# Chapter 4

## Synthesis, characterization, electrochemical and photophysical properties of dithienopyrrolobenzothiadiazole based $\pi$-conjugated polymers and $\pi$-conjugated D- $\pi$ - A- $\pi$ -D type molecule

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

## 4.1 Introduction

Conjugated polymers have gathered tremendous interest from researchers since its discovery in 1970 [1]. Since its discovery there has been consistent improvement through means of modifications in the polymer backbone [2], employing different side-chains [3] and various functional groups [4] as well as use of specific structural units for enhancement in terms of applications [5]. Owing to this, conjugated polymers based materials have found various applications such as a photovoltaics [6], field-effect transistors [7], light-emitting diodes [8], sensors [9], electrochromic devices [10], bioimaging materials [11], drug delivery [12] and as photosensitizers in photodynamic therapy [13]. Conjugated polymers possess distinct benefits of its lightweight and easy solution based processability alongwith its compatibility with flexible substrate. These properties can be used to manufacture low-cost flexible roll to roll printed plastic opto-electronic devices [14].

Thiophene based oligomers and polymers have been widely investigated in material science mainly in organic electronic field owing to their conducting, luminescence and sensing properties [15]. The reason for dominance of polythiophenes in the field of $\pi$-conjugated polymers can be accounted to two factors. The first one is in-fact chemistry of thiophene itself. The numerous synthetic methodologies known for the functionalization of the core thiophene units. The transition metal-catalyzed reactions used for cross-coupling reactions developed within last 20 years provided access to many valuable thiophene-based scaffolds which allowed tuning of the electronic and optical properties of their resultant polymers and polymer-based materials [16]. The second reason is the remarkable physical and chemical characteristics of the polythiophenes. The polythiophenes are usually stable in nature in both conducting and semi-conducting states as well as an unique properties resulted from self-assembly and stacking arrangement on bulk and solid surfaces.

One of the most prominent polythiophene polymers which have been commercialized are poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT-PSS) which have found application as a conducting and hole-transport layers of organic light emitting diodes (OLEDs) and organic solar cells (OSCs). Poly(3-hexylthiophene) (P3HT) is another polythiophene which has been used in semiconductor in organic field effect transistors (OFETs) and OSCs [17].

The donor-acceptor (D-A) alternating co-monomer strategy is often used to impart delocalization in the backbone of the polymer. The electron donating and electron withdrawing properties of alternating monomer efficiently increases the intramolecular charge transfer setting up the push-pull effect which narrows the band gap of the conjugated polymer. Due to these advantages, various thiophene-containing D-A $\pi$-systems have been synthesized and their applications in organic electronics were studied [18]. To setup the push-pull effect through D-A strategy various functional groups are incorporated on the backbone of the polymers. The functional groups such as $–NR_2$, -OR, -OAr, –SR (R= alkyl and Ar= aryl) are electron releasing groups by nature, hence when introduce in the thiophene units, the unit becomes a donor unit. Similarly introducing electron withdrawing groups such as $–NO_2$, -COOR, -CN (R= alkyl) imparts acceptor property to the thiophene units present in the backbone of polymer. In present chapter, we will be using D-A concept to impart increased delocalization along the polymer backbone.

Along with D-A concept, use of fused ring thiophene units in the polymer backbone is often utilized. Fused thiophene ring system possesses rigidity and extended $\pi$-conjugation. The fused ring thiophene system possesses extended $\pi$-conjugation and rigidity. This factor lowers the bandgap of the polymer and enhances the intermolecular interactions observed in the solid films of $\pi$-conjugated polymers.

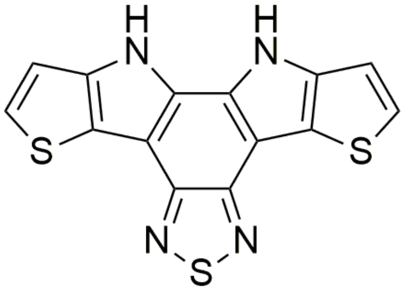


**Figure 4.1** Structure of dithienopyrrolobenzothiadiazole (DTPBT)

Dithienopyrrolobenzothiadiazole (DTPBT) unit have multifused pentacyclic structure in which central core benzothiadiazole units flanked with thiophenes units at 3rd and 6th positions along with two bridging *N*-atoms connecting to 4th and 5th position forming a planar molecule.

Synthesis of ditheniopyrrolobenzothiadiazole (DTPBT) was first reported independently by Cheng [19] and Yu [20] groups in 2012. The synthetic methodology involved the fusion of pyrrole rings with the central benzodithiazole ring through Cadogen reaction [21].

H. Kim *et al* in 2015 reported synthesis of copolymer having DTPBT units coupled with electron rich fluorene units (Figure 4.2). The polymer poly(fluorene-dithienopyrrolobenzothiadiazole) (PFDTPBT) was synthesized by Suzuki coupling reaction and obtained polymer had optical bandgap of 2.15 eV. The blend of polymer PFDTPBT with $PC_{71}BM$ as active layer in bulk heterojunction photovoltaic device showed power conversion efficiency (PCE) of 2.08% [22].

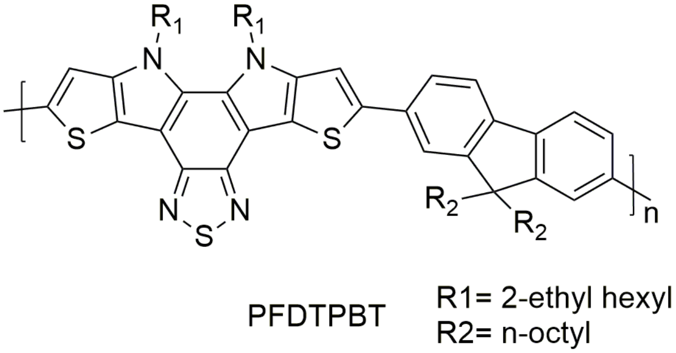


**Figure 4.2** Structure of poly(fluorene-dithienopyrrolobenzothiadiazole) (PFDTPBT)

In 2016, Y. Lie *et al* synthesized dithienopyrrolobenzothiadiazole-benzodithiophene based donor-acceptor polymers [23]. The reported polymers showed an enhanced PCE of 4.31%, due to a broader light absorption and higher hole mobility which was obtained as $1.4 \times 10^{-4}$ $cm^2$ $V^{-1}$ $S^{-1}$.

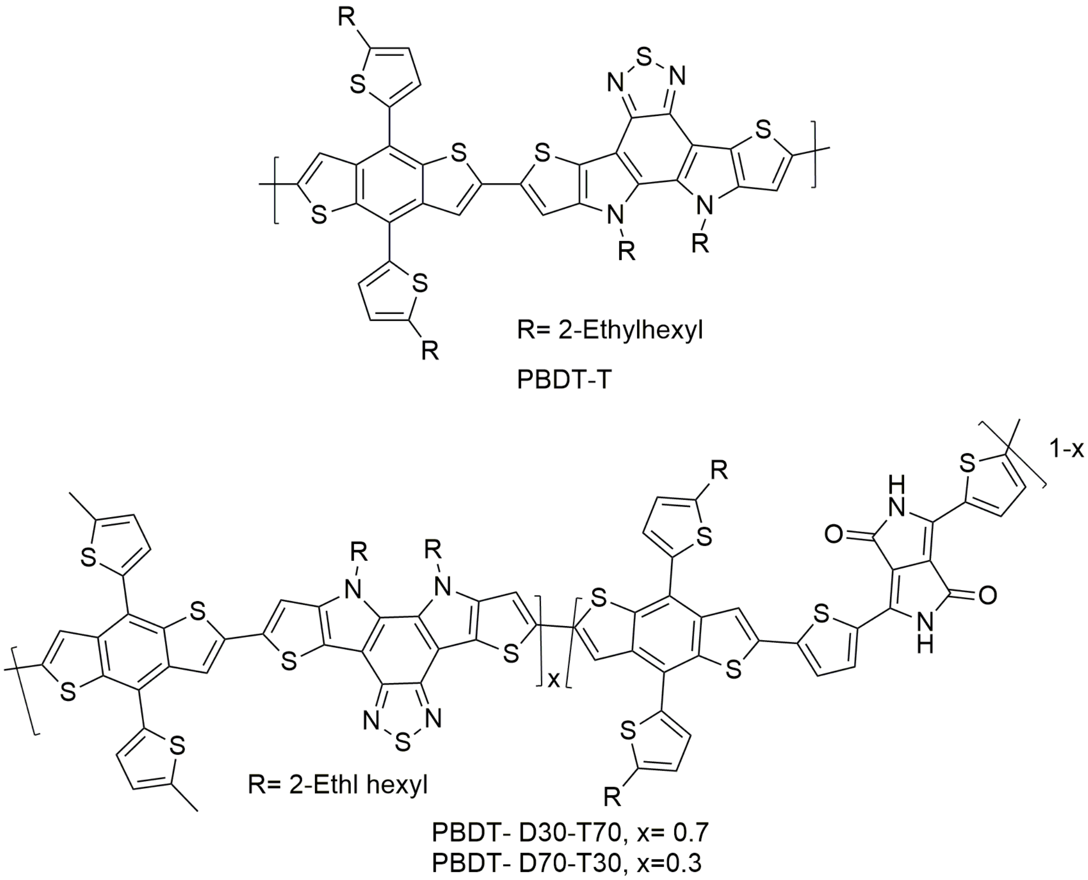


**Figure 4.3** Structures of dithienopyrrolobenzothiadiazole based donor-acceptor polymers

$\pi$-Conjugated polymer based on dialkyl tert-thiophene dicarboxylate (TTD)-DTPBT co-polymer has not been reported till date. DTPBT unit consist of electron-deficient benzodithiazole center linked with electron-rich thiophene with nitrogen atoms. Thus, the DTPBT is an integrated unit of donor-acceptor-donor structure.

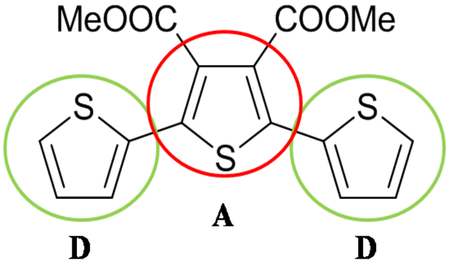


**Figure 4.4** Schematic representation of dialkyl tert-thiophene dicarboxylate (TTD) unit in D-A-D form

TTD units possess central thiophene having dicarboxylate groups linked with thiophene units on either side. The dicarboxylate groups being electron-withdrawing in nature makes central thiophene electron deficient whereas thiophene flanked on either side were acts as donor units. TTD units can be envisioned as an integrated donor-acceptor-donor system. We have synthesized conjugated polymer, poly tert-thiophene-dithienopyrrolobenzothiadiazole (**PTTPBT)** by Stille coupling reaction.

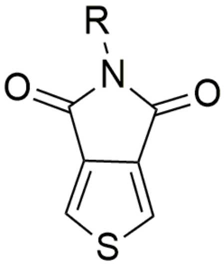


**Figure 4.5** Structure of thieno[*3,4-c*]pyrrole-4,6-dione (TPD)

Thieno[*3,4-c*]pyrrole-4,6-dione (TPD) is one of the most explored and quite promising building block used for the synthesis of $\pi$-conjugated polymers [24]. The first TPD based conjugated polymers was reported by Nielsen *et al* [25] in 2004. The synthesized *n*-alkylated TPD homopolymers obtained were relatively low molecular weight.

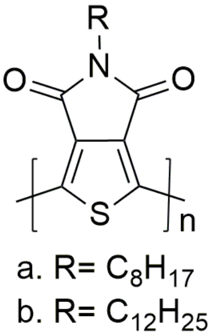


**Figure 4.6** TPD based conjugated polymers

A significant work on TPD units was carried by Leclerc *et al* [26]. In 2012, Leclerc *et al* synthesized several derivatives of TPD based homopolymers. The electron mobility of TPD based homopolymers were observed around $10^{-3}$cm$^2$ V$^{-1}$ s$^{-1}$ in OFET device.

In 2009, Y. Zou *et al* reported D-A type copolymer having TPD units coupled with benzodithiophene units (BDT). The synthesized polymer was low band gap (1.8 eV) and was thermally stable upto 380 °C. Polymer based solar cell demonstrated PCE of 5.5% [27].

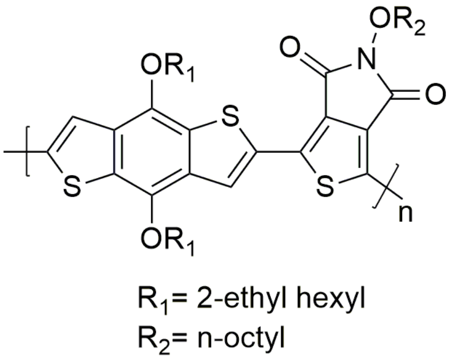


**Figure 4.7** TPD and BDT units based copolymer

K. Lu *et al* reported synthesis of new D-A type conjugated polymers having two dimensional alkyl thiophene substituted BDT units coupled with TPD units having thiophene and *n*-hexyl thiophene units as a spacers between them. Synthesized polymers were low band gap and the bulk heterojunction solar cells fabricated from them showed PCE upto 6.08% [28].

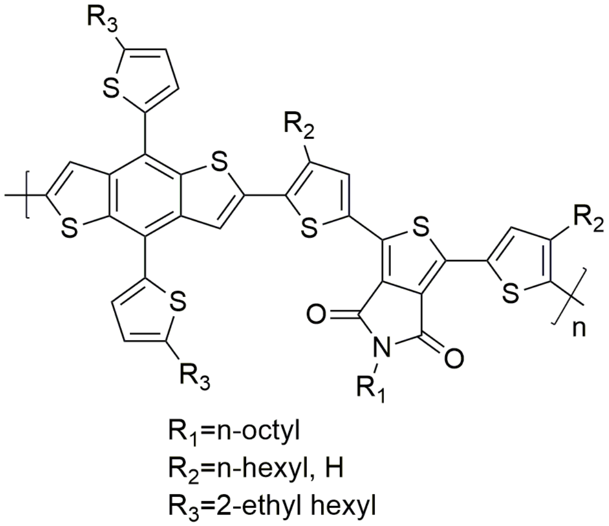


**Figure 4.8** TPD and BDT units based D-A copolymer with thiophene and alkyl thiophene as spacers

TPD possesses rigidity due to fused ring system and have favorable arrangement in the solid state. The *N*-alkylation allows good solubility. The first TPD consisted polymers and their material have low energy band gap which is arise from the stabilization energy acquired from the formation of quinoidal-thiophene-maleimide structure during the excited state [29]. The imide functional groups of TPD effectively pull up the electron from the thiophene ring making TPD molecules as an acceptor unit. TPD is often used as co-monomer coupled with electron-rich unit forming D-A type polymers showing push-pull effect in the backbone of $\pi$-conjugated polymers [30].

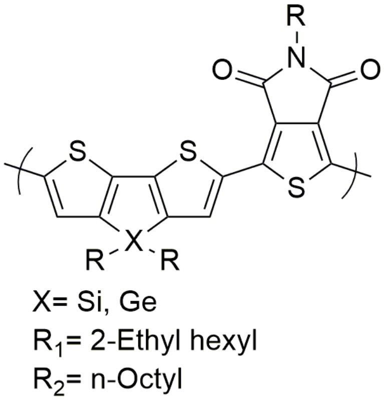


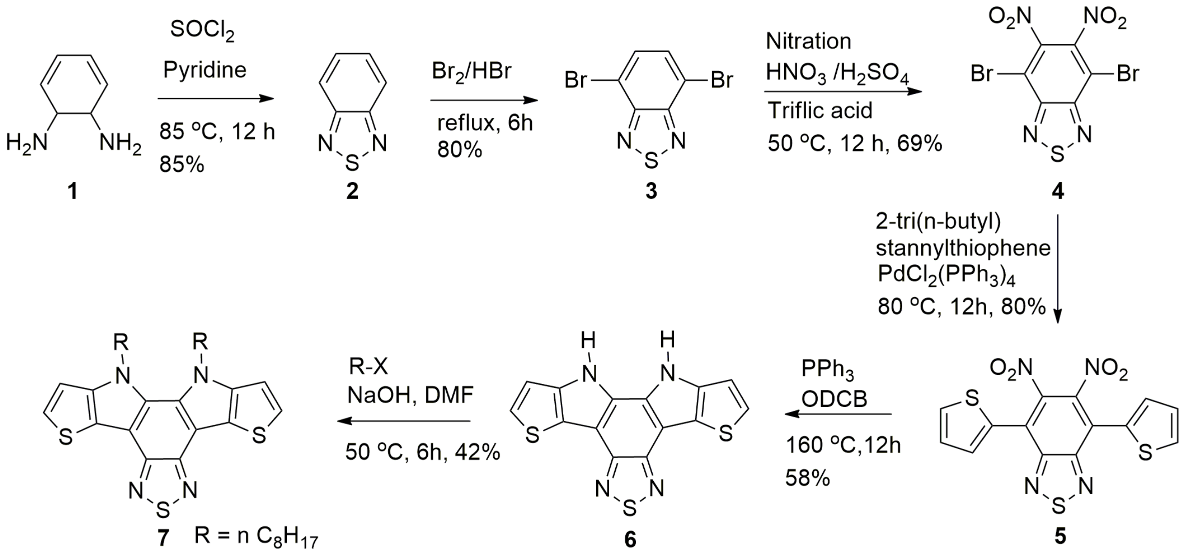
**Figure 4.9** TPD based D-A type polymer

In present chapter, we have synthesized two $\pi$-conjugated polymers (**PTTPBT** and **PTPDPBT)** consisting DTPBT units linked with the diethyl tert-thiophene dicarboxylate units and thieno[ *3, 4-c*]pyrrole-4,6-dione. $\pi$-Conjugated polymers based on dialkyl tert-thiophene dicarboxylate (TTD)-DTPBT co-polymers have not been reported till date. DTPBT unit consist of electron-deficient benzodithiazole center linked with electron-rich thiophene with nitrogen atoms. Thus, the DTPBT is an integrated unit of donor-acceptor-donor structure. While TTD units possess central thiophene having dicarboxylate groups linked with thiophene units on either side. The dicarboxylate groups being electron-withdrawing in nature makes central thiophene electron deficient, whereas thiophene flanked on either side were acts as a donor unit. TTD units can be envisioned as an integrated donor-acceptor-donor system. The synthesized polymers were isolated, purified and characterized by NMR ($^{1}$H and $^{13}$C). The properties of polymers were determined by using gel permeation chromatography (GPC) analysis, UV-visible spectroscopy, thermogravimetric analysis and electrochemical techniques. The measurement of space charge limited current (SCLC) hole mobilities of both polymers **PTTPBT** and **PTPDPBT** was also carried out.

## 4.2. Results and Discussion

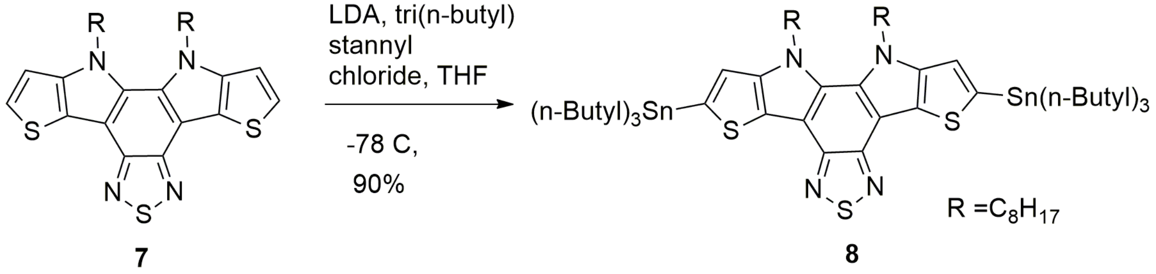
### 4.2.1 Experimental

Polymers, **PTTPBT** and **PTPDPBT** consist of a common monomer 10, 11-dioctyl-10, 11-dihydro-[*1*, *2*, *5*]thiadiazolo[*3*, *4-e*]thieno[*2'*, *3'*:*4*, *5*]pyrrolo[*3*, *2-g*]thieno[*3*, *2-b*]indole (**7**). In case of **PTTPBT** polymer, compound **7** was coupled with diethyl tert-thiophene dicarboxylate (TTD), in which TTD units acts an acceptor owing to its electron withdrawing dicarboxylate groups while DTPBT units acts as a donor unit. Synthesis of compound **7** was carried out according to the method reported in the literature (Scheme 4.1). The synthesis of compound **7** involves multiple steps. In first step, *ortho* phenylene diamine (**1**) was reacted with thionyl chloride to yield benzothiadiazole (**2**), which further brominated by using bromine in hydrobromic acid (HBr) to get dibromo benzothiadiazole (**3**). Compound **3** was nitrated by nitrating mixture ($HNO_3$/$H_2SO_4$:3/2) in trifilic acid giving product dinitro dibromo benzothiadiazole (**4**) in 69% yield. This compound **4** was reacted with 2-tri(*n*-butyl)stannyl thiophene under nitrogen atmosphere in dry THF in presence of tetra(triphenyl)bispalladium dichloride as a catalyst to yield 5, 6-dinitro-4, 7-di(thiophen-2-yl)benzo[*c*]-2, 1, 3-thiadiazole (**5**) in 80%. Compound **5** was cyclized under Cadogen reaction conditions to form dithienopyrrolobenzthiadiazole (**6**) in 58% yield.



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

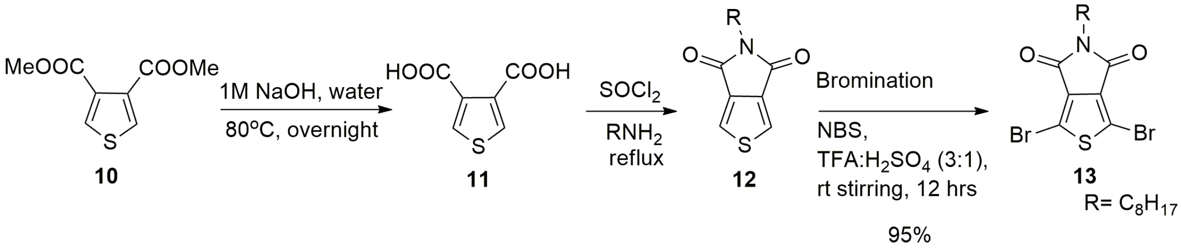
Compound **6** was alkylated by *n*-octyl bromide in DMF using NaOH as a base to form compound **7** with yield of 42%. Compound **7** was first reacted with LDA at -78$^{o}$ C and then reacted with tri-*n*-butylstannyl chloride to yield compound **8** in 90%.



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

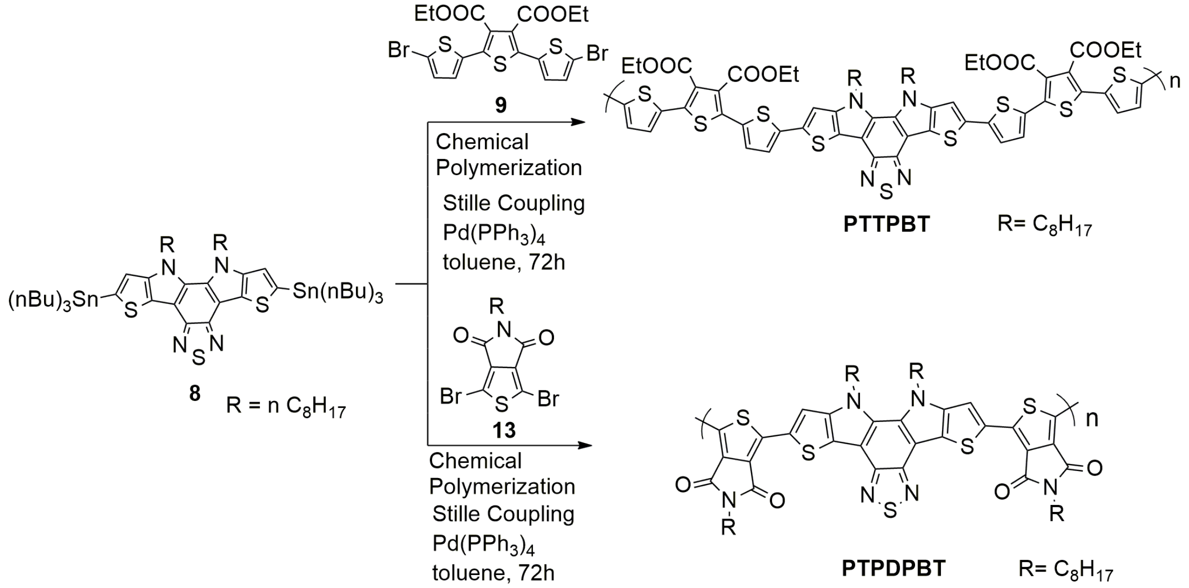
Monomer, diethyl tert-thiophene dicarboxylate was synthesized by the procedure as described in Chapter 3. Synthesis of polymer **PTTPBT** was carried out by the chemical polymerization between compound **8** and dibromo diethyl tert-thiophene dicarboxylate (TTD) (**9**) under Stille coupling reaction conditions. Obtained polymer **PTTPBT** was characterized by NMR ($^{1}$H and $^{13}$C). The molecular weight was determined by GPC analysis.

**PTPDPBT** polymer contained DTPBT units coupled with *n*-octylthieno[*3 ,4-c*]pyrrole-4,6-dione (TPD) units. TPD units inherits electron withdrawing nature from its imide group and due to this property, TPD units have been used as an acceptor unit in many π-conjugated polymers. TPD was synthesized from dimethyl 3, 4-thiophene dicarboxylate (**10**) [31] in overall three steps. First step involved hydrolysis of dimethyl 3,4-thiophene dicarboxylate in aqueous NaOH solution to yield Thiophene 3,4-dicarboxylic diacid (**11**). Thiophene 3,4-dicarboxylic diacid was then converted into TPD through one-pot reaction which included first its reaction with thionyl chloride to form acid chloride which was further reacted with octyl amine to yield *n*-octylthieno[*3, 4-c*]pyrrole-4,6-dione (TPD) (**12**). Bromination of TPD was carried out in TFA:sulfuric acid [3:1] system using NBS at room temperature stirring to get 1, 3-dibromo-5-octylthieno[*3, 4-c*]pyrrole-4, 6-dione (**13**) as a white solid (Scheme 4.3).



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

Synthesis of **PTPDPBT** was carried out *via* chemical polymerization and the procedure was similar to that of **PTTPBT** polymer (scheme 4.4).



**Scheme 4.4** Synthesis of polymer **PTTPBT** and **PTPDPBT** by chemical polymerization.

The synthesized polymer, **PTPDPBT** was characterized by NMR ($^{1}H$ and $^{13}C$) and molecular weight of polymer was determined by GPC analysis.

### 4.2.2 Photophysical properties of polymers

The photophysical properties of polymers, **PTTPBT** and **PTPDPBT** were studied by UV-visible absorption and fluorescence emission spectroscopy. The absorption spectra of **PTTPBT** and **PTPDPBT** were shown in Figure 4.8 and the results are summarized in Table 4.1.

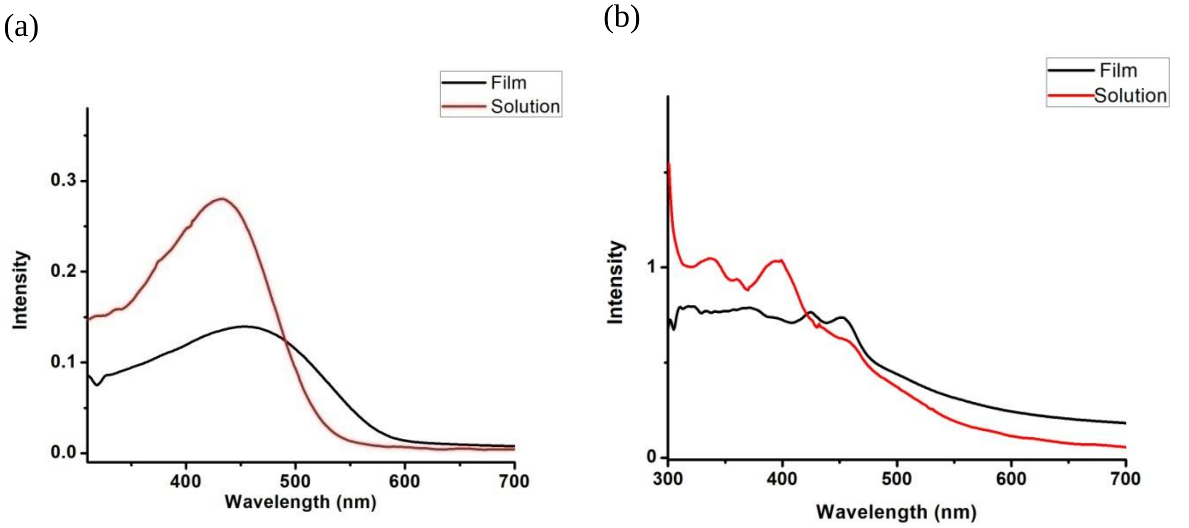


**Figure 4.10** UV-visible spectra of polymers (a) **PTTPBT** and (b) **PTPDPBT** in chloroform solution and thin solid films

Both polymers, **PTTPBT** and **PTPDPBT** showed a broad absorption curve between 230 to 600 nm. Polymer **PTTPBT** was dark red coloured shows single broad peak from 300 to 580 nm region in chloroform solvent (Figure 4.10). The absorption maximum was obtained at 430 nm in the chloroform solution. The broad single peak spectrum might be arising due to both π-π* transitions as well as intramolecular charge transfer (ICT) occurring between the DTPBT units and tert-thiophene dicarboxylate units [21]. The absorption peak gets red-shifted by about 25 nm, when the peaks obtained from solution were compared with solid thin film (Table 4.2). This red-shift confirms the presence of intermolecular interactions and aggregation in the solid state. These interactions were quite favorable as they likely to improve charge mobility in the thin films.

Polymer **PTPDPBT** which was black in color showed spectrum having peaks in region from 300 to 600 nm (obtained from chloroform solution). The absorption maxima were obtained at 340 nm and at 369 nm. The solid thin film UV-visible spectrum shows bathochromic shift of $\lambda_{max}$ from 340 nm, 369 nm to 426 nm and 451 nm (Figure 4.10). This result implies the intermolecular interactions and aggregation present in the solid state.

The emission properties of polymers, **PTTPBT** and **PTPDPBT** were studied by fluorescence spectroscopy. Emission spectra of **PTTPBT** and **PTPDPBT** were shown in Figure 4.11 and results are listed in Table 4.1.

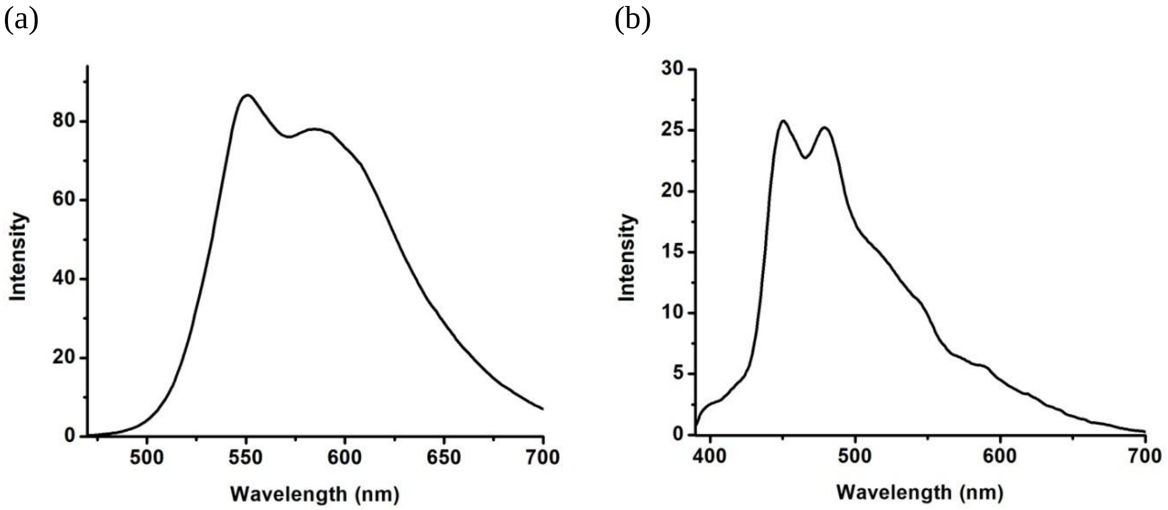


**Figure 4.11** Emission spectra of polymers (a) **PTTPBT** and (b) **PTPDPBT** in chloroform solution.

The emission spectrum of polymer **PTTPBT** ranges from 550 nm to 700 nm having a peak at 550 nm followed by hump at 586 nm as obtained from chloroform solution. The value of stoke shift was found to be 156 nm. Polymer **PTPDPBT** showed emission spectrum ranges from 400 nm to 650 nm and having two distinct peaks at 451 nm and 479 nm. The stokes shift was found to be 166 nm.

The $\lambda_{onset}$ for polymer **PTTPBT** was obtained at 586 nm and it possesses optical bandgap of 2.1 eV, while $\lambda_{onset}$ for polymer **PTPDPBT** was obtained at 650 nm which results the optical bandgap of 1.9 eV.

**Table 4.1** Photophysical properties of polymers, **PTTPBT** and **PTPDPBT**

| Polymer | $\lambda_{max}$ (abs) nm[a] | $\lambda_{max}$ (abs) nm(Film) | $\lambda_{max}$ (em) nm[a] | Stokes Shift (nm) | Onset (nm) | $E_{band\ gap}^{Opt}$(eV)[b] |
|---|---|---|---|---|---|---|
| **PTTPBT** | 430 | 456 | 586, 550 | 156 | 586 | 2.1 |
| **PTPDPBT** | 340, 369 | 426, 451 | 479, 451 | 166 | 650 | 1.9 |

[a] Measured in chloroform.

[b] Estimated from the onset of the absorption in the thin films ($E_g = 1240/(\lambda_{onset}$ eV)

## 4.2.3 Thermal and molecular weight properties of polymers

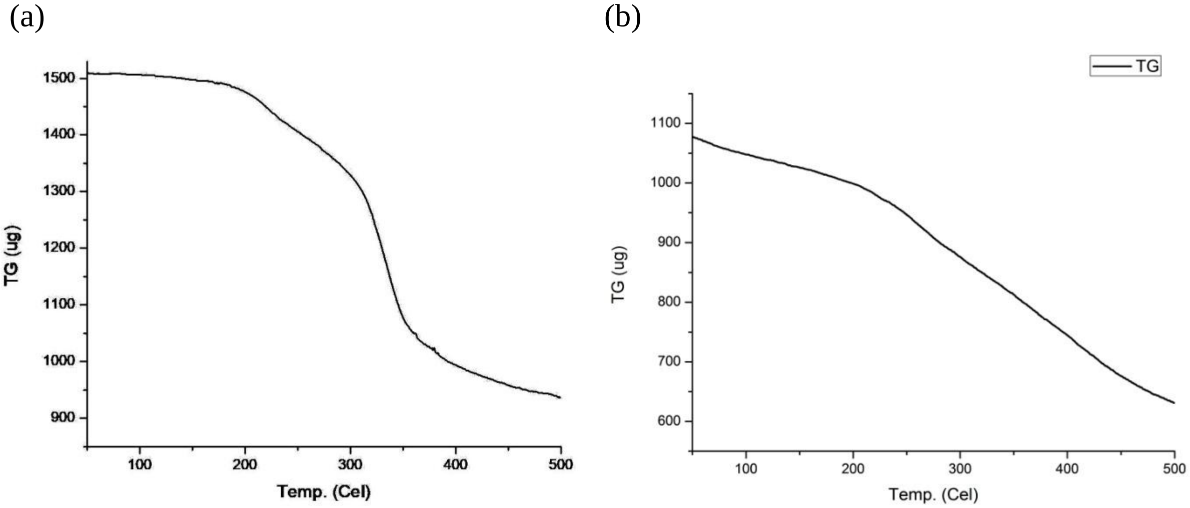


**Figure 4.12** TGA curves of polymers (a) **PTTPBT** and (b) **PTPDPBT**

Thermal properties of both synthesized conjugated polymers were analyzed by thermogravimetric analysis (TGA) at a heating rate of 10 °C/min under nitrogen atmosphere (Figure 4.12). The decomposition temperature (T*d*) of the polymer is defined as the temperature at which, the polymer loses 5% of its weight. The decomposition temperature (T*d*) of **PTTPBT** and **PTPDPBT** were observed at 220 °C and 208 °C respectively, which shows high thermal stability of synthesized polymer in the applications of organic electronic devices.

Weight average molecular weight (Mw), poly-dispersity index (PDI) and decomposition temperatures (T*d*) of both polymers are summarized in Table 4.2.

**Table 4.2** Molecular weight and poly-dispersity index (obtained from GPC analysis) and decomposition temperature T*d* (obtained from TGA) of synthesized polymers

| Polymer | $M_n$ (KDa) | $M_w$ (KDa) | PDI | $T_d$ ($^oC$) |
|---|---|---|---|---|
| **PTTPBT** | 9.44 | 20.65 | 2.18 | 220 |
| **PTPDPBT** | 4.92 | 9.60 | 1.9 | 208 |

## 4.2.3 Electrochemical properties of polymers

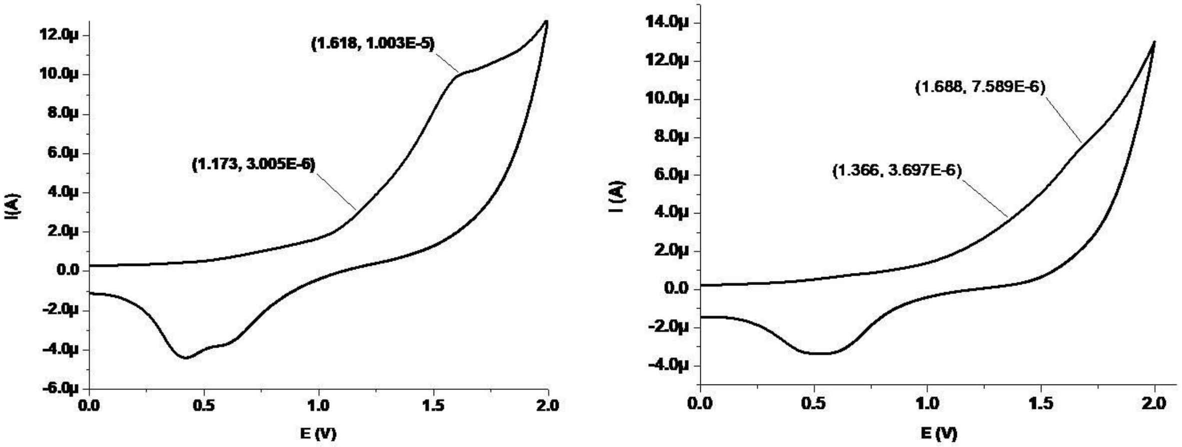

(a)
(b)

**Figure 4.13** Cyclic voltammogram of polymers (a) **PTTPBT** and (b) **PTPDPBT.** (Curves were obtained in $CH_3CN$ solution of ~50 mM $TBAPF_6$ at scan rate of 50 $mVs^{-1}$. $E_{onset(Fc/Fc+)}$ = 0.40 V

The frontier orbital energy levels of the synthesized conjugated polymers were measured using cyclic voltammetry (CV). CV experiments were performed in the dry acetonitrile using $TBAPF_6$ as a supporting electrolyte (~50 mM) using a three-electrode system: a glassy carbon electrode as the working electrode, a Pt wire electrode as the counter electrode and Ag/Ag+ as the reference electrode. Polymer films were casted on the glassy carbon working electrode from its chloroform solution (~10 mg/mL), the films were dried under nitrogen gas flow and were subjected to the CV measurement. The CV of **PTTPBT** showed oxidation potential at 1.61 V and the oxidation peak with an onset at 1.17 V *vs* $Ag^+/Ag$. From the onset of oxidation potential, energy levels of HOMO of polymer **PTTPBT** was estimated to be -5.57 eV. LUMO energy levels of polymer **PTTPBT** was calculated using equation $E_{LUMO} = Eg^{opt} + E_{HOMO}$ (eV) and value obtained was -3.47 eV.

The oxidation potential of **PTPDPBT** polymer was obtained at 1.68 V and its onset for oxidation was found to be 1.36 V. HOMO energy levels of **PTPDPBT** polymer which were estimated from onset of oxidation were obtained as -5.76 eV and its corresponding LUMO energy levels were calculated from the optical bandgap and the HOMO energy level found from CV. The calculated values of LUMO were -3.86 eV (Table 4.3).

**Table 4.3** Electrochemical properties of **PTTPBT** and **PTPDPBT**

| Polymers | $E^{onset}_{oxi}$ (V)[a] | $E_{HOMO}$ (eV)[b] | $E_{LUMO}$ (eV)[c] | $E_{band\ gap}^{opt}$ (eV)[d] |
|---|---|---|---|---|
| **PTTPBT** | 1.17 | -5.57 | -3.47 | 2.1 |
| **PTPDPBT** | 1.36 | -5.76 | -3.86 | 1.9 |

[a] Ag*vs* Ag/AgCl; [b] calculated using the equation: $E_{HOMO} = -(E_{oxi} + 4.8 - E_{(Fc/Fc+)})$, $E_{(Fc/Fc+)} = 0.40$ V; [c] calculated from the equation $E_{LUMO} = Eg^{opt} + E_{HOMO}$ (eV). [d] Estimated from the onset of the absorption in the thin films ($E_g = 1240/(\lambda_{onset}$ eV)

From the result of electrochemical experiments, it can be concluded that HOMO energy levels of **PTTPBT** and **PTPDPBT** polymers were located in an ideal range and can be compared to other reported $\pi$-conjugated polymers [32]. As well as the LUMO energy levels of polymers **PTTPBT** and **PTPDPBT** were obtained as -3.47 and -3.86 eV respectively, and the values were higher than that of $PC_{71}BM$ (-4.0 eV), which ensure favorable energetic electron transfer from donor to acceptor in the photovoltaic devices [33].

### 4.2.4 Space charge limited current (SCLC) hole mobilities of polymers

The photophysical and electrochemical properties of synthesized polymers **PTTPBT** and **PTPDPBT** encourage us to carry out hole mobility measurement. The hole mobility of polymers was measured according to a similar method described in the literature, [20] using a diode configuration of ITO/poly(ethylenedioxythiophene) doped with poly(styrenesulfonate) (PEDOT:PSS)/polymer/Al by taking current-voltage current in the range of 0~6 V and fitting the results to a space charge limited form; the SCLC is described by,

$$J = {}^{9\varepsilon_0\varepsilon_r\mu V^2}\!/_{8L^3}$$

In the equation, $\varepsilon_0$ is the permittivity of free space, $\varepsilon_r$ is the dielectric constant of the polymer, $\mu$ is the hole mobility, $V$ is the voltage drop across the device, and $L$ is the polymer thickness, $V = V_{appl} - V_r - V_{bi}$, where $V_{appl}$ is the applied voltage to the device, $V_r$ is the voltage drop due to constant resistance series resistance across the electrodes, and $V_{bi}$ is the built-in voltage due to the difference in work function of the two electrodes. The resistance of the device was measured using a blank configuration ITO/PEDOT/Al. The dielectric constants of the polymers in our analysis were determined by using the equation of $\varepsilon_r = {}^{Cd}\!/_{A\varepsilon_0}$, where C, *d*, A and $\varepsilon_0$ are the capacitance of the device, the thickness of the polymer film, the area of the device and permittivity of the free space, respectively.

The measured SCLC hole mobilities for synthesized DTPBT-based conjugated polymers are $2.36\times10^{-4} cm^2V^{-1}s^{-1}$ and $2.18\times10^{-4}$ $cm^2V^{-1}s^{-1}$, respectively for polymers,

**PTTPBT** and **PTPDPBT**. The hole mobilities observed for these polymers allows their application to be used as hole transporting materials (HTMs) for organic photovoltaic devices.

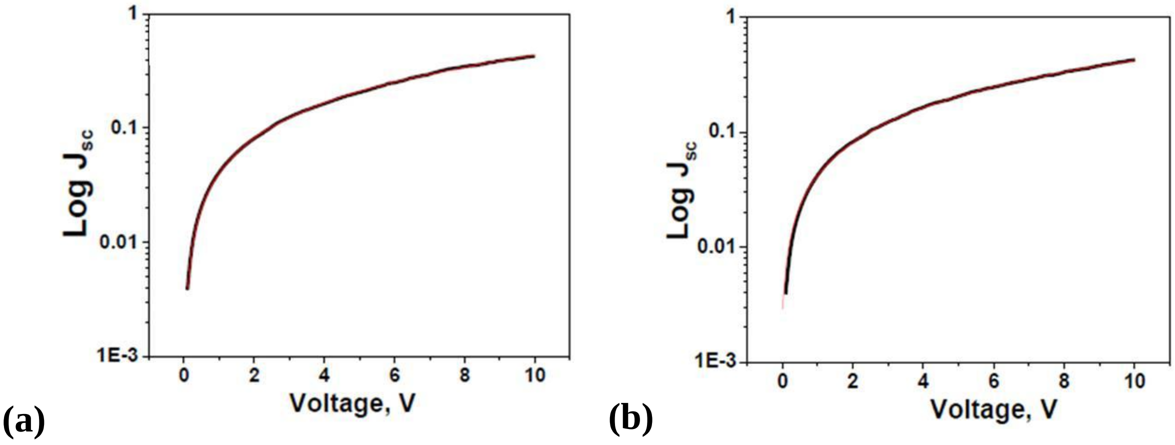


**Figure 4.14** SCLC hole mobility of polymer (a) **PTTPBT** and (b) **PTPDPBT.**

## 4.3 Conclusion

Dithienopyrrolobenzothiadiazole was synthesized and used as donor unit in $\pi$-conjugated polymer against diethyl tert-thiophene dicarboxylate and thieno[*3*,*4*-*c*]pyrrole-4,6-dione as an acceptor units. Chemical polymerization of distannyl dioctyl dithienopyrrolobenzothiazole and diethyl dibromo tert-thiophene dicarboxylate and dibromothieno[*3*,*4*-*c*]pyrrole-4,6-dione were carried out *via* Stille coupling reaction. The obtained conjugated polymers were isolated and purified, characterized by NMR. The photophysical properties such as UV-visible absorption and photo-luminescence were studied from UV-visible absorption and fluorescence spectrophotometer respectively. Polymer **PTTPBT** showed broad absorption peak with absorption maxima at 430 nm while **PTPDPBT** showed absorption maxima at 369 nm. Polymers, **PTPDPBT** showed broad absorption spectrum. Electrochemical properties of polymers were studied by CV in which it was observed that both polymers gave reversible oxidation curves with $E^{onset}_{oxi}$ at 1.17 V and 1.36 V for polymer **PTTPBT** and **PTPDPBT**, respectively. The synthesized polymers, **PTTPBT** and **PTPDPBT** both possessed small band gap of 2.1 eV and 1.9 eV which qualifies their application in the organic-electronic field. The hole mobilities of both polymers were measured and the values obtained were 2.36 $\times10^{-4}cm^2V^{-1}s^{-1}$ and 2.18 $\times10^{-4}cm^2V^{-1}s^{-1}$ for **PTTPBT** and **PTPDPBT**, respectively.

## 4.4 Experimental section

### 4.4.1 General

All chemicals and reagents were purchased from commercial sources and used without further purification unless otherwise noted. THF and toluene were distilled over sodium and benzophenone. Reactions which were moisture sensitive, carried out under nitrogen atmosphere. Reactions were monitored by TLC analysis using Merck silica gel 60 F-254 thin-layer plates. Column chromatography was done on Silica Gel (60-140 mesh). NMR spectra were recorded on Bruker AV-III 400 MHz (for $^1$H) and 100 MHz (for $^{13}$C) spectrometer using $CDCl_3$/DMSO-*D*6 as solvent and chemical shifts are reported in parts per million (δ scale) relative to tetramethylsilane (TMS) as an internal standard. The UV-visible spectra were recorded on model Perkin ElemerLamba 35 UV-visible spectrometer. Fluorescence spectra were recorded on a model HITACHI F-6300 fluorescence spectrometer. The molecular weight and poly dispersity index of polymers were determined by gel permeation chromatography (GPC) using PL gel 5 um MXLED-C column on an Agilent 1100 series liquid chromatography system with THF as an eluent and calibrated with polystyrene as standard. Thermal analysis was recorded on a SII EXSTAR 6000 model thermogravimetric analysis/ simultaneous differential thermal analysis (TG/DTA). CV was performed on Princeton Applied Research 263A potentiostat with a three-electrode cell containing a solution of $TBAPF_6$ (0.1 M) as electrolyte in dry DCM at a scan rate of 50 mV $s^{-1}$. The measurements were calibrated using ferrocene as standard. The electrochemical cell was set up with Pt disk electrodeas the working electrode, a Pt wire as counter electrode, and an Ag/AgCl as reference electrode. Electrochemical experiments were performed under nitrogen atmosphere.

### 4.4.2 Synthesis

#### 4.4.2.1 Synthesis of benzo[*c*]-2,1,3-thiadiazole (2)

*o*-Phenylene diamine (5 g, 46 mmol) was taken in two neck round bottom flask and 10 mL dichloroethane (DCE) and triethyl amine (TEA) (19.3 mL, 139 mmol) were added sequentially. Slow dropwise addition of solution of thionyl chloride (13.5 mL, 185.2 mmol) in DCE was carried out over 45 minutes using pressure equalizer dropping funnel. Reaction mixture was refluxed at 85$^o$ C for 12 hours. Then it was cooled to room temperature and water was added to quench excess thionyl chloride. The product was extracted in dichloromethane (DCM), organic layer was dried over $Na_2SO_4$ and solvent was evaporated under reduced pressure. The crude product thus obtained was subjected to steam distillation to obtain pure product as white crystals. The product was obtained in 85% yield (5.4g). $^1$H NMR ($CDCl_3$): $\delta$ 8.00-8.05 (m, 2H), 7.59-7.63 (m, 2H).

#### 4.4.2.2 Synthesis of 4, 7-dibromobenzo[*c*]-2,1,3-thiadiazole (3)

A solution of bromine (7.06 g, 2.3 mL, 44 mmol) in HBr (20 mL) was added dropwise using pressure equalizer dropping funnel into the solution of compound 2 (2.0 g, 14.7 mmol) in 47 % HBr (30 mL) and then reaction mixture was refluxed for 6 hours. After cooling to the room temperature $NaHSO_3$ solution was added to quench excess bromine. The crude product obtained was filtered and washed with water and then with cold diethyl ether carefully and dried. It was purified by silica gel column chromatography (ethyl acetate:petroleum ether, 1:10). The product was obtained as white crystals in 80% yield (3.46g). $^1$H NMR ($CDCl_3$): $\delta$ 7.75 (s, 2H).

#### 4.4.2.3 Synthesis of 4,7-dibromo-5,6-dinitrobenzo[*c*]-2,1,3-thiadiazole (4)

Triflic acid (trifluoromethane sulfonic acid) (11.1 mL, 128.6 mmol) was taken in a two neck round bottom flask and cooled in ice-salt bath under nitrogen atmosphere. To this fuming $HNO_3$ (2.5 mL conc. $HNO_3$ + 0.8 mL conc. $H_2SO_4$) was added and this nitrating mixture was cooled for 15 minutes. Compound **3** (3.0 g, 10.2 mmol) was added into nitrating mixture portion-wise over 30 minutes. The temperature was then raised to 50$^o$ C and stirred overnight. Then reaction mixture was poured slowly on crushed ice and neutralized with 2N NaOH. The resultant mixture was filtered and washed with water, dried and recrystallized from 95% EtOH. Crystals of compound **4** obtained were directly used for next reaction (2.72 g, 69% yield).

### 4.4.2.4 Synthesis of 5,6-dinitro-4,7-di(thiophen-2-yl)benzo[*c*]-2,1,3-thiadiazole (5)

Compound **4** (0.800 g, 1.65 mmol) was dissolved in dry THF (20 mL) under nitrogen atmosphere in two neck round bottom flask and $Pd(PPh_3)_2Cl_2$ (0.058 g, 0.083 mmol) was added. Then 2-tributyl stannyl thiophene (1.02 mL, 4.13 mmol) was added *via* syringe and reaction mixture was heated at $65^o$ C for 12 hours. The reaction was monitored by TLC. On completion of reaction, the solvent was evaporated under reduced pressure and reaction mixture was washed with water and extracted in DCM which was later dried over $Na_2SO_4$ and concentrated to yield crude product. The crude product was further purified over silica gel column chromatography (20% ethyl acetate in petroleum ether). Bright red solid compound was obtained. Yield: 80% yield (0.65g). $^1$H NMR ($CDCl_3$): $\delta$ 7.76-7.77(dd, 2H), 7.53-7.54 (dd, 2H), 7.25-7.33 (m, 2H).

### 4.4.2.5 Synthesis of dithienopyrrolobenzothiadiazole (DTPBT) (6)

Compound **5** (0.300g, 0.612 mol) was dissolved in *o*-dichlorobenzene (5 mL) in a two neck round bottom flask under nitrogen atmosphere and triphenyl phosphine (1.604 g, 6.12 mol) was added. Reaction mixture was then heated to 160 $^o$C for 12 hours, cooled and purified by silica gel column chromatography (40% ethyl acetate in petroleum ether). The product was obtained as an orange solid (0.260g). $^1$H NMR (DMSO $D_6$): $\delta$ 11.90 (s, 2H), 7.61-7.63 (d, 2H), 7.43-7.44 (d, 2H).

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

In a 100 mL round bottom flask compound **6** (0.260 g, 0.79 mmol) was taken followed by addition of octyl bromide (0.69 mL, 3.98 mmol). To this reaction mixture, NaOH (0.316 g, 7.9 mmol) in DMF/water (2 mL) was added. The reaction mixture was stirred at 50 $^{o}$C for 6 hours. Then excess of water was added in reaction mixture and product was extracted in DCM. Organic layer was dried over $Na_2SO_4$ and then evaporated under reduced pressure to get crude product which was purified by silica gel column chromatography (5% ethyl acetate in petroleum ether). The solid product was obtained in 42% yield (0.214 g). $^1$H NMR ($CDCl_3$): $\delta$ 7.45-7.46 (d, 2H), 7.20-7.22 (d, 2H), 4.50-4.54 (t, 4H), 1.81-1.87 (m, 4H), 1.08-1.27 (m, 20H), 0.80-0.84 (m, 6H).

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

10, 11-dioctyl-10, 11-dihydro-[*1, 2, 5*]thiadiazolo[*3, 4-e*]thieno[*2', 3':4, 5*]pyrrolo[*3, 2-g*]thieno[*3, 2-b*]indole (0.4 g) (0.0007 mol) (1 equivalents) was taken in dry three neck round bottom flask attached with septum. 10 mL of dry THF was added to it and resultant solution was stirred at -78 $^{o}$C under nitrogen atmosphere. LDA (0.224 g) (0.0021 mol) (3 equivalents) was added to the reaction mixture and reaction mixture stirred at -78$^{o}$C for 3 hours. Tributyltin chloride was added to reaction mixture and reaction mixture was again stirred at -78 $^{o}$C for 1 hour. Thereafter, the reaction mixture was allowed to reach at room temperature in overnight time. The reaction mixture was quenched with water addition. The organic contents was extracted in diethyl ether, ether layer was washed with brine and dried over sodium sulfate, concentrated to yield product 10, 11-dioctyl-2, 8-bis(tributylstannyl)-10, 11-dihydro-[*1, 2, 5*]thiadiazolo[*3, 4-e*]thieno[*2', 3':4, 5*]pyrrolo[*3, 2-g*]thieno[*3, 2-b*]indole (**8**) in 90% yield (0.738 g). $^1$H NMR ($CDCl_3$): $\delta$ 0.77-0.83 (6H), 0.91-0.95 (18H), 1.10-1.69 (60H), 4.52-4.59 (4H), 7.17 (2H).

### 4.4.2.8 Synthesis of 5-*n*-octylthieno[*3*,*4*-*c*]pyrrole-4,6-dione (12)

Dimethyl thiophene-3,4-dicarboxylate (**10**) (4.0 g, 20 mmol) was taken in round-bottom flask of 100 mL capacity. To this 20 mL of 1M solution of NaOH was added and the mixture was stirred at 80 $^{o}$C for overnight. The solution was then acidified with HCl to pH=3 and extracted with ethyl acetate, dried over sodium sulfate and concentrated to obtain the yellow solid compound (**11**) (3.44 g). Yield obtained was 80%. Obtained product was dissolved in toluene (50 mL) and 15 mL of thionyl chloride was added to it. The reaction mixture was refluxed for 5 hours. Thereafter, excess of thionyl chloride was distilled off and 3.3 mL of *n*-octyl amine was added to the reaction mixture. The reaction mixture was heated to 200 $^{o}$C for 12 hours. Crude product was washed with water and brine, extracted in ethyl acetate. Dried over sodium sulfate and concentrated under reduced pressure. Further purification was performed by column chromatography on silica gel using petroleum ether:ethyl acetate (10:1) as eluent to obtained white solid product 4.5 g (85% yield). $^{1}$H NMR ($CDCl_3$): $\delta$7.8 (s, 2H), 3.62 (t, 2H), 1.67-1.60 (m, 2H), 1.30 (m, 10H), 0.86 (t, 3H).

### 4.4.2.9 Synthesis of 1,3-dibromo-5-octylthieno[*3*,*4*-*c*]pyrrole-4,6-dione (13).

Compound **12** (2 g, 7.54 mmol) was dissolved in trifluoroacetic acid (20 mL) and sulfuric acid (7.97 mL). NBS (4.45 g, 25 mmol) was added in small portion with constant stirring. The reaction mixture was stirred at room temperature for overnight. Reaction mixture was washed with aqueous sodium thiosulfate solution and the organic compound was extracted in dichloromethane. The crude product was purified by column chromatography on silica gel using petroleum ether/ethyl acetate (1:10) as the eluent to give compound **13** (2.69 g, 85%). $^{1}$H NMR ($CDCl_3$) $\delta$ 3.59 (t, 2H), 1.63 (m, 2H), 1.30-1.25 (m, 10H), 0.87 (t, 3H). $^{13}$C NMR ($CDCl_3$) $\delta$ 14.1, 22.6, 26.8, 28.2, 29.1, 31.7, 38.8, 112.9, 134.7, 160.4.

### 4.4.2.10 Synthesis of poly tert-thiophene-dithienopyrrolobenzothiadiazole (PTTPBT)

The chemical polymerization was carried out using Stille coupling reaction. In 50 mL round bottom flask diethyl 5, 5''-dibromo-[2, 2':5', 2''-terthiophene]-3', 4'-dicarboxylate

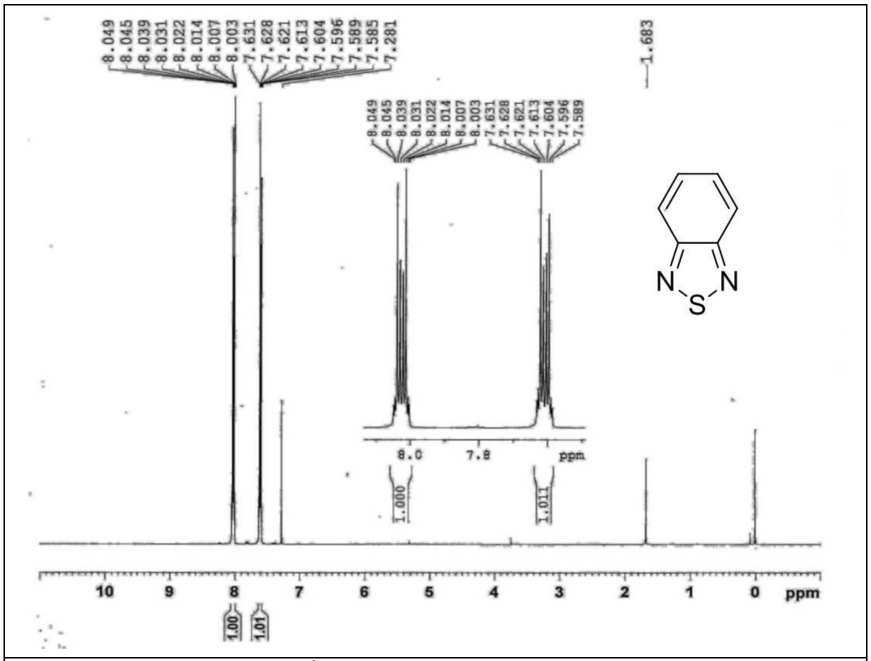
(0.165 g) (0.0003 mol) (1 equivalents) and distannyl dithienopyrrolobenzothiadiazole (0.3 g) (0.0003 mol) (1 equivalents) were dissolved in dry toluene (15 ml) and solution was purged with nitrogen for 15 minutes, thereafter $Pd(PPh_3)_4$(34.7 mg) (0.00003 mol) (0.1 equivalents) was added to the reaction mixture. The reaction mixture was again purged with nitrogen for 15 minutes. The reaction mixture was refluxed for 72 hours under nitrogen atmosphere. The reaction mixture was cooled to room temperature, washed with water and organic content was extracted in chloroform. The chloroform content was concentrated under vacuum; thereafter methanol (300 mL) was added to precipitate the crude polymer. The crude polymer was filtered and washed with methanol. Further purification was carried out by Soxhlet extraction by subsequent washing of hexane and acetone to yield final solid red colored polymer. Yield: 190 mg (76%). GPC: $M_n$= 9.4, PDI= 2.1. $^1$H NMR ($CDCl_3$) $\delta$ 0.81-0.89 (9H), 1.26-1.37 (18H), 1.69-1.89 (13H), 4.30-4.39 (8H), 7.09-7.11 (1H), 7.18-7.19 (2H), 7.31-7.32 (2H), 7.36-7.37 (1H), 7.42-7.44 (1H). $^{13}$C NMR ($CDCl_3$) $\delta$ 14.0, 22.5, 26.2, 27.0, 29.1, 42.8, 61.9, 113.8, 116.5, 124.8, 127.8, 129.1, 130.1, 139.1, 158.7, 163.8.

### 4.4.2.11 Synthesis of poly thieno[*3*,*4*-*c*]pyrrole-4,6-dione-dithienopyrrolobenzothiadiazole (PTPDPBT)

The chemical polymerization was carried out using Stille coupling reaction and the method used for synthesis of **PTTPBT** was followed. Both monomer, 1,3 dibromo-5-octylthieno[*3*,*4*-*c*]pyrrole-4,6-dione (0.084g) (0.0002 mol) (1 equivalents) and distannyldithienopyrrolobenzothiadiazole (0.25g) (0.0002 mol) (1 equivalents) was taken in dry toluene. $Pd(PPh_3)_4$ (23 mg) (0.00002 mol) (0.1 equivalents) was used as a catalyst. Obtained crude polymer was purified by Soxhlet extraction by subsequent extraction by hexane and acetone to remove lower molecular weight fractions. Black colored polymer was obtained with yield of 65% (117 mg). GPC: $M_n$= 4.9, PDI= 1.9. $^1$H NMR ($CDCl_3$) $\delta$ 0.87-0.90 (9H), 1.26-1.34 (34H), 1.70-1.72 (2H), 3.67-3.71 (6H), 7.95 (2H).

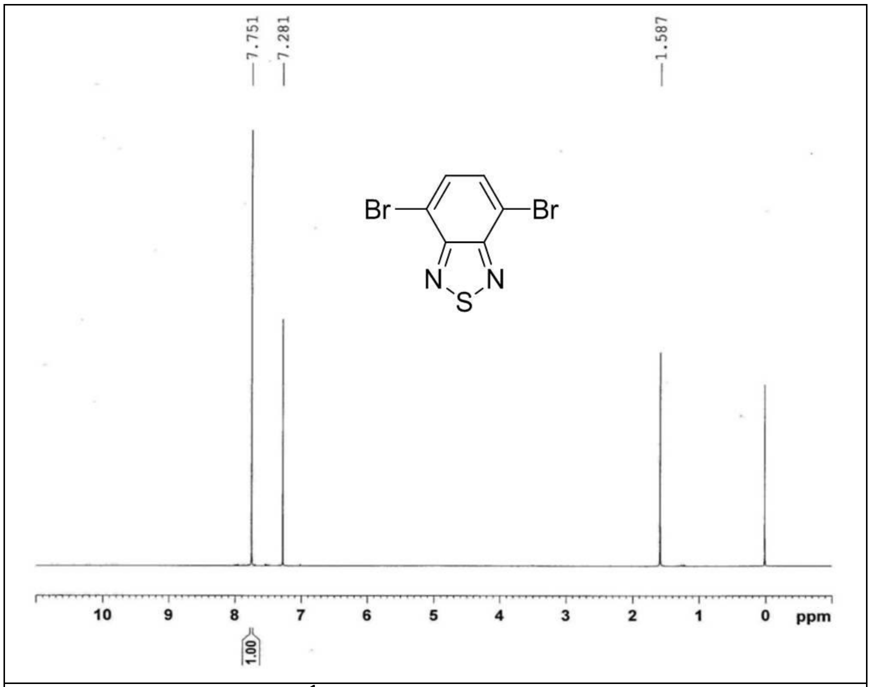
## 4.5 Spectral data

### 4.5.1 Benzo[*c*]-2,1,3-thiadiazole (2)



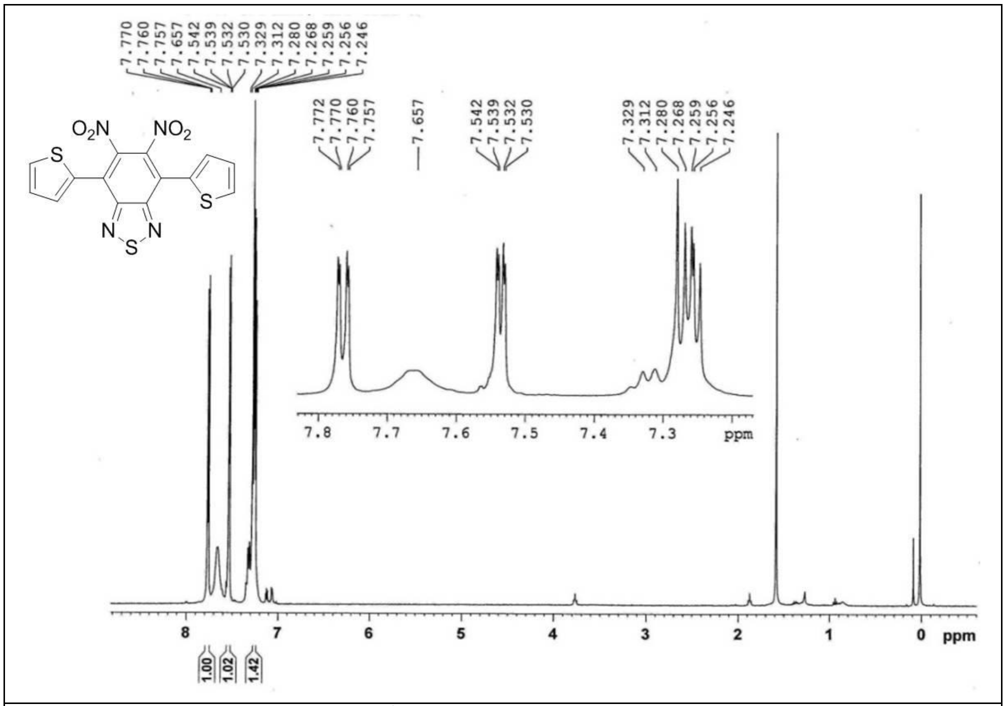
$^1$H NMR spectrum

### 4.5.2 4,7-Dibromobenzo[*c*]-2,1,3-thiadiazole (3)



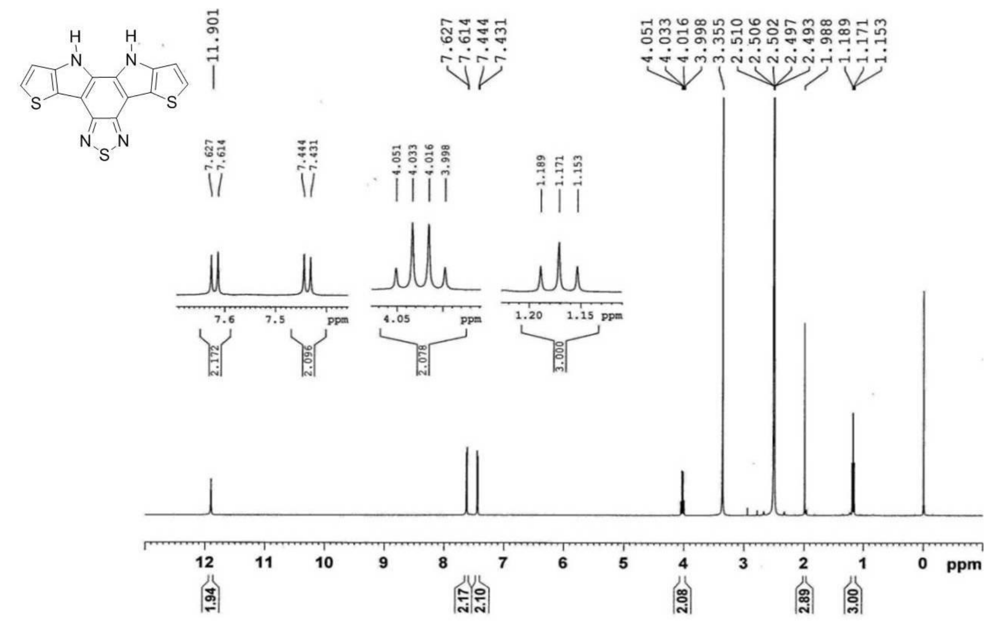
$^1$H NMR spectrum

### 4.5.3 5,6-Dinitro-4,7-di(thiophen-2-yl)benzo[*c*]-2,1,3-thiadiazole (5)



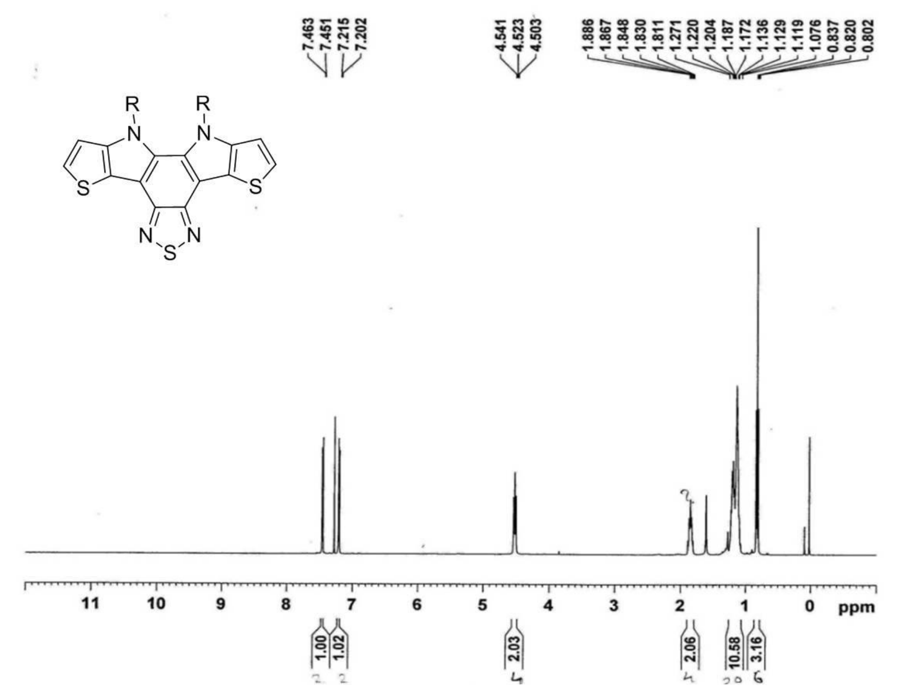
$^1$H NMR spectrum

### 4.5.4 Dithienopyrrolobenzothiadiazole (6)

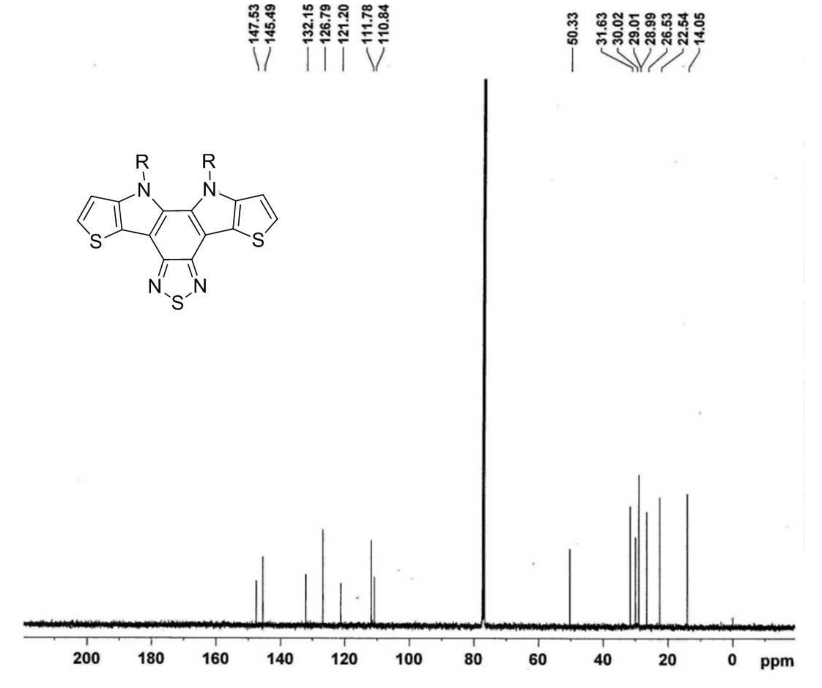


$^1$H NMR spectrum

### 4.5.5 10,11-Dioctyl-10,11-dihydro-[*1,2,5*]thiadiazolo[*34-e*]thieno[*2',3':4,5*] pyrrolo[*3,2-g*]thieno[3,2-b]indole (7) :

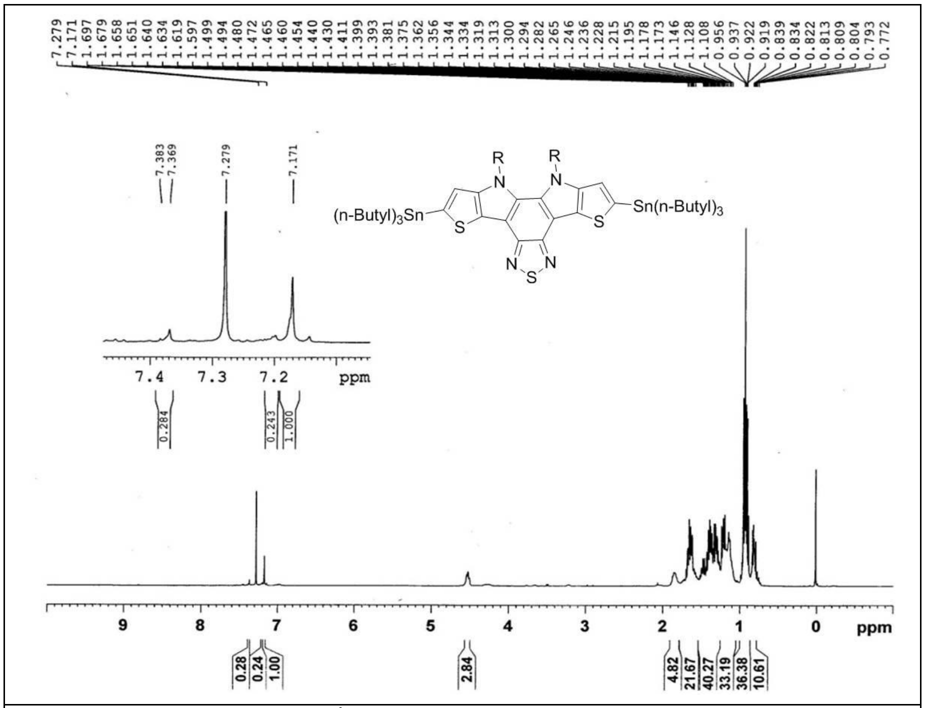


**$^1$H NMR spectrum**



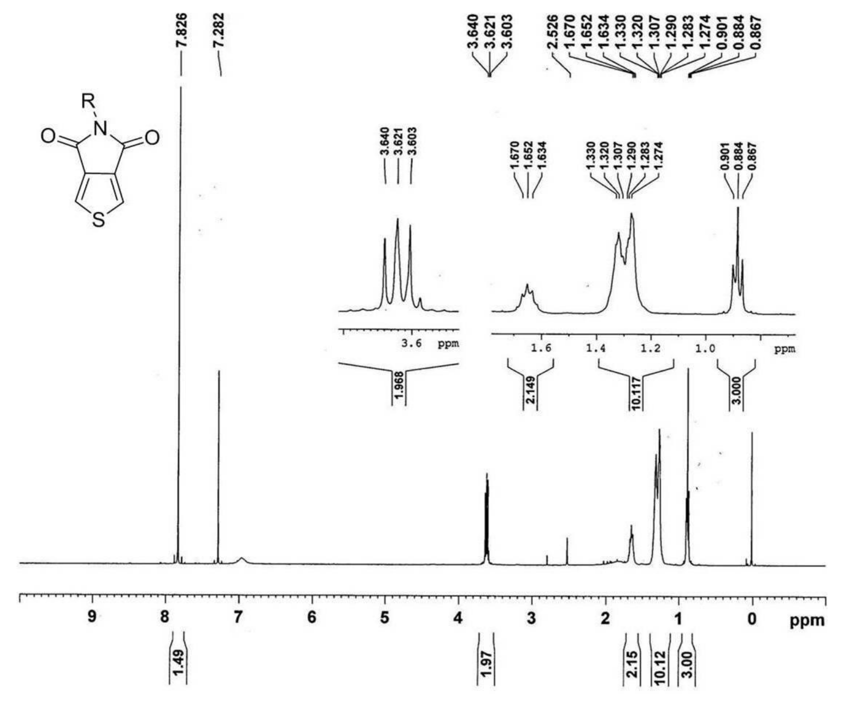
**$^{13}$C NMR spectrum**

### 4.5.6 10,11-Dioctyl-2,8-bis(tributylstannyl)-10,11-dihydro-[*1*,*2*,*5*]thiadiazolo[*3*,*4-e*]thieno[*2'3'*:*4*,*5*]pyrrolo[*3*,*2-g*]thieno[*3*,*2-b*]indole (8)



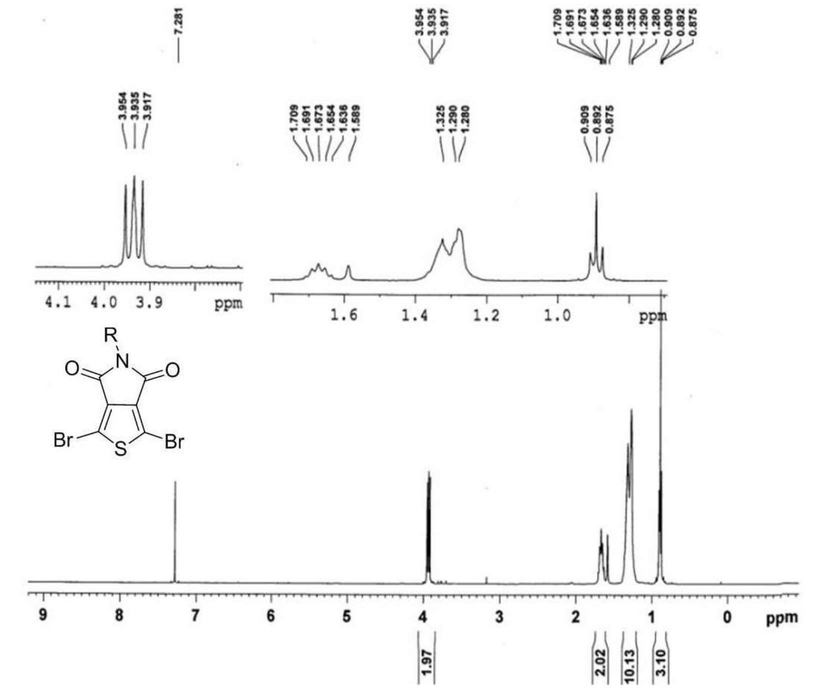
$^1$H NMR spectrum

### 4.5.7 5-*n*-Octylthieno[*3,4-c*]pyrrole-4,6-dione (12)

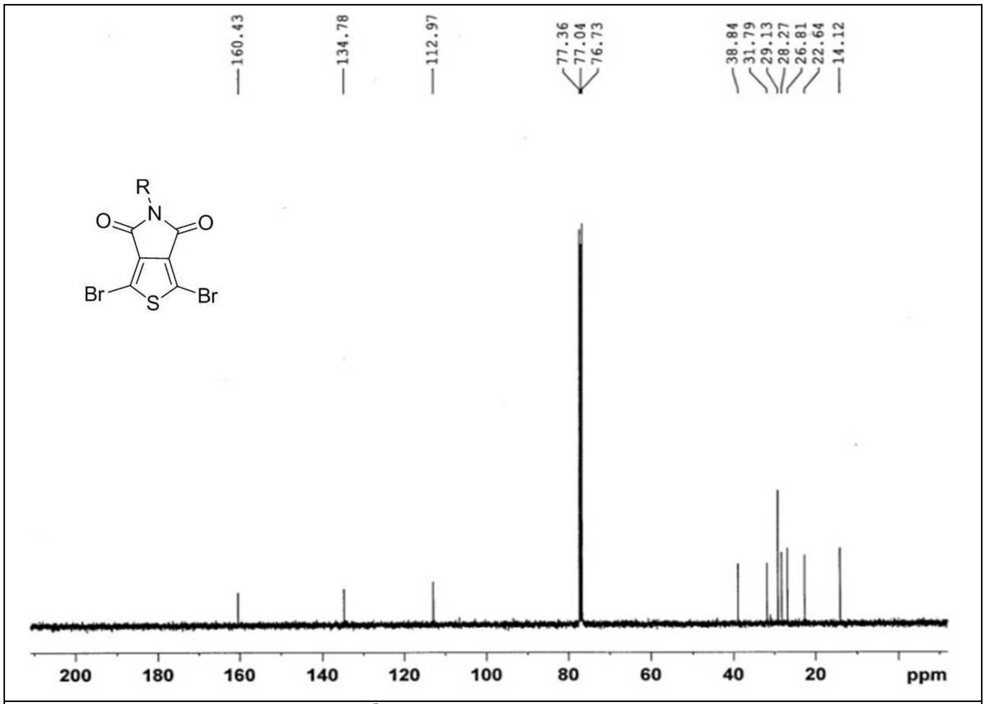


**$^1$H NMR spectrum**

### 4.5.8 1, 3-Dibromo-5-octylthieno[*3,4-c*]pyrrole-4,6-dione (13).

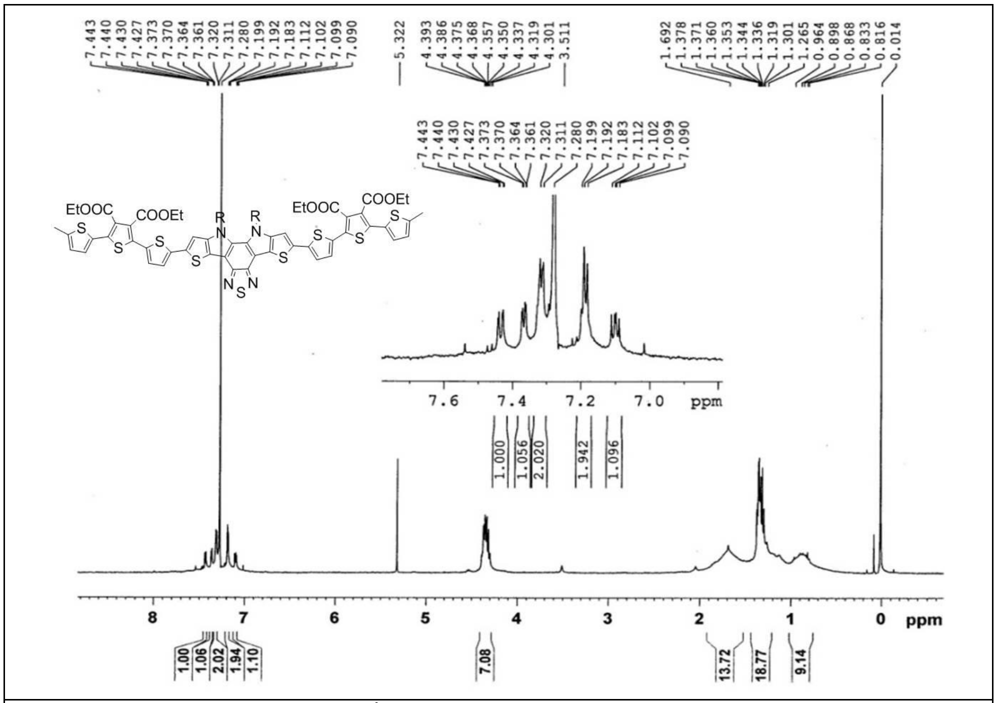


**$^1$H NMR spectrum**

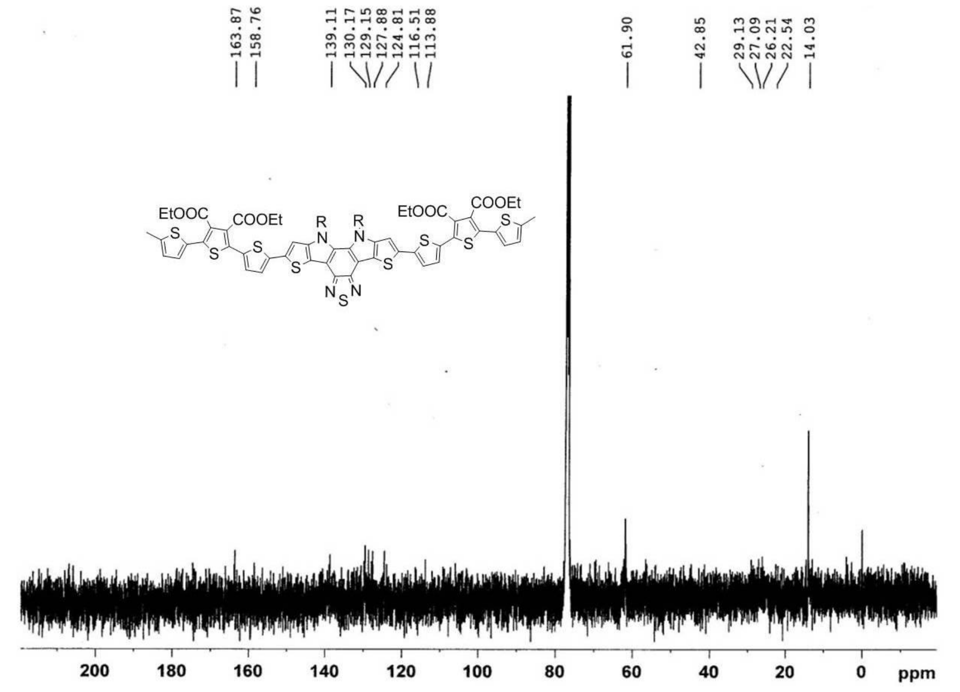


$^{13}$C NMR spectrum

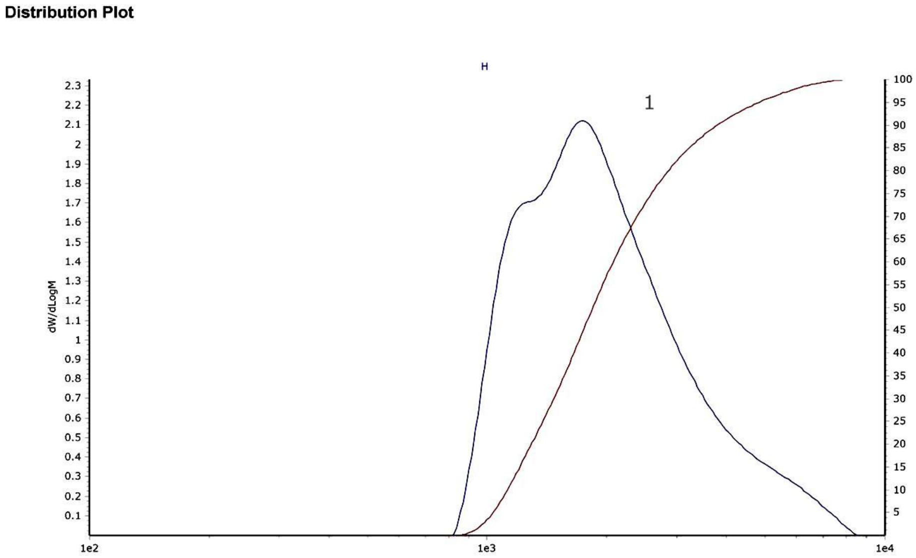
### 4.5.9 Poly tert-thiophene-dithienopyrrolobenzothiadiazole (PTTPBT)



$^{1}$H NMR spectrum



$^{13}$C NMR spectrum

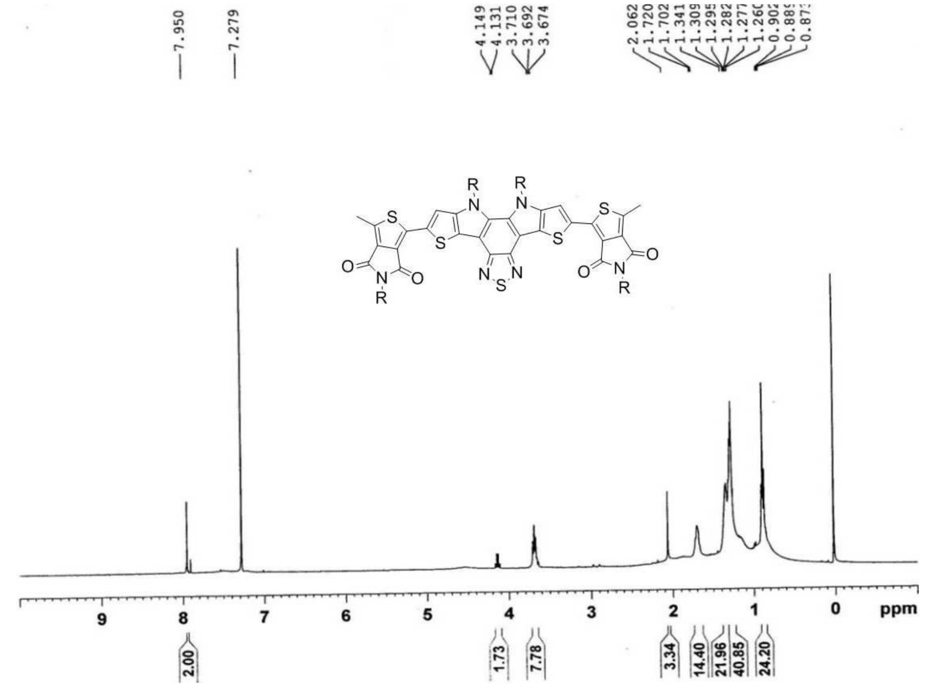


Molecular Weight Averages

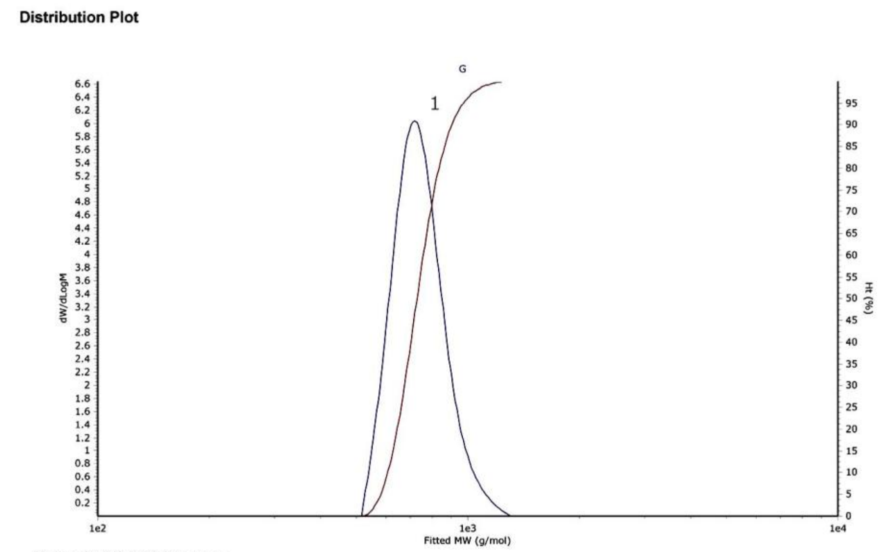
| Peak | Mp (g/mol) | Mn (g/mol) | Mw (g/mol) | Mz (g/mol) | Mz+1 (g/mol) | Mv (g/mol) | PD |
|---|---|---|---|---|---|---|---|
| Peak 1 | 4910 | 9444 | 20654 | 36970 | 48309 | 34972 | 2.187 |

GPC analysis of poly tert-thiophene-dithienopyrrolobenzothiadiazole (PTTPBT)

### 4.5.10 Polythieno[*3,4-c*]pyrrole-4,6-dione-dithienopyrrolobenzothiadiazole (PTPDPBT)



**$^1$H NMR spectrum**



**Molecular Weight Averages**

| Peak | Mp (g/mol) | Mn (g/mol) | Mw (g/mol) | Mz (g/mol) | Mz+1 (g/mol) | Mv (g/mol) | PD |
|---|---|---|---|---|---|---|---|
| Peak 1 | 8203 | 4924 | 9601 | 16037 | 21391 | 15170 | 1.95 |

**GPC analysis of polythieno[*3,4-c*]pyrrole-4,6-dione-dithienopyrrolobenzothiadiazole (PTPDPBT)**

# Chapter 4

## Synthesis, characterization, electrochemical and photophysical properties of dithienopyrrolobenzothiadiazole based $\pi$-conjugated polymers and $\pi$-conjugated D- $\pi$ - A- $\pi$ -D type molecule

## Part b: Dithienopyrrolobenzothiadiazole–Carbazole based $\pi$-conjugated D-$\pi$-A-$\pi$-D type molecule: Synthesis, characterization, photophysical, electrochemical and DFT studies

## 4.6. Introduction

Organic $\pi$-conjugated molecules have acquired significant research interest across the world due to their unique and desirable optical and electronic properties. $\pi$-conjugated molecules have well-defined molecular structures which provide them high degree of conjugation. Owing to these characteristic conjugated molecules are used in development of organic electronic devices like organic light emitting devices (OLEDs), organic field effect transistors (OFETs) and organic photovoltaics (OPVs) [34, 35].

$\pi$-Conjugated molecules consisting of fused thiophene ring systems exhibits extended $\pi$-conjugation facilitating better charge transport and unique electronic features raised from quinoid character accompanied by structural rigidity to the molecule [36]. Sulfur atom of thiophene also provides multiple short intermolecular S-S contacts which increases dimensionality in the conjugated systems [37, 38].

Incorporation of alternating donor (electron rich units) – acceptor (electron deficient units) (D-A) units in the π-conjugated systems, which results in the "push-pull" effect, have been proved extensively advantageous [39]. The intramolecular charge transfer (ICT) interaction arouses from the push-pull effect lowers the resultant band-gap of the $\pi$-conjugated systems. Thus, the tuning of bandgap of π-conjugated systems can be controlled by choosing a suitable donor, acceptor and linking moiety to yield desired result.

Ditheniopyrrolobenzothiadiazole (DTPBT) was synthesized by Cheng [19] and Yu [20] groups independently through fusion of two pyrrole units into the BTD by intermolecular Cadogen annulation resulting in the multifused pentacyclic structure [21]. The DTPBT unit possesses ladder type $\pi$-conjugated systems having enhanced $\pi$-conjugation across the system along with the rigid, large and planar framework resulting in high carrier mobility and high fluorescence properties [40].

Huang *et al* reported four new D-$\pi$-A type molecules having DTPBT units. In these molecules DTPBT were used as $\pi$-spacer. All synthesized molecules showed broad absorption spectra with high molar extinction coefficient which resulted in high light efficiency. Synthesized compounds were used in fabricating dye sensitized solar cells (DSSCs) which showed PCE of 7.55% for dye DTP4 [41].

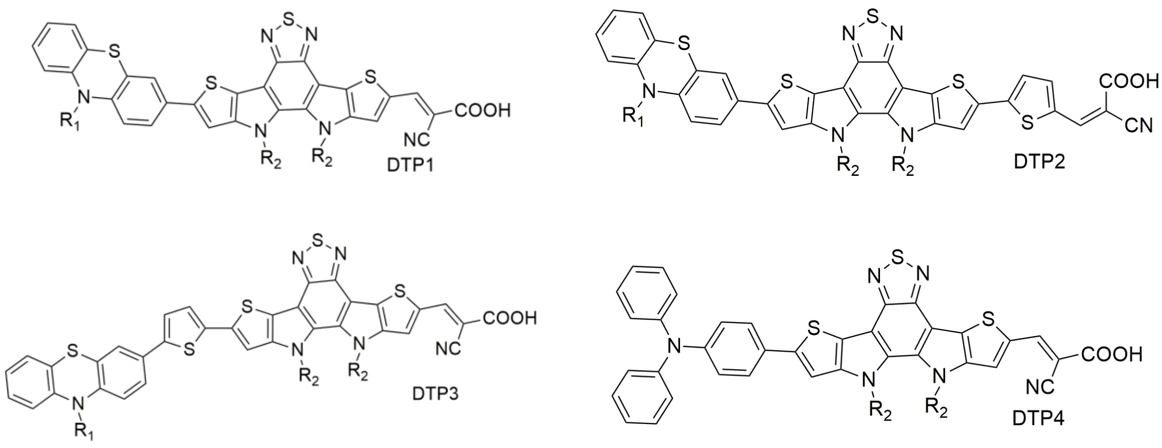


**Figure 4.15** D-$\pi$-A type molecules having DTPBT units as π-spacer

Recently, Lewdon *et al* reported carbazole-benzothiadiazole based D-$\pi$-A-$\pi$-D molecule (Figure 4.16) [42]. The application of synthesized molecule in OLED devices showed good efficiency, with a quantum efficiency as high as 3.13%, indicates that the reported molecule is a promising candidate for red and infrared applications.

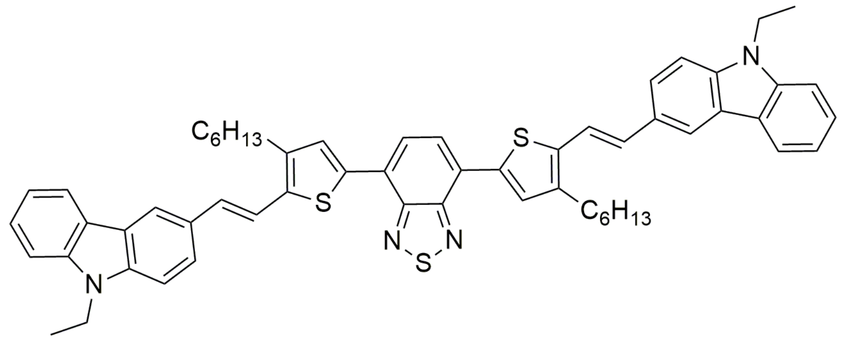


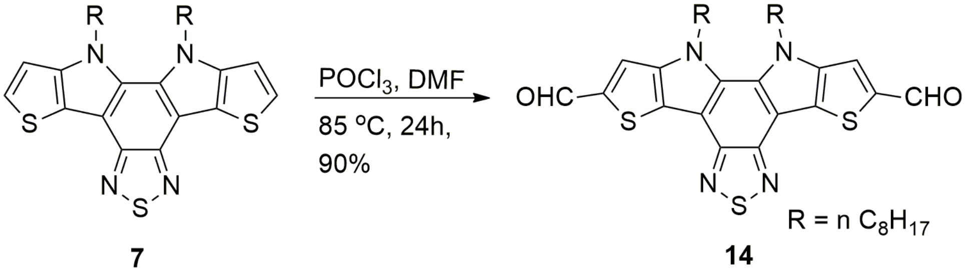
**Figure 4.16** Carbazole-benzothiadiazole based D-π-A-π-D

In present work, DTPBT core has been used to develop a new D-$\pi$-A-$\pi$-D type macromolecule. Carbazole was used as donor units in this $\pi$-conjugated system. The carbazole is among the most popular donor units in the field of organic semiconductors molecules because of its inexpensive and easily modified nature. Nitrogen atom in the carbazole ensures its high electron rich character as well as its structure provides good thermal, morphological stability along with high fluorescence nature [43]. To minimize steric hindrance and to increase the charge transfer bands in the molecule vinyl $\pi$-systems were used as linker between donor (carbazole) and acceptor (DTPBT) units [44]. The new D-$\pi$-A-$\pi$-D type macromolecule was characterized by NMR and HRMS. Photophysical studies were carried out by UV-visible and Fluorescence spectroscopy. Electrochemical properties were studied by CV analysis. Theoretical data were obtained from DFT calculations using *Gaussian 09* software [45].

## 4.7 Results and discussion

### 4.7.1 Synthesis

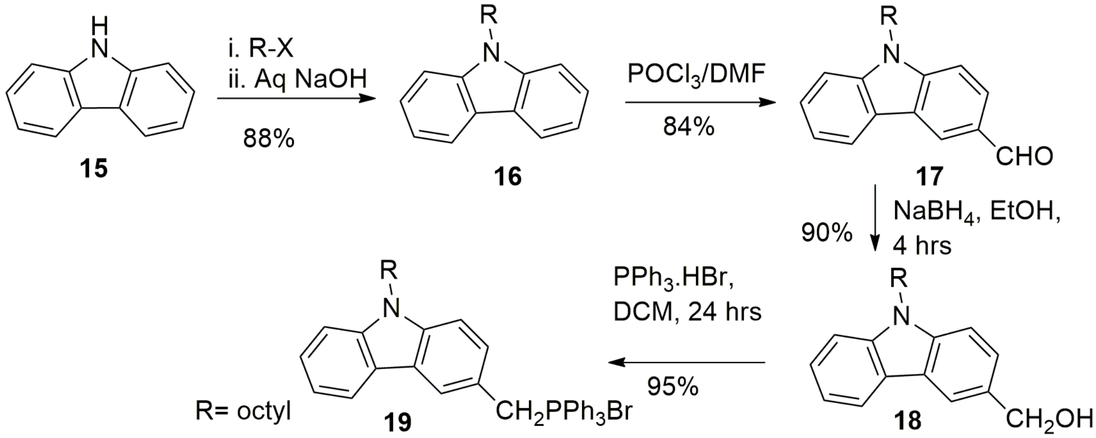
Compound **7** was synthesized using the procedure describe in chapter 4 (Part a).



**Scheme 4.5** Synthesis of compound **14**

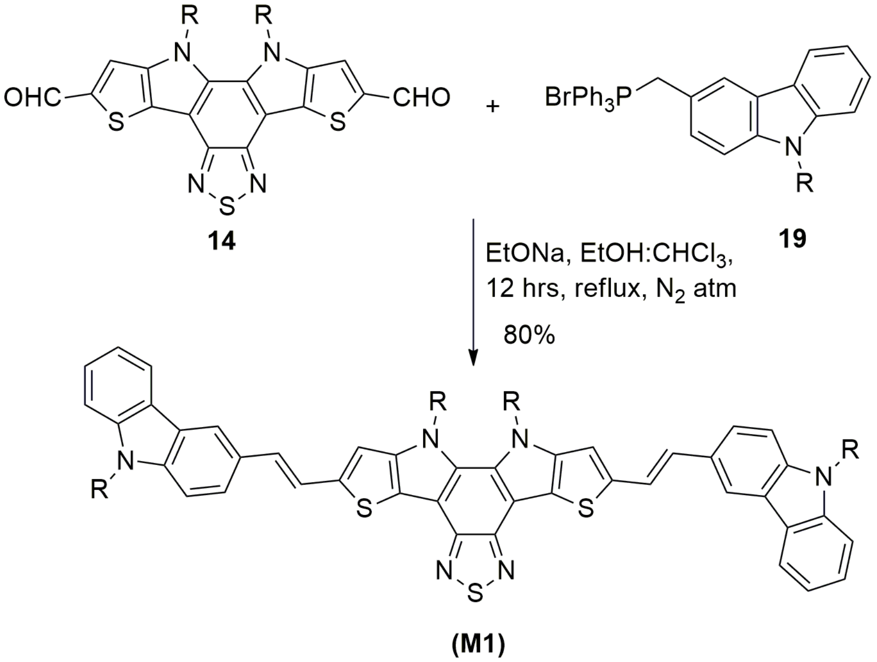
Compound **7** was reacted under Vilsmeier-Heck reaction condition to yield diformyl dioctyl DTPBT (**14**) in about 90% yield.Compound **14** was used as acceptor in the donor- $\pi$ -acceptor- $\pi$ -donor system.

Wittig salt of carbazole (**19**) was synthesized from carbazole by using literature procedure in four steps (Scheme 4.6) [45]. Compound **15** was first reacted with base NaOH and *n*-octyl bromide which yielded *N*-octylcarbazole (**16**) in 88% yield. *N*-octylcarbazole was converted into 3-formyl *N*-octylcarbazole (**17**) by Vilsmayer-Heck reaction using DMF/$POCl_3$. Compound **17** was reduced using $NaBH_4$ to obtain compound **18** which was converted into ((9-octylcarbazol-3-yl)methyl)triphenylphosphonium bromide (Wittig salt) (**19**) by reaction with triphenylphosphonium hydrobromide.



**Scheme 4.6** Synthesis of ((9-octylcarbazol-3-yl)methyl)triphenylphosphonium bromide (**19**)

Compound **M1** was synthesized by Wittig reaction of carbazole wittig salt (**19**) and diformyl dioctyl DTPBT (**14**) using sodium methoxide as base in MeOH as a solvent. The product was purified by column chromatography and characterized by NMR ($^1$H and$^{13}$C) NMR spectroscopy and HRMS.



**Scheme 4.7** Synthesis of compound **M1**

## 4.7.2 Photophysical properties

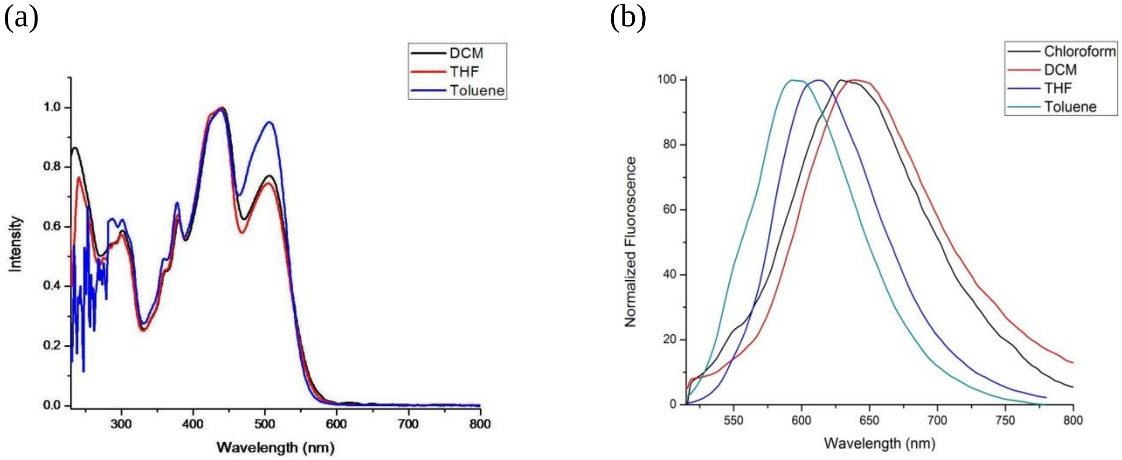


**Figure 4.17** (a) UV-visible spectra of compound **M1** in various solvents (concentration ~10 μM) (b) Emission spectra of compound **M1** in various solvents (concentration ~10 μM)

UV-visible absorption study was carried out by dissolving the compound **M1** in DCM solution having concentration of 10 $^{-5}$M. The UV-visible spectrum of compound **M1** showed two distinct absorption peaks at 506 nm and 441 nm. The intensity of 506 nm peak changes with different solvent. It can be suggested that this peak at 506 nm may arise due to the intramolecular charge transfer. These types of absorption band is characteristic peak of some donor-acceptor organic molecules e.g. benzothiadiazole molecule. The peak at 441 nm was obtained due to $\pi$-$\pi$* transitions.

A solvatochromic fluorescence effect was observed in the compound **M1**. An emission maximum of compound **M1** was observed at 614 nm in the THF solution. Red-shift was observed when solvent was varied from toluene to THF and then to DCM. These types of bathochromic shift are often observed because of the modification of energy levels of excited states arising by the changes in the polarity of the solvents [40]. The stokes shift value calculated for compound **M1** was 110 nm. The energy of observed stokes shift is 0.43 eV.

**Table 4.4** Photophysical properties of **M1**

| Compound | $\lambda_{max}$ (abs) (nm) | $\lambda_{max}$ (em) (nm) | $\lambda_{onset}$(abs) (nm) | $E_{band\ gap}^{Opt}$(eV)$^{b}$ | Stokes Shift (nm) | Stokes shift (eV) |
|---|---|---|---|---|---|---|
| **M1** | 506<br>441 | 614 | 582 | 110 | 110 | 0.43 |

[a] Measured in dichloromethane.

[b] Estimated from the onset of the absorption in the thin films ($E_g = 1240/(\lambda_{onset}$ eV).

The optical band gap of compound **M1** was calculated from UV-visible spectra. The onset of compound was observed at 582 nm. The optical band gap obtained was 2.13 eV.

## 4.7.3 Electrochemical properties

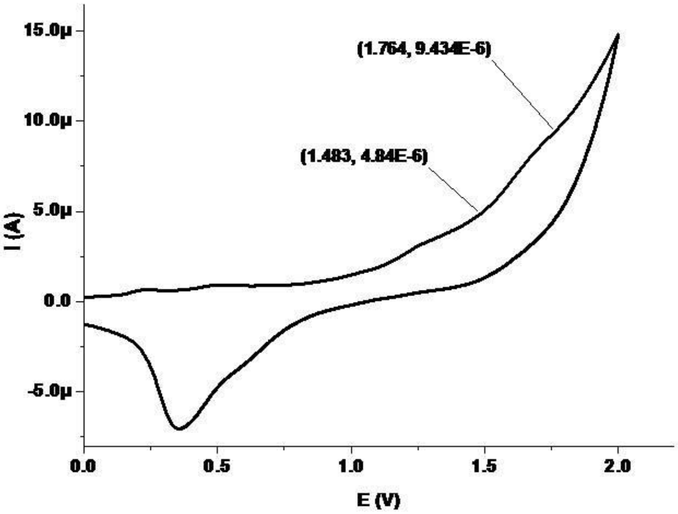


**Figure 4.18** CV curves of compound **M1**. CV curves were performed in $CH_3CN$ solution having (~50 mM) $TBAPF_6$ as supporting electrolyte at scanning rate of 50 mV $s^{-1}$. $E_{onset}$ (Fc/Fc+) = 0.40 V

The frontier orbital energy levels of the synthesized compound **M1** was measured using cyclic voltammetry (CV). CV experiments were performed in the dry acetonitrile using $TBAPF_6$ as a supporting electrolyte (~50 mM) using a three-electrode system: a glassy carbon electrode as the working electrode, a Pt wire electrode as the counter electrode and Ag/Ag+ as the reference electrode. Solid films were casted on the glassy carbon working electrode from its chloroform solution (~10 mg/mL), the films were dried under nitrogen gas flow and were subjected to the CV measurement.

The compound **M1** showed single reversible oxidation peak. Reduction peak was not observed. CV curves showed that oxidation potential ($E^{ox}_{peak}$) occurs around 1.76 V with onset value at 1.48 V. The calculated HOMO and LUMO energy levels were found to be -5.88 eVand -3.79 eV, respectively.

**Table 4.5** Electrochemical properties of **M1**

| Compound | ${}^{a}E^{ox}_{onset}$ (V) | ${}^{b}E_{HOMO}$ (eV) | ${}^{c}E_{LUMO}$ (eV) | ${}^{d}E^{opt}_{bangap}$ (eV) | ${}^{e}E^{theo}_{bangap}$(eV) |
|---|---|---|---|---|---|
| **M1** | 1.4 | -5.88 | -3.79 | 2.1 | 2.4 |

[a] Ag vs Ag/AgCl; [b] calculated using the equation: $E_{HOMO} = -(E_{oxi} + 4.8 - E_{(Fc/Fc+)})$, $E_{(Fc/Fc+)} = 0.40$ V; [c] calculated from the equation $E_{LUMO} = Eg^{opt} + E_{HOMO}$ (eV),[d] calculated optical band-gaps using equation $E_{optical} = 1240/\lambda_{onset}$; [e] from DFT calculation

### 4.7.4 Space charge limited current (SCLC) hole mobility

The photophysical and electrochemical properties of synthesized compound **M1** encourage us to carry out hole mobility measurement. The hole mobility of compound was measured according to method described in the chapter 4 Part a. The measured SCLC hole mobility for compound **M1** was found to be $3.85 \times 10^{-4}$ $cm^2V^{-1}s^{-1}$ (Figure 4.16). The high hole mobility allows the synthesized compound to be used as hole transporting materials (HTMs) for organic photovoltaic devices.

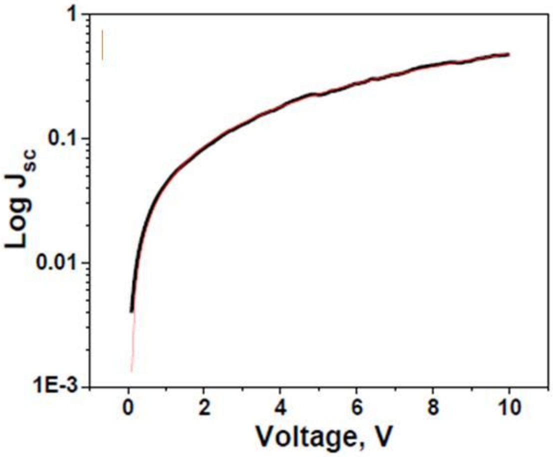


**Figure 4.19** SCLC hole mobility of compound **M1.**

### 4.7.5 Computational studies

DFT calculations often used for in-depth understanding of FMO and other quantum chemical studies of organic molecules. To obtain these data, computational studies of this compound was done with the help of DFT using B3LYP hybrid exchange correlation with basis set 6-31G (d) [46] on *Gaussian 09* software [47].

Energy and geometric optimization of compound were carried out. The optimized geometry of calculated compound **M1** showed quite planar structure. From these data it can be suggested that extended conjugation exists among all the units of the molecule and thus increases effective conjugation length of the molecule.

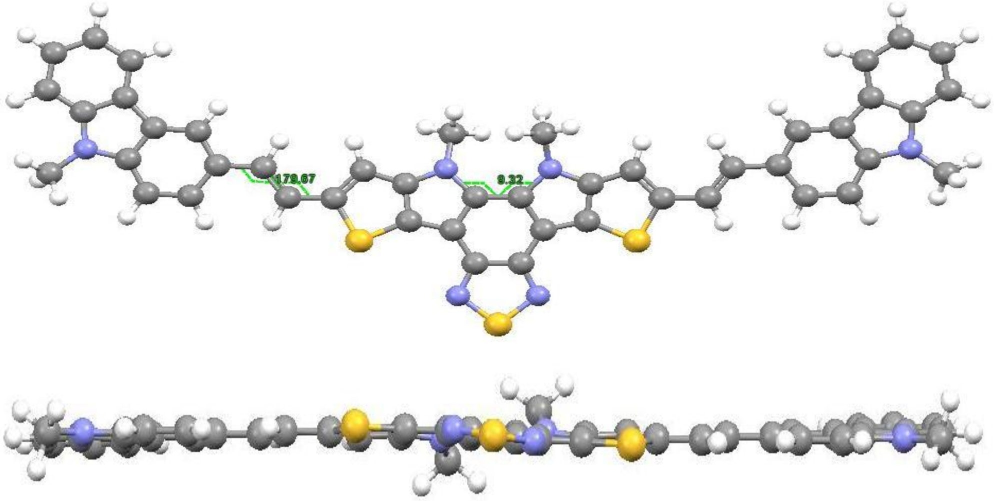


**Figure 4.20** (a) Horizontal view of DFT geometric optimized calculated structure (B3LYP/6-31G (d)) level (b) Vertical view of DFT geometric optimized calculated structure (B3LYP/6-31G (d)) level

The FMO analysis of the DFT data reveals the HOMO levels have bonding interaction located along the length of the molecule, whereas the LUMO levels have bonding interaction located mainly in the core DTPBT ring. It is often assumed that HOMO levels are governed by electron releasing groups which then referred as donor type whereas, LUMO levels are controlled by the electron withdrawing groups of the molecule thereby such units act as acceptor type. In short, the FMO study shows that the periphery carbazole units are donor type while the core DTPBT unit acts as an acceptor type with π bond as a spacer in the molecule.

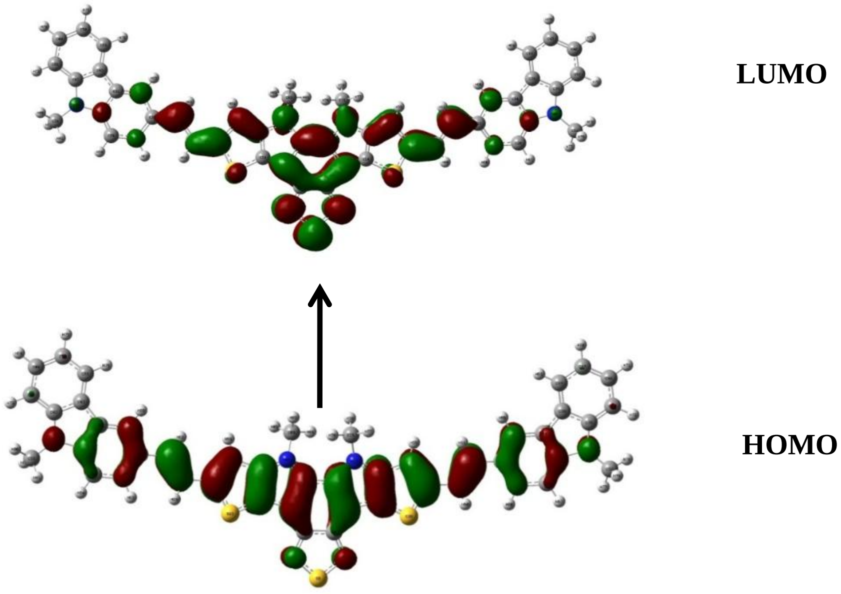


**Figure 4.21** HOMO and LUMO frontier molecular orbitals of compound **M1** calculated from DFT at (B3LYP/6-31G (d)) level representing electronic distribution at ground and excited states

Time-dependent DFT calculations were performed to examine the changes occurring during electronic transitions and thereby the changes reflecting in the HOMO-LUMO energy gaps. The calculated HOMO to LUMO vertical electronic transition was observed at 437 nm.

## 4.8 Conclusion

Compound **M1** was synthesized by Wittig reaction of carbazole wittig salt (**19**) and diformyl dioctyl DTPBT (**14**). The optical band gap of compound **M1** was found to be 2.1 eV. The measured SCLC hole mobility for compound **M1** was found to be $3.85 \times 10^{-4}$ $cm^2V^{-1}s^{-1}$. The high hole mobility allows the synthesized molecule to be used as hole transporting materials (HTMs) for organic photovoltaic devices. The computational data were carried out by DFT calculation. The FMO analysis of the calculated data revealed that HOMO energy levels were distributed overall molecule while LUMO levels were concentrated to the DTPBT core system. Further it suggests that periphery carbazole units are donor type while core unit acts as an acceptor type making this molecule a D-π-A-π-D type conjugated molecule.

## 4.9 Experimental

### 4.9.1 General

All chemicals were reagent grade and were used as purchased. Moisture sensitive reactions were performed under an inert atmosphere of dry nitrogen with dried solvent. Reactions were monitored by TLC analysis using Merck silica gel 60 F-254 thin-layer plates. Column chromatography was done on Silica Gel (60-140 mesh). NMR spectra were recorded on Bruker AV-III 400 MHz (for $^{1}H$) and 100 MHz (for $^{13}C$) spectrometer using $CDCl_3$/DMSO-$D_6$ as solvent and chemical shifts are reported in parts per million (δ scale) relative to tetramethyl silane (TMS) as the internal standard. The UV-visible spectra were recorded on model Perkin ElemerLamba 35 UV-visible spectrometer. Fluorescence spectra were recorded on a model HITACHI F-6300 fluorescence spectrometer. CV was performed on Princeton Applied Research 263A potentiostat with a three-electrode cell containing a solution of $TBAPF_6$ (0.1 M) as electrolyte in dry DCM at a scan rate of 50 mV $s^{-1}$. The measurements were calibrated using ferrocene as a standard. The electrochemical cell was set up with Pt disk electrode as the working electrode, a Pt wire as counter electrode and an Ag/AgCl as reference electrode. Electrochemical experiments were performed under nitrogen atmosphere.

### 4.9.2 Synthesis

#### 4.9.2.1 Synthesis of 10, 11-dioctyl-1, 2, 5-thiadiazolo[*3, 4-e*]thieno[*2', 3':4, 5*]pyrrolo[*3, 2-g*]thieno[*3, 2-b*]indole-2, 8-dicarbaldehyde (14)

DMF (0.9 mL, 11.67 mmol) was taken in a clean dry two neck round bottom flask and cooled in ice-salt bath under nitrogen atmosphere. To this $POCl_3$ (0.9 mL, 9.7 mmol) was added and the mixture was stirred at $0^{o}$ C for 1 hour. To this mixture solution of compound **7** (0.214g, 0.389 mmol) in DCE (20 mL) was added dropwise with the help of syringe through a rubber septum. Reaction mixture was stirred at room temperature for 1 hour and then refluxed ($84^{o}C$) for 24 hours. After completion of reaction, DCE was evaporated and the remaining mass was washed with water and then extracted with DCM.

The organic layer was washed twice time with brine and then dried over anhydrous $Na_2SO_4$.DCM was then evaporated to obtain pure solid compound **14** in 90% yield (0.212 g). $^1$H NMR (400 MHz $CDCl_3$): $\delta$ 10.03 (2H, s), 7.86 (2H, s), 4.56-4.60 (4H, t), 0.835-2.386 (34H, m).

### 4.9.2.2 Synthesis of 9-octylcarbazole (16)

Compound **15** (4.0 g, 23.95 mmol) and KOH (5.36 g, 95.8 mmol) was added to acetone and stirred for 30 minutes. The octyl bromide (6.010 g, 31.13 mmol) was added dropwise with a syringe and stirred at room temperature for 24 hours. Acetone was evaporated; crude product was washed with water and extracted in DCM which was then dried over $Na_2SO_4$. DCM was then evaporated under reduced pressure. Crude product was obtained in 88% yield (5.878 g) which was further purified by silica gel column chromatography (petroleum ether). $^1$H NMR (400 MHz $CDCl_3$):$\delta$ 8.13-8.14 (d, 2H), 7.43-7.52 (m, 4H), 7.24-7.28 (m, 2H), 4.31-4.34 (t, 2H), 1.86-1.93 (m, 2H), 1.26-1.43 (m, 10H), 0.89-0.91 (t, 3H). $^{13}$C NMR (100 MHz $CDCl_3$): $\delta$ 140.4, 125.6, 122.8, 120.4, 118.7, 108.7, 43.1, 31.83, 29.4, 29.2, 29.0, 27.4, 22.6, 14.1.

### 4.9.2.3 Synthesis of 9-octylcarbazole-3-carbaldehyde (17)

DMF (2.67 mL, 34.8 mmol) was taken in a clean dry two neck round bottom flask and cooled in ice-salt bath under nitrogen atmosphere. To this $POCl_3$ (1.3 mL, 13.9 mmol) was added and the mixture was stirred at $0^o$ C for 1 hour. To this mixture solution of compound **16** (1.943 g, 6.96 mmol) in DCE was added dropwise with the help of syringe through a septum. Reaction mixture was stirred at room temperature for 1 hour and then refluxed ($84^o$ C) for 24 hours. After completion of reaction, DCE was evaporated and the remaining mass was stirred with water and then extracted with ethyl acetate. The organic layer was washed with water and then with brine and dried over anhydrous $Na_2SO_4$. After evaporating solvent under reduced pressure, the crude product was subjected to silica gel column chromatography (5% ethyl acetate in petroleum ether). The pure compound **17** was obtained in 83.5% yield (1.78g). $^1$H NMR (400 MHz $CDCl_3$): $\delta$ 10.12 (s, 1H), 8.64 (s, 1H), 8.17-8.19 (d, 1H), 8.02-8.05 (dd, 1H), 7.54-7.58 (m, 1H), 7.47-7.51 (m, 2H), 7.33-7.37 (m, 1H), 4.37-4.33(t, 2H), 1.94-1.87(m, 2H), 1.42-1.25(m, 10H), 0.89-0.86(t, 3H). $^{13}$C NMR

(100 MHz $CDCl_3$)**:** $\delta$ 191.9, 144.1, 141.15, 128.42, 127.2, 126.7, 124.08, 123.0, 122.9, 120.8, 120.3, 109.4, 108.9, 43.4, 31.8, 29.3, 29.2, 28.9, 27.3, 22.6, 14.1.

#### 4.9.2.4 Synthesis of (9-octylcarbazol-3-yl)methanol (18)

Compound **17** (1.785 g, 5.81 mmol) was dissolved in DCM and $NaBH_4$ (0.265g, 6.977 mmol) was added. To this methanol was added slowly (1 mL) and reaction mixture was allowed to stir room temperature under nitrogen atmosphere for 6 hours. On completion of reaction solvent was evaporated, crude product was washed with water, extracted in DCM and dried over sodium sulfate. Crude product was directly used for the next step. Weight of crude product was 1.65g (92% yield).

#### 4.9.2.5 Synthesis of ((9-octylcarbazol-3-yl)methyl)triphenylphosphonium bromide (19)

Compound **18** (1.65g, 5.3 mmol) was dissolved in DCM, triphenylphosphonium hydrobromide (2.015g, 5.87 mmol) was added and reaction mixture was stirred at $40^o$ C for 18 hours. The solvent was evaporated and paste like mass was treated with excess diethyl ether to yield white colored solid powder which was filtered and dried (3.22g, 95% yield).

$^1H$ NMR (400 MHz $CDCl_3$): $\delta$ 7.71-7.79 (m, 10H), 7.60-7.64 (m, 6H), 7.52 (s, 1H), 7.44-7.47 (m, 1H), 7.33-7.38 (m, 2H), 7.14-7.18 (m, 2H), 5.46-7.49 (d, 2H), 4.16-4.19 (t, 2H).

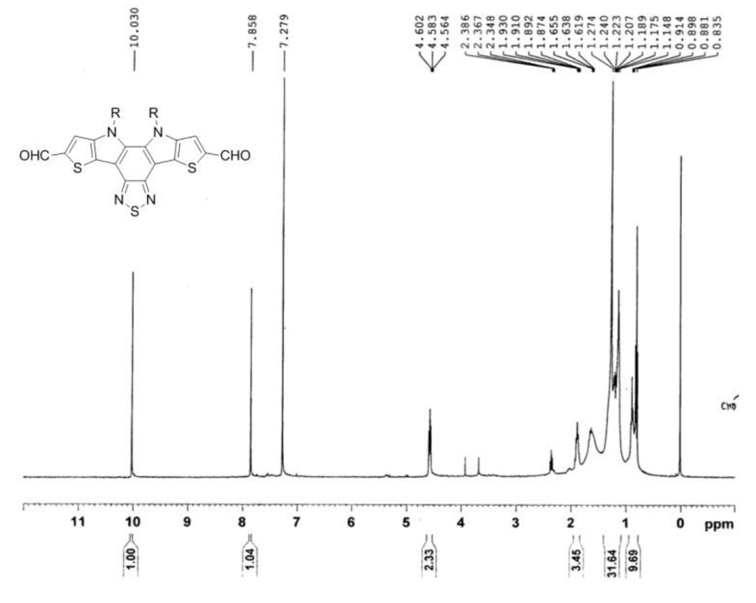
#### 4.9.2.6 Synthesis of 10, 11-dioctyl-2-((*E*)-2-(9-octyl-*9H*-carbazol-2-yl)vinyl)-8-((*E*)-2-(9-octyl-*9H*-carbazol-3-yl)vinyl)-1, 2, 5-thiadiazolo[3, 4-e]thieno[*2', 3':4, 5*]pyrrolo[*3, 2-g*]thieno[*3, 2-b*]indole (M1)

Sodium methoxide was prepared by dissolving sodium metal (23mg, 0.99 mmol) in dry methanol (10 mL) under nitrogen atmosphere. To this solution, mixture of compound **14** (60mg, 0.099 mmol) and compound **19** (188mg, 0.296 mmol) in dry methanol (10 mL) was added using syringe through septum. The reaction mixture was heated at 65 $^oC$ for 24 hours. Then water was added and product was extracted in ethyl acetate. The crude product was purified by silica gel column chromatography (20% ethyl acetate in pet ether). (80% yield, 0.091 g). $^1H$ NMR (400 MHz $CDCl_3$) :$\delta$ 8.25 (s, 2H), 8.16-8.18 (d, 2H), 7.67-7.68

(m, 2H), 7.49-7.54 (m, 2H), 7.40-7.44 (m, 6H), 7.26-7.30 (m, 4H) (merged with $CDCl_3$ signal), 7.14 (s, 2H), 4.47-4.51 (t, 4H), 4.30-4.34 (t, 4H), 1.865-1.918 (m, 8H), 1.19-1.42 (m, 40H), 0.86-0.90 (m, 12H). $^{13}C$ NMR (100 MHz $CDCl_3$)**:** $\delta$ 202.7, 201.0, 147.6, 145.4, 145.3, 140.8, 140.2, 131.6, 128.8, 128.0, 125.9, 124.4, 123.2, 122.8, 120.5, 120.3, 119.6, 119.0, 118.4, 111.0, 109.6, 108.99, 43.2, 31.8, 31.7, 30.1, 29.4, 29.2, 29.1, 29.0, 27.3, 26.6, 22.6, 22.6, 14.1. HRMS : m/z for $C_{74}H_{88}N_6S_3$ [$M^+$] Calculated: 1156.6233, Experimental: 1156.6389.

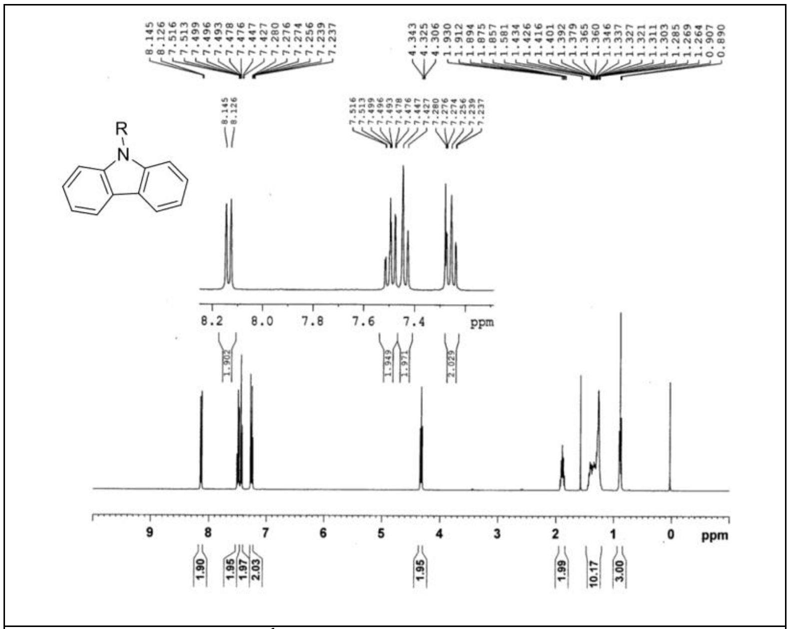
## 4.10 Spectral data

### 4.10.1 10, 11-Dioctyl-1, 2, 5-thiadiazolo[*3*, *4-e*]thieno[*2'*, *3':4*, *5*]pyrrolo[*3*, *2-g*]thieno[*3*, *2-b*]indole-2, 8-dicarbaldehyde (14)

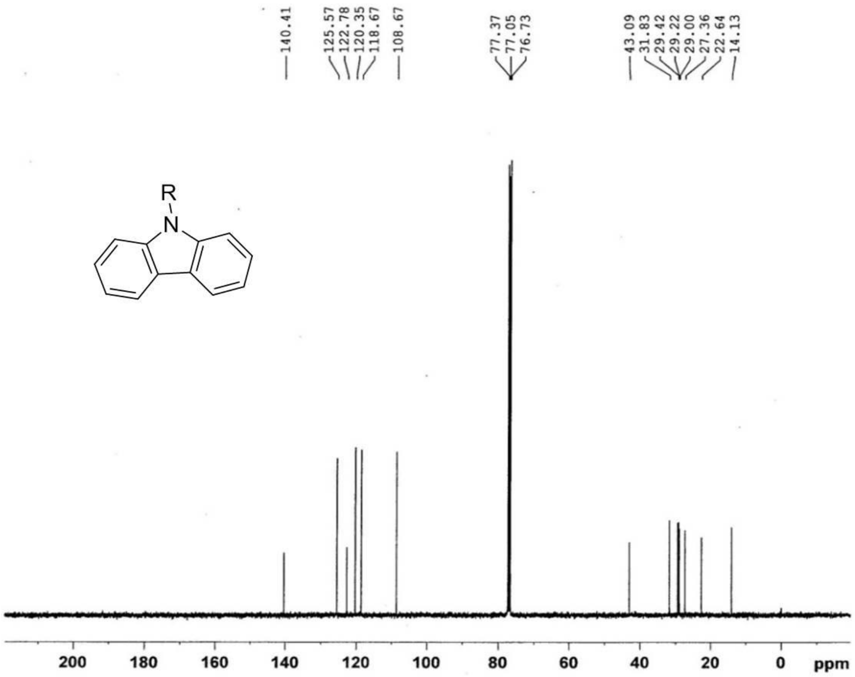


**$^1$H NMR spectrum**

### 4.10.2 9-Octylcarbazole (16)

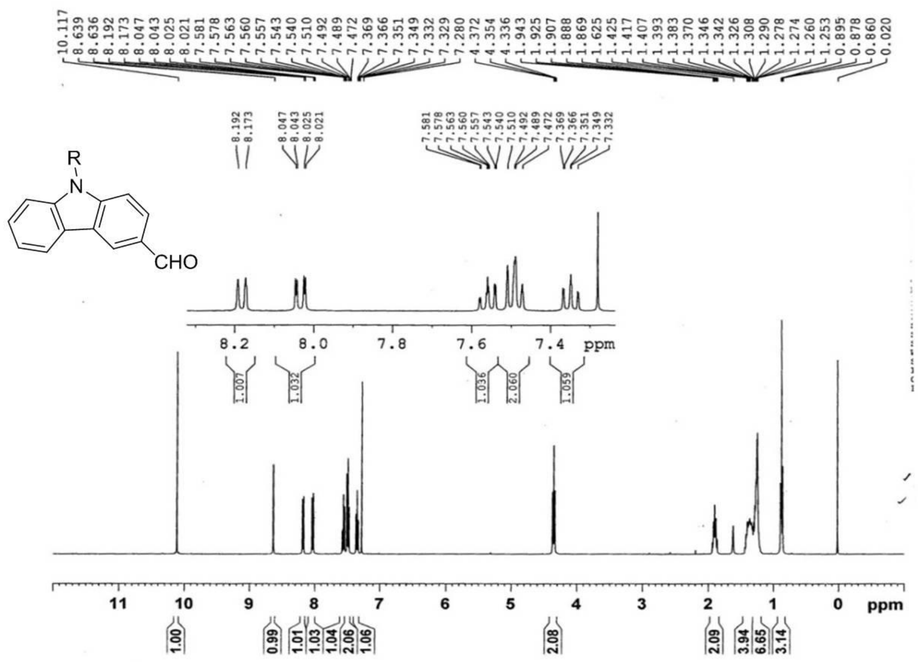


**$^1$H NMR spectrum**

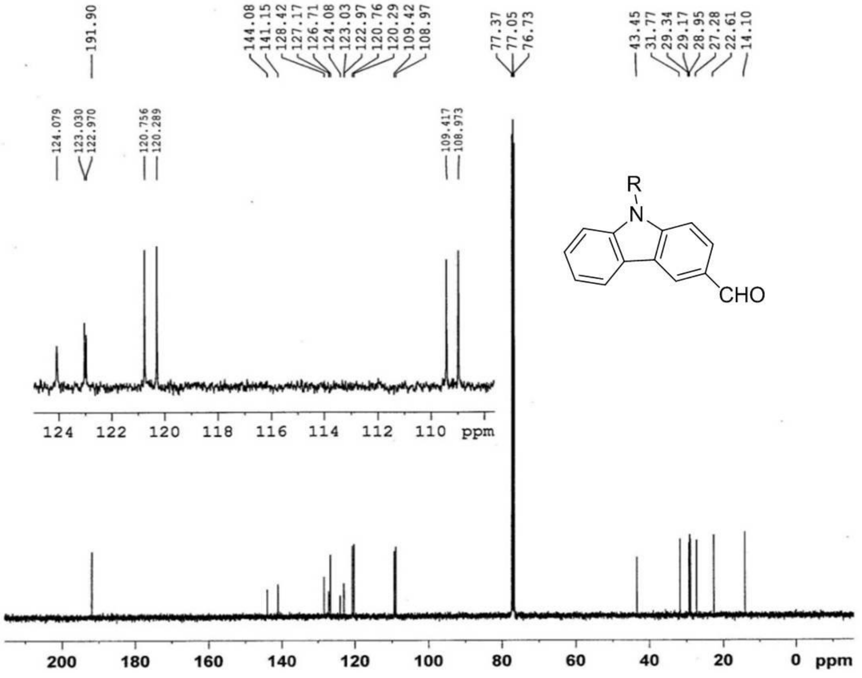


$^{13}$C NMR spectrum

### 4.10.3 9-Octylcarbazole-3-carbaldehyde (17)

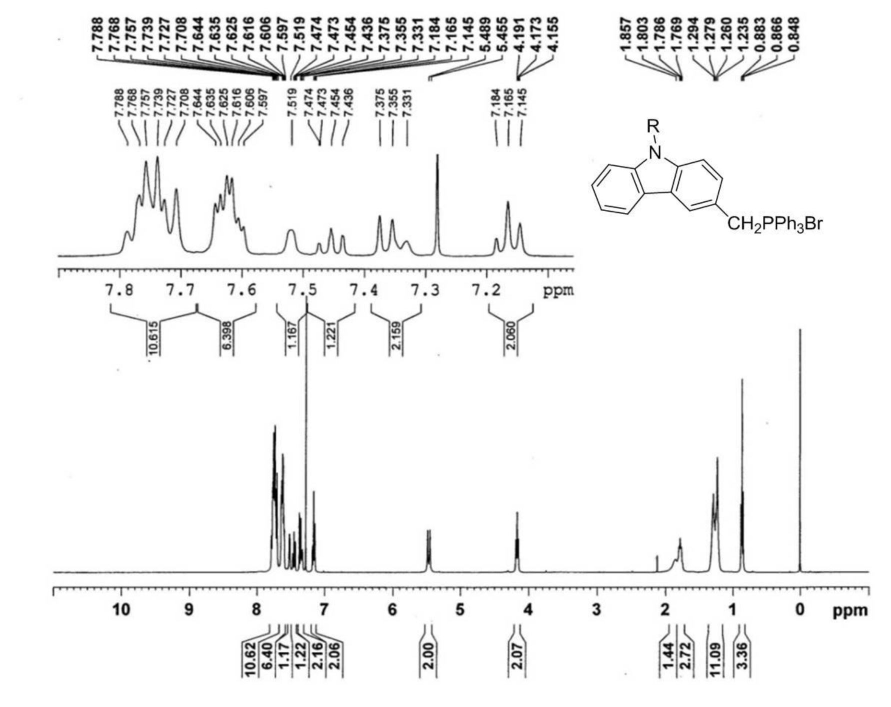


$^1$H NMR spectrum



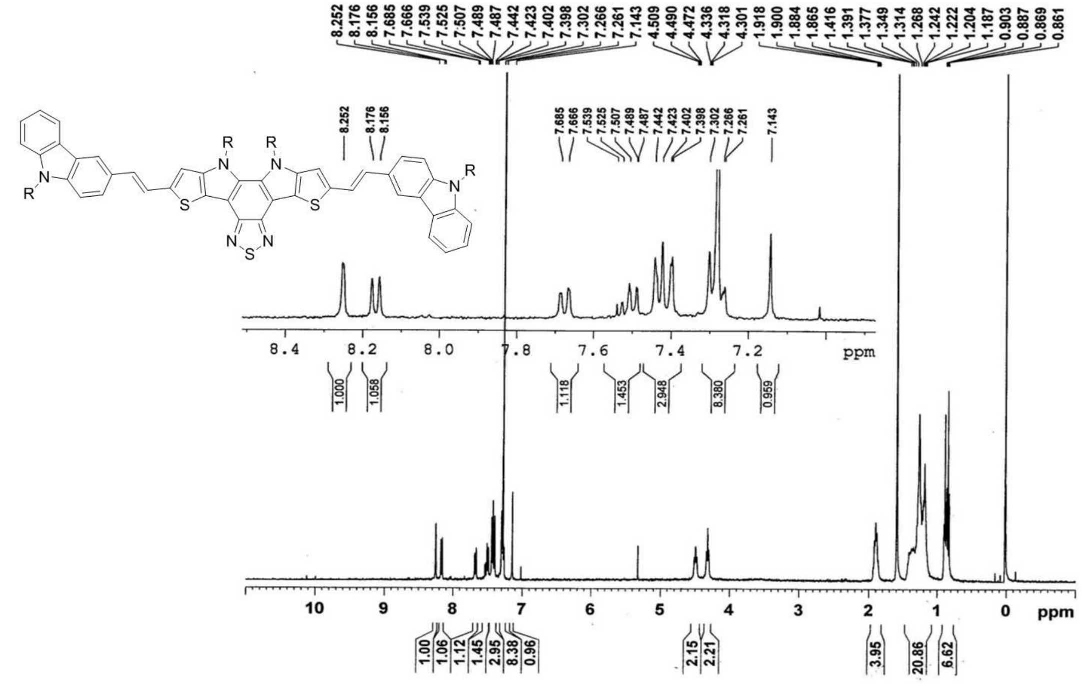
$^{13}$C NMR spectrum

### 4.10.4 ((9-Octylcarbazol-3-yl)methyl)triphenylphosphonium bromide (19)

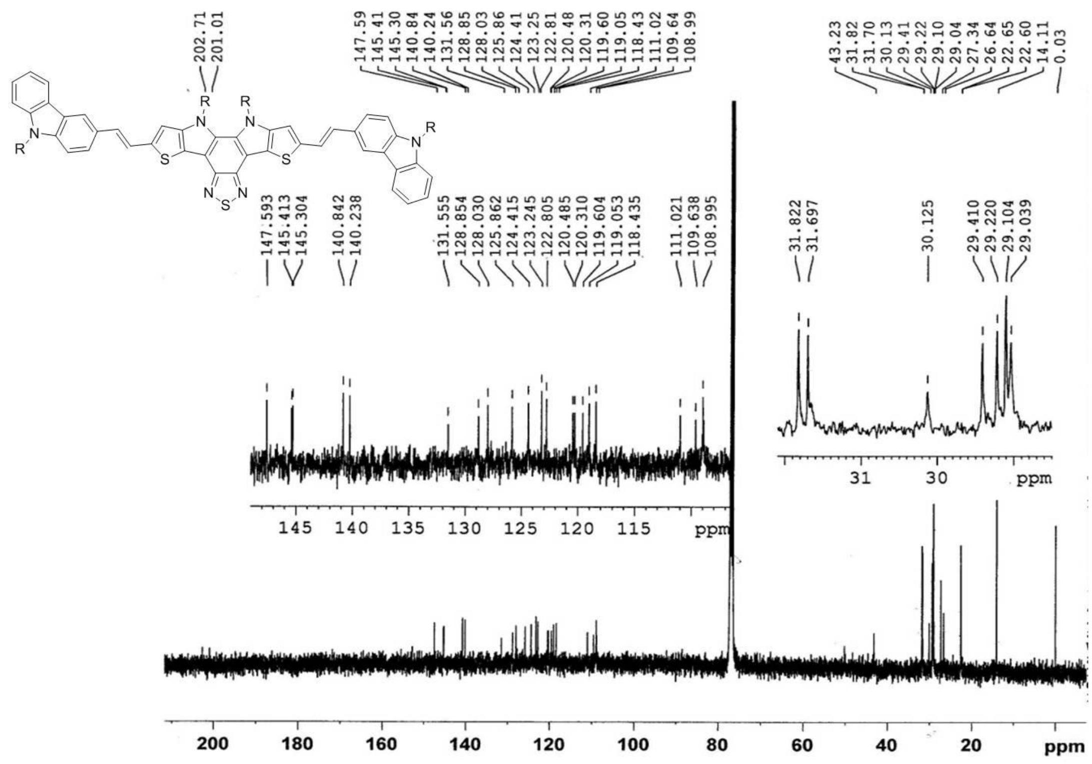


$^1$H NMR spectrum

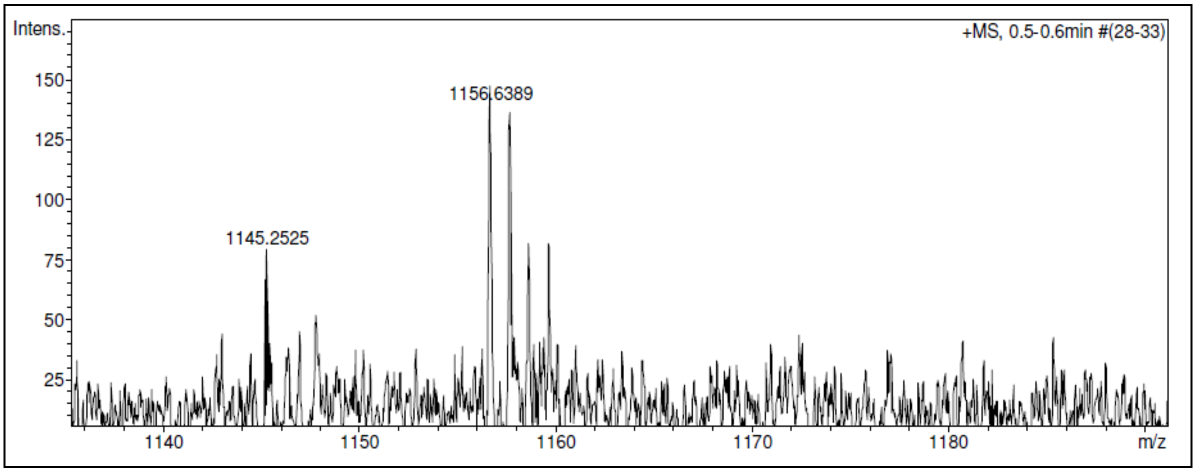
### 4.10.5 10, 11-Dioctyl-2-((*E*)-2-(9-octyl-9H-carbazol-2-yl)vinyl)-8-((*E*)-2-(9-octyl-9H-carbazol-3-yl)vinyl)-1, 2, 5-thiadiazolo[*3, 4-e*]thieno[*2′, 3′:4, 5*]pyrrolo[*3, 2-g*]thieno[*3, 2-b*]indole (M1)



$^1$H NMR spectrum



**$^{13}$C NMR spectrum**



**HRMS data m/z for $C_{74}H_{88}N_6S_3$ [M+] calculated : 1156.6233, Experimental : 1156.6389**

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