Synopsis of thesis entitled

"Synthesis, Characterization and Study of Low Band Gap Conjugated Molecules and Polymers"

To be submitted to

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For the degree of

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in

Chemistry

By

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A synopsis of the thesis

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Title of the Thesis : **"**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 sp2pz 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.

The electronic structure in conducting polymers is determined by the chain symmetry (i.e. the number and kind of atoms within the repeat unit), with the result that such polymers can exhibit semiconducting or even metallic properties.

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 a so called "donor–acceptor" design strategy.

Polythiophenes are most important classes of π-conjugated polymers, as they meet the essential requirements of solubility and processibility 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.

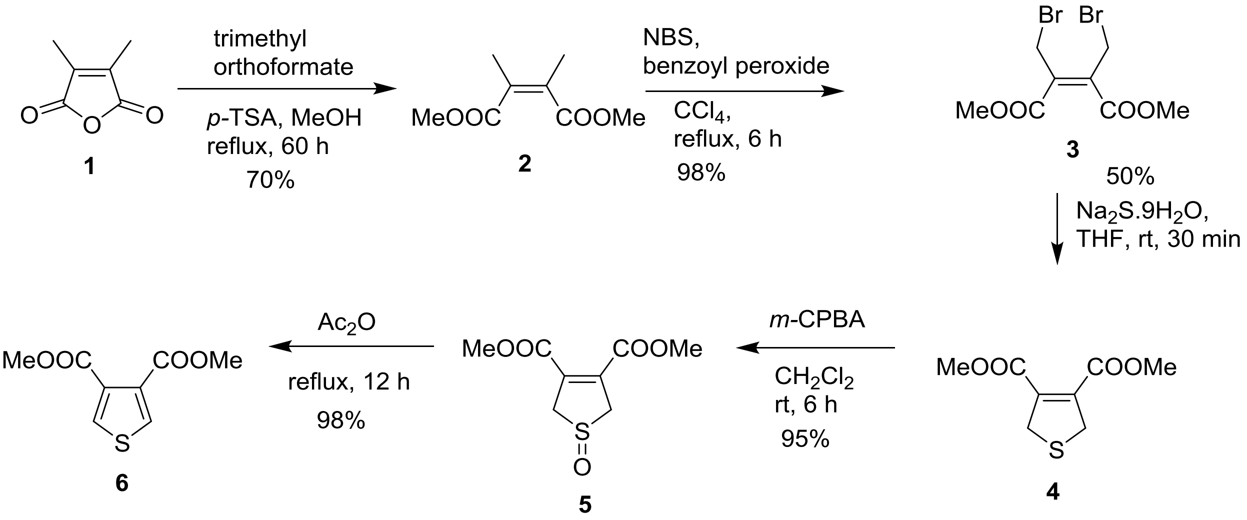
Aim and objective of this work

1. To develop a 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.

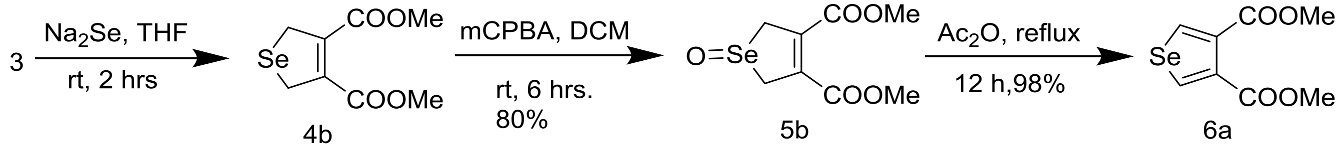
Chapter 2: Synthesis of Donor and Acceptor Units of the Low Band Gap Polymers from Single Precursor–Dimethyl Thiophene Dicarboxylate

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 synthesized BDT and TPD. BDT have been synthesized from p-benzoquinonedithiophene, whereas TPD has been synthesized fromthiophene-3,4-dicarboxylicacid. 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 1).



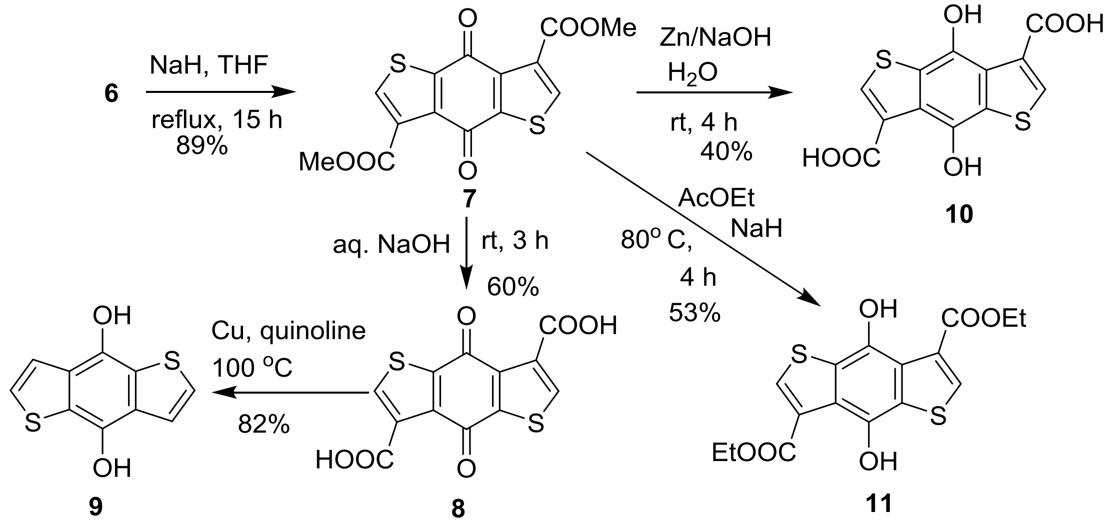
Scheme 1: Synthesis of dimethyl thiophene dicarboxylate (**6**)[6]

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)



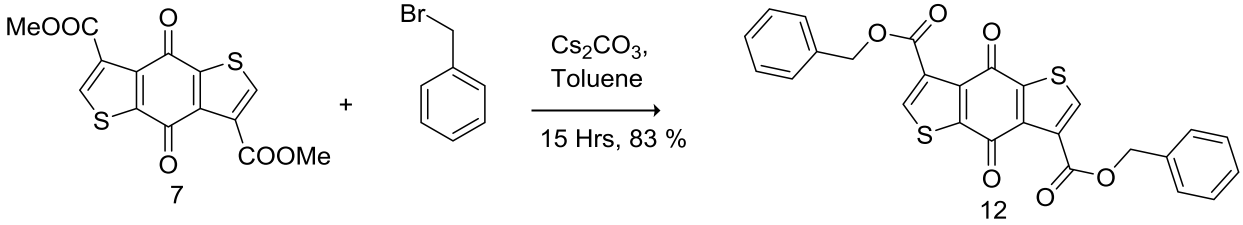
Scheme 2: Synthesis of dimethyl selenophene dicarboxylate (**6a**)

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] Conjugated systems comprising the symmetric, rigid and highly planar BDT unit showed better charge mobility due to presence of efficient π-stacking interaction. Alkoxy substituents at the 4, 8-positionsof BDT improve the solubility of the resulting polymers without steric hindrance in the conjugation. Recently, two dimensional conjugations on BDT units have been reported where the BDT has been functionalized through two perpendicular directions.[9]



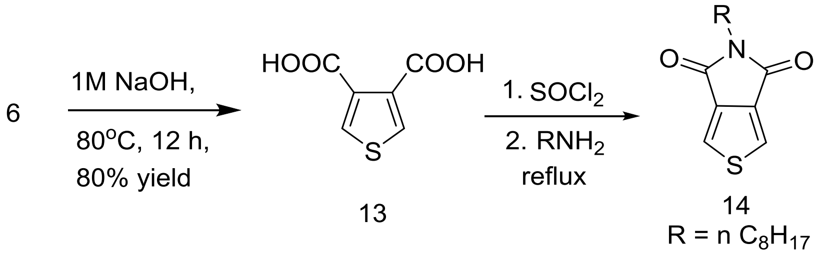
Scheme 3 Synthesis of BDT derivatives from compound **6**[6]

Synthesis of 3,7-dimethyl-4,8-dihydrobenzo[1,2-b:4,5-b']dithiophen-4,8-dione-dicarboxylate (**7**), a precursor to dihydoxy benzodithiophene **9**, was accomplished by new and unconventional approach. Compound **7** 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 **7** was hydrolyzed with aqueous NaOH to afford dicarboxylic acid **8**, which subsequently aromatize and decarboxylated by heating with Cu/quinolone to afford dihydroxy benzodithiophene **9**. When compound **7** was treated with aqueous NaOH solution in presence of Zn powder, it afforded dihydroxy benzodithiophene dicarboxylic acid **10**. Interestingly, when compound **7** was stirred with excess of NaH in ethyl acetate, aromatization with trans-esterification occurred to afford dicarboxylate **11**.



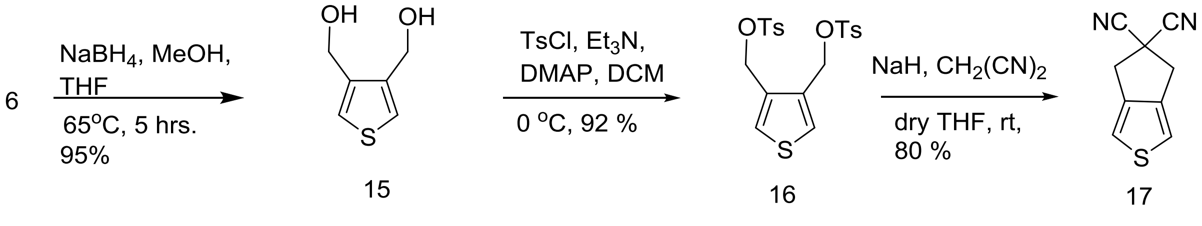
Scheme 4: Synthesis of Dibenzyl diester derivative of BDT (**12**)

Dibenzyl diester derivative of BDT (**12)** was synthesized by treatingcompound **7** with benzyl bromide in presence of Cs_2CO_3 (Scheme 4).Compound **6** was also explored for the synthesis of TPD derivative (**14**). Compound **14** was synthesized from compound **6** in three steps (Scheme 5).



Scheme 5: Synthesis of 5-octyl-thienopyrrole-4,6-dione (**14**)

3, 4 substitutents 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 6: Synthesis of cyclopentathiophene dicarbonitrile (**17**)

Synthesis of compound **17** was carried out from compound **6** in overall 3 steps. Compound **6** was first reduced, then tosylated by TsCl from which cyclopenta ring was formed by reacting with malonitrile to yield compound **17**.

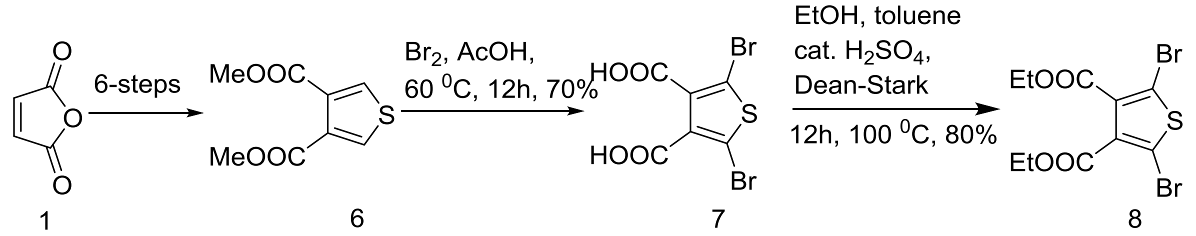
In summary, dimethyl thiophene dicarboxylate, a precursor for conjugated polymers, was synthesized from maleic anhydride in simple six-step synthetic pathway involving mild reagents and in moderate yield. Similarly, dimethyl selenophene dicarboxylate was synthesized. Dimethyl thiophene dicarboxylate diester obtained was successfully converted into TPD and BDT which were useful building blocks for π-conjugated polymer. BDT derivatives 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 **17** showed that ring system is planar and the cyano groups facilitate inter 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

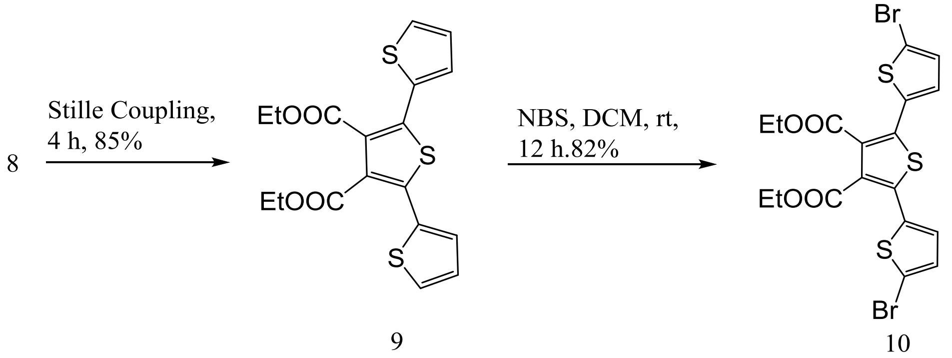
To impart the delocalization in the polymer back bone which provides quinoid character, donor-acceptor alternating co-monomer strategy is often used. The electron donating and electron withdrawing properties of alternating monomer efficiently increases the intramolecular charge transfer setting up the push-pull effect which narrows the band gap of the conjugated polymer[11].

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.



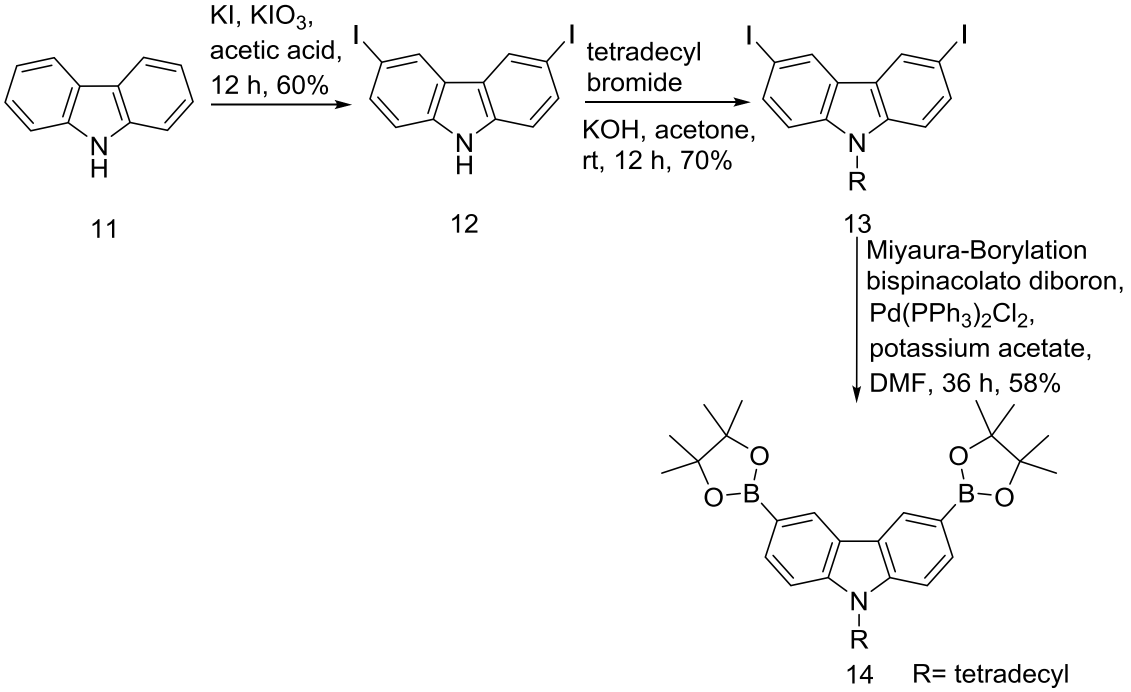
Scheme 7: Synthesis of diethyl 2,5-dibromothiophene-3,4-dicarboxylate (**8**)

Diethyl 2,5-dibromothiophene-3,4-dicarboxylate (**8**)was synthesized from dimethyl thiophene dicarboxylate. Bromination and esterification was carried out to yield compound **8** which was used as a monomer in chemical polymerization (Scheme 7). Compound **8** was further treated with 2-tributylstannylthiopheneunder stille reaction conditions to get diethyl [2,2':5',2"-terthiophene]-3',4'-dicarboxylate compound **(9)**. Compound **9** was brominated in presence of NBS to yield diethyl 5,5"-dibromo-[2,2':5',2"-terthiophene]-3',4'-dicarboxylate (**10**)



Scheme 8: Synthesis ofdiethyl 5, 5"-dibromo-[2,2':5',2"-terthiophene]-3',4'-dicarboxylate (**10**)

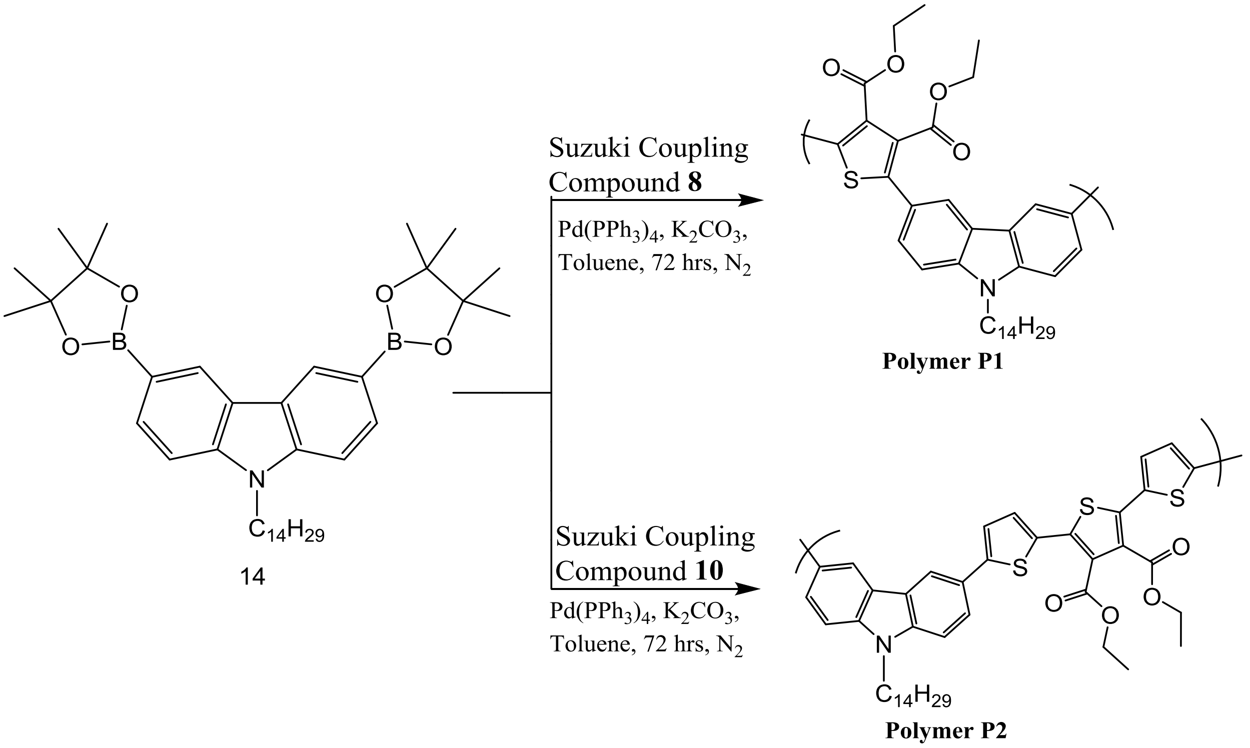
9-Tetradecyl-3,6-bis-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-carbazole (**14**) was synthesized from carbazole in three steps by using reported method (Scheme 9)[12].



Scheme 9 Synthesis of 9-tetradecyl-3, 6-bis-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-carbazole (**14**)

Compound **14** was further treated with compound **8**and compound **10**under Suzuki Miyaura reaction condition to yield **Polymer P1**and **Polymer P2**, respectively (Scheme 10).The synthesized **Polymer P1**and **Polymer P2** were well characterized by ^{1}H NMR, GPC,UV-Vis, 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 disubsituted thiophenes units contributes lesser steric hindrance to the neighboring groups which again benefits the overall conjugation.



Scheme 10: Synthesis of **Polymer P1** and **Polymer P2**

UV-Vis and fluorescence, GPC analysis and TGA data of **Polymer P1** and **Polymer P2** are summarized below (Table 1)

Table 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	**λ_{max}(abs) (nm)**	**λ_{max}(em) (nm)**	**Stokes Shift (nm)**	**Stokes shift (eV)**	**Mw (KDa)**	**Mn (KDa)**	**PDI**	**Td**
Polymer P1	306 249	493	187	1.49	6.9	2.7	2.5	304
Polymer P2	417 303 254	583	166	0.82	8.7	4.0	2.15	264

Compound **8** and compound**10**were synthesized from dimethyl thiophene dicarboxylate**(6**)which were used as acceptor unit and compound **14**was used as donor molecule in the synthesis of π-conjugated **Polymer P1** and **Polymer P2**. The polymers were characterized by ^{1}H NMR, UV-Vis, GPC and TGA techniques. The data shows that with addition of thiophene unit in **Polymer P2** the effective conjugation length of polymer was increased which thus decreases the band gap of the **Polymer P2**.

Chapter 4: Synthesis, Characterization, Electrochemical and Photophysical properties of Dithienopyrrolobenzothiadiazole based π-conjugated polymers and π-conjugated D- π - A- π -D type molecule.

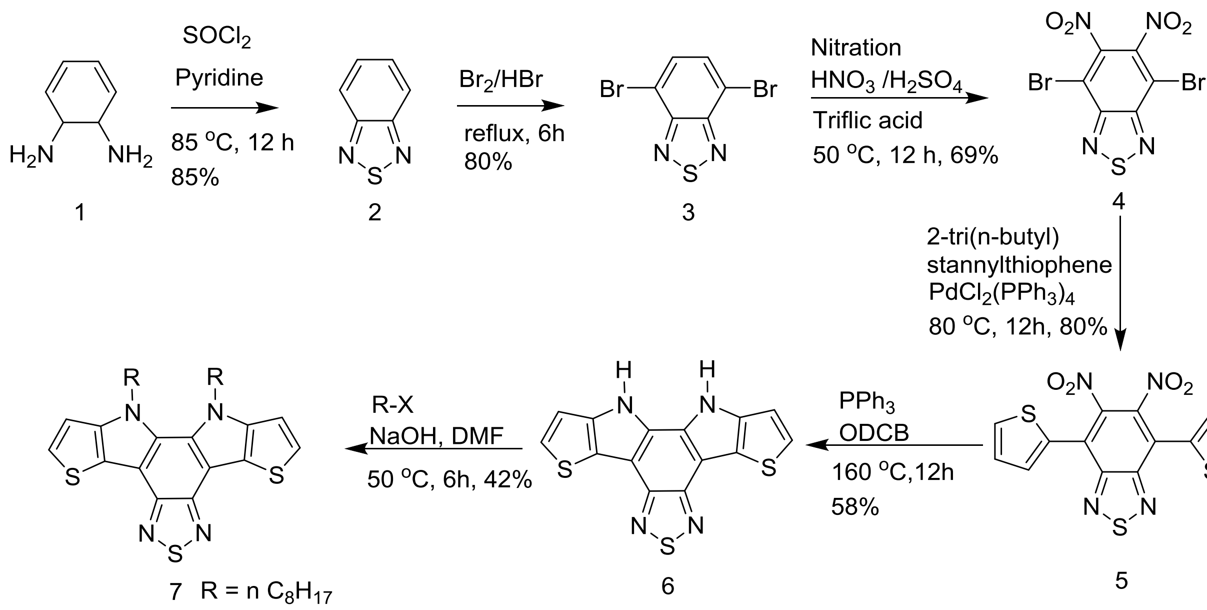
Part a: Synthesis, Characterization, Electrochemical and Photophysical studies of Dithienopyrrolobenzothiadiazole based π-conjugated polymers

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. 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.

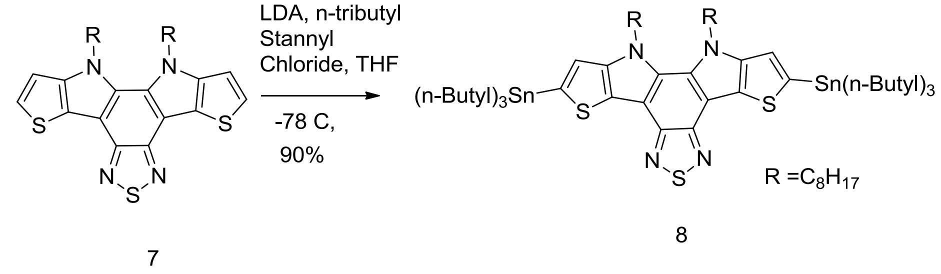
Synthesis and characterization of monomers

DTPBT was synthesized from 5,6-dinitro-4,7-dithienyl-2,1,3-benzothiadiazole (**5**) by intramolecular cadogan annulation (Scheme 11) according to the literature procedure reported by Kato et al.[15]



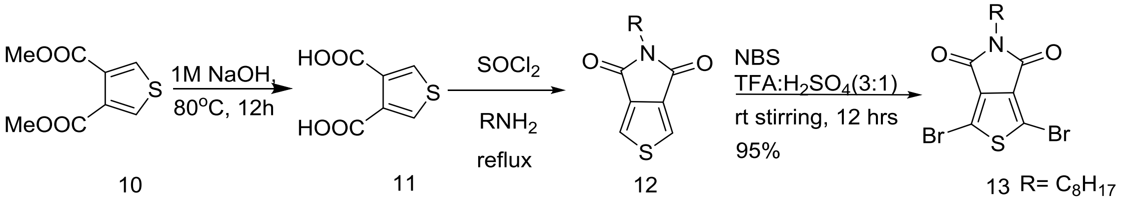
Scheme 11: Synthesis of Dithienopyrrolobenzothiadiazole (DTPBT)

DTPBT-based monomer, distannyldithienopyrrolobenzothiadiazole (**8**) was synthesized according to the literature procedure reported by Carsten et al (Scheme 12)[16].



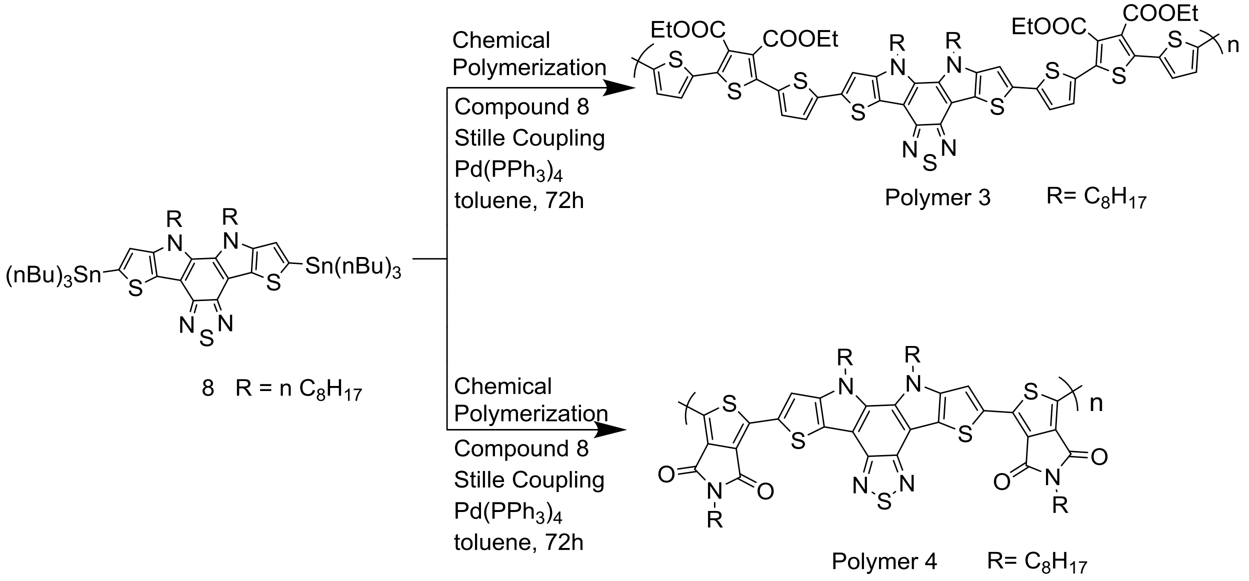
Scheme 12: Synthesis of Distannyldithienopyrrolobenzothiadiazole (**8**)

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 13).



Scheme 13: Synthesis of1, 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 (**14**) 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 **13** and compound **14**were carried out under standard stille coupling conditions. The obtained polymers, **DETTDC-DTPBTD Polymer 3**and **BTD-DTPBTD Polymer 4**were well characterized by ^{1}H NMR, GPC, UV-Vis and fluorescence spectroscopy and cyclic voltammetry analysis



Scheme 13: Synthesis of DTPBT-based conjugated polymers **Polymer 3** and **Polymer 4** by Stille coupling reaction

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-voltammetry. The properties of the synthesized polymers are summarized in Table 2 and Table 3. All the polymers showed good thermal stabilities and good film forming properties. The synthesized polymers **Polymer 3 and Polymer 4** possessed small band gap, 2.1 eV and 1.9 eV respectively.

Table 2 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

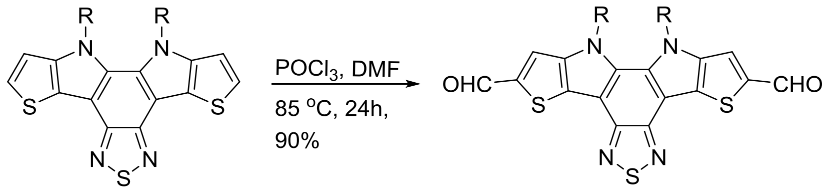
Polymers	λ_{max}(abs) (nm)	λ_{max}(em) (nm)	Stokes Shift (nm)	Stokes shift (eV)	Mw (KDa)	Mn (KDa)	PDI	Td
Polymer 3	430	543 501	113	0.58	20.65	9.44	2.18	220
Polymer 4	369	479 451	110	0.75	9.60	4.92	1.9	208

Table 3 Electrochemical properties of synthesized polymers; a potential v/s Ag/Ag+; calculated from equation $E_{HOMO/LUMO} = -(E_{oxi/red,onset} + 4.8 - E_{Fc/Fc+})$; calculated from equation $E_{LUMO} = E_{HOMO} + Eg_{opt}$.

Polymers	E_{oxid}(V)	E_{HOMO} (eV)	E_{LUMO} (eV)	$E_{band\ gap}^{opt}$ (eV)
Polymer 3	1.17	-5.57	-3.47	2.1
Polymer 4	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 BTD 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 Vilsmayer-Heck condition to yield diformyl dioctyl DTPBT (**16**) (Scheme 14).

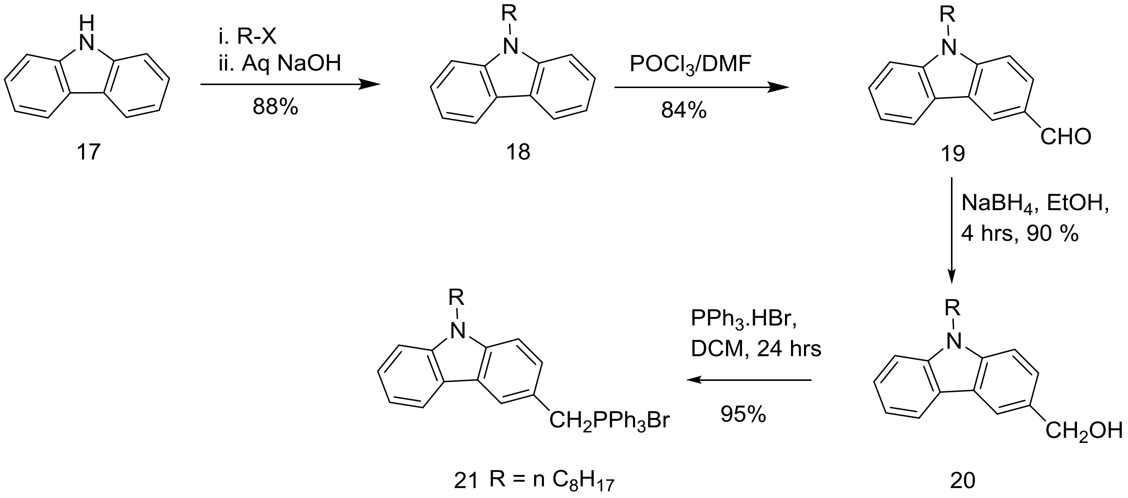


7

16 R = n C_8H_{17}

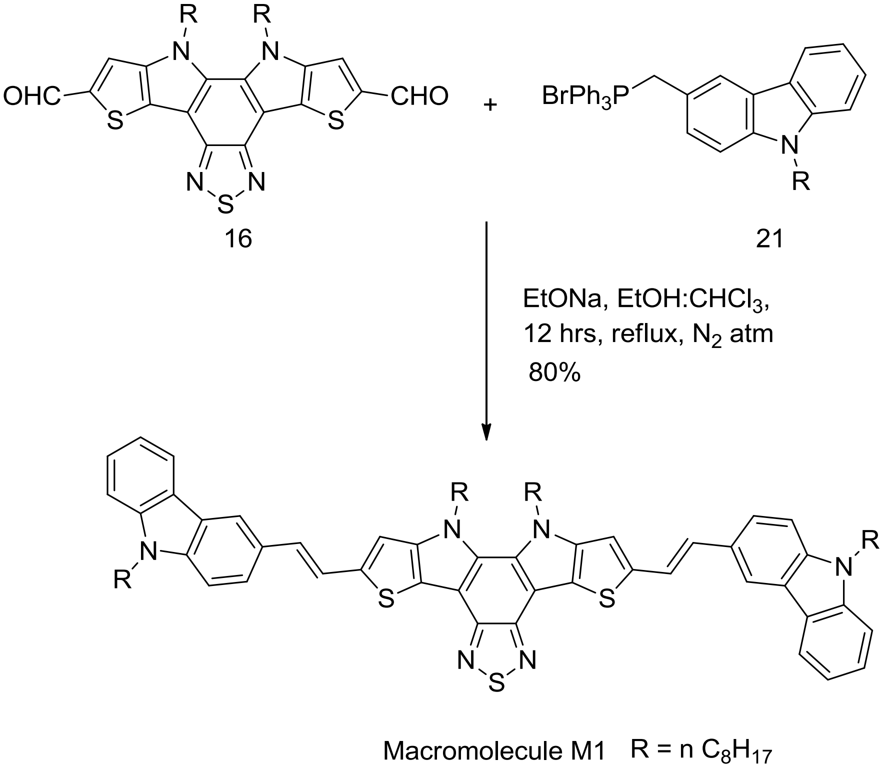
Scheme 14: Synthesis of diformyl DTPBT

Wittig salt of carbazole was synthesized from carbazole (**17**) in four steps by following the literature method (Scheme 15).[18]



Scheme 15: Synthesis of Wittig salt of carbazole (**21**)

Compound **16** was further treated with compound **21**in presence of sodium ethoxide to yield macromolecule (M1) (Scheme 16)



Scheme 16: Synthesis of Macromolecule (M1)

The synthesized macromolecule M1 was well characterized by ^{1}H 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.

Table 4 Photo-physical, electrochemical and DFT calculated properties of Macromolecule M1;

^{a}from absorption data; ^{b}from emission data; ^{c} Ag 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 $E_{LUMO} = Eg^{opt} + E_{HOMO}$ (eV).^{g} calculated optical band-gaps using equation $E_{optical} = 1240/\lambda onset$;

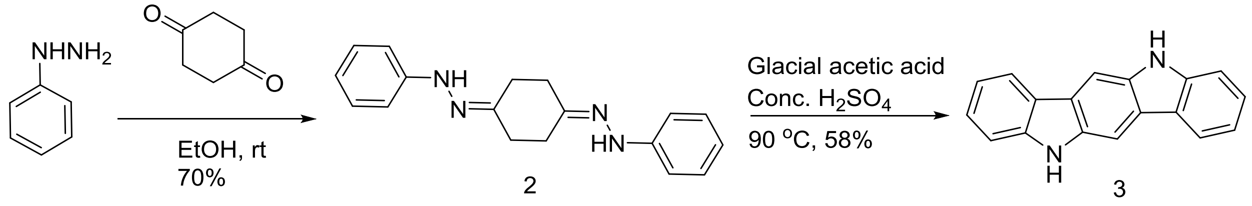
Compound	λ_{max}(abs) (nm)^{a}	λ_{max}(em) (nm)^{b}	Stokes Shift (nm)	Stokes shift (eV)	E $_{oxidation}^{c}$ (V)	E $_{HOMO}^{e}$ (eV)	E $_{LUMO}^{f}$ (eV)	E $_{band\ gap\ optg}$ (eV)
M1	504 437	614	110	0.43	1.48	-5.88	-3.78	2.1

Chapter 5: Indolocarbazole-Benzimidazole based Conjugated Molecules and Trisubsituted Phenyl-Oxazole based π-Conjugated Molecule: Synthesis, Characterization, Photophysical and DFT studies

Part a: Indolo[3,2-b]carbazole-Benzimidazole based conjugated molecules: Synthesis, Photophysical and Computational studies

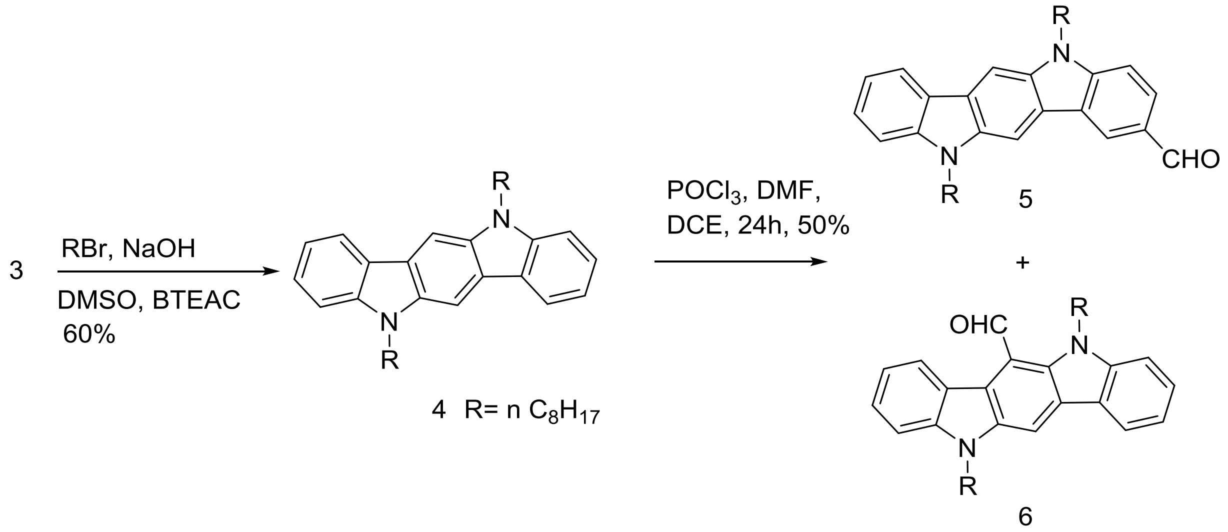
Indolo[3,2-b]carbazole (ICZ) have shown remarkable application in fields of medicinal, biological and material sciences. ICZ derivatives are known for their planar and rigid conjugated structures and due to this it shows remarkable photophysical properties. ICZ derivatives could serve as an excellent 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 we wish to report two new dialkyl ICZ-benzimidazole derivatives, 2-(1H-benzo[d]imidazol-2-yl)-5,11-dioctyl-5,11-Indolo[3,2-b]carbazole (2-BIDICZ) and 6-(1H-benzo[d]imidazol-2-yl)-5,11-dioctyl-5,11-Indolo[3,2-b]carbazole (6-BIDICZ).ICZ (**3**) moiety was synthesized by following reported procedure (Scheme 17).[22]

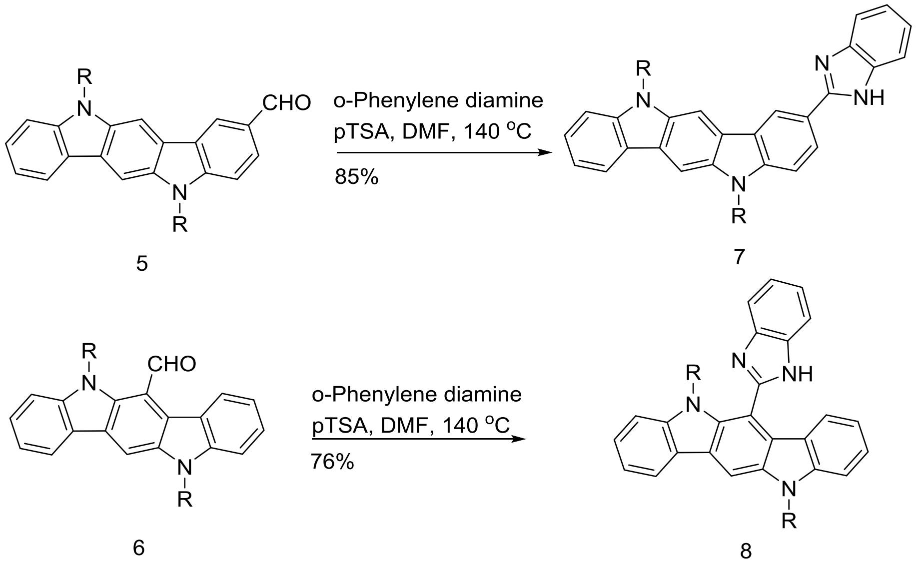


Scheme 17: Synthesis of indolo[3,2-b]carbazole (ICZ)

ICZ was further alkylated with octyl bromide in presence of NaOH. Formylation of alkylated ICZ were carried out by following Vilsmeier-Haack conditions to achieve 5,11-dioctyl-5,11-dihydroindolo[3,2-b]carbazole-2-carbaldehyde (**ICZ-2-aldehyde**) and 5,11-dioctyl-5,11-dihydroindolo[3,2-b]carbazole-6-carbaldehyde (**ICZ-6-aldehyde**) (Scheme 18). The ICZ aldehydes were reacted with ortho phenyl diamine in dry DMF in presence of pTSA at elevated temperature to yield corresponding substituted benzimidazole (Scheme 19).



Scheme 18: Synthesis of ICZ-2-aldehyde andICZ-6-aldehyde

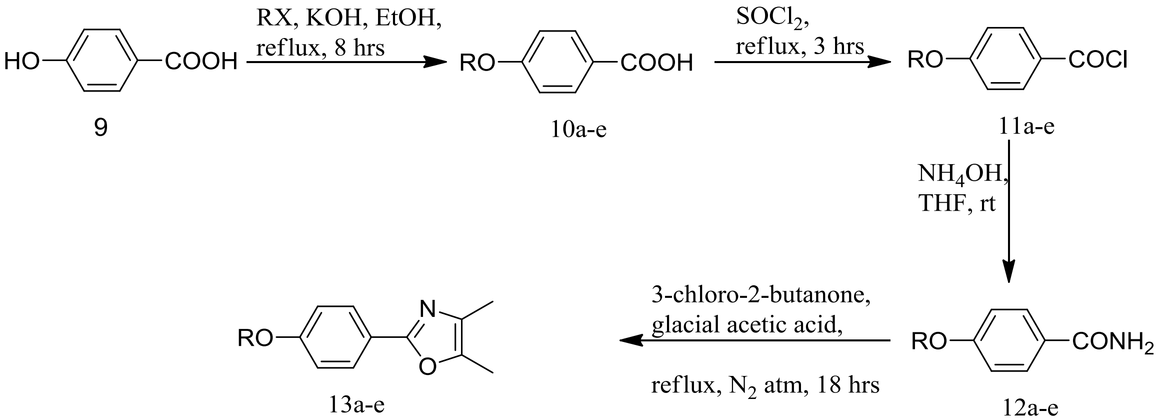


Scheme 19: Synthesis of 2-BIDICZ and 6-BIDICZ

The structures of these two compounds were fully characterized by NMR (^{1}H 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, 2-BIDICZ and 6-BIDICZ were showed remarkable sensitivity towards acid (TFA). Density Functional Theory (DFT) studies showed that 6-BIDICZ is more planar compared to 2-BIDICZ, 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 trisubsituted oxazole derivatives. A simple and practical synthetic methodology was used to achieve the desired molecules.

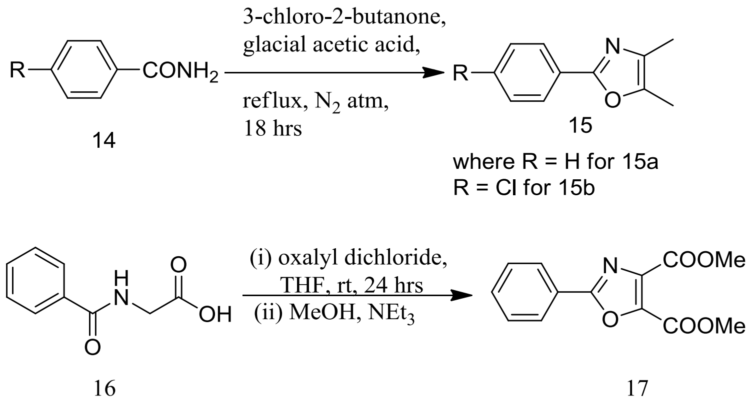


Where R= n-C_3H_7 for 13a, R = n-C_4H_9 for 13b,
R = n-C_6H_{13} for 13c, R = n-C_7H_{15} for 13d &
R = n-C_8H_{17} for 13e

Scheme 20: Synthesis of 2-(4-alkyloxyphenyl)-4,5-dimethyloxazole derivatives[23]

The molecular structures for 2- (4-butyloxyphenyl)-4, 5-dimethyloxazole (**13b**) and 4,5-dimethyl-2-(4-(octyloxy)phenyl)oxazole (**13e**) 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 (Cg), 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.



where R = H for 15a
R = Cl for 15b

Scheme 21 Synthesis of 2-phenyl-4,5-dimethyloxazole (**15a**), 2-(4-chlorophenyl)-4,5-dimethyloxazole (**15b**) and dimethyl-2-phenyloxazole-4,5-dicarboxylate (**17**)[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 (**17**) was also prepared by treating N-benzoyl glycine (**16**) with oxalyl dichloride in dry THF under N_2 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-alkyloxyphenyl)-4, 5-dimethyloxazole derivatives, negative charge was concentrated over N-atom of oxazole ring and O-atom of ethereal linkage compared over the rest of molecule. Subsitution of chloro group showed little effects on charge distribution pattern. In dimethyl 2-phenyloxazole-4, 5-dicarboxylate (**17**) 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 **13b** and compound **13e** 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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