**Additive-assisted supramolecular manipulation of polymer:fullerene blend phase morphologies and its influence on photophysical processes**

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Despite the rapid and significant progress in polymer:fullerene blends for use as the light-harvesting active layer in Organic Photovoltaic (OPV) devices, there is still a lack of complete understanding of the actual phase morphology (*i.e*. the number of phases and the complexity of their microstructure) achieved in the active layer and its correlation to device performance. Clearly, if we want to reach the maximum performance within polymer-fullerene bulk heterojunction (BHJ) solar cells, we need to gain a more in-depth knowledge and control of these multi-component systems in order to correlate their optical and electronic properties with their solid-state microstructure and phase morphology. We will first present a versatile way to manipulate, and thus easily study, such functional two-component, multi-phase blend architectures using poly(2,5-bis(3-tetradecylthiophen-2-yl)thieno[3,2-b]thiophene) (pBTTT): [6,6]-phenyl C61-butyric acid methyl ester (PC61BM) blends (1:1 by weight)1 with the assistance of alkyl-chain methyl esters as additives.2 This allows us to evaluate the effect of the phase morphology of such structures – from fully intercalated to partially and predominantly non-intercalated systems – on the exciton and carrier dynamics, and the efficiency of charge collection, with relevance for future device design and processing. Note that we can extend this additive-assisted manipulation to other polymer: fullerene blends such as the well-studied poly(3-hexylthiophene) (P3HT) and PC61BM system.3 Finally, I will show how these systems can be also applied to investigate the Charge Transfer (CT) -absorption band and -energy levels of these blends and probe whether ‘hot’ states (strongly debated nowadays in the OPV field)4 can play a role depending on the amount of donor:acceptor interface within polymer:PC61BM.

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**Morphology and interface control with fully conjugated block copolymers for organic photovoltaics**

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Weak intermolecular interactions and disorder at junctions of different organic materials limit the performance and stability of organic interfaces and hence the applicability of organic semiconductors to electronic devices. We have demonstrated control of donor-acceptor heterojunctions through microphase-separated conjugated block copolymers. When utilized as the active layer of photovoltaic cells, block copolymer-based devices demonstrate efficient photoconversion well beyond devices composed of homopolymer blends. The 3% block copolymer device efficiencies are achieved without the use of a fullerene acceptor. Resonant soft X-ray scattering and grazing-incidence X-ray diffraction results reveal that the efficient performance of block copolymer solar cells is due to self-assembly into mesoscale lamellar morphologies with primarily face-on crystallite orientations. We can build on these initial results with the combination of Density Functional Theory, Molecular Dynamics simulations and polymer theory to design donor-acceptor block copolymers with control of charge transfer processes. For example, interfaces in conjugated block copolymers are governed by chain flexibility and the interaction parameter. As such, we can present strategies to design block copolymers with suppression of bimolecular recombination through the molecular composition and microstructure.

**Title: Functional Fullerene Interlayers: Bringing High Work Function Cathodes and Unprecedented Efficiencies to Organic Solar Cells**

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**Abstract:**

This poster will describe the synthesis, characterization and device integration of novel fulleropyrrolidines having amine (**C60-N**) or zwitterionic (**C60-SB**) substituents. The fulleropyrrolidines serve as cathode-independent buffer layers and overcome numerous barriers in the fabrication of single junction polymer solar cells. This cathode independence originates from an interfacial energy “pinning” effect, where a work function of 3.65 eV is obtained when a thin layer of **C60-N** is placed in contact with Ag, Cu, or Au. Power conversion efficiencies (PCEs) reached 9.78% for devices employing **C60-N** as the buffer layer and Ag as the cathode, while PCEs exceeding 8.5% were obtained for OPVs independent of the cathode, whether Al, Ag, Cu or Au. Such high efficiencies did not require precise control over interlayer thickness, as **C60-N** and **C60-SB** layers ranging from 5 to 55 nm functioned similarly. Charge mobility studies, ultraviolet photoelectron spectroscopy (UPS) and reflectance spectroscopy show that **C60-N** provides Ohmic contact, while acting as a cathode modification layer and an optical spacer.

Titanium oxide hydrates/ PVAl hybrids based photonic structures for light-management in organic optoelectronic devices

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The Organic Optoelectronics field increasingly focuses on the development of new materials that allow enhanced light management (through use of, e.g., input-/output-coupling structures and waveguides) and, thus, the performance of devices such as organic light-emitting diodes, organic photovoltaic cells, etc.... However, so far, versatile and easy-to-process materials are still lacking that would allow straight-forward manufacturing of such light-management architectures and/or ready integration of them into organic-based optoelectronic devices. In order to address this issue, we have developed solution-processable hybrid materials based on titanium oxide hydrates and polymer matrices such as poly(vinylalcohol) that display refractive indices *n* varying between 1.52 and 2.1 (at 550 nm), are highly transparent in the visible and near infrared regime and allow manufacturing of complex architectures like one- and two-dimensional photonic crystals through simple and inexpensive techniques such as solution-molding. Furthermore, it is possible to widen the spectrum of optoelectronic properties of these hybrids to tailor them for specific applications by simply modifying their formulation through addition of different metals chosen with respect to their chemistry, dimensions, and optical and electronic properties of their oxides. As a proof of concept we analysed the effect of the introduction of Zr, Hf, W, Ga, In, Tl and Eu selected with the aim to improve the refractive index window of the hybrids and/or impart them an enhanced conductivity or emissivity. The optical properties of the obtained structures were then analysed and discussed in light of potential applications.

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**Novel hybrids of W-Ti polyoxometallates and polyalcohols for optical**

**and energy storage applications.**

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Hybrids including organic and metallic species can display new interesting light and redox induced functionalities that can give rise to photoinduced energy- and electron-transfer processes. These properties can be potentially exploited for very different purposes from photoinduced non-linear optic applications to solar energy harvesting and storage to photocatalysis1. Indeed, hybrids of titanium oxide hydrates and polyalcohols show intense photochromic response from colourless to blue2,3 over irradiation to UV-near visible light. This phenomenon results from a photoinduced redox reaction involving the two components of the hybrid which leads to the reduction of the metal centers and consequently to charge transfer mechanisms among the reduced metals. The colouration can be fully reversed over exposure to air.In this work we enhanced the photochromic response of such hybrids by introducing tungsten in the structure of titanium oxide hydrates. Molecular hybrids systems based on titanium-tungsten-polyoxometallates and polyalcohols thus displayed faster, more intense and stable photochromic response respect to the previous set of hybrids. We observed that the enhancement of the photochromic behaviour of the hybrid systems increased with the content of tungsten in mixed metal oxide hydrates structures (up to 100 folds higher than in absence of W) and that this metals act as charge depositories of the hybrids. Our work thus highlighted that the photochromism of these novel materials based on titanium oxide hydrates and polyalcohols can be exploited not only for optical applications but also for solar energy harvesting and storage purposes.

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**Spectral dependence of the internal quantum efficiency of organic solar cells: effect of charge generation pathways**

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The conventional picture of photocurrent generation in organic solar cells involves photoexcitation of the electron donor, followed by electron transfer to the acceptor via an interfacial charge transfer (CT) state [Channel I]. It has been recently shown that the mirror-image process of acceptor photoexcitation leading to hole transfer to the donor is also an efficient means to generate photocurrent [Channel II]. The donor and acceptor components may have overlapping or distinct absorption spectra. Hence, different excitation wavelengths may preferentially activate one Channel or the other. As such the internal quantum efficiency (IQE) of the solar cell may likewise depend on the excitation wavelength. We show that several model organic solar cell blends, notably PCDTBT:PC70BM and PCPDTBT:PC60/70BM, exhibit flat IQEs across the visible spectrum, suggesting that charge generation is occurring either via a dominant single Channel or via both Channels but with comparable efficiency. In contrast, blends of the narrow optical gap copolymer DPP-DTT with PC70BM show two distinct spectrally flat regions in their IQEs, consistent with the two Channels operating at different efficiencies. The observed energy-dependence of the IQE can be successfully modelled as two parallel photodiodes, each with its own energetics and exciton dynamics but with the same extraction efficiency. Hence, an excitation-energy dependence of the IQE in this case can be explained as the interplay between two photocurrent generate Channels, without recourse to more exotic processes.

**A Novel Perfluoroarylated Fullerene Family That Rivals PCBM**

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Fullerenes and fullerene derivatives have been heavily researched for the use in organic photovoltaics. Recently, three new indene‐based fullerene derivatives were investigated, and it was shown that an increase in power conversion efficiency (in comparison to PCBM) was due to a larger open circuit voltage when blended with P3HT.[1](#_ENREF_1) The use of fullerenes containing perfluoroalkyl(aryl) functional groups in organic photovoltaics is limited. In this work, a novel perfluoroarylfullerene family was synthesized and separated by HPLC. Devices using a standard architecture were fabricated and the power conversion efficiencies were measured. Selected fullerene derivatives were investigated for potential use as organic photovoltaics in the lower earth space orbit. Products were characterized by 19F spectroscopy, mass spectrometry, cyclic voltammetry, and time resolved microwave conductivity.

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**Spectroscopic characterization of crystalline non-fullerene organic blends for solar cells**

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Solar cells based on blends of conjugated polymers with fullerenes, such as PC60BM and PC70BM, have been intensively investigated but there are far fewer reports on blends that incorporate non-fullerene electron acceptors. One interesting feature of non-fullerene acceptors is that they typically have higher absorption coefficients than fullerenes and can therefore make a greater contribution to the photocurrent through photoexcited hole transfer to the polymer. Furthermore, they also present a broader platform on which to investigate the effects of blend microstructure on the photophysics of the system and ultimately device performance.

We report an investigation into the nature of photoexcitations in blends of varying ratio of P3HT with the small molecule electron acceptor K12[1] using photoinduced absorption (PIA) spectroscopy, photoluminescence quantum yield, steady-state and time-resolved photoluminescence measurements. K12 has a tendency to crystallize and the performance of devices incorporating blends with P3HT depends strongly on the blend ratio and processing conditions.[2] The results show that optimizing the microstructure requires a delicate balance between crystallization of the K12 and maximizing harvesting of the K12 singlet excitons. Furthermore, the results show that the natural tendency of the K12 to crystallize can cause the microstructure of the blend to evolve over time but that thermal annealing can be used to lock-in the optimum microstructure.

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Stability of inverted organic solar cells with ZnO contact layers deposited from sol-gel precursors

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We report on investigations of the stability of inverted organic solar cells that use a ZnO electron collecting interlayer solution-processed from zinc acetate (ZnAc) or diethylzinc (deZn) precursors. Characterization of the respective solar cells suggests that the two materials initially function similarly in devices, however, we find that the device with ZnO from the deZn precursor (deZn-ZnO) is more stable under long-term illumination than the device with ZnO from the ZnAc precursor (ZnAc-ZnO). A dipolar phosphonic acid which reduces the ZnO work function also improved device performance and stability compared with unmodified ZnAc-ZnO, but caused deZn-ZnO devices to fail very rapidly. X-ray diffraction data suggests that the preferential orientation of the two ZnO films are significantly different and may result in surfaces that differ in their stability within organic solar cells.

**Electrically detected magnetic resonance of polymer:fullerene solar cells**

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Organic solar cells have the potential advantages of low-cost, flexibility and high throughput production. However at present photovoltaic efficiencies are lower than those of other thin film technologies. Using electron paramagnetic resonance techniques we have investigated the spin dependent mechanisms that occur during the operation of polymer:fullerene solar cells.

Conventional EPR lacks the sensitivity to investigate thin film devices due to low spin volumes. Electrically detected magnetic resonance (EDMR) can be many orders of magnitude more sensitive than conventional EPR and detects paramagnetic species by the change in transport current through a device. EDMR is highly selective to the processes relevant to solar cell operation as only spin dependent processes which contribute to the current are detected, for example spin-dependent recombination or hopping transport.

CW and pulsed EDMR measurements have been performed on bulk heterojunction solar cells comprising Poly(3-hexylthiophene-2,5-diyl) (P3HT) or Poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV) with [6,6]-phenyl C61-butyric acid methyl ester (PC61BM) and the nature of the spin dependent transport characterised.

Computational Analysis of Energy Pooling to Harvest Low-Energy Solar Energy in Organic Photovoltaic Devices

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Current photovoltaic energy conversions do not typically utilize low energy sunlight absorption, leaving large sections of the solar spectrum untapped. It is possible, though, to absorb such radiation, generating low-energy excitons, and then pool them to create higher energy excitons, which can result in an increase in efficiency. Calculation of the rates at which such up-conversion processes occur requires an accounting of all possible molecular quantum electrodynamics (QED) pathways. There are two paths associated with the up-conversion. The cooperative mechanism involves a three-body interaction in which low energy excitons are transferred sequentially onto an acceptor molecule. The accretive pathway, requires that an exciton transfer its energy to a second exciton that subsequently transfers its energy to the acceptor molecule. We have computationally modeled both types of molecular QED obtaining rates using a combination of TDDFT and perturbation theory. The simulation platform is exercised by considering up-conversion events associated with materials composed of a combination of high energy absorbing cores of hexabenzocoronene (HBC), and stilbene and low energy absorbing arms of oligothiophene and fluorescein, respectively. In addition, we make estimates for all competing processes in order to judge the relative efficiencies of these two processes.

**Simulation and experimental studies of thiophene-based conjugated polymer morphology and charge carrier dynamics**

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The morphology of blends of thiophene-based conjugated polymers (electron donors) and fullerene derivative molecules (electron acceptors) strongly affects the efficiency of organic solar cells. We use molecular dynamics simulations, and Time Resolved Microwave Conductivity (TRMC) and X-Ray Diffraction (XRD) experiments to determine how physical and chemical features of the donor and acceptor molecules affect morphology. Using simulations, we show how conjugated thiophene-based oligomer architecture affects neat oligomer morphology and how additives and acceptor molecule chemistry can be used to tune blend morphology and phase separation. Experimentally, we show how conjugated thiophene-based polymer architecture and processing conditions affect neat polymer morphology and charge carrier dynamics.

**Photophysics of an Azulene-Functionalized Diketopyrrolopyrrole**

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Understanding the nature of molecular exciton states is critical for the design and implementation of organic photovoltaic (OPV) materials that are fully optimized and that push current device efficiencies into the next realm. As a model system, azulene presents a unique molecular motif that exhibits a long lived (nanosecond), doubly excited S2 state, i.e. it breaks Kasha’s rule with anomalous S2 fluorescence. This presents an opportunity to understand the foundations of exciton kinetics, and it also raises the possibility of designing materials with very long-lived exciton states. Such states would be useful in designing efficient OPV materials, and might potentially enable more exotic mechanisms such as “energy pooling”—which is a mechanism for adding exciton energies as a form of upconversion. First, however, we need to better understand the effect that functionalizing azulene has on its electronic structure and optical properties.

Here, we report the photophysics of one such system: an azulene-diketopyrrolopyrrole conjugate (2-AzDPPF), that features a diketopyrrolopyrrole core linked to two azulene arms through furyl linkers. In order to assess the perturbation of the electronic states of pure azulene as it couples to the core in the conjugate molecule, we have used a combination of experimental techniques and quantum chemical computations—in particular, density functional theory (DFT) and its time-dependent counterpart (TD-DFT). The excited-state properties and kinetics of our system has been discerned through steady-state and time-resolved spectroscopic techniques. To complement these experiments, DFT and TD-DFT were applied to calculate both ground-state and excited-state properties, including nuclear geometries, electronic structure, charge distributions, oscillator strengths, and vibrational modes. This combination of both experimental and theoretical investigations provides a powerful approach for deepening our understanding of the photophysics of our system, helping to guide the future design of new OPV materials.

Using Energy Pooling for Upconversion in Organic Photovoltaics

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**Abstract:**

While organic photovoltaic (OPV) technology is currently improving at a rapid rate, significant challenges remain in reducing energy loss during the charge separation process, in reducing charge recombination, and in the relatively low voltage output of OPV devices. To address these issues we are investigating exciton upconversion in OPV absorber materials. We aim to demonstrate a system in which two “antenna” chromophores transfer their energy to a single “core” chromophore to create an exciton with roughly twice the energy of the initial excitons, a process we call “energy pooling.” Since every harvested exciton loses a fixed amount of energy in the charge generation process, energy pooling halves the energy loss in the charge splitting process while also nearly doubling the output voltage of the system. We aim to build off of the original energy pooling work of Nickoleit *et al* [1] by using a Stilbene-420 and organic dye system to demonstrate energy pooling as an effective method to enhance OPV energy harvesting. We have observed optical upconversion in stilbene-420 when pumping between 660 and 690 nm, resulting in a final excited state identical to that resulting from one-photon absorption at 348 nm, as expected. This work will present results of steady-state and time-resolved optical spectroscopies in the exploration of how upconversion efficiency varies with pump wavelength in stilbene-420, as well as how combination of stilbene-420 with antenna chromophores may facilitate intermolecular upconversion to enable energy pooling. Through the non-linear process of energy pooling we hope to demonstrate a pathway to beating the Shockley-Quiesser limit and raising the efficiency possibilities of OPV.

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**Toward 15% Efficient Excitonic Photovoltaics Based on Resonance Energy Transfer**

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Building the next generation of excitonic solar cells will require a leap in our ability to control the flow of energy in excitonic materials if we are to escape the largely combinatorial engineering processdictated by bulk heterojunction architectures. Energy relay architectures present an exciting possibility both for improving performance and for studying the fundamental of energy transport in excitonic photovoltaic structures. In this work we seek to optimizing energy transport through a cascade of energy transfer setps to a central reaction center, much as occurs in the first-hugely efficient- steps of natural photosynthesis. An experimentally verified theoretical model has been developed which provides a clear path to >15%efficient excitonic photovoltaics using this strategy.



**Studying Recombination Dynamics of High Efficiency Inverted Bulk Heterojunction OPVs with Transient Photovoltage Measurements**

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The field of OPV has seen immense development in recent years from the point of view of materials design, device engineering, and fundamental understanding of the device physics. The recombination loss is an important factor that limits the efficiency of organic solar cells [1]. There are number of models aimed at describing the recombination dynamics in bulk heterojuction devices and mapping the recombination loss pathways [2]. Transient Photo-Voltage (TPV) is a powerful tool to understand the reaction order (defined as the order of how the charge density varies with the recombination rate) as well as the role of traps in the recombination process [3].

In this present work, we examine the polymer PCE-10, an analog of PTB7 that demonstrates efficiencies ~10%, blended with [70]PCBM as the active layer material in inverted BHJ solar cells. We find the device ideality factor of the device by taking the open circuit voltage (VOC) with the variation of optical bias to be 1.31, which is substantially lower than commonly found by simply fitting the JV curve to the ideal diode equation at a single value of optical bias. The TPV technique was then applied to obtain the variation of recombination lifetime (τ1) with the intensity, from which the recombination order and trap state energy was estimated to be 2.9 and 49.4 eV, respectively. The carrier lifetime was determined to be very long, in the millisecond regime, for this material blend at low optical bias.

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**Enhancing the performance of nanostructured zinc oxide and conjugated copolymer based hybrid solar cell by inserting thermally evaporated fullerene (C70) thin film**

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Organic-inorganic hybrid solar cells have been emerging as one of the most interesting approaches for modern day photovoltaics [1]. Nanostructured metal oxide-conjugated polymer based inverted hybrid solar cells have been considered as an alternative to the all-organic bulk heterojunction based solar cells, which attempt to harness advantages from both the organic and inorganic components of the solar cell [2]. Although they promise several advantageous, including tunable band energies and increased electron mobilities, metal oxide-conjugated polymer based solar cells suffer from the low efficiency [3]. The inadequacy in interfacial exciton dissociation efficiency is the major cause for the poor performance. Ideas such as thin interlayer deposition, incorporation of charge transporting nanostructures, metal oxide surface modification with dye or acceptor sensitizing materials, insertion of fullerene (C60) or PCBM between metal oxide and polymer etc. have been employed to improve the efficiency [4]. A thermally evaporated fullerene interlayer can be an interesting method to enhance charge transport, as fullerene will be in its purest form when the vapour is deposited at high vacuum and will provide uniform coverage of the nanostructures. In our present work, we have deposited a thin layer of fullerene (C70) with thermal evaporation over the ZnO nanostructure before the polymer deposition. The fullerene incorporation enhances the solar cell performance and improves electron transfer process in between the metal oxide and conjugated co-polymer (Fig 1).



Fig 1: Current density (J) – Voltage (V) characteristics of the nanostructured ZnO/conjugated polymer based solar cell with and without fullerene (C70) interlayer.

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**Probing Charge Separation Driving Force with Perylene Diimides**

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Our group recently demonstrated the existence of an optimal driving force for charge separation between conjugated polymer donors and a series of fullerene acceptors in OPV active layers.1 It was found that the optimal driving force is different for each conjugated polymer system while using a series of fullerenes with varying reduction potentials.1 We are currently investigating if this same optimal driving force exists for a series of non-fullerene acceptors. Our group has synthesized a new series of 11 core-substituted poly(trifluoromethyl) perylene diimides that differ only in the degree of trifluoromethyl substitution and fluorination of the alkyl imide chain. Poly(trifluoromethyl) perylene diimides were isomerically separated by HPLC and characterized by a combination of 1H and 19F NMR, UV-vis spectroscopy, mass spectrometry, single-crystal X-Ray diffraction, and cyclic voltammetry. The first reduction potentials for this perylene diimide series span 670 mV in dichloromethane. This large span in reduction potentials encompasses the same range of reduction potentials as the fullerenes used in our previous report, which allows us to study the same range of charge separation driving force while using highly tunable small molecule acceptors. This study utilizes time-resolved microwave conductivity as an electrodeless probe of free carriers in the OPV active layer to determine if an optimal driving force for charge separation exist between conjugated polymer donors and perylene diimide acceptors, and if so, whether or not the optimal driving force will be the same as in the series of fullerene acceptors.

(1) Coffey, D. C.; Larson, B. W.; Hains, A. W.; Whitaker, J. B.; Kopidakis, N.; Boltalina, O. V.; Strauss, S. H.; Rumbles, G. *J. Phys. Chem. C.***2012**, *116*, 8916.

**Photoinduced Electron and Hole Transfer and Thermal Charge Recombination Dynamics of TiOPc/C60/P3HT layers**

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**Abstract**

Photoinduced electron and hole transfer (PIET and PIHT) and thermal charge recombination dynamics (CR) of trilayer thin-films comprising titanyl phthalocyanine (TiOPc), regioregular poly(3-hexylthiophene-2,5-diyl) (P3HT) and C60 are studied using time-resolved fs-μs transient absorption spectroscopy. Upon photoexcitation of TiOPc in a P3HT/TiOPc/C60 trilayer, new spectral features in 400-600 nm domain appear instantaneously, followed by an additional slow rise in the ground state bleaching of P3HT. We assign transient absorption signals to the TiOPc anion and cation radical species as well as the P3HT polaron, consistent with bilayer control experiments. These results indicate ultrafast photoinduced carrier generation followed by exciton diffusion-limited carrier generation. The CR time constants for P3HT/TiOPc/C60 trilayer films have been determined to be ~5-10 μs, whereas those for TiOPc/C60 and P3HT/TiOPc are ~700 ns and ~1.5 μs, respectively. These results suggest that thin-film trilayer systems incorporating NIR light absorbing dye can successfully generate charge carriers by photoexciting at NIR spectral domain and evince longer CR dynamics with respect to bilayer D-A systems.

Photophysics and charge transfer in donor-acceptor triblock copolymer photovoltaic materials

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Efficient conversion of solar energy to electricity in low-cost organic photovoltaic (OPV) devices requires the complex interplay between multiple processes and components over various length and time scales. Optimizing device morphology to ensure efficient exciton diffusion and charge transport as well as ensuring efficient charge photogeneration is necessary to achieve optimum performance in new materials. The conjugated polymer electron donor PFM (poly(9,9-diocetylfluorene-co-bis-N,N’-(4-methylphenyl)-bis-N,N’-phenyl-1,4-phenylenediamine)) and electron acceptor F8BT (poly[(9,9-di-n-octylfluorenyl-2,7-diyl)-alt-(benzo[2,1,3]thiadiazol-4,8-diyl)), comprise the novel triblock copolymer PFM-F8BT-PFM. This copolymer is designed to phase separate on the 20-30 nm scale, a domain size ideal for maximizing exciton collection at the donor-acceptor interface. Despite this optimization of domain size, the photophysics of block copolymers at the donor-acceptor interface are not fully understood. Using steady-state and ultrafast spectroscopic characterization including high repetition rate transient absorption spectroscopy, the dynamics of charge and energy transfer of the component polymers and the triblock co-polymer have been investigated. The results demonstrate that for the homopolymers solvent dependent exciton transport processes dominate, while in the triblock copolymer solutions transient spectroscopy provides evidence for interfacial charge separation.

**Geminate Recombination of Charge Carriers in Low Dielectric Constant Solvent**

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Geminate recombination of charges carriers was observed in low dielectric constant solvents (ε) such as THF (ε=7.58) and 2,3-dihydrobenzofuran (DF, ε=4.33). Pulse radiolysis facilitated rapidly creations of cation and anion in a given solvent. Consisting of diffusion bring anion and cation together to become charge transfer (CT) state (contact and solvent separated radical ion pairs) because of the Coulomb attraction, then recombination of anion with cation are either due to proton transfer (PT) or electron transfer (ET) reactions. Low charge density weakening the Coulomb attraction results in solvent separated radical ion pair (SSRIP) so the yield of charge separation (Y) increases with decreasing charge density of ion. Oligo(9,9-dihexyl)fluorenes (Fn,n=1-6) are applied to study the influence of charge density in yield of charge separation (Y). Charge densities of Fn(n=1-6) ions decrease with increasing number of the repeat units (*n*). Based on PT model and Marcus theory, rates of PT and ET decrease with increasing separation distance of radical ion pair. Therefore, lifetimes of radical ion pairs increase with decreasing charge density.

**Mobility of holes on oligo- and polyfluorenes of defined lengths measured by pulse radiolysis time resolved microwave conductivity**

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The high-frequency mobility of positive charges (holes) moving along the backbones of an extensive data set of 7 oligomers (*n* = 2–16) and 6 polymers (<*n*> = 26–138) of fluorene was measured using pulse-radiolysis time-resolved microwave conductivity (PR-TRMC) in benzene. As expected, at 8.9 GHz, the measured isotropic ac mobility, μac,measiso, was observed to be strongly dependent on the lengths of the chains due to the charges encountering chain ends during one microwave cycle. Values of the measured mobility, μac,measiso, ranged from 5 × 10–4 cm2/(V s) for an *n* = 2 repeat unit oligomer to 0.18 cm2/(V s) for a polymer with an average length of <*n*> = 86 repeat units. Global fits to the entire set of lengths extracted the chain-length-independent intramolecular mobility, μacintra, using the Kubo formula, assuming normal diffusion along the contour of the molecule with reflecting boundary conditions at the ends. The effects of chain conformation, chain defects, and polymer length distributions on μac,measiso were considered quantitatively. The best fit to the whole data set, taking into account the polymer length distributions, suggests μacintra = 1.1 cm2/(V s). The possible role of defects was also investigated and the results are compatible with charges encountering defects spaced ~40 repeat units or more. These defects would appear not to be deep traps but barriers to transport that persist on the ~50ps timescale of the experiment.

**Exciton diffusion lengths of 30-40nm measured along single polyfluorene chains with end traps by transient absorption spectroscopy and steady-state fluorescence**

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The average distance that an exciton can travel in its lifetime is an important parameter in organic solar cells. It has also been observed recently that excitons can form significant numbers of charges in <100fs1, suggesting that the initial excitation may occupy a larger volume than the relaxed exciton, and that this process is important in the most efficient solar cells. Typical estimates of the diffusion length in films are around 3-10nm, although possibly as large as 20nm in crystalline domains.2 Attempts at measuring diffusion lengths along a single chain have suggested values of 7nm (P3HT with fullerene end traps)3 and 17nm (pF with fullerene end traps).4

In this work, we perform transient absorption spectroscopy and steady-state fluorescence measurements to estimate diffusion lengths along single polyfluorene chains with end traps. Both a simple diffusion model and a model involving defects along the chain are used to fit the data, taking into account capping efficiency and length distribution of the polymers. The time resolved data also allows the observation of an instant (<100fs) quenching of excitons and we can estimate the number of repeat units involved in this. Possibly due to the full conjugation along the chain to the trap, these data suggest a diffusion length sqrt(Dτ) of 30-40nm, which is longer than those previously observed. The length of the polymer involved in the instant quenching was estimated to be in the range of 4-12 repeat units.

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**Characterization of Benzothiadiazole-containing non-fullerene acceptors for OPV**

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In the past 5 years, there has been significant interest in the viability of non-fullerene acceptors for organic electronic applications with efforts to reduce material costs and improve the absorption overlap with the solar spectrum, especially in the case of organic photovoltaics (OPVs). Here we present results on a family of low band-gap small molecule acceptors based on a benzothiodiazole (BT) core unit. By tailoring the BT core unit with a variety of conjugated moieties, these small molecules exhibit broad absorption features with peak absorbances in the range of 400–640 nm. The photovoltaic performance of one of the small molecules (ORT-BT) suggests efficient dual channel photocurrent generation: channel 1 being exciton formation in the donor with electron transfer to the acceptor, and channel 2 being exciton formation in the acceptor and hole transfer to the donor. These findings are supported by PL quenching and time-resolved microwave conductivity measurements independently probing both channels.

***"In-situ X-ray scattering characterization of Roll-to-Roll printing of organic solar cells”***

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The current efforts to improve the OPV device performance almost exclusively employ spin-coating of the active materials in a protected atmosphere, with efficiencies now reaching 12% for small area devices on the order of millimeter squares. The fabrication conditions by which these very high electrical efficiency cells are currently produced generally cannot be simply transferred to a large-scale roll-to-roll industrial production scheme. The efficiency discrepancy between organic solar cells produced in the laboratory and large-scale devices manufactured in a roll-to-roll printing process need to be addressed before the commercialization of large area printed OPV devices. Correlating the process conditions, the morphology and electrical performance of the OPV devices are critical for solving the challenge of mass-producing high efficient large area organic solar cells.

To solve the above mentioned grand challenge, we developed a mini roll-to-roll compatible printing setup for organic solar cells with the capability to follow the film formation during solvent dry *in situ* with small and wide angle X-ray scattering at Stanford Synchrotron radiation facility. By using this set-up, time resolution down to 10ms was achieved to probe the drying kinetic and crystallization process of the organic semiconductor materials. This set-up also allows to use multiple inks that being delivered to the roll-to-roll printer head with different composition of the active layer between the donor and acceptor materials. We used P3HT/PCBM BHJ as model system to print them on the flexible ITO/PET substrates and characterized the print process using *in situ* /wide angle X-ray scattering (SAXS, WAXS). Wide range process parameters were investigated in details during R2R coating process, including solvent quality, drying temperature, shearing speed in order to obtain the optimized OPV morphology. By extracting the peak intensity, full widths at half maximum (FWHM) and peak position, rich information about the drying process as well as dried film are obtained. Finally the morphology of the OPV devices will be correlated to electrical performance of the device (e.g. VOC , Jsc , FF, PCE), thus shed light on the best protocol for drying process to obtain the highest possible efficiency for the R2R coating of OPV materials on flexible substrates.

All-polymer solar cells, consisting of polymers for both the donor and acceptor, gained significantly increased interests recently, because of their ease of solution processing, potentially low cost, versatility in molecular design, and their potential for good chemical and morphological stability due to entanglement of polymers. Preliminary ex situ experiments using the solution shearing on the all-polymer solar cells employing polymeric donors based on isoindigo and acceptor based on perylenedicarboximide showed a record PCE of 4.8% (average from 20 devices), with an average *J*SC of 9.8 mA cm-2 for all polymer solar cell. The phase separation domain length scale correlates well with the *J*SC and is found to be highly sensitive to the aromatic co-monomer structures used in the crystalline donor polymers. With the PS polymer side chain engineering, the phase separation domain length scale decreased by more than 45%. The PCE and *J*SC of the devices increased accordingly by more than 20%. This demonstrates that a better understanding of tuning polymer phase separation domain size provides an important path towards high performance, all-polymer solar cells. The use of polymer side-chain engineering provides an effective molecular engineering approach that can be combined additional processing parameter control obtained from in situ mini R2R X-ray diffraction method to further elevate the performance of all-polymer solar cells.

Conjugated Phosphonic Acid Modified Zinc Oxide Electron Transport Layers for Improved Performance in Organic Solar Cells

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ABSTRACT. Phosphonic acid modification of zinc oxide (ZnO) electron transport layers in inverted P3HT:ICBA solar cells was studied to determine the effect of conjugated linkages between the aromatic and phosphonic acid attachment groups. For example, zinc oxide treated with 2,6-difluorophenylvinylphosphonic acid, having a conjugated vinyl group connecting the aromatic moiety to the phosphonic acid group, showed a 0.78 eV decrease in the effective work function versus un-modified ZnO, while non-conjugated 2,6-difluorophenylethylphosphonic acid resulted in a 0.57 eV decrease, as measured by Kelvin probe. This resulted in an average power conversion efficiency of 5.89% for conjugated 2,6-difluorophenyvinylphosphonic acid modified solar cells, an improvement over un-modified (5.24%) and non-conjugated phosphonic acid modified devices (5.64%), indicating the importance of the conjugated linkage.

**Designing polymer-based renewable energy materials with massively parallel computing platforms**

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Engineering the morphology of bulk heterojunction solar cells is a key challenge for maximizing their power conversion efficiency. In this work we perform coarse-grained molecular dynamics simulations to investigate how the chemistries of push-pull polymers influence the morphologies that are thermodynamically stable for polymer melts over a range of temperatures. Graphics processing units are used to accelerate simulations, permitting experimentally relevant volumes to be investigated, and simulated diffraction patterns show good agreement between predicted morphologies and experimental films.

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