

Physique et Modèles de Dispositifs Photovoltaïques Plastiques

Ajay K. Pandey

► To cite this version:

Ajay K. Pandey. Physique et Modèles de Dispositifs Photovoltaïques Plastiques. Physique [physics]. Université d'Angers, 2007. Français. NNT: . tel-00345829

HAL Id: tel-00345829 https://theses.hal.science/tel-00345829

Submitted on 10 Dec 2008 $\,$

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers. L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Physique et Modèles de Dispositifs Photovoltaïques Plastiques

Thèse de Doctorat Spécialité : Physique

Ecole Doctorale d'Angers

Présentée et soutenue publiquement

Le 13 Juin 2007 à Angers

par Ajay K. PANDEY

Devant le jury ci-dessous :

Président : M. Pietrick HUDHOMME, Professeur, Université d' Angers, France
 Rapporteurs : M. André MOLITON, Professeur, Université de Limoges, France
 M. Wai-Kin CHAN, Professor, University of Hong Kong, Hong Kong
 Examinateurs : M. Stéphane GUILLEREZ, Ingénieur, INES, CEA Chambéry, France
 M. Jean-Michel NUNZI, Professeur, Université d'Angers, France
 Invité: M. Ifor D.W. SAMUEL, Professor, University of St. Andrews, UK

Directeur de thèse : Pr. Jean-Michel NUNZI

Cellules Solaire Photovoltaïques Plastiques Laboratoire POMA, UMR CNRS 6136 Université d'Angers, bâtiment Db 2, boulevard Lavoisier, 49045 Angers.

ED 363

This thesis is dedicated to

my parents ...Radhika and Harendra Nath Pandey

Résumé

Cette thèse discute le fonctionnement et les mécanismes mis en œuvre dans les cellules solaires en plastique, composées de différents donneurs et accepteurs et dont l'architecture est décrite par hétérojonction/volume-hétérojonction. Une attention particulière a été portée à l'étude les conditions nécessaires pour la fabrication de cellules solaires à fort rendement, ceci de manière à aider au développement de compositions en donneur-accepteur nouvelles et plus efficaces. Une nouvelle classe de dispositifs photovoltaïques a été préparée et leurs rendements électriques ont été caractérisés. Les résultats expérimentaux obtenus avec ces dispositifs permettent une meilleure compréhension des phénomènes de génération et de dissociation d'excitons dans les cellules solaires organiques.

Pour la première fois, le *rubrene*, un matériau organique, semiconducteur et fortement luminescent a été utilisé en tant que donneur dans l'architecture de systèmes organiques. Celui-ci nous a permis de fabriquer un appareil offrant 2 modes de fonctionnement intégrés et qui reposent sur l'utilisation respective de des propriétés photovoltaïques (PV) et électroluminescentes (EL) du rubrene. Un des résultats les plus importants a été obtenu lors de l'application de tensions extrêmement basses (< 1V) exigées pour l'émission de lumière d'un tel dispositif. Ce mode de fonctionnement est décrit comme un processus de conversion vers de plus hautes énergies (up-conversion), un phénomène rarement observé dans les hétérojonctions organiques.

Abstract

This thesis discusses the operation and mechanisms of plastic solar cells made up using heterojunction/bulk-heterojunction of different donors and acceptors. Main emphasis is to highlight and address the forefront requirements for realization of efficient solar cells that would help develop new efficient donor-acceptor compositions. New class of efficient photovoltaic devices are prepared and electrically characterized. The results from these devices provide a better understanding of the exciton generation and dissociation phenomenon in organic solar cells.

For the first time, highly luminescent organic semiconductor material *rubrene* is used as a donor in solar cell architecture, resulting in formation of an organic dual function device with photovoltaic (PV) and electroluminescence (EL) behavior integrated. The intriguing operation of extremely low voltage (< 1V) required for light emission from such dual function device is described as an energy *up-conversion* process; a phenomenon rarely observed in organic heterojunctions.

Contents

Résumé	v
Abstract	vii
Acknowledgements	xi
List of Figures	xv
List of Tables	xxi
Chapter 1	1
Introduction	1
1.1. Physics of plastic solar cells	3
1.1.1 Absorption of photons	5
1.1.2 Exciton formation and diffusion	6
1.1.3 Exciton dissociation at donor-acceptor interface	8
1.1.4 Charge transport and collection	8
1.2. Characterization of plastic solar cells	10
1.3. Outline of the thesis	12
References	16
Chapter 2	18
Polymer based Bulk Heterojunction Solar Cells	
2.1. Introduction	18
2.2. Methanofullerene derivative as acceptor	20
2.2.1 MEH-PPV: Methanofullerene derivative based BHJ solar cells	24
2.2.2. P3HT: Methanofullerene derivative based BHJ solar cells	27
2.3. TiO ₂ : polymer solar cells	36
2.3.1. TiO ₂ : MEH-PPV network	36
2.3.2. TiO ₂ : P3HT network	40
2.4. Conclusions	43
References	44

Chapter 3	46
Model molecular blends and heterostructures	
3.1. Introduction	46
3.1.1. Pentacene-fullerene heterojunction solar cells	47
3.1.2. Thermal and mechanical stability	56
3.1.3. Pentacene/PTCDI-C13 heterojunction solar cells	61
3.1.4. Pentacene :PTCDI-C13 molecular blends	66
3.1.5. Pentacene-PTCDI-C13 : Bilayer vs Blend	72
3.2. Conclusions	75
References	76
Chapter 4	78
Improving open circuit voltage of pentacene solar cells	
4.1. Introduction	78
4.1.1. Effect of metal cathode on Voc	79
4.2. Pentacene dioxane and C60 solar cells	83
4.3. Conclusions	90
References	91
Chapter 5	92
Dual function Rubrene/Fullerene heterojunction: Solar cells and Light- emitting diodes	
5.1. Introduction	92
5.2. Rubrene/C60 heterojunction solar cells	93
5.3. Rubrene/fullerene light-emitting diodes	103
5.4. Conclusions	117
References	118
Chapter 6	120
Size and shape effects on the efficiency of organic solar cells	
6.1. Introduction	120
6.2. Size effects	121
6.3. Shape effects	128
6.4. Conclusions	131
References	132
Summary & Prospects	133
Annexure	136

Acknowledgements

First and foremost, I would like to thank my advisor, Prof. Jean-Michel Nunzi, for providing me with an invaluable opportunity, to work on the challenging and most relevant topic of organic photovoltaic over past three years. He has encouraged me with freedom to explore even the most outrageous ideas I have had during these years. Without his guidance this thesis would have not been successful. I consider it as a great pleasure to work alongside him with always something new to learn.

I would like to thank every one on my thesis jury. Thanks are due to Professors Andre Moliton and Wai Kim Chan for sparing their invaluable time reviewing the manuscript. I want to thank Professor Ifor D.W. Samuel, Professor Pietrick Hudhomme and Dr. Ing. Stéphane Guillerez in addition to my advisor for agreeing to serve on my thesis jury.

I always have enjoyed working in POMA and its wonderful gathering of graduate students, post-docs from all over the world. My thank goes to Prof.

Andre Monteil for providing such a fascinating environment for research and accepting me as a part of it.

I'm indebted to all the graduate students and post-docs, researchers, I have had pleasure to work with: Salima Alem, Gabriela Aldea, Hassina Derbal, Katherine Pacheco, K. N. Narayanan Unni , Kitty Man, Miahela Girtan, Sohrab Ahmadi, Wallace Chan.

I would like to thank all the members of Laboratory CIMMA where all experimental works were performed and our device fabrication facility is installed, my special thanks to Dr. Patrcik Batail, Prof. Jack Cousseau for their help and permission to use the lab and office facilities.

I would like to thank our collaborators here in France and abroad. My thanks to Florent Monestier, Dr. J.J. Simon, Dr. P. Torchio and Dr. L. Escoubas from Institute Fresnel, Marseille for our collaboration on optical modeling of the solar cell architectures.

I'm indebted to Prof. Alexandra Djurišić and Prof. W.K. Chan for providing the opportunity to learn the fabrication and characterization of nano-composite materials in their well-equipped laboratory in Hong Kong. I would like to thank all the group members for their help inside lab and memorable time spent outside. I'm greatly indebted to Wang Hai for his constant supply of TiO₂ samples on which solar cell experiments are performed.

I would like to thank Prof. John E. Anthony of University of Kentucky for his generous gift of pentacene dioxane, Dr. Steven Xiao of Organic Vision, for providing the multi-adduct methanofullerenes and Dr. Bernard Geffroy of CEA Saclay and Dr. David Vaufrey and Dr. Henri Doyeux of Thomson Multimedia Research Labs, Rennes, for EL measurements on the dual devices. Thanks are due to Jérôme Baffreau, Laboratory CIMMA for help in electro-chemical measurements on methanofullerene and to Romain Mallet, SCIAM, Angers for SEM measurements.

I would also like to thank Dr. Mukesh Joshi, for introducing me to the challenging field of organic semiconductors during my master thesis stay at R.R. Center for Advanced Technology, India.

Finally, and most importantly I wish to thank my parents who have supported me emotionally, intellectually and financially for all my life, my brother Arun, and sisters Pushpa and Suman for their love and affection I always had.

List of figures:

Figure 1.1:	Layout of an organic solar cell showing stepwise operation mechanisms	4
Figure 1.2:	Air Mass (AM) 1.5 spectral distribution reaching the earth surface	6
Figure 1.3:	Typical J-V response of a plastic solar cell under simulated illumination.	10
Figure 2.1:	Chemical structures of polymer donors and fullerene derivatives as acceptors used to form BHJ solar cells	20
Figure 2.2:	Absorption spectrum measured in chlorobeneze and chemical structures of MEH-PPV and P3HT	21
Figure 2.3:	Cyclic Voltammograms and absorption spectrums of P1-4	22
Figure 2.4:	Dark J-V response of MEH-PPV: Px devices	25
Figure 2.5:	Device J-V response under illumination intensity of 100 mWcm ⁻²	25
Figure 2.6:	% EQE spectrums of MEH-PPV: P1-P4	27
Figure 2.7:	J-V response, in dark, of different P3HT: Px compositions	28
Figure 2.8:	J-V response of P3HT: Px photoactive layers under illumination intensity of 100 mW cm ⁻²	29
Figure 2.9:	Photo action spectra (EQE) of P3HT: Px devices	30
Figure 2.10:	Atomic force micrographs of P3HT: Px (x= 1,2,3,4), rms roughness tends to increase with increasing adducts	32
Figure 2.11:	High resolution SEM scans on photoactive layers of P3HT: Px	34

Figure 2.12:	2D – inter connected porous network of TiO ₂ used for fabricating solar cells by filling donor polymer inside	37
Figure 2.13:	Energy level alignment at TiO ₂ : MEH-PPV (P3HT) interface required for exciton dissociation and charge collection. J-V response in dark and under illumination of the device TiO ₂ : MEH-PPV device	38
Figure 2.14:	EQE of TiO ₂ filled with MEH-PPV solar cells	39
Figure 2. 15:	J-V response of TiO ₂ : P3HT hybrid network solar cells	40
Figure 2.16:	EQE spectral response of TiO2: P3HT hybrid network solar cells	41
Figure 3.1:	Chemical structure of pentacene and C60	47
Figure 3.2:	Absorption profile of pentacene and C60 thin films	48
Figure 3.3:	Before and after annealing; J-V response of the Pentacene/C ₆₀ heterojunction solar cell with silver cathode.	49
Figure 3.4:	Comparative transmittance of the ITO thin films on glass and on PET substrates	51
Figure 3.5:	Comparative J-V response of pentacene/C ₆₀ heterojunction in dark and under illumination on glass and PET substrate	52
Figure 3.6:	AFM scans on ITO coated glass and PET substrates	54
Figure 3.7:	AFM micrographs showing larger grain formation of pentacene on glass substrate (left) compared to PET	54
Figure 3.8:	Full coverage by C_{60} and inter-grain connectivity of pentacene on ITO coated glass (left) and on PET (right)	55
Figure 3.9:	Thermal stability of pentacne/C60 plastic solar cells	56

Figure 3.10:	Device J _{sc} under different bend radii as shown as a function of applied strain	58
Figure 3.11:	EQE spectrum of pentacene/C60 heterojunction device	59
Figure 3.12:	Energetic evolved controlling the V_{OC} of the pentacene- C_{60} heterojunction solar cells	60
Figure 3.13:	Chemical structure of PTCDI-C13. The HOMO-LUMO of PTCDI-C13 is shown in the adjacent energy level diagram which allows high $V_{OC} \sim 1.6V$	61
Figure 3.14:	Absorption profile of PTCDI-C13 and pentacene thin films (50 nm).	62
Figure 3.15:	Dark and illuminated J-V response of pentacene/ PTCDI- C13 heterojunction device	63
Figure 3.16:	Photo-action spectra of pentacene/PTCDI-C13 heterojunction solar cell	64
Figure 3.17:	AFM micrographs measured on pentacene covered by thin layer of PTCDI-C13	65
Figure 3.18:	Spectral coverage of pentacene: PTCDI-C13 molecular blends. Absorption at 670 nm is shown to increase with loading of pentacene	66
Figure 3.19:	J-V characteristics of the pentacene: PTCDI-C13 blended devices with different wt% of pentacene in the single photoactive layer	67
Figure 3.20:	Exceptionally high EQE achieved with controlled growth of 3:1 blend ration of pentacene and PTCDI-C13	68
Figure 3.21:	Controlling the blend morphology for better PV yield. 1:1 ratio (top), 2:1 (center) and 3:1 (bottom).	70
Figure 3.22:	Comparative absorption profile of pentacene molecular blend and heterostructure	72

Figure 3.23:	J-V response of blend and bilayer pentacene-PTCDI-C13 devices	73
Figure 4.1:	J-V response of pentacene/C ₆₀ heterojunction device with calcium, aluminum and silver cathodes	79
Figure 4.2:	Origin of V_{OC} in pentacene-C ₆₀ heterojunction. M-I-M picture allows V_{OC} variation from 0.3 V to 2.1 V whereas HOMO-LUMO offset permits $V_{OC} \sim 0.5 V_{}$	80
Figure 4.3:	Reflection spectrum of 60 nm thin Ag, Al and Ca thin films on glass substrate	82
Figure 4.4:	Chemical structure of pentacene dioxane	83
Figure 4.5:	Absorption profile of pentacene dioxane	84
Figure 4.6:	J-V response in dark and under illumination intensity of 100 mW cm ⁻²	84
Figure 4.7:	J-V response under different illumination intensity. The Voc obtained is 500 mV	85
Figure 4.8:	AFM micrographs of 50 nm thick pentacene dioxane layers on glass	86
Figure 4.9:	Improved Voc with doped and irregular layer of rubrene on pentacene. J-V response in dark and under illumination intensity of 100 mW cm ⁻²	87
Figure 4.10:	Energetic of pentacene: rub: C_{60} solar cell. The new interface formation at rubrene- C_{60} allows enhanced V_{OC}	88
Figure 5.1:	Chemical structure of rubrene (left) and fullerene C ₆₀ (right)	93
Figure 5.2:	Absorption profile of rubrene and fullerene thin films	94
Figure 5.3:	J-V response of rubrene/fullerene solar cell in dark and under illumination intensities of 10.11	95

Figure 5.4:	Energy-level diagram of rubrene/fullerene heterojunction solar cell	96
Figure 5.5:	AFM micrographs taken on 50 nm thin rubrene layer	97
Figure 5.6:	J-V response with pre and post fabrication thermal treatment of rubrene/fullerene solar cells	98
Figure 5.7:	EQE of the rubrene/C60 solar cells with and without annealing	99
Figure 5.8:	Dark and illuminated J-V response of optimized rubrene/fullerene solar cell at different illumination intensities	101
Figure 5.9:	Photo-physics of a heterojunction solar cell. Photo-excited rubrene electrons under go charge transfer at rubrene-C ₆₀ interface giving rise to photocurrent	102
Figure 5.10:	Energy level diagram showing HOMO-LUMO positions of rubrene with respect to the electrodes	104
Figure 5.11:	J-V-L response of rubrene single layer light emitting diode	104
Figure 5.12:	Semi-log J-V-L response of the rubrene/fullerene heterojunction device. The EL turns on at much lower voltage than expected at ~ 1V	105
Figure 5.13:	EL spectral features of rubrene and rubrene/fullerene light emitting diodes	106
Figure 5.14:	J-V response of rubrene/fullerene heterojunction with different cathode metals.	107
Figure 5.15:	Relative position of rubrene/fullerene HOMO-LUMO energy levels with respect to metal cathode workfunction.	108
Figure 5.16:	Proposed mechanism leading to low voltage operation	110

Figure 5.17:	Combined near IR absorption spectrum of rubrene/fullerene thin film showing non-existence of mid levels facilitating Auger recombination inside the heterojunction device	111
Figure 5.18:	Dual function rubrene/PTCDI-C13 heterojunction; J-V turn on at 1V after external injection is observed with similar EL response (top). PV behavior with expected high Voc of 900 mV is obtained (bottom)	112
Figure 5.19:	Identical EL spectral features of rubrene, rubrene/C ₆₀ and rubrene/PTCDI-C13 devices	113
Figure 5.20:	Current and Power efficiency of rubrene/fullerene OLED	114
Figure 5.21:	Schematic layout of an <i>organic dual device</i>	115
Figure 6.1:	An equivalent circuit of an organic solar cell device	122
Figure 6.2:	Origin of series resistance inside an organic solar cell structure	123
Figure 6.3:	Layout of a heterojunction solar cell device with different active area of 0.03, 0.28 and 0.78 cm ²	124
Figure 6.4:	Different cathode geometries marked as 1, 2, 3 and 4 with constant active area of 0.30 cm ²	124
Figure 6.5:	a) J-V response with Al cathode; 0.78 cm ² (filled triangles), 0.28 cm ² (open circles) and 0.03 cm ² (filled squares). b) J-V	126
Figure 6.6:	Comparative EQE response with Al and Ag cathodes of pentacene/C60 solar cells	128
Figure 6.7:	Semi-log J-V plots for devices with Al cathode structures 1, 2, 3 and 4	129
Figure 6.8:	AFM micrographs showing wave like coverage of pentacene grains by C ₆₀ (left) and pentacene inter-grain connection (right), <i>rms</i> roughness remains the same	130

List of tables:

Table 2.1:	Redox potentials (V) of compounds P0-P4	24
Table 2.2:	Photovoltaic parameters for MEH-PPV: Px (x=1, 2, 3, 4) photoactive layers	26
Table 2.3:	PV parameters of P3HT: Px devices	30
Table 2.4:	RMS roughness of the different fullerene adducts dissolved with P3HT	33
Table 2.5:	PV response of TiO ₂ : polymer solar cells	41
Table 3.1:	PV performance of pentacene/C60 before and after annealing	49
Table 3.2:	Comparative PV performance on ITO coated glass and PET substrates	53
Table 3.3:	PV response of pentacene: PTCDI-C13 blends	69
Table 4.1:	Weak dependence of V_{OC} on the metal work function	81
Table 4.2:	Improving Voc of pentacene-C60 heterojunction solar cells	89
Table 5.1:	Thermal treatment induced improvement in PV parameters of rubrene/C ₆₀ solar cells	99
Table 5.2:	Photo response under different illumination intensities.	101
Table 6.1:	Relating organic-cathode interface with PV parameters of <i>ITO/PEDOT/pentacne/C60/BCP/Al or Ag</i> solar cells	126
Table 6.2:	Device performance with different cathode geometries with constant active area of 0.30 cm ²	130

Chapter 1 Introduction

The impact of greenhouse gases emitted everyday by burning fossil fuels has been a topic of great debate, which points our responsibility of maintaining the ecological balance on the planet earth [1]. With ever-increased global energy demands and limited energy resources to address this requirement, renewable energy sources are of great potential to address our future energy needs without affecting the natural resources. There may be varied opinion about which particular mode of renewable can provide sustainable solution to all our requirements but it is well agreed that solar energy has a great role to play in the future [2].

Solar cells or photovoltaic are well known medium of converting solar energy into electrical energy and are widely used for space applications and at remote locations on the earth. Although the best efficient silicon solar cells are well established and efficient medium of energy conversion, their initial production cost prohibit them to have a direct impact on the rising problem of energy shortage in the different parts of the world.

In past two decades there have been few emerging solutions to bring the PV production cost affordable for immediate applications [3]. Solar cells made up of organic materials are one such promising answer to make renewable energy cost-effective in all different means with added advantages of extremely light weight, flexibility over design and processing techniques. Such ultra thin solar cells, which are generally called *plastic solar cells*, though still in their infancy, have drawn huge attention from the scientific community [4-9].

Plastic solar cells are broadly covered into two different categories; the much studied and current state of art, solution processed polymer based donoracceptor (D-A) bulkheterojunction (BHJ) solar cells and vacuum deposited small organic molecule based D-A heterojunction or blend solar cells [6,8]. A loosely connected third category generally known as organic-inorganic hybrid solar cell compromises a polymer donor with wide band gap inorganic acceptors [11]. While the former two compositions are similar in principle and operation, the latter is closely related to the solution processed BHJ cells.

1.1 Physics of plastic solar cells

An efficient plastic solar cell requires a donor and an acceptor photoactive layer sandwiched between two electrodes either in form of a bilayer, or a single interpenetrated layer of both the donor and the acceptor. In order to allow the incident solar radiation to reach the photoactive layer one of the used electrodes need to be transparent. In plastic solar cells, after absorption inside the photoactive layer the absorbed photon creates an exciton inside the donor, which diffuses along the donor site, up to a certain length, termed as exciton diffusion length (L_D). For generation of photocurrent, dissociation of this exciton is required that happens at the donor-acceptor interface site. After dissociation of exciton into hole and electron, the acceptor takes the electron owing to its high electron affinity (EA) through photo-induced charge transfer. In order to avoid any other competing phenomenon like radiative recombination of the electronhole pair the charge transfer should be fast enough on the time scale < 1 ps [9]. Charges thus separated are transported across the device structure and delivered to the external circuit in presence of electric field caused by the asymmetric work function of the electrodes.

Figure 1.1 shows the geometrical layout of a heterojunction and BHJ organic solar cell. Because of the low diffusion length of exciton, typically < 10 nm in

commonly available organics donor-acceptor composition, a BHJ device structure is preferred for efficient dissociation of excitons since the probability of having an acceptor in proximity of the donor is higher compared to that with a sharp D-A heterojunction.



Figure 1.1: Layout of an organic solar cell (top) showing stepwise operation mechanisms (down). Stepwise mechanisms; absorption of incident photons (1) leads to creation of exciton (2), the exciton diffuses along the polymer chains (3) and gets dissociated at the donor-acceptor interface (4) thus giving rise to free charge carriers (5) which are swept away under influence of an external field.

As shown in figure 1.1, the overall efficiency of a plastic solar cell depends on the individual efficiencies of each step involved, starting with light absorption to exciton formation followed by exciton dissociation and finally the collection of free charge carriers thus created inside the bulk of the photoactive layer. Ideally, each of these steps should satisfy the optimum individual efficiency required for an overall healthy performance from the photoactive layer. In coming sections we discuss the importance and requirement of these steps as per the sequence quantified in figure 1.1.

1.1.1 Absorption of photons

The very first requirement of a good solar cell lies in its absorption spectral matching to that of the incident solar radiation. Generally conjugated organics are materials with high absorption coefficient (~ 10⁵ cm⁻¹) that means, unlike inorganic solar cells, a very thin photoactive layer is sufficient for absorbing almost all the incident solar intensity.

The air mass 1.5 (AM 1.5) solar irradiance spectrum available on the earth surface is shown in figure 1.2; where cumulative irradiance available from sun on a 1m² area of the earth is 1000W. Inset shows the AM 1.5 spectral distribution in terms of % solar irradiance distributed over the range of wavelength regions, ca. ultraviolet (UV), visible, near infrared (IR) and far infrared.



Figure 1.2: Air Mass (AM) 1.5 solar spectral distribution reaching the earth surface

As we can see, the peak irradiance of the AM 1.5 solar spectrum lies around 700 nm with 52% of the total available power extending beyond 750 nm in infrared region of the spectrum. So the photoactive material should have a broad absorption profile with peak absorption featuring around 700 nm for high photocurrent generation.

1.1.2 Exciton formation and diffusion

Working principle of an organic solar cell differs from inorganic solar cells. Absorption of light in the organic D-A photoactive layer results in the formation

of a mobile neutral excited state, referred as *exciton*, rather than free electron-hole pairs as produced in inorganic solar cells. This occurs for the reason that organic semiconductor materials have low dielectric constant (~3), compared to inorganic semiconductors with high dielectric constant (~10). The low dielectric constant of organic semiconductors causes high exciton binding energy (~ 0.3 to 1.eV), thus an energy input much higher than the thermal energy (kT) is required to dissociate such excitons [12]. An energy offset greater than exciton binding energy is thus desired at the highest occupied molecular orbital (HOMO) of the donor and is offered by the low lying lowest occupied molecular orbital (LUMO) of acceptor at the D-A interface. Exciton created in the bulk of photoactive layer diffuses from one site to other and reaches at the D-A interface where it dissociates into electron and hole. Hence for large photocurrent generation, all excitons should reach the D-A interface. Under such circumstances, the exciton diffusion length (L_D) should be greater than the thickness of the photoactive layer.

Since the exciton diffusion length in common organic semiconductors is typically ~10 nm [13], which falls shorter than typical ~100 nm thin photoactive layer required as absorption depth in device structures, hence the majority of excitons are lost through bulk recombination within the photoactive composition. Thus

the low exciton diffusion length limits charge carrier generation in organic solar cells.

1.1.3 Exciton dissociation at donor-acceptor interface

For a current flow and free electrons and holes in the device structure, all photo generated excitons must get dissociated. For the efficient dissociation of excitons, donor semiconductor should have intrinsic high ionization potential (IP) and acceptor should have high electron affinity (EA). This offset creates a potential energy at the donor-acceptor interface. Exciton arriving at this interface dissociates because the binding energy of exciton is lower than the energy offset at the D-A interface. This leads to creation of free charges inside the photoactive layer. Step 4 in Figure 1.1 shows the required energy position at the donoracceptor interface required for exciton dissociation.

1.1.4 Charge transport and collection

Dissociated excitons give rise to free charges inside the photoactive layers. Under space- charge (SC) regime, electrons and holes thus created drift towards the selective electrode under the influence of *built-in field* created by their work function difference. Space-charge conduction is due to electrons injected from an electrode to the LUMO of the semiconductor and holes injected from an electrode to the HOMO of the semiconductor. When both the electrodes form an ohmic contact with a semiconductor layer of thickness *d*, this means the electrodes are able to supply an unlimited number of one-type carriers and the current conduction is then limited by its own space charge.

Considering a trap free semiconductor into which charges are injected with a density n in its LUMO. The charge carrier density decreases with increasing distance from the injection contact by-

$$n(x) = \frac{3\varepsilon\varepsilon_0 V}{4ed^2} \left(\frac{d}{x}\right)^{1/2}$$

While the local field increases accordingly -----

$$F(x) = \frac{3V}{2d} \left(\frac{x}{d}\right)^{1/2}$$

At equilibrium, the total current density equals the difference between the drift and the diffusion current:

$$J = ne\,\mu F - De\!\left(\frac{dn}{dx}\right)$$

Where D is diffusion constant and μ is the carrier mobility.

Neglecting the diffusion term, current density becomes $J = ne\mu F$

Thus current density under SCL regime can be given by [14]

 $J_{SCL} = \frac{9}{8} \epsilon \mu \frac{V^2}{d^3}$, where ϵ is dielectric permittivity. Hence for fast extraction

of photo-generated charges, the photoactive composition should support high

mobility for both the charge carriers i.e. electrons and holes. A balanced mobility is desired when blending donor and acceptor forms the photoactive layer.

1.2 Characterization of plastic solar cells

Solar cell is a device that converts incident solar energy into electrical energy. For characterization of a solar cell its current-voltage (I-V) response is recorded in dark and under illumination. For determination of power conversion efficiency (PCE) of the solar cell, devices are illuminated by light source simulated to solar AM 1.5 spectrum.

Figure 1.3 shows the typical response of a plastic solar cell in dark and under simulated solar illumination.



Figure 1.3: Typical J-V response of a solar cell in dark and under illumination. Relevant PV parameters such as Voc, Jsc and maximum power available from this solar cell are highlighted.

Power conversion efficiency (PCE) of a solar cell is basically the ratio of electrical power generated by it to the optical power incident on it.

Under standard characterization, PCE is given by...

PCE (%) =
$$\frac{\text{Solar cell power output (mW/cm^2)}}{\text{AM 1.5 solar light (100mW/cm^2)}} \times 100$$

From figure 1.2; PCE can be written as

$$\eta(\%) = \left(\frac{V_{oc} \times J_{sc} \times FF}{I_0}\right)$$
1

Where Voc is termed as open circuit voltage, Jsc is short circuit current and FF stands for fill factor. FF is again defined by the ratio of maximum power available from the solar cell to the product of Jsc and Voc measured and is given by

$$FF = \left(\frac{V_m \times J_m}{V_{OC} \times J_{SC}}\right)$$
2

Where V_m corresponds to the maximum voltage point and J_m represents the maximum current point measured from the experimental J-V curves and are pointed in the figure 1.2. In general, FF defines the health of a solar cell by means of maximum available power from the solar cell to the external load.

Unlike silicon solar cells, where the energy difference caused by asymmetric work function of the metal electrode is used as a measure of open circuit voltage,

plastic solar cells often follow the energy offset at the donor-acceptor interface with the measured Voc [15].

Another important characterization of a solar cell is by measuring the external quantum efficiency (EQE) of the photoactive composition used in device geometry. EQE measured in % is basically the ratio of photo generated electrons to the per incident monochromatic photon which is given by the relation

EQE (%) =
$$\left(\frac{100 \times 1240 \times J_{SC}}{\lambda \times I_0}\right)$$
 3

Where I_0 is the incident intensity of the light source (mWcm⁻²), J_{SC} is short-circuit current (mAcm⁻²) and λ is the wavelength of light (nm).

1.3 Outline of the thesis

Since the introduction of BHJ concept [7], efficiency of polymer and fullerene based solar cells are greatly improved. The concept of BHJ advocates the advantage of extended geometrical interface of donor-acceptor by mixing them in a single photoactive layer. It's impressive to mention that present power conversion of such devices have scaled up to 5% from their previous values of 2.5% established in 2001 [8,16-18]. Concept of BHJ formation has been the guiding approach towards development of efficient plastic solar cells in recent years [7,16,17], its worth noting that these BHJ based solar cells have been
improved mostly because of device optimization, mostly the active layer morphology, and is limited to one particular composition of P3HT: PCBM [16,17]. For a broad strategy, new compositions are required in order to generalize the approach.

Aim of this thesis is to elaborate and underline the need and requirements for realization of alternative donor-acceptor compositions for broad understanding of the organic based solar cells behavior, which can be offered as a guideline to optimization of emerging compositions. We find that organic solar cells should be optimized according to the domain size of the D-A species, this also elaborates that the BHJ cannot always be a viable option for optimum PV performance.

In chapter 2, we study the widely known polymer BHJ solar cell compositions such as MEH-PPV or P3HT blended with PCBM. Apart from their different spectral features. We try to understand the significance and limitation of spontaneously created D-A phase separation on exciton dissociation efficiency in such devices. We used multi adducts of commonly used fullerene PCBM as acceptors to understand the limit of BHJ concept in these compositions. Pre defined nano -porous network of TiO₂ layer as acceptor highlights our point on treating every composition as a different system hence special requirements are desired for optimization of efficiency in new compositions.

In chapter 3, we demonstrate the similarity and difference between a heterojunction (HJ) and the BHJ composition using pentacene as a common donor in conjunction with different conformational acceptors. Advantage of HJ and BHJ over each other in this case is described. Like chapter 2, emphasis is on efficient exciton dissociation required for generation of high photocurrent. Additionally, we try to fulfill most of the criterion required for an efficient composition with particular attention on broad spectral coverage and high carrier mobility for efficient charge extraction in and out of the device structure. Further limitations like general post fabrication annealing required for optimum PV operation is avoided by growth of photoactive layers at a substrate temperature. Efficient solar cells are demonstrated on flexible substrate with good thermal and mechanical stability. Low Voc is identified as limiting factor for further increase in efficiency of these model solar cells.

Different strategies of improving the Voc of a low offset D-A composition like pentacene are described in chapter 4. For improving the Voc of pentacene-based compositions, we investigate the performance of a functionalized pentacene derivative and role of a florescent organic semiconductor interlayer between the D-A composition studied in chapter 3. A novel concept is introduced in chapter 5 for realization of smart organic optoelectronic devices having dual function of a solar cell and a light emitting diode integrated in a single device structure. Ultra low power consuming devices are thus realized and shown to work as an energy-creating medium in both modes of PV and EL. New findings are presented bearing potential to restructure our current understanding of organic semiconductor physics.

Finally, in Chapter 6 we investigate the influence of electrode size and shape on the PV behavior of the model solar cell devices. The results presented in this study highlight the loss mechanisms influencing FF and J_{SC} in large area upscaled device structures. Reduction in overall series resistance of the device structure is desired for an improved FF in organic solar cells. Our detailed studies correlate the loss of film quality with the PCE of the large area devices .

References

1. Intergovernmental Panel on Climate Changes, (IPCC), *Fourth assessment report* - *climate changes* 2005, website <u>www.metoffice.gov.uk/</u>

2. K. W. J. Barnham, M. Mazzeri, B. Clive, *Resolving the energy crisis: nuclear or photovoltaics ?*, Nature Materials **5** (2007), 161.

3. B. O'Regan, M. Gratzel, A low-cost, high-efficiency solar cell based on dyesensitized colloidal TiO2 films, Nature **353** (1991), 737.

4. C.W. Tang, *Two-layer organic photovoltaic cell*, Applied Physics Letters **48** (1986), 183.

5. J.J.M. Halls, R.H. Friend, *The photovoltaic effect in a poly (p-phenylenevinylene)/perylene heterojunction*, Synthetic Metals **85** (1997), 1307.

6. P. Peumans, V. Bulovic, S. R. Forrest, *Efficient photon harvesting at high optical intensities in ultrathin organic double-heterostructure photovoltaic diodes*, Applied Physics Letters **76** (2000), 2650.

7. S. E. Shaheen, C. J. Brabec, N. S. Sariciftci, F. Padinger, T. Fromherz, J. C. Hummelen, *2.5% efficient organic plastic solar cells*, Applied Physics Letters **78** (2001), 841.

8. G. Yu, J. Gao, J. C. Hummelen, F. Wudl, A. J. Heeger, *Polymer photovoltaic cells - enhanced efficiencies via a network of internal donor-acceptor heterojunctions*, Science **270** (1995), 1789.

9. N. S. Sariciftci, L. Smilowitz, A. J. Heeger, F.Wudl, *Photoinduced electron-transfer* from a conducting polymer to buckminsterfullerene, Science **258** (1992), 1474.

10. C. J. Brabec, N. S. Sariciftci, J. C. Hummelen, *Plastic solar cells*, Advanced Functional Materials **11** (2001), 15.

11. W.J.E. Beek, M.M. Wienk, R.A.J. Janssen, *Efficient Hybrid Solar Cells from Zinc Oxide Nanoparticles and a Conjugated Polymer*, Advanced Materials **16 (2004)**, 1009.

12. P. G. Dacosta, E. M. Conwell, *Excitons and the band-gap in poly (phenylene vinylene)*, Physical Review B **48** (1993), 1993.

13. D. E. Markov, E. Amsterdam, P. W. M. Blom, A. B. Sieval, J. C. Hummelen, *Accurate measurement of the exciton diffusion length in a conjugated polymer using a heterostructure with a side-chain cross-linked fullerene layer*, Journal of Physical Chemistry A **109** (2005), 5266.

14. M. Pope, C. E. Swenberg, *Electronic Processes in Organic Crystals and Polymers*, Oxford Scientific Publications (1999).

15. C.J. Brabec, A. Cravino, D. Meissner, N. S. Sariciftci, T. Fromherz, M. T. Rispens, L. Sanchez, J.C. Hummelen, *Origin of the Open Circuit Voltage of Plastic Solar Cells*, Advanced Functional Materials **11** (2001), 374.

16. W. Ma, C. Yang, X. Gong, K. Lee, A.J. Heeger, *Thermally Stable, Efficient Polymer Solar Cells with Nanoscale Control of the Interpenetrating Network Morphology*, Advanced Functional Materials **15** (2005), 1617.

17. G. Li, V. Shrotriya, J. Huang, Y. Yao, T. Moriarty, K. Emery, Y. Yang, *High-efficiency solution processable polymer photovoltaic cells by self-organization of polymer blends*, Nature Materials **4** (2005), 864.

18. J. Xue, S. Uchida, Barry P. R, S. R. Forrest, 4.2% *efficient organic photovoltaic cells with low series resistances*, Applied Physics Letters **84** (2004), 3013.

Chapter 2 Polymer based Bulk Heterojunction Solar Cells

2.1 Introduction

As described earlier, an efficient organic solar cell requires donor and acceptor for excited state charge transfer from donor to acceptor. In bulk heterojunction (BHJ) solar cells, donor and acceptor are generally dissolved in a common solvent and spin coating is used for processing an interpenetrated photoactive layer. Usually an acceptor with high EA is required for fast electron withdrawal from donor, which also leads to photoluminescence (PL) quenching of the donor, as electrons are no longer available in its LUMO for bulk recombination yielding PL. Thus quenching of PL is widely used as a measure behind formation of a quality BHJ composition [1, 2]. For efficient exciton dissociation with generally low exciton diffusion length , D-A domain distribution at nano-scale is required while maintaining a good percolation across the D-A phase is essential for charge conduction. Majority of the organic solar cell research is formed on solution processed BHJ compositions of PPV or P3HT based donors with PCBM as preferred acceptor [3, 4]. In recent years, the widely characterized composition of P3HT: PCBM has emerged as the benchmark for PV performance among different D-A compositions [4, 5]. Nevertheless, several parameters have direct influence on the performance of this composition, such as influence of solvent; high temperature annealing and above all spontaneously formed morphology of the D-A photoactive composition [4 - 6].

In this chapter we investigate the effect of different acceptors on the PV performance of solar cells fabricated by using MEH-PPV or *regio-regular* P3HT as donor in terms of donor-acceptor (D-A) domain distribution required for efficient exciton dissociation. The experimentally measured EQE is used as a measure behind effectiveness of the phase separated D-A compositions. Morphological characterizations such as AFM, SEM are used as supporting tool in our observations.

The first part of this chapter forms the studies on devices fabricated using randomly separated D-A BHJ using poly-adducts of fullerene termed as P1, P2, P3 and P4 where P1 represents the well known PCBM and P2, P3 and P4 are adducts with similar functional group as on PCBM.

In the second part, we create a predefined nano-porous network of inorganic acceptor TiO₂ and then fill it with the donor polymers, hence forming a template

rigid D-A BHJ. The amount of pore filling and hence magnitude of exciton dissociation related to measured EQE is used to understand the behavior of MEH-PPV and P3HT behind formation of BHJ. The acceptor strength of all the acceptors from P1-P4 including TiO₂ is almost identical, thus the big difference in acceptor strength is avoided.

2.2 Methanofullerene derivatives as acceptor

Figure 2.1 shows the chemical structures of the polymer donors and fullerene acceptors.



Figure 2.1: Chemical structures of fullerene derivatives as acceptors used to form BHJ solar cells

Before fabricating the solar cells based on polymer donor and fullerene acceptors, we characterized the spectral response of these methanofullerene derivatives by recording the UV-Vis absorption spectrum and their reduction potentials by electro-chemical measurements. Spectral coverage and chemical structures of MEH-PPV and P3HT are shown in figure 2.2.



Figure 2.2: Absorption spectrum measured in chlorobeneze and chemical structures of MEH-PPV and P3HT.

The cyclic voltammogram (CV) of compounds P1-P4 shown in figure 2.3 are recorded in order to get more information on their electron accepting capacities. Values are recorded in a *o*-dichlorobenzene/CH₂Cl₂ (2:1) solution using *n*Bu₄NPF₆ 0.1M as the supporting electrolyte, Fc⁺/Fc as the reference, platinum wires as counter and working electrodes using a scan rate: 100 mV/s. For reference we recorded CV of fullerene C₆₀, shown as P0 in figure 2.3. Relative absorption spectra of P1-P4 recoded in chlorobenzene solvent are also shown.



Figure 2.3: Cyclic Voltammograms and absorption spectrums of P1-P4.

As shown in figure 2.3, each voltammogram displays three reversible reduction waves. The values obtained for compound P0 (C_{60}) are in good agreement with values described in literature [7]. The first one-electron process is assigned to the formation of the anion radical of P0 (C₆₀⁻) at $E_{1/2 \text{ red1}} = -1.09 \text{ V}$ (vs Fc⁺/Fc), the second one-electron process to the formation of the di-anion of P0 ($C_{60^{2-}}$) at $E_{1/2 \text{ red2}}$ = -1.48 V, and the third one-electron process to the formation of the tri-anion radical of P0 (C_{60}^{3-}) at $E_{1/2 \text{ red3}} = -1.91 \text{ V}$. The values obtained for compound P1 (PCBM) are also in good agreement with values described in literature on this compound [8]. Thus by comparison with these two reference compounds, first electron processes of compounds P2, P3 and P4 can be assigned due to the formation of the anion radicals P2⁻, P3⁻ and P4⁻, respectively. In the same way next reduction waves result from the formation of P2²⁻, P3²⁻, and P4²⁻ species, and last reduction waves from the formation of P2³⁻, P3³⁻ and P4³⁻ species. The electron withdrawing effect of the ester groups has no influence on the fullerene moiety as they are separated from C₆₀ by a non-conjugated chain. On the other hand the shift of reduction waves to more negative potentials observed for compounds P0 to P4 is due to the presence of these side chains. This is due to the loss of one, two, three or four double bonds for compounds P1, P2, P3 and P4, respectively: in other words, lower the double bond in a fullerene is, less reducible the fullerene becomes. We find that the LUMO and HOMO orbitals calculated by molecular modeling (using Gaussian 97 software) are shifted in the same way and the LUMO level from P1 to P4 varied by 0.16eV only. Table 2.1 compares the redox potentials of P1-P4.

Compound	E ½ red 1	E ½ red 2	E ½ red 3
P0	-1.09	-1.48	-1.91
P1	-1.16	-1.53	-1.99
P2	-1.23	-1.60	-2.07
P3	-1.23	-1.62	-2.08
P4	-1.30	-1.67	-2.15

Table 2.1: Redox potentials (V) of compounds P0-P4.

2.2.1: MEH-PPV: methanofullerene derivative based BHJ solar cells

We used the fullerene derivates P1-P4 to understand the nature of interface formed within the BHJ of MEH-PPV donor. The loading of such acceptors in the BHJ D-A matrix of MEH-PPV has a determining influence on the PV performance of these devices [9]. It is also known that the higher loading of PCBM in MEH-PPV yields high PCE and EQE [9]. From hereon, $P \times$ will be used for describing various methanofullerene derivatives unless otherwise stated. Solar cells were fabricated by spin coating the MEH-PPV: $P \times$ in the ratio of wt% of 1:4 dissolved in chlorobenzene solvent. Figure 2.4 shows the dark J-V response of the ITO/PEDOT/MEH-PPV: $P \times /BCP/A1$ BHJ devices. The spin coated photoactive MEH-PPV: $P \times$ layer was ~100 nm thick. A 40 nm thin PEDOT layer and an 8 nm thin BCP layer were used as buffer. A 60 nm thin Aluminum cathode was deposited under vacuum.



Figure 2.4: Dark J-V response of MEH-PPV: P× devices

Figure 2.5 shows the device J-V response under illumination intensity of 100 mWcm⁻². All devices were illuminated through the transparent indium tin oxide (ITO) anode.



Figure 2.5: Device J-V response under illumination intensity of 100 mWcm⁻².

As we can see in figure 2.5, the short-circuit current density of P1 to P4 has a decreasing trend although the open circuit voltage doesn't vary much. PCE with PCBM (P1) is 1.4%, which falls to 0.08% for P4. The detailed PV parameters are given in Table 2.2.

Table 2.2: Photovoltaic parameters for MEH-PPV: P× (×=1, 2, 3, 4) photoactive layers.

MEH-PPV: P×	Voc	Jsc	FF	PCE	EQE @ 516 nm
(×=1-4)	(mV)	(mA cm ⁻²)	(%)	(%)	(%)
P1	715	5.48	35.3	1.40	27.51
P2	741	2.72	35.2	0.72	13.75
P3	771	2.24	28.3	0.49	11.18
P4	763	0.32	33.4	0.08	1.74

The external quantum efficiency (EQE) of MEH-PPV devices with P1-P4 is shown in figure 2.6. The best EQE was recorded for P1 with a similar decreasing trend like measured photocurrent from P1 to P4.

The differences observed in EQE indicate that majority of the excitons created in MEH-PPV: P1 are dissociated leading to large photocurrent in this particular composition. Also in table 2.2, the degree of exciton dissociation varies with the increasing adduct on the fullerene ring. As described in electrochemistry section, the acceptor strength of multi adduct fullerene is expected to decrease compared to the mono adduct although the difference is not significantly large. This may reduce the photo generated current Jsc and would slightly increase the Voc of

compositions with multi-adducts, an observation consistent with the results shown in table 2.2.



Figure 2.6: % EQE spectrums of MEH-PPV: P1-P4 solar cells.

2.2.2: P3HT: methanofullerene based BHJ solar cells

For a broad understanding of the nature of effect seen in MEH-PPV: $P \times BHJ$ devices, we made similar devices by replacing the donor MEH-PPV by P3HT. The absorption spectrum, shown in figure 2.2, for P3HT is not very different to that of MEH-PPV, though the device preparation requires different content of acceptor loading in the donor-acceptor matrix [4-6]. It has been known that the performance of P3HT: PCBM solar cells are widely dependent on a number of factors [4-6]. We study the P3HT donor with adducts of fullerene $P \times (\times = 1-4)$. All the devices investigated here are fabricated with 1:1 wt% of P3HT: P \times dissolved

in chlorobenzene. A 90 nm thick photoactive layer was spin coated on the prepared substrates with a 40 nm thin PEDOT layer on transparent ITO. After deposition of photoactive layer, substrates were dried at 100°C in vacuum. An 8 nm thin layer of BCP was evaporated on top of these photoactive layers before deposition of a 60 nm thin Al cathode layer.

Figure 2.7 shows the J-V response measured in dark of P3HT: $P \times$ devices fabricated as described above.



Figure 2.7: J-V response, in dark, of different P3HT: P× compositions.

As evident from the above figure, magnitude of current flow under forward bias differs when compared to MEH-PPV devices. In contrast to figure 2.4, the J-V slope under forward bias for multi adducts is better than the mono adduct (PCBM; P1). This may happen because of the increased solubility of lower content multi adducts (1:1 instead of 1:4) in chlorinated solvent with additional side chains. The photo response under illumination intensity~100 mW cm⁻² of such devices is shown in figure 2.8. A PCE of 1.7% was measured on composition containing P1 acceptor with closely followed values of 1.47 % and 1.32 % for P2 and P3 respectively. PCE measured on P4 acceptor was inferior because of the low Jsc ~ 2.2 mA cm⁻²; though the values for Voc and FF are comparable. Nevertheless this shows in general high degree of photocurrent generation for all adducts of fullerene in P3HT donor matrix compared to that obtained with MEH-PPV donor. The detailed PV parameters are tabulated in Table 2.3.



Figure 2.8: J-V response of P3HT: $P \times$ photoactive layers under illumination intensity of 100 mW cm⁻².

P3HT:P×	Voc (mV)	Jsc (mA cm ⁻²)	FF (%)	PCE (%)	EQE @ 500 nm
					(%)
P1	547	8.70	34.6	1.70	46.28
P2	553	6.79	38.9	1.47	30.04
P3	543	5.83	41.5	1.32	14.8
P4	533	2.19	43.2	0.47	4.36

Table 2.3: PV parameters of P3HT: P× devices

The high photocurrent measured from P3HT: $P \times$ can be described as the difference in the donor content inside the D-A photoactive layer (50% of P3HT) as majority of the photons are expected to be absorbed inside the donor, whereas MEH-PPV based composition represents donor quantity to only 20% inside the photoactive layer. Secondly it is known that P3HT supports better mobility for positive charges (holes) compared to MEH-PPV [6,10] which may make a difference in the final current flow in compositions based on these two donors.



Figure 2.9: Photo action spectra (EQE) of P3HT: P× devices. For reference to EQE spectrum, absorption spectrum of 50 nm thin films P3HT is also shown (left).

For understanding the origin of varying photocurrent, we measured the EQE of all the devices with different fullerene adducts. Experimentally measured EQE spectral response of P3HT: Px devices are shown in figure 2.9.

As shown in figure 2.9, the % EQE spectrum indicates that efficient exciton dissociation occurs inside the P3HT: P1 composition with a decreasing trend to increasing fullerene adducts. At the peak absorption of P3HT, EQE value as high as 46.3% is recorded for P1, which diminishes to 4.3% for P4. The measured photocurrent is consistent with the EQE measurements. This means that P3HT: $P \times BHJ$ is a better system than MEH-PPV: $P \times$, not because of the difference in the carrier mobility as mobility plays a role after exciton dissociation only.

For a closer view we study the morphology of the photoactive layers formed by spin coating of the P3HT: P× compositions. The grown layers on glass substrates were analyzed with atomic force microscope. Figure 2.10 shows the wide scan micrographs of the P3HT: P× layers. As evident from the micrographs; the similar features between P1 and P2 can be seen along with the similarity between P3 and P4. AFM pictures for P3HT: P1 shows homogenous feature with formation of smoother surface. It also shows a similar homogeneous feature with rather high roughness for P3HT: P2 composition. From the picture shown for P3HT: P3, large bumps arising on the surface are easily distinguishable with

even higher surface roughness compared to that with P1 and P2 loaded P3HT. In the final picture for P3HT: P4 we see similar bumps arising with increased surface roughness. The rms roughness values for all compositions are given in table 2.4.



Figure 2.10: Atomic force micrographs scanned on 100 nm thick layer of P3HT: $P \times (\times = 1, 2, 3, 4)$, rms roughness tends to increase with increasing adducts.

As shown in table 2.4, the much higher *rms* roughness values are observed on P3HT: Px (x=2-4) compared to that from P3HT: P1. This is despite the trend of

Composition	<i>rms</i> roughness (nm)		
P3HT: P1	2.2		
P3HT: P2	5.2		
P3HT: P3	15.0		
P3HT: P4	16.0		

Table 2.4: RMS roughness of the different fullerene adducts dissolved withP3HT.

increased solubility of multi adducts with additional side chains. This brings the importance of desired donor-acceptor domain distribution of polymer and fullerene multi adducts into play. Spin coating of donor-acceptor creates a spontaneous phase separated distribution of donor to acceptor species, as the side chain increases, it is expected from the molecular structure of these multi adducts to have unfavorable conformations within the interpenetrated network of donor-acceptor. Such randomly distributed acceptor may prevent the formation of quality D-A BHJ at the required scale.

An experimental quantification of such phenomenon is shown in figure 2.11. The figure shows the surface morphology of P3HT: $P \times$ compositions measured by scanning electron microscope (SEM).



Figure 2.11: High resolution SEM scans on photoactive layers of P3HT: Px taken on identical scale.

High-resolution SEM pictures in above figure reveals a totally different side of the BHJ formation using multi-adduct fullerenes. We observe void like structures in all the photoactive layers, which may bear the signature of low electron density domains. First we compare the SEM scans on P3HT: P1 and P3HT: P2. At scan scale of \geq 100 nm, we observe contrastingly different features. The domains are more condensed in P1 than in P2. We see a reverse trend in P3 and P4. At scan scale \leq 100 nm; the domains are more highly packed in P4 than P3. Such contrasting features certainly point to the conformational differences of fullerene multi-adducts inside the thin D-A photoactive layer. Spontaneous separation at scale lower than the thickness of photoactive layer ~100nm would reduce the effectiveness of the BHJ required for dissociation of photo-generated excitons inside the composition with increased fullerene adducts. This can also be correlated to the EQE response of the devices described earlier. It can be concluded from the identical absorption profiles of the multi adducts shown in figure 2.1 that the difference accounted in EQE spectrum is as because of the effectiveness of the D-A bulk heterojunction formation within the photoactive layer.

Based on above observations a comparison between P3HT and MEH-PPV compositions can be made. As described earlier and also seen across the work reported with MEH-PPV (including MDMO-PPV and other derivatives), for an efficient conversion of incident solar radiation this composition needs 1:4 donor: acceptor or even higher in wt.% ratio [3,9]. One would argue that the decrease in PV performance with increasing adducts may bear a signature of lesser fullerene content in the photoactive composition as going from P1 to P4 causes increase in molecular weight of the fullerene compound (because of the additional functional groups). A donor-acceptor composition based on molar ratio than weight ratio would give a clear picture. Nevertheless, the results obtained here shows morphological implications driving the PV response.

In general practice, the additional loading of acceptor (PCBM; P1) is correlated to the observed PL quenching because of the charge transfer, which is also used as a measure behind effectiveness of the donor-acceptor interpenetrated network formation. This may be true but according to the behavior observed with different adducts of fullerene in P3HT and MEH-PPV we propose that the effectiveness of the BHJ in P3HT and MEH-PPV with different loading of acceptor is based on their domain distribution within the D-A composition. In other words, MEH-PPV is a long chain polymer with random conformation compared to regio-regular P3HT with certain order [6,11]. This raises the requirement for higher loading of PCBM acceptor for an effective heterojunction formation through conformational collapse of the MEH-PPV polymer chain inside the D-A matrix. Such conformational recess may offer higher geometrical interface formation inside the D-A photoactive layer leading to formation of quality BHJ required for an efficient exciton dissociation.

2.3: TiO₂: polymer solar cells

In coming sections above observation is verified by using a pre-defined network of acceptor grown on the substrate and then realization of an interpenetrated D-A network by filling polymer donor inside this network. For such measurements, 2D meso-porous layers of TiO₂ with an average pore size of 20 nm (tuned to the exciton diffusion length limit in common polymer donors ~ 10 nm) and depth thickness of 40 nm was used. Finally the working devices are fabricated by filling the network of TiO₂ by either MEH-PPV or P3HT followed by evaporated metal anode.

2.3.1: TiO₂: MEH-PPV network

Alternatively, the BHJ can be realized in a totally different manner. A predefined pattern of either donor or acceptor at nano-scale can offer better control of D-A domain distribution. A possible solution to create such pre-existing network of polymer D-A is to develop soft lithography for photoactive layers that permit nano-scale patterning of these organic layers. Alternatively, wide band-gap semiconductor TiO₂ can be used to form controlled nano-porous films to offer large surface area similar to conventional BHJ created by the spontaneously phase separated D-A. For this, highly porous TiO₂ layers consisting of 2D interconnected network of anatase crystallites were processed on the ITO substrates.



Figure 2.12: 2D – inter connected porous network of TiO₂ used for fabricating solar cells by filling donor polymer inside.

The titanium-interconnected network was prepared using an optimized recipe [12]; Poly (styrene-block-ethylene oxide) (PS-b-PEO) as a templating agent, while

titanium tetraisopropoxide (TTIP) was used as a TiO₂ precursor; a solution of 1% w/v PS-*b*-PEO was prepared in toluene. A solution of 2.5% w/v of TTIP in toluene was prepared; The PS-b-PEO and TTIP mixed solutions with different volume fractions were used for spin coating onto the ITO. Films of 40 nm thickness were obtained by spin coating; the films were calcinated by heating at 1 °C /min rate up to 400 °C at which large part of the film is converted to TiO₂. The inter-connected TiO₂ image from transmission electron microscope (TEM) is shown in figure 2.12. Titania nano-porous layers thus fabricated on top of transparent ITO conducting layers, had average pore size of ~23 nm. box.



Figure 2.13: Energy level alignment at TiO₂: MEH-PPV (or P3HT) interface required for exciton dissociation and charge collection (left). J-V response in dark and under illumination of the device TiO₂: MEH-PPV device (right).

To fabricate the solar cell, a 50 nm layer of MEH-PPV was spin coated from 8mg/ml xylene solutions on top of TiO₂ porous layers, polymer filled samples were annealed at 100 °C inside a vacuum oven for solvent removal. Finally, 30

nm of gold was evaporated as an anode through a proper shadow mask. Energylevel diagram with respective HOMO-LUMO levels of the TiO₂ and MEH-PPV is shown in figure 2.13, showing energetically favorable charge transfer and collection mechanisms. The J-V characteristics of the hybrid cells measured in dark and under AM 1.5 G solar illumination at 100 mWcm⁻² is also shown in figure 2.13. The devices were illuminated through the transparent ITO, serving here as cathode. The open circuit voltage, Voc and the short-circuit current density Jsc measured for as fabricated cells were 793 mV and 0.32 mAcm⁻² respectively. Such high open circuit voltage satisfies the typical characteristic of MEH-PPV based bulk-heterojunction (BHJ) devices described in section 2.1.1, which appears to be in good agreement with the difference of the HOMO and LUMO of the MEH-PPV donor and TiO₂ acceptor composition shown in figure 2.13.



Figure 2.14: EQE of MEH-PPV filled TiO₂ hybrid solar cell.

The EQE spectrum measured on such devices is shown in figure 2.14. An EQE of 2.5% was measured on MEH-PPV filled TiO₂ solar cells indicating the poor exciton dissociation efficiency responsible for low J_{SC} observed from this device.

2.3.2 TiO₂: P3HT Network

For complete performance comparison of MEH-PPV filled TiO₂ interpenetrated solar cells, we made similar devices by filling the porous network of TiO₂ by P3HT polymer donor. The same fabrication conditions were used as described in section 2.1.4. Figure 2.15 shows the dark and illuminated J-V response of devices prepared with P3HT donor.

The interpenetrated device network has the configuration: ITO/TiO₂: P3HT/Au. A relatively lower open circuit voltage of 300 mV was measured from this device composition with three times higher $J_{SC} = 0.91$ mA cm⁻² compared to that measured on MEH-PPV filled TiO₂. The EQE response is shown in figure 2.16.



Figure 2. 15: J-V response of TiO₂: P3HT hybrid network solar cells.

Table 2.5 compares the PV response of the different polymer donors used with porous TiO₂ interpenetrated hybrid solar cells. The observed PCE is comparable to the existing reports on similar compositions [13, 14].



Figure 2.16: EQE spectral response of TiO₂: P3HT hybrid network solar cells.

TiO ₂ : Donor	Voc (mV)	Jsc (mA cm ⁻²)	FF (%)	PCE (%)	EQE @ 500
					nm (%)
MEH-PPV	793	0.32	35.6	0.09	2.5
РЗНТ	303	0.91	42.5	0.11	3.91

Table 2.5: PV response of TiO₂: polymer solar cells

As we can see from table 2.4, using the same surface area of TiO₂ template, the polymer donor response varies in terms of EQE observed and hence the amount

of photocurrent measured from the similar device architectures. This may question the extent of interpenetrated network formed by MEH-PPV to that using P3HT. The previously discussed low carrier mobility in MEH-PPV remains a concern behind lower Jsc from TiO₂: MEH-PPV device. Assuming desired uniform filling of polymer donor inside the TiO₂ template [15], at the first approximation, the EQE onset close to 675 nm in TiO₂: P3HT as compared to 600 nm in TiO₂: MEH-PPV holds the explanation behind better photocurrent from the P3HT based device. The slightly higher EQE may originate from the better absorption in P3HT over MEH-PPV. Nevertheless, the limited spectral coverage of both these polymer donors highlights the need of alternative D-A compositions.

2.4 Conclusions

In this chapter, we observed that the BHJ formation within the D-A photoactive layer differs significantly for different donors with commonly used fullerene acceptor. The spontaneous nature of domain distribution created in these D-A compositions has direct impact on the photovoltaic performance of solar cell devices. The magnitude of photo-generated exciton differs accordingly and even the best composition of MEH-PPV: PCBM or P3HT: PCBM has limited exciton dissociation; < 50% this shows only half of the photogenerated excitons are dissociated. The organic-inorganic hybrid D-A based BHJ studies confirm conformational differences in MEH-PPV and P3HT hence different strategies for optimal PV response are desired.

The control over the quality of BHJ formation is spontaneous and this highlights why the PV response of these composition changes abruptly. Such wide variation in their PV response offers less clarity to be treated as a guiding approach for general development and enhancement of other D-A compositions. In next chapter, we address these issues by taking control over the growth of D-A photoactive layers at smaller scale using conjugated organic oligomers as model composition to generalize and understand the requirements towards realization of efficient plastic solar cells.

References

1. N. S. Sariciftci, L. Smilowitz, A. J. Heeger, F.Wudl, *Photoinduced electron-transfer from a conducting polymer to buckminsterfullerene*, Science **258** (1992), 1474.

2. C. J. Brabec, N. S. Sariciftci, J. C. Hummelen, *Plastic solar cells*, Advanced Functional Materials **11** (2001), 15.

3. S. E. Shaheen, C. J. Brabec, N. S. Sariciftci, F. Padinger, T. Fromherz, J. C. Hummelen, *2.5% efficient organic plastic solar cells*, Applied Physics Letters **78** (2001), 841.

4. W. Ma, C. Yang, X. Gong, K. Lee, A.J. Heeger, *Thermally Stable, Efficient Polymer Solar Cells with Nanoscale Control of the Interpenetrating Network Morphology*, Advanced Functional Materials **15** (2005), 1617.

5. G. Li, V. Shrotriya, J. Huang, Y. Yao, T. Moriarty, K. Emery, Y. Yang, *High-efficiency solution processable polymer photovoltaic cells by self-organization of polymer blends*, Nature Materials **4** (2005), 864.

6. Y.Kim, S. Cook, S.M. Tuladhar, S.A. Choulis, J. Nelson, J.M. Durrant, D. D.C. Bradley, M. Giles, I. Mcculloch, C-S Ha, M. Ree, *A strong regioregularity effect in self-organizing conjugated polymer films and high-efficiency polythiophene: fullerene solar cells*, Nature Materials **5** (2006), 197.

7. Q. Xie, E. Pérez-Cordero, L. Echegoyen, *Electrochemical Detection of* C₆₀⁶⁻ and C₇₀⁶⁻: *Enhanced Stability of Fullerides in Solution*, Journal of American Chemical Society, **114** (1992), 3978.

8. J. C. Hummelen, B. W. Knight, F. LePeq, F. Wudl, J. Yao, C. L. Wilkins, *Preparation and Characterization of Fulleroid and Methanofullerene Derivatives*, Journal of Organic Chemistry, **60** (1995), 532.

9. S. Alem, R. de Bettignies, J.M. Nunzi, M. Cariou, *Efficient polymer based interpenetrated network photovoltaic solar cells*, Applied Physics Letters **84** (2004), 2178.

10. C. Melzer, E. J. Koop, V.D. Mihailetchi, P.W.M. Blom, *Hole transport in poly(phenylene vinylene)/Methanofullerenebulk-heterojunction solar cells*, Advanced Functional Materials Physics **14** (2004), 865.

11. D. Hu, J. Yu, K. Wong, B. Bagchi, P. J. Rossky, P. F. Barbara, *Collapse of stiff* conjugated polymers with chemical defects into ordered, cylindrical conformations, Nature **405** (2000), 1030.

12. H. Wang, C. C. Oey, A. B. Djurišić, M. H. Xie, Y. H. Leung, K. K. Y. Man, W. K. Chan, A. Pandey, J.M. Nunzi, P. C. Chui, *Titania bicontinuous network strucutres for solar cell applications*, Applied Physics Letters **87** (2005), 023507.

13. C. C. Oey, A. B. Djurišić, H. Wang, K. K. Y. Man, W. K. Chan, M. H. Xie, Y. H. Leung, A. Pandey, J.-M. Nunzi, P. C. Chui, *Polymer-TiO*² solar cells: *TiO*² *interconnected network for improved cell performance*, Nanotechnology **17** (2006), 706.

14. N. Kudo, S. Honda, Y. Shimazaki, H. Ohkita, S. Ito, H.Benten, *Improvement of charge injection efficiency in organic-inorganic hybrid solar cells by chemical modification of metal oxides and organic molecules*, Applied Physics Letters **90** (2007), 183513.

15. A.K. Pandey, J.M. Nunzi, H. Wang, C. C. Oey, A. B. Djurišić, M. H. Xie, Y. H. Leung, K. K. Y. Man, W. K. Chan, *Reverse biased annealing: Effective post treatment tool for polymer/nano-composite solar cells*, Organic Electronics **8** (2007), 396.

Chapter 3 Model molecular blends and heterostructures

3.1 Introduction

As discussed in chapter 2, an efficient solar cell requires control over growth of the photoactive layer so that a uniform matrix of D-A is established. It also requires high carrier mobility for photogenerated charge carriers with good spectral matching to the solar radiation.

For controlled growth of photoactive layer, here we use model devices grown under vacuum using physical vapor deposition process. High mobility semiconductor pentacene is used as donor with fullerene C₆₀ or PTCDI-C13 as different molecular acceptors. We first discuss the devices and their optimization for maximum exciton dissociation required for high photocurrent generation. Pentacene/C₆₀ heterojunction devices are compared to the blend solar cells fabricated on the bulk heterojunction concept by co-deposition of molecular blends of pentacene and PTCDI-C13.

3.1.1. Pentacene-fullerene heterojunction solar cells

Pentacene is the widely studied material with high intrinsic mobility for holes in field-effect transistors [1]. Its low band-gap close to 1.9 eV makes it an appropriate donor to realize an efficient D-A based organic solar cell. The chemical structure of pentacene and C₆₀ are shown in figure 3.1. Pentacene is a planar conjugated molecule with 5 phenyl rings and C₆₀ is conjugated cage like structure with diameter of ~7 nm.



Figure 3.1: Chemical structure of pentacene and C₆₀.

Figure 3.2 shows the absorption spectral profile of pentacene and C_{60} measured on a thin film of 50 nm. While C_{60} strongly absorbs in the wavelength range < 550 nm with decreasing absorption in the long wavelength region, pentacene absorption starts from 500 nm and peaks at 670 nm with an absorption onset extending up to 750 nm.



Figure 3.2: Absorption profile of pentacene and C₆₀ thin films.

As shown in absorption spectrum this D-A composition permits wide spectral coverage of incident solar radiation with pentacene peaking in the range of maximum photon-flux available from the sunlight (refer fig. 1.2).

For maximum absorption inside pentacene layer we fabricated heterojunction devices based on pentacene / C₆₀ by using a 55 nm thin layer of pentacene and 35 nm thin layer of C₆₀ sandwiched between transparent ITO anode and aluminum or silver metal cathode. 40 nm thin PEDOT: PSS and 8 nm thin BCP were used as buffer layers. Current –voltage response of such heterojunction device is shown in figure 3.3 when measured in dark and under illumination. Under illumination intensity of 80 mW cm⁻², short circuit current (Jsc) > 5 mA cm⁻² was measured
from this heterojunction device, which justifies pentacene as a good photovoltaic medium. Rather low open circuit voltage (Voc) of 230 mV was produced. We found the optimal efficiency of 1.4% when the devices were annealed after fabrication at 120°C for 15 min inside inert atmosphere of argon.



Figure 3.3: J-V response before and after annealing; of the pentacene/ C_{60} heterojunction solar cell with silver cathode.

Table 3.1 shows the improvement in photovoltaic parameters after post fabrication annealing.

Table 3.1: PV performance of pentacene/C₆₀ before and after annealing.

Treatment	Voc (mV)	Jsc (mA cm ⁻²)	FF (%)	PCE (%)	
No	230	5.57	42.3	0.67	
120°C	300	6.66	58.3	1.45	

We found similar device behavior in literature where post fabrication annealing at temperature close to 180°C was required to increase the PCE of such heterojunction devices [2,3]. PCE, thus improved, was related to the increased crystalline order in pentacene after high temperature annealing, which supports the enhanced Jsc [2,3]. Indeed, we observed increase in Jsc and Voc on thermally treated device structures and most importantly the much-improved FF of 58.3% that leads to PCE improvement from 0.67% to 1.45%. Improvement in FF comes because of the lowering of the series resistance which may originate by improvement at the various interface involved in this multilayer heterojunction device.

Post fabrication annealing is widely used on plastic solar cells where high temperature $\geq 150^{\circ}$ C is generally required for optimal PV performance [3-6]. Such high temperature treatment can become a limiting factor for realization of devices on flexible substrates.

For optimization of photoactive layer and avoiding the mandatory high temperature annealing, we fabricated similar heterojunction devices by organic deposition at substrate temperature in range of 60-80°C. Comparative pentacene/C₆₀ heterojunction devices are fabricated both on regular glass substrates and flexible PET substrates coated with transparent thin layer of ITO having sheet resistance of 35 Ω/\Box and 15 Ω/\Box respectively. Figure 3.4 compares

the optical transmittance of different ITO coated substrates. A 40 nm thin layer of PEDOT was spin coated before growing organic photoactive layers inside vacuum evaporator.



Figure 3.4: Comparative transmittance of the ITO thin films on glass and on PET substrates.

Devices were made using the same 55 nm layer of pentacene and 35 nm of C₆₀ deposited at constant rate of 0.05 nm/sec. Both pentacene and C₆₀ layers were grown with a heated substrate temperature of 80°C. Further depositions of buffer layer BCP and cathode layer Ag were perfromed without substrate heating: an 8 nm thin layer of bathocuproine (BCP) as buffer was deposited. Devices were completed by deposition of 60 nm Ag through a shadow mask as top electrode, resulting in several devices on each substrate. All depositions were performed under a base pressure lower than 5x10⁻⁷ mbar.

Dark and photo-response of optimized pentacene/C₆₀ solar cells grown at substrate temperature of 80°C on glass and PET substrate (active area 0.03 cm²) are compared in figure 3.5.



Figure 3.5: Comparative J-V response of pentacene/C₆₀ heterojunction in dark and under illumination on glass and PET substrate.

The devices on glass substrates delivered J_{SC} = 7.3 mA cm⁻² and FF = 0.56, whereas values from flexible devices were J_{SC} = 8.8 mA cm⁻² and FF = 0.48. Although similar efficiency of 1.6 % at 80 mW cm⁻² was measured on both substrates, significant difference in J_{SC} and FF on flexible and glass substrates is observed.

Table 3.2 summaries the PV details of the heterojunction device on different substrates.

Substrate	Voc (mV)	Jsc (mA cm ⁻²)	FF (%)	PCE (%)
Glass	300	7.3	56.8	1.6
PET	300	8.8	48.3	1.6

Table 3.2: Comparative PV performance on ITO coated glass and PET substrates

Loss in FF on flexible devices is mainly because of the previously mentioned higher sheet resistance of the ITO films on PET. Higher short circuit current from flexible devices despite high sheet resistance and low optical transmittance of ITO may come from difference in growth of organic layers on soft and hard substrates. In order to understand the possible difference in growth mechanisms of active layers we performed contact mode AFM measurements on identical devices grown on PET and glass substrates. The AFM micrographs measured under contact mode were scanned on working devices where top surface was not covered by metal cathode.

For reference, first we compare the AFM scans of ITO layer on glass and PET substrate. AFM micrographs for ITO on different substrates are shown in figure 3.6. As expected, ITO on glass substrates was smoother than those on flexible PET substrates with *rms* roughness 2 and 7 nm respectively. Despite the higher *rms* roughness of ITO layer on PET, overall surface roughness of organic layers (multilayer representative of ITO/PEDOT/Pentacene/C₆₀/BCP) grown on PET

remained ~ 7 nm whereas much smoother layer of ITO on glass revealed final roughness ~11 nm.



Figure 3.6: AFM scans on ITO coated glass and PET substrates

A closer look on 3D AFM micrographs shown in figure 3.7 on identical scale reveals big grain formation of pentacene on glass substrates whereas pentacene grains on PET substrates were comparatively smaller.



Figure 3.7: AFM micrographs showing larger grain formation of pentacene on glass substrate (left) compared to PET substrate.

Full coverage of pentacene grains by C_{60} *balls* can be clearly seen in 2D AFM micrographs shown in figure 3.8. It is expected that the BHJ is not viable here as

the pentacene domains are much bigger than those of C₆₀. We measured supporting low PV performance when pentacene and C₆₀ were co-deposited.



Figure 3.8: Full coverage by C₆₀ and inter-grain connectivity of pentacene on ITO coated glass (left) and on PET (right) substrates.

The small grain size of pentacene on PET substrates offers better inter-grain coverage and connectivity by much smaller C₆₀ molecules and supports the charge collection through enhanced percolation resulting in higher J_{SC} from flexible devices. While smaller D-A grains are favorable for PV response it may not favor the lateral charge carrier mobility. Low FET mobility measurements on PET substrates compared to glass substrates support our observation where authors reported lower mobility of holes in pentacene field-effect transistor (FET) devices fabricated on PET substrates compared to those fabricated on glass substrates [7].

3.1.2 Thermal and mechanical stability

In order to characterize the thermal and mechanical stability of pentacene/ C_{60} heterojunction devices we studied their PV response at elevated temperature and under bending stress.

For possible thermal degradation devices were treated for 1hr each at increasing temperature range from 40°C to 100°C. For testing the thermal stability, devices were stored inside a glass oven under argon atmosphere for 1 hr each at different temperatures. Figure 3.9 shows the evolution of device stability under prolonged thermal treatment.



Figure 3.9: Thermal stability of pentacne/C₆₀ plastic solar cells

As evident from fig. 3.9, no significant change in Jsc was observed, as it remained fairly stable after each temperature treatment whereas FF fell to 0.42 from its

original value of 0.48 at 100°C. No significant change in Voc was observed and it remained stable at ~300 mV. The fill factor loss appears to come from an increased series resistance of the annealed devices. We suspect some degradation at the organic/metal-cathode interface; possibly caused by the limited thermal stability of the BCP buffer layer.

No significant change in power conversion efficiency up to 80 °C was observed, at 100 °C; loss in FF caused slight drop in efficiency from 1.6 % to 1.4 %, which is fairly stable for practical considerations.

For the effect of mechanical strain on the working device, we applied strain by bending devices across the active area under different bending radii.

Strain is calculated using the given relation [8]

$$\varepsilon = \left(\frac{d_f + d_s}{2R}\right) \frac{\left(1 + 2\eta + \chi \eta^2\right)}{\left(1 + \eta\right)\left(1 + \chi \eta\right)}$$
1

Where R represents the bending radius, d_f the thickness of the ITO layer, d_s the thickness of the PET substrate, $\eta = d_f/d_s$, $\chi = Y_f/Y_s$, and Y_f , Y_s are Young's moduli of the ITO and PET respectively. With d_f and d_s values of 150 nm and 175 μm respectively, η can be approximated to 0, similarly $\chi \sim 24$ with Y_f (ITO) =118 GPa and Y_s (PET) = 5 GPa.

So under above approximation equation (1) can relate strain to bending radius by

$$\varepsilon = \frac{d_s}{2R}$$

Figure 3.10 compares the response of J_{SC} with respect to the applied strain. For reference, current *without any strain* and current after *released strain* are also pointed. % Strain values represent devices under bend radii of 16, 10, 8, 6 and 4 mm respectively. We observed steep drop in J_{SC} with increasing external strain. This comes primarily because of the reduced incident light intensity from the solar simulator as devices were exposed under bend conditions.





Figure 3.10: Device J_{SC} as a function of applied strain (left). Working device under manually applied strain (right).

For strain induced damages, devices when measured after releasing the strain, delivered identical J_{SC} like original devices. This confirms no damage caused to ITO or organic layers under applied mechanical strain. Arrows on left and right in figure 3.10 indicate J_{SC} measured before any applied strain and after the released strain respectively.

Change in Voc and FF under strain remained unchanged to their original values. The external quantum efficiency of this optimized heterojunction is shown in figure 3.11. EQE is measured using the relation described in chapter 1 and given by

EQE (%) =
$$\left(\frac{100 \times 1240 \times J_{SC}}{\lambda \times I_0}\right)$$
 3



Figure 3.11: EQE spectrum of pentacene/C₆₀ heterojunction device

The EQE response has an overlapping signature of the absorption profile of C_{60} in wavelength region < 500 nm with pentacene contribution peaking at 644 nm to 52%. This means that the heterojunction device is able to dissociate more than

half of the excitons created in the photoactive layer of pentacene-C₆₀. This stands even higher than what was measured on polymer BHJ devices discussed in last chapter. Such high dissociation of the photogenerated exciton requires all the excitons created inside bulk of the pentacene and C₆₀ must diffuse to the interface. High EQE indicates the long diffusion length of the excitons formed in pentacene and C₆₀. After dissociation of the exciton the extraction of charges is also efficient as high photocurrent is measured. This is preliminary because of the high intrinsic mobility of both the pentacene and C₆₀. Secondly the inter grain connectivity and coverage of D-A heterojunction supports the sharp percolation for extraction of the charges through the opposite electrodes.



Figure 3.12: Energetic evolved controlling the V_{OC} of the pentacene-C₆₀ heterojunction solar cells.

The limiting factor of this heterojunction device is the low Voc, which is controlled by the offset of pentacene HOMO to C₆₀ LUMO as shown in figure 3.12. Alternative to avoid such low Voc is to have the high HOMO-LUMO offset

at the pentacene-acceptor interface. In next section we describe heterojunction and blend solar cells using pentacene and new acceptor PTCDI-C13 as a solution to low Voc.

3.1.3. Pentacene / PTCDI-C13 heterojunction solar cells

We used PTCDI-C13 as an acceptor in order to replace C₆₀. PTCDI-C13 is a n-type organic semiconductor with high intrinsic mobility for electrons [9]. Figure 3.13 shows the chemical structure of PTCDI-C13. The LUMO position of PTCDI-C13 is reportedly higher than the C₆₀ [10,11].



Figure 3.13: Chemical structure of PTCDI-C13.

Figure 3.14 shows the absorption profile of PTCDI-C13 and pentacene. PTCDI shows good absorption in low wavelength regime and complements the absorption profile of pentacene with peak absorption at 474, 500 and 572 nm while pentacene peaks at 572, 640 and 672 nm. Thus this composition allows

better spectral coverage when compared to pentacene–C₆₀ photoactive composition.



Figure 3.14: Absorption profile of PTCDI-C13 and pentacene thin films (50 nm).

The photovoltaic response of the devices made using heterojunction of pentacene and PTCDI-C13 is shown in figure 3.15. The 45 nm thin photoactive layer each of pentacene and PTCDI-C13 was sandwiched between 40 nm thin PEDOT coated ITO anode and 60 nm thin silver cathodes. An 8 nm thin layer BCP was used as exciton blocking layer before deposition of silver cathode.



Figure 3.15: Dark and illuminated J-V response of pentacene/ PTCDI-C13 heterojunction device (left). Proposed HOMO-LUMO offset at pentacene-PTCDI-C13 interface (right) more consistent to experimentally observed Voc.

We propose, in figure 3.15, a different HOMO-LUMO level to what is available in literature [11]. This is taken from the similar perylene based molecule namely PTCBI and fits with the experimentally observed Voc [12].An expected increase in Voc was observed for this heterojunction device with Voc = 400 mV which is in good agreement with proposed LUMO level of PTCDI-C13. The short-circuit current density; Jsc of 5.0 mA cm⁻² was recorded under illumination intensity of 80 mW cm⁻². With a slightly increased Voc, the PCE recorded reaches to 1.6 % and is similar to that from pentacene-C₆₀ heterojunction devices. This comes primarily because of the much better FF of 64.2% from PTCDI-C13 based devices. For understanding the lower Jsc of 5.0 mA cm⁻² compared to 7.13 mAcm⁻² from C₆₀ devices we measured the EQE of pentacene/PTCDI-C13 heterojunction devices. Figure 3.16 shows the EQE response of this heterojunction device. With slightly different features in the low wavelength region, the peak EQE of 41.3 % was recorded at absorption peak of pentacene (664 nm). This shows that the maximum excitons are generated in the first photoactive layer into the light path through transparent ITO i.e pentacene donor layer.



Figure 3.16: Photo-action spectra of pentacene/PTCDI-C13 heterojunction solar cell.

The EQE of 41.3% from PTCDI-C13 based devices are significantly lower than the EQE of 52.7% obtained from C_{60} based devices. This may come from the low exciton diffusion length of PTCDI-C13 as compared to C_{60} [12].

For understanding the morphological nature of this heterojunction we looked at atomic force images of 45 nm thin pentacene covered by 45 nm thin PTCDI-C13

layers on glass substrates. Figure 3.17 shows the AFM micrographs recorded on this photoactive layer.



Figure 3.17: AFM micrographs measured on pentacene covered by thin layer of PTCDI-C13.

As seen in the AFM micrographs, PTCDI-C13 growth is different than the C₆₀ on the pentacene. PTCDI-C13 is a planar molecule that tends to align differently than the spherical C₆₀ molecules. Hence the requirement for the exciton dissociation may differ based on the domain size of this new acceptor.

In the next section we describe the photoactive layers formed by blending the pentacene with PTCDI-C13 by means of vacuum co-deposition.

3.1.4. Pentacene: PTCDI-C13 molecular blends

Photoactive layers of pentacene and PTCDI-C13 blended in one single layer were fabricated by the co-evaporation of pentacene and PTCDI-C13 from two diagonally separated alumina crucibles while controlling each deposition rate by oscillating quartz crystal monitors under a base pressure < 5x10⁻⁷ mbar. A 90 nm thick photoactive layer made by blending pentacene and PTCDI-C13 in different loading ratio was grown on similar device structure described in section 3.1.2. For taking advantage of pentacene absorption in long wavelength region >600 nm, we fabricated molecular blends (by wt%) in ratio of 1:1, 2:1 and 3:1. The final thicknesses of all the layers were kept constant at 90 nm.

The combined absorption spectrum of the blends with different wt. ratio ca.1: 1. 2:1 and 3:1 are compared in figure 3.18.



Figure 3.18: Spectral coverage of pentacene: PTCDI-C13 molecular blends. Absorption at 670 nm is shown to increase with higher loading of pentacene.

We see two clear trends in the combined spectrum of pentacene and PTCDI. In the low wavelength region: < 600 nm; the downward shift of the spectrum indicates lesser content of PTCDI-C13 while in the longer wavelength region: > 600 nm; we see an increased absorption solely because of the high pentacene content. It's worth mention that the 3:1 blend shows almost balanced absorption through out the visible spectrum.

The photovoltaic response of bulk heterojunction devices fabricated with different loading of pentacene is shown in figure 3.19.



Figure 3.19: J-V characteristics of the pentacene: PTCDI-C13 blended devices with different wt% of pentacene in the single photoactive layer.

We measured increase in all parameters of the devices by increasing the content of pentacene. Voc of the device with 1:1 ratio starts at 210 mV and saturates at 410 mV with higher content of pentacene. The most significant increase is seen in the Jsc, which shows an increasing trend with increase of the pentacene content. High Jsc upto 9 mA cm⁻² was recorded from the 3:1 blend layers of pentacene and PTCDI-C13. As discussed before, we attribute the high photocurrent generation to the balanced absorption in this blend. It means that the photo-generated excitons are created within the bulk of the blended layer, which offers proximity of donor –acceptor sites for dissociation at the D-A interface.

The EQE spectrum measured on 3:1 blended devices confirms the controlled nature of donor-acceptor interface formation within the bulk of the photoactive layer. An exceptionally high EQE of 82.75 % at 664 nm is recorded at the peak absorption of pentacene, as shown in figure 3.20.



Figure 3.20: Exceptionally high EQE achieved with controlled growth of 3:1 blend ration of pentacene and PTCDI-C13.

The higher EQE shows that almost all the excitons generated by incident photons are dissociated giving rise to high photocurrent in this composition. An increased PCE of 2.0% is achieved, which is the highest among the pentacene donor based solar cells [2,3]. Nevertheless, the ~ 83% of EQE obtained from this composition is among the highest for any photoactive composition reported on organic solar cells in the literature [3-6].

Table 3.3 summarizes the PCE of different blends with equal thickness of 90 nm measured under 80 mW cm⁻² illumination intensity.

Tabl	e 3.3: P	V resj	ponse o	of j	pentacene:	PΤ	CD	I-C13	blends
------	----------	--------	---------	------	------------	----	----	-------	--------

Wt % (P: C13)	Voc(mV)	Jsc (mA cm ⁻²)	FF (%)	PCE (%)
1:1	211	1.16	41.4	0.12
2:1	400	3.77	55.3	1.0
3:1	411	8.67	44.9	2.0

In order to understand the performance variation with increased pentacene content inside the blend layer we checked the blend morphology of all three compositions. The AFM pictures scanned on 1:1, 2:1 and 3:1 blend ratio of pentacene to PTCDI-C13 are shown in figure 3.21. A smooth top surface is observed in 1:1 blend with 45 nm equivalent of pentacene and PTCDI-C13 in it. As we increase the pentacene content to 60 nm in 2:1 blend while putting PTCDI-C13 to 30 nm we see rough surface with rising domains. By increasing pentacene

content to 67 nm in 3:1 blend and reducing PTCDI-C13 to 22 nm, nicely ordered thread like *inter-woven structures* with smoother top surface can be seen.



Figure 3.21: controlling the blend morphology for better PV yield. 1:1 ratio (top) , 2:1 (center) and 3:1 (bottom). Red lines used in 3:1 are for guide to eyes.

The 3:1 surface morphology reveals the reason why high photocurrent is observed from this particular blend. This photoactive system nicely combines the advantage of balanced absorption and desired phase separation by controlled growth of D-A blended layer.

By fitting the EQE data of pentacene /PTCDI-C13 heterojunction device we get L_D of 50 nm and 20 nm for pentacene and PTCDI-C13 respectively. Even higher exciton diffusion length up to 65 nm is reported in literature [3]. Thus the L_D greater than pentacene thickness of 45 nm allows all excitons created in pentacene to reach at the pentacene/PTCDI-C13 interface where they dissociate. Unlike the pentacene, the L_D ~ 20 nm in 45 nm thin PTCDI-C13 layer causes loss of photogenerated excitons as they fail to diffuse towards the D-A interface. This explains the low EQE of 41.3% in the heterojunction devices as compared to 83% from blend devices

Assuming that no recombination takes place, by integrating the device EQE spectrum to the AM 1.5 photon flux density we get the simulated photocurrent close to 13 mA cm⁻². The measured photocurrent is 8.7 mA cm⁻² which remains ~33% lower than what can be expected from this composition. This points that the photocurrent generated inside the blend is limited by the charge extraction from the device. However, large mobility for electrons and holes are measured

using field-effect mobility (FET) measurements performed on similar blends [10]. We believe bi-molecular recombination takes place because of imperfectly balanced mobility of electrons and holes inside this D-A blend.

3.1.5. Pentacene- PTCDI: Bilayer vs Blend

In this section we aim to elucidate the advantage and limitation of heterojunction and bulk-heterojunction concept by comparing the performance of pentacene-PTCDI-C13 bilayer to 3:1 blend.

First we look at the combined absorption profile of these two structures. Figure 3.22 compares the absorption profile of 45/45 nm thin bilayer and 90 nm thin blend devices. Hence thickness was kept constant at ~ 90 nm in each case.



Figure 3.22: Comparative absorption profile of pentacene molecular blend and heterostructure.

As visible from previous figure, the absorption profile of the two remains almost identical. A slight difference in absorbance can be seen in the higher wavelength region > 600 nm. This means, ideally, both media should produce similar photocurrent ignoring the interference effects in device structures. In figure 3.23, we compare the J-V response of both devices under incident intensity of 80 mW cm⁻². Jsc from bilayer device is 5.0 mA cm⁻² compared to 8.7 mA cm⁻² from the blend device. The relatively high FF of 64% from heterojunction device to 44% from blend device indicates the recombination of photogenerated charge carriers inside the blend.



Figure 3.23: J-V response of blend and bilayer pentacene-PTCDI-C13 devices

The high bimolecular recombination occurs because of the partially imbalanced mobility of electrons in these blended devices [10] that may lead to build-up of excess electrons causing recombination with incoming holes. Another mechanism working behind such losses may be due to broken or dead ends of the D-A percolation in blended layers compared to heterojunction where the donor-acceptor interface is sharply defined and leads to fast carrier extraction and hence less recombination [13]. However by comparing the performance of pentacene-C₆₀ heterojunction devices to the pentacene-PTCDI blended devices we find that there is no difference in terms of measured photocurrent as almost identical Jsc of 8.8 mA cm⁻² is obtained from both optimized structures. This further elucidates the fact that ideal exciton dissociation achieved by blend devices is limited by the charge extraction from the device that causes loss of Jsc through bulk bimolecular recombination.

As observed through out, the commonly observed PCE limiting parameter of these healthy photoactive devices is their relatively low Voc which doesn't increase much beyond 400 mV even after tuning the acceptor strength using PTCDI-C13. Nevertheless, limitation on Voc comes from the low ionization potential (IP) of pentacene that is ~5.0 eV .In the coming chapters we discuss alternative solutions to address the limited Voc obtained from this molecular donor.

3.2 Conclusion

In this chapter, we demonstrated the matching performance achieved by a heterojunction D-A composition and a blend BHJ composition based on pentacene. Hence heterojunction or bulk-heterojunction concept for realization of efficient solar cell requires a better understanding of D-A domains. Thermally stable and efficient PV operation on flexible substrates is attained by organic layers grown at elevated substrate temperature, which enables us to avoid the need of generally required high temperature pre/post treatment for optimal performance. A PCE of 2.0% is achieved by addressing the desired D-A domain distribution required for an efficient solar cell. Wide and balanced spectral coverage of pentacene-PTCDI-C13 extends up to 730 nm. Almost all the excitons generated within this photoactive system dissociate and generate high photocurrent, which is equal to that achieved from P3HT: PCBM composition. Above all we demonstrated the different requirements for realization of efficient devices based on heterojunction and bulk heterojunction by addressing the D-A domain size control and its distribution within the photoactive layer. Heterojunction devices have limited exciton dissociation as compared to D-A blends, the transport and collection of photo-generated charges is better in the heterojunction than the blend/BHJ D-A layer. The low open circuit voltage is limiting the final PCE.

References

1. N. Yoneya, M. Noda, N. Hirai, K. Nomoto, M. Wada, J. Kasahara, *Reduction of contact resistance in pentacene thin-film transistors by direct carrier injection into a-few-molecular-layer channel*, Applied Physics Letters, **85** (2004), 4663.

2. A. C. Mayer, M. T. Lloyd, D. J. Herman, T. G. Kasen, G. G. Malliaras, *Postfabrication annealing of pentacene-based photovoltaic cells*, Applied Physics Letters, **85** (2004), 6272.

3. S. Yoo, B. Domercq, B. Kipplen, *Efficient thin-film organic solar cells based on pentacene*/ C_{60} *heterojunctions*, Applied Physics Letters , **85** (2004), 5427.

4. F. Padinger, R.S. Rittberger, N.S. Sariciftci, *Effects of postproduction treatments on plastic solar cells*, Advanced Functional Materials, **13** (2003), 85.

5. W. Ma, C. Yang, X. Gong, K. Lee, A.J. Heeger, *Thermally Stable, Efficient Polymer Solar Cells with Nanoscale Control of the Interpenetrating Network Morphology*, Advanced Functional Materials **15** (2005), 1617.

6. G. Li, V. Shrotriya, J. Huang, Y. Yao, T. Moriarty, K. Emery, Y. Yang, *High-efficiency solution processable polymer photovoltaic cells by self-organization of polymer blends*, Nature Materials **4** (2005), 864.

7. H. Klauk, M. Halik, U. Zschieschang, F. Eder, G. Schmid, C. Dehm, *Pentacene* organic transistors and ring oscillators on glass and on flexible polymeric substrates, Applied Physics Letters, **82** (2003), 4175.

8. Z. Suo, E. Y. Ma, H. Gleskova, and S. Wagner, *Mechanics of rollable and foldable film-on-foil electronics*, Applied Physics Letters **74** (1999), 1177.

9. K. N. N. Unni, A. K. Pandey, J. M. Nunzi, *N-channel organic field-effect transistors using N,N0-ditridecylperylene-3, 4, 9, 10-tetracarboxylic diimide and a polymeric dielectric,* Chemical Physics Letters **407** (2005), 95.

10. K.N. N. Unni , A. K. Pandey, S. Alem, J.M. Nunzi, *Ambipolar organic field-effect transistor fabricated by co-evaporation of pentacene and N,N'-ditridecylperylene-3,4,9,10-tetracarboxylic diimide*, Chemical Physics Letters **421** (2006), 554.

11. C. Rost, D.J. Gundlach, S. Karg, W. Rieß, *Ambipolar organic field-effect transistor based on an organic heterostructure*, Journal of Applied Physics, **95** (2004), 5782.

12. P. Peumans, A. Yakimov, S.R. Forrest, *Small molecular weight organic thin-film photodetectors and solar cells*, Journal of Applied Physics, **93** (2003), 6393.

13. M.M. Mandoc, L.J.A. Koster, P.W.M. Blom, *Optimum charge carrier mobility in organic solar cells*, Applied Physics Letters, **90** (2007), 133504.

Chapter 4 Improving open circuit voltage of pentacene solar cells

4.1 Introduction

In the last chapter we find that the low open circuit voltage of pentacene solar cells limits the PCE of these devices. In this chapter we investigate the possible ways of increasing the Voc of an organic solar cell with low energy offset at the donor-acceptor interface and its consequences on the other photovoltaic parameters of the device. First the metal cathode was varied for understanding the origin of Voc in relation to the electrode work function difference.

Secondly, we use the functionalized pentacene with higher IP than the regular pentacene. The increased Voc from this derivative of pentacene stands at 720 mV. In order to tune the D-A interface for high HOMO-LUMO offset, an alternative way is proposed by using high IP donor dyes either by doping or by using a discontinuous layer. This is shown to improve the Voc without loss of photocurrent.

4.1.1: Effect of metal cathode on Voc

We studied pentacene/C₆₀ heterojunction device response by varying the metal cathode work function from 4.7 eV to 2.9 eV by using silver, aluminum and calcium metals. J-V response under illumination is shown in figure 4.1.



Figure 4.1: J-V response of pentacene/C₆₀ heterojunction device with calcium, aluminum and silver cathodes (in dark and under illumination intensity=80mW cm⁻²).

As evident from the above plot we see little difference in Voc by varying the metal cathode work function. The observed difference in Voc is ~ 0.02 V by varying the cathode metal work function by 1.8 eV. Figure 4.2 shows origin of Voc associated with the energy level diagram of pentacene-C₆₀ heterojunction with respect to different metal cathodes.



Figure 4.2: Origin of Voc in pentacene-C₆₀ heterojunction. M-I-M picture allows Voc variation from 0.3 V to 2.1 V whereas HOMO-LUMO offset permits Voc ~0.5 V.

Following the classical metal-insulator-metal (M-I-M) behavior, 0.3V, 0.7V and 2.1 V of Voc is expected with respective Ag, Al and Ca cathodes [1]. Thus calcium cathode must give highest Voc which is exactly opposite in present composition with lowest Voc measured with Ca cathode. The dependence of metal work function on the Voc in pentacene/C₆₀ heterojunction solar cells remains inconclusive [2]. The low energy offset at pentacene/C₆₀ interface seems to control the measured Voc [3].

Table 4.1 compares the measured Voc by varying the cathode metal work function.

Cathode	Work	Voc	Jsc	FF	PCE
metal	function (eV)	(mV)	(mA cm ⁻²)	(%)	(%)
Calcium	2.9	278	4.91	55.3	0.94
Aluminum	4.3	302	6.38	52.2	1.25
Silver	4.7	304	7.53	57.1	1.63

Table 4.1: Weaker dependence of Voc on the metal work function

Voc tabulated in table 4.1, clearly shows the Voc is controlled by the HOMO-LUMO offset at the pentacene-C₆₀ interface and not by the electrode work function difference. Meanwhile, we observed significantly stronger effect of metal work function on J_{sc}. An inverse relation of J_{sc} with increasing metal work function is clearly evident from table 4.1.

As evident from their low workfunction Al and Ca in figure 4.2, form ohmic contacts with C₆₀, hence no barrier for charge (electrons) collection exists at C₆₀-Al or Ca interface. Although Ag forms rectifying contact with C₆₀, the small barrier may get compensated with the interfacial di-pole formation at C₆₀-Ag interface. Alternatively, the difference observed in J_{sc} may originate because of the magnitude of light absorbed inside the device geometry with different metal cathodes [4]. The reflection spectrums of 60 nm thin Ag, Al and Ca films on glass substrate are shown in figure 4.3. At around 700 nm (peak absorption of pentacene) and at normal incidence, Ag reflects 96%; Al reflects 90% and Ca reflects 70%. This may explain why low JSC is observed with Ca cathode. Although the reflection from Al differs by 6% only to Ag, the Jsc variation is significant.



Figure 4.3: Reflection spectrum of 60 nm thin Ag, Al and Ca thin films on glass substrate. This gives quantitative analysis of photocurrent variation observed in table 4.1.

The alternative approach for improving the Voc has also been discussed in chapter 3 by changing the acceptor to PTCDI-C13. In chapter 3, we observed slightly improved Voc using this acceptor, which improves the PCE to 2.0%. Because of existence of limited acceptors an alternative strategy is required for variation at the donor-acceptor interface. We tried to vary the HOMO level of pentacene donor for this purpose a functionalized pentacene was used. In next section the devices made with this functionalized pentacene donor with C₆₀ acceptor are described.

4.2 Pentacene dioxane and C60 solar cells

The chemical structure of pentacene dioxane is shown in figure 4.4. The detailed synthesis and optical properties of this material is described in *reference* 5.



Figure 4.4: Chemical structure of pentacene dioxane (R=H).

Figure 4.5 shows the absorption spectrum of pentacene dioxane compound. When compared to the spectrum of pentacene, shown in last chapter, we clearly see the characteristic long wavelength absorption of pentacene along with the new features in the wavelength regions 420-470 nm. This added contribution comes from the functional group attached to the main pentacene structure as shown in figure 4.4.

This pentacene derivative was designed for applications in organic light emitting diode as a red luminescent material with high photoluminescence quantum yield and can be dissolved in organic solvents for thin film processing [5].



Figure 4.5: Absorption profile of 50 nm thin pentacene dioxane film on glass.

The dark and illuminated J-V response of this new donor with C₆₀ acceptor is shown in figure 4.6. We get an increased open circuit voltage as high as 720 mV from this heterojunction device which is twice more than that obtained with regular pentacene devices, though the photocurrent drops to 3.2 mA cm⁻² which is quite lower than that observed from pentacene/C₆₀ solar cells.



Figure 4.6: J-V response in dark and under illumination intensity of 100 mW cm⁻².
The EQE measurement on this device is consistent with the low photocurrent which shows that much less excitons are dissociated. Thus the PCE of this device remains low at 0.85 %, solely because of the low short-circuit current. The HOMO level of pentacene dioxane is expected to be similar or higher to that of pentacene [5].

For further improvement in Voc without losing on Jsc, we used a 10 nm thick layer of pentacene dioxane on top of 50 nm thick regular pentacene before deposition of 35 nm thick C₆₀ layer. The J-V characteristic with this intrinsic layer device is shown in figure 4.7 where high Voc of 500 mV is measured with slightly improved Jsc of 3.9 mA cm⁻². The improved Jsc shows the contribution coming from regular pentacene. The low Jsc still limits the PCE to even lower value of 0.6%.



Figure 4.7: J-V response under different illumination intensity. The Voc obtained is 500 mV.

Figure 4.7 shows the irregular J-V curve with high slope at short-circuit condition, showing poor shunting of the device structure, which indicates possible morphological effects on the device performance. The AFM scans measured on pentacene dioxane reveals a different nature of grain growth than regular pentacene. Figure 4.8 shows the AFM images of this pentacene derivative.



Figure 4.8: AFM micrographs of 50 nm thick pentacene dioxane layer on glass.

The other possible reason behind low photocurrent can be the mobility mismatch between the two-pentacene layers with lower mobility pentacene dioxane layer [4]. Nevertheless, an improved Voc is obtained by putting an intrinsic layer of pentacene dioxane on pentacene. This shows that the Voc can be tuned by using an alternative donor layer between the pentacene-C₆₀ D-A interface.

For further improving the Voc, without loss of Jsc, we used alternative strategies of blending the higher IP donors in pentacene layer and by using a very thin irregular layer on top of pentacene layer. Firstly, we used a 5 nm thin layer of *rubrene* either blended by co-deposition in the pentacene layer or deposited on top of it. Figure 4.9 shows the J-V response of rubrene *doped* pentacene and rubrene on top of pentacene layer before deposition of C₆₀ acceptor layer. The solar cells thus fabricated delivered increased open circuit voltage of 400 mV.



Figure 4.9: Improved Voc with doped and irregular layer of rubrene on pentacene. Device J-V response in dark and under 100 mW cm⁻² illumination intensity.

The photocurrent recorded for blended rubrene in pentacene layer dropped to 4.95 mA cm⁻² with final PCE of 1.0%. The drop in photocurrent can be looked at in terms of energy level alignment at pentacene/rubrene interface.

Figure 4.10 shows the respective HOMO-LUMO levels of pentacene and rubrene with respect to C₆₀.



Figure 4.10: Energetic of pentacene: rub: C₆₀ solar cell. The new interface formation at rubrene-C₆₀ (broken line) allows enhanced Voc.

The higher lying HOMO level of rubrene at 5.4 eV forms a new interface with C₆₀ LUMO at 4.5 eV. Under this new HOMO-LUMO offset Voc higher than 500 mV is feasible. While the very thin discontinuous layer of rubrene in-between pentacene may not prevent the carrier conduction through pentacene, rubrene blended in pentacene may hamper the flow of holes by breaking the percolation. This may reduce the photocurrent as seen in figure 4.9. The improvement in all PV parameters is observed with thin rubrene layer on pentacene with high characteristic photocurrent from pentacene of 8.74 mA cm⁻² and better FF of 58.0% yielding an improved PCE of 2.0 %, which is better than the PCE of pentacene/C₆₀ solar cells.

Table 4.2 summarizes the PV parameters recorded using different approaches.

Donor	Voc	Jsc	FF	PCE
	(mV)	(mA cm ⁻²)	(%)	(%)
Functionalized	720	3.22	36.5	0.85
pentacene				
Rub. doped	375	4.95	50.6	1.0
pentacene				
Thin rubrene on	400	8.74	58.0	2.0
pentacene				
Funct.pentacene	502	3.89	30.9	0.6
on pentacene				

Table 4.2: Improving V_{OC} of pentacene-C₆₀ heterojunction solar cells characterized under AM 1.5 illumination at 100 mW cm⁻².

In all cases, we see an increased Voc with nature of approach influencing the measured photocurrent from the devices. The best improvement is obtained using thin layer of rubrene in between pentacene and C₆₀.

5.3 Conclusion

In this chapter, we investigated different possible ways of improving the open circuit voltage of pentacene-C₆₀ D-A heterostructure solar cells with optimally improved PCE of 2.0%. A molecular approach to functionalized pentacene offers improved V_{OC} .

The use of luminescent donor such as rubrene improves Voc without affecting the Jsc. This would solve the issue of limited acceptors often putting a restriction in design and development of new D-A compositions. We noticed a recent and similar use of rubrene in improved performance of CuPc/C₆₀ solar cells [6].

References

1. S.-M. Sze, *Semiconductor Devices-Physics and Technology*, 2nd Ed. Wiley & Sons Inc., Singapore, **2001**.

2. V.D. Mihailetchi, P.W.M. Blom, J.C. Hummelen, M.T. Rispens, *Cathode dependence of the open-circuit voltage of polymer:fullerene bulk heterojunction solar cells*, Journal of Applied Physics **94** (2003), 6849.

3. C.J. Brabec, A. Cravino, D. Meissner, N. S. Sariciftci, T. Fromherz, M. T. Rispens, L. Sanchez, J.C. Hummelen, *Origin of the Open Circuit Voltage of Plastic Solar Cells*, Advanced Functional Materials **11** (2001), 374.

4. A.J. Moule', K. Meerholz, *Minimizing optical losses in bulk-heterojunction polymer solar cells*, Applied Physics B **86**, (2007) 721.

5. M.M. Payne, J.H. Delcamp, S.R. Parkin, J.E. Anthony, *Robust soluble pentacene ethers*, Organic Letters, **6** (2004), 1609.

6. M.Y. Chan, S.L. Lai, M.K. Fung, C.S. Lee, T.S. Lee, *Doping-induced efficiency* enhancement in organic photovoltaic devices, Applied Physics Letters, **90** (2007), 023504.

Chapter 5 Dual function Rubrene/Fullerene heterojunction: Solar cells and Light Emitting Diodes

5.1 Introduction

In the last chapter we discussed that using a thin layer of luminescent donor like *rubrene* significantly improves the solar cell response of pentacene/C₆₀ heterojunction solar cells. In this chapter we introduce the novel concept of taking advantage of the luminescent rubrene as donor by integrating the two electronic function ca. PV and EL in one heterojunction device. The single thin film device yields a luminance of 1000 cd/m² at ~2.0 V, with the characteristic yellow color of rubrene. It delivers an open circuit voltage of ~ 1 V when illuminated under simulated AM 1.5 solar conditions. The solar power conversion efficiency of such dual device reaches 3 % with a short-circuit current density of 5.3 mA cm^2 .

5.2 Rubrene/C60 heterojunction solar cells

5, 6, 11, 12-tetraphenylnaphthacene, commonly known as *rubrene*, is widely studied semiconductor with high field-effect mobility for holes [1]. Rubrene is also used as an efficient fluorescent dopant for achieving the white light emission in OLED structures, which make them suitable for display and lighting applications [2]. Its intrinsic high mobility and sufficient spectral coverage to solar emission makes rubrene an alternative to pentacene. For the first time, we have used rubrene as a donor in order to realize an efficient solar cell. Figure 5.1 shows the chemical structure of rubrene molecule. With 4 phenyl rings on the main chain of tetracene, rubrene appears a non-planar molecule.



Figure 5.1: Chemical structure of rubrene (left) and fullerene C60 (right).

The absorption spectral profile of thin sublimed film is shown in figure 5.2. With clear spectral features, rubrene molecule peaks at 335 nm, 495 and 540 nm respectively. The comparative spectral profile of C₆₀ shows a complete spectral overlapping profile.



Figure 5.2: Absorption profile of 50 nm thin rubrene and fullerene films.

We made heterojunction solar cells combining 35 nm-thick rubrene and 25 nm-thick C₆₀ layers sandwiched between indium tin oxide (ITO) and silver electrodes with overlapping area of 0.3 cm². A 40 nm-thick layer of poly (3, 4-ethylenedioxythiophene): poly (styrenesulfonate) (PEDOT: PSS) at the ITO/rubrene interface and an 8 nm-thick layer of bathocuproine (BCP) at the C₆₀/Ag interface were used as buffer layers. Under illumination we expect,

photo-induced charge transfer takes place from the rubrene electron donor to the C₆₀ electron acceptor. Figure 5.3 shows the J-V response of rubrene/fullerene heterojunction solar cell device in dark and under different illumination intensities.



Figure 5.3: J-V response of rubrene/fullerene solar cell in dark and under illumination intensities of 10, 21, 32, 53 and 99 mW cm⁻².

At ~ 100 mW cm⁻², we get a high open circuit voltage *Voc* of 728 mV. Combined with J_{SC} of 3 mA and FF nearly 44%, the PCE of this device is 1.0%. The low forward current just above Voc indicates formation of barrier either for charge collection or conduction. For understanding the origin of such behavior, we compare the respective HOMO-LUMO positions of this D-A composition. Figure 5. 4 shows the energy levels of rubrene and fullerene with respect to used electrodes.



Figure 5. 4: Energy-level diagram of rubrene/fullerene heterojunction solar cell

As we can see in the above figure, there exists an injection barrier of 0.4 eV at the anode-rubrene interface that appears to limit the forward current flow across this heterojunction device. Nevertheless, for solar cell operation under illumination this barrier becomes irrelevant, as it doesn't offer any barrier for charge collection at the anode-rubrene interface.

Also, the HOMO-LUMO offset at the rubrene-fullerene interface suggests possibility of improved Voc close to 900 mV. A better alignment of rubrene on the PEDOT coated ITO anode may improve the PV response of this heterojunction device. For understanding the nature of rubrene growth, we studied AFM scans measured on the 50 nm thin layer of sublimed rubrene on glass substrate. Figure 5. 5 show the AFM micrographs of the rubrene layer with island like growth. A closer look at these micrographs reveals randomly organized islands forming big circular domains.



Figure 5.5: AFM micrographs taken on 50 nm thin rubrene layer.

We have seen in last chapter that the pentacene/C₆₀ layers grown at elevated substrate temperature yield better performance by controlled growth of the organic layers. We studied the effect of temperature on the performance of rubrene/fullerene solar cells as well. Four different sets of devices are studied namely, devices without annealing (WA), devices grown with substrate temperature (ST) of 80°C, devices pre-annealed at 160°C for 5 min before deposition of BCP buffer layer and devices with post-fabrication annealing at 160°C for 5 min.

Figure 5. 6 compare the J-V response of these four different sets of devices under same illumination intensity (99 mW cm⁻²) with active area of 0.3 cm².



Figure 5.6: J-V response with pre and post fabrication thermal treatment of rubrene/fullerene solar cells.

The PV parameters are given in table 5.1 .As summarized in table 5.1; we see that the maximum improvement in Jsc comes from devices fabricated with ST of 80°C. Interestingly the improvement with post-fabrication annealing at 160°C remains inferior to that achieved with pre-fabrication annealing at similar temperature and duration. This indicates the improvement in Jsc from pre-annealed devices comes as because of the preferred conformational overlap of rubrene-C60 at the interface. This is further established with almost similar Jsc observed from devices grown at ST of 80°C, with a much higher Voc of 861 mV. Nevertheless we see high forward current above Voc with all three treatments.

Treatment	Voc (mV)	Jsc (mA cm ⁻²)	FF (%)	PCE (%)
No	728	3.07	43.9	1.0
Post at 160°C	728	3.53	45.5	1.2
Pre at 160°C	702	4.56	44.6	1.45
ST at 80°C	861	4.36	45.5	1.74

Table 5.1: Thermal treatment induced improvement in PV parameters of rubrene/C₆₀ solar cells

For further insight into improved Jsc from pre-annealed devices, we compare the EQE measurements performed on devices with no thermal treatment to those pre-annealed at 160°C. Figure 5.7 compares the EQE of such devices.



Figure 5.7: EQE of the rubrene/C₆₀ solar cells with and without annealing.

The EQE profile of rubrene/ C_{60} solar cells reproduces the overlapping absorption profile of C_{60} and rubrene shown in figure 5.2. This means that excitons are

created across the heterojunction, which happens due to the completely overlapped absorption profile of rubrene and C₆₀. Maximum EQE measured at 454 nm on pre-annealed devices is 52.7% whereas non-annealed devices have maximum EQE of 34.62% at 456 nm. A nearly 20% improved EQE from devices annealed at 160°C before deposition of BCP and Ag cathode indicates efficient exciton dissociation at rubrene/C₆₀ interface. This may happen because of the increased interfacial contact between rubrene and C₆₀ leading to generation of higher photocurrent as observed from such devices.

Indeed further improvement may come by improving the FF and the J_{SC} of these heterojunction solar cells. Figure 5.8 shows the dark and illuminated J-V response of an optimized device structure with 35 nm rubrene and 25 nm C₆₀. The active area of this heterojunction solar cell is 0.03 cm^2 .

At illumination intensity of 97 mW cm⁻², we get even higher Voc of 940 mV with increased J_{SC} and FF values of 5.3 mA cm⁻² and 56.6% respectively. With overall improvement of the PV parameters, the PCE of this optimized structure is 2.9%. Table 5.2 summarizes the photo response of this optimized heterojunction device.



Figure 5.8: Dark and illuminated J-V response of optimized rubrene/fullerene solar cell at different illumination intensities.

Intensity (mW cm ⁻²)	Voc (mV)	Jsc (mA cm ⁻²)	FF (%)	PCE (%)
10	861	0.62	50.7	2.68
21	889	1.23	52.6	2.72
30	900	1.81	53.3	2.89
50	915	3.0	53.6	2.95
97	940	5.3	56.6	2.9

 Table 5.2: Photo response under different illumination intensities

As we can see from the above table an almost linear increase in J_{SC} with respect to increased intensity is observed. This shows weak bi-molecular recombination even at the high intensities close to 100 mW cm⁻². We attribute this to the fast extraction of photogenerated charges made possible by high mobility of rubrene and C₆₀.

A remarkable PCE of 2.9 % using a florescent molecule is exceptional as florescent donors are traditionally considered as poor PV material. Next, we look at the working principle of this solar cell with a florescent donor.

Figure 5.9 shows the schematics of photo-physics taking place inside the device structure.



Figure 5.9: Photo-physics of a heterojunction solar cell. Photo-excited rubrene electrons undergo charge transfer at rubrene-C₆₀ interface giving rise to photocurrent.

Under illumination, photo-induced charge transfer takes place from rubrene donor to fullerene acceptor, leading to the flow of photogenerated current across the device structure. As seen earlier, an overlapping absorption profile of rubrene and C₆₀ makes this composition different from generally discussed D-A compositions with little overlap of their absorption profile. Indeed absorbed photons create excitons in the bulk of this D-A heterojunction device. Excitons created inside the layers then diffuse towards the interface and undergo dissociation. A large barrier of ~ 1 eV for either electrons or holes at the interface leads to strong carrier confinement for dissociated charges, which are then collected with high Voc at respective electrode.

Given, the florescent nature of the donor *rubrene*, under external injection, this heterostrucutre should also work as a light emitting diode. In next section we describe the electroluminescence (EL) behavior of rubrene/fullerene heterojunction device.

5.3 Rubrene/fullerene light emitting diodes

For EL action, sufficient charge injection into rubrene and C₆₀ requires formation of ohmic contact at both electrodes. For this high workfunction anode and low workfunction cathode is required [3]. The heterojunction device described in section 5.2 fulfills this requirement with high workfunction PEDOT coated ITO anode and low workfunction Ag metal cathode. Fullerene C₆₀ is a non-florescent n-type semiconductor, hence charges injected into this heterojunction device need to recombine inside the rubrene layer for photon emission. First, we study a rubrene only device sandwiched between PEDOT coated ITO anode and Ca/Ag metal cathode. Figure 5.10 shows the energy level diagram and different steps required for the EL from the single layer rubrene only device. Electrons are injected into rubrene LUMO through Ca/Ag ohmic contact and holes are injected into the HOMO of rubrene. Once enough carriers of opposite sign are injected, the recombination takes place inside the rubrene bulk, raising a photon of energy equal to its band gap.



Figure 5.10: Energy level diagram showing HOMO-LUMO positions of rubrene with respect to the electrodes.



Figure 5.11: J-V-L response of rubrene single layer light emitting diode.

From the difference in HOMO-LUMO levels shown in above figure 5.10, rubrene has a bandgap of 2.2 eV. In figure 5.11, we see EL turn-on of rubrene *only* device at external potential \geq 2.2 V with luminance of ~300 cd/m² at 3.4 V. The EL spectrum of rubrene shows (figure 5.13) two characteristic peaks at 572 and 608 nm. The CIE color co-ordinates measured are x = 0.55, y = 0.44.

Figure 5.12 shows the semi-logarithmic current-voltage-luminance (J-V-L) response of rubrene/C₆₀ heterojunction device described as a solar cell in section 5.2 with PV response shown in figure 5.8.



Figure 5.12: Semi-log J-V-L response of the rubrene/fullerene heterojunction device. The EL turns on at much lower voltage than expected at ~ 1V.

Interestingly, this rubrene/fullerene heterojunction device delivers a luminance of ~ 1000 cd/m² at a much lower driving voltage than rubrene single layer device

with CIE color coordinates similar to rubrene only device (x = 0.55, y = 0.44). Surprisingly, the EL turn-on voltage of rubrene/fullerene devices is ~ 1 V, which corresponds to half the band gap of the rubrene. As revealed by the J-L-V curves, forward current enters the mA regime at drive voltages as low as 0.88 V, providing enough carriers for recombination within the rubrene layer. This process is found independent on the individual layer thickness of either rubrene or fullerene used in the heterostructure device.

Rise of a photon of energy 2.2 eV under application of 1V looks like an energy *up-conversion* process.



Figure 5.13: EL spectral features of rubrene and rubrene/fullerene light emitting diodes.

As shown in figure 5.13, identical EL-spectral features and CIE co-ordinates for heterojunction and single layer devices rule out the possibility of defect or exciplex luminescence within the bulk or at the rubrene/fullerene heterojunction. EL at a relatively lower voltage than the band gap is reported in distributed heterojunction polymer light emitting diodes. The authors found exciplex formation at the polymer-polymer interface, making it energetically favorable for charge recombination without crossing the junction [4]. Identical spectral features shown in figure 5.13, rules out such possibility in our devices.

To address the origin of charge injection and recombination at extremely low voltages we made similar rubrene/fullerene heterojunction devices with high and low workfunction metals using gold, silver and aluminum as cathodes. The J-V responses of devices made with Al, Ag and Au cathodes are shown in figure 5.14.



Figure 5.14: J-V response of rubrene/fullerene heterojunction with different cathode metals. Although the magnitude of current flow differs, turn-on voltage remains the same at 1V.

As shown in figure 5.14, the forward current in devices with different cathodes differs with respect to the metal work function while turn-on voltage remains the same at ~1 V for all metal cathodes. EL also has a similar response with respect to the drive voltage. The EL turn-on voltages of single or multilayer organic light emitting diodes (OLEDs) are usually sensitive to the metal electrode workfunction and for efficient charge injection; it requires high work function metals as anode and low work function ones as cathode [3].

To understand the low voltage EL phenomenon, it is required to understand the energetic steps involved starting from charge injection at the organic-metal interface. Figure 5.15 shows the energy level diagram of the present heterostructure in conjunction with different metal cathodes.



Figure 5.15: Relative position of rubrene/fullerene HOMO-LUMO energy levels with respect to metal cathode workfunction.

The generally given HOMO-LUMO levels of organic semiconductor are representative of the discrete layers and they may shift significantly when used in contact with other organic or metallic layers because of formation of interfacial dipoles [5,6]. No change in the EL turn-on voltage, while intentionally creating injection barriers at the C₆₀/cathode interface, suggests barrier-less charge injection from the cathode into C₆₀ LUMO. This is expected as because of dipole creation at the metal-organic interface causing either shift in the C₆₀ energy levels downwards or Fermi level pinning of metal cathode to the level of C₆₀ LUMO [7,8]. However, the EL turn-on at extremely low drive voltage remains unresolved.

We propose energy *up-conversion* at organic-organic interface facilitating the EL turn on at such low voltages. Energy up-conversion is an interesting phenomenon in semiconductor physics. In semiconductor heterostructure and quantum dots, energy up-conversion takes place due to *Auger recombination*. Auger recombination is identified as the transfer of energy and momentum released by the recombination of an electron-hole pair to a third particle, *ca.* an electron or hole, giving rise to an energetic electron [9]. Auger recombination in inorganic semiconductors originates under the high carrier concentration regime provided by high doping or by high current density injection [10]. Conjugated

organics are traditionally known low carrier concentration semiconductors and the phenomenon of Auger recombination was never described in the literature.

In present heterojunction device, Auger effect can take place owing to two reasons: primarily as because of the large carrier mobility of the individual materials and secondly, due to the resonant energetic for energy transfer from the LUMO of C₆₀ to the LUMO of rubrene under 1V bias. Indeed, the combination is such that $\Delta E_1 \approx \Delta E_2 \approx 1$ V, where ΔE_1 is the energy difference between the LUMO of C₆₀ and HOMO of rubrene and ΔE_2 is the energy difference between the LUMO of rubrene and C₆₀ as depicted in figure 5.16.



Figure 5.16: Proposed mechanism leading to low voltage operation; energy level alignment at anode-rubrene interface and fullerene-cathode interface makes charge injection barrier less. Rubrene supports high mobility for holes and blocks electrons flow whereas fullerene supports high mobility for electrons and blocks holes. This leads to high charge carrier accumulation and confinement at rubrene/C₆₀ interface leading to formation of an energetic electron responsible for Auger recombination in the heterostructure and EL at lower drive voltage than required becomes possible.

The Auger recombination mechanism behind low voltage EL threshold summarized in figure 5.16, follows: Owing to the large mobility of the compounds and large barrier at the heterojunction, charges of both signs accumulate at the interface under 1V bias (almost flat bands); electrons from C₆₀ recombine with holes from rubrene in a non-radiative process at the interface; the energy ΔE_1 that is released is transferred to an electron that is resonantly excited to the LUMO of rubrene; The electron recombines with the hole in the rubrene layer that is highly luminescent and emits a photon of characteristically higher energy.

This would mean that the LUMO of C₆₀ acts as a stepping-stone to the charge injection into LUMO of rubrene.



Figure 5.17: Combined near IR absorption spectrum of rubrene/fullerene thin film showing non-existence of mid levels facilitating Auger recombination inside the heterojunction device.

One can argue that there should exist a mid energy level required for such energy transfer. We measured the near infrared (IR) absorption spectrum of rubrene/fullerene thin films shown in figure 5.17, which doesn't show any significant absorption down to 1500 nm.

For a better understanding of the phenomenon, we fabricated heterojunction devices using 35 nm rubrene and 30 nm PTCDI-C13.



Figure 5.18: Dual function rubrene/PTCDI-C13 heterojunction; J-V turn on at 1V after external injection is observed with similar EL response (top). PV behavior with expected high Voc of 900 mV is obtained (bottom).

As described in chapter 3, PTCDI-C13 should have identical HOMO-LUMO levels to those of C_{60} [11]. Figure 5.18 shows the expected dual behavior of this heterojunction device. Data shown in figure 5.18 (a) and (b) are representative of two similar devices. PTCDI-C13 is an n-type semiconductor with relatively lower electron mobility as compared to fullerene C_{60} [12]. The freshly characterized devices with PTCDI-C13 have EL turn on at 1.6V. After externally injected current, the EL turn-on starts at 1V, which is similar to the heterojunction devices with fullerene layer. We explain this in terms of trap filled improvement of PTCDI-C13 layer. Under illumination this heterojunction device gives Voc of 900 mV that shows the C₆₀ like identical LUMO positioning of PTCDI-C13 with respect to rubrene HOMO.

The EL spectral features of rubrene only, rubrene/fullerene and rubrene/PTCDI-C13 devices are compared in figure 5.19.



Figure 5.19: Identical EL spectral features of rubrene, rubrene/C₆₀ and rubrene/PTCDI-C13 devices.

No change in EL spectrum observed with rubrene/PTCDI-C13 heterojunction device again confirms no exciplex or mid level emission taking place. Observation of similar low voltage phenomenon with PTCDI-C13 highlights existing C₆₀-like resonant Auger recombination taking place inside this heterojunction device also.

The fact that both electroluminescence and photovoltaic behavior is observed finds explanation from the photovoltaic EQE spectrum shown in Figure 5.7, which shows that essentially the excitons generated in C₆₀ undergo charge transfer at the rubrene/C₆₀ interface, leading to the photovoltaic behavior. Meanwhile, excitons in rubrene do not appear to undergo efficient charge transfer. Then, electron-hole pairs with ~1eV electrochemical potential recombining at the rubrene/C₆₀ interface must create ~2eV excitons in rubrene to yield effective electroluminescence.





Figure 5.20: EL and power efficiency of the rubrene/fullerene (left) and rubrene/PTCDI-C13 (right) OLED device.

Finally we propose the concept of an organic dual function devices (ODD) using organic heterojunction semiconductor. Figure 5.21 shows the schematic requirements of such dual function device that can be used to realize novel optoelectronic applications.



Figure 5.21: Schematic layout of an *organic dual device*, the device compromises one hole transporting layer and one electron transporting layer sandwiched between metal electrodes. Working *mode 1* absorbs solar radiation and creates a net current flow across the circuit whereas *mode 2* requires external voltage source for light emission. An external storage element can store the charges created from the ambient sunlight that can be used as external power to drive the EL action. For incident light to get absorbed and generated light to come out of the device structure, one electrode must be transparent. Inset on right side shows such device working in *mode 2* showing yellow color emission coming through the transparent ITO electrode. Inset shows the rubrene/fullerene dual devices working in *mode 2*.

The high excitation at relatively low voltage in rubrene/C60 and rubrene/PTCDI-

C13 heterojunction is not a signature of disordered energy bands in organic

semiconductor as identical photo-voltage (Voc) of ~900 mV is measured in both cases which is exactly the same as required for an EL onset.

5.4 Conclusion

With the usual paradigm of mandatory photoluminescence quenching required for efficient solar cell operation, a 3% solar cell PCE and 1 lm/watt of EL efficiency from an ODD structure appears exceptional. The EQE for PV in such solar cells reaches 53% at 454nm. Further improvement in PV and EL efficiency can be anticipated from device optimization at various stages. This newly reported efficient mechanism for charge injection and recombination into organic semiconductor structures at low drive voltages can be used as a building block for the realization of much awaited electrically pumped organic lasers where tandem excitation as described here can be used for achieving high current densities at low operating voltages [13,14]. These findings demand an improvement in the current understanding of organic semiconductor device physics. Moreover, the low turn-on voltage offered by the efficient implementation of the Auger recombination scheme should stimulate developments in a new generation of *self-powered* optoelectronic devices suitable for lighting and signalization. More study is required in order to elaborate the underlying physics behind such phenomenon.

References:

1. V.C. Sundar et al., *Elastomeric Transistor Stamps: Reversible probing of charge transport in organic crystals.* Science **303** (2004), 1644.

2. G. Li, J. Shinar, *Combinatorial fabrication and studies of bright white organic lightemitting devices based on emission from rubrene-doped* 4,4'*-bis*(2,2'*-diphenylvinyl*)-1,1'*biphenyl*, Applied Physics Letters 83 (2003), 5359.

3. W. Brutting, S. Berleb, A.G. Muckl, *Device physics of organic light-emitting diodes based on molecular materials*. Organic electronics **2** (2001), 1.

4. A.C. Morteani *et al. Barrier-free electron-hole capture in polymer blend heterojunction light emitting diodes,* Advanced Materials **15** (2003), 1708.

5. H. Vázquez, W. Gao, F. Flores, A. Kahn, *Energy level alignment at organic heterojunctions: Role of the charge neutrality level.* Physical Review B **71** (2005), 041306.

6. L. Lozzi, S. Santucci, S. La Rosa, *Photoemission investigation on copper phthalocyanine:fullerene blend film*. Applied Physics Letters **88** (2006), 133505.

7. J. Y. Lee, *Efficient hole injection in organic light-emitting diodes using C*⁶⁰ as a buffer *layer for Al reflective anodes, Applied Physics Letters*, **88** (2006), 073512.

8. C.J. Brabec, A. Cravino, D. Meissner, N. S. Sariciftci, T. Fromherz, M. T. Rispens, L. Sanchez, J.C. Hummelen, *Origin of the Open Circuit Voltage of Plastic Solar Cells*, Advanced Functional Materials **11** (2001), 374.

9. W. Seidel, A. Titkov, J.P. Andre, P. Voisin, M. Voos, *High-efficiency energy up-conversion by an "Auger Fountain" at an InP-AlInAs type-II heterojunction*, Physical Review Letters **73** (1994), 2356.

10. Sze, S.M. *Semiconductor Devices - Physics and Technology*, 2nd Ed. Wiley& Sons Inc. Singapore, **2001**.

11. P. Peumans, A. Yakimov, S.R. Forrest, *Small molecular weight organic thin-film photodetectors and solar cells*, Journal of Applied Physics, **93** (2003), 6393.

12. K. N. N. Unni, A. K. Pandey, J. M. Nunzi, *N-channel organic field-effect transistors using N,N0-ditridecylperylene-3, 4, 9, 10-tetracarboxylic diimide and a polymeric dielectric,* Chemical Physics Letters **407** (2005), 95.

13. N. Tessler, et al. *Properties of light emitting organic materials within the context of future electrically pumped lasers*. Synthetic Metal **115** (2000), 57.

14. M.A. Baldo , R.J. Holmes, S.R. Forrest, *Prospects for electrically pumped organic lasers*, Physical Review B **66** (2002), 35321.

Chapter 6 Size and shape effects on the efficiency of organic solar cells

6.1 Introduction

We have seen that organic based ultra thin solar cells belong to unconventional family of thin film photovoltaic (PV) devices where their overall thickness of few tens of nanometer becomes comparable to the thickness of the electrodes. At the final stage of this thesis, OSC have been shown to attain PCE close to 5% [1,2]. Throughout the work on this thesis, it was observed that solar cells made with any D-A composition have strong dependence on their active device area with smaller devices yielding better PCE compared to those with larger areas. Also, we observed in the last chapter that reducing the size of rubrene/fullerene device increases the PCE from 1.78% to 2.9% mainly because of improved FF and better Jsc. In this chapter we investigate the nature and origin of area and electrode geometry dependence on the PCE of organic solar cells.
6.2: Size effects

Power conversion efficiency (PCE; η) of a solar cell under AM 1.5 radiation (I₀) mostly depends on the parameters such as open circuit voltage (Voc), short circuit current (Jsc) and fill factor (FF) and is given by

$$\eta = \left(\frac{V_{OC} \times J_{SC} \times FF}{I_0}\right) \tag{1}$$

In general, η scales up either with improved V_{oc} or J_{sc} and this has been recent strategy behind increasing the efficiency of organic solar cells [3].

For understanding the device behavior and effects of different components on the PCE, it is required to look at the working principle of a solar cell. Figure 6.1 shows an equivalent circuit model of a solar cell device.



Figure 6.1: An equivalent circuit of an organic solar cell device showing combination of photo-generator (J_{ph}), diode and resistances (R_s, R_{sh}) defining the experimental J-V behavior of a solar cell.

Also known as the maximum power rectangle, FF depends on Voc and Jsc by

following relation

$$FF = \left(\frac{V_m \times J_m}{V_{OC} \times J_{SC}}\right)$$
(2)

Where V_m and J_m correspond to the values at maximum power available from the device. This in turn depends on the series (R_S) and shunt resistance (R_{SH}) of the device structure through equivalent circuit of solar cell shown in figure 6.1. Thus current – voltage (J-V) characteristics of a solar cell device can be given by

$$J = \left[\left(J_D \times \exp\left(\frac{qV - JR_S}{nKT}\right) - 1 \right) + \left(\frac{V - JR_S}{R_{SH}}\right) - J_{ph} \right]$$
(3)

Where J_D stands for the dark current, q is the electron charge, n is the diode ideality factor, $\kappa \tau$ is the thermal energy and J_{ph} is the photocurrent. It's well known that a non-zero Rs can drastically reduce the efficiency of the solar cell simply by reducing the FF [4].



Figure 6.2: Origin of series resistance inside an organic solar cell structure.

Figure 6.2 associates the origin of overall series resistance through bulk of the organic material and that emerging at metal –organic interface. While bulk

resistance is related to the photoactive organic layer collectively termed as R_0 , interfacial resistances originating at *anode* and *cathode* (including the bulk resistance of respective electrode and resistance at metal-organic interfaces I_1 and I_2) are assigned as R_A and R_c respectively. Collectively, the overall series resistance of the solar cell can be given as $R_s = R_A + R_0 + R_c$. For $R_s \sim 0$ it is desired to minimize the effect of all these individual components.

Previously described heterojunction solar cells with pentacene/ C₆₀ are investigated in this study as many performance limiting constraints such as bimolecular recombination caused by low and unbalanced carrier mobility and commonly observed small exciton diffusion length can be easily overlooked in this combination [5]. Aluminum (Al) and silver (Ag) were used as cathode metals for investigating the interfacial resistance at organic –metal interface and Indium tin oxide (ITO) with sheet resistance of $15\Omega/\Box$ is used as anode. Our multilayer devices have the structure ITO / 40nm PEDOT: PSS / 55nm Pentacene / 25nm C₆₀ / 8nm BCP / 60nm Metal, fabrication details of which is given in chapter 3.

For detailed analysis, we investigate two sets of devices. In the first set, device active area is varied using predefined cathode areas of 0.78 cm², 0.28 cm², and 0.03 cm² on each substrate. Figure 6.3 shows the schematic location of different area devices on the substrate with ITO layer underneath. In order to avoid any cross talk, all these devices are positioned at different corners of the substrate.



Figure 6.3: Layout of a heterojunction solar cell device with different active area of 0.03, 0.28 and 0.78 cm².

In the second set, cathode area is kept constant at 0.30 cm² while shape is varied. As shown in figure 6.4, the shapes are strategically designed to cover different portions/directions with maximum spatial coverage of the photoactive layer. This helps to understand the influence of morphology on the performance of such devices.



Figure 6.4: Different cathode geometries marked as 1, 2, 3 and 4 with constant active area of 0.30 cm².

in figure 6.5. Figure 6.5a compares J-V response with Al cathode. Response of devices with Ag cathode is shown in figure 6.5b.



Figure 6.5: a) J-V response with Al cathode; 0.78 cm² (filled triangles), 0.28 cm² (open circles) and 0.03 cm² (filled squares). b) J-V response with Ag cathode, legends is the same as of Al cathode.

Summary of PV response with varying device area and different cathode metal is given in table 6.1. Although the Voc with Al and Ag cathode remains unchanged we observed significant difference in the Jsc.

Table 6.1: Relating organic-cathode interface with PV parameters of *ITO/PEDOT/pentacne/C₆₀/BCP/Al or Ag** solar cells. *values given in parenthesis represent devices with silver cathode

Area	Voc (mV)	Jsc(mAcm ⁻²)	FF (%)	PCE (%)	$R_s(\Omega \ cm^2)$
0.03	304 (302)	6.38 (7.53)	52.2 (57.1)	1.24 (1.61)	5.51 (2.19)
0.28	310 (310)	5.71 (7.3)	39.1 (42.2)	0.87 (1.2)	16.03 (14.2)
0.78	309 (318)	5.18 (6.78)	32.3 (33.2)	0.67 (0.9)	34.61 (25.3)

As evident from above table, going up scale from 0.03 cm² to 0.78 cm² caused a loss in J_{SC} of 1.20 mA with Al cathode whereas devices with Ag cathodes showed similar trend. Nevertheless, the effect on FF is most prominent irrespective of the metal cathode. All devices were characterized by illuminating through the transparent ITO anode. In order to avoid the contribution from fringe currents, device under characterization was illuminated through a black paper covering the rest of the substrate. Indeed, the positioning of our devices on the underneath ITO anode is such that there was no significant difference in J-V curves even if the whole substrate was illuminated. Series resistance (Rs) obtained from the experimental J-V plots from our cells shades the light on observed losses in the FF. The Rs as small as ~2.0 Ω cm² is obtained for smallest area while values close to 30 Ω cm² were observed on bigger devices (table 6.1). This led to drop in PCE from 1.61 % to 0.90% with Ag cathodes while a overall loss of ~50% in PCE is observed with Al cathodes. Though a big change in Rs is observed, RsH obtained from the experimental curves remained constant within the range of 620-680 Ω cm².

For understanding the nature of losses in Jsc with Al cathode we compare the external quantum efficiency (EQE) of both cells. Figure 6.6 illustrates the EQE measurements on the devices with Al and Ag cathodes of 0.28-cm² areas each. However, spectral features remain the same; significant difference in EQE at the peak absorption of pentacene is observed.



Figure 6.6: Comparative EQE response with Al and Ag cathodes of pentacene/C₆₀ solar cells.

Device with Al cathode yields EQE of 44.45 % whereas that from Ag cathode stands higher at 52.03 %. From previous observation in section 4.1.1, this difference may arise from the difference in amount of light absorbed inside the device structure with Al and Ag cathodes. Also, the Rs remains low with Ag cathodes compared to Al cathodes (refer table 6.1). Low Rs indicates less resistive interface at organic-metal interface with Ag cathode.

6.3: Shape effects

Performance losses caused by spatial variation in inorganic solar cells are generally quantified using various experimental techniques such as Corescan, Cello and imaging techniques like light beam induced current (LBIC) and lock-in thermography (LIT). While inorganic solar cells have low series resistance, these techniques often put upper detection limit [6] on measurable series resistance that might not be applicable to organic solar cells.

The spatially varied cathode geometries shown in figure 6.4 allows us to simultaneously cover different part of the active organic layers which can be compared as a measure of local morphological deformation such as pin holes. Our measurement on devices with different shapes; 1, 2, 3 and 4 suggests no

pronounced effect of morphology on device efficiencies as values obtained for FF and J_{SC} were consistent and well within measurement error limits.

Figure 6.7 represents the evolution of device response with different cathode geometries as depicted in figure 6.4. As evident from figure 6.5 and figure 6.7, we essentially do not see any drop in Voc as all the J-V curves intersect the voltage axis, in the IV quadrant, almost at the same point. This confirms high parallel resistance R_{SH}; ruling out loss of film quality or pinhole defects in bigger devices [7]. Hence we find no profound effect of cathode geometry on the PCE.



Figure 6.7: Semi-log J-V plots for devices with Al cathode structures 1, 2, 3 and 4.

Summary of results are given in table 6.2. For comparison, data for circular devices with active area 0.28 cm² is also given, which essentially appears to be in good agreement with rest of the devices.

Shape	Voc (mV)	Jsc (mA cm ⁻²)	FF (%)	PCE (%)	Rs (Ω cm ²)
1	311	5.17	34.9	0.7	28.24
2	310	5.97	42.8	1.0	14.69
3	312	5.07	43.5	0.85	10.42
4	306	5.76	42.4	0.91	12.43
0.28 cm ²	310	5.71	39.1	0.87	16.03

Table 6.2: Device performance with different cathode geometries with constant active area of 0.30 cm² across the substrate

For reference, we checked the influence of morphology on the device performance. Local AFM micrographs are shown in figure 6.8.



Figure 6.8: AFM micrographs show wave like coverage of pentacene grains by C₆₀ (left) and pentacene inter-grain connection (right), *rms* roughness remains the same.

RMS roughness remains the same over wide scan ranges, which support the claim of defect free morphology giving, rise to high shunt resistance across the device structure.

6.4 Conclusion

This chapter demonstrates the effect of series resistance by varying size and shape of the pentacene/C₆₀ solar cells. Increase in R_s is directly related to the low FF observed on bigger area devices. The commonly preferred Al cathode is shown to limit the charge collection at the C₆₀/cathode interface. A high work function cathode such as Ag is required for barrier free charge collection. We find no profound effect of cathode geometry on the PCE of organic solar cell device. Eventually, the high sheet resistance of ITO puts the limit on further reduction of series resistance in organic solar cells.

References

1. W. Ma, C. Yang, X. Gong, K. Lee, A.J. Heeger, *Thermally Stable, Efficient Polymer Solar Cells with Nanoscale Control of the Interpenetrating Network Morphology*, Advanced Functional Materials **15** (2005), 1617.

2. G. Li, V. Shrotriya, J. Huang, Y. Yao, T. Moriarty, K. Emery, Y. Yang, *High-efficiency solution processable polymer photovoltaic cells by self-organization of polymer blends*, Nature Materials **4** (2005), 864.

3. D. Muhlbacher, M. Scharber, M. Morana, Z. Zhu, D. Waller, R. Gaudiana, C. Brabec, *High photovoltaic performance of a low-bandgap polymer*, Advanced Materials, **18** (2006), 2884.

4. Sze, S.M. Semiconductor Devices - Physics and Technology, 2nd Ed. Wiley& Sons Inc. Singapore, 2001.

5. S. Yoo, B. Domercq, B. Kipplen, *Efficient thin-film organic solar cells based on pentacene*/C₆₀ *heterojunctions*, Applied Physics Letters, **85** (2004), 5427.

6. T. Trupke, E. Pink, R. A. Bardos, M. D. Abbott, *Spatially resolved series resistance of silicon solar cells obtained from luminescence imaging*, Applied Physics Letters, **90** (2006), 093506.

7. M. Al-Ibrahim, H. K. Roth, S. Sensfuss, *Efficient large-area polymer solar cells on flexible substrates*, Applied Physics Letters, **85** (2004), 1481.

Summary & Prospects

In the quest of addressing the requirements described in chapter 1 of this thesis, efficient plastic solar cells using new donor-acceptor compositions with solar power conversion efficiency close to 3% have been realized.

we investigated the limitation of spontaneously formed bulk heterojunction between a polymer donor and acceptor, which shows a more controlled D-A interface is desired for efficient exciton dissociation. A pre-defined wellcontrolled template, either of donor or acceptor, at nano-scale can offer control over photoactive layer morphology towards improve PCE from polymer BHJ solar cells.

We have shown that the organic D-A growth at practical substrate temperature and by matching big donor domains with acceptor leads to efficient heterostructure flexible solar cells. Thus understanding of D-A domain size and distribution is important aspect for realization of efficient solar cells. The external quantum efficiency of 53% from pentacene/C₆₀ heterostructure solar cell is comparable to the present state of art P3HT: PCBM BHJ solar cells. We also demonstrated an efficient molecular bulk-heterojunction solar cell using PTCDI-C13 acceptor and pentacene donor,. This molecular BHJ solar cell attains 83% of quantum efficiency, which is highest for an organic solar cell composition. This contrasting behavior of a heterojunction solar cell to BHJ solar cell using same donor is achieved by tuning the D-A domain distribution required for efficient exciton dissociation at desired scale. In opposition to polymer BHJ approach, the higher loading of donor *pentacene* than acceptor *PTCDI-C13* (in wt. ratio of 3:1) delivers optimum PCE. Thus, while developing new PV compositions, the PL quenching must not be taken as the only criterion.

Low-bandgap donors are desirable for harvesting the maximum solar radiation. The important issue of reduced open-circuit voltage expected from organic donors with low ionization potential (IP) such low-bandgap as polymer/oligomer donors is addressed. With an optical band-gap of 1.9 eV, pentacene belongs to the low-bandgap organic semiconductor family. The results presented by tuning the Voc of pentacene donor, in conjunction with C60 acceptor suggest use of thin layer of alternative donors with higher IP as a potential strategy to address the intrinsic limitation imposed on Voc.

Our studies open a new window for potentially suitable florescent donors to be used in development of efficient plastic solar cells which may eventually pave the way of integrating the lighting and photovoltaic function in one organic donor-acceptor composition. The extremely important experimental findings taking place at organic-organic interface which gives rise to exceptionally low EL action has potential to become a building block for smart optoelectronic device development in near future. Nevertheless, it requires enough new thoughts to arrive up to an acceptable explanation behind origin of such high injection at low driving potential.

Finally, as investigated in chapter 6, the unresolved factor of high series resistance, which limits high power conversion efficiency only to extremely small PV pixels needs to be addressed before moving towards commercialization of fascinating *plastic solar cells*.

Annexure : Experiments and Methods

This sections details the experimental conditions and methods used to fabricate and characterize several devices presented in this thesis.

An 150 nm thick indium tin oxide (ITO) supplied by Merk AG was used as a transparent anode in all device structures described in this thesis. Devices realized on flexible ITO were 175 nm thick and were received from Sheldal Inc. The sheet resistance of the ITO layer used on glass substrate was 15 Ω/\Box . ITO layers were patterned and cleaned following standard cleaning procedure. A 40 nm thick layer of PEDOT supplied by HC Stark or Baytron was spin coated at spinning speed of 4000 rpm in ambient conditions. PEDOT films thus coated on ITO were dried at 120 °C inside vacuum drying oven for 1 hr. Dried substrates with ITO/PEDOT layer on top were transferred inside an Argon filled MBraun Glove Box with oxygen and moisture presence < 0.1 ppm. Deposition of all layers including organics and metal cathodes were performed inside an Edwards evaporation plant installed inside the glove box. All depositions were performed under base pressure $< 2.0.10^{-7}$ mbar. Pentacene , rubrene and BCP were all purchased from Aldrich at highest purity and used without further purifications. C₆₀ was obtained from MER. Aluminum, silver, calcium and gold with highest available purity were used as cathodes. Growth of each layer was monitored insitu using quartz crystal microbalances and were cross checked by Dektak 6M profilometer. UV-Vis absoprtion and transmission spectra were recorded using Lambda 19 spectrometer.

Polymer BHJ devices were prepared first by coating a 100 nm thick layer either of MEH-PPV: PCBM or P3HT:PCBM on top of ITO/PEDOT layers at spin speed of 1000 rpm. Polymer layers thus grown were first dried inside a vacuum dry oven at 100 °C for 1hr before transfer inside the glove box for cathode evaporation. MEH-PPV was supplied by Aldrich and P3HT came from Rieke Metals Inc. PCBM and its derivatives P1-P4 were supplied by Organic Vision.

An 8 nm thin layer of BCP was used in all device structures as a buffer before deposition of metal cathode. Devices were also studied without using the layer of PEDOT and BCP. Main results presented in this thesis are independent of any of these buffer layers. All devices were characterized in dark and under different AM 1.5 spectral illumination intensities from a solar simulator.