

Summary of thesis entitled

**“Synthesis, Characterization and Study of Low
Band Gap Conjugated Molecules and Polymers”**

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Chapter 1: Introduction

Conducting polymers/molecules offered the promise of achieving a new generation of polymers: materials which exhibit the electrical and optical properties of metals or semiconductors and which retain the attractive mechanical properties and processing advantages of polymers.[1] In conjugated polymers, the chemical bonding leads to one unpaired electron (the π electron) per carbon atom. Moreover, π bonding, in which the carbon orbitals are in the sp^2p_z configuration and in which the orbitals of successive carbon atoms along the backbone overlap, leads to electron delocalization along the backbone of the polymer.[2] This electronic delocalization provides the “highway” for charge mobility along the backbone of the polymer chain.

A π -conjugated backbone composed of linked unsaturated units resulting in extended π -orbitals along the polymer chain, thus enabling proper charge transport and optical absorption. The energy levels of polymer should be matching with that of acceptor’s one. Solubility and processability are important features required for the device manufacturing processes, which can be achieved by functionalization of the polymer core with solubilizing substituent

The first generation of conducting organic materials witnessed predominantly carbon-based molecular structures such as linear acenes, polyacetylene, and poly(p-phenylene vinylene) derivatives (PPV). The following generation involved the widespread incorporation of heterocycles into the conjugated backbone, culminating in the popularization of the thiophene unit as a molecular building block, as in the well-known material, poly(3-hexylthiophene), or P3HT. Currently, the standard for high performing conjugated polymers and small molecules utilizes so called “donor–acceptor” design strategy.

Polythiophenes are most important classes of π -conjugated polymers, as they meet the essential requirements of solubility and processability and a wide variety of functionalities can be incorporated through substituent modifications. Polythiophenes containing bulky alkyl groups at the β -position have been employed in the preparation of light-emitting diodes (LEDs) [3], the emission of which ranges from red to blue depending on the extent of conjugation.

The conjugation length depends on the amount of main chain distortion due to substituent on the backbone. The regioregularity of the polythiophene chains for mono/di-substituted polymers in particular, as well as the nature of the substituent play a fundamental role in determining the properties of the materials such as solubility, conductivity, optical properties etc.

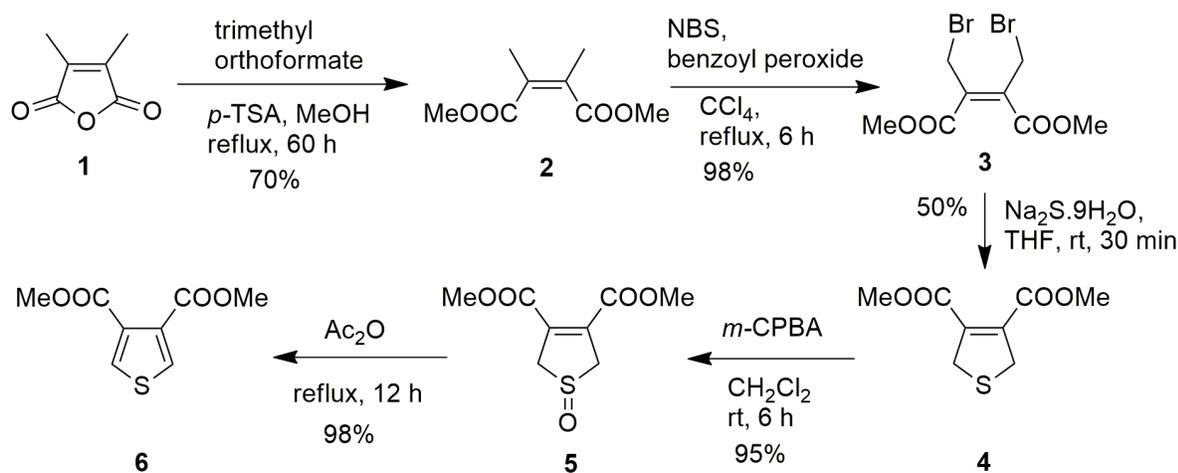
Aim and objective of this work

1. To develop new synthetic methodology for the synthesis of Donor and Acceptor molecules

2. To develop fused conjugated molecules/monomers that can be subjected to polymerization without costlier transition metal catalysts and harsh conditions in terms of temperature and pressure.
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. To develop conjugated small molecules having Donor-Acceptor concept.

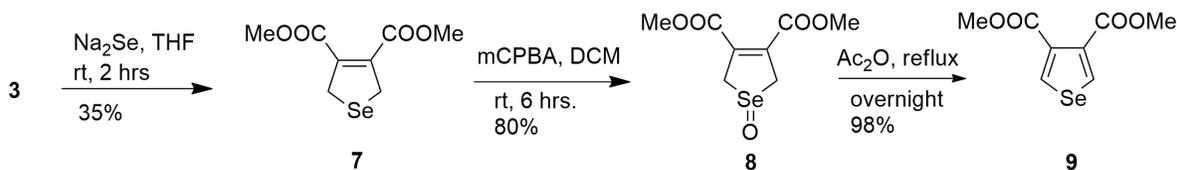
Chapter 2: Synthesis of donor and acceptor units of the low band gap polymers from single precursor–Dimethyl thiophene dicarboxylate

The donor–acceptor concept [4] has been greatly exploited in the conjugated polymers to tune the electronic and structural properties [5]. Benzo[1,2-b:4,5-b']dithiophene (BDT) and thieno[3,4-c]pyrrole-4,6-dione (TPD) are examples of thiophene-fused ring systems which are among the most explored building blocks of conjugated polymers. There are only few methods reported in the literature to synthesize BDT and TPD. BDT have been synthesized from *p*-benzoquinonedithiophene, whereas TPD has been synthesized from thiophene-3,4-dicarboxylic acid. The reported synthetic methods for BDT and TPD are involving multistep. In the present work we report the synthesis of BDT (donor unit) and TPD (acceptor unit), two important building blocks for the conjugated polymers, from a single precursor, dimethyl thiophene-3,4-dicarboxylate (**6**). This compound **6**, in turn, was synthesized from maleic anhydride. The synthesis of dimethyl thiophene dicarboxylate from maleic anhydride (Scheme 2.1).



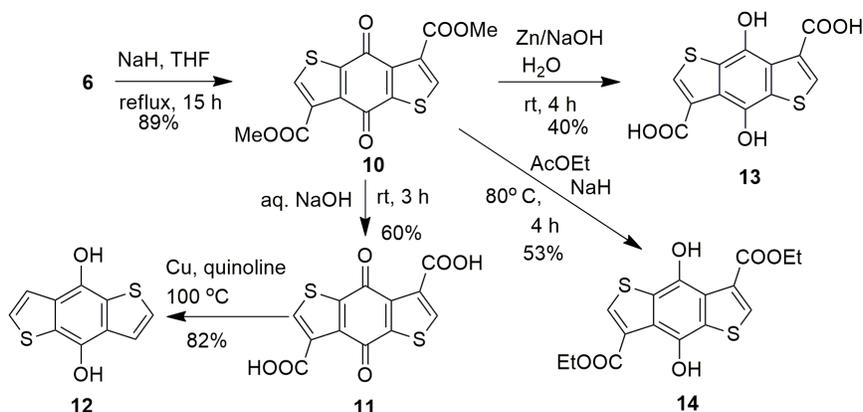
Scheme 2.1 Synthesis of dimethyl thiophene dicarboxylate (**6**) [6].

Oligo-selenophene and polyselenophene are often more rigid compared to its thiophene counterparts. Also, the substituent of the selenophene causes in lesser twisting in the polymers preserving the planarity. Very few routes are available in the literature for the synthesis substituted selenophene. We have synthesized dimethyl selenophene dicarboxylate by similar methodology (Scheme 2.2)



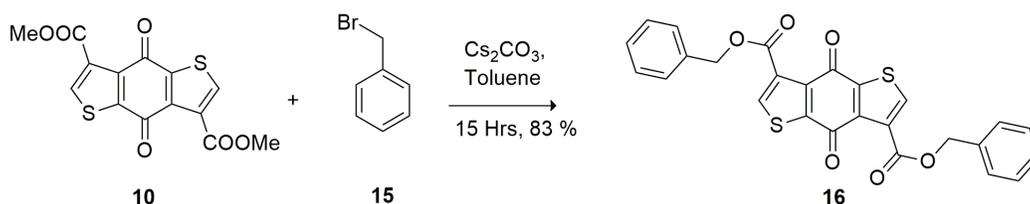
Scheme 2.2 Synthesis of dimethyl selenophenedicarboxylate (9).

BDT and TPD derivatives have been highly exploited as donor and acceptor units, respectively, to synthesize important donor-acceptor (D-A) conjugated polymers. BDT-based polymers were found to be one of the most efficient conjugated polymers for organic photovoltaic application. BDT-based molecules have emerged as prominent building blocks for conjugated systems in the number of organic electronic applications. Initially, these conjugated systems were used as active materials in OFETs [7]. In recent years; these building blocks were used to construct donor conjugated systems for OPV devices. The power conversion efficiencies of the OPV devices using conjugated systems comprising BDT unit have exceeded 8% [8]. The symmetric and large planar character of BDT imparts convenient charge transportation as well as rigidity. The symmetric and large planar character of BDT imparts convenient charge transportation as well as rigidity. Increased charge mobility accounted by the facial π - π stacking of planar conjugated structure of BDT. The salient features of these units are the alkoxy groups at 4 and 8 positions which improve the solubility of polymer and avoid the steric hindrance for adjacent units. Recently, two dimensional conjugations on BDT units have been reported where the BDT has been functionalized through two perpendicular directions [9].



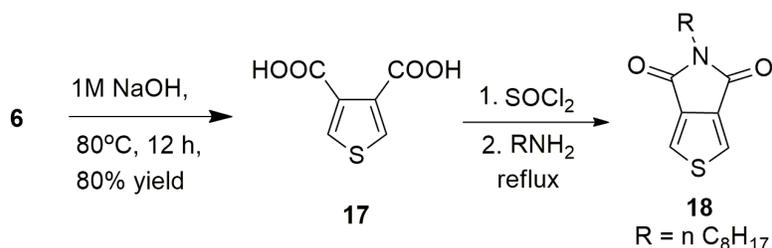
Scheme 2.3 Synthesis of BDT derivatives from compound 6 [6].

Synthesis of 3,7-dimethyl-4,8-dihydrobenzo[1,2-b:4,5-b']dithiophen-4,8-dione-dicarboxylate (**10**), a precursor to dihydroxybenzodithiophene **12**, was accomplished by new and unconventional approach. Compound **10** was obtained by treating compound **6** with an excess of sodium hydride under refluxing condition in dry THF for 15 hours in 89% yield. The diester **10** was hydrolyzed with aqueous NaOH to afford dicarboxylic acid **11**, which subsequently aromatize and decarboxylated by heating with Cu/quinolone to afford dihydroxy benzodithiophene **12**. When compound **10** was treated with aqueous NaOH solution in presence of Zn powder, it afforded dihydroxy benzodithiophene dicarboxylic acid **13**. Interestingly, when compound **7** was stirred with excess of NaH in ethyl acetate, aromatization with transesterification occurred to afford dicarboxylate **14**.



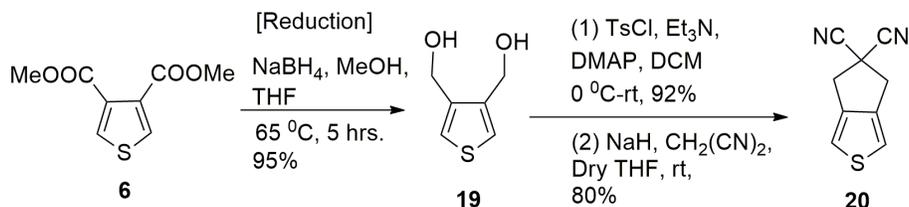
Scheme 2.4 Synthesis of Dibenzyl diester derivative of BDT (**16**)

Dibenzyl diester derivative of BDT (**16**) was synthesized by treating compound **10** with benzyl bromide in presence of Cs_2CO_3 (Scheme 2.4). Compound **6** was also explored for the synthesis of TPD derivative (**14**). Compound **14** was synthesized from compound **6** in three steps (Scheme 2.5).



Scheme 2.5 Synthesis of 5-octyl-thienopyrrole-4,6-dione (**18**)

3, 4 substituents avoid β - β and α - β coupling during electropolymerization [10]. Cyclopenta rings yields lesser steric hindrance and maintains more planarity in conjugated polymers. In present work, cyclopenta-thiophene derivatives are synthesized from compound **6**.



Scheme 2.6 Synthesis of cyclopentathiophenedicarbonitrile (**20**)

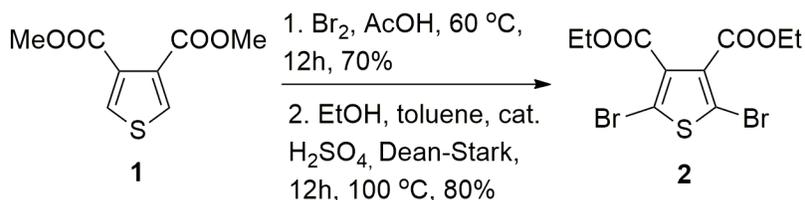
Synthesis of compound **20** was carried out from compound **6** in overall 2 steps. Compound **6** was first reduced, then tosylated by TsCl from which cyclopenta ring was formed by reacting with malonitrile to yield compound **20**.

In summary, dimethyl thiophene dicarboxylate, a precursor for conjugated polymers, was synthesized from maleic anhydride in simple six-step synthetic pathway involving mild reagents and in moderate yield. Similarly, dimethyl selenophene dicarboxylate was synthesized. Dimethyl thiophene dicarboxylate diester obtained was successfully converted into TPD and BDT derivatives which were useful building blocks for π -conjugated polymer. TPD, BDT and CPT derivative were synthesized, characterized by NMR and SCXRD.

Single crystal data revealed that benzodithiophene dicarboxylate derivative forms 1D-molecular sheet type structures in solid state. Along with these theoretical studies showed that conversion of quinone derivative to benzoquinone derivative decreases the bandgap of the molecules. Crystal data of compound **20** showed that ring system is planar and the cyano groups facilitate intermolecular H-bonding. Theoretical data suggest cyano exerts electron withdrawing effect on this CPT ring system.

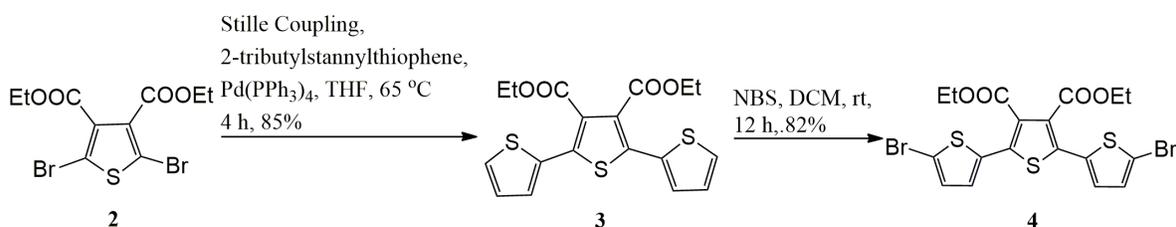
Chapter 3: Thiophene-3,4-dicarboxylate and carbazole based π -conjugated polymer: Synthesis, characterization and structure-property relationship studies

One of the most popular approach is modulation of band-gap, in which essentially the energy difference between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) is modified by incorporating electron-releasing groups (alkyl, aryl etc) or electron withdrawing groups (-CN, -COOR) in the backbone of the polymer chain. These modifications changes optical and redox properties of the polymer which overall affects the charge transport properties of the materials. The electron donating and electron withdrawing properties of alternating monomer efficiently increases the intramolecular charge transfer and setting up the push-pull effect which narrows the band gap of the conjugated polymers. The underlying concept is that the interaction between alternating electron-rich donors and electron-deficient acceptors results in a compressed band-gap *via* molecular orbital hybridization and *via* intramolecular charge transfer. N-fused heterocyclic ring systems have been reported as good donor units in the literature. The carbazole units are one of the most exploited and well-studied systems in the prospect. Unique feature of carbazole systems includes that N-atom in the molecule increases electron density and hence contributes to its hole-transporting ability. The fused system provides it good thermal and morphological stability as well as high fluorescence properties. In present case, the thiophene dicarboxylate units owing to their ester groups possesses electron-withdrawing nature, thus if incorporated in polymer-backbone these units will act as acceptor units.



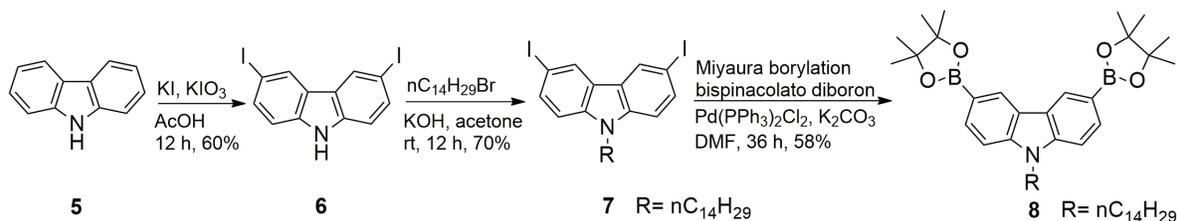
Scheme 3.1: Synthesis of diethyl 2,5-dibromothiophene-3,4-dicarboxylate (**2**)

Diethyl 2,5-dibromothiophene-3,4-dicarboxylate (**2**) was synthesized from dimethyl thiophene dicarboxylate. Bromination and esterification was carried out to yield compound **2** which was used as a monomer in chemical polymerization (Scheme 3.1). Compound **2** was further treated with 2-tributyl stannylthiophene under stille reaction conditions to get diethyl [2,2':5',2''-terthiophene]-3',4'-dicarboxylate compound (**3**). Compound **3** was brominated in presence of NBS to yield diethyl 5,5''-dibromo-[2,2':5',2''-terthiophene]-3',4'-dicarboxylate (**4**)



Scheme 3.2 Synthesis of diethyl 5,5''-dibromo-[2,2':5',2''-terthiophene]-3',4'-dicarboxylate (**4**)

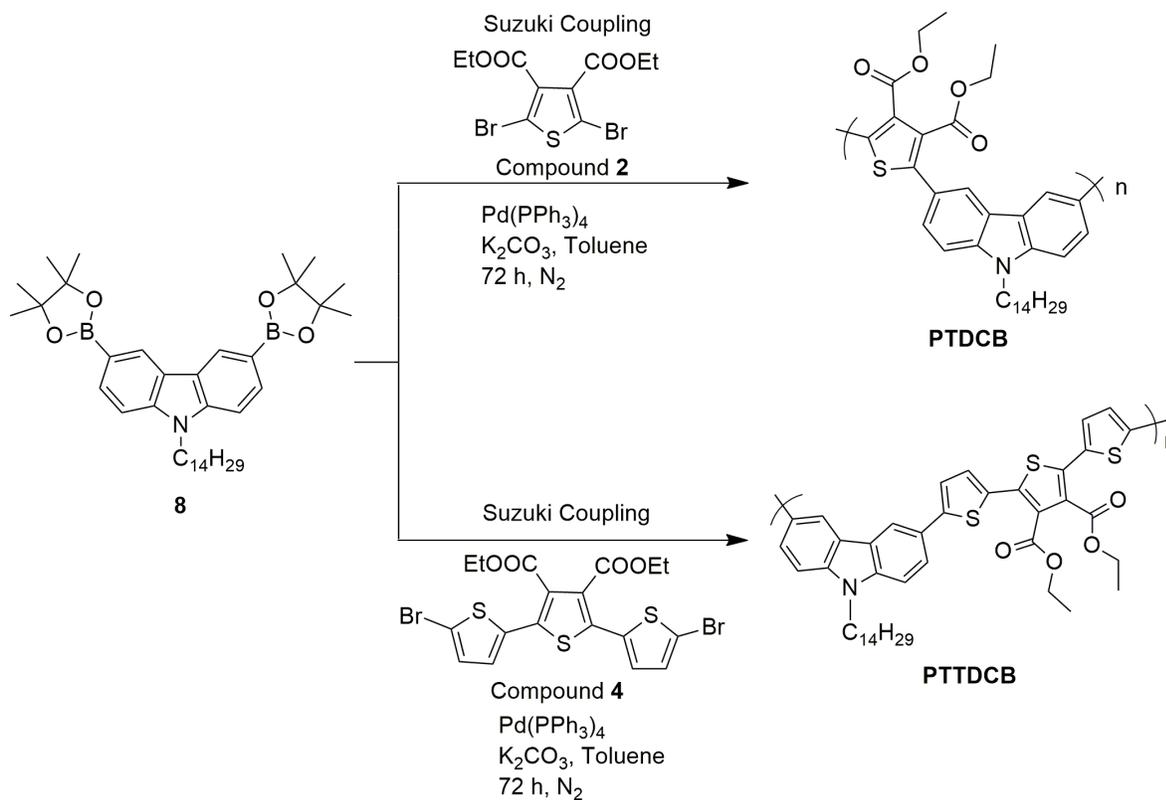
9-Tetradecyl-3,6-bis-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-carbazole (**8**) was synthesized from carbazole in three steps by using reported method (Scheme 3.3) [12].



Scheme 3.3 Synthesis of 9-tetradecyl-3,6-bis-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-carbazole (**8**)

Compound **8** was further treated with compound **2** and compound **4** under Suzuki Miyaura reaction condition to yield **PTDCB** and **PTTDCB**, respectively (Scheme 3.4). The synthesized polymers **PTDCB** and **PTTDCB** were well characterized by ^1H NMR, GPC, UV-visible and electrochemical techniques.

Addition of thiophene units in the polymer imparts dual advantage one being increase in the conjugation along the polymer backbone which will increase effective conjugation length of the polymer as well as 2,5 disubstituted thiophenes units contributes lesser steric hindrance to the neighboring groups which again benefits the overall conjugation.



Scheme 3.4 Synthesis of **PTDCB** and **PTTDCB**

UV-visible and fluorescence, GPC analysis and TGA data of **PTDCB** and **PTTDCB** are summarized below (Table 3.1)

Table 3.1 Photo-physical properties (abs - absorption and em - emission values), Molecular weight Mw, Mn, Poly-Dispersity Index (obtained from GPC analysis), decomposition temperature Td (obtained from TGA)

Polymer	$\lambda_{\max}(\text{abs})$ (nm)	$\lambda_{\max}(\text{em})$ (nm)	Stokes Shift (nm)	Stokes shift (eV)	Mw (KDa)	Mn (KDa)	PDI	Td
PTDCB	306 249	493	187	1.49	6.9	2.7	2.5	304
PTTDCB	417 303 254	583	166	0.82	8.7	4.0	2.15	264

In summary Compound **2** and compound **4** were synthesized from dimethyl thiophene dicarboxylate (**1**) which were used as acceptor unit and compound **8** was used as donor molecule in the synthesis of π -conjugated **PTDCB** and **PTTDCB**. The polymers were characterized by ^1H NMR, UV-Vis, GPC and TGA techniques. The data shows that with addition of thiophene unit in **PTTDCB** the effective conjugation length of polymer was increased which thus decreases the band gap of the **PTTDCB**.

Chapter 4: Synthesis, characterization, electrochemical and photophysical properties of dithienopyrrolobenzothiadiazole based π -conjugated polymers and π -conjugated D- π - A- π -D type molecule

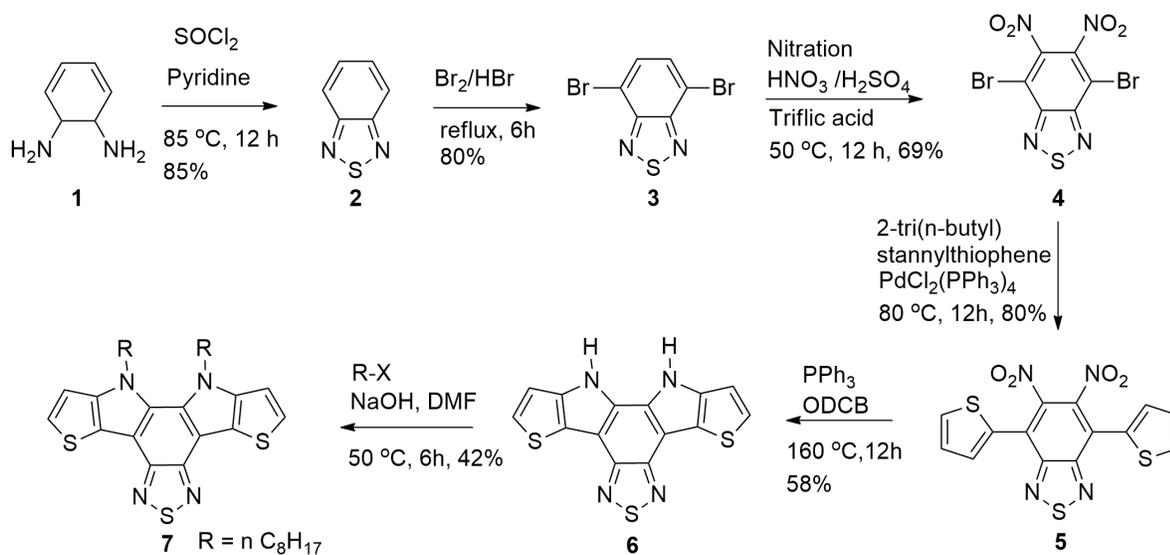
Part a: Tert-thiophene-dithienopyrrolobenzothiadiazole(PTTPBT) and thieno[3,4-*c*]pyrrole-4,6-dione-dithienopyrrolobenzothiadiazole(PTPDPBT) based conjugated polymers

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 [13] Furthermore, rigid structures can reduce the rotational disorder around interannular single bonds to lower the reorganization energy, which is beneficial to improve charge mobility [14]. On the basis of aforementioned points, we have synthesized nitrogen bridged donor-acceptor multifused dithienopyrrolobenzothiadiazole (DTPBT) by intramolecular Cadogan annulation, to prepare two novel copolymers with two different monomers.

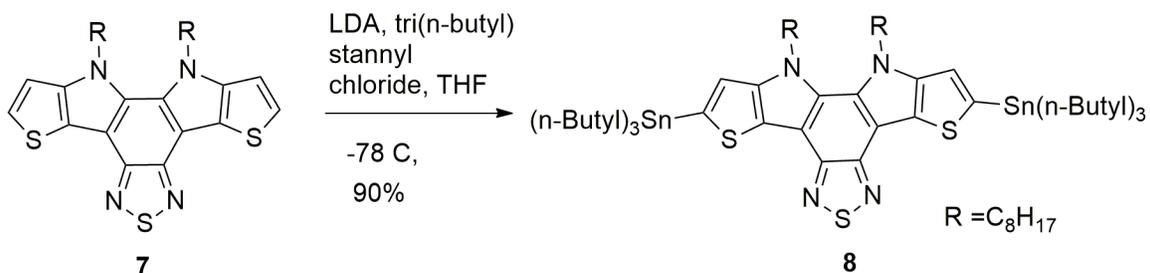
Synthesis and characterization of monomers

DTPBT was synthesized from 5,6-dinitro-4,7-dithienyl-2,1,3-benzothiadiazole (**5**) by intramolecular cadogan annulation (Scheme 4.1) according to the literature procedure reported by Kato *et al* [15].



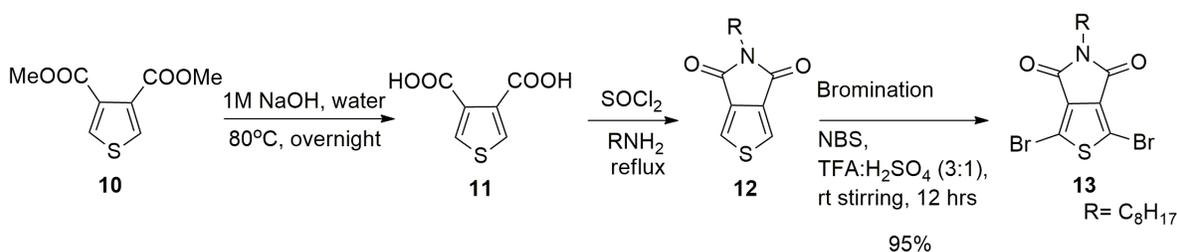
Scheme 4.1 Synthesis of 10, 11-dioctyl-10, 11-dihydro-[1, 2, 5]thiadiazolo[3, 4-e]thieno[2', 3':4, 5] pyrrolo[3, 2-g]thieno[3, 2-b]indole (**7**)

DTPBT-based monomer, distannyldithienopyrrolobenzothiadiazole (**8**) was synthesized according to the literature procedure reported by Carsten *et al* (Scheme 4.2) [16].



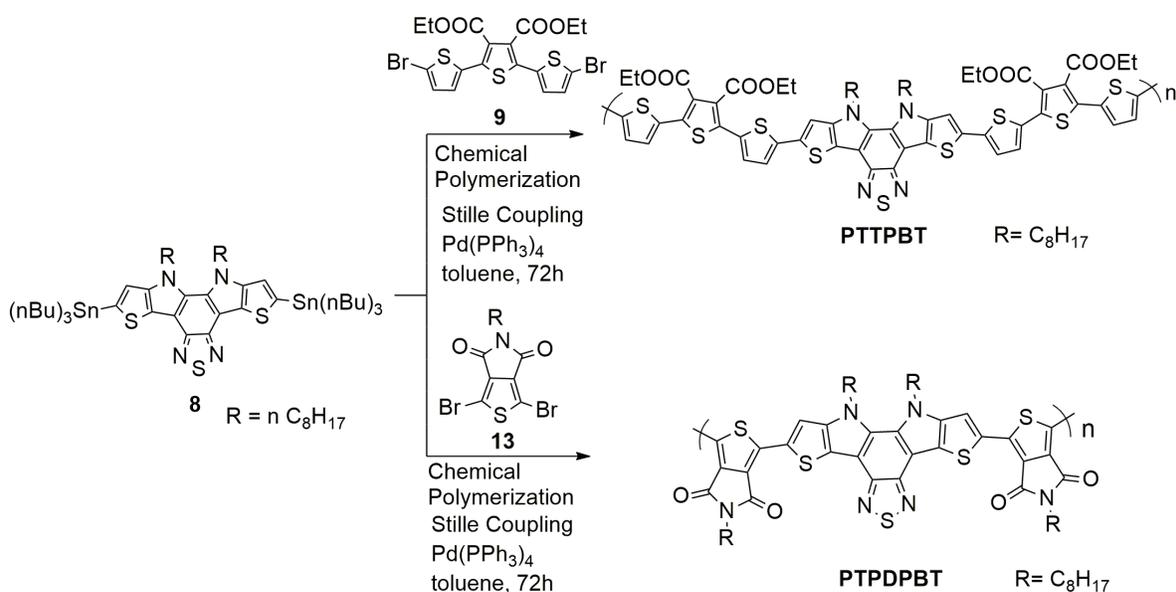
Scheme 4.2 Synthesis of 10, 11-dioctyl-2, 8-bis(tributylstannyl)-10, 11-dihydro-[1, 2, 5]thiadiazolo[3, 4-e]thieno[2', 3':4, 5]pyrrolo[3, 2-g]thieno[3, 2-b]indole (**8**).

Thieno[3,4-c]pyrrole-4,6-dione (TPD) is one of most promising molecule in the field of conjugated polymer. Many conjugated polymer having TPD as one of its unit showed excellent OPV, OFET properties. Imide-fused thiophene containing conjugated polymers have also demonstrated excellent photovoltaic properties as electron acceptor for OPV. The symmetric structure of TPD makes regioisomer-free polymers as well the alkyl substituent possesses minimum steric hindrance to the neighboring groups. Compound **13** was synthesized from diethyl thiophene diester (**10**) (Scheme 4.3).



Scheme 4.3: Synthesis of 1,3-dibromo-5-octyl-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione(**13**)

Similarly, diethyl 5,5''-dibromo-[2,2':5',2''-terthiophene]-3',4'-dicarboxylate (**9**) was synthesized from diethyl 2,5-dibromothiophene-3,4-dicarboxylate according to the procedure mentioned in the Scheme 8, Chapter 3. Chemical polymerization of compound **8** with compound **9** and compound **13** were carried out under standard stille coupling conditions. The obtained polymers, **PTTPBT** and **PTPDPBT** were well characterized by ^1H NMR, GPC, UV-Vis and fluorescence spectroscopy and cyclic voltammetry analysis



Scheme 4.4 Synthesis of DTPBT-based conjugated polymers **PTTPBT** and **PTPDPBT** by Stille coupling reaction.

The synthesized DTPBT-based conjugated polymers were characterized by ^1H 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-voltammetry. The properties of the synthesized polymers are summarized in Table 4.1 and Table 4.2. All the polymers showed good thermal stabilities and

good film forming properties. The synthesized polymers **PTTPBT** and **PTPDPBT** possessed small band gap, 2.1 eV and 1.9 eV respectively.

Table 4.1 Photo-physical properties (abs absorption and em emission values), Molecular weight Mw, Poly-Dispersity Index (obtained from GPC analysis) and decomposition temperature Td (obtained from TGA) of synthesized DTPBT-based polymers

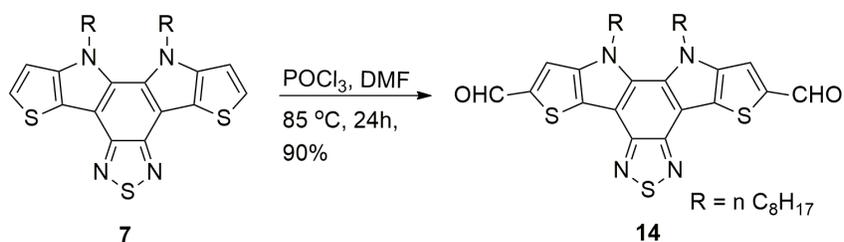
Polymers	$\lambda_{\max}(\text{abs})$ (nm)	$\lambda_{\max}(\text{em})$ (nm)	Stokes Shift (nm)	Stokes shift (eV)	Mw (KDa)	Mn (KDa)	PDI	Td
PTTPBT	430	543 501	113	0.58	20.65	9.44	2.18	220
PTPDPBT	369	479 451	110	0.75	9.60	4.92	1.9	208

Table 4.2 Electrochemical properties of synthesized polymers; a potential v/s Ag/Ag⁺; calculated from equation $E_{\text{HOMO/LUMO}} = - (E_{\text{oxi/red,onset}} + 4.8 - E_{\text{Fc/Fc}^+})$; calculated from equation $E_{\text{LUMO}} = E_{\text{HOMO}} + E_{\text{gopt}}$

Polymers	$E_{\text{oxid}}(\text{V})$	$E_{\text{HOMO}}(\text{eV})$	$E_{\text{LUMO}}(\text{eV})$	$E_{\text{band gap}}^{\text{opt}}(\text{eV})$
PTTPBT	1.17	-5.57	-3.47	2.1
PTPDPBT	1.36	-5.76	-3.86	1.9

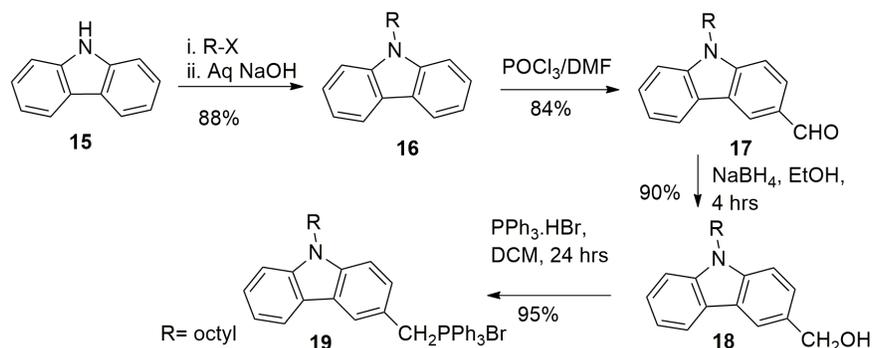
Part b: Dithienopyrrolobenzothiadiazole–Carbazole based π -conjugated D- π -A- π -D type molecule. Synthesis, Characterization, Photophysical, Electrochemical and DFT studies

Conjugated D–A materials find numerous applications as active layers for solar cells, organic light emitting diodes (OLEDs) and electrochromic devices. Ladder type π -conjugated system with fully fused polycyclic skeleton incorporating various heteroatoms like nitrogen, silicon and boron are of growing interest owing to their rigid structural framework which ensures enhanced π -conjugation and dense molecular packing in solid state which ultimately leads to high fluorescence ability and high carrier mobility. Benzothiadiazole unit and 4,7-di(thiophen-2-yl) benzothiadiazole (DTBT) unit are the most commonly used acceptor units in D–A systems [17]. It is of great interest to planarize the DTBT structure by connecting 3-positions of two outer thiophenes with the 5- and 6- position of the central BTB core *via* two bridging atoms. Here, we report the synthesis of macromolecule M1, based on carbazole and DTPBT. Its optical, redox and electronic properties were studied. Dioctyl-DTPBT (**7**) was formylated under Vilsmyer-Heck condition to yield diformyl dioctyl DTPBT (**14**) (Scheme 4.5).



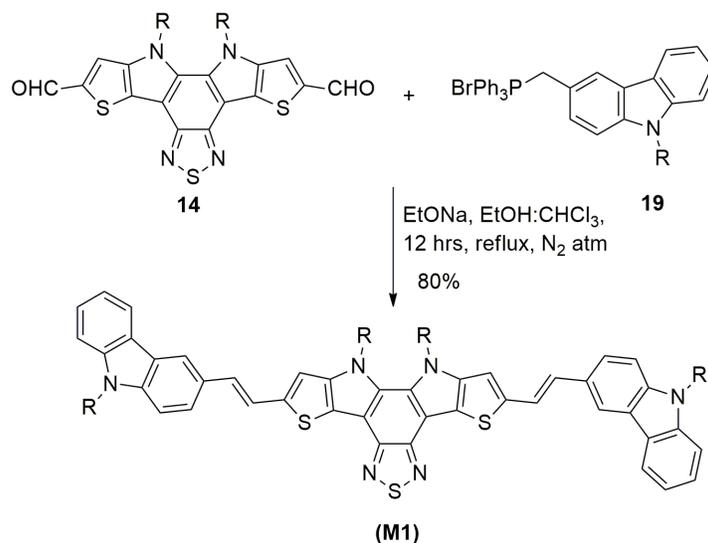
Scheme 4.5 Synthesis of compound **14**

Wittig salt of carbazole was synthesized from carbazole (**15**) in four steps by following the literature method (Scheme 4.6) [18].



Scheme 4.6 Synthesis of Wittig salt of carbazole (**19**)

Compound **19** was further treated with compound **14** in presence of sodium ethoxide to yield macromolecule (M1) (Scheme 4.7)



Scheme 4.7 Synthesis of Macromolecule (M1)

The synthesized macromolecule M1 was well characterized by ^1H and ^{13}C NMR, HRMS, UV-Vis and fluorescence spectroscopy and cyclic voltammetry analysis. The computational data were carried out by DFT calculation on *Gaussian 09* software using 6-31G basis set with B3LYP hybrid exchange-correlation. The FMO analysis of the calculated data revealed that HOMO energy levels were distributed overall molecule while LUMO levels were concentrated to the DTPBT core system. Further, it also suggests that periphery carbazole units are donor type while core unit acts as an acceptor type making this molecule a D-A-D type conjugated molecule. The optical, electronic and theoretical band-gaps were calculated using UV-visible spectroscopy, cyclic-voltammetry and density functional theory (DFT), respectively. All the properties of Macromolecule M1 are summarized in Table 4.3.

Table 4.3 Photo-physical, electrochemical and DFT calculated properties of Macromolecule M1;

^afrom absorption data; ^bfrom emission data; ^cAg vs Ag/AgCl; ^e calculated using the equation: $E_{\text{HOMO}} = -(E_{\text{oxi}} + 4.8 - E_{(\text{Fc}/\text{Fc}^+)})$, $E_{(\text{Fc}/\text{Fc}^+)} = 0.86 \text{ V}$; ^f calculated from the equation $E_{\text{LUMO}} = E_{\text{g}}^{\text{opt}} + E_{\text{HOMO}}$ (eV). ^g calculated optical band-gaps using equation $E_{\text{optical}} = 1240/\lambda_{\text{onset}}$;

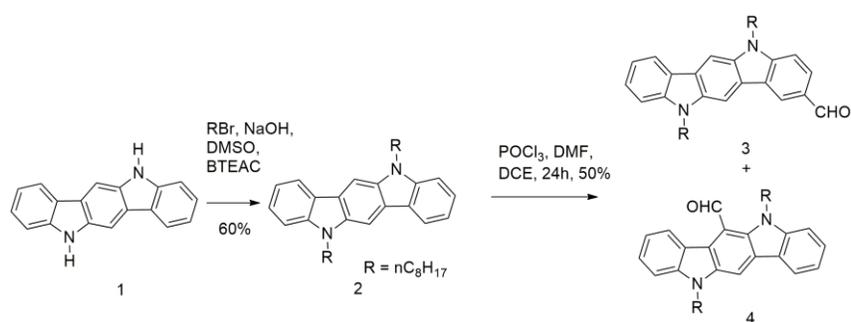
Compound	$\lambda_{\text{max}}(\text{abs})$ (nm) ^a	$\lambda_{\text{max}}(\text{em})$ (nm) ^b	Stokes Shift (nm)	Stokes shift (eV)	E oxidation ^c (V)	E HOMO ^e (eV)	E LUMO ^f (eV)	E band gap optg (eV)
M1	504 437	614	110	0.43	1.48	-5.88	-3.78	2.1

Chapter 5: Indolocarbazole-benzimidazole based conjugated molecules and trisubstituted phenyl-oxazole based π -conjugated molecules: Synthesis, characterization, photophysical and DFT studies

Part a: Indolo[3,2-*b*]carbazole-benzimidazole based conjugated molecules: Synthesis, computational and photophysical studies

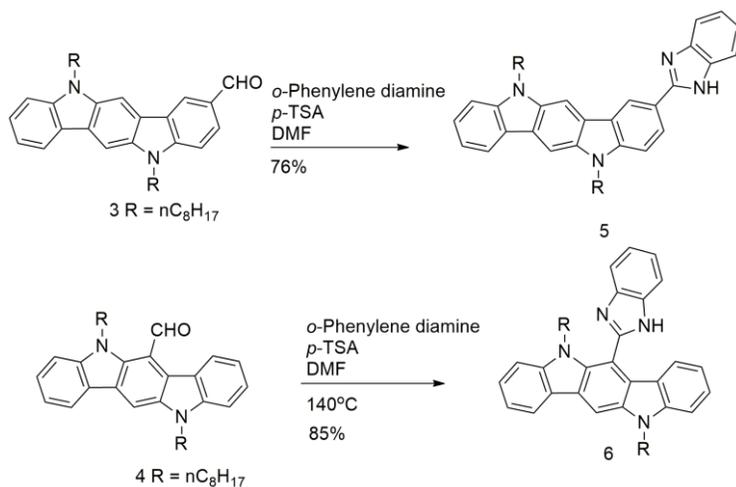
Indolo[3,2-*b*]carbazole (ICZ) have shown remarkable application in fields of medicinal, biological and material sciences. ICZ derivatives are known for their planar and rigid conjugated structures and due to this it shows remarkable photophysical properties. ICZ derivatives could serve as an excellent hole-transporting materials and organic thin-film transistor (OTFT) materials [19]. Several ICZ derivatives were synthesized and used as luminescence and hole-transporting materials in the OLEDs [20]. Carbazole-benzimidazole based ratiometric fluorescent probes have been recently reported by S. Goswami *et al* [21]. The reported carbazole-benzimidazole based sensor showed high and reversible sensitivity for volatile acid vapors.

In this chapter reports new dialkyl ICZ-benzimidazole derivatives which were synthesized from dioctyl ICZ derivatives obtained by double Fischer cyclization of bisarylhydrazones. The dioctyl ICZ were further reacted under Vilsmeier-Haack reaction condition to yield structural isomers dioctyl ICZ-2-aldehyde and dioctyl ICZ-6-aldehyde. Both aldehydes were separately reacted with *ortho*-phenylene diamine to yield 2-(1H-benzo[d]imidazol-2-yl)-5,11-dioctyl-5,11-Indolo[3,2-*b*]carbazole (compound **5**) and 6-(1H-benzo[d]imidazol-2-yl)-5,11-dioctyl-5,11-Indolo[3,2-*b*]carbazole (compound **6**). Compound **5** and compound **6** were characterized by NMR spectroscopy and High-resolution Mass-spectrometry (HRMS). UV-visible absorption studies and fluorescence studies were analyzed. The responses of compounds against the TFA in fluorescence were measured. The computational studies were done to develop the understanding regarding acidic response by the synthesized compounds. [22]



Scheme 5.1 Synthesis of dioctyl ICZ-2-aldehyde (**3**) and dioctyl ICZ-6-aldehyde (**4**) from ICZ (**1**).

The ICZ aldehydes were reacted with *ortho*-phenyl diamine in dry dimethyl formamide [DMF] in presence of *p*-TSA at elevated temperature to yield corresponding substituted benzimidazole (Scheme 5.2).

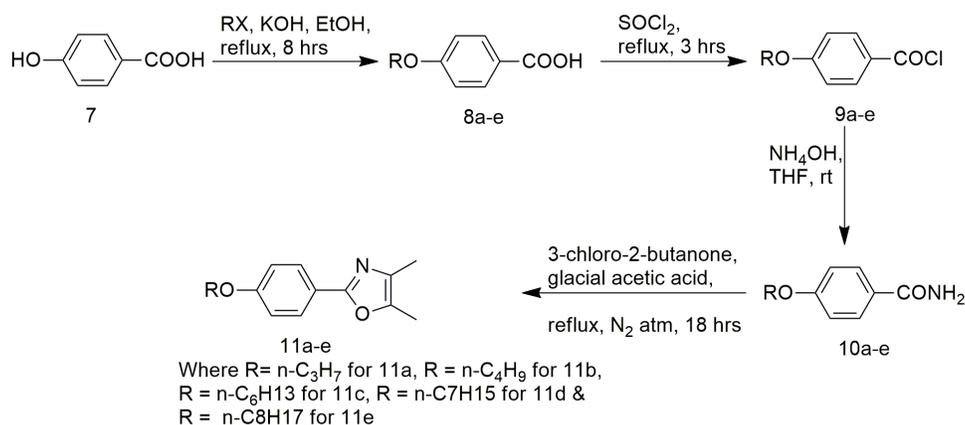


Scheme 5.2: Synthesis of 2-(1H-benzo[d]imidazol-2-yl)-5,11-dioctyl-5,11-Indolo[3,2-*b*]carbazole (**5**) and 6-(1H-benzo[d]imidazol-2-yl)-5,11-dioctyl-5,11-Indolo[3,2-*b*]carbazole (**6**)

The structures of these two compounds were fully characterized by NMR (^1H and ^{13}C) and HRMS spectroscopy methods. Their photochemical and electrochemical properties were studied by UV-vis absorption spectroscopy and fluorescence spectroscopy and electrochemical methods. Fluorescence study results reveal that compounds, **5** and **6** were showed remarkable sensitivity towards acid (TFA). Density Functional Theory (DFT) studies showed that **5** is more planar compared to **6**, which resulted in the increase in the conjugation thereby decreases the band gap. The optimized structures of both compounds and their protonated forms were calculated by density functional theory calculations.

Part b: Series of 2, 4, 5-trisubstituted oxazole: Synthesis, characterization and DFT studies

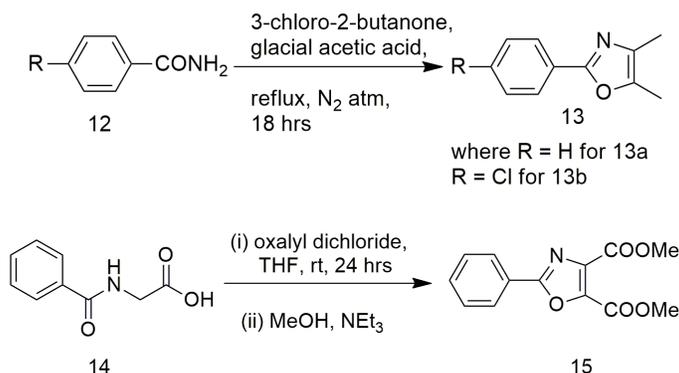
Oxazoles have been found as subunits in numerous natural products. Oxazole is also a valuable precursor in various biochemical as well as synthetic transformations. Oxazole derivatives have shown activity against inflammation, diabetes, bacterial infection, cardiovascular disease, viral and cancer. Owing to these facts, oxazole derivatives have attracted considerable attention in field of medicinal research, and resulted in development of numerous investigations on their synthesis and biological activities during the last decade. However, very little efforts have been paid to the synthesis of trisubstituted oxazoles. In present work we report the synthesis of 2-(4-alkyloxyphenyl)-4,5-dimethyloxazole derivatives and other trisubstituted oxazole derivatives. A simple and practical synthetic methodology was used to achieve the desired molecules.



Scheme 5.3 Synthesis of 2-(4-alkyloxyphenyl)-4, 5-dimethyloxazole derivatives (**11a-e**)

The molecular structures for 2-(4-butyloxyphenyl)-4, 5-dimethyloxazole (**11b**) and 4,5-dimethyl-2-(4-(octyloxy)phenyl)oxazole (**11e**) were elucidated by SCXRD. The C12-H12a group associated with the methylene moiety which is indeed in a close proximity to the ethereal linkage and the centroid of the benzene ring (C_g), essentially involved in the intermolecular C-H... π , (distance 2.89 Å) donor-acceptor interactions, arranging the molecules linearly.

Principally, the oxazole moiety of the asymmetric molecule is involved in C-H...N donor-acceptor interaction, arranging the neighbouring molecule parallel. Overall, the asymmetric molecule forms an aggregate of three molecules. In fact, C10-H10b and N8 groups of oxazole moiety are mainly involved C-H...N (distance 2.55 Å) weak H-bonding interactions and arranging the molecules linearly.



Scheme 5.4 Synthesis of 2-phenyl-4,5-dimethyloxazole (**13a**), 2-(4-chlorophenyl)-4,5-dimethyloxazole (**13b**) and dimethyl-2-phenyloxazole-4,5-dicarboxylate (**15**) [24]

2-(4-chlorophenyl)-4,5-dimethyloxazole was synthesized by reaction of chloro-butanone and 4-chloro benzamide while dimethyl-2-phenyloxazole-4,5-dicarboxylate (**15**) was also prepared by treating N-benzoyl glycine (**14**) with oxalyl dichloride in dry THF under N₂ atmosphere followed by treatment with methanol in presence of triethyl amine.

DFT calculated electrostatic potential maps of these compounds showed. Substituents on oxazole ring showed significant effect on the overall charge distribution pattern. It reveals that in 2-(4-alkoxyphenyl)-4, 5-dimethyloxazole derivatives, negative charge was concentrated over N-atom of oxazole ring and O-atom of etheral linkage compared over the rest of molecule. Substitution of chloro group showed little effects on charge distribution pattern. In dimethyl 2-phenyloxazole-4, 5-dicarboxylate (**15**) carbonyl oxygen atoms of ester groups were effectively able to alter the charge distribution of molecule.

In summary, a series of 2,4,5-trisubstituted oxazole were prepared and characterized by standard spectroscopic methods and X-ray crystallography. The crystal structures of compound **11b** and compound **11e** shows significant nonbonding intermolecular interactions such as C-H... π , C-H...N and C-H...O interactions, forming a fascinating 1D and 3D molecular networking, respectively. DFT calculated electrostatic potential maps were obtained and effects of different substitutions on charge distribution pattern were analyzed.

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List of Publications

The research papers published based on work presented in this thesis:

1. **V. Kadam**, P. Bhatt, H. Karmakar, S. Zade and A. Patel, 2019. Benzimidazole-Substituted Indolo [3, 2-b] carbazoles: Acid-Responsive Probes. *ChemistrySelect*, 4, (13), pp.3948-3952.
2. **V. Kadam**, A. Patel and S. Zade, 2016. Single precursor for the synthesis of donor and acceptor units of the low band gap polymers: Synthesis of benzodithiophene and thienopyrroledione from maleic anhydride. *Tetrahedron Lett.*, 57, (24), pp.2608-2611.
3. **V. Kadam**, S. Shaikh and A. Patel, 2016. A series of 2, 4, 5-trisubstituted oxazole: Synthesis, characterization and DFT modelling. *J. Mol. Struct.*, 1114, pp.181-188.