

A Synopsis of the thesis entitled
Synthesis, Characterization and Study of
Conjugated Materials

To be submitted to M. S. University of Baroda



For the Degree
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DOCTOR OF PHILOSOPHY

In Chemistry

By

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Chapter 1: Introduction

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 silicon electronics have solved many of the challenges associated with our increased use of electronics, though there are limits to what silicon can do¹. Chemists are synthesizing a wealth of new organic materials in the field of organic electronics, that create novel properties, which are impossible to replicate with silicon. These materials hold tremendous promise to expand our electronic landscape in ways that will radically change the way society interacts with technology.²

High performing small molecules and polymers have gained considerable interest of researchers, in the field of organic electronics for potential applications such as polymer solar cells (PSCs), organic light emitting diodes (OLEDs),³ organic field effect transistors (OFETs) and organic thin film transistors (OTFTs). In the past few years, several molecules have been reported leading to the enhanced charge carrier mobilities as a result of induced dipole-dipole interactions, close intermolecular packing and shorter π - π distances.⁴ a few examples are N-heteroacenes, azulene derivatives, diketopyrrolopyrrole (DPP)-based polymers, iso-indigo (IIG) and its derivatives-based small molecules and polymers, indigo-based polymers, phenyl-flanked and thiophene-flanked benzodipyrrolidone (BDPDP and BDPDT)-based polymers, dihydropyrroloindoleione (DPID)-based polymers etc.⁵

These materials are used to build electronic structures,⁶ 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.⁷

The basic requirements for development of conjugated polymers are mentioned below.

1. **Good solution processibility:** This facilitates the device fabrication through common solution-based printing and patterning techniques, easily adaptable to the large area substrates.
2. **Suitable HOMO-LUMO energies/band-gap:** HOMO-LUMO energy levels alignment at metal-organic and organic-organic interfaces are important for device performance.

3. **High charge carrier mobilities:** This is associated with excellent overlap between the π -systems of the adjacent molecules and strong electronic coupling between the adjacent molecules.
4. **Good air stability:** Not due to degradation of chemically unstable neutral materials, but due to the susceptibility of the corresponding radical anions to H₂O or O₂ in air, which can seriously suppress ET processes. It has also been experimentally found that for air stable transistors the LUMO level of semiconductors should be below 4.0 eV with respect to the vacuum level.

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Chapter 2: Synthesis, characterization and study of extended isoindigo based donor-acceptor conjugated polymers

In recent years, a plethora of conjugated polymers has been explored as a new-generation optoelectronic materials for organic electronic devices, such as organic light-emitting diodes (OLEDs), organic field effect transistors (OFETs) and organic photovoltaics (OPVs).¹⁻⁴ Optoelectronic devices based on organic conjugated molecules and polymers possess many desirable characteristics, such as low-cost fabrication, flexibility, lightweight and ease of use over wide surface area. Donor-acceptor (D-A) conjugated polymers have garnered significant interest in recent years as one of the most important classes of organic semiconductor materials, owing to their excellent performance in organic optoelectronic devices and their ability to be tailored to specific structures to manipulate the semiconducting properties.⁵⁻⁹

Some reported conjugated units that are used to obtain π -extended isoindigo derivatives isoindigo based conjugated building blocks include benzodifurandione (I), benzodipyrroledione (II),¹⁰ naphthodifurandione (III), naphthodipyrroledione (IV), thieno[3,2-*b*]thiophene (V), dithiophene (VI), pyrazine (VII), benzene (VIII), tetrafluorobenzene (IX), and 1,2-dithiophenylethene (X) (Fig. 2.1).

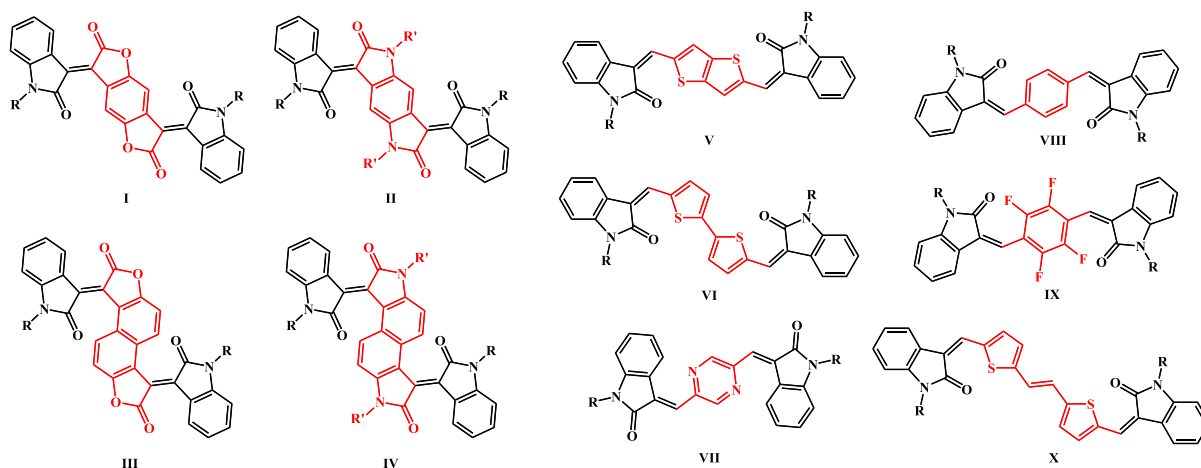
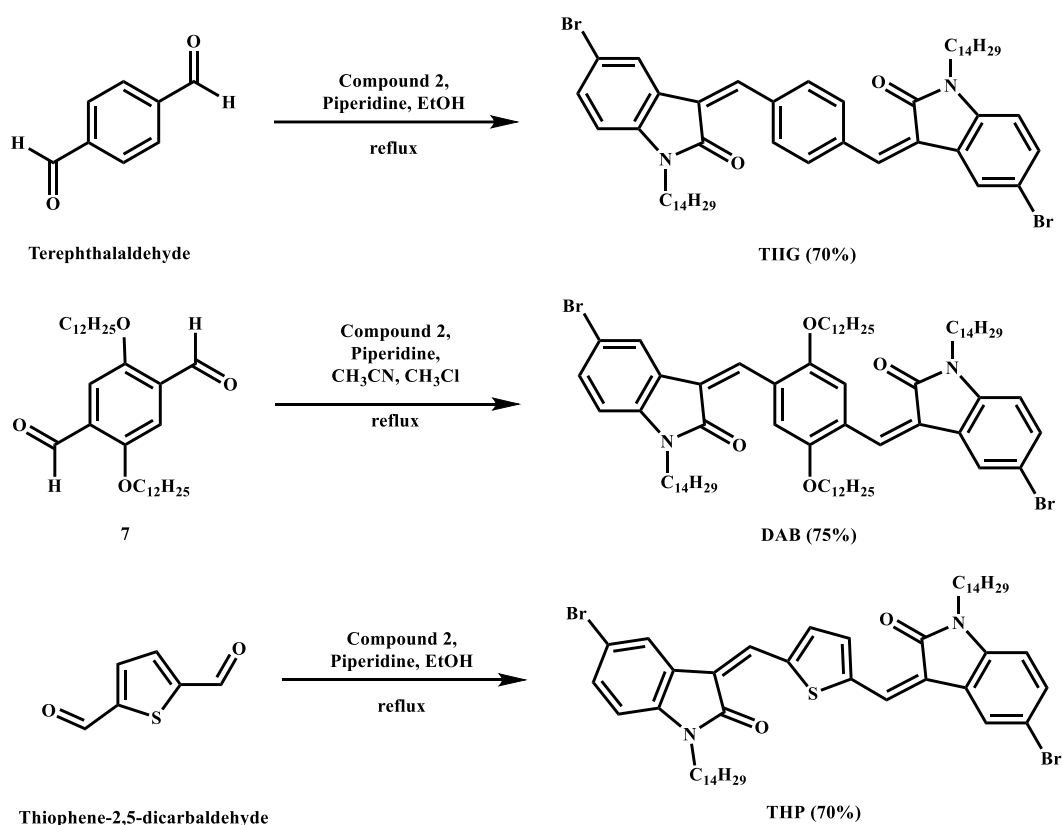


Figure 2.1 Representative structures of reported π -extended isoindigo derivatives.

However, half of these π -extended isoindigo derivatives require complex, lengthy and expensive preparation of the central conjugated moieties. In our previous research work, we have successfully introduced *p*-dimethylenbenzene as conjugated spacer to get π -extended isoindigo, which showed good hole mobility when incorporated within the polymer backbone. Here, we report two additional π -extended isoindigo with dialkoxy-*p*-dimethylenbenzene and

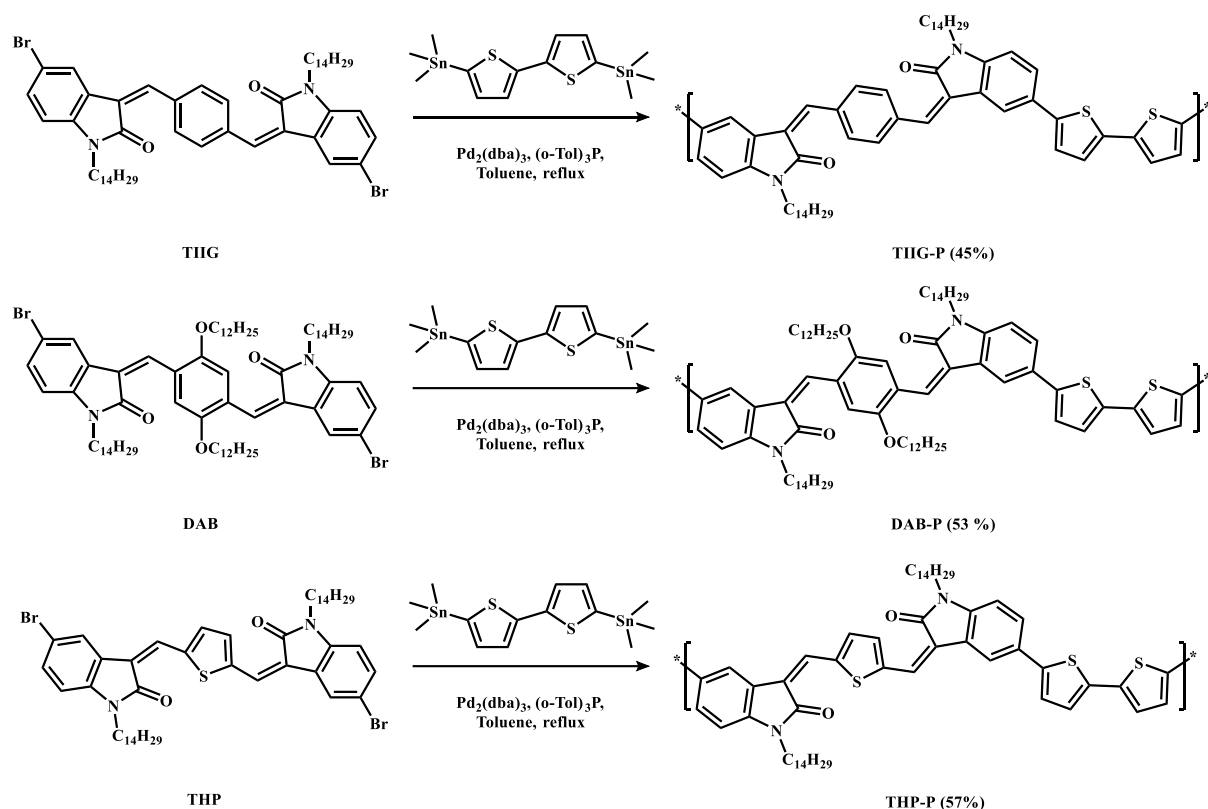
2,5-dimethylenethiophene as central spacer and copolymerized them with 2, 2'-dithiophene to yield D-A-type conjugated polymers.

The π -extended benzene-, dialkoxybenzene-, and thiophene-fused isoindigo (compounds **TIIG**, **DAB**, and **THP**) are synthesized by Knoevenagel-type coupling reaction between *n*-tetradecylindolin-2-one (compound **2**) and corresponding dialdehydes (terephthalaldehyde, compound **7**, and thiophene-2,5-dicarbaldehyde) using piperidine as base as per Scheme 2.1



Scheme 2.1 Synthesis of π -extended isoindigo compounds **TIIG**, **DAB**, and **THP**.

The π -extended isoindigo based D-A type conjugated polymers namely **TIIG-P**, **DAB-P** and **THP-P** were synthesised by Stille coupling reaction between 5,5'-bis(trimethylstannyl)-2,2'-bithiophene unit and π -extended isoindigo compounds **TIIG**, **DAB** and **THP** using Pd₂(dba)₃ and tri-*o*-tolylphosphine as the catalyst-ligand system in refluxing toluene (Scheme 2.4). The obtained crude polymers **TIIG-P**, **DAB-P** and **THP-P** are purified by sequential Soxhlet extraction technique using methanol, petroleum ether, toluene and chloroform, respectively. The chloroform was evaporated under reduced pressure and polymers were collected and dried under vacuum at 60 °C.



Scheme 2.2 Synthesis of π -extended D-A-type conjugated polymers.

Three novel π -extended isoindio-based monomers (**TIIG**, **DAB** and **THP**) were synthesized by double Knoevenagel condensation reaction. The synthesised compounds (**TIIG**, **DAB** and **THP**) were polymerised with 5,5'-bis(trimethylstannyl)-2,2'-bithiophene to form conjugated low band-gap D- π -A polymers. The synthesised polymers were well characterised by NMR, UV-Visible, GPC, TGA and electrochemical techniques. Photo physical properties of **TIIG-P**, **DAB-P** and **THP-P** showed broad absorption spectra and the band gap values were found to be 2.55 eV, 2.16 eV and 2.15 eV, respectively. All the conjugated polymers showed moderate to good solubility in common organic solvents and showed sufficiently high thermal stability. The polymers showed HOMO energy levels (~ -5.0 eV) whereas LUMO energy level are ranging from -2.4 eV to -2.9 eV. The structural aspects of polymers, **TIIG-P**, **DAB-P** and **THP-P** were studied by DFT calculations on model polymers (by replacing *N*-alkyl by *N*-ethyl groups) comprising of the repeat unit of each parent copolymer indicates that π -extended isoindigo and bithiophene units are highly planar, whereas dihedral angle between these units in the polymers is $\sim 30^\circ$. The optimized structures of polymers showed that polymers **TIIG-P** and **DAB-P** were linear, whereas polymer **THP-P** showed wavy arrangement of commoners. The calculated bandgap values for model polymers, **TIIG-P**, **DAB-P** and **THP-P** were found to be 2.11 eV, 2.21 eV and 2.11 eV respectively. The powder X-ray diffraction (PXRD)

analysis showed the inherent amorphous nature of the polymers. Moreover, the diffraction peaks of polymers suggest that polymer **THP-P** exhibited greater crystallinity compared to polymer **TIIG-P** and polymer **TIIG-P** surpassing polymer **DAB-P** in this aspect. The measured Space-Charge-Limiting Current (SCLC) hole mobilities were found to be $7.11 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, $6.43 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and $8.19 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for polymers **TIIG-P**, **DAB-P** and **THP-P**, respectively. The obtained high hole mobilities of the synthesized polymers showed the great potential for their applications in organic electronic devices.

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Chapter 3: Synthesis and study of dithienopyrrolobenzothiadiazole (DTPBT) -isoindigo based conjugated polymers and their SCLC hole mobilities

Over the past few decades, there has been significant research and development of conjugated polymers as active materials for various organic electronic devices. These materials have shown promise and have been extensively studied for applications in organic light-emitting diodes (OLEDs), organic field-effect transistors (OFETs), and organic photovoltaics (OPVs).¹ The development of various conjugated polymer materials with improved performance, such as higher charge carrier mobility, better stability, and increased absorption efficiency, has been a focus of research in the field of organic electronics.² This ongoing research aims to further advance the efficiency and functionality of organic electronic devices for practical applications.³

Dithienopyrrolobenzothiadiazole (DTPBT) is a ladder-type conjugated molecule that exhibits interesting electronic and optical properties.⁴ It consists of an electron-deficient 2,1,3-benzothiadiazole (BT) unit covalently fused with two outer electron-rich thiophene units through two embedded pyrrole rings.⁵ The multifused pentacyclic structure of DTPBT is of interest due to its unique electronic and optical properties. It exhibits good charge transport characteristics, making it suitable for applications in organic electronic devices such as organic solar cells, organic field-effect transistors, and organic light-emitting diodes.⁶

DTPBT-based D-A polymers, which are developed by copolymerizing DTPBT-scaffold with various conjugated scaffolds like fluorine, carbazole, cyclopenta[2,1-*b*:3,4-*b'*]dithiophene, benzo[1,2-*b*:4,5-*b'*]dithiophene, 3-fluorothieno[3,4-*b*]thiophene, bis-(2-thiophenyl)benzo[1,2-*b*:4,5-*b'*]dithiophene, diketopyrrolopyrrole, etc. have been explored for organic electronic devices.⁷ Structures of these reported DTPBT-based conjugated polymers are summarised in Figure 3.1.

According to the literature study, DTPBT-based conjugated polymers incorporating co-monomers such as benzo[1,2-*b*:4,5-*b'*]dithiophene, 3-fluorothieno[3,4-*b*]thiophene, and diketopyrrolopyrrole¹⁸ exhibit higher SCLC (Space Charge Limited Current) hole mobilities. This can be attributed to the rigid and coplanar structures of these co-monomers, which facilitate efficient charge transport.⁸

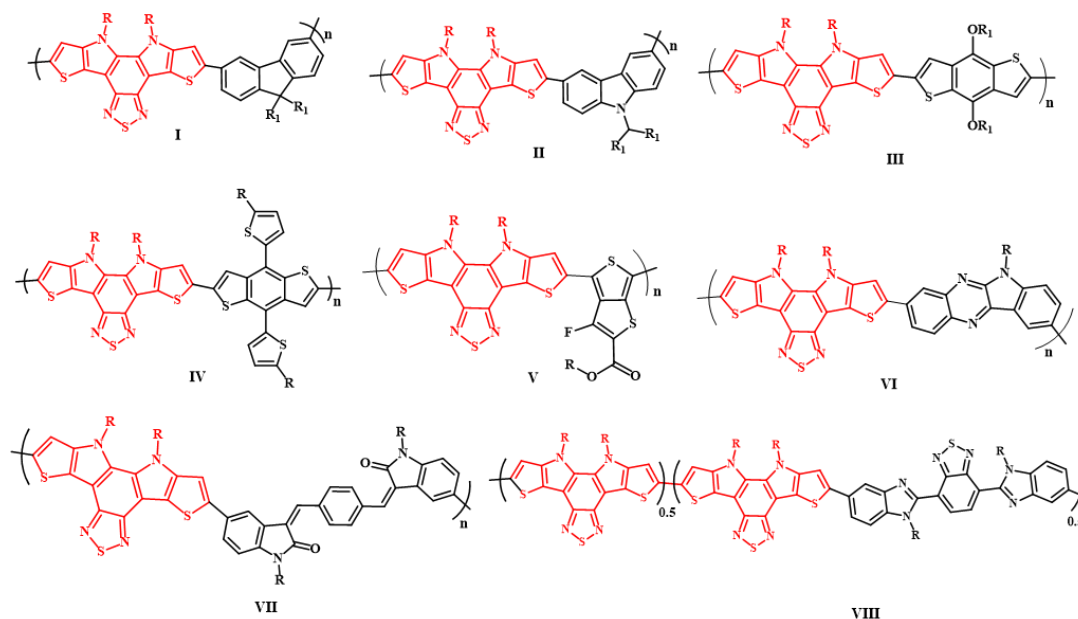
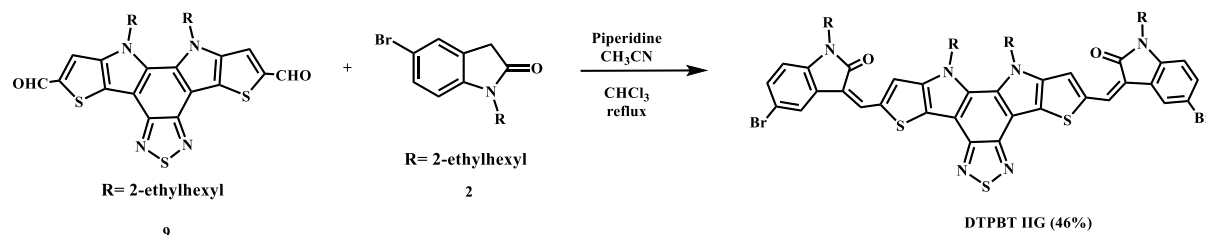


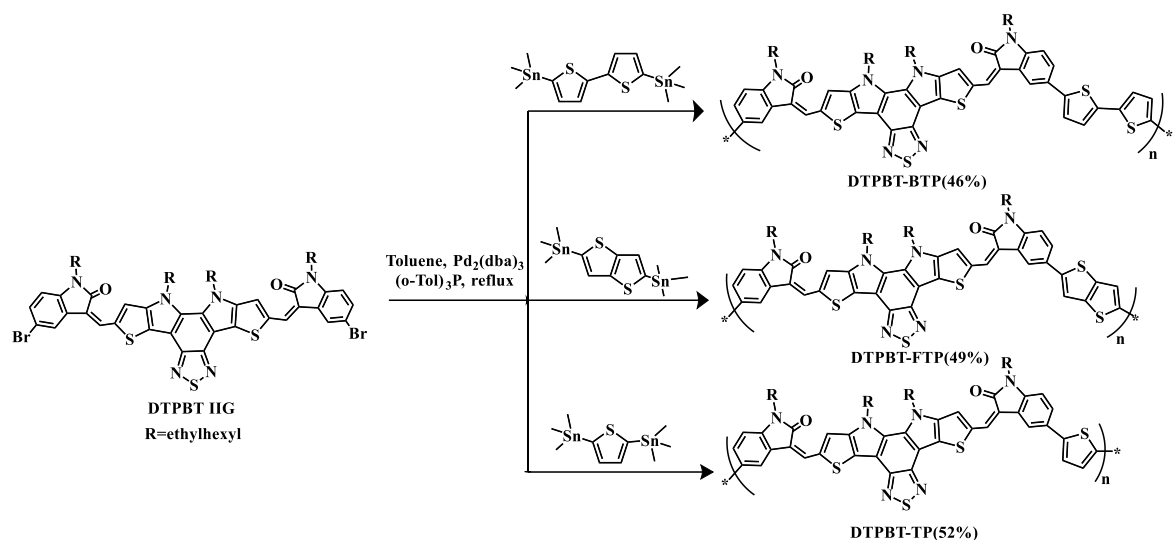
Figure 3.1 Representative structures of reported π -extended DTPBT based polymers

π -Extended DTPBT-isoindigo based compound **DTPBT IIG** was synthesised by Knoevenagel condensation reaction between DTPBT-dialdehyde with 2-ethylhexylindoline-2-one in presence of piperidine in acetonitrile/chloroform solvent system to synthesise compound **DTPBT IIG**.⁹



Scheme 3.1 Synthesis of **DTPBT IIG**

Donor-acceptor type π -extended DTPBT based conjugated polymers were synthesised *via* Stille coupling reaction (**Scheme 3.2**). Polymers **DTPBT-BTP**, **DTPBT-FTP** and **DTPBT-TP** were synthesized by treating compound **DTPBT IIG** with 5,5'-bis(trimethylstannyl)2-2'-bithiophene, 2,5-bis(trimethylstannyl)thieno[3,2-*b*] thiophene and 2,5-bis(trimethylstannyl)thiophene, respectively in presence of $\text{Pd}_2(\text{dba})_3$ catalyst tri-*o*-tolyl phosphine in toluene. The resulting polymers were purified by Soxhlet extraction technique using methanol, petroleum ether, toluene, acetone and chloroform.



Scheme 3.2 Synthesis of π -extended D-A-type conjugated polymers **DTPBT-BTP**, **DTPBT-FTP** and **DTPBT-TP**.

Three novel DTPBT based conjugated building block was synthesised using a double Knoevenagel condensation reaction and characterised by various analysis techniques like ^1H and ^{13}C NMR and MALDI-TOF analysis.

These monomers were then polymerized with 5,5'-bis(trimethylstannyl)-2,2'-bithiophene, 2,5-bis(trimethylstannyl)thieno[3,2-*b*] thiophene, 2,5-bis(trimethylstannyl)thiophene to form conjugated low band-gap **D- π -A** polymers. The synthesized polymers (referred to as **DTPBT-BTP**, **DTPBT-FTP**, and **DTPBT-TP**) underwent comprehensive characterization using various techniques. Nuclear Magnetic Resonance (NMR) spectroscopy was employed to analyse the chemical structure of the polymers. UV-Visible spectroscopy was used to study their absorption properties, revealing broad absorption spectra. The band gap values were determined to be 1.87 eV for **DTPBT-BTP**, 1.85 eV for **DTPBT-FTP**, and 1.86 eV for **DTPBT-TP**. These values indicate that the polymers have a low band gap, which is desirable for organic electronic devices. The polymers were also characterized using Gel Permeation Chromatography (GPC) to determine their molecular weight and molecular weight distribution. Thermogravimetric Analysis (TGA) was employed to assess the thermal stability of the polymers. Additionally, electrochemical techniques were utilized to investigate their electrochemical properties. The results of the characterization revealed that the synthesized polymers exhibit moderate to good solubility in common organic solvents. This solubility is beneficial for processing these polymers into thin films or other device architectures.

Furthermore, the polymers demonstrated high thermal stability, indicating their suitability for practical applications where elevated temperatures may be encountered. The energy levels of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) were also determined. The HOMO energy levels were found to be below -5.0 eV for all the polymers. The LUMO energy levels ranged from -3.7 eV to -3.4 eV. These energy level values suggest that the polymers have appropriate energy levels for facilitating charge transport and efficient device performance in organic electronic devices. Based on the preliminary characterization data, it can be concluded that the newly synthesized conjugated polymers **DTPBT-BTP**, **DTPBT-FTP** and **DTPBT-TP** hold promise as potential candidates for various organic electronic devices. Further studies and optimizations can be conducted to explore their specific applications and enhance their performance in specific device architectures.

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Chapter 4: Synthesis and study of donor-acceptor type π -conjugated polymers based on carbazole and isoindigo units

In recent years, considerable research efforts have been made to design the non-fullerene acceptors. Non-fullerene D-A small molecules have adjustability of electronic energy levels, absorption profiles, solubility parameters, and self-assembly tendencies, which makes them preferable to fullerene derivatives.¹ The significant benefits of solution-processed bulk heterojunction (BHJ) polymer solar cells (PSC), including their low weight, affordability, and flexibility, make them an economical choice.² Although they have significantly improved recently, organic solar cells power conversion efficiencies (PCEs) still fall short of blends of polymer donors and fullerene acceptors, which surpass 10% efficiency.³

The N-fused heterocyclic ring systems suggests a category of compounds that are considered effective donor units.⁴ The choice of these units is backed by references in the literature, indicating that this is a recognized and studied area in the field. Carbazole units are highlighted as one of the most exploited and well-studied systems in the context of N-fused heterocyclic ring systems. The fused system of carbazole is noted for providing good thermal and morphological stability. This is crucial for the performance and durability of materials in electronic devices. Carbazole is recognized for its high fluorescence properties, which can be beneficial in certain applications, such as light-emitting devices.⁵

Carbazole-based polymers have been synthesized by various researchers, indicating the interest and exploration of this material in the scientific community. The passage mentions that these polymers have been investigated for applications in organic photovoltaic cells (OPVs), organic field-effect transistors (OFETs),⁶ and organic light-emitting diodes (OLEDs). This suggests a broad range of potential uses for these materials in different electronic devices. The deep-lying highest occupied molecular orbital (HOMO) energy level of carbazole derivatives is ascribed to their high open-circuit voltage (Voc).⁷

Several copolymers of carbazoles with different monomer combinations like dithinopyrrolbenzthiadiazole, 2,2'-bithiophene, bis(2-methylacrylonitrile), 1,1'-(5,5''-dimethyl-[2,2':5',2''-terthiophene]-3',4'-diyl)bis(2-methoxyethan-1-one) have been explored for organic electronic devices. Structures of these reported conjugated copolymers are summerised in Figure 4.1.

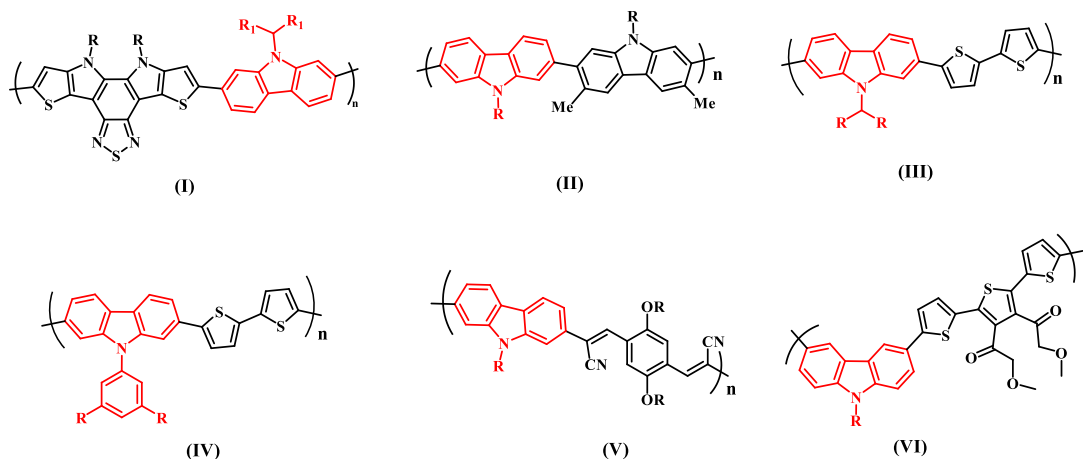
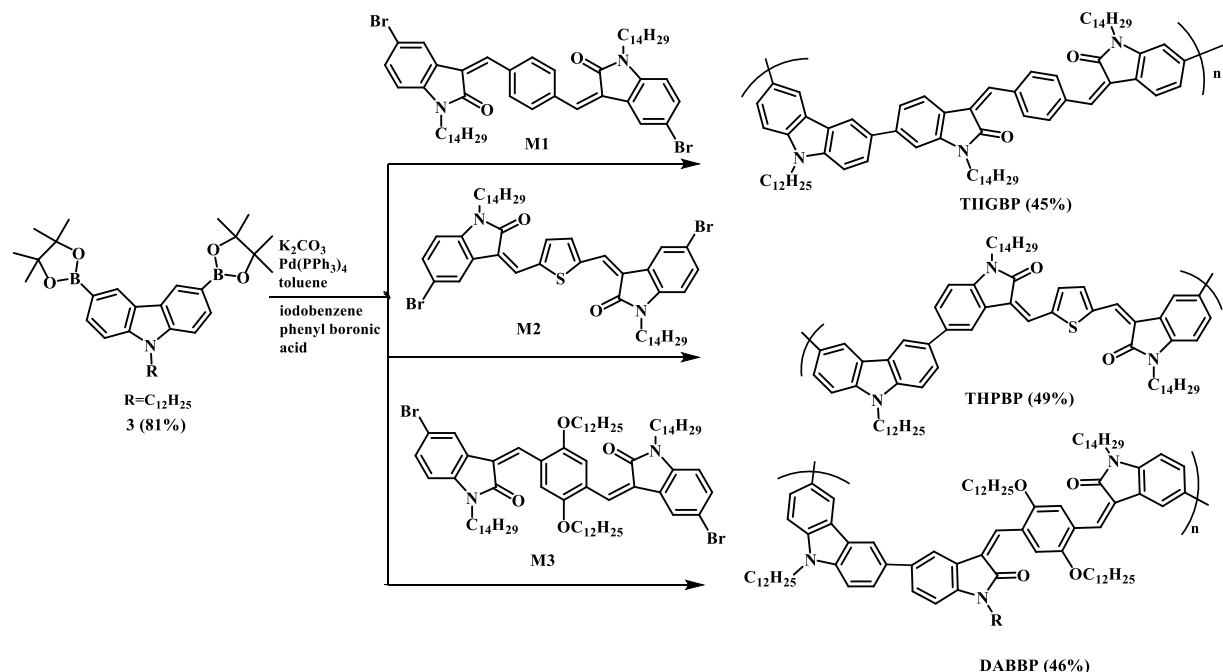


Figure 4.1 Representative structures of reported π -extended carbazole based polymers

D-A-type π -conjugated polymers are synthesized from 9-dodecyl-3,6-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-carbazole (**3**) via modified literature procedure.⁸ Compound (**3**) is coupled with three different isoindigo units (**M1**, **M2** and **M3**) in presence of Pd-catalyst like tertakis(triphenylphosphine)palladium (0) ($\text{Pd}(\text{PPh}_3)_4$), iodobenzene, phenyl boronic acid and potassium carbonate (K_2CO_3) in refluxing toluene (Scheme 4.1).⁹ The obtained crude polymers **TIIGBP**, **THPBP** and **DABBP** are purified by sequential Soxhlet extraction technique using methanol, petroleum ether, toluene and chloroform, respectively.



Scheme 4.1 Synthesis of carbazole based D-A-type conjugated polymers **TIIGBP**, **THPBP** and **DABBP**.

The polymerisation of borylated carbazole with three different π -extended isoindigo unit was carried out in presence of Pd-catalyst. The synthesised polymers were well characterised by NMR, UV-Visible, GPC, TGA and electrochemical techniques. Photophysical properties of **TIIGBP**, **THPBP** and **DABBP** showed broad absorption spectra and the band gap values were found to be 2.45 eV, 2.04 eV and 2.17 eV, respectively. All the conjugated polymers showed moderate to good solubility in common organic solvents and showed sufficiently high thermal stability. The GPC analysis of polymers showed that the chain length of polymers was 12, 18 and 18 comonomer units for polymers **TIIGBP**, **THPBP** and **DABBP** respectively. Thermogravimetric analysis (TGA) of polymers was showed that all polymers are quite stable up to 290 °C. The HOMO energy levels were found to be below -5.0 eV for all the polymers. The LUMO energy levels of polymers were found to be in the range of -2.67 eV to -2.21 eV.

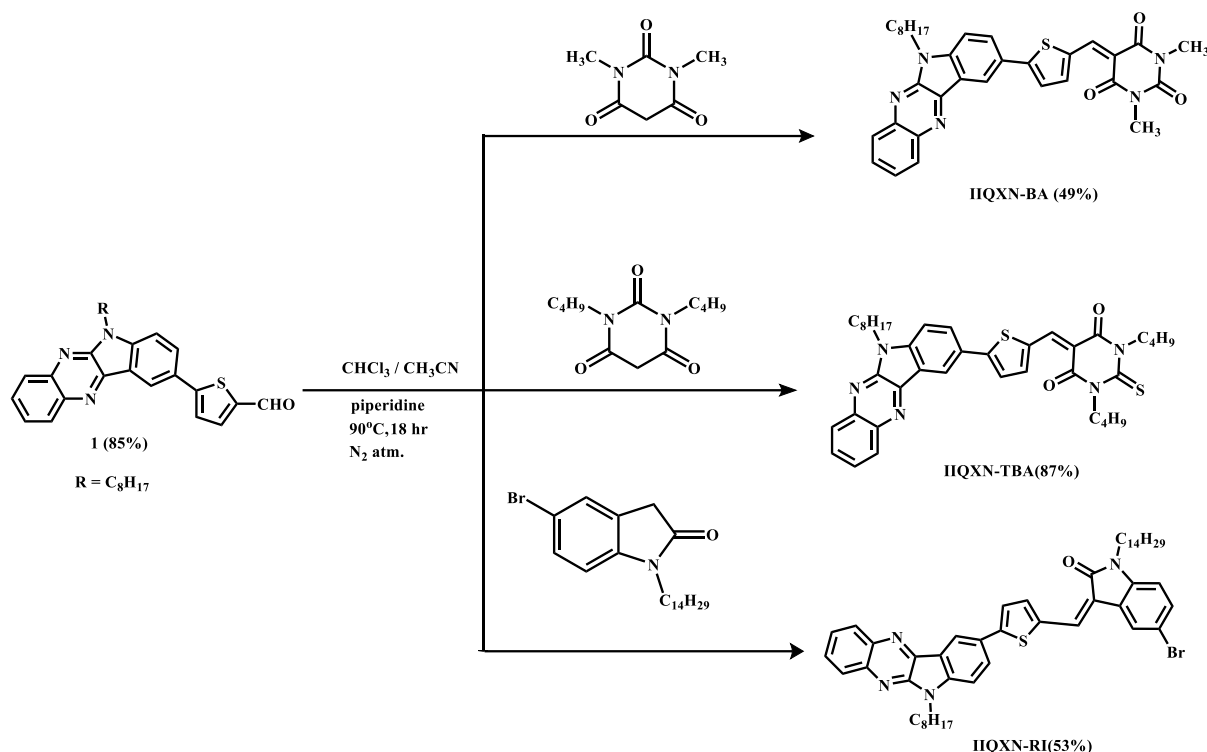
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Chapter 5: Synthesis and study of indoloquinoxaline based D- π -A molecules and their application as fluorescent probe for hypochlorite detection

Donor- π -acceptor (D- π -A) conjugated molecules are indeed important materials in the field of optoelectronics and have gained significant attention in recent years due to their unique electronic properties and potential applications.¹ These molecules are designed to have a specific molecular structure consisting of three main components: an electron-donating group (D), a π -spacer, and an electron-accepting group (A). This design facilitates intramolecular charge transfer (ICT) and leads to a variety of interesting spectroscopic and optoelectronic features. The donor (D) is typically a group or moiety within the molecule that has a relatively higher electron density or is capable of donating electrons. Common D groups include electron-rich aromatic rings or heterocycles with lone pair electrons.² 6*H*-Indolo[2,3-*b*]quinoxaline is a versatile compound with unique properties, making it valuable for various applications in the field of organic electronics, including OLEDs, solar cells, and conjugated polymers. Its ability to form strong π - π interactions and its extended π -conjugation are key factors contributing to its utility in these applications.³ 6*H*-Indolo[2,3-*b*]quinoxaline has been used as an electron-transporting and emitting layer in organic light emitting diodes (OLEDs).⁴ It serves as organic sensitizers for dye-sensitized solar cells (DSSCs).⁵ It is used as hole-injection materials in multi-layered OLEDs. The compound has been incorporated into a conjugated polymer, resulting in a polymer with very high SCLC (Space Charge Limited Current) hole mobility.⁶ A single crystal X-ray diffraction study of the indoloquinoxaline-based compound revealed strong π ... π interactions and a high planar framework.⁷

Compound **1** is being treated with various acceptor moieties (barbituric acid, thiobarbituric acid, and reduced isatin) under Knoevenagel condensation reaction conditions in the presence of piperidine to produce three different compounds, **IIQXN-BA**, **IIQXN-TBA**, and **IIQXN-RI**. Knoevenagel condensation is a common organic reaction used to form carbon-carbon double bonds.



Scheme 5.1 Synthesis of compounds, **IIQXN-BA**, **IIQXN-TBA**, and **IIQXN-RI**.

Three novel indoloquinoxaline-based D- π -A molecules **IIQXN-BA**, **IIQXN-TBA**, and **IIQXN-RI** were synthesized and characterized using various spectroscopic techniques. These compounds were then investigated for their ability to detect ClO^- ions, and the findings indicate their sensitivity and selectivity in this regard. Three novel molecules, **IIQXN-BA**, **IIQXN-TBA**, and **IIQXN-RI**, based on indoloquinoxaline were synthesized. Characterization of all the three compounds **IIQXN-BA**, **IIQXN-TBA**, and **IIQXN-RI** was performed using techniques such as IR (Infrared), NMR (Nuclear Magnetic Resonance), and HRMS (High-Resolution Mass Spectrometry). All three synthesized compounds (**IIQXN-BA**, **IIQXN-TBA**, and **IIQXN-RI**) exhibited excellent sensitivity and selectivity towards ClO^- ions. The detection was achieved through green emission, which was visible to the naked eye. Compound **IIQXN-BA** and compound **IIQXN-RI** showed a "TURN ON" type of fluorescent probe behavior in response to ClO^- ions. Compound **IIQXN-TBA** exhibited a "TURN OFF" type of fluorescent probe behavior upon interaction with ClO^- ions. The mechanism of intramolecular charge transfer (ICT) towards ClO^- ions was confirmed through ^1H NMR studies. The molecules were subjected to electrochemical studies, revealing HOMO energy levels at approximately -5.1 eV and LUMO energy levels at approximately -3.4 eV. The theoretical band gap value for the interaction of the molecules with ClO^- (M- ClO) was found to be 3.40 eV, while the band gap values for compounds **IIQXN-BA**, **IIQXN-TBA**, and **IIQXN-RI** were

2.87 eV, 2.69 eV, and 2.88 eV, respectively. The thermal stabilities of the compounds were determined using thermogravimetric analysis (TGA). All three compounds exhibited good thermal stability, with stability maintained above 300°C.

Overall, a detailed characterization of the synthesized molecules and their promising properties as fluorescent probes for the detection of ClO^- ions were carried out.

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