

International joint supervision of thesis

UNIVERSIDADE ESTADUAL PAULISTA “JÚLIO DE MESQUITA FILHO”

Programa de Pós-graduação em Ciência e Tecnologia de Materiais

and

UNIVERSITÉ DE PAU ET DES PAYS DE L’ADOUR

Ecole Doctorale Sciences Exactes et leurs Applications

Edilene Assunção da Silva

FABRICATION AND CHARACTERIZATION OF ORGANIC SOLAR CELLS
BASED ON NANOSTRUCTURED LOW-BANDGAP POLYMERS

Brazilian supervisor: Prof. Dr. Clarissa de Almeida Olivati

French supervisor: Dr. Christine Lartigau-Dagron

2018

UNIVERSIDADE ESTADUAL PAULISTA “JÚLIO DE MESQUITA FILHO”

FACULDADE DE CIÊNCIAS E TECNOLOGIA

FACULDADE DE FÍSICA

PROGRAMA DE PÓS-GRADUAÇÃO EM CIÊNCIA E TECNOLOGIA DE
MATERIAIS

EDILENE ASSUNÇÃO DA SILVA

FABRICAÇÃO E CARACTERIZAÇÃO DE CÉLULAS SOLARES BASEADAS EM
POLÍMEROS ORGÂNICOS LOW-BANDGAP NANOESTRUTURADOS

Presidente Pudente

2018

EDILENE ASSUNÇÃO DA SILVA

FABRICAÇÃO E CARACTERIZAÇÃO DE CÉLULAS SOLARES BASEADAS EM
POLÍMEROS ORGÂNICOS LOW-BANDGAP NANOESTRUTURADOS

Tese apresentada como requisito à
obtenção do título de Doutora à
Universidade Estadual Paulista "Júlio de
Mesquita Filho" - Programa de Pós-
Graduação em Ciência e Tecnologia de
Materiais, sob a orientação da Profa. Dra.
Clarissa de Almeida Olivati e da Profa.
Dra. Christine Lartigau-Dagron.

Presidente Prudente
2018

da Silva, Edilene Assunção.

Fabrication and characterization of organic solar cells based on nanostructured low-bandgap polymers / Edilene Assunção da Silva, 2018
127 f. : il.

Orientadora: Clarissa de Almeida Olivati

Tese (Doutorado)-Universidade Estadual Paulista. Faculdade de Ciências, Bauru, 2018

1. Polímeros low-bandgap. 2. Langmuir-Schaefer. 3. Medidas elétricas. 4. Dispositivos fotovoltaicos orgânicos. I. Universidade Estadual Paulista. Faculdade de Ciências. II. Título.

ATA DA DEFESA PÚBLICA DA TESE DE DOUTORADO DE EDILENE ASSUNÇÃO DA SILVA, DISCENTE DO PROGRAMA DE PÓS-GRADUAÇÃO EM CIÊNCIA E TECNOLOGIA DE MATERIAIS, DA FACULDADE DE CIÊNCIAS - CÂMPUS DE BAURU.

Aos 05 dias do mês de julho do ano de 2018, às 09:30 horas, no(a) Anfiteatro VII, reuniu-se a Comissão Examinadora da Defesa Pública, composta pelos seguintes membros: Prof^a Dr^a CLARISSA DE ALMEIDA OLIVATI - Orientador(a) do(a) Departamento de Física / UNESP/ Câmpus de Presidente Prudente, Prof. Dr. ROBERTO MENDONÇA FARIA do(a) Departamento de Física e Ciência dos Materiais / Universidade de São Paulo, Prof. Dr. HENRIQUE DE SANTANA do(a) Departamento de Química / UNIVERSIDADE ESTADUAL DE LONDRINA, Prof^a. Dr^a. MARYSTELA FERREIRA do(a) Campus Sorocaba / Universidade Federal de São Carlos, Profa. Dra. CHRISTINE DAGRON-LARTIGAU do(a) Institut des Sciences Analytiques et de Physico-chimie pour l'Environnement et les Matériaux / Université de Pau et des Pays de l'Adour, sob a presidência do primeiro, a fim de proceder a arguição pública da TESE DE DOUTORADO de EDILENE ASSUNÇÃO DA SILVA, intitulada **Fabrication and characterization of organic solar cells based on nanostructured lowbandgap polymers..** Após a exposição, a discente foi arguida oralmente pelos membros da Comissão Examinadora, tendo recebido o conceito final: APROVADA. Nada mais havendo, foi lavrada a presente ata, que após lida e aprovada, foi assinada pelos membros da Comissão Examinadora.

Clarissa Olivati

Prof^a Dr^a CLARISSA DE ALMEIDA OLIVATI

Roberto Mendonça Faria

Prof. Dr. ROBERTO MENDONÇA FARIA

Henrique de Santana

Prof. Dr. HENRIQUE DE SANTANA

Marystela Ferreira

Prof^a. Dr^a MARYSTELA FERREIRA

Christine Dagron-Lartigau

Profa. Dra. CHRISTINE DAGRON-LARTIGAU

*To my mother who always
encouraged me to pursue my wishes,
the importance of facing upfront the
arduous circumstances, and
endeavouring to achieve my goals.*

Acknowledgements

To Pr. Dr Clarissa de Almeida Olivati for accepting to be my supervisor in more one step of my scientific carrier, for the laughter that softens greatly the typical pitfalls of the research path and for the support and recognition given to me over the years, working as my “scientific mother”.

To Pr. Dr Christine Lartigau- Dagron for kindly receiving me at her laboratory, for being patient to guide a student from a rather different field, and for supervising me on my time abroad.

To Pr. Dr Roberto Mendonça Faria for accepting to participate on the jury, and for receiving me at his institution, and providing me with all necessary assistance while working there.

To Pr. Dr Marystela Ferreira for the acceptance of my invitation to be part of this defence and for the always nice and delightful manner with which she has treated me.

To Prof. Henrique Santana who was directly involved with this work by the collaboration on obtaining data for the thesis, and now for collaborating on the final text.

To Pr. Dr Neri Alves that helped me with insights on the qualification jury and who is always available when needed, besides being an exemplary human being and professional inspiring all his “science children”, of which I consider myself one of them.

To Dr Roger Hiorns for accepting to be part of the qualification jury, for teaching me the first steps of the organic Chemistry synthesis, and for supporting me during my time abroad.

To Pr. Dr Carlos José Constantino and MSc José Diego Fernandes for the Raman measurements and all the time spent analysing and discussing the data with me.

To my family, in especial to my mom, who is always by my side (even if distant physically) making this journey worthwhile.

To my friend Dr Maria Luisa Braunger who taught me the basis of my research field and that near or far acts as my big sister supporting me scientifically and personally.

To Dr Alberto Gregori who, as a fellow researcher and boyfriend, helped me greatly during my path on polymer synthesis and gives me all the necessary support scientifically and emotionally.

To my group friends from LOFF, in especial, Jessé, Lulu, Kaique and Jéssyka who were my buddies at all moments and definitely lightened my scientific quotidian.

To my friends from LaDSor, in particular, Gabriel that helped me with innumerable measurements of impedance and evaporation.

To Pr. Dr Deuber Lincoln da Silva Agostini for the partnership with our laboratory always offering his space, equipment and any kind of support promptly.

To Luiz Felipe that, apart from my personal friend, was essential for the realization of the AFM measurements at *Universidade Federal do Mato Grosso do Sul* (UFMS).

To my dear friend Wissem who assisted me to obtain the polymers, encouraging me on the final moments and for taking part of his time to synthesize more materials afterwards.

To Francineide Lopes Araújo and Daniel Roger Bezerra Amorim that thought me and stayed with during all the fabrication process and OPV tests of the spin-coat based devices.

To my friends and colleagues from my time at EPCP-IPREM, highlighting, Rayane, Aurélie, Enkyung, Shuanlong, Meera, Hugo and Tonimar. And to the other friends I met during the period abroad for arising my feeling of having found a second home.

Capes and CNPQ for the financial support.

RESUMO

Células solares poliméricas atraem grande interesse nessa área de pesquisa, devido ao baixo custo, processo de fabricação de grandes áreas, materiais de manuseio leves e a possibilidade de sua fabricação por diversas técnicas. Para uma boa eficiência dos dispositivos fotovoltaicos, a camada ativa deve conter uma boa absorção da luz solar. Em termos de *bandgap*, isto quer dizer que quanto menor o *bandgap* maior o fluxo de fótons absorvidos. Uma maneira de realizar isto com os materiais poliméricos é a síntese de um polímero no qual o *bandgap* óptico tem a capacidade de aumentar a captura da luz solar, os chamados polímeros *low-bandgap*. A organização estrutural da camada ativa possui um papel importante na performance de dispositivos, inclusive dos fotovoltaicos, e a técnica Langmuir-Schaefer (LS) proporciona a capacidade de fabricar filmes nanoestruturados e com controle de espessura, podendo servir de base para construção de melhores dispositivos. Dentro deste contexto, o objetivo deste trabalho foi sintetizar polímeros *low-bandgap* e, posteriormente fabricar e caracterizar filmes LS destes polímeros e de suas blendas com um derivado de fulereno, o PCBM, para a aplicação dos mesmos como camada ativa de células solares. Foram fabricados filmes LS dos polímeros e de suas misturas com PCBM e realizadas medidas de caracterização. Estes filmes foram caracterizados por meio de medidas elétricas (corrente vs. Tensão, espectroscopia de impedância e voltametria cíclica), morfológica (microscopia de força atômica) e óptica (Ultravioleta-Visível, Espalhamento Raman e transmissão no infravermelho). Com os filmes de Langmuir e as medidas morfológicas foi possível observar as características específicas de como é a conformação de cada polímero na forma de filme. As medidas ópticas confirmam a absorção em altos comprimentos de onda esperados para estes polímeros. Nas medidas elétricas os resultados mostraram diferentes condutividades para os mesmos materiais quando mudado os tipos de eletrodos. Os dispositivos fotovoltaicos dos filmes LS fabricados não alcançaram bons valores de eficiência. Filmes *spin-coating* destes polímeros testados como camada ativa dos dispositivos, em atmosfera controlada, revelaram eficiência de até 0.6%.

Palavras-chave: polímeros *low-bandgap*, Langmuir-Schaefer, medidas elétricas, dispositivos fotovoltaicos orgânicos.

ABSTRACT

Polymeric solar cells attract great interest in this area of research due to the potential low cost, large area fabrication process, lightweight physical feature and the possibility of fabricating these cells by several techniques. To achieve good efficiency in the photovoltaic devices the active layer must have an efficient absorption of sunlight. In terms of bandgap, this means that the smaller the bandgap the greater the flux of photons absorbed. One way to accomplish this, with the polymeric materials, is the synthesis of a polymer in which the optical bandgap has the ability to increase the capture of sunlight, the so-called low-bandgap polymers. The structural organization of the active layer plays an important role in the performance of devices, including in photovoltaic devices, and the Langmuir-Schaefer (LS) technique provides the ability to manufacture nanostructured films with thickness control, which can serve as a basis for building better devices. In this context, the aim of this work was to synthesize low-bandgap polymers for later manufacturing and characterization of LS films of these polymers and their blends with a fullerene derivative, PCBM, and test them as active layer of solar cells. LS films of such polymers and their blends with PCBM were made and characterization measurements were performed. These films were characterized by electrical (current vs. voltage, impedance spectroscopy and cyclic voltammetry), morphology (atomic force microscopy) and optical (ultraviolet-visible, Raman scattering and infrared) measurements. Through the Langmuir films and the morphological measurements, it was possible to observe the specific characteristics of how it is the conformation of each polymer in film form. Optical measurements confirmed the absorption at high wavelengths expected for these polymers. In the electrical measurements, the results showed different conductivities for the same materials when the types of electrodes were changed. The photovoltaic devices manufactured from LS technique have not reached good efficiency values. When spin-coated active layers were tested as OPV devices in a controlled atmosphere the efficiency achieved up to 0.6%.

Keywords: low-bandgap polymers, Langmuir-Schaefer, electrical measurements, organic photovoltaic devices.

RESUMÉ

Les cellules solaires polymériques attirent un grand intérêt dans ce domaine de recherche, en raison du faible coût, du procédé de fabrication de grandes surfaces, des matériaux de manutention légers et de la possibilité de leur fabrication par diverses techniques. Pour une bonne efficacité des dispositifs photovoltaïques, la couche active doit contenir une bonne absorption de la lumière du soleil. En termes de *bandgap*, cela signifie que plus le *bandgap* est petit, plus le flux de photons absorbés est grand. Une manière d'accomplir ceci avec les matériaux polymères est la synthèse d'un copolymère alterné dans lequel le *bandgap* optique est diminué, ce que l'on appelle des polymères *low-bandgap*. L'organisation structurale de la couche active joue un rôle important dans la performance des dispositifs, y compris les dispositifs photovoltaïques, et la technique Langmuir-Schaefer (LS) permet de fabriquer des films nanostructurés avec contrôle de l'épaisseur, qui peuvent servir de base pour construire de meilleurs dispositifs. Dans ce contexte, l'objectif de ce travail était de synthétiser des polymères *low-bandgap* et ensuite de fabriquer et caractériser des films LS de ces polymères et leurs mélanges avec un dérivé de fullerène, le PCBM, pour leur application en tant que couche active de cellules solaires. Les films LS des polymères et leurs mélanges avec PCBM ont été fabriqués et des mesures de caractérisation ont été effectuées. Ces films ont été caractérisés par des mesures électriques (courant vs tension, spectroscopie d'impédance et voltampérométrie cyclique), morphologiques (microscopie à force atomique) et optiques (UV-visible, diffusion Raman et transmission infrarouge). Par les films de Langmuir et les mesures morphologiques, il a été possible d'observer les caractéristiques spécifiques concernant la conformation de chaque polymère sous forme de film. Des mesures optiques confirment l'absorption aux longueurs d'onde élevées attendues pour ces polymères. Dans les mesures électriques, les résultats ont montré des conductivités différentes pour les mêmes matériaux lorsque les types d'électrodes ont été changés. Les dispositifs photovoltaïques des films LS fabriqués n'ont pas atteint de bonnes valeurs d'efficacité. Les films *spin-coating* de ces polymères testés en tant que couche active des dispositifs, sous atmosphère contrôlée, ont montré une efficacité allant jusqu'à 0,6%.

Mots clés: polymères *low-bandgap*, Langmuir-Schaefer, mesures électriques, dispositifs photovoltaïques organiques.

List of figures

Figure 1 - Illustration of a) sp^2 carbon, and b) the interactions (bonding) - (anti-bonding) between the HOMO / LUMO levels of an organic semiconductor.	21
Figure 2 – Structure of a low-bandgap copolymer containing a DPP unit and a CPDT unit. Where R= dodecyl or methoxyethoxy ethoxy ethyl.....	23
Figure 3 - Low-bandgap conjugated polymers. Where R = alkyl chain. Extracted from [59].	24
Figure 4- Illustration of the charge separation principle of a solar cell. Extracted from [66].	26
Figure 5 - Representation of a polymeric OPV device with homojunction structure. ...	28
Figure 6 - Representation of different structures: a) bilayer, b) BHJ and c) ideal ordered BHJ, of organic solar cells. Figure adapted from [17].	29
Figure 7- Energy levels of the numerical materials BHJ of P3HT: PCBM a) conventional, b) inverted.....	30
Figure 8- Representation of a double junction tandem cell.....	30
Figure 9 - Characteristic J-V curve of a photovoltaic device.	31
Figure 10 - Illustration of an interdigitated electrode.....	33
Figure 11 - Representation of Ossila ITO substrates a) as received b) after metal evaporation.	33
Figure 12 – Devices architecture for the devices with active layer spin-coated based. Adapted from [84].	34
Figure 13 - Chemical structure of a) $PC_{61}BM$ and b) $PC_{71}BM$. Figure extracted from [85].	34
Figure 14 - Structure of the polymers a) PCPDTDPP_ C_{12} and b) PCPDTDPP_Met. ...	35
Figure 15 - Representation of the lateral chain insertion procedure. R = side chain.	36
Figure 16 - Schematic representation of the Bromination procedure.....	37
Figure 17 - Procedure performed for the synthesis of the low-bandgap polymers.	38
Figure 18 - Π -A isotherm for an amphiphilic material in the Langmuir trough and its compression phases of molecules as the pressure increases.....	40
Figure 19 - Layout of the a) LB and b) LS techniques.....	41
Figure 20 - Stages of a spin-coating film formation. Retrieved from [98].....	42
Figure 21 - a) Epoxy solution and b) cover glasses for encapsulation.	44
Figure 22 – Representative system of the encapsulation process.....	44

Figure 23 - Schematic illustration of the basic components of an XPS system.	45
Figure 24 - Side view of optical beam deflection detection in AFM measurement.	48
Figure 25 - Structure of the diode type photovoltaic devices with configuration a) direct and b) indirect.	50
Figure 26 - Measurement system for electrodes a) IDEs and b) ITOs.	50
Figure 27 - Oriel Verasol solar simulator in operation.	51
Figure 28 - Mask with aperture for measuring the photovoltaic devices efficiency.	51
Figure 29 – Graphs of a) Real and imaginary impedance versus frequency and b) Real impedance versus imaginary impedance, for circuits with a capacitor and a resistor connected in parallel, in alternating current.	54
Figure 30 - Schematic representation of an electrochemical cell for CV experiments. Extracted from [117].	55
Figure 31 – Surface pressure–area isotherms of the PCBM.	58
Figure 32 - Surface pressure–area isotherms of the a) PCPDTDPP_C ₁₂ and b) PCPDTDPP_Met (in blue), and their mixtures with PCBM (in green)	59
Figure 33 - AFM images of low-bandgap polymer LS films deposited via Langmuir-Schaefer.	61
Figure 34 - AFM images of low-bandgap polymers mixed with PCBM deposited via Langmuir-Schaefer.	62
Figure 35 - High-resolution X-ray photoelectron spectroscopy scans of the C 1s, O 1s peaks of the pristine PCBM, polymers and its mixture films.	63
Figure 36 - High-resolution X-ray photoelectron spectroscopy scans of the N 1s, S 2p peaks of the pristine polymers and the polymer:PCBM films.	64
Figure 37 - Absorption spectra of PCPDTDPP_C ₁₂ and PCPDTDPP_Met samples.	66
Figure 38 – Pictorial representation of (a) H- and (b) J-aggregates in P3HT. Figure extracted from [156].	67
Figure 39 - Absorption spectra of PCPDTDPP_C ₁₂ :PCBM and PCPDTDPP_Met:PCBM samples	68
Figure 40 – Raman spectra for a) PCBM, b) PCPDTDPP_C ₁₂ and c) PCPDTDPP_Met LS films.	70
Figure 41 - Raman spectra for PCPDTDPP_C ₁₂ : PCBM for different regions of the LS films.	71
Figure 42 - Raman spectra for PCPDTDPP_Met: PCBM for different regions of the LS films.	72

Figure 43 - FTIR spectra recorded from drop-cast films of a) PCBM, b) PCPDTDPP_C ₁₂ and c) PCPDTDPP_C ₁₂ :PCBM on Ge (transmission mode).	73
Figure 44 - FTIR spectra recorded from drop-cast films of a) PCBM, b) PCPDTDPP_Met and c) PCPDTDPP_Met:PCBM on Ge (transmission mode).	74
Figure 45 - Cyclic voltammograms for Pt/ PCPDTDPP_C ₁₂ and Pt/PCPDTDPP_Met systems in 0.100 mol L ⁻¹ LiClO ₄ /ACN solution, $v = 50$ mV/s.	75
Figure 46 - In situ Raman spectra for a)Pt/PCPDTDPP_C ₁₂ , b) Pt/PCPDTDPP_Met obtained using radiation at a wavelength of 532 nm.	77
Figure 47 - Bode phase plots generated for a) Pt/PCPDTDPP_C ₁₂ and b) Pt/PCPDTDPP_Met systems in 0.100 mol L ⁻¹ LiClO ₄ /ACN solution at different potentials.	78
Figure 48 – Current vs. Voltage curves for the LS films of PCPDTDPP_ C ₁₂ and PCPDTDPP_Met on the fabricated day and on the following week.	79
Figure 49 - Current versus voltage curves for the LS films of a) PCPDTDPP_C ₁₂ , b) PCPDTDPP_Met during the encapsulation process, c) PCPDTDPP_C ₁₂ and d) PCPDTDPP_Met at the time just after encapsulating.	80
Figure 50 – Interdigitated substrate 6 months after film manufacturing encapsulated on the digits area.	81
Figure 51 - Current versus voltage curves for LS films of a) PCPDTDPP_C ₁₂ and PCPDTDPP_Met and b) PCPDTDPP_C ₁₂ /PCBM and PCPDTDPP_Met/PCBM.	81
Figure 52 - I vs. Curves V, in linear scale, of the devices a) ITO/PEDOT: PSS/C ₁₂ :PCBM/Al, b) ITO/C ₁₂ : PCBM/PEDOT:PSS/Al, c) ITO/PEDOT: PSS/Met:PCBM/Al and d) ITO/Met:PCBM/PEDOT:PSS/Al.	84
Figure 53 - I vs. Curves And, on a monologarithmic scale, of the devices a) ITO/PEDOT:PSS/C ₁₂ :PCBM/ Al, b) ITO/C ₁₂ :PCBM/PEDOT:PSS/Al, c) ITO/PEDOT:PSS/Met:PCBM/Al, and d) ITO/Met:PCBM/ PEDOT:PSS/Al.	85
Figure 54 - Z' vs. f curves for LS films with the ITO/PEDOT:PSS/Polymer:PCBM/Al and ITO/Polymer:PCBM/PEDOT:PSS/Al configurations.	87
Figure 55 - Z'' vs. f curves for LS films with the ITO/PEDOT:PSS/Polymer:PCBM/Al and ITO/Polymer:PCBM/PEDOT:PSS/Al configurations.	89
Figure 56 - Z'' vs. Z' curves for LS films with the ITO/PEDOT:PSS/Polymer:PCBM/Al and ITO/Polymer:PCBM/PEDOT:PSS/Al configurations.	90
Figure 57 – Plots of a) Z' vs. f, b) Z'' vs. f and c) Z'' vs. Z' for ITO/PEDOT:PSS/Met:PCBM/Al LS film with 20 layers.	91

Figure 58 - J vs. V curves for the a) ITO/PEDOT:PSS/C ₁₂ :PCBM/Al, b) ITO/C ₁₂ :PCBM/PEDOT:PSS/Al, c) PCBM/PEDOT: PSS/Al devices, under the illumination of a solar simulator (100 mW/cm ² - AM 1.5).	93
Figure 59 - Schematic representation of the OPV devices with spin-coating BHJ active layer.	95
Figure 60 - J-V curves for the ITO/PEDOT:PSS/C ₁₂ :PC ₆₁ BM/Ca/Al and ITO/PEDOT:PSS/C ₁₂ :PC ₇₁ BM/Ca/Al devices under dark and illuminated.	96
Figure 61 - J-V curves for the ITO/PEDOT:PSS/Met:PC ₆₁ BM/Ca/Al and ITO/PEDOT:PSS/Met:PC ₇₁ BM/Ca/Al devices under dark and illuminated.	97
Figure 62 - J-V curves for the ITO/PEDOT:PSS/Met:PC ₇₁ BM/Ca/Al and ITO/PEDOT:PSS/Met:PC ₇₁ BM/Ca/Al devices under dark and illuminated.	98
Figure 63 - Energy diagram of the materials used on the OPV devices.	99
Figure 64 - AFM images for the spin films from CHCl ₃ solutions of the a) C ₁₂ :PC ₆₁ BM, b) C ₁₂ :PC ₇₁ BM, d) Met:PC ₆₁ BM, e) Met:PC ₇₁ BM, and from CB solutions of the c) C ₁₂ :PC ₇₁ BM, f) Met:PC ₇₁ BM, all of them over the ITO/PEDOT:PSS system.	100

List of tables

Table 1 – Chemical composition of the LS films surface of the low-bandgap polymers.	65
Table 2 - Results obtained by CV and UV-visible optical absorption measurements for the PCPDTDPF films.	77
Table 3- Calculated RR values for the devices in constant voltage.	86
Table 4 - Photovoltaic parameters obtained for the OPV devices of the polymers:PCBM blends deposited via LS and with different geometries.....	93

List of abbreviations

AFM	Atomic Force Microscopy
BHJ	Bulk heterojunction Solar Cell
CPDT	Cyclopentadithiophene
CV	Cyclic Voltammetry
DPP	diketopyrrolopyrrole
E_{gap}	Gap energy
E'_{ox}	oxidation potential onset
ETL	Electron Transporting Layer
f	frequency
FF	Fill Factor
HOMO	Highest Occupied Molecular Orbital
HTL	Hole Transporting Layer
I	electric current
I_0	intensity of incident light
ITO	Indium Tin Oxide
J	density of current
J_{max}	density of current that maximize FF
J_{SC}	Short-Circuit Current Density
k_{cell}	cell constant
LS	Langmuir-Schaefer
LUMO	Lowest Unoccupied Molecular Orbital
NBS	N-bromosuccinimide
NMR	Nuclear Magnetic Resonance
OPV	organic photovoltaic
PCBM	phenyl-C ₆₁ -butyric acid methyl ester
PC ₆₁ BM	phenyl-C ₆₁ -butyric acid methyl ester
PC ₇₁ BM	phenyl-C ₇₁ -butyric acid methyl ester
PCE	Power Conversion Efficiency
PEDOT:PSS	poly(3,4-ethylenedioxythiophene)-poly(styrene sulfonate)
R	electrical resistance
V_{OC}	Open-Circuit Voltage
V_{max}	voltage that maximize FF
XPS	X-Ray Photoelectron Spectroscopy
Z^*	electrical impedance (complex quantity)
λ_{ex}	excitation wavelength
λ_{max}	wavelength of maximum absorption
ρ	electrical resistivity
ω	angular frequency

Summary

Chapter 1: Introduction.....	18
1.1 Organic Semiconductors.....	20
1.2 Low-bandgap polymers	22
1.3 Organic photovoltaic devices (OPVs)	25
1.4 Principles of organic solar cell operation.....	25
1.5 Solar cell architectures.....	27
1.6 Analysis of the J-V curve for a photovoltaic device.....	31
Chapter 2: Materials and Methods.....	33
2.1 Substrates	33
2.2 Materials	34
2.3 Methods	35
2.3.1 Polymers synthesis processes	35
2.3.2 Magnetic Nuclear Resonance	38
2.3.3 Size Exclusion Chromatography	39
2.3.4 Langmuir and Langmuir-Schaefer films	39
2.3.5 LS films of the low-bandgap polymers	41
2.3.6 Spin-coating technique	42
2.3.7 PVD films.....	43
2.3.8 Encapsulation process.....	43
2.3.9 X-ray Photoelectron Spectroscopy (XPS).....	45
2.3.10 Optical Characterization in Ultraviolet-Visible (UV-Vis)	46
2.3.11 Fourier-transform infrared (FTIR) absorption spectroscopy.....	46
2.3.12 Raman spectroscopy	47
2.3.13 Atomic Force Microscopy (AFM).....	48
2.3.14 Electrical characterization in direct current (DC).....	49
2.3.15 Alternating current (AC) measurements.....	51
2.3.16 Cyclic Voltammetry	54
2.3.17 Profilometry analysis.....	55
Chapter 3 – Thin films, morphological and optical characterization results.....	57
3.1 Langmuir films	57
3.2 Atomic Force Microscopy	60
3.3 X-ray Photoelectron Spectroscopy (XPS)	63
3.4 UV-Vis spectroscopy	66

3.5	Raman spectroscopy	69
3.6	FTIR Spectroscopy	72
Chapter 4 – Electrical and electrochemical measurements results.....		75
4.1	Cyclic Voltammetry.....	75
4.2	Interdigitated Electrodes (IDE).....	79
4.2.1	Measurements in direct current	79
4.3	Diode structure.....	83
4.3.1	Direct Current Measurements.....	83
4.3.2	Alternating current measurements.....	86
4.4	Results of the OPV performance of the LS films	92
Chapter 5 – OPV devices from spin-coating films.....		95
Chapter 6 - Conclusions		102
Complementary information		104
References		106
Appendix		124

Chapter 1: Introduction

It is clear that the current energy regimen, which is mainly based in non-renewable and pollutant energy sources, is unsustainable and reveals great consequences for the societal, economical, geopolitical and environmental issues [1]. The increase of the world energy demand caused the search for new alternatives to the conventional fossil sources. The photovoltaic devices offer the availability of generating clean and renewable electricity, where the spectral region of the solar emission is divided in around 5% on the UV-Visible, 43% on the visible and 52% on the infrared region of the electromagnetic spectrum, therefore the production of such devices is a viable process [2]. If completely converted into electricity, one hour of solar irradiation could supply all the earth energetic demand for one year [3]. It is estimated that in three weeks the sun can emit the same energy contained in all the remaining fossil reservations of the world [4]. Thus, researches that have as aim the development of this energy source are essential for the energetic picture.

Concerning the solar cells types, the Organic Photovoltaic (OPV) devices are among the most promising technologies that can be used to produce low-cost energy with the advantage of semitransparency, flexibility, aesthetics, and solution processability [5], besides is easily applicable in several products, it has manufacturing costs significantly lower when compared to the inorganic technologies, it shows short energy payback times and low environmental impact during manufacturing and operations [6]. The first generation of solar cells was based on a single layer of organic material located between two electrodes with appropriate work function where, in the 1980s the first OPV cell was demonstrated by Weinberger et al. [7] using a thin film of trans-polyacetylene as a photosensitive material, with 0.1% efficiency, which paved the way for the research of the polymers for application in solar cells.

Contrary to inorganic solar cells, absorption of a photon produces a neutral excited state (exciton) and not free charge carriers. Thus, a new architecture for solar cells was reported in 1986, the bilayer heterojunction, which consists of two different organic layers to separate the charges, where one layer is the acceptor (n-type) material then responsible for the transport of electrons and the other layer is the donor (p-type) material which is in charge of the transport of holes, this constituted an attempt to improve the OPV photocurrent. A device with this architecture, consisting of a phthalocyanine layer as a p-type and a perylene derivative as n-type, having the ITO electrode and a silver contact

above the active layer caused an increase in efficiency of solar cells to about 1% [8]. But, the bilayer heterojunction devices are greatly limited by the small effective interfacial area between the donor and the acceptor [9,10]. This is a key parameter due to the short diffusion length of excitons in organic materials as polymers, estimated at about 10 nm [11]. Therefore, in order to increase this interface area between the donor and the acceptor materials, which also leads to an increase in charge generation, the bulk heterojunction (BHJ) device was created. In 1992, the photoinduced electron transfer between a conjugated polymer and fullerene (C₆₀) was reported [12], opening a huge improvement in organic solar cells area. Now the two materials of interest are mixed together and subsequently deposited onto the desired substrate [13].

The OPVs area has advanced a lot in recent decades, with frequent reports of studies showing > 10% efficiency produced in laboratories [6,14], which is commonly considered a benchmark for commercial viability [15]. This progress can be largely attributed to the development of new light-absorbing polymers. From homopolymers that have been extensively studied as P3HT and MDMO-PPV [16,17], many other polymers with more complex structures have been introduced with improved capture of sunlight, charge generation, and charge transport properties [18].

Among the various semiconductor polymers that have been studied in recent decades, low-bandgap polymers - that have a typical bandgap of less than 1.5 eV and near-infrared (NIR) absorption - appear as one of the categories more intriguing for research as polymeric solar cells [19–21]. For the polymeric OPV devices, the NIR absorption allows the generation of the NIR photocurrent, which consists of a way of increasing the short-circuit current, and consequently the efficiency of the cell. In addition, according to the molecular model, most low-bandgap semiconductor polymers have more delocalized π electrons, greater conjugation length and higher polymer chains planarity when compared to other polymers [22,23]. These characteristics lead to a decrease in the energy level of the higher occupied molecular orbital (HOMO) of the donor polymer, easiness of the intermolecular hole transport, and equilibrium in the transport of the electrons and holes between the electron donor polymer and the electron acceptor material. As a result, studies have been observed in which solar cells based on low-bandgap polymers reach efficiencies above 10%, thus, revealing materials that can be commercialized [24,25].

The morphology of devices manufactured from organic materials affects significantly their conductivity [26]. In thin films form, the morphology changes can

occur according to the chosen deposition technique. There are many techniques available for the production of films from organic materials [27–29], among them it is possible to highlight the Langmuir deposition techniques [30,31], which are commonly used for the manufacture of films in which greater ordering and good control at the molecular level are desired [32,33]. The Langmuir-Blodgett technique is a complicated way of making films from non-amphiphilic rigid materials [34,35]. For such cases, the Langmuir-Schaefer technique is more common, which does not have this type of restriction [36].

The aim of this work was to study and characterize optical and electrically low-bandgap polymers that were synthesized during the internship abroad, utilizing the Langmuir-Schaefer technique to build photovoltaic devices of these polymers. Thereby enabling the improvement of the overall organic film conformation and, thus improving the device operation. As well as building different device architectures, analysing the result of this architecture in the final performance of the cell.

1.1 Organic Semiconductors

Organic semiconductors are carbon-based materials and possess semiconductor characteristics. The atoms of an organic semiconductor molecule are bounded by π -conjugated bonds, while the molecules are linked together by the weak van der Waals force. This type of bond gives organic semiconductor materials their unique features, such as: flexibility, lightness, and low sublimation point, which facilitates their processing [37]. In organic semiconductors, the Highest Occupied Molecular Orbital (HOMO) and Lower Unoccupied Molecular Orbital (LUMO) are the valence band and conduction band analogue described for the inorganic semiconductors, respectively. The HOMO and LUMO of the organic materials represent the hybridization of π -conjugated bonding and anti-bonding electrons [38].

Organic semiconductors are composed of organic molecules that are formed by a π -conjugated system. The carbon atoms are hybridized in the sp^2 form, with three covalent bonds (σ type) with the neighbouring atoms (Figure 1.a). The remaining p orbitals of the carbon atoms form a cloud of delocalized electrons through the formation of weaker π bonds. This type of bond forms a quasi-unidimensional structure for conjugated organic semiconductors. The π -bonding system can assume different configurations according to the wave function superposition of the electrons and the neighbouring atoms. For

example, in Figure 1.b) it is possible to observe two different states for the π bonds, with the bonding and anti-bonding states corresponding to different energy levels.

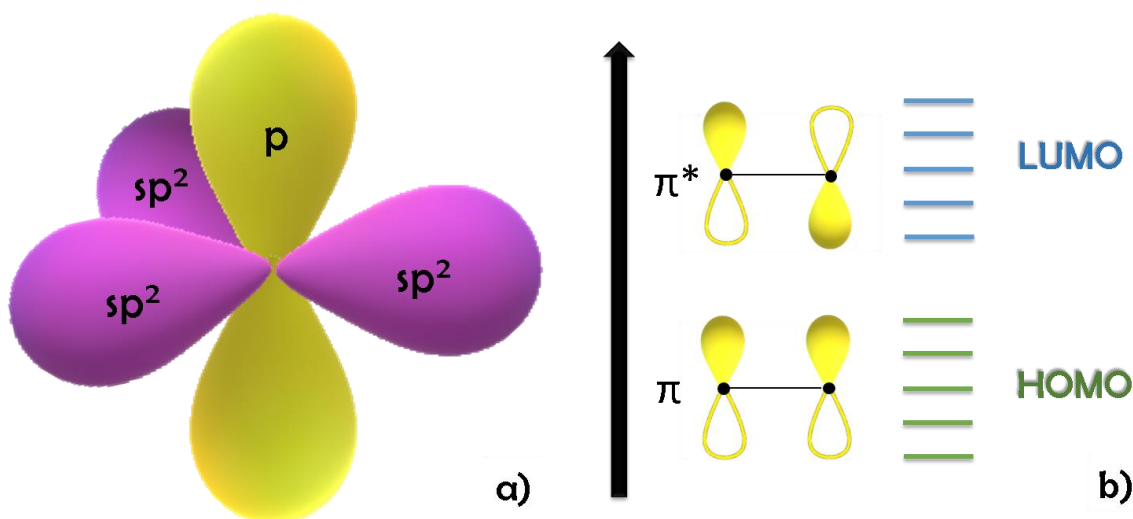


Figure 1 - Illustration of a) sp^2 carbon, and b) the interactions (bonding) - (anti-bonding) between the HOMO / LUMO levels of an organic semiconductor.

The HOMO and LUMO of the organic semiconductors refer to the energy bands corresponding to different states of π bonds hybridization that will result in different energy levels of an organic semiconductor.

After Alan J. Heeger, Alan G. MacDiarmid and Hideki Shirakawa discovered that the conductivity of polyacetylene could be magnified significantly by chemical doping [39], the interest in the conjugated polymers rose considerably. This discovery also caused them to be awarded the Nobel Prize in Chemistry in 2000. The transport properties of semiconductor polymers are dominated by disorder due to partial crystallinity, nonhomogeneous doping, or the disarrangement that is created during the synthesis or material processing [40].

As an explanation for the transports in these polymers, solitons, polarons and bipolarons [41] emerged as important concepts that are associated with the non-linear configurations formed due to the delocalization of the charges. Conductive polymers are more susceptible to structural distortions than inorganic ones. In this way, the electronic excitation is strongly related to the distortions of the chain [42], therefore, the charge carrier in a polymer is different from a free electron in a metal or the electron-hole pair in an inorganic semiconductor. Solitons are used as charge carriers in the case of degenerate conjugated polymers, more precisely for trans-polyacetylene [43], whereas polarons and bipolarons are considered as the carriers of charges for non-degenerate conjugated polymers [44].

The conductivity of the conjugated polymers is generated due to the charge carriers and their movement along the chain where there are the π -conjugated systems. However, bulk conductivity cannot be analysed by considering only charge transfers in a single conjugate pathway, since the polymeric systems are disordered. For this, it is also necessary to evaluate the existence of electronic hopping between the polymer chains [45,46].

There are studies that report how transport by polarons in the conjugated polymers occurs. But specifically, for these polymers applied to solar cells, there are several theoretical and experimental studies that suggest that the light excitation effect in these pristine polymers produces not only oxides but also pairs of polarons, which are electrons and holes with a weaker Coulomb attraction [47,48]. Not long ago, it was reported that these pairs of polarons, formed in the polymer domains, play a significant role in the photovoltaics operation, being as important for the final efficiency of the cell as the excitons [49]. However, for the case of the copolymers it is still unclear the contribution of these pairs of polarons to the total efficiency of the devices, and perhaps discrepancies between the theoretical values using some models and an above-expected experimental value occur from the negligence of these charges [50].

1.2 Low-bandgap polymers

Generation of electricity in OPVs can be summarised through five processes: i) the absorption of light and the generation of the exciton in the photoactive organic semiconductors; ii) Exciton diffusion towards the donor/acceptor heterojunction, iii) separation of the photo-induced charges and subsequent generation of charge carriers; iv) transportation of charge carriers and v) their collection at each electrode [51]. Another aspect of the organic semiconductors is to exhibit lower carriers mobility in comparison with inorganic semiconductors [52], because of this the thickness of the photovoltaic layer in the OPVs should be chosen carefully once the devices performance is highly dependent on that [53]. Therefore, the absorption range of the semiconductors should be higher to compensate for the thinner photoactive layer.

Besides focusing on the thickness, an efficient way to extend the light absorption range by the active layer is to decrease its optical bandgap, which for polymeric materials are the so-called low-bandgap polymers. Inside this class, there is mainly the presence of

polymers that have typically the bandgap energy smaller than 1.5 eV ($E_g < 1.5$ eV). The most efficient method of synthesizing low-bandgap polymers is to alternately copolymerize an electron donor (D) with an electron acceptor (A) monomer [19]. This strategy induces an intramolecular charge transfer between the D and A units of the polymer backbone, resulting in a redistribution of the molecular orbitals of D and A. This hybridization of the molecular orbitals generates new occupied and unoccupied orbitals with a narrow bandgap of the copolymers of type D-A.

If a semiconductor polymer has a bandgap of 2.0 eV, it can absorb photons up to 620 nm which corresponds to the harvesting of 25% of the total solar energy flux. With the extension of this absorption to a value up to 1100 nm ($E_g = 1.1$ eV), for example, the harvest of sunlight would increase to 77% [54]. Particularly, due to this ability to collect a large portion of the solar spectrum, several low-bandgap polymers have been used as the p-type component in high efficient polymer solar cells [55].

In the present work, two low-bandgap polymers were used with a Pyrrolo[3,4-c]pyrrole-1,4-dione (DPP) derivative as the A unit and a cyclopentadithiophene derivative (CPDT) as the D unit forming the copolymer D-A. They are shown in Figure 2.

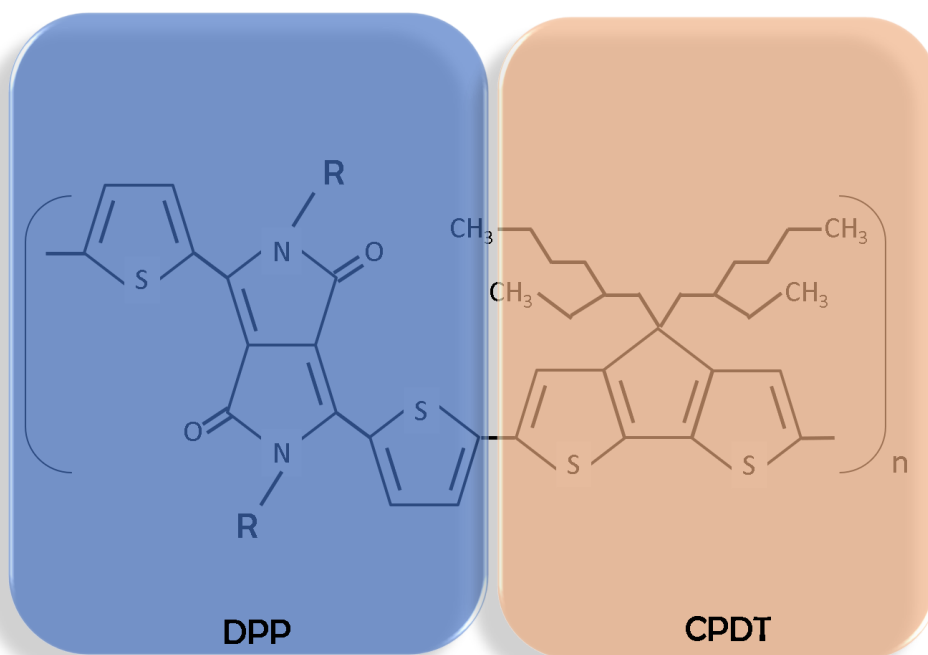


Figure 2 – Structure of a low-bandgap copolymer containing a DPP unit and a CPDT unit. Where R= dodecyl or methoxyethoxy ethoxy ethyl.

The CPDT portion containing a thiophene derivative is widely used in various copolymers used for electronic devices [56]. Up to now, most of the D units in the semiconductor polymers that show higher efficiencies are thiophene derivatives [57]. The

sulphur atom in thiophenes releases more electrons than nitrogen and oxygen due to the lower electronegativity of the sulphur compared to these two, which makes the thiophene to be richer in π electrons than the analogues with nitrogen and oxygen (pyrrole and furan). Therefore, thiophene derivatives exhibit strong electron donor characteristics along with the effective π - π packing and with high hole mobility. In contrast to the D units, a greater variety of A units has been developed, because the electron deficient nature of the A units can be effectively adjusted by replacing groups that capture or release electrons in unit A [54]. Notably, the absorption, energy levels and bandgaps of the semiconductor polymers are controlled primarily by the choice of unit A. As a consequence, the proper choice of the A unit in D-A type copolymers is critically important to obtain high-performance polymer solar cells [58].

Hence, there are several types of low-bandgap polymers, which are classified according to acceptor unit, among them are those based on 2,1,3-Benzothiadiazole (BT), Diketopyrrolopyrrole (DPP), Isoindigo, Thieno [3,4-c] pyrrole-4,6-dione (TPD), Benzo[1,2-b,4,5-b]dithiophene-based polymers (BDT), fluorinated thieno[3,4-b] thiophene (T34T), among other types [54]. Some examples of low bandgap polymers are shown in Figure 3.

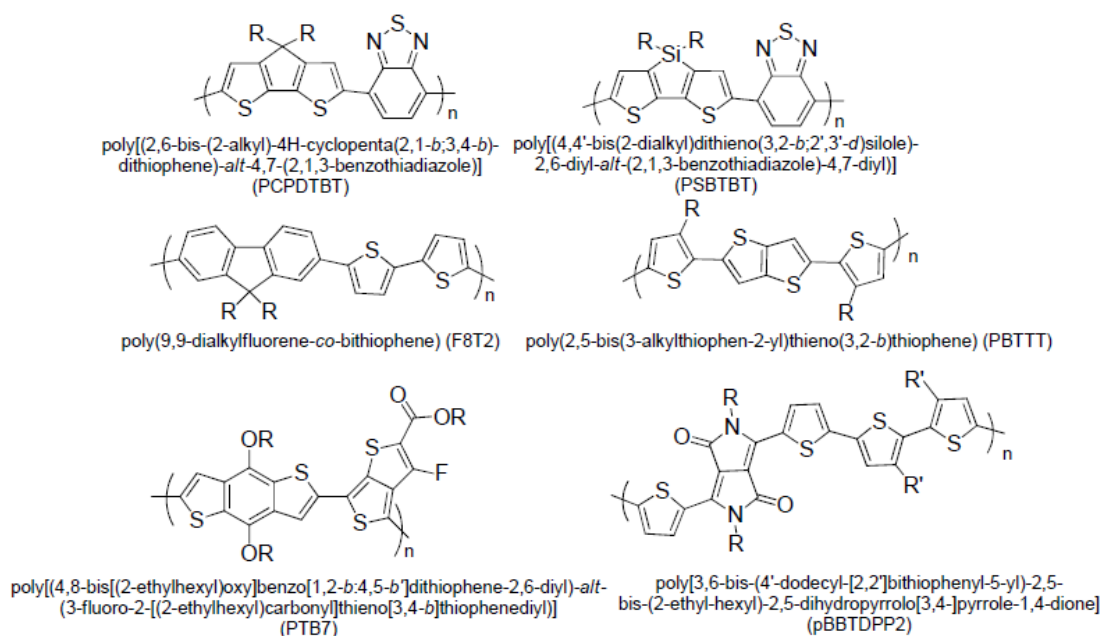


Figure 3 - Low-bandgap conjugated polymers. Where R = alkyl chain. Extracted from [59].

DPP derivatives usually have evidenced absorption bands in the visible region. DPP-based thiophenes have well-defined conjugated structures and exhibit good mobility of charge carriers, both for holes and electrons [60]. Therefore, polymers and small

molecules have attracted considerable attention, and more materials DPP-based for the OPVs have been developed [61,62]. It is also noteworthy to mention that when compared to the thiophene derivatives (DT) with BT-based (DTBT), the thiophene copolymerized with the DPP-based acceptor unit form polymers that have much lower bandgap values [34].

1.3 Organic photovoltaic devices (OPVs)

Photovoltaic devices are semiconductor diodes that convert light radiation into electrical energy. The structure of an OPV device is similar to the organic light emitting devices (OLEDs). The substrate/anode to construct these devices must be a transparent material in order to allow light to pass through. Thereby, it is used a glass or plastic substrate covered by a thin layer of a transparent conducting oxide, and the most commonly used is the ITO (Indium-Tin oxide), however, can also be applied FTO (Fluorine doped Tin-Oxide), silver nanowires, metallic thin films, graphene and carbon nanotubes [63–65]. And the cathode is usually made from a metal such as Aluminium, Magnesium, Calcium or Silver [3,13]. The photoactive layer is composed of electron donor materials such as p-type polymers, and electron acceptors such as fullerene and its derivatives, which can assume different types of architectures.

1.4 Principles of organic solar cell operation

The operation of the organic solar cells can be summarized in five steps: i) Photon absorption leading to the exciton generation; ii) Exciton diffusion towards the donor/acceptor heterojunction; iii) Exciton dissociation in the heterojunction iv) Charges transport and v) Charges collection by the electrodes. Figure 4 shows these steps which are described in more details below.

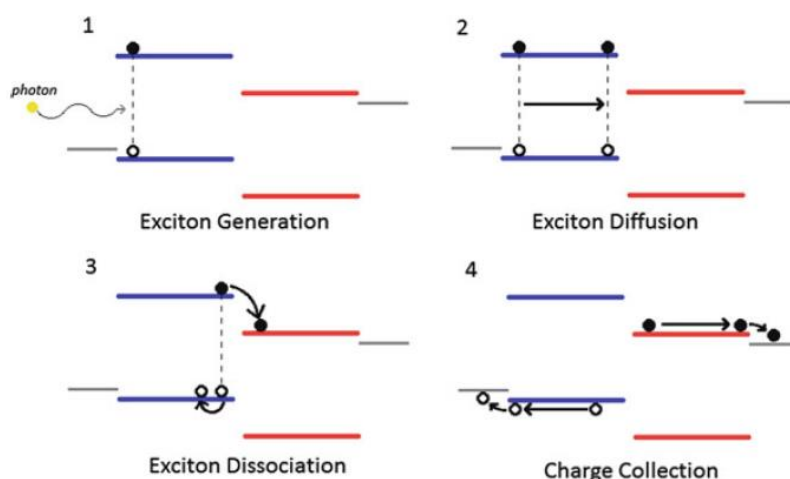


Figure 4- Illustration of the charge separation principle of a solar cell. Extracted from [66].

- i. **Exciton generation:** With a photon absorption, an electron in the organic semiconductor is excited from HOMO to LUMO. However, due to the low dielectric constant and the wave functions of the electrons and holes located in the organic semiconductors [67], there is a strong Coulomb attraction in the electron-hole pair. This pair is called exciton, and the bonding energy between them ranges from 0.1 to 1.4 V [67].
- ii. **Exciton diffusion:** In order to convert the luminous energy into electrical energy in the device, the exciton must reach the interface for the dissociation to occur. Thus, it is necessary for the exciton to travel a certain distance in sufficient time to avoid radiative de-excitation. The transport of these excitons occurs mainly by diffusion since these entities do not suffer influence of internal fields since they are electrically neutral [4].
- iii. **Exciton dissociation:** With the exciton generation and diffusion the next issue is to separate the electron-hole pair with the aim to create free charges that will generate electricity afterwards. In conjugated polymers, the binding energy of the exciton is approximately 0.3 eV, higher in 10 times than the thermal energy [68]. This contributes to the tendency of the exciton to stay connected or to desexcitate. To avoid this from happening Tang *et al.* proposed the use of two different organic materials, with optimal alignment of their energy levels which can result in efficient solar cells [8]. The junction formed between these two materials is called heterojunction. In order to achieve the excitons dissociation, it is necessary that the energy difference between the donor and acceptor LUMO levels is greater

than the binding energy of the exciton [69]. It is also generally accepted that the difference between the LUMOs of D and A should be higher than 0.3 eV [70].

- iv. Charges transport: After the exciton dissociation each element of the electron-hole pair must reach the electrodes within its lifetime. The main forces that act to transport the holes to the cathode and the electrons to the cathode are the drift and diffusion currents [71]. Where the drift current corresponds to the movement of the charge carriers along the gradient of the potential within the solar cell, the chosen electrodes are an important part in this type of conduction. While the diffusion current comes from the fact that the carriers diffuse to the opposite direction of the heterojunction that has the highest concentration of electrons and holes [37]. In this step is important to take into account the importance of the blend films morphology, since this parameter is closely related to the charge carriers recombination [49].
- v. Charges collection by the electrodes: After travelling through the polymers and electron accepting molecules, it is necessary that the charges achieve the electrodes, and thus completing the electric circuit. The recombination speed in the regions surrounding the electrodes is crucial for the possibility of this step [72]. Another aspect to be taken into account is that the electrodes have a working function difference sufficient to control the current flow, causing the holes to move towards the anode (higher working function) and the electrons towards the cathode (low working function) [73].

1.5 Solar cell architectures

OPV devices formed by a single layer of polymer (Figure 5) or conjugated organic molecules do not show good efficiency. One of the causes is that the electric field generated by the two electrodes is rarely high enough for the complete dissociation of the electrostatic bonds of about 100 to 500 meV between the polarons of the photogenerated excitons [74]. Moreover, since the device is made from a single layer, even the electrons dissociated by the application of an external electric field will recombine before reaching

the electrodes. This facility to recombine occurs because both, positive and negative, charge carriers are dissociated and carried on the same active layer.

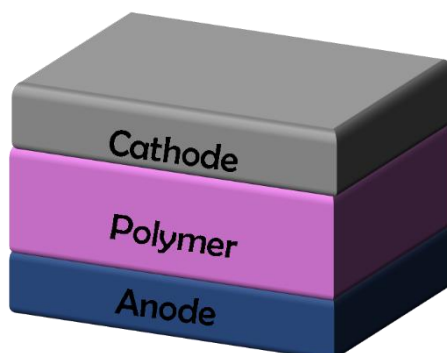


Figure 5 - Representation of a polymeric OPV device with homojunction structure.

The formation of a heterojunction by Tang et al. in 1986 was first shown in the form of a bilayer solar cell [8]. In the bilayer cell (Figure 6.a) the active layer is composed of a planar heterojunction that contains two materials with different working functions. In this framework, there is a single and well-defined interface between donor and acceptor where the excitons dissociate more efficiently when compared to the system with only one material in the active layer. A significant disadvantage of bilayer solar cells is that the short diffusion length of the exciton of organic materials limits the thickness of the donor and acceptor layers. For this reason, if these layers are too thick, the excitons generated further from the heterojunction can desexcitate before reaching it. Also, the active layers must be shaped to ensure that the phase separation between the donor and the acceptor is comparable to the dissociation length of the exciton.

One of the most important advances in the area of OPVS occurred in 1995 with the discovery of bulk heterojunction (BHJ) structure (Figure 6.b) [13]. This type of structure is commonly formed by mixing the donor and acceptor materials in solution which is then passed onto the substrate using, generally, the spin-coating technique [75,76]. The resulting film is a nanoscale interpenetrating network between the donor and the acceptor materials, which causes a large interfacial area favouring the excitons dissociation. In contrast with flat (bilayer) heterojunction devices, the charge carriers in a BHJ cell are generated throughout the device bulk [77]. However, it is argued that due to the inherent spatial charge effects in the BHJ structure, the fill factor (directly linked to cell efficiency) is usually low and that the disordered structure will eventually be limited by several high series resistances [78]. In this way there is also the ordered BHJ structure (Figure 6.c), which is intrinsically the same as the normal BHJ, however, the donor and acceptor materials have direct paths to their respective electrodes and,

consequently, they are expected to perform well. Nevertheless, in order to manufacture polymeric devices with an ordered BHJ structure, techniques requiring either highly specialized instrumentation or more developed synthesis and processing (which are more expensive), not being a practical implementation method, neither in research or in the industrial production processes [17].

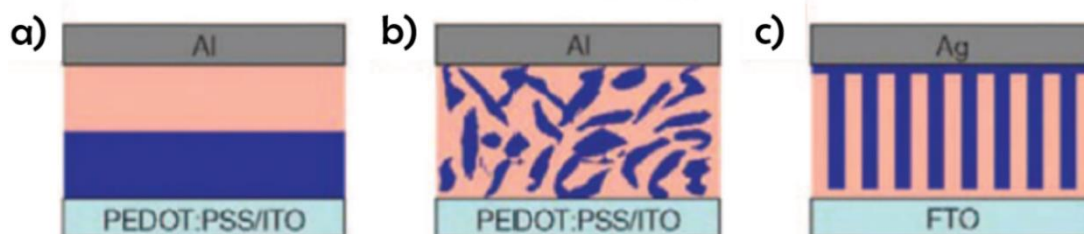


Figure 6 - Representation of different structures: a) bilayer, b) BHJ and c) ideal ordered BHJ, of organic solar cells. Figure adapted from [17].

In addition to the active layer and electrodes, other intermediate layers are employed to manufacture solar cells in order to increase their efficiency. In a conventional device, over the semi-transparent electrode, the ITO for instance, it is normal to use a layer to collect holes, such as poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT: PSS), MoO_3 , NiO , V_2O_5 , WO_3 , among others. The inclusion of such layers helps to provide an effective charge collection, as well as contributes to the removal of potential pinholes on the ITO surface [79]. Subsequent to this layer is deposited the active layer containing the p and n-type materials, thus forming the heterojunction (bilayer or BHJ). Onto this organic layer is transferred an electron transport layer (ETL), such as LiF, Ca and ZnO, which also has the function of protecting the active layer during the cathode deposition and extending the lifetime of the device [1,80]. Following these steps, the upper electrode, like the aluminium, is deposited on these layers. In the inverted devices the electron collecting layer is deposited after the ITO, and the hole transport layer (HTL) before the metal, which requires a change in the upper electrode, and silver is commonly used [24,51,65]. The definition of the two geometries relates to the direction in which the flow of the charges occurs, this can be observed in Figure 7.

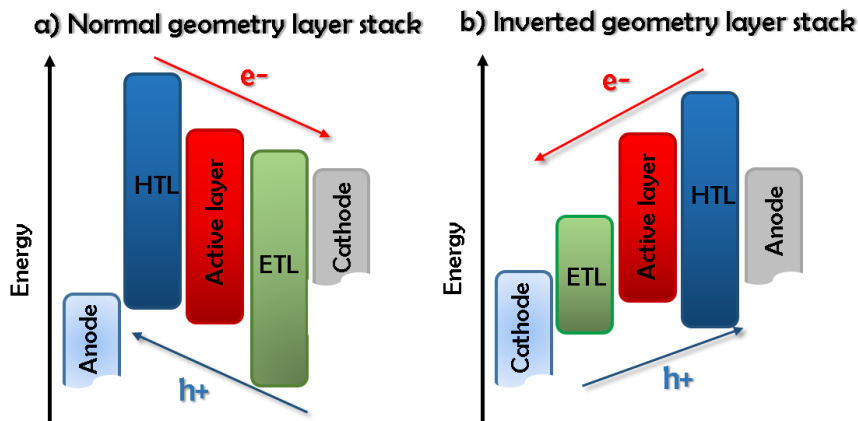


Figure 7- Energy levels of materials in polymer:fullerene BHJ solar cells for a) conventional, b) inverted geometry.

For a more efficient exploitation of solar radiation, a proposition is to stack in series multiple photoactive layers with complementary absorption spectra, thus constructing a tandem solar cell [81]. In a typical double-junction tandem cell, its structure consists of an initial layer with a wide-bandgap material, an intermediary layer, and a layer with a low-bandgap material. Figure 8 shows a double junction cell and the absorption spectra of the active layers of such devices. When compared to devices that do not have the tandem structure, this structure reduces the loss of photovoltage during the conversion processes inside the cell [81]. A tandem solar cell has been proven to improve the efficiency of polymer-based photovoltaic devices by about 40-50% [82].

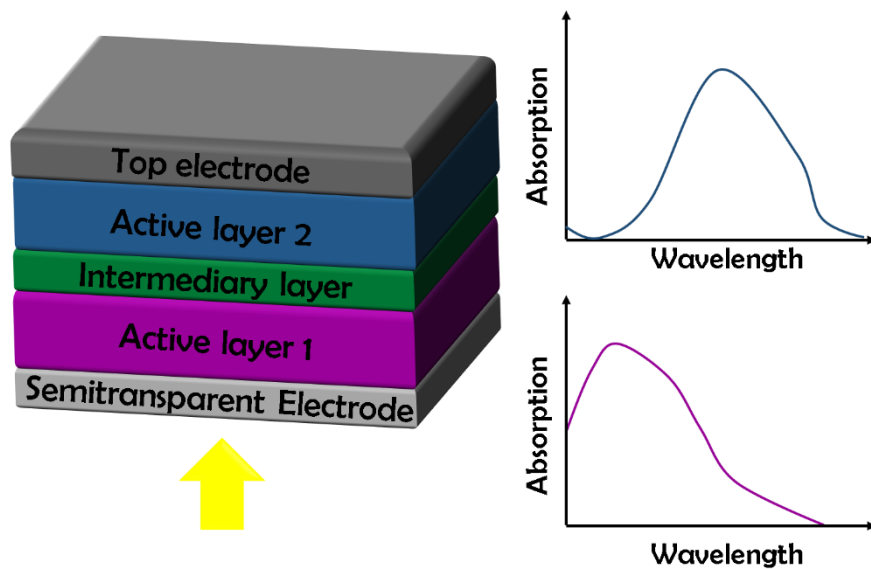


Figure 8- Representation of a double junction tandem cell.

Despite the aforementioned advantages, tandem solar cells present several difficulties in the association of their subcells. Charge carriers of the upper and lower layers recombine in the intermediate layers, which must be chosen to allow efficient

recombination and must be transparent to reduce optical losses. Furthermore, the corresponding current between the subcells must be achieved in order to prevent the charge accumulation in any one of the subcells, that ultimately influences the drop in total efficiency. Finally, during the manufacturing process, it is also important that the layers deposited on the top of the others do not damage the layers below. These factors represent the challenges in the manufacture of cells that have this architecture. The choice of each layer and the techniques used to do so constitute a great difficulty in the manufacture of tandem cells [37].

1.6 Analysis of the J-V curve for a photovoltaic device

The electrical response of each photovoltaic device is obtained by characteristic curves of current density versus applied voltage (J-V). Figure 9 shows a hypothetical characteristic curve for a device in the dark and under illumination. This is a representation of the behaviour closest to the ideal in a photovoltaic cell. The curve in the dark represents the response to a rectifier diode where there is electrical current only for direct polarization, *i.e.* when the highest work function electrode is connected to the positive terminal of the voltage source and the lower work function electrode to the negative. The open circuit voltage (V_{OC}) and the short circuit current density (J_{SC}) are represented in the curve under illumination.

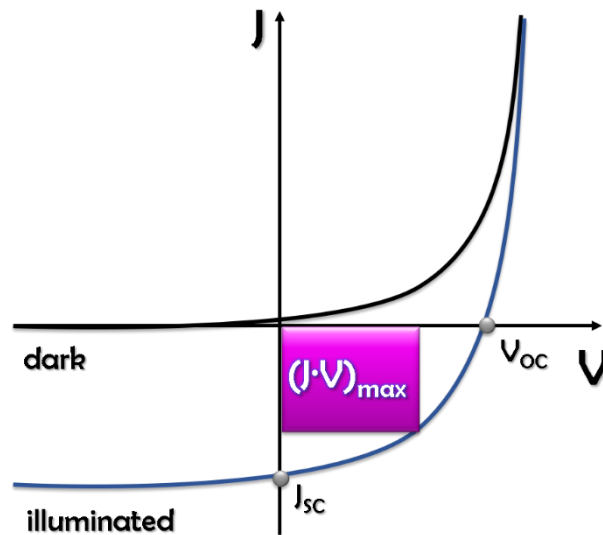


Figure 9 - Characteristic J-V curve of a photovoltaic device.

The amount of electrical energy that can be obtained from a photovoltaic cell is the ratio of the maximum power supplied by the device (represented by the area of the rectangle in Figure 9) and the power related to the J_{SC} and V_{OC} values. This ratio is a

measure of how much the J vs. V of a photovoltaic device differs from that of an ideal cell [83] and is called the fill factor, FF, and can be calculated by the expression (1):

$$FF = \frac{(JV)_{max}}{J_{sc}V_{oc}} \quad (1)$$

where J_{max} and V_{max} are values for current density and applied voltage that maximize the product, leading to the rectangle of larger area in the fourth quadrant of the curve J vs. V. The conversion efficiency of a photovoltaic device, η , relates the maximum power generated by the cell and the incident light power in such a way that:

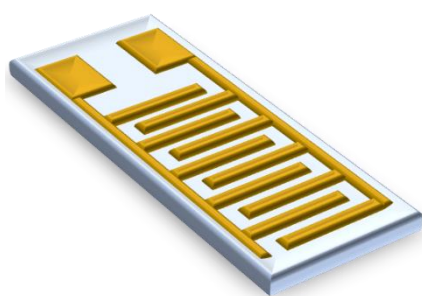
$$\eta = FF \frac{J_{sc}V_{oc}}{I_0} \quad (2)$$

where I_0 is the intensity of the incident light on the device in W/cm^2 .

Chapter 2: Materials and Methods

2.1 Substrates

The substrates used for the electrical characterizations in direct current and for the absorption in the UV-Vis were the interdigitated electrodes (IDEs) manufactured and supplied by the National Nanotechnology Laboratory (LNNano) of the National Centre for Research in Energy and Materials (CNPEM), an illustration of this substrate with its dimensions can be seen in Figure 10.



Number of digits: 25 pairs
Width of the digits: 100 μm
Length of the digits: 8000 μm
Height of the digits: 120 nm

Figure 10 - Illustration of an interdigitated electrode.

Glass substrates covered with ITO (Indium-tin-oxide) were used for AFM measurements, electrical measurements in alternating current and the photovoltaic devices. For the electrical measurements of the LS films, the ITOs were commercially acquired from Ossila, and they have a pattern as shown in Figure 11.a). Whilst, Figure 11.b) presents the ITO after evaporation of the metal with the suitable mask. The ITOs used for the morphological measurements have the dimension of 1 x 1 cm and they were purchased from Delta technology. Meanwhile, the ITO used for spin-coated films was fabricated at University of São Paulo on the *Grupo de Polímeros*, and its structure is presented in Figure 12, and the procedure can be found on the thesis of Daniel Roger Bezerra [84].

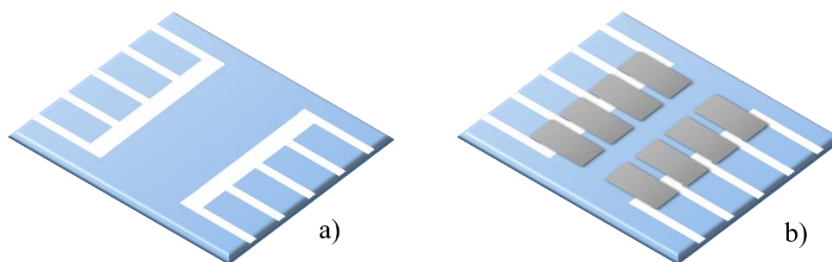


Figure 11 - Representation of Ossila ITO substrates a) as received b) after metal evaporation.

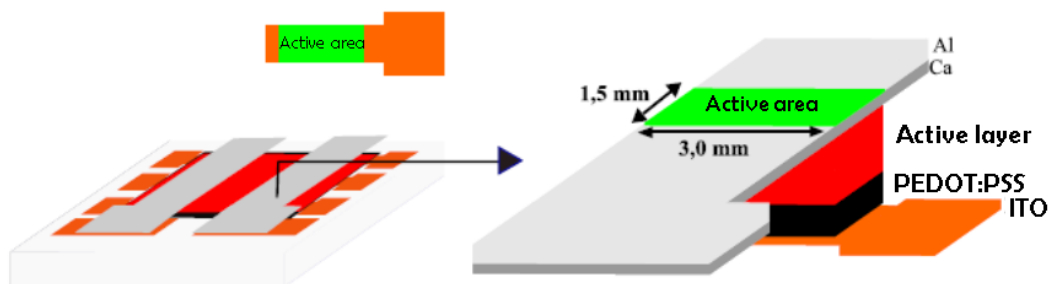


Figure 12 – Devices architecture for the devices with active layer spin-coated based. Adapted from [84].

Prior to use, all substrates were cleaned in acetone, and then isopropyl alcohol, both boiling.

2.2 Materials

For this thesis, the electron acceptor materials chosen were [6,6]-Phenyl C₆₁(71) butyric acid methyl ester, PC₆₁BM (Figure 13.a and b), CAS number 160848-22-6, ref. number 684457 and PC₇₁BM, CAS number 609771-63-3, ref. number 684465. As the conductive polymer for the active layer Poly (3,4-ethylenedioxythiophene) -poly (styrenesulfonate), PEDOT: PSS, reference number 483095, all commercially acquired from Sigma Aldrich. Synth chloroform was used as the solvent for the films. The main polymers used as the active layer of photovoltaic devices were synthesized at the *Université de Pau et des Pays de l'Adour (UPPA)*, France, under the guidance of Professor Christine Lartigau-Dagron, and the synthesis is presented in the Methods section. For encapsulation of the devices was used the epoxy solution of encapsulation for photovoltaic and OLEDs purchased from the company Ossila.

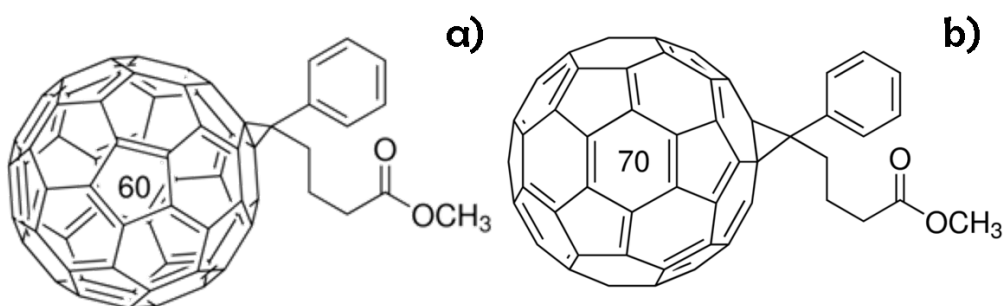


Figure 13 - Chemical structure of a) PC₆₁BM and b) PC₇₁BM. Figure extracted from [85].

2.3 Methods

2.3.1 Polymers synthesis processes

The low-bandgap polymers synthesized during the period outside were Poly[4,4'-diethylhexyl- 4H - cyclopenta [2,1-b;3,4-b'] dithiophene - alt - 2,5 - didodecyl - 3,6 - bis (thiophen-2-yl)pyrrolo[3,4-c]-pyrrole-1,4-dione] (PCPDTDPP_C₁₂) and the poly[4,4'-diethylhexyl - 4H - cyclopenta [2,1-b;3,4-b'] dithiophene – alt - 2,5 - di(2-(2-(2-methoxyethoxy)ethoxy) ethyl-3,6-bis (thiophen-2-yl) pyrrolo [3,4-c] -pyrrole-1,4-dione] (PCPDTDPP_Met), which can be seen in Figure 14.a) and b), respectively.

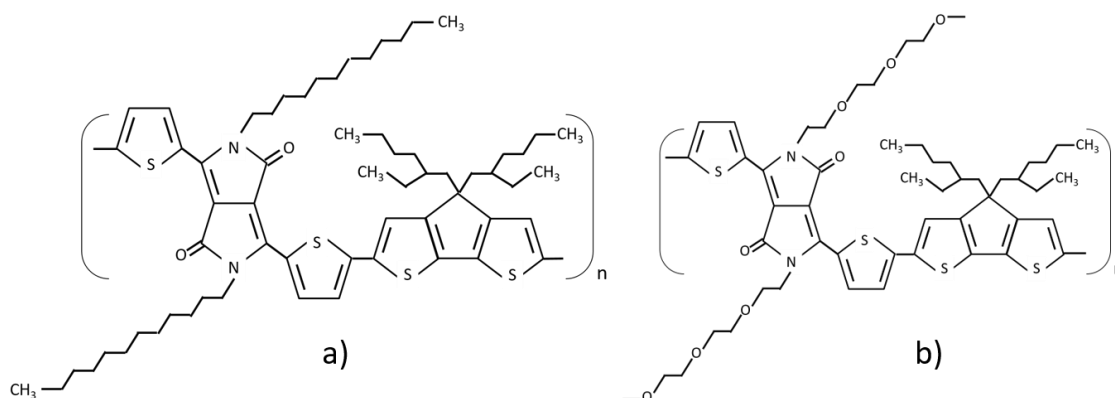


Figure 14 - Structure of the polymers a) PCPDTDPP_C₁₂ and b) PCPDTDPP_Met.

With the purpose to attain these polymers, it was necessary to obtain their constituent monomers, the monomer that forms the p-type part of the low-bandgap polymers was the 4,4-Bis(2-ethylhexyl)-2,6-bis (trimethylstannyl)-4H-cyclopenta [2,1-b:3,4-b ']'dithiophene, CPDT, which was commercially purchased from 1-Materials, and it is present in the two synthesized polymers. The other monomer was different for both cases, whereas for PCPDTDPP_C₁₂ the 2,5-Dodecyl-3,6-bis (5-bromothiophen-2-yl) pyrrolo [3,4-c] pyrrole was used for the synthesis of the polymer, for the PCPDTDPP_Met the monomer used was the 2,5-(methoxyethoxy)ethane-3,6-bis(5-bromothiophen-2-yl) pyrrolo[3,4-c] pyrrole-1,4-dione, these two monomers are part of the group of materials that receive the abbreviation DPP [65,86]. For the synthesis of these DPP derivatives, it was firstly used the 3,6-Dithiophene-2-yl-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione, which had previously been synthesized by the PhD Alberto Gregori, who belonged to the French polymer group (EPCP, IPREM, UPPA - France). The procedure used for both monomers was the same, herein the procedure is described in the following topic.

2.3.1.1 Lateral chain insertion procedure

Aiming to couple the side chains to the 3,6-Dithiophene-2-yl-2,5-dihydropyrrolo [3,4-c]pyrrole-1,4-dione monomer, a common procedure was used for both. The procedure, represented by Figure 15, consists of:

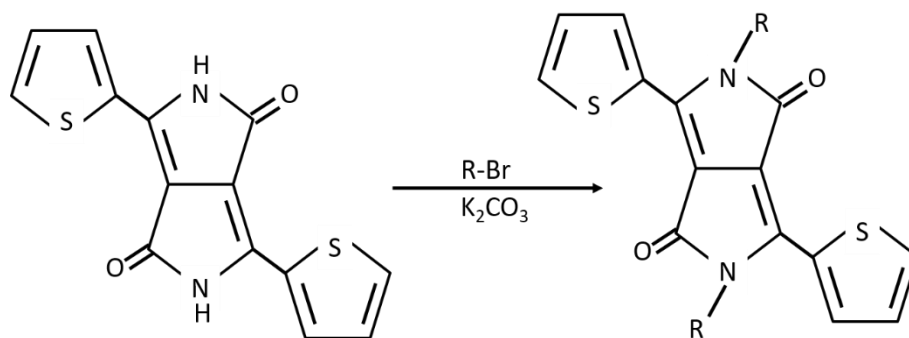


Figure 15 - Representation of the lateral chain insertion procedure. R = side chain.

In a two-neck reaction flask with a magnetic stir bar was put an equivalent (1 eq) of DPP in anhydrous Dimethylformamide (DMF), this solution was then stirred under an inert atmosphere of nitrogen. After 1 h, 6 eq of anhydrous potassium carbonate (K₂CO₃) and 0.01 eq of 18-crown-6 were added along with 3 eq of 1-Bromododecane to the PCPDTDPP_C₁₂, or 3.2 eq 1-(2-Bromoethoxy)-2-(2-methoxyethoxy)ethane to the PCPDTDPP _MET. The mixture was allowed to stir overnight at 120 °C. The following day, after reaching room temperature, the mixture was filtered and washed with methanol. Filtration was carried out a few times. The final product was left under vacuum for complete removal of the solvent.

2.3.1.2 General Bromination Procedure of DPP Derivatives

In order to enable the polymerization, it was necessary to functionalize the DPP monomer derivative. This functionalization was performed through the bromination of these molecules. The scheme can be seen in Figure 16, and followed by the description of the procedure:

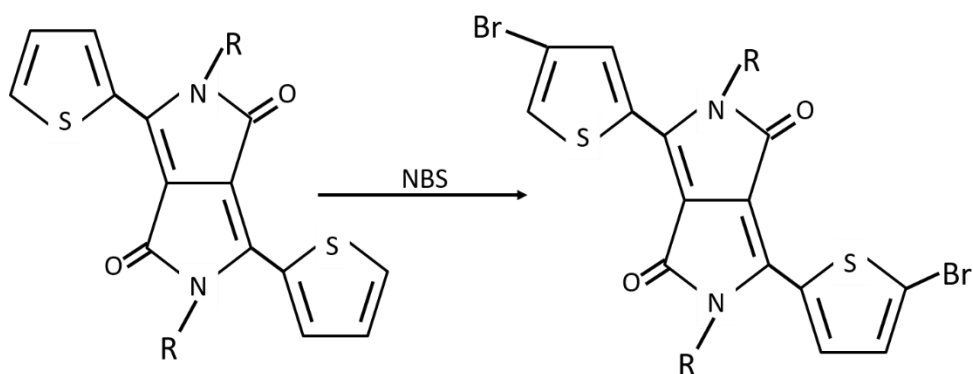


Figure 16 - Schematic representation of the Bromination procedure

A one-neck reaction flask with a magnetic stir bar was filled with 1 eq of the DPP derivative (C_{12} or Met) in chloroform. After 30 min stirring the solution at room temperature, 2.5 eq of N-Bromosuccinimide (NBS) was added in small portions to the solution already in the dark, to avoid reaction with light. The solution was stirred in the dark for 3h at 60 °C. After reaching room temperature, the mixture was filtered and washed with methanol. The final product was left under vacuum for complete removal of the solvent.

2.3.1.3 Synthesis of polymers

A solution with equimolar amounts of CPDT and DPP derivatives (1 eq) in chlorobenzene was prepared in a Schlenk tube with screw cap. To the stirred solution was added 2 mol% of tris(dibenzylideneacetone)dipalladium(0), $Pd_2(dba)_3$, and 10 mol% of tri(o-tolyl)phosphine, $(tolyl)_3P$. The mixture was heated to 150 °C for 24h. The representative polymer synthesis scheme is shown in Figure 17. The result of this reaction was precipitated in methanol, filtered and purified by Soxhlet extractor.

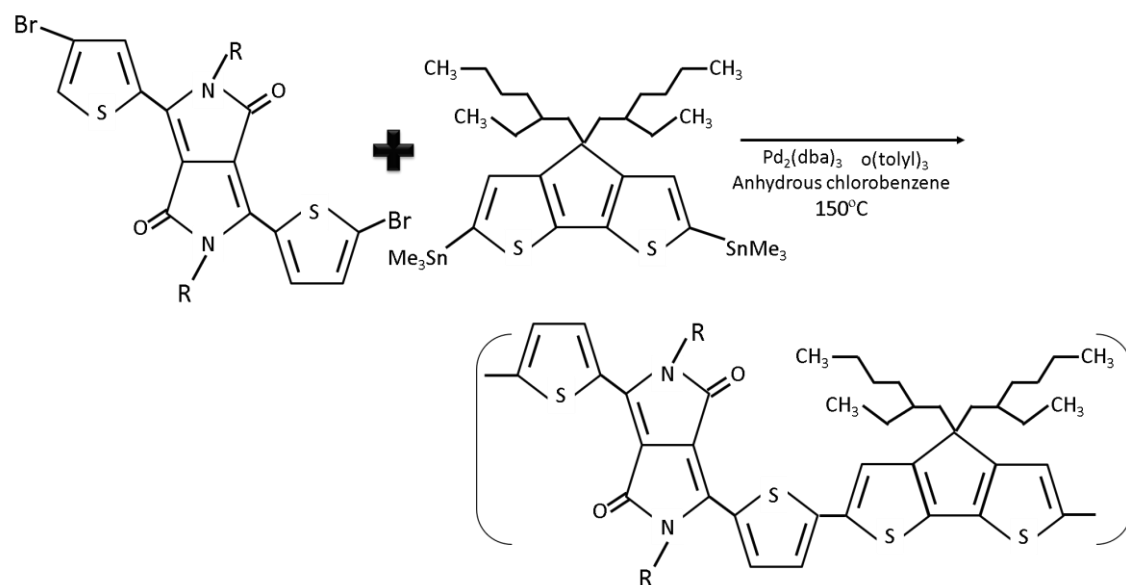


Figure 17 - Procedure performed for the synthesis of the low-bandgap polymers.

Purification by Soxhlet extractor was carried out washing the product with the successive solvents: methanol and acetone - for the extraction of the small molecules, petroleum ether - for extraction of the oligomers, cyclohexane - for extraction of low molecular weight polymers and chloroform where it was the desired product. The steps occurred long enough until the extracted contents were colourless. From the fraction contained in the chloroform, the solvent was removed, and the polymer was allowed to dry completely under vacuum.

2.3.2 Magnetic Nuclear Resonance

In all stages of monomer synthesis, Nuclear Magnetic Resonance (NMR) equipment was used as the main way to analyse the obtainment of the desired product. NMR is a technique that allows the determination of the molecular structure through the analysis of the magnetic properties of the atomic nucleus and the surrounding electrons. And for this reason, it is the most important technique employed during the organic synthesis evaluation of the monomer structures, enabling to proceed to the next step of the synthesis.

Common components of the NMR instrumentations are (i) a magnet for providing static magnetic field (B_0), (ii) devices for generating a second magnetic field in the radio frequencies and receiving the resulting NMR signal, (iii) device to place the sample on the magnet, (iv) equipment to stabilize the B_0 and optimize the signal (v) computers to control the operation and process the signals obtained [87].

NMR measurements were performed on Bruker UltraShield 400 Magnet equipment, under the supervision of the technician Abdel Khoukh. The NMR samples must be dissolved in solvents containing deuterium in place of Hydrogen, and deuterated chloroform (CDCl_3) is a commonly used solvent, especially in this work. Thereby, a small amount of the material should be well dissolved and then transferred to a specific tube that comes with the equipment.

2.3.3 Size Exclusion Chromatography

Size Exclusion Chromatography (SEC) is a chromatographic method in which the molecules that are in solution are separated by their size. The column used is filled with materials containing many pores. When dissolved, molecules of different sizes pass through the column, the molecules that dissolve at slow pace move more slowly through the column because they penetrate deep into the pores, whereas those that dissolve quite well pass quickly through the column, since they do not penetrate deeply into the pores. Consequently, large molecules come out before the column and the small ones later, which effectively separates the molecules by size. This is the principle for the SEC method [88].

There are many names given to different types of size exclusion chromatography, but all are based on the same principle. Historically the average pores were made of gel, hence Gel Permeation Chromatography (GPC) which is still a term widely used by the industry.

2.3.4 Langmuir and Langmuir-Schaefer films

Langmuir and Langmuir-Schaefer films are interesting for application in several areas of basic science [35,89] as well for technological application [90,91]. Langmuir films are formed at the air-water interface and are obtained by spreading a small amount of, generally, amphiphilic molecules into the liquid subphase inside a container called Langmuir trough. For this procedure, the material of interest is dissolved in a very volatile and water immiscible solvent. When formed by ideal amphiphilic materials, these films can form a monolayer, in which the hydrophilic part of the molecules comes in contact with water, while the hydrophobic portion is placed towards the air. Fatty acids are examples of materials with this typical behaviour [92,93].

The trough is made of Teflon to avoid reaction with any material inserted in it, and has as main accessories the movable barriers, the surface pressure sensor, and the

dipper (submersion system of the substrate). The pressure sensor measures the surface pressure (π) by the Wilhelmy method [94]. By decreasing the area occupied by the film, the surface pressure curves versus area per molecule (π -A), the so-called isotherms, are obtained. For many materials, especially fatty acids and phospholipids, pressure isotherms may have distinct regions which can be associated with the compression stages of the films in the trough, a model representing one of the isotherms types is shown in Figure 18.

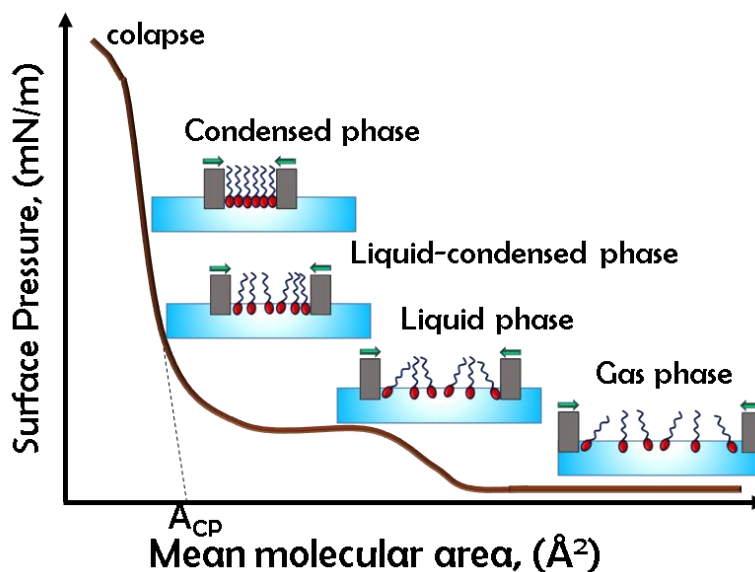


Figure 18 - π -A isotherm for an amphiphilic material in the Langmuir trough and its compression phases of molecules as the pressure increases.

In this case, it is possible to make an analogy with thermodynamics, in which initially the molecules are dispersed and not interacting with each other, corresponding to the gaseous phase. With the compression of the barriers and consequent approximation of the molecules begins to occur some interaction between them, which can be related to the liquid phase. Before reaching the most compact state and with the highest density of molecules a transition may occur. After that, the molecules reach the “solid phase” where the films are well ordered and with good molecular packing, forming a monolayer with a thickness of around molecules magnitude. And if this compression of the films is continued, there will be a disturbance of the molecules in the solid state, causing them to collapse. It is possible to study the molecular interactions and the probable conformation of the materials through the analysis of surface pressure isotherms. One possible information to extract from this graph is the area occupied in the solid state that can be estimated by the tangent line in the solid-state area (A_{SP}).

When in the solid state, the Langmuir film can be transferred onto a solid substrate, at a constant pressure, which can be immersed vertically forming the Langmuir-Blodgett film (Figure 19.a) or horizontally forming the Langmuir-Schaefer (Figure 19.b).

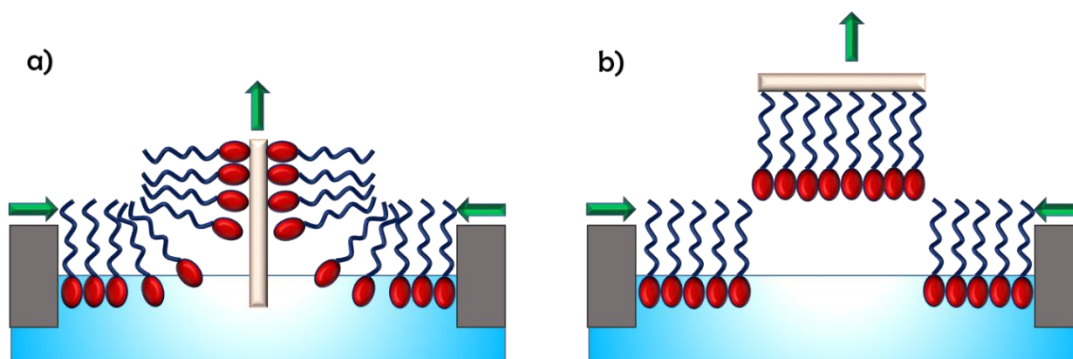


Figure 19 - Layout of the a) LB and b) LS techniques.

These techniques allow the control of film thickness, homogeneous deposition of monolayers, and the deposition of films layers on several types of solid substrates [95,96]. In the specific case of LS, which was used in this work, to ensure a better deposition the substrate approach in the monolayer is performed slowly when the Langmuir film is at the chosen pressure. Then the substrate is raised staying attached with the hydrophobic part of the molecules present in the trough, as can be seen in Figure 19.b.

2.3.5 LS films of the low-bandgap polymers

For the fabrication and study of the Langmuir films, the low-bandgap polymers were dissolved in chloroform, the room temperature was maintained at 23 °C. The trough KSV model 5000 was cleaned with chloroform for complete removal of previous traces, the subphase was filled with ultrapure water obtained from a Millipore system with a resistivity of 18.2 MΩ. The solutions had a concentration of 0.2 mg/ml for the pristine polymers and 0.3 mg/ml for the PC₆₁BM (that will be referred, from now on, in the LS films experiments as PCBM) molecules and for the blends of polymers:PCBM having a 1: 1 mass ratio [57,97]. In the Langmuir software, data concerning the solutions that would be spread were provided, such as: the molecular mass of the material (in the case of polymers it is used the mass of the monomer), the solution concentration and the volume spread. In the case of mixtures, the molecular mass was calculated from the weighted average between the polymer monomer and the PCBM masses.

Therefore, the solutions were spread with microsyringes on the subphase of the water, then a time of 15 minutes was allowed for total evaporation of the solvent, then the compression of the movable barriers with speed of 10 mm/min was initiated. By

performing this process, the isothermal curves were obtained, which were analysed for the sake of choosing the parameters for the deposition.

For the deposition of these films on solid substrates, the pressure of 20 mN/m was selected for the PCPDTDPP_C₁₂ and its mixture with PCBM, and 25 mN/m for PCPDTDPP_Met and its mixture with PCBM. Consecutive horizontal manual depositions on the solid substrates were performed to make the LS films.

2.3.6 *Spin-coating technique*

The spin-coating technique, also called spin-cast, is a technique commonly used for uniform deposition of thin films on flat substrates. This technique depends on some factors, such as: solvent volatility, viscosity and concentration of the solvent-solute, angular velocity and time [98]. The procedure consists of pouring an excessive amount of the desired solution into the centre of the substrate, which is then set to rotate at the pre-defined angular velocity and time, the fluid is spread through the centrifugal force thusly.

Figure 20 illustrates the formation stages of a spin-coated film. In step 1 with the excess spread of the solution, the interaction of the solution is only with the substrate and the gravitational force. As the rotation begins in step 2 the rotational force is the dominant process, the fluid starts to be expelled from the substrate forming a liquid film which is not yet homogeneous. In step 3, at the end of the spinning process, the action of viscous forces arises, which causes an increase in homogeneity, forming a uniform film. In the last step (4), stabilization of the film takes place followed by the entire solvent evaporation.

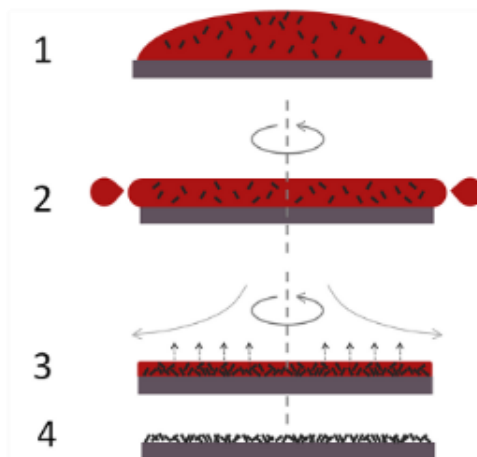


Figure 20 - Stages of a spin-coating film formation. Retrieved from [99].

This technique was used to fabricate the PEDOT: PSS layers for the devices and the films of the blends between polymers and PCBM to test as a photovoltaic device. This material, previously filtered, was deposited with the angular velocity of 3000 rpm for a time of 60s for the PEDOT:PSS. While for the polymer:PC₆₁₍₇₁₎BM solutions in chloroform and chlorobenzene at a concentration of 10 mg/ml (1:1), the deposition parameters were 1500 rpm for 60s.

2.3.7 PVD films

The Physical Vapor Deposition (PVD) can be carried out by means of different techniques, such as: thermal evaporation, sputtering, cathode arcs and ion deposition [88]. In this work the thermal evaporation was implemented, which consists of placing the material of interest in a high boiling point metal container, then a current is applied in this system, raising the temperature of the material in the container causing its evaporation. The whole process takes place in a vacuum chamber that facilitates the evaporation process, additionally, this causes practically only the evaporated particles to reach the substrates positioned to receive the material in evaporation, upon reaching the substrates the evaporated particles condensate and return to solid state. The control of the evaporation speed and film thickness is carried out by a quartz scale that is coupled inside the chamber.

For the evaporation of contact metals in the photovoltaic devices from LS films, the Boc Edwards evaporator model Auto 306 Evaporation System was used. The pressure conditions in the vacuum chamber were approximately 10^{-6} Torr. Through the quartz microscale, it was possible to obtain the value of 70 nm of thickness for the Aluminium films and the evaporation rate was approximately 0.8 nm/s. For the spin-coated films, the evaporation occurred on an evaporator inside of a glovebox model MB Evap, with the subsequent deposition of Calcium at a rate of 2.0 nm/s reaching thickness of 40 nm and the Aluminium was deposited at 0.5 nm/s and 60 nm. The devices based on spin-coated active layers and their characterization were performed at the *Grupo de Polímeros “Prof. Bernhard Gross”* of the *Instituto de Física de São Carlos* (USP - São Carlos/SP - Brazil), under the supervision of Professor Roberto Mendonça Faria.

2.3.8 Encapsulation process

The materials present in the active layers of the OPV devices may suffer degradation due to several factors, with humidity and oxygen among the main degrading

agents [100], and a process that is widely reported to decrease the system contact with such elements is the encapsulation. The encapsulation process was performed using the epoxy solution (Figure 21.a), glass plates with a 12 mm x 15 mm area and a thickness of 0.55 mm (Figure 21.b) and a micropipette.

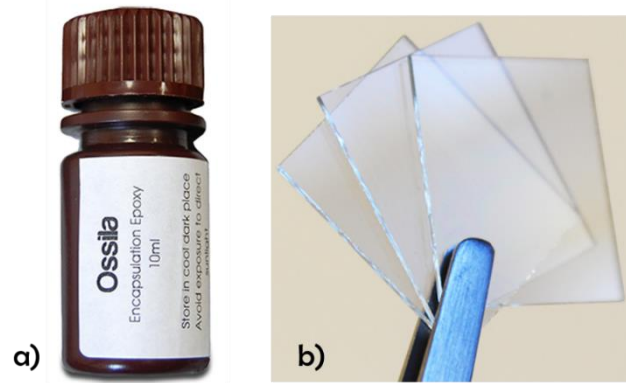


Figure 21 - a) Epoxy solution and b) cover glasses for encapsulation.

Then for the IDE and ITO devices, a small drop was placed on the area of interest and the cover glass is deposited with tweezers which are handled to ensure the removal of any existing air bubbles. Thereafter, the system is placed altogether under an Ultraviolet UV lamp and configuration 300 W 230 V E27 for 1 min, and then assessed if the cover glass is securely attached to the device surface. This process can be better seen in Figure 22.

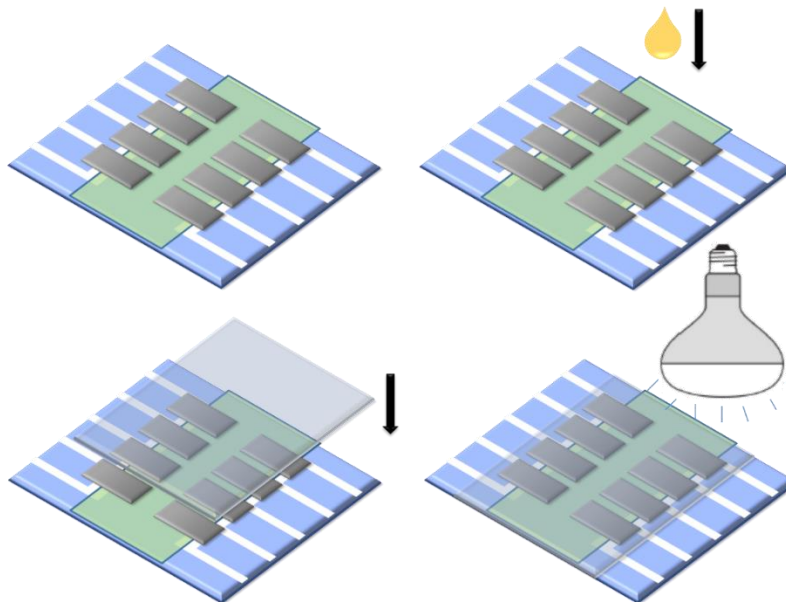


Figure 22 – Representative system of the encapsulation process.

2.3.9 X-ray Photoelectron Spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) is an atomic spectroscopic technique, which is adequate to provide atomic and molecular information concerning the material surface. Furthermore, this technique can furnish a quantitative analysis of the surface composition, it also receives the name of electron spectroscopy for chemical analysis (ESCA). XPS involves the irradiation of a sample with X-rays and the kinetic energy analysis of photoemitted electrons which are generated close to the sample surface (about 5 nm), and the system can be seen in Figure 23. The photoelectron kinetic energy is measured, and the emitting atom (except H and He) can be determined from the typical electron kinetic energy. Moreover, the high resolution of the photoelectron spectrometer enables chemical information on the atomic bonds [1,2].

XPS is utilized to probe core-levels and subsequently to analyse the composition and electronic states of the sample surface by energy-dispersive analysis of the emitted core photoelectrons. There is a specific binding energy related to each core atomic orbital for every element, thus, a specific set of peaks in the photoelectron spectrum determines the element. In an analysed sample then, a particular set of peaks at characteristic energies reveal which element is there, additionally, the intensity of the peaks is associated to the element concentration [2].

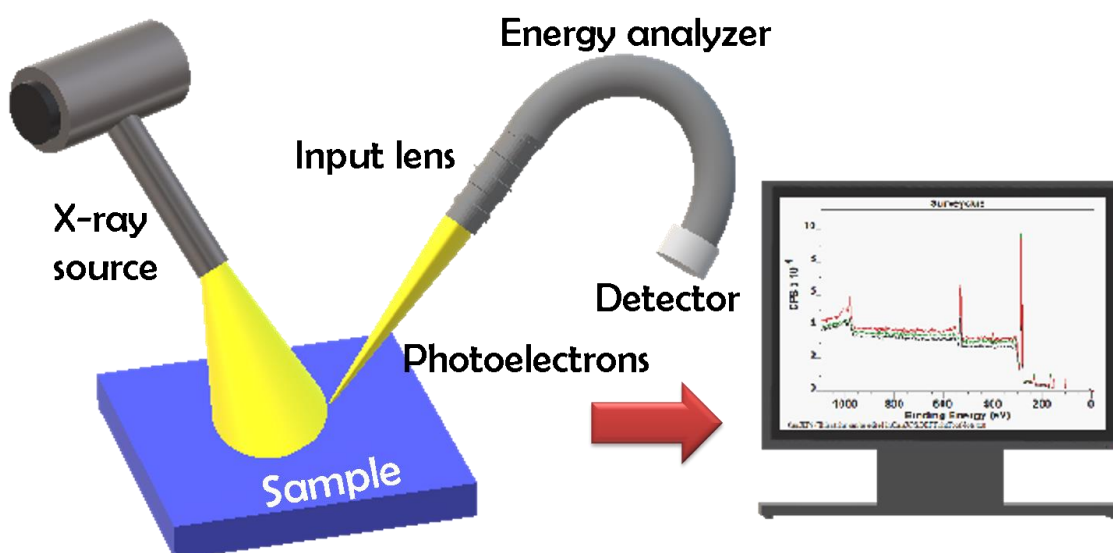


Figure 23 - Schematic illustration of the basic components of an XPS system.

XPS measurements of 10 layers LS films were carried out using a K-Alpha X-ray Photoelectron Spectrometer, with a micro-focused monochromatic Al K α source (Al K α 1486.6 eV, spot diameter of about 400 μ m, power 72 W), this happened on at a pressure of $2 \cdot 10^{-7}$ mbar. This equipment utilizes a hemispheric analyser, a transfer

column and an MCP (microchannel plate) detection. XPS analyses and interpretations were done by Christian Njel and Rémi Dedryvere at IPREM, Pau, France.

2.3.10 Optical Characterization in Ultraviolet-Visible (UV-Vis)

UV-Vis spectroscopy involves electronic transitions related to the absorption of electromagnetic radiation whose energy is in the region of the visible, reaching up to the near infrared or ultraviolet region. This spectroscopy determines the absorbance of solutions or films with defined optical paths [101]. The electron transitions occurring in the UV-Vis region of the spectrum happen due to radiation absorption from specific binding types or functional groups in the molecules. The absorption wavelength is given by the energy required for the electronic transition, on the other hand, the intensity depends on the probability of this transition to arise [102].

The electrons that contribute to the absorption in an organic molecule are: (1) those that participate directly in the formation of the bond between the atoms and, in this way, are associated with more than one atom; (2) unbound or non-shared outer electrons that are largely located on some atoms: oxygen, halogens, sulphur, and nitrogen. The transitions $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ are in most spectroscopic absorption applications of organic compounds, owing to the fact that the energies required for these processes bring the absorption peaks to an experimentally convenient spectral region. Both transitions rely upon the presence of an unsaturated functional group for the π orbitals. The term chromophore applies to these unsaturated absorber centres [103].

Regarding the optical absorption characterization of the low-bandgap polymers and their mixtures with PCBM, it was used the Varian Cary 100 UV-Vis spectrophotometer equipment. The spectra were performed in the wavelength range from 300 to 900 nm, for the solutions in chloroform inside a quartz cuvette and for the films in the glass of the IDE substrates. The results are presented in terms of unitary absorbance.

2.3.11 Fourier-transform infrared (FTIR) absorption spectroscopy

The FTIR absorption spectroscopy encompasses absorption phenomena which are in the IR radiation energy (4000 a 10 cm^{-1}), and they are related to the transition between two vibrational or rotational energy states of the molecule [104]. Inside the large range of the IR spectrum, the region used in this work is the mid-IR (middle infrared) that goes from 4000 to 200 cm^{-1} , for a long time this spectral region has been used for qualitative organic analysis and structure determinations. The IR radiation does not incite

the same types of electronic transitions found for UV-vis radiation, because this radiation is not energetic enough. Absorption of IR radiation is then limited largely to molecular species that contain small energy differences between various vibrational and rotational states [103].

To absorb IR radiation, a molecule has to be subjected to a net change in dipole moment as it vibrates or rotates. Merely in these circumstances (resonance) the alternating electric field of radiation can interact with the molecule and cause changes in the amplitude of one of its motions. The FTIR spectra were acquired in the equipment Tensor 27 from Bruker, in the range from 4000 to 400 cm^{-1} , on germanium substrates.

2.3.12 Raman spectroscopy

Raman spectra are obtained through the irradiation of a sample using a powerful laser source of near-IR monochromatic radiation. Meanwhile, the irradiation is happening, the scattered irradiation spectrum, at a specific angle, is measured with a suitable spectrometer. Raman scattering derives from the same type of quantized vibrational alterations related to IR absorption. In Raman spectroscopy, the incident radiation is scattered by the molecule with an energy slightly different from the energy of the incident radiation, in a way that this difference is in the IR region. This process involves a variation of the molecule polarizability due to the incident radiation. Despite the astonishing resemblance between Raman and IR spectra, a reasonable amount of differences prevails between the groups that are IR active and Raman active, thus they consist of two complementary techniques.

The origin of Raman spectra is given in the following form: Radiation from a source over the sample produces scattering at all angles, and the incident radiation causes excitation to a virtual level and subsequent re-emission of a photon of lower or higher energy, the resulting Raman spectrum consists of lower frequency emissions called Stokes scattering and higher-frequency emissions termed anti-Stokes scattering. Elastically scattered radiation is of the same frequency as the excitation beam and is called Rayleigh scattering.

The Raman spectra were acquired by using a micro-Raman Renishaw spectrograph, model in-via, coupled to a Leica microscope, and it is equipped with a CCD detector and laser at 633 nm, the measurements were carried out over the metal of the gold IDE substrate for the PCBM, the low-bandgap polymers and their mixtures

2.3.13 Atomic Force Microscopy (AFM)

Atomic Force Microscopy (AFM) allows the attainment of the individual atoms resolution on conductive and insulating surfaces [103]. This technique does not employ optical elements for the acquisition of the image, as a matter of fact, the acquisition is obtained by the measure of the interaction force between a tip and the surface of the sample. In this procedure, a flexible and force-sensitive cantilever performs a standard movement on the surface of the sample. The force acting between the cantilever and the sample surface causes instantaneous deflections that are determined by optical means, as schematized in Figure 24. During surface scanning, the force at the tip is kept constant by upward and downward movement of the tip, which provides the topographical information.

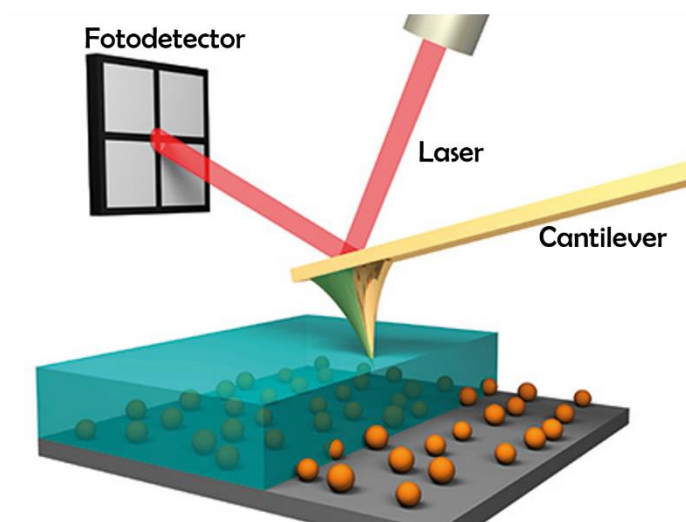


Figure 24 - Side view of optical beam deflection detection in AFM measurement.

One of the disadvantages of the measurements through the contact mode is that, since the cantilever is in constant contact with the sample surface, and the force applied by it is not low enough to avoid damaging the sample surface, this may cause the distortion of the acquired image. This operation mode is particularly problematic for less rigid materials, such as biological samples [105], polymers [106] and even silicone-based materials [107]. The surface damage problem has been reasonably overcome due to a process in which the tip comes into contact with the surface briefly and periodically, and is then removed from the surface, this process was called a tapping mode.

LS films of the low-bandgap polymers and their mixtures with PCBM were deposited on ITO (10 layers), after which they were characterized morphologically on a nanometre scale through AFM, using the Park XE7 microscope, operation tapping mode.

The topographic images obtained were analysed using the XEI software for the treatment of the images and calculation of the average roughness of the samples.

2.3.14 Electrical characterization in direct current (DC)

Direct current (dc) measurements provide the resistance value and the dc conductivity (σ_{dc}) of the analysed material, using the Ohm's Law. The electrical characterization is important for understanding the phenomena that occur in the bulk of the material. Nonetheless, this characterization presents a great challenge, which is the great range of behaviours that the materials can present. For example, for the same polymer, the electrical measurements can reveal completely different results with the change of deposition technique [108]. Since non-doped semiconducting organic polymers normally exhibit high resistance [109,110], it is necessary an equipment with high measurement sensitivity to detect precisely the electrical conductivity and the possible changes originating from a modification in the film structure, as well from the insertion of another material to the polymer.

For DC measurements, the Keithley model 238 source measure unit was used, this equipment has the capability to provide a current or a constant voltage as a stimulus parameter while obtaining the stimulus-response (voltage or current) at the measuring terminals, making it possible to acquire current versus voltage curves, I vs. V , of semiconductors and other devices [111].

In this work, to measure the intrinsic conductivities, σ_{dc} , of the low-bandgap polymers and their mixtures with PCBM, measurements were performed on LS films containing these materials in parallel contact structure (interdigitated gold electrodes - Figure 10). In order to evaluate the behaviour of these materials as photovoltaic devices, measurements were carried out in perpendicular contact, a diode type structure, which was obtained by PEDOT: PSS deposition and BHJ layer of the polymer: PCBM on the transparent ITO electrode, both in direct and reverse configuration, this structure can best be observed in Figure 25.

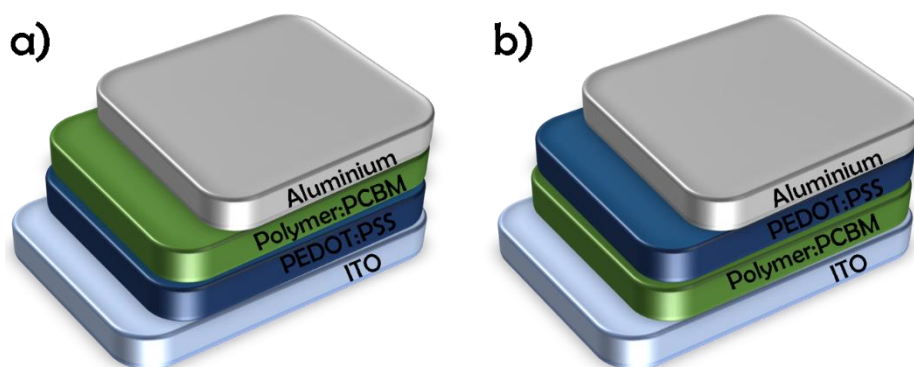


Figure 25 - Structure of the diode type photovoltaic devices with configuration a) direct and b) indirect.

The dc measurements were performed in the Keithley 238 source measure unit and consisted in applying tension and the subsequent attainment of the corresponding current, providing the I vs. V curves. For these measures, a voltage of -10 to 10 V was applied in steps of 0.1 V and with waiting time of 1 s between each step. The contact between the films and the measurement system is given by pressure contact, and the sample holders used for such experiments onto the IDE and ITO substrates are shown in Figure 26.

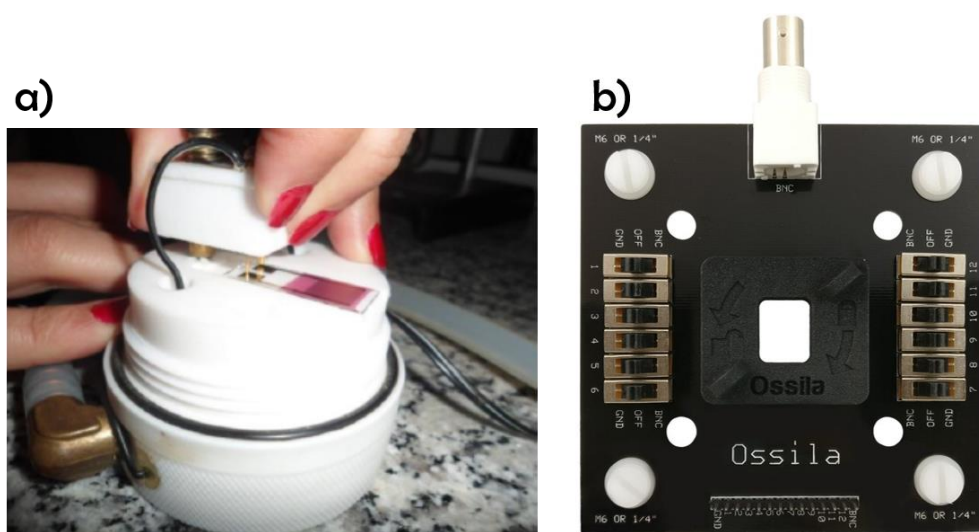


Figure 26 - Measurement system for electrodes a) IDEs and b) ITOs.

The measurements mentioned above were performed in the dark, and for the devices manufactured in IDE and ITO, the photoconductivity and photovoltaic device test was performed, respectively. For that, the samples were put under illumination using the solar simulator Oriel Verasol (100 mW/cm^2 - AM 1.5), shown in Figure 27.

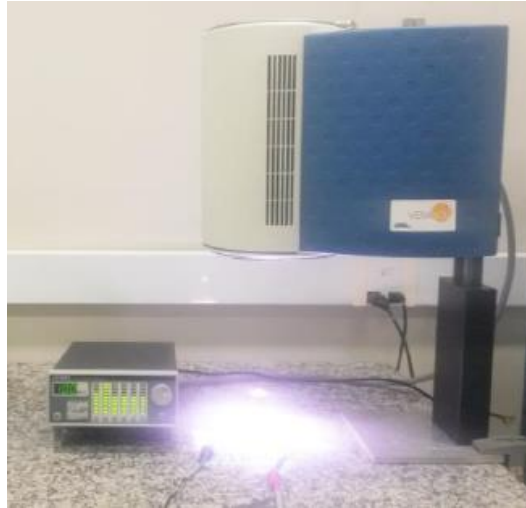


Figure 27 - Oriel Verasol solar simulator in operation.

For these measurements under illumination, on top of the devices was placed the photovoltaic mask, acquired in Ossila, in order to restrict the active area of each digit from which information about the efficiency of the manufactured devices is extracted. This mask can be seen in Figure 28, where it can be seen that the active area for each digit is 2.56 mm^2 .

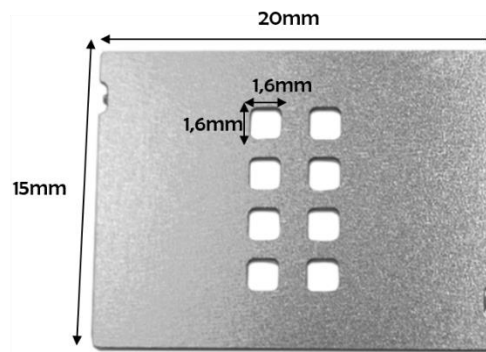


Figure 28 - Mask with the apertures for measuring the photovoltaic devices efficiency.

The spin-coating based were characterized at the Source meter Keithley 2400 in dark to verify the devices quality and under illumination from the Oriel Solar Cell Simulator class AAA (100 mW/cm^2 - AM 1.5 G) to examine the photovoltaic parameters. The range of the applied voltage for such measurements was from -2 to 2 V and it was performed on a sealed chamber to avoid air and moisture contact.

2.3.15 Alternating current (AC) measurements

In many circuits, the electric current is not stationary and varies with time. These are called alternating current (ac) circuits and the ratio between current and voltage in this system is called impedance. Thus, the measurements performed for the samples in this

scheme is called impedance spectroscopy. The impedance spectroscopy is a method of characterizing the electrical properties of several materials and their interfaces with electrically conductive electrodes. It can be used to investigate the dynamics of any solid or liquid material: ionic, semiconductors, ionic/electronic and even insulators [112].

In impedance spectroscopy measurements, a material is placed between two electrodes, where after the application of an electric stimulus, a response is obtained. In AC impedance measurements, an alternating voltage of the sinusoidal type is used as the voltage source, where it is possible to extract information such as the real and imaginary impedances.

Similar to other electrical measurements, impedance spectroscopy can provide information such as: conductivity, dielectric constant, carrier mobility, charge generation and recombination, interface effects, injection and accumulation. Models are used for purposes of representing the interpretation and analysis of results. A commonly used model that supports the interpretation of several results is based on the reproduction of equivalent circuits.

Since it is known that measurements in alternating current have alternating voltage and currents and that can be written in a complex way:

$$V^*_{(t)} = V_0 e^{i\omega t} \quad e \quad I^*_{(t)} = I_0 e^{i(\omega t - \phi)} \quad (3)$$

Where V_0 is the voltage amplitude, I_0 is the current amplitude, ω is the angular frequency ($\omega = 2\pi f$), ϕ is the phase angle between the current and the voltage. The complex impedance Z^* is defined as:

$$Z^* = Z' + iZ'' = \frac{V^*_{(t)}}{I^*_{(t)}} \quad (4)$$

Where Z' is the real part, and Z'' is the imaginary part of the electrical impedance. The phase angle is given by:

$$\phi = \tan^{-1} \frac{Z''}{Z'} \quad (5)$$

The expected spectra for a resistor, a capacitor or an association between both, when subjected to an alternating voltage, $V^*_{(t)} = V_0 \sin(\omega t)$, show different features depending on how this association happens. Impedance measurements for polymers can be quite complex to analyse and compare with circuit association. However, the RC circuit in parallel is the most commonly used for analysis of impedance curves [113–115].

For the case of a resistor and a capacitor associated in parallel to each other and in series with the AC source using the equation 6:

$$\frac{I^*(t)}{V^*(t)} = \frac{1}{Z^*} = \frac{1}{Z_R^*} + \frac{1}{Z_C^*} \quad (6)$$

And replacing the terms $Z_R^* = R$ e $Z_C^* = 1/i\omega C$, it is obtained $1/Z^* = 1/R + i\omega C$, via mathematical manipulation, it is possible to get the equation 5, and its real and imaginary components are represented in Figure 29.a):

$$Z^* = \frac{R}{1 + (\omega RC)^2} - \frac{\omega R^2 C}{1 + (\omega RC)^2} i \quad (7)$$

Thus, the real and imaginary terms can be written in the following form:

$$Z' = \frac{R}{1 + (\omega RC)^2} = Re(Z^*) \quad (8)$$

$$Z'' = -\frac{\omega CR^2}{1 + (\omega RC)^2} = -Im(Z^*) \quad (9)$$

Expressing the imaginary term as a function of the real term it is possible to obtain the following equation:

$$\begin{aligned} -Im(Z^*) &= \omega RC \cdot Re(Z^*) \\ \omega RC &= \frac{-Im(Z^*)}{Re(Z^*)} \end{aligned} \quad (10)$$

Replacing the equation (10) in the real term of the impedance, we have:

$$[Re(Z^*)]^2 + [-Im(Z^*)]^2 - R \cdot Re(Z^*) = 0$$

Using the mathematical tool of completing the square it gives origin to the equation (9):

$$\left[Re(Z^*) - \frac{R}{2} \right]^2 + [-Im(Z^*)]^2 = \left(\frac{R}{2} \right)^2 \quad (11)$$

The equation (9) represents a circumference centred at $(R/2, 0)$ and radius $R/2$. The characteristic impedance spectrum for RC circuits in series has the feature presented in Figure 29.b).

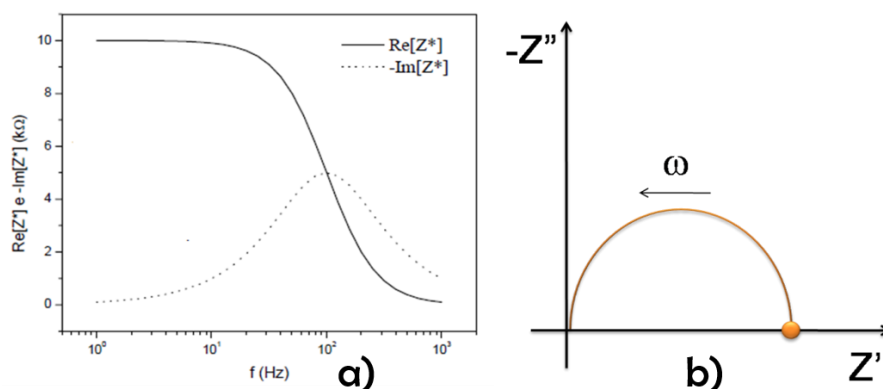


Figure 29 – Graphs of a) Real and imaginary impedance versus frequency and b) Real impedance versus imaginary impedance, for circuits with a capacitor and a resistor connected in parallel, in alternating current.

This electric circuit has a time constant, $\tau_0 = RC$, which is related to the dielectric relaxation of the material [112]. The semicircle indicates the existence of a relaxation time, but in real materials is very common to find several relaxation times in the impedance planes [116,117]. In practice, experimental data rarely form a complete semicircle centred on the real axis of the complex plane, and in many cases, the superposition of arcs occurs. The physical interpretation of elements distributed in an equivalent circuit is quite complex, however, it supports the understanding of ac electronic transport.

Thus, alternating current electrical measurements were performed on the LS films transferred onto the ITO using the Impedance Analyzer Solartron 1260A from 1 Hz to 1 MHz (50 mV ac) varying the dc component (bias) from 0-5 V. And from the measured results the following spectra were obtained: Real impedance vs. frequency (Z' vs. f), Imaginary impedance vs. frequency ($-Z''$ vs. f) and Imaginary impedance vs. Real impedance ($-Z''$ vs. Z').

2.3.16 Cyclic Voltammetry

Electrochemistry consists of a resourceful tool to examine reactions including electron transfers and it associates the flow of the electrons to chemical modifications. The main point of electrochemistry resides in the facility to control a reaction driving force and the capability to measure thermodynamic and kinetic parameters [118]. Voltammetry consists of a group of electroanalytical methods in which the information of the analysed sample is obtained through the measurement of the current as a function of an applied potential under conditions that cause polarization of an indicator, or working electrode [103]. Cyclic voltammetry (CV) is a potential-controlled "reversal"

electrochemical experiment, whereas a stationary electrode, immersed in a solution without stirring, provides a current as a function of a triangle-shaped excitation potential signal. The potential variation over time is linear and reaches a defined value, thenceforth the sweeping is inverted and the potential moves towards the first applied potential. On the inversion potentials, there are two processes: oxidation and reduction, which are controlled, mainly, by the analyte diffusion. CV is a popular tool to study electrochemical reactions, in Organic Chemistry this technique is specially employed to analyse synthetic pathways and to studies of electrochemically generated free radicals. More specifically CV is often applied to investigate the reduction and oxidation processes of molecular species [119].

The CV measurements were carried out using an Autolab PGSTAT 302N potentiostat/galvanostat coupled with a microcomputer with NOVA 1.8 software, under the responsibility of Prof. Dr Henrique Santana (UEL - Londrina/PR - Brazil). The supporting electrolyte was a solution of 0.1 mol L⁻¹ lithium perchlorate (LiClO₄) in acetonitrile (ACN). The cell was composed of an Ag/AgCl as the reference electrode, a 0.50 cm² platinum plate as the counter electrode and the drop-cast polymers films over ITO substrates as the working electrode. The experimental setup is shown in Figure 30.

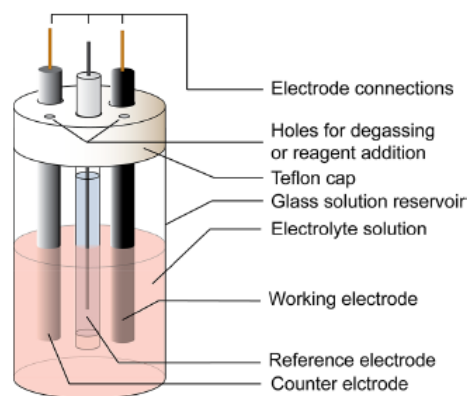


Figure 30 - Schematic representation of an electrochemical cell for CV experiments. Extracted from [118].

2.3.17 Profilometry analysis

For electrical and OPV measurements the thickness is an important factor to be considered, especially, for the OPV this element can alter significantly the optical path of light, which is responsible for the light absorbance by the cell. For this reason, it is important to know the thickness of the active layers used in the devices [120]. A profilometer utilizes a diamond stylus that is moved across the sample for a specific

distance and contact force. The vertical displacement of the stylus is measured depending on its horizontal position [121], the data is obtained and captured by a software.

The thicknesses of the LS and spin-cast films of the pristine polymer and the organic bulk heterojunctions, were determined by a Veeco model Dektak 150 profilometer, in the *Grupo de Polímeros* of the *Instituto de Física de São Carlos* (USP - São Carlos/SP - Brazil), under the supervision of MSc Marcos Felipe Bom Sampaio. Prior to the data acquisition, the films over ITO substrates were scraped with an aluminium tip, forming a valley where the bottom achieves the substrate surface.

Chapter 3 – Thin films, morphological and optical characterization results

3.1 Langmuir films

The organization of the active layer has an important role in the performance of devices, including the photovoltaics [97,122], and the LB and LS techniques provide the ability to manufacture nanostructured films with thickness control, and can serve as a basis for developing better devices [123]. Before making the deposition onto solid substrates it is fundamental to investigate the Langmuir films, this analysis is performed through the surface pressure versus area by molecule (π -A) isotherms. From the outcome of the isotherms, valuable information can be extracted concerning the used materials, such as: the probable conformation, the area that molecules/monomers are occupying in the Langmuir trough and the ideal pressure for deposition (which corresponds to the pressure that the molecules are close together, in a more organized way).

An attempt to fabricate LB films of the synthesized polymers was performed, nevertheless, this was not achievable. The reason why this occurred is that the low-bandgap polymers do not have an amphiphilic structure and more particularly form a rather rigid monolayer, standard for the materials utilized in the trough [26,124], thereby the LB deposition is hindered, the addition of a fatty acid may enable this type of deposition [74,125]. Since the goal is to manufacture BHJ devices composed by the polymer and the electron acceptor molecule, it is not appealing to insert the fatty acid within. Hence, the LS technique was chosen because it was the most appropriated one to produce organized films in order to create the active layer of the devices.

Since the final device contains as active layer the mixture between two materials, the discussion was conducted considering the isotherms of the pristine materials and their mixture along with the air-water interface. The incorporation of fullerenes in thin films is crucial for the preparation of many optoelectronic devices, hence there has already been carried out a considerable amount of studies containing fullerene derivatives on surfaces and interfaces [126–129]. Thus, first it was fabricated a PCBM Langmuir film, Figure 31 shows the isotherm from a 0.3 mg/ml solution of PCBM in chloroform, it is compelling to start with the interpretation of this result because it is possible to find many literature reports regarding fullerene-type monolayers.

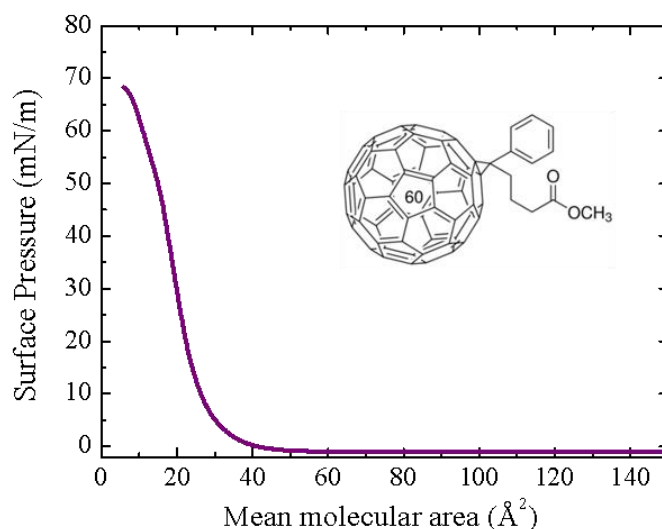


Figure 31 – Surface pressure–area isotherms of the PCBM.

Examining the graph shown in Figure 31, one can notice the absence of the usual sharp phase transitions of the typical molecules isotherms, and this is a strong indication that this is a liquid-expanded isotherm, according to Harkins' classification [130]. The area per repeating unit found for PCBM at the air-water interface was 29 Å^2 , as already reported larger areas per molecule for the C_{60} (the sphere constituent of PCBM) in a Langmuir trough are expected [128,129]. However, when concerns the fullerene derivatives that possess functional groups this area it was shown to be consistently smaller, actually the area per molecule in the isotherm from the current work corroborates a previous literature result for fullerenes when there is a stable film compression [131]. A quite common explanation is that firstly the functional group of the molecule generally is oriented toward the water, and this can be a major contribution for the area found through the graph. Researches about the behaviour of fullerenes after spreading on the air-water interface revealed that its films do not form a true monolayer, therefore the plausible causes are the non-amphiphilic nature of these compounds and the aggregation phenomenon that arises from the strong fullerene-fullerene interactions [127,132].

In Figure 32, it is possible to see the pristine polymers and their mixture with PCBM isotherms attained at the Langmuir trough. The area per monomer found for these polymers was 65 Å^2 for the PCPDTDPP_ C_{12} (a) and 116 Å^2 for the PCPDTDPP_Met (b), since there is no previous literature from these exact polymers and we could not make the theoretical calculations, their monomer areas are unknown.

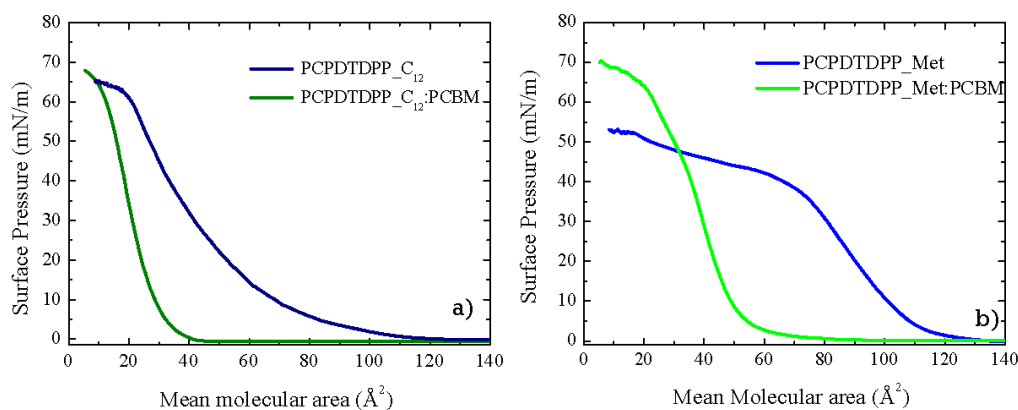


Figure 32 - Surface pressure–area isotherms of the a) PCPDTDPP_C₁₂ and b) PCPDTDPP_Met (in blue), and their mixtures with PCBM (in green)

In regard to the isotherms, it can be observed that the polymers, like the PCBM, can be classified as a liquid-expanded type, not achieving the phase related to a condensed phase either. However, the overall isotherm behaviours are quite divergent from one another. The PCPDTDPP_C₁₂ presents no distinct phase transitions and has a rather steady upward trend until it reaches the collapse pressure at 65mN/m. While the PCPDTDPP_Met starts to raise the pressure values (corresponding to the transition from the “gas” to the “liquid” state) at a high mean area of 120 Å², and another steep change in the slope of the graph occurs at approximately 35 mN/m, which can be related to a coexistence of two phases [133], and/or the formation of bilayers from the monomers within the air-water interface [134], another characteristic that differentiates the isotherm of this polymer, in contrast to the other one, is its lower collapse surface pressure (53mN/m). The lower surface pressure attained for this film indicates a lower resistance of the monolayer structure to compression for the mixed film, which must be closely related to the low compressibility of the liquid-expanded film, and this may cause the formation of thinner layers of polymeric chains at the interface upon compression. This outcome can be the responsible for the difference in thickness of the solid films for both polymers, even when the same quantity of layers were deposited onto the substrate [135,136].

Comparing now the isotherms of the pristine polymers (in blue) to the isotherms arising from the co-spreading of the polymer and the PCBM (in green), one first thing it can be stated is a really low miscibility between the two materials. This conclusion is done because a sign that they are miscible with each other is the presence of a collapse pressure in between the ones found for the two materials separated [130], and as can be seen in Figure 32, for both cases the mixture collapse pressures are roughly the same that

of PCBM, probably indicating the PCBM dominant characteristic on the interface. The PCPDTDPP_C₁₂: PCBM film occupies an area per molecule of 30 Å², which is quite close to the area achieved by PCBM itself, besides the shape of the curve is also fairly similar to this pristine molecule (Figure 31). This may indicate a conformation where the PCBM molecules are working as a matrix at the air-water interface, where the polymer is lying on top of it, forming aggregates islands or bilayers. Discussing the surface pressure isotherms of PCPDTDPP_Met:PCBM, regarding the graph shape, it is unequivocal to assert its resemblance with the PCBM isotherm, including the collapse pressure features. Concerning its area per repeating unit (52 Å²), it stays between the ones found for each material apart, although this area is yet closer to the one of the PCBM molecules. Thereby, for this case, the PCBM molecules seem to be mingled with the polymers chains of the PCPDTDPP_Met, however, some parts of the polymer may be lying above the mixed monolayer, affirmation based on the fact that mean molecular area is below the average between the area of the two materials.

3.2 Atomic Force Microscopy

Nanoscale morphology of 10 layers LS films of the pristine polymers and mixed with PCBM deposited onto ITO was investigated via AFM using the tapping mode, as described in the section 2.3.13. Generally, the research reporting these class of polymers display characterization of spin-coating films from the polymers dissolved in dichlorobenzene [137–139]. This fact can complicate the comparison between our results and literature since both, technique and solvent, influence considerably on the obtained image. The 9 x 9 µm topographic images of the pristine polymer LS films are presented in Figure 33, a difference in topography between the two polymers is evident. The PCPDTDPP_C₁₂ exhibits a quite irregular structure with high agglomerates and some valleys, its root mean square (rms) roughness is 50 nm. In the AFM image of the PCPDTDPP_Met LS film, the topography is more homogeneous, its rms roughness is very low with 4.3 nm, even having more agglomerates, they are smaller in size and height than PCPDTDPP_C₁₂. These analyses seem to be in accordance with the isotherms results, because the film that presented smaller mean molecular area (PCPDTDPP_C₁₂) at the Langmuir trough has big polymer agglomerates on the film, while for the PCPDTDPP_Met which showed larger area indicating more space between the polymers chains and more homogeneous structure, the agglomerates are noticeably smaller.

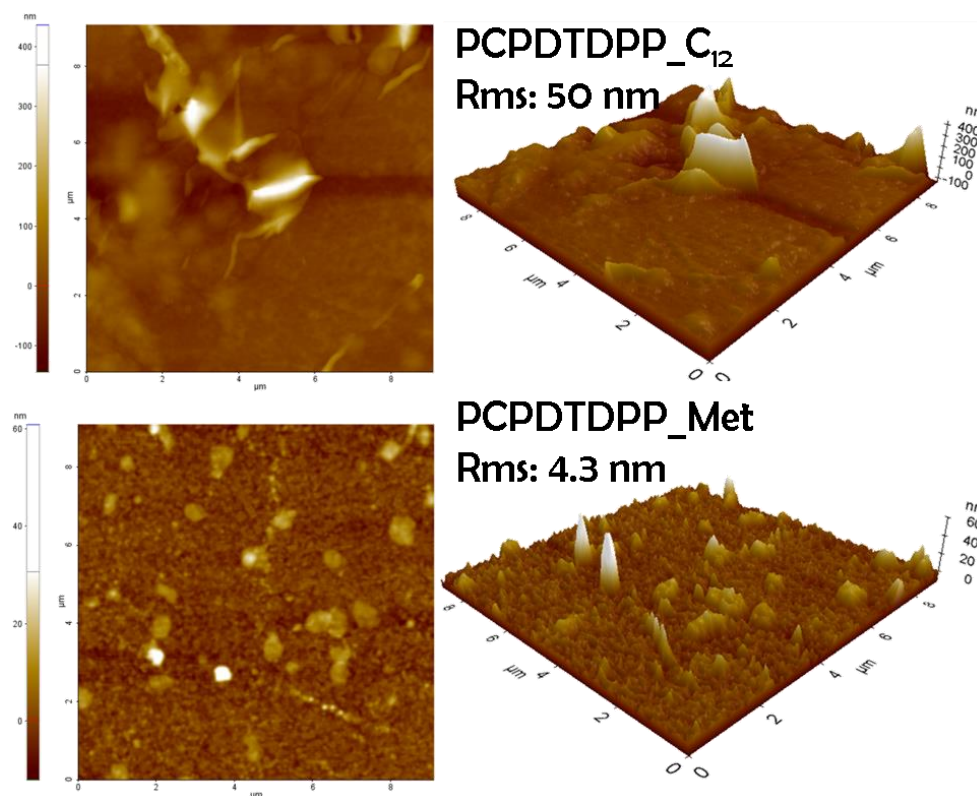


Figure 33 - AFM images of low-bandgap polymer LS films deposited via Langmuir-Schaefer.

In published research concerning polymeric OPV devices is common to find topographic images of polymer:PCBM films [140,141], whether is using spin-coating [142] and drop-cast technique [143,144], after annealing treatment [145] and with the inclusion of additives that has the aim to improve the device performance [75]. Ergo, it is interesting to analyse the mixed films morphology, because the use of different treatments, techniques or materials modify significantly the morphology. Thus, topographic images of the low-bandgap polymers with PCBM were carried out, the images are presented in Figure 34. In these images is confirmed the higher roughness for the PCPDTDPP_C₁₂ (36 nm), when compared to the PCPDTDPP_Met (7.3 nm), even after they were mixed with PCBM.

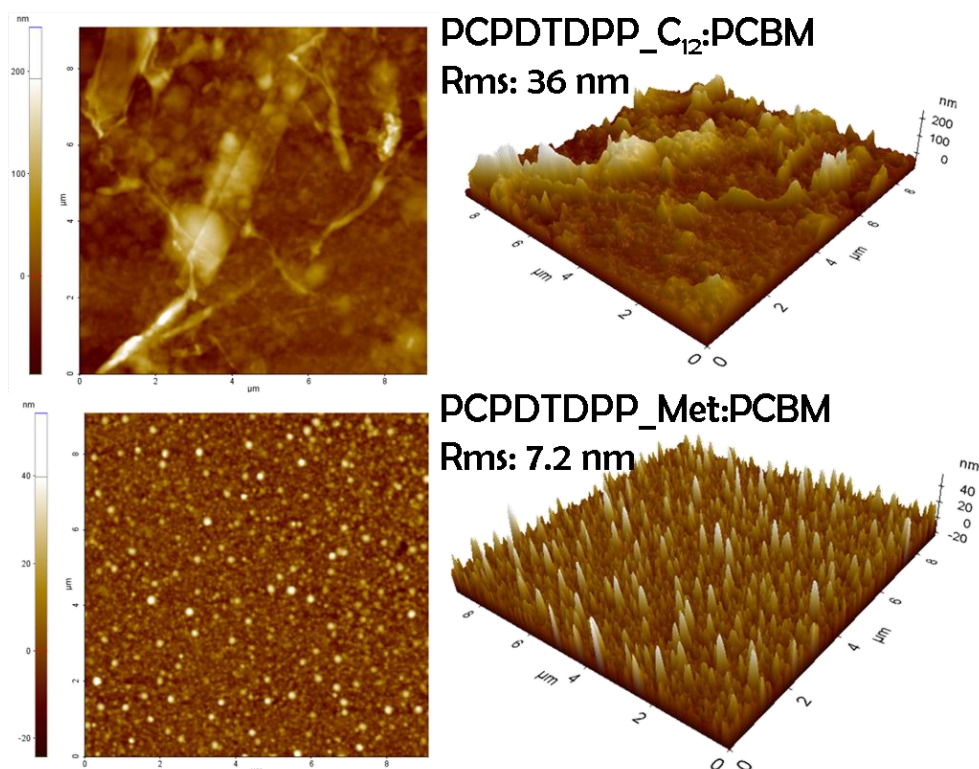


Figure 34 - AFM images of low-bandgap polymers mixed with PCBM deposited via Langmuir-Schaefer.

Establishing a relationship between these images and the ones of the pristine materials, it happens a divergence on the behaviour of the two samples, whereas the PCPDTDPP_C₁₂:PCBM LS film shows a drop in roughness and the PCPDTDPP_Met:PCBM an increase. Notwithstanding, the overall films conformation is kept similar with subtle differences, among them it can be emphasized that the image of the PCPDTDPP_Met:PCBM displays smaller and more amount of domains that are homogeneously dispersed along the film relating to the image of its pristine form. With this image, it can be concluded that, as observed in the surface pressure isotherms, the interaction between the PCPDTDPP_Met and PCBM is stronger than the interaction between this last and the PCPDTDPP_C₁₂ indicated by the most significant topographic changes. This validates the interpretation of how it is the conformation already at the air-water interface, where the PCPDTDPP_C₁₂ is over the PCBM, thus the characteristic observed on the image of the pristine polymer is similar for its mixture, and the PCPDTDPP_Met contains some portions side by side with the PCBM, consequently modifying the general image features.

3.3 X-ray Photoelectron Spectroscopy (XPS)

Surface properties are critical to the end-use or performance of the polymeric device. These properties can be associated with the adhesion, biological compatibility, permeability, crazing, chemical reactivity, electrical, wear and optical properties [146]. Therefore, XPS technique appears as another alternative to analyse with more details the films surfaces, which is also useful to quantify atomic fractions, which is especially important when dealing with mixed films, as already reported in the literature [143,147,148].

In order to evaluate which elements were present on the surface of the pristine polymers, the PCBM and the polymer:PCBM films, the XPS analysis was performed. XPS survey scans showed that carbon, oxygen, sulphur and nitrogen are present in all the samples that had the polymers. Figure 35 presents high-resolution scans of the C 1s and O 1s, peaks for the pristine PCBM, PCPDTDPP_C12, PCPDTDPP_Met and the PCPDTDPP:PCBM mixed films.

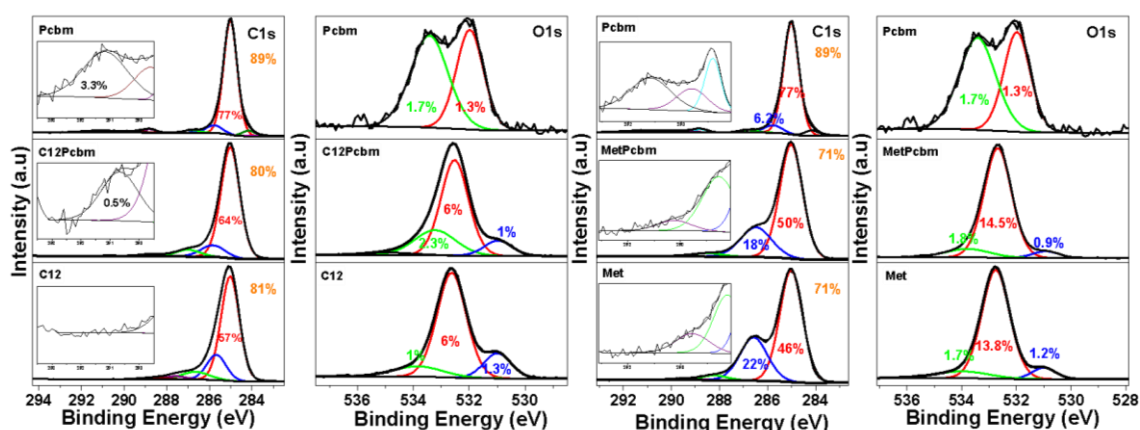


Figure 35 - High-resolution X-ray photoelectron spectroscopy scans of the C 1s, O 1s peaks of the pristine PCBM, polymers and its mixture films.

High-resolution scans of the C 1s and O 1s peaks are shown first in Figure 35 once these peaks are present on the PCBM films as well, and it is possible to make a comparison between them. Therefrom, for both polymers can be stated that after the PCBM addition to the polymers happened a decrease of the characteristic peaks of the low-bandgap polymers, at 286.5eV and 531eV for the PCPDTDPP_Met and 531 eV for the PCPDTDPP_C12, at the same time there is the increase of the peak around 285 eV and a peak at 290 eV appears, both arising from the PCBM addition.

Figure 36 shows the high-resolution scans of the elements found solely on the polymers with the N 1s and S 2p peaks. As expected the PCBM addition to the polymers causes a drop of the elements due to the low-bandgap polymers (Sulphur and nitrogen).

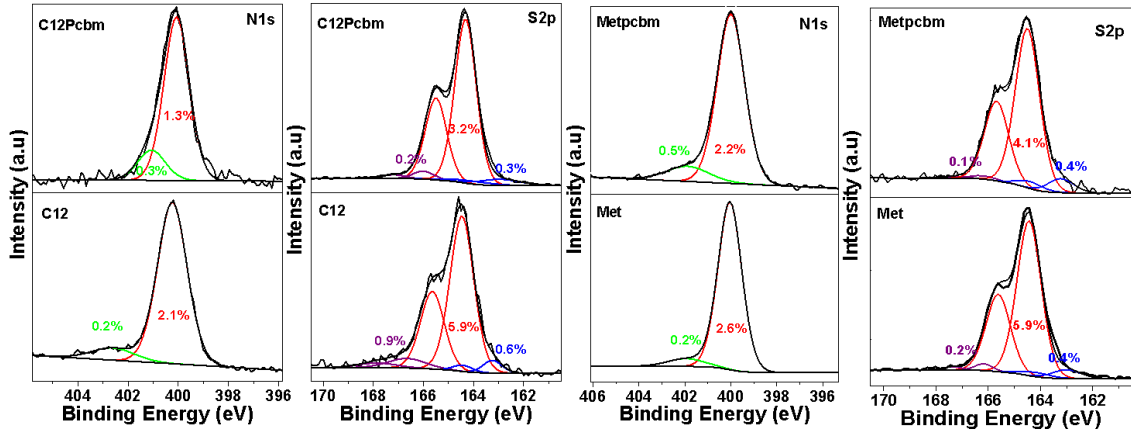


Figure 36 - High-resolution X-ray photoelectron spectroscopy scans of the N 1s, S 2p peaks of the pristine polymers and the polymer:PCBM films.

Since the AFM and Langmuir films measurements provide some explanation concerning the films morphology the materials proportion on the mixtures still remains a question. Aiming to find out the amount of the PCBM in these films some calculations were performed according to the XPS data. For that, the following steps were used:

The mixture PCBM + low-bandgap polymer can result in the equation 12:

$$x_{PCBM} + (1 - x)_{polymer} \quad (12)$$

where x corresponds to the mol.% of PCBM in the mixture.

It should be noted that in the expression of the number of moles, to get rid of the chain length of polymers, we consider only one brick in the chain. If R_n is defined as the molar ratio between the PCBM and the polymer considered, as seen on equation below:

$$R_n = x_{PCBM} + (1 - x)_{polymer} \rightarrow x_{PCBM} = \frac{R_n}{(1 + R_n)} \quad (13)$$

The mass ratio R_m is deduced from the molar ratio, $R_m = R_n \cdot R_M$, with R_M corresponding to the ratio between the molar mass of PCBM and that of the brick of the polymer chain. From the mass ratio R_m , the mass percentage (wt.%) of PCBM within the mixture can be determined by $PCBM_{wt.\%} = \frac{R_m}{(1 + R_m)}$. Let X be the experimental ratio between the total amount of carbon, and the total amount of sulphur and nitrogen measured by XPS, then $X_{polymer} = C^T / (S^T + N^T)$.

Since sulphur and nitrogen are only present in the polymers. It is, therefore, possible to extract the proportion of PCBM in the mixtures, as it follows:

$$X_{mix} = \left(\frac{C^T}{S^T + N^T} \right)_{mix} = (1 + R_n) \cdot X_{polymer} = (1 + R_n) \cdot \left(\frac{C^T}{S^T + N^T} \right)_{polymer} \quad (14)$$

Therefore:

$$R_n = \frac{X_{mix} - X_{polymer}}{X_{polymer}} \rightarrow R_m = R_M \cdot \frac{X_{mix} - X_{polymer}}{X_{polymer}} \quad (15)$$

And, the total percentage amount of PCBM on the samples is given by:

$$PCBM_{wt.\%} = \left(\frac{R_M \cdot \frac{X_{mix} - X_{polymer}}{X_{polymer}}}{1 + R_M \cdot \frac{X_{mix} - X_{polymer}}{X_{polymer}}} \right) \quad (16)$$

Using the equations aforementioned, Table 1 was constructed with the main results. Analysing the table content, it can be stated that the PCPDTDPP_C₁₂ interacted in a way with PCBM that the surface contains practically the same amount of the two materials, while for the PCPDTDPP_Met the presence of the PCBM is mainly within the film bulk or in more separated domains. Taking into account the depth (few nanometers) that this technique can reach inside the film, the conformation assumptions made for the Langmuir technique may be correct where the PCPDTDPP_C₁₂ and the PCBM form a bilayer of a molecule magnitude causing them to have almost the same amount at the surface, as for the PCPDTDPP_Met the portion of polymer that does not interact with the PCBM form cluster regions which give origin to the elevated amount of polymer on the surface. This outcome was also observed through the AFM measurements.

Table 1 – Chemical composition of the LS films surface of the low-bandgap polymers.

Film	X ratio	R _n	R _m	Mol.% PCBM	Wt.% PCBM
PCPDTDPP_C ₁₂	8.9	0	0	0	0
PCPDTDPP_C ₁₂ :PCBM	17.1	0.92	0.83	48	45
PCPDTDPP_Met	8.4	0	0	0	0
PCPDTDPP_Met:PCBM	11.3	0.34	0.31	25	24

3.4 UV-Vis spectroscopy

The absorption spectra of the solutions in chloroform and of the solid polymer films are shown in Figure 37.

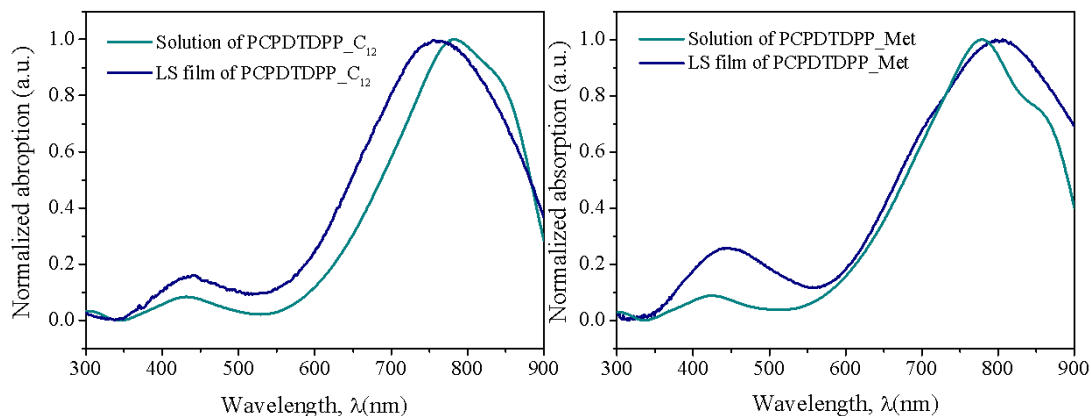


Figure 37 - Absorption spectra of PCPDTDPP_C₁₂ and PCPDTDPP_Met samples.

The absorption spectrum of PCPDTDPP_C₁₂ in chloroform solution has two bands with maximum absorption (λ_{max}) centred at 431 and 782 nm, and the LS film from this material also possess two bands centred at 440 and 754 nm. The PCPDTDPP_Met solution features two absorption bands as well, with λ_{max} in 424 and 780 nm, whilst in the LS film these bands are centred at 444 and 806 nm. The absorption spectra show the polymers large solar spectrum overlapping.

The energy conversion efficiency of organic solar cells relies upon some factors, among them the photons absorption and, the charge carriers separation and transport [149]. Semiconducting polymers often used for the photovoltaic research and that have satisfactory conversion factors are the polyphenylene-vinylene and the polythiophenes, in spite of revealing promising results their absorption spectra show small overlapping of the solar emission spectrum. In the search for more efficient solar cells, one useful approach was to focus on the synthesis of new materials, whose optical bandgap is tuned to improve the harvest of sunlight. In fact, approximately 40% of the total solar energy is on the range from 650 to 1100 nm [150], for this reason, the low-bandgap polymers are an interesting option in order to cover this absorption range, mainly on the NIR region. Therefore, these polymers are useful for the purpose of increasing efficiency.

Thus, on the UV-Vis spectra the two bands are related to the two portions of the low-bandgap polymers, the first band has its origin due to the CPDT portions, while the largest band centred at a higher energy value comes from the intramolecular charge transfer (ICT) between the CPDT and the DPP units, G. Chen *et al.* reported the same

attributions for a similar polymer [151]. The films of the two polymers showed a broadening of the absorption bands compared to the spectra from the solution in chloroform, this behaviour indicates a strong intermolecular interaction in solid state [150] and a certain level of organization [28]. Despite this similarity, the LS films absorption spectra present distinct features between the two polymers when compared to their respective solutions spectra. While the PCPDTDPP_Met exhibit a redshift, expected result for the film, once this outcome suggests a longer conjugation length (lower energy), caused by the strong interaction of the donor-acceptor portions within the repeating units of the polymer chains, depicting the more ordered structure of the material in solid state [55,76,137]. The PCPDTDPP_C₁₂ presents a blueshift in the transition from solution to film, a study containing a polymer with a similar structure in a solution of o-dichlorobenzene (ODCB) and spin-coating films also revealed such aftereffect [152], in the cited study this difference is not discussed though. Nonetheless, other reports where this phenomenon occurs, not only the blueshift but a broadening of the spectra as well, is attributed to the H-aggregates basing in the exciton model [153,154], and this type of aggregates are originated, mainly, from the intrachain Coulomb interactions [155]. In the H-aggregates, the interaction between the main chains happens in a way that the monomers stack over one another forming a face-on configuration, where the stacking between the chains are perpendicular to the molecular plan [156], Figure 38 displays the conformation of P3HT when it is established the H-aggregates which contribute to the blueshift and the J-aggregates which normally induce a redshift.

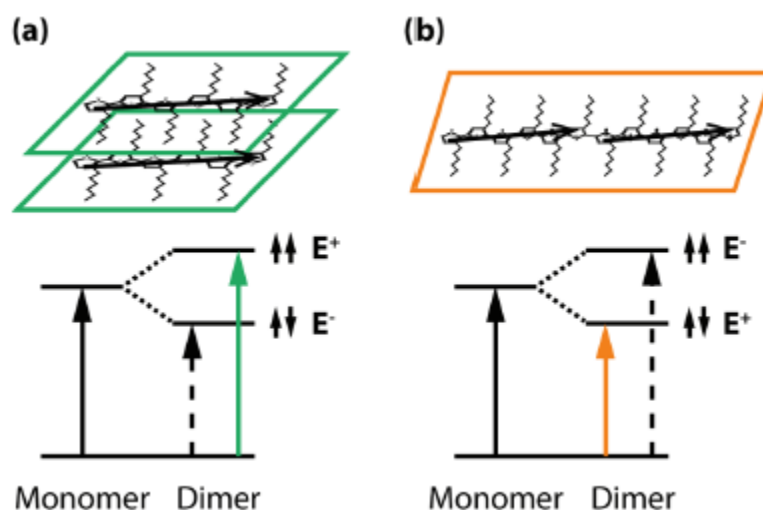


Figure 38 – Pictorial representation of (a) H- and (b) J-aggregates in P3HT. Figure extracted from [157].

Figure 39 shows the absorption spectra in UV-Vis of the polymers with PCBM in chloroform solution and LS films.

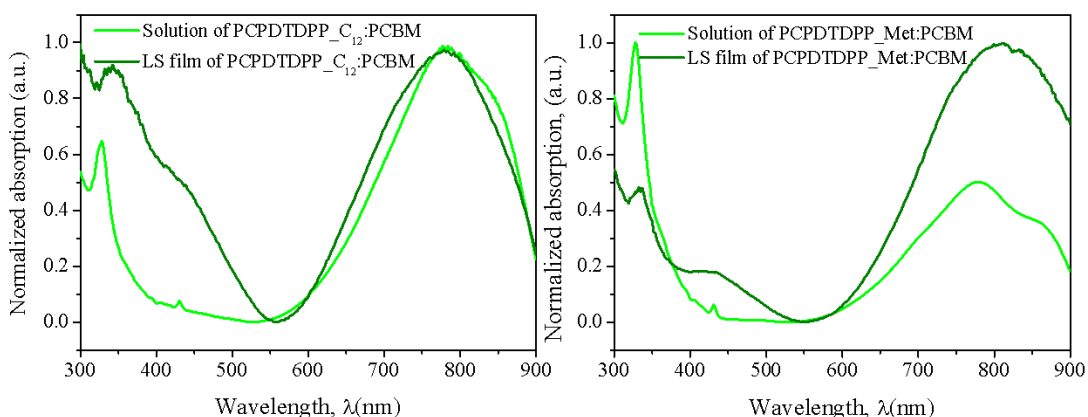


Figure 39 - Absorption spectra of PCPDTDPP_C₁₂:PCBM and PCPDTDPP_Met:PCBM samples .

The solution spectrum of PCPDTDPP_C₁₂:PCBM have two peaks, at 328 and 431 nm which are related to the PCBM that possess in its spectrum three feature peaks of fullerene derivatives, the [6-6]-addition at 260 nm, 330nm (C₆₀) and 430 nm ([6,6]-addition in C₆₀) [138,139]. This spectrum also presents a band centred at 782 nm associated with the pristine polymer, thus it is clear the characteristics of the two materials in the optical response. Regarding the film, the first peak of the PCBM is shifted to 343 nm, arising a shoulder which seems to be the first band that appears on the spectrum of the pristine polymer film and it may be overlapping the small PCBM peak (430nm), and the band related to the PCPDTDPP_C₁₂ is at 781 nm.

Now, for the PCPDTDPP_Met:PCBM solution spectrum, there are the PCBM peaks at 328 and 431 nm, like the other polymer and the polymer band at 779 nm. Concerning the aforementioned LS films, it happens a shift of the spectrum, particularly, on the PCBM peak to 335 nm and the polymer band to 812 nm, besides it emerges an intermediary band centred at 435 nm, which is presumably related to the first band of the polymer spectrum.

Thereafter, with regard to the mixed films, comparing the solutions to the solid films, the overall behaviour is that the PCBM peak is redshifted for both polymer:PCBM mixtures, while the band associated to the interaction between the polymer portions is kept unchanged for the PCPDTDPP_C₁₂:PCBM, for the PCPDTDPP_Met/PCBM it redshifts 33 nm, thereby for both mixed films a certain degree of general ordering and a greater conjugation length are emerging when they pass to film form [140].

3.5 Raman spectroscopy

Raman spectroscopy is among the optical spectroscopy techniques that furnish a probe for several optoelectronic properties of organic semiconductors and may provide essential information concerning the thin film morphology [158] since this technique is sensitive to changes in the local order or in the conformational properties [159]. Some works also used Raman technique to investigate the conformational changes of molecules after the operation of a device [160], and to analyse the phase segregation when there are two materials combined [161]. Therefore, Raman spectroscopic measurements were performed in order to evaluate the studied materials (low-bandgap polymers and the PCBM) and to verify possible structural changes due to: time, electrical stimulus, and interaction between the materials.

Firstly, the spectra of PCBM and low-bandgap polymers as bulky neat materials were collected and are shown in Figure 40, using the excitation laser line at 633 nm. The outcome of the PCBM spectrum (Figure 40.a) is a strong photoluminescence signal, not being possible the observation of any Raman bands, as already reported [162,163]. The spectra of the polymers PCPDTDPP_ C₁₂ and PCPDTDPP_ Met shown in Figure 40.b) and c), respectively, are similar, presenting quite the same centre positions and relative intensities for the Raman bands. There are three strong bands at 1512, 1409 and 1364 cm⁻¹, which are tentatively attributed to thiophene C=C/C-C stretching/shrinking, thiophene ring C=C stretching, and DPP C=C and (C-N+C-C) stretching modes, respectively, as reported for related polymers [164–166]. Other well-defined bands are seen at 1229 cm⁻¹ assigned to C-H bending, at 1075 cm⁻¹ to C-N and C-H stretching, and at 709 cm⁻¹ to C-S stretching modes [165,167]. Moreover, there is a broadband from 2740 to 2900 cm⁻¹, which is related to C-H and C=O stretching modes [168].

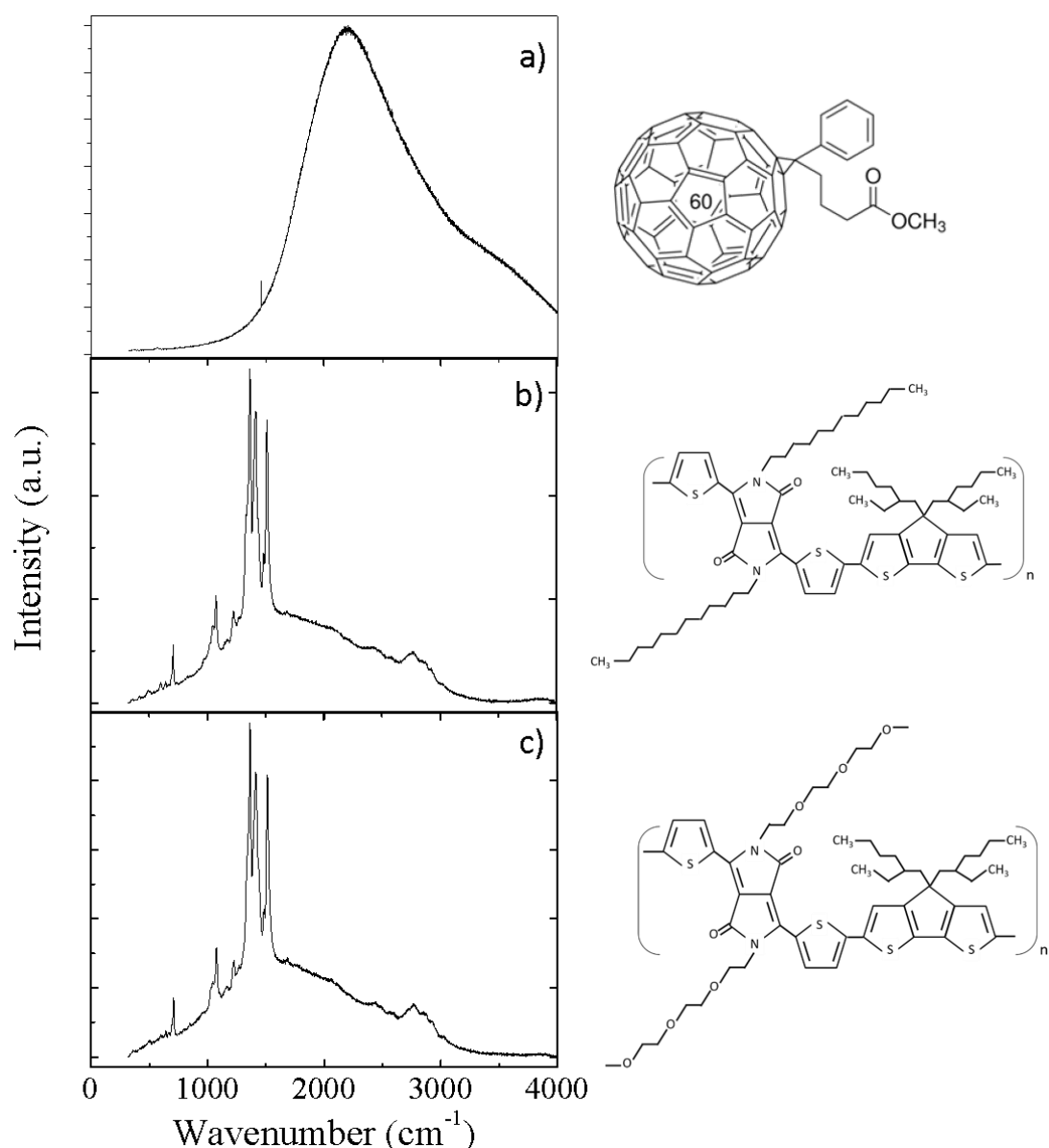


Figure 40 – Raman spectra for a) PCBM, b) PCPDTDPP_C12 and c) PCPDTDPP_Met LS films.

It was also obtained the Raman scattering of the LS films from the mixture between PCBM and low-bandgap polymers. The spectra were taken from different regions of the films in order to analyse the compositions and possible interactions. In Figure 41 is displayed the image of the LS film of PCPDTDPP_C12 and the Raman spectra for four distinct regions of the sample that was transferred onto IDE substrates. Observing all the spectra, it is possible to notice the fluorescence band from the PCBM (around 2200 cm^{-1}) and the characteristic Raman bands for the polymers. This confirms the presence of both materials forming the LS films onto IDE electrodes. Besides, the absence of new bands or significative spectral changes, such as centre shift and relative intensities, indicate the materials keep their chemical integrity (no chemical interactions). Concerning composition yet, the black spots on the optical image show a stronger relative

PCBM fluorescence band (Figure 41.e), which indicates higher concentration of PCBM in this region.

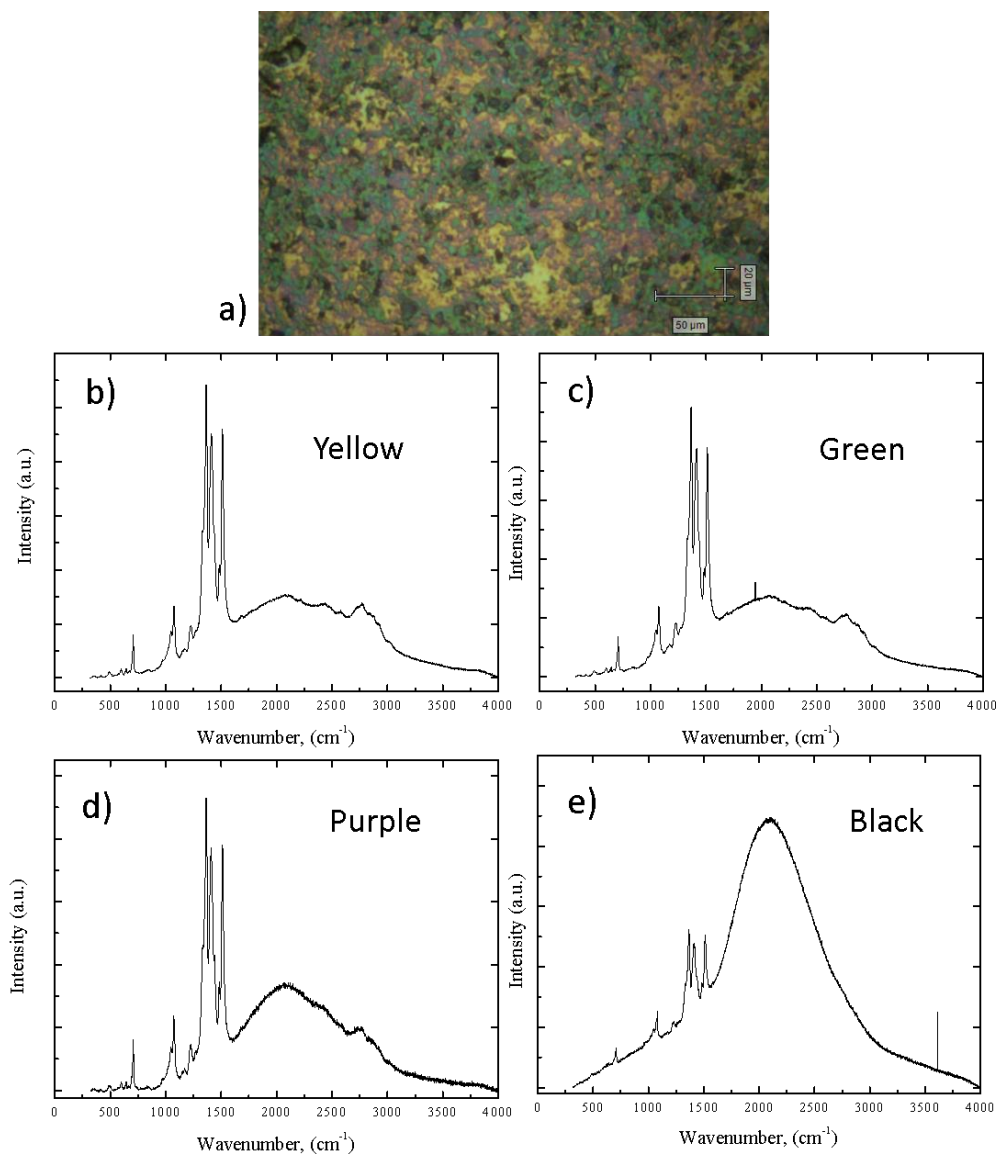


Figure 41 - Raman spectra for PCPDTDPP_C12:PCBM for different regions of the LS films.

Performing the same measurements for the PCPDTDPP_Met:PCBM LS films, it was attained the Raman spectra in Figure 42. This film presented three clear different regions: for the two light regions (Figure 42.a and b) appear the same behaviour of the other polymer, suggesting again the existence of both materials on the sample and only physical interaction has occurred. Notwithstanding, the black clusters reveal only the PCBM fluorescence band on its spectrum, which demonstrates the complete absence or remarkably low amount of the polymer in such region.

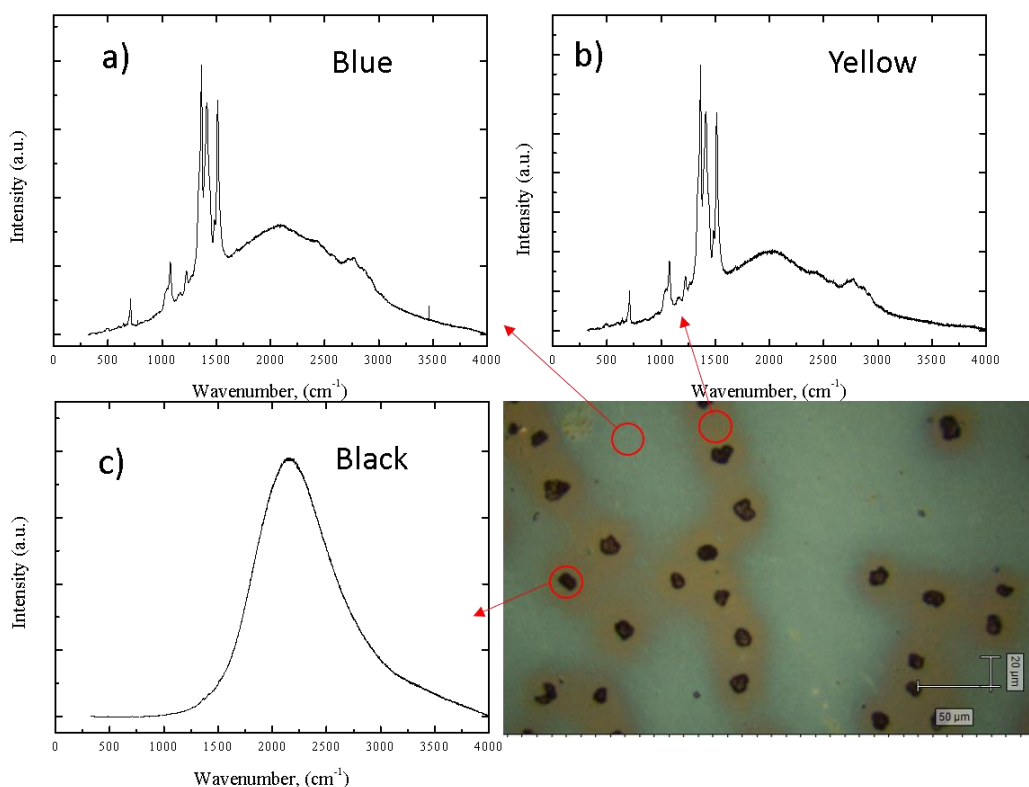


Figure 42 - Raman spectra for PCPDTDPP_Met:PCBM for different regions of the LS films.

Thus, the LS film morphology of the two polymers when mixed with possesses different features. It looks like the miscibility between PCPDTDPP_C₁₂ and PCBM is higher, once both materials are in all distinct regions for PCPDTDPP_C₁₂, while for PCPDTDPP_Met well-defined clusters of PCBM are observed, which probably are already formed in the Langmuir trough during the compression of such films. Due to instabilities of the electrical measurements, Raman scattering of LS films over time (from hours to days) and after electrical stimulus was analysed, but it did not present any morphological (optical microscopy) and spectral (Raman scattering) modifications.

3.6 FTIR Spectroscopy

As a complement for the Raman scattering analysis, FTIR absorption spectroscopy measurements were performed. The chemical composition of the pristine polymers and their mixture with PCBM was observed using FTIR results.

Figure 40 shows the measured FTIR spectra of the PCBM, PCPDTDPP_C₁₂ and PCPDTDPP_C₁₂:PCBM mixed samples. Curve a) in Figure 43 is for the PCBM sample; despite some noises, the main peaks of PCBM can be found in it. The absorption bands at 2918 and 2850 cm⁻¹ can be attributed to the C-H stretching mode transition in CH₂

groups for the asymmetric and symmetric stretches, respectively; the peak at 1737 cm^{-1} to the C=O group, the 754 cm^{-1} to the Aryl-H bending vibration, and other peaks at 526, 1186 and 1424 cm^{-1} are related to characteristic peaks of fullerene [169–171]. Curve b) in Figure 43 is from PCPDTDPP_C₁₂ samples, this spectrum also contains the peaks associated to the C-H stretching (2920 and 2850 cm^{-1}), a peak at 1664 cm^{-1} corresponding to the C=O of the DPP unit, the band from 1510 to 1545 cm^{-1} to the C=C and C-C stretching modes on thiophene, from 1438 to 1460 cm^{-1} can be attributed to the C-H bending mode and the C-N stretching, at 1404 cm^{-1} to the C=C stretching on the thiophene ring, the peak at 1377 cm^{-1} to the C=C and (C-N+C-C) stretching modes localized on the DPP unit [136,172,173]. There are some peaks, not so well-defined, between 980 and 1300 cm^{-1} related to the C-S stretching and C-H bending coupled to thiophene ring stretches, and at 806 cm^{-1} to the C-H out of plane [174].

As for curve c), the results are quite similar to the polymer, with a more defined C=O peak due to the presence of the PCBM, nevertheless, no chemical interaction seems to be happening, as seen in Raman scattering.

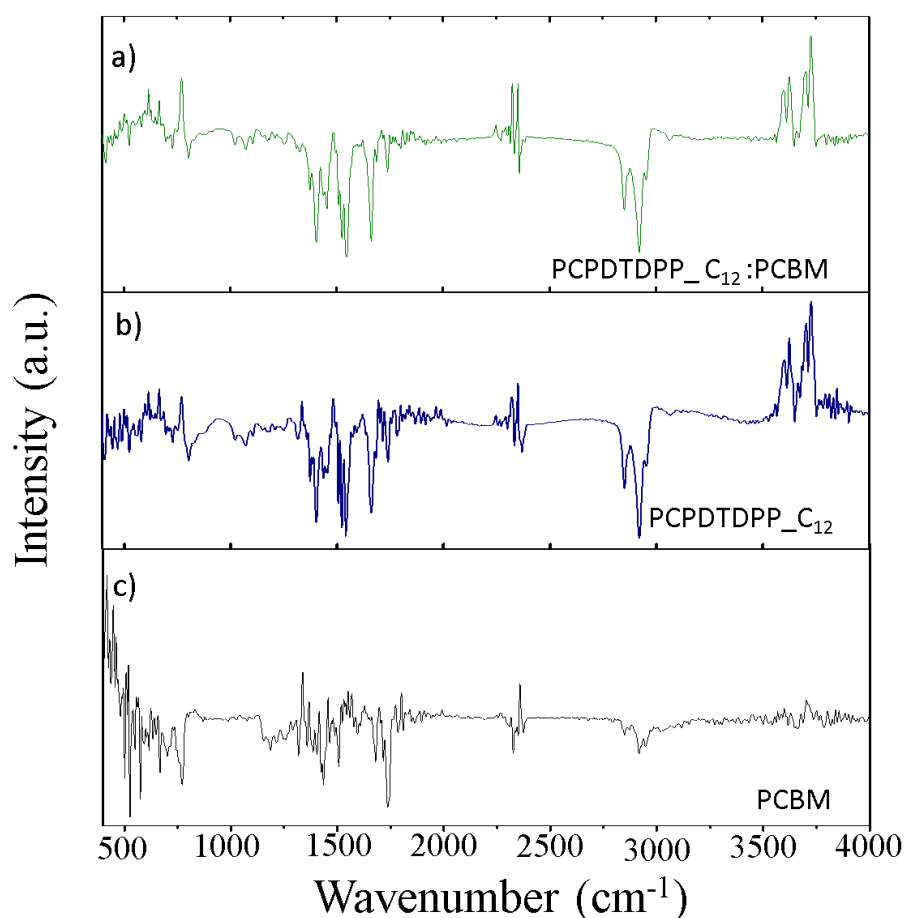


Figure 43 - FTIR spectra recorded from drop-cast films of a) PCBM, b) PCPDTDPP_C₁₂ and c) PCPDTDPP_C₁₂:PCBM on Ge (transmission mode).

Figure 44 depicts the FTIR spectra for the PCPDTDPP_Met, PCPDTDPP_Met:PCBM and the pristine PCBM (as in Figure 43.a), to make clear the comparison among them. In general, the pristine PCPDTDPP_Met shows the same peaks as the ones found for the PCPDTDPP_C₁₂. The most noteworthy difference is the increase in the region from 1000-1150 cm⁻¹ because the polymer in Figure 44.b has C-O bonds in the structure, and the C-O-C asymmetric stretching mode is within this region. For this polymer as well, the interaction between the polymer and the PCBM was merely physical, as already evaluated through Raman scattering.

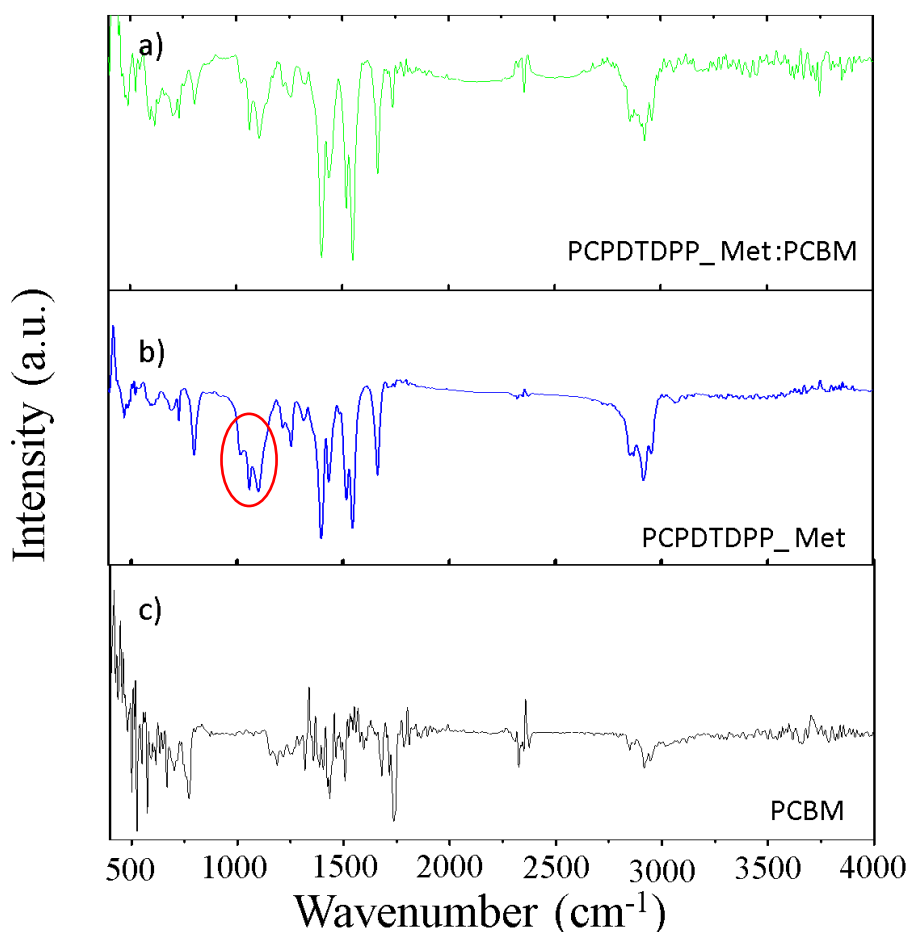


Figure 44 - FTIR spectra recorded from drop-cast films of a) PCBM, b) PCPDTDPP_Met and c) PCPDTDPP_Met:PCBM on Ge (transmission mode).

FTIR transmission measurements over time were carried out, but they did not present any considerable modifications in the spectra. The PCBM band centred at 1750 cm⁻¹ is in the mixture, however apparently did not occur any shifts/inversions or upsurge of bands.

Chapter 4 – Electrical and electrochemical measurements results

4.1 Cyclic Voltammetry

CV is a satisfactory tool to analyse the redox processes of a molecular species, and these processes provide a way to investigate the electronic bandgap diagram of the chosen material. Whereas the HOMO and LUMO of a material are related to the ionization potential (by oxidation potential) and the electron affinity (by reduction potential), respectively [175]. The energy diagram of the active layer of solar cells, notably the donor and acceptor materials, must be studied to observe if they fulfil the energy requirements to generate photocurrent [176].

Figure 45 shows the cyclic voltammograms for the drop-casting films of the a) PCPDTDPP_C₁₂ and b) PCPDTDPP_Met on a platinum substrate, in a 0.1 mol L⁻¹ solution of LiClO₄ in acetonitrile, the sweeping was carried out at a scan rate of 50 mV s⁻¹.

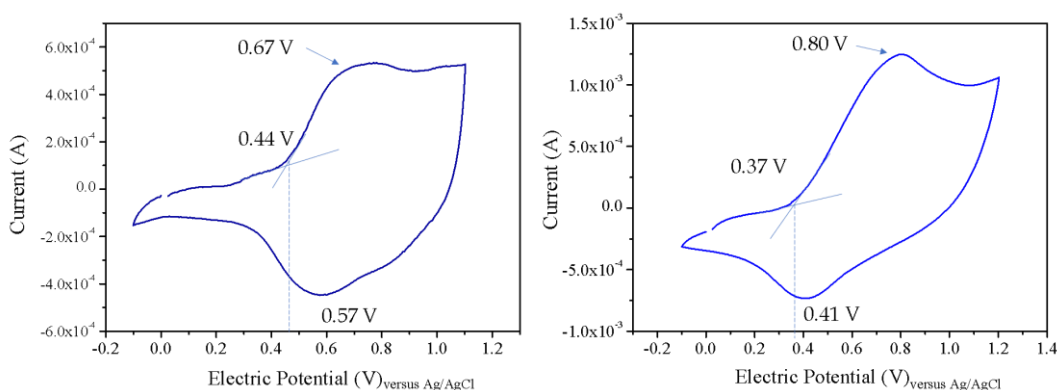


Figure 45 - Cyclic voltammograms for Pt/PCPDTDPP_C₁₂ and Pt/PCPDTDPP_Met systems in 0.100 mol L⁻¹ LiClO₄/ACN solution, $\nu = 50 \text{ mV s}^{-1}$.

Both polymers, PCPDTDPP_C₁₂ and PCPDTDPP_Met, revealed one clear oxidation peak at 0.67 and 0.80 V and reduction at 0.57 and 0.41 V, respectively. As it happens for other DPP-based copolymers, there is a reversible p-doping/dedoping (oxidation/reduction) process in the positive potential range for the polymers [177].

From literature, to attain accurate redox potentials, the reference electrode is calibrated by the Ferrocene/Ferrocenium (Fe/Fe⁺), whose redox potential is estimated to have an absolute energy level of -4.80 V in vacuum [178,179]. Thus, the equation to ascertain the HOMO is $E_{\text{HOMO}} = [(E_{\text{ox}} - E_{1/2(\text{Fc}/\text{Fc}^+)}) + 4.8]$, while for the LUMO level is $E_{\text{LUMO}} = [(E_{\text{red}} - E_{1/2(\text{Fc}/\text{Fc}^+)}) + 4.8]$. Yan Ji *et al.* tested the CV of Fe/Fe⁺ versus Ag/AgCl in order to determine the $E_{1/2(\text{Fe}/\text{Fe}^+)}$ which was found to be 0.37 V [180]. Hence, substituting

the $E_{1/2} (Fc/Fc^+)$ value, the HOMO and LUMO energy levels can be calculated using the equations 17 and 18.

$$E_{HOMO} = -e(E_{ox} + 4,43)V \quad (17)$$

$$E_{LUMO} = -e(E_{red} + 4,43)V \quad (18)$$

Where E_{ox} is the onset oxidation potential vs Ag/AgCl, and the E_{red} the onset reduction potential.

From the curves in Figure 45, the E_{HOMO} calculated for the PCPDTDPP_C₁₂ was 4.87 eV ($E_{ox} = 0.44$ V), while for the PCPDTDPP_Met was 4.80 eV ($E_{ox} = 0.37$ V). At the same time, as a result of the difficulty to identify the onset reduction potential, it was not possible to extract the E_{LUMO} , which hindered the estimation of the electronic bandgap energy. In spite of the electrochemical bandgap being usually higher than the optical bandgap in conjugated polymers, an outcome generally attributed to the formation of free ions in the electrochemical experiment rather than a neutral excited state [181]. The optical bandgap can be used in many cases as an approximation for electronic bandgaps, this was already reported for some low-bandgap polymers based on DPP [152].

Thence, the optical bandgap energy (E_{gap}) was obtained from the UV-Vis absorption measurements, the wavelength related to the optical bandgap is attained by the edge of the absorption spectrum of the film [151], and allows the calculation of the E_{gap} .

$$E_{gap} = \frac{hc}{\lambda} = \frac{1240}{\lambda} eV \quad (19)$$

where h represents the Planck's constant in eV·s and c the speed of light in vacuum, in m/s.

The E_{gap} determined for the films were 1.27 eV ($\lambda_{onset} = 976$ nm) for the PCPDTDPP polymer containing the C₁₂ branch on the DPP unit and 1.21 eV ($\lambda_{onset} = 1023$ nm) for the DPP Met-branched polymer. These results are in accordance with the ones obtained by spin-coating deposition for other similar types of low-bandgap polymers [151,182,183]. From the E_{HOMO} and E_{gap} computed heretofore, it is conceivable to estimate the LUMO energy level, E_{LUMO} , by means of the relation $E_{LUMO} = E_{HOMO} - E_{gap}$. This relation was also used by C. Duan et al. to calculate the LUMO energy level for an organic copolymer to produce solar cells [179]. Thus, an energy diagram can be created from the values found above, which is a suitable method once the charge transfer process is considered reversible being established solely by the process thermodynamics. Table 2

depicts the values aforementioned attained for the two polymers, that will be used to estimate the energy diagrams.

Table 2 - Results obtained by CV and UV-visible optical absorption measurements for the PCPDTDPP films.

Polymer	E_{ox} (V)	E_{HOMO} (eV)	E_{gap} (eV)	E_{LUMO} (eV)
PCPDTDPP_C12	0.44	4.87	1.27	3.60
PCPDTDPP_Met	0.37	4.80	1.21	3.59

To analyse what happens with the chemical species during the redox process, measurements of *in situ* Raman were carried out for different applied potentials, and Figure 46 displays the results.

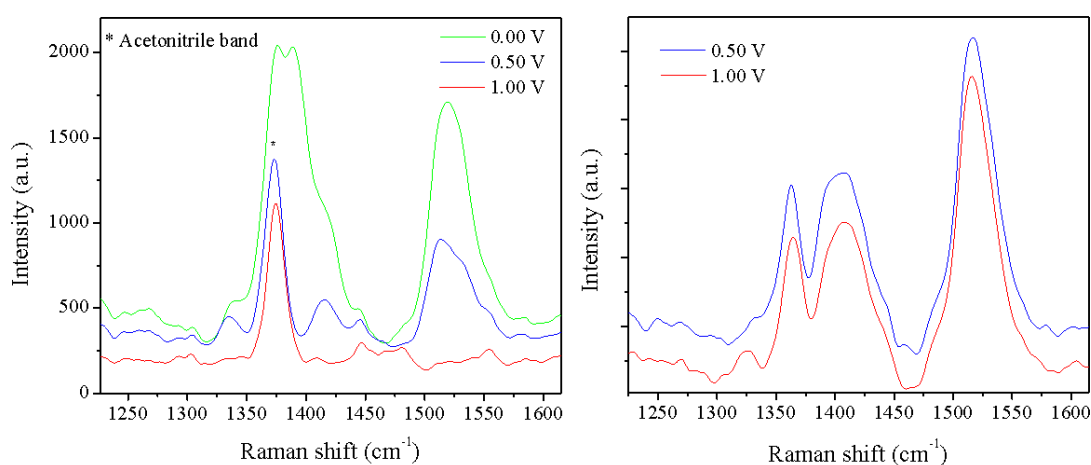


Figure 46 - *In situ* Raman spectra for a) Pt/PCPDTDPP_C12, b) Pt/PCPDTDPP_Met obtained using radiation at a wavelength of 532 nm. * acetonitrile band

The PCPDTDPP_C12 (Figure 46.a) when under application of a constant potential of 0.00 and 0.50 V shows the bands at 1514, 1445, 1416, 1388 and 1335 cm^{-1} and PCPDTDPP_Met (Figure 46. b) under 0.50 and 1.00 V at 1514 and 1408 cm^{-1} . The bands at 1388, 1416/1408 and 1514 cm^{-1} probably are characteristic bands of the radical cation and dication segments related to the characteristic frequencies of the thiophene ring, as observed in previous studies [184]. When oxidised at +1.00 V, the Raman spectrum of the PCPDTDPP_C12 (Figure 46.a) had a drastic intensity loss, probably due to the degradation effect.

With the purpose to better comprehend the transport mechanism of the ions on the polymer film/solution interface, the Bode diagrams were obtained on the different applied potentials. The Bode-phase diagram was represented to identify the influence of different processes for charge transfer in the conductivity of each system. For the Bode-phase plots, at low frequencies, there are two stages of charge transfer processes assigned

to the polaronic (radical cation) and bipolaronic (dication) conduction in the polymer matrix, while at high frequencies the sign is related to the electronic conduction [185,186]. Figure 47 depicts Bode plots at potentials of +0.50 and +0.90 V (considering to reach a stage before the process of degradation) for the Pt/PCPDTDPP_C₁₂/LiClO₄-ACN system, and +0.50 and +1.00 V for the Pt/PCPDTDPP_Met/LiClO₄-ACN system.

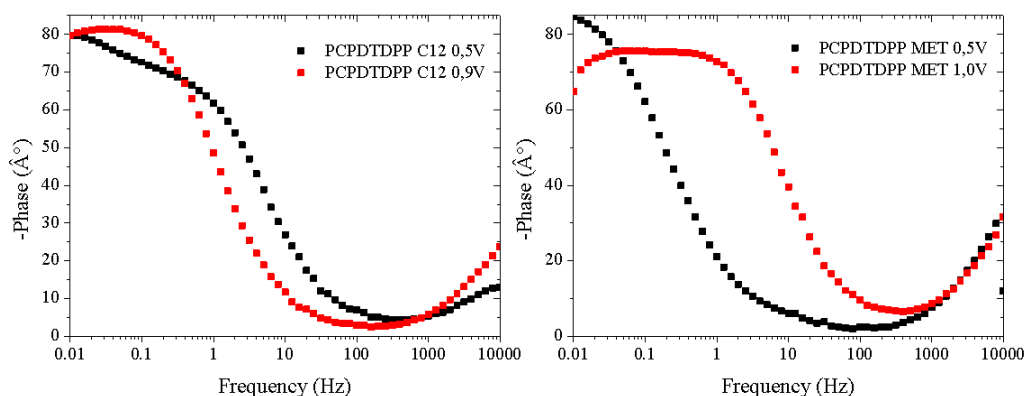


Figure 47 - Bode phase plots generated for a) Pt/PCPDTDPP_C₁₂ and b) Pt/PCPDTDPP_Met systems in 0.100 mol L⁻¹ LiClO₄/ACN solution at different potentials.

The Bode phase plots of the Pt/polymer/LiClO₄-ACN systems (Figure 47) when potentials of +0.50 V (black curves) were applied, showed a wide phase form for the C₁₂ derivative polymer going from 0.01 to 1 Hz that is mostly related to polaronic conduction, but with some contribution of the bipolaronic transport, since it has this broad phase in this frequency range [187]. In this same potential, the Met-based polymer has apparently only the polaronic input, with a time constant probably centred in less than 0.01 Hz. When a higher potential was applied, the polymers presented distinct behaviours, the PCPDTDPP_C₁₂ under +0.90 V, shifted the plot to lower frequencies, with the time constant staying in a range between 0.01 and 0.3 Hz, associated only to the polaronic conduction, and the phase angle in this range was kept roughly the same. While for the PCPDTDPP_Met, at +1.00 V, the Bode plot shifted to higher frequency with a broad phase from 0.03 to 3 Hz, as already reported by A. D. Batiste *et al.* [188], this broad range indicates the contribution of both polaron and bipolaron conduction, it happened a slight decrease in the phase angle. Regarding all cases, the phase assigned to the electronic conduction was verified at low phase angles, which through the rise of the applied potential increased a little for the C₁₂-based polymer and did not show significant changes for the Met branched polymer.

4.2 Interdigitated Electrodes (IDE)

4.2.1 Measurements in direct current

Initially, the films revealed an irregular electrical performance, where the electrical conductivity could change over time, not in a homogeneous way though, which was verified on the first tested samples. To demonstrate such behaviour, Figure 48 shows the current versus voltage (I x V) curves of the LS films from the low-bandgap polymers deposited onto IDE substrate, on the fabrication day and on the following week.

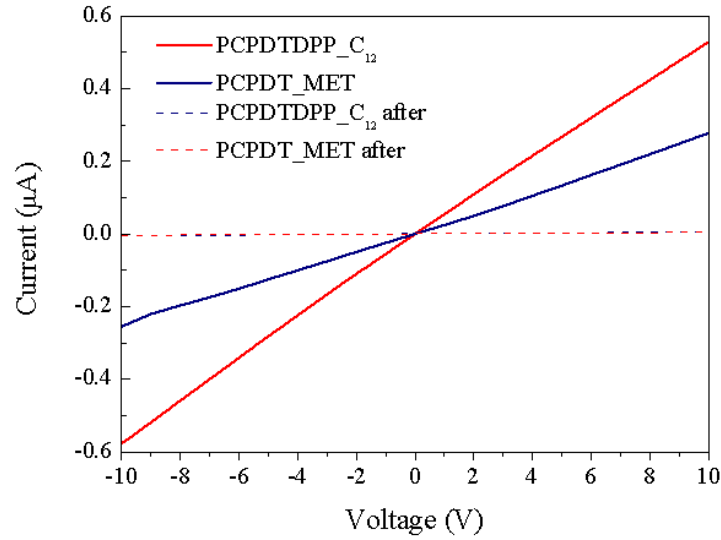


Figure 48 – Current vs. Voltage curves for the LS films of PCPDTDPP_C₁₂ and PCPDTDPP_Met on the fabrication day and on the following week.

The linear behaviour presented by these curves enables obtaining the films electrical resistance, R , for this electrode configuration. This outcome represents an ohmic character for the films with this set up [189], possibly due to the Au/polymer/Au contact interface. In this way, to calculate the conductivity, σ_{dc} , Ohm's law can be used, which through the combination between the equations: $V = R \cdot I$ e $R = \rho \frac{l}{A}$, once the conductivity is given by the inverse by the resistivity ρ , ultimately this value can be found from $\sigma = 1/\rho$. The source measure unit apply a tension and record the corresponding current, this allows to attain R ($1/R$ is the graph slope), and using this resistance calculate the conductivity, although it still necessary to find out the l/A ratio, related to the system geometry. Regarding the IDE, the geometric factor used to proceed with the calculations is the cell constant κ [cm^{-1}]. The cell constant takes into account the electrodes digit number, width, length and height [190]. The electrode used for this work has a cell constant of 5.1 m^{-1} [89].

The electrical conductivities computed from the curves on Figure 48 were $3.2 \cdot 10^{-7} \text{ S} \cdot \text{m}^{-1}$, $4.2 \cdot 10^{-9} \text{ S} \cdot \text{m}^{-1}$ for the PCPDTDPP_C₁₂ and $3.5 \cdot 10^{-9} \text{ S} \cdot \text{m}^{-1}$, $1.9 \cdot 10^{-7} \text{ S} \cdot \text{m}^{-1}$ for the PCPDTDPP_Met, on the fabrication day and on the following week, respectively. This result evidences the considerable changes in the electrical features of the produced films over time, even though the samples were stored within an N₂ atmosphere inside of a glovebox. These conductivity variations continued happening over more time has passed in a non-monotonic manner. Aiming to stabilize electrically the samples, encapsulation products were purchased to work as a procedure to decrease greatly the films contact with oxygen and moisture, which are normally pointed out as degradation agents of organic polymers [191–193].

Figure 49 depicts the I vs. V plots for the whole process, from fabrication to days after encapsulating, to evaluate the possibility of stabilizing the films and, concomitantly the encapsulation process.

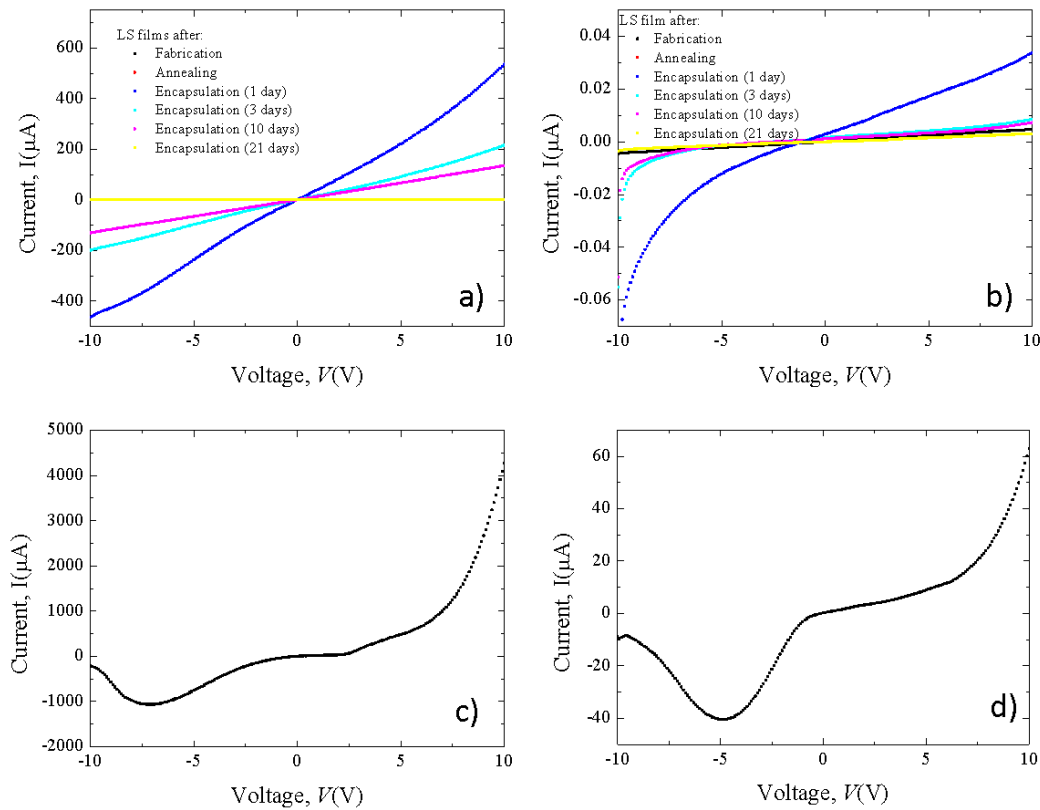


Figure 49 - Current versus voltage curves for the LS films of a) PCPDTDPP_C₁₂, b) PCPDTDPP_Met during the encapsulation process, c) PCPDTDPP_C₁₂ and d) PCPDTDPP_Met at the time just after encapsulating.

From Figure 49, the encapsulation effects on the electrical conductivities of the films can be seen. The first measurements (black curves in a and b) shows the plots for the film prior to any treatment and after annealing (overlapped by the yellow curve on

Figure 49.a), right after encapsulation results are shown on the Figure 49.c) and d), where a high epoxy effect (not completely dry yet) can be observed as soon as it is deposited onto the films, for instance, the conductivity rises up to 5000 times for a material and 600 for the other. As the responsible manufacturer claims that for the encapsulated devices be inserted on a glovebox, it is necessary to perform a de-gas on it for, at least, 24 h for complete oxygen and moisture removal. Thence, a possible vestige of the elements aforementioned and the incomplete epoxy drying can be the responsible for such result. In this way, it was noticed that in 3 weeks the conductivity gets near to the initial measured value which is kept steady enough after that. Despite the waiting for the epoxy drying after encapsulation, once this technique is performed the polymeric films becomes reasonably stable. Another example that allows the clear observation of the protection provided by the encapsulation is noticed in Figure 50, in this image the PCPDTDPP_Met LS films, that was initially blue, keeps the original colour exclusively on the encapsulated area. The mixed samples were also tested and presented similar outcome when compared to the result of the pristine polymers.

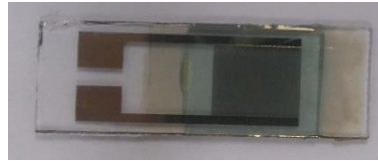


Figure 50 – Interdigitated substrate 6 months after film manufacturing encapsulated on the digits area.

Deriving out of this, to continue the work, the samples fabricated from this moment were always encapsulated. Thereupon, I x V dc measurements were carried out in order to compare the inherent conductivity of the pristine low-bandgap polymers and their mixtures with PCBM. Figure 51 displays the plots of such measures.

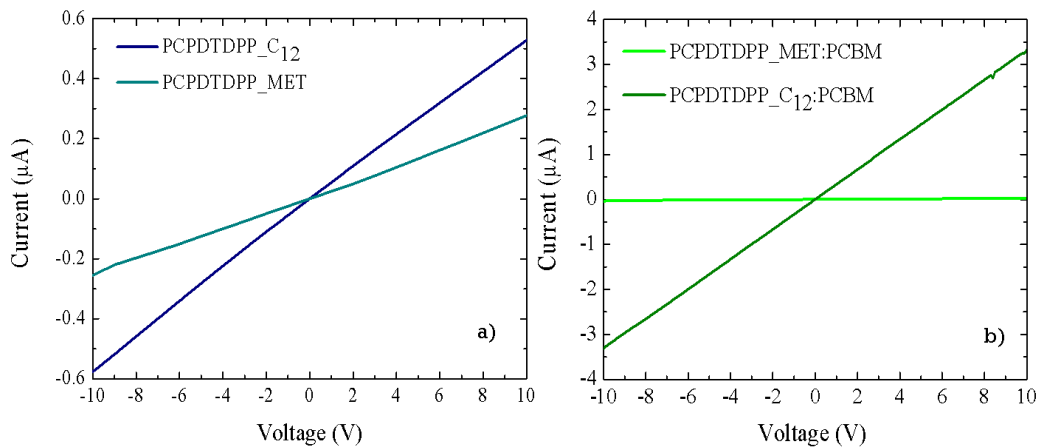


Figure 51 - Current versus voltage curves for LS films of a) PCPDTDPP_C12 and PCPDTDPP_Met and b) PCPDTDPP_C12/PCBM and PCPDTDPP_Met/PCBM.

After setting up the processes, it was done the films conductivity calculations and comparison between the different materials. The intrinsic conductivities in direct current (σ_{dc}) computed for the LS films were $2.8 \cdot 10^{-7}$, $1.3 \cdot 10^{-7}$, $1.7 \cdot 10^{-6}$ and $1.4 \cdot 10^{-8}$ S m⁻¹, for the PCPDTDPP_C12, PCPDTDPP_Met, PCPDTDPP_C12:PCBM and PCPDTDPP_Met:PCBM, respectively. Through these results, it can be concluded that the polymer type, as well as their mixture with PCBM, interfere directly with the film conductivity. In the comparison between the two pristine polymers, the PCPDTDPP_C12 revealed higher conductivity. Nonetheless, when analysed the polymer:PCBM films, the behaviour found for each polymer was distinct, where for the PCPDTDPP_C12 the PCBM helped to improve the film conductivity, while for the PCPDTDPP_Met:PCBM the conductivity decreased compared to its pristine polymer.

It is not quite usual the conductivity measures on IDE for low-bandgap polymers, especially using the Langmuir deposition techniques. A previous group work [134], however, fabricated LB films onto gold IDE of two low-bandgap polymers: *poly[(4,4-bis(2-ethylhexyl)-cyclopenta-[2,1-b:3,4-b']dithiophene)-2,6-diyl-alt-(2,1,3-benzothiadiazole)-4,7-diyl]*, PCPDTBT and the *poly[(4,4'-dioctyldithieno[3,2-b:2',3'-d]silole-2,6-diyl)-alt-(2,1,3-benzothiadiazole)-4,7-diyl]*, PDTSTBT mixed with amphiphilic molecules that enabled the LB films production [74], these films depicted conductivities on the 10^{-8} and 10^{-9} S·m⁻¹ magnitude order, close values to the ones obtained on the current work.

The difference on the conductivity for the PCPDTDPP films may be explained by the polymers structure, more precisely the lateral chains present on the DPP units, since the conformation they adopt in film form can change the inter/intrachain interactions influencing on the carriers' transport, the influence of side chains on a device performance is well reported for many polymers, such as P3ATs [194,195]. The isotherm areas attained in the Langmuir trough, the morphologies on the AFM and the Raman images also show the high structural dissimilarities on the films surfaces of the polymers, strongly suggesting conformational changes. However, as the conductivity between the pristine polymers is not so distinct, the way the interaction between low-bandgap polymers and PCBM occurs seems to have a higher influence on the final result. For the material that, through the analysis of previous measurements, apparently interacts more efficiently with the PCBM, PCPDTDPP_Met, shows a decrease in an order of magnitude in the conductivity when in the mixture. This probably means that this interaction is decreasing the intrachain transport processes, hindering the positive and negative

polarons transport. Once the intrinsic conductivity of conjugated polymers is usually low according to the small number of impurities within the chains, which can be inserted during the synthesis or on the manipulation [196]. Whilst for the PCPDTDPP_C₁₂:PCBM the inverse process is taking place showing a boost in the conductivity value.

4.3 Diode structure

4.3.1 Direct Current Measurements

Figure 52 presents the plots of the dc electrical characterization for the devices ITO/PEDOT:PSS/C₁₂:PCBM/Al and ITO/C₁₂:PCBM/ PEDOT:PSS/Al in a), containing 20 layers LS film of the polymer:PCBM mixture, and 40 layers of PCPDTDPP_Met:PCBM LS films, for the devices with ITO/PEDOT:PSS/Met:PCBM/Al and ITO/Met:PCBM/PEDOT:PSS/Al configuration b). The PEDOT:PSS layer of the devices was spin-coated at 3000 rpm for 60 s, and performed annealing at approximately 120 °C for 10 min [100,197]. The LS films solution had a concentration of 0.3 mg ml⁻¹ (1:1 weight ratio) in chloroform, and the Al was evaporated at a rate of de ~0,8 nm s⁻¹ with a thickness of 70 nm controlled by the evaporator, the active area of the electrodes is 4 mm². The contact electrodes used in this characterization possess work functions of 4.7 eV for the ITO and 4.3 eV for the Al [76,198,199]. This difference on the work function of both and the presumed defects between the metal and the semiconductor interface induce the formation of a Schottky barrier [200–202]. As a consequence, the

curves obtained in these measurements is a rectifying diode. For this characterization, voltages from -10 to 10 V were applied.

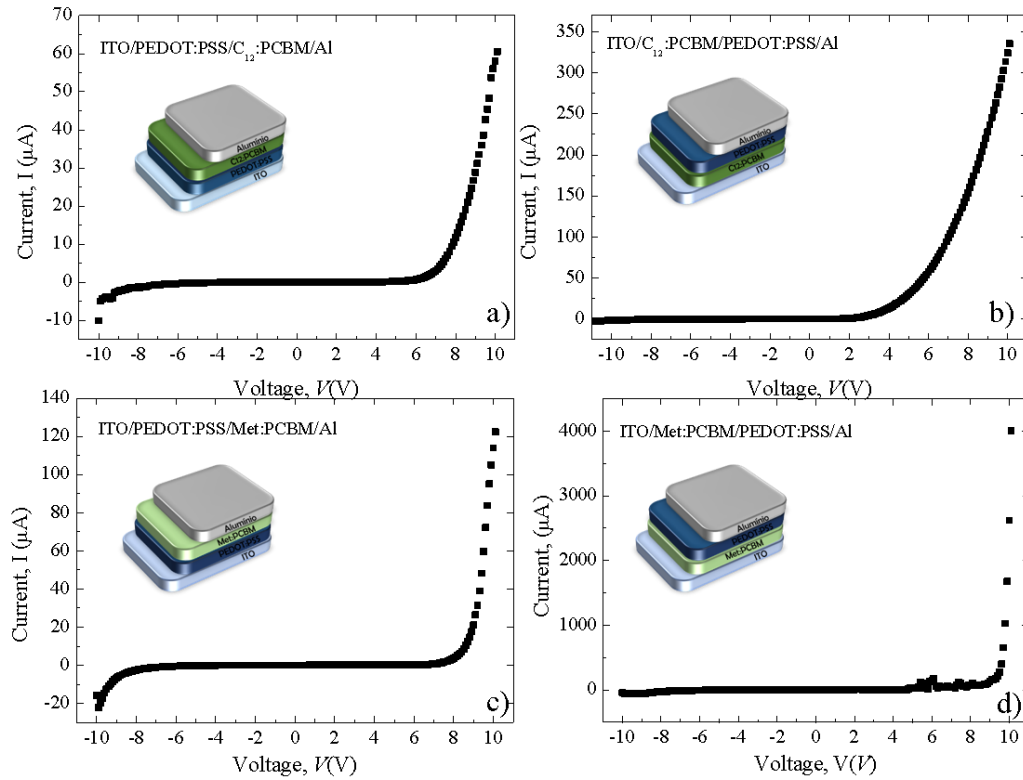


Figure 52 - I vs. Curves V, in linear scale, of the devices a) ITO/PEDOT: PSS/C₁₂:PCBM/Al, b) ITO/C₁₂:PCBM/PEDOT:PSS/Al, c) ITO/PEDOT: PSS/Met:PCBM/Al and d) ITO/Met:PCBM/PEDOT:PSS/Al.

The device with the structure ITO/Met:PCBM/PEDOT:PSS/Al presented much higher current than the other configurations, however this curve exhibited many noises starting around 3V, which can have as origin the formation of a quite irregular layer of PEDOT:PSS over the PCPDTDPP_Met:PCBM, causing a non-homogenous carrier transport system and simultaneously highlighting the PEDOT:PSS intrinsic feature (for instance, the high current value). The lowest current was attained for the ITO/PEDOT:PSS/C₁₂:PCBM/Al device. Comparing one polymer with itself but inverted structures, the devices encompassing the PEDOT:PSS over the active layer displayed higher currents. The reason for that possibly relies on the fact that this configuration enhances the conduction process and the electronic injection, the PEDOT:PSS being more influencing on the measured current, or even originated from experimental issues arising from the challenging deposition of this layer over the polymer:PCBM LS film. The threshold voltages achieved for the devices was 5, 3, 6 and 8V for the a) ITO/PEDOT:PSS/C₁₂:PCBM/Al, b) ITO/C₁₂:PCBM/PEDOT:PSS/Al, c) ITO/PEDOT:PSS/Met:PCBM/Al and d) ITO/Met:PCBM/PEDOT:PSS/Al, respectively. It is worth pointing out that there is a more efficient transport for the active layer

Met:PCBM on the diode-like devices, which can be related to the films thicknesses where for the C₁₂:PCBM 20 layers is around 200 nm, value way higher than the measured thickness for the Met:PCBM 40 layers ~130 nm.

Figure 53 displays the I vs. V curves in mono-logarithmic scale that offers another way to analyse the diode-like devices, from that it can be extracted the rectification ratio (RR), which is useful to examine the rectification behaviour of a diode. A rectification ratio of a contact is calculated from the ratio between the forward and reverse-bias polarized currents, as illustrated by the equation $RR = \frac{I_{forward}}{I_{Reverse}}$ [203]:

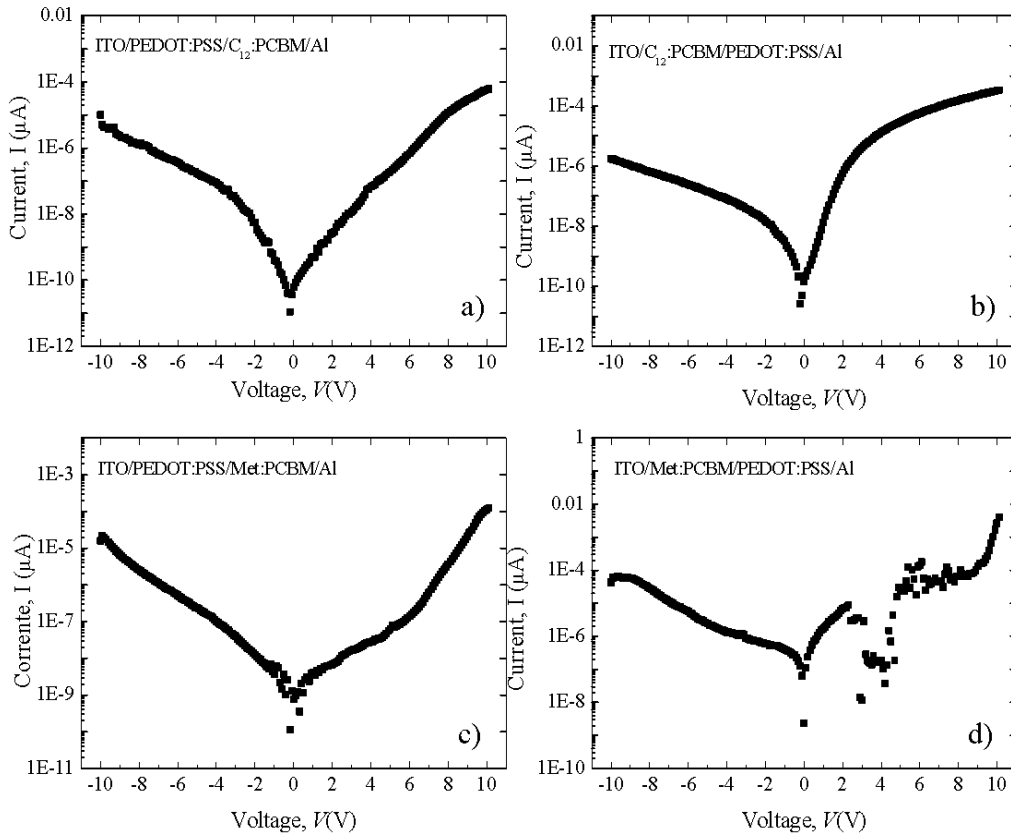


Figure 53 - I vs. Curves And, on a monologarithmic scale, of the devices a) ITO/PEDOT:PSS/C₁₂:PCBM/Al, b) ITO/C₁₂:PCBM/PEDOT:PSS/Al, c) ITO/PEDOT:PSS/Met:PCBM/Al, and d) ITO/Met:PCBM/PEDOT:PSS/Al.

Analysing the graphs from the Figure 53, it is possible to observe that a rectifying behaviour happens for all the studied devices, despite this ratio is very distinct for each measured sample. As mentioned before, the ITO/Met:PCBM/PEDOT:PSS/Al device presents significant noise around 3 V that only decreases at ~ 6 V. The rectification ratios

were calculated on the voltages of -10 and 10 V and they are illustrated in *Table 3*. These factors were computed for voltages above the threshold voltages.

Table 3- Calculated RR values for the devices in constant voltage.

Device	Rectification ratio (RR)
ITO/PEDOT:PSS/C ₁₂ :PCBM/Al	12
ITO/C ₁₂ :PCBM/PEDOT:PSS/Al	190
ITO/PEDOT:PSS/Met:PCBM/Al	6
ITO/Met:PCBM/PEDOT:PSS/Al	68

In comparison with organic polymers curves from literature, the RR estimated did not have the typical found factors with magnitudes of 10^3 and 10^4 [204–207]. Nevertheless, in our case the active layer is a BHJ from the polymer and the PCBM, besides there is yet the PEDOT:PSS layer between the electrodes which usually do not possess high RR values [208], thus the final ratio result comes from the interaction of materials with one another and with the electrodes. Moreover, the deposition technique used on the devices confection influences considerably on this ratio, and published results generally utilize other techniques [209].

4.3.2 Alternating current measurements

The Z' versus V plots obtained for the ITO/PEDOT:PSS/Polymer:PCBM/Al and ITO/Polymer:PCBM/PEDOT:PSS/Al devices are presented in Figure 54, in these devices the PEDOT:PSS was spin-coated and the low-bandgap polymers were deposited *via* LS technique in a total of 40 layers of the PCPDTDPP_Met and 20 layers of the PCPDTDPP_C₁₂ (number of layers chosen due to previous experimental trial). The data extracted from these plots present, in general, a steady trend where the Z' is kept rather constant, and these plateaus appeared in low and high frequencies. The high frequencies plateaus are quite clear on the impedance curves, nonetheless is not well-defined at low frequencies and concomitantly this last plateau varied according to the applied dc bias. For the ITO/PEDOT:PSS/C₁₂:PCBM/Al configuration, the variation in the low-frequency plateau can be identified clearly, while for the devices containing other configurations, such characteristic becomes apparent solely after certain applied dc bias. The change on the low-frequency plateau according to the dc bias may be attributed to the impedance of the Al/PEDOT or Al/polymer interface caused by a potential barrier, as it was already

demonstrated for the interface between aluminium and polyphenylene-vinylene [210] and polythiophene [194].

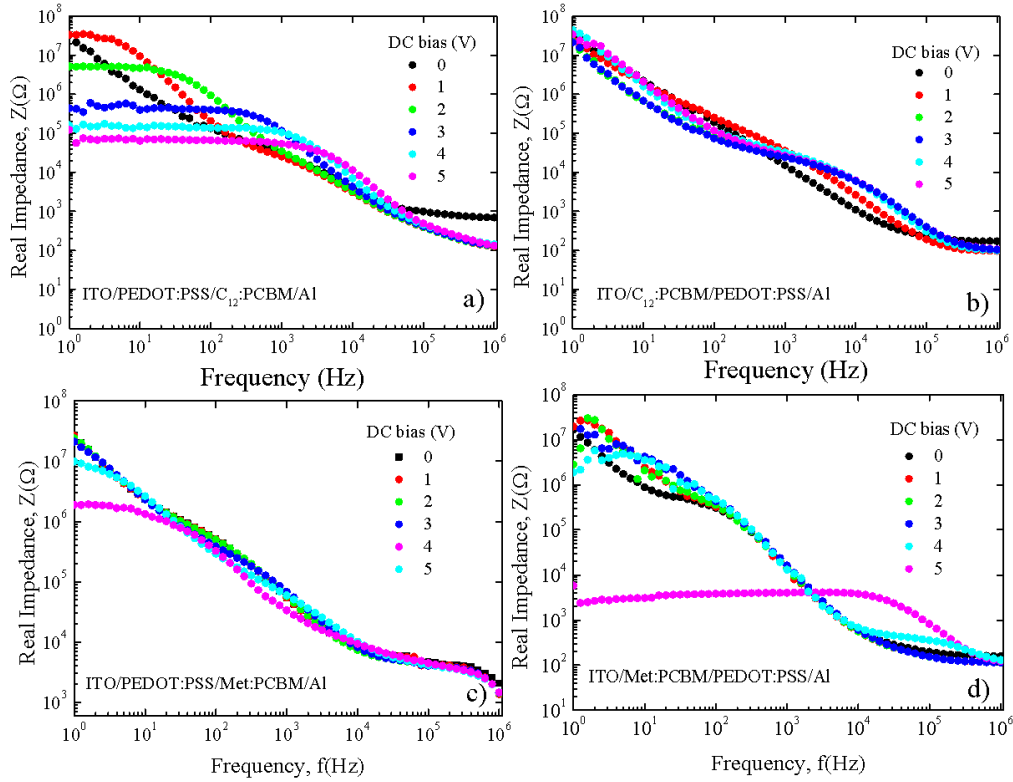


Figure 54 - Z' vs. f curves for LS films with the ITO/PEDOT:PSS/Polymer:PCBM/Al and ITO/Polymer:PCBM/PEDOT:PSS/Al configurations.

For the devices fabricated with PCPDTDPDPP_C₁₂, the one with the structure ITO/PEDOT:PSS/C₁₂:PCBM/Al (Figure 54.a) shows as an overall feature the drop on the real impedance Z' according to the rise of the applied dc voltage, whereas the frequency goes from $\sim 10^4$ a $\sim 10^7$ Ω. In this plot, it also occurs an upward trend on the frequency range of the first plateau as the dc bias is augmented, for instance at 1 V the plateau frequency is up to 5 Hz, while for 5V, $3.5 \cdot 10^3$ Hz. The most distinct curve appears on the 0 V plot, which is associated with the impedance of the C₁₂:PCBM/Al interface because of the potential barrier.

Figure 54.b) depicts the curves for the ITO/C₁₂:PCBM/PEDOT:PSS/Al device, for this structure the applied dc bias interfered less relevantly on the Z' outcome when compared to the conventional architecture. All the plots seem to possess a plateau for the frequencies under 1 Hz, nevertheless, the curves for 0 and 1 V show a rather same behaviour, in contrast with the curves starting from 2 V which are quite similar with each other. For the 2-5 V plots, the steady impedance region has an inflexion point around 10^4 Ω, such constant region is not detected for the lower applied bias. Meanwhile, at high

frequencies (from 10^5 Hz) there is a plateau with roughly the same resistance, around 150 Ω , for all the different biases. This constant region can be attributed to the impedance of the ITO and PCPDTDPP_C₁₂ interface.

The real impedance response for the ITO/PEDOT:PSS/Met:PCBM/Al device is depicted in Figure 54.c), the obtained responses were rather analogous for any bias, highlighting only the 5 V plot reveals a noticeable change, whereas the low-frequencies plateau is more evident. At the same time, on the high-frequencies ($\sim 5 \cdot 10^5$ Hz), there is a constant level at about $3 \cdot 10^3$ Ω , probably related to the impedance of the ITO/PEDOT:PSS interface due to the barrier between them.

Finally, the ITO/Met:PCBM/PEDOT:PSS/Al device in spite of the noise at low-frequencies, the corresponding resistances stay between $2 \cdot 10^7$ Ω (0V) e $2 \cdot 10^6$ Ω (4V), and the tendencies of the curves are quite similar until reaching 4 V. On the low-frequencies there is a constant impedance curve with high resistance, the 0 V plot shows somewhat a different aspect in this region since it has 2 plateaus (one can only be seen altogether in frequencies lower than 1 Hz). As proposed by Olivati *et al.* for OC₁OC₆-PPV LB films [210], this steady behaviour on the impedance at low-frequencies occurs owing to the interface impedance of the material that is in contact with the Aluminium (for our case, PEDOT:PSS/Al), which is generated by a potential barrier that disappears with the application of high fields and tunnelling happens. At high frequencies ($\sim 1,3 \cdot 10^4$ Hz), the plateaus are within a fairly close value for the samples under distinct biases, the reciprocal resistance for this region is 460 Ω (active layer/ITO interface). When 5 V was applied over the sample, apparently there was sort of a disruption of the Met:PCBM layer, which is in between the ITO and the PEDOT:PSS layer, prevailing the PEDOT:PSS characteristics such as the lower resistance on the magnitude of 10^3 Ω [211].

Figure 55 displays the Imaginary impedance *versus* frequency, Z'' vs. f , of the ITO/PEDOT:PSS/Polymer:PCBM/Al and ITO/Polymer:PCBM/PEDOT:PSS/Al devices with the same configurations described on the Z' vs. f plots discussion section. Performing an overall analysis of the Z'' vs. f spectra, two main outcomes took place: no relaxation peak appeared until determinate dc bias was applied or these peaks shifted to high frequencies as the dc bias increased.

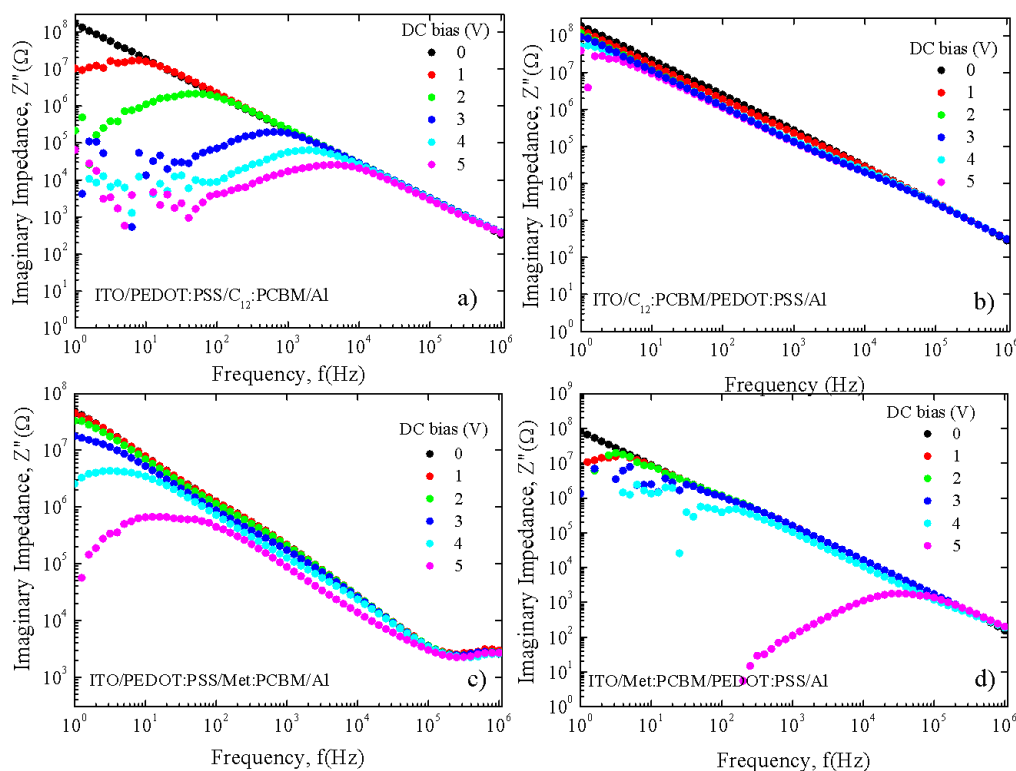


Figure 55 - Z'' vs. f curves for LS films with the ITO/PEDOT:PSS/Polymer:PCBM/Al and ITO/Polymer:PCBM/PEDOT:PSS/Al configurations.

Examining the imaginary impedance plots, the ITO/PEDOT:PSS/ C_{12} :PCBM/Al device observed on Figure 55.a) showed the propensity of the high-frequency shift according to the rise of the employed bias. Now, the ITO/ C_{12} :PCBM/PEDOT:PSS/Al device (Figure 55.b) conveys the impression of having a non-defined peak at a high-frequency from the applied potential of 3V, whilst in low-frequencies only at 5V there is a sign of the formation of the relaxation variable. The Z'' vs. f curves on Figure 55.c) of the ITO/PEDOT:PSS/Met:PCBM/Al device only the 5 V spectrum possess a clear relaxation peak in low-frequency region (63 Ω), noticing though that at 4 V the plot appears to have a peak on Z'' at the range from 1 to 10 Hz, at the same time at high frequencies all the plots present the formation of a relaxation maximum, although it is not well-defined. Despite the noises on the measurements in Figure 55.d), the general behaviour of the suchlike polymer in other architecture (Figure 55.c) also happens in this case, notwithstanding the 5 V curve displaces to high frequencies and low imaginary impedances abruptly, possibly to the effect cited previously about the PEDOT:PSS dominating the spectrum shape.

The Argand diagrams, where the Z'' vs. Z' graphs, for the aforementioned devices are shown in Figure 56.

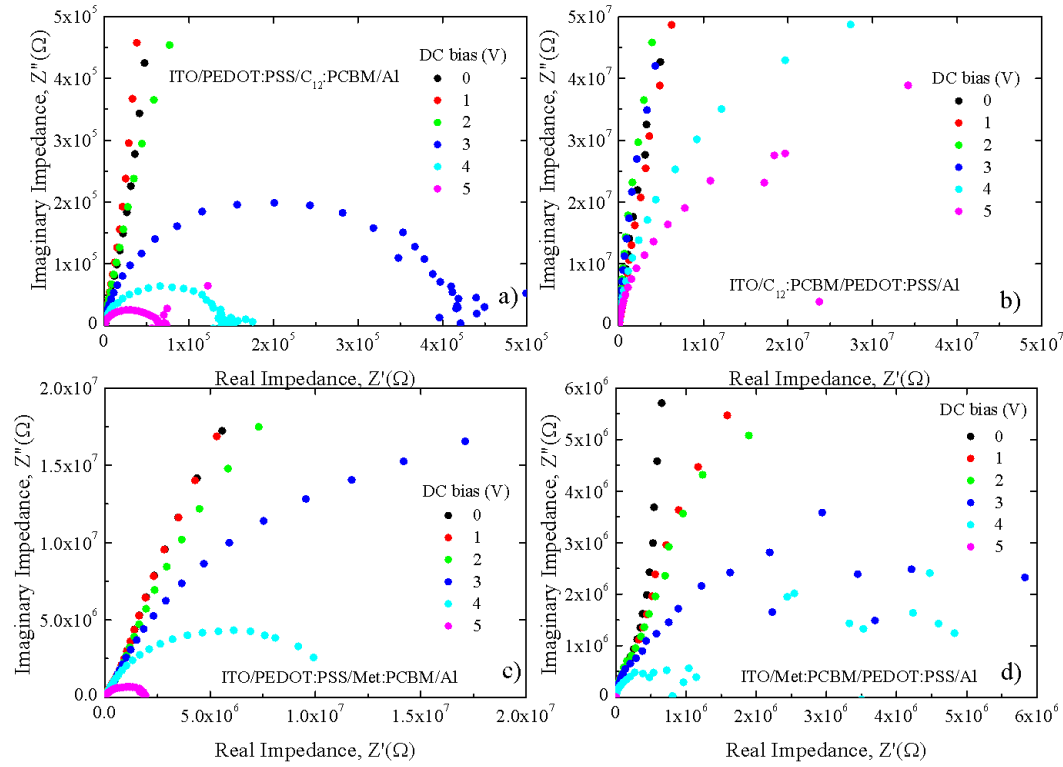


Figure 56 - Z'' vs. Z' curves for LS films with the ITO/PEDOT:PSS/Polymer:PCBM/Al and ITO/Polymer:PCBM/PEDOT:PSS/Al configurations.

Investigating the Argand diagrams (Figure 56), a feature that stands out for all the analysed devices, the centre of the semi-circular arc moves towards the origin axis while the bias keeps growing. The semicircle diameter of the diagram is associated with the total resistance of the device [115,212]. Another similarity among the curves is that they only present a single semicircle, and since there is more than one interface on the system (which could create more semicircles [115]), this result means probably the overlapping of two or more semicircles. In the devices with the structure where the PEDOT:PSS is between the ITO and the polymer film (Figure 56.a and c), the semicircle closes more evidently, while for the other configuration is not clear the semicircle development as can be seen on Figure 56.d, or this effect does not occur at all (Figure 56.b). This last-mentioned behaviour indicates a really high total resistance. The 5 V plot for the ITO/ Met:PCBM/PEDOT:PSS/Al device (Figure 56.b) does not appear on the image because its semicircle diameter is too small, due to the low resistance, which could be detected also on the $Z' \text{ e } Z''$ vs. f plots.

The impedance can vary according to several factors, among them: the intensity of the applied dc voltage [213], the sample temperature [214,215], the deposition technique of the device layers [216], and the layers' thicknesses [117,217]. Previously,

devices containing 20 layers of PCPDTDPP_Met were fabricated, but it was only possible to perform the measurements on the device with the structure ITO/PEDOT:PSS/Met:PCBM/Al, once the ITO/Met:PCBM/PEDOT:PSS/Al device with this amount of layers presented short-circuit precluding any electrical measure. Figure 57 depicts the impedance measurements, Z' vs. f , Z'' vs. f e Z'' vs. Z' , for the ITO/PEDOT:PSS/Met:PCBM/Al device fabricated with Met/PCBM 20 layers via LS technique.

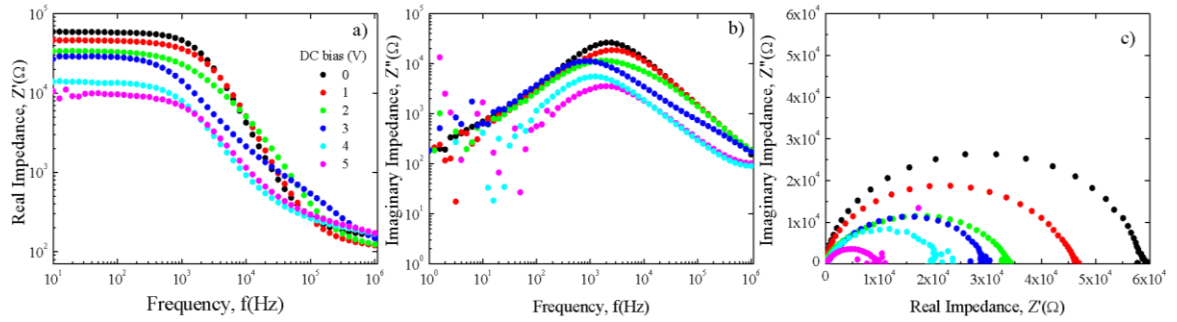


Figure 57 – Plots of a) Z' vs. f , b) Z'' vs. f and c) Z'' vs. Z' for ITO/PEDOT:PSS/Met:PCBM/Al LS film with 20 layers.

Comparing the curves in Figure 57 to the identical 40 layers device it is noticeable the difference between the two devices. In a first glance the change on the shape of the curve is quite clear, whereas, on the 20 layers sample, the data that can be obtained through the graphs are more evident, like the interface resistances, the relaxation peaks and the total device resistance. Moreover, the global impedance values are another aspect to be evaluated. Thus, the 40 layers device showed real impedances around 10^7 - $10^8 \Omega$, and the one containing 20 layers presented the Z' values between $\sim 10^4 \Omega$ (at 5 V) e $\sim 10^5 \Omega$ (at 0 V). On the Z'' vs. f measurements, the thicker active layer device did not show well-defined relaxation peaks, as for the less thick, these maxima appear clearly since the application of a 0 V voltage. On the Argand diagram, the 20 layers film enables the observation of the total resistances (through the semicircle results) regardless of the applied bias, in contrast with the thicker analogous sample that due to its high resistance only had closed circles after the employment of 4 V dc bias. These distinct outcome according to the modification of the active layer thicknesses are rather common and well reported in the literature [117,213,217].

Finally, probing the ac electrical results for the 20 layers device, from the real impedance, displayed on Figure 57.a, Z' decreases with the drop of the employed dc voltage, however, unlike the ITO/PEDOT:PSS/C₁₂:PCBM/Al the first plateaus do not shift so considerably as the bias kept being applied. The imaginary impedance versus frequency (Figure 57.b) showed explicit relaxation peaks for all voltages, although it

presented a non-monotonic behaviour as the bias rose, this fact is more perceptible on the 3 and 4 V plots. In the Figure 57.c, the semicircles on the Z'' vs. Z' graph had a drop on the diameter at the Z' axis as the voltage kept going upward.

In a Argand diagram, by applying different dc bias, in the region equivalent to the high frequencies (near the origin axis) many devices present a linear shape when a line is drawn with slope of 45° , in fact Garcia-Belmonte *et al.* showed this outcome for a ITO/PEDOT:PSS/P3HT:PCBM/Al device. This aftereffect is attributed to a system whose the carriers transport is determined by the diffusion-recombination between the non-absorbing contacts [218,219]. Nevertheless, for all the devices tested on the current work the attained results did not reveal such feature, yet the curves in this frequency region were quite distinct for each voltage applied due to the constant phase element (CPE), which is related to microscopic materials properties arising from surface defects and local charge inhomogeneities [220–222].

4.4 Results of the OPV performance of the LS films

The devices manufactured for this first step were fabricated with the BHJ active layer of the low-bandgap polymers PCDPTDPP_C₁₂ and PCDPTDPP_Met with the PCBM using the Langmuir-Schaeffer technique. For the holes injection, a PEDOT: PSS layer was added, which can be inserted between the ITO and the active layer [223,224], or between the active layer and the contact electrode in inverted devices [193,225].

Figure 58 shows the curves J vs. V , under the solar simulator illumination, for low-bandgap polymers in BHJ structure with PCBM, where the devices are in the direct configurations (ITO/PEDOT:PSS/C₁₂:PCBM/Al and ITO/PEDOT:PSS/Met:PCBM/Al) and inverted (ITO/C₁₂:PCBM/PEDOT:PSS/Al and ITO/Met:PCBM/PEDOT:PSS/Al). Normally, for the inverted structure of OPV devices, the ideal is to work with silver [45] as the upper electrode, but the fabricated samples using such top electrode, have been short-circuited.

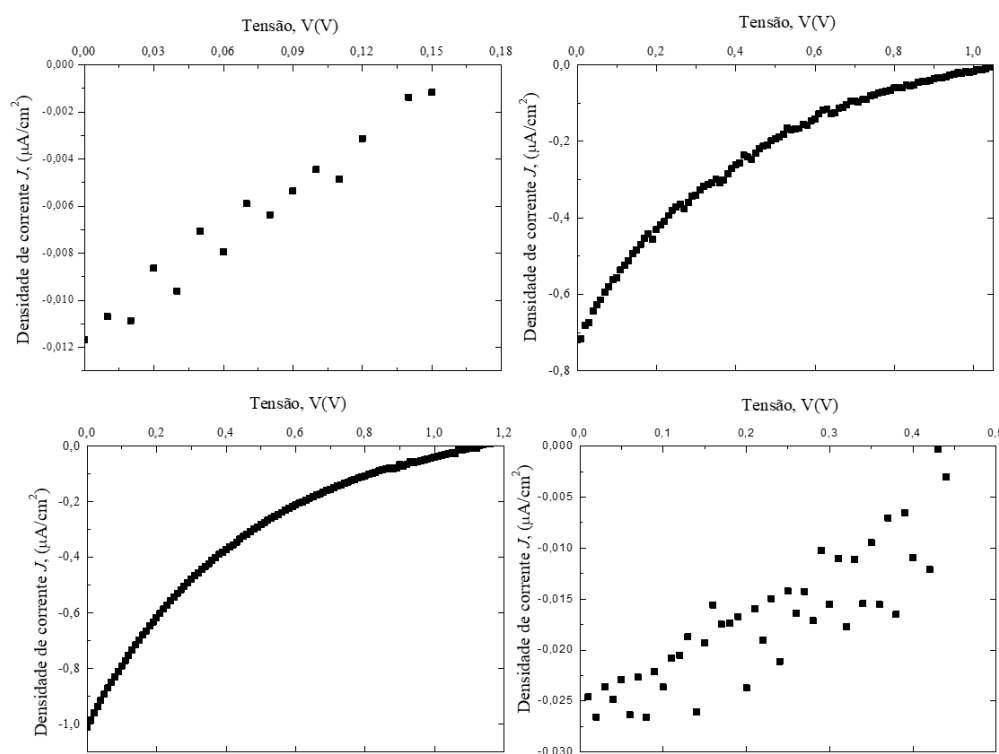


Figure 58 - J vs. V curves for the a) ITO/PEDOT:PSS/C₁₂:PCBM/Al, b) ITO/C₁₂:PCBM/PEDOT:PSS/Al, c) PCBM/PEDOT:PSS/Al devices, under the illumination of a solar simulator (100 mW/cm² - AM 1.5).

Through the J vs. V measures under illumination it is possible to observe that, even if at different scales and noisy measurements (Figure 58.a), the photovoltaic effect occurred. Thus, using the equations for the solar cells described in section 1.6, Table 4 was constructed and it contains the parameters for the organic photovoltaic devices. It is possible to observe that these curves are distinct from the ideal curves for photovoltaic devices. This fact could be related to series and parallel resistances. The shunt resistance affects the generated current, decreasing power and short circuit current (I_{sc}). Otherwise, the V_{oc} is affected by parallel resistance. Among the main general causes of low efficiency of the solar cells is the contact of the devices with air and humidity [173].

Table 4 - Photovoltaic parameters obtained for the OPV devices of the polymers:PCBM blends deposited via LS and with different geometries.

Device	$J_{max}(\mu A/cm^2)$	$V_{max}(V)$	$J_{sc}(\mu A/cm^2)$	$V_{oc}(V)$	FF
PEDOT:PSS/C₁₂:PCBM	0.11	0.005	0.15	0.01	0.29
C₁₂:PCBM/ PEDOT:PSS	0.22	0.49	0.72	1.05	0.15
PEDOT:PSS/Met:PCBM	0.33	0.47	1.01	1.15	0.13
Met:PCBM/PEDOT:PSS	0.014	0.29	0.44	0.025	0.36

In addition to the difficulty of manufacturing the devices that require different techniques for each of its constituent parts. Even if the samples are encapsulated, they end up being determined moments in contact with the ambient atmosphere until the encapsulation moment, which can reduce but not completely eliminate this effect. The lack of intermediate layers that would aid in separating the charges until they reach the electrodes that collect them is another pitfall that contributed to the attained result. Examples of these layers are: lithium fluoride (LiF) between the active layer and the aluminium in the direct structure devices, and the zinc oxide (ZnO) between the ITO and the active layer in the indirect configuration devices. In addition, switching the upper electrode to silver in cases of inverted electrodes is an essential form to furnish an upgrade for the final product.

Chapter 5 – OPV devices from spin-coating films

The majority of the OPV devices is fabricated via spin-coating technique [226–228], thus after the difficulties to achieve efficient devices with the experimental set up, the attempt of making a device comparable with literature was performed at *Grupo de Polímeros* of the *Instituto de Física de São Carlos* (USP - São Carlos/SP - Brazil), under the supervision of Professor Roberto Mendonça Faria, with the assistance of Francineide de Araújo Lopes e Daniel Roger Bezerra Amorim. However, the spin-coating method requires a big amount of material, the measures were performed more towards the end and the parameters were not thoroughly optimized.

For that, the first step was to make the mixed solutions of the low-bandgap polymers with the PC₆₁BM and the PC₇₁BM, as it was the first step the chosen proportion was 1:1 wt% of the two materials to make the solution at a concentration of 10 mg/ml in chloroform, this solution was stirred overnight. For this experiments only the conventional structure was tried, whereas the ITO was the bottom electrode, and the PEDOT:PSS worked as the anode buffer layer using the same parameters described previously (40 nm), for the active layer, containing the donor and acceptor material, was used the PCBM:polymer BHJ that was spin-coated from a chloroform solution at 1500 rpm for 90 s with thickness around 120 nm, as a cathode window layer Calcium (40 nm) was evaporated onto the active layer, and as the top electrode the Al (60 nm) was used again. Therefore, four structures were manufactured: ITO/PEDOT:PSS/C₁₂:PC₆₁BM/Ca/Al, ITO/PEDOT:PSS/C₁₂:PC₇₁BM/Ca/Al, ITO/PEDOT:PSS/Met:PC₆₁BM/Ca/Al and ITO/PEDOT:PSS/Met:PC₇₁BM/Ca/Al. Figure 59 shows the schematic representation of the spin-coated bulk-heterojunction OPV devices.

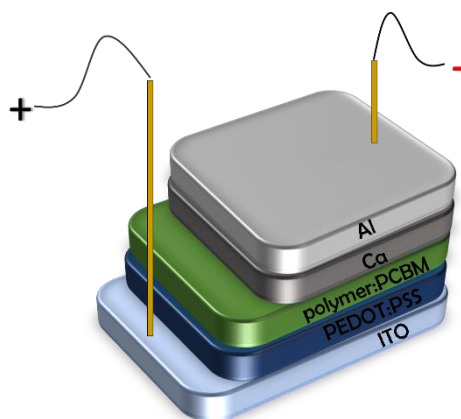


Figure 59 - Schematic representation of the OPV devices with spin-coating BHJ active layer.

Before choosing the parameters, several polymers films with different spin speeds were fabricated over the PEDOT:PSS layer, then analysed the structure on AFM and thickness on the Profilometry equipment, from that it was selected the spin speed to assure about 100 nm film thickness. The surface of the ITO and the PEDOT:PSS was also examined. The UV-Vis of the spin-coated films were carried out, the PCPDTDPP_C12 showed a redshift of 10 nm in comparison with the LS film while the PCPDTDPP_Met presented the same absorption maximum peak. In Figure 60 it is possible to see the J vs. V curves for the devices of the PCPDTDPP_C12:PCBM films. The active area used to attain the current density curves under the solar simulator illumination is $4.5 \cdot 10^{-2} \text{ mm}^2$.

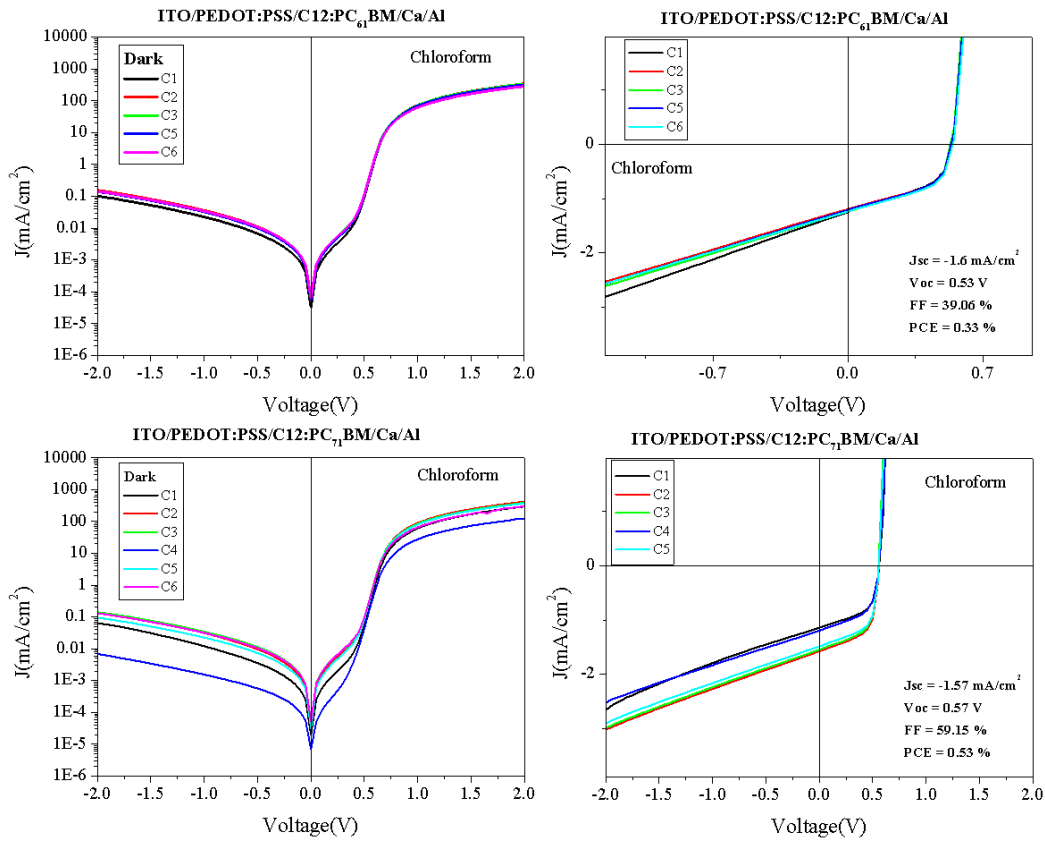


Figure 60 – J-V curves for the ITO/PEDOT:PSS/C12:PC₆₁BM/Ca/Al and ITO/PEDOT:PSS/C12:PC₇₁BM/Ca/Al devices under dark and illuminated.

The J vs. V plots in Figure 60 show the data obtained for the devices when in dark and under illumination of a solar simulator. Firstly, discussing the curves in the dark the rectification ratios are quite high, for the blends with the PC₆₁BM Figure 60.a) this factor is around 3000 for all the measured digits, the curve for the C12: PC₇₁BM sample the RR is also about 10^3 even reaching a 10^4 in the navy-blue curve. Concerning the curves under illumination, the J_{SC} and the V_{OC} for both devices were quite similar, the highest found difference was on the fill factor, FF, which also lead to the higher PCE = 0.53%

when the polymer was mixed to the PC₇₁BM. Figure 60 depicts the J vs. V curves in dark and light for the PCPDTDPP_Met: PC₆₁₍₇₁₎BM blends in CHCl₃.

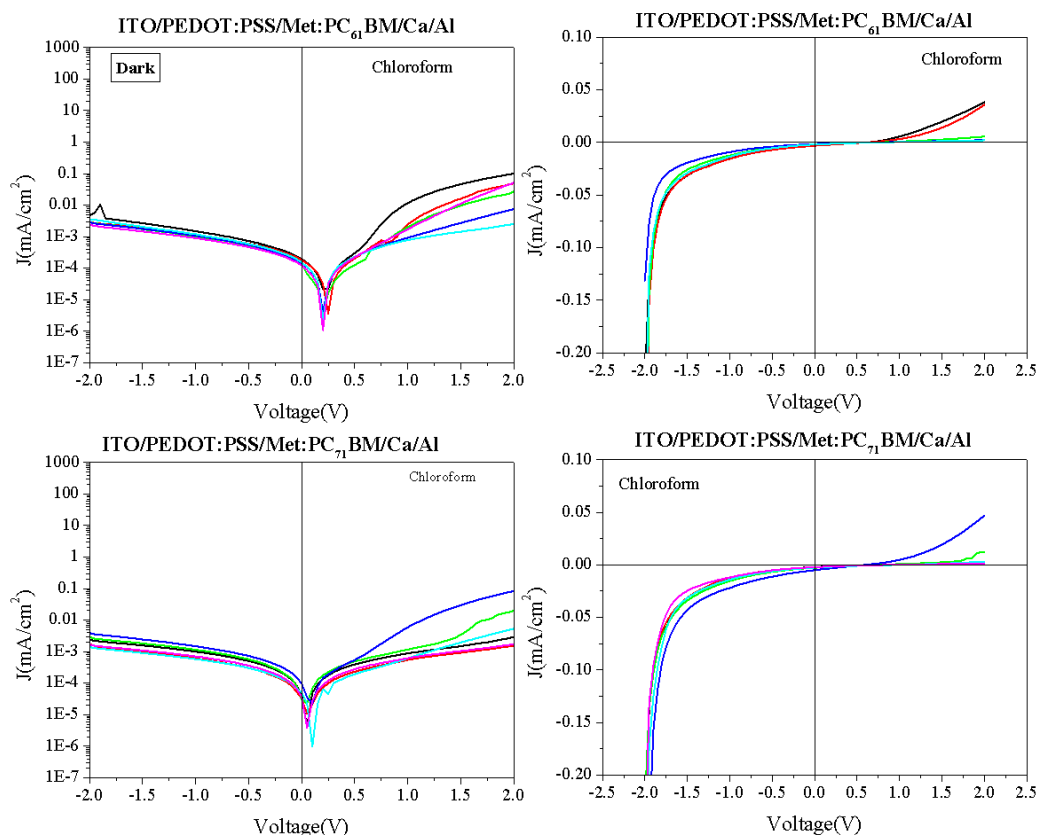


Figure 61 - J-V curves for the ITO/PEDOT:PSS/Met:PC₆₁BM/Ca/Al and ITO/PEDOT:PSS/Met:PC₇₁BM/Ca/Al devices under dark and illuminated.

The curves in dark (left side of Figure 61) revealed quite low RR values, showing the weak diode characteristic of these devices. The RR obtained were at the same order of the device fabricated by LS technique. Despite appearing the photovoltaic effect on the illuminated curves, the efficiency is $\sim 10^{-4}\%$, similar to the LS-based devices as well. This polymer presented a problem in dissolving properly in chloroform, and maybe the non-dissolution or the conformation of this polymer compared to the C₁₂ derivative was not favourable to attain the OPV devices. The solvent plays an important role in the solubility of a material, its conformation [197] and morphology as thin films [229,230]. Additionally, chlorobenzene (CB) derivatives constitute solvents highly used in the OPV devices, specially built from low-bandgap polymers [150,231]. Ergo, solutions of the polymers mixed to the PC₇₁BM in CB were utilized to make devices to test the photovoltaic ability. Figure 62 displays the J vs. V curves, under dark and illumination, for the devices containing the polymer:PC₇₁BM assembled utilizing the CB as the solvent.

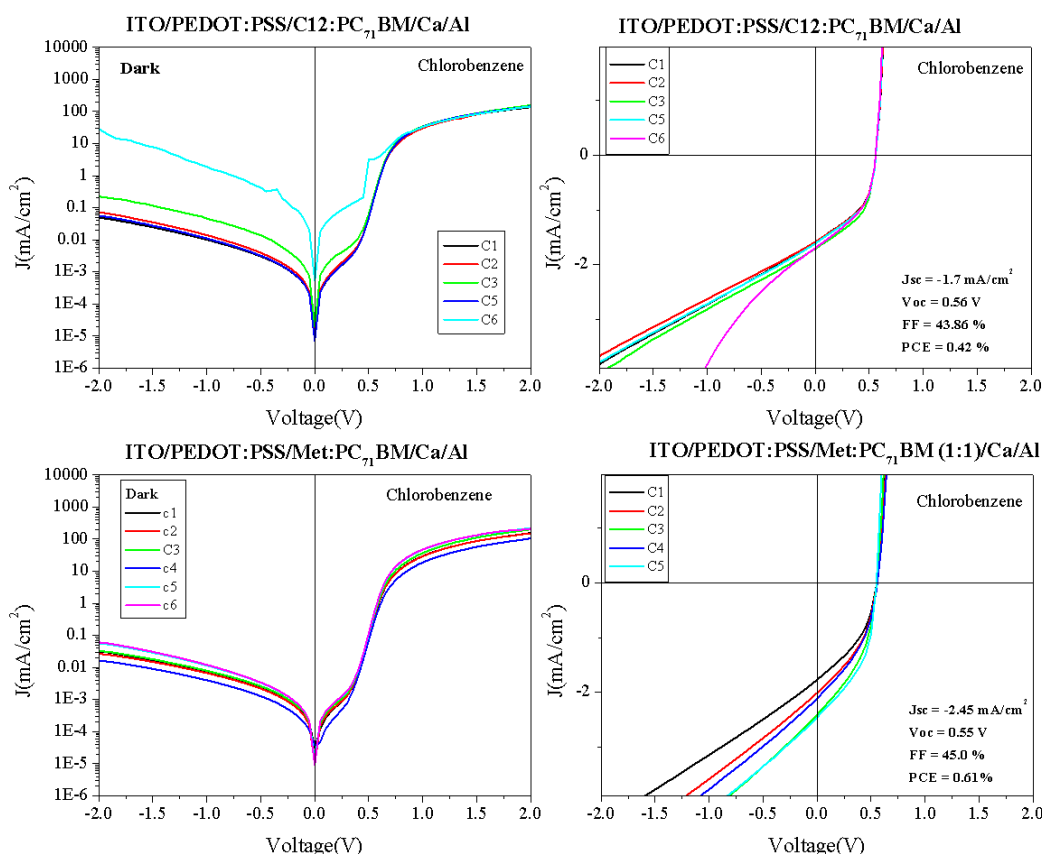


Figure 62 - J-V curves for the ITO/PEDOT:PSS/Met:PC₇₁BM/Ca/Al and ITO/PEDOT:PSS/C12:PC₇₁BM/Ca/Al devices under dark and illuminated.

Ignoring the cyan curve for the current density in dark for the PCPDTDPP_C12:PC₇₁BM (Figure 62.a), the rectification ratios found stayed between 700 and 3000, while for the PCPDTDPP_Met:PC₇₁BM with the light off (Figure 62.c) the RR was kept at 10^3 as it happened for the same sampled manufactured from a CHCl₃ solution. In the OPV curves, the C12 device showed an increase in the power conversion efficiency as a result of the solvent modification. As for the OPV device based on PCPDTDPP_Met, the use of CB caused the growth of the photovoltaic effect plainly visible on the graph, as a consequence the PCE rose up to 1000 times more than the sample from the CHCl₃ solution, reaching a PCE of 0.61%. There is a small decrease in the V_{oc} of the Met in relation to the C12 sample, and this is a result expected when a material has lower oxidation potential than other [152].

Comparing the attained results for all the fabricated devices, from the considerable PCE achieved, they are within the efficiency range estimated for low-bandgap polymers with rather similar structure reported in the literature which presented PCE values between 0.05 and 1.7% [61,139,152]. However, there are many things that could improve the performance of the devices, such as: the detailed study of the

proportion between the polymer:fullerene, changes of solvents, the solution concentration, the set of the temperature annealing, the use of other intermediary layers, the test as OPV of the inverted device structure and the insertion of additives that tune the domains of the films, taking all these examples into account, the cell showed a good efficiency result.

The LUMO-LUMO offset between the polymers and the PC₆₁₍₇₁₎BM need to be enough to have a sufficient driving force for charge separation, and it is usually estimated that a minimum offset of ~0.4 eV between the LUMO levels of electron donor and acceptor is necessary for efficient photoinduced charge transfer. Therefore, it would be expected that the using the PC₇₁BM, where the LUMO-LUMO offset is 0.7 eV, should produce a better device performance than when utilizing the PC₆₁BM where this value is 0.1 eV, this can be seen on the energy diagram, constructed from the UV-Vis and Voltammetry results, in Figure 63. Although, this does not appear on the J_{SC} outcome, which is normally the variable that is affected by such effect [152]. As shown in previous studies, a driving force below 0.2 eV can restrict or perhaps inhibit the charge dissociation at the polymer-fullerene interface [232,233]. Nonetheless, the charged carriers that are produced appear to be extracted fairly efficiently, as suggested by a reasonable FF of ~0.40.

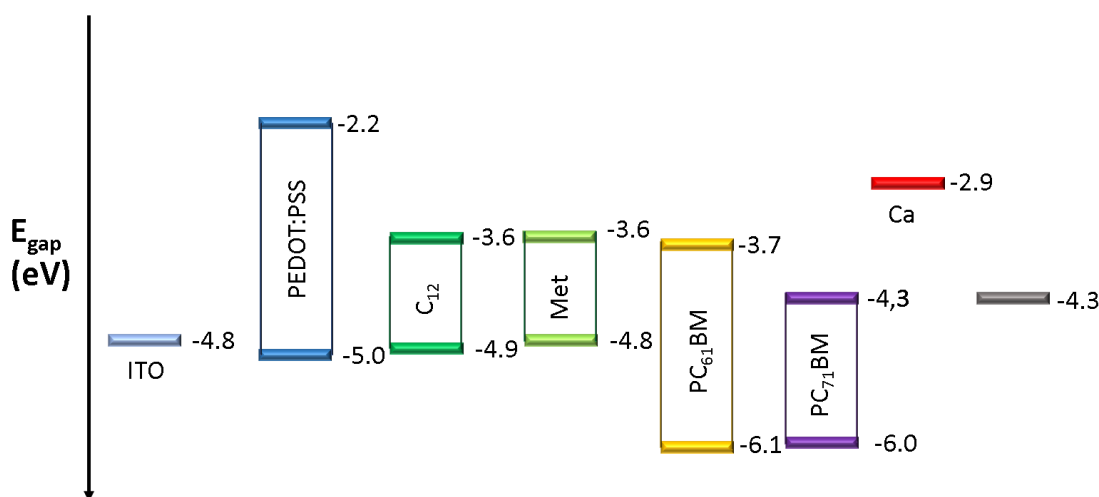


Figure 63 – Energy diagram of the materials used on the OPV devices.

Another fact that stood out is the lack of a tendency for the current to reach its saturation value, which happened for all the devices but more evidently for the ones fabricated with CB solutions. The saturation current is associated with the material properties and the junction configurations [234]. When the saturation occurs, it suggests that all photogenerated excitons are dissociated into free carriers and all carriers are

collected at the electrodes without any bimolecular recombination [235]. Thus, it seems in this current work that the recombination is rather high for the studied devices.

The morphology of the active layer in a bulk heterojunction solar cell is also important to the overall photovoltaic performance. Spin-coating from different solvents affect charge separation efficiency and charge carrier mobility [232]. The morphology of the active layers was investigated by AFM (Figure 64), that consist of the images of the fabricated configurations: ITO/PEDOT:PSS/PCPDTDPP_C₁₂:PC₆₁BM, ITO/PEDOT:PSS/PCPDTDPP_Met:PC₆₁BM, ITO/PEDOT:PSS/PCPDTDPP_C₁₂:PC₇₁BM and ITO/PEDOT:PSS/PCPDTDPP_Met:PC₇₁PBM in chloroform solutions, and the ITO/PEDOT:PSS/polymers:PC₇₁PBM devices in chlorobenzene solution.

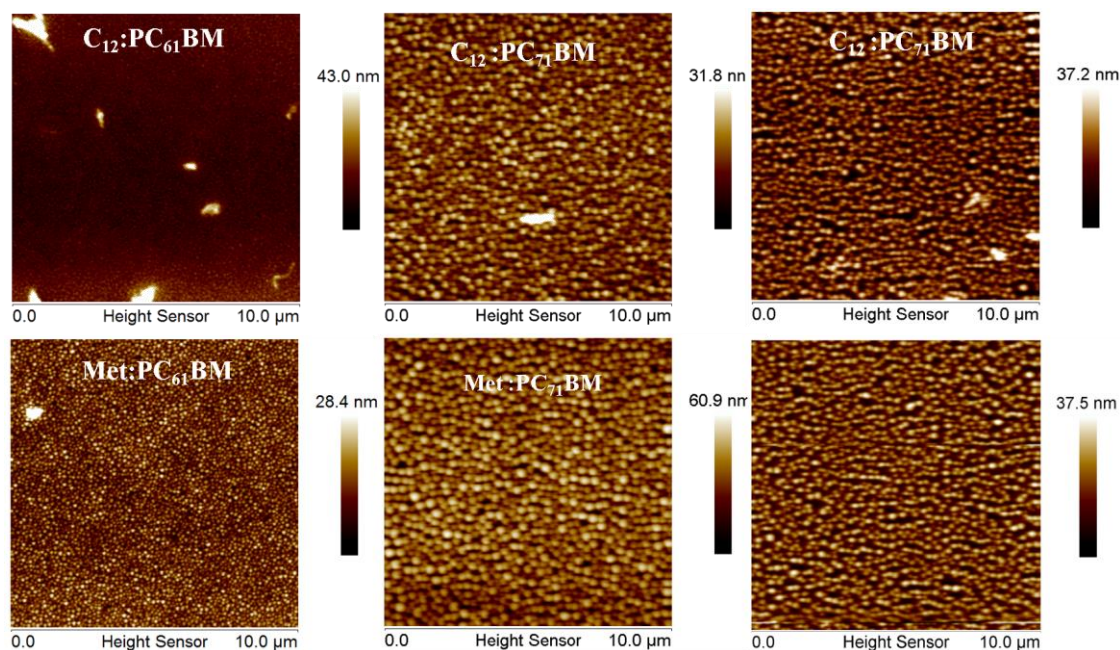


Figure 64 – AFM images for the spin films from CHCl₃ solutions of the a) C₁₂:PC₆₁BM, b) C₁₂:PC₇₁BM, d) Met:PC₆₁BM, e) Met:PC₇₁BM, and from CB solutions of the c) C₁₂:PC₇₁BM, f) Met:PC₇₁BM, all of them over the ITO/PEDOT:PSS system.

All blends presented homogeneous films (their roughness remained between 2-8 nm), even though the domains had rather different sizes, it is clear the bigger domains for the PCPDTDPP/Met based films, this increase also happens when the fullerene derivative used is the PC₇₁BM and for the devices fabricated from CB solutions when compared to the CHCl₃. From the devices done using the CHCl₃ (Figure 64.a, b, d and e), it looks like the PC₆₁BM interacted more distinctly with each polymer, result also observed on the LS characterizations. The films uniformity may indicate that a relative intimate mixing of the two components exists that itself would not prevent charge generation.

The images for the films using the CB as solvent on (Figure 64.c and f), also showed the difference on the interaction of the fullerene with each polymer. Again, the portions have smaller sizes for the PCPDTDPP_C₁₂ film. Correlating with the suchlike samples fabricated from the chloroform solution, the domains displayed divergent features, where the distance between the clusters is higher for the CB, and this modification on the morphology, probably coming from a global conformation change, can be the responsible for the contrasting outcome on the OPV device of the PCPDTDPP_Met samples.

Chapter 6 - Conclusions

Low-bandgap polymers, PCPDTDPP_C₁₂ and PCPDTDPP_Met, were synthesized during the period of the PhD in France possessing high molecular weight they were envisioned, mainly, to be used as active layer for solar cells. Nonetheless, besides this technological application, the knowledge concerning these polymers is indispensable, therefore, these materials underwent optical, morphological, conformational and electrical characterization, and furtherly they were tested as OPV devices.

Langmuir films revealed the influence of the DPP unit branch of each polymer on the monolayer conformation, where it can be seen the rather distinct surface pressure isotherms curves. The insertion of PC₆₁BM at the Langmuir through showed the great interaction of the polymers with this fullerene derivative, although this interaction resulted in different conformation on the Langmuir films. This trend seems to be also happening for the solid films, which can be observed by the LS films AFM images, where after PCBM addition the pristine polymer character is still the film strongest feature.

The UV-Vis spectra displayed the low optical bandgap of the films, seeing through its high wavelengths, emphasizing that the PCPDTDPP_Met has the smallest bandgap when compared to the DPP alkylated-chain polymer. These spectra present typical optical absorption of low-bandgap polymers, however, the PCBM addition caused a redshift on the PCPDTDPP_Met spectrum, the same effect did not occur for the PCPDTDPP_C₁₂. Raman scattering and FTIR results did not indicate any chemical changes on the solid films after the PCBM introduction onto them, and no degradation of films over time. These measurements also confirmed the disparity of the polymer self-assembly onto the substrates.

From XPS results the surface analysis could be more precise, and it showed that the amount of the PCBM on the surfaces presented substantial discrepancy seeing on the polymer:PCBM ration, given by the conformation of each polymer since the Langmuir through until after its deposition over the solid substrate.

In the electrochemistry measures, the cyclic voltammetry provided a manner to estimate the energy diagrams of the polymers, making it possible a better analysis of the system interfaces. While the Raman *in situ* enlightened the conditions of the chemical species during the redox process. Finally, in the Bode phase plots, when applied a low

potential the polymers seem to have polaronic and electronic transport, and in high potentials, there is also the bipolaronic conduction for the PCPDTDPP_Met films.

In the electrical measurements in direct current, it can be stated that the thin films without encapsulating do not present good stability. The LS film from pristine PCPDTDPP_C₁₂ showed higher conductivity in the IDE than the pristine PCPDTDPP_Met in the dc electrical measurements, and while the PCBM presence apparently tuned the conductivity outcome of the PCPDTDPP_C₁₂, the opposite happened for the PCPDTDPP_Met:PCBM films. Notwithstanding, for the alternating current electrical measurements, on the Schottky diode curves, the PCPDTDPP_Met-based devices revealed the highest conductivity. The impedance outcome, arising from the ac current graphs, demonstrated high total resistances for all the researched polymers. Accentuating that the devices with ITO/PEDOT:PSS/Polymer:PCBM/Al configuration had the smaller total resistances when compared to the ITO/Polymer:PCBM/PEDOT:PSS/Al configuration.

Regarding the OPV devices for the LS films, the J vs. V curves did not present a typical OPV plot, besides the low fill factor and not photovoltaic parameters. The spin-coating films, fabricated under controlled atmosphere, depicted better J vs. V plots, and an efficiency up to 0.6%, nevertheless, the devices with the PCPDTDPP_Met:PCBM as active layer only showed efficiency when chlorobenzene substituted the chloroform as the processing solvent.

Complementary information

⌘ Published and accepted papers:

- a) Silva, E. A.; Oliveira, V. J. R.; Braunger, M. L.; Constantino, C. J. L.; Olivati, C. A. *Poly(3-octylthiophene)/stearic Acid Langmuir and Langmuir-Blodgett films: Preparation and characterization*. **Materials Research**, v.17, p.1442 - 1448, 2014.
- b) Bento, Danielly C. da Silva, Edilene A. Olivati, Clarissa A. Louarn, G. Santana, Henrique. *Characterization of the interaction between P3ATs with PCBM on ITO using in situ Raman spectroscopy and electrochemical impedance spectroscopy*. **Journal of Materials Science. Materials in Electronics**, v. 26, n. 10, p. 7844-7852, 2015.
- c) Silva, Edilene A.; Caseli, Luciano; Olivati, Clarissa A. *Organization of polythiophenes at ultrathin films mixed with stearic acid investigated with polarization modulation infrared reflection/absorption spectroscopy*. **Colloids and Surfaces A- Physicochemical and Engineering aspects**, v.529, p.628 - 633, 2017.
- d) Oliveira, V. J. R.; Silva, E. A; Olivati, C. A. *Fabricação e caracterização de filmes finos de OC8OC8-PPV aplicados em dispositivos sensores de umidade*. **Journal of Experimental Techniques and Instrumentation (JETI)**, v.1, p.27 - 40, 2018.
- e) Braunger, Maria Luisa; A. da Silva, Edilene; Awada, Hussein; R. de Oliveira, Vinícius Jessé; S Silva, Hugo; Bégué, Didier; Hiorns, Roger C.; Lartigau-Dagron, Christine; A. Olivati, Clarissa. *Langmuir and Langmuir-Blodgett films of Low - bandgap Polymers*. **Polymer International**, v. 66, p. 1-7, 2018.
- f) Vinicius Jessé Rodrigues de Oliveira, Edilene Assunção da Silva, Maria Luisa Braunger, Hussein Awada, Henrique de Santana, Roger Hiorns, Christine Lartigau-Dagron, Clarissa de Almeida Olivati. *Molecular organization relationship of low-bandgap polymers at the air-water interface and in solid films*. **Journal of Molecular Liquids**.

⌘ Submitted or on final stage

- a) Lucas V. L. Citolino, Edilene A. da Silva, Clarissa A. Olivati. Langmuir-Schaefer films of P3HT mixed with stearic acid: influence of the amphiphilic molecule addition on the film nanostructure. *Journal of Polymer Science Part B: Polymer Physics*.
- b) Edilene A. da Silva, Maria Luisa Braunger, Clarissa A. Olivati. Fabrication, Characterization and VOCs sensing characteristics of Langmuir-Blodgett films from poly(3-alkylthiophene) derivatives mixed with stearic acid.
- c) Lucas K. M. Roncaselli, Edilene A. Silva, Maria Luisa Braunger, Marystela Ferreira, Henrique de Santana, Clarissa A. Olivati. Regioregularity and nanostructure effect in the physical/chemical properties of polythiophene derivatives films.

References

- [1] L. Lu, T. Zheng, Q. Wu, A.M. Schneider, D. Zhao, L. Yu, Recent Advances in Bulk Heterojunction Polymer Solar Cells, *Chem. Phys. Lett.* 115 (2015) 12666–12731. doi:10.1021/acs.chemrev.5b00098.
- [2] J. Turner, A. V. Parisi, D.J. Turnbull, Reflected solar radiation from horizontal , vertical and inclined surfaces : Ultraviolet and visible spectral and broadband behaviour due to solar zenith angle , orientation and surface type, *J. Photochem. Photobiol. B Biol.* 92 (2008) 29–37. doi:10.1016/j.jphotobiol.2008.03.006.
- [3] A.M. Bagher, Introduction to Organic Solar Cells, *Sustain. Energy.* 2 (2014) 85–90. doi:10.12691/rse-2-3-2.
- [4] B.G.A.L. Borges, Estudo da estrutura eletrônica e transferência de carga de polímeros derivados do tiofeno com aplicação em dispositivos fotovoltaicos, Universidade Federal do Rio de Janeiro, 2015.
- [5] T. Ameri, P. Khoram, J. Min, C.J. Brabec, M.O.E.L.U. Mo, Organic Ternary Solar Cells : A Review, (2013) 1–22. doi:10.1002/adma.201300623.
- [6] M.C. Scharber, N.S. Sariciftci, Efficiency of bulk-heterojunction organic solar cells, *Prog. Polym. Sci.* (2013) 1–13. doi:10.1016/j.progpolymsci.2013.05.001.
- [7] B.R. Weinberger, M. Akhtar, S.C. Gau, Polyacetylene photovoltaic devices, *Synth. Met.* 4 (1982) 187–197.
- [8] C.W. Tang, Two layer organic photovoltaic cell, *Appl. Phys. Lett.* 48 (1986) 183–185. doi:10.1063/1.96937.
- [9] M. Theander, A. Yartsev, D. Zigmantas, V. Sundström, W. Mammo, M.R. Andersson, O. Inganäs, Photoluminescence quenching at a polythiophene/C60 heterojunction, *Phys. Rev. B.* 61 (2000) 957–963.
- [10] J.J.M. Halls, K. Pichler, R.H. Friend, S.C. Moratti, A.B. Holmes, Exciton diffusion and dissociation in a poly(p-phenylenevinylene)/C60 heterojunction photovoltaic cell, *Appl. Phys. Lett.* 68 (1996) 3120–3122. doi:10.1063/1.115797.
- [11] C. Deibel, V. Dyakonov, Polymer-fullerene bulk heterojunction solar cells, *Reports Prog. Phys.* 73 (2010) 096401. doi:10.1088/0034-4885/73/9/096401.
- [12] N.S. Sariciftci, L. Smilowitz, A.J. Heeger, F. Wudl, Photoinduced Electron Transfer from a Conducting Polymer to Buckminsterfullerene., *Science* (80-.). 258 (1992) 1474–1476. doi:10.1126/science.258.5087.1474.
- [13] 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* (80-.). 270 (1995) 1789–1791. doi:10.1126/science.270.5243.1789.
- [14] R.P. Singh, O.S. Kushwaha, Progress towards efficiency of polymer solar cells, *Adv. Funct. Mater. Lett.* 8 (2017) 2–7. doi:10.5185/amlett.2017.7005.
- [15] S. Holliday, Y. Li, C.K. Luscombe, Progress in Polymer Science Recent advances in high performance donor-acceptor polymers for organic photovoltaics, *Prog. Polym. Sci.* 70 (2017) 34–51. doi:10.1016/j.progpolymsci.2017.03.003.

- [16] J.M. Chem, J. Wang, C. Lu, J. Hsu, M. Lee, Y. Hong, T. Perng, Efficient inverted organic solar cells without an electron selective layer, *J. Mater. Chem.* 21 (2011) 5723–5728. doi:10.1039/c0jm04269b.
- [17] F. Liu, Y. Gu, J.W. Jung, W.H. Jo, T.P. Russell, On the morphology of polymer-based photovoltaics, *J. Polym. Sci. Part B Polym. Phys.* 50 (2012) 1018–1044. doi:10.1002/polb.23063.
- [18] C. Liu, K. Wang, X. Gong, A.J. Heeger, Low bandgap semiconducting polymers for polymeric photovoltaics, *Chem. Soc. Rev.* 45 (2016) 4825–4846. doi:10.1039/C5CS00650C.
- [19] E. Bundgaard, F.C. Krebs, Low band gap polymers for organic photovoltaics, *Sol. Energy Mater. Sol. Cells.* 91 (2007) 954–985. doi:10.1016/j.solmat.2007.01.015.
- [20] B.C.J. Brabec, C. Winder, N.S. Sariciftci, J.C. Hummelen, A. Dhanabalan, P.A. Van Hal, R.A.J. Janssen, A Low-Bandgap Semiconducting Polymer for Photovoltaic Devices and Infrared Emitting Diodes, *Adv. Funct. Mater.* 12 (2002) 709–712. doi:10.1002/1616-3028(20021016)12.
- [21] I. Etxebarria, J. Ajuria, R. Pacios, Polymer: fullerene solar cells: materials, processing issues, and cell layouts to reach power conversion efficiency over 10 %, a review, *J. Photonics Energy.* 5 (2015) 1–25. doi:10.1117/1.JPE.5.057214.
- [22] Y. Li, Molecular Design of Photovoltaic Materials for Polymer Solar Cells: Toward Suitable Electronic Energy Levels and Broad Absorption, *Acc. Chem. Res.* 45 (2012) 723–733.
- [23] H. Chen, J. Hou, S. Zhang, Y. Liang, G. Yang, Y. Yang, Polymer solar cells with enhanced open-circuit voltage and efficiency, *Nat. Photonics.* 3 (2009) 649–653. doi:10.1038/NPHOTON.2009.192.
- [24] C. Interlayer, S. Liao, H. Jhuo, P. Yeh, Y. Cheng, Y. Li, Y. Lee, S. Sharma, S. Chen, Dual-Doped Zinc Oxide Nano-Film as, *Sci. Rep.* 4 (2014) 1–7. doi:10.1038/srep06813.
- [25] J. Chen, C. Cui, Y. Li, L. Zhou, Q. Ou, Single-Junction Polymer Solar Cells Exceeding 10 % Power Conversion Efficiency, *Adv. Mater.* 27 (2014) 1035–1041. doi:10.1002/adma.201404535.
- [26] B. de Boer, P.F. van Hutten, L. Ouali, V. Grayer, G. Hadziioannou, Amphiphilic, Regioregular Polythiophenes, *Macromolecules.* 35 (2002) 6883–6892. doi:10.1021/ma011591w.
- [27] F.J. Pavinatto, L. Caseli, O.N. Oliveira, Chitosan in nanostructured thin films, *Biomacromolecules.* 11 (2010) 1897–1908. doi:10.1021/bm1004838.
- [28] L. Gaffo, V. Zucolotto, M.R. Cordeiro, W.C. Moreira, O.N. Oliveira, F. Cerdeira, M.J.S.P. Brasil, Structural aspects of Langmuir–Blodgett and cast films of zinc phthalocyanine and zinc hexadecafluorophthalocyanine, *Thin Solid Films.* 515 (2007) 7307–7312. doi:10.1016/j.tsf.2007.03.050.
- [29] H. Bai, G. Shi, Gas Sensors Based on Conducting Polymers, *Sensors.* 7 (2007) 267–307. doi:10.3390/s7030267.
- [30] R. Rella, P. Siciliano, F. Quaranta, T. Primo, L. Valli, L. Schenetti, A. Mucci, Gas

- sensing measurements and analysis of the optical properties of poly [3-(butylthio)thiophene] Langmuir–Blodgett films, *Sensors Actuators B Chem.* 68 (2000) 203–209.
- [31] R. Rodríguez, J. Ignés-Mullol, F. Sagués, E. Quiñoá, R. Riguera, F. Freire, Helical sense selective domains and enantiomeric superhelices generated by Langmuir–Schaefer deposition of an axially racemic chiral helical polymer, *Nanoscale*. 8 (2016) 3362–3367. doi:10.1039/C5NR07990J.
- [32] M. Sano, A. Kamino, J. Okamura, S. Shinkai, Self-Organization of PEO-graft-Single-Walled Carbon Nanotubes in Solutions and Langmuir-Blodgett Films, *Langmuir*. 17 (2001) 5125–5128.
- [33] M.L. Braunger, A. Barros, M. Ferreira, C.A. Olivati, Electrochimica Acta Electrical and electrochemical measurements in nanostructured films of polythiophene derivatives, *Electrochim. Acta*. 165 (2015) 1–6. doi:10.1016/j.electacta.2015.02.232.
- [34] Aoki Atsushi, Fukuyama Shinya, Organic Thin Film Solar Cell Composed of Hetero-Deposited Langmuir-Blodgett Films, *Electrochemistry*. 78 (2010) 178–180. doi:10.5796/electrochemistry.78.178.
- [35] J. Sołoducho, J. Cabaj, A. Swist, Structure and sensor properties of thin ordered solid films., *Sensors (Basel)*. 9 (2009) 7733–52. doi:10.3390/s91007733.
- [36] M.K. Ram, M. Adami, M. Sartore, M. Salerno, S. Paddeu, C. Nicolini, Comparative studies on Langmuir-Schaefer films of polyanilines, *Synth. Met.* 100 (1999) 249–259. doi:10.1016/S0379-6779(99)00024-7.
- [37] W.C.H. Choy, ed., *Organic Solar Cells: Materials and Device Physics*, 1st ed., Springer-Verlag London, London, 2013. doi:10.1007/978-1-4471-4823-4.
- [38] V.C. Gonçalves, *Síntese e caracterização de derivados do politiofeno para utilização em sensores*, Universidade de São Paulo, 2010.
- [39] C.K. Chiang, C.R. Fincher, Y.W. Park, A.J. Heeger, H. Shirakawa, E.J. Louis, S.C. Gau, A.G. MacDiarmid, A.J. Heeger, E.J. Louis, S.C. Gau, Electrical conductivity in doped polyacetylene, *Phys. Rev. Lett.* 39 (1977) 1098–1101. doi:10.1103/PhysRevLett.39.1098.
- [40] C.O. Yoon, M. Reghu, D. Moses, A.J. Heeger, Y. Cao, T. Chen, X. Wu, R.D. Rieke, Hopping transport in doped conducting polymers in the insulating regime near the metal-insulator boundary: polypyrrole, polyaniline and polyalkylthiophenes, *Synth. Met.* 75 (1995) 229–239.
- [41] J. Bredas, G. Street, Polarons, bipolarons, and solitons in conducting polymers, *Acc. Chem. Res.* 1305 (1985) 309–315.
- [42] A.J. Heeger, Semiconducting and Metallic Polymers: The Fourth Generation of Polymeric Materials †, *J. Phys. Chem. B*. 105 (2001) 8475–8491. doi:10.1021/jp011611w.
- [43] C. Kuhn, Solitons, polarons, and excitons in polyacetylene: Step-potential model for electron-phonon coupling in π -electron systems, *Phys. Rev. B*. 40 (1989) 7776–7787.

- [44] A.G. Macdiarmid, Synthetic metals : a novel role for organic polymers, *Synth. Met.* 125 (2002) 11–22.
- [45] J. Nelson, Polymer:fullerene bulk heterojunction solar cells, *Mater. Today*. 14 (2011) 462–470. doi:10.1016/S1369-7021(11)70210-3.
- [46] R.R. Lunt, T.P. Osedach, P.R. Brown, J.A. Rowehl, V. Bulovic, Practical Roadmap and Limits to Nanostructured Photovoltaics, *Adv. Mater.* 23 (2011) 5712–5727. doi:10.1002/adma.201103404.
- [47] B. Schweitzer, V.I. Arkhipov, H. Bässler, Field-induced delayed photoluminescence in a conjugated polymer, *Chem. Phys. Lett.* 304 (1999) 365–370. doi:10.1016/S0009-2614(99)00260-2.
- [48] E.L. Frankevich, A.A. Lymarev, I. Sokolik, F.E. Karasz, S. Blumstengel, R.H. Baughman, H.H. & Hörhold, Polaron-pair generation in poly(phenylene vinylenes), *Phys. Rev. B*. 46 (1992) 9320–9324.
- [49] J. Guo, H. Ohkita, H. Benten, S. Ito, Charge Generation and Recombination Dynamics in Poly (3-hexylthiophene)/ Fullerene Blend Films with Different Regioregularities and Morphologies, *J. Am. Chem. Soc.* 132 (2010) 6154–6164. doi:10.1002/adma.200903528.(11).
- [50] R. Tautz, E. Da Como, T. Limmer, J. Feldmann, H. Egelhaaf, E. Von Hauff, V. Lemaure, D. Beljonne, S. Yilmaz, I. Dumsch, S. Allard, U. Scherf, Structural correlations in the generation of polaron pairs in low-bandgap polymers for photovoltaics, *Nat. Commun.* 3 (2012) 970–978. doi:10.1038/ncomms1967.
- [51] A.J. Heeger, 25th Anniversary Article : Bulk Heterojunction Solar Cells : Understanding the Mechanism of Operation, *Adv. Energy Mater.* 26 (2014) 10–28. doi:10.1002/adma.201304373.
- [52] A.F. Nogueira, I. Montanari, J. Nelson, J.R. Durrant, C. Brabec, Charge Recombination in Conjugated Polymer / Fullerene Blended Films Studied by Transient Absorption Spectroscopy, *J. Phys. Chem. B*. 107 (2003) 1567–1573.
- [53] A.J. Moulé, J.B. Bonekamp, K. Meerholz, The effect of active layer thickness and composition on the performance of bulk-heterojunction solar cells, *J. Appl. Phys.* 100 (2006) 094503. doi:10.1063/1.2360780.
- [54] J.W. Jung, J.W. Jo, E.H. Jung, W.H. Jo, Recent progress in high efficiency polymer solar cells by rational design and energy level tuning of low bandgap copolymers with various electron-withdrawing units, *Org. Electron.* 31 (2016) 149–170. doi:10.1016/j.orgel.2016.01.034.
- [55] A. Punzi, F. Nicoletta, G. Marzano, C.G. Fortuna, J. Dagar, T.M. Brown, G.M. Farinola, Synthetic Routes to TEG-Substituted Diketopyrrolopyrrole-Based Low Band-Gap Polymers, *European J. Org. Chem.* 2016 (2016) 3233–3242. doi:10.1002/ejoc.201600406.
- [56] J. Mei, SOLUTION-PROCESSABLE ORGANIC SEMICONDUCTING MATERIALS FOR PHOTOVOLTAIC APPLICATIONS, Universidade da Florida, 2010.
- [57] Y.-J. Cheng, Sh.-H. Yang, C.-S. Hsu, Synthesis of conjugated polymers for organic solar cell applications, *Chem. Rev.* 109 (2009) 5868–923. doi:10.1021/cr900182s.

- [58] Z. He, C. Zhong, S. Su, M. Xu, H. Wu, Y. Cao, Enhanced power-conversion efficiency in polymer solar cells using an inverted device structure, *Nat. Photonics*. 6 (2012) 591–595. doi:10.1038/NPHOTON.2012.190.
- [59] A. Gregori, *Synthesis of Conjugated Polymers and Adhesive Properties of Thin Films in OPV Devices*, Université de Pau et des Pays de L'Adour, 2015.
- [60] L. Bürgi, M. Turbiez, R. Pfeiffer, F. Bienewald, H.-J. Kirner, C. Winneswisher, High-Mobility Ambipolar Near-Infrared Light-Emitting Polymer Field-Effect Transistors, *Adv. Mater.* 20 (2008) 2217–2224. doi:10.1002/adma.200702775.
- [61] J. Mei, K.R. Graham, R. Stalder, S.P. Tiwari, H. Cheun, J. Shim, M. Yoshio, C. Nuckolls, B. Kippelen, R.K. Castellano, J.R. Reynolds, Self-Assembled Amphiphilic Diketopyrrolopyrrole-Based Oligothiophenes for Field-Effect Transistors and Solar Cells, (2011) 2285–2288. doi:10.1021/cm1036869.
- [62] O. V Kozlov, V.G. Pavelyev, H.D. De Gier, R.W.A. Havenith, P.H.M. Van, J.C. Hummelen, M.S. Pshenichnikov, Ultrafast electron and hole transfer in bulk heterojunctions of low-bandgap polymers, *Org. Photonics Photovolt.* 4 (2016) 24–34. doi:10.1515/oph-2016-0003.
- [63] P.P. Boix, J. Bisquert, M. Sessolo, H.J. Bolink, Solar Energy Materials & Solar Cells Simultaneous determination of carrier lifetime and electron density-of-states in P3HT: PCBM organic solar cells under illumination by impedance spectroscopy, *Sol. Energy Mater. Sol. Cells.* 94 (2010) 366–375. doi:10.1016/j.solmat.2009.10.015.
- [64] R.-H. Hsu, Yu-Chen; Tseng, Lin-Chieh; Lee, Graphene oxide sheet-polyaniline nanohybrids for enhanced photovoltaic performance of dye-sensitized solar cells, *J. Polym. Sci. Part B Polym. Phys.* 52 (2014) 321–332. doi:10.1002/polb.23416.
- [65] L. Dou, J. You, Z. Hong, Z. Xu, G. Li, R. a Street, Y. Yang, 25Th Anniversary Article: a Decade of Organic/Polymeric Photovoltaic Research., *Adv. Mater.* 25 (2013) 6642–71. doi:10.1002/adma.201302563.
- [66] W.C.H. Choy, *Organic Solar Cells: Materials and Device Physics (Green Energy and Technology)*, 2013. doi:10.2174/97816080528511060101.
- [67] B.A. Gregg, M.C. Hanna, Comparing organic to inorganic photovoltaic cells: Theory, experiment, and simulation Comparing organic to inorganic photovoltaic cells: Theory, experiment, and simulation, *J. Appl. Phys.* 93 (2003) 3605–3614. doi:10.1063/1.1544413.
- [68] C. Deibel, D. Mack, J. Gorenflot, A. Schöll, S. Krause, F. Reinert, D. Rauh, V. Dyakonov, Energetics of excited states in the conjugated polymer poly(3-hexylthiophene), *Phys. Rev. B.* 81 (2010) 1–5. doi:10.1103/PhysRevB.81.085202.
- [69] I.F.L. Dias, D. Javier, C. Chávez, M. Munhoz, L.C. Poças, M. Aurélio, H. De Santana, J. Leonil, Desenvolvimento de Dispositivos Fotovoltaicos e Diodos Emissores de Luz de Corantes Naturais : novos parâmetros de sustentabilidade Development of Photovoltaic and Light Emitters Diodes Devices of Natural Dyes : new parameters of sustainability, *Semin. Ciências Exatas e Tecnológicas.* 37 (2016) 81–94. doi:10.5433/1679-0375.2016v37n2p81.
- [70] M.C. Scharber, D. Mühlbacher, M. Koppe, P. Denk, C. Waldauf, A.J. Heeger, C.J.

- Brabec, Design rules for donors in bulk-heterojunction solar cells - Towards 10 % energy-conversion efficiency, *Adv. Mater.* 18 (2006) 789–794. doi:10.1002/adma.200501717.
- [71] L.J.A. Koster, E.C.P. Smits, V.D. Mihailetschi, P.W.M. Blom, Device model for the operation of polymer/fullerene bulk heterojunction solar cells, *Phys. Rev. B - Condens. Matter Mater. Phys.* 72 (2005) 1–9. doi:10.1103/PhysRevB.72.085205.
- [72] C.M. Proctor, M. Kuik, T.-Q. Nguyen, Charge carrier recombination in organic solar cells, *Prog. Polym. Sci.* 38 (2013) 1941–1960. doi:10.1016/j.progpolymsci.2013.08.008.
- [73] J. Brabec, A. Cravino, D. Meissner, N. Sariciftci, T. Fromherz, M. Rispens, L. Sanchez, J. Hummelen, Origin of the open circuit voltage of plastic solar cells, *Adv. Funct. Mater.* 11 (2001) 374–380. doi:10.1002/1616-3028(200110)11.
- [74] M.L. Braunger, Fabrication and electrical characterization of solar cells from organic thin films, UNESP, 2015.
- [75] J.K. Lee, W.L. Ma, C.J. Brabec, J. Yuen, J.S. Moon, J.Y. Kim, K. Lee, G.C. Bazan, A.J. Heeger, Processing additives for improved efficiency from bulk heterojunction solar cells., *J. Am. Chem. Soc.* 130 (2008) 3619–23. doi:10.1021/ja710079w.
- [76] Y. Sun, G.C. Welch, W.L. Leong, C.J. Takacs, G.C. Bazan, A.J. Heeger, Solution-processed small-molecule solar cells with 6.7% efficiency., *Nat. Mater.* 11 (2012) 44–8. doi:10.1038/nmat3160.
- [77] F. Yang, M. Shtein, S.R. Forrest, Controlled growth of a molecular bulk heterojunction photovoltaic cell, *Nat. Mater.* 4 (2004) 37–41. doi:10.1038/nmat1285.
- [78] G. LI, V. SHROTRIYA, J. HUANG, Y. YAO, T. MORIARTY, K. EMERY, Y. YANG, High-efficiency solution processable self-organization of polymer blends, *Nat. Mater.* 4 (2005) 864–868. doi:10.1038/nmat1500.
- [79] G. Li, R. Zhu, Y. Yang, Polymer solar cells, *Nat. Photonics.* 6 (2012) 154–161. doi:10.1038/nphoton.2012.11.
- [80] C.J. Traverse, M. Young, S. Wagner, P. Zhang, P. Askeland, M.C. Barr, R.R. Lunt, Efficient zinc sulfide cathode layers for organic photovoltaic applications via n-type doping, *J. Appl. Phys.* 115 (2014) 1–5. doi:10.1063/1.4878155.
- [81] Z. He, B. Xiao, F. Liu, H. Wu, Y. Yang, S. Xiao, C. Wang, T.P. Russell, Y. Cao, Single-junction polymer solar cells with high efficiency and photovoltage, *Nat. Mater.* 6 (2015) 1–6. doi:10.1038/nphoton.2015.6.
- [82] Y. Liu, J. Zhao, Z. Li, C. Mu, W. Ma, H. Hu, K. Jiang, H. Lin, Aggregation and morphology control enables multiple cases of high-efficiency polymer solar cells, *Nat. Commun.* 5 (2014) 1–8. doi:10.1038/ncomms6293.
- [83] Application Note Series Electrical Characterization of Photovoltaic Materials and Solar Cells with the Model 4200-SCS Semiconductor Characterization System, Keithley Appl. Note Ser. Number 3026. (2011).
- [84] D.Ro.B. Amorim, Análise teórico-experimental sobre mecanismos de transporte

em células solares orgânicas de P3HT e PCBM, USP, 2018.

- [85] Sigma Adrich, (n.d.). http://www.sigmaaldrich.com/catalog/product/aldrich/684449?lang=pt®ion=BR&gclid=Cj0KEQjwxbDIBRCL99Wls-nLicoBEiQAWroh6i7cHQZjzHAGmV5VivUSa-FeFvkoj_9oj_gDIRZlk1YaAthe8P8HAQ.
- [86] J.C. Bijleveld, B.P. Karsten, S.G.J. Mathijssen, M.M. Wienk, D.M. de Leeuw, R. a. J. Janssen, Small band gap copolymers based on furan and diketopyrrolopyrrole for field-effect transistors and photovoltaic cells, *J. Mater. Chem.* 21 (2011) 1600. doi:10.1039/c0jm03137b.
- [87] J.B. Lambert, E.P. Mazzola, Nuclear magnetic resonance spectroscopy: An introduction to principles, applications, and experimental methods, Pearson Education Inc., Upper Saddle River, New Jersey, 2003.
- [88] S. Arul, M. Easwaramoorthi, M. Meikandan, Different types of PVD coatings and their demands - A review, *Int. J. Appl. Eng. Res.* 9 (2014) 26417–26430.
- [89] P. Alessio, R.F. de Oliveira, P.H.B. Aoki, J.D. a. S. Pereira, M.L. Braunger, L.N. Furini, M. Vieira, S.R. Teixeira, a. E. Job, C. a. T. Saenz, N. Alves, C. a. Olivati, C.J.L. Constantino, Molecular Architecture and Electrical Properties in Evaporated Films of Cobalt Phthalocyanine, *J. Nanosci. Nanotechnol.* 12 (2012) 7010–7020. doi:10.1166/jnn.2012.6583.
- [90] D. Çaycı, S.G. Stanciu, İ. Çapan, M. Erdoğan, B. Güner, R. Hristu, G. a. Stanciu, The influence of the surface morphologies of Langmuir Blodgett (LB) thin films of porphyrins on their gas sensing properties, *Sensors Actuators B Chem.* 158 (2011) 62–68. doi:10.1016/j.snb.2011.05.033.
- [91] C. Nicolini, R. Narizzano, V. Bavastrello, New materials by organic nanotechnology and their applications, *Recent Res. Dev. Mater. Sci.* 661 (2005) 1–24. [http://old.arpal.gov.it/Pubbl/paper/New Materials by Organic Nanotechnology a.pdf](http://old.arpal.gov.it/Pubbl/paper/New_Materials_by_Organic_Nanotechnology_a.pdf) (accessed April 8, 2014).
- [92] Y. Ren, K. Iimura, T. Kato, Structure of Barium Stearate Films at the Air/Water Interface Investigated by Polarization Modulation Infrared Spectroscopy and π -A Isotherms, *Langmuir.* 17 (2001) 2688–2693. doi:10.1021/la000872e.
- [93] A. Chyla, S. Kucharski, R. Janik, J. Sworakowski, M. Bieńkowski, Two-component Langmuir and Langmuir-Blodgett films containing monomeric and polymeric alkylheteroaromates: surface plasmon resonance and electrical conductivity, *Thin Solid Films.* 284–285 (1996) 496–499. doi:10.1016/S0040-6090(95)08375-8.
- [94] F.J. Pavinatto, Interação entre quitosana e modelos de membrana celular : filmes de Langmuir e Langmuir-Blodgett (LB), Universidade de São Paulo, 2010.
- [95] C. Curcino, C. Vieira, Universidade de São Paulo Instituto de Química, (2010).
- [96] M.C. Petty, Molecular electronics: from principles to practice, 2007. doi:10.1002/9780470723890.
- [97] Y. Kim, S. Cook, S.M. Tuladhar, S.A. Choulis, J. Nelson, J.R. Durrant, D.D.C. Bradley, M. Giles, I. McCulloch, C.-S. Ha, M. Ree, A strong regioselectivity effect

- in self-organizing conjugated polymer films and high-efficiency polythiophene:fullerene solar cells, *Nat. Mater.* 5 (2006) 197–203. doi:10.1038/nmat1574.
- [98] A. MARLETTA, PROPRIEDADES ÓPTICAS DE SEMICONDUTORES ORGÂNICOS À BASE DE POLÍMEROS EMISSORES DE LUZ, Universidade de São Paulo, 2001.
- [99] Spin Coating: A Guide to Theory and Techniques, (n.d.). <https://www.ossila.com/pages/spin-coating> (accessed May 5, 2017).
- [100] a. H. Reshak, M.M. Shahimin, N. Juhari, R. Vairavan, Photovoltaic characteristics of hybrid MEH-PPV-nanoparticles compound, *Curr. Appl. Phys.* 13 (2013) 1894–1898. doi:10.1016/j.cap.2013.07.023.
- [101] J.R. Cordeiro, Síntese e Aplicação de Polímeros Condutores em Sensores Olfativos, Universidade de São Paulo, 2010.
- [102] P. Alessio, Poliuretana contendo corante azóico e espaçador tipo bis- carbonato como material para fabricação de filmes nanoestruturados, Universidade Estadual Paulista, 2008.
- [103] D.A. Skoog, F.J. Holler, T.A. Nieman, Principles of Instrumental Analysis, 6th ed., Thomson Brooks/Cole, Orlando, 2007.
- [104] P. Alessio, Sensores para sistemas líquidos diluídos combinando Raman amplificado em superfície (SERS) e língua eletrônica, Unesp, 2012.
- [105] M. Fritz, M. Radmacher, J.P. Cleveland, M.W. Allersma, R.J. Stewart, R. Giesemann, P. Janmey, C.F. Schmidt, P.K. Hansma, Imaging Globular and Filamentous Proteins in Physiological Buffer Solutions with Tapping Mode Atomic Force Microscopy, *Langmuir*. 11 (1995) 3529–3535.
- [106] G. Bar, Y. Thomann, R. Brandsch, H. Cantow, Factors Affecting the Height and Phase Images in Tapping Mode Atomic Force Microscopy. Study of Phase-Separated Polymer Blends of Poly (ethylene-co-styrene) and Poly (2,6-dimethyl-1,4-phenylene oxide), *Langmuir*. 13 (1997) 3807–3812.
- [107] Q. Thong, D. Inniss, Fractured polymer / silica fiber surface studied by tapping mode atomic force microscopy, *Surf. Sci. Lett.* 290 (1993) L688–L692. doi:10.1016/0039-6028(93)90582-5.
- [108] E.A. da Silva, Efeito da adição de moléculas anfifílicas na formação de filmes langmuir e langmuir- blodgett de derivados alquilados do politiofeno: aplicação em sensores, Universidade Estadual Paulista, 2014.
- [109] S. Barth, H. Ba, H. Rost, H.H. Ho, Extrinsic and intrinsic dc photoconductivity in a conjugated polymer, 56 (1997) 3844–3851.
- [110] J. Kumar, R.K. Singh, S. Chand, V. Kumar, R.C. Rastogi, R. Singh, Dc Electrical Conduction and Morphology of Poly(3-Octylthiophene) Films, *J. Phys. D. Appl. Phys.* 39 (2006) 196–202. doi:10.1088/0022-3727/39/1/029.
- [111] Low Level Measurements Handbook - 7 th Edition Precision DC Current, Voltage, and Resistance Measurements, 7th ed., Tektronix, n.d. <http://www.tek.com/sites/tek.com/files/media/document/resources/LowLevelHan>

- [112] J.R. Macdonald, E. Barsoukov, Impedance spectroscopy: theory, experiment, and applications, John Wiley & Sons, 2005.
- [113] J.I. Basham, T.N. Jackson, D.J. Gundlach, Predicting the J-V Curve in Organic Photovoltaics Using Impedance Spectroscopy, *Adv. Energy Mater.* 4 (2014) 1–7. doi:10.1002/aenm.201400499.
- [114] J. Bisquert, L. Bertoluzzi, I. Mora-Sero, G. Garcia-Belmonte, Theory of impedance and capacitance spectroscopy of solar cells with dielectric relaxation, drift-diffusion transport, and recombination, *J. Phys. Chem. C.* 118 (2014) 18983–18991. doi:10.1021/jp5062144.
- [115] D.K. Mahato, T.P. Sinha, Electrical impedance and electric modulus approach of double perovskite $\text{Pr}_2\text{ZnZrO}_6$ ceramics, *J. Mater. Sci. Mater. Electron.* 24 (2013) 4399–4405. doi:10.1007/s10854-013-1416-7.
- [116] M. Glatthaar, N. Mingirulli, B. Zimmermann, T. Ziegler, R. Kern, M. Niggemann, A. Hinsch, A. Gombert, Impedance spectroscopy on organic bulk-heterojunction solar cells, *Phys. Status Solidi Appl. Mater. Sci.* 202 (2005) 125–127. doi:10.1002/pssa.200521149.
- [117] S. Taibl, G. Fafilek, J. Fleig, Impedance spectra of Fe-doped SrTiO_3 thin films upon bias voltage: inductive loops as a trace of ion motion, *Nanoscale.* 8 (2016) 13954–13966. doi:10.1039/C6NR00814C.
- [118] N. Elgrishi, K.J. Rountree, B.D. McCarthy, E.S. Rountree, T.T. Eisenhart, J.L. Dempsey, A Practical Beginner's Guide to Cyclic Voltammetry, *J. Chem. Educ.* 95 (2018) 197–206. doi:10.1021/acs.jchemed.7b00361.
- [119] G.A. Mabbott, An introduction to cyclic voltammetry, *J. Chem. Educ.* 60 (1983) 697. doi:10.1021/ed060p697.
- [120] R.P.C. Bauer, Organic Photovoltaic Devices: Atmospheric Fabrication and Characterization, University of Saskatchewan, 2016.
- [121] N. Seidler, Polythiophene Nanofibres for Optoelectronic Applications, University College of London, 2014.
- [122] M. Zukalová, A. Zukal, L. Kavan, M.K. Nazeeruddin, P. Liska, M. Grätzel, Organized mesoporous TiO_2 films exhibiting greatly enhanced performance in dye-sensitized solar cells., *Nano Lett.* 5 (2005) 1789–1792. doi:10.1021/nl051401l.
- [123] M.C. Tanese, G.M. Farinola, B. Pignataro, L. Valli, L. Giotta, S. Conoci, P. Lang, D. Colangiuli, F. Babudri, F. Naso, L. Sabbatini, P.G. Zambonin, L. Torsi, D. Chimica, C. Fisica, F. Accascina, D. Ingegneria, C.N.R. Iccom, E. Tires, Poly(alkoxyphenylene-thienylene) Langmuir-Schäfer Thin Films for Advanced Performance Transistors, *Chem. Mater.* 18 (2006) 778–784.
- [124] E. Amado, J. Kressler, Interactions of amphiphilic block copolymers with lipid model membranes, *Curr. Opin. Colloid Interface Sci.* 16 (2011) 491–498. doi:10.1016/j.cocis.2011.07.003.
- [125] A. Sakai, S.H. Wang, L.O. Péres, L. Caseli, Controlling the luminescence

- properties of poly(p-phenylene vinylene) entrapped in Langmuir and Langmuir–Blodgett films of stearic acid, *Synth. Met.* 161 (2011) 1753–1759. doi:10.1016/j.synthmet.2011.06.019.
- [126] S.S. Gayathri, A. Patnaik, Electrical rectification from a fullerene[60]-dyad based metal-organic-metal junction., *Chem. Commun. (Camb).* (2006) 1977–1979. doi:10.1039/b602203k.
- [127] W.R. Lindemann, W. Wang, F. Fungura, J. Shinar, R. Shinar, D. Vaknin, The effect of cesium carbonate on 1-(3-methoxycarbonyl)propyl-1-phenyl[6,6]C61 aggregation in films, *Appl. Phys. Lett.* 105 (2014). doi:10.1063/1.4901444.
- [128] J.-F. ois Nierengarten, Chemical modification of C 60 for materials science applications, *New J. Chem.* 28 (2004) 1177–1191.
- [129] N.C. Maliszewskyj, P.A. Heiney, D.R. Jones, R.M. Strongin, M.A. Cichy, A.B. Smith, Langmuir Films of C60, C60O, and C61H2, *Langmuir.* 9 (1993) 1439–1441. doi:10.1021/la00030a001.
- [130] Gareth Roberts, Langmuir-Blodgett Films, 1990. doi:10.1017/CBO9781107415324.004.
- [131] M.C. Petty, Langmuir-Blodgett Films: an introduction, 1st ed., Cambridge University Press, Cambridge, 1996.
- [132] R. Marczak, V.T. Hoang, K. Noworyta, M.E. Zandler, W. Kutner, F. D’Souza, Molecular recognition of adenine, adenosine and ATP at the air–water interface by a uracil appended fullerene, *J. Mater. Chem.* 12 (2002) 2123–2129. doi:10.1039/b202461f.
- [133] M.J. Hwang, K. Kim, Poly(ethylenimine) as a subphase stabilizer of stearic acid monolayers at the air/water interface: surface pressure-area isotherm and infrared spectroscopy study, *Langmuir.* 15 (1999) 3563–3569. doi:10.1021/la9804029.
- [134] M.L. Braunger, E.A. da Silva, H. Awada, V.J. de Oliveira, H.S. Silva, D. Bégué, R.C. Hiorns, C. Lartigau-Dagron, C. de Almeida Olivati, Langmuir and Langmuir-Blodgett films of low-bandgap polymers, *Polym. Int.* (2018) 1–24. doi:10.1002/pi.5604.
- [135] A. Pawlicka, R. Faria, M. Yonashiro, Effect of polymer molecular weight on Langmuir monolayers and the deposition of Langmuir-Blodgett films of poly (3-butylthiophene) and stearic acid, *Thin Solid Films.* 244 (1994) 723–727. <http://www.sciencedirect.com/science/article/pii/0040609094905584> (accessed August 31, 2013).
- [136] E.A. da Silva, L. Caseli, C. de A. Olivati, Organization of polythiophenes at ultrathin films mixed with stearic acid investigated with polarization-modulation infrared reflection–absorption spectroscopy, *Colloids Surfaces A Physicochem. Eng. Asp.* 529 (2017) 628–633. doi:10.1016/j.colsurfa.2017.06.035.
- [137] C. Kanimozhi, N. Yaacobi-Gross, E.K. Burnett, A.L. Briseno, T.D. Anthopoulos, U. Salzner, S. Patil, Use of side-chain for rational design of n-type diketopyrrolopyrrole-based conjugated polymers: what did we find out?, *Phys. Chem. Chem. Phys.* 16 (2014) 17253–17265. doi:10.1039/c4cp02322f.
- [138] S.P. Senanayak, A.Z. Ashar, C. Kanimozhi, S. Patil, K.S. Narayan, Room-

- temperature bandlike transport and Hall effect in a high-mobility ambipolar polymer, *Phys. Rev. B - Condens. Matter Mater. Phys.* 91 (2015) 1–16. doi:10.1103/PhysRevB.91.115302.
- [139] S. Izawa, K. Hashimoto, K. Tajima, Synthesis, characterization, and photovoltaic properties of diketopyrrolopyrrole-oligothiophene/fullerene dyads, *Synth. Met.* 162 (2012) 2201–2205. doi:10.1016/j.synthmet.2012.10.018.
- [140] A.L. Ayzner, C.J. Tassone, S.H. Tolbert, B.J. Schwartz, Reappraising the need for bulk heterojunctions in polymer-fullerene photovoltaics: The role of carrier transport in all-solution-processed P3HT/PCBM bilayer solar cells, *J. Phys. Chem. C.* 113 (2009) 20050–20060. doi:10.1021/jp9050897.
- [141] Z. Jin, J. Wang, PIN architecture for ultrasensitive organic thin film photoconductors., *Sci. Rep.* 4 (2014) 1–7. doi:10.1038/srep05331.
- [142] J.J. Benson-Smith, L. Goris, K. Vandewal, K. Haenen, J. V. Manca, D. Vanderzande, D.D.C. Bradley, J. Nelson, Formation of a ground-state charge-transfer complex in polyfluorene/[6,6]- phenyl-C61 butyric acid methyl ester (PCBM) blend films and its role in the function of polymer/PCBM solar cells, *Adv. Funct. Mater.* 17 (2007) 451–457. doi:10.1002/adfm.200600484.
- [143] J. Peet, J.Y. Kim, N.E. Coates, W.L. Ma, D. Moses, A.J. Heeger, G.C. Bazan, Efficiency enhancement in low-bandgap polymer solar cells by processing with alkane dithiols, *Nat. Mater.* 6 (2007) 497–500. doi:10.1038/nmat1928.
- [144] H. Hoppe, T. Glatzel, M. Niggemann, W. Schwinger, F. Schaeffler, A. Hinsch, M.C. Lux-Steiner, N.S. Sariciftci, Efficiency limiting morphological factors of MDMO-PPV:PCBM plastic solar cells, *Thin Solid Films.* 511–512 (2006) 587–592. doi:10.1016/j.tsf.2005.12.071.
- [145] Y.-C. Huang, Y.-C. Liao, S.-S. Li, M.-C. Wu, C.-W. Chen, W.-F. Su, Study of the effect of annealing process on the performance of P3HT/PCBM photovoltaic devices using scanning-probe microscopy, *Sol. Energy Mater. Sol. Cells.* 93 (2009) 888–892. doi:10.1016/j.solmat.2008.10.027.
- [146] L. Name, F. Name, O. Training, P. Training, C. Darin, R.O. Training, M. Kimberly, G. Deepa, E. Board, E. Principal, I. Primary, F. Systems, E.B. Study, N. Co-investigator, Surface analysis of polymers by XPS and static SIMS, 2005. doi:10.1007/s13398-014-0173-7.2.
- [147] Y. Yao, J. Hou, Z. Xu, G. Li, Y. Yang, Effects of solvent mixtures on the nanoscale phase separation in polymer solar cells, *Adv. Funct. Mater.* 18 (2008) 1783–1789. doi:10.1002/adfm.200701459.
- [148] S.R. Dupont, E. Voroshazi, D. Nordlund, K. Vandewal, R.H. Dauskardt, Controlling interdiffusion, interfacial composition, and adhesion in polymer solar cells, *Adv. Mater. Interfaces.* 1 (2014) 1–8. doi:10.1002/admi.201400135.
- [149] C. Soci, I. Hwang, D. Moses, Z. Zhu, D. Waller, R. Gaudiana, C.J. Brabec, A.J. Heeger, Photoconductivity of a Low-Bandgap Conjugated Polymer **, *Adv. Funct. Mater.* 17 (2007) 632–636. doi:10.1002/adfm.200600199.
- [150] D. Deng, L. Gu, Synthesis and photovoltaic properties of new near infrared absorption polymers based on C and N-bridged dithiophene and

- diketopyrrolopyrrole units, *J. Mater. Sci. Mater. Electron.* 24 (2013) 3029–3035. doi:10.1007/s10854-013-1207-1.
- [151] G. Chen, C. Chiang, D. Kekuda, S. Lan, C. Chu, K. Wei, Synthesis and Characterization of a Narrow-Bandgap Polymer Containing Alternating Cyclopentadithiophene and Diketo-Pyrrolo-Pyrrole Units for Solar Cell Applications, *J. Polym. Sci. Part A Polym. Chem.* 48 (2010) 1669–1675. doi:10.1002/pola.
- [152] A.P. Zoombelt, S.G.J. Mathijssen, M.G.R. Turbiez, M.M. Wienk, R. a. J. Janssen, Small band gap polymers based on diketopyrrolopyrrole, *J. Mater. Chem.* 20 (2010) 2240–2246. doi:10.1039/b919066j.
- [153] R. Saini, A. Mahajan, R.K. Bedi, D.K. Aswal, a. K. Debnath, Solution processed films and nanobelts of substituted zinc phthalocyanine as room temperature ppb level Cl₂ sensors, *Sensors Actuators, B Chem.* 198 (2014) 164–172. doi:10.1016/j.snb.2014.03.027.
- [154] P. Ehrenreich, S.T. Birk, E. Zimmermann, H. Hu, K. Kim, J. Weickert, T. Pfadler, L. Schmidt-mende, H-aggregate analysis of P3HT thin films-Capability and limitation of photoluminescence and UV / Vis spectroscopy, 2 (2016) 1–8. doi:10.1038/srep32434.
- [155] F.C. Spano, C. Silva, H- and J-Aggregate Behavior in Polymeric Semiconductors, *Rev. Adv.* 65 (2014) 477–500. doi:10.1146/annurev-physchem-040513-103639.
- [156] G. Pescitelli, L. Di Bari, N. Berova, Application of electronic circular dichroism in the study of supramolecular systems., *Chem. Soc. Rev.* 43 (2014) 5211–33. doi:10.1039/c4cs00104d.
- [157] O.G. Reid, R.D. Pensack, Y. Song, G.D. Scholes, G. Rumbles, Charge photogeneration in neat conjugated polymers, *Chem. Mater.* 26 (2014) 561–575. doi:10.1021/cm4027144.
- [158] S. Wood, J.R. Hollis, J. Kim, Raman spectroscopy as an advanced structural nanoprobe for conjugated molecular semiconductors, *J. Phys. D. Appl. Phys.* 50 (2017) 073001 (1-32). doi:10.1088/1361-6463/50/7/073001.
- [159] S. Falke, P. Eravuchira, A. Materny, C. Lienau, Raman spectroscopic identification of fullerene inclusions in polymer/fullerene blends, *J. Raman Spectrosc.* 42 (2011) 1897–1900. doi:10.1002/jrs.2966.
- [160] W.C. Tsoi, D.T. James, J.S. Kim, P.G. Nicholson, C.E. Murphy, D.D.C. Bradley, J. Nelson, J. Kim, The Nature of In-Plane Skeleton Raman Modes of P3HT and Their Correlation to the Degree of Molecular Order in P3HT : PCBM Blend Thin Films, *J. Am. Chem. Soc.* 133 (2011) 9834–9843. doi:10.1021/ja2013104.
- [161] E. Klimov, W. Li, X. Yang, G.G. Hoffmann, J. Loos, Scanning Near-Field and Confocal Raman Microscopic Investigation of P3HT - PCBM Systems for Solar Cell Applications, *Macromolecules.* 39 (2006) 4493–4496. doi:10.1021/ma052590x.
- [162] X. Wang, D. Zhang, K. Braun, H.J. Egelhaaf, C.J. Brabec, A.J. Meixner, High-Resolution spectroscopic mapping of the chemical contrast from nanometer domains in P3HT:PCBM organic blend films for Solar-Cell applications by, *Adv.*

- Funct. Mater. 20 (2010) 492–499. doi:10.1002/adfm.200901930.
- [163] X. Wang, H.J. Egelhaaf, H.G. Mack, H. Azimi, C.J. Brabec, A.J. Meixner, D. Zhang, Morphology related photodegradation of low-band-gap polymer blends, *Adv. Energy Mater.* 4 (2014) 1–12. doi:10.1002/aenm.201400497.
- [164] C. Francis, D. Fazzi, S.B. Grimm, F. Paulus, S. Beck, S. Hillebrandt, A. Pucci, J. Zaumseil, Raman spectroscopy and microscopy of electrochemically and chemically doped high-mobility semiconducting polymers, *J. Mater. Chem. C* 5 (2017) 6176–6184. doi:10.1039/C7TC01277B.
- [165] P. Roy, A. Jha, V.B. Yasarapudi, T. Ram, B. Puttaraju, S. Patil, J. Dasgupta, Ultrafast bridge planarization in donor- π -acceptor copolymers drives intramolecular charge transfer, *Nat. Commun.* 8 (2017). doi:10.1038/s41467-017-01928-z.
- [166] S. Wood, J. Wade, M. Shahid, E. Collado-Fregoso, D.D.C. Bradley, J.R. Durrant, M. Heeney, J.-S. Kim, Natures of optical absorption transitions and excitation energy dependent photostability of diketopyrrolopyrrole (DPP)-based photovoltaic copolymers, *Energy Environ. Sci.* 8 (2015) 3222–3232. doi:10.1039/C5EE01974E.
- [167] J. Calvo-Castro, M. Warzecha, A.J. McLean, C.J. McHugh, Impact of substituent effects on the Raman spectra of structurally related N-substituted diketopyrrolopyrroles, *Vib. Spectrosc.* 83 (2016) 8–16. doi:10.1016/j.vibspec.2015.12.004.
- [168] M. Doris, F. Aziz, H. Alhummany, T. Bawazeer, N. Alsenany, A. Mahmoud, R. Zakaria, K. Sulaiman, A. Supangat, Determining the Effect of Centrifugal Force on the Desired Growth and Properties of PCPDTBT as p-Type Nanowires, *Nanoscale Res. Lett.* 12 (2017) 1–11. doi:10.1186/s11671-017-1851-0.
- [169] T. Sharma, R. Singhal, R. Vishnoi, P. Sharma, A. Patra, S. Chand, G.B.V.S. Lakshmi, S.K. Biswas, Electronic excitation induced modifications of optical and morphological properties of PCBM thin films, *Nucl. Instruments Methods Phys. Res. Sect. B Beam Interact. with Mater. Atoms.* 379 (2016) 176–180. doi:10.1016/j.nimb.2016.03.029.
- [170] J. Wu, G. Yue, Y. Xiao, H. Ye, J. Lin, M. Huang, Application of a polymer heterojunction in dye-sensitized solar cells, *Electrochim. Acta.* 55 (2010) 5798–5802. doi:10.1016/j.electacta.2010.05.025.
- [171] S.H. Yoo, J.M. Kum, S.O. Cho, Tuning the electronic band structure of pcbm by electron irradiation, *Nanoscale Res. Lett.* 6 (2011) 1–7. doi:10.1186/1556-276X-6-545.
- [172] X. Jiang, J. Ding, A. Kumar, Polyurethane-poly(vinylidene fluoride) (PU-PVDF) thin film composite membranes for gas separation, *J. Memb. Sci.* 323 (2008) 371–378. doi:10.1016/j.memsci.2008.06.048.
- [173] C.D. Weber, C. Bradley, M.C. Lonergan, Solution phase n-doping of C₆₀ and PCBM using tetrabutylammonium fluoride, *J. Mater. Chem. A* 2 (2014) 303–307. doi:10.1039/C3TA14132B.
- [174] D. Kelkar, A. Chourasia, Electrical and Magnetic Conduction Properties of

- Polythiophene Doped with FeCl₃, *Macromol. Symp.* 327 (2013) 45–53. doi:10.1002/masy.201350505.
- [175] G. Zotti, G. Schiavon, The polythiophene puzzle. Electrochemical and spectroelectrochemical evidence for two oxidation levels, *Synth. Met.* 31 (1989) 347–357. doi:10.1016/0379-6779(89)90802-3.
- [176] A. Shafiee, M.M. Salleh, M. Yahaya, Determination of HOMO and LUMO of [6,6]-Phenyl C61-butyric 3-ethylthiophene Ester and Poly (3-octyl-thiophene-2, 5-diyl) Acid through Voltametry Characterization, *Sains Malaysiana*. 40 (2011) 173–176.
- [177] T. Haefele, K. Kita-Tokarczyk, W. Meier, Phase Behavior of Mixed Langmuir Monolayers from Amphiphilic Block Copolymers and an Antimicrobial Peptide, *Langmuir*. 22 (2005) 1164–1172. doi:10.1021/la0524216.
- [178] J. Pommerehne, H. Vestweber, W. Guss, R.F. Mahrt, H. Bässler, M. Porsch, J. Daub, Efficient two layer leds on a polymer blend basis, *Adv. Mater.* 7 (1995) 551–554. doi:10.1002/adma.19950070608.
- [179] C. Duan, W. Cai, F. Huang, J. Zhang, M. Wang, T. Yang, C. Zhong, X. Gong, Y. Cao, Novel silafluorene-based conjugated polymers with pendant acceptor groups for high performance solar cells, *Macromolecules*. 43 (2010) 5262–5268. doi:10.1021/ma100616f.
- [180] Y. Ji, H. Niu, H. Zhang, W. Wu, J. Cai, Ch. Wang, X. Bai, W. Wang, Synthesis and electrochromic properties of polybismaleimides containing triphenylamine units, *J. Solid State Electrochemistry*. 18 (2014) 1537–1544. doi:10.1007/s10008-013-2371-1.
- [181] D. Baran, A. Balan, S. Celebi, B. Meana Esteban, H. Neugebauer, N.S. Sariciftci, L. Toppare, Processable multipurpose conjugated polymer for electrochromic and photovoltaic applications, *Chem. Mater.* 22 (2010) 2978–2987. doi:10.1021/cm100372t.
- [182] J. You, L. Dou, Z. Hong, G. Li, Y. Yang, Recent trends in polymer tandem solar cell research, *Prog. Polym. Sci.* 38 (2013) 1909–1928. doi:10.1016/j.progpolymsci.2013.04.005.
- [183] Y.-C. Pao, C.-T. Yang, Y.-Y. Lai, W.-C. Huang, C.-S. Hsu, Y.-J. Cheng, Synthesis and field-effect transistor properties of a diseleno[3,2-b:2',3'-d]silole-based donor–acceptor copolymer: investigation of chalcogen effect, *Polym. Chem.* 7 (2016) 4654–4660. doi:10.1039/C6PY00765A.
- [184] H. De Santana, E.C.R. Maia, D.C. Bento, T.N.M. Cervantes, G.J. Moore, Spectroscopic study of poly(3-alkylthiophenes) electrochemically synthesized in different conditions, *J. Mater. Sci. Mater. Electron.* 24 (2013) 3352–3358. doi:10.1007/s10854-013-1254-7.
- [185] G. Lillie, P. Payne, P. Vadgama, Electrochemical impedance spectroscopy as a platform for reagentless bioaffinity sensing, *Sensors Actuators, B Chem.* 78 (2001) 249–256. doi:10.1016/S0925-4005(01)00821-8.
- [186] D.C. Bento, E.C.R. Maia, T.N.M. Cervantes, C. de Almeida Olivati, G. Louarn, H. de Santana, Complementary study on the electrical and structural properties of

- poly(3-alkylthiophene) and its copolymers synthesized on ITO by electrochemical impedance and Raman spectroscopy, *J. Mater. Sci. Mater. Electron.* 26 (2014) 149–161. doi:10.1007/s10854-014-2377-1.
- [187] D. Cristina, B. Guy, L. Henrique, Structural stability and improved properties of poly (3- alkylthiophenes) synthesized in an acid medium, *J. Mater. Sci. Mater. Electron.* 27 (2016) 5371–5382. doi:10.1007/s10854-016-4437-1.
- [188] A. Domingues, B. Danielly, C. Bento, H. De Santana, Structural stability of poly (3-methylthiophene) and poly (3 , 4- ethylenedioxythiophene) in the ITO / PEDOT : PSS / P3MT system, *J. Mater. Sci. Mater. Electron.* 28 (2017) 1514–1521. doi:10.1007/s10854-016-5690-z.
- [189] S.M. Sze, K.K. Ng, *Physics of Semiconductor Devices*, 3rd ed., John Wiley & Sons, Hoboken, 2007.
- [190] W. Olthuis, W. Streekstra, P. Bergveld, Theoretical and experimental determination of cell constants of planar-interdigitated electrolyte conductivity sensors, *Sensors Actuators B Chem.* 24–25 (1995) 252–256. <http://www.sciencedirect.com/science/article/pii/0925400595850538> (accessed April 2, 2014).
- [191] A. Tournebize, M. Seck, A. Vincze, A. Distler, H. Egelhaaf, C.J. Brabec, A. Rivaton, H. Peisert, T. Chassé, Solar Energy Materials & Solar Cells Photodegradation of Si-PCPDTBT : PCBM active layer for organic solar cells applications : A surface and bulk investigation, *Sol. Energy Mater. Sol. Cells.* 155 (2016) 323–330.
- [192] W.D. Callister, *Materials science and engineering: An introduction*, 7th ed., John Wiley & Sons, Inc., 2007. doi:10.1016/0025-5416(87)90343-0.
- [193] H.-L. Yip, A.K.-Y. Jen, Recent advances in solution-processed interfacial materials for efficient and stable polymer solar cells, *Energy Environ. Sci.* 5 (2012) 5994. doi:10.1039/c2ee02806a.
- [194] L.V. de L. Citolino, M.L. Braunger, V.J.R. Oliveira, C.A. Olivati, Study of the Nanostructure Effect on Polyalkylthiophene Derivatives Films Using Impedance Spectroscopy, *Mater. Res.* 20 (2017) 1–8. doi:10.1590/1980-5373-mr-2016-0670.
- [195] I. Watanabe, K. Hong, M.F. Rubner, Langmuir-Blodgett manipulation of poly(3-alkylthiophenes), *Langmuir.* 6 (1990) 1164–1172. doi:10.1021/la00096a024.
- [196] T. Blythe, D. Bloor, *Electrical properties of polymers*, 2nd ed., Cambridge University Press, Cambridge, 2005.
- [197] D.E. Motaung, G.F. Malgas, C.J. Arendse, S.E. Mavundla, D. Knoesen, Structural and photo-physical properties of spin-coated poly(3-hexylthiophene) thin films, *Mater. Chem. Phys.* 116 (2009) 279–283. doi:10.1016/j.matchemphys.2009.03.028.
- [198] M. Li, K. Gao, X. Wan, Q. Zhang, B. Kan, R. Xia, F. Liu, X. Yang, H. Feng, W. Ni, Y. Wang, J. Peng, H. Zhang, Z. Liang, H. Yip, X. Peng, Y. Cao, Y. Chen, Solution-processed organic tandem solar cells with power conversion efficiencies >12%, *Nat. Photonics.* 11 (2016) 85–90. doi:10.1038/nphoton.2016.240.
- [199] T.-B. Song, N. Li, *Emerging Transparent Conducting Electrodes for Organic Light*

- Emitting Diodes, *Electronics*. 3 (2014) 190–204. doi:10.3390/electronics3010190.
- [200] A.J.H. H. TOMOZAWA, D. BRAUN, S.D. PHILLIPS, R. WORLAND, Metal-polymer Schottky barriers on processible polymers, *Synth. Met.* 28 (1989) 687–690. doi:doi.org/10.1016/0379-6779(89)90591-2.
- [201] W.E. Spicer, I. Lindau, P. Skeath, C.Y. Su, P. Chye, Unified mechanism for schottky-barrier formation and III-V oxide interface states, *Phys. Rev. Lett.* 44 (1980) 420–423. doi:10.1103/PhysRevLett.44.420.
- [202] R.A. Zoppi, M.-A. De Paoli, Aplicações tecnológicas de polímeros intrinsecamente condutores: Perspectivas atuais, *Quim. Nova*. 16 (1993) 560–568.
- [203] H. Koralay, N. Tuğluoğlu, K.B. Akgül, Ş. Çavdar, Analysis of Hopping Conduction and Space Charge Limited Currents in Nearly Ideal Metal/Semiconductor Contacts, *Gazi Univ. J. Sci.* 27 (2014) 901–907.
- [204] C. Olivati, Estudo das propriedades elétricas e ópticas de dispositivos eletroluminescentes poliméricos., Universidade de São Paulo, São Carlos, 2004. <http://www.teses.usp.br/teses/disponiveis/76/76132/tde-08122010-094137/> (accessed March 6, 2014).
- [205] A.J. Heeger, Semiconducting polymers: the Third Generation, *Chem. Soc. Rev.* 39 (2010) 2354. doi:10.1039/b914956m.
- [206] N.S. Sariciftci, D. Braun, C. Zhang, V.I. Srdanov, A.J. Heeger, G. Stucky, F. Wudl, Semiconducting polymer-buckminsterfullerene heterojunctions: Diodes, photodiodes, and photovoltaic cells, *Appl. Phys. Lett.* 62 (1993) 585–587. doi:10.1063/1.108863.
- [207] G. Liang, T. Cui, K. Varahramyan, Electrical characteristics of diodes fabricated with organic semiconductors, *Microelectron. Eng.* 65 (2003) 279–284. doi:10.1016/S0167-9317(02)00901-2.
- [208] H.P. Kim, S.J. Lee, A.R. bin Mohd Yusoff, J. Jang, A high performance organic photovoltaic utilizing PEDOT:PSS and graphene oxide, *RSC Adv.* 6 (2016) 28599–28606. doi:10.1039/C6RA04376C.
- [209] A. Singh, M. Katiyar, A. Garg, Understanding the formation of PEDOT:PSS films by ink-jet printing for organic solar cell applications, *RSC Adv.* 5 (2015) 78677–78685. doi:10.1039/C5RA11032G.
- [210] C.A. Olivati, M. Ferreira, A.J.F. Carvalho, D.T. Balogh, O.N. Oliveira, H. Von Seggern, R.M. Faria, Polymer light emitting devices with Langmuir-Blodgett (LB) films: Enhanced performance due to an electron-injecting layer of ionomers, *Chem. Phys. Lett.* 408 (2005) 31–36. doi:10.1016/j.cplett.2005.03.144.
- [211] T. Stöcker, A. Köhler, R. Moos, Why does the electrical conductivity in PEDOT:PSS decrease with PSS content? A study combining thermoelectric measurements with impedance spectroscopy, *J. Polym. Sci. Part B Polym. Phys.* 50 (2012) 976–983. doi:10.1002/polb.23089.
- [212] U. Simon, G. Schön, G. Schmid, The Application of Au₅₅ Clusters as Quantum Dots, *Angew. Chemie Int. Ed. English*. 32 (1993) 250–254. doi:10.1002/anie.199302501.

- [213] A. Sun, H. Huang, C. Chu, Y. Li, Effect of the pore size of TiO₂ porous film on humidity sensitive properties of TiO₂/NaPSS composite films, *Sensors Actuators B Chem.* 160 (2011) 1335–1339. doi:10.1016/j.snb.2011.09.071.
- [214] J.B. González-campos, E. Prokhorov, G. Luna-Bárcenas, A.M. Galván, I.C. Sanchez, S.M. Nuño Donlucas, B. Garcia-Gaitan, Y. Kovalenko, Relaxations in chitin: Evidence for a glass transition, *J. Polym. Sci. Part B Polym. Phys.* 47 (2009) 932–943. doi:10.1002/polb.21690.
- [215] S. Pati, Impedance Spectroscopy of Nano-Grain ZnO Thin Films, *Int. J. Recent Innov. Trends Comput. Commun.* 3 (2015) 6441–6446.
- [216] C. Silva Martin, M. Dassie Maximino, M. Santos Pereira, C. de Almeida Olivati, P. Alessio, The role of film composition and nanostructuration on the polyphenol sensor performance, *AIMS Mater. Sci.* 4 (2016) 27–42. doi:10.3934/matricsci.2017.1.27.
- [217] W. Chen, S. Yang, Dye-sensitized solar cells based on ZnO nanotetrapods, *Front. Optoelectron. China.* 4 (2011) 24–44. doi:10.1007/s12200-011-0207-0.
- [218] G. Garcia-Belmonte, A. Munar, E.M. Barea, J. Bisquert, I. Ugarte, R. Pacios, Charge carrier mobility and lifetime of organic bulk heterojunctions analyzed by impedance spectroscopy, *Org. Electron. Physics, Mater. Appl.* 9 (2008) 847–851. doi:10.1016/j.orgel.2008.06.007.
- [219] J. Bisquert, Theory of the Impedance of Electron Diffusion and Recombination in a Thin layer, *J. Phys. Chem. B.* 106 (2002) 325–333. doi:10.1021/jp011941g.
- [220] L. Xu, Y.-J. Lee, J.W.P. Hsu, Charge collection in bulk heterojunction organic photovoltaic devices: An impedance spectroscopy study, *Appl. Phys. Lett.* 105 (2014) 123904. doi:10.1063/1.4896633.
- [221] T. Ripolles-Sanchis, A. Guerrero, J. Bisquert, G. Garcia-belmonte, Diffusion-Recombination Determines Collected Current and Voltage in Polymer : Fullerene Solar Cells, *J. Phys. Chem. C.* (2012).
- [222] E. Barsoukov, J.R. Macdonald, *Impedance Spectroscopy*, 2005. doi:10.1002/0471716243.
- [223] S. Middya, A. Layek, A. Dey, P.P. Ray, Morphological impact of ZnO nanoparticle on MEHPPV:ZnO based hybrid solar cell, *J. Mater. Sci. Mater. Electron.* 24 (2013) 4621–4629. doi:10.1007/s10854-013-1453-2.
- [224] T. Kim, J. Kim, T.E. Kang, C. Lee, H. Kang, M. Shin, C. Wang, B. Ma, U. Jeong, T. Kim, B.J. Kim, Flexible , highly efficient all-polymer solar cells, *Nat. Commun.* 6 (2015) 1–7. doi:10.1038/ncomms9547.
- [225] G. Perrier, R. De Bettignies, S. Berson, N. Lemaître, S. Guillerez, Impedance spectrometry of optimized standard and inverted P3HT-PCBM organic solar cells, *Sol. Energy Mater. Sol. Cells.* 101 (2012) 210–216. doi:10.1016/j.solmat.2012.01.013.
- [226] C. Chen, W. Chang, K. Yoshimura, K. Ohya, J. You, An Efficient Triple-Junction Polymer Solar Cell Having a Power Conversion Efficiency Exceeding 11 %, (2014) 5670–5677. doi:10.1002/adma.201402072.

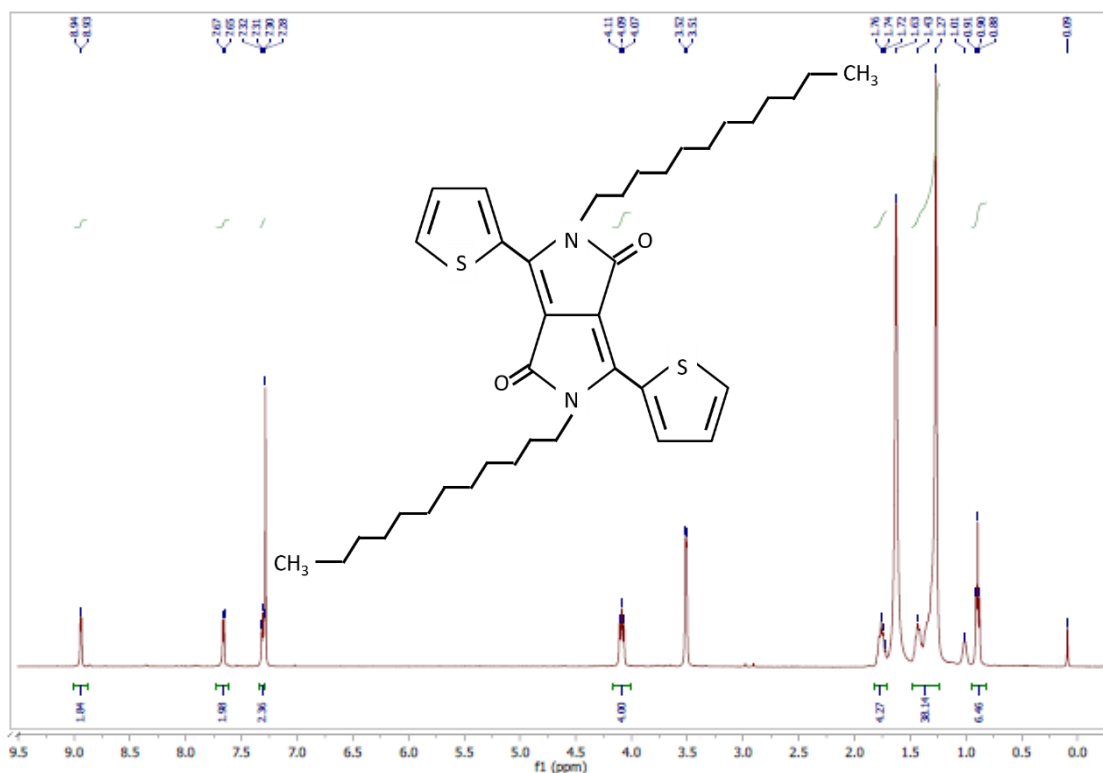
- [227] S. Na, G. Wang, S. Kim, T. Kim, S. Oh, B. Yu, T. Lee, D. Kim, Evolution of nanomorphology and anisotropic conductivity in solvent-modified PEDOT : PSS films for polymeric anodes of polymer solar cells, 1 (2009) 9045–9053. doi:10.1039/b915756e.
- [228] P.-T. Wu, H. Xin, F.S. Kim, G. Ren, S. a. Jenekhe, Regioregular Poly(3-pentylthiophene): Synthesis, Self-Assembly of Nanowires, High-Mobility Field-Effect Transistors, and Efficient Photovoltaic Cells, *Macromolecules*. 42 (2009) 8817–8826. doi:10.1021/ma901829d.
- [229] O. Oklobia, T.S. Shafai, B. Friedel, T.J.K. Brenner, C.R. McNeill, U. Steiner, N.C. Greenham, G. Li, G. Lu, S. Li, H. Tang, X. Yang, G. Lu, L. Li, J. Li, Y. Wang, X. Yang, S.J. Lou, J.M. Szarko, T. Xu, L. Yu, T.J. Marks, L.X. Chen, W.-H. Baek, T.-S. Yoon, H.H. Lee, Y.-S. Kim, Precise construction of PCBM aggregates for polymer solar cells via multi-step controlled solvent vapor annealing, *J. Mater. Chem.* 11 (2010) 1736–1745. doi:10.1021/ja2085564.
- [230] F.S.U. Fischer, D. Trefz, J. Back, N. Kayunkid, B. Tornow, S. Albrecht, K.G. Yager, G. Singh, A. Karim, D. Neher, M. Brinkmann, S. Ludwigs, Highly crystalline films of PCPDTBT with branched side chains by solvent vapor crystallization: Influence on opto-electronic properties, *Adv. Mater.* 27 (2015) 1223–1228. doi:10.1002/adma.201403475.
- [231] A. Riaño, P. Mayorga Burrezo, M.J. Mancheño, A. Timalina, J. Smith, A. Facchetti, T.J. Marks, J.T. López Navarrete, J.L. Segura, J. Casado, R. Ponce Ortiz, The unusual electronic structure of ambipolar dicyanovinyl-substituted diketopyrrolopyrrole derivatives, *J. Mater. Chem. C*. 2 (2014) 6376–86. doi:10.1039/C4TC00714J.
- [232] A.P. Zoombelt, M. Fonrodona, M.M. Wienk, A.B. Sieval, J.C. Hummelen, R.A.J. Janssen, Photovoltaic performance of an ultrasmall band gap polymer, *Org. Lett.* 11 (2009) 903–906. doi:10.1021/ol802839z.
- [233] A.P. Zoombelt, M. Fonrodona, M.G.R. Turbiez, M.M. Wienk, R.A.J. Janssen, Synthesis and photovoltaic performance of a series of small band gap polymers, *J. Mater. Chem.* 19 (2009) 5336. doi:10.1039/b821979f.
- [234] N.M. Ravindra, B. Prasad, Saturation current in solar cell: an analysis, *Sol. Cells*. 2 (1980) 109–113.
- [235] Z. He, C. Zhong, X. Huang, W.Y. Wong, H. Wu, L. Chen, S. Su, Y. Cao, Simultaneous enhancement of open-circuit voltage, short-circuit current density, and fill factor in polymer solar cells, *Adv. Mater.* 23 (2011) 4636–4643. doi:10.1002/adma.201103006.

Appendix

Monomer synthesis: NMR spectra

In this section the NMR spectra obtained for each step are presented, they consist of the verification of the synthesis of the side chain insertion process to the DPP monomer and its bromination, processes necessary for the final polymerization of the DPP with the CPDT. These results are not discussed in this section because they are not the focus of the doctoral work.

- *2,5-Didodecyl-3,6-dithiophene-2-yl-2,5-dihydropyrrolo[3,4-*c*]pyrrole-1,4-dione*



DPP: 0.500 g, 1.66 mmol

K₂CO₃ anhydrous: 1.1 g, 8.01 mmol

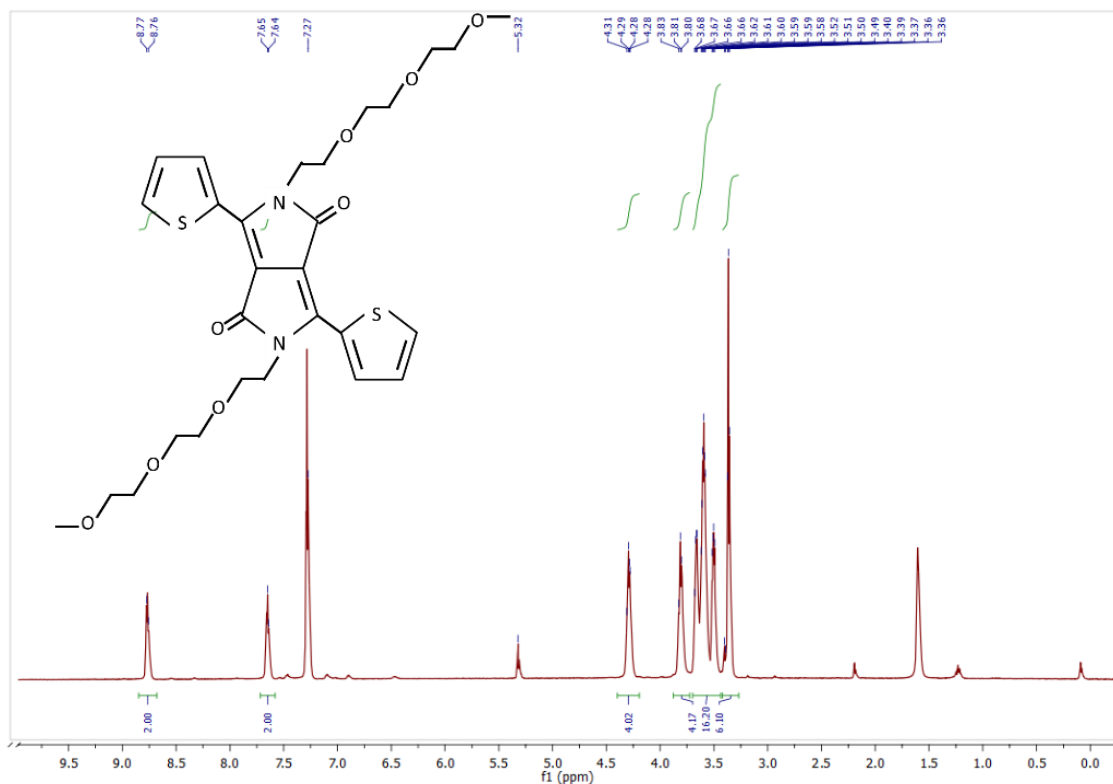
C₁₂H₂₅Br: 1.1 g, 5.04 mmol

18-Crown-6: 15 mg, 0.05 mmol

Yield: 0,674 g, 1.05 mmol, 64%

¹H NMR (CDCl₃, 400 MHz) δ (ppm): 8.93 (d, 2H), 7.65 (d, 2H), 7.30 (t, 2H), 4.09 (t, 4H), 0.8-1.8 (m, 48H).

- 2,5-(methoxyethoxy)ethane--3,6-dithiophene-2-yl-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione



DPP: 0.886 g, 2.94 mmol

K₂CO₃ anhydrous: 2.4 g, 17.64 mmol

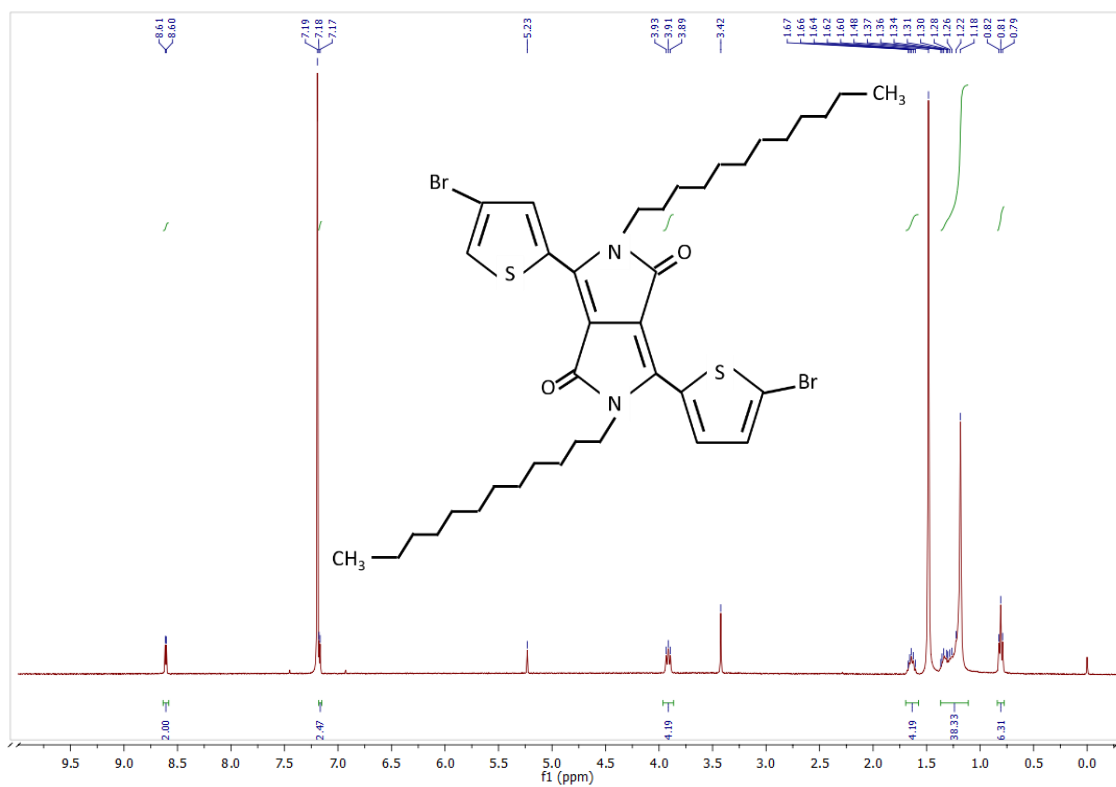
MetEtBr: 2 g, 8.81 mmol

18-Crown-6: 16 mg, 0.06 mmol

Yield: 1.13 g, 1.90 mmol, 67%

¹H NMR (CDCl₃, 400 MHz) δ (ppm): 8.76 (d, 2H), 7.64 (d, 2H), 7.27 (t, 2H), 4.28 (t, 4H), 3.3-3.8 (m, 26H).

- 2,5-Dodecyl-3,6-bis(5-bromothiopen-2-yl)pyrrolo[3,4-c]-pyrrole-1,4-dione



DPP_C₁₂ 492 mg, 0.77 mmol

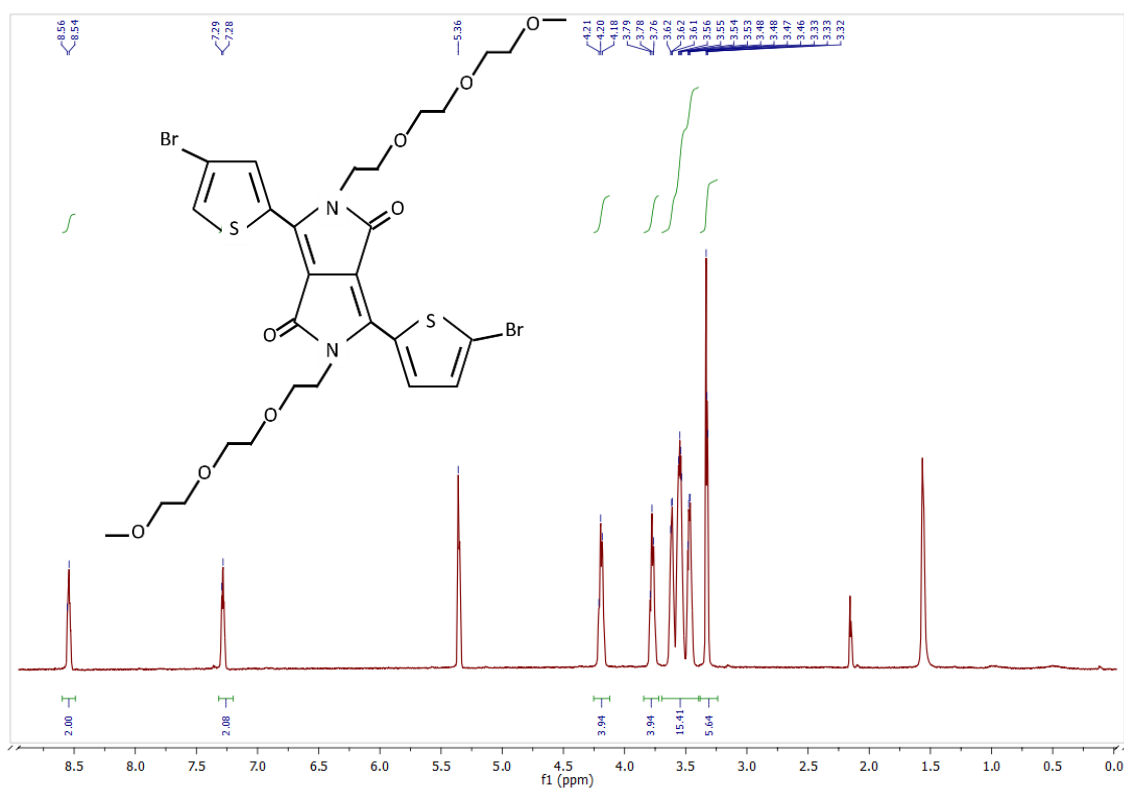
NBS: 343 mg, 1.93 mmol

CHCl₃: 20 ml

Yield: 384 mg, 0.48 mmol, 62%

¹H NMR (C₂D₂Cl₂, 400 MHz) δ (ppm): 8.60 (d, 2H), 7.17 (d, 2H), 3.91 (t, 4H), 0.8-1.7 (m, 48H).

- 2,5-(methoxyethoxy)ethane-3,6-bis(5-bromothiophen-2-yl)pyrrolo[3,4-c]-pyrrole-1,4-dione



DPP_Met 0,9 g, 1.51 mmol

NBS: 670 mg, 3.78 mmol

CHCl₃: 20 ml

Yield: 633 mg, 0.57 mmol, 56%

¹H NMR (C₂D₂Cl₂, 400 MHz) δ (ppm): 8.54 (d, 2H), 7.28 (d, 2H), 4.20 (t, 4H), 3.3-3.8 (m, 26H).