Contents

Page No.

List of Figures i-viii
List of Tables ix
List of Abbreviations / Symbols xi-xiv
Preface xv-xx

Chapter – 1 Introduction & Literature Survey **1-38**
1.1. Introduction 1
1.2. Conducting Polymers 2
1.2.1. π-conjugated Organic Semiconductors 3
1.2.2. Charge Transport in Organic semiconductor 5
1.2.3. Doping in Conducting Polymers 6
1.2.3.1. Chemical Doping 6
1.2.3.2. Photo Doping 7
1.2.3.3. Electrochemical Doping 8
1.2.4. Charge Carrier in Conducting Polymers 8
1.3. Organic Electronic Devices 11
1.3.1. Organic Schottky Barrier Diode 12
1.3.2. Organic Field Effect Transistor (OFET) 13
1.3.2.1. Working Mechanism of OFET 14
1.3.3. Organic Photo Transistor (OPT) Configuration 16
1.3.3.1. Working Mechanism of Organic Phototransistor 16
1.3.3.2. Photoexcitation and Photocurrent Generation 17
1.3.3.3. Operation Modes of Phototransistor 17
1.3.3.4. Key Parameter of Organic Photodetectors 18
1.3.4. Charge Transport in Organic Electronic Devices 19
1.3.5. Time Resolved Microscopic Second Harmonic Generation (TRM-SHG) 20
1.4. Limitation of Conducting Polymer in Electronic Devices 24
1.5. Approaches to Enhance the Performance of Organic Electronic Devices 25
1.5.1. Molecular Orientation of Polymer Backbones 25
1.5.1.1. Types of Molecular Orientation 26
1.5.1.2. Different Approaches for Molecular Orientation 27
1.5.2. Blending with Nanomaterials 32
1.5.2.1. Conventional Nanomaterials 33

1.5.2.1.1. Different type of Conventional Nanomaterials 33

1.5.2.1.2. Disadvantages of Conventional Nanomaterials 35

1.5.2.2 Organic Graphitic Carbon Nitride (g-C_3N_4) and (C_3N_5) 35

1.6. Existing Problems and Objective of Thesis 36

Chapter – 2 Experimental and Instrumentations 39-66

2.1. Introduction 39

2.2. Materials 40

2.3. Materials Synthesis 41

2.3.1. Synthesis of C_3N_5 41

2.3.2. Dielectric Synthesis 42

2.3.2.1. Li-Al_2O_3 Ion-Conducting Gate Dielectric Solution Synthesis 42

2.3.2.2. Poly (methyl methacrylate) (PMMA) Dielectric Preparation 43

2.3.3. Polymer ink Preparation 43

2.3.3.1. Preparation of Polymer Solution 43

2.3.3.2. Preparation of Polymer/C_3N_5 Solution 43

2.4. Thin Film Fabrication Techniques 44

2.4.1. Spin Coating 44

2.4.2. Floating Film Transfer Method 45

2.4.3. Unidirectional Floating Film Transfer method 46

2.4.4 Polydimethylsiloxanes (PDMS) Mold 47

2.5. Device Fabrication 48

2.5.1. Substrate Preparation 48

2.5.2. Metal-Insulator-Metal (MIM) Device Fabrication 49

2.5.3. Active Layer Fabrication of OFETs 50

2.5.4. Electrode Deposition using Thermal Vapour Evaporator 50

2.6. Characterization Tools 52

2.6.1. Structural Characterization 52

2.6.1.1. X-ray Diffraction (XRD) 52

2.6.1.2. Fourier Transform Infrared Spectroscopy (FTIR) 53

2.6.1.3. X-ray Photoelectron Spectroscopy (XPS) 55

2.6.2. Optical Characterizations 56

2.6.2.1. UV-Visible Spectroscopy 56

2.6.3. Surface and Morphological Characterizations 57

2.6.3.1. Atomic Force Microscopy (AFM) 57
2.6.3.2. Scanning Electron Microscopy (SEM) 58
2.6.4. Electrochemical Characterizations 60
2.6.4.1. Cyclic Voltammetry 60
2.6.5. Electrical Characterization 62
2.6.5.1. Capacitance vs. Frequency Measurement 62
2.6.5.2. Leakage Current Measurement 63
2.6.5.3. Thin Film Transistor Characterizations 63
2.6.5.4. Current vs Time (*I-t*) Characterization 64
2.6.5.5. Time Resolved Microscopic Second Harmonic Generation Technique 64
Chapter – 3 **Exploring Anisotropic Charge Transport in Highly Oriented P4T2F- HD Thin Films via Second Harmonic Generation (SHG) Analysis** **67-82**
3.1. Introduction 67
3.2 Materials and Methods 69
3.2.1. Thin Film and OFET Fabrication 69
3.3. Results and Discussion 71
3.3.1. Structural Characterization 71
3.3.2. Optical Characterization 72
3.3.3. Surface Characterization 73
3.3.4. Electrical Characterizations 73
3.3.5. TRM-SHG Measurement 75
3.4. Conclusion 81
Chapter – 4 **Fabrication of Highly Sensitive Flexible Phototransistors through Unidirectional Floating Film Transfer Method Using P4T2F-HD Thin Film** **83-102**
4.1. Introduction 83
4.2. Materials and Methods 86
4.2.1. Materials 86
4.2.2. Device Fabrication 86
4.3. Results and Discussion 87
4.3.1. Dielectric Characterizations 87
4.3.1.1. Surface Characterization 87
4.3.1.2. Leakage Current Characterization 88
4.3.2. P4T2F-HD Thin Film Characterizations 89

4.3.2.1. XRD Analysis 89
4.3.2.2. Optical Analysis 90
4.3.2.3. Surface Characterizations 92
4.3.3. Electrical Characterizations of OPTs 92
4.3.3.1. OPTs Sensing Measurement 93
4.3.3.2. Flexibility Measurement 99
4.3.3.3. Stability Measurement 100
4.4. Conclusion 102
Chapter – 5 **Fabrication of NIR Sensitive-Low Operating Voltage Phototransistor with Unidirectional Organic Polymer.** **103-120**
5.1. Introduction 103
5.2. Materials and Methods 105
5.2.1. Materials 105
5.2.2. Dielectric Synthesis 105
5.2.3. Device Fabrication 105
5.3. Results and Discussion 107
5.3.1. Dielectric Characterizations 107
5.3.1.1. XRD Analysis 107
5.3.1.2. Optical Analysis 107
5.3.1.3. Surface Characterization 108
5.3.1.4. Leakage Current and Areal Capacitance Measurement 109
5.3.2. DPP-TTT Thin Film Characterizations 110
5.3.2.1. XRD Analysis 110
5.3.2.2. Optical Analysis 111
5.3.2.3. Surface Characterization 111
5.3.3. Electrical Characterizations 112
5.3.3.1. Optical Sensing of OPTs 114
5.4. Conclusion 118
Chapter – 6 **Direct Visualization of Carrier Motion in DPP-TTT/C_3N_5 Blended Organic Thin Film Transistor by Optical Second Harmonic Generation.** **121-148**
6.1. Introduction 121
6.2. Materials and Methods 124
6.2.1. Materials 124
6.2.2. Preparation of Exfoliated C_3N_5 Nanosheets from Bulk C_3N_5 125

6.2.3. Thin Film Fabrication 125
6.2.4. Device Fabrication 126
6.3. Results and Discussion 127
6.3.1. Characterization of C_3N_5 127
6.3.1.1. XRD Analysis 127
6.3.1.2. FTIR Analysis 128
6.3.1.3. Optical Analysis 128
6.3.1.4. Xray Photo Spectroscopy (XPS) 129
6.3.1.5. Morphological Study 130
6.3.2. Characterization of DPP/C_3N_5 Blend Solution 131
6.3.3. DPP-TTT/C_3N_5 Thin Film Characterizations 132
6.3.3.1. XRD Analysis 132
6.3.3.2. Optical Analysis 134
6.3.3.3. Morphological Characterization 136
6.3.3.4. Cyclic Voltammetry 137
6.3.4. Electrical Characterization of OFETs 138
6.3.5. SHG measurement 141
6.4. Conclusion 148
Chapter – 7 Summary and Future Work 149-154
References 155-168
List of Publications
Conferences/Workshops Attended
Research Visit

List of Figures

Figure No.	Figure Caption	Page No.
Figure 1.1	Represents the log scale of conductivity range of the conjugated polymers.	**3**
Figure 1.2	Types of organic conjugated semiconductors (a) small molecules, and (b) semiconducting polymers	**5**
Figure 1.3	Illustrates the formation of both negative and positive polarons, as well as bipolarons, in polythiophene (b) schematic for bond length alteration during oxidation and reduction.	**10**
Figure 1.4	Depicts (a) soliton formation along a trans-polyacetylene chain, while (b) presents an illustration of three distinct solitons and their associated band structures.	**11**
Figure 1.5	Schematic of (a) organic diode (b) band positions of Al/P3HT/ITO Schottky diode	**13**
Figure 1.6	Illustrates (a) different configurations of OFETs, and (b) presents the corresponding transfer characteristics.	**14**
Figure 1.7	Schematic representation of the operational mechanism of a phototransistor.	**16**
Figure 1.8	Represents the schematic for the three different types of orientation occurred in conducting polymer thin films.	**27**
Figure 1.9	Represents the schematic of (a) off-centered spin coating (b) Solution shearing (c) Epitaxial crystallization for organic thin films.	**30**
Figure 1.10	Schematic of floating film transfer method.	**31**
Figure 1.11	Schematic representation for the Unidirectional floating film transfer method.	**32**
Figure 2.1	Chemical structure (a) DPP-TTT, (b) P4T2F-HD, (c) C_3N_5.	**41**
Figure 2.2	Schematic representation of C_3N_5 synthesis from its precursor.	**42**

Figure 2.3	Photographs of (a) Spin coating instruments (b) schematic representation of the steps involved in spin coating process.	**45**
Figure 2.4	(a) Photographs of the FTM thin film (b) schematic representation of FTM and their steps involved during film fabrication.	**46**
Figure 2.5	(a) Schematic representation of the UFTM (b) photographs of the UFTM thin film.	**47**
Figure 2.6	Schematic Representation of PDMS mold preparation.	**48**
Figure 2.7	Schematic representation for the substrate cleaning.	**49**
Figure 2.8	Schematic representation of the MIM (p+-Si/dielectric/Al) device fabrication.	**50**
Figure 2.9	(a) Representation of the OFETs fabrication (b) photographs of the nickel shadow mask (c) optical images of the shadow mask.	**51**
Figure 2.10	(a) Schematic representation of XRD (b) instrument image of the thin film XRD	**53**
Figure 2.11	(a) Schematic representation of the FTIR (b) photographs of the FTIR instrument.	**54**
Figure 2.12	Represents the Photographs of the XPS instrument (curtsy to CIFC IIT BHU), (b) working principle of the XPS	**55**
Figure 2.13	(a) Photographs of The UV instrument (b) photograph of the polarizer.	**57**
Figure 2.14	(a) Schematic representation of the AFM (b) photographs of the AFM instruments	**58**
Figure 2.15	(a) Schematic representation of the SEM (b) instrument image	**60**

Figure 2.16	(a) Schematic representation of the CV instrument (b) instruments photographs of cyclic voltammetry.	**62**
Figure 2.17	(a) Setup of TRM-SHG (b) Schematic representation of the TRM-SHFG setup.	**65**
Figure 3.1	Represents the schematic of the Unidirectional floating film Transfer Method (UFTM)	**70**
Figure 3.2	(a) **S**chematic representation for the out-of-plane instrument, (b) out-of-plane XRD pattern of P4T2F-Thin film.	**71**
Figure 3.3	(a) Represents the Polarized spectra of P4T2F-HD, the inset image represents the thin film fabricated by UFTM in which the red arrow shows the direction of flow, and the black arrow presents the polarizer position. (b) represents the polarized absorbance from 0^o - 360^o	**72**
Figure 3.4	(a) Represents the AFM image of P4T2F-HD (b) 3D AFM image of P4T2F-HD	**73**
Figure 3.5	(a) Represents the Output characteristics of perpendicular aligned film (b) the Output characteristics of parallel aligned film (c) represents the schematic of film expansion with channel alignment (d) represents the thin transfer characteristics of parallel and perpendicular aligned film.	**75**
Figure 3.6	(a) Setup of the Optical Apparatus for Time-Resolved Magneto-Second Harmonic Generation (TRM-SHG) Exploration. (b) Schematic of the Circular Electrode Configuration, (c) Structure of the Examined Specimen.	**77**
Figure 3.7	(a) Shows the stamped thin film from the orientation thin film, and lines on the thin films show the orientation polymer chains (b) time-resolved SHG image of the device	**78**

Figure 3.8 Represents the time-resolved SHG image of the device with different time intervals from 0 to 500ns. **80**

Figure 4.1 Schematic represents the fabrication of OPTs. **87**

Figure 4.2 (a) 2D AFM image of PMMA thin film, (b) 3D-AFM imager of PMMA, (c) SEM image of PMMA thin film (d) cross-sectional SEM image of PMMA dielectric. **88**

Figure 4.3 Leakage current vs applied voltage for PMMA dielectric. **89**

Figure 4.4 (a) Out of plane XRD pattern of thin film (b) represents the in plane XRD pattern of thin film. **90**

Figure 4.5 (a) Represents the image of UFTM thin film on air-liquid interface (b) represents the polarized UV-Spectrum of P4T2F (c) & (d) represents the polarized image of thin film in which green arrow represents the flow direction while yellow double-sided arrow presents the polarizer direction **91**

Figure 4.6 Represents AFM image of P4T2F thin film, (b) SEM image of P4T2F-HD, thin film. **92**

Figure 4.7 (a) Represents the output characteristics of the device (b) represents the transfer characteristics of device. **93**

Figure 4.8 Represents the drain current versus gate voltage with variable light intensity (b) represents the sensitivity of device at different gate voltage with varying in the intensity of light (c) represents the responsivity of device at different gate voltage with varying in the intensity of light (d) represents the detectivity of device at different gate voltage with varying in the intensity of light **95**

Figure 4.9 (a) Represents the shift in the threshold voltage with light intensity (b) represents the sensitivity with light intensity at V_{GS} = -80V (c) represents the responsivity with light intensity at V_{GS} = -80V (d) represents the detectivity with light intensity at V_{GS} = -80V **97**

Figure 4.10 (a) Represents the transient response of device (b) Represents the photo response under different wavelength (c) represents the I_D-V_G with different bending cycle parallel to channel width (d) represents the I_D-V_G with different bending cycle, bending is parallel to channel length **100**

Figure 4.11 Represents the transfer characteristics of device under dark conditions with different no. of days (b) represents the transfer characteristics under illumination with different no. of days (c) represents the mobility v/s days (d) represents the on/off ratio v/s days **101**

Figure 5.1 Schematic diagram of Li-Al_2O_3/DPP-TTT OFET fabrication. **107**

Figure 5.2 (a) GIXRD pattern of the Li-Al_2O_3 thin film (b) UV-spectrum of the dielectric thin film. **108**

Figure 5.3 (a) 2D AFM image (b) 3D image of the Li-Al_2O_3 dielectric thin film. **109**

Figure 5.4 (a) Leakage current versus applied voltage Li-Al_2O_3 dielectric thin film, (b) capacitance vs. frequency plot of Li-Al_2O_3 dielectric thin film in Metal-Insulator-Metal (MIM) geometry. **109**

Figure 5.5 GIXRD pattern of (a) in plane, and (b) out of plane DPP-TTT thin film. **110**

Figure 5.6 (a) UFTM thin film image and in inset thin film transferred on quartz substrate in which blue arrow shows the direction of flow and double-sided red arrow shows the polarizer direction (b) polarized visible/NIR absorption spectra of DPP-TTT thin film. **111**

Figure 5.7 (a) AFM image of DPP-TTT thin film (b) Roughness profile of the DPP-TTT thin films. **112**

Figure 5.8 (a) Schematic for the channel orientation, (b) Output characteristics of Perpendicular (c) output characteristics of Parallel, (d) Transfer characteristics of OFETs with $(I_D)^{1/2}$ Vs. V_G. **113**

Figure 5.9 (a) Represents the device schematic under light exposure (b) Photocurrent versus time of OFET under Different wavelengths of light. (c) Transfer characteristics of OFET under different power Intensity of light, (d) plotted graph in log (10) plot of Transfer characteristics in Dark and Under light illumination of different power of light in ($\mu W/cm^2$). **114**

Figure 5.10 (a) Threshold voltage and Darin current under different illumination power. (b, & c) sensitivity, and detectivity v/s light intensity in accumulation and depletion mode respectively, (d)) Transient response of the device under 830nm at 730$\mu W/cm^2$. **116**

Figure 6.1 (a) XRD pattern of the bulk C_3N_5 (b) FTIR spectra of C_3N_5 **127**

Figure 6.2 (a) UV-visible absorption spectra of C_3N_5 (b) transformed Kubelka-Munk function versus photon energy for C_3N_5 **128**

Figure 6.3 High-resolution deconvoluted elements (a) C1s, (b) N1s, (c) XPS survey of C_3N_5 **129**

Figure 6.4 Represents the Sem image of (a) bulk C_3N_5 (b) exfoliated C_3N_5 (c) elemental survey of C_3N_5 (d) represents the elemental mapping of carbon and nitrogen **130**

Figure 6.5 FTIR spectra of DPP-TTT/C_3N_5 blend solution **132**

Figure 6.6 (a) GIXRD pattern of DPP-TTT and DPP-TTT/C_3N_5 (3%). (b) represents the shifting in the (100) peak of the DPP-TTT/C_3N_5 (3%) with respect to pristine DPP-TTT **134**

Figure 6.7 (a) Represents the thin film with polarizer red double-sided arrow shows the direction of polarizer and blue arow presents the direction of flow. (b) Polarized spectra of thin film, (c) Normalized UV-VIS absorption spectrum of DPP-TTT and DPP-TTT/ C_3N_5 hybrid film. (d) A_{0-0}/A_{0-1} ratio (black half-filled hexagonal) and exciton bandwidth (red diamond) as a function of C_3N_5 (wt.%) concentration in DPP-TTT **136**

Figure 6.8 (a) & (b) AFM height profile and its 3D image of the DPP-TTT thin film, respectively, (c) & (d) AFM height profile and corresponding 3D image of the DPP-TTT/C_3N_5(3%) hybrid thin film, respectively. **137**

Figure 6.9 CV curve of DPP-TTT and DPP-TTT/C_3N_5(3%) hybrid thin film. **138**

Figure 6.10 (a) Output characteristics of DPP-TTT (b) Output characteristics DPP-TTT/C_3N_5 (3%) **139**

Figure 6.11 (a) Represents the device schematic (b) Transfer characteristics of DPP-TTT/C_3N_5 (c) SQRT Id-Vg of DPP-TTT/C_3N_5. (d) represents the mobility v/s C_3N_5 fraction. **140**

Figure 6.12 Optical configuration for Second Harmonic Generation (SHG) analysis, and the sample architecture for Field-Effect Transistor (FET) evaluations. **142**

Figure 6.13 SHG image of (a) DPP-TTT OFETs with different time interval (b) DPP-TTT/C_3N_5 OFETs with different time interval **144**

Figure 6.14 Represents the pixel position of (a) DPP-TTT OFET under different time interval, (b) DPP-TTT/ C_3N_5 (3 %) OFET under different time interval, (c) represents the position of the charge carrier of DPP-TTT and DPP-TTT/C_3N_5 calculated from the SHG image **145**

List of Tables

Table No.	Table Caption	Page No.
Table 4.1	Comparative study of current work with previously reported.	**98**
Table 5.1	Summary of OFETs Parameters	**116**
Table 5.2	Comparative study of current work with previously reported.	**118**

µA	:	Microampere
µL	:	Microlitre
ºC	:	Degree Celsius
1D	:	One dimensional
2D	:	Two dimensional
3D	:	Three dimensional
AFM	:	Atomic Force Microscopy
Al	:	Aluminum
Au	:	Gold
cm	:	Centimetre
CCD		Charge-Coupled Device
CV	:	Cyclic Voltammetry
DI	:	Deionized
DPP-TTT	:	Poly[2,5-(2-octyl-dodecyl)-3,6-diketopyrrolopyrrole-alt-5,5-(2,5-di(thien-2-yl)thieno[3,2-b]thiophene)]
EDS/ EDAX	:	Energy dispersive X-ray spectroscopy
EFISHG	:	Electric field induced second harmonic generation
eV	:	Electron volt
FTIR	:	Fourier transform infrared
FTM	:	Floating Film Transfer method
UFTM	:	Unidirectional Floating Film Transfer method
HOMO	:	Highest Occupied Molecular Orbital
h / hr	:	Hour(s)
HR-TEM	:	High resolution transmission electron microscopy

ITO	:	Indium Tin Oxide
LS	:	Langmuir Schaefer
LUMO	:	Lowest Unoccupied Molecular Orbital
min	:	Minute(s)
M_W	:	Weight average molecular weight
Mn	:	Number average molecular weight
nm	:	nanometer
NIR		Near-infrared
OFET	:	Organic Field Effect Transistor
OPT	:	Organic phototransistor
OLED	:	Organic Light-Emitting diodes
OTFT	:	Organic thin film Transistor
OSP	:	Organic Semiconducting Polymers
PDIOTFT	:	Polydispersive index
PED	:	Polymer Electrochromic Device
P4T2F-HD	:	Poly(3,3′-dihexyldecyl-4″,4‴-difluoro[2,2′:5′,2″:5″,2‴-quaterthiophene]-5,5‴- diyl)
P3HT	:	Poly(3-hexylthiophene-2,5-diyl)
PBTTT	:	Poly[2,5-bis (3- tetradecylthiophen-2-yl) thieno[3,2- b]thiophene]
PT	:	Polythiophene
rr-P3HT	:	Regioregular- poly(3-hexylthiophene-2,5-diyl)
s	:	Second
S	:	Siemen
SAED	:	Selected area electron diffraction patttern
SBD	:	Schottky barrier diodes

T	:	Temperature
TBAP	:	Tetrabutyl ammonium perchlorate
TEM	:	Transmission electron microscopy
TMDs		Transition metal dichalcogenides
TOF		Time of flight
TRM-SHG	:	Time Resolved Microscopic Second Harmonic Generation
UV–Vis	:	UV Visible
V	:	Volt
W		Watt
XPS	:	X–ray photoelectron spectroscopy