

Supplementary Information

Synthesis and Photovoltaic Properties of Thieno[3,2-b]thiophenyl Substituted Benzo[1,2-b:4,5-b']dithiophene Copolymers

Zeyun Xiao, Jegadesan Subbiah, Kuan Sun, David J. Jones, Andrew B. Holmes and Wallace W. H. Wong*

School of Chemistry, Bio21 Institute, the University of Melbourne, 30 Flemington Road, Parkville, Victoria 3010, Australia.

Table of contents

General Experimental Information	2
High temperature GPC traces of P1 and P2	3
Differential scanning calorimetry (DSC) data	5
UV-vis absorption spectrum of polymers in chloroform solution	5
Photoluminescence spectra	5
UV-vis absorption spectrum of blend films of polymer and PC ₇₁ BM	6
Bulk heterojunction solar cell device data	7
Space charge limited current (SCLC) measurement	8
¹ H NMR spectrum of compounds	10

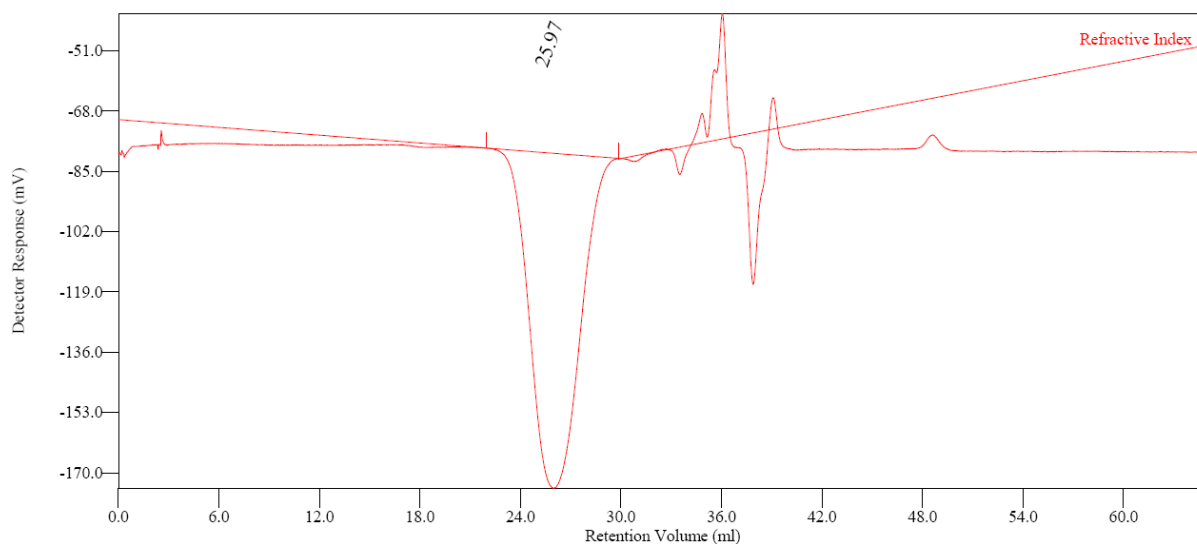
General Experimental Information

Unless noted, all materials were reagent grade and used as received without further purification. Chromatographic separations were performed using standard column methods with silica gel (Merck 9385 Kieselgel 60). Thin layer chromatography was performed on Merck Kieselgel 60 silica gel on glass (0.25 mm thick).

Infrared (IR) spectra were obtained on a Perkin Elmer Spectrum One FT-IR spectrometer and UV-vis spectra were recorded using a Cary 50 UV-Vis spectrometer. Photoluminescence was measured with a Varian Cary Eclipse fluorimeter. Melting points were determined on a Büchi 510 melting point apparatus. ^1H NMR and ^{13}C NMR spectra were carried out on a 400 MHz spectrometer. All NMR data was referenced to the chloroform signal and peak multiplicity was reported as follows: s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, dd = doublets of doublets, m = multiplet, br = broad). Differential scanning calorimetry (DSC) experiments were performed on a Perkin-Elmer Sapphire DSC.

High temperature gel permeation chromatography (HT-GPC): Molecular weights of polymer were characterized by HT-GPC performed in 1,2,4-trichlorobenzene (TCB) with 500 ppm 3,5-di-tert-butyl-4-hydroxytoluene (1.0 mL/min) at 120°C using a Malvern Viscotek 350A HT-GPC system with a Refractive Index Detector, a Viscotek 2600 Photodiode Array Detector, a Viscometry Detector, a series of four Malvern high temperature columns (1×Guard + 3×HT6000M), and OmniSEC Software. The GPC was calibrated with narrow polydispersity polystyrene standards (Malvern PolyCal PS standards, MW from 1050 to 4.2×10^6), and molecular weights are reported both as polystyrene equivalents based on the refractive index detector, and absolute values using universal calibration based on a combination of the refractive index detector and the viscosity detector. The sample was dissolved in TCB with 500 ppm BHT at a concentration around 2.5 mg/mL at 120 °C for 2 hours before injection.

Cyclic voltammetry (CV) experiments were performed at a sweep rate of 50 mV/s. CVs were carried out in a three-electrode cell consisting of a glassy carbon working electrode, a platinum wire auxiliary electrode, and a Ag/Ag⁺ pseudo-reference electrode. The supporting electrolyte was 0.10 M tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) in CH₃CN. The solutions were deoxygenated by sparging with argon prior to each scan and blanketed with argon during the scans. The glassy carbon working electrode was prepared by polishing with 5 mm alumina and washed and dried before the polymer was drop-casted on the electrode from chlorobenzene solution to form a film. Ferrocene/ferroceium redox couple was used as the internal standard. The HOMO energy level was calculated from the onset of the oxidation potential of the polymer using the following: $E_{\text{HOMO}} = -(4.8 + E_{\text{ox onset}})$ eV.



Conventional Calibration - Homopolymers : Results

Peak RV - (ml)	25.970
Mn - (Daltons)	28,908
Mw - (Daltons)	56,141
Mz - (Daltons)	100,236
Mp - (Daltons)	44,199
Mw / Mn	1.942
Percent Above Mw:	0
Percent Below Mw:	0
Mw 10.0% Low	9,898
Mw 10.0% High	168,874
Wt Fr (Peak)	1.000
RI Area - (mvml)	300.71
UV@510nm Area - (mvml)	0.00

Annotation	
Method File	Unsaved Method (CCal-0004.vcm)
Limits File	
Date Acquired	Oct 17, 2013 - 20:27:16
Solvent	TCB
Acquisition Operator	admin : Administrator
Calculation Operator	admin : Administrator
Column Set	3 HT columns
System	HT GPC Malvern
Flow Rate - (ml/min)	1.000
Inj Volume - (ul)	200.0
Volume Increment - (ml)	0.00333
Detector Temp. - (deg C)	120.0
Column Temp. - (deg C)	120.0
OmniSEC Build Number	406

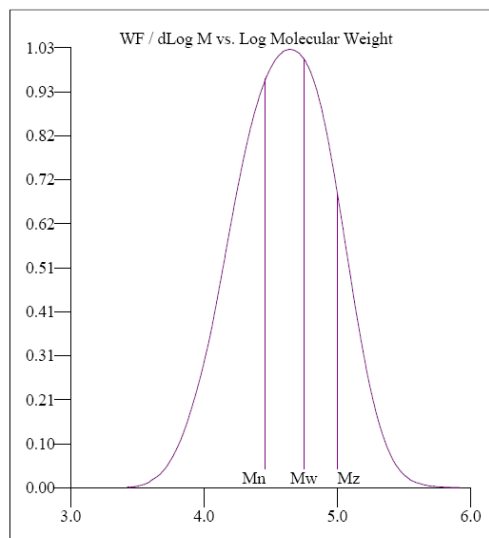
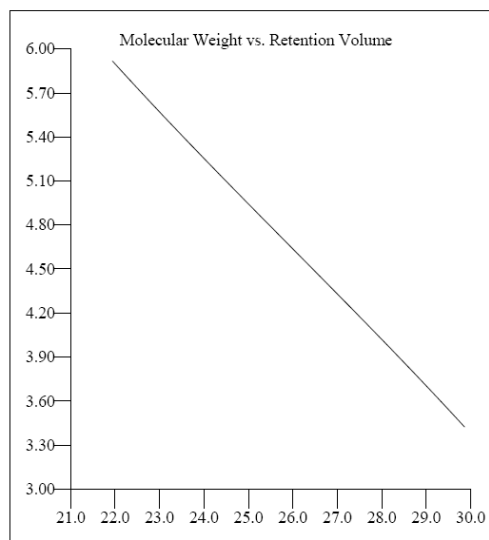
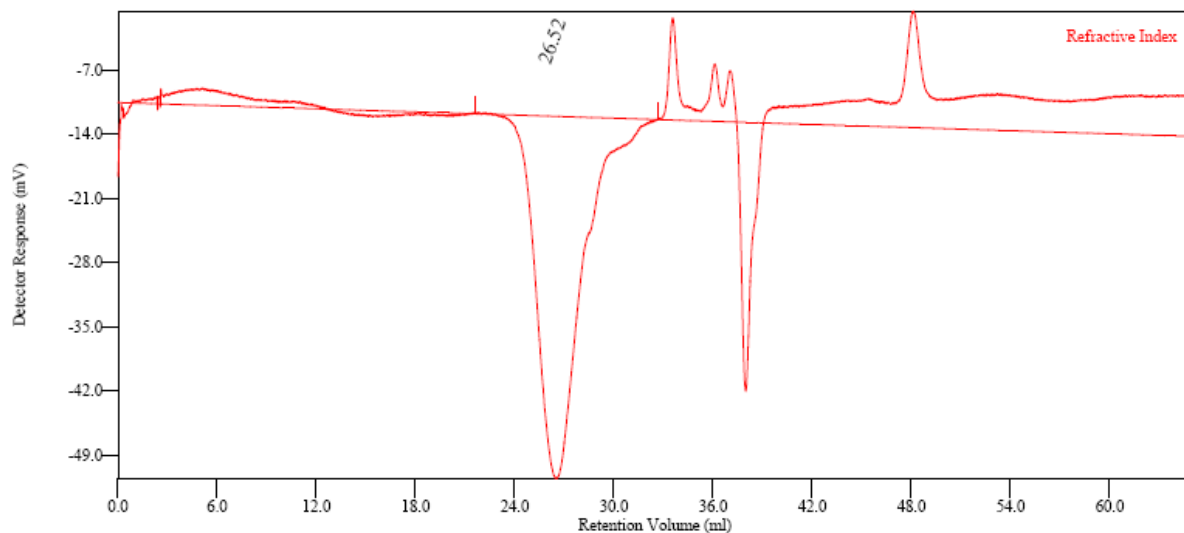


Figure S1. High temperature GPC trace of P1.



Warning: No flow rate marker was found.

Conventional Calibration - Homopolymers : Results

Peak RV - (ml)	26.523
Mn - (Daltons)	10,512
Mw - (Daltons)	34,657
Mz - (Daltons)	88,134
Mp - (Daltons)	28,481
Mw / Mn	3.297
Percent Above Mw:	0
Percent Below Mw:	0
Mw 10.0% Low	2,877
Mw 10.0% High	109,586
Wt Fr (Peak)	1.000
RI Area - (mVml)	116.74
UV@510nm Area - (mVml)	0.00

Annotation	
Method File	CCDemo-0007-0000.vcm
Limits File	
Date Acquired	Jul 19, 2013 - 06:09:21
Solvent	TCE
Acquisition Operator	admin : Administrator
Calculation Operator	admin : Administrator
Column Set	3 HI columns
System	HT GPC Malvern
Flow Rate - (ml/min)	1.000
Inj Volume - (ul)	200.0
Volume Increment - (ml)	0.00533
Detector Temp. - (deg C)	120.0
Column Temp. - (deg C)	120.0
OmniseC Build Number	406

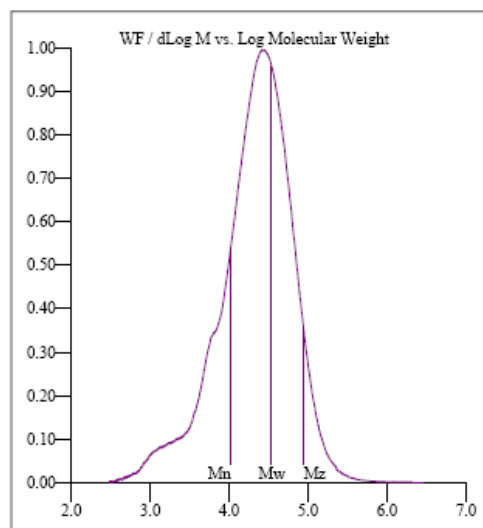
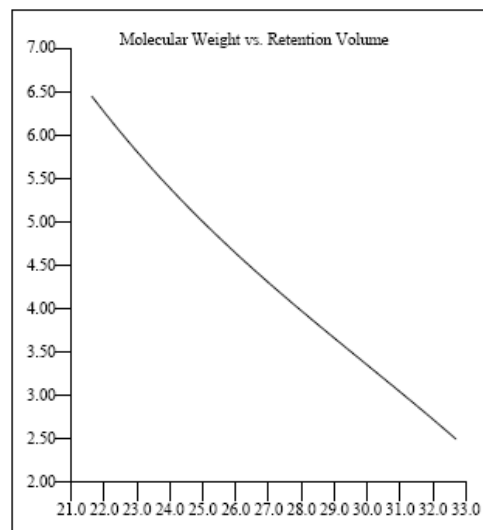


Figure S2. High temperature GPC trace of **P2**.

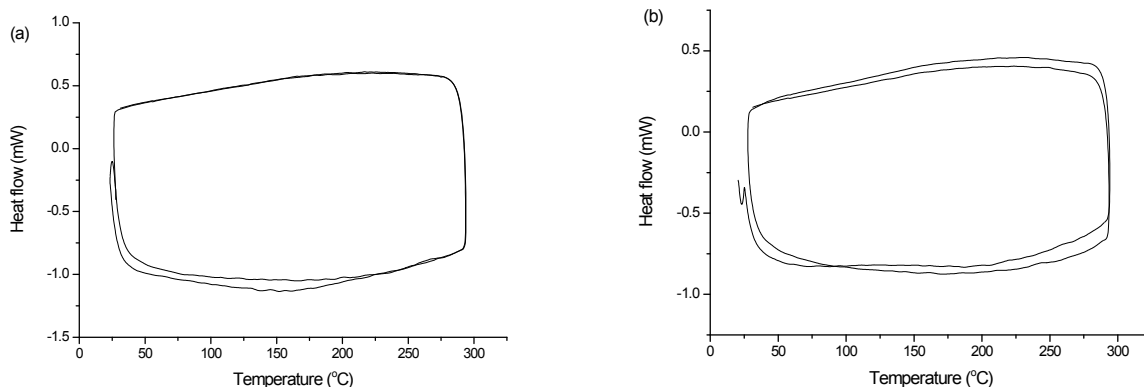


Figure S3. Differential scanning calorimetry data for polymers (a) **P1** and (b) **P2**.

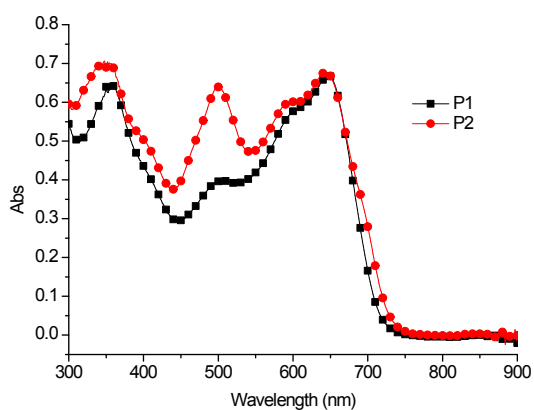


Figure S4. Solution UV-vis absorption spectrum of polymers **P1** and **P2** in chloroform (0.04 g/L).

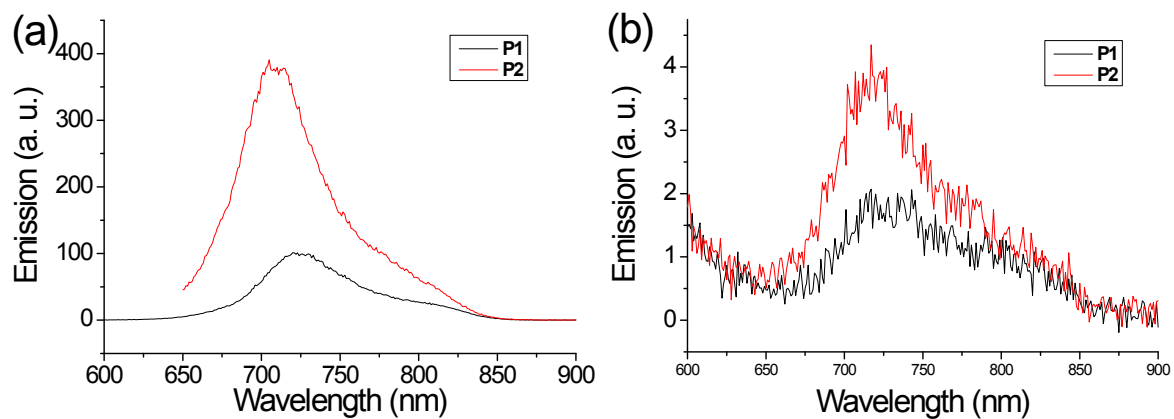


Figure S5. Solution and solid film emission spectra of polymers **P1** and **P2**.

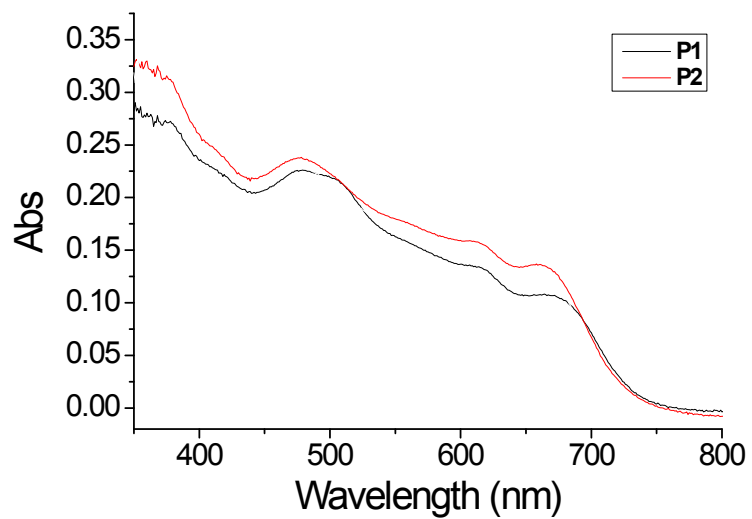


Figure S6. Absorption spectra from films of polymers **P1** and **P2** blended with PC₇₁BM in a 1:2 weight ratio.

Solar cell device data

Table S1 Additional photovoltaic data of the polymer and PC₇₁BM blend films.^{a,b}

Active layer	V_{oc} (V)	J_{sc} (mA cm ⁻²)	FF	PCE (%)
P1 :PC ₇₁ BM (1:2)	0.85	10.2	45	3.87
P2 :PC ₇₁ BM (1:2) ^c	0.96	3.5	37	1.26
P2 :PC ₇₁ BM (1:2) ^d	0.92	2.6	37	0.88
P2 :PC ₇₁ BM (1:2) ^{c,d}	0.94	2.6	35	0.84

^a Inverted structure. ^b weight ratio. ^c with 2.5% of DIO. ^d Thermally annealed at 120 °C for 3 min.

SCLC measurement

The space charge limited current (SCLC) in the polymers were studied using hole-only devices to find the charge-transport properties. The hole-only devices, consisting of active layer sandwiched between a PEDOT:PSS coated ITO electrode and Au counter-electrode as the electron-blocking contact, were fabricated as shown in Fig. S8. From the current density as a function of voltage data, the hole mobility in the space-charge limited current (SCLC) region can be estimated using the Mott-Gurney equation.

Hole only device

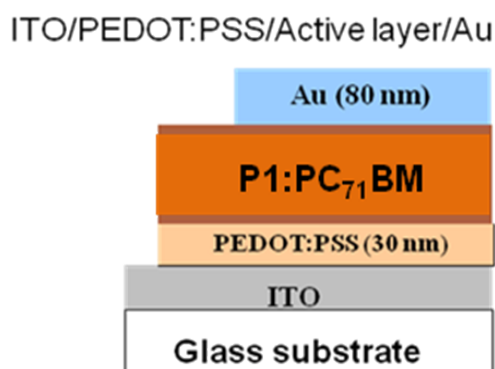


Figure S6. Configuration of the hole only device.

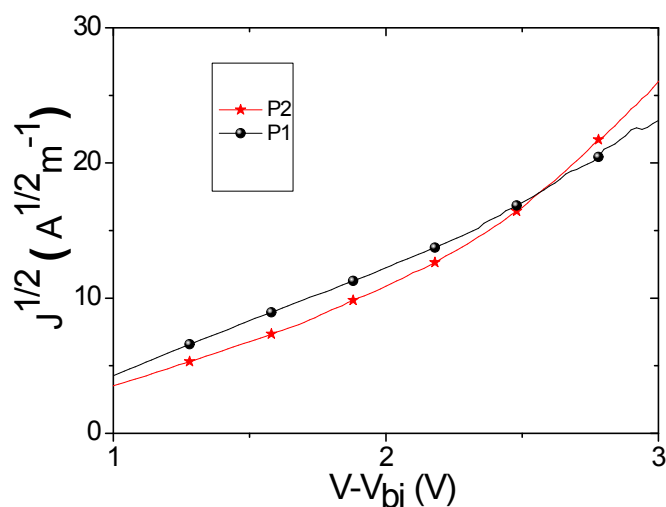
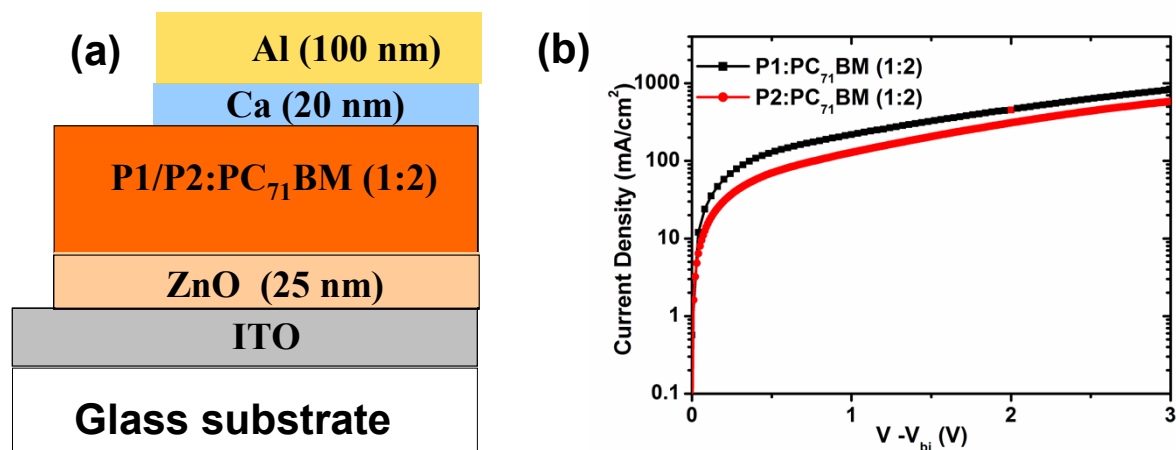


Figure S7. Hole only device: $J^{1/2}$ - V plots of the dark currents of hole-only with films of polymers **P1** and **P2** blended with PC₇₁BM in a 1:2 weight ratio.

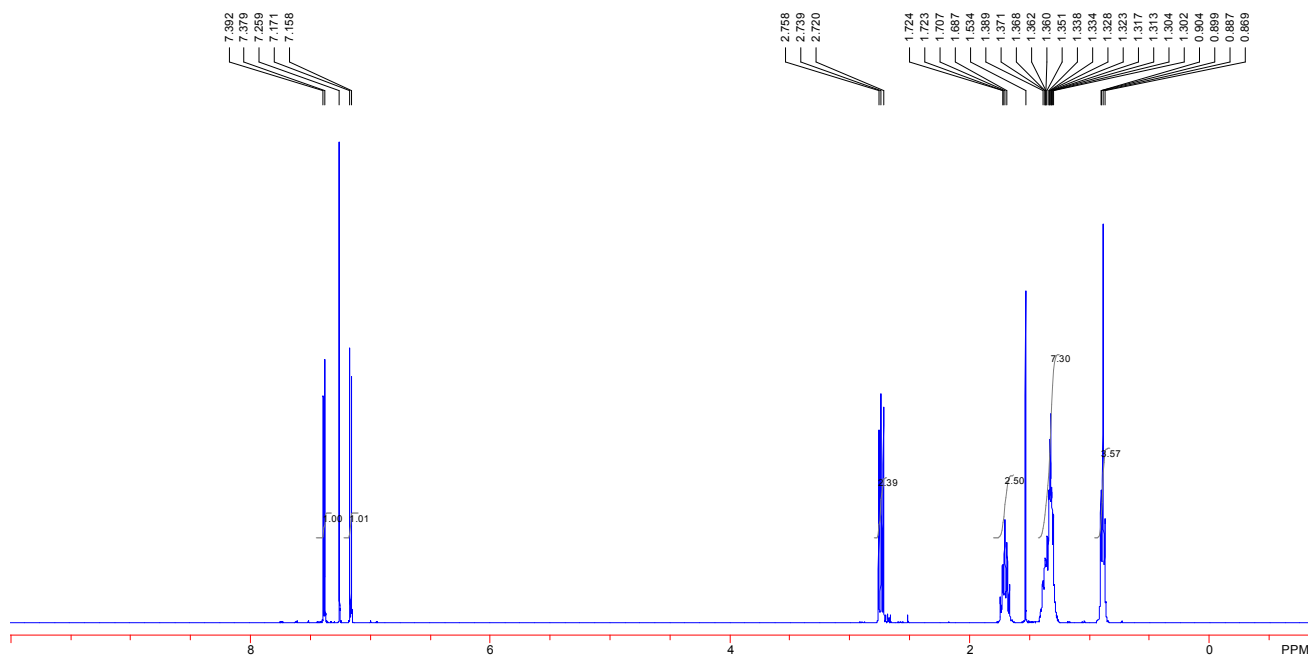
Electron only device



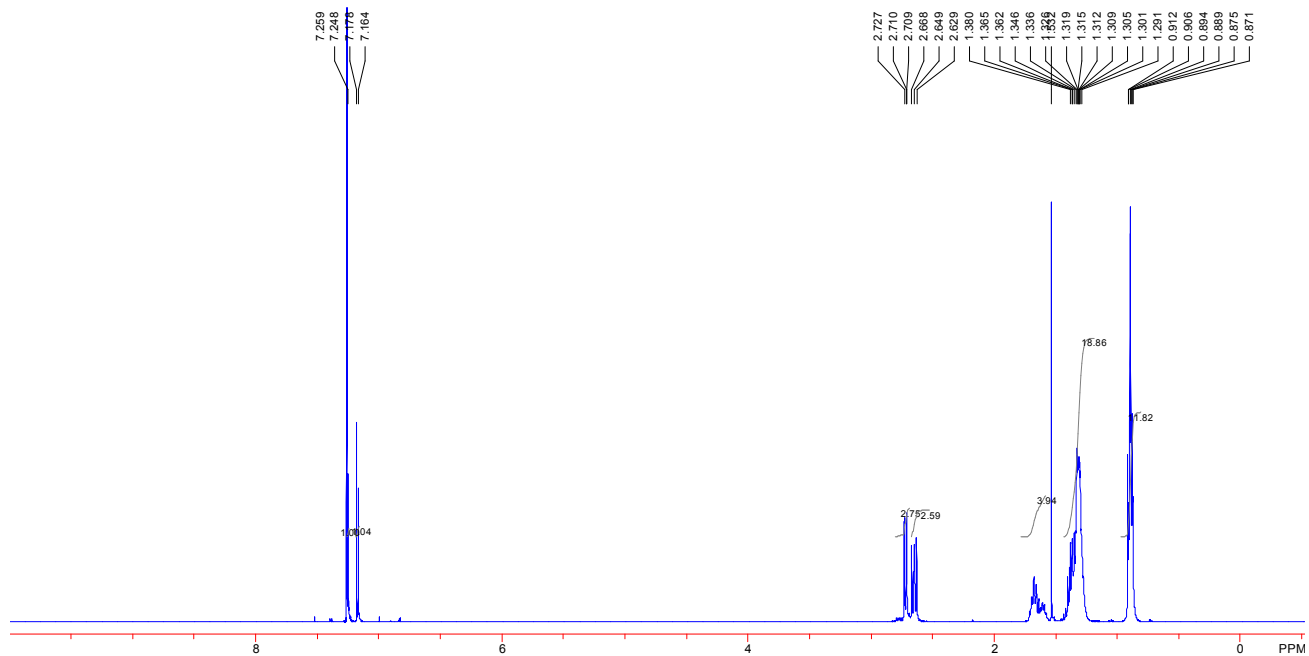
Active layer	Hole Mobility (cm^2/Vm)
P1:PC ₇₁ BM	1.9×10^{-4}
P2:PC ₇₁ BM	1.1×10^{-4}

Figure S8. The electron mobility was measured by the space charge limited current (SCLC) method using an electron-only device with a structure of ITO/ZnO/Active layer/Ca/Al. a) Device structure; b) Current density vs. voltage curve.

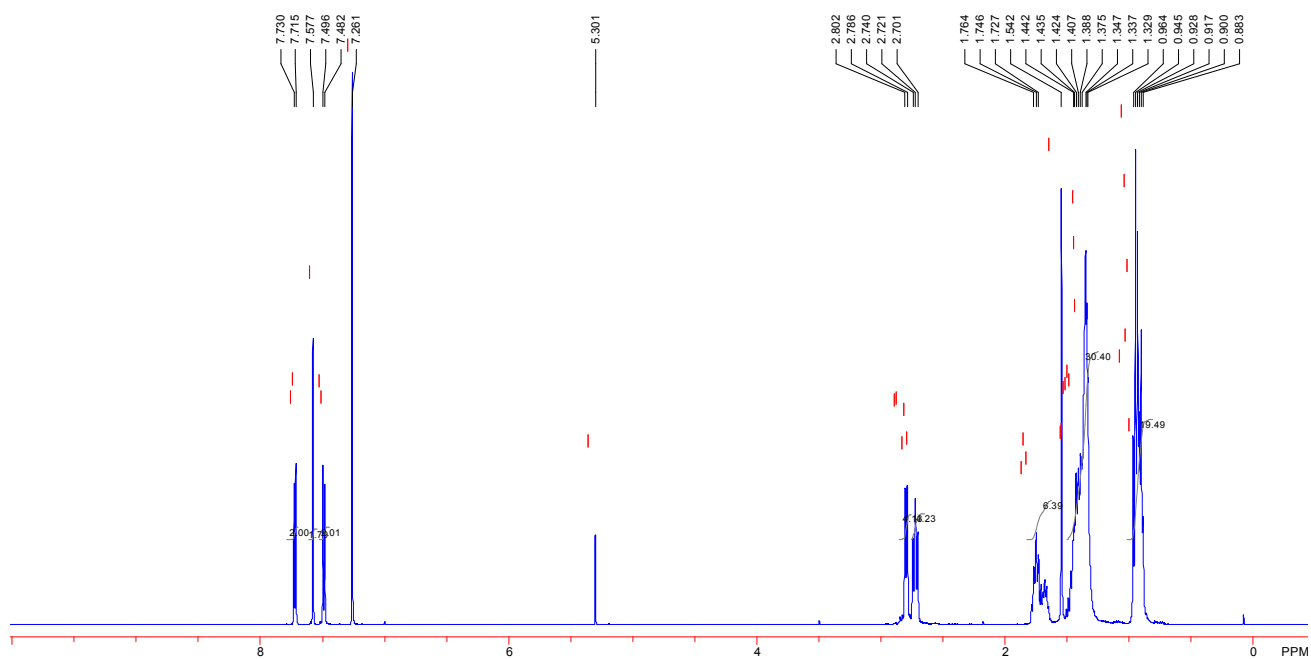
NMR Spectra



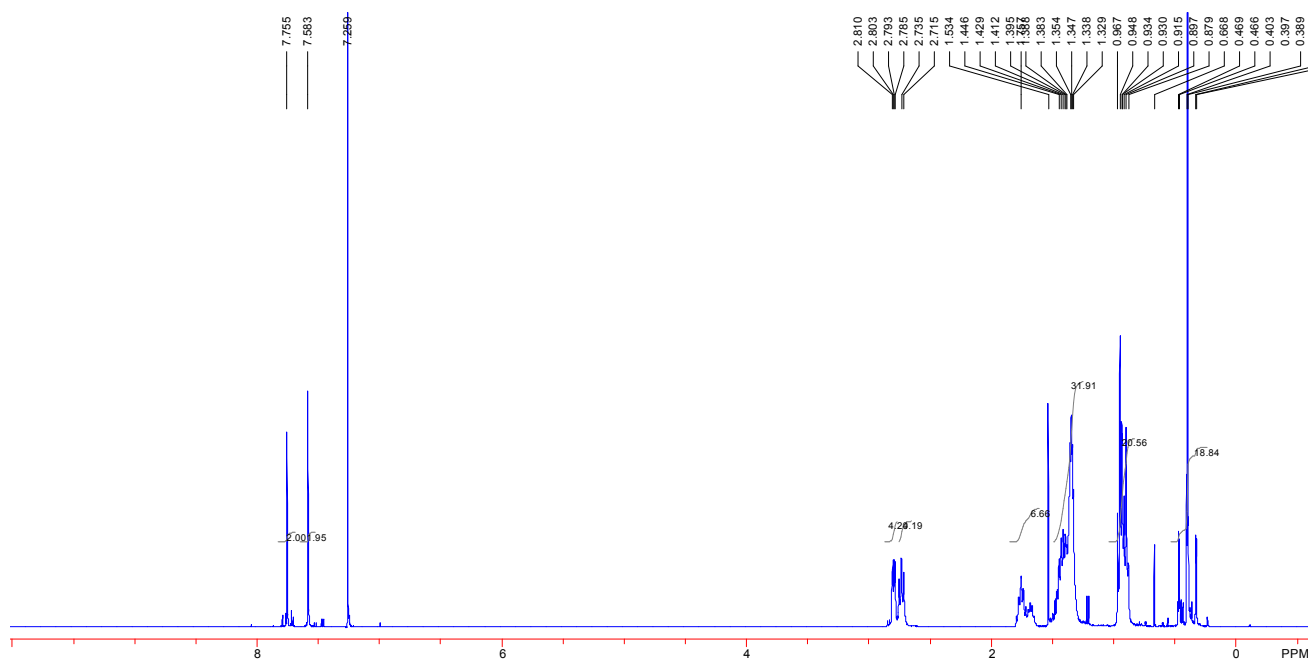
¹H NMR spectrum of compound 6



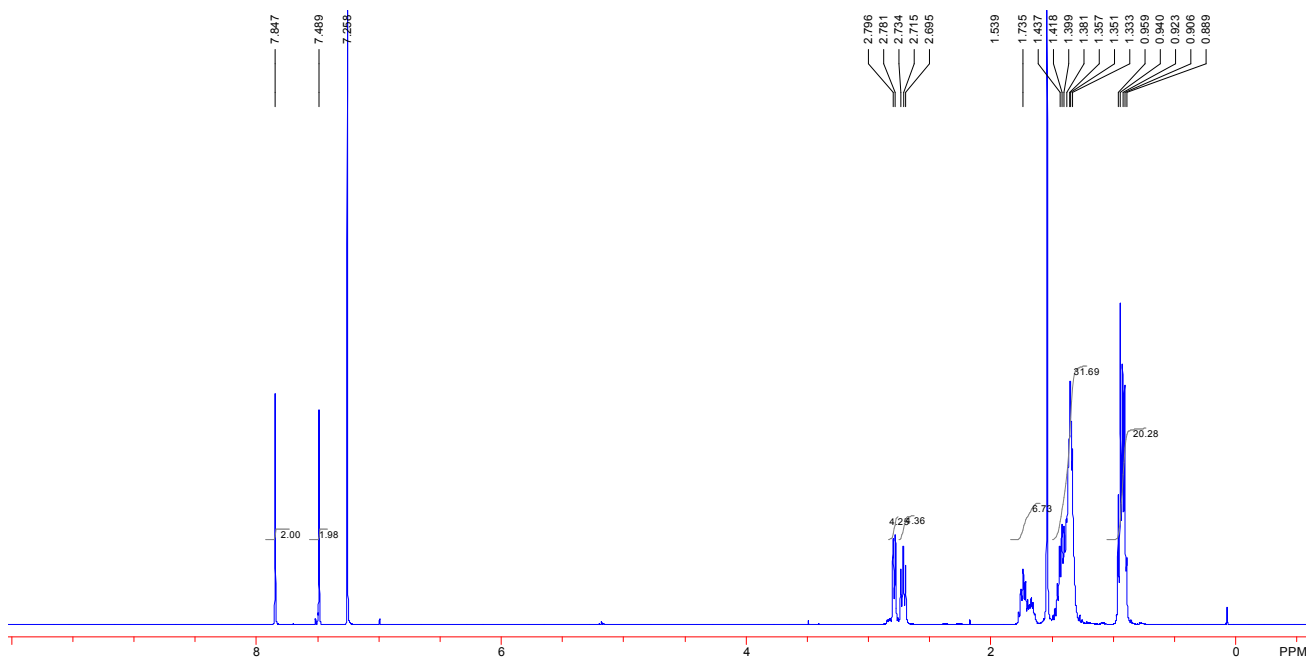
¹H NMR spectrum of compound 7



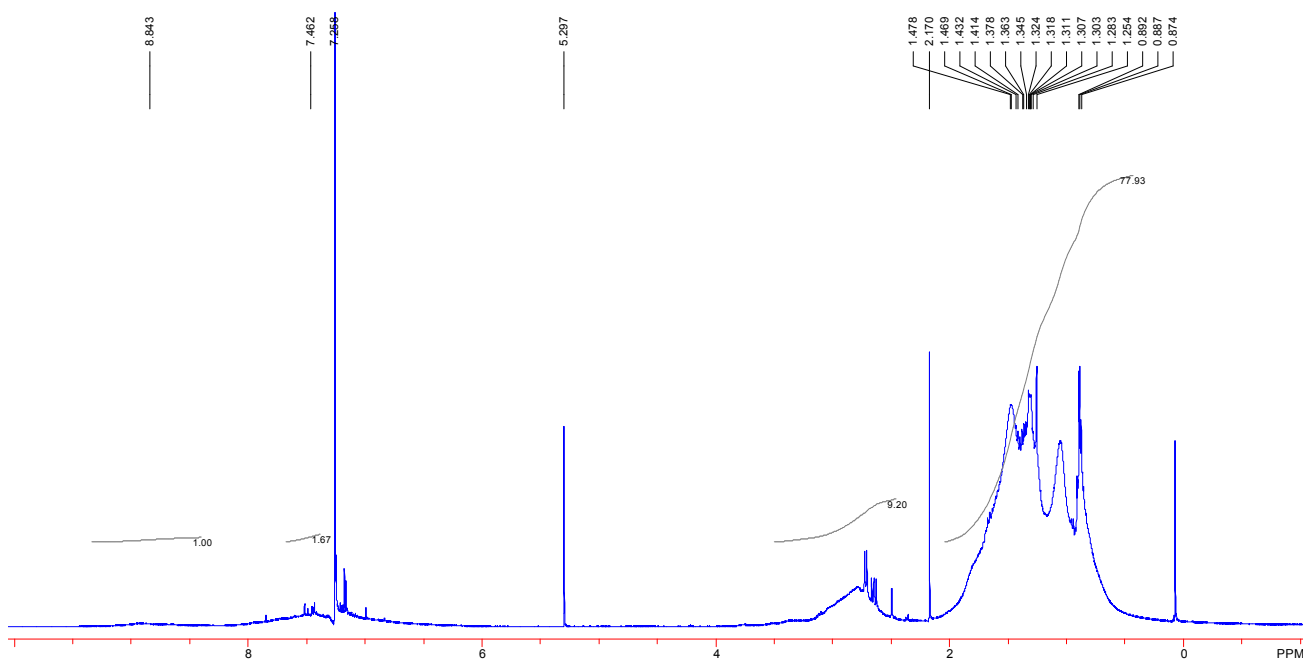
^1H NMR spectrum of compound **8**



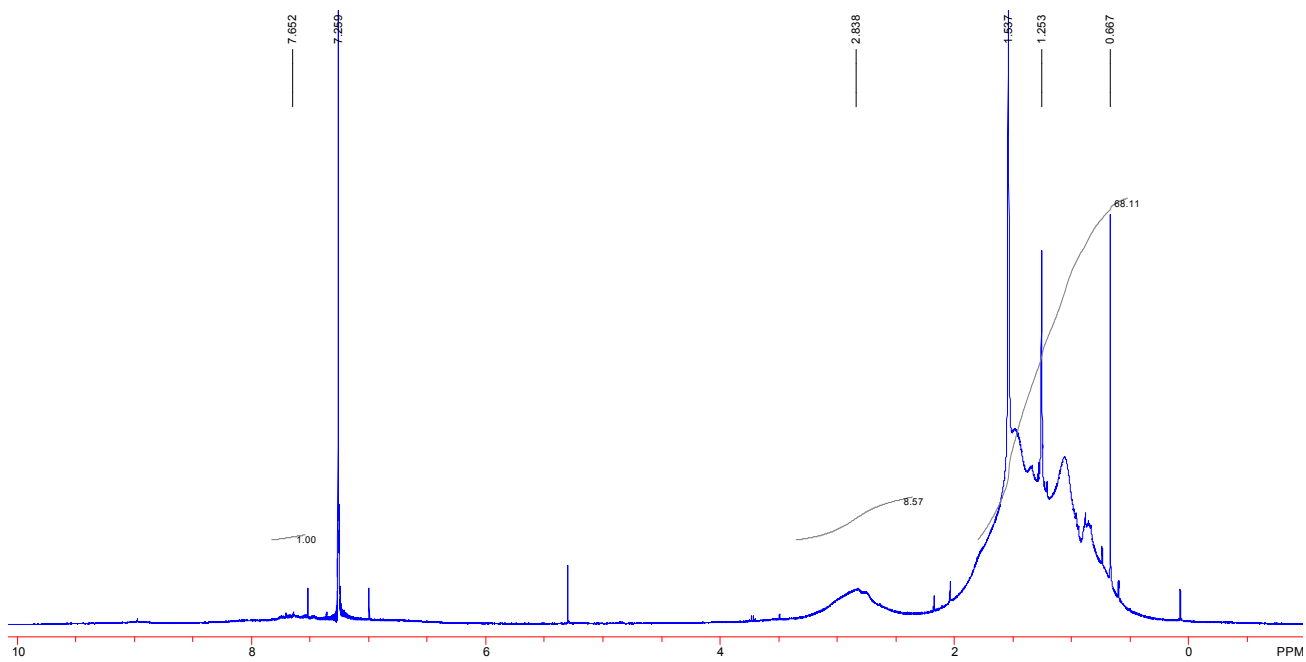
^1H NMR spectrum of compound **9**



^1H NMR spectrum of compound **10**



^1H NMR spectrum of polymer **P1**



^1H NMR spectrum of polymer **P2**