Supporting information

For

Effect of structural isomerism in BODIPY based donor-acceptor co-polymers on their photovoltaic performance

Gourav Tarafdar[1], Upendra K. Pandey*[1], Sanchita Sengupta[1,3], Praveen C. Ramamurthy*[1,2]

[1]Interdisciplinary Centre for Energy Research, Indian Institute of Science, Bangalore-560012, India.

[2]Materials Engineering, Indian Institute of Science, C. V. Raman Avenue, Bangalore-560012, India.

[3]Department of Chemical Sciences, Indian Institute of Science Education and Research (IISER) Mohali, Punjab-140306, India.

Email: praveen@iisc.ac.in ; upendrap@iisc.ac.in

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1. Materials and methods

Thiophene-3-carboxylic acid, 1-Octyne, *iso*-propyl magnesium chloride (*i*-PrMgCl), tris(dibenzylideneacetone)dipalladium(0), o-tolyl phosphine, trimethyl tin chloride ($SnMe_3Cl$, 1 M in hexane) and 9,9-Dihexylfluorene-2,7-diboronic acid bis(1,3-propanediol) ester were obtained from Sigma Aldrich chemical company and used without further purification. 3,4-Dihydroxybenzaldehyde, Pyrrole, 1-Bromohexane, N-bromosuccinamide, Chloranil and 2,3-Dicloro-5,6-dicyano-1,4-benzoquinone (DDQ) were obtained from Spectrochem Pvt ltd. Tetrahydrofuran (THF) was dried over sodium/benzophenone ketyl and distilled prior to use. *n*-BuLi (1.6 M in hexane) was obtained from Acros Chemicals and used as such. Silica gel of 60-120 mesh was used for column chromatography. P3HT of 4001 EE grade was obtained from Rieke Metals, USA and $PC_{61}BM$ from Nano-C corporation. All other reagents and solvents were obtained from commercial suppliers and used without further purification.

Proton nuclear magnetic resonance spectra were recorded using a BRUKER NMR spectrometer with TMS as the internal standard. All the spectra were recorded in $CDCl_3$. Optical studies of the polymer were carried out from the absorption spectra which was measured using Perkin Elmer Lambda 35 spectrophotometer.

Electrochemical properties were determined from the cyclic voltammograms which were recorded using a CH660D CH instrument. 0.1M electrochemical grade tetrabutylammonium hexaflourophosphate was used with acetonitrile as the electrolyte. Electrochemical cell comprised of three electrodes, Ag/AgCl as the reference electrode, platinum wire as the counter electrode and a glassy carbon electrode as the working electrode. The measurements for the polymers were done by drop casting polymer solution in chloroform on the glass carbon electrode to form a film at the tip.

UPS studies were performed using Kratos Axis Ultra DLD. In Ups, we used UV source (He 1) energy of 21.22 eV for recording the spectrum. Vacuum in the chamber at 1e-8 Torr. Calibration was performed with Ag metal foil with the correction of two He 1 and 2 secondary onset values.

Molecular weight of the polymer was determined by gel permeation chromatography (GPC) using Malvern Viscotek GPC instrument using T6000M-T3000 column in series with THF as eluent at 35 degree Celsius at a flow rate of 1mL/min. The results were analysed by using omnisec software. The sample peak was compared with a standard curve plotted with calibration plots obtained using polystyrene calibration standards.

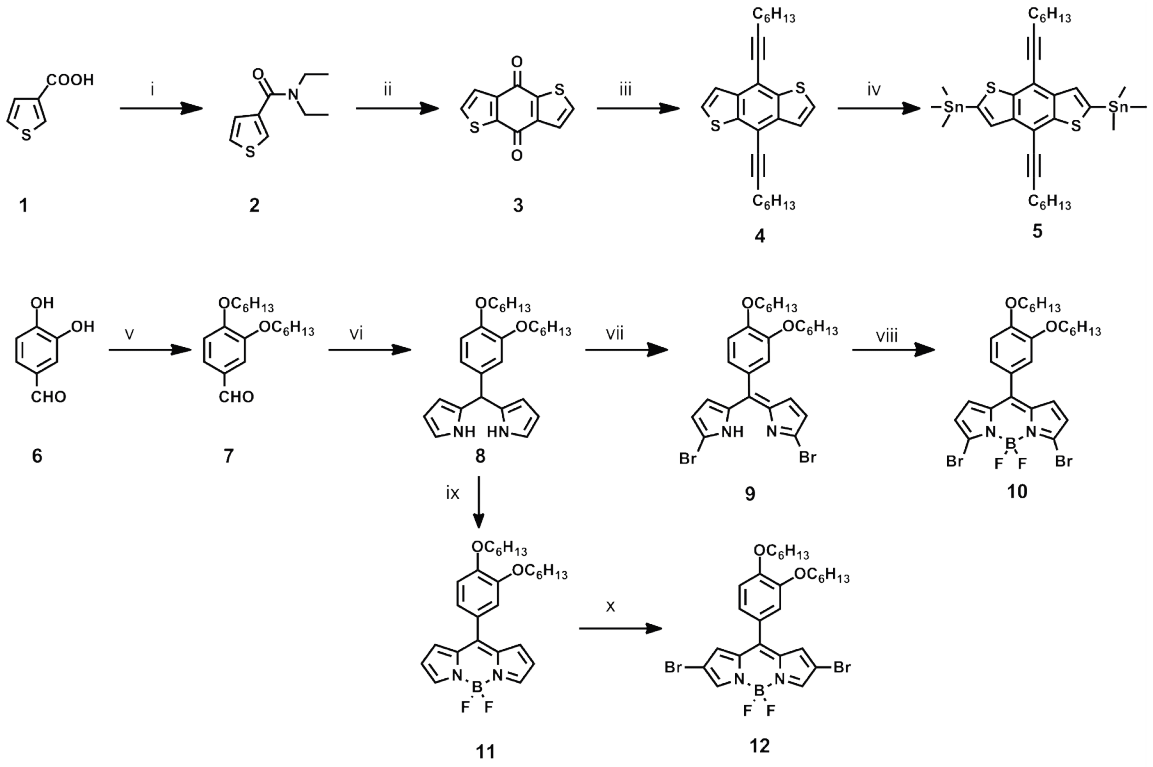
Fluorescence solution measurements were performed with Hitachi F7000 fluorescence spectrophotometer equipped with R928F photomultiplier expandable up to 900 nm. Various excitation

wavelengths were used to perform the fluorescence measurements. Standard software FL Solutions was used for the measurement and analysis of the data. Absolute fluorescence quantum yield of samples were measured with quantum yield measurement set-up equipped with 60 phi integrating sphere with sample holder and quantum yield calculation program provided with F7000 from Hitachi. Time Resolved Photoluminescence (TRPL) studies were performed on HORIBA Jobin Yvon TCSPC lifetime system integrated with a HORIBA Fluorhub Single Photon Counting Controller and HORIBA DeltaDiode C1 controller. For excitation laser model DD-470L from HORIBA scientific with peak wavelength of 469 nm was used.

Atomic force microscopy (AFM) was used to measure the surface roughness and phase contrast imaging using a Bruker ICON Scan Analyst.

2. Synthesis procedure:

The synthesis of monomers the benzodithiophene and BODIPY monomers were carried out following the procedure previously reported by Sengupta et al. [1]



Scheme S1: Synthesis of monomers (i) $(COCl)_2$, diethylamine (ii) *n*-BuLi (iii) *i*PrMgCl, Octyne, $SnCl_2$/HCl (iv) *n*-BuLi, $SnMe_3Cl$ (v) KOH/DMF, $C_6H_{13}Br$ (vi) pyrrole, TFA (vii) N-bromosuccinamide, chloranil (viii) Et_3N, $BF_3.Et_2O$ (ix) DDQ, Et_3N, $BF_3.Et_2O$ (x) N-bromosuccinamide.

a) Synthesis of monomers

(*N*,*N*-diethyl)thiophenecarboxylamide (**2**) : 3g (23.4 mmol) of thiophene-3-carboxylic acid (**1**) was added to about 5 ml of dichloromethane taken in a round bottomed flask fitted with $CaCl_2$ guard tube. The solution was cooled on an ice bath and 11.9 g (93.6 mmol) of oxalyl chloride was added dropwise. The reaction mixture was stirred at room temperature overnight. The excess oxalyl chloride was removed under vacuum and the acyl chloride intermediate was dissolved in 10 ml of dry dichloromethane. The solution of acid chloride was then added dropwise to the solution containing diethylamine 3.4g (46.8 mmol) in 30ml of dry dichloromethane in a two necked round bottomed flask fitted with a $CaCl_2$ guard tube and cooled on an ice bath. The reaction mixture was stirred for 3 hours at room temperature following which it was washed thoroughly with water. The organic fraction was dried using anhydrous sodium sulphate, concentrated and purified by silica gel column chromatography using ethyl acetate: hexane (3:10) mixture as eluent. 4.2 g (98% yield) of pure product was obtained as an oily liquid .

Benzo[1,2-b:4,5-b']dithiophene-4,8-dione (**3**): Compound **2** (4.2 g, 22.9 mmol) obtained from the previous step was dissolved in freshly distilled THF. The solution was cooled to 0°C and 15.8 ml of *n*-BuLi was added dropwise while stirring under inert atmosphere. The solution was stirred at room temperature for 3 h and subsequently poured into a beaker bcontaining ice-water. Yellowish precipitate appears almost immediately and the mixture is stirred overnight. The precipitate is later filtered out using Buchner apparatus and washed well with water, methanol and hexane successively and dried under vacuum. 1.9 g (59.3% yield) of yellow solid is obtained as product.

4,8-Di(oct-1-yn-1-yl)benzo[1,2-b:4,5-b']dithiophene (**4**): 290 mg (2.7 mmol) of 1-Octyne was dissolved in 8 ml of freshly distilled THF in a two necked round bottomed flask fitted with a condenser. 1.2 ml (2.4 mmol) of 2M *i*-PrMgCl in THF was added to it and the solution was heated to 60°C and stirred for about 100 min at that temperature. 100 mg (0.45 mmols) of **3** was added to the solution and stirred for 2 h at 60°C. A solution of 700 mg $SnCl_2$ in 1.6 ml of 10% HCl was added to the reaction mixture and then stirred at 65°C for 2 h. The reaction mixture was then poured into 50 ml of water and extracted with hexane. The organic fraction was dried over anhydrous sodium sulphate and concentrated under vacuum. White solid product was obtained by recrystallization of the yellowish crude from ethanol (160 mg, 90% yield). ^{1}H NMR spectrum (400 MHz, $CDCl_3$) δ (ppm): 7.58-7.56 (2H, d), 7.49-7.50 (2H, d), 2.62-2.65 (4H, m), 1.71-1.75 (4H, m), 1.57-1.62 (4H, t), 1.38-1.40 (8H, t), 0.91-0.95 (6H, t).

(4,8-di(oct-1-yn-1-yl)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl) bis(trimethylstannane) (**5**): 200mg (0.49 mmol) of **4** was dissolved in dry THF. The solution was cooled to -78°C and 1.2 ml of *n*-BuLi as a 1.6M solution in THF (1.97 mmol) was added dropwise while stirring under inert atmosphere. The reaction mixture was stirred at -78°C for 1 h following which 1.97 ml of trimethyltin chloride as a 1M solution in hexane (1.97 mmol) was added. The reaction mixture was stirred overnight at room temperature. The reaction was quenched by adding water and extracted with diethyl ether. **6** was obtained as yellow crystalline solid on recrystallization from ethanol solution of the crude (214 mg, 60% yield). ^{1}H NMR spectrum (400 MHz, $CDCl_3$) δ (ppm): 7.61 (2H, s), 2.63-2.67 (4H, t), 1.72-1.74 (4H, m), 1.55-1.65 (4H, m), 1.38-1.41 (8H, t), 0.92-0.95 (6H, t), 0.37-0.52 (18H). FTIR: 2934 cm^{-1}, 2854 cm^{-1} (C-H stretch), 2225 cm^{-1} (C ≡ C stretch), 1461 cm^{-1}, 1427 cm^{-1} (thiophene ring C=C stretch), 770 cm^{-1}(C=C bending), 530 cm^{-1} (C-Sn stretch).

3,4-bis(hexyloxy)benzaldehyde (**7**): 1.5g (10.8 mmol) of 3,4-dihydroxybenzaldehyde (**7**) and 5.9g (43.2 mmol) of K_2CO_3 were dissolved in 50 ml of DMF. 1-bromohexane (4.3g, 26.0 mmol) was added to it and the reaction was refluxed at 80°C for 4 hours under inert atmosphere. DMF was removed under reduced pressure and the crude was dissolved in ethyl acetate and washed with water. The organic layer was dried over anhydrous sodium sulphate and concentrated under vacuum. Silica gel column chromatography was done with 30 % ethyl acetate in hexane as the eluent (3.2 g, 97% yield). ^{1}H NMR spectrum (400 MHz, $CDCl_3$) δ (ppm): 9.83 (1H, s), 7.40-7.43 (2H, m), 6.94-6.96 (1H, m), 4.04-4.09 (4H, q), 1.81-1.89 (4H, m), 1.48 (4H, m), 1.34-1.35 (8H, m), 0.89-0.92 (6H, t).

2,2'-((3,4-bis(hexyloxy)phenyl)methylene)bis(1H-pyrrole) (**8**): 2g (6.53 mmol) of **7** was dissolved in 12 ml of distilled pyrrole in a two necked round bottomed flask under nitrogen atmosphere. TFA (50 µl, 0.65 mmol) was added to the solution and the reaction was stirred at room temperature for 30 min in dark. The reaction was quenched by adding 0.1 N NaOH solution and extracted with dichloromethane. The organic part was washed with water and brine and dried over anhydrous sodium sulphate. The crude was purified through silica column chromatography using 10% ethyl acetate in hexane as the eluent. (2.4 g, 87% yield) ^{1}H NMR spectrum (400 MHz, CDCl3) δ (ppm): 7.92 (2H, brs), 6.76-6.82 (2H, m), 6.68-6.71 (2H, m), 6.14-6.17 (2H, q), 5.93-5.94 (2H, m), 3.95-3.99 (2H, t), 3.89-3.92 (2H, t), 1.72-1.83 (4H, m), 1.41-1.48 (4H, m), 1.29-1.36 (8H, m), 0.88-0.92 (6H, m).

2-((3,4-bis(hexyloxy)phenyl) (5-bromo-2H-pyrrol-2-ylidene) methyl)-5-bromo-1H-pyrrole (**9**): 1g (2.37 mmol) of **8** was dissolved in 20 ml of dry THF under nitrogen atmosphere. The solution was cooled to -

78°C and a solution containing 0.884 g (4.97 mmol) of N-bromosuccinamide in 10 ml of dry THF was slowly added to it. The reaction was stirred for 1 hour turns dark red. THF was removed and the crude was dissolved in dry dichloromethane. 1.16 g (4.73 mmol) of chloranil was added to the solution and stirred at room temperature for 1h. The reaction mixture was then passed through a silica filter column and washed with dichloromethane to obtain the brominated dipyrromethene (**9**). The crude was taken as such for the next step.

10-(3,4-bis(hexyloxy)phenyl)-3,7-dibromo-BODIPY (**10**): The crude from the previous reaction was dissolved in 20 ml of dry dichloromethane and 4 ml of triethylamine was added to it followed by addition of 4 ml of $BF_3.Et_2O$. The reaction mixture was stirred overnight at room temperature. 20 ml of 0.1 N NaOH was added to the reaction mixture and extracted with dichloromethane. **10** was purified from the crude by silica column chromatography using 20% dichloromethane in hexane as eluent (843 mg, 71% yield). ^{1}H NMR spectrum (400 MHz, $CDCl_3$) δ (ppm): 7.02-7.08 (2H, m), 6.96-6.98 (2H, m), 6.86-6.87 (1H, m) 6.53-6.54 (2H, m), 4.07-4.10 (2H, t), 3.99-4.02 (2H, t), 1.81-1.89 (4H, m), 1.2-1.4 (12H, m), 0.90-0.95 (6H, m). FTIR: 2940 cm^{-1}, 2860 cm^{-1} (C-H stretch), 1608 cm^{-1} (aromatic C=C stretch), 1487 cm^{-1} (B-F stretch), 1300 cm^{-1} (C-O stretch), 1125 cm^{-1} (C=N stretch), 616 cm^{-1} (C-Br stretch).

10-(3,4-bis(hexyloxy)phenyl)-BODIPY (**11**): 250 mg (0.59 mmol) of **8** was dissolved in 20 ml of dry toluene under nitrogen atmosphere and 134mg (0.59 mmol) of DDQ was added. The reaction mixture was stirred for 40 min in dark. 1ml of triethylamine was added to it followed immediately by addition of 1 ml of BF3.Et2O. The reaction mixture was stirred overnight at room temperature. 20 ml of 0.1 N NaOH was added to the reaction mixture and extracted with dichloromethane. The organic layer was washed several times with water and dried over anhydrous sodium sulphate. The crude was purified using silica column chromatography using 50% dichloromethane in hexane as eluent. 185 mg (67% yield) of **11** was obtained upon recrystallization from dichloromethane-cyclohexane system. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) δ (ppm): 7.91 (2H, s), 7.13-7.17 (2H, m), 6.98-7.01 (3H, m), 6.54-6.55 (2H, m), 4.08-4.11 (2H, t), 4.01-4.05 (2H, t), 1.8-1.92 (4H, m), 1.49-1.52 (4H, m), 1.34-1.39 (8H, m), 0.89-0.95 (6H, q).

10-(3,4-bis(hexyloxy)phenyl)-2,8-dibromo-BODIPY (**12**): 100 mg (0.214 mmol) of **11** was dissolved in 16 ml of DMF:DCM solution (1:1). 92 mg (0.514 mmol) N-bromosuccinamide was dissolved in 8 ml of DCM and was added dropwise to the solution under inert atmosphere. The reaction mixture was stirred overnight at room temperature. The crude was purified by silica column chromatography using 30% dichloromethane in hexane as eluent to obtain 110 mg (74% yield). ^{1}H NMR spectrum (400 MHz,$CDCl_3$) δ (ppm): 7.81 (2H, s), 7.08-7.14 (2H, m), 6.99-7.02 (3H, m), 4.09-4.12 (2H, t), 4.03-4.06 (2H, t), 1.82-

1.92 (4H, m), 1.49-1.54 (4H, m), 1.35-1.40 (8H, m), 0.90-0.95 (6H, q). 3122 cm^{-1} (alkenyl C-H stretch), 2940 cm^{-1}, 2860 cm^{-1} (alkyl C-H stretch), 1595 cm^{-1} (aromatic C=C stretch), 1480 cm^{-1} (B-F stretch), 1347 cm^{-1} (C-O stretch), 1252 cm^{-1} (C=N stretch), 583 cm^{-1} (C-Br stretch).

b) Synthesis of polymers

All the polymerization reactions were carried out in anhydrous toluene at a temperature of 110°C. The completion of reaction was monitored by complete consumption of starting materials using thin layer chromatography (TLC). After completion of the reactions toluene was the removed and chloroform added to the mixture. 10 mg of the Pd-removal agent, 4,4-diethyl-1-phenylthiosemicarbazide was added to the solution and stirred for 1 hour. The polymer was then precipitated from the solution by adding methanol and filtered. The crude polymer obtained was purified through Soxhlet extraction using methanol, hexane and chloroform as the consecutive solvents. The chloroform fraction was collected and evaporated to obtain the respective polymers.

P1: 110 mg (0.15 mmol) of **5** and 94 mg (0.15 mmol) of **11** were dissolved in 10 ml of dry toluene and degassed with nitrogen for 15 min. 1.5 mg of Tris(dibenzylideneacetone) dipalladium(0) and 10 mg of Tri(*o*-tolyl)phosphine were added to the solution and the mixture was degassed for another 15 min. The reaction mixture was then refluxed at 110°C for 48 h. After purification, 85 mg of the polymer (65% yield). ^{13}C NMR spectrum (100 MHz, $CDCl_3$) δ (ppm): 149.76, 149.63, 147.74, 147.60, 138.93, 136.25, 134.95, 128.45, 128.43, 128.40, 124.01, 123.44, 122.26, 109.62, 109.56, 109.52, 109.47, 32.02, 31.02, 29.80, 22.80, 22.33, 14.20.

P2: 110 mg (0.15 mmol) of **5** and 94 mg (0.15 mmol) of **11** were dissolved in 10 ml of dry toluene and degassed with nitrogen for 15 min. 1.5 mg of Tris(dibenzylideneacetone) dipalladium(0) and 10 mg of Tri(*o*-tolyl)phosphine were added to the solution and the mixture was degassed for 15 min. The reaction mixture was then refluxed at 110°C for 24 h. 55 mg of the purified polymer was obtained (42% yield). ^{13}C NMR spectrum (100 MHz, $CDCl_3$) δ (ppm): 139.29, 124.48, 124.09, 123.99, 123.53, 115.96, 114.08, 33.83, 31.94, 31.64, 31.46, 30.23, 29.53, 29.37, 29.18, 28.98, 22.70, 14.11.

P3: 75 mg (0.15 mmol) of 9,9-Dihexylfluorene-2,7-diboronic acid bis(1,3-propanediol) ester (**13**) and 94 mg (0.15 mmol) of **10** were dissolved in 10 ml of dry toluene and degassed with nitrogen for 15 min. 1.5 mg of Tris(dibenzylideneacetone) dipalladium(0) and 10 mg of Tri(*o*-tolyl)phosphine were added to the solution and the mixture was degassed for another 15 min. 2 ml of 2M K_2CO_3 solution in distilled water was added to the reaction mixture. The reaction mixture was then refluxed at 110°C for 48 h. After the

general purification process 90 mg of the polymer was obtained (75% yield). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.02, 147.56, 141.11, 140.80, 135.64, 129.31, 127.66, 126.19, 123.21, 119.75, 119.00, 115.57, 111.71, 68.47, 68.26, 30.59, 30.33, 28.68, 28.24, 24.69, 22.63, 21.65, 21.44, 12.96.

P4: 75 mg (0.15 mmol) of 9,9-Dihexylfluorene-2,7-diboronic acid bis(1,3-propanediol) ester (13) and 94 mg (0.15 mmol) of **11** were dissolved in 10 ml of dry toluene and degassed with nitrogen for 15 min. 1.5 mg of Tris(dibenzylideneacetone) dipalladium(0) and 10 mg of Tri(*o*-tolyl)phosphine were added to the solution and the mixture was degassed for another 15 min. 2 ml of 2M K_2CO_3 solution in distilled water was added to the reaction mixture. The reaction mixture was then refluxed at 110°C for 48 h. After the general purification process 78 mg of the polymer was obtained (65 % yield). ^{13}C NMR (126 MHz,) δ 150.86, 149.82, 141.82, 139.47, 136.43, 134.76, 129.73, 129.63, 127.91, 127.49, 127.28, 126.76, 124.75, 123.52, 123.36, 119.34, 118.55, 54.40, 39.50, 30.48, 28.62, 22.69, 21.54, 12.97.

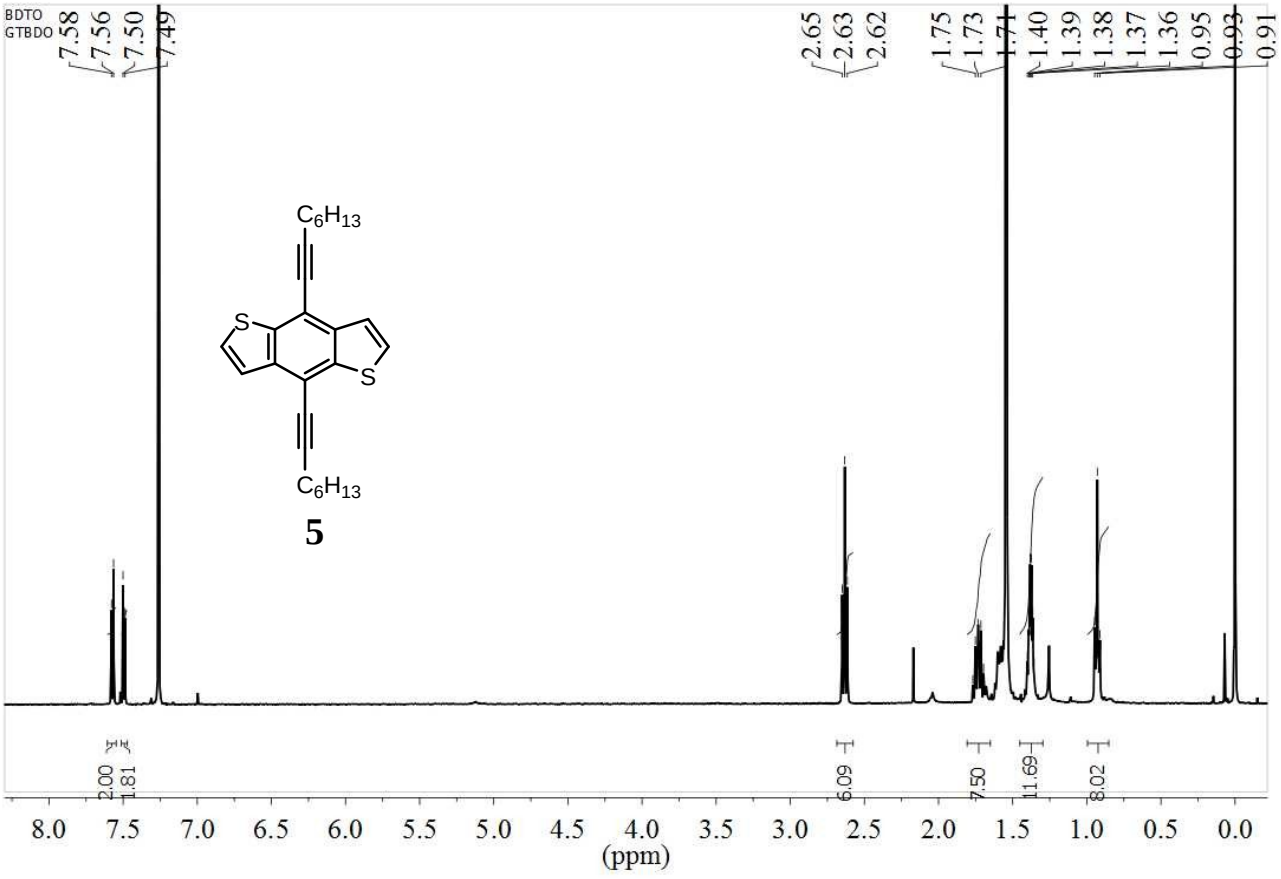


Figure S1: ^{1}H NMR spectrum of **4** in $CDCl_3$

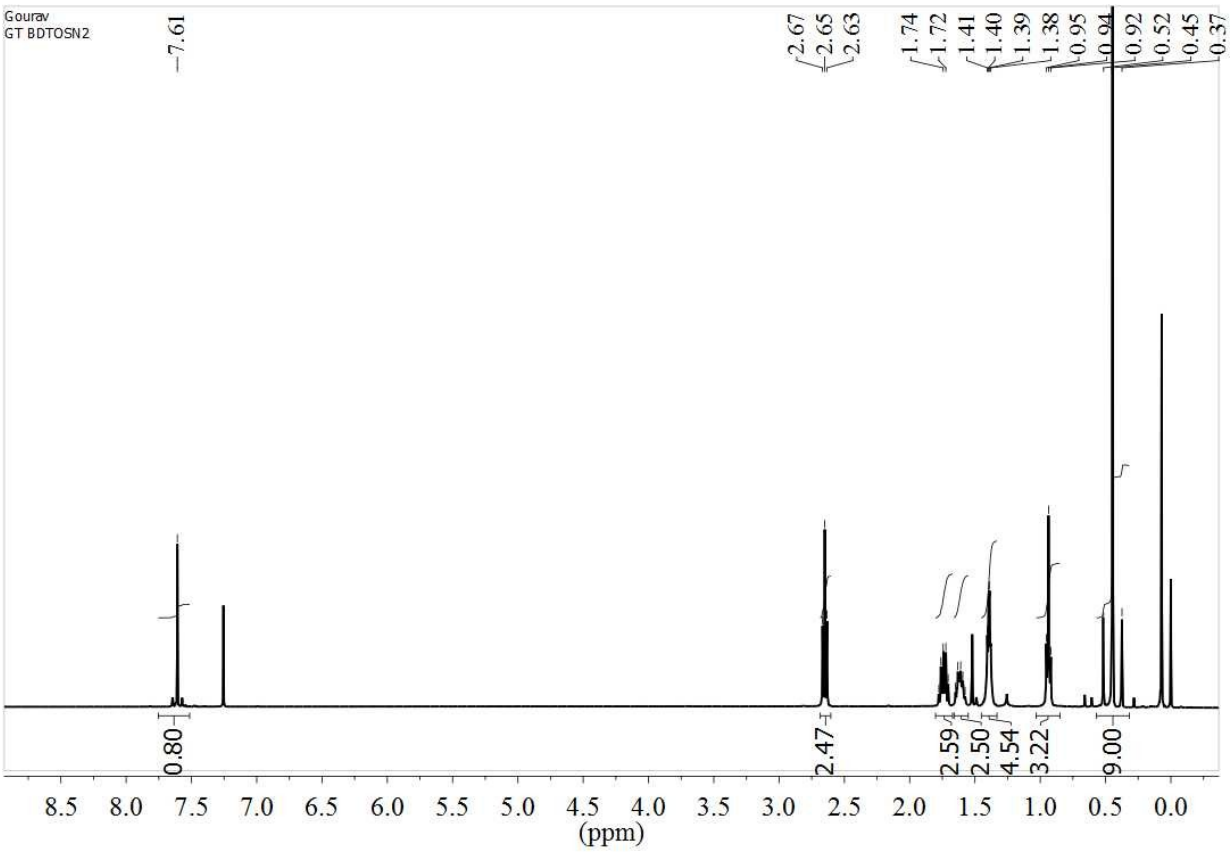


Figure S2: ^{1}H NMR spectrum of **5** in $CDCl_3$

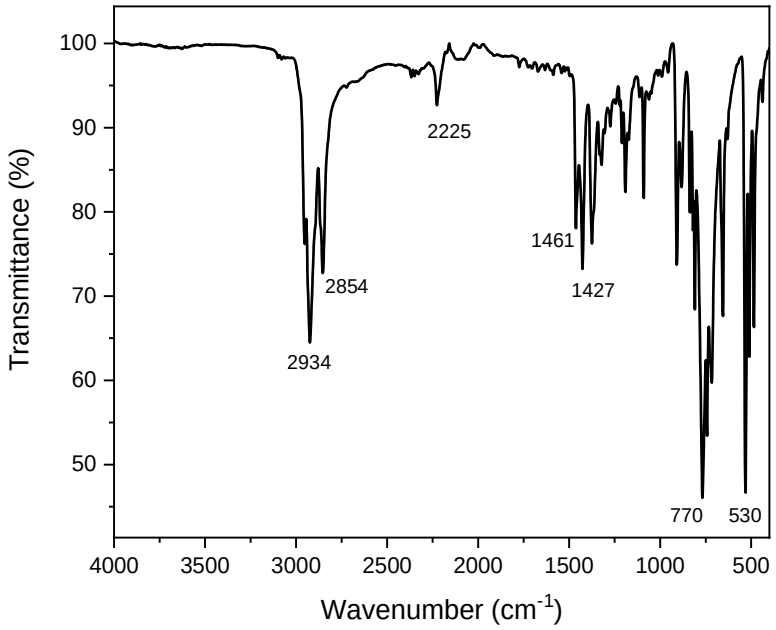


Figure S3: FTIR spectrum of **5**

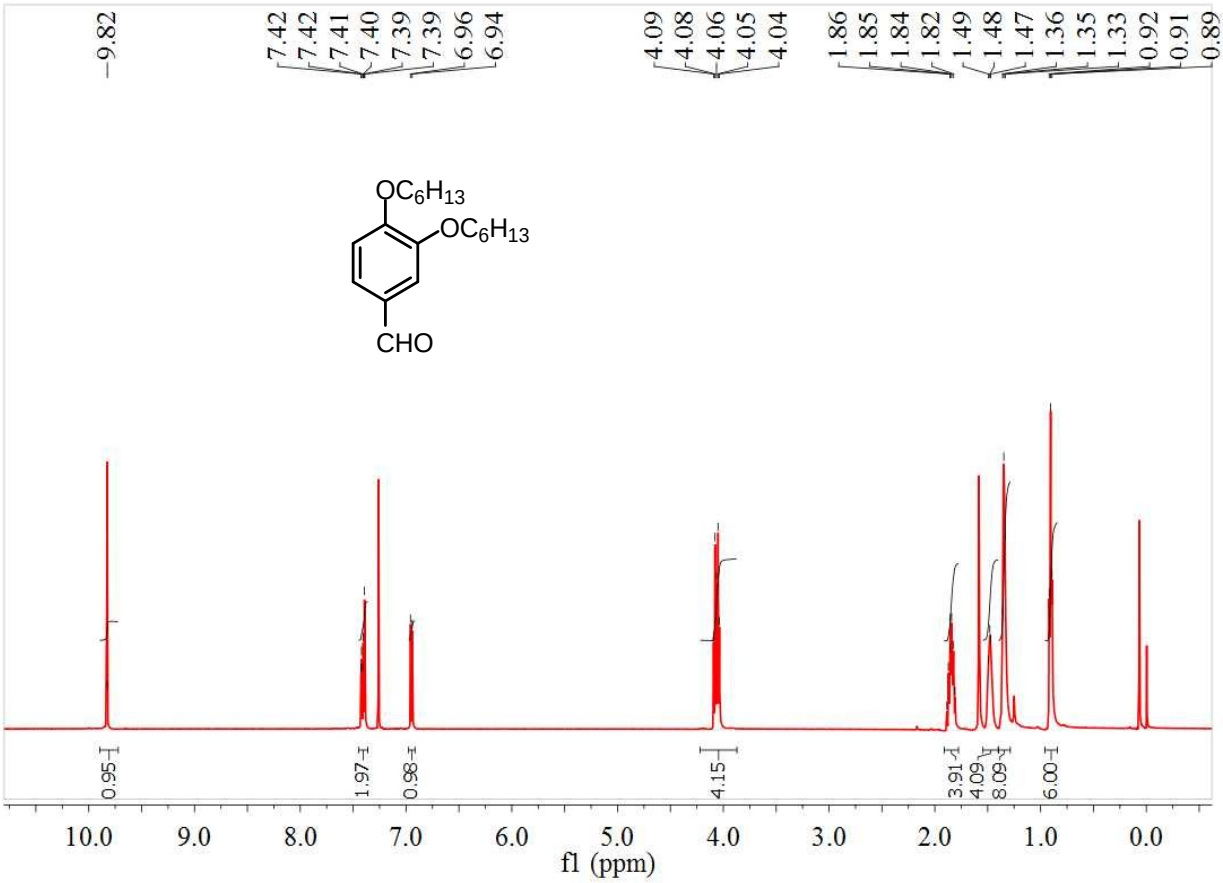


Figure S4: ^{1}H NMR spectrum of **7** in $CDCl_3$

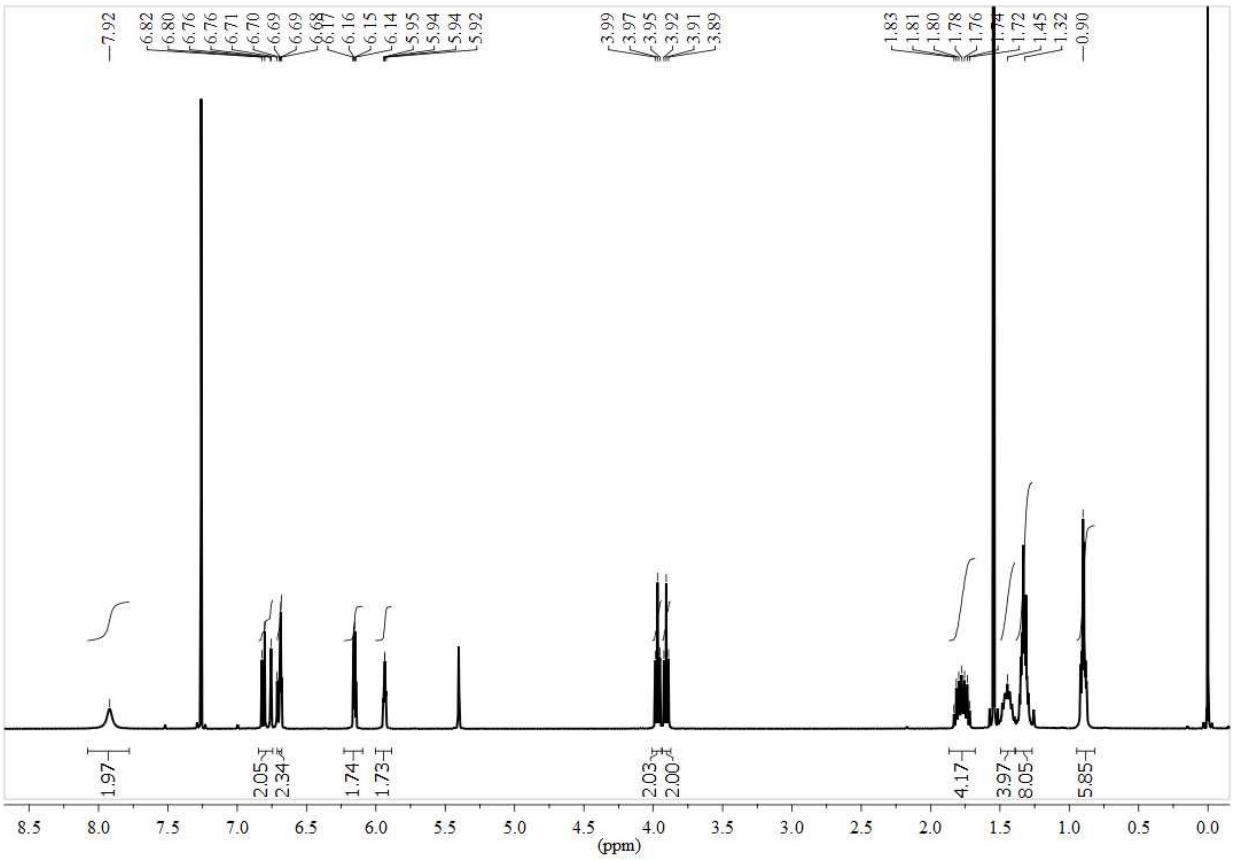


Figure S5: ^{1}H NMR spectrum of **8** in $CDCl_3$

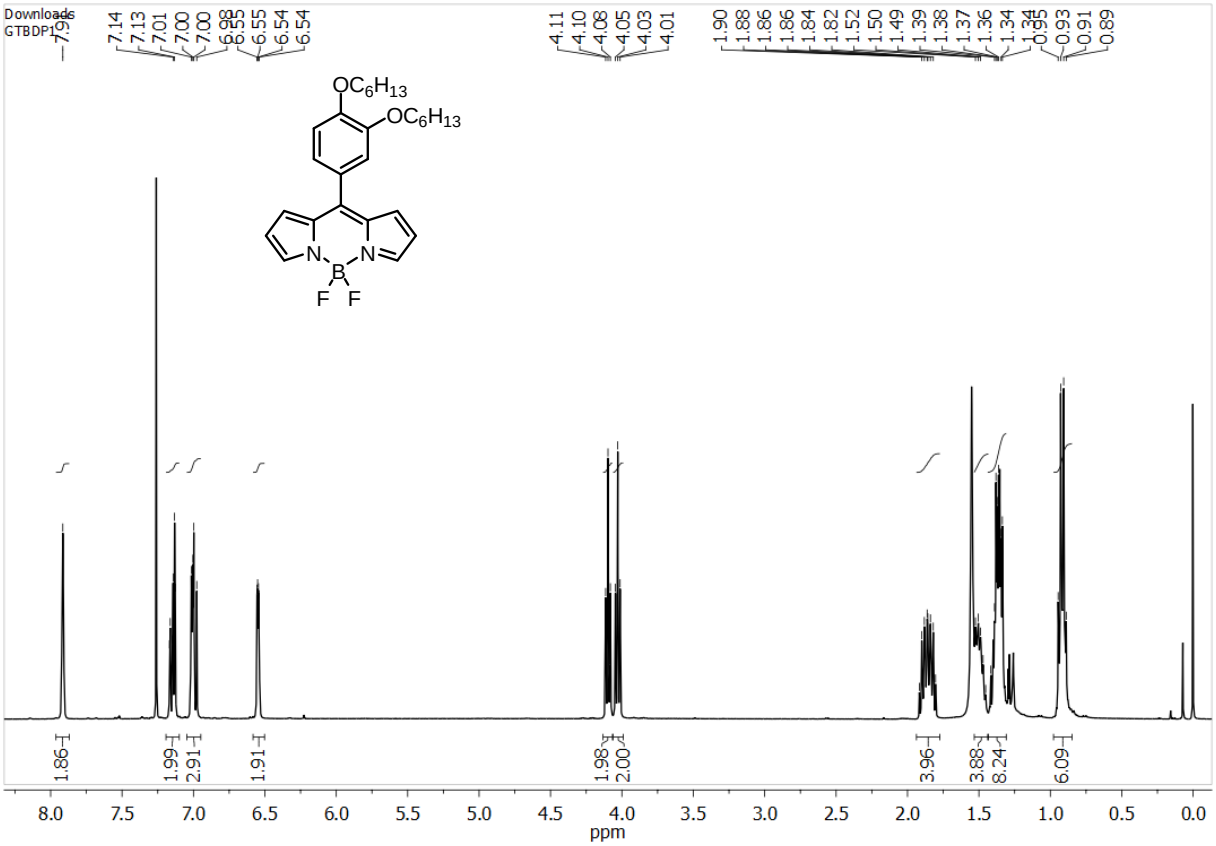


Figure S6: ^{1}H NMR spectrum of **11** in $CDCl_3$

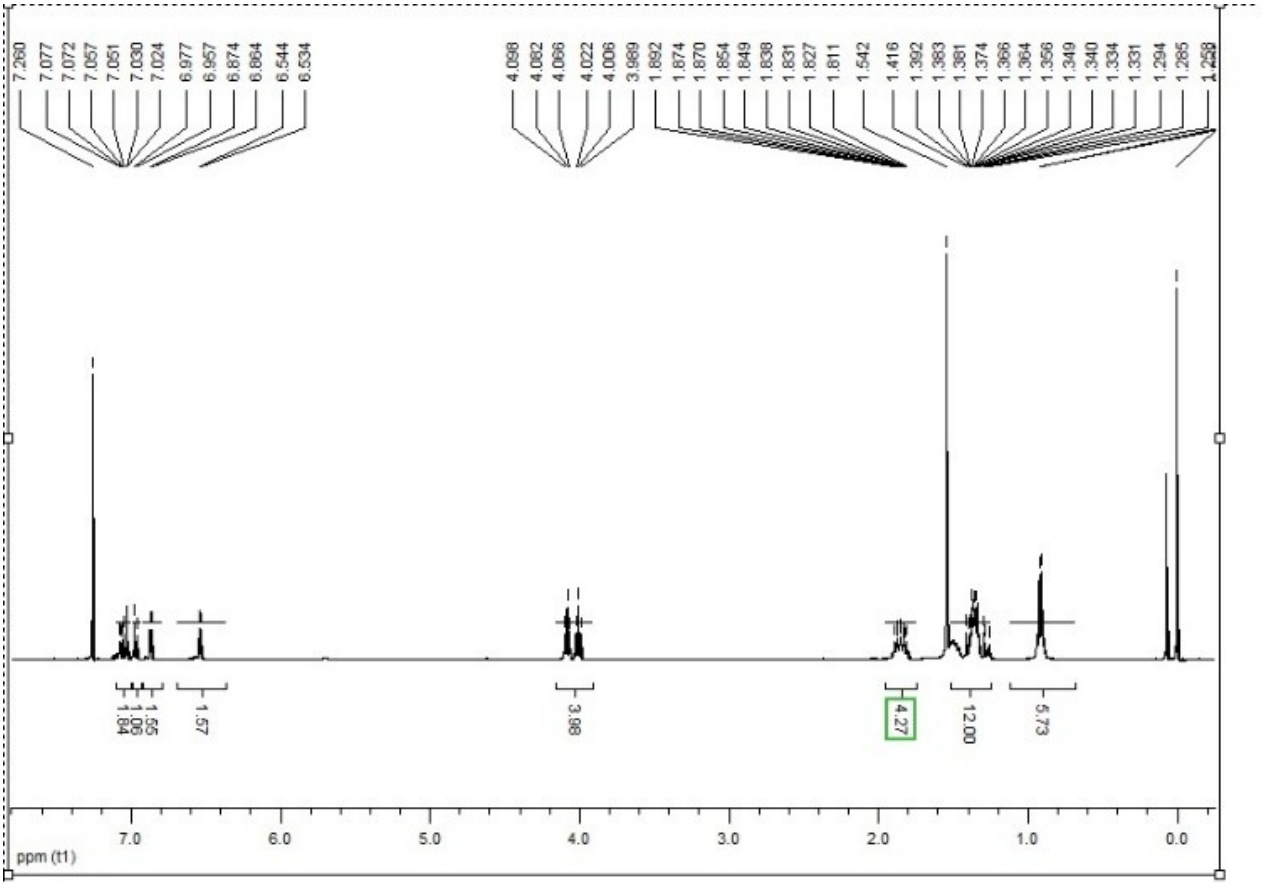


Figure S7: ^{1}H NMR spectrum of **10** in $CDCl_3$

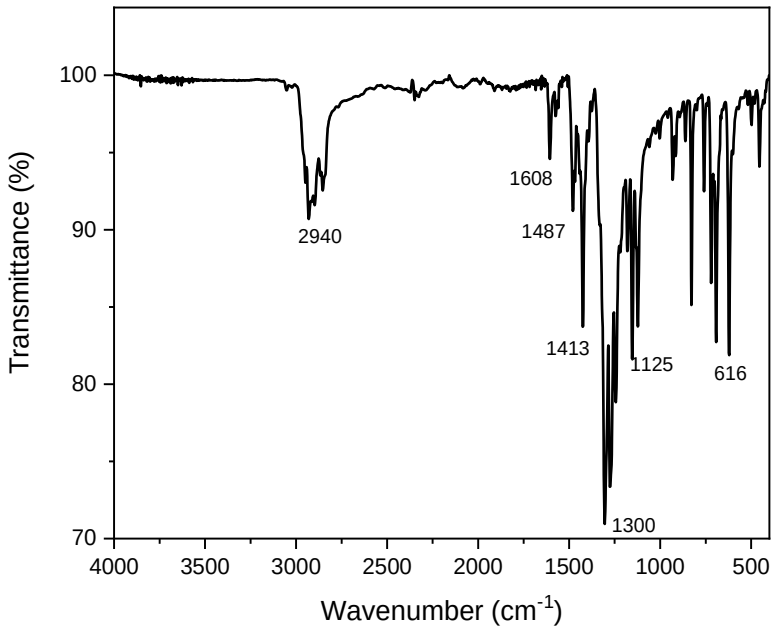


Figure S8: FTIR spectrum of **10** in $CDCl_3$

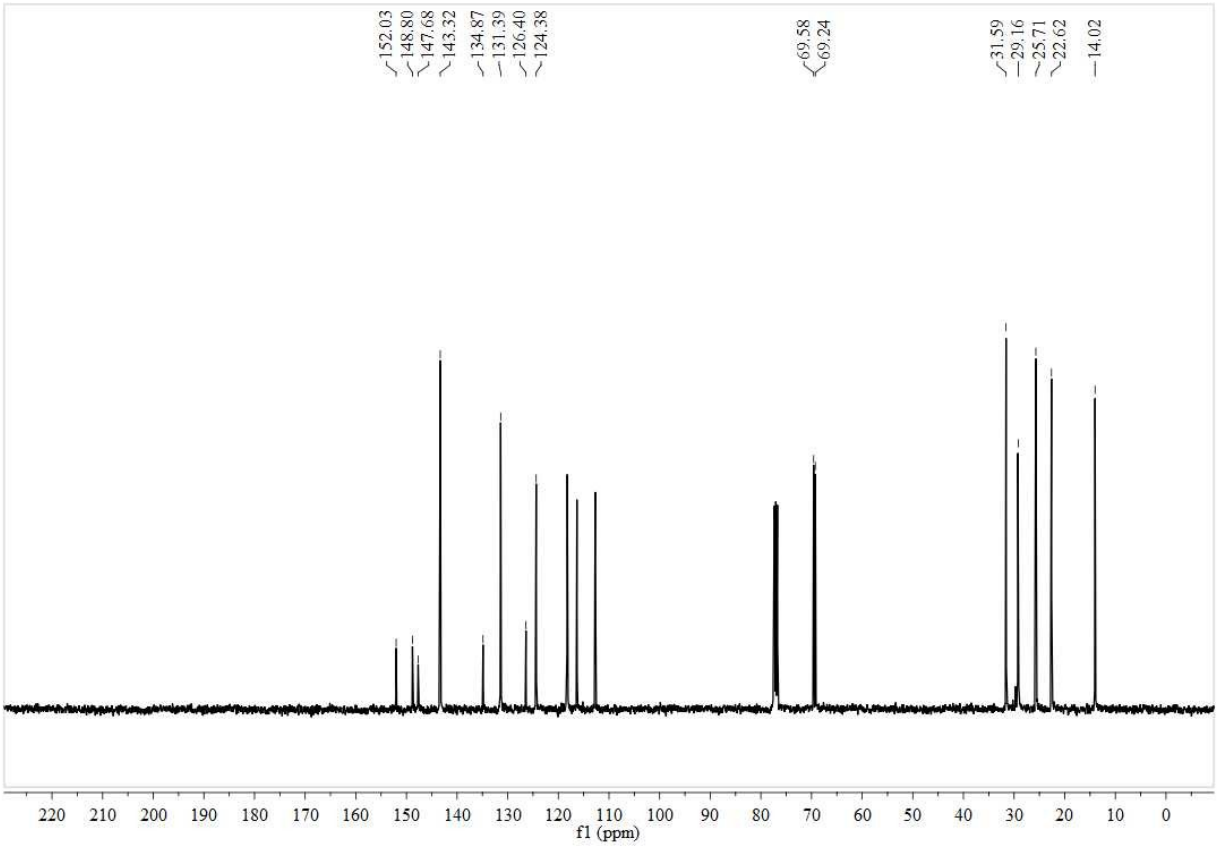


Figure S9: ^{13}C NMR spectrum of **11** in $CDCl_3$

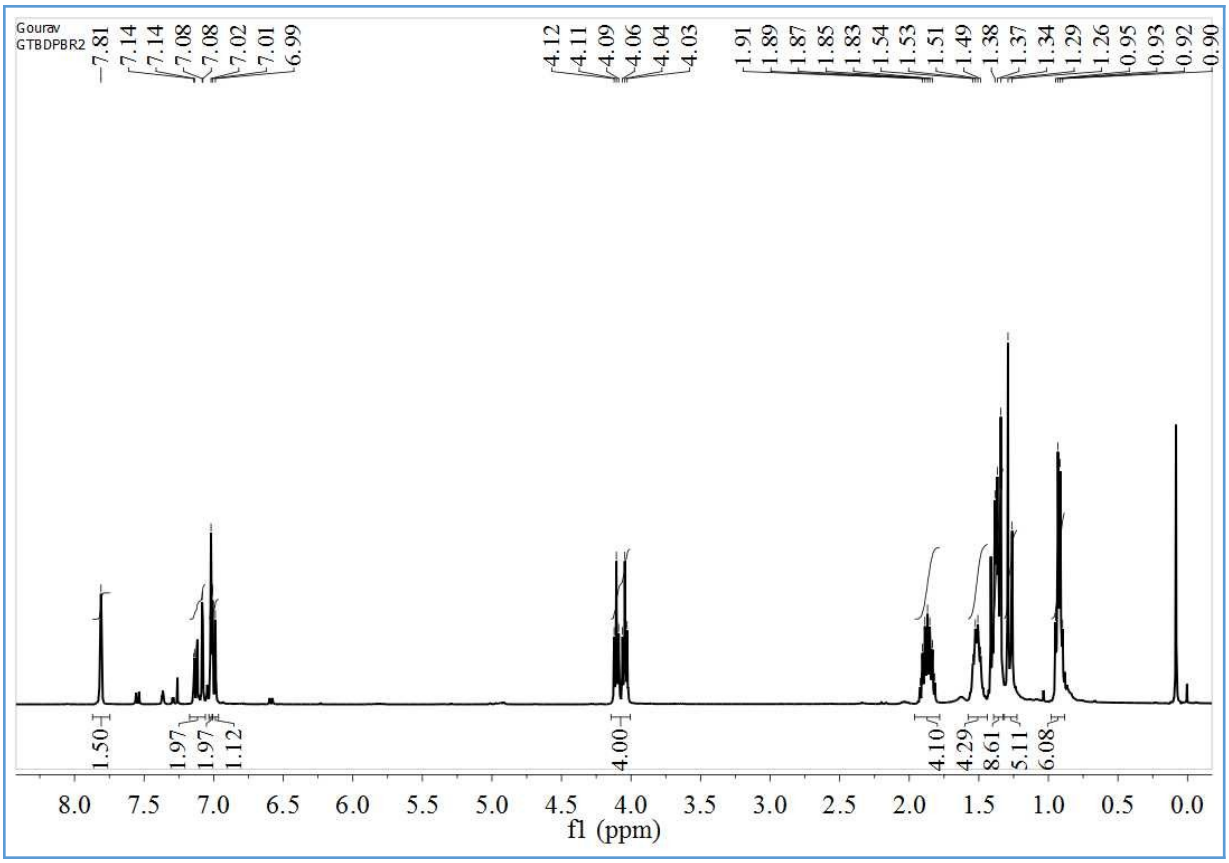


Figure S10: ^{1}H NMR spectrum of **12** in $CDCl_3$

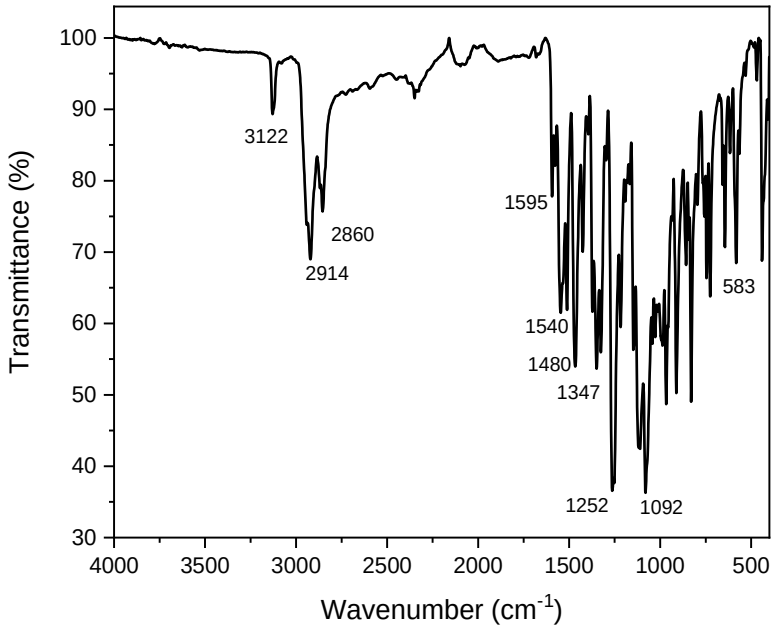


Figure S11: FTIR spectrum of **12**

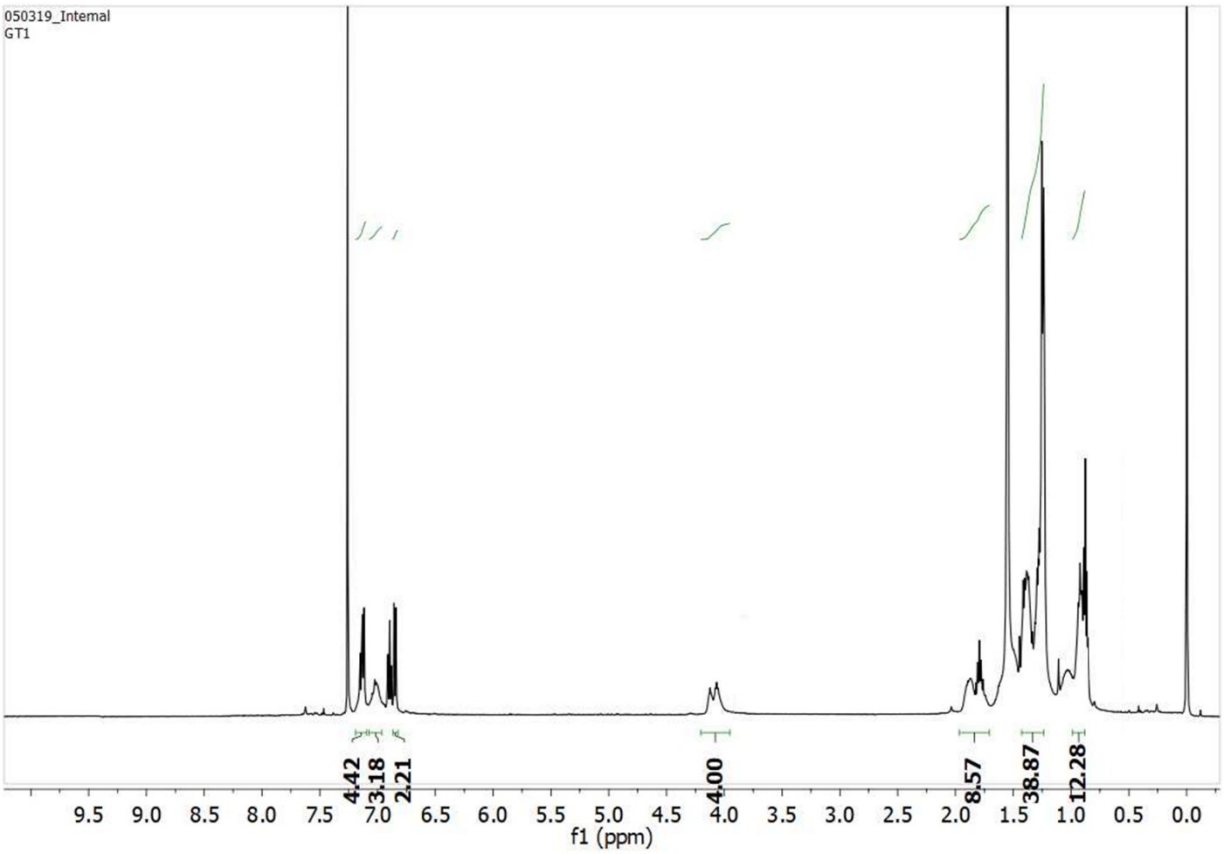


Figure S12: ^{1}H NMR spectrum of **P1** in $CDCl_3$

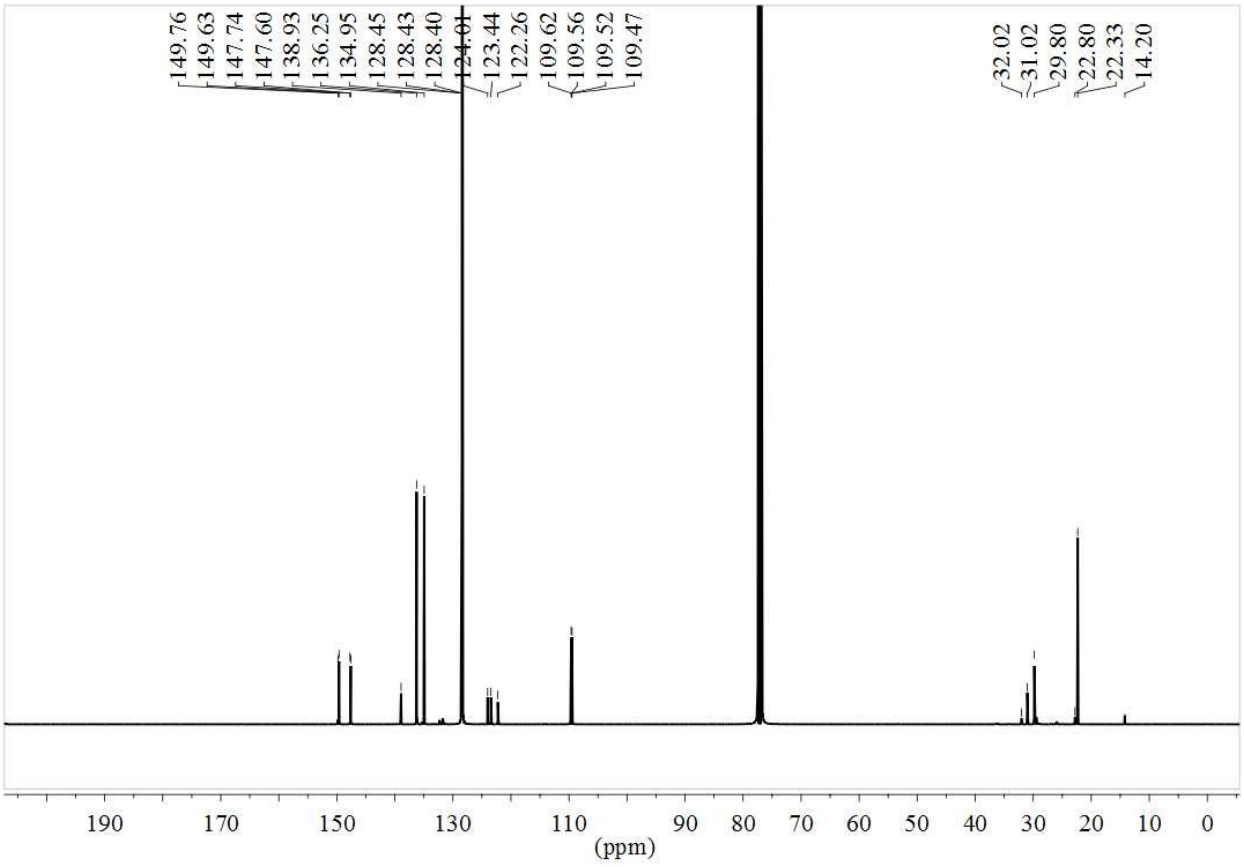


Figure S13: ^{13}C NMR spectrum of **P1** in $CDCl_3$

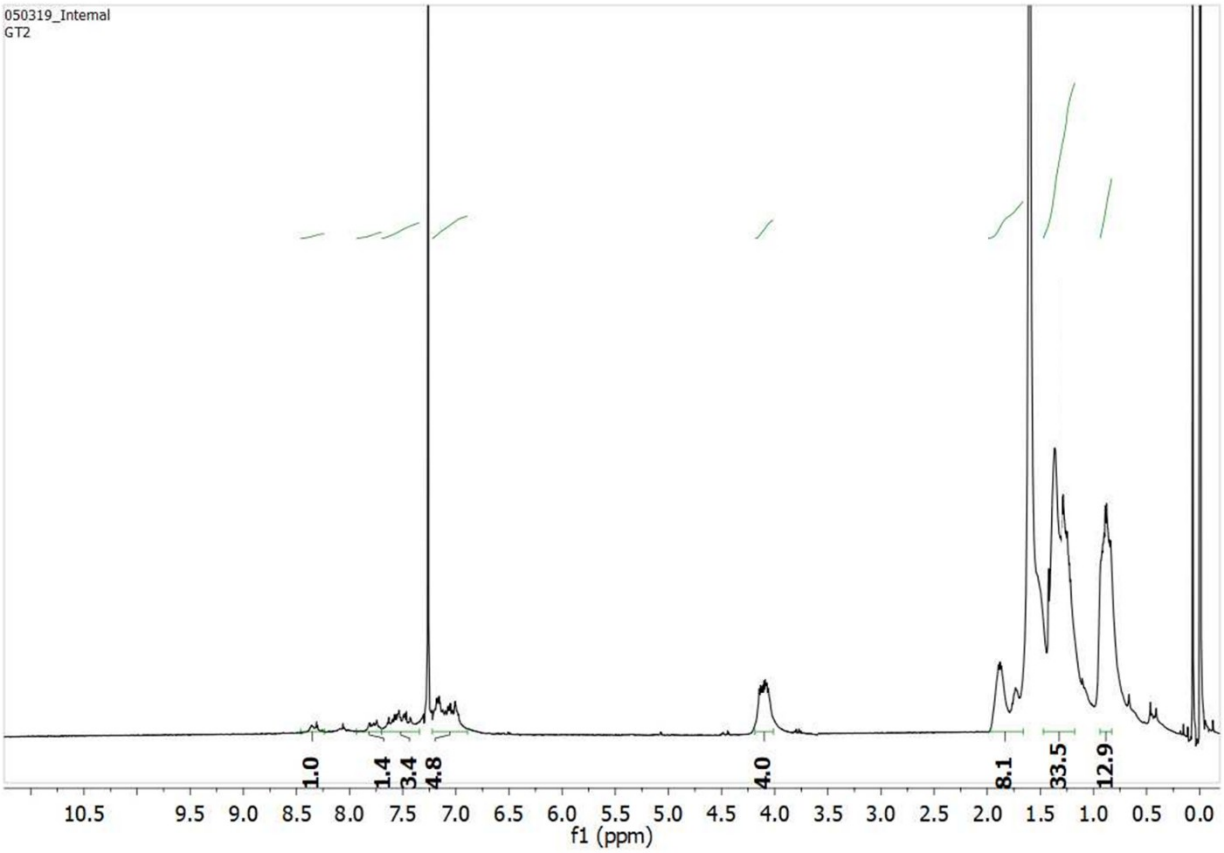


Figure S14: ^{1}H NMR spectrum of **P2** in $CDCl_3$

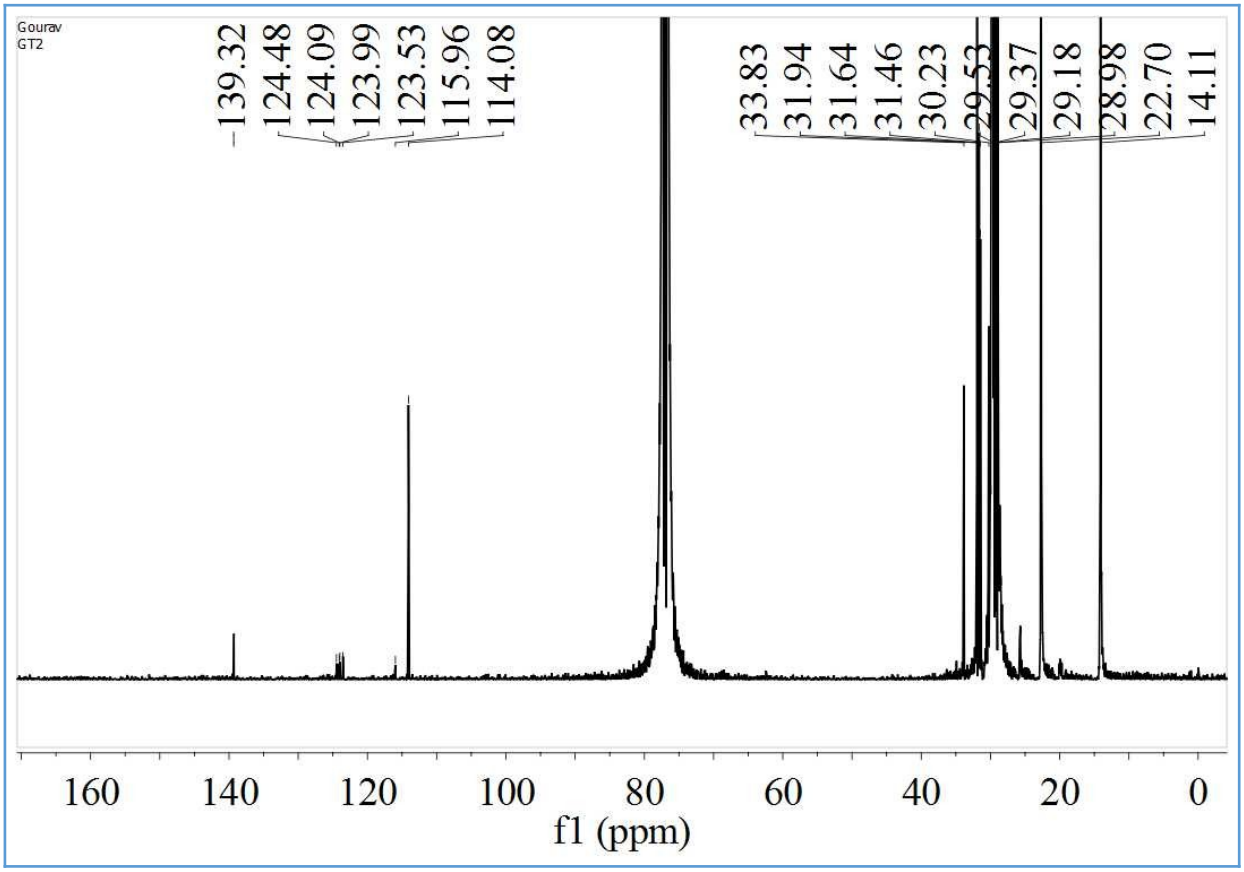


Figure S15: ^{13}C NMR spectrum of **P2** in $CDCl_3$

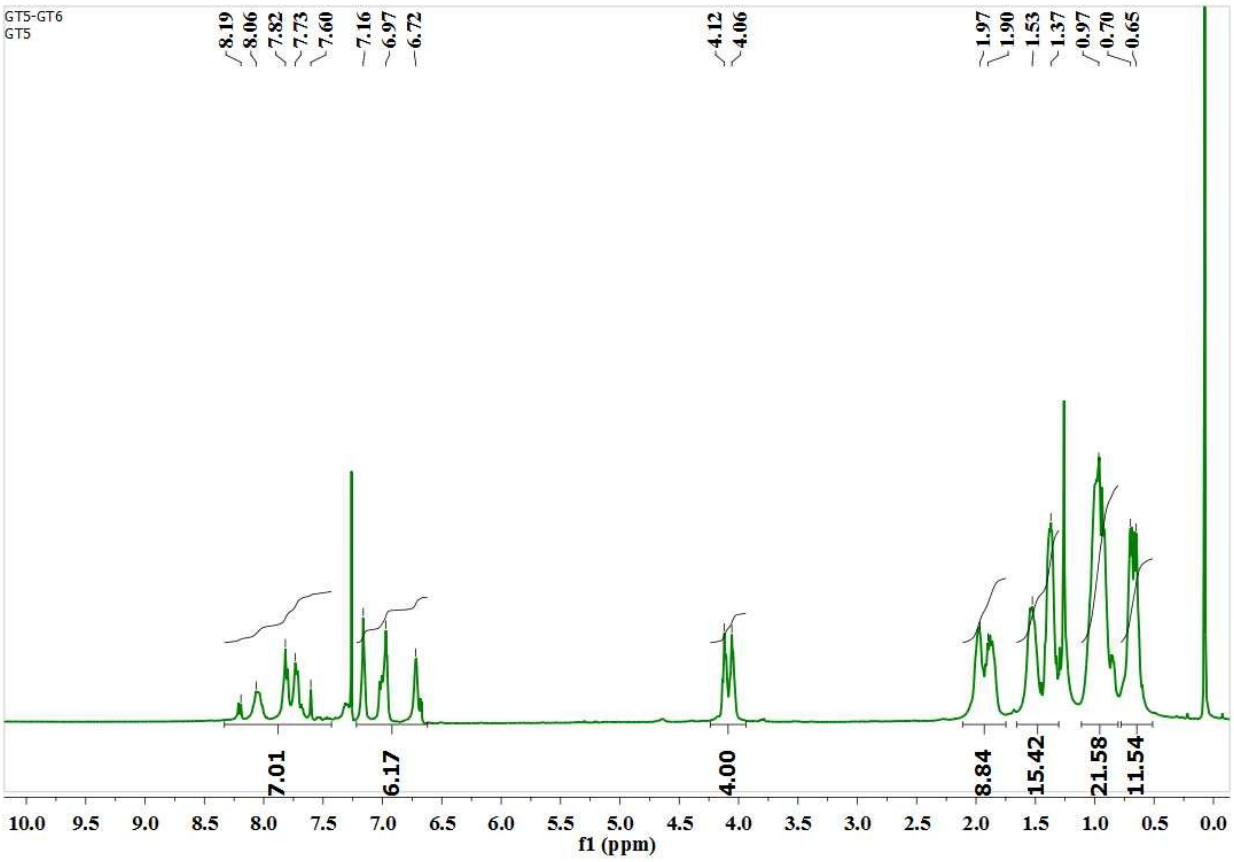


Figure S16: ^{1}H NMR spectrum of **P3** in $CDCl_3$

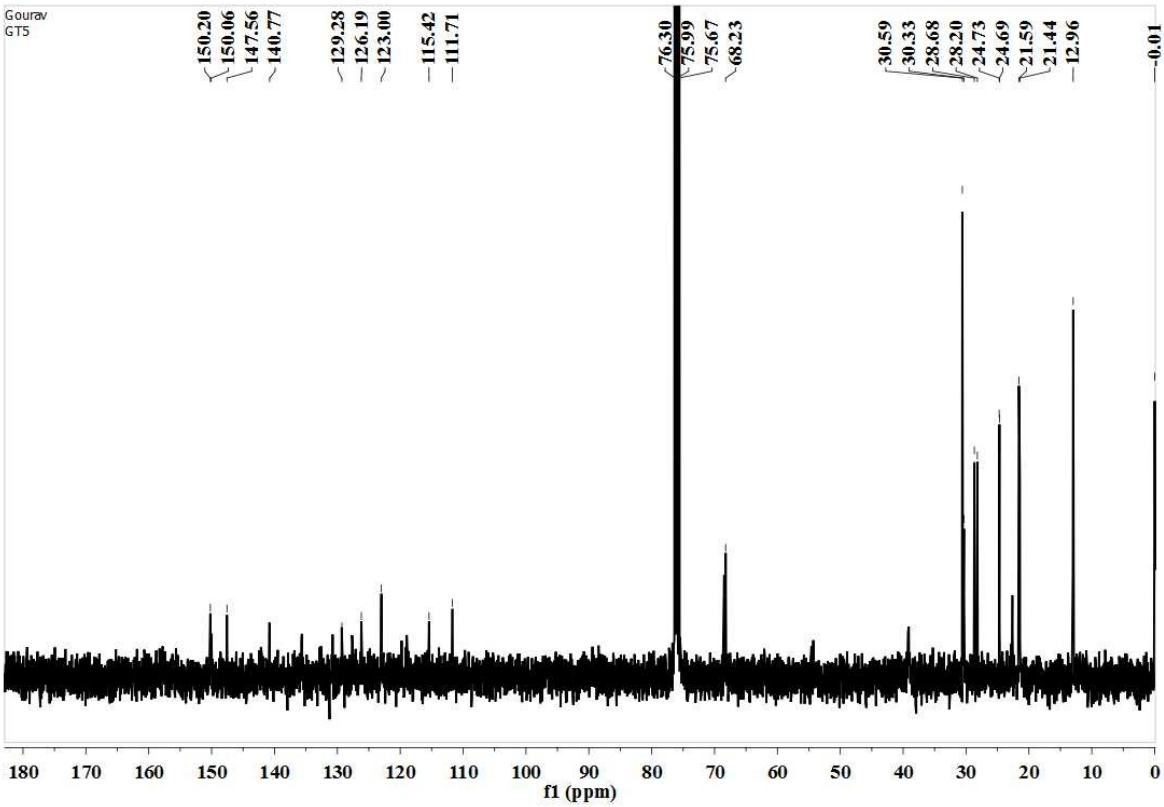


Figure S17: ^{13}C NMR spectrum of **P3** in $CDCl_3$

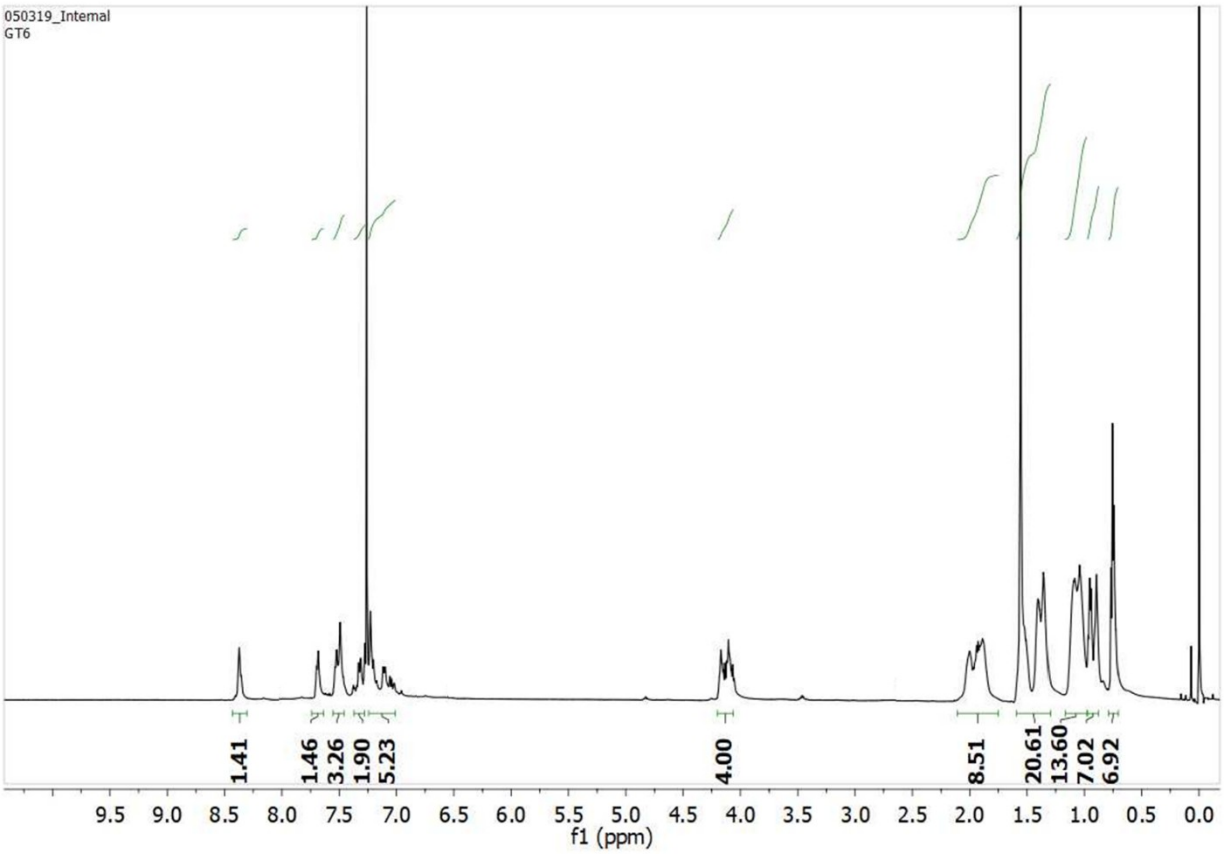


Figure S18: ^{1}H NMR spectrum of **P4** in $CDCl_3$

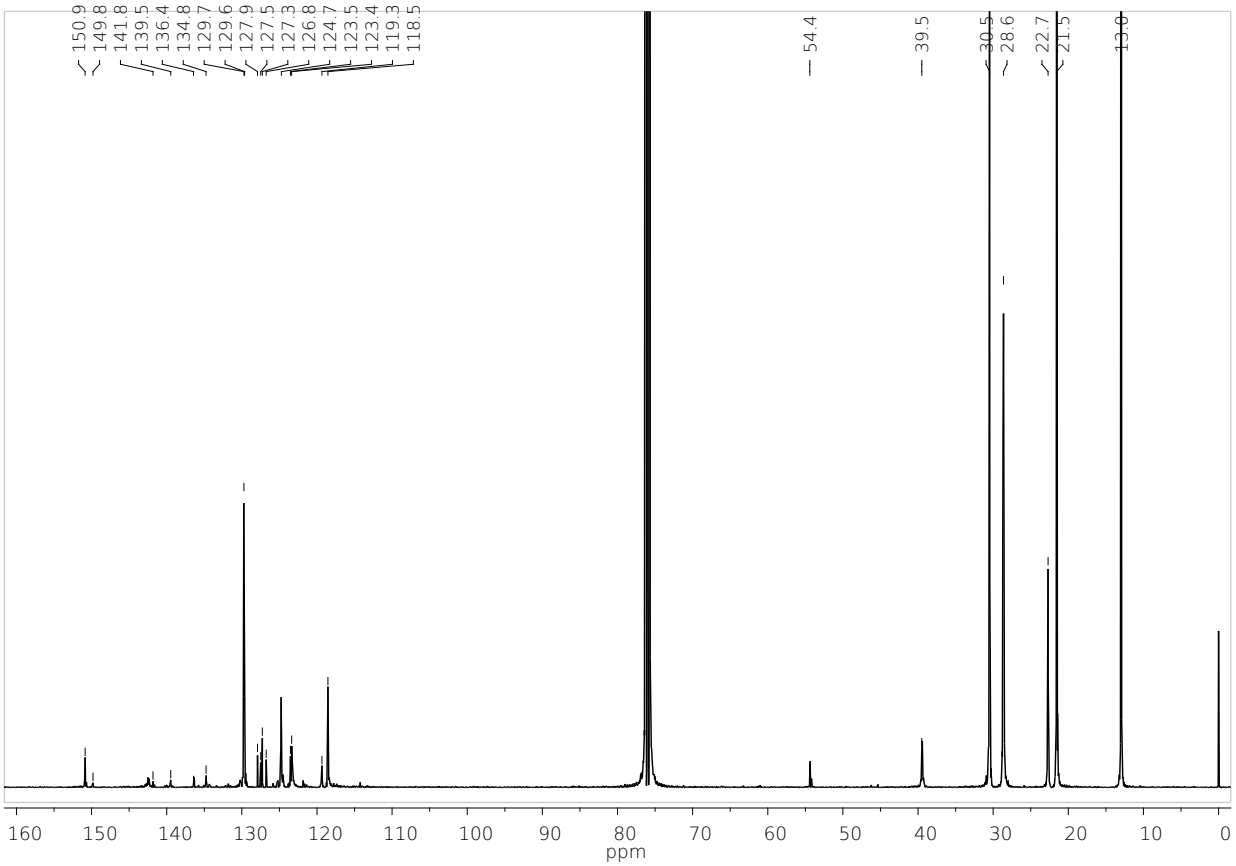


Figure S19: ^{13}C NMR spectrum of **P4** in $CDCl_3$

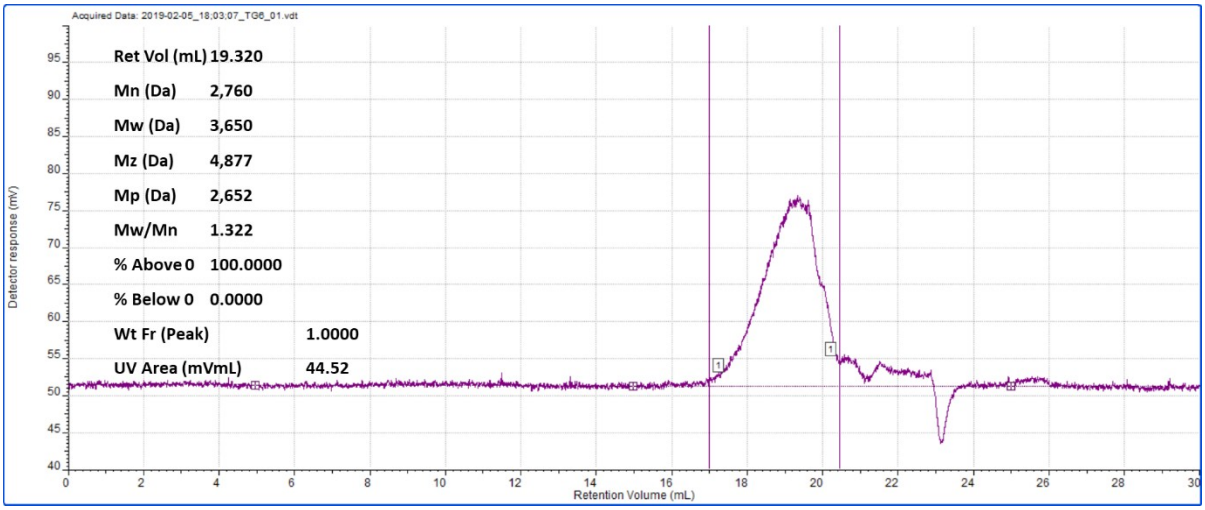


Figure S20: GPC spectrum for **P1** in THF

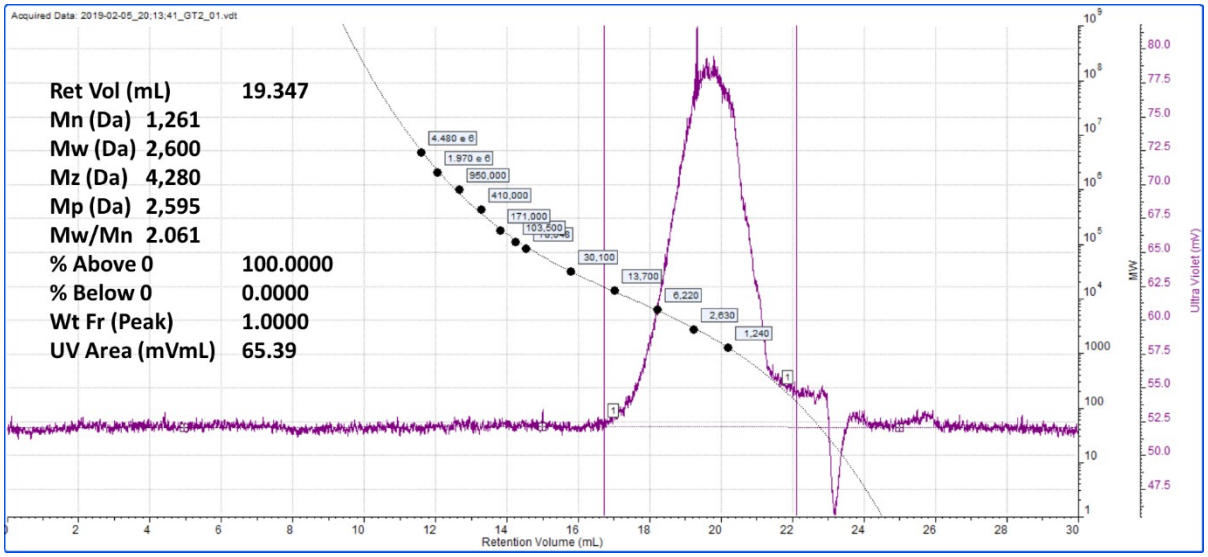


Figure S21: GPC spectrum for **P2** in THF

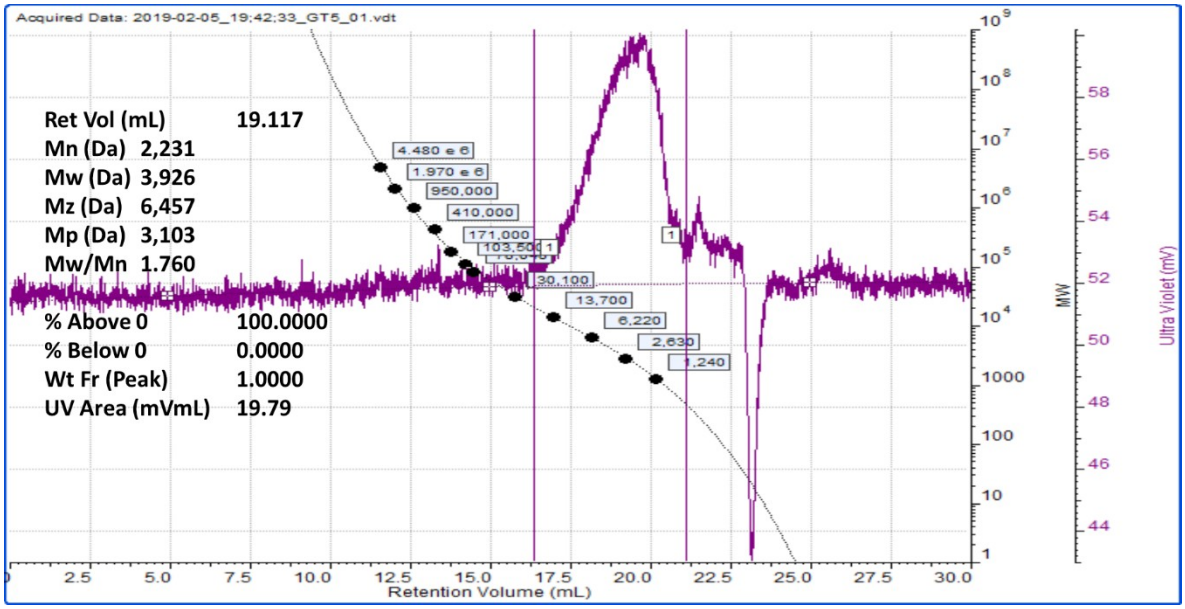


Figure S22: GPC spectrum for **P3** in THF

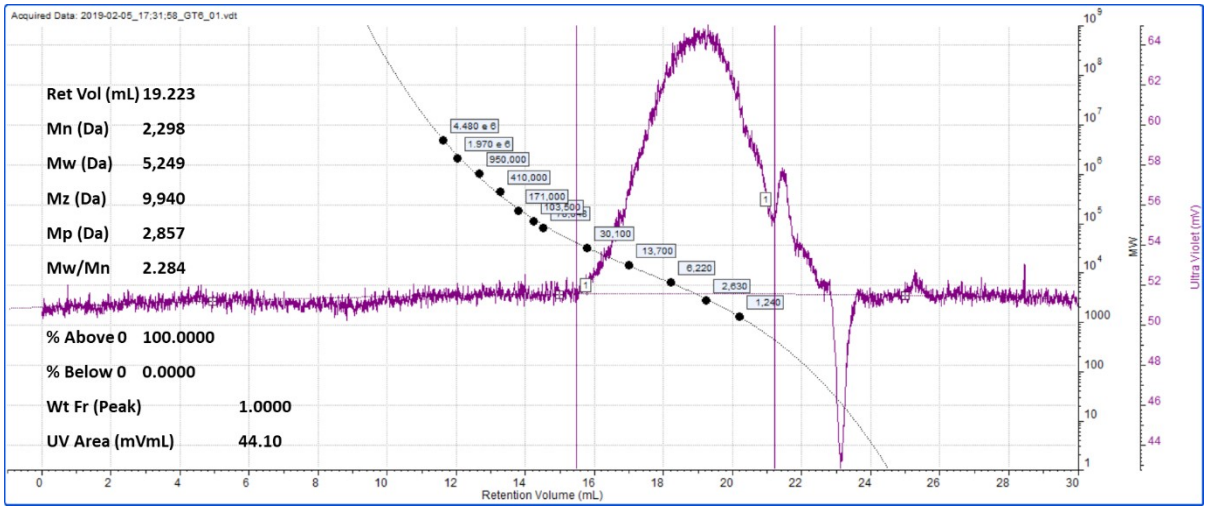


Figure S23: GPC spectrum for **P4** in THF

3. Optical studies

a. Energy transfer in **P1** and **P2.**

Emission spectra were measured for **P1** and **P2** by exciting at the donor and acceptor absorption wavelengths as well as at CT bands at 696 nm and 725 nm (Fig S16). Fluorescence quantum yield measurements were performed for **P1** and **P2** by absolute method using an integrating sphere set up and quantum yields of 0.017 and 0.002 were obtained for **P1** and **P2** respectively. The quenching of fluorescence as well as smaller value of quantum yield for **P2** indicate that electron transfer is more effiicient in **P2** compared to **P1**. Evaluation of gibbs free energy change for photoinduced electron transfer (ΔG_{CS}) suggest an increased driving force for photoinduced electron transfer for **P2** (~ - 0.61 eV) compared to P1 (~ - 0.17 eV). [1] Fluorescence lifetime measurements were performed for polymers P1 and P2 in chloroform using time correlated single photon counting (TCSPC) measurement technique. The fluorescence lifetimes of P1 and P2 were measured upon excitation of 669 nm and decay of emission bands at 843 nm and 776 nm were studied for **P1** and **P2** respectively. The obtained decay data were fitted with triexponential decay and the errors in the fitting parameters were minimized by keeping the $\chi 2$ values close to unity. The lifetime for the decay of emission band of P2 was ~ 0.31 ns corresponding to a much faster decay compared to that of P1 for which a slower lifetime of ~ 1.37 ns was obtained (see Figure S16 for fluorescence decays and fits). This observation is consistent with the fact that **P2** shows more efficient electron transfer than **P1** and higher quenching with a shorter fluorescence lifetime compared to that of **P1**.

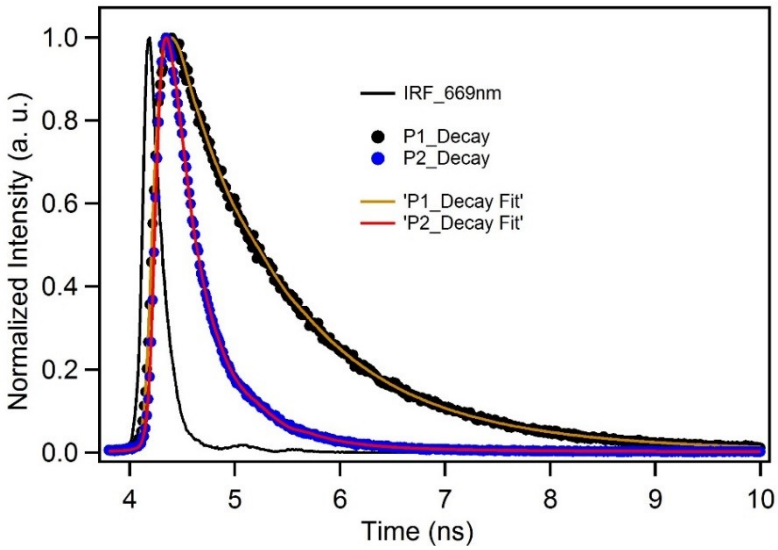


Figure S24: Time resolved fluorescence spectra of **P1** and **P2** in chloroform upon excitation at 669 nm and fluorescence decays as well as fitted data are shown.

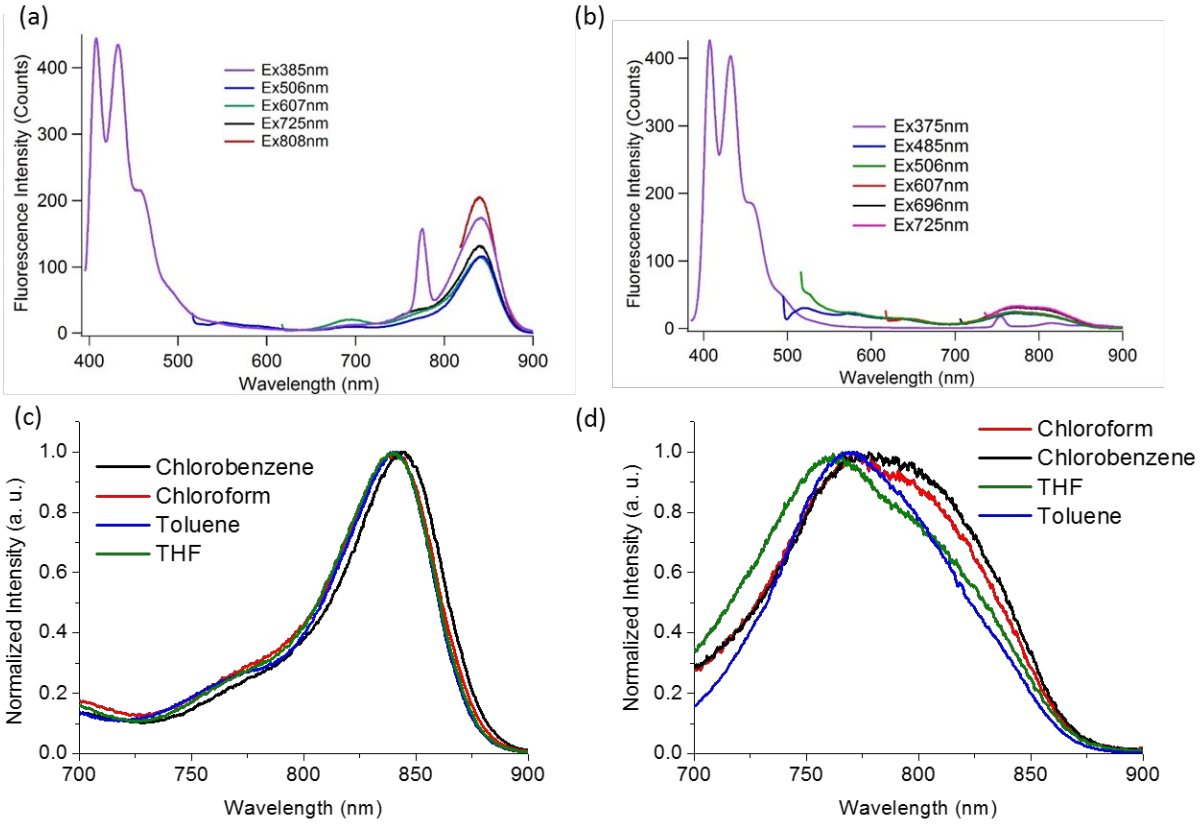


Figure S25: Fluorescence spectra of (a) **P1** for different excitation wavelengths (b) **P2** for different excitation wavelengths (c) **P1** in different solvents (excitation at 607 nm) (d) **P2** in different solvents (excitation at 607 nm)

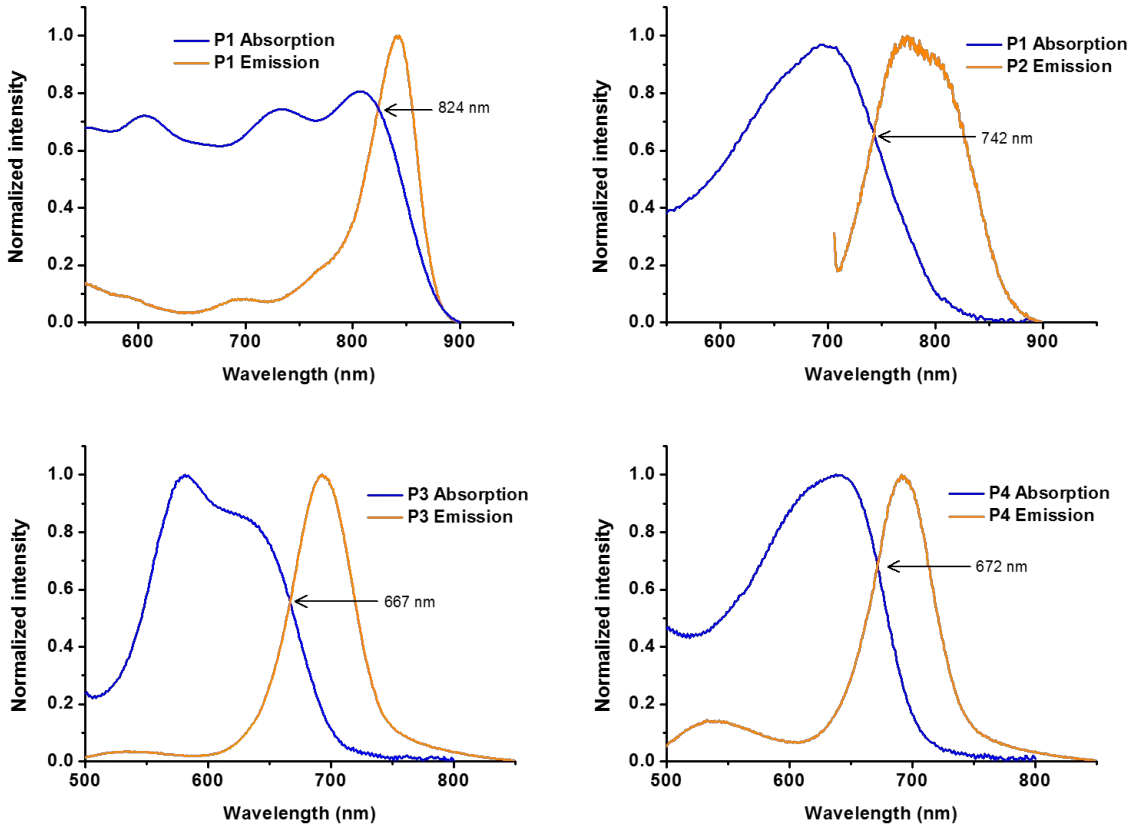


Figure S26: Calculation of band gap from absorption and emission spectra from polymer solutions in dichlorobenzene

Table S1: TD-DFT calculations for **P1**

Wavelength (nm)	Oscillator strength	Transition
716.47	0.6587	HOMO → LUMO
610.99	0.3490	HOMO-1 → LUMO; HOMO → LUMO + 1
508.06	0.3106	HOMO – 3 → LUMO
487.47	0.4458	HOMO – 2 → LUMO + 1; HOMO – 3 → LUMO
463.27	0.3480	HOMO – 3 → LUMO + 1; HOMO – 4 → LUMO

Table S2: TD-DFT calculations for **P2**

Wavelength (nm)	Oscillator strength	Transition
698.40	0.5550	HOMO → LUMO

525.48	0.6004	HOMO - 2 → LUMO
415.45	0.9618	HOMO → LUMO + 2

Table S3: TD-DFT calculations for **P3**

Wavelength (nm)	Oscillator strength	Transition
605.24	0.9336	HOMO → LUMO
545.88	0.2278	HOMO - 1→ LUMO
489.87	0.7729	HOMO-1 → LUMO, HOMO-1 → LUMO+1, HOMO → LUMO+1, HOMO -2 → LUMO
409.77	0.2190	HOMO - 2→ LUMO+1, HOMO - 4→ LUMO, HOMO - 4→ LUMO+1,

Table S4: TD-DFT calculations for **P4**

Wavelength (nm)	Oscillator strength	Transition
608.55	0.8918	HOMO → LUMO, HOMO → LUMO+1
421.14	0.2297	HOMO-2→ LUMO, HOMO-5→ LUMO
390.46	0.9724	HOMO-3 → LUMO, HOMO-3→ LUMO+1, HOMO-5→ LUMO

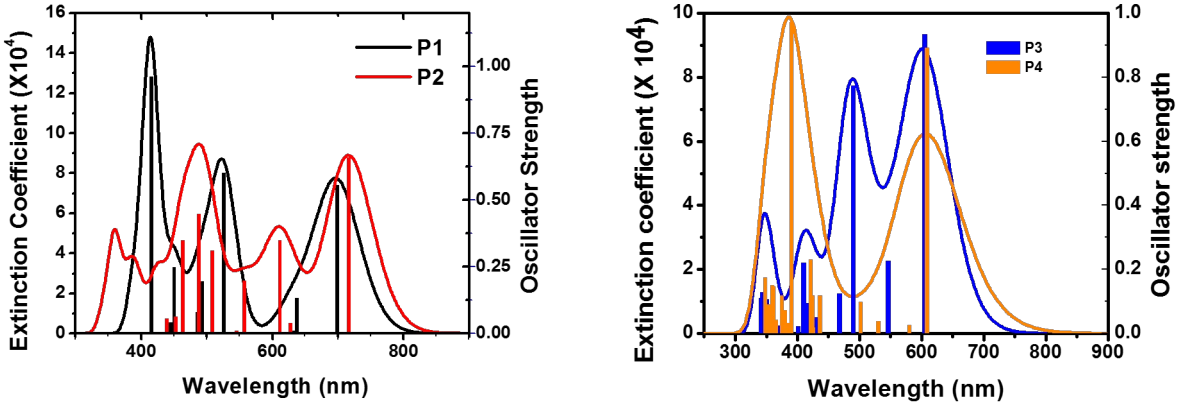


Figure S27: Simulated absorption spectra for the polymers using TD-DFT calculations on Gaussian08..

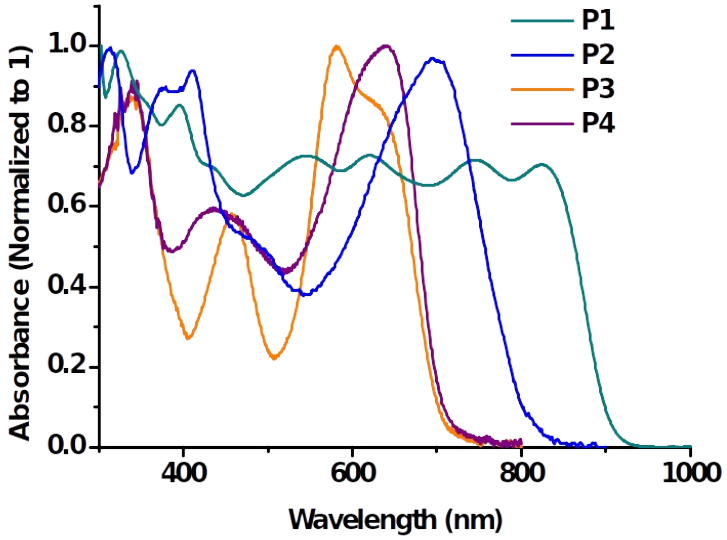


Figure S28: UV-vis absorption in Chloroform solution.

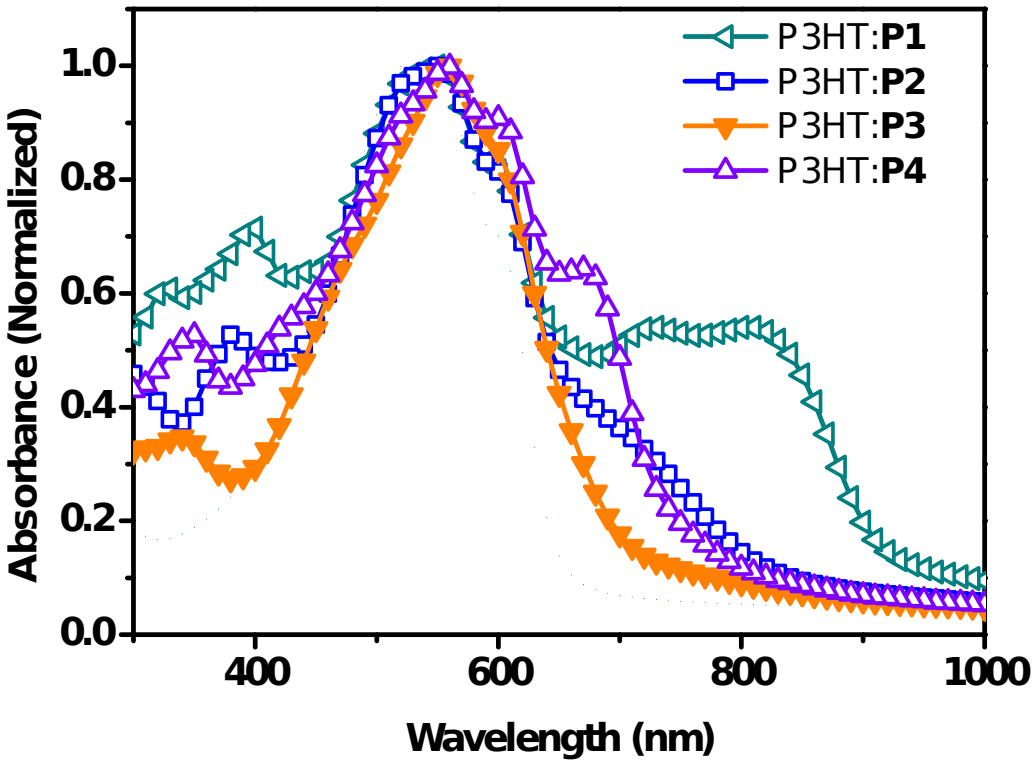


Figure S29: Absorption spectra of blend films.

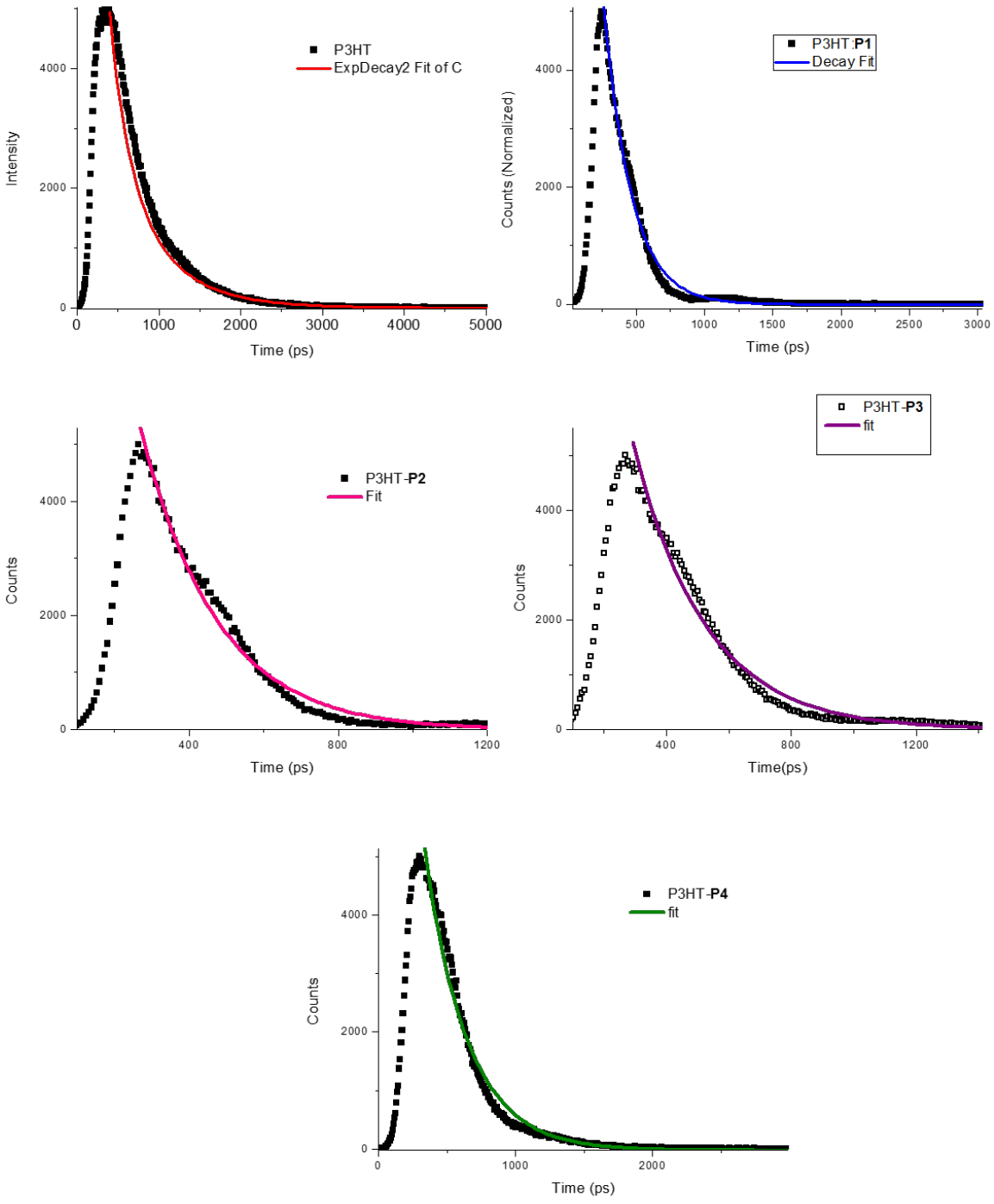


Figure S30: Time Resolved Photoluminescence decay plots along with the fits

4. Cyclic Voltammetry:

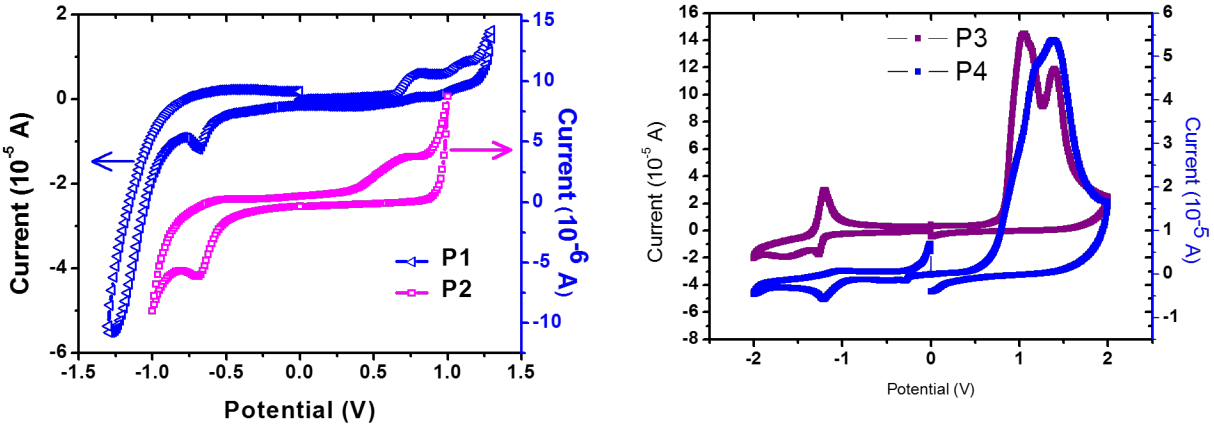


Figure S31: Cyclic voltammetry of the polymer films

Energy of the HOMO and the LUMO are calculated using the following relations [2]:

$$E_{HOMO} = -\left(E_{onset}^{OX} + 4.8 - E_{Fc}\right)$$

$$E_{LUMO} = -\left(E_{onset}^{i} + 4.8 - E_{Fc}\right)$$

E_{FC} was measured to be 0.12 V against the Ag/Ag^{+} electrode used for the measurements.

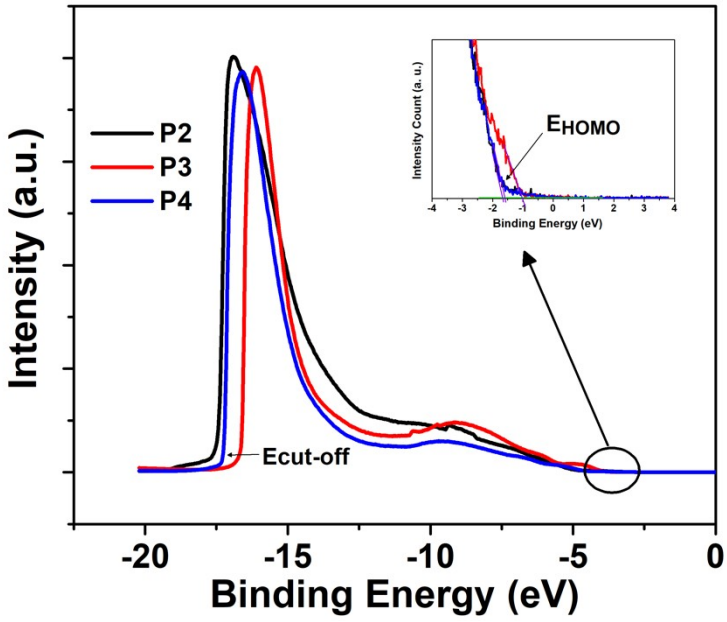


Figure S32: UPS spectra for polymers.

5. Morphology

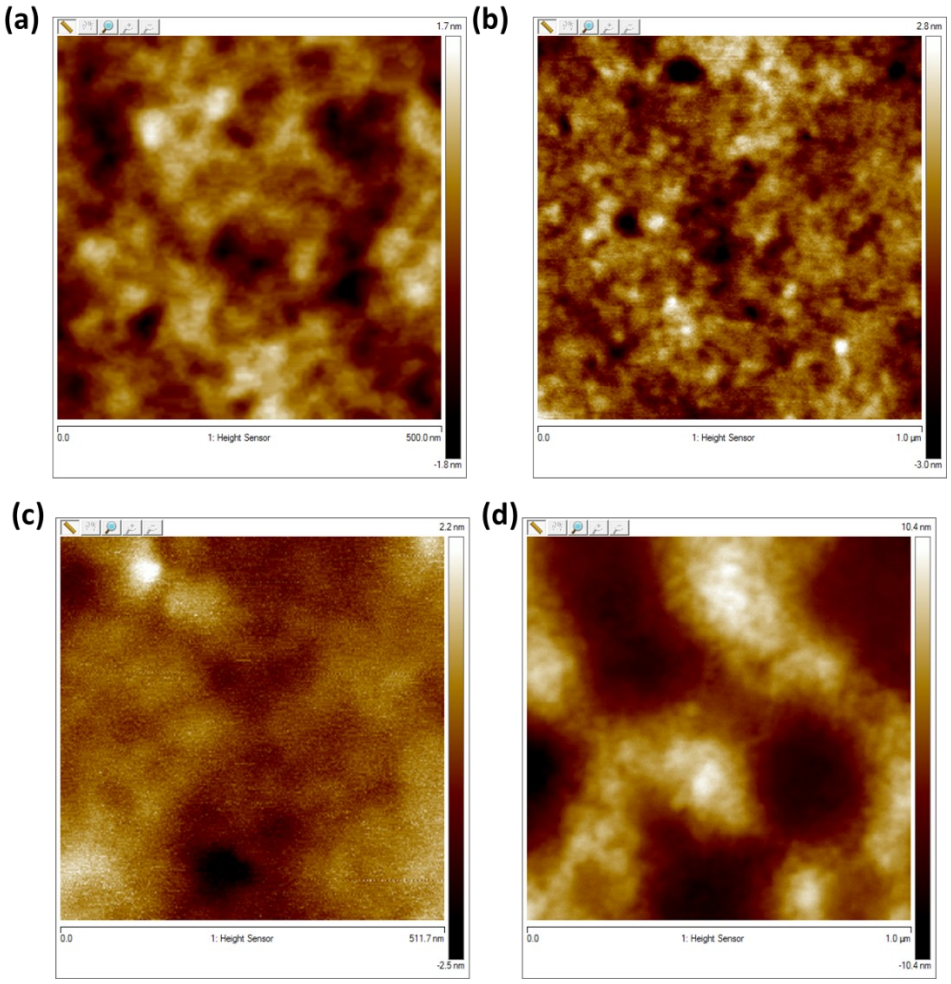


Fig S33: Height images from Atomic force microscopy for blend films (a) P3HT:PCBM (b) P3HT:P1 (c) P3HT:P2 (d) P3HT:P3

Table S5: Roughness for blend films as calculated from Atomic force microscopy

	σ_{RMS} (nm)
P3HT: $PC_{61}BM$	0.610
P3HT:P1	0.803
P3HT:P2	0.596
P3HT:P3	3.93
P3HT: $PC_{61}BM$:P3	1.05

6. SCLC mobility measurements:

Hole only devices were fabricated using the configuration of ITO/PEDOT:PSS/polymer/Au and J-V current was measured under dark. The J-V curve was then fitted using the modified Mott Gurney equation to obtain the mobility values (μ_h).

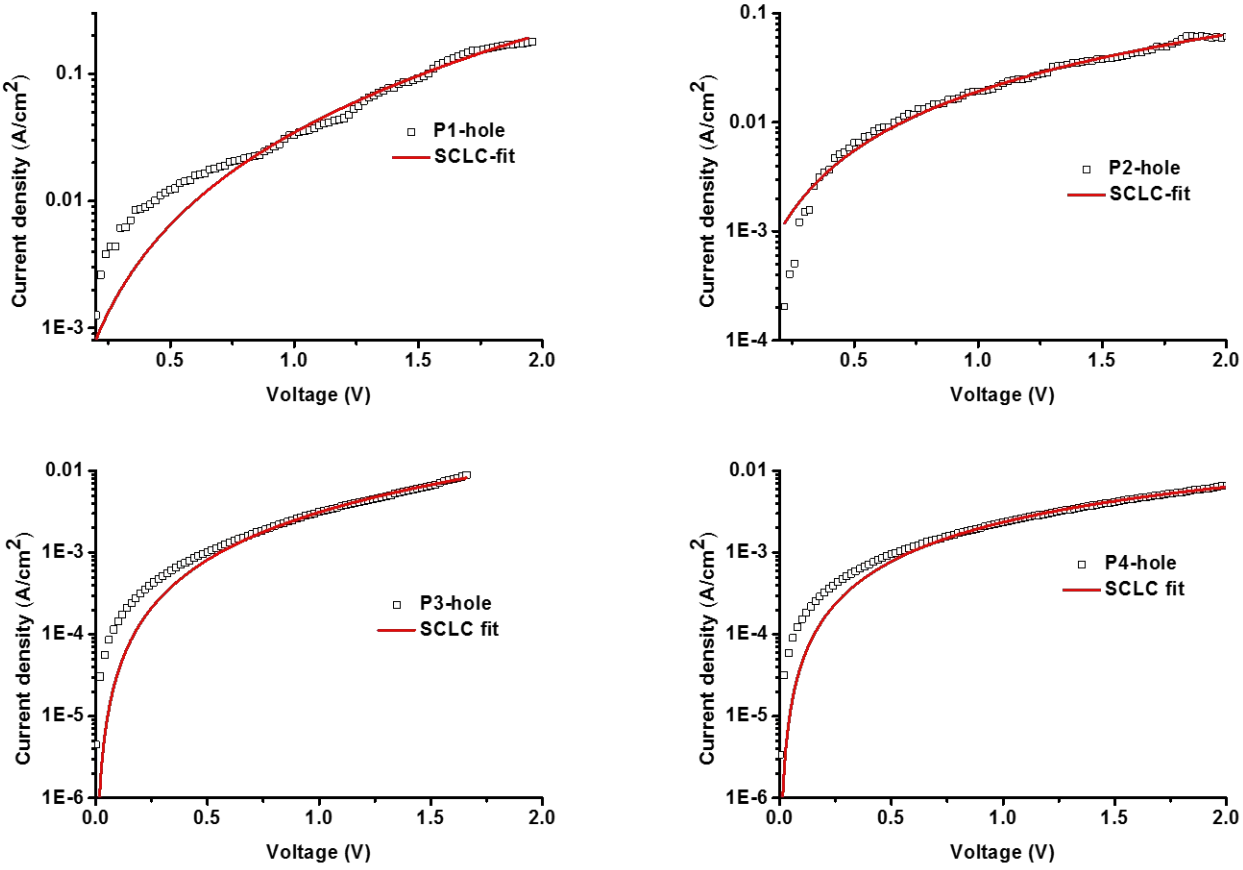


Figure S34: J-V curves for hole only devices of **P1**-**P4 for** SCLC measurements.

Electron only devices were fabricated using the configuration of ITO/Al/polymer/Al and J-V current was measured under dark. The J-V curves were then fitted using the Mott Gurney equation to obtain the mobility values (μ_e).

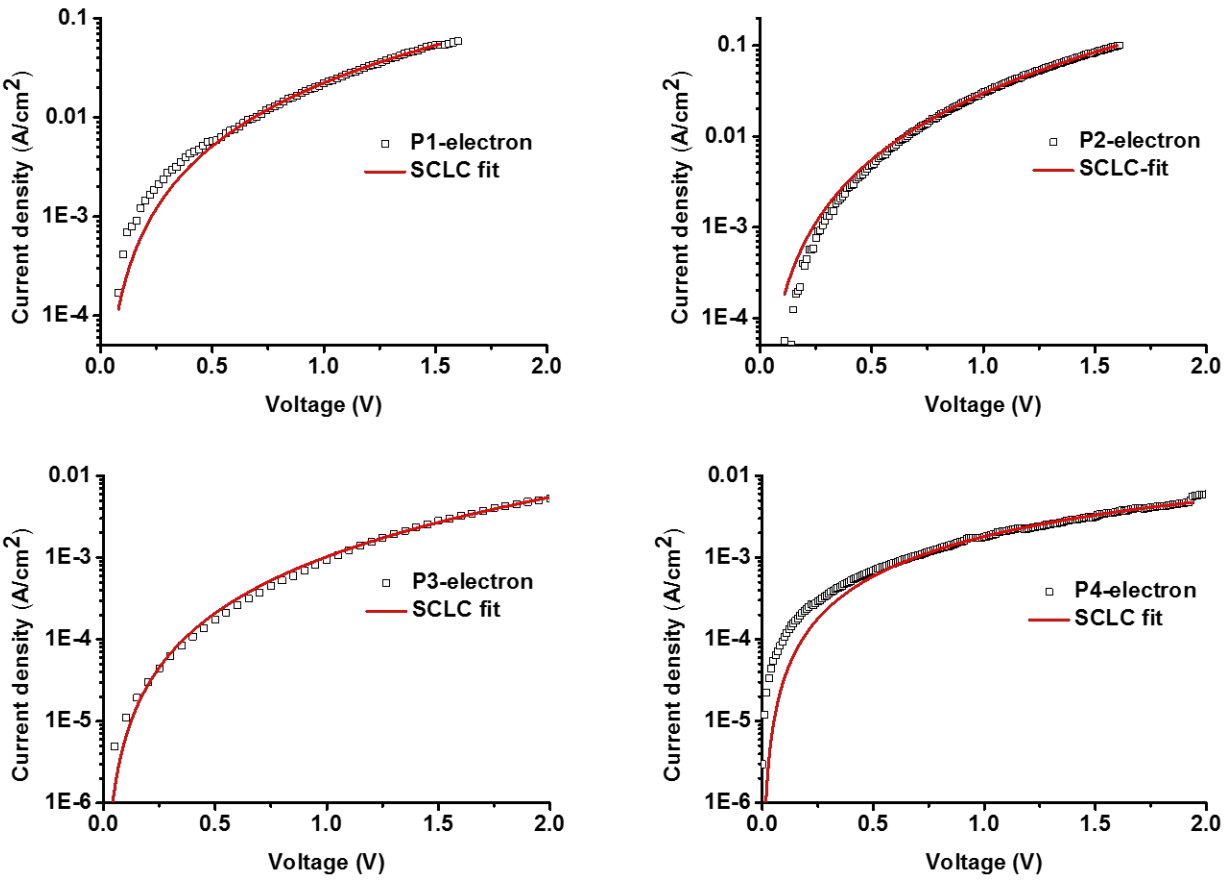


Figure S35: J-V curves for electron only devices of **P1-P4 for** SCLC measurements.

7. Solar cell fabrication:

The solar cells were fabricated on prepatterned ITO-coated substrates of ~12 ohm/cm^2 from Xinyan Technology Limited, Taiwan. The ITO substrates were sequentially cleaned in an ultrasonicator bath using deionized water with soap solution (Hellmanex III, 3% in deionized water), deionized water, acetone and isopropyl alcohol subsequently. The ITO Substrates were then dried using nitrogen gas followed by UV ozone (Novascan, USA) treatment for 20 min. The electron transporting layer ZnO was spin coated from di-ethyl zinc solution (DEZ), (15% in toluene (Aldrich)), solution prepared from mixing DEZ with tetrahydrofuran in 1:6 (vol/vol) inside glove box. ZnO coated substrates were than annealed at 130° C for 20 minutes in ambient with humidity less than 35% RH, resulting ~30 nm thick film. ZnO coated samples were then

immediately transferred inside the glove box (Jacomax, O_2 < 5 ppm, H_2O < 5 ppm) for spin coating of the active layers of P3HT:P1-P4. The polymer (P1-P4), P3HT and $PC_{61}BM$ were dissolved in chlorobenzene and stirred overnight in dark to make 30 mg/ml solutions. Active layer was spin coated on ZnO layer for 60 seconds at 1000 rpm (thickness ~ 120 nm) and then annealed at 140° C for 15 minutes. Finally, top contact of MoO_3 and Ag with a thickness of < 10 nm and 120 nm respectively was evaporated (Angstrom USA) at a base pressure of 3.6 x 10^{-6} mbar in order to complete the device. The active area of the device was 9 mm^2, calculated with the overlap area of top and bottom contact of the sample.

Table S6: Photovoltaic parameters for ternary devices

	η (%)	**V_{OC} (V)**	**J_{SC} (mA/cm^2)**	**FF**
P3HT:$PC_{61}BM$:P1	0.00008 ± 0.00006	0.62 ± 0.03	.0005 ± 0.00003	0.26 ± 0.01
P3HT: $PC_{61}BM$:P2	0.16 ± 0.08	0.59 ± 0.02	1.72 ± 0.8	0.15 ± 0.01
P3HT: $PC_{61}BM$:P3	1.18 ± 0.04	0.64 ± 0.01	4.17 ± 0.18	0.47 ± 0.003
P3HT: $PC_{61}BM$:P4	0.38 ± 0.18	0.54 ± 0.14	2.58 ± 0.98	0.28 ± 0.02

Reference:

[1] S. Sengupta, U. K. Pandey, and E. U. Athresh, "Regioisomeric donor-acceptor-donor triads based on benzodithiophene and BODIPY with distinct optical properties and mobilities," *RSC Adv.*, vol. 6, no. 77, pp. 73645–73649, 2016.

[2] L. Pan *et al.*, "Role of oxadiazole moiety in different D–A polyazothines and related resistive switching properties," *J. Mater. Chem. C*, vol. 1, no. 30, pp. 4556–4564, 2013.