



VILNIUS UNIVERSITY
CENTER FOR PHYSICAL SCIENCES AND TECHNOLOGY
UNIVERSITÉ DE PAU ET DES PAYS DE L'ADOUR

Meera Stephen

**Charge Transport and Novel Poly(fullerene)s in Organic
Photovoltaics**

Summary of doctoral thesis,
Technological sciences, Material engineering (08 T)

Vilnius, 2016

The work described in this thesis has been carried out at Vilnius University (Lithuania) and Université de Pau et des Pays de l'Adour (France) during 2013-2016.

This research has been funded by the European Union Seventh Framework Program (FP7-PEOPLE-2011-ITN) under grant agreement ESTABLIS no. 290022

Supervisors:

Prof. Dr. Gytis Juška (Vilnius University, Technological Sciences, Material Engineering – 08 T).

Dr. Roger C. Hiorns (Université de Pau et des Pays de l'Adour, Physical Sciences, Chemistry – 03P).

Thesis defended at the united Vilnius University and CPST Physics Research Council:

Chairman:

Prof. Habil. Dr. Saulius Antanas Juršėnas (Vilnius University, Technological Sciences, Material Engineering – 08 T).

Members:

Prof. Dr. Vidmantas Gulbinas (Vilnius University, Technological Sciences, Material engineering – 08T);

Prof. Dr. Vytautas Getautis (Vilnius University, Technological Sciences, Material engineering – 08T);

Prof. Dr. Piétrick Hudhomme (Université Angers, Technological Sciences, Material engineering – 08T);

Prof. Dr. Laurence Vignau (Ecole Nationale Supérieure de Chimie Biologie et Physique de Bordeaux, Technological Sciences, Material engineering – 08T).

The dissertation will be defended on 26th of October in 2016, 16:00 in auditorium No. 212 in Faculty of Physics, Vilnius University, Saulėtekio av. 9, LT-10222, Vilnius, Lithuania.

Summary of dissertation sent on 26th of September 2016.

The dissertation is available at Vilnius University, Center of Physical science and technology libraries and on internet: www.vu.lt/lt/naujienos/ivikiu-kalendorius

VILNIAUS UNIVERSITETAS
FIZINIŲ IR TECHNOLOGIJOS MOKSLŲ CENTRAS
UNIVERSITÉ DE PAU ET DES PAYS DE L'ADOUR

Meera Stephen

**Krūvio pernaša ir nauji polifulerenai
organinėse fotovoltinėse sistemose**

Daktaro disertacijos santrauka
Technologijos mokslai, medžiagų inžinerija (08 T)

Vilnius 2016

Disertacija rengta 2013-2016 metais Vilniaus ir de Pau et des Pays de l'Adour universitetuose.

Moksliniai tyrimai finansuoti iš Europos Sąjungos FP7 programos (FP7-PEOPLE-2011-ITN) grantu ESTABLIS Nr. 290022 lėšų.

Moksliniai vadovai:

prof. habil. dr. Gytis Juška (Vilniaus universitetas, technologijos mokslai, medžiagų inžinerija – 08 T)

Dr. Roger C. Hiorns (Po universitetas (Université de Pau et des Pays de l'Adour, Prancūzija), fiziniai mokslai, chemija – 03P)

Disertacija ginama Vilniaus universiteto Medžiagų inžinerijos mokslo krypties taryboje:

Pirmininkas – prof. habil. dr. Saulius Antanas Juršėnas (Vilniaus universitetas, technologijos mokslai, medžiagų inžinerija – 08T).

Nariai:

Prof. dr. Vidmantas Gulbinas (Fizinių ir technologijos mokslų centras, technologijos mokslai, medžiagų inžinerija – 08T);

Prof. Vytautas Getautis (Fizinių ir technologijos mokslų centras, technologijos mokslai, medžiagų inžinerija – 08T);

Prof. dr. Piétrick Hudhomme (Anžė universitetas, Prancūzija, technologijos mokslai, medžiagų inžinerija – 08T);

Prof. dr. Laurence Vignau (Bordo nacionalinė chemijos, biologijos ir fizikos mokykla, technologijos mokslai, medžiagų inžinerija – 08T).

Disertacija bus ginama 2016 m. spalio 26 d. 16⁰⁰ val. VU Fizikos fakulteto 212 auditorijoje, Saulėtekio al. 9, LT-10222, Vilnius, Lietuva.

Disertacijos santrauka išsiuntinėta 2016 m. rugsėjo 26 d.

Su disertacija galima susipažinti Vilniaus universiteto, Fizinių ir technologijos mokslų centro bibliotekose ir VU interneto svetainėje adresu: www.vu.lt/lt/naujienos/ivikiu-kalendorius

Santrauka

Pastarąjį dešimtmetį atsinaujinančios energijos šaltinių poreikis skatino intensyvius nebrangių organinių saulės elementų (OPV - angl. Organic Photovoltaics) tyrimus. Dėka savo lankstumo, plastiškumo, galimybės padengti įvairius paviršius OPV gali būti naudojami įvairiose nišinėse srityse. Kadangi visos organinės elektronikos sritys pasižymi tarpdiscipliniškumu, todėl ir progresas OPV srityje reikalauja glaudaus chemikų bei fizikų bendradarbiavimo.

Ši disertacija susideda iš dviejų skirtingų, bet tarpusavyje susijusių, temų. Pirmąją dalį sudaro išsamūs saulės imitatoriumi apšviestų organinių saulės elementų degradacijos tyrimai. Fotogeneruotų krūvininkų ištraukimas tiesiškai kylančia įtampa (photo-CELIV - angl. photo-induced charge carrier extraction by linearly increasing voltage) ir lėkio trukmės (TOF - angl. time of flight) metodai buvo pasitekti siekiant nustatyti fotodegradacijos įtaką krūvininkų pernašai šiuose elementuose. Pirmiausia buvo tirti plačiausiai paplitę P3HT:PCBM aktyvios srities elementai. Siekiant ištirti negrįžtamą degradacijos mechanizmą buvo atlikti išsamūs krūvininkų judrio, tankio bei rekombinacijos tyrimai. Progresuojant degradacijai pastebėtas padidėjęs prilipusių krūvininkų kiekis bei išaugusi bimolekulinė rekombinacija, tai rodo idealios morfologijos, stebėtos nedegredavusiuose P3HT:PCBM bandiniuose, suardymą. Analogiški tyrimai taip pat buvo atlikti su benzoditiofeno (BDT) – diketopirolopirolio (DPP) grupės polimerais, turinčiais skirtingas šonines grandines. Ekstracinių srovės kinetikų analizė leido nustatyti prilipimo būsenų susidarymą, kuris buvo vienas pagrindinių vyraujančių efektų, įtakojančių krūvio ekstrakciją.

Šios disertacijos antrąją dalį sudaro fotovoltiniams prietaisams skirtų naujų polifulerenų sintetinimas. Neseniai atrastas erdviškai didžiulių grupių panaudojimo cheminėje sintezėje būdas, suteikia galimybę kontroliuoti atšakų prijungimo vietą bei patį polimerizacijos procesą. Naudojant 2,5-bis(oktiloksi)tereftalaldehidą bei PCBM komonomerus erdviškai kontroliuojamoje azometino ilido ciklo prijungimo polimerizacijos reakcijoje (SACAP - angl. Sterically controlled Azomethine ylide Cycloaddition Polymerization) buvo gautas didelės molekulinės masės, termiškai stabilus polimerus. Taip

pat, buvo įrodyta, kad didelių chromoforų panaudojimas leidžia sintetinti fulereno-dažų polimerus bei oligomerus ir tai įmanoma atlikti naudojant SACAP metodiką, pasitelkus DPP ko-polimerizuotą su C₆₀ bei PCBM. Tai yra pirmas kartas, buvo susintetinti polimerai, savo grandinėleje turintys organinio dažo fragmentą bei fulereną. Gautos medžiagos buvo charakterizuotos pasitelkus NMR (¹H, ¹³C ir 2D HSQC), GPC, sugerties spektrą, fluorescencijos emisiją, TGA bei DSC siekiant pagrįsti šių naujų medžiagų struktūrą bei savybes. Šių polifulerenų tinkamumas OPV buvo patvirtintas naudojant šias medžiagas kaip akceptorius tūrinės heterosandūros (BHJ - angl. bulk heterojunction,) celėse. Dėl aukštesnio LUMO lygmens (lyginant su PCBM) buvo nustatyta didesnė atviros grandinės įtampa nei naudojant PCBM, tai patvirtino modeliavimo rezultatus. Celės, pagamintos naudojant polifulerenus, yra stabilios šiluminiam stresui, todėl prognozuojamas jų tarnavimo laikas turėtų būti žymiai ilgesnis, nei naudojant PCBM. Manoma, kad trumpo jungimo srovės sumažėjimas celėse PCBM pakeičiant polifulerenais vyksta dėl neidealaus maišymosi su donoro polimeru.

Introduction

Increasing global energy demand and raising concerns of preserving the environment has urged humankind to look for fossil fuel free alternatives.¹ Research in renewable energy is moving to the forefront in a variety of fields owing to its increasing relevance in today's world. Among various renewable energy technologies, solar energy is an incredibly abundant² and extremely clean source, which remains underexploited to date.³ The growth of solar photovoltaics (PV) has been tremendous recently, with more than 60% of all PV capacity in operation worldwide by the end of 2014 being added over the past three years.⁴ However, in developing and emerging economies, obtaining PV installations at affordable rates remains a common challenge.

The first practical photovoltaic cell was developed in 1954 at Bell Laboratories, which soon became popular for space applications.⁵ The field of PV technology has since seen many innovations and is traditionally divided into three generations. The first generation is mainly based on mono/polycrystalline Si wafers, second generation on amorphous Si and other thin film technologies such as CIGS and CdTe, and finally the third generation based on organic materials.⁶

The use of organic materials for photovoltaic applications can potentially reduce the fabrication costs and enable bulk production of modules *via* printing processes. The most exciting aspect of this kind of solar cells is perhaps their light weight and flexibility, making them promising for niche applications such as building integrated photovoltaics, smart windows (which are partially transparent) and custom designed products. The world record efficiency for organic solar cells (OSC) stands at ~12% today as certified by the National Renewable Energy Laboratory (NREL).⁷ Last decade has seen a steady growth in efficiencies of these devices but their relatively low stability remains a bottleneck, which is still poorly understood.

Consequently, there has been a paradigm shift in the research focus from efficiency to stability in the recent years. Owing to the very nature of interdisciplinarity in the field of organic photovoltaics (OPV), any progress towards a more reliable device calls for the close cooperation of chemists and physicists.

This dissertation comprises of two distinct but interconnected topics. The first part looks into bulk charge transport in OPV devices employing charge extraction techniques. The effects of prolonged light exposure on the charge carrier transport are documented and analyzed in the former part. Photo-induced charge carrier extraction by linearly increasing voltage (photo-CELIV) and time of flight (TOF) techniques are made use of to probe charge carrier mobility and recombination at varying times of degradation. Firstly, benchmark devices based on poly(3-hexylthiophene) (P3HT) : phenyl-C₆₁-butyric acid methyl ester (PCBM) active layer are studied. Comprehensive investigations of charge carrier mobility, density and recombination are performed to get an insight into the consequent efficiency losses. Furthermore, the photo-degradation of a series of novel benzodithiophene (BDT) – diketopyrrolopyrrole (DPP) based polymers with different side-chains is documented. Analysis of extraction current transients indicated the progressive formation of trap states as being the most predominant effect influencing the process of charge extraction.

A second part of this work deals with synthesis of novel poly(fullerene)s for photovoltaic applications. Even though PCBM has been widely used as an acceptor material in OPV applications due to its efficient electron accepting and charge transport properties, it possesses some undesirable characteristics with regard to morphological stability. Fullerene spheres are known to diffuse through the active layer film forming large phase separated domains non-ideal for photovoltaic performance. Additionally they undergo light induced dimerization even in inert atmosphere, which was suggested to constitute a possible device degradation mechanism for OPV.⁸

In an attempt to alleviate this problem, we prepared polymers incorporating fullerenes in the main-chain so that the movement of individual spheres within the film is restricted. A recently discovered route where the use of sterically cumbersome groups provided for a certain degree of control over the additions to the fullerene sphere is explored to provide for main-chain poly(fullerene)s. The use of 2,5-bis(octyloxy)terephthalaldehyde and PCBM as co-monomers afforded high molecular weight, thermally stable polymers *via* the Sterically controlled Azomethine ylide Cycloaddition Polymerization (SACAP). Furthermore, the inclusion of large chromophore units to yield fullerene-dye alternating

polymers and oligomers is proved to be feasible with the SACAP route, where DPP is co-polymerized with both C₆₀ and PCBM. This is the first time that alternating polymers containing dyes and fullerene in the main-chain have been prepared. Detailed characterizations using NMR (¹H, ¹³C and 2D HSQC), GPC, UV-Visible absorption, fluorescence emission, TGA and DSC are carried out to substantiate the structure and properties of these new materials. Moreover, their photovoltaic properties are validated by using them as acceptor materials in bulk heterojunction (BHJ) cells. They are found to yield high open circuit voltages relative to PCBM, as a result of raised LUMO levels, confirming predictions from modeling studies. The devices incorporating these novel materials were also found to be stabilized in response to thermal stress, their *burn-in* phases being greatly reduced.

Main objectives

1. To document the photo-oxidative degradation behavior of P3HT:PCBM solar cells in terms of charge carrier transport – mobility, density and recombination.
2. To correlate the side-chain induced variations in photo stability of devices based on a series of BDT-DPP polymers with charge transport parameters.
3. To synthesize and characterize polymers consisting of fullerene units in the main-chain.
4. To evaluate the photovoltaic properties and possible resulting stability of solar cells incorporating synthesized poly(fullerene)s.

Novelty

All experiments, synthetic and electrical, described in this thesis are original and have not been reported before.

Layout of the thesis

The first chapter provides an introduction to the basics of working of organic solar cells as well as its history and progress. Further, it discusses the process of charge transport in

disordered organic materials and the two main types of degradation of active layer – photo-oxidative and morphological.

The second chapter discusses the methods used to study charge transport during this thesis – photo-CELIV and TOF. It highlights the advantages of these methods in studying working OSCs as well as explains the experimental set up and schematics.

The third chapter provides the data and results obtained for P3HT:PCBM during photo-oxidative degradation. Photo-CELIV and integral TOF transients are documented and analysed during the process of degradation.

The fourth chapter presents the study of charge transport in a series of BDT-DPP polymers in an effort to account for the variation of photo stability brought about the distinct side chains. It also provides excerpts from previously published data to provide the necessary background to clarify the motivation of present work.

The fifth chapter discusses the synthesis and characterization of three different main-chain poly(fullerene)s. The Sterically controlled Azomethine ylide Cycloaddition Polymerization (SACAP) is explored to prepare polymers based on C₆₀ as well as PCBM units.

The sixth chapter presents the photovoltaic performance results of synthesized poly(fullerene)s. It details the device fabrication and optimization procedures. It also reports on thermal stability of devices incorporating poly(fullerene)s with respect to control devices made with PCBM.

1. Probing charge transport in working OPV devices

The incoherent hopping of charge carriers and dispersive transport properties confers a high degree of complexity to the problem of probing charge transport in disordered organic systems. The fundamental transport properties, particularly mobility and recombination are subject to statistical distributions rather than single unique values and are influenced by a range of parameters such as temperature, electric field, morphology of film, purity and regio-regularity of the molecule used, etc.,^{9,10,11} Several techniques such as photo-induced carrier extraction by linearly increasing voltage (photo-CELIV), time of flight (TOF),

double injection (DoI), Field effect transistors (FETs), space charge limited currents (SCLC), impedance spectroscopy, etc. are utilized for the characterization of charge transport in organic semiconductors¹². Among these techniques, photo-CELIV possesses the unique ability to study OPV devices with thicknesses and configurations optimized for real-life working conditions.

The technique of CELIV was introduced about fifteen years ago by Juška *et al.*¹³ to study charge transport in microcrystalline silicon at first and was soon applied in conjugated organic systems.¹⁴ Conventionally, a linearly increasing voltage (triangular pulse) is applied to extract thermally generated carriers and the mobility is obtained from the peak extraction time of the corresponding transient. In organic semiconductors, where the thermally generated carriers are low, an input light pulse is typically employed to photo-generate the charges, wherein it is referred to as photo-CELIV.¹⁵ The method was recognized to have overcome certain limitations of the traditionally used time of flight (TOF) technique, including the possibility to study highly dispersive transients as commonly observed in organic disordered systems.¹⁶ It also allows the study of systems with high bulk conductivity and relatively short dielectric relaxation time (τ_o) in contrast to TOF.¹³ Moreover, the requirement of surface photogeneration limits applicability of TOF in optimized devices. However, TOF with volume photogeneration condition at high light intensities can be used in thin devices to obtain information on charge carrier recombination. These two techniques are employed in the work herein to record and analyze degradation in OPV devices.

The issue of degradation in polymer solar cells is complex owing to the plethora of degradation pathways that occur within the many layers comprising the device architecture. Significant literature can be found on this problem, including some excellent reviews^{17,18} and the identification of numerous factors such as oxygen,¹⁹ water,^{20,21} light,^{22,23} heat^{24,25} and mechanical stresses²⁶ as some of the crucial degradation triggers. The decline in photovoltaic performances with time is largely due to the combined action of interrelated parallel mechanisms at different locations of the device, at specific kinetics. This makes the realization of a holistic understanding and the identification of root causes of degradation

challenging.²⁷ Indeed, while many of the degradation pathways can be reduced to some extent by employing efficient barrier layers, degradation arising from evolution of the active layer needs to be addressed intrinsically.

1.2 Photo-Degradation in P3HT:PCBM Solar Cells

Among the many π -conjugated polymers developed for potential organic electronic applications, poly(3-hexylthiophene) (P3HT) is perhaps the most extensively studied. Despite the fact that new promising materials with improved properties exists today, P3HT remains of significant importance as a prototypical benchmark hole conductor material in OPVs. Chapter 3 details the effect of photo-induced degradation in the presence of oxygen on bulk charge transport in P3HT:PCBM based devices. Previous works have shown that in P3HT:PCBM devices with inverted structure, the degradation under illumination in dry air affects mainly the active layer, consisting of a reversible part, which is assigned to oxygen-induced doping and an irreversible part, which is due to photo-oxidation.²⁸ To elaborate, a partial recovery of J_{sc} and thus the efficiency was observed on heat treatment of the degraded devices. The work herein was intended to study the irreversible part of degradation and hence all samples (pristine and degraded) were annealed under vacuum at 140°C for 5 minutes prior to measurements.

The degradation of devices (non-encapsulated) were carried out by exposing them to AM 1.5 irradiation in dry synthetic air (80 % N₂, 20 % O₂, 0 % H₂O). The extent of degradation was monitored by UV/Vis-absorption spectroscopy and the optical density loss was categorized against the J_{sc} loss. To deconvolute the effect of possible electrode degradation, the degradation of partial devices (without top electrode) were compared with that of complete devices in similar conditions, and were found to follow similar kinetics.

CELIV transients were analysed to determine charge carrier mobility, density and microsecond scale dynamics through the process of degradation.

(a)

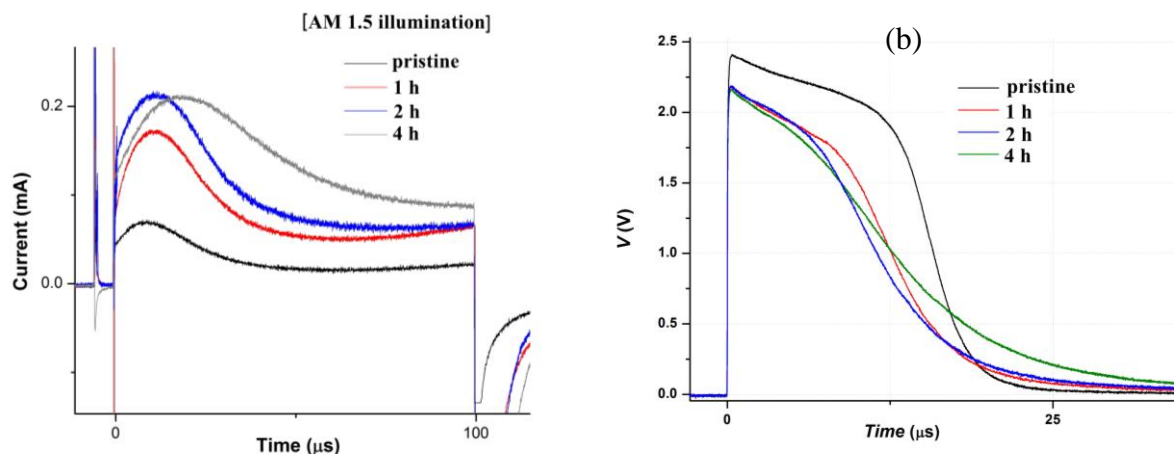


Figure 1. (a) Overlay of Photo-CELIV transients at IV applied voltage, $5 \mu\text{s}$ delay time and 10^4 V/s ramp rate and; (b) Overlay of saturated TOF transients, for samples with varying extents of degradation

The calculated mobilities from photo-CELIV were found to show a reduction of the blend mobility of the order of four times over the degradation time. The photo-CELIV mobility could be argued to be the average mobility of both charge carriers, however, the characteristic t_{max} is said to be predominantly influenced by faster carrier, which becomes significant when the electron and hole mobilities extremely differ from each other.²⁹

These transients also provide with relevant information regarding trapping, as observed in the overlay of transients shown in Figure 1. Apart from the amplitude, a significant difference between the curves is the distinct tailing for degraded samples. Transients corresponding to longer degradation times fail to achieve complete extraction within the applied pulse duration, indicating the presence of traps. The trapping effect is also evident from the peaks getting broader, owing to a more dispersive transport.

Furthermore, CELIV measurements in the dark revealed an increase in equilibrium carrier concentration four-fold within 4 h of illumination, in good agreement with previous reports^{30,31,32} and is often attributed to the effect of doping of the active layer by oxygen.

TOF measurements at high light intensities forming a space charge region within the reservoir of charges created, gives a quick view of whether the bimolecular recombination in the test system follows Langevin mechanism. Figure 1(b) shows that the saturated transient for the pristine sample clearly exhibits a plateau region before the main current decay which is a signature of reduced Langevin recombination, as expected in regio-regular

P3HT-PCBM blends. With progressive degradation, it is apparent that the extracted charge from the reservoir significantly reduces and the decay becomes increasingly featureless. The observed tailing of the transients is in line with trapping effect observed in photo-CELIV transients.

To sum, while photo-CELIV measurements reveal a reduction in average mobilities of a blend, an increased number of traps are evidenced from both photo-CELIV as well as high light intensity TOF measurements. Indeed, the increase in Langevin reduction factors with degradation determined from TOF measurements confirms the destruction of ideal nanomorphology reported for pristine P3HT:PCBM blends.

1.3 Photo-Degradation in BDT-DPP based Solar Cells

Current state of the art polymer semi-conductors based on low band gap polymers are decorated with a selection of linear and/or branched solubilizing side-chains. So far the impact of these side-chains on the polymer order, phase separation and electronic properties has been investigated only in benchmark materials and few studies report on their impact on photostability. While in some cases the presence of side-chains itself is reported to trigger photo-degradation,^{33, 34} optimizing the substituent chains/functional groups allows for optimum and stable photovoltaic performances.

Chapter 4 deals with the study of photo-degradation in solar cell devices based on a series of benzodithiophene (BDT) – diketopyrrolopyrrole (DPP) based polymers, with varying side-chains, using charge extraction measurements.

across the polymer series during the process of degradation. Measurements as described in section 1.2 were carried out to distinguish the apparent variations in photostability brought about by the distinct side chains.

Based on the analyses of the photo-CELIV and TOF transients, it was concluded that increase in trapped carriers play the most dominant role in determining charge transport properties of the blend on a macroscopic time scale. Since the devices were glass encapsulated, this behaviour is considered to be arising from inherent properties of the blend rather than external triggers from water or oxygen ingress. However, complementary studies are required to single out the potential effects of side-chain variation in terms of charge transport and photo-stability. More time-resolved measurements as well as methods that can quantify the number of trap states are considered desirable to this end.

The present study also highlighted the significance of inherent photo-thermal stability of active layer blends. The degradation of devices herein have been evidently driven by evolution of the blend morphology, as reported by Morse et al.³⁵ It is well known from the literature that the diffusion of fullerene molecules within the BHJ is one of major contributors of this undesirable phenomenon. Recent work in our group revealed the potential of oligofullerenes in combating the fast initial degradation of OPV devices on exposure to thermal stress, effectively improving their shelf-lives.³⁷ This concept is further exploited in the following chapters, which details the formation of stable main-chain poly(fullerene)s via a one-pot synthetic route and further discusses their photo-physical and photovoltaic properties.

2. Novel poly(fullerene)s in OPV

As previously discussed, the degradation of OPV devices arising from evolution of the active layer is a problem that needs to be addressed intrinsically. Active layer BHJs consisting of a mix of conjugated polymers and modified fullerenes often form phase-separated microstructures arising from limited polymer-fullerene miscibility. While maximizing the interfacial area facilitates exciton dissociation, reasonably sized pure domains are required for efficient charge transport to electrodes by forming complementary percolative pathways that minimize charge recombination.³⁸ Many studies have shown that the performance of the device as a whole is linked to the morphology of the blend film, *i.e.*, the packing of molecules and size of domains formed. The active layer morphology can be controlled by varying parameters, like chemical composition,^{39,40} choice of solvent,^{41,42} presence of additives^{43,44} and post-deposition techniques like thermal annealing^{45,46} or slow drying.⁴⁷ While such developments definitely helped improve the device performance, it is now recognized that the microstructure evolves over time once it has been formed during production of the device. Small organic molecules like PCBM tend to diffuse slowly or recrystallize over time especially at elevated temperature.⁴⁸ The best structure for device performance will in all probability not be the thermodynamically most stable. Such gradual changes in the microstructure eventually leads to a decline of the photovoltaic performance of the concerned devices. Morphology changes are clearly observed with prolonged times of device operation where the presence of light and temperature are inevitable.

PCBM is found reasonably well dispersed within the donor polymer rich phase after initial processing.⁴⁹ Under elevated temperatures typically reached during realistic working conditions, the enhanced molecular mobility acquired enables the PCBM molecules to diffuse through the film to form aggregates.⁵⁰ This lateral phase separation is found to enhance the PCEs during the initial few minutes (for temperatures $\sim 100^{\circ}\text{C}$) in blends with crystalline systems like P3HT due to improved percolation paths.⁵¹ However, at longer times (>30 min) larger domains of the order of tens of micrometers are formed by molecular diffusion of PCBM out of the polymer matrix.⁵² The major consequence of temperature on BHJ devices is thus the reduced interfacial area between the donor polymer

and the acceptor fullerene. Electrically, this means that the current drawn from the device under illumination at short circuit drops.^{52,53}

Additionally, in the presence of light, PCBM is prone to dimerization in solution⁵⁴, neat films⁵⁵ as well as potential active layer blends.⁵⁶ While the process of dimerization reduces the density of nucleation sites, it does not stop the growth of clusters.⁵⁷ The photo-induced dimerization and subsequent polymerization of fullerenes was found to occur in inert atmosphere by a [2+2] cycloaddition between (6,6) bonds on two adjacent fullerene cages^{58,59} and was found to be reversible at temperatures of *ca* 100 °C.⁶⁰ Oxygen greatly inhibits this process, attributed to O₂ molecules quenching the photoexcited triplet state, which is thought to be a necessary precursor to the photo-polymerization process.⁶⁰ In addition, light exposure has been reported to greatly accelerate the diffusion of any present O₂ molecules into interstitial voids of the fullerene lattice in the neat solid phase, ultimately forming oxidized fullerene end-products instead.⁶¹ Such photochemical reactions in the fullerene phase were reported to drive the intrinsic photo-degradation in many active layer blends in inert atmosphere.⁶²

A possible route to remediating these problems is by incorporating C₆₀ into polymers.⁶³ While C₆₀ is commonly integrated as moieties pendent to the main-chain,⁶⁴ as single additions on C₆₀ are the simplest to control, such polymers can tend to allow the C₆₀ to overly aggregate,⁶⁵ presumably due to the high degree of freedom that each sphere has. By incorporating C₆₀ into the main-chain of the polymer the ability for the sphere to move is reduced.

Chapter 5 details the syntheses of novel poly(fullerene)s to this end by employing the so-called sterically controlled azomethine ylide cycloaddition polymerization (SACAP). This route exploits the use of sterically cumbersome comonomers to ensure that the formation of tris-adducts is reduced, thereby diminishing crosslinking and increasing solubility. This polymerization, based on the so-called Prato chemistry, is thus shown to provide high molecular weight materials under certain strictly controlled conditions.

The first part of the chapter follows up on the work reported by Ramanitra *et al.*, where the feasibility of incorporating PCBM instead of C₆₀ as co-monomer in obtaining

poly(fullerene) structures is exemplified. Synthesis and detailed characterization of an alternating poly(fullerene) based on terephthalaldehyde and PCBM units is reported. The product poly{[bispyrrolidino(phenyl-C₆₁-butyric acid methyl ester)]-*alt*-[2,5-bis(octyloxy)benzene]} (PPCBMB) is found to be soluble in common organic solvents and displays molecular weights (M_w) >25000 g mol⁻¹ from GPC data, against polystyrene standards. When compared to the SACAP of C₆₀, it is found that PCBM permits the formation of even higher molecular weight polymers with greater solubilities and easier handling.

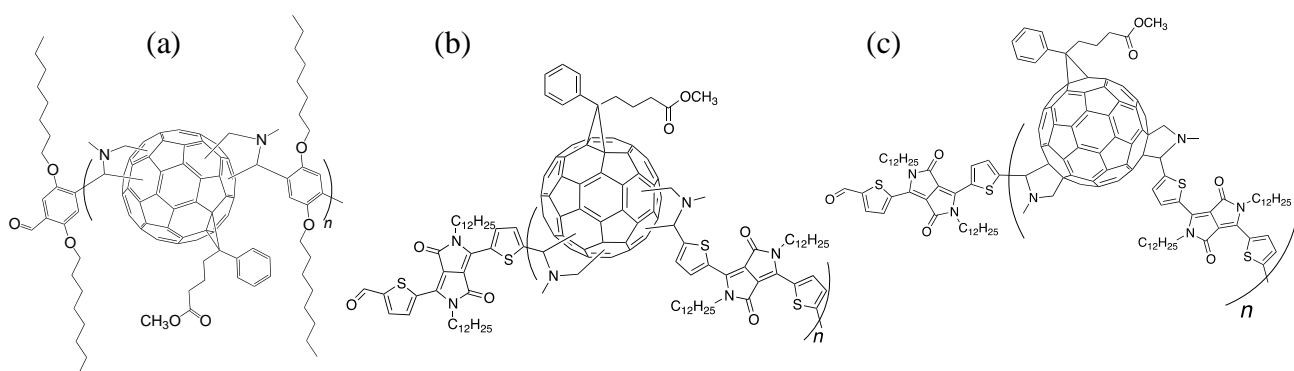


Figure 3. Structures of (a) PPCBMB ; (b) PDPF ; and (c) PDPPCBM

A second part of the chapter reports on inclusion of dye moieties to obtain polymers and oligomers made of alternating dye and fullerene units, with an extended absorption in the visible region. The SACAP route is employed with diketopyrrolopyrrole (DPP) as co-monomer to yield polymers and oligomers with molecular weights greater than 5600 g mol⁻¹ with C₆₀ and greater than 11200 g mol⁻¹ with PCBM. The products obtained are named poly[(dodecyl dithiophene-diketopyrrolopyrrole)-*alt*-bispyrrolidinofullerene] (PDPF) and poly[(dodecyl dithiophene-diketopyrrolopyrrole)-*alt*-(bispyrrolidino-phenyl-C₆₁-butyric acid methyl ester)] (PDPPCBM).

All the poly(fullerene)s synthesized herein are found to be thermally stable upto 300^oC from TGA analyses. Their LUMO energy levels are found to be raised with respect to PCBM, accordingly increasing with subsequent additions to the fullerene sphere.

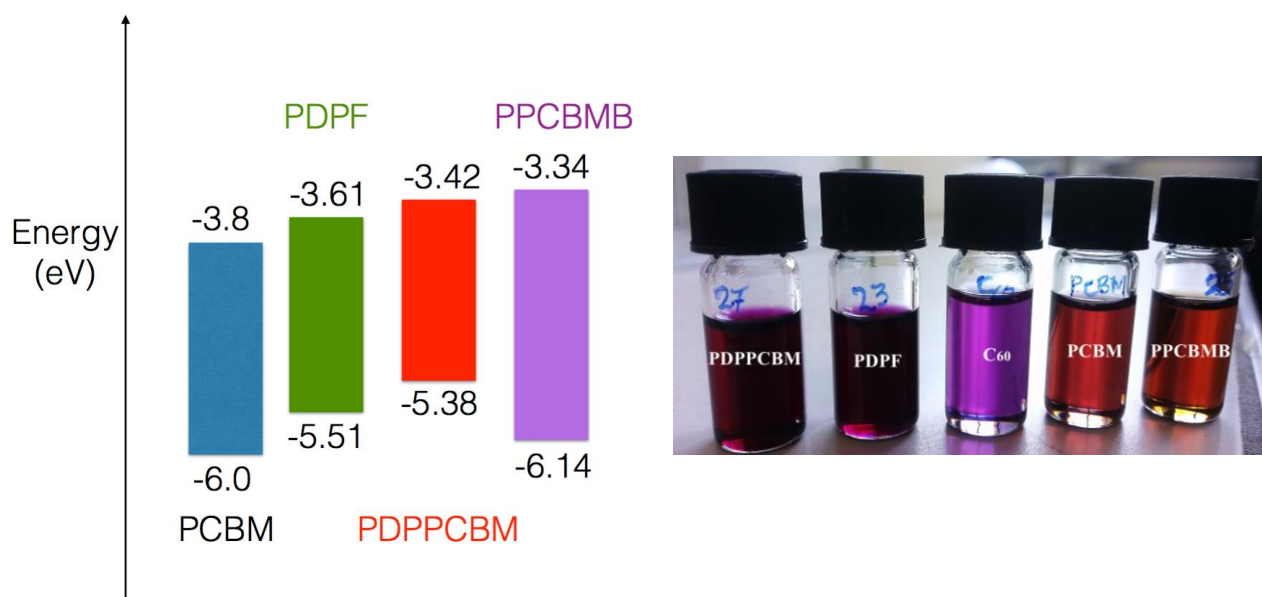


Figure 4 Energy levels of HOMO/LUMO for PDPF, PDPPCBM and PPCBMB relative to PCBM (left); and solutions of PDPPCBM, PDPF, C₆₀, PCBM and PPCBMB in toluene (right)

Chapter 6 discusses the photovoltaic properties of OPV devices incorporating PDPF, PPCBMB and PDPPCBM as acceptors in active layer blends with P3HT, Si-PCPDTBT and KP115. In general, the PCEs are limited by reduced short circuit currents on employing poly(fullerene)s in the active layer. Such reductions in short circuit currents likely originate from a non-ideal intermixing of donor and acceptor moieties, as discerned from photoluminescence quenching measurements. While replacing the relatively small fullerene spheres with large macromolecules such as the oligo/poly(fullerene)s, the donor:acceptor intermixing becomes non-optimal for charge transfer, as reported for many polymer : polymer BHJs in the literature.⁶⁶

However, the raised LUMO levels afforded higher open circuit voltages from devices employing poly(fullerene)s. The photo-CELIV mobilities of poly(fullerene) containing blends were found to be similar to those obtained for blends with PCBM. Interestingly, the poly(fullerene)s were able to stabilize the devices against thermal degradation, with their burn-in phases greatly suppressed. More studies on controlling the morphology of these blends needs to be carried out to unlock their full potential.

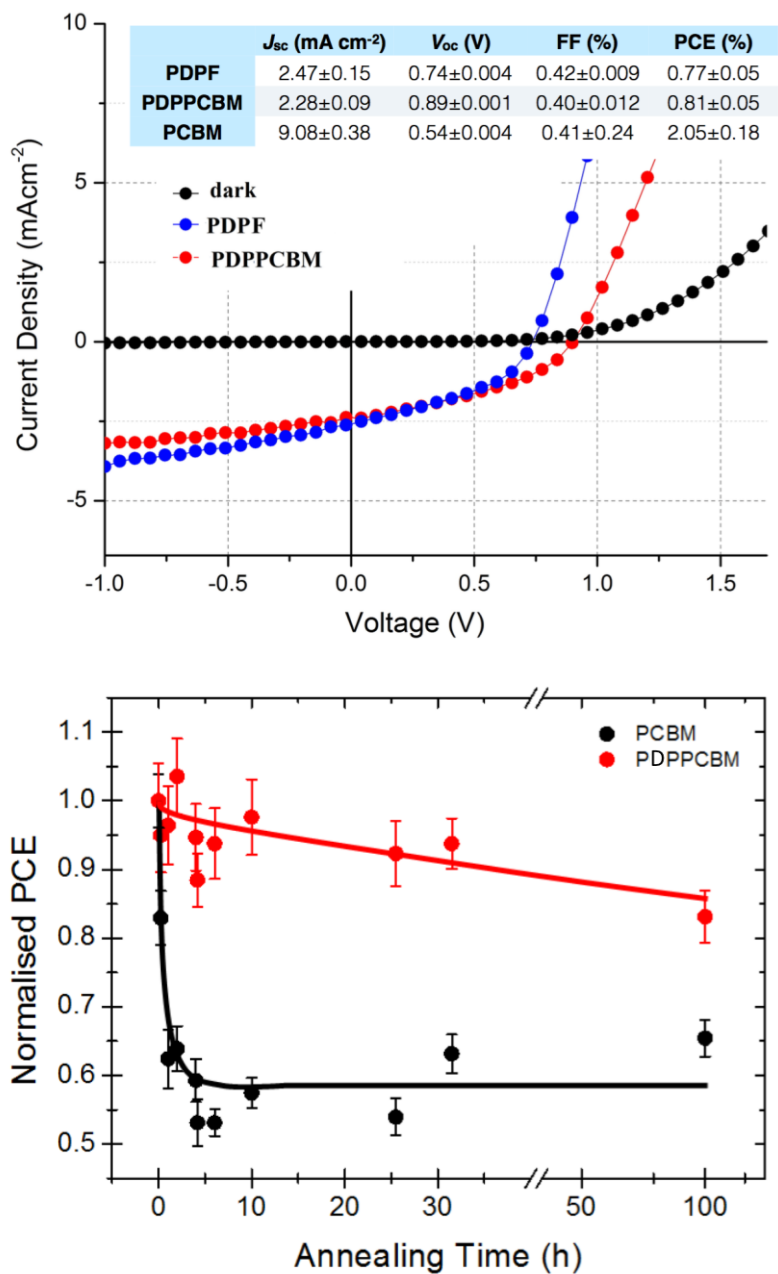


Figure 5. Current density – voltage (JV) curves of KP115:PDPF and KP115:PDPPCBM based devices with inset table showing summary of photovoltaic characteristics.(above) ; and evolution of normalized PCEs for KP115:PDPPCBM and KP115:PCBM based devices, clearly showing the enhanced stability of the former.

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Personal profile of the author

1. First name Meera
2. Second name Stephen
3. Birth date 1989.03.16
4. Birth place Kerala, India
5. Contacts meera.stephen@ff.vu.lt, Ph:+37067235363

6. Education/work History

- **PhD in Materials Engineering** (ongoing) 2013-2016
Vilnius University, *co-tutelle* with Université de Pau et des Pays de l'Adour
- **Project Assistant**, Indian Institute of Science, Bangalore, India 2011-2012
- **M.Sc Analytical Chemistry** 2009-2011
St. Joseph's Post Graduate & Research Centre, Bangalore, India
- **B.Sc Physics, Chemistry, Maths** 2006-2009
St. Joseph's College, Bangalore, India