Chapter 2

SYNTHESIS AND CHARACTERISATION OF MONOMERS

2.1 Introduction
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Conjugated polymeric systems attract research communities worldwide because, they constitute a new class of materials which bind together desired semiconducting properties with mechanical flexibility and in some cases, biocompatibility. Such a practical combination is not observed in metals, inorganic semiconductors or non-conjugated saturated polymers.

The advent of conducting polymers has created new opportunities for fundamental studies in solid-state physics. This type of materials constitute another fascinating crossover of chemistry and physics. Herein, we present the synthesis and characterization of monomers which are used for preparing the desired conjugated polymers. Detailed description of experimental procedures are presented.
2.1 Introduction

There has been substantial research effort to tackle the energy shortage, one of the greatest issues in the twenty first century and to look for new sources of energy.\textsuperscript{1,2} The direct conversion of light into electricity has been achieved via inorganic solar cells, based on the photovoltaic effect, but come with a high manufacturing cost.\textsuperscript{3,4} More recently, a new form of low cost solar cells based on organic semiconductors has emerged, which offer the potential for light weight, mechanically flexible and easy to process.\textsuperscript{5} For a conjugated polymer to fit in organic photovoltaic solar cell, it should possess favourable physical and chemical properties, i.e., it should possess large absorption coefficient; low band gap; high charge mobility; favourable blend morphology; environmental stability; suitable HOMO/ LUMO level and solubility for achieving reasonable device efficiency.\textsuperscript{6-10}

In order to harvest as much solar spectrum as possible, several structures of promising building blocks for potential high performance materials were developed. The control of band gap of π-conjugated systems has been in the centre of the synthetic chemistry of functional π-conjugated polymers for more than twenty years. Various structural factors affect the magnitude of band gap of a material, like bond length alteration, resonance effect, planarity, the introduction of electron-withdrawing or electron-releasing substituents and intermolecular interactions.\textsuperscript{11,12} The insertion of double bonds between aromatic rings represent a simple and straightforward way of reducing ΔE.\textsuperscript{13} Covalent rigidification of π-conjugated systems represents an efficient strategy for
band gap control and opens interesting perspectives for applications in photonic systems such as nonlinear optics, light-emitting devices or solar cells.\textsuperscript{14}

Introduction of electron-releasing or electron-withdrawing groups represents the most immediate way to tune the HOMO and LUMO energy levels of a conjugated system. Electron-withdrawing groups induce a decrease of the HOMO level which results in a stabilization of the neutral state of the system.\textsuperscript{15,16} H. Cha et al have investigated the molecular packing structures of two conjugated polymers based on alkoxy naphthalene, one with cyano-substituent and one without, to determine the effects of electron-withdrawing cyano-groups on the performance of bulk-heterojunction solar cells. A bulk-heterojunction device fabricated with the cyano-substituted polymer: PC\textsubscript{71}BM blend has a higher $V_{OC}$, a higher fill factor (FF) and a lower short circuit current $J_{SC}$ than that of the noncyano-substituted polymer: PC\textsubscript{71}BM blend. Thus, the cyano-substitution of conjugated polymers may be an effective strategy for optimizing the domain size and crystallinity of the polymer: PC\textsubscript{71}BM blend, and for increasing $V_{OC}$ by tuning the HOMO and LUMO energy levels of the conjugated polymer (Fig 2.1). But the introduction of cyano groups leads to a strong decrease of solubility, which must be taken into account when designing the target system.\textsuperscript{17} Variation of the substituent on the aromatic unit in the main chain represents an effective way to perturb molecular orbitals or tune the solubility.
Fig. 2.1: Structures of two conjugated polymers based on alkoxy naphthalene, one with cyano-substituent and one without, to determine the effects of electron-withdrawing cyano groups on the performance of bulk-heterojunction solar cells

Introduction of electron-donor groups to a conjugated system produces an increase of the HOMO level, generally accompanied by a reduction of $\Delta E$. Linear alkyl chain enhances the long-range order in the polymer, through lipophilic interactions between the alkyl chains, this effect being particularly important in regioregular polymers.\textsuperscript{18-20} Strong electron donors such as alkoxy or alkylsulfanyl groups produce a large increase of the HOMO level. The conversion of a polyaromatic chain into a conjugated system with an enhanced quinoid character (fused heterocycles like fluorene, carbazole, quinoxaline etc) is one of the most efficient approaches for band gap reduction. A major drawback of some of these fused systems lies in their limited stability, which has led several groups to combine them with more stable building blocks to obtain multicyclic precursors.\textsuperscript{21-24}

In addition to the energy level tuning, the polymer solubility also affects the physical properties of the polymer, such as processibility, phase behaviour, structural order and charge transport properties. Branched alkyl chains are more effective than their linear counterparts for inducing solubility, but affect the $\pi-\pi$ interaction, and the charge carrier mobility.
Large sized alkyl chains will lengthen $\pi-\pi$ stacking distance and reduce carrier mobility. Bridging atoms that connects two aromatic rings also play a unique role in high performance materials.

### 2.2 Common building blocks for conducting polymers

Ethylene (double bond) is a commonly adopted spacer or bridge in conjugated polymers. Introduction of vinylene spacers between aromatic units helps to reduce the torsional angle thereby lowering the band gap of the conducting polymer. Another advantage of vinylene and ethylenic bond between the rings is to impart restricted rotation of the rings due to the cis or trans configuration of the double bond. Further lowering of the band gap has been achieved by placing an electron withdrawing cyano group on one of the vinyl carbons that helps in stabilizing the quinoidal state. V. Seshadri et al reported that conjugated polymers with band gaps of 1.2 eV were prepared from two isomeric monomers consisting of thieno[3,4-b]thiophene and cyanovinylene units. In another work, H. Padhy synthesized two $\beta$-cyanothiophene vinylene based polymers containing cyclopentadithiophene (CPDT-CN) and dithienosilole (DTS-CN) units. The effects of the bridged atoms (C and Si) and cyanovinylene groups on their thermal, optical, electrochemical, charge transporting, and photovoltaic properties were investigated (Fig 2.2).
Benzene ring is the most fundamental building block for polymer solar cell materials whereby they can be coupled via single bonds as in PPP or fused to ribbons such as in poly (n)acenes. Poly (p-phenylene) shows poor solubility in common organic solvents which limits its application in organic electronics. Introduction of alkyl or alkoxy chain on the backbone will increase the solubility. Poly(phenylene vinylenes) (PPV) based polymers were one of the first semiconducting polymer species investigated for BHJ application.

T. Kietzke et al reported polymer blend solar cells with an external quantum efficiency of more than 30 % and a high overall energy conversion efficiency (ECE) of up to 1.7 % using a blend of M3EH–PPV (poly[2,5-dimethoxy-1,
4-phenylene-1,2-ethenylene-2-methoxy-5-(2-ethylhexyloxy)-(1,4-phenylene-1,2-ethenylene)) (Fig.2.3) and CN−ether−PPV (poly[oxa-1,4-phenylene-1,2-(1-cyano)ethenylene-2,5-dioctyloxy-1,4-phenylene-1,2-(2-cyano)ethenylene-1,4-phenylene]).34(b)

![Fig.2.3: Structure of M3EH–PPV](image)

Introducing acetylenic groups into the PPV structure form PPE-PPV showing outstanding optoelectronic properties and has successfully been used in solar cells. N. Tore et al incorporated silver nanoparticles in the active layer of anthracene containing poly(p-phenylene-ethynylene)-alt-poly(p-phenylene vinylene): phenyl-C61-butyric acid methyl ester) based bulk hetrojunction solar cells and found that the power conversion efficiency and also the life time of the cell were improved.34(c)

Thiophene has become one of the most commonly used building blocks in organic electronics due to its excellent optical and electrical properties as well as exceptional thermal and chemical stability.35 Solubilizing moieties attached to the ring structure increases the solubility of polythiophenes. The band gap of the polythiophene can also be tuned by inductive and/or mesomeric effect from the heteroatom containing substitution. Of particular interest today are copolymers incorporating thiophene based fused rings, which allow high carrier mobilities or high efficiencies. Using a design strategy
similar to that used for regiosymmetric P3ATs, various kinds of rings have been successfully incorporated in polythiophene backbones.\textsuperscript{36} Two frequently encountered thiophene-based conjugated polymers in literature are poly(3,4-ethylenedioxy thiophene) poly(styrene sulfonate) (PEDOT-PSS,) in conducting and hole transport layers for organic light emitting diodes (OLEDs) and PSCs and regioregular poly(3-hexylthiophene) (P3HT) as a hole transporting material in organic field effect transistors (OFETs) and PSCs \textsuperscript{37} (Fig 2.4).

![Fig. 2.4: Structure of (a) PEDOT-PSS and (b) P3HT](image)

Fluorene based polymers have been widely explored as organic electronic material in the field of OLED, OFET and PVs due to their high photoluminescence quantum yield, high thermal and chemical stability, good film-forming properties and good charge transport properties. Polyfluorene, however, has a band gap of \(~3.0\) eV, which limits its application in solar cells. Therefore, fluorene is normally copolymerized with electron withdrawing moieties to construct polymers with band gap \(\geq 2.0\) eV. Palladium catalysed cross-coupling reaction is normally adopted for the polymerization due to the ease of halogenation at the 2,7-position of fluorene unit.
C. E. Song et al synthesized a set of novel conjugated polyfluorene copolymers, poly[(9,9’-didecylfluorene-2,7-diyl)-co-(4,7’-di-2-thienyl-2’,1’,3’-benzothiadiazole-5, 5-diyl)-co-(pyrene-1,6-diyl)] via Pd(II)-mediated polymerization. The field effect carrier mobilities and optical, electrochemical, and photovoltaic properties of the copolymers were systematically investigated \cite{38,39} (Scheme 1).

\begin{center}
\textbf{Scheme 1: Synthesis of the copolymers}
\end{center}

Fused heterocycles represent an important class of building blocks to achieve either low band gap or high carrier mobility depending on the orientation of the fused ring to the polymer main chain. They are one of the most frequently studied classes of organic materials due to their highly conjugated $\pi$-bonding systems, chemical stability, and tunable electronic properties. The fused system tends to favour the quinoidal mesomeric structure, resulting in the band gap being as low as 1.0 eV. Monomers with fused rings like carbazole, cyclododithiophene are useful building blocks to prepare low band gap polymers due to their coplanarity \cite{40-50} (Fig 2.5).
Fig. 2.5: Chemical structures of selected fused heterocycle-based polymers

Z. Feiz et al reported the first synthesis of a fused germandacenedithiophene monomer and its polymerization with 2,1,3-benzothiadiazole by Suzuki polycondensation. The bridging hetero atom has also been shown to have a significant effect on the crystallinity of the polymer. The crystalline polymers demonstrated higher charge carrier mobilities ideal for a number of applications including bulk heterojunction solar cells. The improved crystallinity has been rationalised on the basis of the longer C–Ge bond length compared to the C–C bond, which changes the geometry of the fused ring allowing stronger π-π interactions to occur.\textsuperscript{51}

2.3 Results and discussion

2.3.1 Synthesis of monomers

One of the monomers, benzene-1,4-diboronic acid used in polymer synthesis was obtained from Sigma Aldrich and used without further
purification. All the other monomers were synthesized on the basis of reported procedures and were characterized by spectroscopic techniques. HPLC grade solvents were used for the synthesis of monomers.

### 2.3.1.1 Synthesis of fluorene based monomers

2,7-Dibromofluorene\(^5\) (M1) was prepared by the bromination of 9H-Fluorene. The dibromofluorene was treated with 1-bromoocetane in the presence of KOH and a phase transfer catalyst in DMSO to give 2,7-dibromo-9,9-dioctyl fluorene\(^5\) (M2). The above product was treated with n-butyl lithium and 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane in dry THF at -78°C to form 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene\(^5\) (M3) (Scheme 2). The \(^1\)H NMR spectrum of M3 showed multiplets at \(\delta\) 0.59-2.05 due to alkyl protons. It showed multiplets at \(\delta\) 7.73-7.83 due to aromatic protons.

![Scheme 2: Synthesis of fluorene based monomers](image_url)
In another reaction, 2,7-dibromofluorene (M1) on air oxidation in the presence of KOH in THF gave 2,7-dibromofluorenone\textsuperscript{55} (M4). The synthetic route for the preparation of the compounds is presented in (Scheme 3). The $^1$H NMR spectrum of M4 showed multiplets at $\delta$ 7.28-7.66 due to aromatic protons.

\[
\begin{array}{c}
\text{Br} \quad \text{Br} \\
\text{Br} \quad \text{Br}
\end{array} \xrightarrow{[\text{O}]} \quad \begin{array}{c}
\text{Br} \\
\text{Br}
\end{array} \quad \text{M4}
\]

Scheme 3: Synthesis of 2,7-dibromofluorenone

2.3.1.2 Synthesis of quinoxaline based monomers

A solution of 3,6-dibromo-1,2-phenylenediamine on refluxing with acenaphthene quinone in ethanol and few drops of acetic acid gives 5,8-dibromoacenaphthyl quinoxaline (M5) as the product. 5,8-Dibromo-2,3-diphenyl quinoxaline (M6) was formed when 3,6-dibromo-1,2-phenylenediamine was treated with benzil. 10,13-Dibromodibenzo[a,c]-phenazine (M7) was prepared by refluxing 3,6-dibromo-1,2-phenylenediamine with phenanthrene-9,10-dione in ethanol/ acetic acid.\textsuperscript{56} (Scheme 4). The $^1$H NMR spectrum of all quinoxaline based monomers showed multiplets in the aromatic region.
2.3.1.3 Synthesis of thiophene based monomers

In the synthesis of 3,4-dimethoxy thiophene $^{57}$ (M8), first step involves the condensation of diethyl thiodiglycolate and diethylxalate to give the 3,4-dihydroxythiophene dicarboxylic ester followed by methylation using freshly prepared dimethyl sulphate. This was followed by the hydrolysis of the ethyl ester with conc. HCl to form 3,4-dimethoxythiophene 2,5-dicarboxylic acid. Finally, the above product was decarboxylated at 160°C to obtain the 3,4-dimethoxy thiophene as dark coloured liquid which was purified with column chromatography to yield a colourless liquid as the final product (Scheme 5). The $^1$H NMR spectrum of dimethoxythiophene showed a
singlet at $\delta$ 3.8 due to methoxy hydrogens and another singlet at $\delta$ 6.2 due to aromatic hydrogens.

\[
\text{Scheme 5: Synthesis of 3,4-dimethoxy thiophene}
\]

3,4-dihexyl-2,5-dibromothiophene\textsuperscript{58} was prepared by bromination of 3,4-dihexylthiophene with NBS in chloroform/acetic acid. The synthetic route for the preparation of the compounds is presented in Scheme 6. The $^1$H NMR spectrum of the compound M9 showed multiplets at $\delta$ 0.89-2.51 due to aromatic protons.

\[
\text{Scheme 6: Synthesis of 3,4-dihexyl-2,5-dibromothiophene}
\]

2.3.1.4 Synthesis of cyanovinylene based monomers

2,3-bis(4-bromophenyl)acrylonitrile\textsuperscript{59}(M10) was prepared by adding a solution of NaOH in ethanol to a mixture of 4-bromophenylacetonitrile and 4-bromobenzaldehyde in ethanol.
3-(4-bromophenyl)-2-(5-bromothiophen-2-yl) acrylonitrile (M11) was prepared by using 4-bromophenyl acetonitrile and 2-bromothiophene-5-aldehyde. 2,2’-(thiophene-2,5-diyl)-bis-(3-(4-bromophenyl) acrylonitrile) (M12) was formed by treating 4-bromophenyl acetonitrile and 2,5-thiophene dialdehyde (Scheme 7). The $^1$H NMR spectrum of the cyanovinylene compounds showed multiplets in the aromatic region and signals corresponding to the vinyl protons.

![Scheme 7: Synthesis of cyanovinylene based monomers](image)

2.3.1.5 Synthesis of 3,6-Dibromo-N-(2-ethylhexyl)carbazole

3,6-Dibromo-N-(2-ethylhexyl) carbazole$^{50}$ (M13) was prepared by treating a solution of 3,6-dibromocarbazole with potassium carbonate and 2-ethylhexylbromide. The synthetic route for the preparation of the compounds is presented in (Scheme 8). The $^1$H NMR spectrum of the compound M13 showed multiplets at $\delta$ 7.23-8.17 due to aromatic protons. The spectrum of M13 showed multiplets at $\delta$ 0.85-2.01 due to aliphatic protons. It also showed another multiplet around $\delta$ 4 due to $\text{–N-CH} –$ protons.
2.3.1.6 Synthesis of 4,7-Dibromo-5,6-bis(decyloxy)benzo[c][1,2,5]oxadiazole

1,2-Bis(decyloxy)benzene was synthesised from catechol by treating it with 1-bromooctane and NaOH which was then nitrated with HNO₃. Next step involves the cyclisation of 1,2-dinitro-4,5-bis(decyloxy) benzene to form 5,6-bis(decyloxy)benzo[c][1,2,5]oxadiazole which was then brominated with bromine in acetic acid to form 4,7-Dibromo-5,6-bis(decyloxy)benzo[c][1,2,5]oxadiazole (Scheme 9). The ¹H NMR spectrum of the compound M14 showed multiplets at δ 0.9 - 1.8 due to aliphatic protons. The spectrum showed multiplets at δ 4.2 due to protons attached to alkoxy group.

Scheme 9: Synthesis of 4,7-Dibromo-5,6-bis(decyloxy)benzo[c][1,2,5]oxadiazole
2.4 Experimental procedure

2.4.1 Synthesis of fluorene based monomers

2.4.1.1 2,7-Dibromofluorene (M1)

To a solution of 9H-fluorene (6 g, 36 mmol), iron (III) chloride (92 mg, 1.6 mmol) in CHCl₃ (100 mL) at 0°C, 4 mL bromine was added drop by drop. The mixture was stirred for 12 h. After the reaction, it was poured into 50 mL water. The precipitate was washed with NaHCO₃ and NaHSO₃ solution. The organic layer was extracted with CHCl₃. The organic layer was dried over anhydrous magnesium sulphate. After filtration, the solvent was removed using rotary vacuum evaporation, and the residue was recrystallized from ethanol resulting in white crystalline product. Yield: 75%. M.P: 161-166°C. ¹H NMR (400 MHz, CDCl₃): δ 7.66 (s, 2H), 7.60-7.59 (d, 2H), 7.51-7.49 (d, 2H), 3.87 (s, 2H).

2.4.1.2 2, 7-Dibromo-9,9-dioctyl-9H-fluorene (M2)

KOH solution (10mL, 50 %) and 1-Bromooctane (5.60 g, 29.0 mmol) was added drop wise to a mixture of 2,7-dibromo-9H-fluorene (3.88g, 12.0 mmol), tetrabutyl ammonium bromide (0.0225 g, 0.0975 mmol) in DMSO (50.0 mL) under N₂ atmosphere. The reaction mixture was stirred at 80°C for 2 days. The mixture was poured into H₂O (500 mL). The organic layer was extracted with dichloromethane. The combined organic layer was dried over anhydrous MgSO₄. The solvent was removed under reduced pressure. The crude product was purified by recrystallization from hexane to yield colourless crystals. Yield: 89%. M.P: 59-63°C. ¹H NMR (400 MHz, CDCl₃), δ: 7.51 (s, 2H), 7.45 (m, 4H), 1.90 (m, 4H), 1.25-0.86 (m, 24H),
0.83 (t, 6H). $^{13}$C NMR (CDCl$_3$, 100 MHz), ppm: 153.2, 139.8, 131.2, 126.2, 122.3, 121.1, 46.4, 41.8, 31.7, 29.6, 29.0, 23.9, 22.8, 14.1. MS m/z : 548.4.

**2.4.1.3 2,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene(M3)**

To a stirred solution of 2,7-dibromo-9,9-dioctyl fluorene (5.0 g, 9.1 mmol) in THF (70 ml) at -78 °C was added drop wise n-butyl lithium in hexane (7.6 ml, 2.5 M, 19 mmol) at -78 °C. The mixture was warmed to 0 °C for 15 min and cooled back to -78 °C. 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4 g, 21.5 mmol) was added rapidly to the solution. The resulting mixture was warmed to room temperature and stirred for 24 h. The mixture was poured into water and extracted with diethyl ether. The organic extract was washed with brine and dried over magnesium sulphate. The solvent was removed under reduced pressure, and the crude product was purified by column chromatography, eluting with 2% ethyl acetate and hexane to give 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene as a pale yellow solid. Yield: 65%. $^1$H NMR (400 MHz, CDCl$_3$), $\delta$: 7.83 (d, 2H), 7.76 (s, 2H), 7.73 (d, 2H), 2.05 (m, 4H), 1.44 (s, 24H), 1.25-1.09 (m, 24H), 0.82 (t, 6H). MS m/z: 642

**2.4.1.4 2,7-dibromofluorenone(M4)**

Into a 100mL three-necked flask equipped with a mechanical stirrer, a snorkel and an air condenser were fitted, 2, 7-dibromo-9-fluorene (1.620 g, 5 mmol), KOH (0.280 g, 5 mmol) and THF (15 mL) were added. The reaction mixture was stirred at room temperature while the solution was kept lower than the snorkel, and air was introduced for 5 min every 30 min to ensure that there was sufficient oxygen with minimal loss of solvent. At
the completion of the reaction, the reaction mixture was filtered to remove KOH and the filtrate was concentrated to obtain the crude product.

![Diagram of 2,7-dibromofluorenone](image)

The crude product was washed with water (3 * 100 mL) and dried to give 2,7-dibromofluorenone as a yellow solid, Yield: 98%. M.P: 203-205°C. $^1$H NMR (400 MHz, CDCl$_3$), ppm: 7.66 (dd, 2H), 7.52 (dd, 2H), 7.28 (s, 2H).

$^{13}$C NMR (CDCl$_3$, 100 MHz), ppm: 191.1, 142.4, 137.7, 135.4, 128.0, 123.5, 122.0. Elemental Analysis calculated for C$_{13}$H$_6$Br$_2$O: C, 46.20; H, 1.79. Found C, 46.44; H, 1.81.

2.4.2 Synthesis of quinoxaline based monomers

2.4.2.1 5,8-Dibromoacenaphthyl quinoxaline (M5)

![Diagram of 5,8-Dibromoacenaphthyl quinoxaline](image)
A solution of 3,6-dibromo-1, 2-phenylenediamine (0.15 g, 0.56 mmol) and acenaphthenequinone (0.10 g, 0.55 mmol) in ethanol (20 mL) and few drops of glacial acetic acid was heated to reflux for 1h, and cooled to 0°C. The precipitate formed was separated by filtration and washed with ethanol to afford 5,8-dibromoacenaphthyl quinoxaline as light yellow solid. Yield: 75%.

$^{1}$H NMR (400 MHz, CDCl$_3$), $\delta$: 8.54 (d, 2H), 8.15 (d, 2H), 7.92 (s, 2H), 7.89-7.86 (m, 4H)

2.4.2.2 5,8-Dibromo-2,3-diphenyl quinoxaline (M6)

A solution of 3,6-dibromo-1, 2-phenylenediamine (1.0 g, 3.8 mmol) and benzil (0.80 g, 3.8 mmol) in ethanol (40 mL) and few drops of glacial acetic acid was heated to reflux for 1h, and cooled to 0°C. The precipitate formed was isolated by filtration and washed with ethanol to afford 5,8-dibromo-2,3-diphenyl quinoxaline as light yellow solid. Yield: 80%. M. P: 221°C. $^{1}$H NMR (400 MHz, CDCl$_3$), $\delta$: 7.92 (s, 2H), 7.64 (m, 4H), 7.37 (m, 6 H). $^{13}$C NMR (CDCl$_3$, 100 MHz), ppm: 123.7, 128.4, 129.6, 130.2, 133.1, 137.9, 139.4, 154.14. GC-MS: m/z=439.9
2.4.2.3 10,13-Dibromodibenzo[a,c]phenazine(M7)

A solution of 3,6-dibromo-1,2-phenylenediamine (1.03 g, 3.9 mmol) and phenanthrene-9,10-dione (0.81 g, 3.9 mmol) in 42 mL ethanol/ acetic acid (20:1) was heated to reflux for 2 h, and cooled to 0°C. The precipitate formed was isolated by filtration and washed with ethanol to afford 10, 13-dibromodibenzo [a,c] phenazine as yellow solid. Yield: 78%. M.P: 317°C. $^1$H NMR (CDCl$_3$): $\delta$ 9.48 (dd, 2 H), 8.57 (dd, 2 H), 8.04 (s, 2H), 7.87-7.83 (dt, 2 H). $^{13}$C NMR (CDCl$_3$, 100 MHz), ppm: 123.1, 124.2, 127.3, 128.4, 129.6, 131.3, 132.7, 132.9, 143.5. GC-MS: m/z = 437.9

2.4.3 Synthesis of thiophene based monomers

2.4.3.1 Diethyl thiodiglycolate

In a 500 mL round bottom flask, thiodiglycolic acid (100 g, 0.666 mol) was dissolved in dry ethanol (250 mL) and conc. sulphuric acid (10 mL) was added drop wise to it. The resulting mixture was refluxed for 24 h. The excess methanol was evaporated and the residue was dissolved in ethyl acetate, washed with saturated sodium bicarbonate solution until the aqueous layer was neutral. The organic layer was dried over sodium sulfate and the solvent was removed on a rotary evaporator to afford a light yellow liquid. Yield: 89%. M.P: 69-72°C. $^1$H NMR (400 MHz, CDCl$_3$), $\delta$: 4.2 (q, 4H), 3.4 (s, 4H), 1.4 (t, 6H).

2.4.3.2 3,4-Dimethoxy-2,5-dicarbethoxythiophene

A solution of 10.5 g of sodium metal in 100 mL of dry ethanol was cooled at 0–5°C. To this, a solution of 26.7 g of diethyl thiodiglycolate and 26.7 g of diethyl oxalate was added and stirred. The temperature was maintained at 0°C. The sodium salt was precipitated as a yellow solid. The
reaction was completed by heating the reaction mixture to reflux for 2 h. After cooling, the solid was filtered and dried. The sodium salt of diester (15 g, 54.3 mmol) was taken in 65 mL of freshly distilled dimethyl sulfate and the mixture was heated at 100°C for 1 h. The excess dimethyl sulfate was distilled at low pressure and the crude product was dissolved in ethyl acetate (100 mL) and washed with cold 5% NaOH solution (50 mL). The organic layer was extracted and dried over sodium sulfate and solvent was evaporated to afford the compound as a pure light yellow solid. Yield: 64%. \(^1\)H NMR (400 MHz, CDCl₃), δ: 4.1 (q, 4H), 3.9 (s, 6H), 4.1 (q, 4H), 1.2(t, 6H).

2.4.3.3 3,4-Dimethoxy thiophene-2,5-dicarboxylic acid

In a 100 mL round bottom flask 3,4-dimethoxy-2,5-dicarbethoxy thiophene (9 g, 34.6 mmol) was taken and 10% NaOH (50 mL) was added to it. The mixture was refluxed for 1 h. The reaction mixture was cooled to room temperature and conc. HCl was added to it with stirring. The precipitate thus formed was collected in a Buchner funnel and dried in an oven to give the above product as a white solid. Yield: 84%. \(^1\)H NMR (400 MHz, CDCl₃), δ: 10.2 (s, 2H), 4 (s, 6H)

2.4.3.4 3,4-Dimethoxythiophene(M8)
A 100 mL dry three necked round bottom flask was charged with 3,4-dimethoxy thiophene-2,5-dicarboxylic acid (9 g, 43.3 mmol), copper chromite (0.56 g, 4% mol) and dry quinoline (30 ml). The mixture was heated at 160°C for 4 h under argon atmosphere. The reaction mixture was vacuum distilled and the pink liquid obtained was dissolved in 50 mL of ethyl acetate and washed repeatedly with 5% HCl and water. The organic layer was dried over anhydrous Na₂SO₄, filtered and the solvent was evaporated to give a crude brown coloured liquid. The crude compound was purified by column chromatography using silica gel as the adsorbent and eluting using ethyl acetate/ petroleum ether mixture (v/v) to afford the product as colourless liquid, Yield: 56 %. B.P.110°C (17 bar). ¹H NMR (400 MHz, CDCl₃), δ: 6.2 (s, 2H), 3.8 (s, 6H). ¹³C NMR (CDCl₃, 100 MHz), ppm : 57, 36, 96, 35, 147, 90. MS (EI); m/z= 144

2.4.3.5 3,4-Dihexyl-2,5-dibromothiophene (M9)

In a round-bottom flask, 3,4-dihexylthiophene (3.2 g, 12 mmol) and a mixture of chloroform/acetic acid 50:50 (50 mL) were stirred and kept at 30°C; NBS (4.48 g, 25.2 mmol) was slowly added. After complete addition, the reaction mixture was refluxed for 15–20 min, cooled to room
temperature and diluted with an equal volume of water, the chloroform layer was separated and washed (3 times) with sodium carbonate solution and once with water. The dibromo derivative was obtained as yellowish oil. Yield: 90 %. $^1$H NMR (400 MHz, CDCl$_3$), δ: 2.51(t, 4H), 1.31 (m, 20H), 0.89(t, 6H).

2.4.4 Synthesis of Cyanovinylene based monomers

2.4.4.1 2,3-Bis(4-bromophenyl)acrylonitrile (M10)

4-Bromophenylacetonitrile (1.96 g, 10 mmol) and 4-bromobenzaldehyde (1.85 g, 10 mmol) were dissolved in ethanol (50 mL). To the mixture was added drop wise a solution of NaOH (50 mg) in ethanol (30 mL) under nitrogen atmosphere. The reaction mixture was stirred at room temperature for 1h. The product was obtained as a white precipitate. It was filtered, and washed with water to give a white powder. Yield: 91%. $^1$H NMR (CDCl$_3$): δ 7.77 (d, 2H), δ 7.62-7.52 (m, 6H), 7.45 (s, vinylic proton).

2.4.4.2 3-(4-bromophenyl)-2-(5-bromothiophen-2-yl) acrylonitrile (M11)

4-Bromophenylacetonitrile (1.96 g, 10 mmol) and 2-bromothiophene-5-aldehyde (1.91 g, 10mmol) were dissolved in 50 mL of dry ethanol under nitrogen atmosphere in 100 mL three-necked round-bottomed flask. A
mixture of 50 mg of sodium hydroxide and 30 mL of dry ethanol was added slowly, and the crude product was precipitated in the reaction mixture. The reaction mixture was stirred for 1 h at room temperature, and the precipitate was filtered and washed with water. A yellow powder was obtained. Yield: 85%. \( ^1H \) NMR (400 MHz, CDCl\(_3\)), \( \delta \): 7.8 (s, vinylic proton), 7.2 (d, 2H), 7.42-7.4 (m, 4H).

2.4.4.3 2,2’-(thiophene-2,5-diyl)-bis-(3-(4-bromophenyl) acrylonitrile) (M12)

4-Bromophenylacetonitrile (1.96 g, 10 mmol) and 2,5-thiophene dialdehyde (0.70 g, 5 mmol) were dissolved in 50 mL of dry ethanol under nitrogen atmosphere in 100 mL three-necked round-bottomed flask. A mixture of 50 mg of sodium hydroxide and 30 mL of dry ethanol was added slowly, and the crude product was precipitated in the reaction mixture. The reaction mixture was stirred for 1 h at room temperature, and the precipitate was filtered and washed with water. A yellow powder was obtained. Yield: 80%. \( ^1H \) NMR (400 MHz, CDCl\(_3\)), \( \delta \): 8.1 (s, vinylic protons), 7.3 (d, 2H), 7.8-7.9 (m, 8H).
2.4.5 Synthesis of 3,6-Dibromo-N-(2-ethylhexyl)carbazole (M13)

To a solution of 3,6-dibromocarbazole (6.5 g, 20 mmol) dissolved in 50 mL of anhydrous DMF was added potassium carbonate (5.5 g, 40 mmol). The mixture was allowed to stir for 1 h, after which 2-ethylhexylbromide (5.8 g, 30 mmol) was added drop wise. The reaction was allowed to reflux for 2 days. It was cooled, the mixture was poured into water and extracted with chloroform three times and the combined organic layer was dried over anhydrous magnesium sulfate. The solvent and the unreacted 2-ethylhexylbromide were removed under reduced pressure and the residue was purified by column chromatography with hexane and ethyl acetate (v/v) to afford the compound as a waxy solid. Yield: 80%. M.P: 62-63 °C. $^1$H NMR (400 MHz, CDCl$_3$), $\delta$: 8.17 (s, 2H), 7.60-7.52 (d, 2H), 7.30-7.23 (d, 2H), 4.15-4.09 (m, 2H), 2.01-1.97 (m, 1H), 1.35-1.25 (m, 8H), 0.96-0.85 (m, 6H).

2.4.6 Synthesis of benzo[c][1,2,5]oxadiazole

2.4.6.1 1,2-Bisdecyloxybenzene

Sodium hydroxide (8 g, 0.2 mol) was dissolved in methanol (200 mL) at 0°C for 30 min; catechol (10 g, 90.8 mmol) was added slowly. The solution turned to deep green and finally dark. At this time, 1-bromodecane (42.5 mL, 0.2 mmol) was added to the mixture drop wise. The mixture was refluxed in dry nitrogen atmosphere with stirring. After 8 h, the reaction mixture was cooled to room temperature and the solvent was evaporated under reduced pressure. The organic layer was separated using ethyl acetate, dried over anhydrous magnesium sulfate (MgSO$_4$) and concentrated. The compound obtained was triturated from methanol. Yield: 75 %. $^1$H NMR
2.4.6.2 1,2-Dinitro-4,5-bis(decyloxy)benzene

65% HNO₃ (20 mL) was added drop wise to a two-necked round bottom flask containing 1,2-bis(decyloxy)benzene (10 g, 25 mmol), CH₂Cl₂ (140 mL), and AcOH (140 mL) and was cooled to 10°C. The reaction mixture was warmed to room temperature and stirred for 1 h. The mixture was cooled to 10°C and conc HNO₃ (50 mL) was added drop wise. The mixture was warmed to room temperature and stirred for 40 h before being poured into ice water. The CH₂Cl₂ layer was separated and the aqueous phase extracted with CH₂Cl₂. The organic phases were combined, washed sequentially with water, sat. NaHCO₃ (aq), and brine, and dried with MgSO₄. Concentration under vacuum gave a crude product that was recrystallized from EtOH. Yield: 95%. ¹H NMR (400 MHz, CDCl₃), δ: (s, 2H), 4.3 (t, 4H), 1.9 (m, 4H), 1.4-1.6 (m, 28H), 1.3 (t, 6H).

2.4.6.3 5,6-Bis(decyloxy)benzo[c][1,2,5]oxadiazole

A mixture of 1,2- dinitro-4,5-bis (decyloxy) benzene (2.848 g, 6 mmol), NaN₃ (1.95g, 30 mmol), and n-Bu₄NBr (0.39 g, 1.2 mmol) was heated under reflux in toluene (10 mL) for 12 h. At this point, the starting material has been consumed (TLC); PPh₃ (1.9 g, 7.2mmol) was added and the mixture was heated under reflux for additional 24 h. The reaction mixture was cooled to room temperature and filtered through a short silica plug; the plug was rinsed with CH₂Cl₂. Evaporation of the solvents from the combined organic phases, under reduced pressure, afforded a crude solid that was recrystallized (EtOH) to yield an off-white solid Yield: 63%. ¹H NMR
(400 MHz, CDCl$_3$), $\delta$: 7.2 (s, 2H), 4.3 (t, 4H), 1.9 (m, 4H), 1.3-1.4 (m, 28H), 1.1 (t, 6H).

**2.4.6.4 4,7-Dibromo-5,6-bis(decyloxy)benzo[c][1,2,5]oxadiazole (M14)**

AcOH (10 mL) and Br$_2$ (2 mL, 25 mmol) were added sequentially to a solution of 5,6-bis (decyloxy) benzo[c][1,2,5] oxadiazole (2.5 g, 6 mmol) in CH$_2$Cl$_2$ (80 mL). The resulting mixture was stirred in the dark for 3 days at room temperature. The reaction mixture was poured into aqueous NaOH solution (10 g in 200 mL). The organic compounds were extracted with CH$_2$Cl$_2$; the combined organic extracts were washed with brine and concentrated under reduced pressure to afford a crude solid that was purified through column chromatography to yield a white solid. Yield: 79%. $^1$H NMR (400 MHz, CDCl$_3$), $\delta$: 4.2 (t, 4H), 1.8 (m, 4H), 1.2-1.3 (m, 28H), 0.9 (t, 6H).

**2.5 Conclusion**

A series of monomers were successfully synthesized. The strategies used for synthesizing the monomers were discussed in this chapter. All the compounds synthesized were spectroscopically characterized.
References


Chapter 2


Synthesis and Characterisation of Monomers


Synthesis and Characterisation of Monomers


