show that this is not the case: including more than a small amount of delocalisation results in an increase in the barrier to charge separation [4]. This means that if delocalisation were to improve charge separation efficiencies, it would have to do so via non-equilibrium kinetic effects that are not captured by a thermodynamic treatment of the barrier height.

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2:30 PM BREAK

3:30 PM *EP05.10.04
Determining the Driving Force for Photo-Induced Electron Transfer in Sensitized Organic Materials Garry Rumbles1,2,3, 1National Renewable Energy Laboratory, Lakewood, Colorado, United States; 2Chemistry and Biochemistry, University of Colorado Boulder, Boulder, Colorado, United States; 3Renewable and Sustainable Energy Institute, University of Colorado Boulder, Boulder, Colorado, United States.

This presentation will discuss charge carrier generation and recombination in conjugated polymer and molecular thin films that have been sensitized using molecular electron acceptors at low concentration. Carrier generation is detected using time-resolved microwave conductivity and transient absorption spectroscopy.

A number of fullerene and macrocycle electron acceptors will be discussed, where the driving force for photo-induced electron transfer is controlled primarily by the reduction potential of the acceptors species, and is calculated using the Rehm-Weller equation. The importance the solid-state microstructure of the polymer in controlling the yield and lifetime of the long-lived carriers will be examined, when the primary excitation is an excited singlet-state located on the acceptor. In addition, charge carrier generation in pentacene will be examined, where the triplet excitations are produced from singlet-fission, and a series of electron acceptors capable of dissociating these low energy species is explored.

4:00 PM EP05.10.05
Direct 3D Imaging of the Bulk Heterojunction Microstructure in Organic Solar Cell Artem Levitsky and Gitti L. Frey; Technion–Israel Institute of Technology, Haifa, Israel.

In the realm of functional materials, properties correlate with internal microstructure. This is true for iron alloys, for example, where the carbon-iron phase diagram determines the abundance of different phases, but their size and distribution, determines the steel’s strength. Similarly, performances of organic electronic devices should correlate with film morphology, i.e. film microstructure. However, identifying the types of phases, domain size, composition and distribution is experimentally because all components are organic and often amorphous. Hence, until now, organic electronic film morphologies were speculated based on indirect and non-comprehensive measurements. Here we show a new approach for directly imaging the microstructure of organic electronic films. This is achieved by selective diffusion and retention of organometallic molecules into different phases. We demonstrate this methodology for correlating the performance of high efficiency organic solar cells with their microstructure. The diffusing molecules are Atomic Layer Deposition (ALD) precursors and their diffusion and in-situ conversion to the respective metal oxide depends on free volume in each domain. Under such conditions, presence of metal oxide particles, easily identified by electron microscopy techniques, effectively maps selected domains in the film. Using this technique, we are able to fully map the BHJ microstructure, i.e. size and distribution of the different phase domains composing the BHJ. We find that the microstructure depends on blend composition and processing technique. Finally, the visual imaging of the BHJ allows us to directly correlate the microstructure with device performance shoowing that the obtained microstructure determines solar cells performance.

4:15 PM EP05.10.06
Relationship Between Charge-Transfer State Properties and Non-Radiative Voltage Losses in Organic Bulk-Heterojunction Solar Cells Flurin D. Eisner, Mohammed Azzouzi, Zuoping Fei, Martin Heeney and Jenny Nelson; Imperial College London, London, United Kingdom.

The primary pathway to efficiency losses in bulk-heterojunction organic solar cells (BHJ-OSCs) is believed to be the non-radiative decay of a charge-transfer (CT) state to the ground state via energy transfer to vibrational modes. It has been suggested that the open circuit voltage in OSCs is largely determined by the energy of the donor-acceptor CT state[1], and thus many recent studies have focussed on increasing the energy of CT states by minimizing the energy offset between the donor and acceptor. This relationship can be rationalized by the understanding that a higher overlap of the vibrational modes of the CT and ground states increases the rate of non-radiative recombination. However, some recent studies have found that increasing the CT state energy does not always result in a reduction in the non-radiative voltage losses [2], which suggests that other properties of the CT state to ground state transition affect the trend.

Here, we systematically investigate the relationship between CT state properties and voltage losses in BHJ-OSCs by using a series of increasingly fluorinated PBDB-T donors, in conjunction with a variety of different fullerene and non-fullerene acceptors. Firstly, we show that by depressing both the HOMO and LUMO through fluorination of the donor, the energy of the donor-acceptor CT state can be effectively moved closer to the first excited state. Secondly, by performing a detailed voltage loss analysis of the various blends we find that the non-radiative voltage losses do not reduce systematically...
These photophysical studies provide the fundamental understanding of how different electron acceptor materials can impact the charge generation strategies for s-SWCNT-based optoelectronic applications. The detailed photodynamics of the heterojunctions between (6,5) s-SWCNTs and four different perylene diimide (PDI) based electron acceptors. PDI-based electron acceptors have been distinguished as a potential alternative of fullerene-based acceptors by their superior characteristics such as broader absorption, greater spectral tunability, cheaper cost, and higher robustness. The physics of organic semiconductors is often controlled by large electron-hole Coulomb interactions and by large spin exchange energies. I will discuss recent strategies that allow these interactions to be harnessed for efficient device operation. For LEDs, 3:1 statistical formation of triplet:singlet excitons through electron-hole recombination limits efficiency if the triplet state is non-emissive, but is recovered for systems with reduced exchange energy and strong spin-orbit coupling in organo-metallic systems or for system where triplet-triplet collisions produce singlet excitons efficiently. For organic PV systems, long-range charge separation from the donor-acceptor heterojunction must overcome a substantial Coulomb barrier, which we find always sets up a measurable optical Stark shift that we measure to be 200 meV or more. Whether this separation is ultrafast (sub-picosecond) or slow (>10 psec) depends on the ‘excess’ energy provided by the photogenerated exciton to the separating electron-hole pair, both for fullerene acceptor systems and those with non-fullerene acceptors. Long-time binuclear recombination should show similar spin statistics to LED operation, causing significant non-radiative recombination for triplet formation where there is easy access to a low-lying localized triplet states. I will present evidence that though fullerene systems...
generally show rapid bimolecular triplet formation, this can process can be very strongly reduced in some non-fullerene acceptor systems.

8:30 AM EP05.11.02
The Impact of Driving Force on Recombination Dynamics in Nonfullerene Organic Solar Cells Yifan Dong1, Hyojung Cha1, Jiangbin Zhang2, Ernest Pastor1, Pabitra Shakya Tuladhar1, Iain Muckleloch1,3, James R. Durrant1 and Artem Bakulin1; 1Imperial College London, London, United Kingdom; 2University of Cambridge, Cambridge, United Kingdom; 3King Abdullah University of Science and Technology, Thuwal, Saudi Arabia.

Nonfullerene organic solar cells have demonstrated superior performance compared to the ones with fullerene acceptors. Despite the major world-wide effort in device development and spectroscopic studies, the specific photophysics of nonfullerene acceptor-based materials (NFAs) remains unclear, and it is still not fully understood what controls charge separation and recombination processes.

Here, we compare charge carrier dynamics in polymer:acceptor systems using NFA IDTBR and fullerene PC71BM. Transient absorption spectroscopy shows that when blending with PBDBT4T-2OD, IDTBR based blend exhibits enhanced geminate recombination compared to PCBM-based blend. This limits the charge generation and hence the short circuit current in devices.

We also employ pump push photocurrent spectroscopy from 300 K to 77 K to further elucidate the cause of efficiency loss. These measurements reveal presence of bound charge transfer states and long-lived trapped carriers as well as allow the estimation their respective binding energies.

8:45 AM EP05.11.03
Non-Geminate Recombination Limits Fill Factor in Polymer:ITIC Bulk Heterojunction Solar Cells Jafar I. Khan1, Yuliar Firdaus2, Pierre M. Beauinte and Frédéric Laquai; King Abdullah University of Science and Technology, Jeddah, Saudi Arabia.

Nonfullerene acceptors have emerged as promising fullerene replacements in organic photovoltaics and recently power conversion efficiencies have surpassed 14%. Despite the rapid progress, fundamental understanding of the photo-physical processes is still lacking and identifying the loss mechanisms in devices is important for future material design and device optimization. Here, we investigate the impact of polymer side chain substitution in BDT-thiophene copolymers on the performance of three bulk heterojunction solar cells that use ITIC as nonfullerene acceptor: PBDBT2HT:ITIC (2.5%), PBDBT2HT:ITIC (4.2%) and PBDBT2FT:ITIC (9.8%). All blends absorb across a wide spectral region due to the complementarity of the donor polymer and ITIC acceptor absorption spectra. Transient spectroscopy has been used to monitor excitation generation, diffusion, and dissociation as well as charge carrier recombination in all three systems. We observe significantly more geminate recombination in the alkoxy-substituted PBDBT2HT:ITIC blend in addition to nongeminate recombination of free charges, limiting both the short circuit current and fill factor. The alkylthiophene-substituted PBDBT2HT:ITIC blend exhibits less geminate recombination but significant nongeminate recombination, limiting the fill factor to about 40%, while backbone fluorination in PBDBT2FT:ITIC leads to fast and efficient charge separation and significantly reduced non-geminate recombination, resulting in fill factors in excess of 60%. Time-delayed collection field measurements showed that charge generation in PBDBT2FT:ITIC is field-independent, while a weak field dependence is observed for the other two systems. Our findings provide important structure-property relations and design rules for new nonfullerene materials.


9:00 AM EP05.11.04
Charge Generation and Recombination in Dilute Organic Solar Cells Anna Jungbluth1, Gareth Moore2, Alberto Privitera1, Ivan Ramirez1, Josue F. Martinez Hardigree2, Natalie Banerji1 and Moritz Riede1; 1University of Oxford, Oxford, United Kingdom; 2University of Bern, Bern, Switzerland.

Organic solar cells have attracted interest over the last decades as low-cost, light-weight and scalable alternatives to silicon solar cells. The tunability of optoelectronic properties of organic materials provide clear advantages and considerable work is being done to develop new and better donor and acceptor materials. For years it was thought that high amounts of donor molecules were needed for efficient charge separation in the bulk heterojunction.

Surprisingly, this has been proven wrong in recent years. Efficiencies >5% have been demonstrated for fullerene systems with donor concentrations of less than 10%. The working principles of these dilute solar cells are not yet well understood. Since dilute solar cells are an excellent model system for more complicated systems, understanding the underlying photophysical processes of dilute solar cells is key for advancing our knowledge of the working principles of organic solar cells in general.

In this work we investigate charge generation and recombination processes in low donor concentration organic solar cells as a function of donor percent and microstructure. We use vacuum deposition techniques to fabricate thin films and full devices with 5 mol.%, 10 mol.% and 50 mol.% donor concentration. The effect of microstructure is investigated by comparing mixed film heterojunctions formed with C60 as electron acceptor, paired with either α-Sexithiophene or 1,1-bis-(4-bis(4-methyl-phenyl)-amino-phenyl)-cyclohexane (TAPC) as electron donor materials, which individually grow in crystalline and amorphous layers respectively.

Electron paramagnetic resonance (EPR) measurements are performed to determine the charge species generated in the active layer upon illumination. In the case of the α-Sexithiophene:C60 system with low donor concentration, EPR measurements reveal the presence of triplet states on C60 and α-Sexithiophene molecules as well as free charges generated at the interface. While free charges and α-Sexithiophene triplets remain present in the high donor concentration system, the C60 triplets are quenched. We will evaluate the effect of the quenched C60 triplet by correlating the information gained through EPR with a photophysical characterization of full devices obtained through current-voltage and external quantum efficiency measurements. Our measurements are further enhanced through X-ray measurements of the microstructure of the films to obtain a full picture of the effects of donor percentage on charge generation and recombination.

9:15 AM EP05.11.05
Terahertz Spectroscopy to Study Charge Carriers in Photoexcited and Doped Organic Semiconductors Natalie Banerji1; Department of Chemistry and Biochemistry, University of Bern, Bern, Switzerland.

While transient absorption (TA) spectroscopy gives information about the population of photogenerated excitons and charges, both the population and short-range mobility of charge carriers determines the photoconductivity dynamics in optical-pump-THz-probe (OPTP) measurements. By combining both techniques, the evolution of only the mobility at different times after photoexcitation can be extracted. This is then further substantiated by the mobility and localization parameters obtained from analyzing the real and imaginary parts of the complex photoconductivity spectra at selected time delays with an appropriate model. Here, we have undertaken such a study with pBDTT:PCBM blends having controlled phase morphologies, which are excellent model
systems to study the charge carriers in organic photovoltaics (OPVs). We can thus follow changes in the short-range mobility as the charges evolve between different neat and intermixed regions of the blend.

Moreover, we have investigated thin films of a narrow-bandgap conjugated polyelectrolyte, which was shown to become self-doped (conductive) upon dialysis treatment. The doping is directly evident in the absorption spectrum, where a polaron band appears around 1200 nm. Charges are thus present in the ground state and we have investigated their short-range mobility properties using time-domain THz spectroscopy (TDTS, without need of photocexcitation). Those are compared to the carrier properties of photo-generated charges in blends of the corresponding non-ionic polymer backbone with PCBM. We have also carried out TA spectroscopy in solutions and thin films of the doped system, with pumping in either the excitonic or the polaronic band. Surprisingly similar, correlated and very short-lived dynamics were observed. All data was compared to un-doped reference systems and the fluorescence-dependence was recorded. This brought novel insights to the electronic structure of doped conjugated polymers.

9:45 AM EP05.11.06
Electron-Driven Proton Transfer from Water to a Model Heptazine-Based Molecular Photocatalyst
Emily J. Rabe and Cody Schlenker; University of Washington Chemistry Department, Seattle, Washington, United States.

In the field of photocatalytic hydrogen evolution from water, the conjugated heptazine unit has received significant attention due to intense research interest in 2-dimensional poly(heptazine imides), commonly referred to as carbon nitride or g-C3N4. These conjugated organic materials are readily synthesized from earth abundant materials and act as photoelectrodes, both absorbing photons and transferring charge to drive the redox process. Despite intense research interest over the past decade, the mechanism of photocatalytic activity remains largely enigmatic. In part due to its structural ambiguity, the activity has been attributed to a variety of processes including free carrier generation, active defect sites, and excitonic interactions at the heptazine core. To avoid this ambiguity, we chose to study 2,5,8-tris(4-methoxyphenyl)-1,3,4,6,7,9-b-heptaazaphenalene (TAHz), an ary-functionalized heptazine molecule to study the role of the heptazine core. Using time-resolved multichannel photoluminescence (PL) spectroscopy, we kinetically reveal a new emission feature that emerges in aqueous dispersions of TAHz. We attribute this new PL peak to a state with significant intermolecular charge-transfer (CT) character that forms when photoexcited TAHz accepts an electron from hydrogen-bonded H2O. Using global analysis, we spectrally and kinetically resolve overlapping emission features and observe a prompt CT PL decay component exhibiting a kinetic isotope effect of 2.9. We attribute this isotopic dependence to CT quenching by electron-driven proton transfer from water in the TAHz:H2O complex. Radical detection with terephthalic acid confirm hydroxyl radicals form when TAHz is illuminated in water as a result of this photochemical transformation. Our interpretations are consistent with recent theoretical predictions that g-C3N4-based photocatalysts can participate in electron-driven proton transfer with H2O, forming neutral hydrogenated heptazine and hydroxyl radicals. This significant finding points towards the possibility of incorporating heptazine-based materials in devices for artificial photosynthesis.

10:00 AM BREAK

SESSION EP05.12: Singlet and Triplet Dynamics
Session Chairs: Richard Friend and Naomi Ginsberg
Thursday Morning, November 29, 2018
Hynes, Level 2, Room 208

10:30 AM *EP05.12.01
Exciton Fission and Fusion in Organic Crystals
Chris Bardeen; University of California, Riverside, Riverside, California, United States.

Exciton fission is an energy downconversion process (1 high energy excitation → 2 low energy excitations) while exciton fusion is an energy upconversion (2λ1 process. Both are of practical interest because they provide routes to boost solar energy conversion efficiencies by 30% or more. Organic semiconductors like tetracene and rubrene are uniquely well-suited to perform this energy repackaging because the Frenkel character of the excitons leads to energetically distinct singlet and triplet bands, which can exchange energy via spin-allowed fission and fusion processes. We will describe efforts to understand the photophysical steps involved in singlet fission using time-resolved transient absorption, photoluminescence and magnetic field effects. The roles of molecular packing and crystal morphology in controlling the fission rate will be emphasized. The dynamics of the triplet pair state produced by fission suggest that the triplet excitons may be able to diffuse independently while maintaining spin coherence. For singlet fission, these nonequilibrium spin state distributions can play an important role in both the ultimate triplet yield and the observation of experimental quantities like delayed fluorescence. We will describe time-resolved experiments and Monte Carlo simulations that look at how spin dynamics affect fission and triplet-triplet annihilation. The inverse of singlet fission is triplet-triplet fusion or annihilation, where a pair of triplet excitons fuse into a high-energy singlet state. A new approach to triplet state sensitization involves absorption of low energy photons by semiconductor nanocrystals followed by energy transfer to the molecular triplet states. This approach provides a way to generate large populations of triplets by near-infrared excitation. Interestingly, we also find that upconversion via triplet fusion can occur in certain molecular crystals even in the absence of sensitizers, possibly due to the presence of low-energy intermolecular states.

11:00 AM EP05.12.02
Understanding Singlet Fission Dynamics in Endothermic Systems Using Ultrafast Spectroscopy
Arya Thampi and Akshay Rao; Cavendish Laboratory, University of Cambridge, Cambridge, United Kingdom.

Singlet fission is the spin allowed process of formation of free triplets from a photo-excited singlet, observed in organic molecules such as pentacene, tetracene, their chemical derivatives, conjugated polymers, perylenedimides etc. The dynamics and yield of singlet fission have been understood to be dependent on several factors. To facilitate singlet fission, the energetics of the molecule must be such that the triplet energy lies close to half of singlet energy and this difference in energy was previously thought to be a limiting factor to the efficiency of fission. Prime examples for this were the fast (fs) fission in pentacene, an exothermic system, and slow (ps) fission in tetracene, an endothermic system. However, recently (1,2) it has been shown that singlet fission is fast and efficient in an endothermic system, TIPS- tetracene, where the singlet decays to form vibrationally coherent correlated triplet pair states (TT) under 200 fs, despite the conventional idea that endothermic systems exhibit slower picosecond- timescale singlet fission. In addition to the energetics of the molecules, molecular packing in the solid state is an important parameter as well, since the proximity of molecules to form TT states is crucial to this process.
In this study, we use a series of modified anthracene molecules, with varying endothermicity, to explore the effect of energetics and molecular packing to the dynamics of singlet fission. These molecules are blue-shifted in energy (HOMO-LUMO gap) by approximately 180 meV with respect to the well-studied endothermic fission molecule, TIPS- tetracene. Singlet fission in TIPS- tetracene is a two-step process in which singlets decay to form TT states under 200 fs, and in a few nanoseconds, decouple to form free triplets (1). The latter process of decoupling of the TT states to form free triplets has been shown to be temperature independent (3), though it is counter-intuitive that a thermodynamic factor such as endothermicity has no bearing on this step in the process of singlet fission. The strategic chemical modifications on the anthracene derivatives used in this study are utilized to understand the process of decoupling of triplets in more detail as it provides a larger gap to play with on the energetic landscape between singlets and triplets. We use transient absorption spectroscopy, transient photoluminescence (PL) spectroscopy, magnetic- field dependent steady state PL, temperature dependent PL among other methods in this work. The scope of this work is to understand long-standing questions related to the fundamental nature of SF, which when incorporated in solar cells can improve the power conversion efficiencies by more than 30% (4).

(1) H. L. Stern et al., Nat. Chem. 9, 1205–1212 (2017)

11:15 AM EP05.12.03
Correlation of Molecular Packing and Excited State Dynamics During Singlet Fission
Grayson Doucette1, Christopher Girecio2, Eric Kennehan1, John Asbury1, Haw-Tyng Huang1 and Arani Biswas1; 1The Pennsylvania State University, University Park, Pennsylvania, United States; 2The Ohio State University, Columbus, Ohio, United States.

Continuous control of through space coupling between singlet fission chromophores is a sought-after goal to study the dynamics of intermediates present during the singlet fission reaction. Such fine control of intermolecular interactions may be reserved to ab initio studies for now, but experiments carried out focused on altering the packing of 6,13-bis(tribispropylsilyl)pentacene (TIPS-Pn) thin films are steps toward that end. Without chemical alteration to TIPS-Pn, recent work has demonstrated the direct fabrication of solution cast polymorphs. These polymorphs enable studies of correlated triplet pair intermediates and their associated separation process under slightly different packing motifs. Transient absorption in both the visible and mid-infrared on the ultrafast and nanosecond timescales suggest a correlated triplet pair separation process occurring via triplet transfer. Furthermore, hole and electron transfer integrals qualitatively support the variation in triplet separation with packing geometry. Future modifications to processing conditions and ultrafast experiments will then drive toward even finer control in interchromophore coupling to study the impact of singlet energetics on triplet separation.

11:30 AM EP05.12.04
Exciton Diffusion Dynamics in Perylene Diimides Mediated by Singlet Fission
Ferdinand C. Grozema and Kevin M. Felter, Delft University of Technology, Delft, Netherlands.

The SF process is proposed as one of the strategies to optimize and surpass the Schockly-Queisser limit for (organic) single junction photovoltaic cells. The SF process involves splitting a photoexcited singlet state (S1) into two distinct triplet excited states (T1+T1). This enables harvesting two charges for only one absorbed photon. The process occurs analogously in quantum dot materials where it is called carrier multiplication (MEG). In order to control the SF process and design better chromophores with higher SF efficiencies and rates, fundamental knowledge is required on the underlying principles. One crucial aspect of SF are the energy requirements and dependence on not only solid state packing, but also of chemical substitution. PDIs are excellent study materials to study the influence of chemical substitution on both solid state packing and the energetics. A variety of SF studies on the rate and efficiency in PDIs has been performed using transient. The favourable electronic coupling and energetics of perylene diimides (PDIs) are known to result in efficient singlet fission and triplet up- conversion. A secondary effect of these processes is its significant effect on excition diffusion. This research is part of a systematic study to determine the influence of fission and up-conversion on excition diffusion in PDI derivatives and the effect of temperature.

In order gain information on the singlet fission and excition diffusion, we first studied planar heterojunctions composed of a smooth TiO2 electron acceptor film and physical vapour deposited PDI using the flash photolysis time resolved microwave photoconductivity technique (FP-TRMC). The photoconductance measurements reveal a triplet of triplet exciton diffusion on the packing of the PDI derivative mediated by singlet fission. Furthermore, as illustrated by the figure below, we observe a strong temperature effect on photoconductivity indicating either enhanced excition diffusion and/or UC/SF rate enhancement. Secondly we studied the effect of temperature on the photoluminescence and transient absorption to get direct evidence for a temperature effect on the excitonic species and therefore the singlet fission process. We have determined that the triplet concentration is influenced by temperature as a result of singlet fission. We determined an activation energy for the singlet fission process to occur for a particular type of perylene diimide solid state structure.

We conclude that exciton diffusion and singlet fission in perylene diimide crystals are thermally activated and show a chemical structure dependence on the extent of both singlet fission and excition diffusion. We determined an exciton diffusive properties as well as a singlet fission rate and activation energy.

11:45 AM EP05.12.05
Singlet Fission and Exciton Dynamics in Amorphous Rubrene
Drew Finton, Elizabeth DeJong, Vincent Zoutenbier and Ivan Biaggio; Physics, Lehigh University, Bethlehem, Pennsylvania, United States.

We used molecular beam deposition in high vacuum to obtain both amorphous and multicroystalline rubrene thin films, and studied how the fluorescence dynamics induced by short pulses varies in samples grown under different conditions. These investigations showed that by this method it is possible to obtain a truly amorphous rubrene film where singlet fission does not occur: in such samples we have observed a single exponential decay of the fluorescence, similar to what is seen for molecules in solution. On the other hand, as the film morphology changes as a function of the deposition condition and nano- or microcrystal regions arise, singlet excition fission starts being enabled and the dynamics of the short-pulse induced fluorescence shows the typical signs of exciton fission and triplet fission: a fast transient followed by a delayed fluorescence caused by triplet exciton fission. We discuss the insights that we obtained on the effect of molecular ordering and size of crystalline regions on singlet excition fission and triplet excition fusion.
Singlet fission, a spin-allowed process of spontaneous exciton multiplication, has the potential to enhance the efficiency of photovoltaic devices by utilizing two triplet excitons generated from one singlet exciton. The majority of studies to date have emphasized understanding and optimizing the first step of singlet fission, where the overall singlet intermediate state—the "correlated triplet pair"—is produced from a singlet photoexcitation. Few studies have examined later steps, where the triplet pair may separate and spin correlation may be lost. Here we examine transient absorption of 6,6-bis(triisopropylsilylethynyl)pentacene (TIPS-Pn) films at cryogenic temperatures (78–295 K). We evaluate time constants obtained from global analysis and show that their temperature dependence is inconsistent with an exclusively thermally activated process. Instead, we find that the trends can be modeled by a triplet-triplet energy transfer process involving simultaneous two-electron exchange. The fitted reorganization energy and electronic coupling agree closely with values calculated using density matrix renormalization group quantum-chemical theory. We conclude that the dissociation of the correlated triplet pair to separated (but spin-entangled) triplet excitons in polycrystalline TIPS-Pn occurs by triplet-triplet energy transfer with a hopping time constant of approximately 3.5 ps at room temperature.

In select molecular systems, singlet excitons (S₁) created from the absorption of a photon can undergo a process where it efficiently splits into two triplet excitons (2T₂). This process of singlet fission has the potential of realizing high efficiency solar cells that exceed the Shockley-Queisser limit [1]. In this study we investigate a hexacene derivative [2] using pump energy dependent ultrafast transient absorption spectroscopy to study the mechanisms that limit the singlet fission rate and efficiency. Hexacene is a unique system to study the singlet fission processes because of its small T₁ energy (~0.5 eV) compared to the S₁ energy (~1.5 eV). Therefore, in contrast to other singlet fission systems such as tetracene and pentacene which are close to isoenergetic, singlet fission in hexacene is highly exothermic. The significant degree of electronic coupling compounded with large exothermicity gives the possibility of hexacene to undergo singlet fission from one singlet to either yield three triplets or yield two triplets and phonons.

In this hexacene system we find the singlet fission rate of 470 fs which is in line with previous studies [3][4]. Such a short time scale of singlet fission allows it to out-compete other relaxation channels, and hence giving it a high efficiency. Comparing with pentacene, the other system with exoergic singlet fission (~100 fs fission rate), even though hexacene is more exoergic than pentacene the singlet fission rate is observed to be much slower. The proposed phonon bottleneck effect causing this divergence is experimentally explored through transient absorption spectroscopy, yielding corroborative evidence. By inducing more energy into the system through systematically varying the pump excitation to shorter wavelengths, singlet fission mediated by multiple phonon interactions is directly probed. A prolonged singlet fission rate is observed with higher pump energies. Individual singlet and triplet spectra show that their temperature dependence is inconsistent with an exclusively thermally activated process. Instead, we find that the trends can be modeled by a triplet-triplet energy transfer process involving simultaneous two-electron exchange. The fitted reorganization energy and electronic coupling agree closely with values calculated using density matrix renormalization group quantum-chemical theory. We conclude that the dissociation of the correlated triplet pair to separated (but spin-entangled) triplet excitons in polycrystalline TIPS-Pn occurs by triplet-triplet energy transfer with a hopping time constant of approximately 3.5 ps at room temperature.

Singlet Fission in Synthetic Carotenoid-Proteins Jenny Clark, Daniel Polak and Andrew Musser; University of Sheffield, Sheffield, United Kingdom.

Singlet fission is the process whereby one photon creates two triplet excited states. If both triplet states could be harvested by a single-junction solar cell, the solar cell efficiency would increase by up to 1/3. There has been much academic and industrial interest in developing new materials for singlet fission, but to date no material has proved ideal.

Carotenoids are the most widespread of the natural pigments, important for photosynthesis, vision, human health and industry. Work on astaxanthin [1,2] (the pigment which colours lobster) shows that carotenoids are good candidates for singlet fission sensitizers for solar cells: they have strong absorption and fast (<100fs) singlet fission, independent of energetic driving force. There are hundreds of naturally occurring carotenoids and each of them can form a range of different dimer or aggregate structures (eg H- or J-aggregates).

To determine how carotenoid structure affects singlet fission, and how to exploit carotenoids or other polyene-type systems as singlet fission sensitizers, we use model systems to create identical dimer structures of a range of carotenoids. The model systems are made of synthetic ‘maquette’ proteins that hold the carotenoids in a specific dimer geometry. I will describe details of the photophysics of singlet fission in polyenes, showing that singlet fission is surprisingly robust to changes in conformation and does not depend on either the aggregate or intramolecular structure.


3:30 PM *EP05.13.05/CM04.10.05
Functional Imaging of Energy Flow in Materials at the Nanoscale Milan Delor, Hannah Weaver, QinQin Yu and Naomi S. Ginsberg; University of California, Berkeley, Berkeley, California, United States.

The ability of energy carriers to move within and between atoms and molecules underlies virtually all biochemical and material function. Understanding and controlling energy flow, however, requires observing it on ultrasmall and ultrafast spatiotemporal scales, where energetic and structural roadblocks dictate the fate of energy carriers. We therefore developed a universal, non-invasive optical scheme that leverages interferometric scattering to track energy transport in four dimensions of spacetime with few-nanometer precision and directly correlate it to material morphology. We visualize exciton, charge, and heat transport in polyacene, silicon and perovskite semiconductors and elucidate, in particular, how grain boundaries impact energy flow through their lateral- and depth-dependent resistivities. We reveal new strategies to interpret energy transport in disordered environments that will direct the design of defect-tolerant materials for the semiconductor industry of tomorrow.

4:00 PM EP05.13.06/CM04.10.06
The Evolving Excitonic Properties of Organic Molecules During Self-Assembly Cathy Y. Wong; University of Oregon, Eugene, Oregon, United States.

The electronic structure and exciton dynamics of organic molecules can change dramatically upon aggregation. The exciton dynamics of molecules in solution and in thin films of aggregates can be measured using transient absorption spectroscopy, but the exciton dynamics of intermediate aggregation states during thin film formation are typically unknown since measurements cannot be performed quickly enough to collect accurate transient absorption spectra of these species. By increasing the speed of data collection, the exciton dynamics of evolving material systems can be measured. A novel implementation of transient absorption spectroscopy is introduced that can measure transients with up to a 45 ps pump-probe time delay in one shot. The exciton dynamics measured during the solution deposition of a thin film is validated by comparing the initial exciton dynamics of the solution and the final exciton dynamics of the dry film to traditional transient absorption measurements. The exciton dynamics of intermediate aggregation states will be presented for the first time. The information gained using this technique can be used to modify environmental parameters during the film formation process to kinetically trap aggregates with exciton dynamics tailored for a particular application.

4:15 PM EP05.13.07/CM04.10.07
Diffraction Before Destruction—Unraveling Structure-Function Relationships in Organic Semiconductors with an Ultra-Fast X-Ray Laser Christopher J. Takacs1, Kathryn O'Hara2, Karsten Bruening1, Hans-Georg Steinrueck2, Christopher J. Tassone1, Mengning Liang3, Michael L. Chabinyc2 and Michael F. Toney1; 1Stanford Univ, Menlo Park, California, United States; 2University of California, Santa Barbara, Santa Barbara, California, United States; 3SLAC National Accelerator Laboratory, Menlo Park, California, United States.

Charge and ion transport of organic semiconductors depends strongly on both molecular structure and morphology. Our fundamental understanding of structure-function relationships has improved greatly in recent years; however, conventional high-resolution structural probes such as x-ray and electron scattering/microscopy are severely restricted by radiation damage and new structural probes are needed. Towards this end, we present initial results from nano-beam diffraction experiments at the Linac Coherent Light Source (LCLS), a source of high-intensity, ultra-short, and coherent hard x-ray pulses from several molecular and polymeric materials. Known as “diffraction-before-destruction”, a single femtosecond x-ray pulses yields useable diffraction images in weakly diffracting and disordered samples before radiation damage can propagate (e.g. sample explosion). This removes the previous limitations of sample damage present in synchrotron and electron microscopy methods. Furthermore, the focused beam (150 nm diameter) is small enough that significant anisotropy in the scattering patterns is observed, yielding insight into polymorphism, strain, and grain-boundaries through statistical analysis of hundreds (and eventually millions) of diffraction images. Combined with complementary high-resolution transmission electron microscopy images and atomistic simulations, the results suggest a distribution of packing structures coexist in thin films and that engineering likely packing motifs has the potential to improve both the electronic and ionic transport properties of these materials.

4:30 PM *EP05.13.08/CM04.10.08
Probing Single Molecular Dynamics at Ultrafast Time Scales and in Nanoscale Volumes Nick F. van Hulst1, 2; 1ICFO - Institute of Photonic Sciences, Castelldefels, Spain; 2ICREA - Catalan Institute for Research and Advanced Studies, Barcelona, Spain.

Tracing of individual molecules both in space and in time, provides super-resolution images of intra- and inter-molecular dynamic processes, all beyond the ensemble [1,2]. A host of important dynamic processes occurs on fs-ps timescale, such as electronic relaxation/dephasing, energy & charge transfer, vibrational relaxation, photo-dissociation-ionization, photo-isomerization. Yet capturing fast dynamics is fundamentally limited by the ns lifetime of the detected fluorescence. For the ensemble, fs-ps resolution is conventionally obtained by transient absorption and 2D electronic spectroscopy (2D-ES). Here first, we challenge ultrafast transient absorption of a single molecule and have set out to probe the non-linear ultrafast response of the single molecule using a broadband laser in an effective 3-pulse scheme with fluorescence detection. 2D-ES of single molecules is getting into reach [3].
Next, stimulated emission has the advantage of coherence and unity quantum efficiency, compared to fluorescence. Moreover depleting the excited state rapidly reduces photoassociation. Thus, we have set out to directly detect the stimulated emission from individual molecules and Qdots at ambient conditions, to disentangle ultrafast charge dynamics in the excited state, on fs-ps timescale [4]. Finally, we enhance the sensitivity and resolution using the local optical near-fields of plasmonic nano-antennas. Critical to the optimal coupling and enhancement is the positioning of the molecule at the local nanoscale hotspot of a resonant antenna. We apply deterministic scanning and stochastic mapping of the nanoscale plasmon-molecule interaction, to optimize the coupling strength and ultrafast interaction [5,6]. We apply the enhancement to photosynthetic complexes, LH2 [7], to detect first single FMO complexes at room temperature and assess their photon correlation.

The presented nanoscale ultrafast spectroscopy on individual molecules is of direct importance for pathway-specific detection of energy transfer and charge separation, directly and locally in light-harvesting systems [1].

Acknowledgements
This research was funded by ERC Adv.Grant 670949-LightNet; MINECO Severo Ochoa SEV-2015-0522, FIS2015-69258-P and FIS2015-72409-EXP; the Catalan AGAUR (2017SGR1369), Fundació Privada Cellex, Fundació Privada Mir-Puig, and Gencat CERCA program.

References

EP05.14.01
Effect of Nematic Order on Charge Transport in Conjugated Polymers Wenlin Zhang1, Scott Milner2 and Enrique Gomez2; 1Chemical Engineering, University of Michigan, Ann Arbor, Michigan, United States; 2Chemical Engineering, The Pennsylvania State University, University Park, Pennsylvania, United States.

Nematic order, in the bulk or at interfaces, is ubiquitous for semiflexible conjugated polymers. The effect of liquid crystalline order on charge transport, however, remains unclear. Using an analytical model, we show that nematic order leads to an enhancement in charge mobilities when compared to isotropic chains. We also predict a quadratic dependence of the charge mobility on molecular weight of the chains. This is because uniaxially aligned chain backbones lead to rod-like intra-chain trajectories of charge carriers. Analysis of the probability of forming hairpin defects also shows that increasing persistence length can enhance charge transport in conjugated polymers. We speculate that the prevalence of nematic order in conjugated polymers may explain the reported increase in charge mobilities with molecular weight.

EP05.14.02

A bulk heterojunction (BHJ) structure by co-evaporation of organic photovoltaics (OPVs) provides the large donor-acceptor interface, which facilitates efficient charge separation. However, it is difficult to control directly the morphology of the co-evaporated BHJ layer because of random blend of donor and acceptor molecules. Many efforts have been made for structure control of BHJ layer by introducing a new substitute in molecule and combining additive molecules in solution. In our previous work, we reported highly efficient OPV cells by inserting CuI molecular orientation control layer under the zinc phthalocyanine (ZnPc):C60 co-evaporated BHJ layer. It is estimated that higher light absorption coefficient was obtained by controlled ZnPc lying-down π-d interaction between ZnPc molecules and CuI in ZnPc:C60 co-evaporated BHJ layer. This research was funded by ERC Adv.Grant 670949-LightNet; MINECO Severo Ochoa SEV-2015-0522, FIS2015-69258-P and FIS2015-72409-EXP; the Catalan AGAUR (2017SGR1369), Fundació Privada Cellex, Fundació Privada Mir-Puig, and Gencat CERCA program.

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References

SESSION EP05.14: Poster Session II: Structural, Charge Transport and Photophysical Characterization Session Chairs: Rodrigo Noriega and Ni Zhao
Thursday Afternoon, November 29, 2018
8:00 PM - 10:00 PM
Hynes, Level 1, Hall B

EP05.14.01
Effect of Nematic Order on Charge Transport in Conjugated Polymers Wenlin Zhang1, Scott Milner2 and Enrique Gomez2; 1Chemical Engineering, University of Michigan, Ann Arbor, Michigan, United States; 2Chemical Engineering, The Pennsylvania State University, University Park, Pennsylvania, United States.

Nematic order, in the bulk or at interfaces, is ubiquitous for semiflexible conjugated polymers. The effect of liquid crystalline order on charge transport, however, remains unclear. Using an analytical model, we show that nematic order leads to an enhancement in charge mobilities when compared to isotropic chains. We also predict a quadratic dependence of the charge mobility on molecular weight of the chains. This is because uniaxially aligned chain backbones lead to rod-like intra-chain trajectories of charge carriers. Analysis of the probability of forming hairpin defects also shows that increasing persistence length can enhance charge transport in conjugated polymers. We speculate that the prevalence of nematic order in conjugated polymers may explain the reported increase in charge mobilities with molecular weight.

EP05.14.02

A bulk heterojunction (BHJ) structure by co-evaporation of organic photovoltaics (OPVs) provides the large donor-acceptor interface, which facilitates efficient charge separation. However, it is difficult to control directly the morphology of the co-evaporated BHJ layer because of random blend of donor and acceptor molecules. Many efforts have been made for structure control of BHJ layer by introducing a new substitute in molecule and combining additive molecules in solution. In our previous work, we reported highly efficient OPV cells by inserting CuI molecular orientation control layer under the zinc phthalocyanine (ZnPc):C60 co-evaporated BHJ layer. It is estimated that higher light absorption coefficient was obtained by controlled ZnPc lying-down π-d interaction between ZnPc and CuI. However, information of the ZnPc molecular orientation in ZnPc:C60 film has not been obtained by various measurements, such as XRD, XAFS, and TEM, due to its low crystallinity in ZnPc:C60 film. Hence, we report that the identification of molecular orientation in ZnPc:C60 film by Infrared reflection absorption spectroscopy (IR-RAS), which is enabled to measure the molecular orientation in amorphous film. We succeed in calculating the molecular orientation angle in co-evaporated films on various substrates by IR-RAS. The CuI (5-nm-thickness)/PEDOT:PSS/ITO substrate (CuI substrate) and ZnPc (20-nm-thickness)/CuI/PEDOT:PSS/ITO substrate (ZnPc substrate) were prepared to investigate the molecular orientation control by π-d interaction and π-π interaction, respectively. On these substrates, ZnPc:C60 co-evaporated BHJ layer was evaporated in the vacuum chamber. IR-RAS measurement was done under in-situ conditions during evaporation of ZnPc:C60 film. The orientation angles of ZnPc molecules calculated by IR-RAS in ZnPc:C60 film on various substrates. Orientation angles of ZnPc molecules in ZnPc:C60 films on PEDOT:PSS reference, CuI substrate (π-d interaction) and ZnPc substrate (π-π interaction) are 60 degrees, 45 degrees, and 38 degrees at 10 nm or less thickness regions, respectively. These results indicates that π-π interaction between ZnPc and ZnPc molecules is stronger than π-d interaction between ZnPc molecules and CuI in ZnPc:C60 co-evaporated BHJ layer.

EP05.14.03
Revisiting the Use of Transient Photovoltage Measurements as a Probe of Recombination in Thin-Film Solar Cells Mohammed Azzouzi1, Philip Calado1, Thomas Kirchartz2, 3, Piers Barnes1 and Jenny Nelson1; 1Department of Physics and Centre for Plastic Electronics, Imperial College London, London, United Kingdom; 2IEK-5-Photovoltaics, Forschungszentrum Jülich, Jülich, Germany; 3Faculty of Engineering and CENIDE, University of Duisburg-Essen, Duisburg, Germany.
Transient photovoltage (TPV) measurements have been frequently used to study the recombination lifetime of thin-film solar cells. TPV uses the decay of a small optically-induced voltage perturbation to probe the charge dynamics of devices at open circuit. The transient response to a short pulse of light in modelled devices was simulated using a drift diffusion model. Whilst for high mobility systems the lifetime inferred from the simulated TPV measurement matches well with the input lifetime, in cases where charge-carrier mobilities in the active layer are lower than $10^3$ cm$^2$V$^{-1}$s$^{-1}$, the extracted lifetime deviates strongly from the input lifetime value and is highly dependent on mobility. In such low-mobility cases, the simulated charge carrier dynamics show bi-exponential behaviour where the fast decay at early times reflects the recombination of charges in the bulk, while the second, slower decay relates to charges that accumulate near the interfaces. The inhomogeneous spatial distribution of charge carriers in a device at open circuit reduces the recombination rate close to the interfaces, making net recombination dependent on how fast charges can diffuse into the bulk to recombine. As the open-circuit voltage is related to the majority carrier quasi-Fermi levels near the interfaces, its decay is most strongly related to this second slower decay of the charges. Following this observation we developed a new technique to monitor the charge-carrier density during the TPV experiment. We applied this method alongside conventional TPV to measure the recombination dynamics in different systems, including bulk heterojunctions comprised of P3HT with both a fullerene acceptor (PCBM) and non-fullerene acceptor (O-IDTBR). We observed that while the TPV lifetime of the fullerene and non-fullerene devices were similar in magnitude (7µs and 3µs respectively), the recombination lifetime of the non-fullerene system was significantly faster at 0.1µs compared to 2µs. These findings reconcile the relationship between the fill-factor and the recombination dynamics of the measured devices. By studying the parameters influencing the photovoltage and charge carrier decays, we present a method to estimate the mobility of these devices, and hence estimate the diffusion length of carriers in the active layer.

E05.14.04

Electron Accumulation Enhances Efficiency Bottleneck for Hydrogen Production in Carbon Nitride Photocatalysts Wenzxing Yang1, Robert Godin1, Hatie Kasap2, Benjamin Moss1, Yifan Dong1, Sam J. Hillman1, Ludmilla Steier1, Erwin Reiner1 and James R. Durrant1; Department of Chemistry and Centre for Plastic Electronics, Imperial College London, London, United Kingdom; 2Department of Chemistry, Christian Doppler Laboratory for Sustainable SynGas Chemistry, University of Cambridge, Cambridge, United Kingdom.

A deep understanding of the photoinduced charge-transfer dynamics of photocatalysts is a vital pre-requisite for developing efficient and economical devices for water splitting and CO2 reduction. Graphitic carbon nitrides (g-C$_3$N$_4$) are an emerging cheap and efficient photocatalyst for water splitting. However, the photophysical studies of the g-C$_3$N$_4$ have, to date, lagged far behind rapid improvements in reported efficiency due to its tendency to aggregation in solution presents a significant technical challenge for measurement. Herein, we report a thorough photophysical and charge-transfer study of a stable dispersion of a cyanamide surface functionalized melon-type carbon nitride (NCN-CN$_x$), on a timescale ranging over 12 orders of magnitude (from fs to s) using transient absorption spectroscopy. Fluence-dependence studies reveal that the bimolecular reaction of the photogenerated electrons and holes in NCN-CN$_x$s can be well described by the random walk model developed previously for the metal oxide. Remarkably, the addition of hole scavengers, 4-MBA, into NCN-CN$_x$ was found to lead to an unprecedented ultrafast decay phase (~ few ps) of the electron signals of the NCN-CN$_x$, faster than the diffusion limitation of 4-MBA. We show conclusively that this ultrafast decay is not a result of hole extraction by the scavenger. Rather, it is due to the accelerated electron-hole recombination resulting from electron accumulation in NCN-CN$_x$s (to be around $10^{29}$to$10^{31}$cm$^{-3}$) after holes have been extracted on the ~ ns to µs timescale. Strikingly, under the charge accumulation condition, the recombination kinetics are found no longer controlled between the photogenerated electron/hole pairs, but rather controlled by the accumulation of electrons and the photogenerated holes. Quantitative studies reveal that the acceleration of the recombination process can be described as $t_{rs} \sim [e]^{-2}$. Further hydrogen production and spectroscopic measurements reveal that this charge accumulation limits the further photogenerated charges under steady state, in correlation with the decrease of the enhancement of the hydrogen production quantum yield at the low light intensity. An addition of an electron mediator, methyl viologen (MV$^2-$), is able to extract the accumulated electrons from the NCN-CN$_x$s and thereby enhance hydrogen production NCN-CN$_x$s by more than 30 %. These results emphasize the kinetic impact of electron accumulation in g-C$_3$N$_4$ materials and highlight the importance of efficient charge extraction on systems exhibiting a strong carrier density dependent recombination but slow electron transfer kinetics.

E05.14.05

Exciton Binding Energy of Organic Materials—Ground-State vs Excited-State Donor-Acceptor Complexes Andreas Opitz1, Paul Beyer1, Norbert Koch1,2,3 and Wolfgang Brütting4; 1Institut für Physik, Humboldt-Universität zu Berlin, Berlin, Germany; 2IRIS Adlershof, Humboldt-Universität zu Berlin, Berlin, Germany; 3Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Berlin, Germany; 4Institut für Physik, Universität Augsburg, Augsburg, Germany.

Organic semiconductors are materials with a high exciton binding energy (EBE), which significantly impacts their electronic and optical properties. The EBE is the difference between the electronic gap (sometimes referred to as charge transport gap) and the lowest transition energy of photon induced electron accumulation in g-C$_3$N$_4$ materials and highlight the importance of efficient charge extraction on systems exhibiting a strong carrier density dependent recombination but slow electron transfer kinetics.

E05.14.06

Non-fullerene acceptors (NFA) in bulk heterojunctions of organic solar cells (OSCs), such as derivatives of the fused-ring acceptor ITIC, have been shown to outperform fullerenes in terms of performance and stability. Therefore, power conversion efficiencies of up to 20% are envisioned e.g. for tandem cells [1]. This new optimism in the field of OSCs originates from the advantageous and versatile properties of NFAs including tunable band gaps to match the energetic levels of the donor molecules, increased absorption in comparison to fullerenes, and tunability of morphological properties. As for fullerenes it is accepted that energetic quantities and other properties such as the mobility are strongly related to the nanoscale morphology [2]. This means that order and disorder in materials enriched and interfacial domains, respectively, might play a decisive role in efficient charge separation, explaining the observation of ultrafast electron transfer followed by highly probable separation despite LUMO level offsets of <0.1 eV.

For fullerene-based bulk heterojunctions analytical transmission electron microscopy has been an indispensable tool for visualizing nanoscale domains of different compositions and order. Due to relatively large differences in optical excitations, low energy-loss spectroscopic imaging (ESI) could provide segmentations in 2D and 3D [3]. However, electronic structures of NFAs are close to those of the donors, and hence show similar optical excitation features and energies. Thus, differences in ESI signals between acceptor and donor reduce for bulk heterojunctions including NFAs. Here, we demonstrate that applying pattern recognition algorithms on spatially resolved energy-loss data overcomes the reduced signal problem for plasmonic and inner-shell excitations. We show that the nanoscale morphology of NFA acceptor blends correlates with processing parameters. We discuss different donor polymers (PCE10 and PCE12) mixed with ITIC and IDTBR derivatives, two NFAs enabling high efficiency with these donor polymers, and visualize changes in resulting domain structures of the blends, before and after heat treatment. We find varying extents of interfaces between mixed or less-ordered phases and enriched/pure domains of different materials. This implies that also for NFA blends, changes in energy levels, depending on the ordering at the nanoscale, are important for efficient charge separation. This is supported by detailed spectral analysis of interfaces by seminal experiments using ultra-low voltage scanning electron microscopy [4] and novel studies using a structure-preserving laterally resolved energy-loss method presented in this work.

4. cf. RR Schröder et al., MRS-Fall Meeting 78, Symposium EP05
the composition and thickness of the layer. The analysis of the measurements at 80K showed the presence of two different paramagnetic species, a static and a mobile one, distinguished by two different g-tensors. We attributed the static species to trap states and the mobile ones to free charges. At increasing doping concentration, the number and the mobility of free charges increase. Conversely, the trap states show a different behaviour remaining static at all doping concentrations. The same analysis was performed at different temperatures (T=80K - 280K) elucidating the thermally-activated de-trapping mechanism underlying the doping process and shedding light on the dynamics of the species involved. Our results appear well in accordance with the statistical model proposed by Tietze.2 In this model, a pivotal role is played by trap states: only after all traps are filled during the doping process, free charges are generated. The model describes our results regarding the effects of doping concentration and temperature on the equilibrium populations and the dynamics of the two species well.

In addition, we are currently performing a similar analysis using further model systems to test the validity. The overall analysis will provide further details towards a direct and definitive understanding of the molecular doping in organic semiconductors.

References

EP05.14.10
Diffusion-Limited Delayed Fluorescence as a Signature of Singlet Fission and Triplet Fusion of Correlated Triplets Kazuhiro T. Seki1, Yoriko Sonoda1 and Ryuzi Katoh2; 1National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Japan; 2Nihon University, Koriyama, Japan.

The Singlet fission (SF) has attracted a broad interest in the communities of physical chemistry and organic electronics. The SF is a way to improve the quantum efficiency of organic devices by splitting an excited singlet exciton into a pair of long-lived triplet excitons. However, the fundamental processes caused by the SF are not fully understood.

Since the transition from the excited triplet state to the ground singlet state is spin forbidden, deactivation of triplet excitons requires a long-time, allowing them to dissociate and migrate over long distances. To date, the effects of diffusion on triplet fusion have been studied mainly for second order reactions where fusion is assumed to occur between any triplet pair regardless of whether they are the same pair generated by singlet fission. We focus on geminate triplet fusion where triplets may undergo diffusion but still recombine with the counter triplet generated by singlet fission; delayed fluorescence originates from diffusion mediated reversible geminate fusion of triplets. We show that occurrence of singlet fission followed by triplet fusion processes can be corroborated by studying the kinetics of delayed fluorescence; if delayed fluorescence decays by a power law with an exponent of 3/2, the delayed component of fluorescence could be attributed to geminate fusion of triplet pairs generated by singlet fission. We have also shown the temperature and the magnetic field effects on the kinetics of delayed fluorescence. By combining the static and kinetic aspects of the magnetic field effects on the fluorescence, a considerable amount of information on singlet fission and triplet fusion kinetics can be obtained.


EP05.14.11
Molecular Origin of the Anisotropic Orientation of Molecules in Organic Light Emitting Diodes Pascal Friederich1,2, Vadim Rodin1, Florian von Wrochem1, Reinder Coehoorn3 and Wolfgang Wenzel1; 1Karlsruhe Institute of Technology, Karlsruhe, Germany; 2University of Toronto, Toronto, Ontario, Canada; 3Materials Science Laboratory, Sony Deutschland GmbH, Stuttgart, Germany; 4Eindhoven University of Technology, Eindhoven, Netherlands.

Molecular orientation anisotropy of the emitter molecules used in organic light emitting diodes (OLEDs) can give rise to an enhanced light-outcoupling efficiency, when their transition dipole moments are oriented preferentially parallel to the substrate. A similar effect is observed when the anisotropic orientation of molecules with electrostatic dipole moments leads to the spontaneous buildup of an electrostatic potential perpendicular to the substrate. This so-called giant surface potential (GSP) effect can as well be exploited in organic electronics applications. Here, the orientation anisotropy of widely used organic semiconductors is investigated using a simulation approach which mimics the physical vapor deposition process of amorphous thin films. Our simulations reveal for all studied systems significant orientation anisotropy which is in agreement with experimental results for the emitter orientation as well as the GSP effect. We find that the electrostatic interaction between the dipole moments of the molecules limits the orientation strength while short range van der Waals interactions between molecules and the surface during deposition act as driving force for the anisotropic orientation.

EP05.14.12
Optoelectronic Properties of the Interface Between Si and SiC and α-Hexathiophene—A Comparative Study Hannah Schamoni, Oliver Bienek, Felix Eckermann and Martin Stutzmann, Walter Schöttrück Institute and Physics Department, Technical University Munich, Garching, Germany.

The combination of organic and inorganic semiconductors is a promising approach towards new materials for applications such as solar cells and light emitting devices, as they open up the possibility to simultaneously benefit from the advantages of both material types. Not least due to the broad variety of organic semiconductors, it is possible to tailor the properties of the heterojunctions in many different ways. In order to identify the most promising hybrid systems, a detailed knowledge about the specific organic/inorganic interface is essential. In this work, selected model systems of different organic and inorganic materials are fabricated and characterized optoelectronically. Via an organic molecular beam deposition (OMBD) system, thin films of the small molecule α-hexathiophene (6T) are deposited on two inorganic semiconductors, namely hydrogen-terminated silicon (Si) and hydroxyl-terminated silicon carbide (SiC). The resulting hybrid systems are characterized by current-voltage measurements in the dark, under illumination and at different temperatures, and by Kelvin Probe Force Microscopy. Combining the results of all these measurements provides a detailed view of the interface optoelectronic properties. In particular, we compare Si substrates of different doping types and doping concentrations to each other and to n-type doped 6H-SiC substrates, which exhibit significantly different current-voltage characteristics. Surprisingly, the potential difference between 6T and Si or SiC amounts to approximately 0.2 eV in all hybrid systems investigated. As this value therefore seems independent of the choice of inorganic semiconductor, it is assumed to originate from an interfacial dipole. Our work of combining different measurement techniques to systematically investigate the optoelectronic properties of hybrid systems of 6T and Si or SiC helps to develop a fundamental understanding of organic/inorganic semiconductor interfaces. This will eventually enable the tailoring of hybrid systems to meet the requirements of specific applications.

EP05.14.13
Spontaneous Formation of Aligned, Periodic Patterns During Crystallization of Organic Semiconductor Thin Films John S. Bangsund, Thomas R. Fielitz, Trevor J. Steiner, Kaicheng Shi and Russell J. Holmes; Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, Minnesota, United States.
Thin glassy films of multiple organic semiconductors are found to spontaneously form periodic, highly-aligned surface patterns by a simple annealing process. These grating-like surface structures are formed as the crystal growth front propagates across the sample by a stress-relaxation-driven wrinkling mechanism, and are aligned laterally along the crystallization front. The wavelength of these patterns can be tuned from 800 nm to 2,400 nm by varying film thickness and annealing temperature, and aligned pattern domain sizes on the millimeter length scale are obtained. Large differences in pattern periodicity are observed for thin films of different materials at a constant thickness, suggesting that a wider range of pattern wavelengths could be accessed by controlling materials properties. The pattern formation mechanism reported here is distinct from previous reports involving stress across a bilayer as wrinkling is associated with crystallization of a single layer, making the technique particularly amenable to device integration. These structures could be used as self-assembled diffraction gratings, distributed feedback cavities for organic lasers, or as scattering layers to enhance outcoupling in organic light-emitting devices.

EP05.14.14
The Research on Molecular Orientation and Characterization of the OLED Emitters Sungyong Sohn1, Kwang Han Park1, Hyungju Ahn2, Sungjune Jung2, Soon-Ki Kwon1 and Yun-Hi Kim3; 1Department of Materials Engineering and Convergence Technology and ERI, Gyeongsang National University, Jinju, Korea (the Republic of); 2Pohang Accelerator Laboratory, Pohang, Korea (the Republic of); 3Department of Chemistry and Research Institute for Natural Science, Gyeongsang National University, Jinju, Korea (the Republic of); 4Department of Creative IT Engineering, Pohang University of Science and Technology, Pohang, Korea (the Republic of).

We analyzed the scattered X-ray intensities of the host and host-dopant emitters, which have the spectra of in-plane and out-of-plane scattering to the plane and azimuthal intensity profiles for a plot of orientation distribution using grazing incidence wide-angle X-ray diffraction (GI-WAXD) measurement for high-efficiency organic light-emitting diodes (OLEDs).

In blue fluorescent emitters, we found that a non-doped anthracene derivatives have the highly rigid structure and thermal stability because p-naphthylxylene groups in 9,10-positions were highly twisted to anthracene core with steric hindrance of xylene groups. The OLEDs with non-doped emitters with 2,3-diphenyl groups showed high-efficiency of 5.21 cd/A due to enhanced carrier mobility with well-aligned π-stacking structure toward out-of-plane by the face-on orientation by GI-WAXD analysis. In phosphorescent emitters, we have used the tetrahedral silicon-based host materials with electron transporting (ET) property and investigated on the preferential host orientation. The ET hosts had good morphological stability as well as balanced charge-carrier transport by pyridyl-substituted linker in the devices. The Ir(ppy)3-doped or Firpic-doped devices showed high-efficiency of 53.54 cd/A or 11.08 cd/A, respectively. In thermally activated delayed fluorescence emitters, we found that the molecular orientation of emitting materials with diphenylamine derivative containing malononitrile had different horizontal and/or random orientations as a function of para or meta linker position. It showed 12.5% difference of the device efficiency. These improved device efficiency was confirmed by the enhanced out-coupling efficiency with well-aligned stacking structure in the emitters with horizontal molecular orientation to in-plane and out-of-plane analysis using GI-WAXD analysis. A study on the relationship between device characteristics and molecular orientation using GI-WAXD analysis for the emitting materials will contribute to basic research on molecular design for high efficiency OLEDs.

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EP05.14.15
Hidden Structure Ordering Along Backbone of Fused-Ring Electron Acceptors Enhanced by Ternary Bulk Heterojunction Yiquan Xiao, MSE, The Chinese University of Hong Kong, Hong Kong, Hong Kong.

Fused-ring electron acceptors (FREAs), as a family of non-fullerene acceptors, have achieved tremendous success in pushing the power conversion efficiency of organic solar cells. Here, the detailed molecular packing motifs of two extensively studied FREAs – ITIC and ITIC-Th are reported. It is revealed for the first time the long-range structure ordering along the backbone direction originated from favored end group π-π stacking. The backbone ordering could be significantly enhanced in the ternary film by the mutual mixing of ITIC and ITIC-Th, which gives rise to an improved in-plane electron mobility and better ternary device performance. The backbone ordering might be a common morphological feature of FREAs, providing explanations to previously observed small open circuit voltage loss and superior performance of FREA-based devices and guide the future molecular design of high-performance non-fullerene acceptor.

EP05.14.16

Organic semiconductors have traditionally been regarded as being delicate with respect to degradation in oxygenated/aqueous conditions, especially in the presence of light. We have recently found that, in fact, numerous examples of organic semiconductors exist where these materials support true photocatalytic redox cycles, often with good stability. One general reaction which proceeds efficiently is the photocatalytic reduction of oxygen to hydrogen peroxide. We have found that both n-type, p-type, and ambipolar semiconductors; small molecules and polymers, can generate peroxide in a wide pH range of 1-12. The p-type materials are additionally suitable for the fabrication of photocathodes, allowing the creation of peroxide-generating photoelectrochemical cells – something previously impossible with inorganic semiconductors. In our work we have made a number of free-standing photocatalytic and photoelectrochemical platforms to produce peroxide, and also have discovered the presence of catalytic peroxide production in the biorganic semiconductors.

EP05.14.17
Quantum Beats of a Multie exciton State in Rubrene Drew Finton, Eric Wolf, Vincent Zoutendier and Ivan Biaggio; Physics, Lehigh University, Bethlehem, Pennsylvania, United States.

We have observed quantum beats in the photoluminescence dynamics of the organic molecular crystal rubrene following photoexcitation by a femtosecond pulsed laser. The application of a magnetic field up to 0.3 T, created by a neodymium permanent magnet, produces periodic modulations in the photoluminescence dynamics. The beat frequency ranges between 0.6 GHz to 1.3 GHz and is dependent upon the relative orientation of the magnetic field and the crystalline axes. The amplitude of the beats increases with increasing magnetic field strength, peaking at about 5% of the non-oscillatory background. These beats are indicative of a multie exciton state consisting of a spin-coherent pair of triplet excitons existing during the singlet-to-triplet exciton fission conversion process.

EP05.14.18
High Speed Wire-Bar Coating of Fullerene- and Non-Fullerene-Based Organic Solar Cells with PCE>10% Neha Chaturvedi, Hanlin Hu, Sukumar
Having recently surpassed the 13% threshold, organic photovoltaics (OPV) are once again becoming promising contenders for low-cost solution-processed thin film photovoltaics. The commercialization of large area OPV devices will require, among other things, the capability of coating active layers at high speed in ambient condition without losing fidelity with the champion devices fabricated by spin coating. For a long time, the focus of OPV research was limited to fullerene based acceptor PC$_{61}$BM and PC$_{71}$BM. The fullerene based acceptors have been widely used, but have several limitations, including lower absorption coefficient, and often require a solvent additive for successful processing. In recent years, non-fullerene acceptors (NFAs) have emerged as a new concept to overcome the limitations associated with fullerene based acceptors and have also been shown to yield highly efficient OPV devices without the use of solvent additives.

In this work, we used blends of the donor polymer PTB7-Th, more commonly known as PCE10 : PC$_6$BM (fullerene based) and PCE10: EH-IDTBR (NFA) as active layer materials. We used spin coating (SC) and wire-bar coating (WBC) to fabricate active layers of the two systems with thickness ranging from 50 to 250 nm. The fullerene based solar cells based on WBC PTB7-Th:PC$_6$BM demonstrated a PCE of 10.2 % comparable to 10.1% for the best spin-coat device. Devices based on NFAs also showed excellent performance with PCE of 10.8% for WBC vs. 10.6% for SC devices. We also fabricated ternary organic solar cells based on NFAs using PCE10:EH-IDTBR:EHDIFB as a photoactive layer and find that the device based on WBC and SC active layer achieved the similar efficiency of 11%. We found that WBC maintained performance parity with SC for active layer thickness <100 nm, but outperformed SC, sometimes significantly, for active layers >100 nm. Systematic comparison of the OPV device figures of merit indicated differences due primarily to the fill factor (FF), pointing to transport-related limitations in thicker solar cells prepared by SC. Indeed, various measurements of carrier transport confirmed the superior carrier mobility achieved in active layers prepared by WBC. Our measurements point to enhancement in the electron mobility as the primary source of the difference. Morphological investigation of the photoactive layers also pointed to enhanced aggregation and coarsening, which we attributed in part to the acceptor domains. Further investigation into the active layer formation kinetics using in situ optical diagnostics reveal the spin-cast ink based on chlorobenzene dried 3-4 times faster than the WBC one. We ascribe the significant differences in electron mobility to the kinetics of solidification and aggregation of acceptor domains. As far as we know, this is the first report where a scalable coating technique appears to outperform the well-known SC technique, considered for years to be the champion processing method for organic solar cells.

**EP05.14.19**

**Tuning of Organic Thin-Film Microstructure Using Graphene as a Growth Template**

Jacob G. Kühnholz, Ole Albrektsen, Martin A. Højgaard, and Jakob Kehlstrup-Hansen.

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Photodetectors made from organic semiconductors is an area of great interest since these materials can be tailored through chemical synthesis techniques and processed as thin-films over large areas at low cost. However, a remaining challenge is the low carrier mobility that makes these materials less suitable for high bandwidth-applications. A possible solution is to combine an organic semiconductor with a graphene layer with superior transport properties, which could form the basis for improved photodetector devices. This requires the ability to control the organic thin-film microstructure, which strongly influences both the optical absorption and the exciton diffusion processes. In this work, we study the growth of the organic semiconductor 5,5"-bis(naphth-2-yl)-2,2':5',2''-terthiophene (NaT3) by investigating the influence of the growth substrate (graphene vs. SiO2) and of the substrate temperature. The resulting thin-films are characterized by atomic force microscopy, x-ray diffraction, and fluorescence spectroscopy. On SiO2, the NaT3 molecules form a polycrystalline film with grains consisting of upright-standing molecules that form distinct terraces and with an average grain size that depends on substrate temperature. In contrast, we observe a significantly different morphology of the thin-film when deposited on graphene. Here, the NaT3 molecules form smaller grains with no observable terraces and with different molecular orientations. At high substrate temperature, a discontinuous thin-film is observed where the molecules assemble into elongated nanofiber morphologies. This gives rise to significantly different optical properties. The NaT3 thin-films on graphene exhibit a much stronger fluorescence signal than the similar thin-films on SiO2, while the NaT3 nanofiber structures emit polarized fluorescence.

**EP05.14.20**

**How Can We Engineer Hierarchical Structures and Pattern Functional Organic Materials?**

Shengyang Chen, Bastian Haehnle, Alexander J. Kuehe, Ioan Botiza, Paul Stavrinou, and Natalie Stingelin.

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Organic materials continue to make an impact on a wide variety of optoelectronic applications due to an ever-increasing chemical design space, novel tools to assemble these interesting materials, and the advancement of novel device architectures and devices. One important aspect thereof is how to achieve assembly not only on the molecular and on the meso-scale, but also on the hundreds of nanometer to micrometer scale. Various devices and applications, indeed, require the active material to be patterned and/or to be deposited at pre-determined locations. In areas, such as the bioelectronics field, step-changes may be achieved when more complex, multidimensional architecture that mimic the hierarchical structures of, e.g., tissues or bones could be man-made using stimuli-responsive functional organic materials. Other potential lies in nano- and micro-engineering multifaceted structures to realize new media with unique interactions with electromagnetic radiation. This would lead to new possibilities to harvest light and manipulate light-matter interactions. Here we use model systems to demonstrate hierarchical assembly of organic nanoparticles, covering a range of systems, from inert polystyrene particles to conjugated polymer emitter particles made, e.g., of polyfluorene-co-divinylbenzene (PF-co-DVB)[1]. We show that surface relief structures can be used to direct this process. Thereby, simple geometrical relationships can be employed to program the particles to deposit into specific sites and patterns: from ordered to disordered arrangements; hexagonally-packed, cubic-packed or random-packed structures; to single layer vs. multilayer architectures. This opens a versatile design platform in terms of the fabrication of multifunctional nano- and microstructures with hierarchies for use in the field of photonics (e.g., in solar cells, light-emitting diodes and optical display devices over large areas), bioelectronics and beyond.


**EP05.14.21**

**Coarse-Grained Approach for Modelling Absorption Strength in Organic Semiconductors**

Alise Virbule, Johannes Lischner and Jenny Nelson.

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Organic semiconductors, such as conjugated polymers, have attracted great interest as candidate materials for solar cells, light-emitting diodes and other photonic applications. The performance of such devices depends upon many properties of the materials, including the spectral range and strength of the optical absorption. Several studies have shown that changes in molecular packing and conformation within in a polymer film can influence the absorption strength. Widely used electronic structure methods such as time-dependent density functional theory cannot access the length scales necessary to study the...
effect of polymer conformation on the optical properties, especially for polymers with large repeat units or high persistence length, so instead coarse-grained methods need to be employed. In this work I am using an extended Hubbard Hamiltonian parameterized from first principles calculations to calculate the optical properties of different types of oligomers and study how their absorption strength depends on chain length. The long-term goal of this project is predicting spatially averaged optical properties of a macromolecular material using the knowledge of the excited states of atomic scale building blocks and of the molecular conformations present in the film. Such methods will help understand the macroscopic absorption properties of known compounds and thus aid the design of new organic materials exhibiting high optical absorption.

EP05.14.22
Machine Learning Based Ab Initio Numerical Study of Charge Transport within Non-Crystalline Organic Semiconductors Waldemar Kaiser, Jonas Lederer and Alessio Gagliardi; Technical University of Munich, Munich, Germany.

Organic semiconductors (OSC) are considered as highly feasible for the use in opto- and bioelectronic applications. The relatively low charge carrier mobility limits its current applicability. Insight into electronic structure-property relations is required to understand how to enhance the mobility. Various groups have been working towards a better understanding of the dependence of the mobility both relying on chemical intuition as well as using theoretical approaches covering structural information from molecular dynamics (MD) over transport properties using kinetic Monte Carlo (kMC) [1-3]. Mentioned numerical methodologies provide insight of transport for small perturbations from a crystalline structure. However, there is a lack of description for strongly non-crystalline structures such as solution processed OSCs due to the high computational effort associated with the calculation of all individual transition rates required for precise kMC studies.

In this work, we present a machine learning (ML) based ab-initio multi-scale simulation for charge transport within strongly non-crystalline OSCs using pentacene as a case study. ML allows for efficient and effective modeling of transport properties and helps to overcome conventional physical models that rely on empirical parametrizations or semi-empirical calculations. Using MD and density functional theory (DFT), we generate training data for the coupling integrals between adjacent molecules (dimers) of pentacene. The ML algorithm bases on the kernel ridge regression including an optimized set of descriptors for the respective dimers. To cover the range from the coupling integrals to charge mobilities, we couple the ML algorithm with our off-lattice kMC software [4]. The center of mass positions of the molecules within a non-crystalline pentacene film are used to generate the Voronoi tessellation which allows computing charge hopping across amorphous structures. ML helps to estimate coupling integrals within the Marcus theory without the need for a precomputation of each dimer configuration. We overcome existing ab-initio simulations by a tremendous reduction of computational demand and allow a generalized description for a wide range of structural disorder within the organic layer without a need to compute coupling integrals from scratch. We show how the directionality of the charge transport is influenced by varying the degree of crystallinity. Furthermore, we compute the field- and temperature dependence for non-crystalline pentacene layers stacked on top of a silicon oxide substrate, as used for thin-film transistors, and compare our ML-based approach with empirical kMC results.


EP05.14.23
Dopant Diffusion in Sequentially Doped Poly(3-hexylthiophene) Studied by Infrared and Photoelectron Spectroscopy Patrick N. Reiser1,2, Lars Müller1,2, Vipilan Sivanesan1,2, Robert Lovricic1,2, Stephen Barlow1, Seth R. Marder3, Annamariucci Pucci1,2,4, Wolfgang Jaegermann1,2, Eric Mankel1,2 and Sebastian Beck1,2,3,4,5,6,7,8, Materials Science Department, Surface Science Division, TU Darmstadt, Darmstadt, Germany; 2InnovationLab, Heidelberg, Germany; 3Kirkhoff Institute for Physics, Heidelberg University, Heidelberg, Germany; 4Institute for High-Frequency Technology, TU Braunschweig, Braunschweig, Germany; 5Center for Organic Photonics and Electronics and School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, Georgia, United States; 6Centre for Advanced Materials, Heidelberg University, Heidelberg, Germany.

A key to enable high-performing organic electronic devices is given by proper interface engineering of organic layers. Doped organic transport layers are used to improve charge carrier injection and to reduce ohmic losses. The diffusion of dopants into adjacent layers is known to cause exciton quenching in photo-active layers and to reduce the long-term stability of many types of organic electronic devices. On the other hand, the diffusivity of dopants can be beneficially used in a sequential deposition scheme that allows for doping and at the same time high order of the matrix material. Here, we investigate the diffusion of a bulk sequentially deposited p-dopant in poly(3-hexylthiophene) (P3HT) thin films using non-destructive in-situ infrared (IR) spectroscopy and photoelectron spectroscopy (PES). The dopant diffusion is resolved by differentially evaluating electron transfer in the bulk and at the surface for varying dopant coverage. Using PES and IR spectroscopy, it is possible to determine the concentration at which both charge transfer and dopant incorporation into the polymer film saturate. By means of PES we find that charged dopants are less mobile in the diffusion process than neutral molecules. A comparison of the diffusivity in semi-crystalline and fully amorphous P3HT indicates that semi-crystalline P3HT yields a higher capacity for dopants varying dopant coverage. Using PES and IR spectroscopy, it is possible to determine the concentration at which both charge transfer and dopant incorporation into the polymer film saturate. By means of PES we find that charged dopants are less mobile in the diffusion process than neutral molecules. A comparison of the diffusivity in semi-crystalline and fully amorphous P3HT indicates that semi-crystalline P3HT yields a higher capacity for dopants.

EP05.14.24
Temperature Influence on the Charge Carrier Mobility and on Langevin Reduction Coefficient in Organic Bulk-Heterojunction Solar Cells—Effects of DIO Additive Roberto M. Faria1, Daniel Roger B. Amorim1, Francineide L. Araújo1 and Douglas J. Coutinho2; 1Univ of Sao Paulo, Sao Carlos, Brazil; 2Câmpos Toledo, Technical Federal University of Paraná, Toledo, Brazil.

We have derived an analytical expression for the photocurrent of organic bulk-heterojunction solar cells, taking into account second-order kinetics for bimolecular recombination. Concomitantly, we have carried out current-voltage measurements (J-V) in dark and under 1 Sun illumination, at different temperatures, in devices made with PTB7-Th:PC71BM blends, processed either from a solution of pure chlorobenzene or from a mixture of chlorobenzene and the co-solvent 1,8-diiodooctane (DIO). It is already known that DIO additive selectively dissolves the fullerene and reduces the domain sizes of PC71BM forming a donor-acceptor bicontinuous interpenetrating network, resulting in an increase of the device external quantum efficiency. From the adjustments obtained by the Mott-Gurney equations on the measurements in dark, and that of the photocurrent equation on the photovoltaic responses, we analyzed the effect of temperature on the charge carriers mobility and on the Langevin reduction factor. It was evident that the effect of DIO on the morphology of the active layer improves the conduction process by hopping, and decreases the recombination coefficient. This improvement of the photocurrent response is most probably due to the fragmentation of the PCBM aggregates and their better permeation in the polymer matrix of PTB7-Th:PC71BM, which facilitates the dissociation of charge transfer states at PTB7-Th:PC71BM interfaces.

EP05.14.25
Revisiting Charge Transfer Energies for Organic Photovoltaics Shahidul Alam1,2, Aman Anand1,2, Christian Friebel1,2, Johannes Ahner2, Stephanie
Hoppener1, 1, Martin D. Hager1, 1, Ulrich S. Schubert1, 2 and Harald Hoppe1, 1; 1Center for Energy and Environmental Chemistry Jena (CEEC Jena), Friedrich Schiller University Jena, Jena, Germany; 2Laboratory of Organic and Macromolecular Chemistry (IOMC), Friedrich Schiller University Jena, Jena, Germany; 1Jena Center for Soft Matter (JCSM), Friedrich Schiller University Jena, Jena, Germany.

Traditionally the photo-induced charge transfer occurring at the donor-acceptor interface within an organic semiconductor (bulk) heterojunction is considered to be driven by the energy level offset between the corresponding lowest unoccupied molecular orbitals (LUMO) of the same. Commonly, these energy offsets between LUMO levels of donor and acceptor are taken from cyclic voltammetry (CV) characterization of organic semiconductors in film or solution. Besides some obvious limitations for transferring these energy levels from solution to film, this model does not seem to be applicable in all cases. We found several cases in which novel non-fullerene acceptors do not exhibit successful charge transfer, even though energetics suggests so. Various spectroscopic, morphological and structural characterization methods have been used for finding an explanation.

EP05.14.26 Photothermal Patterning of Semiconductor Polymer Microstructures Justin Mulvey1, Ian Jacobs2, Tucker Murray4, Owen Lee5, Zaira I. Bedolla-Valdez2 and Adam J. Moule1; 1University of California, Davis, Davis, California, United States; 2University of Cambridge, Cambridge, United Kingdom.

Thin film organic semiconductors (OSC) are widely studied for applications in organic thin film transistors (OTFT) and organic photovoltaic’s (OPVs) because they are light weight, flexible, and are compatible with inexpensive roll-to-roll processing. One challenge for implementation of OSC’s devices is the difficulty to patterning the surface of devices. Traditional inorganic patterning methods such as soft lithography or photore sist are unable to consistently produce submicron scale surface patterns. Our research group recently developed a solution processing technique to pattern OSC called photothermal patterning. For this method, a laser is used to locally heat a solvent-swollen polymer film in a theta solvent. The laser increases the temperature enough to induce dissolution of the irradiated polymer and thereby creates a patterned polymer with diffraction limited resolution. Before photothermal patterning can be implemented for industrial-scale large-area patterning of OSC devices, a better understanding of etching rate and solvent quality is required. Here, etching rate is studied as a function of light intensity and organic solvent using thin films of poly(3-hexylthiophene)(P3HT) and other OSCs. The relationship between patterning depth, laser power, dwell time, irradiation wavelength, local temperature change, and solvent quality are studied to obtain reproducible patterning parameters. With a better understanding of etching rate, photothermal patterning can potentially be used for large-area submicron OSC patterning.


Various ultra-low-bandgap polymers with an optical bandgap \( E_g \) of around 1.1–1.3 eV have been developed and employed for polymer solar cells (PSCs) because achievable short-circuit current density \( J_{sc} \) increases with lowering \( E_g \). Nevertheless, PSCs consisting of ultra-low-bandgap polymers routinely lagged behind their conventional low-bandgap polymer analogues. Here, we study an intrinsic limit for photocurrent generation using ultra-low-bandgap polymers with an \( E_g \) of around 1.1–1.3 eV.

We measured femtosecond transient absorption for these polymer films, and found that singlet excitons generated in these polymers rapidly decay with negligible photon emission. The non-radiative decay rate scales exponentially with the bandgap \( E_g \), which is so called “energy gap law”. Our results suggest unavoidable disadvantage for ultra-low-bandgap polymers. Accordingly, we will discuss optimal design concept for high efficient PSCs.

EP05.14.28 Optical and Electrical Properties of Mixed-Solution and Sequentially Processed poly(3-alkylthiophene): F4TCNQ Films Owen Lee1, Zaira I. Bedolla-Valdez2, Alejandra N. Ayala-Oviedo1, Alexa A. Portillo1 and Adam J. Moule1, 1; 1Chemical Engineering, University of California, Davis, Davis, California, United States; 2Materials Science & Engineering, University of California, Davis, Davis, California, United States.

Doping semiconducting polymers often results in a drastic reduction in the solubility of the polymer. While much research has been conducted on the electrical and optical properties of thin films of poly(3-alkylthiophenes) (P3ATs) with side chain lengths between 3 and 9 deposited using a range of solvents [1], little research has been done on the effect of the doping method on the optical and electrical properties of these films. Previous work from our group compared the optical and electrical properties of P3HT:F4TCNQ films prepared via a mixed-solution method to the properties of films doped sequentially. Previously we showed that that films doped sequentially exhibited higher conductivities than those doped using the mixed-solution method. Furthermore, we showed that the choice of sequential doping solvent controls whether or not dopant anions are inserted into crystalline domains within the solid polymer matrix [2]. Here, we generalize these conclusions for other sequentially doped P3ATs using a variety of doping solvents. Using UV-Vis spectroscopy, we show that it is possible to control the doping level of P3AT films by varying the dopant concentration and solvent quality. Four-bar conductivity measurements confirm that sequentially doped P3ATs generally exhibit higher conductivities than those processed via mixed-solution. This indicates that the electrical advantages of the sequential doping process are not limited to P3HT films.

EP05.14.29 Quantum Tunneling on Metal/N-Doped Polymer Semiconductor Shin Sakiyama and Katsushiko Fujita; Kyushu University, Kasuga, Japan.

Efficient n-type doping was not established since the dopants dose not dissolve in same organic solutions of polymer semiconductors. Evaporative Spray Deposition using Ultra-dilute Solution (EDSU) method enabled it recently. We have already reported efficient n-type doping of poly(2-methoxy-5-(2’-methyl-hexyloxy)-p-phenylenevinylene) (MEH-PPV: LUMO: 3.1 eV, HOMO: 5.2 eV). The high doping efficiency as much as 15% was realized. In our group we compared the optical and electrical properties of P3HT:F4TCNQ films prepared via a mixed-solution method to the properties of films doped sequentially. Previously we showed that that films doped sequentially exhibited higher conductivities than those doped using the mixed-solution method. Furthermore, we showed that the choice of sequential doping solvent controls whether or not dopant anions are inserted into crystalline domains within the solid polymer matrix [1]. Here, we generalize these conclusions for other sequentially doped P3ATs using a variety of doping solvents. Using UV-Vis spectroscopy, we show that it is possible to control the doping level of P3AT films by varying the dopant concentration and solvent quality. Four-bar conductivity measurements confirm that sequentially doped P3ATs generally exhibit higher conductivities than those processed via mixed-solution. This indicates that the electrical advantages of the sequential doping process are not limited to P3HT films.
at Al/MEH-PPV junction at the high doping concentration.

In order to evaluate depletion layer width on Al/MEH-PPV junction, C-F measurement was carried out. As a result of the calculation, the depletion layer width of the 0.2 wt% doped device was 16.3 nm, the 2.0 wt% doped device was 9.3 nm, and the 10.0 wt% doped device was 3.3 nm. These results suggest that the depletion layer narrows as the doping concentration increases and the rectification property disappears in the 10 wt% doped device by quantum tunneling. The depletion layer width when quantum tunneling was observed in the p-type organic device, Au/ZnPc:0.3% F4-TCNQ/Au, was 5.2nm. Compared with this depletion layer width of 5.2 nm at metal / p-type organic semiconductor junction, it can be said that the value of 3.3 nm calculated this time is sufficiently narrow to observe quantum tunneling.

EP05.14.30
Fundamentals of Contact Resistance Extraction in Organic Field-Effect Transistors
Hyoseok Kim, Gyeongsang National University, Jinju, Korea (the Republic of).

For the last decade, there has been massive evolutions in organic electronic devices and their novel applications such as organic field-effect transistors (OFETs), organic light-emitting diodes (OLEDs) and organic photovoltaics (OPVs). Moreover, a wide range of printing techniques has proven the process innovation with soluble materials. The limited source of contact electrodes, however, makes the barrier for the commercialization of the printing process with the soluble materials composed of metallic and non-metallic conductors.

Those devices are basically composed of two- or three-terminal contacts which have the interfaces of metal/semiconductor (SC), dielectric/SC and SC/SC. Thus, the interfacial engineering is predominant to realize those devices for flexible application. A crucial issue concerning charge injection at the interface of electrode/organic semiconductor is recently rising in order to improve the electrical performance of diodes and FETs.

This presentation gives an investigation on charge injection via the modification of electrodes with self-assembled monolayers (SAMs) in organic electronic devices. Functionalized SAMs with fluorine at the end group plays a substantial role to improve charge injection through a dipolar effect to decrease barrier height at the electrode/semiconductor interface in a planar diode and organic field effect transistors (OFETs). This is extended to significant enhancement of electrical performance such as field effect mobility and contact resistance in OFETs.

In addition, for a practical application of the extraction technique mentioned above, we particularly suggested the simple interface control engineering to reduce contact resistance and improve electrical characteristics in n-type OFETs with the semiconductor (PNDI2OD-T2). Inkjet-printed Ag metals are implemented for the n-type polymer OFETs as electrodes. Then, it is introduced by the two types of SAMs, thiolphenol (TP) and pentafluorobenzene thiol (PFBT) for the electrodes. Throughout the suppression of the Schottky barrier height with TP in the OFETs, the electron injection is prominently improved as observed previously. We also demonstrated that all solution-processed n-type OFETs can be polarity-inversed by the interface treatment of PFBT onto the inkjet-printed Ag electrode. A remarkable improvement, therefore, was found for the OFETs with the TP-Ag electrodes with high electron mobility of 0.11 cm²/Vs. Additionally, largely low contact resistance of 480 kΩ*cm confirms that TP-Ag can be a great candidate for an excellent electrodes compatible with inkjet-printing for the n-type semiconductors. It indicates that the work function of the inkjet-printed Ag electrodes is variable for a massive scope by the simple interface engineering. As a result, it may be commonly applied for the fabrication of all solution-processed electronics for a variety of applications.

EP05.14.31
Growth Domain Size of Conjugated Polymer Film by Kinetic Control of Metastable States for High-Performance N-Type Field-Effect Transistors
Yeon-Ju Kim, Kyoungtae Hwang, YeonSu Choi and Dong-Yu Kim; Gwangju Institute of Science and Technology, Gwangju, Korea (the Republic of).

Organic field effect transistors (OFETs) have attracted much interest for future electronics because they can have flexibility with processing from solution at low temperature. Recently many researches make an attempt to control the film morphology which directly correlated to the charge transporting ability of conjugated polymers. In this work, we demonstrated optimized poly[(N,N'-bis(2-octyldodecyl)-naphthalene-1,4,5,8-bist(carboximide)-2,6-diyl)-alt-5,5’-(2,2’-bithiophene)] (PNDI2OD-T2) film morphologies, which are obtained by precisely regulating the solidification rate in the metastable state using a novel simple method. The kinetic control in the metastable state brings about dramatic morphological changes in both polymer domain sizes and molecular packing structures. The optimized PNDI2OD-T2 films provide significantly increased electron mobilities up to 3.99 cm²/Vs, which is a significant improvement in performance by nearly 100-fold as compared to conventional spin-coated devices. The observation of low activation energy according to the temperature-dependent behavior in optimized thin films can support the achievement of high electron mobilities of semiconducting polymers.

EP05.14.32
Long-Range Coherent Charge Transport in Physisorbed Molecular Layers
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The charge transport in molecular ensembles is intrinsically related to a series of carrier-molecule quantum interactions which result in a variety of chemical and biological phenomena. Its understanding has paved the way for the development of novel device concepts, such as organic transistors, organic light-emitting diodes, and biosensors [1]. At the nanoscale, such interactions are commonly described as either direct tunneling for the 1-10 nm range or activated hopping for longer distances. However, the continuous transition between coherent tunneling and activated conduction as a function of the barrier width remains unknown for physisorbed molecules. This work describes the first experimental evidence of long-range (> 10 nm) coherent tunneling occurring for physisorbed small-molecule semiconductors-based vertical junctions. By investigating the charge transport in copper-phthalocyanine (CuPc) thin films, we have identified the sequential tunneling as the long-range charge transport mechanism. Such a sequential coherent process is not only different from the direct tunneling but intrinsically distinct from the hopping conduction. Consequently, a gradual transition from direct tunneling to sequential tunneling, within the 10-22 nm barrier width, to hopping conduction can be verified. The evidence of coherent charge transport across long distances has implications for a variety of quantum effects that have not been previously confirmed for films with thicknesses larger than a few nanometers [2]. Therefore, our results contribute to bridging the gap between molecular and organic electronics [3,4].

Acknowledgments:

References:

EP05.14.33
Controlled Self-Assembly of 1D Nanoscale Materials and Their Resulting Photophysical Properties

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Efficiency of organic optoelectronic devices is dependent on the intermolecular interactions of molecular assemblies that can favor charge transfer or radiative recombination. My work pertains to understanding whether directional charge transfer seen in extended crystals of 7,8,15,16-tetrazaterrylene is an intrinsic property of the 1D n-type semiconductor or an extrinsic property caused my subtle defects in the p-stack direction. We use solvent vapor annealing to crystallize nanoscale aggregates (<500 nm), and extended, highly ordered, crystals microns long. We probe the effect that order has on directional charge separation in these species using single molecule techniques and polarized optical excitation coupled with time resolved photoluminescence spectroscopy, this produces photoluminescence decays that have power law signatures, indicative of the presence of charge separated states. The observation of enhanced power-law photoluminescence decay at critical stages of crystal growth support intrinsic charge separation favoring a promising molecular design platform for organic semiconductor materials.

Global Equilibrium and Non-Equilibrium Theory of Hopping Exciton Transport in Disordered Semiconductors

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The phenomenon of exciton diffusion is found to play a role in a remarkably wide range of physical systems including disordered organic semiconductors, nanocrystalline quantum dots, semiconducting carbon nanotubes and photosynthetic biological systems. Moreover, there is a growing interest in describing the electronic exciton energy transfer because exciton dynamics determines function in many technological applications. For example, thin film organic solar cells exciton diffusion drives charge separation, in organic light emitting diodes it determines the brightness and color of the device, in scintillator detectors it controls the response function and yield, while in quantum communication systems it facilitates photon antibunching.

We develop a temperature dependent theory for singlet exciton hopping transport in disordered semiconductors. It draws on the transport level concept within a Förster transfer model and bridges the gap in describing the transition from equilibrium to non-equilibrium time dependent spectral diffusion. We test the validity range of the developed model using kinetic Monte Carlo simulations and find agreement over a broad range of temperatures. It reproduces the scaling of the diffusion length and spectral shift with the dimensionless disorder parameter and describes in a unified manner the transition from equilibrium to non-equilibrium transport regime. We find that the diffusion length in the non-equilibrium regime does not scale with the the third power of the Förster radius. The developed theory provides a powerful tool for interpreting time-resolved and steady state spectroscopy experiments in a variety of disordered materials, including organic semiconductors and colloidal quantum dots.

Direct Characterization of Nanoscale Molecular Ordering in Organic Optoelectronic Materials Using 4-Dimensional Scanning Transmission Electron Microscopy

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The local ordering of the constituent molecules can directly affect the charge transfer and efficiency of the organic electronic devices and solar cells. Efforts to understand the ordering has involved theories and simulations, and experimental characterization, such as using X-ray diffraction. While these methods have provided important information about the ordering, more detailed information on how the ordering forms at the nanoscale level and how it affects the local and overall properties has remained difficult to determine. To fill the gap in the characterization, it is required to develop a new experimental method that uses a small (nanoscale) probe. Here we present the new 4-dimensional scanning transmission electron microscopy (4D-STEM) that can determine the detailed structure of molecular ordering in organic semiconductors. Our 4D-STEM uses a highly coherent electron probe that generates the diffraction signals directly from the local ordering, which are then captured by a new-generation pixelated fast STEM detector. By scanning the probe over a large area, we acquire a few tens of thousands of nanodiffraction patterns from one organic sample. We then subsequently analyze the patterns using intensity variance and angular correlation functions to convert them into a real space map of the ordering, which can reveal the details of the type, size, connection, and distribution of the ordering with unprecedented precision. We will present the data from two materials, P3HT and IDTBT, and demonstrate how the local ordering, which we control using different synthesis parameters, affects their physical and electronic properties.

Radiative Recombination and Exciplexes in All-Polymer Organic Semiconductor Bulk-Heterojunctions

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Organic bulk-heterojunctions of conjugated polymers and fullerenic derivatives have been used extensively in organic photovoltaic devices in the past two decades. Although blends of conjugated polymers and fullerenic derivatives exhibit efficient exciton dissociation upon solar illumination, the solar power
conversion efficiency reached using these materials is at least a factor of two less than that predicted by the Shockley-Queisser theoretical limit. Non-radiative recombination of charge carriers due to efficient exciton quenching by fullerene derivatives is a significant factor preventing organic bulk-heterojunction materials from reaching the Shockley-Queisser limit. Therefore, in recent years there has been greater interest in developing and understanding fullerene-free organic bulk-heterojunctions that are expected to be less prone to non-radiative recombination.

The goal of our work is to understand the influence of altering the radiative decay rate (using the Purcell Effect) of charge transfer excitons on photovoltaic performance. In this study, we investigate radiative recombination and charge transfer excitons at the interface of electron donor:acceptor blends of two polycarbonate-based conjugated co-polymers. The heterojunction formed by the two phases is a type-II heterojunction, in which efficient charge separation is expected to occur. Photoluminescence spectroscopy shows quenching of emission from both polymers in the blends. An additional low-energy emission peak is observed in the blends which is not present in the spectra of either polymer alone. Quenching is more efficient in a 1:1 donor:acceptor blend than in a 1:2 donor:acceptor blend and in the 1:1 blend, the additional emission peak is more intense. In addition, the blends have longer photoluminescence lifetimes than the individual polymers. These measurements indicate that efficient photo-induced charge transfer occurs in the blend, and the additional low-energy emission peak observed in the blend can be attributed to emissive charge transfer excitons (i.e., exciplexes). Future work includes measuring the photoluminescence and quantum efficiency of the conjugated polymer donor:acceptor blends and calculating the radiative decay rates. Plasmonic nanostructures will be incorporated in the organic semiconductor blend that are resonant with the exciplex emission. This will allow us to study the impact of the Purcell effect on charge transfer and exciplex emission. Additionally, electroluminescence and photocurrent measurements of all-polymer bulk-heterojunction devices containing resonant plasmonic nanostructures will be studied to understand if accelerated radiative recombination of charge transfer excitons can be beneficial to photovoltaic device performance.

EP05.14.38
Mechanism of Geminate Polaron Pair Generation in π-Conjugated Polymers

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In this work, we address the mechanism of geminate-charge generation in neat semi-crystalline polymeric semiconductors by means of delayed photoluminescence (PL) [1,2]. We implement time-dependent and steady-state PL spectroscopies to study the yield and recombination rate of geminate polarons. We compare the dynamics of delayed PL at varying magnetic field and temperature. We find that there are significant magnetic field effects on the recombination, which increases the relative quadrature signal of the CW PL with the increase of the magnetic field. This points to charge-transfer intermediate states between singlet excitons and geminate polaron pairs, with strongly mixed singlet and triplet character.


EP05.14.39
Doping Induced Solubility Control Patterning for Organic Thin-Film Transistors

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Moore’s law for computing is driven by the development of methods to scale-down the size of individual transistors in integrated circuits using photolithography. A major obstacle for scaling organic thin-film transistors (OTFTs) is the lack of a patterning method comparable to photolithography. Traditional photolithography cannot be applied to organic semiconductors because of high mutual solubility/miscibility between polymers and cross-linking often leads to formation of defects that reduce the electronic performance. Our research group recently developed a new and potentially scalable patterning technology for organic semiconductors called dopant-induced solubility control (DISC) which is compatible with digital direct-write patterning and sequential roll-to-roll (R2R) solution coating. Using DISC patterning process, it is possible to stack mutually soluble materials and laterally pattern polymer films with light, achieving sub-micrometer, optically limited feature sizes. In the present work we demonstrate that DISC processing enables OTFTs fabrication with short channels that will increase switching speeds. We fabricated short channel transistors with doped polymers for the drain and source electrodes. This presentation will detail how short channel OTFTs were fabricated using all solution processes. We will also detail the performance advantages of short channel OTFTs as well as discuss the lifetime issues associated with dopant drift.

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EP05.14.40
Effect of Disorder on the Thermoelectric Properties of Semiconducting Polymers

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Organic thermoelectric (TE) materials hold tremendous potential to address the ever-increasing demand for sustainable and renewable energy resources. Recently, a ZT~0.25 has been reported in PEDOT: PSS, upon optimizing the carrier concentration. This, combined with advantages such as low cost, easy synthesis, and an inherently low thermal conductivity, makes polymers a very attractive choice for commercially viable TE applications such as large-scale Peltier coolers and electricity generation from waste heat is naturally limited sources. A long-standing problem in TE materials is the interdependence of transport coefficients, which makes it difficult to simultaneously increase the Seebeck coefficient and the conductivity. We find that numerical transport models can play a key role in predicting the optimum structural characteristics and aid the design and development of novel materials for TE applications. In this work, we investigate the TE properties of disordered organic semiconductors, and establish the effect of carrier concentration, disorder and correlation in energy on the TE Seebeck coefficient, electrical conductivity, and the Lorenz number. Our charge transport model is based on electron hopping between localized sites with a Gaussian disorder model for their energies. We iteratively solve the non-linear Pauli master equation to compute the time-averaged occupational probabilities of the sites from which relevant transport quantities are calculated. Our results show that large overlap between localized electronic states can improve the electrical conductivity without adversely affecting the Seebeck coefficient. Positional disorder affects the overlap between neighboring states and aids in the formation of conduction paths with an increased probability of carriers in high energy sites, ultimately leading to simultaneous increase in electrical conductivity and Seebeck coefficient. We introduce positional correlation to investigate the role of partial ordering and find that it negatively affects conductivity. On the other hand, energetic disorder widens the density of states and leads to increased energy gap between neighboring sites, thus hindering transport and adversely affecting both conductivity and Seebeck. Surprisingly, correlation in energies of nearby sites has no effect on the TE properties. We also find that Lorenz number increases with Seebeck coefficient, largely deviating from the Sommerfeld value and the universal trend observed across all materials exhibiting band transport, and it deviates further with increasing positional and energetic disorder. We conclude that controlling energetic and positional disorder allows us to decouple conductivity and Seebeck coefficient. Decreasing correlation and increasing positional disorder while minimizing energetic disorder simultaneously improves both Seebeck and conductivity resulting in a higher TE power factor.

Semiconducting polymers are the subject of much interest and study as active elements in a number of electronic devices. Among these devices, organic photovoltaics are particularly attractive due to their potential light weight, low cost and mechanical flexibility. Crucial to the performance of photovoltaic devices is the generation of charge carriers, which occurs through the dissociation of excitons. A clear understanding of exciton formation, dissociation, and recombination in OPVs is necessary for the design of more efficient devices. We focus on the stability of exciton and the energetics of their dissociation and separation into charge carriers that can then be transported to the electrodes. Excitons are excited electron and hole pair bound by a Coulomb interaction. For separation into individual carriers, the binding energy of the exciton must be overcome. We use a model Hamiltonian based on the tight binding approximation to describe the exciton binding energy and its dissociation potential, for an exciton confined to a 1D lattice. Our model takes into account polaronic effects arising from the reorganization of nuclei and from polarization of the surrounding dielectric, which substantially stabilize the separated carriers and affect the exciton dissociation potential. We examine the effects of an applied electric field on the dissociation potential, and relate the field strength necessary to unbind the hole-electron pair to the maximum attractive Coulomb force between them. We then study the exciton at a 1D donor-acceptor interface, which polarizes the exciton. We explain the exciton polarization by observing how its dissociation potential is altered by the interface. The interface not only polarizes the exciton but makes it easier to be unbound by an external factor, as evidenced by a reduced electric field strength necessary for charge separation.


Interfacial chemistry at organic-inorganic contact critically determines function of a wide range of molecular and organic electronic devices and other systems. The chemistry is, however, difficult to understand due to the lack of easily accessible in-operando spectroscopic techniques that permit access to interfacial structure on a molecular scale. Herein we compare two analogous junctions formed with identical organic thin film and different liquid top-contacts (water droplet vs. eutectic gallium indium alloy) and elucidate the puzzling interfacial characteristics. Specifically, we fine-tune the surface topography of the organic surface using mixed self-assembled monolayers (SAMs): single component SAM composed of rectifier (2,2’-bipyridyl-terminated n-undecanethiolate; denoted as SC11BIPY) is systematically diluted with non-rectifying n-alkanethiolates of different lengths (denoted as SCn where n=8, 10, 12, 14, 16, 18). Characterization of the resulting mixed SAMs in wettability and tunneling currents with the two separate liquid top-contacts allow us to investigate the role of phase segregation and gauche defect in the SAM/liquid interfaces. The results reported here show the difference in length between SC11BIPY and SCn is translated into nanoscopic pits and gauche-conformer defects on the surface, and the difference in contact force—hydrostatic vs. user pressures—and hence conformity of contact accounts for the difference in wettability and rectification behaviors. Our work provides an insight into the role of molecule-electrode interfacial defects in performance of molecular-scale electronic devices.


The study of charge transport by quantum tunneling phenomena across organic thin films has been actively studied for many years in various academic fields. In molecular electronics, while single-component self-assembled monolayers (SAMs) have been previously main organic component, little has been investigated on how heterogeneity of monolayer affects the charge transport behavior across it. Here we focus on binary mixed SAMs composed of two different n-alkanethiolates of different lengths formed on ultraflat template-stripped gold substrate. Electrical characterization of mixed SAMs using liquid eutectic gallium-indium alloy reveals that the surface topography of monolayer largely depends on the difference in length between the thiolates, and the surface heterogeneity is translated into the distribution of tunneling current density. As the length difference is more significant, more phase segregation takes place, leading to increase in the modality of Gaussian fitting curves. Consequently, statistical analysis permits access to deconvolution of tunneling currents, mirroring the phase segregated surface. Our work provides an insight into the role of surface topography in performance of molecular-scale electronic devices.

EP05.14.44 Crystal Structures and Superradiance of Organic Semiconductors at 2D Limit. Beilei Sun, Xin Xu, Zefeng Chen and Jianbin Xu; The Chinese University of Hong Kong, Sha Tin District, Hong Kong.

Organic semiconductors (OSCs) have attracted great attention for decades because they offer intriguing prospects for high throughput, low-temperature processing of electronic circuitry on flexible substrates. However, previous studies mainly focused on bulk single crystal or polycrystalline or amorphous thin films with disorders and grain boundaries. The intrinsic properties of OSCs in the vicinity of the device interfaces are rarely studied, although the interfaces have important influence on the electronic and optoelectronic properties of device. We have prepared high quality few-layer thin films of N,N'-diterdecyleneperylene 3,4,9,10-tetracarboxylic diimide (PTCDI-C12) by physical vapor transport (PVT) method and further characterized the crystal structure and optical properties of the first three layers in the proximity of the substrate. It is found that the first layer adopts a different molecular packing arrangement, whilst the overlayers exhibit different optical properties. Superradiance is observed in the single and bilayer as well as trilayer films, but decreases with the increase of film thickness and then disappears in the bulk material. The superradiance intensity shows an opposite trend as the sample temperature increased. The intensity at 140 K is about 9 times of that at 290K. The linewidth becomes narrower at lower temperature. The full half width at maximum (FWHM) drops from 10 nm at room temperature to 4.3 nm at 140 K.


Graphene plasmonics has attracted widespread attention in recent years due to their rapid frequency tunability, long plasmon lifetime, and strong light confinement. However, the two-dimensional (2D) nature of graphene imposes stringent requirements on the underlying substrate and limits the plasmon enhancement modes that can be excited. One of the solutions to overcome the limited performance of 2D graphene plasmons is through the fabrication of self-assembled graphene nanotubes. We have realized the 3D graphene nanotubes using the plasma in a reactive ion etching (RIE) system to trigger a surface tension based self-folding caused by grain coalescence in a tin sacrificial hinge. The parameters in the RIE process have also been tuned to control the gap size within nanotubes, and also achieve extremely high aspect ratio (length/radius ~ 10,000) tubes. The radial coupling of plasmons at the opening of the tube creates a virtual uniform cross-section area of extremely strong field enhancement as compared to the rapidly decaying fields in 2D graphene. If
small longitudinal gaps are introduced in the nanotubes, propagating surface and edge modes are achieved with intensity based on the gap length between these edges. The propagating modes in the high aspect ratio nanotubes can be utilized for plasmonic waveguides with extremely high propagation lengths. Furthermore, the self-assembled multi-layered (Al2O3/Graphene/Al2O3) nanotubes can be fabricated with an array of horizontally short discontinuous graphene segments as long as the outer layers are maintained as continuous. The smaller aspect ratio graphene segments undergo not only radial plasmon coupling but also a longitudinal coupling between the discontinuous segment openings, creating strong uniform field throughout the volume of the multi-layered tube. The lower contact area of the 3D graphene tubes with the underlying substrate leads to a lower capacitive coupling that causes significant ohmic losses through non-radiative plasmon relaxation due to coupling between plasmons and substrate carriers in metallic and semiconducting substrates. The lower plasmon damping leads to a 13 times stronger field that extends throughout the completely closed graphene tubes as opposed to corner confined weaker field in 2D ribbons on a silicon substrate. The stronger fields throughout the tube structure exhibit a fourfold enhancement in sensitivity and overcome the need to bind targeted molecules to the surface of graphene as exhibited by the example of A/G protein. The 3D graphene nanotubes achieve distinct edge and volumetric enhancement modes while simultaneously increasing the compatibility of graphene with diverse substrates without deterioration in plasmonic properties for application in novel optical and electronic devices.

EP05.14.48

Thermally Activated Delayed Fluorescence Based on Diphenyl-Sulfone Derivatives with Different Molecular Configuration
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Thermally activated delayed fluorescence (TADF) is a promising candidate for light-emitting diodes that can be used as the sensitizer, and the overall conversion efficiency of the triplets into singlets approach 80%. Besides, the operation lifetime of the blue OLED using STTA emission was elongated by ~3x due to separation of charge recombination zone in the sensitizer layer and the overall conversion efficiency of the triplets into singlets approach 80%. Besides, the operation lifetime of the blue OLED using STTA emission was elongated by ~3x due to separation of charge recombination zone in the sensitizer layer and the overall conversion efficiency of the triplets into singlets approach 80%.

EP05.14.47

Universal Triplet Diffusion and Singlet Blocking Layer for Sensitized Triplet-Triplet Annihilation in Solid-State Thin Films with Different Sensitizers
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Sensitized triplet-triplet annihilation (STTA) involves two components: a triplet-triplet annihilation (TTA) material where two triplets can fuse to a singlet for light emission, and a sensitizer material to provide the triplets to the TTA material. Typically, the sensitizer has a lower singlet energy than the TTA material, which results in singlet quenching (SQ) of the TTA signal in solid-state optoelectronic devices (such as organic light-emitting diodes), lowering the efficiency. Here, we show that a triplet diffusion and singlet blocking (TDSB) layer between the sensitizer and TTA material allows the triplet exciton to diffuse from sensitizer to TTA but blocks the singlet quenching of TTA emission by sensitizer. Obviously, the TDSB layer should exhibit a triplet energy lower than the sensitizer and higher than TTA material, as well as a higher singlet energy than both sensitizer and TTA material. The TDSB layer can be applied to several sensitizer systems, such as phosphorescent (Ph) and thermally-activated delayed fluorescent (TADF) materials whose efficient interconversion (ISC) process converts singlets into triplets for sensitizing TTA emission. With incorporation of the TDSB layer into a solid-state thin film, a 6.13-times enhancement in the STTA signal was observed using a TADF-sensitizer under optical pumping. Efficient STTA emission was also observed with a Ph-sensitizer in an electrically-pumped organic light-emitting diode (OLED). The exciton dynamics were analyzed with transient electroluminescence (TrEL) and transient photoluminescence (TrPL), which provide direct evidence for reduced singlet quenching with the insertion of a TDSB layer. Finally, an electrically-pumped device that generates 75% triplet excitons in a conventional fluorescent dye can also provide sufficient triplets to be used as the sensitizer, and the overall conversion efficiency of the triplets into singlets approach 80%. Besides, the operation lifetime of the blue OLED using STTA emission was elongated by ~3x due to separation of charge recombination zone in the sensitizer layer and the emission zone in the TTA layer.

EP05.14.46

Direct Measurement of the Energetic Landscape of Solution-Processed Organic Photovoltaic Devices
Vincent Lami and Yana Vaynzof; Kirchhoff-Institut für Physik and Centre for Advanced Materials, Ruprecht-Karls-Universität Heidelberg, Heidelberg, Germany.

Organic optoelectronic devices such as light-emitting or photovoltaic diodes have been under extensive investigation in the last decades, resulting in remarkable improvements in their performance. Most literature reports in this field include energy level diagrams to illustrate how the energetic landscape in the device varies through the various device layers. Consequently, these energy level diagrams are used to interpret device performance and comment on the efficiency of physical processes such as charge separation, charge injection or extraction. Despite the importance of such energy level diagrams, they are currently constructed by combining energetic values for individual device components as obtained by different techniques, e.g. cyclic voltammetry, density functional theory calculations, Kelvin probe and photoemission spectroscopy. Additionally, these diagrams are often formed without taking into account interfacial effects, such as dipole formation or band bending, that may arise as different materials are put into contact. Herein, we demonstrate that combining ultra-violet photoemission spectroscopy (UPS) with gas cluster ion beam (GCIB) sputtering, allows for a damage-free depth profiling and hence, an accurate determination of the energetic landscape of solution-processed active layers or multi-layers. We utilize the widely investigated model material system poly[3-hexylthiophene] (P3HT) and C61-butyric acid methyl ester (PC60BM), but also demonstrate that our method is applicable to a large variety of other novel organic material systems. By fitting the obtained UPS spectral maps, we are able to not only quantify the positions of the donor and acceptor energy levels, but also obtain compositional information with a higher vertical depth resolution than that available from X-ray photoemission spectroscopy profiling. Our results allow us to accurately and reliably measure the photovoltaic bandgap (the energetic difference between the lowest unoccupied molecular orbital of the acceptor and the highest occupied molecular orbital of the donor) and correlate it to the measured open circuit voltage of the device. Our method opens the way to quantify the energy losses in organic photovoltaic systems and develop new routes for their suppression.

EP05.14.45

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Remarkable improvements in the performance of organic photovoltaic devices have been achieved in recent years through non-radiative plasmon relaxation due to coupling between plasmons and substrate carriers in metallic and semiconducting substrates. The lower plasmon damping leads to a 13 times stronger field that extends throughout the completely closed graphene tubes as opposed to corner confined weaker field in 2D ribbons on a silicon substrate. The stronger fields throughout the tube structure exhibit a fourfold enhancement in sensitivity and overcome the need to bind targeted molecules to the surface of graphene as exhibited by the example of A/G protein. The 3D graphene nanotubes achieve distinct edge and volumetric enhancement modes while simultaneously increasing the compatibility of graphene with diverse substrates without deterioration in plasmonic properties for application in novel optical and electronic devices.

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When developing chromophores for non-linear optical (NLO) applications, synthetic control of the ground and excited state properties of the chromophore is critical. In this regard, the influence of a number of structural motifs on NLO performance have been elucidated including but not limited to changing donor/acceptor groups, varying π-conjugation length, and including transition metals in the electronic transitions of the molecules. This work focuses on the influence of Zn(II) coordination and the ancillary ligands attached to Zn(II) on the photophysical properties of 2,3-di-2-pyridinyl-benzo[g]quinoxaline (dpyb). Only subtle changes are observed in the ground state absorption spectra of dpyb upon coordination of Zn(II) regardless of the nature of the halide ligand. Conversely, Zn(II) coordination strongly influences the excited state properties of dpyb. The iodide complex behaves significantly differently than the chloride and bromide complexes. Coordination of Zn(II) leads to an enhancement of the singlet state lifetime relative to dpyb. This effect is more pronounced in the chloride and bromide complexes. The fluorescence quantum yield is also enhanced upon Zn(II) coordination to dpyb. We also observe a faster bimolecular quenching constant for the quenching of the singlet state by dissolved oxygen in solution for dpyb relative to all of the Zn(II) complexes. dpyb has an intersystem crossing quantum yield on the order of 0.9. All of the Zn(II) complexes have intersystem crossing yields on the order of 0.6. The large variations in the fluorescence quantum yields, intersystem crossing efficiencies, and fluorescence lifetimes paint a very interesting kinetic picture in this series of complexes. The rate constants for radiative decay, non-radiative decay, and intersystem crossing are all largest in dpyb. The radiative decay rate constants for the Zn(II) complexes are all slowed by a factor of two relative to dpyb. Non-radiative decay from the singlet state has negligible influence on the excited states of the chloride and bromide complexes; k<sub>n</sub> in these complexes is two orders of magnitude slower than in dpyb and the iodide complex.

Barrier-free (Ohmic) contacts are a key requirement for efficient organic optoelectronic devices, such as organic light-emitting diodes, solar cells, and field-effect transistors. Here, we propose a simple and robust way of forming an Ohmic hole contact on organic semiconductors with a high ionization energy (IE). The injected hole current from high-work-function metal-oxide electrodes is improved by more than an order of magnitude by using an interlayer for which the sole requirement is that it has a higher IE than the organic semiconductor. Insertion of the interlayer results in electrostatic decoupling of the electrode from the semiconductor and realignment of the Fermi level with the IE of the organic semiconductor. The Ohmic-contact formation is illustrated for a number of material combinations and solves the problem of hole injection into organic semiconductors with a high ionization energy up to 6 eV.

Reference:

EP05.14.50
Universal Strategy for Ohmic Hole Injection into Organic Semiconductors with High Ionization Energies Naresh B. Kotadiya1, Hao Lu1, Anirban Mondal1, Yutaka Ie1, Denis Andrienko1, Paul WM Blom1 and Gert-Jan AH Wetzelaer1; 1Max Planck Institute for Polymer Research, Mainz, Germany; 2Department of Soft Nanomaterials, Osaka University, Institute of scientific and industrial research, Osaka University, Osaka, Japan.

A series of novel carbazole-imidazole derivatives with a large energy bandgap and triplet state over 3.4 and 2.8 eV, respectively, were synthesized conjugating three carbazole moieties and one imidazole moiety to exhibit the bipolar behavior. Their highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) were approximately at 2.3 and 5.7 eV, respectively. In particular, by well design to firm the molecular structure, these compounds showed the excellent thermochemical properties with high glass transition (T<sub>G</sub>) of more than 190 °C and high decomposed temperature of approximately 450 °C. The T<sub>G</sub> is greater than the highest thermal specification of 150 °C for automotive electronics, corresponding to the better thermal reliability. Employing as host materials of blue phosphorescent organic light emitting device (OLED), a layer structure of indium-tin-oxide anode/4,4'-cyclohexyldienebis[N,N-bis(4-methylphenyl)benzenamine]/N,N-dicarbazolyl-3,5-benzene/ host: iridium(III)b(is)[4,6-(di-fluorophenyl)pyridinato-N,Cl]picolinate (Flrpic)/ diphenylbis(4-(pyridin-3-yl)phenyl)disilane/ lithium fluoride/ aluminum cathode. The Flrpic was well-known high blue phosphorescent emitter. Our preliminary high efficiency phosphorescent OLED exhibited the max. current efficiency of 58.7 cd/A, max. power efficiency of 59.3 lm/W, max. external quantum efficiency of 28.6%. By moving the main recombination from the region close to electron transporting layer to the center of emitting layer, the operation lifetime exhibited 2 times improvement. The further improvement in device performance is possible.

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Synthesis and Characterization of Meso-Substituted BODIPYs—Exploration of the Optical and Photophysical Properties and the Formation of Thin Films Cruz Pamechi1, 2; 1UNAM, Mexico city, Mexico; 2Chemistry, IECN, Mexico city, Mexico.

Four BODIPY-fluorene based fluorophores were synthesized using a donor-π-bridge- acceptor (D-π-A) motif. They were studied via their structural analysis, the measurement of their photophysical and optical properties and a theoretical DFT study, to plunge deeper into their electronic structure and transitions bestowing such features. We present four different structures as we change the π bridge, in the first one BODIPY 1, we have the BODIPY core substituted in the meso position with a fluorene moiety in the BODIPY 2 we have the BODIPY core directly attached to the ethynylfluorenone moiety, in BODIPY 3 we have a phenyl group attached to the ethynylfluorenone moiety; finally in the BODIPY 4 we have a phenyl group attached to an ethynylfluorenone moiety. In this work, we present the synthesis of novel meso-BODIPY derivatives, the spectroscopic characterization, structural analysis of X-Ray diffraction, and the study of the photophysical properties, such as: absorption, emission, and fluorescence quantum yield. Quantum chemical calculations were performed to analyzed the conduct of the compounds in the excited state.

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Investigation of Locally-Excited and Charge-Transfer Optical Transitions in a Series of Porphyrins Thomas M. Cooper1, Joy Haley1, Weijie Su2,
In order to investigate locally-excited and charge-transfer optical transitions in multiple-chromophore-molecular-complexes, we synthesized eight new porphyrins containing 5,15-attached diphenyl amine(DPA) or benzothiazole(BT) connected to the porphyrin core either through a phenyl-alkynyl fluorescent bridge or with an alkynyl-fluorene bridge. We also synthesized a series of these porphyrins containing a central Zn atom. We will describe the effects of electron donors(DPA), acceptors(BT), conjugation through the linker(phenyl-alkynyl vs. alkynyl bridge) and the presence of a central Zn atom on ground state absorption, emission and triplet state absorption spectra. We will also present DFT and TDDFT calculations of optical transitions, natural transition orbitals, triplet state energies and spin densities.

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**Tuning Excited-State Absorption of Aromatic Hydrocarbons via Structural Modifications**

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Excited-state absorption (ESA) plays a critical role in the effectiveness of nonlinear optical processes such as reverse-saturable absorption and effective-three-photon absorption. By favorably controlling the intensity and energy of the ESA, the nonlinear performance can be enhanced. However, examples of how to tune ESA are sparse. This work shows how structural modifications across two separate series of molecules can greatly influence ESA. The first series is a group of anthanthrene derivatives to which a varying number of phenyl or t-butyl-phenyl substituents are added. The shape of the ESA spectra remain consistent but the maxima red shift from 585 nm (parent anthanthrene) to 645 nm (four t-but-phenyl substituents). There are also two oxidized derivatives, anthanthrones, which show strong, broad ESA in the visible with weaker transitions observed to nearly two μm. The anthanthrones have stronger ESA in the visible than the anthanthrenes, with ESA extinction coefficients around 30,000 M−1 cm−1. Another noticeable difference is that the intersystem crossing yields are also much larger for the anthanthrones (>0.8) than the anthanthrenes (~0.3). This follows El Sayed’s rule as the anthanthrene derivatives likely contain nπ* states. The second series is a group of naphthalene carbonitrile derivatives containing electron donating groups (either dimethylamino or piperidinyl) in the 2, 3, or 4 positions. These changes dramatically change the energy of the ESA transitions, with shifts in the maxima greater than 100 nm. These modifications also impact the singlet state, as fluorescence lifetimes and quantum yields are significantly larger in the 3-substituted compounds (10.1 ns/0.76) than the 4-substituted (0.48 ns/0.05). Another significant effect of the varying substitution positions is the singlet-triplet energy gap, which can be tuned from 0.65 eV (2-position) to 1.01 eV (4-position).

**EP05.14.56**

**Nature and Role of Charge-Transfer States in Organic Solar Cells**

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The charge-transfer (CT) states appearing at the donor-acceptor interfaces in organic solar cells (OSCs) mediate exciton dissociation, charge generation, and charge recombination. Current work on OSCs based on non-fullerene acceptors (NFAs) points out that by using blends with a small energy offset between the CT state and highly luminescent local excitation (LE) state of the low-gap material it is possible to significantly minimize the voltage losses.1 Here we compare how the static and dynamic disorders and hybridization between the CT and LE states impact the radiative and non-radiative recombination rates and consequently the voltage losses in PTB7-Th:IEICO and PTB7-Th:PC71BM OSCs that are representative examples of small-energy offset NFA and typical fullerene-based OSCs, respectively.1 We have also developed a three-state vibronic model2 that explicitly considers the electronic and vibrational couplings between the CT and LE states and show that the use of the three-state model is mandatory in order to obtain a reliable description of the optical absorption features related to the CT states in blends with small-energy offset between CT and LE states.


**EP05.14.57**

**All-Organic Infrared-to-Visible Up-Conversion Organic Light-Emitting Diodes with Infrared Sensitivity Beyond 1.1μm**

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Infrared (IR)-to-visible up-conversion organic light-emitting diodes (OLEDs) have attracted a great deal of research interest because they offer the potential to convert an invisible infrared image to a visible image without pixilation in the device, thus enabling a high-quality image at a significantly low cost. However, all-organic IR-to-visible up-conversion OLEDs with an organic IR sensitizer as well as an organic visible emitter show very limited IR sensitivity up to around 830 nm. Detecting photons at longer IR wavelengths requires lower bandgap organic semiconductors. Here, all-organic IR-to-visible up-conversion OLEDs with an IR sensitivity up to 1200 nm were fabricated using a novel low bandgap polymer as the organic IR sensitizing layer. This low bandgap polymer showed a strong absorption in the near-IR wavelengths from 700nm to 1200nm. To evaluate the novel low bandgap polymer as the near-IR sensitizer, the near-IR photodetectors are first fabricated with a PC61BM as the acceptor in the photactive layer. The near-IR photodetector showed detectivity higher than 1013Jones in the multi-spectral region (300-1100nm) and the maximum detectivity of 3.0×1011Joules at the wavelength of 1000 nm due to significantly reducing dark current (8.8 × 104mA/cm²·V). Using the novel low bandgap polymer as the IR sensitizing layer, IR-to-visible up-conversion OLEDs were fabricated with an IR sensitivity up to 1,200 nm. The IR up-conversion OLED successfully converted invisible near-IR light of 700nm-1200nm directly to visible green light with a peak emission wavelength of 520 nm. This is the very first report of all-organic IR-to-visible up-conversion OLED with near-IR sensitivity beyond 1100 nm which Si-based photodetectors cannot offer.