
Table of Contents

Dedication.....	I
Certificate.....	II
Declaration.....	III
Acknowledgement.....	IV
Table of Contents.....	VI
List of Abbreviations.....	XIII
Chapter 1	1
Introduction	1
Organic materials for electronics.....	2
Characteristics of organic semiconductors	3
Structural properties.....	3
Conjugated structure	3
Solubilizing side chains.....	3
Optical and electronic properties	4
Charge carrier mobility	9
Solid state morphology	12
Conformational rigidity of monomers and effect of alkyl chain orientation.....	15
Effect of molecular weight	17
Effect of structural reorganization and resonance stabilization.....	18
Aim and objective.....	31
References	32
Chapter 2	43
Polycyclic Fused Aromatic Pyrrole-based Conjugated Polymers	43
Introduction	45
Part-A: Synthesis, characterization and electrochemistry of monomers	52
Results and discussion.....	52
Synthesis of polycyclic fused aromatic pyrrole-based monomers.....	52
Characterization of the synthesized polycyclic fused aromatic pyrrole-based monomers.....	54

Electrochemical properties of the synthesized polycyclic fused aromatic pyrrole-based monomers	54
Conclusion	57
Experimental procedures	58
General procedures	58
Synthesis of tricyclic fused aromatic pyrrole-based monomers	58
Synthesis of 2,1,3-benzothiadiazole, 1 :.....	59
Synthesis of 4,7-dibromo-2,1,3-benzothiadiazole, 2 :	59
Synthesis of 4,7-bis((trimethylsilyl)ethynyl)-2,1,3-benzothiadiazole, 3 :	59
Synthesis of 3,6-bis((trimethylsilyl)ethynyl)benzene-1,2-diamine, 4 :	60
Synthesis of <i>N,N'</i> -(3,6-bis((trimethylsilyl)ethynyl)-1,2-phenylene)diacetamide, 5 :.....	60
Synthesis of 1,8-dihydropyrrolo[3,2- <i>g</i>]indole (BDP):.....	61
Synthesis of 1,8-dioctyl-1,8-dihydropyrrolo[3,2- <i>g</i>]indole (DOBBDP) and 1,3,8-trioctyl-1,8-dihydropyrrolo[3,2- <i>g</i>]indole (TOBDP):.....	61
Synthesis of tetracyclic fused aromatic pyrrole-based monomers.....	62
Synthesis of 2,3-dihydrazinylnaphthalene, 6 :	63
Synthesis of 2,2'-(naphthalene-2,3-diylbis(hydrazin-2-yl-1-ylidene))(2 <i>E</i> ,2' <i>E</i>)-dipropionate, 7 :	63
Synthesis of diethyl 1,10-dihydrobenzo[<i>e</i>]pyrrolo[3,2- <i>g</i>]indole-2,9-dicarboxylate, 8 :	64
Synthesis of 1,10-dihydrobenzo[<i>e</i>]pyrrolo[3,2- <i>g</i>]indole (NBP):.....	64
Synthesis of 1,10-dioctyl-1,10-dihydrobenzo[<i>e</i>]pyrrolo[3,2- <i>g</i>]indole (DONBP):	64
Spectral data	66
Part-B: Synthesis, characterization and electrochemistry of conjugated polymers ...	80
Results and discussion	80
Electrochemical polymerization of synthesized monomers	80
Electrochemical properties of PNBP	84
Synthesis of copolymer PMNBP from NBP	85
Thermogravimetric analysis of PMNBP	86
Molecular weight and solubility properties of PMNBP	87
Photo-physical and conductivity properties.....	87
Electrochemical properties of polymers	89
Conclusion.....	90

Experimental procedures	91
General procedures	91
Synthesis of monomer and polymers	92
Synthesis of 3,4-(dioctyloxy)benzaldehyde:	92
Synthesis of PMNBP from NBP :	92
Spectral data	94
References	97
Chapter 3	100
From 1879 to 2018: Indophenine to Indophenine Polymers.....	100
Introduction	102
Part-A: Development of the synthetic routes for fused bi-isatyls: Synthesis and characterization of novel fused bi-isatyls.....	114
Results and discussion.....	114
Synthetic approaches to synthesize novel fused bi-isatyls	114
Conclusion.....	120
Experimental procedures	121
General procedures	121
Sandmeyer synthetic approach	121
Synthesis of QxN	121
Acid catalyzed condensation-cyclization reaction of 1,2-phenylenebis(oxamic acid)	122
Synthesis of QxDN :	122
Oxidation reaction of stabilized Boc-protected polycyclic fused aromatic pyrrole-based compound di-tert-butyl pyrrolo[3,2-g]indole-1,8-dicarboxylate (DBoc-BDP)	123
Synthesis of di-tert-butyl pyrrolo[3,2-g]indole-1,8-dicarboxylate (DBoc-BDP):	123
Synthesis of di-tert-butyl 2,3,6,7-tetrabromopyrrolo[3,2-g]indole-1,8- dicarboxylate (DBoc-TBr-BDP):	123
Oxidation reaction of <i>N</i> -alkylated polycyclic fused aromatic pyrrole-based compound 1,8-dioctyl-1,8-dihydropyrrolo[3,2-g]indole (DOBBDP).....	124
Synthesis of fused bi-isatyl product 4,5-dibromo-1,8-dioctyl-1,8- dihydropyrrolo[3,2-g]indole-2,3,6,7-tetraone (DBr-DOBBDP-BIs):	124
Oxidation reaction of <i>N</i> -alkylated polycyclic fused aromatic pyrrole-based compound 1,10-dioctyl-1,10-dihydrobenzo[<i>e</i>]pyrrolo[3,2-g]indole (DONBP).....	125

Synthesis of fused mono-isatyl product 1,10-dioctyl-1,10-dihydrobenzo[<i>e</i>]pyrrolo[3,2- <i>g</i>]indole-2,3-dione (DONBP-MIs):	125
Synthesis of 1,10-dioctyl-1,10-dihydrobenzo[<i>e</i>]pyrrolo[3,2- <i>g</i>]indole-2,3,8,9-tetraone (DONBP-BIs):	126
Spectral data	127
Part-B: Synthesis, characterization and electrochemical study of novel fused bi-isatyls and novel indophenine polymers	137
Results and discussion	137
Synthesis and characterization of fused bi-isatyl monomers DBr-DDBDP-BIs and DTNBP-BIs	137
Synthesis of novel indophenine polymers DBr-BDP-INDPH and NBP-INDPH	139
Thermal properties of monomers and polymers, molecular weight and solubility of polymers	140
Photo-physical properties of monomers	142
Photo-physical properties of polymers	144
Electrochemical properties of monomers	147
Electrochemical properties of polymers	148
Organic Field Effect Transistor (OFET) device characterization of polymers	150
Conclusion	152
Experimental procedures	153
General procedures	153
Synthesis of monomers	153
Synthesis of 1,8-didodecyl-1,8-dihydropyrrolo[3,2- <i>g</i>]indole (DDBDP):	154
Synthesis of 4,5-dibromo-1,8-didodecyl-1,8-dihydropyrrolo[3,2- <i>g</i>]indole-2,3,6,7-tetraone (DBr-DDBDP-BIs) and 4,5,6,7-tetrabromo-1,8-didodecyl-1,8-dihydropyrrolo[3,2- <i>g</i>]indole-2,3-dione (TBr-DDBDP-MIs):	154
Synthesis of 1,10-ditetradecyl-1,10-dihydrobenzo[<i>e</i>]pyrrolo[3,2- <i>g</i>]indole (DTNBP):	156
Synthesis of 1,10-ditetradecyl-1,10-dihydrobenzo[<i>e</i>]pyrrolo[3,2- <i>g</i>]indole-2,3,8,9-tetraone (DTNBP-BIs):	156
General procedure for the synthesis of indophenine polymers	157
Spectral data	159
References	172
Chapter 4	179

Heterocyclic Fused Aromatic Dithienopyrrolobenzothiadiazole (DTPBT)-Based Conjugated Polymers	179
Introduction	181
Results and discussion	187
Synthesis of monomers and polymers	187
Structural aspects of monomers	192
Molecular weight and thermal properties of polymers	198
Photo-physical properties of polymers	199
Electrochemical properties of polymers	201
Space charge limited current (SCLC) hole mobilities of polymers	203
Conclusion	204
Experimental procedures	205
General procedures	205
Synthesis of monomers	206
Synthesis of 4,7-dibromo-5,6-dinitro-2,1,3-benzothiadiazole, 3 :	206
Synthesis of 5,6-dinitro-4,7-di(thiophene-2-yl)-2,1,3-benzothiadiazole, 4 :	206
Synthesis of DTPBT :	207
Synthesis of DTPBT-C8 :	207
Synthesis of TP-M1	208
Synthesis of TP-M2	208
Synthesis of compound 6	209
Synthesis of INQx-M3	210
Synthesis of compound 8	210
Synthesis of compound 9	211
Synthesis of BIIG-M4	212
Synthesis of compound 10	212
Synthesis of compound 11	212
Synthesis of compound 12	213
Synthesis of compound 13	213
Synthesis of BTD-IMD-M5	213
General procedure for synthesis of DTPBT-based polymers TP-TP-IMD , TP- INQx and TP-BIIG	214
Spectral data	216
Chapter 5	243

Synthesis, Characterization and Study of Novel Conjugated Molecules.....	243
Part-A: Constructing a self-assembling C ₃ -symmetric covalently linked (fused) donor-acceptor-type molecule containing hexaazatriphenylene core	243
Introduction	245
Results and discussion	251
Synthesis of hexaazatriphenylene core containing molecule HAT-IPN	251
Photo physical properties and dynamic light scattering studies	255
Electrochemistry of HAT-IPN	258
Thermogravimetric analysis, differential scanning calorimetry and atomic force microscopy of HAT-IPN	260
Conclusion	262
Experimental procedures	263
General procedures	263
Synthesis of hexaazatriphenylenehexacarbonitrile, 2 :	264
Synthesis of hexaazatriphenylenehexacarboxamide, 3 :	264
Hexaazatriphenylenehexacarboxamide, 3 :	264
Synthesis of hexaazatriphenylenehexacarboxylic acid, 4 :	264
Synthesis of hexaazatriphenylenehexacarboxylic acid trisanhydride, 5 :	265
Synthesis of 1,2-dioctyloxybenzene, 7 :	265
Synthesis of 1,2-dinitro-4,5-dioctyloxybenzene, 8 :	266
Synthesis of 4,5-dioctyloxybenzene-1,2-diaminium chloride, 9 :	266
4,5-dioctyloxybenzene-1,2-diaminium chloride, 9	266
Synthesis of HAT-IPN :	267
Spectral data	269
Part-B: Synthesis, photophysical, electrochemical and single crystal X-ray diffraction study of (Z)-2-phenyl-3-(5-(4-(thiophen-2-yl)benzo[c][1,2,5]thiadiazol-7-yl)thiophen-2-yl)acrylonitrile.....	274
Introduction	274
Results and discussion	276
Synthesis of compound 5	276
Single crystal X-ray diffraction (SCXRD) study of compound 5	277
Photo-physical properties of compound 5	280
Electrochemical properties of compound 5	281
Thermogravimetric analysis of compound 5	282

Conclusion.....	282
Experimental procedures	283
General procedures	283
Synthesis of compounds 1 and 2 :.....	283
Synthesis of 4,7-di(thiophen-2-yl)-2,1,3-benzothiadiazole (compound 3):..	283
Synthesis of 5-(4-(thiophen-2-yl)benzo[<i>c</i>][1,2,5]thiadiazol-7-yl)thiophene-2- carbaldehyde (compound 4):.....	284
Synthesis of (Z)-2-phenyl-3-(5-(4-(thiophen-2-yl)benzo[<i>c</i>][1,2,5]thiadiazol-7- yl)thiophen-2-yl)acrylonitrile (compound 5):	285
Spectral data	286
References	291
List of Conferences Attended and List of Publications	XIV