

Project 01: Optimization of Nanoscale Interfaces in Organic PV Active Layers

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Overview

The primary steps in the operation of organic PV are the absorption of light, energy migration towards donor-acceptor heterojunctions in typical distributed heterostructure morphologies, dissociation of the exciton at the heterojunction, then formation of mobile carriers in a multistep process.¹ Nanoscale interfaces connect the various domains within the active layer of an organic solar cell. They delineate the continuous domains of material optimized for electron or hole transport, and they play a critical role in exciton dissociation.² When an exciton dissociates across an interface, for example between polymer and PCBM domains, the separated charges are initially bound by nuclear reorganization and Coulomb attraction, forming geminate polaron pairs and possibly charge-transfer excitons.^{3,4} Mobile carriers must then be released through an activated de-trapping process or by a built-in electric field. In polymer heterojunctions with molecular acceptors, the nature of the local interaction across molecular interfaces can vary substantially due to the fantastic diversity of relative donor-acceptor orientations [David review], with some orientations leading to stable charge-transfer exciton states, while others destabilising such states. Challenges for researchers include designing active layer materials and controlling their organization to optimize harvesting of light, transferring that energy to an interface, irreversibly dissociating the exciton, then forming mobile carriers with high yield. Our team will address charge generation processes at nanoscale interfaces by focusing on heterojunctions of conjugated polymers and carbon nanotubes. Our motivation to focus on this particular material system is two-fold. Carbon nanotubes are not only promising electron transporting materials with charge mobilities orders of magnitude higher than organic semiconductors, but also they are well defined structurally, and polymer interactions with the nanotube are dictated by its chirality, such that the range of local interactions at the interface will be limited compared to the situation in blends with molecular acceptors. In this project, we will explore various conjugated polymer:carbon nanotube systems with the global objective of unravelling the nature of local electronic coupling across nanoscale interfaces, with particular interest exciton dissociation processes. Our specific objectives are: (i) to investigate excitonic processes in model conjugated polymer:carbon nanotube systems by means of temperature-dependent, time-dependent optical probes (time-resolved photoluminescence spectroscopy, transient absorption spectroscopy, multidimensional coherent electronic spectroscopy); (ii) to conceive, fabricate, and optimise photovoltaic diodes incorporating the polymer:nanotube composites investigated by optical spectroscopy; (iii) to discover new materials for application in organic PV based on the understanding emerging from the previous two objectives.

This activity will integrate all four groups, and sample exchange will occur at all levels of the project. The proposed workplan exploits the expertise of each group, and combines it in such a way to optimise the impact for the broader NSERC photovoltaic strategic network.

Carbon Nanotube Photovoltaic Devices

It is evident that in order to improve efficiency beyond the 5% level, a superior electron transporter is required. To this end, carbon nanotubes (CNTs) have emerged as potentially ideal components of numerous optoelectronic devices due to their excellent electrical conductivity, electrochemical stability, high aspect ratio, and high surface area. Recently, the discovery of efficient photoinduced electron transfer from various chromophores to CNTs, which effectively act as electron acceptors, has attracted widespread attention and highlighted their potential application in photovoltaics. In fact, this concept has led to the fabrication of functional photovoltaic devices in which nanotubes are dispersed within conjugated polymers. In preliminary studies, the reported nanotube-based photovoltaic devices have

performed with relatively low power conversion efficiencies ($\sim 0.04\%$). Nevertheless, these proof-of-concept experiments open an opportunity for development of materials that will increase future device efficiencies. The significantly poorer performance of CNTs, relative to their C_{60} analogs, can be explained by several factors, including their inherently poor solubility (which precludes homogeneous dispersion), the presence of metallic impurities within most commercially available samples (resulting in diminished charge carrier mobility), and the inevitable mixtures of semiconducting and metallic nanotubes that result from all known synthetic methods (where metallic nanotubes can lead to short circuits within devices). However, the inherent advantage of CNTs over C_{60} is a much higher electron mobility, which translates to a greater potential for reaching high power conversion efficiencies. Current work in the A. Adronov group aims to address each of these nanotube limitations using chemical processing, purification, and functionalization strategies en route to nanotube-based photovoltaic devices that meet and exceed the standards set by C_{60} . Recently, we have studied the interaction of single-walled carbon nanotubes (SWNTs) with a variety of conjugated polymers, and have found that conjugated polymers, appropriately functionalized with solubilizing groups, are capable of efficient and irreversible binding to the surface of CNTs. The resulting supramolecular complexes form stable molecular dispersions in appropriate solvents, even when all excess unbound polymer is removed, thereby solving the nanotube solubility problem while preserving their favourable conductivity properties. More importantly, it has been found that photoluminescence of the adsorbed polymer is quenched by the nanotubes with an efficiency in excess of 95%, suggesting that photoinduced electron transfer from the polymer to the nanotubes may be a dominant relaxation pathway. Therefore, these complexes promise to serve as the basic photoactive components of photovoltaic devices. In addition, Nunzi and co-workers have shown that shortened, covalently-functionalized SWNTs can be incorporated within the active layer of organic PV devices, and these materials result in device efficiencies in excess of 3.5%.⁵ Again, this illustrates that, by removing metallic SWNTs via functionalization, it is possible to dramatically improve device performance. We will therefore focus on continued exploration of organic PV devices that incorporate SWNTs, with the aim of further improving their performance.

In the next stage of this project, we will focus on the specific investigation of poly-3-hexylthiophene (P3HT)-nanotube complexes, which have been shown to form extremely strong interactions and have led to highly soluble nanotube materials. The P3HT-nanotube complexes will be prepared in the Adronov Group, and will be processed to remove all unbound polymer. This will enable fundamental studies on the electronic interactions between the polymer and nanotube. The Silva Group will investigate the mechanism of polymer photoluminescence quenching by transient absorption and photoluminescence measurements. Specifically, we will pump the optical absorption of P3HT chains with femtosecond laser pulses and probe the evolution of photoluminescence spectrum using an optically triggered streak camera, and signatures of energy or charge transfer to the carbon nanotube by means of the transient absorption signature in the nanotube (ground-state bleach and photoinduced absorption of excitons). This will reveal whether energy or electron transfer is occurring in these systems. If electron transfer is responsible for the fluorescence quenching, it will be possible to quantify the charge-separation lifetime within this system. Further insight into the nature of interactions between P3HT and carbon nanotubes will be unravelled by two-dimensional electronic spectroscopy (2DES). In a 2DES measurement, four laser beams are incident on the sample, and the pulse timings are varied, leading to three time periods (τ_1, τ_2 , and τ_3) between field interactions. One beam is selected as a reference, and the phase matching condition among the other three beams, $\mathbf{k}_{\text{sig}} = \mathbf{k}_a + \mathbf{k}_b + \mathbf{k}_c$, leads to signal emitted in the reference direction. In a 2DES measurement, time period τ_1 (the time between fields \mathbf{k}_a and \mathbf{k}_b) is scanned while the emitted signal is detected using a spectrometer for a selected τ_2 value. During a rephasing measurement, field \mathbf{k}_a is incident on the sample first ($\tau_1 > 0$) and a photon echo can occur during the emission time period, τ_3 . For nonrephasing measurements, field \mathbf{k}_a is incident second ($\tau_1 < 0$), and no echo occurs. Together the rephasing and nonrephasing spectra form a complete signal that, after Fourier transformation, can lead to fully absorptive lineshapes in the real part of the 2DES. The Scholes Group has played a leading role in the development and implementation of these techniques for the study of multichromophoric systems, in particular conjugated polymers and

photosynthetic light-harvesting systems. Upon excitation with an ultrashort optical pulse, vibrational coherences, superpositions of vibrational states in the ground and electronic excited manifolds, are generated, and they can be probed via the evolution of the resulting vibrational wavepacket in the time domain. Electronic coherences also result upon excitation with ultrashort pulses, and these can live for as long as picoseconds in certain systems. The Scholes Group has recently demonstrated how electronic and vibrational coherences can be distinguished by decomposing the total two-dimensional electronic spectral signal into rephasing and non-rephasing components.⁵ We will explore the polymer:nanotube electronic coupling by comparing electronic coherence dynamics in the composite with those of isolated polymer chains in solution. Polymer:nanotube electronic coupling will alter the electronic coherence dynamics with respect to the non-interacting polymer chains, and charge-transfer interactions will result

To place the understanding gained by the ultrafast optical probes in context, we will fabricate and characterise photovoltaic diodes. The incorporation of semiconductor-enriched (covalently-functionalized) SWNTs in a P3HT:PCBM bulk heterojunction (BHJ) solar cell has recently been successfully validated in the team of J-M. Nunzi.⁶ The result is a remarkable increase in the open circuit voltage of the cell: from 0.58 to 0.83 V; while preserving state of the art current and fill-factor figures. Therefore, SWNT doping permits to reach the maximum theoretical open circuit voltage given by the HOMO – LUMO energy difference between P3HT and PCBM, without the usual 0.3V bias that limits the maximum efficiency of a single polymer:fullerene BHJ solar cell to about 10% efficiency.⁷ We attribute the effect to improved charge transport within the fullerene part of the blend that permits carrier collection with limited potential drop (improved mobility balance). Interestingly, the as-fabricated cells do not require mandatory thermal annealing or solvent treatment to reach optimal performances; improved crystallinity of the P3HT phase was evident using UV-Vis transmission spectroscopy and X-Ray scattering. Based on the above functionalization techniques, we will first develop and optimize low band-gap polymer based BHJ solar cells with an aim of breaking the above 10% theoretical limit. The next step will consist of removing totally the C₆₀ component from the BHJ and replacing it with zigzag or chiral (n-m ≠ 3p) SWNT. We will thus build, characterize and optimize low band-gap near-infrared harvesting solar cells. By the end of the program, a combination of current equilibrated low and large band gap solar cells in a stacked (using silver nano-particles) tandem structure will enable us to compete towards the 15% record power conversion efficiency.⁸

The Nunzi group will continue to fabricate and characterize bulk heterojunction (BHJ) PV devices within the context of the samples described above, by spin-coating PEDOT-PSS onto ITO-coated glass, followed by deposition of the active layer containing different compositions of the PT-SWNT complexes (ranging from 0.01 to 0.5%) within a matrix of P3HT and PCBM. These devices will then be coated with sequential layers of LiF and Al as the electron collector. Through the use of facilities available in the Nunzi group, we will fully characterize device performance and stability, as a function of SWNT concentration in the active layer, annealing time, and LiF thickness. The ultimate goal of this work will be to identify the device parameters that will enable consistent and significant improvement to device performance in SWNT-containing devices to that of the standard P3HT-PCBM devices. The Nunzi Group has capabilities for complementary time-resolved optical spectroscopies to those of the Silva Group discussed above, such as time-correlated single-photon counting and various quasi-steady-state probes. Basic characterisation of photoluminescence lifetimes with lower temporal resolution will be carried out on working devices at Queens.

The Scholes and Silva Groups have established collaborations with Garry Rumbles (NREL), and he will remain a collaborator for this project by applying time-resolved microwave conductivity techniques to understand charge generation and transport in the polymer:nanotube composites described in this proposal. In these experiments, the time evolution of the photoconductivity is probed with nanosecond time resolution by measuring the transient absorption of microwave radiation by charge carriers. This is a powerful electrodeless electrical probe that is very complementary to the time-resolved optical probes of excitons and charges available in the Silva and Scholes Groups.

We anticipate that these studies will require year 2 to complete in the global way described here. Once these initial studies are complete, we will focus on the investigation of new conjugated polymer-SWNT complexes with different (lower) polymer bandgaps, which will define iterative processes of sample preparation, ultrafast spectroscopic investigation, and device characterisation that will take us through year 5 of the network. The Adronov group has found that appropriately functionalized poly(2,7-carbazole) polymers also bind extremely well to SWNTs, leading to extremely exfoliated nanotube structures. In addition, these polymers are able to selectively bind to specific nanotube chiralities, allowing enrichment of specific semiconducting SWNTs. The Adronov group will continue to investigate the interactions of these polymers with SWNTs, and will specifically focus on optimizing the selectivity for specific semiconducting SWNT types. These new materials will also be characterized by ultrafast spectroscopic probes in the Silva and Scholes groups, and will be incorporated within BHJ PV devices in the Nunzi group, as detailed above.

In addition to the principal activity described above, we opt to include the following activities in the revised proposal, as we consider that they have a high potential for impact. The HQP funded by the project will focus on the principal thrust described above, but other HQP involved in the Network will participate as well in the following activities. Some aspects of this work is well underway as described in the report for Year 1, and they will continue for the remainder of the network cycle.

Spectral Engineering in Organic Devices (GS, AA, J-MN, GR)

Spectral engineering encompasses ways of improving the capture of incident light by a device. This is an important optimization for organic solar cells because it is desirable to keep devices thin for improved carrier transport and it is also desirable to supplement the absorption spectra of active layers (e.g. polymers) to improve the spectral cross-section for light absorption. We will investigate two spectral engineering optimizations.

(a) Polymer Bandgap Tuning in Polymer-SWNT Complexes for Improving Solar Energy Capture

Photosynthetic organisms provide inspiring models for spectral engineering. They employ special light harvesting pigment-protein complexes to increase the spatial and spectral cross section for absorption of incident light.⁹ That excitation energy is subsequently funnelled to reaction centre complexes where the first steps converting it to chemical potential take place. The biochemical isolation of light-harvesting proteins and the discovery of their structure in conjunction with investigations using a variety of spectroscopic techniques have allowed us to gain considerable insights into the cascade of highly efficient electronic energy transfer (EET) steps that serve to funnel absorbed light energy to reaction centres. Such experimental measurement of the EET dynamics can be compared to theoretical models, thus considerably improving our understanding of EET and how it can be used to funnel excitation energy. Thus it has been learned how additional concepts need to be considered in conjunction with Förster's original theory, and we have recently reviewed this topic in detail.¹⁰ How we learn to integrate some of these principles into organic solar cells remains an interesting question¹¹. In this project we aim to use organic synthesis to prepare a series of low-bandgap polymers based on fused bithiophene, dithienopyrrole, and fluorene monomers. The resulting polymers will be investigated for their ability to interact with SWNTs, selectively disperse specific SWNT chiralities, and expand the absorption range of the polymer-nanotube complexes throughout the entire visible spectrum (and into the infrared). The photophysical properties of the resulting polymer-nanotube complexes will be fully characterized by the Silva and Scholes research groups, and will be incorporated within BHJ PV devices in the Nunzi group.

(b) Plasmonics for Photon Trapping

Organic solar cells do not fully benefit from the high absorption cross section of organic materials. Indeed, owing to their sub-wavelength thickness and to the presence of a mirror like electrode,

absorption inside the active photovoltaic layer is not simply optimized. It strongly depends on the thickness of the layers,¹² but also on the reflectivity of the metal cathode.¹³ Several experimental studies have evidenced the gain provided by the plasmon resonance bound to metal nanoparticles on the efficiency of organic solar cells¹⁴. Electromagnetic modeling using the Finite Difference Time Domain method predicts a potential 50% conversion efficiency increase using silver nanoparticles deposited on the ITO side of P3HT:PCBM BHJ-cells.¹⁵ The gain in light harvesting is significant and we implemented the technique at Queen's: both using silver nanoparticles fabricated by reduction of silver nitrate and functionalized using thiol-derivatives, or by evaporating metal nano-aggregates on top of the transparent conducting oxide using our vacuum deposition system.¹⁶ We propose to use dual channel time correlated single photon counting, a technique that was recently implemented at Queen's, to study both the enhancement of the absorption cross section and exciton diffusion by coupling to the metal nanoparticle resonances in the photovoltaic polymer films of interest for the realization of efficient single junction and tandem solar cells. It is worth mentioning that we already measured luminescence cross section enhancements of more than one order of magnitude as well as significant exciton diffusion enhancements in the vicinity of noble-metal nanoparticles.¹⁷

Chain-Chain Aggregates and Consequences for Excitons (CS, GS, GR)

Understanding the complex interdependence between film microstructure (dictated by supramolecular order) and the semiconductor properties of π -conjugated polymers is of fundamental importance in materials physics, but it is also of practical interest for the development of real-life applications in photovoltaics based on this class of materials. Regioregular poly(3-hexylthiophene) (rrP3HT) is a model material to explore the role of supramolecular order in the physics of polymeric semiconductors. In thin films it self-organizes into two-dimensional π -stacked lamellar structures, with co-facial interchain separation of 3.8 Å. These structures allow for two-dimensional charge-transport, resulting in field-effect mobilities of order $0.1 \text{ cm}^2 (\text{Vs})^{-1}$, approaching those of amorphous Silicon. The role of exciton coherence during early dissociation dynamics is of key importance to understand how photocarrier generation is different in rrP3HT compared to other materials showing lower supramolecular order. We speculate that the semiconductor polymers implemented in eventual technologies will be low-band-gap regioregular co-polymers displaying two-dimensional electronic dispersion. It is therefore of both fundamental and practical importance to develop profound understanding of excitonic properties in rrP3HT as a model material, and in parallel to unravel how these properties correlate with photocurrent generation.

We find that an H-aggregate model describes quantitatively the steady-state absorption and photoluminescence spectra in rrP3HT, and it allows us to extract the excitonic coupling J_0 , manifested by the exciton bandwidth W .^{18,19} Exploiting the model, we have shown that W correlates with the fractional volume of the film forming microcrystallites, which is a simple means of quantifying the quality of supramolecular order in rrP3HT films. In turn, the degree of microcrystallinity correlates with the charge transport properties. Namely, we find that the field-effect mobility is most weakly dependent on gate voltage in film microstructures displaying the highest degree of micro-crystallinity.²⁰ The linear absorption spectrum thus provides a direct, simple means to predict the charge transport properties in rrP3HT films, and we will correlate W values measured this way with external quantum efficiency spectra measured in photovoltaic diodes based on rrP3HT:PCBM blends.

We propose to measure time-resolved PL spectra in rrP3HT:PCBM blends at low temperature (4 K), with femtosecond time resolution, by means of Kerr-gate optical schemes. This will permit us to measure the time evolution of the relative 0-0 and 0-1 vibronic peak intensities, which in turn will permit us to unravel the evolution of exciton coherence. We will also measure time-resolved anisotropy. The decay of this function is a signature of energy transport. Recently we have shown how such experiments can be extended to enable us to examine how quantum-coherence assists excited state dynamics. In a conventional transient absorption anisotropy experiment the components of the signal polarized parallel and perpendicular to the polarization of the exciting pulse are recorded as a function of

the delay between the pump and the probe ultrashort laser pulses, T . The anisotropy decay as a function of T is then retrieved as the difference between the two components, normalized by the total intensity decay. The time profile of that decay provides information about transition dipole moment reorientation during the excited state lifetime. Thus time-resolved anisotropy has been extensively exploited to study electronic energy transfer in various kinds of multichromophoric systems.²¹ To study coherent energy transfer directly, a new ultrafast experiment, called two-time anisotropy decay (TTAD), was specifically designed.²² The principle is to measure the anisotropy decay not only as a function of T , like in the conventional anisotropy decay experiments, but also as a function of τ in a three-pulse heterodyne detected transient grating experiment. We found, remarkably, that coherence is preserved along PPV conjugated polymer chains during the migration of excitation energy, even at room temperature. We now need to determine the implications of this observation for energy migration in the presence of charge transfer, because there is an intimate relationship between energy and charge transfer in strongly interacting systems, while the symmetry is broken at an interface. We found for MEH-PPV that coherence does not survive interchain transfer, but little is known now about energy migration throughout the lamellar domain in rrP3HT. The objective of the combined measurements proposed here is to unravel the role of exciton coherence in charge separation mechanisms, and its dependence on film microstructure, in polymer-based photovoltaic diodes.

Collaborative Project Management

The principal investigators of this team, coordinated by Silva, will ensure that collective progress is maintained by holding project meetings on a biyearly basis, once during the broader network meeting, and once mid- year between network meetings. The first such meeting was held at Queen's University on 11 July 2011, in which the PIs discussed the collaborative project for years 2-5. This meeting involved talks by HQP participating in the project, followed by round-table style discussions. We will alternate the location of these meetings between the four institutions of the project.

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