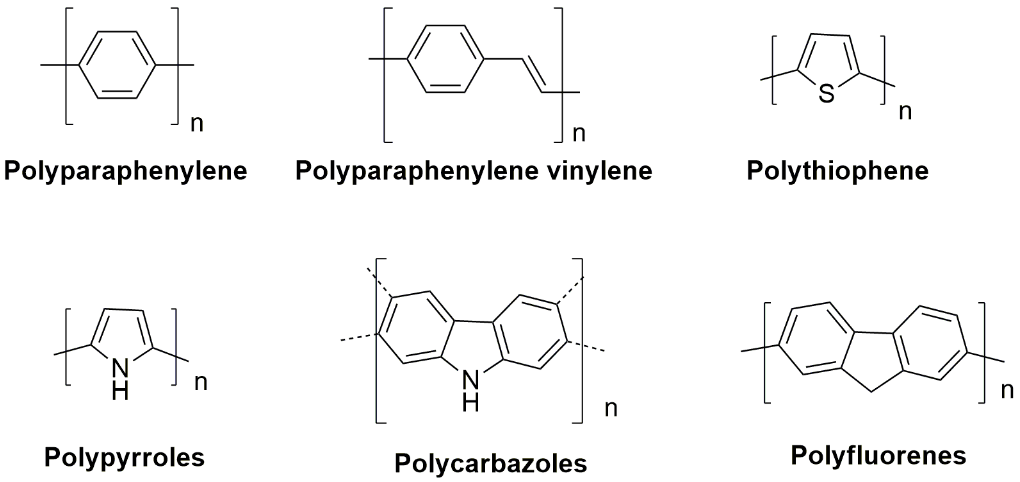
Chapter 3

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

3.1 Introduction

Synthetic polymers have brought remarkable changes in our daily life by replacing many naturally produced materials. Numerous commodity and engineering polymers have been found the applications in our everyday life. This impact drives the search of more new polymeric material which possesses interesting properties in terms of mechanical, electrical, optical or magnetic and thus can replace existing materials to make things more efficient. The daunting tasks which synthetic chemists facing, are to develop the polymers which have combination of mechanical, electrical and optical desirable properties. The applications of these polymers can revolutionize the current semiconductor industry. Due to these factors conjugated polymers which possess π-electrons have gathered immense attention from researcher all over the world.

The first breakthrough in the field of conducting polymers was obtained by synthesis of polyacetylene in 1977 [1]. The polyacetylene showed strong absorption in UV-visible region but polymers were not stable under ambient condition and were quite insoluble in organic solvents due to which no processability were obtained for device applications. From 1980s onwards the problems related to solubility and stability was solved by polymer chemists [2] and several new classes of conjugated polymers were developed which includes poly(*p*-phenylene)s [3], poly(p-phenylenevinylene)s [4], polythiophenes [5], polypyrroles [6], polyanilines [7], polyfluorenes [8] and polycarbazoles [9].



Polyparaphenylene Polyparaphenylene vinylene Polythiophene

Polypyrroles Polycarbazoles Polyfluorenes

Figure 3.1 Some classes of conjugated polymers [3-9]

Polythiophenes are among the most investigated and highly explored conjugated polymers which were used as an active components in numerous organic electronic and molecular electronic devices [10]. Garnier and co-workers in 1989 found that shorter-conjugated oligomers such as α-sexithiophene (6T) also used in organic field-effect transistors (OFETs) as an active material [11]. In 1993, organic light emitting diodes (OLEDs) were developed from well-defined end-capped oligothiophenes, while in 1995 octithiophene were shown having properties of organic semiconductors (OSCs) [12]. Since last 15 years numerous reports on fuctionalized oligo and polythiophenes are published. These novel materials are termed as a third generation of advanced conjugated materials. The driving force behind this continuous research on new polythiophene based material lays the versatility of thiophene unit itself which can be functionalized by either α and β position.

Numerous polythiophenes based oligomers/polymers have been investigated for its applications in OFETs. The FET based on polythiophene [13], α, ω-dialkyloligothiophenes [14] and poly(3-hexyl)thiophene [15] which showed high charge mobility.

Many new scaffolds of thiophene units were synthesized by chemical modifications as well various methodolgy were developed which attributed to huge examples of polythiophene based FETs. The functionalization of core thiophene units affords fine tuning of properties such as optical, electronic and electro-optical [16]. In typical conjugated polymer, the π band is divided into π and π^* bands. Since each band can hold two electrons per atom (spin up and spin down), the π band is filled and the π^* band is empty. The energy difference between the highest occupied state in the π band and the lowest unoccupied state in the π^* band is the $\pi \pm \pi^*$ energy gap, Eg. Because Eg depends upon the molecular structure of the repeat unit, synthetic chemists are provided with the opportunity and the challenge to control the energy gap by design at the molecular level [10].

One of the most popular approach is modulation of band-gap, in which essentially the energy difference between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) is modified by incorporating electron-releasing groups (alkyl, aryl etc) or electron withdrawing groups (-CN, -COOR) in the backbone of the polymer chain. These modifications changes optical and redox properties of the polymer which overall affects the charge transport properties of the materials [17]. The electron donating and electron withdrawing properties of alternating monomer efficiently increases the intramolecular charge transfer and setting up the push-pull effect which narrows the band gap of the conjugated polymers. The underlying concept is that the interaction between alternating electron-rich donors and electron-deficient acceptors results in a compressed band-gap *via* molecular orbital hybridization and *via* intramolecular charge transfer.

N-fused heterocyclic ring systems have been reported as good donor units in the literature [18]. The carbazole units are one of the most exploited and well studied systems in the prospect. Carbazole have several advantages as it is inexpensive and easily modifiable molecule. Carbazole possesses *N*-atom in the molecule which increases electron density and thus contributes to its hole-transporting ability. The fused system provides good thermal and morphological stability as well as high fluorescence properties. Carbazole (Figure 3.2 (b)) is a nitrogen-bridged biphenyl analogous as well as isoelectronic to fluorene (Figure 3.2 (a)).

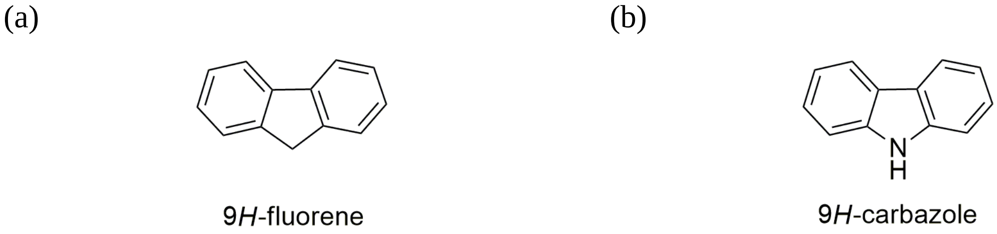


Figure 3.2 Schematic structures of (a) Fluorene and (b) Carbazole

Polyfluorenes have been exploited due to their great potential as a blue emitters in polymer based LEDs [19]. Carbazole possesses nitrogen atom which increases the electron-donating effect of overall molecule, causing the elevation of the HOMO energy levels of the corresponding polycarbazoles when compared to polyfluorenes [18]. These effects further improve the charge injection and charge transport properties of the material. The materials which had oligomers and polymers based on the carbazoles investigated for optoelectronic applications as transistors and LEDs [18] showed higher charge transport properties compared to polyflourenes. Carbazole based polymers have been synthesized by various researchers [20] and their applications as organic photovoltaic cells (OPVs), organic field effect transistors (OFETs), and organic light emitting diodes (OLEDs) have been investigated [21].

The bulk heterojunction (BHJ) based on polycarbazole as a donor material was reported in 2006 first time by J. Li *et al* [22]. The highly soluble polycarbazole (PCz) was used as a donor material with perylene tetracarboxydiimide (PDI) as an acceptor material to fabricate bulk heterojunction solar cells. The HOMO energy levels of polycarbazole based polymers lies in range of -5.2 to -5.8 eV which were sufficiently above the fullerenes, hence, it was appropriate to use them as donor units. The photovoltaic device fabricated using this polymer exhibited a high external quantum efficiency (EQE) of 16% at 490 nm and a power efficiency of 0.6% under illumination with solar light (Figure 3.3).

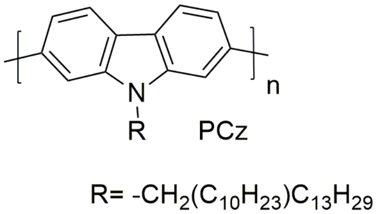


Figure 3.3 Structure of poly [*N*-(2’-decyltetradecyl)carbazole]-2,7-diyl

In 1997, G. Sotzing *et al* reported synthesis and electrochemical polymerization of series of bis-heterocycle-*N*-substituted carbazoles (Figure 3.4). The synthesized polymers showed optical bandgap between 2.4 and 2.5 eV. The polymers were showing multiple colored electrochromic displays up on variation of redox state of polymers [23].

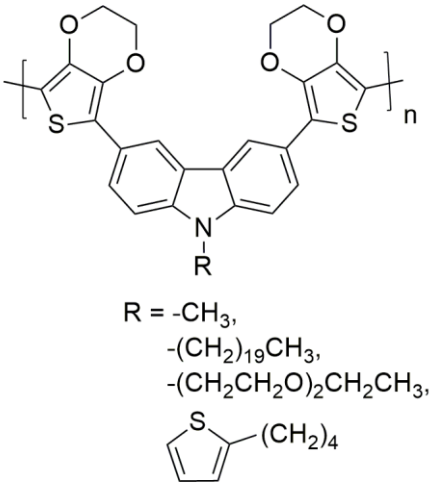


Figure 3.4 Structure of carbazole based polymers [23]

In 2009, Park *et al* reported co-polymer based on carbazole-benzothiadiazole (PCDTBT) (Figure 3.5). The bulk heterojunction solar cell fabricated using PCDTBT and PCBM showed 6% power conversion efficiency (PCE). The internal quantum efficiency of the BHJ solar cell was close to 100%, which meant that every absorbed photon result in a separated pair of charge carriers and that all photogenerated carriers were collected at the electrodes [24].

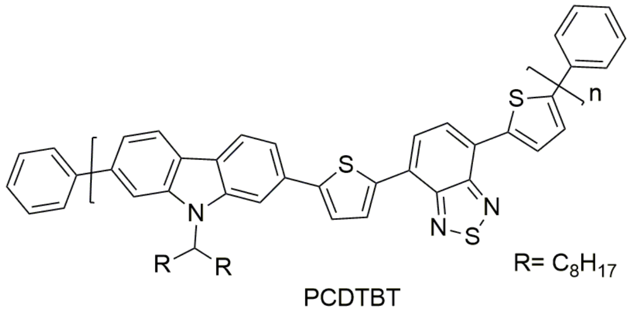
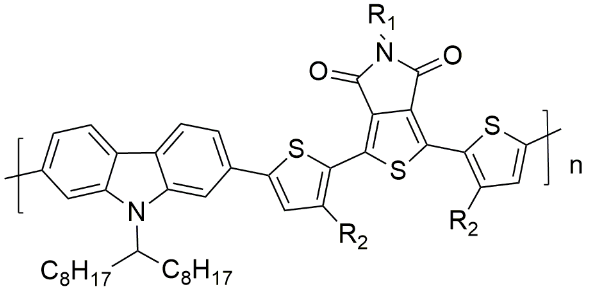


Figure 3.5 Structure of carbazole-benzothiadiazole (PCDTBT) polymer

In 2012, A. Najari *et al* reported synthesis of novel co-polymers based on thieno-[*3,4-c*]pyrrole-4,6-dione (TPD) coupled with 2,7-carbazole units (Figure 3.6). The polymers were synthesized by Suzuki reaction showed good solubility with superior thermal and air stability. The polymers showed low band gap nature and possess low Highest Occupied Molecular Orbital (HOMO) energy levels. Polymers were used as an active material in photovoltaic cells and showed PCE up to 1.8% [25].



$R_1= C_8H_{17}$, $R_2=$ H [PCDTTPD]; yield=76%
$R_1= C_8H_{17}$, $R_2= C_8H_{17}$ [PCDTTPD-ic]; yield=28%
$R_1= CH_2CH(C_6H_{13})C_8H_{17}$, $R_2=$ H [PCDTTPD-C_6C_8] yield=37%

Figure 3.6 Structure of co-polymers based on thieno-[*3,4-c*]pyrrole-4,6-dione (TPD) and 2,7-carbazole units

Low band gap co-polymers based on carbazole with diketopyrrolopyrrole units have been independently reported by Leclerc group and Hashimoto group [26]. The measured hole mobility of polymer P2 (Figure 3.7) was 0.02 cm^2 $V^{-1}s^{-1}$ which indicating that it has excellent charge transport properties. The efficiencies obtained from cells using phenyl-C_{61}-butyric acid methyl ester ($PC_{61}BM$) as an acceptor were 2.26% and 1.6% for polymer P2 and polymer P1, respectively (Figure 3.7).

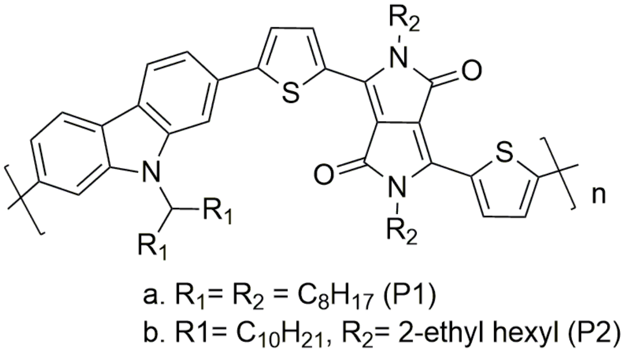


Figure 3.7 Structure of diketopyrrolopyrrole-carbazole based co-polymers

G. Sathiyan *et al* in 2018, reported polymer having carbazole units coupled with thiophene units through cyanovinylene as a spacer. The obtained polymer poly (*2E, 2'E*)- 3, 3'-(9-hexyl-*9H*-carbazole-3, 6-diyl) bis (2- (5- methylthiophen-2yl) acrylonitrile (CN-PICTAN) showed broad absorption and emission range with optical band gap of 2.1 eV. Bulk heterojunction OPV device was fabricated with CN-PICTAN:$PC_{61}BM$ (1:1.5) which showed PCE of 1.23% which improved to 1.73% after device was annealed at 100 ^{o}C [27] (Figure 3.8).

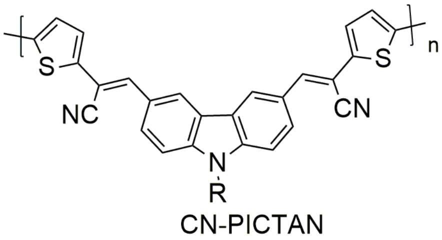


Figure 3.8 Structure of carbazole based conjugated polymer CN-PICTAN

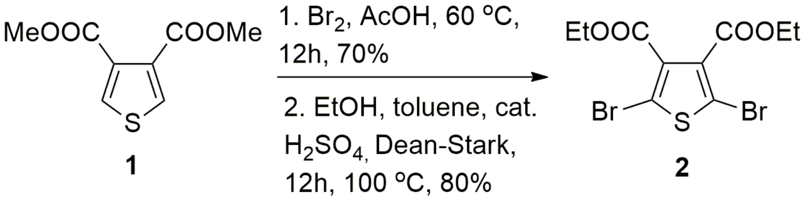
In present chapter, we have synthesized two novel π-conjugated polymers, poly[diethyl-2-(9-tetradecyl-9*H*-carbazol-3-yl)thiophene-3, 4-dicarboxylate] **(PTDCB)** and poly[diethyl-5-(9-tetradecyl-9*H*-carbazol-3-yl)-[2, 2':5', 2''-terthiophene]-3',4'-dicarboxylate **(PTTDCB)**. The diester groups of thiophene units owing to their electron-withdrawing nature will acts as an acceptor unit when attached to electron-rich units of carbazole which provide push-pull type interaction and hence, lowering the band-gap. Both polymers were synthesized through Suzuki coupling reaction. Synthesized polymers were characterized by

NMR (^{1}H and ^{13}C) and Gel permeation chromatography (GPC). Further the properties of both polymers were studied by UV-visible and electrochemical techniques. The measurement of space charge limited current (SCLC) hole mobility of polymer **PTTDCB** was also carried out.

3.2 Results and Discussion

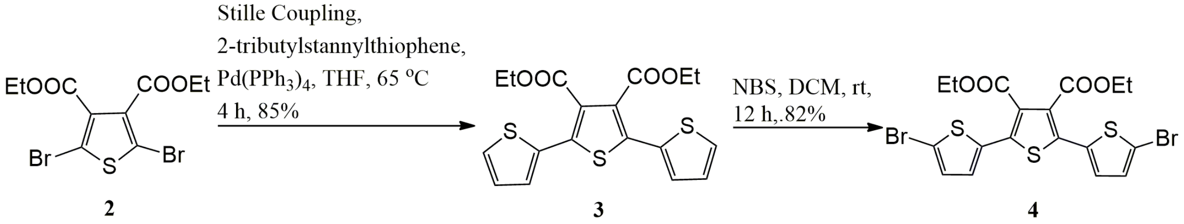
3.2.1 Experimental

3,4-Dimethyl thiophene dicarboxylate was synthesized from maleic anhydride through multiple steps synthetic methodology describe in chapter 2 [28]. 3,4-Dimethyl thiophene dicarboxylate (**1**) was first brominated using bromine-acetic acid yielding 2,5-dibromothiophene-3,4-diacid which was further converted to diester by treating with ethanol (Scheme 3.1).



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

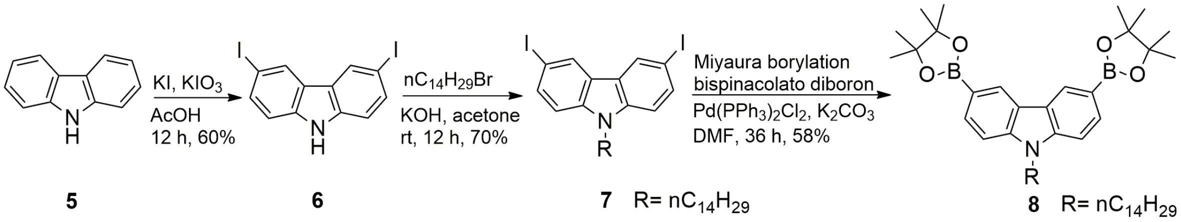
Compound **2** was further treated with 2-tributylstannylthiophene under Stille reaction conditions to obtain diethyl [2,2':5',2''-terthiophene]-3',4'-dicarboxylate (**3**). Compound **3** was brominated in presence of NBS to yield diethyl 5,5''-dibromo-[2,2':5',2''-terthiophene]-3',4'-dicarboxylate (**4**) (Scheme 3.2).



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

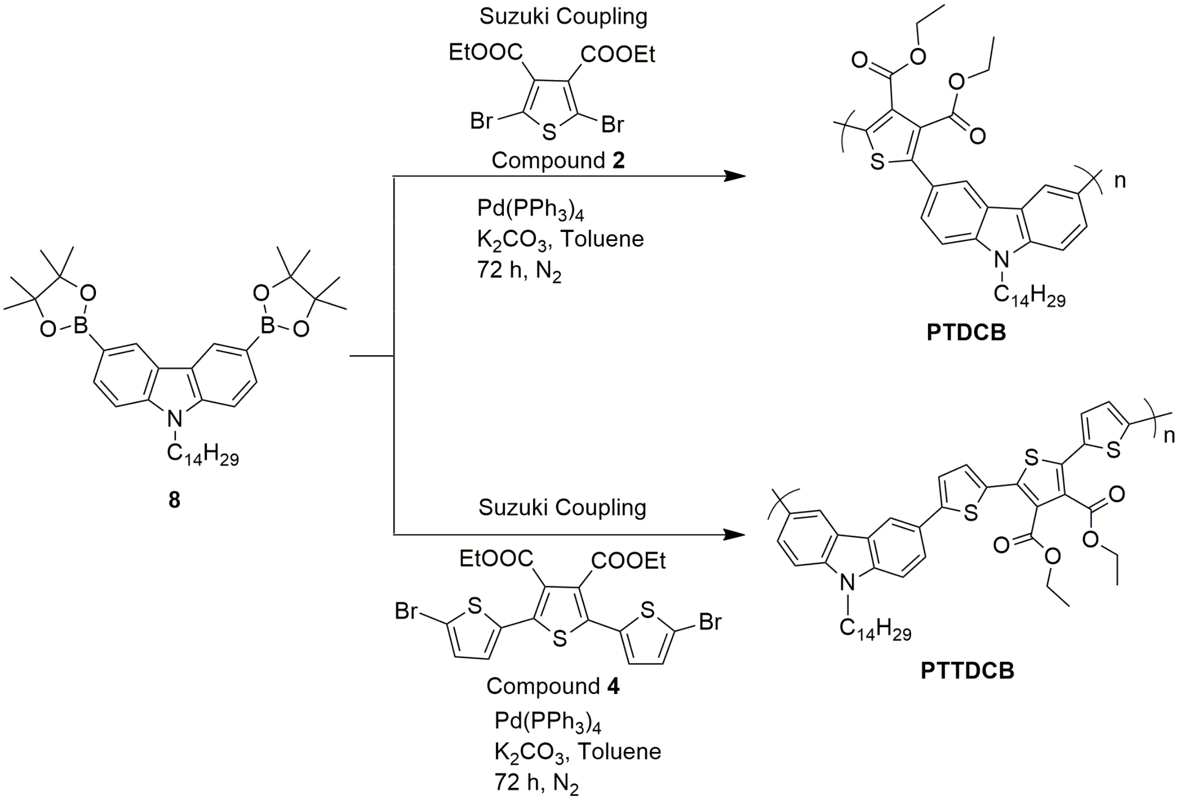
Addition of thiophene units in the **PTTDCB** polymer increases the conjugation along the polymer backbone which will increases effective conjugation length of the polymer as well. Moreover, 2,5-disubsituted thiophene units contributes lesser steric hindrance to the neighboring groups.

9-*n*-Tetradecyl-3,6-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9*H*-carbazole (**8**) was used as monomer for the synthesis of polymers, **PTDCB** and **PTTDCB.** Compound **8** was synthesized in three step synthetic methodology [29]. To synthesize compound **8**, compound **5** was converted in to diiodo carbazole (**6**) by reacting with iodine-iodate mixture. Compound **6** was alkylated in presence of base to get compound **7**. The alkylated compound **7** was further treated with bis(pinacolato)diborane under Miyaura borylation reaction conditions to get desired compound **8** (Scheme 3.3).



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

Compound **8** was further treated with compound **2** and compound **4** under Suzuki Miyaura reaction condition to yield polymers, **PTDCB** and **PTTDCB**, respectively (Scheme 3.4).



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

The synthesized polymers, **PTDCB** and **PTTDCB** were well characterized by NMR (^{1}H and ^{13}C), GPC, UV-visible and electrochemical techniques. The SCLC hole mobility measurement of **PTTDCB** was also carried out.

3.2.2 Photophysical properties of polymers

The photo-physical properties of both the polymers were studied by UV-visible spectroscopy. The chloroform solutions of the polymers as well as thin films on quartz glass casted from chloroform solution were used to determine the photophysical properties. Both polymers showed multiple band absorption spectra with complex band splitting patterns in the solution as well as in the film state.

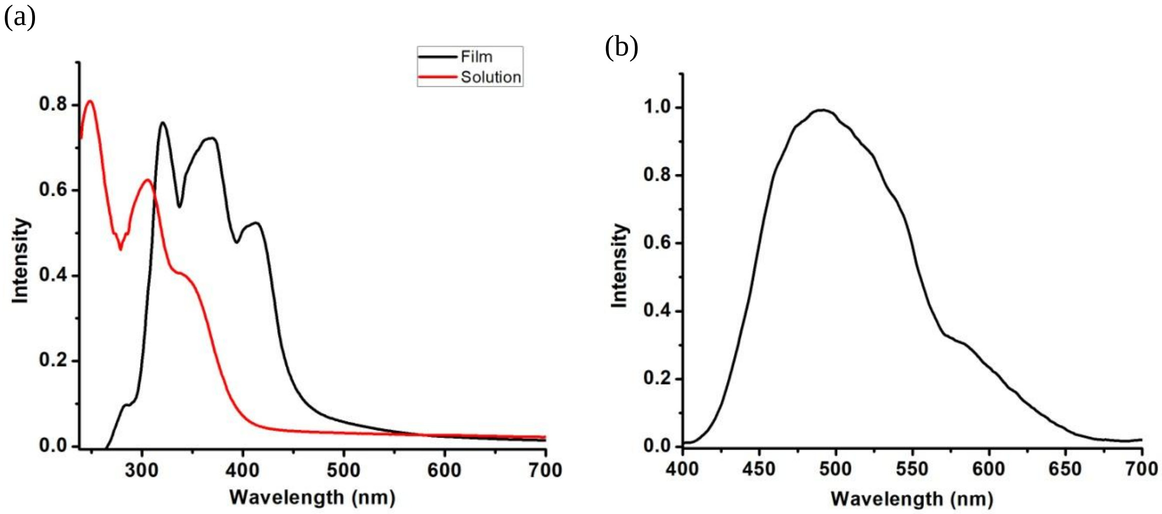


Figure 3.9 (a) UV-visible spectra of **PTDCB** in chloroform and in the film state (b) Emission spectrum of **PTDCB** in chloroform.

UV-visible absorption study of **PTDCB** was carried out in chloroform solution having concentration of 10^{-5} M (Figure 3.9). **PTDCB** shows two prominent peaks for absorption spectra at 249 nm and 306 nm and a hump was observed at 360 nm. The onset of absorption was obtained at 400 nm for **PTDCB** which corresponds to the 3.1 eV bandgap in solution spectra. UV-visible absorption of solid films of **PTDCB** showed broader absorption pattern compared to solution state. The absorption maxima of **PTDCB** were red-shifted from 249 nm and 306 nm in solution state to 308 nm and 368 nm in film state. The onset of absorption of **PTDCB** was red-shifted to 435 nm in film state which corresponds to bandgap of 2.8 eV. The red-shift in the absorption in solid state can be attributing to the enhancement in π-π interaction in solid state with combination of donor-acceptor interaction between carbazole units and thiophene diester units. The emission spectra of **PTDCB** showed broad curve ranging from 400 nm to 650 nm with peak at 493 nm. The Stokes shift calculated from UV-visible spectra of **PTDCB** was 187 nm (Table 3.1).

(a) (b)

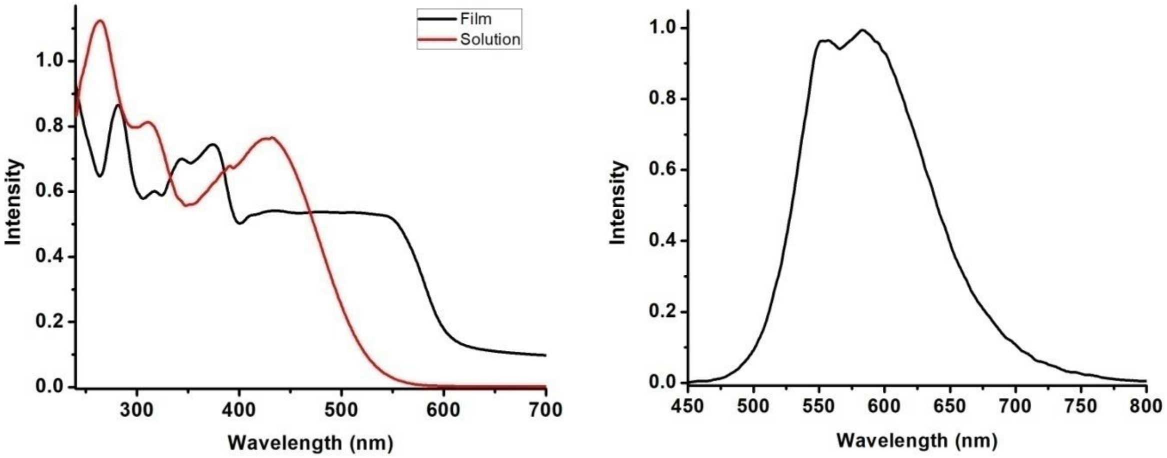


Figure 3.10 (a) UV-visible spectra of solution (in chloroform) and film of **PTTDCB**. (b) Emission spectrum of **PTTDCB**

UV-visible and fluorescence studies of **PTTDCB** were carried out by dissolving the polymer in chloroform having concentration of 10^{-5} M (Figure 3.10). Absorption spectra showed that three peaks observed at 254 nm, 303 nm and 417 nm in solution state. The UV-visible absorption spectra of solid film of **PTTDCB** was recorded and it was observed that the absorption peaks were red-shifted when compared to solution spectra. The absorption maxima of **PTTDCB** in solution was measured at 303 and 417 nm. In solid film spectra absorption maxima were red-shifted to 375 nm and 543 nm. These red-shift were attributed from the π-π interaction occurred in the solid state and the interaction caused from donor-acceptor units in the polymer backbone. The onset of **PTTDCB** was observed at 577 nm. Fluorescence spectrum showed that emission of the polymer ranges from 470 nm to 740 nm, the emission maxima was observed at 583 nm. The Stokes shift calculated for the polymer was 187 nm (Table 3.1).

Table 3.1 Photophysical properties of polymers

Polymer	λ_{max}(abs) nm^a	λ_{max}(abs) nm(Film)	λ_{max}(em) nm^a	Stokes Shift (nm)	Onset (nm)(Film)	$E_{band\ gap}^{Opt}$(eV)^b
PTDCB	306, 249	412, 368	493	187	435	2.8
PTTDCB	417, 303	543, 375	583	166	577	2.1

^{a}Measured in chloroform.

^{b}Estimated from the onset of the absorption in the thin films (E_g = 1240/(λ_{onset} eV)

3.2.3 Thermal and molecular weight properties of polymers

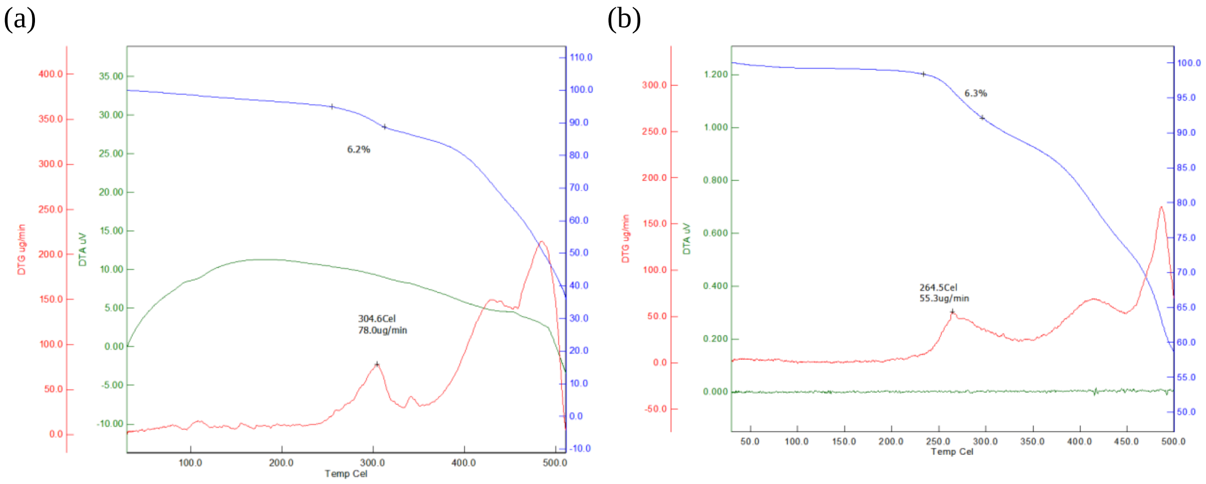


Figure 3.11 Thermogravimetric analysis (TGA) curves of polymers (a) **PTDCB** and (b) **PTTDCB**

Thermal properties of both synthesized conjugated polymers were analysed by thermogravimetric analysis (TGA) at a heating rate of 10 °C/min under nitrogen atmosphere (Figure 3.11). 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 **PTDCB** and **PTTDCB** were observed at 304 °C and 264.5 °C respectively, which shows high thermal stability of synthesized polymers 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 3.2.

Table 3.2 Molecular weight and poly-dispersity index (obtained from GPC analysis) and decomposition temperature T*d* (obtained from TGA) of synthesized polymers

Polymer	Mn(KDa)	Mw(KDa)	PDI	T_d(°C)
PTDCB	2.7	6.9	2.51	304
PTTDCB	4.0	8.7	2.15	264.5

3.2.4 Electrochemical properties

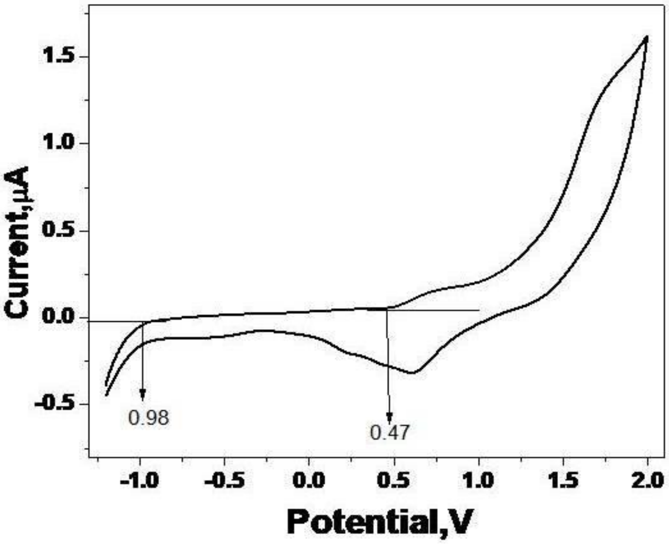


Figure 3.12 Cyclic voltammogram of **PTTDCB** (curves were obtained in CH_3CN) solution of 0.1M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) at 50 mVs^{-1}. E_{onset} (Fc/Fc+) = 0.40 V

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) and a three electrodes 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. Electrochemical properties of **PTTDCB** were determined by cyclic voltammetry (CV). The cyclic voltammogram shows oxidation peak with an onset at 0.47 V *vs* Ag/AgCl (Figure 3.12). From the onset of oxidation potential, energy level of HOMO of **PTTDCB** was estimated to be -5.67 eV. LUMO energy levels of **PTTDCB** were calculated using equation $E_{LUMO} = Eg^{opt} + E_{HOMO}$ (eV) and value obtained were -3.37 eV. The values of CV experiments are provided in Table 3.3.

Table 3.3 Electrochemical properties of **PTTDCB**

Polymer	E^{onset}_{oxi}(V)[a]	E_{HOMO} (eV)[b]	E_{LUMO} (eV)[c]	E_g^{opt}(eV)[d]
PTTDCB	0.47	-5.676	-3.376	2.3

[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)

3.2.5 Space charge limited current (SCLC) hole mobility of polymer

The photophysical and electrochemical properties of synthesized **PTTDCB** encourage us to carry out hole mobility measurement. The hole mobility of polymer was measured according to a similar method described in the literature, [30] 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, ε_0 is the permittivity of free space, ε_r is the dielectric constant of the polymer, μ 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 ε_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 mobility for **PTTDCB** was found to be 4.36 × 10^{-4} $cm^2V^{-1}s^{-1}$ (Figure 3.13). The high hole mobility allows the synthesized polymer to be used as hole transporting materials (HTMs) for organic photovoltaic devices.

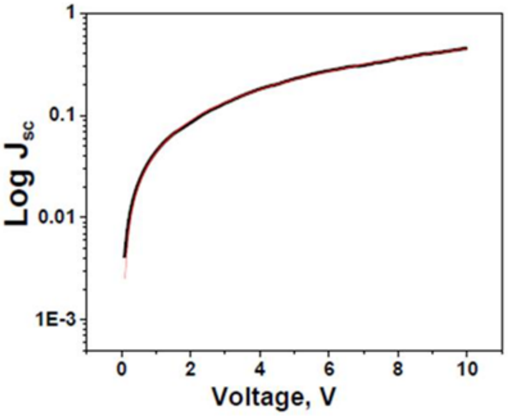


Figure 3.13 SCLC hole mobility of **PTTDCB**

3.3 Conclusion

Two new monomers namely, diethyl dibromo thiophene dicarboxylate (**2**) and diethyl tert-thiophene dicarboxylate (**4**) were synthesized from dimethyl thiophene dicarboxylate. Both monomers were further polymerized with 9-*n*-tetradecyl-3,6-bis

(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9*H*-carbazole (**8**) under Suzuki Miyaura coupling reaction condition to get the desired D-A low band gap conjugated polymers, **PTDCB** and **PTTDCB**, respectively.

The polymers were isolated and characterized by NMR (^{1}H and ^{13}C), UV-visible, GPC, TGA and electrochemical techniques. The structure-property relationships were established by comparing both polymers. **PTDCB** have optical band gap of 2.8 eV while **PTTDCB** have 2.1 eV. Both polymers showed high thermal stability. **PTTDCB** which possessed low band gap nature; hence, its electrochemical properties were measured by CV analysis which showed that **PTTDCB** exhibited reversible oxidation potential, which is an important characteristic of polythiophenes. The hole mobility of **PTTDCB** was found to be 4.36×10^{-4} cm^{2}V^{-1}s^{-1}. The high hole mobility allows the polymer to be used as hole transporting materials (HTMs) for organic photovoltaic devices. Overall comparing the two polymers, it was concluded that by incorporation of addition thiophene units in the polymer chain the effective conjugation length was increased and consequently it decreases the band gap of the polymer.

3.4 Experimental section

3.4.1 General

All chemicals were reagent grade and used as purchased. Moisture sensitive reactions were performed under an inert atmosphere of dry nitrogen with dried solvent. THF was dried over sodium/benzophenone and was distilled prior to use. 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). ^{1}H and ^{13}C NMR spectra were recorded on Bruker AV-III 400 MHz 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 the internal standard. The UV-visible spectra were recorded on model Perkin ElemerLamba 35 UV-visible spectrometer at room temperature. The polymer thin film on glass substrate obtained by drop casting method. Fluorescence spectra were recorded on a model HITACHI F-6300 fluorescence spectrometer. The concentration of solution was kept 10^{-5} M for the measurement of absorption spectra and emission spectra. The molecular weight and poly dispersity index (PDI) 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 standards. Thermal analyses were recorded on a SII EXSTAR 6000 model thermogravimetric analysis/ simultaneous differential thermal analysis (TG/DTA). Cyclic Voltammetry (CV) analysis was performed on Princeton Applied Research 263A potentiostat with a three-electrode cell containing a solution of tetrabutylammonium hexafluorophosphate ($TBAPF_6$) (~50mM) as an electrolyte in dry DCM at a scan rate of 100 mV s^{-1}. The measurements were calibrated using ferrocene as standard. The electrochemical cell was set up with Pt disk electrode as the working electrode, a Pt wire as counter electrode, and Ag/AgCl as reference electrode. Electrochemical experiments were performed under nitrogen atmosphere.

3.4.2 Synthesis

Dimethyl 4,5-thiophene dicarboxylate (**1**) was synthesized from maleic anhydride in six step synthetic methodology mention in chapter 2 [23].

3.4.2.1 Diethyl 2, 5-dibromothiophene-3,4-dicarboxylate (2)

In a clean dry 100 mL round bottom flask 1.04 g (0.005 mol) dimethyl 4,5-thiophene dicarboxylate was taken. To this 5 mL of glacial acetic acid was added and the resultant solution was stirred at room temperature. To the resultant solution 3.31 g (0.02 mol) of bromine was added dropwise. After complete addition of bromine, water condenser was attached to the round bottom flask and content was heated to 80 ^{o}C for 12 hours. The reaction mixture was poured in to cold water and then extracted with ethyl acetate. The organic layer was washed with sodium thiosulfate, dried over sodium sulfate and concentrated by evaporation. The solid yellow compound was obtained. The crude 2,5-dibromo thiophene-3,4-dicarboxylic acid (**1a**) 0.6 g (0.0018 mol) was taken in clean dry 150 mL round bottom flask. 10 mL of absolute ethyl alcohol was added to flask and homogenous mixture was prepared by stirring the contents. Dean-stark apparatus was placed on the round bottom flask. The resulting reaction mixture was refluxed after addition of 30 mL of toluene and 1 mL of concentrated sulfuric acid for 12 hours. After completion of the reaction, the reaction mixture was concentrated and extracted in ethyl acetate with prior water wash. Organic layer was dried over sodium sulfate and concentrated to yield diethyl 2, 5-dibromothiophene-3,4-dicarboxylate as a pale yellow oil. 0.56 g. (80% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 1.35-1.39 (t, 6H, J= 7 Hz), 4.34-4.39 (q, 4H, J= 7 Hz). ^{13}C NMR (100 MHz $CDCl_3$): δ 14.0, 62.0, 115.7, 133.7, 161.5.

3.4.2.2 Diethyl 5, 5''-dibromo-[2, 2':5', 2''-terthiophene]-3', 4'-dicarboxylate (4)

Diethyl 2,5-dibromothiophene-3,4-dicarboxylate (**2**) 0.6 g (0.0018 mol) was taken in clean and dry two neck round bottom flask fitted with water condenser and with septum on other neck. The assembly was kept under nitrogen atmosphere. Freshly distilled THF (15 mL) was added to the two neck round bottom flask. To this reaction mixture 2 mol % of $Pd(PPh_3)_4$ was added and stirred at room temperature for 15 minutes. Thereafter, 2.2 equivalents of 2-tributylstannylthiophene (1.49 g) (0.004 mol) was added by syringe from septum. The reaction mixture was refluxed for 4 hours at 65 ^{o}C and then cooled and excess of THF was evaporated under vacuum. The crude residue was washed with water and extracted in DCM, dried over sodium sulfate and concentrated to yield crude product. Further purification was carried out by column chromatography using SiO_2 and (10:1) pet ether: ethyl acetate solvent system. The purified product, diethyl [2, 2':5', 2''-terthiophene]-3', 4'-dicarboxylate was obtained as a clear oil with yield of 0.51 g, 85%. Diethyl [2, 2':5', 2''-terthiophene]-3',4'-dicarboxylate, 0.48 g (0.0012 mol) was taken in clean dry 100 mL round bottom flask. To this 25 mL of DCM was added and the mixture was stirred at room temperature. 2.0 Equivalent of NBS 0.427 g (0.0024 mol) was added in portion wise to the reaction mixture with constant stirring at room temperature. Thereafter, the reaction mixture was stirred at room temperature for 12 hours. After completion of reaction, the reaction mixture was washed with sodium thiosulfate solution followed by water and then extracted in DCM, dried over sodium sulfate and concentrated. 0.55 g. (82%).^{1}H NMR ($CDCl_3$): δ 1.30-1.34 (t, 6H, J= 7.2 Hz), 4.29-4.35 (q, 4H, J= 7.2 Hz), 7.03-7.04 (d, 2H, J= 4Hz), 7.10-7.11 (d, 2H, J= 4Hz). ^{13}C NMR (100 MHz $CDCl_3$): δ 13.9, 61.6, 127.5, 127.8, 128.7, 129.8, 132.5, 137.9, 163.7.

3.4.2.3 3, 6-Diiodo-9*H*-carbazole (6)

To the solution of glacial acetic acid (10 mL), 3.0 g (0.017 mol) carbazole was dissolved by stirring the solution at room temperature. The solution of KI (3.9 g) (0.023 mol) and KIO_3 (5.68 g) (0.026 mol) dissolved in 10 mL water was added to the reaction mixture. The reaction mixture was then heated to 80°C for 48 hours. After completion of reaction, the reaction mixture was cooled, filtered and washed with saturated sodium carbonate to yield crude product. Crude product was further purified by crystallization in methanol to yield 5.15 g (60%) 3,6-diiodo-9*H*-carbazole as a white solid compound. ^1H NMR (400 MHz $CDCl_3$): δ 7.22-7.24 (d, 2H), 7.68-7.71 (dd, 2H), 8.13 (s, 1H), 8.34 (s, 1H).

3.4.2.4 3, 6-Diiodo-9-*n*-tetradecyl-9*H*-carbazole (7)

In 100 mL round bottom flask 1.3 g (0.023 mol) of KOH pellets were taken in 30 mL of acetone and the solution was stirred at room temperature for 15 minutes. To this solution, 1 g (0.006 mol) 3,6-diiodo-9*H*-carbazole was added and the content were stirred for 30 minutes at room temperature. Thereafter, 2.15 g (0.007 mol) of *n*-tetradecyl bromide was added to the reaction mixture dropwise. The reaction mixture was stirred for 12 hours at room temperature. Excess of solvent was evaporated under vacuum and crude product was repeatedly washed with water, extracted in DCM, dried and concentrated to yield white solid product, 3,6-diiodo-9-*n*-tetradecyl-9*H*-carbazole 1.02 g. (70%). M.P 74 °C. ^1H NMR (400 MHz $CDCl_3$): δ 0.88-0.91 (t, 3H), 1.23-1.31 (m, 22H), 1.80-1.81 (m, 2H), 4.20-4.24 (t, 2H), 7.17-7.19 (d, 2H), 7.71-7.73 (d, 2H), 8.33 (s, 2H). ^{13}C NMR (100 MHz $CDCl_3$): δ 14.1, 22.7, 27.2, 28.8, 29.3, 29.4, 29.4, 29.5, 29.6, 29.6, 29.7, 31.9, 43.2, 81.6, 110.9, 123.9, 129.3, 134.4, 139.4.

3.4.2.5 9-*n*-Tetradecyl-3, 6-bis(4, 4, 5, 5-tetramethyl-1, 3, 2-dioxaborolan-2-yl)-9*H*-carbazole (8)

In a dry three neck round bottom flask attached with condenser under nitrogen atmosphere, 0.8 g (0.0013 mol) 3,6-diiodo-9-*n*-tetradecyl-9*H*-carbazole (**7**) was taken. To this 20 mL of dry DMF was added and solution was stirred to dissolve the compound. Bis pinacolato diboron (1.0 g) (0.0039 mol) (3 equivalents) and potassium acetate (0.50 g) (0.0052 mol) (4 equivalents) was added to the reaction mixture and thereafter the reaction mixture was purged with nitrogen for 15 minutes. $Pd(PPh_3)_4Cl_2$ (91 mg) (0.00013 mol) (0.1

equivalents) was added to the reaction mixture and again nitrogen purged for 15 minutes. The reaction mixture was heated at 120 ^{o}C for 36 hours under nitrogen atmosphere. The completion of reaction was confirmed by disappearance of starting material on TLC. The reaction mixture was diluted with water and then crude product was extracted in DCM. The organic layer was washed with brine and dried over sodium sulfate, concentrated under vacuum to yield crude product. Further purification was carried out by column chromatography using SiO_2 (10% ethyl acetate in pet ether solvent system). The product was obtained as a colourless oil (0.46 g) with 58% of yield. ^{1}H NMR ($CDCl_3$): δ 0.87-0.89 (t, 6H), 1.23-1.26 (m, 22H), 1.40 (s, 24H), 1.82-1.88 (m, 3H), 4.30-4.33 (t, 2H), 7.40-7.42 (d, 2H), 7.90- 7.93 (d, 2H), 8.68 (s, 2H).

3.4.2.6 Poly[diethyl-2-(9-tetradecyl-9*H*-carbazol-3-yl)thiophene-3, 4-dicarboxylate] (PTDCB)

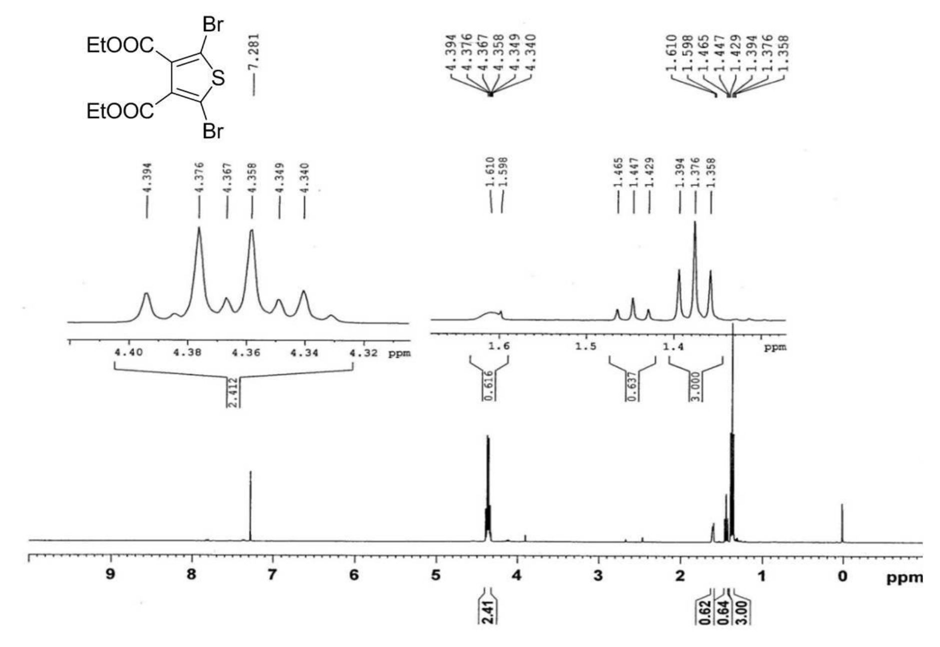
In a dry three neck round bottom flask attached with condenser under nitrogen atmosphere, diethyl 2, 5-dibromothiophene-3, 4-dicarboxylate (**2**) (0.115 g) (0.0003 mol) (1.0 equivalents) was dissolved in 30 mL of dry toluene. To this solution 9-*n*-tetradecyl-3, 6-bis(4, 4, 5, 5-tetramethyl-1, 3, 2-dioxaborolan-2-yl)-9*H*-carbazole (**8**) (0.2 g) (0.0003 mol) (1.1 equivalents) and potassium carbonate (0.124 g) (0.0009 mol) (3 equivalents) dissolved in degassed water was added. The reaction mixture was purged with nitrogen for 15 minutes, thereafter, $Pd(PPh_3)_4$ (34 mg) (0.00003 mol) (0.1 equivalents) was added and reaction mixture was heated to 110^{0}C for 72 hours. Thereafter, iodobenzene was added to the reaction mixture and reaction mixture was refluxed for further 3 hours, followed by addition of phenyl boronic acid. Excess of solvent was removed under vacuum and crude mass was dissolved in chloroform. The resultant mixture was washed with water and brine, dried over sodium sulfate and concentrated. The concentrated solution was poured in 300 mL methanol and left overnight to precipitate out the product. The precipitates were filtered off, washed with methanol and dried. 0.151 g (81 %) of dark brown colored solid was obtained. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.86-0.88 (3H), 1.18-1.26 (18H), 1.38-1.68 (4H), 1.91 (2H), 4.21-4.29 (2H), 4.35-4.42 (2H), 7.43-7.60 (2H), 7.70-7.74 (1H), 7.86-7.88 (1H), 8.2 (1H), 8.28-8.39 (1H). ^{13}C NMR (100 MHz $CDCl_3$): δ 13.8, 14.1, 22.7, 27.3, 29.0, 29.4, 29.4, 29.5, 29.6, 29.6, 29.7, 31.9, 43.4, 61.3, 108.9, 119.0, 121.3, 122.5, 122.7, 127.1, 127.3, 127.7, 128.4, 128.8, 129.1, 129.4, 132.2, 140.1, 162.4.

3.4.2.7. Poly[diethyl-5-(9-tetradecyl-9*H*-carbazol-3-yl)-[2, 2':5', 2''-terthiophene]-3', 4'-dicarboxylate (PTTDCB)

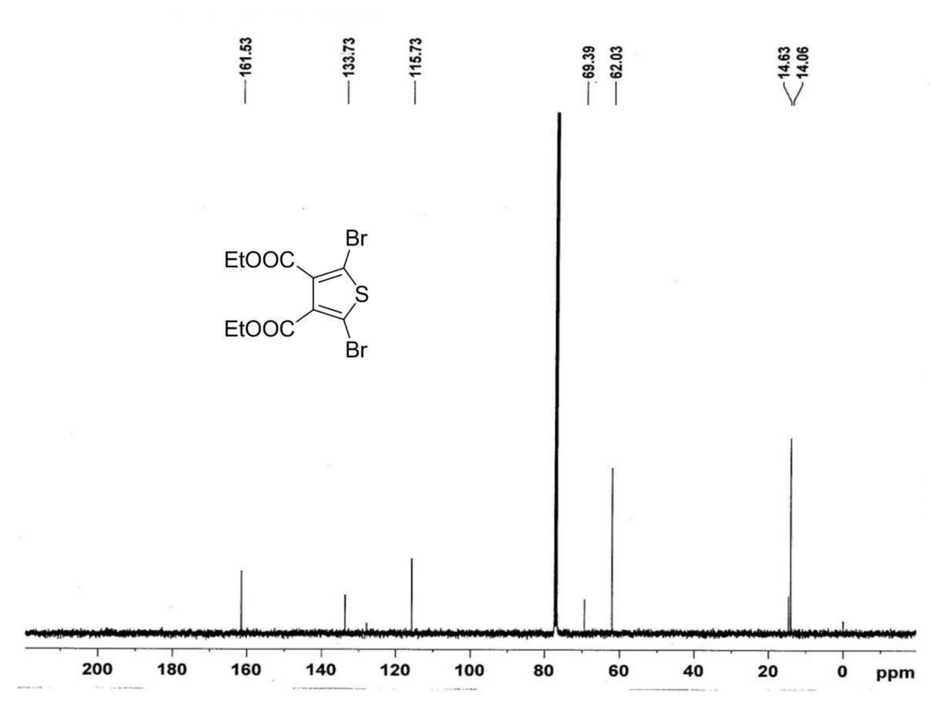
In a dry three neck round bottom flask attached with condenser under nitrogen atmosphere, diethyl 5, 5''-dibromo-[2, 2':5', 2''-terthiophene]-3',4'-dicarboxylate (**4**) (0.165g) (0.0003 mol) (1.0 equivalents) was dissolved in 30 mL dry toluene. To this solution 9-*n*-tetradecyl-3, 6-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9*H*-carbazole (**8**) (0.2 g) (0.0003 mol) (1.1 equivalents) and potassium carbonate (0.124 g) (0.0009 mol) (3 equivalents) dissolved in degassed water was added. The reaction mixture was purged with nitrogen for 15 minutes, thereafter, $Pd(PPh_3)_4$ (34 mg) (0.00003 mol) (0.1 equivalents) was added and reaction mixture was heated at 110 ^{o}C for 72 hours. After 72 hours iodobenzene was added to the reaction mixture and the reaction mixture was refluxed for 3 hours, followed by addition of phenyl boronic acid and refluxed for further 3 hours. Excess of solvent was removed under vacuum and crude mass was dissolved in chloroform. The organic solution was washed with water and brine, dried over sodium sulfate and concentrated. The concentrated solution was poured in 300 mL methanol and left overnight to precipitate out. The precipitates were filtered off, washed with methanol and dried. To remove lower molecular weight fraction polymer was washed with hexane in Soxhlet apparatus for 24 hours. 0.218 g (89%) Dark red colored powder was obtained. ^{1}H NMR (400 MHz $CDCl_3$): δ 0.87-0.88 (3H), 1.28-1.38 (24H), 1.90 (2H), 4.34-4.39 (4H), 7.06 (1H), 7.13-7.77 (6H), 7.82 (1H), 8.38-8.39 (1H). ^{13}C NMR (100 MHz $CDCl_3$): δ 14.0, 14.1, 22.7, 27.3, 29.0, 29.3, 29.5, 29.6, 31.9, 43.3, 61.8, 109.3, 117.6, 117.9, 119.0, 122.5, 123.2, 124.5, 126.5, 127.2, 128.4, 128.5, 128.8, 129.0, 129.6, 131.9, 132.1, 140.7, 163.6.

3.5 Spectral data

3.5.1 Diethyl 2, 5-dibromothiophene-3, 4-dicarboxylate (2)

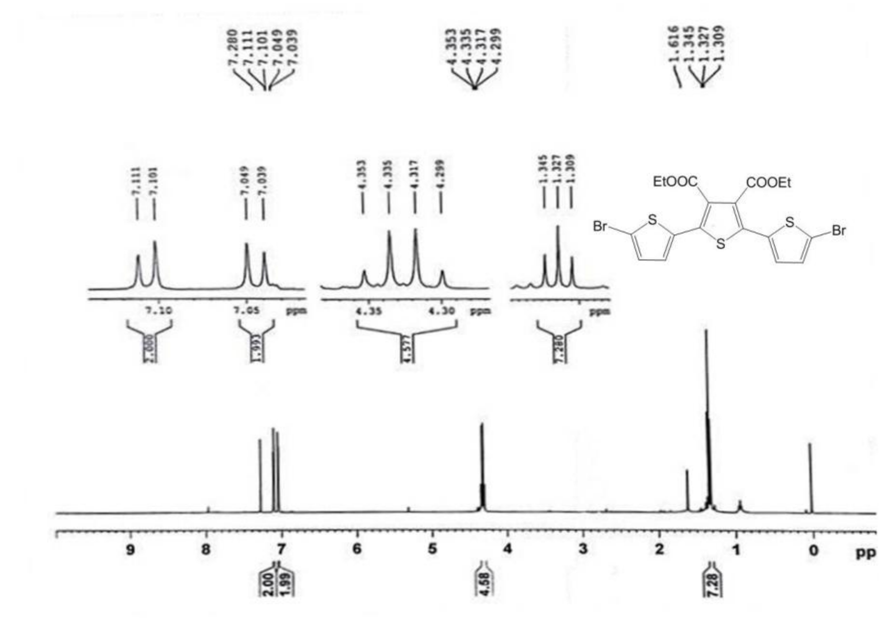


^{1}H NMR spectrum

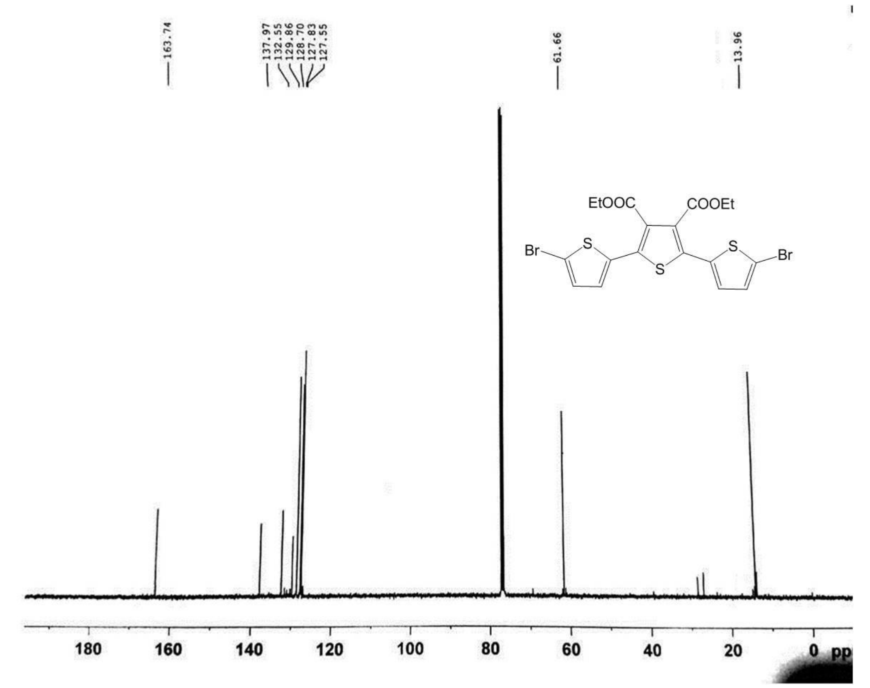


^{13}C NMR spectrum

3.5.2 Diethyl 5, 5''-dibromo-[2, 2':5', 2''-terthiophene]-3', 4'-dicarboxylate (4)

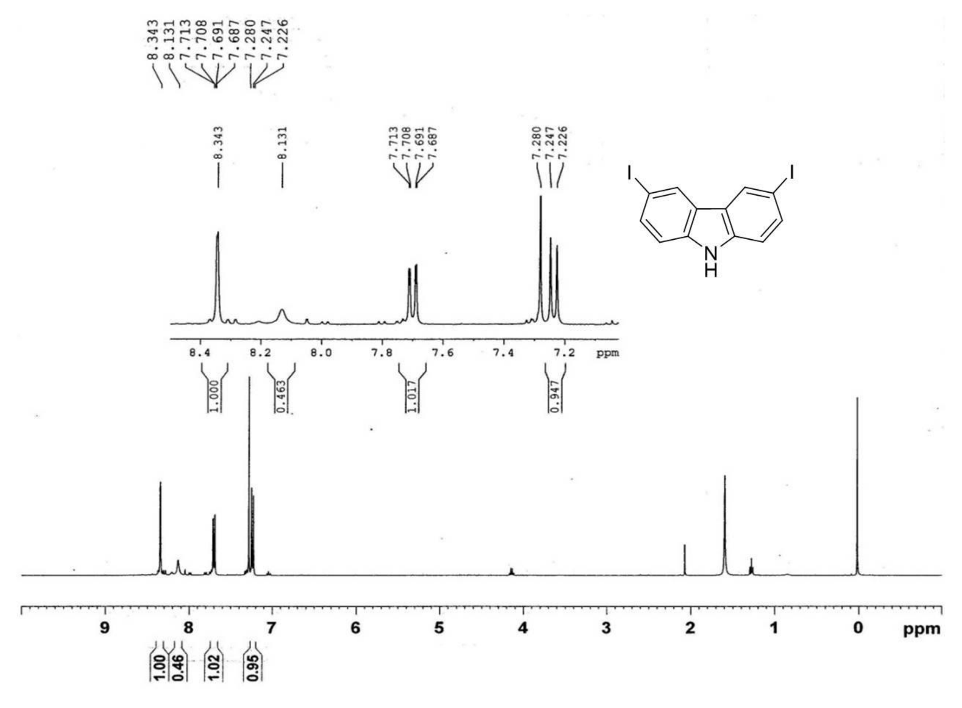


^1H NMR spectrum



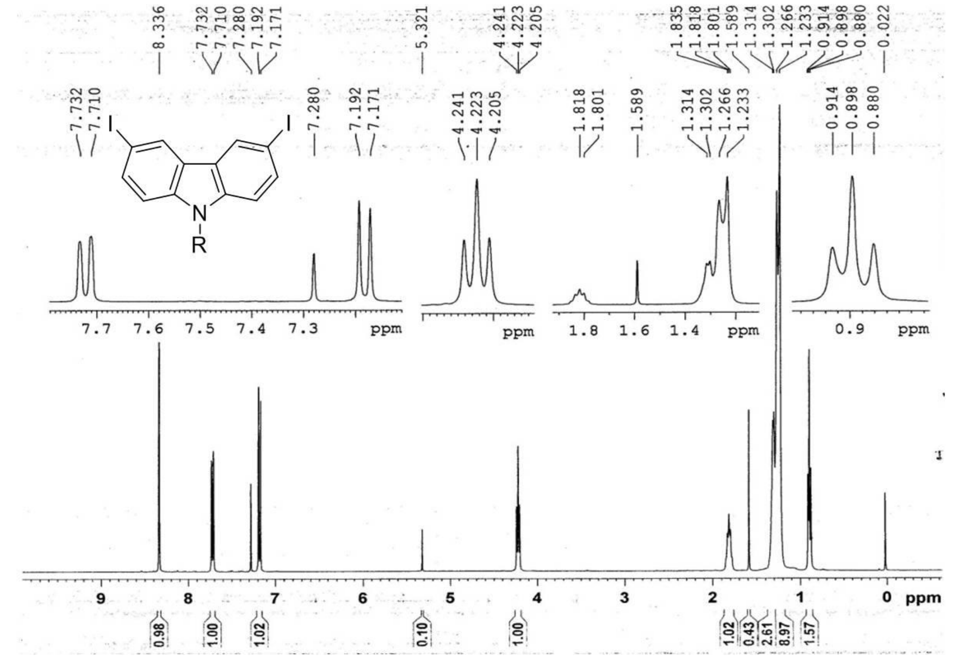
^{13}C NMR spectrum

3.5.3 3, 6-Diiodo-9H-carbazole (6)

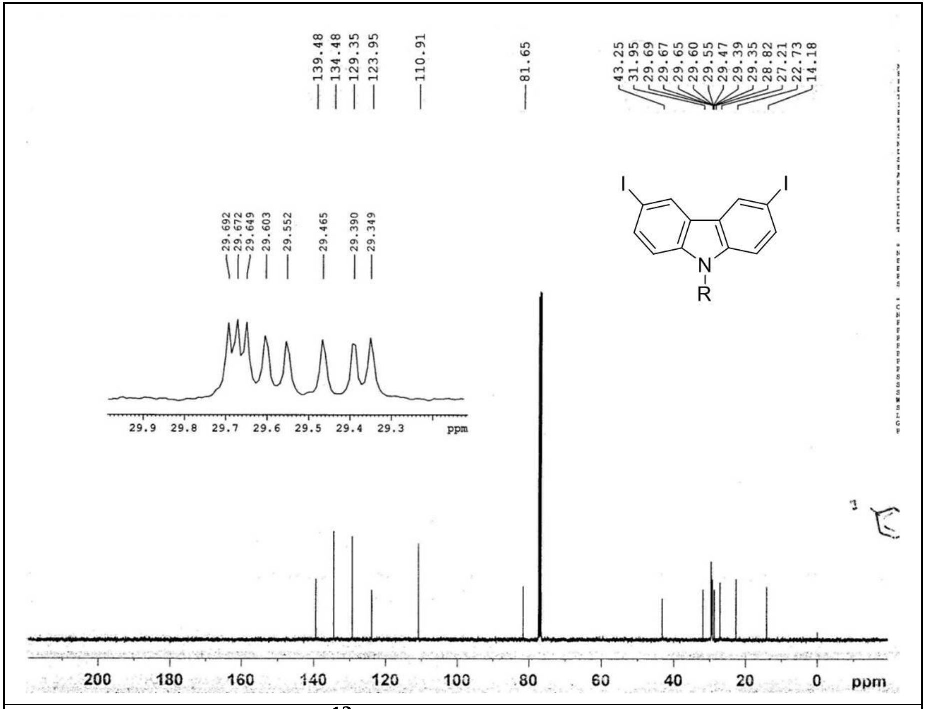


^{1}H NMR spectrum

3.5.4 3, 6-Diiodo-9-*n*-tetradecyl-9*H*-carbazole (7)

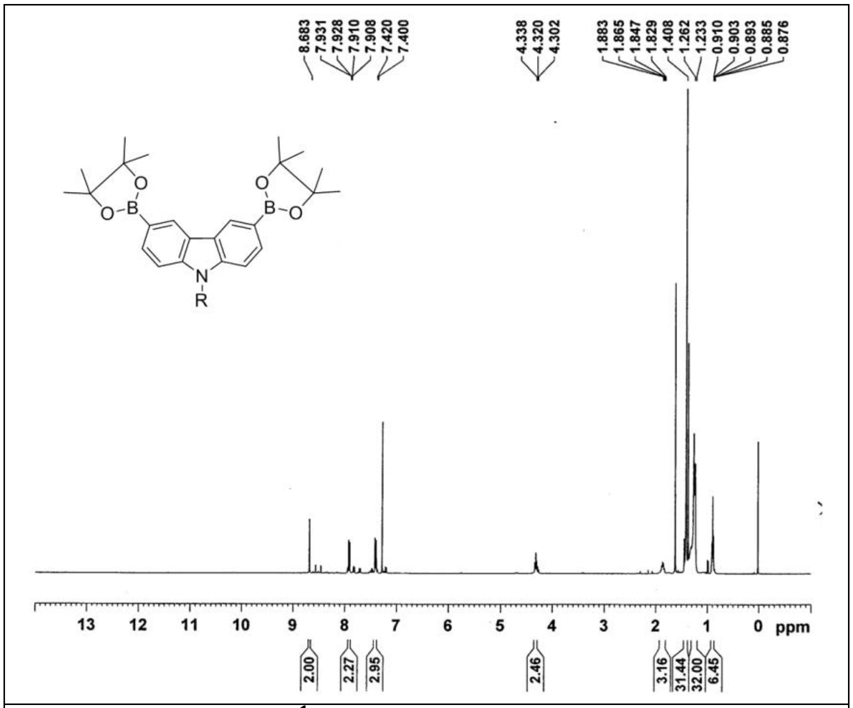


^{1}H NMR spectrum



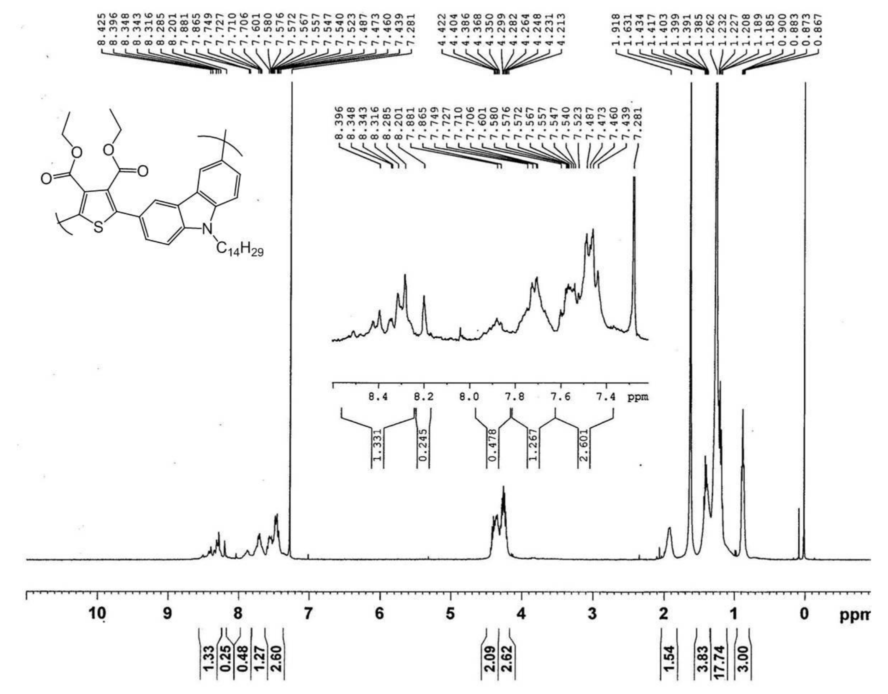
^{13}C NMR spectrum

3.5.5 9-*n*-tetradecyl-3, 6-bis(4, 4, 5, 5-tetramethyl-1, 3, 2-dioxaborolan-2-yl)-9*H*-carbazole (8)



^{1}H NMR spectrum

3.5.6 Poly[diethyl-2-(9-tetradecyl-9*H*-carbazol-3-yl)thiophene-3, 4-dicarboxylate] (PCBTD)



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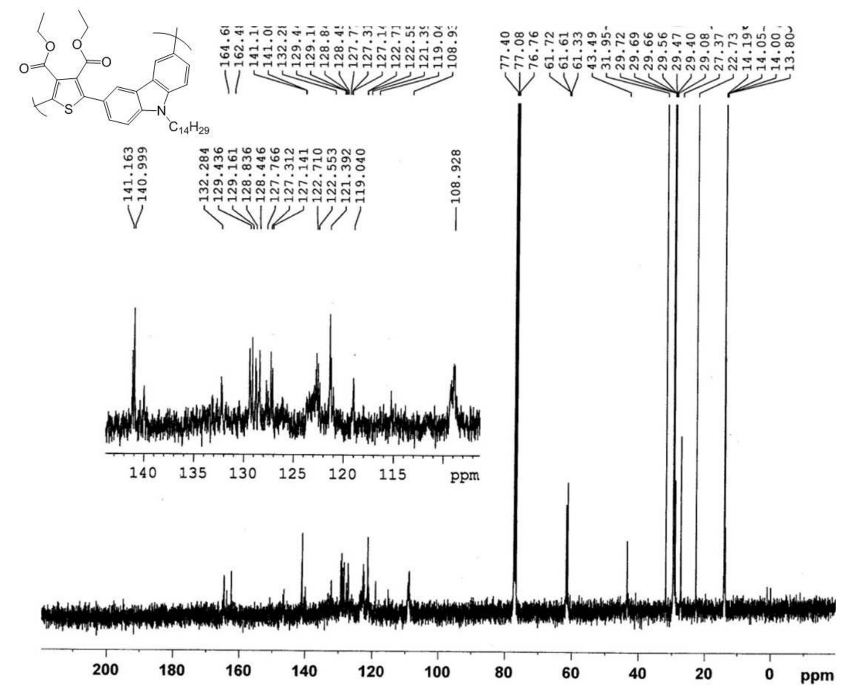

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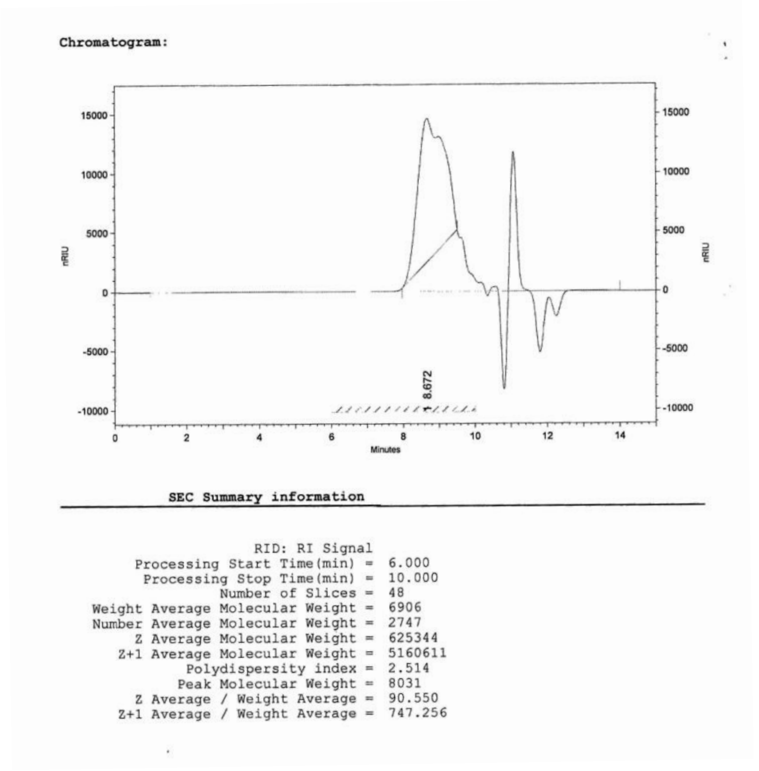

SEC Summary information

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        Polydispersity index =  2.514
         Peak Molecular Weight =  8031
     Z Average / Weight Average =  90.550
   Z+1 Average / Weight Average =  747.256
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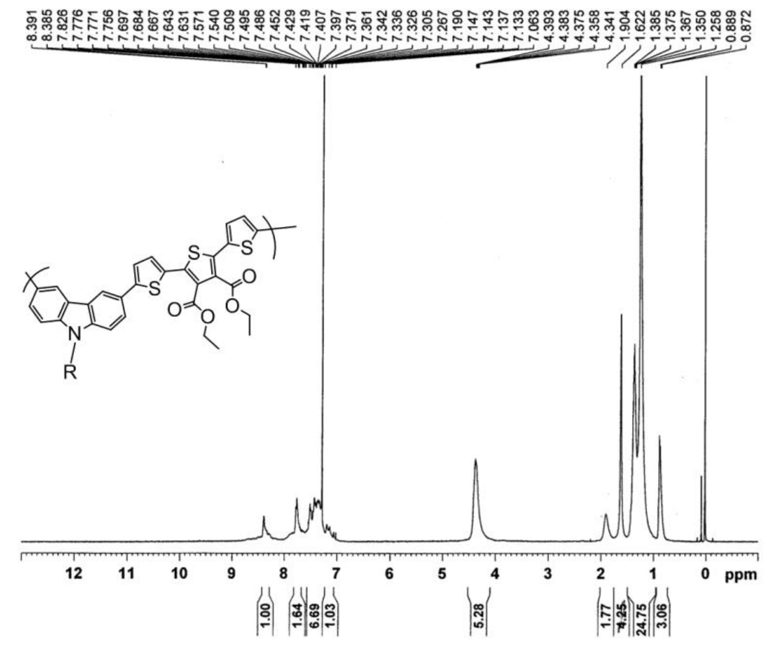
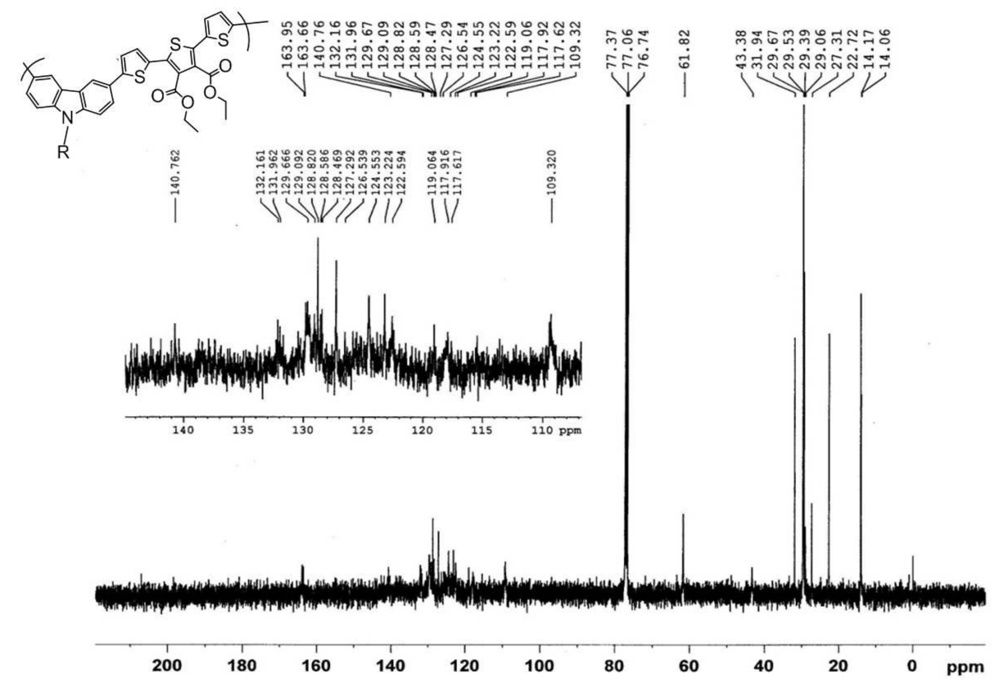
GPC of **PCBTD**

3.5.7 Poly[diethyl-5-(9-tetradecyl-9*H*-carbazol-3-yl)-[2, 2':5', 2''-terthiophene]-3', 4'-dicarboxylate] (PCBTTD)



^{1}H NMR spectrum



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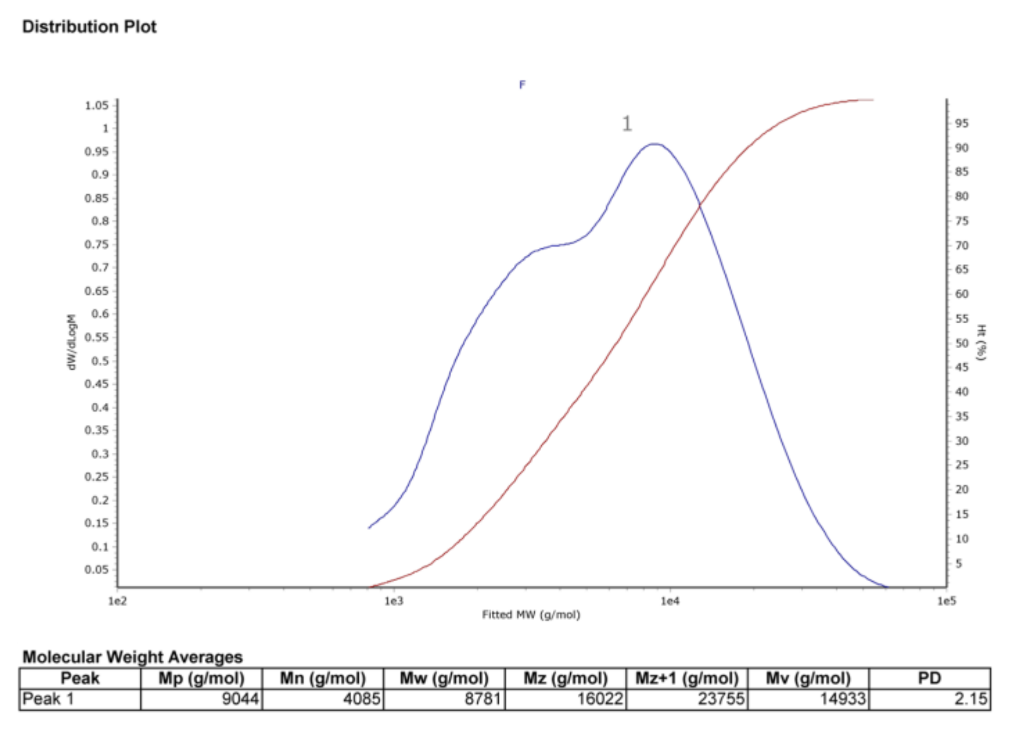

Molecular Weight Averages

Peak	Mp (g/mol)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mz+1 (g/mol)	Mv (g/mol)	PD
Peak 1	9044	4085	8781	16022	23755	14933	2.15

GPC of **PCBTTD**

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