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SYNTHESIS OF SOME FLUORENE-THIOPHENE COPOLYMERS

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SYNTHESIS OF SOME FLUORENE-THIOPHENE COPOLYMERS

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JULY 12, 2007

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List of abbreviation

HOMO: Highest occupied molecular orbital

LUMO: Lowest unoccupied molecular orbital

DMF: Dimethyl formamide

NBS: N-Bromosuccinamide

TEAOH: Tetraethylammonium hydroxide

DME: Dimethoxy ethane

HAc: Acetic acid

THF: Tetrahydrofuran

LED: Light emitting diodes

Mn: Number average molecular weight.

Mw: weight average molecular weight.

SEC: Size exclusion chromatography.

1 INTRODUCTION

A polymer is a substance composed of molecules with large molecular mass consisting of repeating units connected by covalent chemical bonds. In some cases the repetition unit is linear. In other cases the chains are branched or interconnected to form three-dimensional net works. The small molecules that combine with each other to form polymer molecules are termed as monomers. Polymers can be both synthetic and natural.

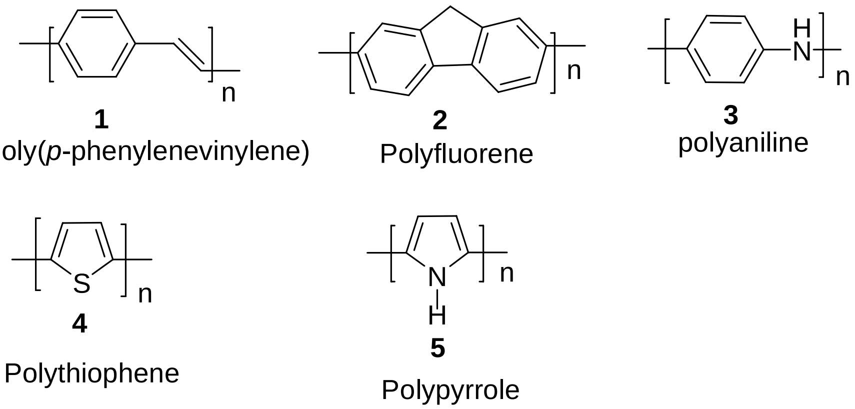
The history of natural polymer dates with the beginning of time in the natural world and natural polymers have been used by man starting from the prehistoric times. Among the natural polymers are wood, cellulose, natural rubber and so forth.

The development of synthetic polymer stared in the 20th century. In 1907, Leo Baekeland created the first completely synthetic polymer, Bakelite, by reacting phenol and formaldehyde at precisely controlled temperature and pressure. Subsequent work by Wallace Carothers in the 1920s demonstrated that polymers could be synthesized rationally from their constituent monomers. Synthetic polymers today find application in nearly every industry and area of life. Polymers are widely used as adhesives and lubricants, as well as structural components for products ranging from children's toys to aircrafts. Among polymeric materials that are widely used today are polyethylene, polyvinylchloride, polystyrene, nylon, polymethylmetaacrylate.[1] Originally, it was believed that all polymers were non-conductors hence synthetic polymers were extensively used by the electronic industry for their insulating properties. But in 1977, polyacetylene could be made to conduct electricity when exposed to iodine vapor and this opened a new era of polymer science[2].

MacDiarmid, a professor of chemistry at the University of Pennsylvania and co-discoverer of the field of conducting polymers, more commonly known as "synthetic metals", was the chemist responsible in 1977 for the chemical and electrochemical doping of poly acetylene. It was found that a thin film of poly acetylene could be oxidized with iodine vapor, increasing its electrical conductivity a billion times. Poly acetylene is a semiconductor on its own, but when the polymer is doped its conductivity is increased. The doping of poly acetylene by oxidation with a halogen (e.g., iodine) is called p-doping. On the other hand, doping by reduction with and alkali metal (e.g., sodium) is called n-doping.

Recently, conducting polymers are used for the manufacture of electronic device such as light emitting diodes, photovoltaic cells, sensors, electronic coatings, actuators (artificial muscles), electromagnetic shields, batteries, non-linear optical devices, high quality self emissive displays and similar devices which are applicable on numerous kinds of portable and stationary utensils. [2] For polymeric materials to conduct electricity the band gap (the energy difference between the highest occupied molecular orbital and the lowest unoccupied molecular orbital) must be low. One way to achieve low band gaps in conjugated polymers is to create an alternating arrangement of aromatic and quinoid units along the polymer chain there by reducing the bond length alteration.[3] The second major factor which affects the band gap of conducting polymer is the effective conjugation length. The effective conjugation length which is dependent up on the torsion angle between the repeating units along the polymer back bone can be controlled by choosing sterically hindered units along the polymer back bone or by introducing bulky side chains to twist the unit out of plane.[4] Band gap can also be controlled by incorporating electron withdrawing and donating groups in the main polymeric chains. Thus, by modifying one of these properties polymers with controlled band gaps and thus, specific electrical properties can be synthesized.

Polyacetylene, the first conjugated conducting polymer synthesized, has certain limitations such as improcessability and instability toward air oxidation in the doped state. As a result the research in conducting polymers focuses on aromatic polymers such as poly(*p*-phenylenevinylenes) (**1**), polyfluorenes (**2**), polyanilines (**3**), polythiophenes (**4**) and polypyrroles (**5**) [1] (Fig. 1) and their copolymers. These aromatic polymeric materials are more stable than the non-aromatic polyacetylene.

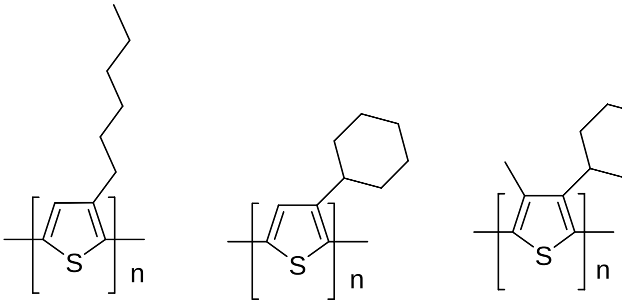


1 Poly(*p*-phenylenevinylene)
2 Polyfluorene
3 polyaniline
4 Polythiophene
5 Polypyrrole

Figure 1: Some aromatic conjugated polymers.

Polythiophene can be synthesized by electrochemical and chemical oxidation reactions as well as by processes involving chemical coupling reactions.[5] It has been intensively studied for its good conductivity, thermal stability and ease of fuctionalization.[6] The latter property permits to overcome its intrinsic insolubility[7] by introducing alkyl chains at the 3-positon of the thiophene ring, thus providing soluble and processable materials. Moreover, the functionalization of the thiophene leads to a new material, which combines the typical physical property of the poly conjugated backbone with those of the inserted functional groups.

Besides increasing the solubility compared to unsubstituted polythiophene, the addition of different bulky side chains can be utilized to control the optical property of the polymer. As shown in Figure 2, the solvating side chains in three substituted polythiophenes affect the color of the light emitted by the polymers.[1]



6 Red
7 Green
8 Blue

Figure 2: Polythiophenes with solvating side chains which tune the color of emission.

Polyfluorene-based materials have been investigated extensively because of the many attractive properties they possess, as active components of organic light emitting diodes [8, 9] and because of their thermal and chemical stability .[9] Polyfluorene-based materials can emit color across the entire visible range, possess high thermal stability, and can easily be functionalized at the methylene bridge for fine tuning of emissive properties. The polyfluorene backbone provides planarity; side groups at C-9 can give polymer processablity and solubility.[9] These characteristics make polyflorene homo- and co-polymers attractive components for luminescent materials in organic light emitting diodes. Clearly, polyfluorenes are seen as one of the most promising classes of electroluminescent polymers; however, as in the case of all polymer-based light emitting diodes, the problem of stability remains and hinders their industrial applications.

The first reported polyfluorenes were prepared by an oxidative coupling reaction using $FeCl_3$, which is prone to produce partially and irregularly cross-linked material (i.e., polyfluorens linked at positions other than 2 and 7). But recently highly conjugated polyfluorenes could be synthesized by coupling reactions such as those of Yamamoto [10] Stille [11] and Suzuki.

The ability to functionalize polyfluorene at the methylene bridge without distorting the conjugation between monomer units has been utilized as a method to help control undesirable properties and improve thermal properties of the polymer along with processibility[12]. Copolymerization of fluorene monomer derivatives with different aromatic moieties allows for color tuning through the modification of the band gap. To extend the optical absorption to longer wavelengths, synthesis of alternating fluorene copolymers, which contain blocks of electron accepting and electron donating moieties along the polymer backbone, have been developed.[13] Copolymerization of fluorene with aryl partners allowed for structural control. In particular, pendant functionalization offers an attractive possibility of developing new materials that in addition to their intrinsic polymer electronic properties incorporate specific properties of the functionalities. [14]

Copolymers consisting of 9.9-substituted fluorenes and low band gap monomers such as **9**, **10**, **11**, **12** and **13**(Fig. 3) [15], have been synthesized.

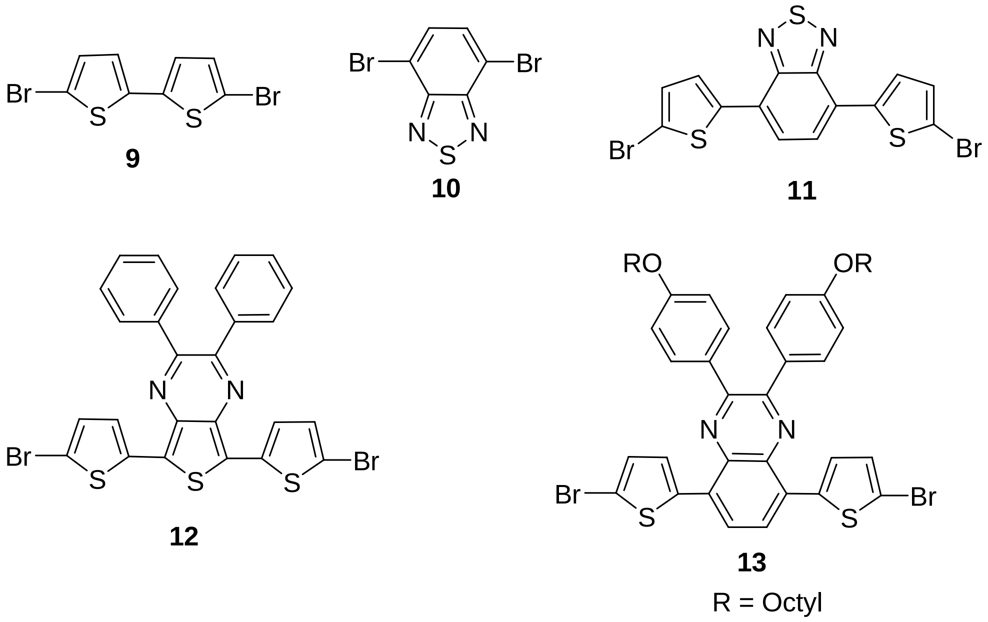


Fig. 3. Some low band gap co-monomers.

Thus, copolymerization can serve as a way of manipulating the electronic properties, specially the band gap, provided that the right kinds of monomers are used for the copolymerization. Consequently derivatizaition of the polymer chain with functionalized and straight chain pendant groups together with copolymerization are the most common ways of manipulating both electrical and physical properties of the polymeric materials.

2. LITRATURE REVIEW

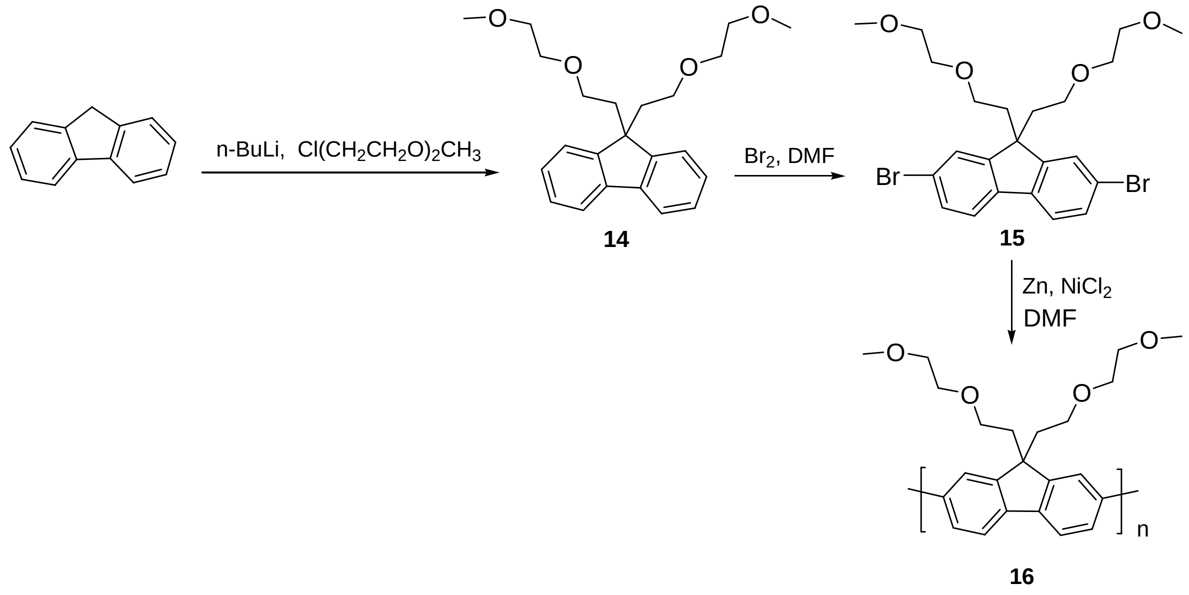
Low band gap conjugated polymers have attracted considerable interest in recent years to obtain intrinsically conducting materials.[16] Because low optical band gap conjugated polymers may improve the efficiency of organic photovoltaic devices by increasing the absorption in the visible and near infrared region of the solar spectrum, the synthesis of low band gap material is of interest for the development of plastic solar cells. This polymer solar cells are becoming attractive because they show potential advantage over silicon based solar cells.[17] The main limitation to their application are lower power conversion efficiency and instability compared to Silicon based solar cells, but their cost of production is low. Among parameters that help control the band gap of polymeric materials by modification of HOMO and LUMO level of a conjugated polymers as discussed some where in this paper are bond length alternation, inter-ring torsion angle [18] and incorporation of alternating electron donating and accepting substituents along the polymer backbone. [19]

In this regard, polyfluorene copolymers show attractive properties in the optoelectoronic devices such as light emitting diodes and field effect transistors. The high mobility, stability and high photoluminescence efficiency have made these classes of material suitable for use in light emitting devices[20]. The copolymerization approach that has been widely used in preparation of conducting polymers is of particular interest for fluorene-based polymers since the electronic properties of polyfluorene cannot easily be tuned by other conventional chemical methods of modification. High molecular weight copolymers consisting of 9,9-dialkylfluorene and various aromatic units like thiophene can be synthesized by using Suzuki coupling reactions. The resulting polymeric material is soluble in conventional organic solvent such as aromatic hydrocarbons, tetrahydrofuran and chlorinated hydrocarbons.

2.1 THE FLUORENE MONOMERIC SUB-UNIT

Fluorene belongs to a family of biphenyl methane derivatives. It exists as a white crystalline solid at room temperature and melts at 114-116 ^{o}C. Fluorene serve as a starting material for the synthesis of polyfluouenes and its derivatives like the 9,9-dialkylated polyfluorenes. Substituents at carbon atom 9 are usually incorporated to modify the polymer processablity.

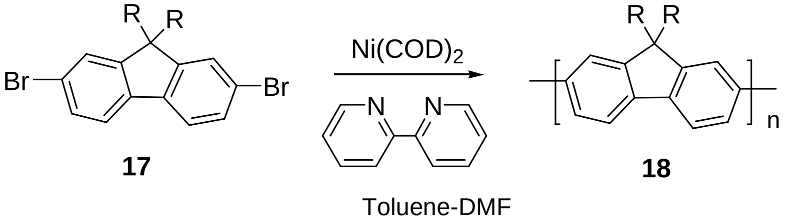
Synthesis of polyfluorene begins by functionalizing the benzylic carbon at the 9-position. For example, **16** was synthesized by Pei *et al.* starting from fluorene. Thus, lithiation of fluorene followed by treatment with 1-chloro-2-(2-methoxy ethoxy)-ethane at -40^{0}C yielded 9-(3,6-dioxaheptyl)fluorene (**14**). Bromination of **14** with molecular bromine in DMF followed by polymerization using zinc as the reductant and reactive nickel(0) as a catalyst, produced **16**.[21]



Scheme 1: Synthetic route to **16.**

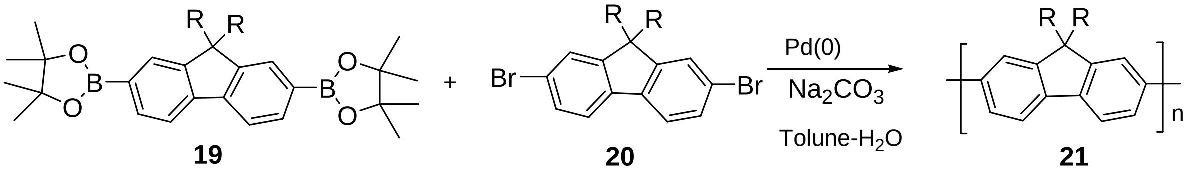
Before brominating compound **14**, one can easily conduct polymerization using 4:1 molar mixture of iron (III) chloride in chloroform [21], but complete removal of the residual iron from the polymer is difficult.

Many polyfluorene derivatives have been prepared by the nickel-mediated Yamamoto polymerization (Scheme 2) [22]



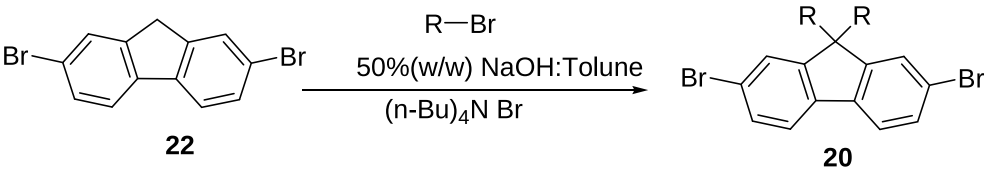
Scheme 2: Yamamoto polymerization.

One drawback to this procedure is that polymers with a degree of polymerization greater than 50 are difficult to obtain due to low solubility in the highly polar aprotic reaction medium[23]. A superior method is the Suzuki reaction, which is based on the palladium-catalyzed reaction of mixed phenylboronic acid and aryl bromides to give biphenyls[24]. The polymerization method has been modified such that polymers with molecular weights ranging from 10,000 to 50,000 Da are prepared in high yield with good quality. Both Yamamoto and Suzuki polymerization have been used to synthesize a variety of 9,9-substituted polyfluorenes with various physical and electrical properties.



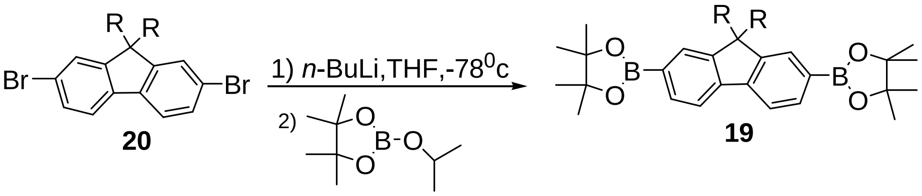
Scheme 3: Suzuki coupling of 9,9-substituted fluorenes.

2,7-Dibromo-9,9-dialkylfluorene (**20**) is prepared by phase transfer catalysis reaction which involves the use of two phase system composed of equal volumes of toluene and 50% (W/W) aqueous NaOH, and tetrabutylammonium bromide as a phase transfer catalyst (Scheme 4). The advantage of this reaction is that it can be implemented on 2,7-dihalogenated fluorene, and eliminates the risk of halogenating the side chain or functional group of the side chain.



Scheme 4: Synthesis of 9,9-dialkylfluorene using phase transfer catalysis.

The other intermediate for the Suzuki coupling reaction shown in Scheme 3 is the borolane **19**, which is prepared from 2,7-dibromo-9,9-dialkylfluorene (**22**) by using a strong base like *n*-BuLi for the formation of aryl lithium through lithium bromine exchange. Subsequent treatment of the lithiated species with 2-isopropoxy-4”,4”,5”,5”-tetramety1-1, 3,2-dioxaborolane gives the borolane **19**. (Scheme 5)

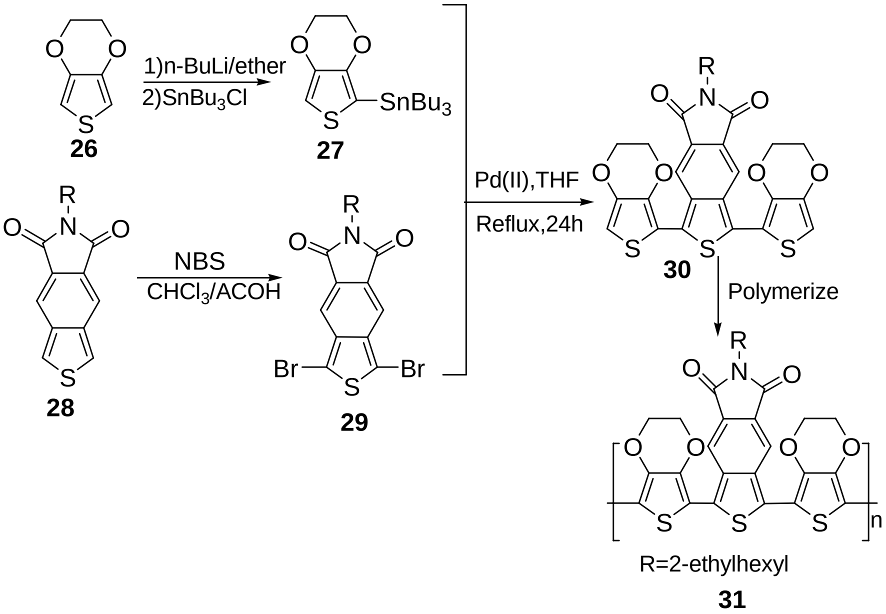


Scheme 5: Synthetic route towards borolane **19.**

2.2 THE THIOPHENE MONOMERIC SUBUNITS

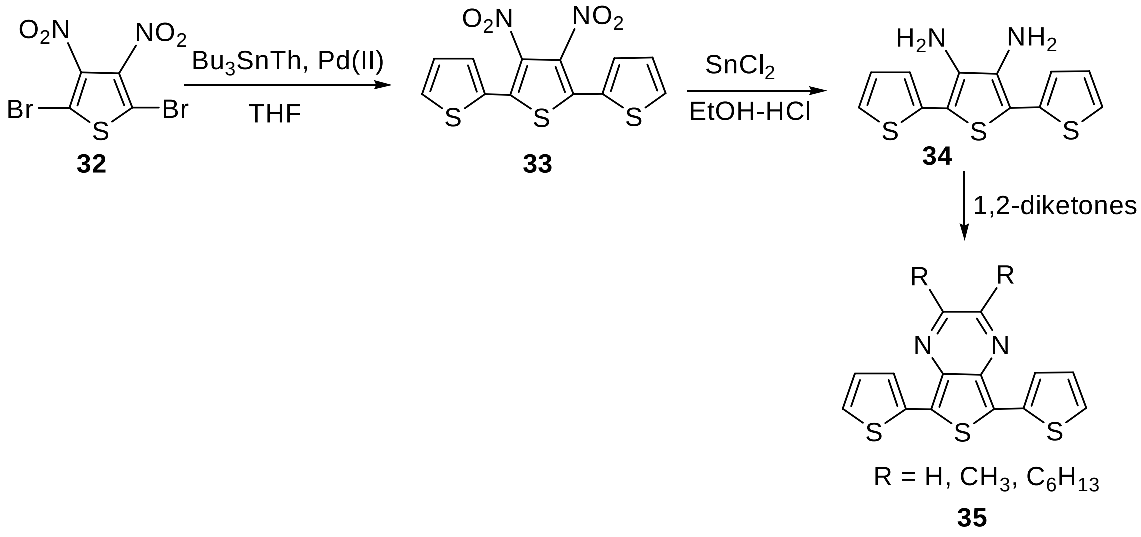
Thiophene is a heterocyclic five-membered unsaturated aromatic compound that contains sulfur in its rings. Its polymer, polythiophene, results from the polymerization of thiophene, a sulfur heterocycle that can become conducting when electrons are added or removed from the conjugated π -orbital via doping. A variety of reagents have been used to dope polythiophenes. Iodine and bromine produce high conductivities but are unstable and slowly evaporate from the material. Organic acids such as trifluoroacetic acid, propinoic acid and sulfonic acids produce polythiophenes with lower conductivities than iodine, but with higher environmental stabilities. Unsubstituted polythiophenes are conductive after doping, and have excellent environmental stability compared with some other conducting polymers such as polyacetylene, but are intractable and are soluble only in solutions like mixtures of arsenic trichloride and arsenic pentafluoride. But up on attaching alkyl substituents at 3- and 4 positions, polythiophenes that are soluble in common organic solvents can be synthesized. The introduction of flexible side chains on to the backbone improves the solubility and processability allowing a more complete characterization of the material [25]. Also such introduction modifies the electronic properties of the polymer enlarging the possibilities for industrial applications [25] Polythiophenes with substituents other than alkyl groups have also been investigated by Xiao *et al.*, among which those with electron donating alkoxy groups have displayed promising electrical and optical properties. Incorporation of an alkoxy group at the 3-postion of the thiophene ring yields polymers with optical absorption maximum at 475-530 nm, higher or comparable with those of poly-3-alkyl thiophenes [25]. This can be attributed to both the electron donating effect of the alkoxy group and the more coplanar conformation of poly(3-alkoxythiophene) as compared to that of poly(3-alkyl thiophene).

The recent trend in the synthesis of thiophene-based polymers starts with the preparation of terthiophene and its derivatives. In this regard Sonomez *et al.* [18] synthesized poly-1,3-bis(2’(3’-ethylenedioxy)thienyl)-benzothiophene–N-2”-ethylhexyl-4,5-dicarboximide (**31**) starting from ethylenedioxythiophene (**26**) as depicted in Scheme 6.



Scheme 6: Synthetic route toward polymer **31**.

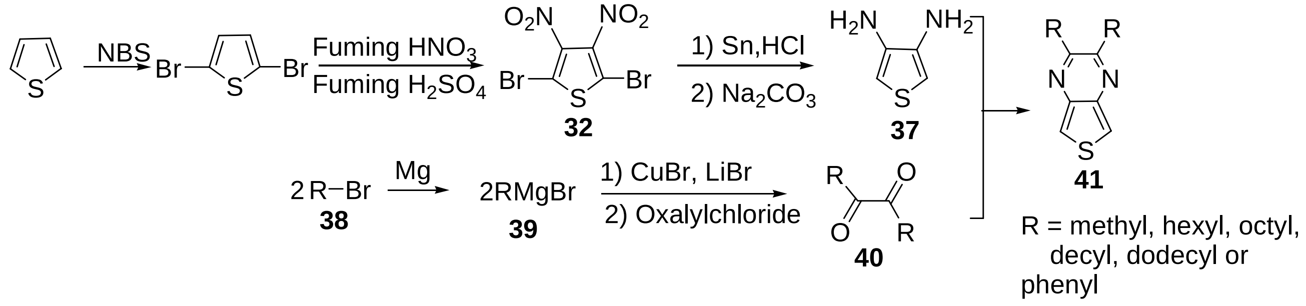
The presence of an acceptor units, the benzothiophen–N-2’-ethylhexyl-4,
5-dicarboximide between two 3,4-ethylenedioxythiophene donor units was intended to decrease the LUMO and increase the HOMO energy levels, resulting in a low band gap.
The synthesis of monomer **35,** as described by Yamashita *et al.*, begins with the Stille coupling reaction of 2,5-dibromo-3,4-dinitrothiophene with tributyl (thien-2-y1) stannane in the presence of catalytic bis(triphenylphosphine)palladium(II) dichloride gave the dinitro compound **33**.[26] Reduction of the dinitro compound **33** in to diamine **34** took place with $SnCl_2$ in ethanol-HCl. Condensation of the intermediate compound **34** with 1,2 –diketones yielded compounds **35** as depicted in Scheme 7.



Scheme 7: Synthetic route toward monomer **35**.

As described by Yamashita *et al.*, reduction of the dinitro compound can also be effected using iron powder in an acetic acid

Thieno-(3,4-b)-pyrazines (**41**) were shown to be excellent precursors for the production of low band gap conjugated polymers. These compounds can be synthesized starting from thiophene as described by Rasmussen *et al.* (Scheme 8). [27] α-Diones **40**, could be obtained by treating the Grignard reagent **39** with oxalylchloride. Finally, condensation of 3,4-diaminothiopene **37** with the α- diones **40** readily occurred at room temperature in an ethanol solution (Scheme 8).

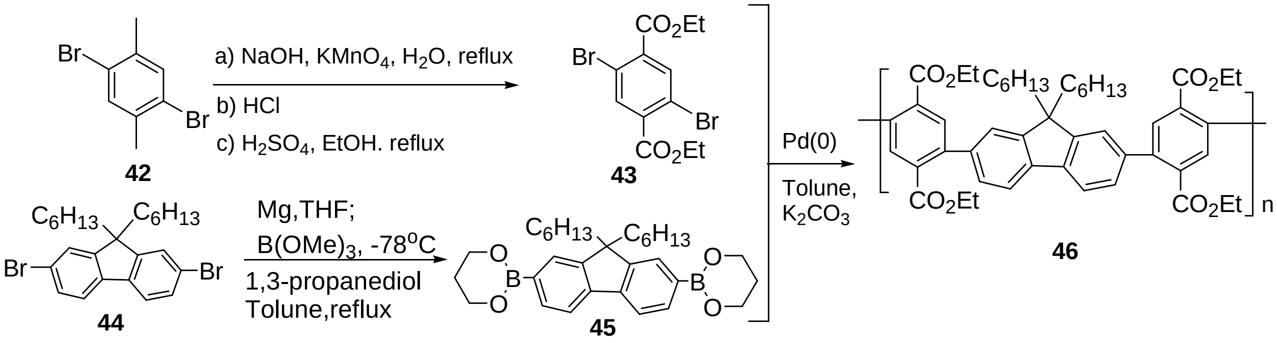


Scheme 8: Synthesis of thieno-[3,4-b]-pyrazines.

2.3 SYNTHESIS OE CONJUGATED POLYFLUORENE COPOLYMERS

Co-polymers consist of chains with two or more linkages usually implying two or more different types of monomer units. Copolymerization of fluorene and donor-acceptor groups in to the polymer chains is suggested to give promising materials for photo diodes and solar cells.[28] This approach may also enable materials with optical absorption below the high band gap of polyfluorene, essential for photo diodes capable of absorbing a large fraction of solar spectrum, and therefore suitable for solar cells. In particular, pendant fuctionalization of polyfluorene offers an attractive possibility of developing new materials that, in addition to their intrinsic polymer electronic properties, incorporate specific properties of the functionalities[14]. The copolymerization approach that has been

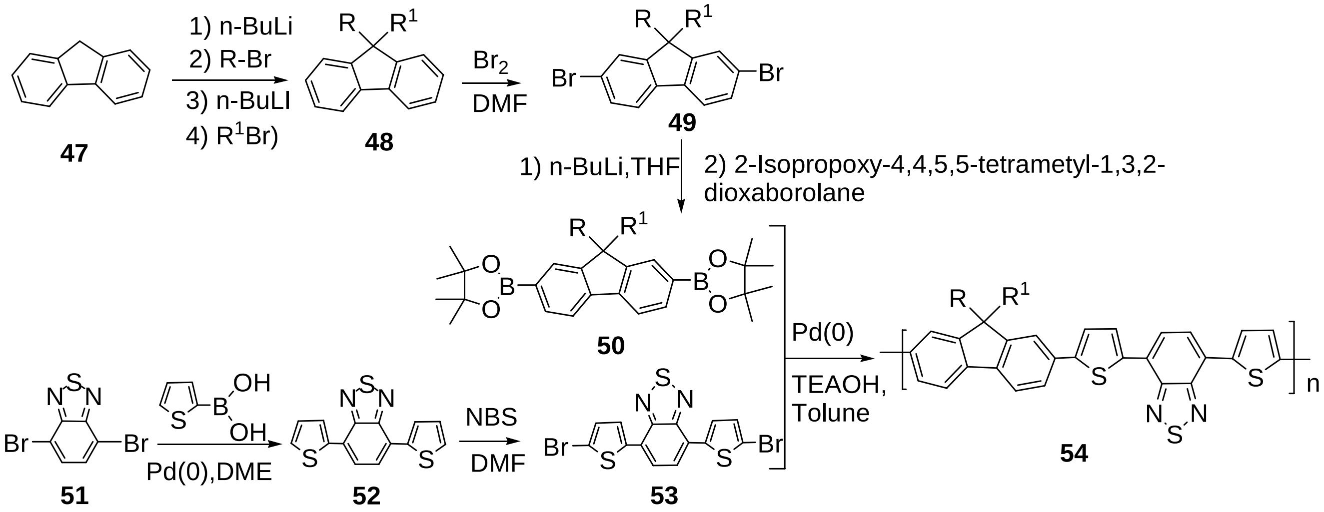
widely used in the preparation of traditional polymers, is of particular interest for fluorene-based polymers, since the electronic properties of polyfluorene are not easy to be tuned by conventional chemical modification.[14] In this regard, the copolymer of phenylene-fluorene that enabled the tunabliity of HOMO and LUMO energy levels in the range of 0.4-0.5 eV while the blue light emission was maintained were synthesized as depicted in Scheme 9.



Scheme 9: Synthetic route towards polymer **46**.

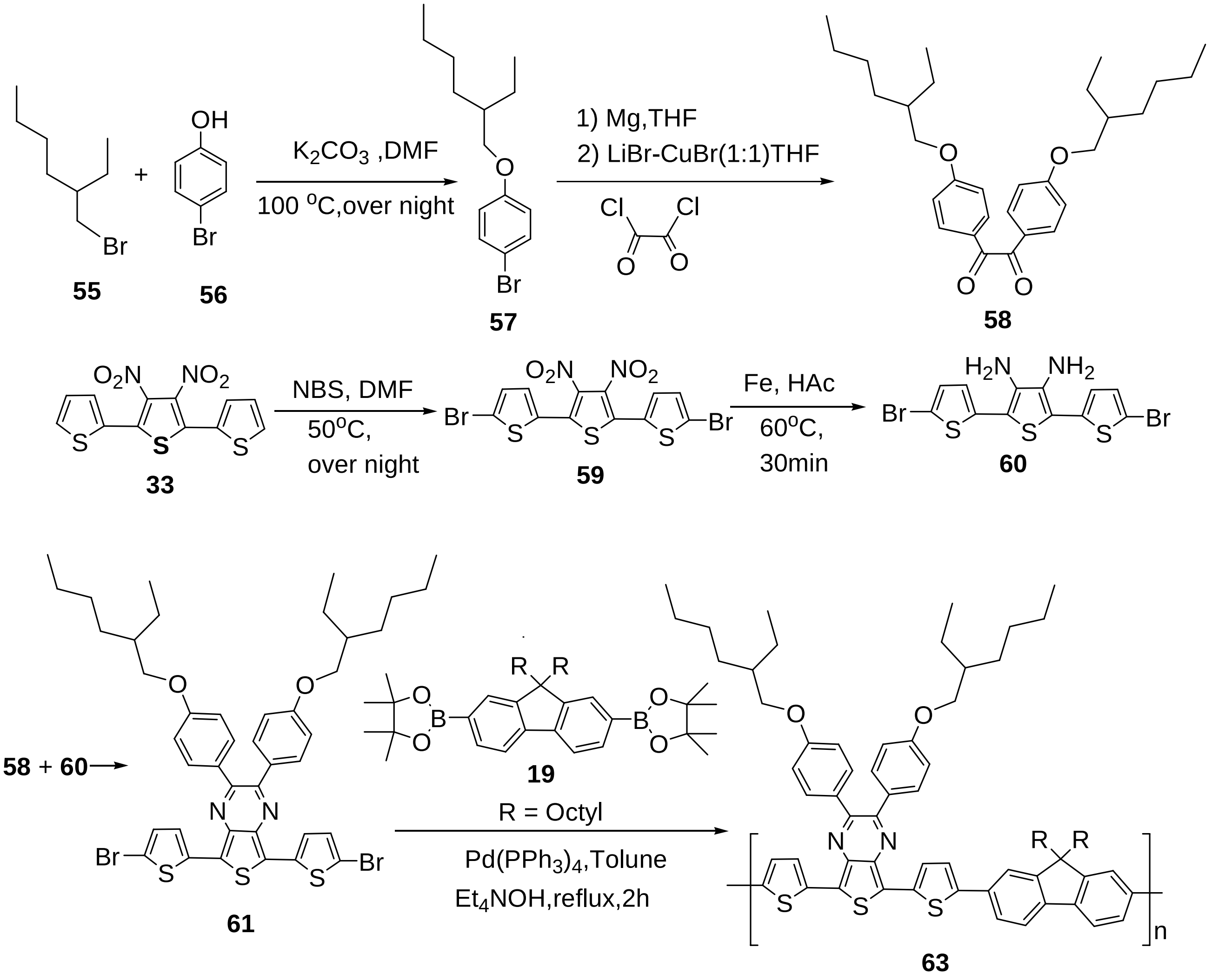
Alternating conjugated copolymers are most often prepared via transition metal catalyzed polycondensations. Recently the Suzuki poly condensation is used for the synthesis of copolymers in preference to the Stille coupling reactions. The Suzuki route is potentially more versatile than the Stille reaction because the reaction tolerates a large number of functional groups and boronic acid derivatives are easier to handle [16].

According to Inganas *et al.,* the purpose of copolymers of fluorene and thiophene-benzothiazole-thiophene structures has been to generate optical absorption at lower energies by reducing the band gap of the homo polymer polyfluorene. [16] The homo polymer will have absorption mainly in the UV and blue part of the visible spectrum, and therefore has particularly poor match to the solar spectrum. It is therefore necessary to include absorption at the green and red or near IR part of the spectrum. Accordingly, the synthesis of copolymers of fluorene and thiophene-benzothiazole- thiophene units was reported (Scheme 10). [16] The polymerization was carried out using the Suzuki coupling reaction with $(PPh_3)_4Pd(0)$ as a catalyst and Et_4NOH as a base (Scheme10).



Scheme10: Synthetic route towards polymer **54**.

Another alternating polyfluorene copolymer that absorbs near IR having high molecular weight and low band gap was reported by Zhang *et al.* [29]. The synthesis of this polymer is depicted in Scheme 11.



Scheme 11: Synthesis of polymer **63**.

3. OBJECTIVES OF THE PROJECT

The aim of this MSc project work is to synthesize some polyfluorene copolymers with terthiophene donor-acceptor-donor sub-units. It involves the synthesis of fluorenes with different 9,9-dialkyl substituents, the synthesis of terthiophenes with donor-acceptor-donor substituents, and co-polymerization of the 9,9-dialkyl fluorenes with functionalized terthiophenes by Suzuki-type polymerization reaction using palladium(0) as catalyst. The intermediate compounds and the polymers will be characterized by spectroscopic means, including NMR, FT-IR and UV-VIS. The physical properties of the polymers will be studied for possible applications as LEDs and other high technology devices.

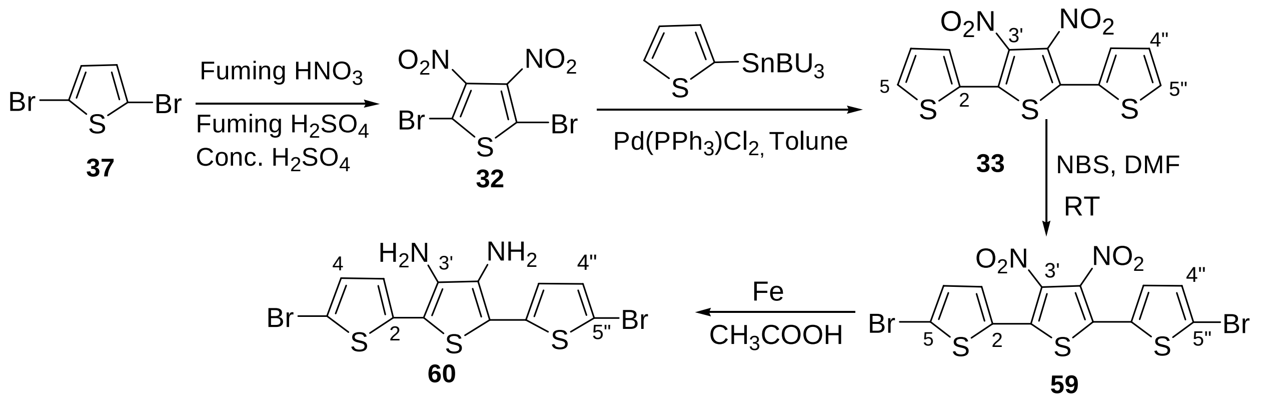
4. RESULTS AND DISCUSSION

In the course of this work, four copolymers based on substituted fluorene and terthiophene derivatives were synthesized using modified Suzuki coupling polymerization reactions. These were, poly-2, 7-(9,9-dioctylfluorene-*alt*-5,5-(5,7-bis 2-thiophene)-2,3-bis-(4-octyloxy-phenyl thieno-(3,4-b)- pyrazine (**84**), poly-2,7-(9,9-dioctylfluorene-*alt*-5,5-(3,4 –di (2-hexyloxy benzlidene imino)-2,2': 5,2"-terthiophene (**85**), poly-2,7-(9,9-dietylhexyllfluorene-*alt*-5,5-(3,4–di(2-hexyloxy benzlidene imino)-2,2': 5,2"-tertthiophene (**86**) and poly-2,7-(9,9-dioctylfluorene-5,5-(5,7-bis-2-thiophen)-2,3-bis-(4-octyloxy-phenylthieno(3,4-b)pyrazine-*ran*-2,7-(9,9-dioctylfluorene-5,5-bis(2"-thienyl)-4,4-dipentyl-2,2'-bithazole-5",5"-diyl (**87**). The syntheses started first by the preparation of the required monomers for the co polymerization reaction as indicated in Schemes13, 14 and 16.

4.1 Syntheses of Thiophene-based Monomers

4.1.1 Synthesis of 5,7-bis-(5-bromo-thiophen-2-yl)-2,3-bis-(4-octyloxy-phenyl)-thieno(3,4-b)pyrazine (66)

The synthesis of 5,7-bis-(5-bromothiophen-2-yl)-2,3-bis-(4-octyloxyphenyl)-thieno-(3,4-b)-pyrazine began by nitrating 2,5-dibromothiophene (**37**). Thus, treatment of 2,5-dibromothiophene (**37)** with a mixture of conc. H_2SO_4, fuming H_2SO_4 and fuming HNO_3 gave 2,5-dibromo-3,4-dinitrothiophene (**32**) in 95.5 % yield. Compound **32** was used for Stille coupling reaction with tributyl(thiophen-2-y1)stannane in the presence of palladium(II)dichloride to give2,5-dithiophen-3,4-dinitrothiophene (**33**) in 72.3%, which in turn was brominated using NBS in DMF at RT to provide 5,5"-dibromo-3',4'-dinitro-2,2':5',2"-terthiophene(**59**) in 84.6% yield (Scheme 12). Compound **59** was further reduced with iron and acetic acid to afford diamine (**60).** The above compounds (**33**, **59** and **60**) were characterized based on their spectroscopic behaviors as discussed below.



Scheme 12: Synthesis of 5,5"-dibromo-3',4'-diamino-2,2':5',2"-terthiophene (**60**).

The ^{1}H-NMR spectrum of compound **33** showed three signals in the in the aromatic region. A two hydrogen doublet of doublet centered at δ 7.63 with *J* = 5.2 and 1.2 Hz is due to H-5 and H-5”, which are equivalent and couple with H-4 and H-3. Another two-proton doublet of doublet at δ 7.56 (*J* = 3.6 and 1.2 Hz) is due to H-3 and H-3”, which are equivalent and couple with H-4 and H-5. The remaining doublet of doublet at δ 7.2 (*J* = 5.2, 3.6 Hz), which integrates for two hydrogens, is due to H-4 and H-4”,which are equivalent and couple with H-5 and H-3 (Table 1).

The ^{13} C-NMR and DEPT-135 spectra of compound **33** signify six carbon signals, of which the signals at δ 136.0, δ 133.9 and δ 128.1 are quaternary and belong to C-2’, C-3’and C-2, respectively. The remaining three signals due to methine groups of the thiophene moiety appeared at δ 131.2, 131.1 and 128.4and can be accounted for C-4, C-5 and C-3, respectively.

The ^{1}H-NMR spectrum of compound **59** indicated only two signals in the aromatic region of the spectrum. The two-proton doublet (*J* = 4 Hz) is assignable to H-4 and H-4”. The remaining two-proton doublet (*J* = 4 Hz) is due to H-3 and H-3”. The FT-IR spectrum of compound **59** shows aromatic C-H stretch at 3097 cm^{-1}, over tone combination region at 1700 cm^{-1}, 1696 cm^{-1}, 1685 cm^{-1}, and 1653 cm^{-1}, asymmetric $\mathrm{N}\overset{\text{—}}{\text{- - -}}\mathrm{O}$ stretch at 1543 cm^{-1}, symmetric$\mathrm{N}\overset{\text{—}}{\text{- - -}}\mathrm{O}$ stretch at 1386 cm^{-1}, C-N stretch at 797 cm^{-1}, out of plane ring vibration

at 476 cm^{-1}, out of plane-C-H bend at 755 cm^{-1}, C=C ring stretch at 1559, 1415, 1386 cm^{-1}. The FT-IR data along with ^{1}H-NMR data agree with the structure of compound **59**.

The ^{1}H-NMR spectrum of compound **60** showed that there are a total of three signals in the spectrum, two of which in the aromatic region and the remaining one in the aliphatic region of the spectrum. The two-hydrogen doublet at δ 7.05 (J = 6 Hz) is due to H-4 and H-4”. The other doublet signal at δ 6.86 (J = 6 Hz) is assignable to H-3 and H-3”. The broad four-proton singlet which appeared at δ3.7 is due to the two equivalent amine protons (Table 1). The^{13}C-NMR and DEPT-135 spectrum of compound **60** displayed that there are six signals, of which, four are quaternary and two are methine carbon signals. The quaternary carbon signals that appeared at δ 137.21, 133.95, 110.89 and 109.8 are attributable to C-2, C-2’, C-3’, and C-5, respectively, and the remaining two-carbon signals at δ 130.54 and 124.46 are due to C-4 and C-3, respectively. The data from ^{1}H-NMR, ^{13} C-NMR and DEPT-135 agree with the structure of compound **60** (Table 2).

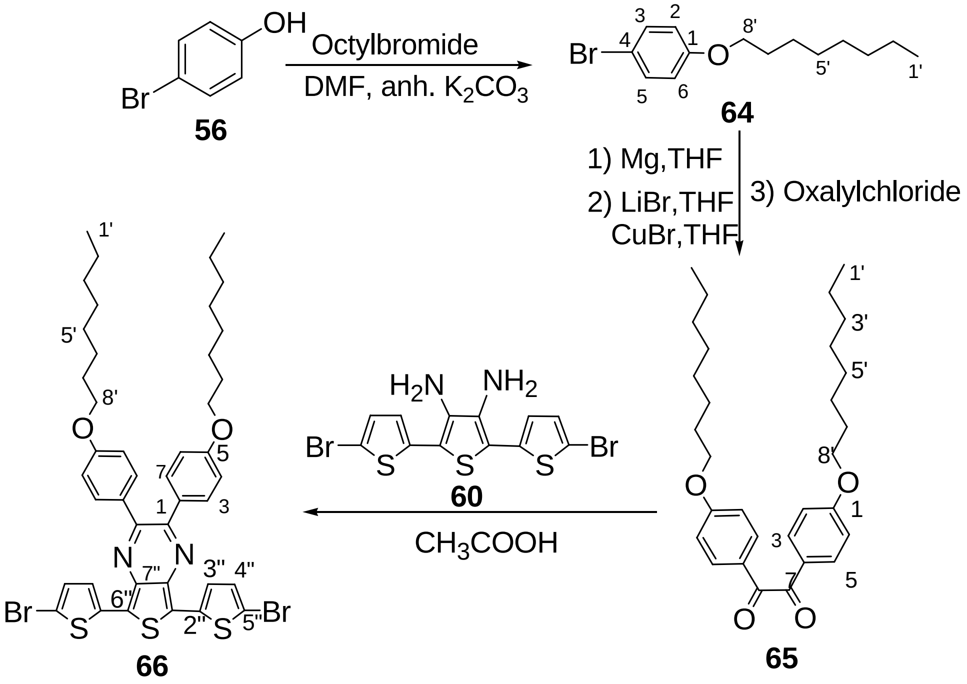
Table1.^{1}H-NMR (400.13, $CDCl_3$) data (δppm) of compounds **33, 59** and **60.**

33	**59**	**60**
7.63 (*dd* ,*J* = 5.2, 1.2 Hz, 2H, H-5, H-5”)	7.35 (*d*, *J* = 4 Hz, 1H, H-4, H-4”)	7.05 (*d* ,*J* = 6 Hz, 2H, H-4, H-4”)
7.57 (*dd* , *J* = 3.6,1.2 Hz, 2H, H-3, H-3”)	7.16 (*d* , *J* = 4 Hz, 1H, H-3, H-3”)	6.86 (*d* , *J* = 6 Hz, 2H, H-3, H-3”)
7.20 (*dd* ,*J* = 5.2, 3.6 Hz, 2H, H-4, H-4”)		3.70 *Broad singlet*, 4H, two NH_2

Table2. ^{13}C-NMR (100.6 MHz, $CDCl_3$) data (δppm) of compounds **33** and **60.**

Carbon	**33**	**60**
2, 2”	128.06	137.21
3, 3”	128.44	124.46
4, 4”	131.29	130.54
5, 5”	131.18	109.80
2’, 5’	135.98	133.95
3’, 4’	133.86	110.89

One of the building blocks for compound **64** was 1,2-bis-(4-(octyloxyphenyl)- ethane-1,2-dione, which was synthesized starting from *p*-bromophenol **56** (Scheme 13). The reaction began by alkylating *p*-bromophenol using 1-bromooctane in the presence of anhydrous K_2CO_3 to provide *p*-bromooctyloxybenzene (**64**) in 68% yield. Compound **64** was subjected to Grignard reaction with Mg in THF and the resulting Grignard reagent was added to a suspension of LiBr/CuBr mixture. Up on adding oxalylchloride to the above mixture as described by Kenning *et al.*[27] 1, 2-bis–(4-octyloxyphenyl)-ethane-1,2-dione (**65**) was obtained, which was purified by silica gel column chromatography using 4.5:0.5 pet ether:ethyl acetate as eluent. The final step in the synthesis of 5,7-bis-(5-bromo-thiophen-2-yl)-2,3-bis-(4-octyloxy- phenyl)-thieno-(3,4-b)-pyrazine (**66**) was the condensation of diamine **60** with 1,2-bis-(4-octyloxyphenyl)-ethane-1,2-dione (**65**). Compound **66** was obtained in a pure form after chromatography on silica gel using a 3:2 mixture of petroleum ether:toluene as eluent. The identities of compounds **64**, **65** and **66** were confirmed based on their spectroscopic data as discussed below.



Scheme 13: Synthesis of 5,7-bis-(5-bromothiophen-2-yl)-2,3-bis-(4-octyloxyphenyl)-thieno-(3,4-b)- pyrazine (**66**).

The ^{1}H-NMR spectrum of **64** showed a three-proton triplet peak at δ 0.92 which is due to the terminal methyl group (H-1'). The ten-proton multiplet between δ 1.5-1.3 is due to five methylene groups and the two-proton quintet at δ 1.8 is due to the CH_2 at C-7' while the two-proton triplet at δ 3.93 is due to the H-8'. In the aromatic region, the one-proton doublet at δ 6.81 (*J* = 6.2 Hz) is due to H-2 and H-6 while the remaining one-proton doublet at δ 7.38 (*J* = 6.2 Hz) is due to H-3 and H-5 (Table 3).

The ^{13} C-NMR spectrum of compound **64** showed four resonances in the aromatic region, of which two are due to quaternary carbon atoms. The quaternary carbon signals at δ 158.27 and 112.55, respectively, are attributed to C-1 and C-4. The remaining peaks in the aromatic region arise from the methine carbon atoms of the benzene ring moiety. The signals at δ 132.19 is due to C-3 and C-5, where as the signal at δ 116.29 is due to C-2 and C-6. In the aliphatic region of the spectrum, there are eight signals. The signal at δ 68.0 is due to C-8' and the remaining signals a δ 31.86, 29.29, 29.4, 29.22, 26.06, 22.72 and14.16 are due to C-3', C-7', C-5', C-4', C-6' C-2', and C-1’, respectively. Thus, the data obtained from ^{1}H-NMR and ^{13}C-NMR along with DEPT-135 agrees with the structure of compound **64** (Table 4).

The ^{1}H-NMR spectrum of compound **65** showed a doublet at δ 7.49 (J = 8.8 Hz), which integrated for four protons and is due to H-3 and H-7, which couple with their neighboring *ortho* protons. The remaining doublet signal at δ 6.96 (J = 8.8 Hz) that again integrates for four protons is due to H-4 and H-6. In the aliphatic region of the spectrum there are four signals. The one that appeared at δ 4.05, which integrates for four protons, is due to the methylene protons on the carbon atoms attached to the oxygen. The two-proton quintet at δ 1.8, which integrates for four hydrogen is due to CH_2 groups at C-7’. A twenty-proton unresolved multiplet ranging from δ 1.2 - 1.6 is due to ten CH_2 groups on the side chain. Finally, the six-proton triplet at δ 0.95 is due to the terminal methyl groups.

The ^{13} C-NMR spectrum and DEPT-135 of compound **65** confirmed the presence of three quaternary carbons, two non-equivalent methine, seven methylene and one methyl groups. The signal at δ 193 is assigned to the two equivalent carbonyl groups. The peak at δ 68 is due to the oxygenated methylene groups and the peak at δ 14 is due to the terminal methyl groups. The remaining signals at δ 31.79, 29.29.00, 29.20, 29.02, 25.95 and 22.65 are due to C-3’, C-7’, C-5’, C-4’, C-6’and C-2’, respectively.

The FT-IR spectrum of compound **65** showed bands at 2924 and 2855 cm^{-1} due to stretching vibrations of the CH_3 and CH_2 groups, respectively. The carbonyl-stretching band appeared at 1661 cm^{-1}. In addition, the bands at 1602 and 1510 cm^{-1} are attributed to the C=ring stretching vibration. The asymmetric and symmetric C-O-C stretching bands appeared at 1263 and 1163 cm^{-1}, respectively. The IR data along with the ^{1}H-NMR and ^{13}C-NMR data agrees very well with structure **65**.

The UV-Vis spectrum of compound **66** was recorded in $CHCl_3$ and showed two absorption bands at 358 and 559 nm. The FT-IR spectrum showed asymmetric C-H stretching of CH_3 groups at 2852 cm^{-1}; symmetrical bending vibration of CH_3 group at 1360 cm^{-1}; scissoring vibration of CH_2 groups at 1466 cm^{-1}; C⎓C ring stretching at 1604 cm^{-1} and 1511 cm^{-1}; out of plane C-H bending vibration of aromatic compound at 778 cm^{-1}, ring C=C bending vibration at 668 cm^{-1}, and asymmetric C-O-C stretching at 1176 cm^{-1}.

Table3. ^{1}H-NMR (400.13MHz, $CDCl_3$) data (δppm) of Compounds **64 - 66**.

64	**65**	**66**
7.38 (*d, J* = 6.2 Hz, 2H, H-3, H-5)	7.94 (*d, J* = 8.8 Hz, 4H, H-3, H-5)	7.52 (*d, J* = 8.8 Hz, 4H, H-3, H-5)
6.81 (*d*, *J* = 6.2 Hz, 2 H, H-2, H-6)	6.96 (*d*, *J* = 8.8 Hz, 4 H, H-2, H-6)	7.23 (*d, J* = 4 Hz, 2 H, H-4”)
3.93 (*t*, 2H, H-8’)	4.05 (*t*, 4 H, H-8’)	6.86 (*d*, J = 8.8 Hz, 4 H, H-2, H-6)
		7.00(*d, J* = 4 Hz, 2H,H-3”)
1.8 (*q*, 2 H, H-7’)	1.8 (*m*, 4 H, H-7’)	4.1 (*t*, 4 H, H-8’)
1.3-1.5 (*m*, 10 H, H-2’ to H-6’)	1.6-1.2 (*m*, 10 H, H-2’to H-6’)	1.75 (*q*, 4 H, H-7’)
0.92 (*t*, 3 H, H-1’)	0.95 (*t*, 6H, H-1’)	1.6-1.2 (*m*, 20 H, H-2’to H-6’)
		0.95 (*t*, 6 H, H-1’)

The ^{1}H-NMR spectrum of compound **66** displayed four doublet peaks in the aromatic region. Among these two of them are due to thiophenic protons and the remaining two are due to the protons on the benzene rings. The four-proton doublet at δ 7.52 (*J* = 8.8 Hz) is due to H-3 and H-7 while the four-proton doublet at δ 6.82 (*J* = 8.8 Hz) is due to H-4 and H-6. The two-proton doublet at δ 7.23 (*J* = 4 Hz) is attributable to H-4” while the two-proton doublet at δ 7.00 (*J* = 4 Hz) is assignable to H-3”. The methylene protons attached to the oxygenated carbon at C-8’ resonate at δ 4.1 (triplet). The four-proton multiplet at δ 1.75 is due to H-7'. The remaining methylene proton resonances appear between δ 1.2 and 1.6 are unresolved. The signal due to the terminal methyl protons appears at δ 0.9 as a triplet (Table 3).

Table 4. ^{13}C-NMR (100.6 MHz, $CDCl_3$) data (δppm) of compounds-**64-66**.

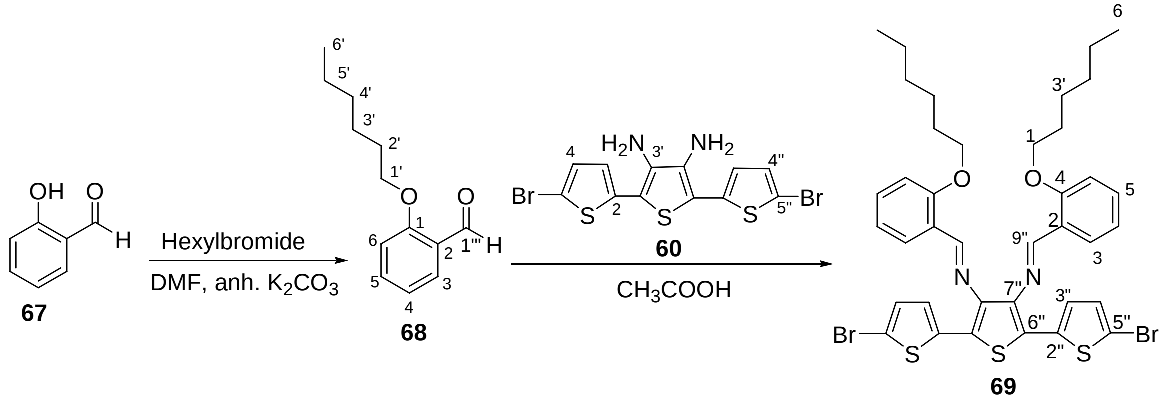
Carbon	**64**	**65**	**66**
1	156.27	164.50	160
2	116.29	114.72	114.17
3	132.19	132.36	129.74
4	112.55	126.11	131.15
5	132.19	114.72	129.74
6	116.29	132.36	114.17
7	-	193.57	153.04
1'	14.16	14.16	14
2'	22.06	22.06	22
3'	31.86	31.86	31.8
4'	29.20	29.20	29.2
5'	29.4	29.4	29.3
6'	29.4	29.4	26
7'	29.29	29.29	30.9
8'	68.25	68.25	68
2"			137.5
3"			123.65
4"			131.5
5"			114.35
6"			136.19
7"			123.5

In the ^{13}C-NMR spectrum of compound **66** (Appendix 1), there are 11 peaks in the aromatic region and eight peaks in the aliphatic region. This coupled with the DEPT-135 spectrum(Appendix 2) confirmed the presence of seven quaternary carbons, four methine carbons, seven methylene groups and one methyl group. The quaternary carbon signals that appeared at δ 160.0, 153.04, 137.5, 136.2, 131.2, 123.5 and 114.4 are due to C-5, C-1, C-2", C-7", C-2, C-6" and C-5", respectively, while the methine carbon signals appeared at δ 137.5, 129.0, 123.6 and 114.1, respectively, and are attributed to C-4", C-3, C-3" and C-6. The signal at δ 14.0 is due to methyl group and the remaining six signals are due to –CH_2- groups next to CH_3 groups (Table 4).

The ^{1}H-NMR, ^{13}C-NMR and FT-IR spectra recorded for compound **66** are in good agreement with the structure assigned for the compound.

4.1.2 Synthesis of 5,5”-dibromo 3’,4’di(2-hexyloxy-benzylideneimino)-2,2’:5’,2”-terthiophene (69)

The synthesis of 5,5”-dibromo 3’,4’di(2-hexyloxy-benzylideneimino)-2,2’:5’,2”-terthiophene (**69**) is shown in Scheme 14. Thus, salicylaldehyde was deprotonated with anhydrous K_2CO_3 and was alkylated with hexylbromide in DMF. The resulting *ortho*-hexyloxybenzaldehyde (**68**) was condensed with 5,5”-dibromo 3’,4’-diamino-2,2’:5’,2”-terthiophene (**60**) in glacial acetic acid to afford compound **69**, which was obtained in pure form after silica gel column chromatography using a 1:1 mixture of pentane and CH_2Cl_2 as eluent.



Scheme 14: Synthesis of **69**.

Both compound **68** and **69** were characterized based on their ^{1}H- and ^{13}C-NMR spectral data. Thus, the ^{1}H-NMR spectrum of compound **68** indicated the presence of five signals in the aromatic region and six signals in the aliphatic region of the spectrum. The one-proton singlet at δ 10.5 is due to the aldehydic hydrogen. The signals at δ 7.82 (*dd*, 1H), 7.52 (*dt*, 1H), 6.95 (*unresolved*, 2H) are assignable to H-3, H-5, H-4 and H-6, respectively. The two-proton triplet at δ 4.15 is due to the methylene protons at C-1’. The eight-proton muliplet between δ 1.9-1.3 is due to the four-methylene groups at C-2’, C-3’, C-4’ and C-5’ and the triplet signal at δ 0.9 is attributable to the terminal CH_3 group at C-6’.

In the ^{13}C-NMR spectrum of compound **68**, thirteen carbon resonances occurred, of which seven appeared in the aromatic region and the remaining six appeared in the aliphatic region. The aldehydic carbonyl carbon resonance appeared at δ 189.84. The signal due to the oxygenated methylene carbon at C-1’ appeared at δ 68.49. The terminal methyl group at C-6’ resonated at δ 13.99 as shown in Table 6. Thus, the ^{1}H- and ^{13}C-NMR spectra along with the DEPT-135 spectrum are in good agreement with the structure of compound **68**.

Likewise, the structure of compound **69** was confirmed based on its ^{1}H-NMR and ^{13}C-NMR spectra (Appendix 4). In addition, the FT-IR and UV-Vis spectra gave further support to the structure of compound **69.** Thus, the ^{1}H-NMR spectrum of compound **69** showed aromatic proton resonances at δ 8.31 (*dd,* 2H,), 7.6 (*dt,* 2H), 7.06 (*t*, 1H), 7.00 (*d*, 2H), and 6.85 (*d*, 2H). In the aliphatic region of the spectrum three signals appeared. The two-proton triplet at δ 3.8 is due to the methylene protons on the oxygenated carbon atoms of the side chains. Four methylene proton resonances appeared in the region between δ 1.6-1.1. The remaining six-proton triplet at δ 0.85 is due to the terminal CH_3 groups of the side chains (Table 5).

Table 5. ^{1}H-NMR (400.13 MHz, $CDCl_3$) data (δppm) of compounds **68**, **69**.

68	**69**
10.5 (*s*, 1H, H-1”)	8.90 (s, 2H, H-9”)
7.82 (*dd*, J = 7.6, 1.6 Hz, 1H, H-3)	8.31 (*dd*, J = 7.6, 1.6 Hz, 2H, H-3
7.52 (*dt*, J = 7.2, 1.6 Hz, 1H, H-5)	7.6 (*dt*, J = 8, 1.6 Hz, 1H, H -5
6.95 (*m*, 2H, H-4, H-6)	7.1 (*t*, 1H, H-2)
4.15 (*t*, 2H, H-1’)	7 (*d*, J = 4 Hz, 2H, 4”)
1.9-1.3 (*m*, 8H, H-2’ to H-5’)	6.955 (*d,J* = 4 Hz 2H, H-3”)
0.9 (*t*, 3H, H-6’)	6.85 (*d*, 2H,H-4)
	3.8 (*t*, 4H, H-1’)
	1.6-1.1 (*m*, 8H, H-2’ to H-5’)
	0.85 (*t*, 6H,H-6’)

The ^{13}C-NMR and DEPT-135 (Appendix 3) spectra of compound **69** revealed the presence of six quaternary carbons, seven-methine carbons, five methylene groups, and one methyl group. Six of these signals appeared in the aliphatic region and the remaining thirteen in the aromatic region. Table 6 shows the assignments of the carbon signals.

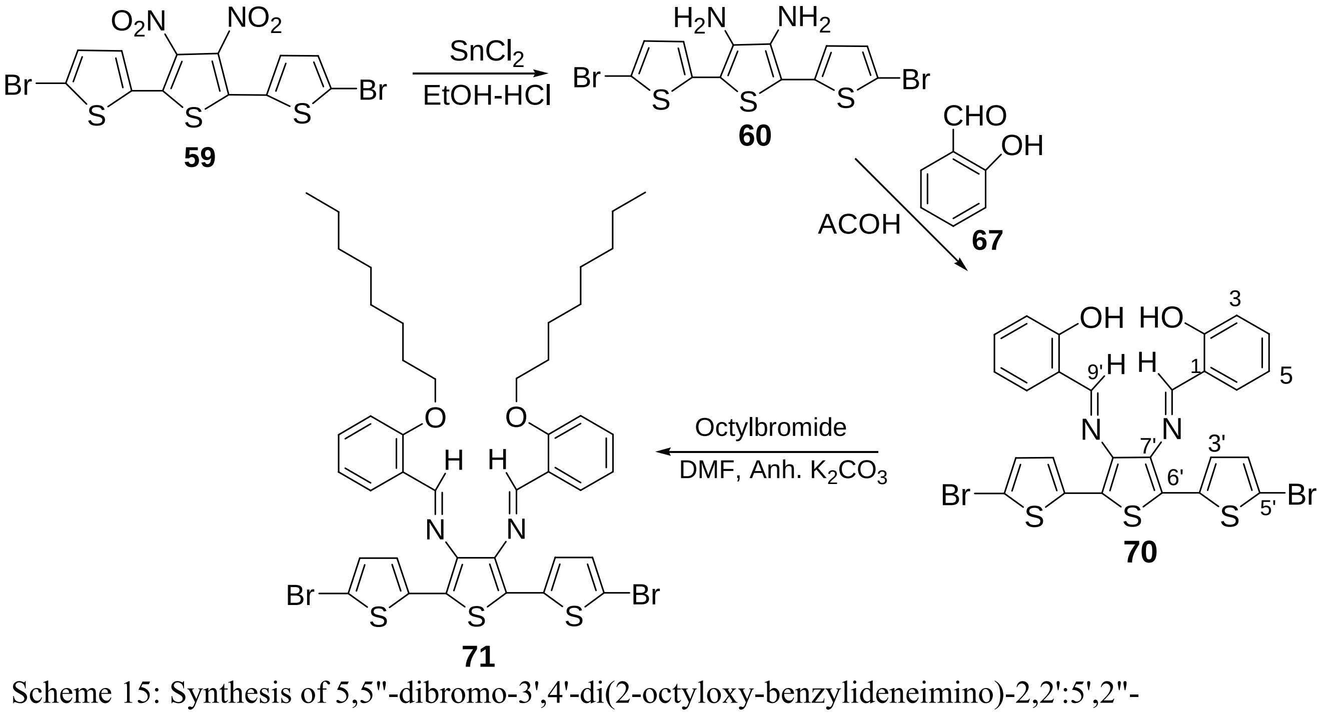
The UV-Vis spectrum of compound **69** which was recorded in $CHCl_3$ solution displayed two absorption bands at 352 and 418 nm. The FT-IR spectrum of compound **69** showed asymmetrical C-H stretching of methyl groups at 2954 cm^{-1}, C-H asymmetrical stretching of methylene groups at 2867 cm^{-1}, symmetrical bending vibration of CH_3 groups at 1368 cm^{-1}, CH_2 scissoring at 1430 cm^{-1}, methylene rocking at 1159 cm^{-1}, asymmetrical C-O-C stretching at 1238 cm^{-1}, symmetrical stretching of C-O-C at 1044 cm^{-1}, the C=C ring stretching at 1593 cm^{-1}, out of plane C-H bending at 779, and 757 cm^{-1}.

Table 6: ^{13}C-NMR ($CDCl_3$, 100.6 MHz) data (δppm) for compound **68**, and **69**.

Carbon	**68**	**69**
1'''	189.84	160.38
2	124.84	121.65
1	161.57	159.55
6	112.48	111.97
5	135.92	129.46
4	120.40	120.66
3	128.09	127.83
1'	68.49	68.45
2'	29.02	28.74
3'	25.71	25.50
4'	31.49	31.49
5'	22.56	22.53
6'	13.99	14.06
2''	-	140.38
7''	-	123.75
4''	-	132.99
5''	-	113.92
3''	-	124.69
6''	-	137.03

4.1.3 Synthesis of 5,5”-dibromo3’,4’-di(2-octyloxy-benzylideneimino)-2,2’:5’,2”-terthiophene (71)

The synthesis of 5,5”-dibromo 3’,4’-di(2-octyloxy-benzylideneimino)-2,2’:5’,2”-terthiophene (71) is shown in Scheme 15. Thus, reduction of compound **59** with $SnCl_2$ in a mixture of ethanol and HCl following the procedure described by Kitamura *et al.*,[26] afforded 5,5“-dibromo-3,4-diamino-2,2’:5’2”-terthiophene (**60**) which was subsequently condensed with salicylaldehyde (**67**) in the presence of acetic acid to afford compound **70**. Alkylation of compound **70** with 1-bromooctane and anhydrous K_2CO_3 in DMF yielded compound **71.** The confirmations of the structures of compounds **70** and **71** were mainly based on their ^{1}H- and ^{13}C-NMR spectral data as described below.



Scheme 15: Synthesis of 5,5"-dibromo-3',4'-di(2-octyloxy-benzylideneimino)-2,2':5',2"-terthiophene (**71**).

The ^{1}H-NMR spectrum of compound **70** indicated the presence of six signals. The two-proton broad singlet at δ 12.35 is due to the acidic OH protons and the two-proton singlet at δ 8.6 is attributed to the olefinic hydrogens on the imine carbon atoms. The doublet of triplet peak at δ 7.42, which integrates for two protons, is due to H-6. The doublet of doublet peak centered at δ

7.23 (*J* = 7.6, 1.2 Hz) which integrates for two protons is due to H-4. A two-proton broad singlet at δ 7.04 is due to H-3, and a four-proton broad singlet at δ 7.02 is due to H-3' and H-4' of the thiophene moiety. The remaining one-proton doublet of triplet at δ 6.91 is due to H-5.

The ^{13}C-NMR spectrum of compound **70** revealed 13 carbon resonances, all of which are in the aromatic region. Out of the 13 carbon resonances, six appeared at δ 160.6, 137.7, 135.5, 122.1, 118.5 and 113.7 and are attributed to the quaternary carbons C-2, C-2', C-6', C-1 ,C-3',and C-5, respectively. The remaining seven signals which appeared at δ
δ 169, 134, 133, 130, 125, 119 and 117 are due to methine carbons and are assigned to C-4', C-4, C-6, C-3', C-5and C-4, respectively.

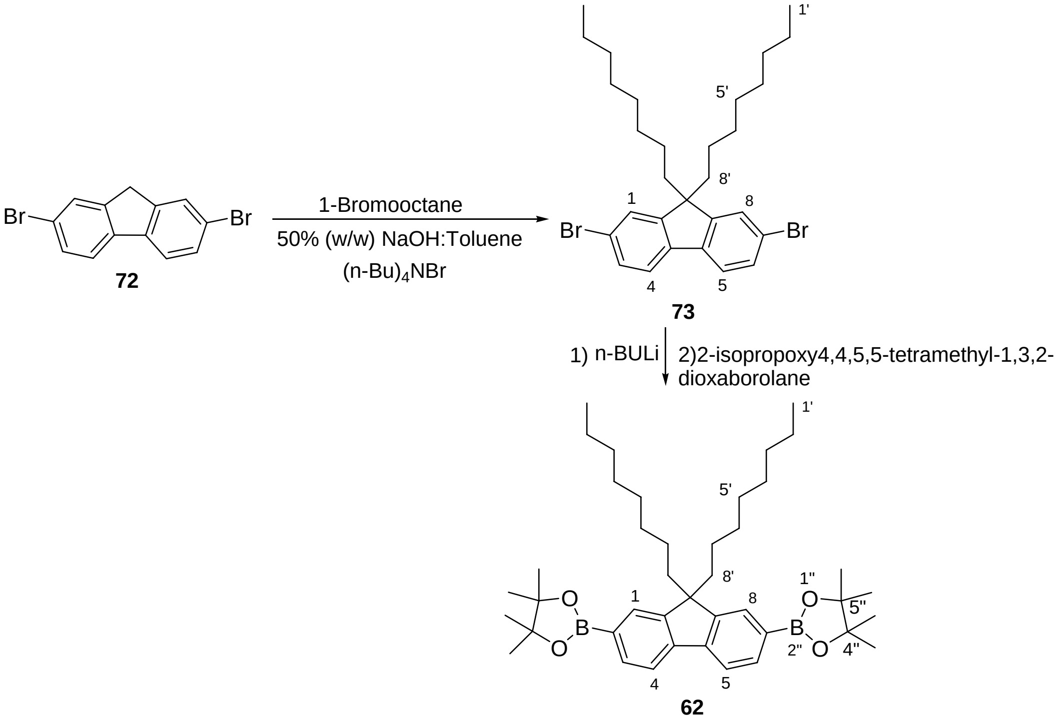
The ^{1}H-NMR spectrum of compound **71** showed that there are six proton signals in the aromatic due to the thiophenic and aromatic protons. The presence of an octyl side chain was also evident from the ^{1}H-NMR spectrum. The ^{13} C-NMR and DEPT-135 spectra of compound **71** confirmed the presence of six quaternary and seven methine carbon resonances in the aromatic region. The carbon resonances due to the octyl side chain appeared in the region between δ 14 and 70 in agreement with the structure of compound **71**.

The ^{1}H- and ^{13}C-NMR spectra of compound **71** showed that there were also signals due to an impurity. Thus attempts were made to purify compound **71** by silica gel column chromatography. However, it was not possible to remove the impurity completely. Thus no further efforts were made to make a copolymer out of compound **71**.

4.2 SYNTHESIS OF FLUORENE-BASED MONOMERS

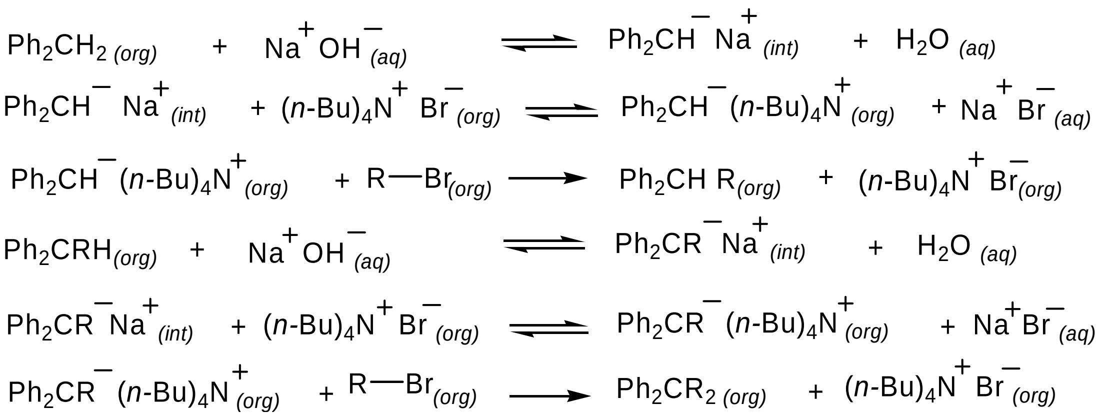
4.2.1 Synthesis of 2,7-bis-(4’,4’,5”,5”-tetramethyl-1,3,2-dioxaboralane)-9,9-dioctylfluorene (62).

The general route for the synthesis of 2,7-bis-(4’,4’,5”,5”-tetramethyl-1,3,2-dioxa-boralane)-9,9-dioctylfluorene (**62**) is depicted in Scheme 16.



Scheme 16: Synthesis of 2,7-bis-(-4",4"5",5"-tetramethyl-1,3,2-dioxaborolane)-9,9-dioctylfluorene (**62**).

2,7-Dibromofluorene (**72**), the precursor for the synthesis of 9,9-dioctyl-2,7-dibromofluorene, was synthesized by Zekarias Yacob, [30] by treating fluorene with Br_2 in $CHCl_3$: HOAC at 0˚C. The synthesis of 9,9-dioctyl-2,7-dibromofluorene (**73**) was achieved in 91.2% yield, from 2,7-dibromofluorene (**72**) using a two- phase system composed of 50% w/w aqueous NaOH and toluene, in the presence of tetrabutylammonium bromide as a phase transfer catalyst. It was observed that immediate reaction took place as soon as tetrabutylammonium bromide catalyst was added. In this system, hydroxide ions are transported from the aqueous layer to the organic layer by the phase transfer catalyst and fluorene is deprotonated to form 9-fluorenyl anion, which acts as a nucleophile and attacks 1-bromooctane. The mechanism of the phase transfer catalysis is depicted in Scheme 17.[30] Compound **73** was obtained as a yellow solid, which melted at 50.0 - 52.9°C after recrystallization from isopropyl alcohol.



$$Ph_2CH_{2\,(org)} + Na^+\,OH^-_{(aq)} \rightleftharpoons Ph_2CH^-\,Na^+_{(int)} + H_2O_{(aq)}$$
$$Ph_2CH^-\,Na^+_{(int)} + (n\text{-Bu})_4N^+\,Br^-_{(org)} \rightleftharpoons Ph_2CH^-\,(n\text{-Bu})_4N^+_{(org)} + Na^+\,Br^-_{(aq)}$$
$$Ph_2CH^-\,(n\text{-Bu})_4N^+_{(org)} + R{-}Br_{(org)} \longrightarrow Ph_2CH\,R_{(org)} + (n\text{-Bu})_4N^+\,Br^-_{(org)}$$
$$Ph_2CRH_{(org)} + Na^+\,OH^-_{(aq)} \rightleftharpoons Ph_2CR^-\,Na^+_{(int)} + H_2O_{(aq)}$$
$$Ph_2CR^-\,Na^+_{(int)} + (n\text{-Bu})_4N^+\,Br^-_{(org)} \rightleftharpoons Ph_2CR^-\,(n\text{-Bu})_4N^+_{(org)} + Na^+Br^-_{(aq)}$$
$$Ph_2CR^-\,(n\text{-Bu})_4N^+_{(org)} + R{-}Br_{(org)} \longrightarrow Ph_2CR_{2\,(org)} + (n\text{-Bu})_4N^+\,Br^-_{(org)}$$

Scheme 17: Mechanism of the phase transfer catalysis.

The ^1H-NMR spectrum of compound **73** showed three peaks integrating for six protons in the aromatic region and four peaks in the aliphatic region. The doublet of doublet peak centered at δ 7.54 (J = 6.4, 2.0 Hz) is due to H-3 and H-6, which are chemically equivalent and have *ortho* couplings with H-4 and H-5, respectively. The broad singlet peak at δ 7.49 is due to H-4 and H-5 while the remaining doublet peak centered at δ 7.47 is due to H-1 and H-8, which are chemically equivalent and have *meta* couplings with H-3 and H-6, respectively. A multiplet signal at δ 1.9 is due to the CH_2 groups next to the C-9 position of the fluorene moiety. The multiplet peak between δ 1.4-1.05 which integrates for 20 protons is due to ten-methylene groups on the octyl side chains. The triplet signal at δ 0.85, which integrates for six protons is due to the two terminal methyl groups on the octyl side chains. The four-proton multiplet peak at δ 0.65 is attributed to the C-7' metyhylene protons. As described by Ding *et al.*, these protons are located on the top of conjugated plane and are shielded by the π electrons of the fluorene ring moiety, and consequently their resonance appeared at higher field in the spectrum [31] (Table7).

The ^{13}C-NMR spectrum of compound **73** displayed a total of 15-carbon resonances, of which six appeared in the aromatic region and nine appeared in the aliphatic region. The DEPT-135 spectrum revealed one methyl, seven methylene and three methine carbons.

The remaining four-carbon resonances are due to quaternary carbons (Table 8). The FT-IR spectrum of compound **73** indicates an asymmetric C-H stretching of CH_3 groups at 2954 cm^{-1}, asymmetric C-H stretching of CH_2 groups at 2926 cm^{-1}, CH_2 scissoring at 1448 cm^{-1} and rocking at 808 cm^{-1}. In addition, absorption bands due to in-plane C-H bending were observed at 1060 and 1004 cm^{-1} in agreement with the structure of compound **73**.

Table7. ^{1}H-NMR (400.13 MHz,$CDCl_3$) data (δppm) of compounds **73** and **62.**

73	**62**
7.54 (*dd*, *J* = 6.4, 2.0 Hz,2H, H-3, H-6)	7.83 (*dd*, *J* = 7.6, 0.8 Hz, 2H, H-3, H-6)
7.49 (*Broad singlet*, 2H, H-4, H-5)	7.77 (*Broad singlet*, 2H, H-1, H-8)
7.47 (*d*, *J* = 2 Hz, 2H, H-1, H-8)	7.75 (*dd*, *J* = 7.6 Hz, 2H, H-4, H-5)
1.9 (*m*, 4H, H-8’)	2.00 (*m*, 4H, H-8’)
1.4-1.05 (*m*, 20H, H-2’ to H-6’)	1.4 (*s*, 24H, H-6’’ to H-9’’)
0.85 (*t*, 6H, H-1’)	1.25-1.00 (*m*, 20H, H-2’ to H-6’)
0.65 (*m*, 4H, H-7’)	0.85 (*t*, 6H, H-1’)
	0.55 (*m*, 4H, H-7’)

2,7-Dibromo-9,9-dioctylfluorene (**73**) was converted to the corresponding diborolane **62** by halogen-metal exchange with *n*-BuLi in THF at-78˚C followed by the addition of 2-isopropoxy-4’,4’,5”,5”-tetramethy1-1,3,2-dioxborolane according to the procedure reported by Ranger *et al.* [32] . Unlike the literature procedure, the time required for the reaction was decreased from 24 hours to 5 hours and the crude product was recrystallized from isopropyl alcohol rather than purification by column chromatography. The dioxborolane **62** was obtained in pure form and was characterized based on its melting point, FT-IR, ^{1}H- and ^{13}C-NMR data.

The FT-IR spectrum of compound **62** showed an aromatic C-H stretching at 2973 cm^{-1}, and aromatic ring modes at 1577 and 1467 cm^{-1}, out of plane C-H bending at 700 cm^{-1}, aromatic ring bending at 633cm^{-1}, and asymmetric C-H stretching of CH_3 at 2850 cm^{-1}. Bands due to asymmetric C-B-O stretching appeared at 1256 cm^{-1}. In addition, a band due to an asymmetric Ar-B stretching was observed at 1426 cm^{-1}. The ^{1}H-NMR spectrum of compound **62**(Appendix 5) displayed three signals in the aromatic region. The two-proton doublet of doublet at δ 7.83 (*J* = 7.6, 0.8 Hz) is due to H-3 and H-6, while the two-proton broad singlet at δ 7.77 is attributed to H-1 and H-8. The two-proton doublet of doublet at δ 7.75 (*J* = 7.6, 0.8 Hz) is assigned to H-4 and H-5. In the aliphatic region of the spectrum, a four-proton multiplet appeared at δ 2.00, which is due to H-8'. The singlet signal at δ 1.4, which integrates for twenty-four protons is due to the protons on the four-methyl groups of the dioxaborolane moieties. The 20-proton multiplet at δ 1.25-1.00 is due to ten methylene groups on the octyl side chains. The six-proton triplet at δ 0.85 is assigned to the terminal methyl groups and the multiplet signal at δ 0.55, which integrates for four protons, is due to the C-7' methylene protons as described above (Table 7).

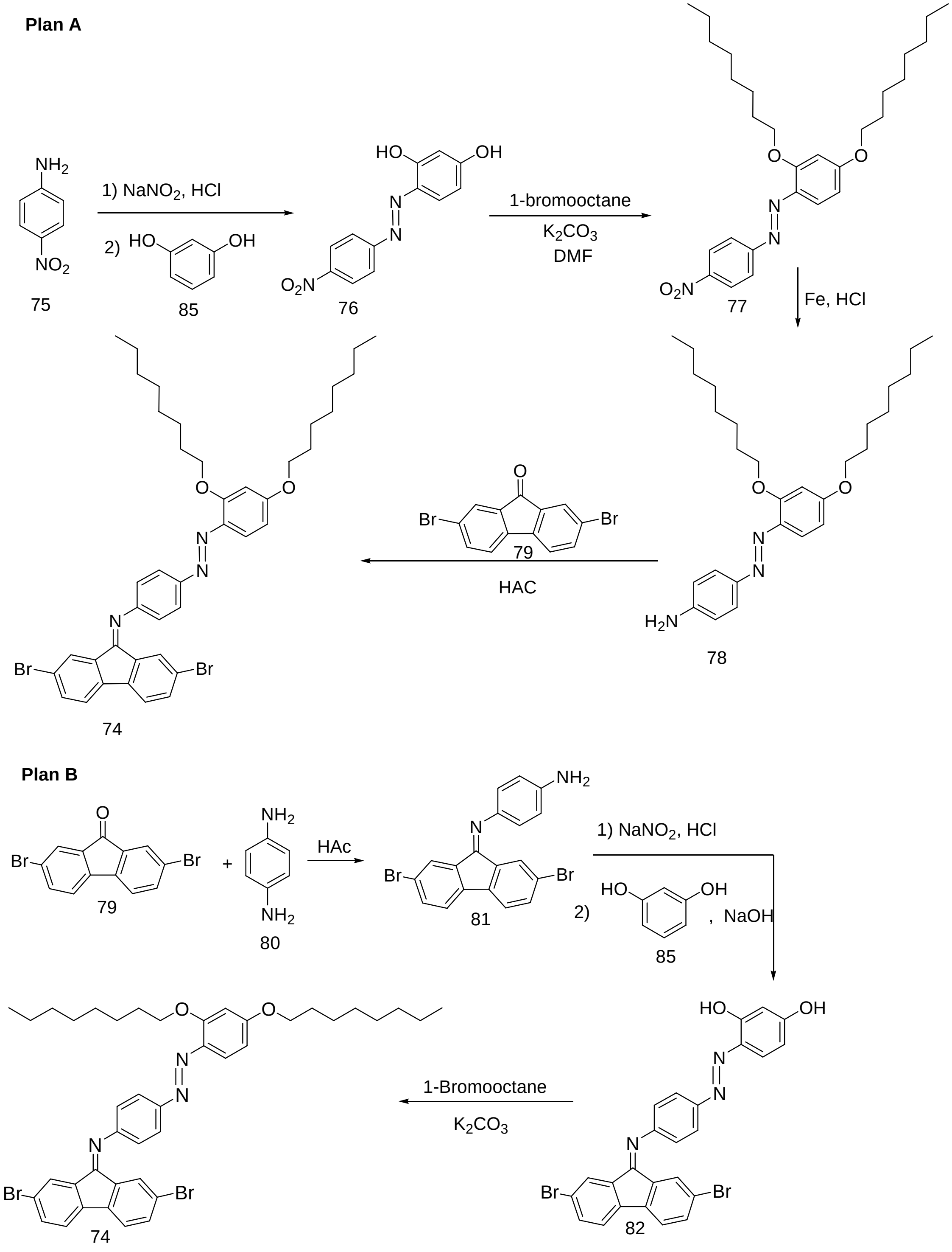
The ^{13}C-NMR (Appendix 6) and DEPT-135 spectra of compound **62** confirmed the presence of five methyl, seven methylene and two quaternary carbon resonances in the aliphatic region. It also displayed the presence of three quaternary and three methine resonances in the aromatic region. Since the compound is symmetrical, only half of the carbon signals were observed in the ^{13}C-NMR spectrum (Table 8).

Table8. ^{13}C-NMR (100.6 MHz,CDCl$_3$) data (δppm) of compounds **73** and **62.**

Carbon	**73**	**62**
1	130.18	133.66
2	121.12	128.91
3	121.53	119.94
4	126.22	128.91
5	126.22	128.91
6	121.53	119.94
7	121.12	128.91
8	130.18	133.66
9	55.71	55.18
10	152.58	150.48
11	139.09	143.92
12	139.09	143.92
13	152.58	150.48
1’	14.10	14.08
2’	22.63	22.60
3’	31.29	31.79
4’	29.18	29.16
5’	29.21	29.21
6’	29.89	29.94
7’	23.66	23.94
8’	40.18	40.10
1”	-	-
2”	-	-
3”	-	-
4”	-	83.72
5”	-	83.72
6”	-	24.94
7”	-	24.94
8”	-	24.94
9”	---	24.94

4.2.2. ATTEMPTS TOWARDS THE SYNTHESIS OF [4-(2,4-BIS-OCTYLOXY-PHENYLAZO)-PHENYL]-2,7-DIBROMOFLUOREN-9-YLIDENE-AMINE (74)

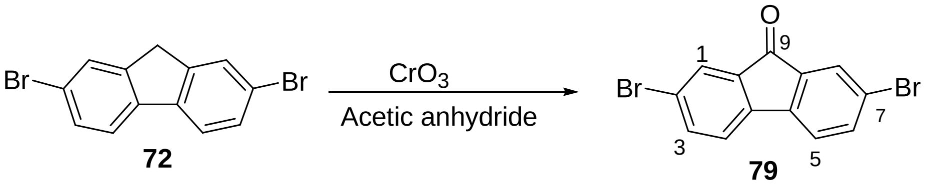
In the course of this project work, attempt was made to synthesize compound **74.** Our original synthetic plan is shown in Scheme **18.** Although our efforts to prepare compound **74** did not succeed, we have synthesized several of the intermediate compounds shown in Scheme **18** and characterized them. The discussion that follows describes the syntheses and characterization of these compounds.



Scheme 18. Plan towards the synthesis of compound **74**.

4.2.2.1. Synthesis of 2,7-dibromofluorenone (79).

2,7-Dibromofluorenone (**79**), the by-product that was formed during alkylation of 2,7-dibromofluorene (**72**), was synthesized by the oxidation of the benzylic C-9 position of 2,7-dibromofluorene (**72**). Following a similar procedure like that employed by Ranger *et al.,*[32] 2,7-dibromofluorene was treated with CrO_3 in the presence of acetic anhydride. Compound **79** was obtained as a yellow solid in 98% yield, which was recrystallized from isopropyl alcohol.



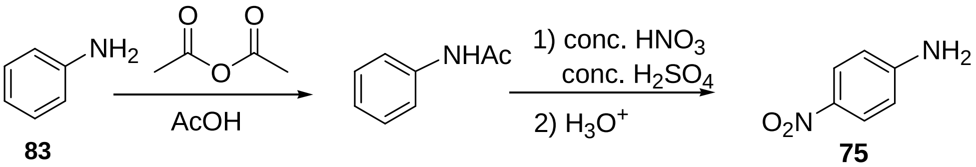
Scheme 19: Synthesis of 2,7-dibromofluorenone (**79**).

The FT-IR spectrum of compound **79** showed a strong carbonyl absorption band at 1725 cm^{-1}. In addition, the FT-IR spectrum revealed C$\underset{- - -}{\text{—}}$C ring stretching bands at 1592, 1459 and 1419 cm^{-1}. The ^{1}H-NMR spectrum of compound **79** showed a two-proton broad singlet at δ 7.76 due to the equivalent protons at C-1 and C-8. The doublet peak at δ 7.65 (J = 8 Hz) is due to the protons at C-3 and C-5, which couple with the *ortho* hydrogens at C-4 and C-6, respectively. The remaining two-proton doublets at δ 7.4 (J = 8 Hz) are due to the hydrogens at C-4 and C-6 (Table 9).

The ^{13}C-NMR and DEPT-135 spectra of compound **79** suggested the presence of four quaternary carbon atoms, all of which are in the aromatic region. Out of the four quaternary carbon signals, the one that appeared at δ 190 accounts for the carbonyl group at C-9. The DEPT-135 spectrum also indicated the presence of three methine groups (Table10) in agreement with the structure of **79**.

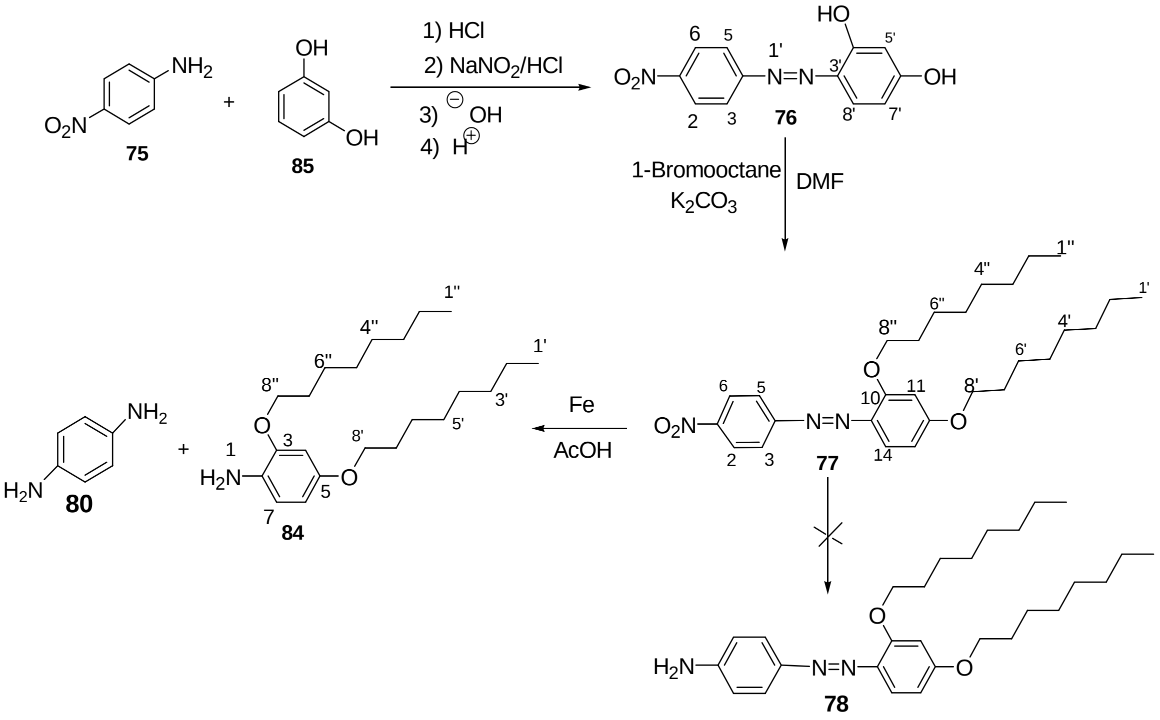
4.2.2.2. Synthesis of (2,4-bis-octyl-phenyl)-(4-amino-phenyl)-diazine (78)

The synthesis of (2,4-bis-(octyl)-phenyl)-(4-aminophenyl)-diazine (7**8)** began from aniline (Scheme 19). Thus, aniline was first protected by converting it to acetanilide with acetic anhydride in acetic acid. Subsequent treatment of acetanilide with concentrated HNO_3 and H_2SO_4 resulted in *p*-nitroacetanilide, which was subsequently hydrolyzed with 10% H_2SO_4 solution. After the solution was rendered alkaline with 20% NaOH solution, a precipitate was formed which was recrystallized from ethanol to afford *p*-nitroaniline (**75**), which melted at 145.5-148.2 ^{0}C.



Scheme 20: Synthesis of *p*-nitroaniline.

p-Nitroaniline was diazotized using conc. HCl and $NaNO_2$ to yield *p*-nitrobenzene diazonium chloride, which was subsequently treated with resorcinol to give rise to compound **76**. The alkylation of compound **76** was effected using 1-bromooctane in the presence of K_2CO_3 to give compound **77** in 63 % yield. Finally, the attempted reduction of the nitro group of compound **77** with iron in acetic acid at 40˚C gave an unexpected result. Instead of giving the expected amine **78**, compound **77** fragmented to give amine **84** and presumably *p*-phenylenediamine (**80**). Tables 9 and 10 summarize the ^{1}H- and ^{13}C-NMR spectral data for compounds **79**, **77** and **84**.



Scheme 21: Attempted synthesis of [2,4-bis-(octyloxy)phenyl-(4-amino-phenyl)]-diazene (**78**).

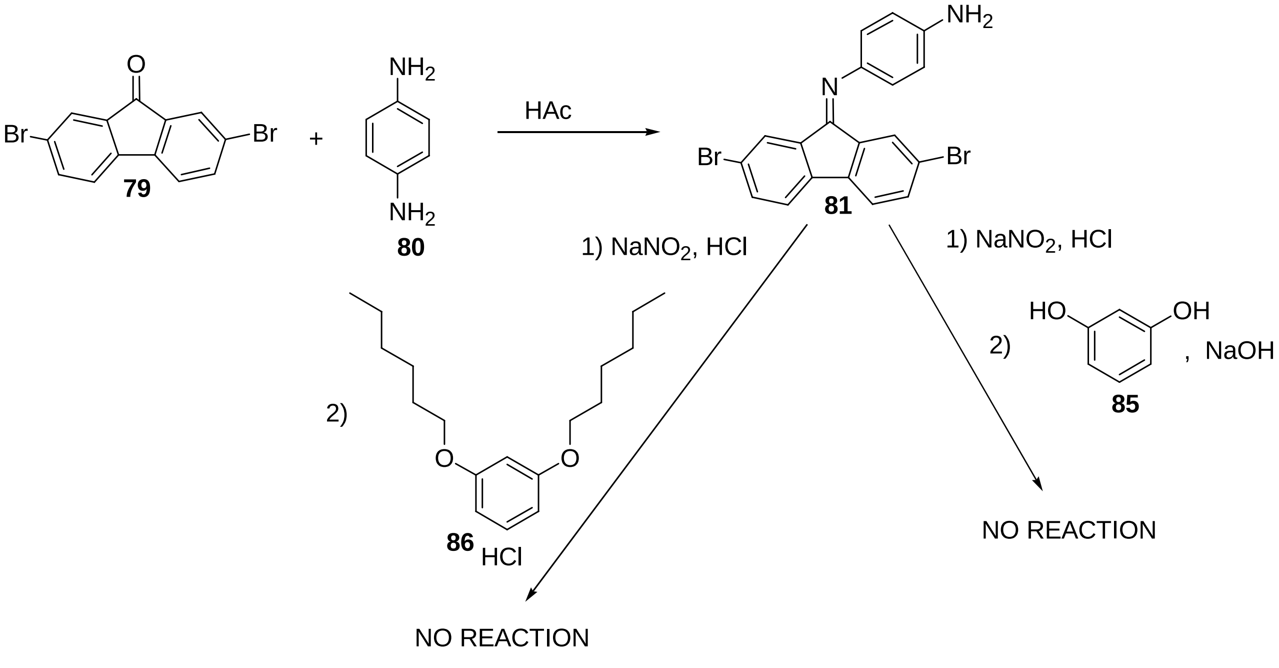
Table 9:^{1}H-NMR(CDCl$_3$, 400.13 MHz) data (δppm) for compound **79**, **77** and **84.**

79	**77**	**84**
7.76 (*Broad singlet*, 2H, H-1, H-8)	8.35 (*d*, *J* = 9.6 Hz, 2H, H-2, H-6)	6.65 (*d*, *J* = 8.4 Hz, 1H, H-7)
7.65 (*d*, *J* = 8Hz, 2H, H-3, H-6)	8.00 (*d*, *J* = 9.6 Hz, 2H, H-3, H-5)	6.47 (*d*, *J* = 2.4 Hz, 1H, H-4)
7.4 (*d*, *J* = 8 Hz, 2H, H-4, H-5)	7.82 (*d*, *J* = 8.8 Hz, 1H, H-14)	6.35 (*dd*, *J* = 8.4, 2.4 Hz, 1H, H-6)
	6.65 (*d*, *J* = 2.4 Hz, 1H, H-11)	3.97 (*t*, 2H, H-8”)
	6.60 (*dd*, *J* = 2.4, 8.8 Hz, 1H, H-13)	3.89 (*t*, 2H, H-8’)
	4.19 (*t*, 2H, H-8”)	3.6 (*Broad singlet*, 2H, NH$_2$)
	4.05 (*t*, 2H, H-8’)	1.8 (*m*, 4H, H-7’, 8’and H-7’,H-7”)
	1.95 (*q* ,2H, H-7”)	1.4-1.2 (*m*, 20H, H-2’to H-6’,H-2” to H-6”)
	1.84 (*q*, 2H, H-7’)	0.9 (*t*, 3H, H-1’ and H-1’’)
	1.7-1.3 (*m*, 20H, H-2’to H-6’ and H-2 to H-6’’)	
	0.9 (*t*, 6H, H-1’ and H-1”)	

Table 10: ^{13}C-NMR ($CDCl_3$, 100.6 MHz) data (δppm) for compounds **79**,**77** and **84.**

Carbon	**79**	**77**	**84**
1	127.87	156.69	-
2	123.34	124.68	129.76
3	137.48	123.08	147.76
4	121.84	147.83	100.86
5	121.84	123.08	152.5
6	137.48	124.68	105.06
7	123.34	-	115.21
8	127.86	-	-
9	190.91	136.92	-
10	142.27	159.70	-
11	135.30	100.61	-
12	135.30	164.84	-
13	142.27	106.80	-
14	-	118.16	-
1’,1”	-	14.13	14.1
2’,2”	-	22.29	22.6
3’,3”	-	31.81	29.49
4’,4”	-	29.16	29.2
5’,5”	-	29.25	29.3
6’	-	26.02	26.1
7’	-	29.31	29.40
8’	-	68.56	68.3
8”	-	69.61	68.6
7’’	-	29.35	29.44
6”	-	26.07	26.1

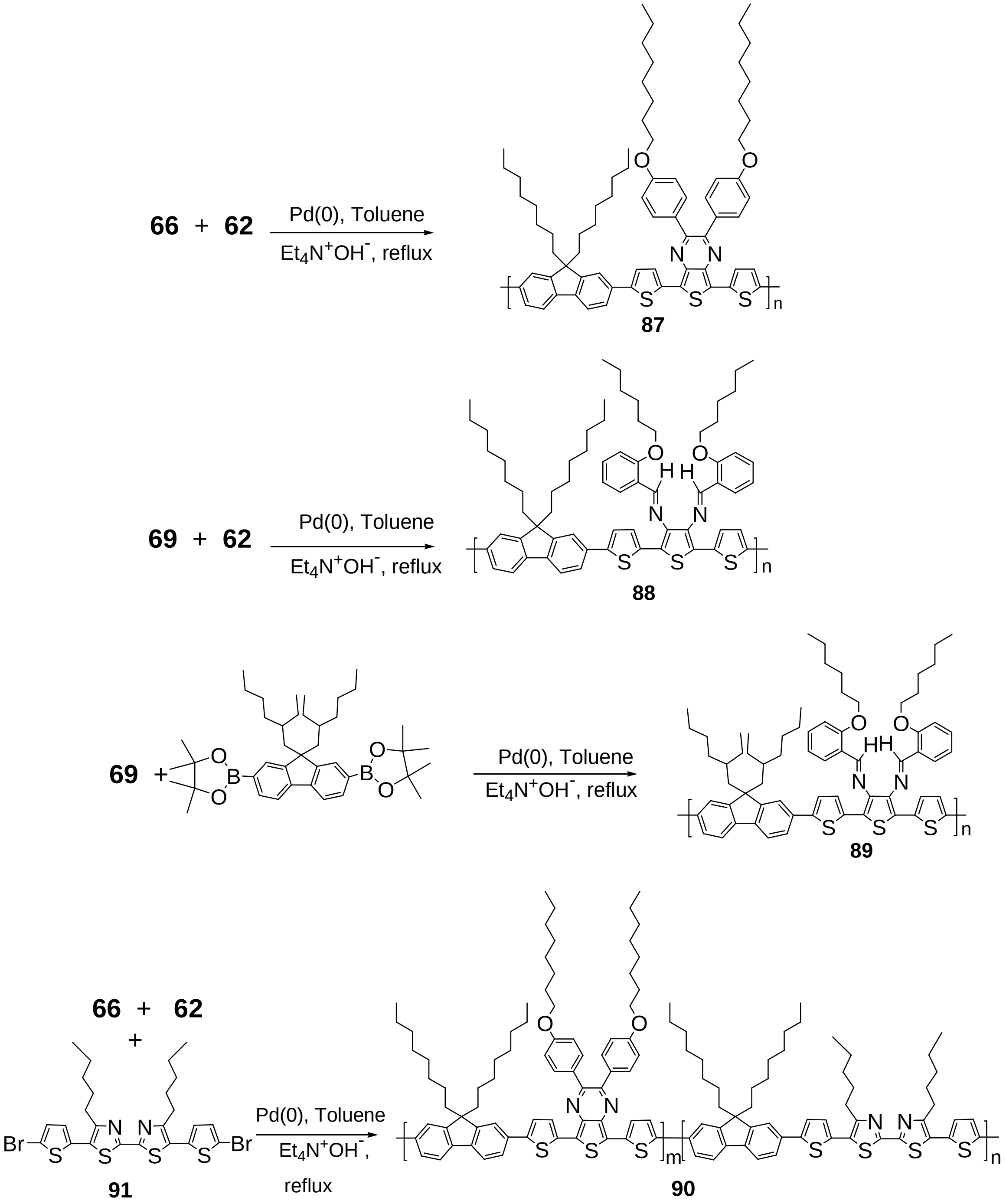
Having failed to secure the crucial intermediate compound **78** some more attempts were made to explore the condensation reactions of 2,7-dibromofluorenone (**79**) with several amines. Thus, the prolonged reaction of 2,7-dibromofluorenone with *p*-nitroaniline in acetic acid and a small amount of *p*-toluenesulfonic acid failed to give any condensation product. The failure of *p*-nitroaniline to undergo the condensation reaction is presumably due to the strong electron-withdrawing ability of the nitro group, which renders the amino group essentially non-nucleophilic. A similar attempt to effect a condensation between compound **84** and 2,7-dibromofluorenone gave no condensation product. However, the condensation of *p*-phenylenediamine with 2,7-dibromofluorenone occurred readily in warm acetic acid to give a brick-red precipitate, which could be collected by filtration. (Scheme19). The condensation product had very poor solubility in common organic solvents and therefore was not characterized properly using NMR spectroscopic techniques. Attempts to effect diazo coupling reactions between this compound and 1,3-dihexyloxy benzene failed to work. A similar diazo coupling reaction with resorcinol did not give any coupling product.



Scheme 22. Attempted at diazo coupling reactions.

5. SYNTHESIS OF THE COPOLYMERS

The overall goal of this synthetic work was the synthesis of conjugated copolymers of substituted fluorenes with donor-acceptor-donor segments. Thus, the monomers, whose syntheses were discussed in the previous sections, were polymerized using a modified Suzuki coupling reaction with tetrakis(triphenylphosphine)palladium(0) as a catalyst and tetraethylammonium hydroxide as the base, instead of K_2CO_3 or $NaHCO_3$, which were used for the standard Suzuki polymerizations. The use of tetraethylammonium hydroxide instead of K_2CO_3 or $NaHCO_3$ reduces the reaction time to 2-4 hours compared to the 24 hours required for the standard Suzukipolymerization.[33] The low molecular weight oligomers and unreacted starting materials were separated by Soxhlet extraction with ether and the higher molecular weight and chloroform-soluble materials were extracted with chloroform and precipitated from methanol as described in the Experimental section. Scheme 23 shows the reactions that led to the syntheses of the copolymers.



Scheme 23: Synthesis of co-polymers.

All polymers obtained in the course of this study are soluble in $CHCl_3$.The colors of co-polymer **87** and **90** are green in $CHCl_3$ solution while co-polymer **88** and **89** turned out to be red. The molecular weight of polymer **87** was determined by size exclusion chromatography using polystyrene standards at Chalmers University of Technology, Sweden. The Mn and Mw were found to be 11,000 and 32,000, respectively. The UV-Vis spectra (Table 11, Appendix7 and 8) of $CHCl_3$ solutions of the polymers were recorded. The absorption maxima of the polymers varied from 388 nm to 649nm (Table 11). The electronic spectra of conjugated polymers indicate the extent of π orbital overlap. The energy gap between $\pi \longrightarrow \pi^*$ transition is directly affected by the degree of conjugation. The higher the conjugation length the smaller the energy gap between the two transitions. Thus, the UV-Vis spectra gave us an insight in to the extent of conjugation and hence the band gap.

Table 11: Some characteristics of polymers 87 - 90.

Polymer	Appearance	UV-Vis (λ_{max} in nm)
87	Green, solid	429 nm, 649 nm
88	Red, solid	394 nm, 484 nm
89	Red, solid	388 nm, 478 nm
90	Green, solid	438 nm, 630 nm

The polymers were also subjected to FT-IR spectroscopic studies. Asymmetric and symmetric stretching bands of methyl and methylene group were observed between 2950 and 2846 cm^{-1}. An absorption band around 1600 cm^{-1} is due to C=C-C ring stretching which appeared in the IR spectra of all polymers. Symmetrical bending vibrational bands were observed for polymers **87**, **88**,and **89** at 1346, 1368 and 1369 cm^{-1}, respectively. Bands due to scissoring of CH_2 groups occurred at 1466, 1457, 1457 and 1458 cm^{-1}, respectively, for polymers **87**, **88**, **89** and **90**. The bands at 752 and 753 cm^{-1} in the IR spectra of polymers **87** and **88,** respectively, were attributed to out of plane C-H bending of aromatic systems.

6 CONCLUSION

Conjugated polymers have been studied in great detail as electroluminescent materials for use in light emitting diodes. In this regard polyfluorene based materials have been investigated extensively because of the many attractive properties they possess. However, their wide applications have been greatly restricted by their susceptibility to oxidation at C-9 position, very low durability during use and their intractability. In order to overcome these defects a lot of modifications have been made. Among these are functionalizing fluorene at the methylene bridge without distorting the conjugation length and copolymerizing the fluorene with aromatic sub units like thiophene. In this project work, four poyfluorene copolymers containing donor-acceptor-donor segments were synthesized. The fluorene subunits contained octyl and 2-ethyl hexyl pendant groups at the C-9 position. The donor-acceptor-donor segments were derived from terthiophene. The monomers were synthesized following the different routes indicated in Schemes13, 14 and 16. The polymerization reactions were conducted by modified Suzuki coupling reactions using Pd(0) as a catalyst and tetraethylammonium hydroxide as a base. The colors of the polymers **87** and **90** are green in $CHCl_3$ solution and polymer **88** and **89** are red. Polymer **87** had a reasonably high molecular weight as determined by SEC measurements. All of the polymers prepared in the course of this project work are soluble in chloroform. The physical properties of all polymers and their possible applications in light emitting diodes and other high technology materials will be studied in collaboration with physicists.

7. EXPERIMENTAL

7.1. MATERIALS AND METHODS

All of the compounds prepared in the course of the synthetic work were purified and characterized by UV-Vis, FT-IR and NMR techniques. ^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Bruker Avance 400.13 MHz spectrometer with $CDCl_3$ as a solvent and are reported in δ units. The solvent signal was used as internal standard. The UV-Vis spectra of the monomers and polymers were recorded in chloroform using SPECTRONIC GENESYS 2PC spectrophotometer with a 1 cm cell at room temperature. Infrared spectra were obtained using a PERKIN ELMER infrared spectrophotometer. FT-IR spectra of the crystalline compounds were obtained as KBr pellets. Melting points were measured using LEICA GALEN^{TM} III compound microscope melting point apparatus and are uncorrected.

7.2. REAGENTS

2,5-Dibromothiophene (Aldrich), potassium carbonate (Aldrich), sodium sulfate (Aldrich), $PdCl_2$ (BDH), *N*-bromosuccinimide (NBS) (Aldrich), *n*-octyl bromide (Aldrich), *n*-hexylbromide (Aldrich) DMF (Aldrich), $CHCl_3$ (BDH), methanol (BDH), diethyl ether (BDH), petroleum spirit (BDH), acetone (BDH), ethyl acetate (Aldrich), n-pentane (BDH), magnesium (Aldrich), tetrabutylammonium hydroxide (Aldrich), tetrabutylammonium bromide (Aldrich), *p*-bromophenol (Aldrich),oxalylchloride (Aldrich), NaOH(Aldrich), phenylboric acid (Aldrich), aniline (BDH), toluene (BDH), propan-2-ol (BDH), LiBr (Aldrich), CuBr (Aldrich), tributyl(thiophen-2-yl)stannene (Aldrich), 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaboralane(Aldrich), bromobenzene (Aldrich), *p*-phenyldiamine (Sigma), ethanol (Analar), acetic acid (Analar), iron (Fluka), resorcinol (Riedel-deHaën), *p*-nitroaniline (Riedel-de Haën) were bought and used as received. Tetrahydrofuran (THF) was dried over Na-benzophenone under nitrogen atmosphere. Analytical grade methanol and chloroform were purchased from BDH. *n*-Butyl lithium (2.4M in hexane), were received from Aldrich and were used without further purification. Pd(0) used in the course of this project work was prepared in the laboratory by Addisu Getachew[34]. Silica gel 60 (43-63 μm) was used as a stationary phase for column chromatography. 0.25 mm silica gel pre-coated plates (Fluka) were used for thin layer chromatography.

7.3. PROCEDURES

1. Preparation of Acetanilide.

In 500 mL round bottom flask equipped with a reflux condenser, aniline (500 mL), acetic anhydride (60 mL), glacial acetic acid (50 mL) and of zinc dust (1 g) were placed. The mixture was then refluxed for 30 min and then poured in to a beaker containing ice-cold water (1250 mL). The mixture was stirred while the product crystallized. The crude product was filtered by suction and the solid residue was washed three times with ice cold water. The product was dried and its yield was 83.5g.

2. Preparation of *p*-Nitroaniline (75)

To acetanilide (81.58g, 0.6mol) which was placed in a 500 mL Erlenmeyer flask, conc. H_2SO_4 (60 mL) was added. The mixture was swirled until most of the acetanilide dissolved and the flask was placed in an ice bath. In another flask, the nitrating mixture was prepared by adding cold conc. H_2SO_4 (160 mL) drop-wise to cold conc. HNO_3 (60 mL) (ice-water bath). Using a Pasteur pipette small portions of the mixed acids was added to the cooled H_2SO_4 solution of acetanilide by swirling the mixture thoroughly after each addition. After 20 min., including the time required for the addition of the nitrating mixture, ice water (112 mL) was added. The suspension of nitroacetanilde was allowed to stand for 5 min. with occasional stirring.

3. HYDROLYSIS OF *p*-NITROACETANILIDE

p-Nitroacetanilide obtained in the above experiment was refluxed with 10% H_2SO_4 (981 mL) solution for 1 hour. The solution was rendered alkaline with 20% NaOH solution that gave a precipitate. The precipitate was filtered by suction. The residue was washed three times with distilled water. The solid residue was dried and then recrystallized from ethanol to afford 17.2 g of a crystalline product, which was collected by suction filtration. The crystals were dried and the melting point was determined to be 145.5-148.8°C (Lit (148.5-149.5°C).

4. Synthesis of 4-(4-nitrophenylazo)-benzene-1,3-diol (76)

p-Nitroaniline (12 g, 0.086 mol), was placed in a one-liter beaker and water (32 mL) and conc. HCl (20 mL) were added to it. The content of the beaker was warmed to give a clear solution. The beaker was placed in an ice bath and cooled to 20°C during which *p*-nitroaniline hydrochloride separated in a finely divided crystalline form. To this cooled mixture a cold (3°C) solution of $NaNO_2$ (12 g, 0.086 mol) in water (60 mL) was added slowly with stirring. The diazonium salt solution was kept in an ice bath for 45 min. at a temperature of 6°C (solution A).
In a one-liter Erlenmeyer flask containing a solution of resorcinol (12g) in 22% NaOH solution (64 mL), water (80 mL) was added (solution B).
Solution B was cooled in an ice bath and to it a solution of *p*-nitrobenzene diazonium chloride (solution A) was added with stirring. To this mixture conc. HCl was added gradually with vigorous stirring, making the mixture strongly acidic to Congo red paper. The solution was filtered with gentle suction filtration and the solid residue was washed with water until it became free from acid. The residue was air-dried which gives 25.04 g of the product. FT-IR (KBr) ν_{max} (cm^{-1})**:** 3398, 1653, 1594, 1477, 1338, 1209, 1160, 1107, 1043.

5. Synthesis of (2,4-bis-octyloxyphenyl)-(4-nitrophenyl)-diazene (77)

In a three-necked round bottom flask 4-(4-nitrophenylazo) benzene-1,3-diol (10 g), DMF (80 mL) and anhydrous K_2CO_3(34 g) was added. The mixture was stirred at 100°C and 1-bromooctane (13.4 mL) was added drop-wise from a pressure-equalizing dropping funnel. The mixture was heated under nitrogen atmosphere for 8 h and the progress of the reaction was checked by TLC. The mixture was then cooled to room temperature and filtered by suction. The filtrate was acidified with 2M HCl and extracted with diethyl ether. The extract was washed with 1M NaOH solution followed by brine solution. It was then dried over anhydrous sodium sulfate and the ether was removed by rotary evaporator to affording compound **77 (**11.8 g, 63%). ^{1}H-NMR ($CDCl_3$. 400.13 MHz)**:** δ 8.3 (*d*, *J* = 9.6 Hz, 2H,H-2, H-6), 8.0 (*d*, *J* = 9.6 Hz, 2H,H-3, H-

5), 7.8 (*d*, *J* = 8.8 Hz, 1H,H-14), 6.6 (*d*, *J* = 2.4 Hz, 1H, H-11), 6.6 (*dd*, *J* =, 8.8, 2.4 Hz, 1H, H-13), 4.1 (*t*, 2H, H-8"), 4.0 (*t*, 2H, H-8'), 1.9 (*q*, 2H, H-7"), 1.8 (*q*, 2H, H-7'), 1.7-1.3 (*m*, 20H, H-2'to H-6' and H-11'), 0.9 (*t*, 6H, H-1'); ^{13}C-NMR($CDCl_3$, 100.6 MHz)**:** δ 156.69,124.68, 123.08, 147.83, 123.08, 124.68, 136.92, 159.70, 100.61, 164.84, 106.80, 118.16, 29.35, 14.13, 22.29, 31.81, 29.25, 26.02, 29.31, 68.56, 69.61.

6. Synthesis of 2,7-Dibromofluoren-9-one (79).

To a suspension of 2,7-dibromofluorene (6.38 g) in acetic anhydride (110 mL), CrO_3 (4.8 g) was added at room temperature. The reaction mixture was stirred for 5 h and the solution was then added to 2%HCl (200 mL of) solution. The suspension was then filtered off by suction and washed with cold water. The product was recrystallized from isopropyl alcohol to provide compound **79** (6.44 g, 98%) as a yellow solid yield. Mp.198-202°C; FT-IR (KBr)ν_{max} (cm^{-1})**:** 1725, 1708, 1592, 1445, 1419, 1244, 1181, 1055, 821, 780, 683, 471; ^{1}H-NMR ($CDCl_3$, 400.13 MHz): δ 7.7 (*Broad singlet*, 2H, H-1,H-8,), 7.6 (*d*, *J* = 8 Hz, 2H, H-3, H-6), 7.4 (*d*, *J* = 8 Hz, 2H, H-4, H-5); ^{13}C-NMR ($CDCl_3$, 100.6 MHz)**:** δ 190.9, 142.2, 137.4, 135.3, 127.8, 123.3, and 121.8.

7. Attempted synthesis of 2,7-dibromofluoren-9-ylide-(4-nitrophenyl)-aniline .

In a 500 mL RB flask 2,7-dibromofluoren-9-one (1 g, 0.003mol)) was dissolved in acetic acid (100 mL). To this was added *p*-nitroaniline (0.412 g, 0.003 mol) and was refluxed at 100°C with stirring while following the progress of the reaction by TLC. The reaction was continued for 15 days and the formation of no product was observed.

8. Synthesis of octyloxy-*p*-bromobenzene (64)

To a mixture of *p*-bromophenol (10 g, 0.06mol) and DMF (80 mL) in three-necked round bottom flask, anhydrous potassium carbonate (35 g) was added. The mixture was stirred at 100°C and 1-bromooctane (9.88 mL, 0.06 mol) was drop-wise from a pressure-equalizing dropping funnel. After the addition was complete, heating continued under nitrogen atmosphere for 5 h. and the progress of the reaction was followed by TLC. The mixture was then cooled to room temperature and filtered. The filtrate was acidified with 2 M HCl and extracted with diethyl ether, and the extract was washed with 1 M NaOH followed by brine solution. It was then dried over anhydrous Na_2SO_4 and the solvent was removed by rotary evaporator to afforded compound **64** (11.16g, 68%) as a yellowish liquid. ^{1}H-NMR ($CDCl_3$, 400.13 MHz)**:** δ 7.3 (*d*, *J* = 6.2 Hz, 2H, H-3, H-5), 6.8 (*d, J* = 6.2 Hz, 2H, H-2, H-6), 3.93(*t*, 2H, H-8'), 1.8 (*q*, 2H, H-7'), 1.3-1.5 (*m*, 10H, H-2'to H-6'), 0.92 (*t*, 3H, H-1'); ^{13}C-NMR ($CDCl_3$, 100.6 MHz)**:**δ 158.2, 132.1, 116.2, 112.5, 68.2, 31.8, 29.4, 29.2, 26.0, 22.0, 14.1.

9. Synthesis of 1,2-bis- (4-(octyloxy)-phenyl)-ethane-1,2-dione (65)

A Grignard reagent was prepared by dropwise addition of 1-bromo-4-octyloxy benzene (8.0 g, 0.028 mol) in THF (20 mL) to a suspension of magnesium (0.8 g, 0.0334 mol) in THF (18 mL). In a separate flask, a solution of LiBr (5.17 g. 59.4 mmol) in THF (20 mL) was added to a stirred suspension of CuBr (4.28 g, 29.7 mmol) in THF (20 mL). The mixture was stirred until it became homogenous and was cooled to -15°C using an immersion cooler. The Grignard reagent was added to the LiBr/CuBr suspension and after 10 minutes, oxalylchloride (1.89 g, 14.88mmol) was then added. The mixture was kept at -15 °C for 30 min. and was quenched with saturated NH_4Cl. The organic layer was separated, washed with saturated NH_4Cl dried over anh. Na_2SO_4 and the solvent was removed to afford compound **65 (**7.1 g) as a pale yellow oil. Silica gel column chromatography was conducted using pet spirits:ethyl acetate (4.5:0.5) as eluent to give 3.1 g pure product as a pale yellow solid.

FT-IR (KBr)ν_{max} (cm^{-1})**:** 2924, 2855, 1661, 1602, 1573, 1263, 1232, 1163, 888, 842, 765, 649, 619 and 411; ^{1}H-NMR ($CDCl_3$. 400.13 MHz): δ 7.9 (*d*, *J* = 8.8 Hz, 4H, H-3, H-5), 6.9 (*d*, *J* = 8.8 Hz, 4H, H-2, H-6), 4.0 (*t*, 4H, H-8'), 1.8 (*m*, 4H, H-7'), 1.6-1.2 (*m*, 10H, H-2'to H-6'), 0.95 (*t*, 6H, H-1'); ^{13C}-NMR ($CDCl_3$, 100.6 MHz)**:** δ 193.5, 164.5, 132.3, 126.1, 114.7, 68.5, 31.8, 29.2, 26.0, 22.7, 14.1

10. Synthesis of 2,5-dibromo-3,4-dinitrothiophene (32)

Concentrated H_2SO_4 (74.3 mL), fuming H_2SO_4 (114.3 mL), and fuming HNO_3 (63 mL) were combined in a one-liter round bottom flask and cooled over an ice bath. 2,5-dibromothiophene (20 mL, 22.94 g, 94.79 mmol) was added dropwise to maintain a temperature of 20-30^{o}C. The mixture was allowed to react for a total of 8 h and then poured onto ice (515 g). The solid product was recovered by vacuum filtration, washed with distilled water, and recrystallized from hot isopropyl alcohol to give compound **32** (30.04 g, 95.5%). Mp.135.3-136^{o}C.

11. Synthesis of 2,5-dithiophene-3, 4-dinitrothiophene (33).

To a solution of 2,5-dibromo-3,4-dinitrothiophene (10 g, 30 mmol) and tributyl (thiophen-2-yl)stannane (19 mL, 55.47 g, 60.2 mmol) in toluene (110 mL), $PdCl_2(PPh_3)_2$ (0.422 g) was added. The mixture was refluxed for 12 h under nitrogen atmosphere and the solvent was removed over a rotary evaporator. The residue was taken-up in hexane and the resulting solid was separated by suction filtration to afford compound **33** (7.38 g , 72.3%). Mp**.**143-143.6^{o}C. ^{1}H-NMR ($CDCl_3$, 400.13 MHz)**:** δ 7.6 (*dd*, *J* = 5.2 1.2 Hz, 2H, H-5, H-5”), 7.5 (*dd*, *J* = 3.6, 1.2 Hz, 2H, H-3, H-3”), 7.2 (*dd*, *J* = 5.2, 3.6 Hz, 2H, H-4, H-4”); ^{13}C-NMR ($CDCl_3$, 100.6 MHz)**:** δ 135.9, 133.8, 131.2, 131.1, 128.4, 128.0.

12. Synthesis of 5,5’’-Dibromo-3, 4-dinitro-2, 2’: 5’, 2’’-terthiophene (59).

2,5-Dithiophen-3,4-dinitrothiophene(5 g, 0.0146 mol) was dissolved in DMF (50 mL) at room temperature. To this was added a solution of NBS (5.2 g, 0.029 mol) in DMF (50 mL) dropwise from a pressure equalizing dropping funnel. The mixture was stirred for 16 h under nitrogen atmosphere and the resulting pale-yellow precipitate was filtered by suction and was washed five times with methanol. The product was dried and weighed to give compound **59** (6.18 g, 84.6%). FT-IR (KBr)ν_{max} (cm^{-1})**:** 3097, 1700, 1696, 1685, 1653, 1559, 1553, 1415, 1386, 1335, 1278, 797; ^{1}H-NMR ($CDCl_3$, 400.13 MHz)**:** δ 7.345 (*d*, *J* = 4 Hz, 1H, H-4, H-4”), 7.16 (*d*, *J* = 4Hz, 1H, H-3, H-3”).

13. Synthesis of 5,5’’-dibromo-3,4-diamino-2,2’:5’,2’’-terthiophene (60).

5,5’’-Dibromo-3`,4`-dinitro-2,2’:5’,2’’-terthiophene (2 g,4.03mmol), iron powder (0.451 g, 8.05mmol) and acetic acid (25 mL) were mixed and heated at 40^{o}C for 45 min. The mixture was then basified with dil. NaOH solution and was extracted with ether, washed with brine and dried over anh. Na_2SO_4. Removal of the solvent afforded compound **60** (1.23 g). as a greenish-yellow solid. ^{1}H-NMR ($CDCl_3$. 400.13 MHz): δ 7.0 (*d*, *J* = 6 Hz, 2H, H-4, H-4”), 6.8 (*d*, *J* = 6 Hz, 2H, H-3, H-3”), 3.7(*Broad singlet*, 4H, 2 X NH_2); ^{13}C-NMR ($CDCl_3$, 100.6 MHz)**:** δ 137.2, 133.9, 130.5, 124.4, 110.8,109.8.

14. Synthesis of 5,7-bis-(5-bromo-thiophen-2-yl)-2,3-bis-(4-octyloxy-phenyl)-thieno (3,4-b)pyrazine (66).

5,5’’-Dibromo-3`,4``-dinitro-2,2’:5’,2’’-terthiophene (1 g, 2.29 mmol) and 1,2-bis [4-(2-octayloxy)-phenyl] ethane-1, 2-dione (1.07 g, 2.29 mmol) were dissolved in acetic acid (55 mL) and heated at 60^{o}C for 5 h. The mixture was then cooled to room temperature and the precipitate was collected by filtration, washed with water and MeOH and dried to yield a dark solid (1.3 g) which was chromatographed using pet ether:ethyl acetate (4.5:0.5) as eluent to afford 0.65 g). The product contained impurities and was thus further chromatographed on a silica gel column using a mixture of pet ether: toluene (3:2) as eluent to afford compound **66** (0.40 g) in a pure form. FT-IR (KBr)ν_{max} (cm^{-1})**:** 2923, 2852, 2361, 1604, 1511, 1466, 1429, 1360, 1248, 1176, 969, 830, 792, 778, 605, 478; ^{1}H-NMR($CDCl_3$. 400.13 MHz)**:** δ 7.52(*d*, *J* = 8.8 Hz, 4H, H-3, H-5), 7.23 (*d*, *J* = 4 Hz, 2H, H-4”), 7.00 (*d*, *J* = 4 Hz, 2H, H-3”), 6.86 (*d*, *J* = 8.8 Hz, 4H, H-2, H-6), 4.1 (*t*, 4H, H-8’), 1.75 (*q*, 4H, H-7’), 1.6-1.2 (*m*, 20H, H-2’ to H-6’), 0.95 (*t*, 6H, H-1’); ^{13}C-NMR ($CDCl_3$, 100.6 MHz): δ 160, 153, 137, 136, 131.5, 131.1, 129, 123.8, 123.5, 114.3, 68, 31.8, 30.9, 29.3, 29.2, 26, 22,14.

15. Attempted reduction of (2,4-bis-octyloxyphenyl)-(4-nitrophenyl)-diazene (77).

(2,4-Bisoctyloxyphenyl)-(4-nitrophenyl)-diazene (4.48 g, 9.27 mmol), iron powder (0.8 g, 14 mmol) and acetic acid (100 mL) were mixed and heated to 40°C for 3 h. The mixture was cooled and was then poured on to cold 2N NaOH solution. The alkaline solution was extracted with ether, washed with brine, dried over anh. Na_2SO_4, and the solvent was removed to afford 2.62 g a product, which after silica gel column chromatography with CH_2Cl_2: $CH_3COOC_2H_5$ (3:2) as eluent gave rise to 1.62 g of an unexpected product. This product was characterized as 2,4-dioctyloxyaniline.

16. Attempted synthesis of (2,4-bis-octyloxy-phenyl)-(2,7-dibromo-fluoren-9-ylidene)-amine.

2,7-Dibromofluorenone (1.45 g, 4.29 mmol) was allowed to react with 2,4-dioctyloxyaniline (1.5 g, 4.3 mmol) in acetic acid (150 mL) in the presence of methane sulfonic acid as a catalyst. The progress of the reaction was checked by TLC. The reaction was allowed to continue for 10 days and during this time no product was observed.

17. Synthesis of 2,7-dibromo-9, 9-dioctylfluorene (73).

2,7-Dibromofluorene (20 g, 61.7 mmol) was reacted with *n*-bromooctane (23.83 g, 22 mL, 123.9 mmol) in a two-phase system composed of toluene (133 mL) and aqueous NaOH (50%W/W) (133 mL) using tetrabutylammonium bromide (2 g, 6.2 mmol) as a phase transfer catalyst. The mixture was heated at 60°C under nitrogen atmosphere and the progress of the reaction was followed by TLC. After the reaction was complete, the mixture was diluted with ethyl acetate (200 mL), and the organic layer was separated and was washed with water thoroughly, dried over anh. Na_2SO_4 and the solvent was removed to give an oily product. Addition of small amount of MeOH and CH_2Cl_2, followed by removal of solvent using a rotary evaporator gave a solid product. The product was recrystallized from isopropyl alcohol (30.82 g, 91.2% yield).
Mp**:** 50-53.9°C; FT-IR (KBr)ν_{max} (cm^{-1})**:** 2954, 2926, 2853, 1622, 1448, 1415, 1060, 808; ^1H-NMR ($CDCl_3$,.400.13 MHz)**:** δ 7.5 (*dd*, *J* = 6.4, 2Hz, 2H, H-3, H-6), 7.4 (*Broad singlet*, 2H, H-4,

H-5), 7.4 (*d*, *J* = 2 Hz, 2H, H-1, H-8), 1.9 (*m*, 4H, H-8'), 1.4-1.05 (*m*, 20H, H-2' to H-6'), 0.85 (*t*, 6H, H-1'), 0.65 (*m*, 4H, H-7'); ^{13}C-NMR ($CDCl_3$, 100.6 MHz): δ 152.5, 139.0, 130.1, 126.2, 12.5, 55.7, 40.1, 31.7, 29.8, 29.2, 29.1, 23.6, 22.6, 14.1.

18. Synthesis of 2,7-bis (4`,4`,5`,5``-tetramethyl-1,3-2-dioxaborolane)-9,9-dioctyl fluorene (62).

To a solution of 2,7-dibromo-9,9-dioctyl fluorene (14 g, 25.55 mmol) in THF (150 mL) at -78^{o}C, a 2.5 M solution of *n*-BuLi (22 mL) was added by a syringe and the mixture was stirred at –78^{o}C for one h. 2-Isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (11 mL) was added rapidly to the reaction mixture and the resulting solution was warmed for 5 h. The mixture was poured in to water (150 mL) and extracted with ether. The organic extracts were washed with brine and dried over anh. Na_2SO_4. After filtration, the solvent was removed by rotary evaporation to gave a crude product (16 g) that was reccrystallized from isopropyl alcohol to afford compound **62** (12.5g, 76.3%) as needle-like crystals. Mp: 127-131^{o}C; FT-IR (KBr)ν_{max} (cm^{-1})**:** 2973, 2950, 2926, 2855, 1608, 1577, 1477,1467, 1426, 1370, 1346, 1328, 1256, 1143, 1079, 966, 826,700, 633; ^{1}H-NMR($CDCl_3$, 400.13MHz)**:** δ7.83 (*dd*, *J* = 7.6, 0.8 Hz, 2H, H-3, H-6), 7.7 (*Broad singlet*, 2H, H-1, H-8), 7.75 (*dd*, *J* = 7.6 Hz, 2H, H-4, H-5), 2.00 (*m*, 4H, H-8'), 1.4 (*s*, 24H, H-6" to H-9"), 1.25-1.00 (*m*, 20H, H-2' to H-6'), 0.85 (*t*, 6H, H-1'), 0.55 (*m*, 4H, H-7'); ^{13}C-NMR ($CDCl_3$, 100.6 MHz)**:** δ 150.4, 143.9, 133.6, 128.9, 119.3, 83.7, 55.1, 40.1, 31.7, 29.9, 29.2, 29.1, 24.9, 23.9, 22.60,14.0.

19. Synthesis of poly-2, 7-(9,9-dioctylfluorene-*alt*-5,5-(5,7-bis 2-thiophene)-2,3-bis- (4 octyloxy-phenyl thieno(3,4-b)pyrazine (87).

Compound **66** (0.2212g, 25.5mmol) was mixed with 2,7-bis-(4',4',5",5"-tetramethyl-1,3,2-dioxaborolane-2-yl)-9,9-dioctylfluorene (**62**) (0.165 g, 25.5 mmol), tetrakistri-phenylphosphine palladium(0) (20 mg) and toluene (12 mL) and was refluxed for 10 min. under nitrogen atmosphere. Tetraethylammonium hydroxide (1 mL, 20% by weight in water) was introduced and the mixture was refluxed for 2 h. Bromobenzene (55 mg) was added and after 1 h phenylboronic acid (44 mg) was introduced. The mixture was allowed to reflux for 1 h, cooled to room temperature and the polymer was precipitated by slowly adding the mixture in to MeOH, filtered, washed with MeOH and dried. The resulting solid was dissolved in chloroform, and was washed with ammonia (twice) and with water (twice) and was concentrated to a small volume and the polymer was reprecipitated from MeOH, filtered and dried. The dark-colored solid was Soxhlet extracted with ether and chloroform. The chloroform portion was concentrated to a small volume and the polymer was reprecipitated from MeOH, filtered and dried to afford polymer **87** (0.205 g).

FT-IR(KBr)ν_{max}(cm^{-1})**:** 3420, 2922, 2846, 2360, 2342, 1653, 1600, 1509, 1466, 1411, 1346,1212, 1170, 1075, 982, 832, 668, 418; UV-Vis(λmax) nm: 429, 649.

20. Synthesis of 5,5``-dibromo-3`,4``-diamino-2,2`:5`,2``-terthiophene (60).

Compound **59** (2.5 g, 5.04 mmol) was suspended in EtOH (28 mL) and concentrated HCl (55 mL). To this was added a solution of anhydrous $SnCl_2$ (50 g) in EtOH (60 mL) and the mixture was stirred at room temperature for 18 h and poured in to a cold 25% NaOH solution. Toluene (200 mL) was added to the above mixture, and then, the reaction mixture was shaken vigorously and filtered through celite. The phases were separated and the aqueous layer was extracted with toluene. The combined organic layer was washed with brine and dried over anh Na_2SO_4. After removal of the solvent by rotary evaporation, compound **60** (1.3 g) was obtained.

^{1}H-NMR ($CDCl_3$, 400.13 MHz)**:** δ 7.0 (*d*, *J* = 6 Hz, 2H, H-4, H-4”), 6.8 (*d*, *J* = 6 Hz, 2H, H-3, H-3”), 3.7 (*Broad singlet*, 4H, 2 X NH_2); ^{13}C-NMR($CDCl_3$, 100.6 MHz)**:** δ 137.2, 133.9, 130.5, 124.4, 110.8, 109.8.

21. Synthesis of 5,5``-dibromo-3’,4``-di(iminometyl-phenol)-2,2`:5’’,2``-terthiophene (70).

5,5``-Dibromo-3`,4`-diamino-2,2`:5`,5``-terthiophene (1.2 g, 0.0028 mol) and salicylaldehyde (0.68 g, 0.0056 mol) were dissolved in acetic acid (60 mL) and heated to 60°C for 1 h. The mixture was cooled to room temperature and the precipitate was filtered, washed with water and MeOH, and dried to yield compound **70** (1.67 g).

^{1}H-NMR (CDCl$_3$. 400.13 MHz)**:** δ 12.35(*s*, 2H, -2OH), 8.6 (*s*, 2H, alkenic hydrogen), 7.42 (*dt*, 2H, H-12), 7.23 (*dd*, *J* = 7.6, 1.2 Hz, 2H, H-10), 7.044 (*broad singlet*, 2H, H-11), 7.02 (*broad singlet*, 4H, H-3', H-4'), 6.91 (*dt*, 1H, H-9); ^{13}C-NMR(CDCl$_3$, 100.6 MHz): δ 160.6, 137.7, 135.5, 122.0, 118.5, 113.7, 169, 134, 133, 130, 125, 119, 117.

22. Attempted synthesis of 5,5``-dibromo-3`,4``-di((2-octyloxy-benzylidene)-amine)-2,2`:5'',2``-terthiophene (71).

To a mixture of compound **70** (1.4g, 0.0022 mol) and DMF (50 mL) in a two-necked round bottom flask, K$_2$CO$_3$, (5 g) was added. The mixture was heated at 100^{o}C under nitrogen atmosphere and 1-Bromooctane (0.9 g, 0.0047 mol) was added drop-wise from a pressure equalizing dropping funnel. The progress of the reaction was checked by TLC. The mixture was cooled to room temperature and filtered using fluted filter paper. The filtrate was acidified using 2M HCl and extracted with CH$_2$CH$_2$ and the extract was washed with NaOH followed by brine solution; and dried over anhydrous Na$_2$SO$_4$. The solvent was removed using rotary evaporator to afford 1.16 g impure product was obtained. After silica jel column chromatography using 2.5:2.4:0.1 mixture of phenol: Toluene: ethylacetate, respectively again an impure product was obtained.

23. Synthesis of 2-hexyloxy-benzaldehyde (68).

Salicylaldehyde (10 g, 0.082 mol), K$_2$CO$_3$ (20 g) and DMF (20 mL) were placed in a two-necked round bottom flask and heated at 100^{o}C. To this was added drop-wise *n*-hexylbromide (13.6 g, 11.55 mL, 0.094mol) from a pressure equalizing dropping funnel. The progress of the reaction was checked by TLC. After the reaction was complete, the mixture was cooled to room temperature and filtered. The filtrate was acidified using 2M HCl and extracted with CH$_2$Cl$_2$ and the extract was washed with NaOH followed by brine solution, and dried over anhydrous Na$_2$SO$_4$. The solvent was removed under reduced pressure to afford compound **68** (12.03 g).

^{1}H-NMR (CDCl$_3$. 400.13 MHz)**:** δ 10.5 (*s*, 1H, H-1"), 7.82 (*dd*, *J* = 7.6, 1.6 Hz, 1H, H-3), 7.52 (*dt*, *J* = 7.2,1.6 Hz, 1H, H-5), 6.95 (*m*, 2H, H-4, H-6), 4.15 (*t*, 2H, H-1'), 1.9-1.3 (*m*, 8H, H-2' to

H-5’), 0.9 (*t*, 3H, H-6’); ^{13}C-NMR(CDCl$_3$, 100.6 MHz)**:** δ 189.8, 161.5 135.9, 128.0, 124.8, 120.4, 112.4, 31.4, 29.0, 25.7, 22.5,13.9.

24. Synthesis of 5,5``-dibromo-3`,4``-di((2-hexyloxy-benzylidene)-amine)-2,2`:5’’,2``-terthiophene (69).

5,5``-Dibromo-3,4-diamino-2,2`:5`,2`-terthiophene (2.4 g, 0.08 mol) and 2-hexyloxy-benzaldehyde (2.3 g, 0.016 mol) were dissolved in acetic acid (60 mL) and heated at 60^{o}C for 1 h. The mixture was cooled to room temperature and the precipitate was filtered, washed with water followed by MeOH, and dried over anh. Na$_2$SO$_4$ to afford a solid product (2.2 g), which was chromatographed over a column of silica gel using a mixture of CH$_2$Cl$_2$:n-pentane (3:2)_ to afford compound **69** (1.8 g). FT-IR (KBr) ν_{max} (cm^{-1})**:** 3420, 2954, 2867, 2359, 1593, 1574, 1456, 1430, 1368, 1238, 1159, 1044, 779, 757, 463; ^{1}H-NMR (CDCl$_{3.}$ 400.13 MHz)**:** δ 8.90 (*s*, 2H, H-9”), 8.31 (*dd*, *J* = 7.6,1.6 Hz, 2H, H-3), 7.6 (*dt*, *J* = 8,1.6,Hz, 1H, H-5), 7.1 (*t*, 1H, H-2), 7.0 (*d*, *J* = 4 Hz, 2H, H-4”), 6.95 (*d*, *J* = 4 Hz, 2H, H-3”), 6.85 (*d*, 1H, H-4), 3.8 (*t*, 4H, H-1’),1.6-1.1 (*m*, 8H, H-2’ to H-5’), 0.85 (*t*, 6H. H-6’); ^{13}C-NMR (CDCl$_3$, 100.6 MHz)**:** δ 160.5, 159.5, 140.3, 137.0, 132.9, 129.4,127.8, 124.6, 123.7, 121.6, 120.6, 113.9, 111.9, 68.4, 31.4, 28.7, 25.5, 22.5, 14.0; UV-Vis (λmax) nm: 352, 418.

25.Poly-2,7-(9,9-dioctylfluorene-*alt*-5,5-(3,4-di-(2-hexyloxybenzlideneimino)-2,2’:5,2”-tertthiophene (88).

Compound **69** (0.22 g, 27 mmol) was mixed with 2,7-bis (4’,4’,5”,5”-tetramethyl-1,3,2-dioxaborolane-2-yl)-9,9-dioctylfluorene(0.174 g, 27 mmol), tetrakistriphenylphosphine palladium(0) (20 mg) and toluene (12 mL) and the mixture was refluxed for 10 min. under nitrogen atmosphere. Tetraethylammonium hydroxide (1 mL, 20% by weight in water) was introduced and the mixture was refluxed for 1½ h. Bromobenzene (58 mg) was added and after 1 h phenylboronic acid (46 mg) was introduced. The mixture was allowed to reflux for 1 h, cooled to room temperature and the polymer was precipitated by slowly adding the mixture in to MeOH, filtered, washed with MeOH and dried. The dark-colored solid was dissolved in chloroform, and was washed with ammonia (twice) and with distilled was (twice), concentrated to a small volume and the polymer was repreciptatd from MeOH. The dark colored solid was collected by filtration and was Soxhlet extracted with ether and chloroform. The chloroform portion was concentrated to a small volume and the polymer was reprecipitated from MeOH, dried and filtered to afford polymer **88** (0.158 g).

FT-IR (KBr)ν_{max} (cm^{-1})**:** 3422, 2925, 2852, 1617, 1596, 1457, 1368, 1297, 1239, 1159, 1079, 997, 870, 817, 752; UV-Vis (λmax) nm**:** 394, 484.

26. Poly-2,7-(9,9-diethylhexylfluorene-*alt*-5,5-(3,4–di-(2-hexyloxybenzlideneimino)-2,2’: 5,2”-terthiophene (89).

Compound **69** (0.252 g, 30.9 mmol) was mixed with 2,7-bis (4’,4’,5”,5”-tetramethyl-1,3,2-dioxaborolane-2-yl)-9,9-dioctylfluorene (0.200 g, 30.9 mol), tetrakistriphenyl- phosphine palladium(0) (20 mg) and toluene (12 mL) and was refluxed for 10 min. under nitrogen atmosphere. Tetraethylammonium hydroxide (1 mL, 20% by weight in water) was introduced and the mixture was refluxed for 1½ h. Bromobenzene (67 mg) was added and after 1 h phenylboronic acid (53.2 mg) was introduced. The mixture was allowed to reflux for 1 h, cooled to room temperature and the polymer was precipitated by slowly adding the mixture in to MeOH, filtered, washed with MeOH and dried. The dark-colored solid was dissolved in chloroform, and was washed with ammonia (twice) and with distilled was (twice), concentrated to a small volume and the polymer was reprecipitated from MeOH. The dark colored solid was collected by filtration and was Soxhlet extracted with ether and chloroform. The chloroform portion was concentrated to a small volume and the polymer was reprecipitated from MeOH, dried and filtered to afford polymer **89** (0.149 g).

FT-IR (KBr) ν_{max} (cm^{-1})**:** 4321, 2955, 2926, 2854, 1616, 1596, 1457, 1369, 1297, 1271, 1209, 1080, 996, 869, 818, 753;Uv-Vis (λmax) nm**:** 388, 478.

27. Synthesis of -1,3-heptyloxy benzene (86).

To a mixture of resorcinol (10 g, 0.09 mol) and DMF (100 mL) in a two-necked round bottom flask, K_2CO_3 (35 g) was added. The mixture was heated at 100^{o}C under nitrogen atmosphere and heptylbromide (32.55 g, 0.18 mol,) was added from a pressure equalizing funnel drop-wise. The progress of the reaction was followed by TLC. After the reaction was complete, the mixture was cooled to room temperature and filtered. The filtrate was acidified using 2M HCl and extracted with ether and the extract was washed with NaOH followed by brine solution, dried over anhydrous Na_2SO_4 and the solvent was removed using a rotary evaporator to afford compound **86** (23.83 g). ^{1}H-NMR ($CDCl_3$. 400.13 MHz)**:** δ 7.2 (*m*, 1H, H-6), 6.55 (*m*, 3H, H-2, H-4, H-6), 4.00 (*t*, 4H, H-8'), 1.85 (*m*, 4H, H-7'), 1.6-1.3 (*m*, 16H, H-2' to H-5'), 1.00 (*t*, 6H, H-6'); ^{13}C-NMR($CDCl_3$, 100.6 MHz)**:** δ 160, 129, 106, 101, 67, 31. 9, 29.4, 29.2, 26.1, 22.6, 14.1.

28. Attempted synthesis of *N*- (2,7-dibromo-fluoren-9-ylidene)-benzene-1,4-diamine

2,7-Dibromofluorenone (2.25 g, 0.007 mol) and *p*-phenylenediamine (0.72 g, 0.007 mol) were dissolved in acetic acid (75 mL) and heated to 60°C for 2 h. The mixture was then cooled to room temperature and the precipitate was collected by filtration, washed with water and MeOH and dried to yield a brick-red solid (2.2 g). The solid compound was insoluble in common organic solvent.

29. Poly-2,7-(9,9-dioctylfluorene-5,5-(5,7-bis-2-thiophen)-2,3-bis-(4-octyloxy-phenyl)thieno(3,4-b)pyrazine-*ran*-2,7-(9,9-dioctylfluorene-5,5-bis(2"thienyl)-4,4 dipentyl-2,2'-bithazole-5",5"-diyl (90).

Compound **66** (0.111g, 0.124mmol) was mixed with 2,7-bis-(4',4',5",5"-tetramethyl-1,3,2-dioxaborolane)-9,9-dioctylfluorene (0.159g,0.247mmol) and 5,5-bis(5-bromo-thienyl)-4,4'-dipentyl-2,2'-bithazole-5",5"-diyl[35] (77.3mg,0.124mmol), tetrakistriphenyl phosphine palladium (0) (20 mg) and toluene (12 mL) and was refluxed for 10 min. under nitrogen atmosphere. Tetraethyl-ammonium hydroxide (1 mL, 20% by weight in water) was introduced and the mixture was refluxed for 2 h. Bromobenzene (54 mg) was added and after 1 h phenylboronic acid (43 mg) was introduced. The mixture was allowed to reflux for 1 h, cooled to room temperature and the polymer was precipitated by slowly adding the mixture in to MeOH, filtered, washed with MeOH and dried. The dark-colored solid was dissolved in chloroform, and was washed with ammonia (twice) and with distilled was (twice), concentrated to a small volume and the polymer was repreciptatd from MeOH. The dark colored solid was collected by filtration and was Soxhlet extracted with ether and chloroform. The chloroform portion was concentrated to a small volume and the polymer was reprecipitated from MeOH, dried and filtered to afford polymer **90** (0.205 g). FT-IR (KBr) ν_{max} (cm^{-1})**:** 3447, 2923, 1654, 1508, 1458, 1246; UV-Vis (λ_{max}) nm**:** 438, 630.

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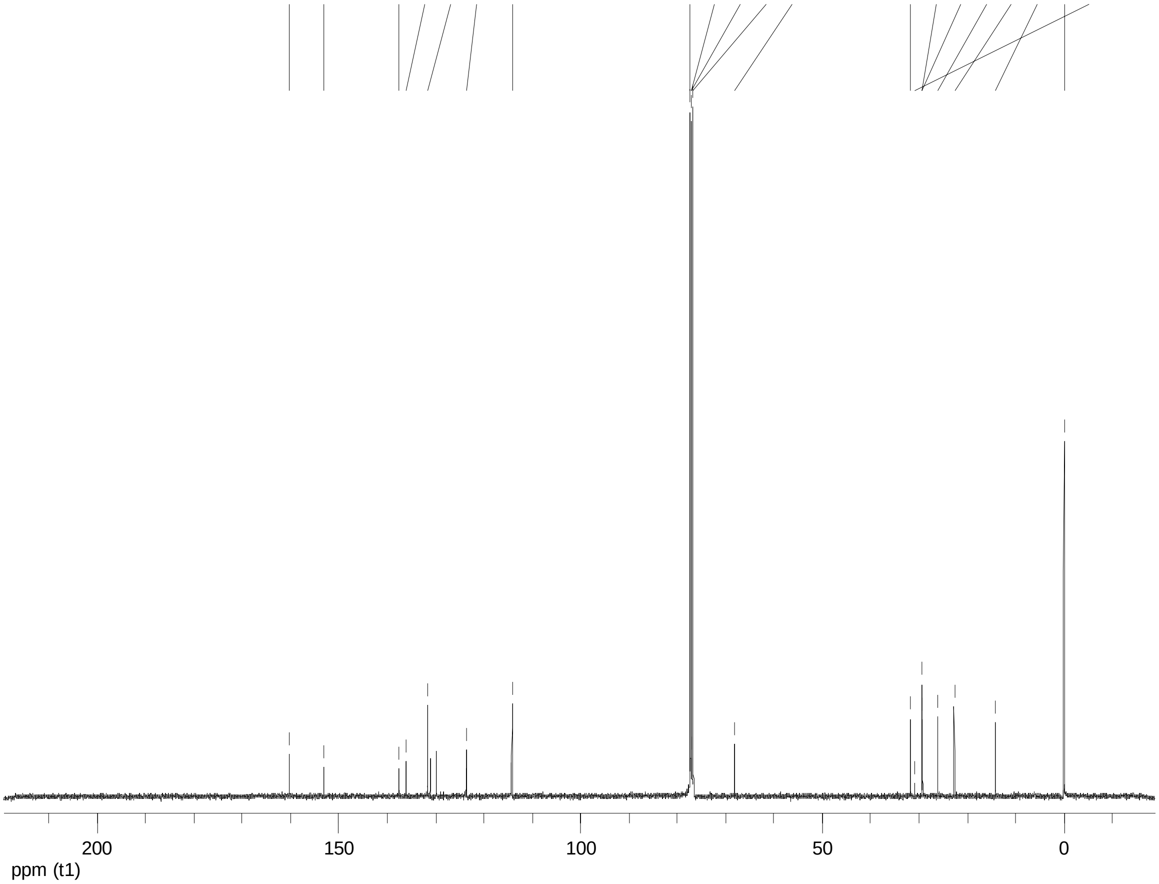
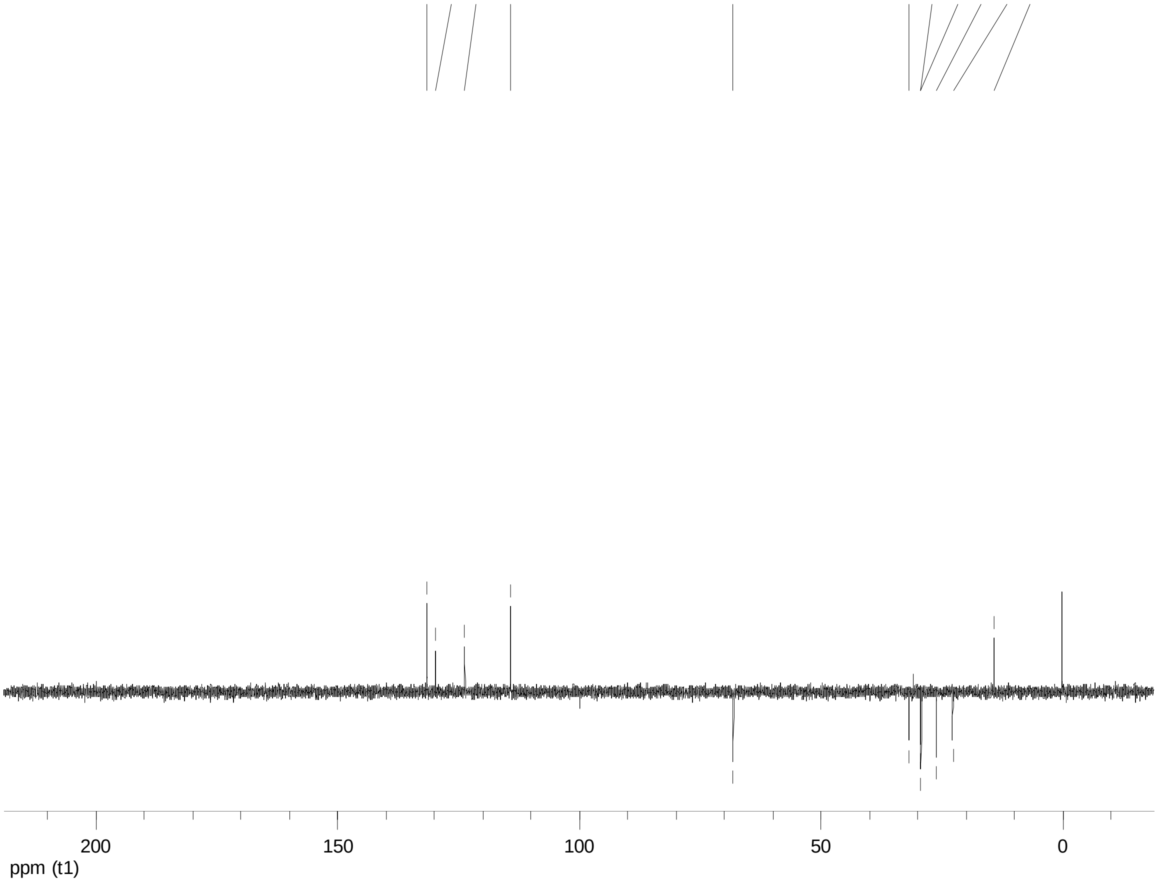
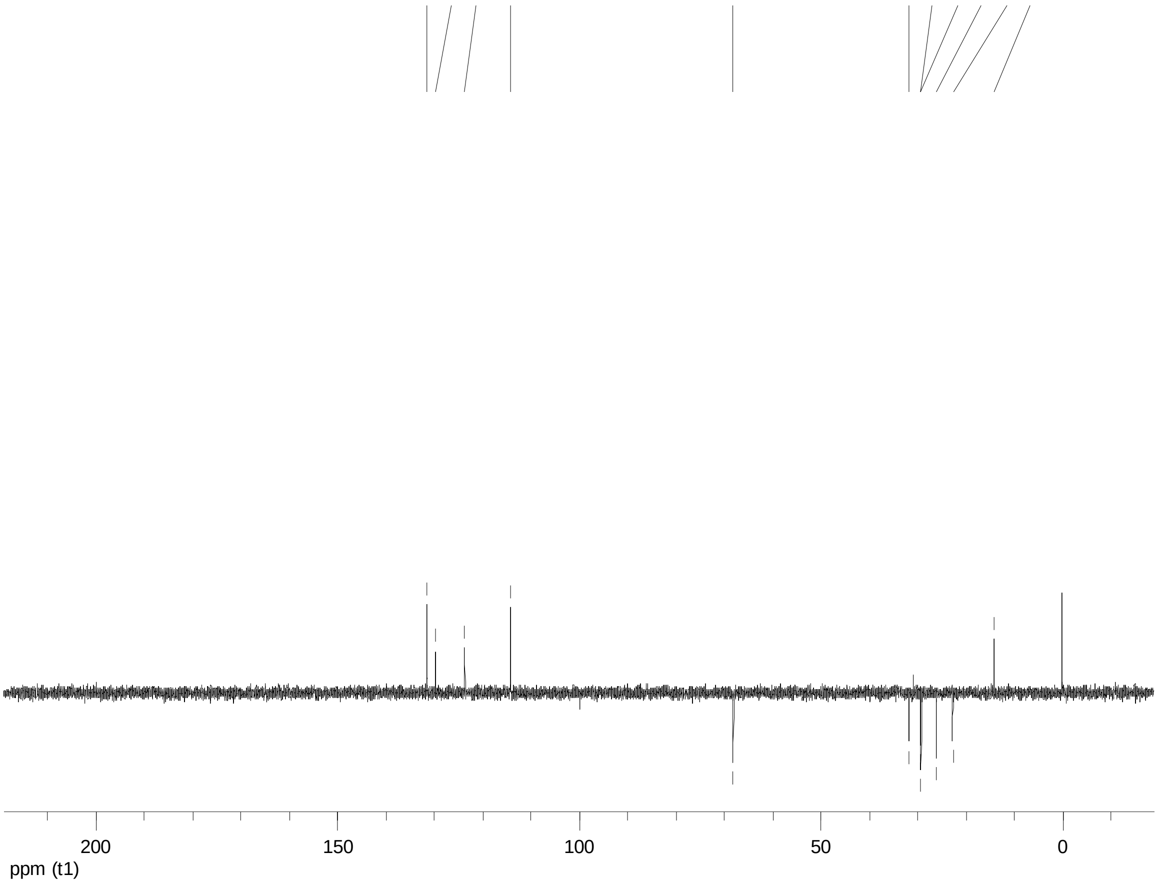
8. Appendices



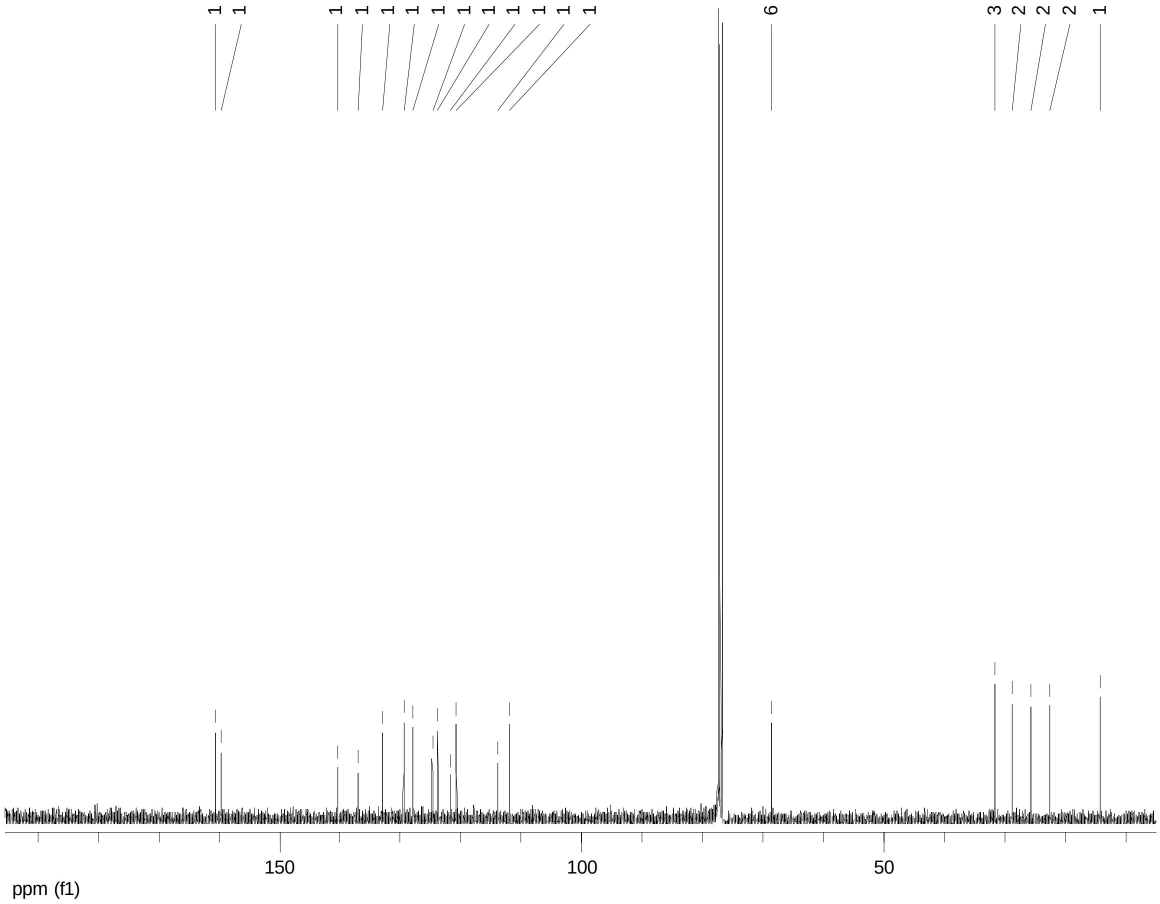
App.1: ^{13}C-NMR spectra of 5,7-bis-(5-bromo-thiophen-2-yl)-2,3-bis-(4-octyloxy-phenyl)-thieno(3,4-b)pyrazine(**66**)



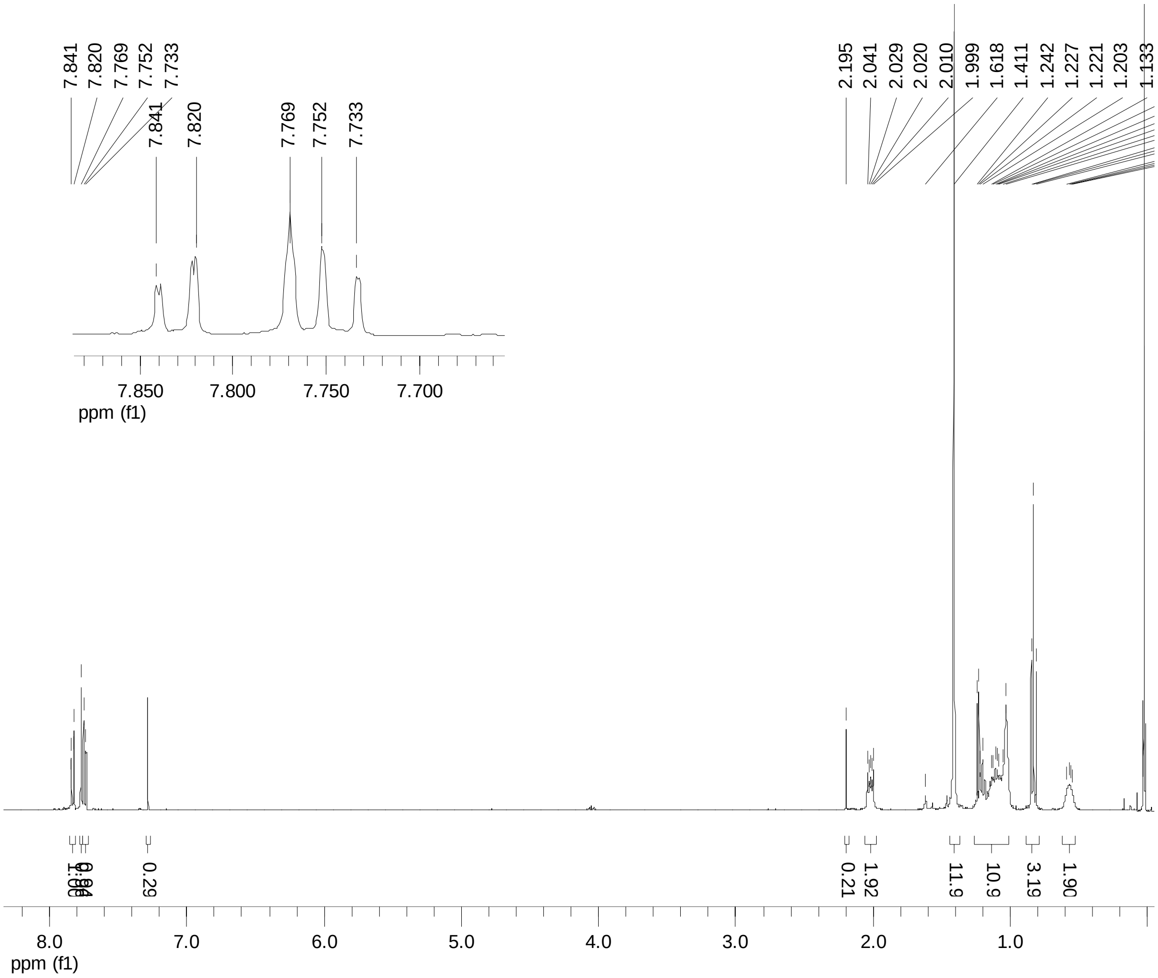
App.2: DEPT-135-spectra of 5,7-bis-(5-bromo-thiophen-2-yl)-2,3-bis-(4-octyloxy-phenyl)-thieno (3,4-b) pyrazine (**66**)



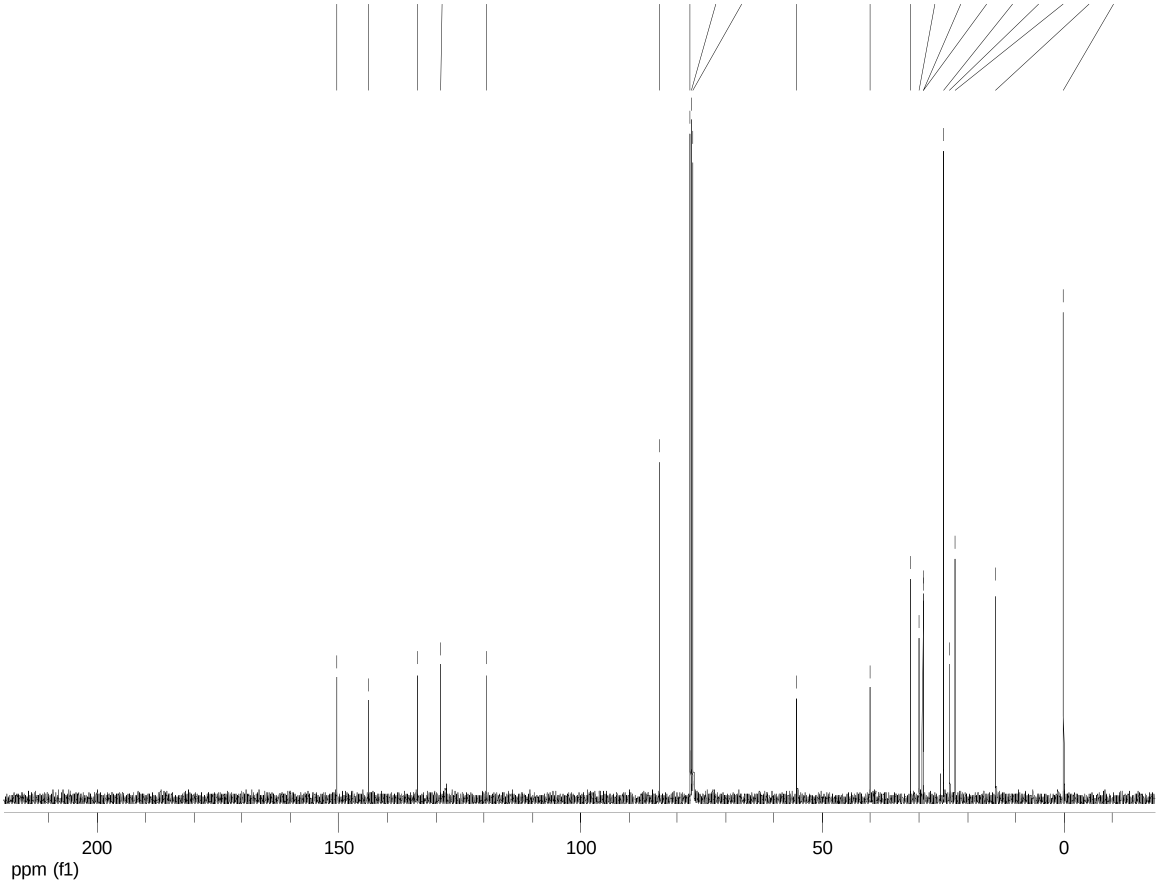
App.3: DEPT-135- spectra of 5,5”-dibromo-3’,4’-di-(2-hexyloxy-benzylideneimino)-2,2’:5’,2”-terthiophene.



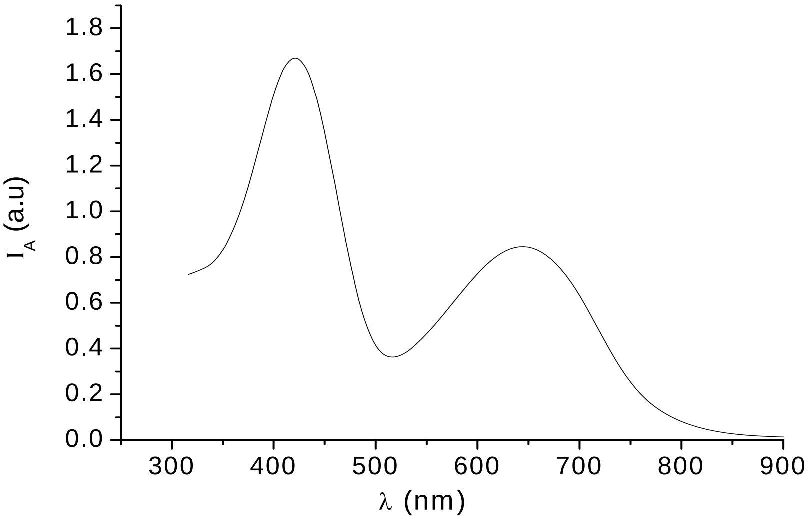
App.4: ^{13}C-NMR spectra of 5,5”-dibromo-3’,4’-di-(2-hexyloxy-benzylideneimino)-2,2’:5’,2”-terthiophene.



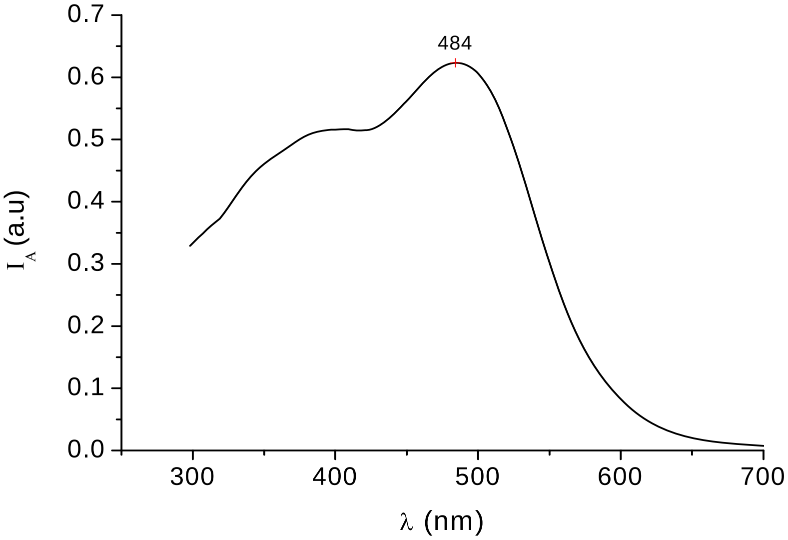
App.5: ^{1}H-NMR spectra of 2,7-bis-(4’,4’5”,5”-tetramethyl-1,3,2-dioxaboralane)-9,9-dioctylfluorene (**62**)



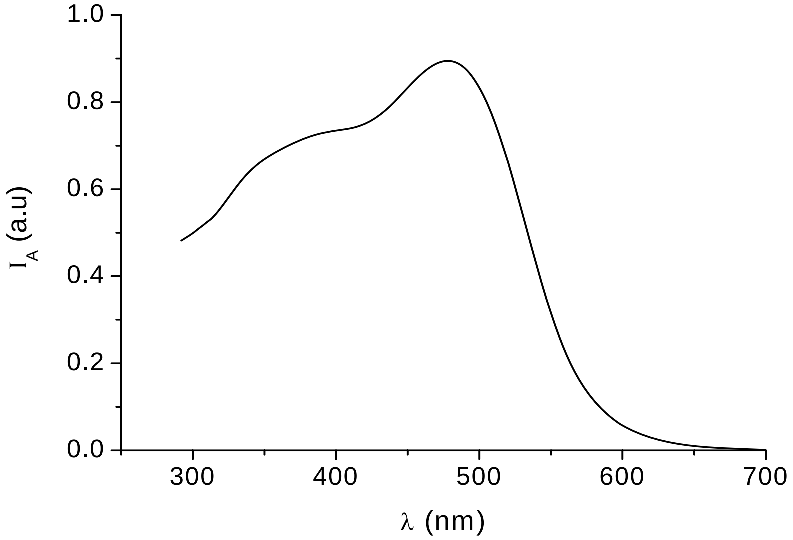
App.6: ^{13}C-NMR spectra of 2,7-bis-(4’,4’5”,5”-tetramethyl-1,3,2-dioxaboralane)-9,9-dioctylfluorene (**62**)



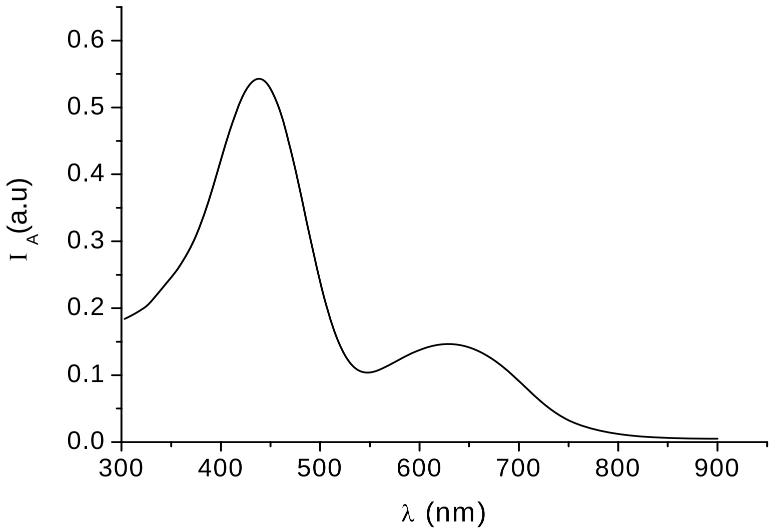
App.7: UV-Vis spectra of polymer **87**



App 8: UV-Vis spectra of polymer **88**



App.9: UV-Vis spectra of polymer **89**



App.10: UV-Vis spectra of polymer **90**

DECLARATION

I, the undersigned, declare that this project is my original work and has not been presented for any degree in any other university and that all sources of material used for the project have been duly acknowledged.

Name: Yadessa Melaku

Signature:

This project has been submitted for examination with my approval as a university advisor.

Name: Wendmiagegn Mammo

Signature:

Date and place of submission: Department of Chemistry
Addis Ababa University
July 2007