A synopsis of the thesis entitled

Synthesis, Characterization and Electrochemical Studies of Low Band-gap Conjugated Molecules and Polymers

To be submitted as a partial fulfilment for the award of the degree of

DOCTOR OF PHILOSOPHY

in

Chemistry

By

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The thesis will be presented in form of the following chapters:

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Part-B: Synthesis, characterization and electrochemistry of conjugated polymers

Chapter 3: From 1879 to 2018: Indophenine to Indophenine Polymers

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Chapter 1

Introduction

Organic materials for electronics

We live in an increasingly electronic world, with computers occupying a central part of our lives. In 2012, there were an estimated 30 - 40 processors per person, on average, with some individuals surrounded by as many as 1000 processors on a daily basis. While the miniaturization of silicon-based electronic structures have created an electronic world full of affordable, high performing devices, still there are things that silicon-based electronics cannot do and will never be able to do. Organic materials, whether used in combination with silicon or not, hold the potential to expand our electronic world in unimaginable ways. Chemists have worked with several different types of organic materials in the field of organic electronics. These materials include small molecules and polymers; fullerenes, nanotubes, graphene, and other carbon-based molecular structures; ensembles of molecules and molecular structures; and hybrid materials. These materials are used to build electronic structures, which are integrated into electronic devices. Some of these devices are already commercial realities and being used on a widespread basis. For example, both small molecules and polymers are being used in the manufacture of OLED displays (e.g., TV and cell phone displays), Organic Solar Cells , and OFETs.[1]

Conjugated polymers and molecules

Conjugated polymers are composed of alternating single and double bonds between covalently bound carbon atoms, leading to one unpaired electron (the π electron) per carbon atom. The sp^2p_z hybridized π orbitals overlap along the backbone, leading to the electron delocalization which provides pathway for charge transport along the polymer chain. Due to low-cost, light-weight, and flexibility advantages, electronic devices based on conjugated polymers are a promising cost-effective alternative to inorganic materials-based electronics. Conjugated polymers can be classified as hole or electron transporting (HT or ET) or ambipolar materials according to the type of orderly transferring charge carriers. Over the past two decades, significant evolution has been achieved in the preparation of HT conjugated polymers; some of the HT polymers shows extremely high hole mobilitiy (> 1 $cm^2 V^{-1} s^{-1}$), similar to that of amorphous silicon. The basic requirements for development of conjugated polymers are good solution processability, suitable HOMO-LUMO energies/bandgap, high charge carrier mobilities and deep LUMO levels to provide good air stability.[2,3] Polymers that have alternating electron rich donor and electron poor acceptor conjugated repeating units typically have low bandgaps where the HOMO energy levels resemble to HOMO of the electron rich unit, while the LUMO resembles the electron poor unit. The substituents on the donor and acceptor units can affect the band gap. The energy level of the HOMO of the donor can be increased by attaching electron donating groups (EDG), such as thiophene and pyrrole. Similarly, the energy level of the LUMO of the acceptor is lowered, when electron withdrawing groups (EWG), such as nitrile, thiadiazole and pyrazine, are attached. In addition to the D-A strategy, forced planarization by covalently fastening adjacent aromatic units in the polymer backbone provides an effective way to reduce the band gap and enhance the intrinsic charge mobility.[4,5] In this regard, extensive research effort has been focused on the design and synthesis of coplanar electron-rich donors and electron-deficient acceptors having multifused aromatic or heteroaromatic structures.[6,7] In recent years, quinoidal molecules have attracted considerable interest as a new class of semiconducting materials for organic electronics, over the multifused planar conjugated molecular building blocks, because of their highly planar structure and favoured π–π stacking which in turn, leads to the efficient charge transport in solid state.[8,9] Focusing the advantages of incorporating aromatic fused ring structures and quinoidal structures along the polymer backbone, we have synthesized and studied, monomers having fused ring systems as well as monomers which will favour quinoidal backbone formation upon polymerization. We have also synthesized conjugated polymers form these monomers and studied them electrochemically.

Aim and objective of this work

1. Development of fused conjugated molecules/monomers that can be subjected to polymerization without costlier transition metal catalysts and harsh conditions in terms of temperature and pressure.
2. Development of such conjugated fused molecules which, up on polymerization, can promote and stabilize quinoidal structure along the polymer backbone.
3. To develop conjugated polymers having a push-pull effect and having a better matched energy levels (for efficient electron/hole transfer between all layers and the electrodes of the device), that can compete favorably with other available materials for organic electronics.
4. Development of conjugated small molecules having Donor-Acceptor concept.

Chapter 2

Polycyclic Fused Aromatic Pyrrole-based Conjugated Polymers

Introduction

Pyrrole is five membered heterocyclic aromatic compound, which has remarkably lower oxidation potential than that of other five membered heterocyclic aromatic monomers, like thiophene and furan. Polypyrrole exhibits promising candidature for many commercial applications like **electronic devices**, **functional membranes**, **electrochromic windows and displays**, **solid electrolytic capacitors**, **anti-electrostatic coatings**, **wires**, **microactuators**, **biosensors and gas sensors** etc. because of its higher conductivity, facile synthesis and good environmental stability. Polypyrrole films have remarkable influence in the field of **molecular electronic devices**, **solid-state 'batteries'** and **chemically modified electrodes and sensors** due to their solid-state properties[10]. Fused rings help to achieve planar and more rigid polymer backbone, which in turn leads to enhanced effective π conjugation, reduced chain-folding and lower band-gap. Moreover, rigid fused ring structure lowers the reorganization energy of the polymer, which facilitates intermolecular hoping and charge career mobility[11].

Part-A

Synthesis, characterization and electrochemistry of monomers

Focusing the advantages of incorporation of fused aromatic pyrrole-based building blocks in to the polymer backbone, we have synthesized a series of polycyclic fused aromatic pyrrole-based building blocks, namely 1,8-dihydropyrrolo[3,2-g]indole (benzodipyrrole) 1 (BDP), 1,8-dioctyl-1,8-dihydropyrrolo[3,2-g]indole (N,N'-dioctylbenzodipyrrole) 2 (DOBDP), 1,3,8-trioctyl-1,8-dihydropyrrolo[3,2-g]indole (N,N'-diocyl-3-octylbenzodipyrrole) 3 (TOBDP), 1,10-dihydrobenzo[e]pyrrolo[3,2-g]indole (naphthobipyrrole) 4 (NBP) and 1,10-dioctyl-1,10-dihydrobenzo[e]pyrrolo[3,2-g]indole (N,N'-dioctylnaphthobipyrrole) 5 (DONBP).

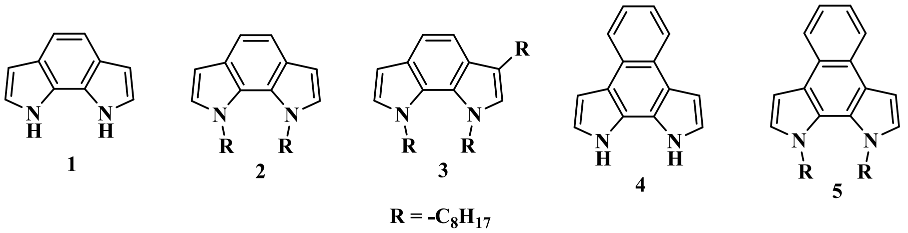
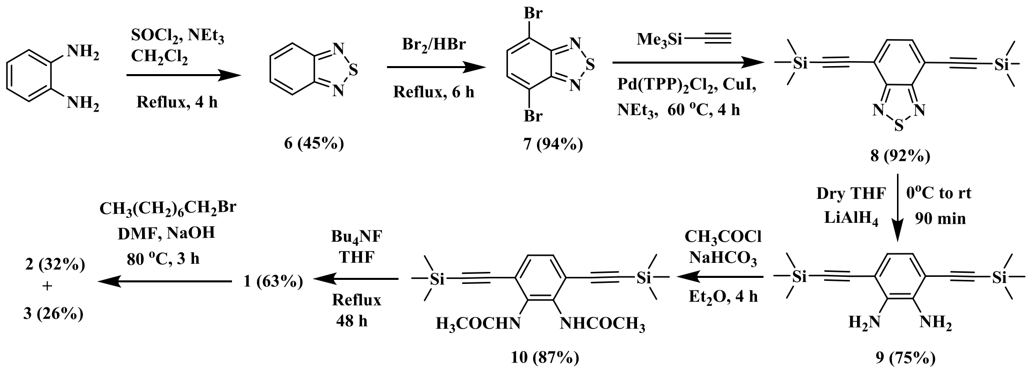
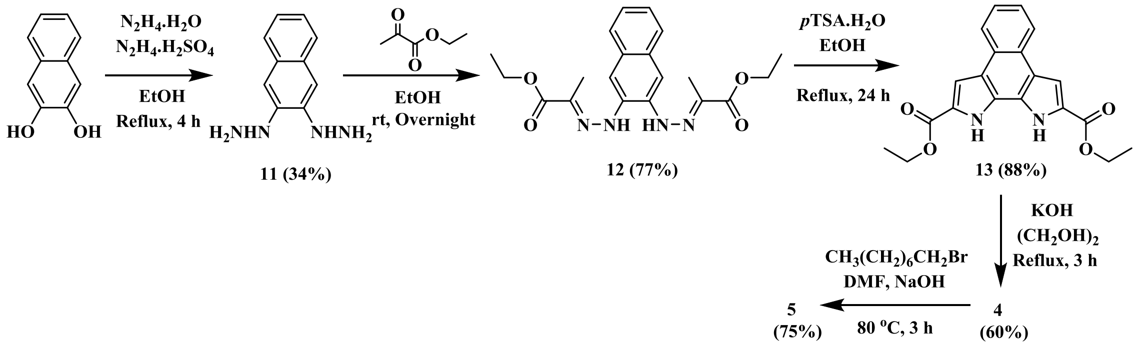


Figure 1[11] Synthesized polycyclic fused aromatic pyrrole-based monomers

Synthesis and characterization of polycyclic fused aromatic pyrrole-based monomers



Scheme 1[11] Synthesis of compounds **1**, **2** and **3**



Scheme 2[11] Synthesis of compounds **4** and **5**

Compound **1** was synthesized by tetra-*n*-butylammonium fluoride (TBAF)-mediated intramolecular cyclization of ortho-alkynylaniline using the modification of the literature procedure reported by Yasuhara *et al.*[12] in 63% yield (Scheme 1). Alkylation reaction of compound **1** using excess of 1-bromooctane and NaOH in DMF afforded compounds **2** and **3**. Naphthobipyrrole **4**[13] was synthesized as shown in Scheme 2 using the modification of the literature procedure reported by Roznyatovskiy *et al.*[14] *N,N´*-dioctylnaphthobipyrrole **5** was synthesized by alkylation reaction of compound **4** using excess of 1-bromooctane and NaOH in DMF at 80 °C for 3 h. All the synthesized compounds are characterized by ^{1}H, ^{13}C and mass spectroscopy.

Electrochemistry of synthesized monomers

The redox properties of the synthesized monomers **1-5** were studied by cyclic-voltammetry (CV). CV experiments were performed in the dry acetonitrile solution of compounds **1-5** (~ 5 mM) and $TBAPF_6$ as a supporting electrolyte (~ 50 mM) using three electrodes system: Pt disc electrode as working electrode, Pt wire electrode as counter electrode and Ag/Ag^+ as a reference electrode. All monomers showed irreversible oxidation waves in cyclic voltammogram. The onset oxidation potentials, measured from the CVs were utilized to calculate the Highest Occupied Molecular Orbital (HOMO) levels of the synthesized monomers. In case of BDP-based monomers (**1**, **2** and **3**), introduction of alkyl substituents in to the BDP scaffold elevated the HOMO levels. While in case of NBP-based scaffolds (**4** and **5**), introduction of alkyl substituents lowered the HOMO levels.

Monomer	E_{oxi} (V) v/s Ag/Ag^+	$E_{oxi\ onset}$ (V) v/s Ag/Ag^+	HOMO [a] (eV)
Compound 1	+ 1.22	+ 0.78	− 5.22
Compound 2	+ 0.86	+ 0.71	− 5.15
Compound 3	+ 0.74	+ 0.63	− 5.07
Compound 4	+0.70	+ 0.55	− 4.99
Compound 5	+ 0.72	+ 0.60	− 5.04

Table 1[11] Electrochemical properties of synthesized monomers **1-5**; [a] calculated from the equation: $E_{HOMO} = -(E_{oxi,onset} + 4.8 - E_{onset\ (Fc/Fc+)})$, $E_{onset\ (Fc/Fc+)} = 0.36$ V.

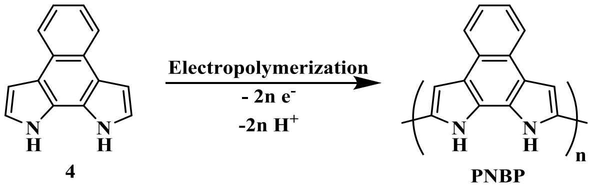
Part-B

Synthesis, characterization and electrochemistry of conjugated polymers

Out of synthesized monomers, compound **4** (naphthobipyrrole) was opted as a choice of monomer for the formation of homopolymer as well as copolymer contemplating advantages like tetracyclic fused aromatic pyrrole-based structure, good β-β´-reactivity of pyrrolic positions towards electrophilic reactions and stability towards aerial oxidation.

Synthesis, characterization and electrochemistry of homo-polymer of naphthobipyrrole by electro-chemical polymerization

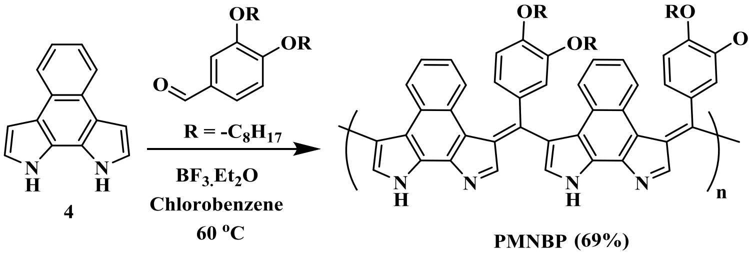
Electrochemical polymerization technique has advantage that it forms a layer of conducting material directly on to the surface of electrode, so that solubility and processability needs for synthesized polymers can be avoided. Compound **4** (naphthobipyrrole) polymerizes electrochemically when cycled repeatedly between −0.2 V to 1.1 V forming a continuous polymeric film on the surface of the working electrode.



Scheme 3 Synthesis of homo-polymer **PNBP** from compound **4** *via* electrochemical polymerization

The synthesized homo-polymer PNBP is an electro-active polymer, exhibiting electrochromic properties as evidenced by scan rate dependence cyclic voltammetry and spectroelectrochemical studies of PNBP film coated on ITO electrode.

Synthesis, characterization and electrochemistry of co-polymer of naphthobipyrrole



Scheme 4[11] Synthesis co-polymer **PMNBP** from compound **4** and 3,4 (dioctyloxy)benzaldehyde.

Compound **4** (naphthobipyrrole) shows predominant reactivity at carbon 3 and 8 (i.e., the β-pyrrolic positions). To synthesize copolymer **PMNBP**, compound **4** was reacted with 3,4-(dioctyloxy)benzaldehyde in presence of $BF_3.Et_2O$ to afford **PMNBP**; in which monomeric naphthobipyrrole units are connected by substituted methylene bridges via β-position of fused-pyrroles (Scheme 4). Source of substituted methylene bridge is 3,4-(dioctyloxy)benzaldehyde, which also confers the solubility to the resulting co-polymer **PMNBP**. The synthesized co-polymer **PMNBP** is characterized by ^1H and ^{13}C NMR spectroscopy, gel permeation chromatography, UV-visible spectroscopy, cyclic voltammetry and thermogravimetric analysis. The conductivity of PMNBP was found to be 0.124 mS cm^{-1}. **PMNBP** turned out to be an electro-active low band-gap polymer, having good film forming properties with a lower oxidation potential and good thermal stability.

Polymer	λ_{max} (nm)	$E_{oxi,onset}$ (V) v/s Ag/Ag$^+$	E_{HOMO} (eV) ^{a}	E_{LUMO} (eV) ^{b}	E_g^{opt} (eV) ^{c}	M_w Dalton	PDI	T_d °C
PMNBP	586, 715	+0.61	−4.94	−3.51	1.43	4878	1.22	239

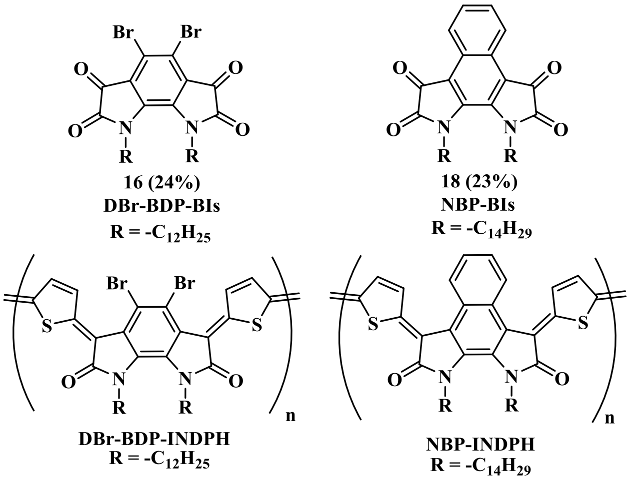
Table 2[11] Photo-physical, electro-chemical properties, Molecular weight M_w, Poly-Dispersity Index (obtained from GPC analysis), decomposition temperature T_d (obtained from TGA) of PMNBP; ^{a} calculated using equation $E_{HOMO} = -(E_{ox,onset} + 4.8 - E_{onset\ (Fc/Fc+)})$, $E_{onset\ (Fc/Fc+)} = 0.47$ V; ^{b} calculated using equation $E_{LUMO} = E_g^{opt} + E_{HOMO}$ eV; ^{c} calculated using equation $E_g^{opt} = 1240/\lambda_{onset}$(nm) eV.

Chapter 3

From 1879 to 2018: Indophenine to Indophenine Polymers

Introduction

Compared to the various conjugated molecular building blocks, quinoidal molecular building blocks offer several advantages like highly planar structure, favourable π-π staking which in turn leads to the efficient charge transport in the solid state, efficient delocalization of π-electrons resulting in to the reduced band-gaps and amphoteric redox behaviour which makes them good candidates as both n-type and p-type semiconductors when properly polarized. Till now, very few quinoidal molecules have been reported, amongst which, most of the quinoidal molecules show n-channel FET behaviour. Recently, N-dodecyl indophenine has been reported to show promising ambipolar charge-transport performance with electron mobility of about 10^{-3} $cm^2V^{-1}s^{-1}$ and hole mobility of about 10^{-2} $cm^2V^{-1}s^{-1}$ in OFETs.[9,15] All above said facts and figures motivated us to take this promising quinoidal molecule, indophenine to the next level. Driven by this idea, we designed monomers bi-isatyls, which would give exactly the same reaction with thiophene in presence of concentrated sulfuric acid, like isatin. Indophenine reaction with these monomers will lead to the polymers, having quinoidal backbone just like indophenine. Preliminary DFT calculations showed that these indophenine polymers are low band-gap polymers (<1.3 eV) due to their quinoidal nature of bonding.



16 (24%)
DBr-BDP-BIs
R = $-C_{12}H_{25}$

18 (23%)
NBP-BIs
R = $-C_{14}H_{29}$

DBr-BDP-INDPH
R = $-C_{12}H_{25}$

NBP-INDPH
R = $-C_{14}H_{29}$

Figure 2 Structures of the synthesized novel fused bi-isatyls and corresponding indophenine polymers

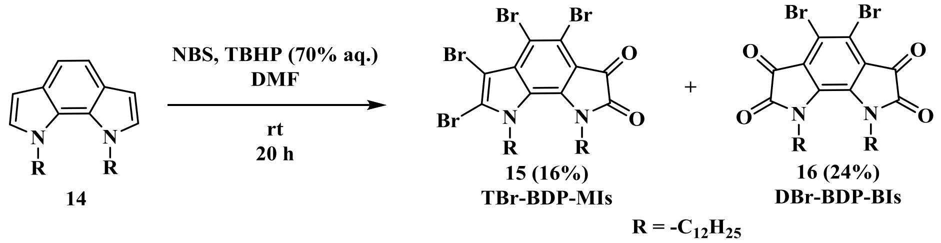
Part-A

Development of the synthetic routes for fused bi-isatyls: synthesis, characterization and electrochemical study of novel fused bi-isatyls

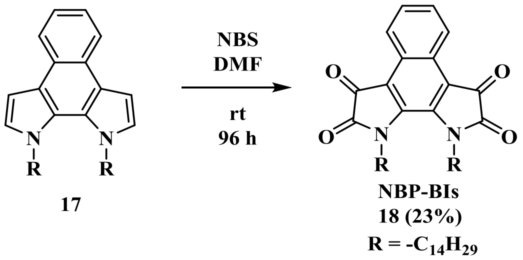
Synthesis and characterization of novel fused bi-isatyls

The novel fused bi-isatyls were synthesized by oxidizing the corresponding polycyclic benzodipyrrole and naphthobipyrrole scaffolds. Following the reported procedures of synthesis of isatin from indole, we have tried many oxidizing agents involving PCC, PCC-SiO_2, CrO_3-Jones oxidation, H_2O_2, TBHP, IBX-$CeCl_3$ mediated oxidation, I_2-KOH mediated iodination followed by oxidation using $NaIO_4$, etc. to convert bi-pyrrole in to bi-isatyl, but in all the cases, we ended up with either decomposition of starting materials or sticky side products which could not be isolated and characterized.

The benzodipyrrole (BDP)-based fused bi-isatyl compound **16** (DBr-BDP-BIs) was synthesized by oxidation of compound **14** using N-bromosuccinamide and tert-butyl hydroperoxide (70% aqueous solution) in DMF at room temperature (Scheme 5). The naphthobipyrrole (NBP)-based fused bi-isatyl compound **18** (NBP-BIs) was synthesized by oxidation of compound **17** using N-bromosuccinamide in DMF at room temperature (Scheme 6).



Scheme 5 Synthesis of BDP-based novel fused bi-isatyl compound **15** (DBr-BDP-BIs) from compound **14**



Scheme 6 Synthesis of NBP-based novel fused bi-isatyl compound **18** (NBP-BIs) from compound **17**

All the synthesized molecules were characterized by ^{1}H, ^{13}C and DEPT-135 NMR spectroscopy and UV-visible spectroscopy.

Monomer	**λ_{max} [ab] (nm)**	**λ_{onset} (nm)**	**E_g^{opt} (eV)**
DBrBDP-BIs	340, 570	692	1.79
NBP-BIs	318, 517	710	1.74

Table 3 Photo-physical properties of synthesized bi-isatyls and optical band-gaps calculated using equation $E_g^{opt} = 1240/\lambda_{onset}$(nm) eV.

Electrochemistry of synthesized monomers

The redox properties of the synthesized monomers **16** and **18** were studied by cyclic-voltammetry (CV). CV experiments were performed in the dry acetonitrile solution of compounds **16** and **18** (~ 5 mM) and TBAPC as a supporting electrolyte (~ 50 mM) using three electrodes system: Pt disc electrode as working electrode, Pt wire electrode as counter electrode and Ag/Ag^+ as a reference electrode. All monomers showed irreversible oxidation and reduction waves in cyclic voltammogram. The onset oxidation and reduction potentials, measured from the CVs were utilized to calculate the Highest Occupied Molecular Orbital (HOMO) and Lowest Unoccupied Molecular Orbital (LUMO) levels of the synthesized monomers.

Monomer	**E_{oxi} [a] (V)**	**$E_{oxi,onset}$ [a] (V)**	**E_{HOMO} [b] (eV)**	**E_{red} [a] (V)**	**$E_{red,onset}$ [a] (V)**	**E_{LUMO} [b] (eV)**	**E_g^{el} [c] (eV)**
DBr-BDP-BIs	+ 1.89	+ 1.12	− 5.56	− 1.01	− 0.60	− 3.83	1.73
NBP-BIs	+ 1.91	+ 1.18	− 5.62	− 0.71	− 0.51	− 3.93	1.69

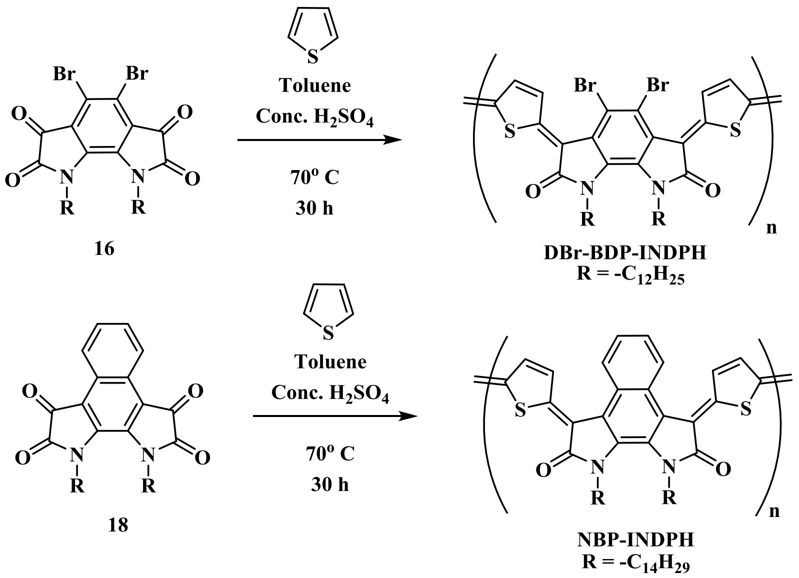
Table 4 Electrochemical properties of synthesized bi-isatyls; [a] potential v/s Ag/Ag^+; [b] calculated from equation $E_{HOMO/LUMO} = -(E_{oxi/red,onset} + 4.8 - E_{Fc/Fc+})$; [c] calculated from equation $E_g^{el} = E_{LUMO} - E_{HOMO}$.

Both of the synthesized novel fused bi-isatyls were proven to be low band-gap molecules from optical as well as electrochemical band-gap measurements using UV-visible spectroscopy and cyclic voltammetry.

Part-B

Synthesis, characterization and electrochemical study of novel indophenine polymers

Indophenine polymers are named after the famous Indophenine reaction between isatin and thiophene in presence of concentrated sulfuric acid which yields intensely blue coloured compound, Indophenine. The benzodipyrrole and naphthobipyrrole-based indophenine polymers DBr-BDP-INDPH and NBP-INDPH were synthesized according to the reported synthetic procedure for indophenine reaction (Scheme 7). The monomers DBr-BDP-BIs and NBP-BIs were reacted with thiophene in presence of concentrated sulphuric acid in anhydrous toluene. The synthesized polymers were purified by soxhlet extraction and characterized by ^{1}H NMR spectroscopy, gel permeation chromatography, UV-visible spectroscopy, cyclic voltammetry and thermogravimetric analysis.



Scheme 7 Synthesis of indophenine polymers DBr-BDP-INDPH and NBP-INDPH

Polymer	λ_{max} ab (nm)	λ_{onset} (nm)	E_g^{opt} (eV)	M_w Dalton	PDI	T_d °C
DBr-BDP-INDPH	**568**	**918**	**1.35**	**13973**	**2.76**	**229**
NBP-INDPH	**444, 544**	**975**	**1.27**	**10819**	**1.3**	**214**

Table 5 Photophysical properties ([ab] absorption values), Molecular weight M_w, Poly-Dispersity Index (obtained from GPC analysis), decomposition temperature T_d (obtained from TGA) and calculated optical band-gaps of synthesized indophenine polymers using equation $E_g^{opt} = 1240/\lambda_{onset}$.

Polymer	E_{oxi} a (V)	$E_{oxi,onset}$ a (V)	E_{HOMO} b (eV)	E_{red} a (V)	$E_{red,onset}$ a (V)	E_{LUMO} b (eV)	E_g^{el} c (eV)
DBr-BDP-INDPH	**+ 1.72**	**+ 1.06**	**− 5.50**	**− 1.16**	**− 0.54**	**− 3.90**	**1.60**
NBP-INDPH	**--** e	**+ 0.97**	**− 5.41**	**− 1.14**	**− 0.65**	**− 3.79**	**1.62**

Table 6 Electrochemical properties of synthesized indophenine polymers; [a] potential v/s Ag/Ag^+; [b] calculated from equation $E_{HOMO/LUMO} = -(E_{oxi/red,onset} + 4.8 - E_{Fc/Fc+})$; [c] calculated from equation $E_g^{el} = E_{LUMO} - E_{HOMO}$; [e] unresolved peak.

To the best of our knowledge, these indophenine polymers are the first in its class. Both indophenine polymers showed significantly lowered optical as well as electrochemical band-gaps compared to the synthesized bi-isatyl monomers owing to the extension of the delocalisation of electrons and quinoidal backbone formation. Both polymers showed good thermal stabilities and film forming properties.

Chapter 4

Heterocyclic Fused Aromatic Dithienopyrrolobenzothiadiazole (DTPBT)-Based Conjugated Polymers

Introduction

In recent years, all-solution processed polymer devices have attracted tremendous academic and industrial interests. To realize low-cost, lightweight, large-area and flexible electronic devices, conjugated polymer materials play the most important role. A conjugated polymer should possess low optical band gap with excellent hole/electron mobility for efficient charge transport.[16] The widely used strategy to produce a low band gap polymer is to polymerize an electron-rich donor (D) monomer with an electron-deficient acceptor (A) monomer along the conjugated polymer backbone. In addition to the D-A strategy, forced planarization by covalently fastening adjacent aromatic units in the polymer backbone provides an effective way to reduce the band gap and enhance the intrinsic charge mobility.

The electronic interactions between the donor and the acceptor units in a D-A copolymer can be greatly enhanced, if the neighbouring electron-rich donor and electron-deficient acceptor units along the polymer backbone are covalently locked and conformationally rigidified into a coplanar inter-fused D-A assembly.[17] Furthermore, rigid structures can reduce the rotational disorder around interannular single bonds to lower the reorganization energy, which is beneficial to improve charge mobility.[18,19] On the basis of aforementioned points, we have synthesized nitrogen bridged donor-acceptor multifused dithienopyrrolobenzothiadiazole (DTPBT) by intramolecular Cadogan annulation, to prepare three novel copolymers, having fused ring structures along the backbone by copolymerizing DTPBT with three different monomers having different structural rigidity.

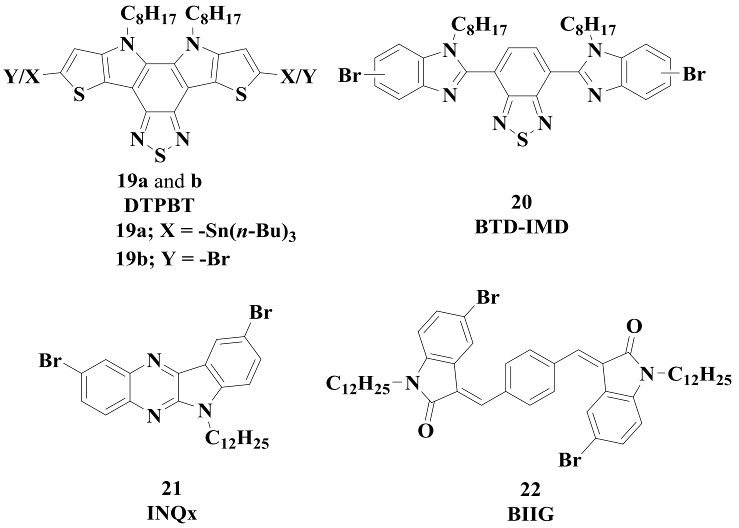
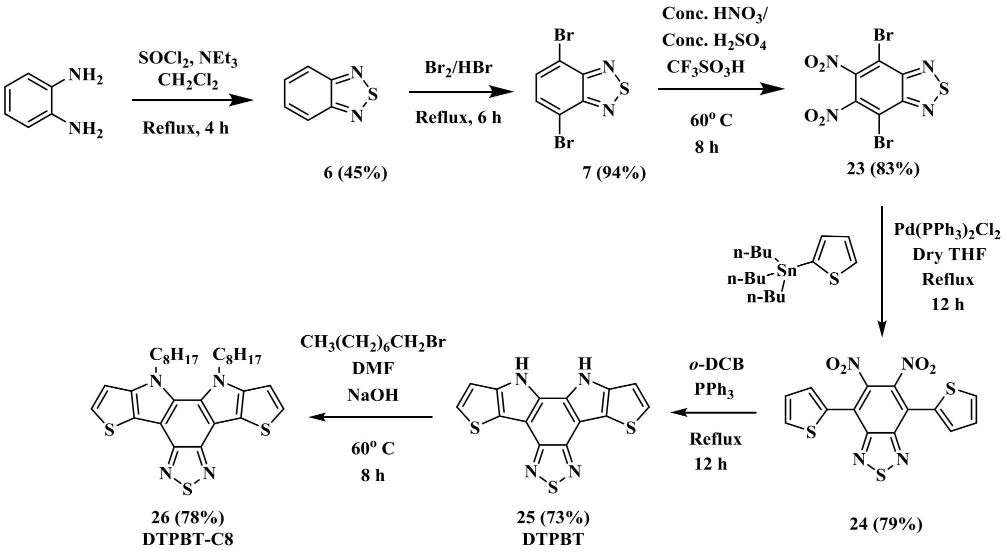


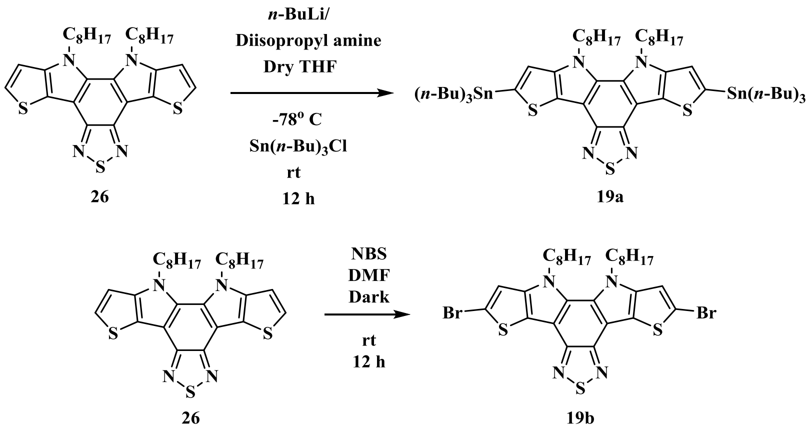
Figure 3 Synthesized heterocyclic fused aromatic monomers

Synthesis and characterization of monomers

A nitrogen-bridged donor-acceptor type multifused dithienopyrrolobenzothiadiazole (**DTPBT**) was synthesized from 5,6-dinitro-4,7-dithienyl-2,1,3-benzothiadiazole (compound **24**) by intramolecular cadogan annulation (Scheme 8) according to the literature procedure reported by Kato *et al.*[20] DTPBT-based monomers **19a** and **b** were synthesized according to the literature procedure reported by Carsten *et al*[21] (Scheme 9).

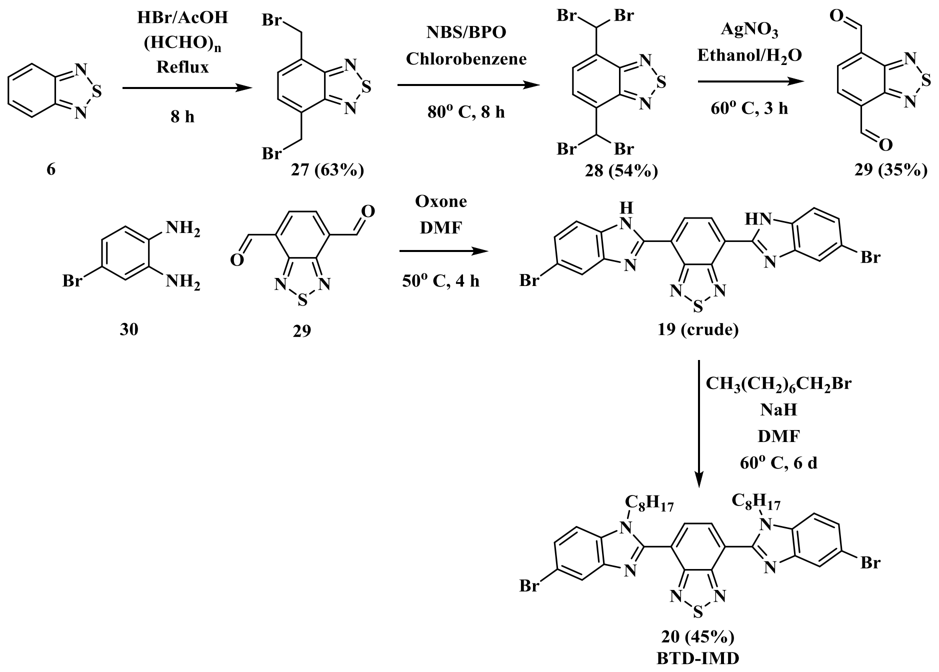


Scheme 8 Synthesis of DTPBT and DTPBT-C8

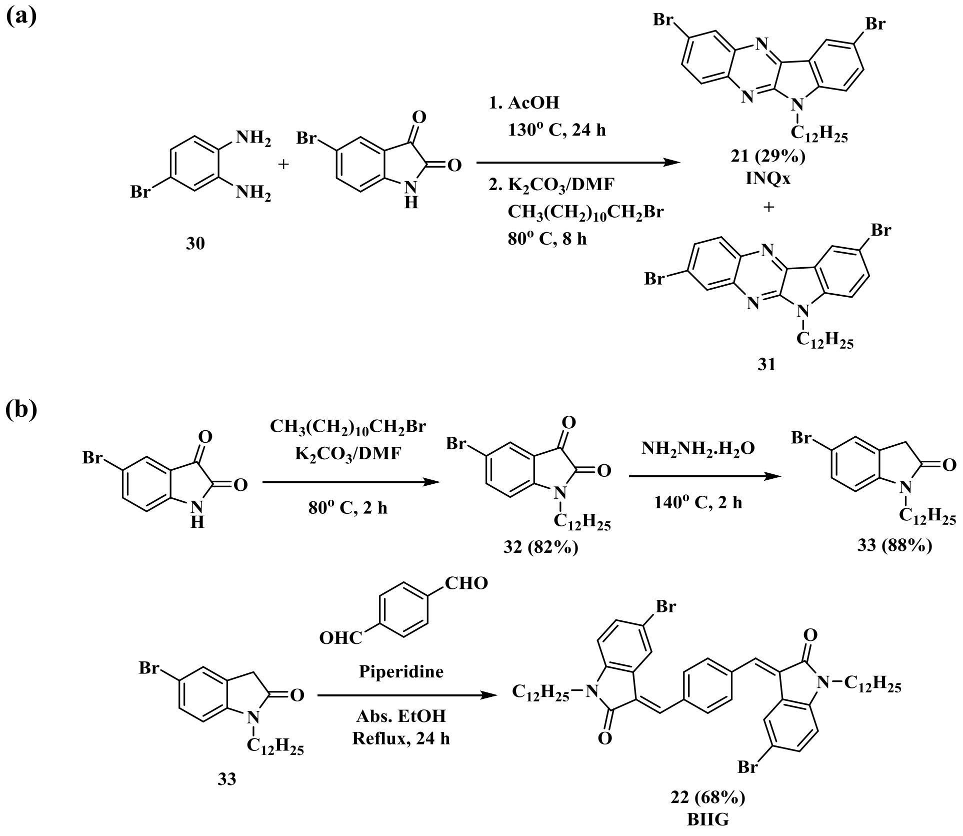


Scheme 9 Synthesis of DTPBT-based monomers

An acceptor-acceptor-acceptor type benzothiadiazole-imidazole based monomer BTD-IMD (compound **20**) was synthesized by reacting 2,1,3-benzothiadiazole-4,7-dicarbaldehyde (compound **29**) with 4-bromo-1,2-diaminobenzene (compound **30**) in DMF using OXONE as an oxidizing agent, according to the modified literature procedure reported by Sriramoju *et al*[22] followed by N-alkylation of the crude reaction mass using sodium hydride (60% mineral oil suspension) in anhydrous DMF (Scheme 10). 4-bromo-1,2-diaminobenzene (compound **30**) was synthesized according to the modified literature procedure reported by Zhu *et al.*[23]



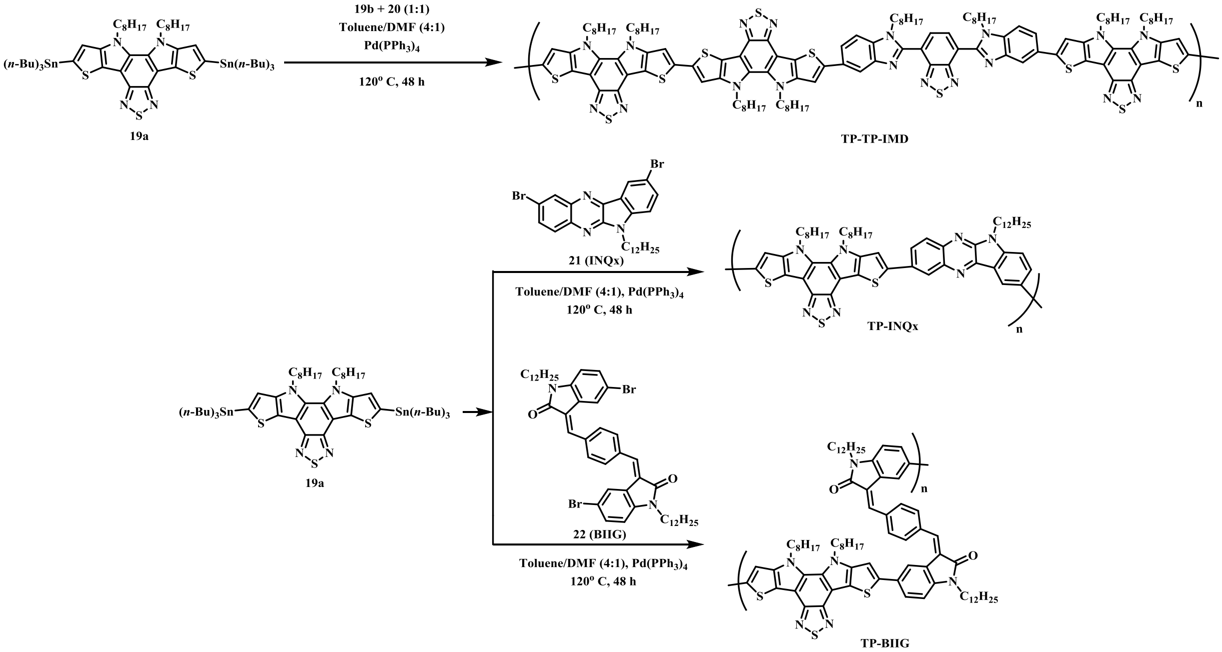
Scheme 10 Synthesis of acceptor-acceptor-acceptor type benzothiadiazole-imidazole based monomer **BTD-IMD**



Scheme 11 Synthesis of isatin-based monomers **INQx** and **BIIG**

An isatin-based co-planar multifused heterocyclic monomer **INQx** (compound **21**), having indoloquinoxaline structure, was synthesized according to the modified literature procedure reported by Dong *et al.*[24] (Scheme 11a) in two steps; first step involved condensation reaction between 5-bromoisatin and 4-bromo-1,2-diaminobenzene in refluxing acetic acid. The crude product obtained from the first step was subjected to the *N*-alkylation reaction using *n*-dodecylbromide and potassium carbonate in DMF. The second isatin based co-planar heterocyclic monomer **BIIG** (compound **22**), having benzene fused iso-indigo structure, was synthesized by knoevenagel-type condensation reaction between 5-bromo-*N*-dodecylindolin-2-one (compound **33**) and terephthalaldehyde using piperidine as a base in refluxing ethanol (Scheme 11b), according to the modified literature procedure reported by Li *et al.*[25] All the synthesized monomers were characterized by ^{1}H and ^{13}C NMR spectroscopy.

Synthesis, characterization and electrochemical studies of DTPBT-based conjugated polymers



Scheme 12 Synthesis of DTPBT-based conjugated polymers **TP-TP-IMD**, **TP-INQx** and **TP-BIIG** by stille coupling reaction

DTPBT-based conjugated polymers, namely **TP-TP-IMD**, **TP-INQx** and **TP-BIIG**, were synthesized by stille coupling reaction between distannyl derivative of DTPBT (compound 19a) and corresponding dibromo derivatives (compounds **19b**, **20**, **21** and **22**) using $Pd(PPh_3)_4$ as catalyst in toluene/DMF (4:1) under nitrogen atmosphere. The obtained polymers were further purified by sequential soxhlet extraction using different solvents like methanol, acetone, petroleum ether and chloroform. The synthesized DTPBT-based conjugated polymers were characterized by ^{1}H NMR spectroscopy, thermogravimetric analysis and gel permeation chromatography. Moreover, photo-physical and electrochemical properties of the synthesized polymers were studied using UV-visible spectroscopy and cyclic-voltametry. The properties of the synthesized polymers are summarized in Table 7 and 8. All the polymers showed good thermal stabilities and good film forming properties.

Polymer	**$\lambda_{max}{}^{ab}$ nm**	**$\lambda_{max}{}^{em}$ nm**	**$\lambda_{onset}{}^{ab}$ nm**	**$E_g{}^{opt}$ eV**	**T_d °C**	**M_w Dalton**	**PDI**
TP-TP-IMD	374, 507	408, 432, 623	717	1.73	310	5818	1.57
TP-INQx	375, 513	408, 432, 637	674	1.84	375	13186	3.48
TP-BIIG	379, 475	408, 432, 619	626	1.98	321	12227	3.24

Table 7 Photo-physical properties (^{ab} absorption and ^{em} emission values), Molecular weight M_w, Poly-Dispersity Index (obtained from GPC analysis), decomposition temperature T_d (obtained from TGA) and calculated optical band-gaps of synthesized DTPBT-based polymers using equation $E_g^{opt} = 1240/\lambda_{onset}$.

Polymer	**$E_{oxi}{}^{a}$ (V)**	**$E_{oxi,onset}{}^{a}$ (V)**	**$E_{HOMO}{}^{b}$ (eV)**	**$E_{red}{}^{a}$ (V)**	**$E_{red,onset}{}^{b}$ (V)**	**$E_{LUMO}{}^{c}$ (eV)**
TP-TP-IMD	+1.07	+0.81	−5.25	−1.55	−1.27	−3.52
TP-INQx	+1.52	+1.05	−5.49	−1.46	−1.17	−3.65
TP-BIIG	--^{e}	+1.23	−5.67	−1.55	−1.18	−3.69

Table 8 Electrochemical properties of synthesized polymers; ^{a} potential v/s Ag/Ag+; ^{b} calculated from equation $E_{HOMO/LUMO} = -(E_{oxi/red,onset} + 4.8 - E_{Fc/Fc+})$; ^{c} calculated from equation $E_{LUMO} = E_{HOMO} + E_g^{opt}$; ^{e} unresolved peak.

Chapter 5

Synthesis, Characterization and Study of Novel Conjugated Molecules

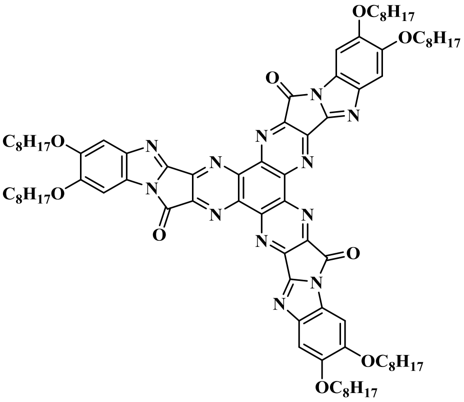
Part-A

Constructing a self-assembling C_3-symmetric covalently linked (fused) donor-acceptor-type molecule containing hexaazatriphenylene core

Introduction

Fused polycyclic aromatic cores, demonstrating the extended π-conjugation have gained significant attention in the field of organic electronics.[26] Many linear and star-shaped molecules comprised of the polycyclic aromatic core and extended π-conjugation have been identified as an active component in optoelectronic devices. Recently, 1,4,5,8,9,12-hexaazatriphenylene (HAT) and its extended derivatives have been demonstrated as good n-type semiconducting materials. These HAT-based materials, when properly substituted, show self-assembling behaviour both in solution and bulk state to form one-dimensional columnar-type aggregates.[27,28] Though having self-assembling nature, most of these reported large polycyclic aromatic molecules are either showing n-type or p-type semiconducting characteristics. The construction of electron donor-acceptor ensembles, capable of transporting electrons and holes at the same time is important for their application in organic field effect transistors (OFETs) and organic light emitting field effect transistors (OLETs).[29] The prime requirement for building highly ordered donor-acceptor assemblies is strong interaction between electron donor-acceptor pairs as a result of complementary electronic characters. Regardless of the advances in these self-assembly systems, breakthroughs in new materials development are largely limited by the scarcity of the strongly interacting donor-acceptor pairs.

An alternate approach to this is to construct D-A systems by electron-rich groups conjugated with electron deficient groups, which can self-assemble into columns, thereby forming a single molecule that is proficient of showing both n-type and p-type behaviour. We have constructed a C_3-symmetric covalently linked donor-acceptor-type molecule in which the n-type hexaazatriphenylene core has been fused with three p-type di-amino-di-alkoxybenzene moieties by imidazolo-pyrrolone type linkage, forming a 13 fused ring system, HAT-IPN.

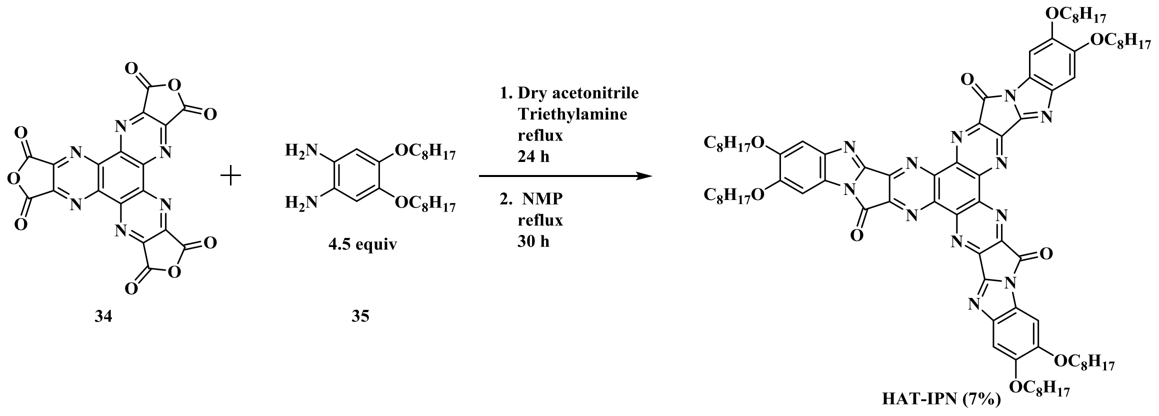


HAT-IPN

Figure 4 Structure of C_3-symmetric donor-acceptor type HAT-IPN

Synthesis, characterization and study of HAT-IPN

HAT-IPN with six *n*-octyloxy groups was synthesized by the condensation-cyclisation reaction of corresponding hexaazatriphenylenehexacarboxylic acid trisanhydride **5** with 4,5-diamino-1,2-dioctyloxybenzene **10** (Scheme 1). The compound **5** was synthesized according to the procedure reported by Kanakarajan *et al.*[30] and compound **10** was synthesized according to the literature procedure reported by Nagarjuna *et al.*[31]



Scheme 13 Synthesis of HAT-IPN from compound **34** and **35**

The synthesized HAT-IPN was characterized by ^{1}H and ^{13}C NMR and elemental analysis. The UV-visible absorption spectra of HAT-IPN exhibit absorption resulting from the monomers as well as from the aggregates. The emission spectra showed combined emission from both the molecules and aggregates, as suggested by the broadening of the emission peak. The relative fluorescence emission quantum yield of HAT-IPN in methanol is measured to be 23.1% with the reference of quinine sulfate (54%) in 0.01 M H_2SO_4 solution. The ambipolar (D-A) character and electrochemical stability of HAT-IPN were confirmed by cyclic-voltammetry. Cyclic-voltammogram of HAT-IPN was recorded using three electrode system: Pt-disc electrode as working electrode, Pt wire as a counter electrode and Ag/Ag^+ as a reference electrode. Electrochemical properties of HAT-IPN are summarized in Table 9. Donor-acceptor nature of HAT-IPN is also evident from DFT calculated frontier orbitals. LUMOs are mainly located in the central HAT core, whereas the HOMOs have contributions largely coming from the peripheral dialkoxybenzoimidazole part.

Compound	**E_{oxi}[a] (V)**	**E_{red}[a] (V)**			**E_{HOMO}[b] (eV)**	**E_{LUMO}[b] (eV)**
		1st	2nd	3rd		
HAT-IPN	+0.64	−0.77	−1.17	−2.05	−5.44	−4.03

Table 9 Electro-chemical properties of HAT-IPN; [a] V vs Fc/Fc^+ in THF; [b] Calculated using E_{oxi} and E_{red} of the first oxidation and first reduction peak using the equation: $E_{HOMO/LUMO} = -(E_{oxi/red} + 4.8)$, $E_{(Fc/Fc+)} = 0.65$ V.

Moreover, the self-assembling tendency of the HAT-IPN was demonstrated by the ^{13}C NMR spectroscopy, dynamic light scattering, differential scanning calorimetry and atomic force microscopy, indicating the formation of one-dimensional π-stacked aggregates.

Part-B

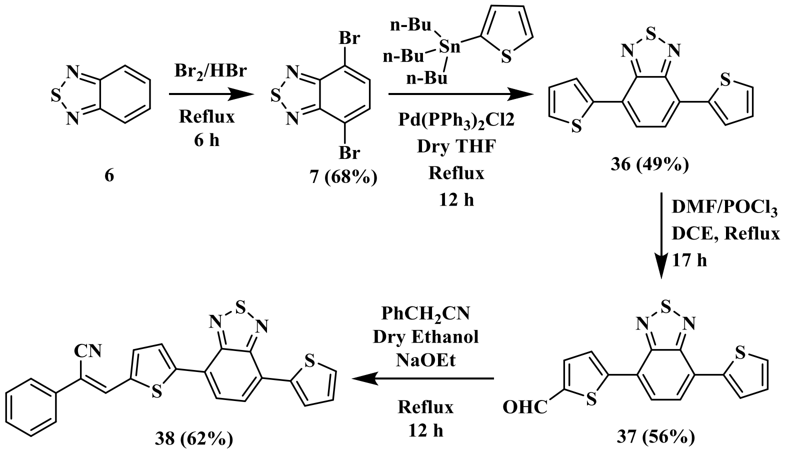
Synthesis, photophysical, electrochemical and single crystal X-ray diffraction study of (Z)-2-phenyl-3-(5-(4-(thiophen-2-yl)benzo[c][1,2,5]thiadiazol-7-yl)thiophen-2-yl)acrylonitrile

Introduction

2,1,3-Benzothiadiazole (BTD) derivatives are outstanding compounds due to their electron-withdrawing properties and have been used as units of electron acceptors for conducting materials.[32] The highly electron-deficient BTD unit is one of the most popular building blocks in organic electronics. BTD can conjugatively link with an electron-rich molecule to form low band gap functional polymers or small molecules, and materials prepared in this manner showed usefulness in organic light emitting diodes (OLEDs), dye sensitized solar cells (DSSCs), light-harvesting and other optical or electronic functional devices. Molecularly hybridized push−pull type materials, where the alternating arrangement of electron rich and electron-deficient units along the π-conjugated backbone effectively controls the frontier molecular orbitals. BTD is often the electron-deficient unit of choice for such materials.[33]

BTD- based small molecules are becoming increasingly popular for devising hybrid solar cells, because of high electron mobility and excellent chemical and physical stability of inorganic semiconductors. Recent studies have demonstrated that formation of self-assembled monolayer of conjugated molecules on the surface of the inorganic semiconductors can lead to the formation of interfacial dipoles, which in turn, can improve the work function of substrate materials.[34,35] These type of small conjugated molecules can act as interfacial modifiers (IMs), which enhances charge injection from metals in to organic materials. J. Yu and co-workers have prepared and examined one of such IMs, having cyano-acrylic acid as anchoring group and showed increase in electron affinity at the polymer-inorganic semiconductor interface and formation of dipoles, which are oriented away from the semiconductor surface. We have synthesized a new conjugated donor-acceptor type compound having cyano-benzylic anchoring group, (*Z*)-2-phenyl-3-(5-(4-(thiophen-2-yl)benzo[c][1,2,5]thiadiazol-7-yl)thiophen-2-yl)acrylonitrile (compound **38**) by a multi-step synthetic route.

Synthesis and characterization



Scheme 14[33] Synthesis of (*Z*)-2-phenyl-3-(5-(4-(thiophen-2-yl)benzo[c][1,2,5]thiadiazol-7-yl)thiophen-2-yl)acrylonitrile (compound **38**)

BTD-based novel highly conjugated molecule **38** was synthesized in four steps; 4,7-dibromo-2,1,3-benzothiadizole **7** was treated with 2-(tri-*n*-butylstannyl)thiophene in presence of $Pd(PPh_3)_2Cl_2$ to get compound **36** in 49% yield. Mono-formylation of compound **36** by following vilsmeier-haack reaction conditions, yielded compound **37** in 56 % yield, which was subjected to knoevenagel condensation reaction with benzyl cyanide using sodium ethoxide in dry ethanol to get desired compound **38** in 62% yield. The synthesized molecule was characterized by ^{1}H and ^{13}C NMR spectroscopy as well as by single crystal X-ray diffraction spectroscopy.

Photo-physical and electrochemical properties

The photophysical properties of compound **38** were studied using UV-visible spectroscopy. The absorption and emission spectra of **38** were carried out in methanol. Synthesized compound **38** possess the dual-band nature; one lower energy band is ranging in between 250-340 nm which is due to π-π^* transition of the conjugated backbones, while second higher energy band ~~is~~ ranging from 400-520 nm due to the charge transfer transition between donor and acceptor. The optical, electronic and theoretical band-gaps were calculated using UV-visible spectroscopy, cyclic-voltametry and density functional theory (DFT), respectively. The thermal stability of the synthesized compound was determined by thermogravimetric analysis (TGA). All the properties of compound **38** are summarized in Table 10.

Compound	λ_{max} ^{a} **(nm)**	λ_{max} ^{b} **(nm)**	λ_{onset} ^{a} **(nm)**	T_d ^{c} **(^{o} C)**	E_{oxi} ^{d} **(V)**	E_{HOMO} ^{e} **(eV)**	E_{LUMO} ^{f} **(eV)**	E_g $^{opt\ g}$ **(eV)**	E_g $^{cal\ h}$ **(eV)**
38	379, 463	605	548	336	+ 1.92	− 5.86	− 3.59	2.27	2.80

Table 10[33] Photo-physical, thermo-gravimetric, electrochemical and DFT calculated properties of compound **38**; ^{a} from absorption data; ^{b} from emission data; ^{c} obtained from TGA; ^{d} vs $Ag/AgNO_3$; ^{e} calculated using the equation: $E_{HOMO} = -(E_{oxi} + 4.8 - E_{(Fc/Fc+)})$, $E_{(Fc/Fc+)} = 0.86$ V; ^{f} calculated from the equation $E_{LUMO} = E_g^{opt} + E_{HOMO}$ (eV).^{g} calculated optical band-gaps using equation $E_{optical} = 1240/\lambda_{onset}$; ^{h} calculated band-gaps using DFT.

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