

Supporting Information

Synthesis of Semiconducting Polymers through Soluble Precursor Polymers with Thermally Removable Groups and Their Application to Organic Transistors

Taisuke Uemura, Masashi Mamada, Daisuke Kumaki, Shizuo Tokito^{*}

*Graduate School of Science and Engineering, Yamagata University, 4-3-16 Jonan, Yonezawa, Yamagata ,992-8510
JAPAN*

tokito@yz.yamagata-u.ac.jp

Contents:

1. Instruments	2
2. Materials	2
3. Synthesis	2
4. TGA measurements	5
5. UV spectra	6
6. IR spectra	7
7. Device fabrications.....	8
8. FET characteristics	9
9. NMR spectra	10
10. References	17

1. Instruments

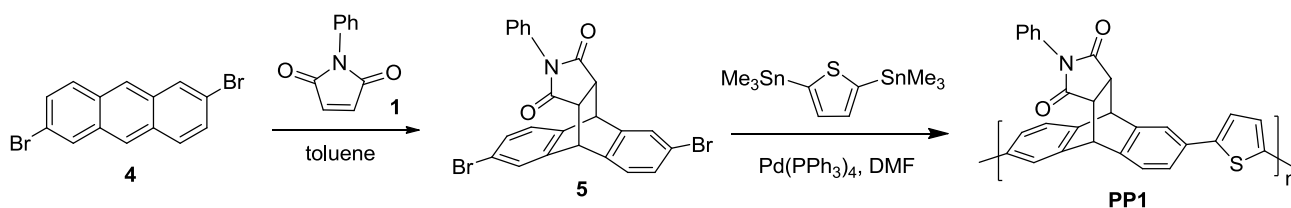
^1H -NMR and ^{13}C -NMR spectra were recorded on a JEOL 500 MHz JNM-ECX instrument. Chemical shifts were calibrated to the corresponding deuterated solvents. Thermogravimetry-Differential Thermal Analysis (TG-DTA) was performed on a SII TG/DTA 6200 unit under a N_2 atmosphere with a heating rate of $10\text{ }^\circ\text{C}$ per minute. Differential Scanning Calorimeter (DSC) was performed on a TA Instruments DSC Q200 unit with a heating rate of $10\text{ }^\circ\text{C}$ per minute. The UV/VIS spectra were measured using a Hitachi High-Tech. U-4100 UV-VIS-NIR spectrometer. The light source consisted of Deuterium (D2) and Tungsten Iodide (50W) lamps for the ultraviolet and visible regions respectively. FT-IR spectra were measured using a Shimadzu FTIR-8400S spectrometer. Mass spectra were collected on JEOL JMS-T100GC instrument equipped with a direct probe ionization. Molecular weights were determined by gel permeation chromatography (GPC) TOSOH HCL-8120 using chloroform as a solvent and calibrated with polystyrene standards. Atomic force microscopy (AFM) was performed on a Nanoscope V (Burrker) in tapping-mode. The elemental analyses were performed with Perkin Elmer 2400 series II CHNS/O elemental analyzer.

2. Materials

N-Phenylmaleimide (CAS: 941-69-5), diethyl azodicarboxylate (CAS: 1972-28-7) were purchased from Tokyo Kasei Co., Ltd. Toluene dehydrated (CAS: 108-88-3), *N,N*-dimethylformamide dehydrated (CAS: 68-12-2) were purchased from Kanto Chemicals. $\text{Pd}(\text{PPh}_3)_4$ (CAS: 14221-02-4) was purchased from Aldrich Chemical Co. The materials were used without further purification.

2,6-Dibromoanthracene (**4**)¹, *N*-*n*-hexylmaleimide (**2**)², 2,5-bis(trimethylstannyl)thiophene³ and 5,5'-bis(trimethylstannyl)-2,2'-bithiophene⁴ were prepared according to the reported procedure.

3. Synthesis



5

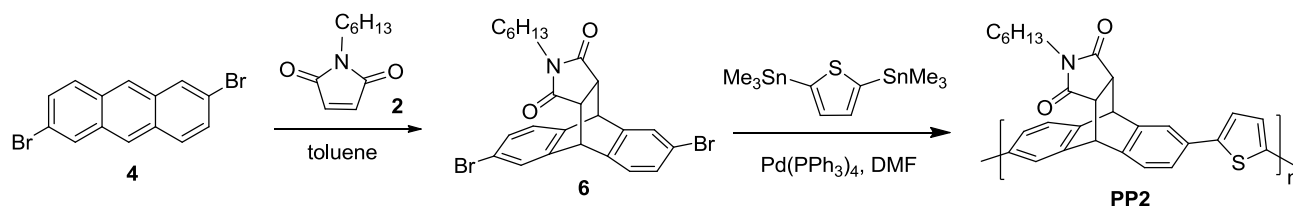
To a solution of *N*-phenylmaleimide (0.346 g, 2.0 mmol) in 30 mL of toluene was added 2,6-dibromoanthracene (0.672 g, 2.0 mmol) and the mixture was refluxed for 16 h. After cooling to room temperature, the solvent was removed under pressure. The residue was purified by column chromatography on a silica gel using chloroform to give the compound **5** (0.99 g, 98%) as a colorless solid.

Mp: $250\text{ }^\circ\text{C}$. ^1H -NMR: δ /ppm (500 MHz, CDCl_3 , Me_4Si) = 7.57 (d, 1H, $J = 1.49\text{ Hz}$); 7.51 (d, 1H, $J = 1.49\text{ Hz}$); 7.39-7.32 (m, 5H); 7.29 (d, 1H, $J = 7.92\text{ Hz}$); 7.20 (d, 1H, $J = 7.92\text{ Hz}$); 6.57 (dd, 2H, $J = 2.48$ and 7.92 Hz); 4.84 (d, 1H, $J = 2.97\text{ Hz}$); 4.83 (d, 1H, $J = 2.97\text{ Hz}$); 3.37 (d, 1H, $J = 2.97\text{ Hz}$); 3.36 (d, 1H, $J = 2.97\text{ Hz}$). ^{13}C -NMR: δ /ppm (125 MHz, CDCl_3) = 175.3, 142.9, 140.4, 139.5, 131.1, 130.3, 130.0, 129.2, 129.0, 128.9, 128.2, 127.6, 126.7, 126.2, 126.0, 125.3, 121.1, 120.7, 46.4, 46.3, 45.1, 45.0. MS/FD: m/z 509 (M^+ , 100%, showing expected

bromine isotope peaks). IR: $\nu_{\text{max}}/\text{cm}^{-1}$ = 3051, 2990, 1777, 1711, 1597, 1494, 1460, 1380, 1162, 1061, 968, 914, 881, 832, 812, 760. Anal. Calcd. For $\text{C}_{24}\text{H}_{15}\text{Br}_2\text{NO}_2$: C, 56.61; H, 2.97; N, 2.75. Found: C, 57.00; H, 2.72; N, 2.70.

PP1

A solution of **5** (0.400 g, 0.786 mmol), 2,5-bis(trimethylstannyl)thiophene (0.322 g, 0.786 mmol), $\text{Pd}(\text{PPh}_3)_4$ (27 mg, 0.0236 mmol) in 12 mL of anhydrous DMF was stirred for 2 h at 130 °C under N_2 atmosphere. After cooling to room temperature, the reaction solution was poured into a mixture of methanol (70 mL) and concentrated hydrochloric acid (3 mL) and stirred for 1 h. The suspension was filtered to give the polymer, which was purified by Soxhlet extraction with methanol, acetone to remove low molecular weight fractions. The residue was extracted with chloroform, precipitated in 50 mL of methanol to give the polymer **PP1** (128 mg, 38%) as a light yellow solid. ^1H -NMR: δ/ppm (500 MHz, CDCl_3 , Me_4Si) = 7.69 (d, 1H, J = 5.45 Hz); 7.62 (d, 1H, J = 5.45 Hz); 7.47-7.26 (m, 9H); 6.56 (br, 2H); 4.96 (br, 2H); 3.45 (br, 2H). ^{13}C -NMR: δ/ppm (125 MHz, $\text{DMSO}-d_6$) = 175.8, 143.4, 143.2, 143.1, 141.7, 140.3, 139.3, 137.8, 133.5, 133.2, 131.3, 129.1, 128.8, 126.3, 125.7, 125.6, 124.9, 124.6, 124.5, 124.3, 124.2, 122.4, 121.7, 46.8, 45.6. GPC (CHCl_3): M_n = 8,000, M_w = 13,300. IR: $\nu_{\text{max}}/\text{cm}^{-1}$ = 3061, 2960, 1780, 1710, 1498, 1474, 1374, 1178, 773. Anal. Calcd. For $\text{C}_{28}\text{H}_{17}\text{NO}_2\text{S}$: C, 77.94; H, 3.97; N, 3.25; S, 7.43. Found: C, 72.92; H, 4.38; N, 3.93; S, 6.66.



6

To a solution of *N*-*n*-hexylmaleimide (0.362 g, 2.0 mmol) in 48 mL of toluene was added 2,6-dibromoanthracene (0.672 g, 2.0 mmol) and the mixture was refluxed for 22 h. After cooling to room temperature, the solvent was removed under pressure. The residue was purified by column chromatography on a silica gel using hexane/ethyl acetate (4/1) to give the compound **6** (0.80 g, 77%) as a colorless solid.

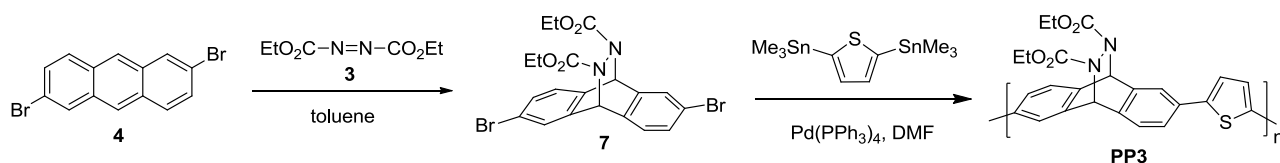
Mp: 146 °C. ^1H -NMR: δ/ppm (500 MHz, CDCl_3 , Me_4Si) = 7.52 (d, 1H, J = 1.49 Hz); 7.43 (d, 1H, J = 1.98 Hz); 7.33 (dd, 1H, J = 1.98 and 7.92 Hz); 7.28 (dd, 1H, J = 1.49 and 7.92 Hz); 7.23 (d, 1H, J = 7.92 Hz); 7.14 (d, 1H, J = 7.92 Hz); 4.73 (d, 2H, J = 2.97 Hz); 3.16 (d, 1H, J = 2.97 Hz); 3.15 (d, 1H, J = 2.97 Hz); 3.11 (t, 2H, J = 7.43 Hz); 1.26-1.10 (m, 4H); 0.95-0.70 (m, 4H); 0.86 (t, 3H, J = 2.48 Hz). ^{13}C -NMR: δ/ppm (125 MHz, CDCl_3) = 176.1, 143.1, 140.4, 139.8, 137.1, 130.1, 129.9, 128.2, 127.5, 126.6, 125.9, 121.0, 120.5, 46.2, 46.1, 44.8, 44.7, 38.7, 31.2, 27.1, 26.1, 22.3, 14.0. MS/FD: m/z 517 (M^+ , 100%, showing expected bromine isotope peaks). IR: $\nu_{\text{max}}/\text{cm}^{-1}$ = 2913, 2853, 1769, 1686, 1602, 1465, 1406, 1345, 1138, 1063, 963, 927, 837, 774. Anal. Calcd. For $\text{C}_{24}\text{H}_{23}\text{Br}_2\text{NO}_2$: C, 55.73; H, 4.48; N, 2.71. Found: C, 55.79; H, 4.49; N, 2.59.

PP2

A solution of **6** (0.300 g, 0.580 mmol), 2,5-bis(trimethylstannyl)thiophene (0.238 g, 0.580 mmol), $\text{Pd}(\text{PPh}_3)_4$ (20 mg, 0.0174 mmol) in 16 mL of anhydrous toluene was stirred for 18 h at 130 °C under N_2 atmosphere. After cooling to room temperature, the reaction solution was poured into a mixture of methanol (30 mL) and

concentrated hydrochloric acid (2 mL) and stirred for 1 h. The suspension was filtered to give the polymer, which was purified by Soxhlet extraction with methanol, acetone to remove low molecular weight fractions. The residue was extracted with chloroform, precipitated in 50 mL of methanol to give the polymer **PP2** (115 mg, 45%) as a light yellow solid.

$^1\text{H-NMR}$: δ/ppm (500 MHz, CDCl_3 , Me_4Si) = 7.62 (d, 1H, J = 9.41 Hz); 7.53 (d, 1H, J = 9.41 Hz); 7.45-7.36 (m, 3H); 7.32-7.30 (m, 1H); 7.26-7.18 (m, 2H); 4.84 (d, 2H, J = 3.47 Hz); 3.23 (br, 2H); 3.10 (br, 2H); 1.06-1.04 (m, 2H); 0.98-0.97 (m, 2H); 0.85-0.84 (m, 2H); 0.77-0.75 (m, 2H); 0.70 (t, 3H, J = 6.93 Hz). $^{13}\text{C-NMR}$: δ/ppm (125 MHz, $\text{DMSO}-d_6$) = 176.6, 143.2, 143.0, 142.0, 140.6, 139.3, 137.8, 133.4, 133.0, 125.6, 124.8, 124.2, 124.1, 122.1, 121.6, 46.6, 45.4, 38.6, 31.3, 31.2, 26.1, 22.2, 14.0. GPC (CHCl_3): M_n = 12,800, M_w = 26,000. IR: $\nu_{\text{max}}/\text{cm}^{-1}$ = 2927, 1698, 1396, 1363, 1340, 1219, 1173, 1137, 773. Anal. Calcd. For $\text{C}_{28}\text{H}_{25}\text{NO}_2\text{S}$: C, 76.51; H, 5.73; N, 3.19; S, 7.29. Found: C, 73.78; H, 5.56; N, 2.91; S, 6.34.



7

To a solution of diethyl azodicarboxylate (6.6 mL, 14.58 mmol, 2.2 M in toluene solution) in 12 mL of toluene was added 2,6-dibromoanthracene (0.700 g, 2.08 mmol) and the mixture was refluxed for 16 h. After cooling to room temperature, the solvent was removed under pressure. The residue was purified by column chromatography on a silica gel using hexane/ethyl acetate (4/1) to give the compound **7** (0.75 g, 71%) as a colorless solid.

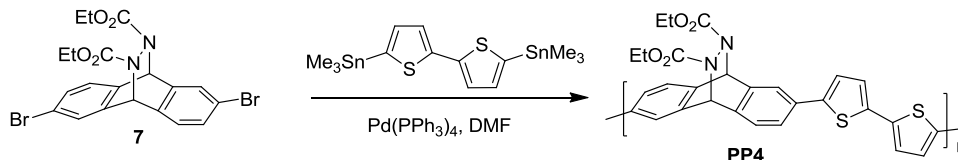
Mp: 176 °C. $^1\text{H-NMR}$: δ/ppm (500 MHz, CDCl_3 , Me_4Si) = 7.60 (s, 1H); 7.51 (s, 1H); 7.37-7.36 (m, 2H); 7.31 (d, 1H, J = 7.92 Hz); 7.23 (d, 1H, J = 7.92 Hz); 6.22 (s, 2H); 4.06-4.18 (m, 4H); 1.19 (br, 6H). $^{13}\text{C-NMR}$: δ/ppm (125 MHz, CDCl_3) = 157.6, 143.4, 140.2, 138.1, 134.7, 130.7, 128.9, 127.2, 126.3, 124.5, 121.8, 121.0, 62.9, 62.8, 59.4, 14.4. MS/FD: m/z 510 (M^+ , 100%). IR: $\nu_{\text{max}}/\text{cm}^{-1}$ = 2982, 1753, 1723, 1607, 1463, 1370, 1330, 1275, 1233, 1128, 1060, 920, 879, 920, 766. Anal. Calcd. For $\text{C}_{20}\text{H}_{18}\text{Br}_2\text{N}_2\text{O}_4$: C, 47.08; H, 3.56; N, 5.49. Found: C, 47.10; H, 3.37; N, 5.54.

PP3

A solution of **7** (0.300 g, 0.588 mmol), 2,5-bis(trimethylstannyl)thiophene (0.241 g, 0.588 mmol), $\text{Pd}(\text{PPh}_3)_4$ (20 mg, 0.0176 mmol) in 15 mL of anhydrous DMF was stirred for 20 h at 110 °C under N_2 atmosphere. After cooling to room temperature, the reaction solution was poured into a mixture of methanol (80 mL) and concentrated hydrochloric acid (3 mL) and stirred for 1 h. The suspension was filtered to give the polymer, which was purified by Soxhlet extraction with methanol, acetone to remove low molecular weight fractions. The residue was extracted with chloroform, precipitated in 100 mL of methanol to give the polymer **PP3** (105 mg, 41%) as a light yellow solid.

$^1\text{H-NMR}$: δ/ppm (500 MHz, CDCl_3 , Me_4Si) = 7.71 (s, 1H); 7.62 (s, 1H); 7.50-7.39 (m, 4H); 7.26-7.25 (m, 2H); 6.34 (s, 2H); 4.22-4.08 (m, 4H); 1.21 (br, 6H). $^{13}\text{C-NMR}$: δ/ppm (125 MHz, CDCl_3) = 157.9, 143.1, 143.0, 142.5, 140.9, 137.0, 135.3, 133.6, 133.3, 126.2, 124.8, 124.6, 124.4, 124.2, 123.4, 123.0, 120.0, 62.8, 62.7, 60.2, 14.4.

GPC (CHCl_3): $M_n = 9,800$, $M_w = 13,800$. IR: $\nu_{\text{max}}/\text{cm}^{-1} = 2978, 1748, 1700, 1618, 1477, 1370, 1302, 1265, 1218, 1126, 1099, 866, 811, 772$. Anal. Calcd. For $\text{C}_{24}\text{H}_{20}\text{N}_2\text{O}_2\text{S}$: C, 66.65; H, 4.66; N, 6.48; S, 7.41. Found: C, 65.76; H, 4.63; N, 6.16; S, 7.22.



PP4

A solution of **7** (0.150 g, 0.294 mmol), 5,5'-bis(trimethylstannyl)-2,2'-bithiophene (0.145 g, 0.294 mmol), $\text{Pd}(\text{PPh}_3)_4$ (10 mg, 0.0088 mmol) in 12 mL of anhydrous DMF was stirred for 20 h at 110 °C under N_2 atmosphere. After cooling to room temperature, the reaction solution was poured into a mixture of methanol (70 mL) and concentrated hydrochloric acid (2 mL) and stirred for 1 h. The suspension was filtered to give the polymer, which was purified by Soxhlet extraction with methanol, acetone to remove low molecular weight fractions. The residue was extracted with chloroform, precipitated in 80 mL of methanol to give the polymer **PP4** (64 mg, 42%) as a yellow solid.

$^1\text{H-NMR}$: δ/ppm (500 MHz, CDCl_3 , Me_4Si) = 7.71 (s, 1H); 7.61 (s, 1H); 7.49-7.39(m, 4H); 7.22-7.20 (m, 2H); 7.15 (d, 1H, $J = 2.97$ Hz) 6.35 (s, 2H); 4.24-4.08 (m, 4H); 1.22 (br, 6H). $^{13}\text{C-NMR}$: δ/ppm (125 MHz, CDCl_3) = 157.9, 142.5, 142.3, 140.8, 137.0, 136.9, 136.8, 135.2, 133.5, 133.2, 126.2, 124.7, 124.6, 124.4, 124.2, 123.4, 122.9, 120.0, 62.8, 60.1, 14.4. GPC (CHCl_3): $M_n = 8,500$, $M_w = 11,600$. IR: $\nu_{\text{max}}/\text{cm}^{-1} = 2977, 1749, 1697, 1617, 1479, 1370, 1302, 1265, 1217, 1126, 1099, 867, 792, 770$. Anal. Calcd. For $\text{C}_{28}\text{H}_{22}\text{N}_2\text{O}_4\text{S}_2$: C, 65.35; H, 4.31; N, 5.44; S, 12.46. Found: C, 63.92; H, 4.20; N, 5.22; S, 12.20.

4. TGA measurements

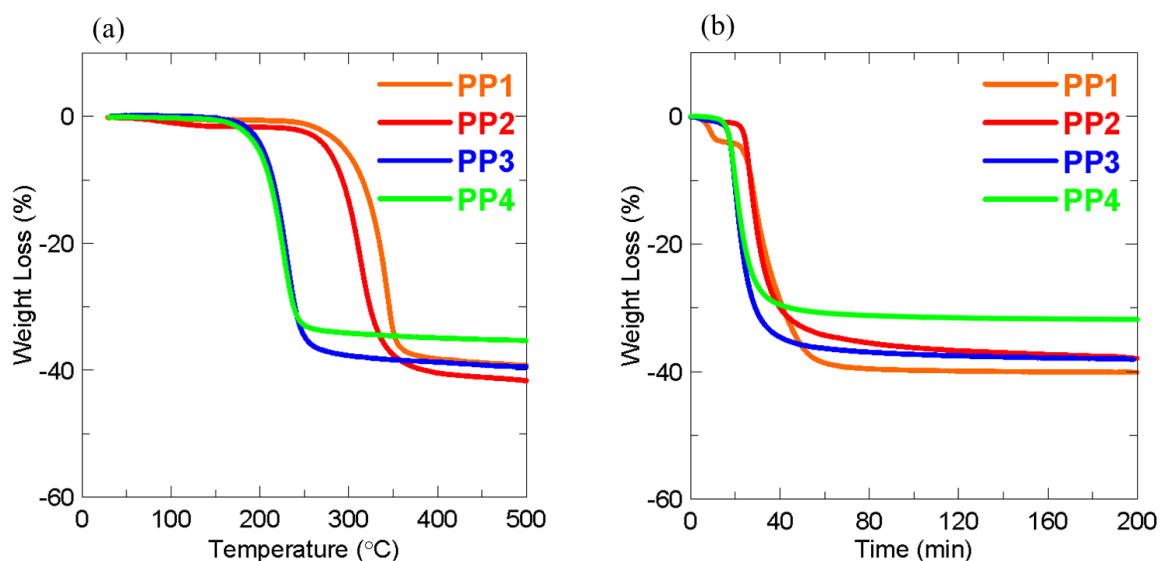


Figure S1. (a) TGA measurements of **PP1-PP4**. (b) Isothermal TGA measurements of **PP1-PP4** at 5% weight loss temperatures (T_{d5}), which are 295 °C for **PP1**, 275 °C for **PP2**, 203 °C for **PP3**, and 198 °C for **PP4**.

5. UV spectra

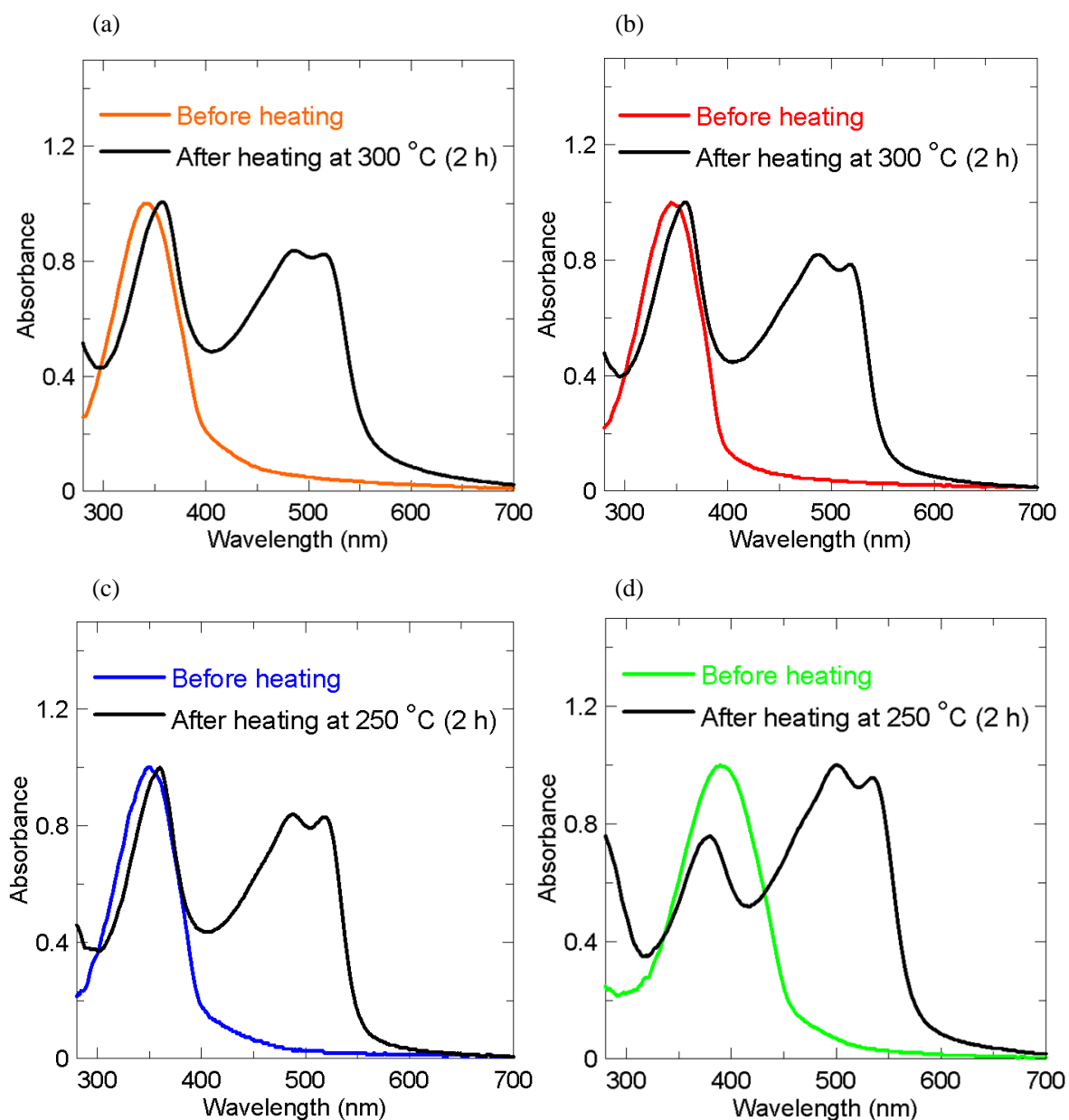


Figure S2. Absorption spectra of precursor polymers (a) **PP1**, (b) **PP2**, (c) **PP3**, and (d) **PP4** before and after heating.

6. IR spectra

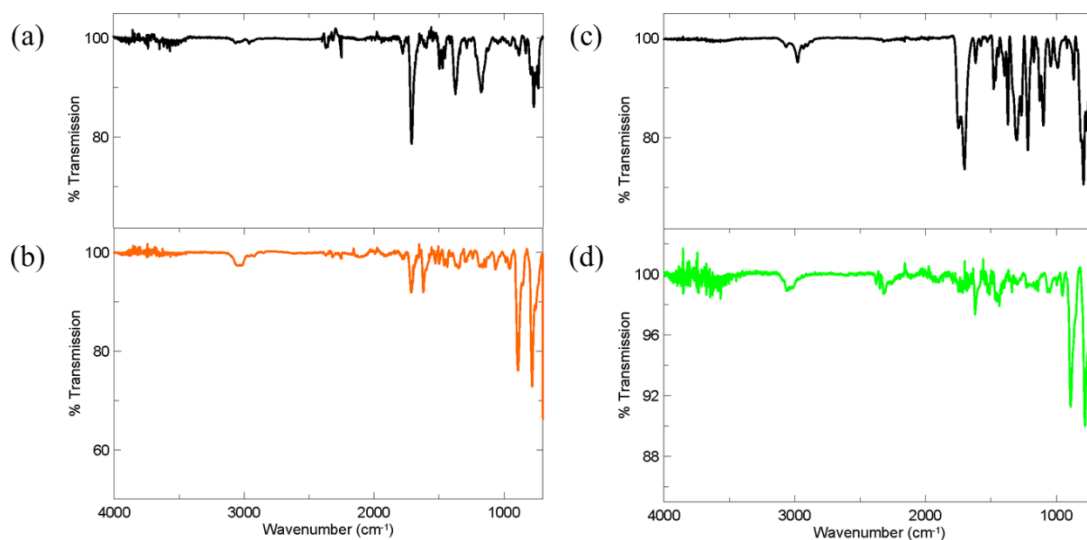


Figure S3. FT-IR spectra of films for (a) as-coated **PP1**, (b) **PP1** heated at 350 °C for 5 h, (c) as-coated **PP4**, and (d) **PP4** heated at 250 °C for 2 h.

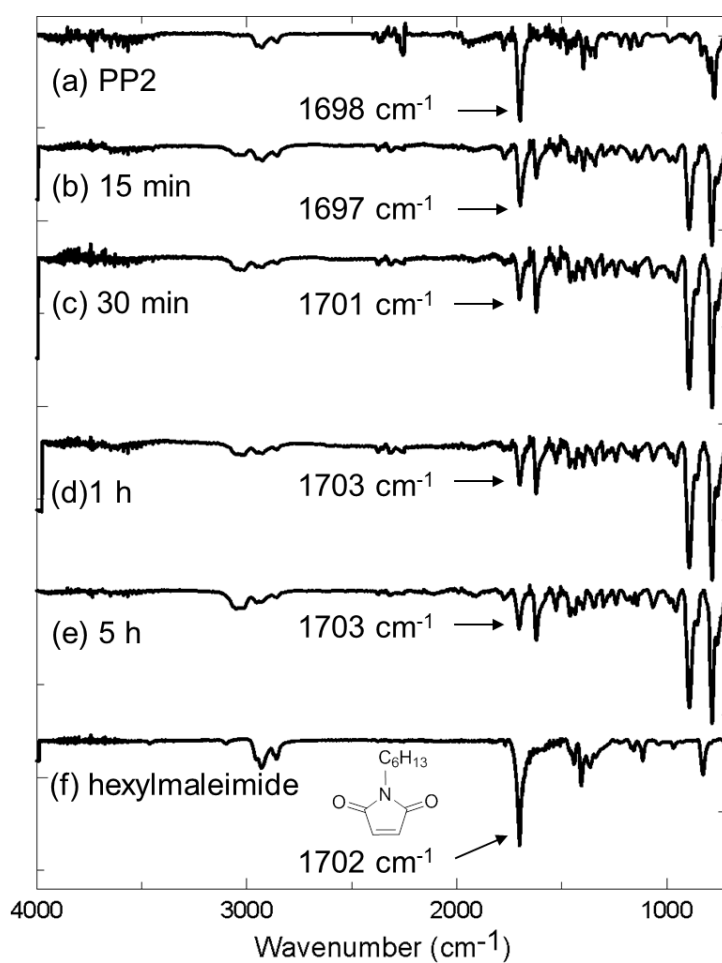


Figure S4. FT-IR spectra of films for (a) as-coated **PP2**, and annealed **PP2** at 350 °C for (b) 15 min, (c) 30 min, (d) 1 h, and (e) 5 h, and (f) neat liquid of *N-n*-hexylmaleimide.

7. Device fabrications

The HMDS (hexamethyldisilazane) treatment was carried out by immersing the substrate in HMDS at room temperature for >10 h. OFETs were constructed on heavily doped n-type silicon wafers covered with thermally grown silicon dioxide (200 nm) which was cleaned by piranha solution. The silicon dioxide acts as a gate dielectric layer, and the silicon wafer serves as a gate electrode. Precursor polymers were spin-coated from the chloroform solution (0.3 wt %) with 2000 rpm for 30 sec, followed by thermal heating under nitrogen atmosphere to convert to polymer semiconductor. Gold was used as source and drain electrodes (50 nm) and deposited on the organic semiconductor layer through a shadow mask with $L/W = 75/2100$ μm . The FET measurements were carried out at room temperature in a glovebox without exposure to air with a semiconductor parameter analyzer (4200-SCS, KEITHLEY). Mobilities (μ) were calculated in the saturation regime by the relationship: $\mu_{\text{sat}} = (2I_{\text{D}}L)/[WC_{\text{ox}}(V_{\text{G}}-V_{\text{th}})^2]$ where I_{D} is the source-drain saturation current; C_{ox} (4 F) is the oxide capacitance; V_{G} is the gate voltage and V_{th} is the threshold voltage. The latter can be estimated as the intercept of the linear section of the plot of $V_{\text{G}} (I_{\text{D}})^{1/2}$

8. FET characteristics

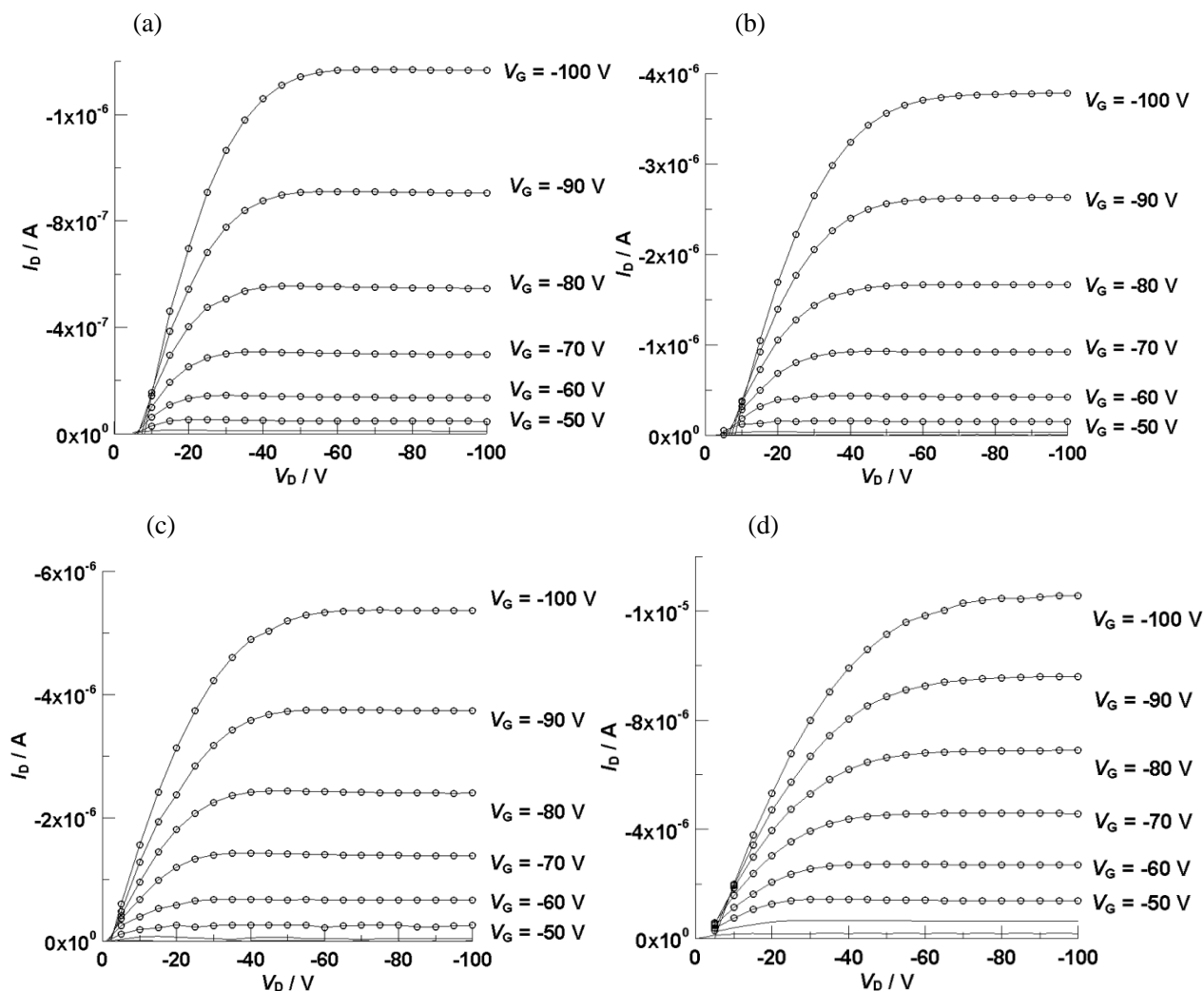
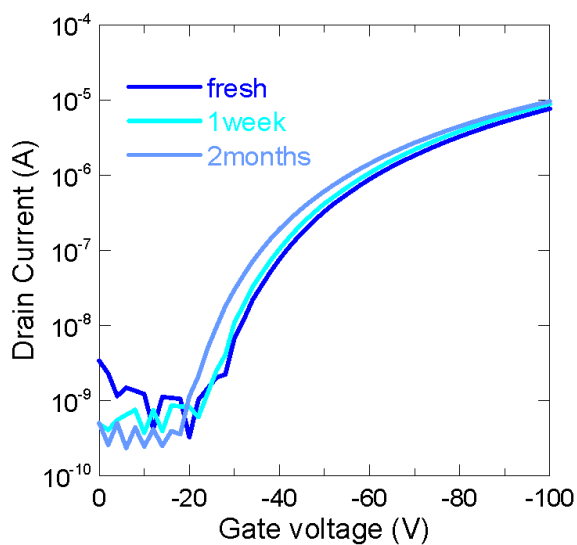


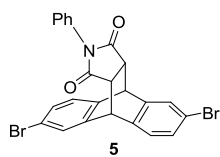
Figure S5. Output characteristics for OTFTs using **P1** films from (a) **PP1**, (b) **PP2** and (c) **PP3** and **P2** film from (d) **PP4**.



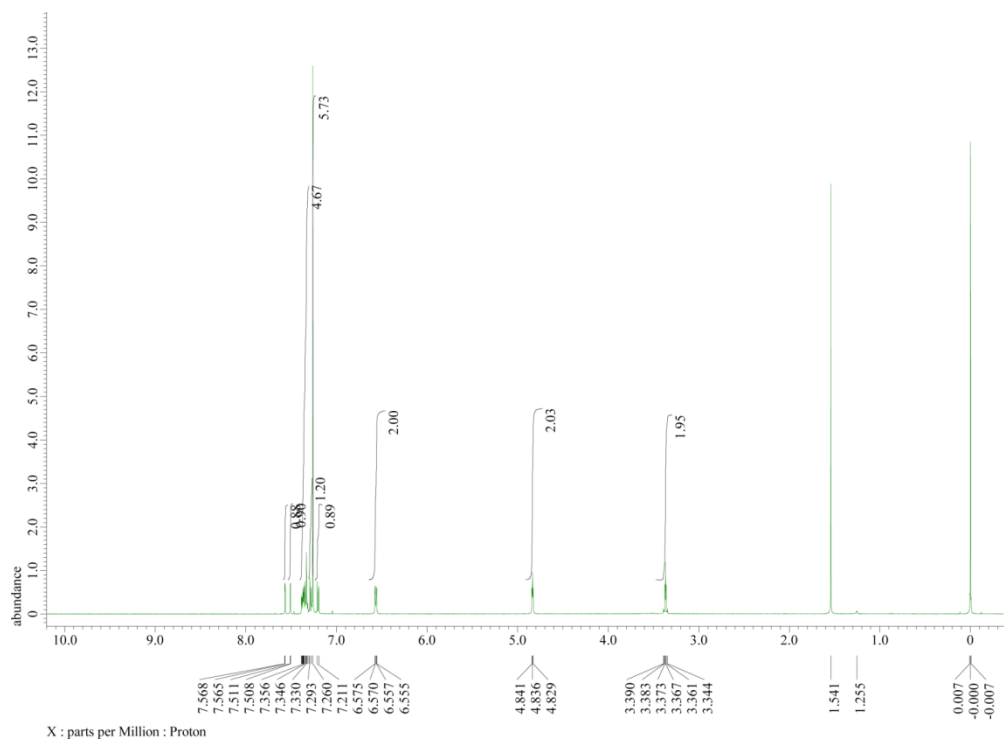
	μ (cm ² / Vs)	On / Off	V_{th} (V)
fresh	0.010	10 ⁴	-43
1week	0.011	10 ⁴	-42
2months	0.010	10 ⁴	-37

Figure S6. Changes in the transfer characteristic of **P1** film from **PP3** by time upon exposure to air.

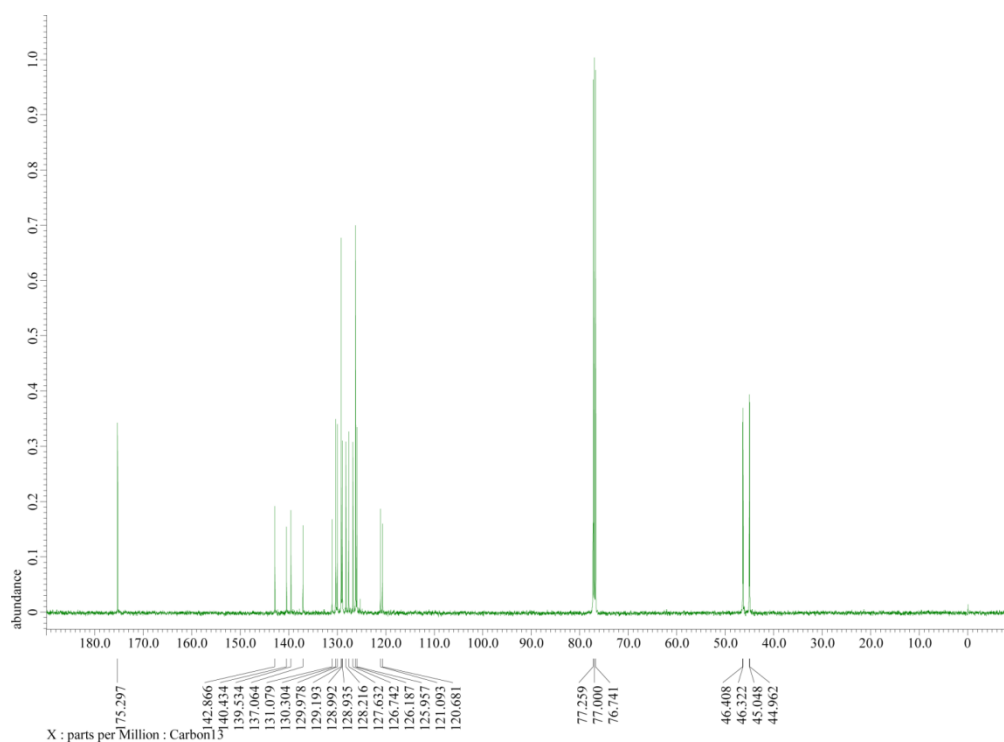
9. NMR spectra

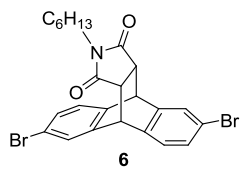


^1H -NMR spectrum (500 MHz, CDCl_3 , Me_4Si)

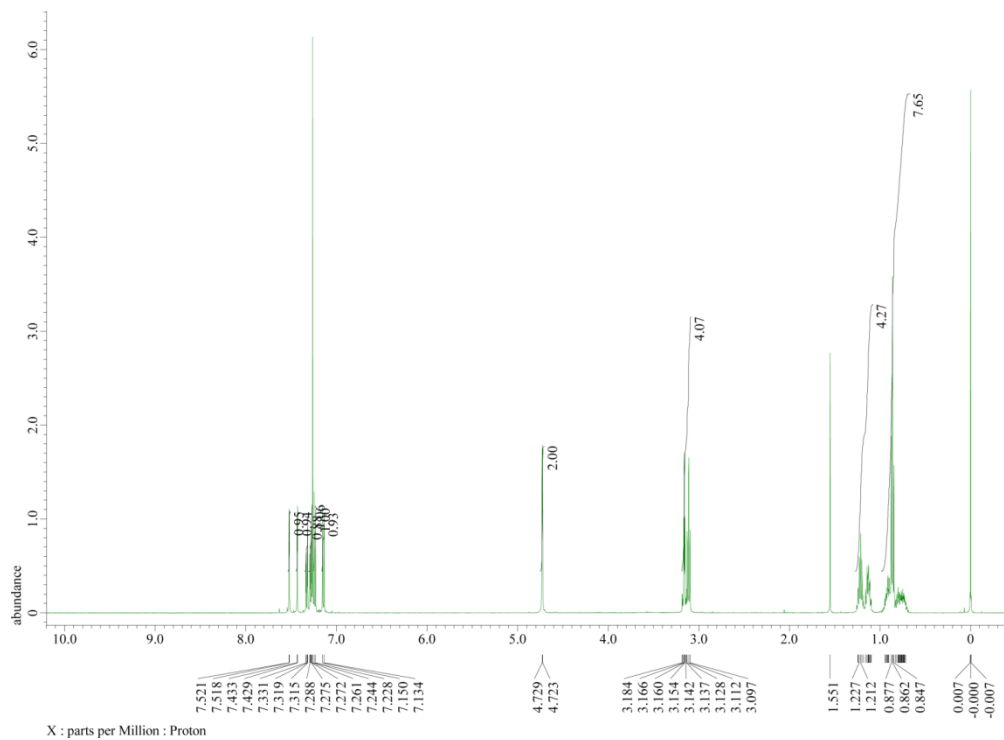


^{13}C -NMR spectrum (125 MHz, CDCl_3 , Me_4Si)

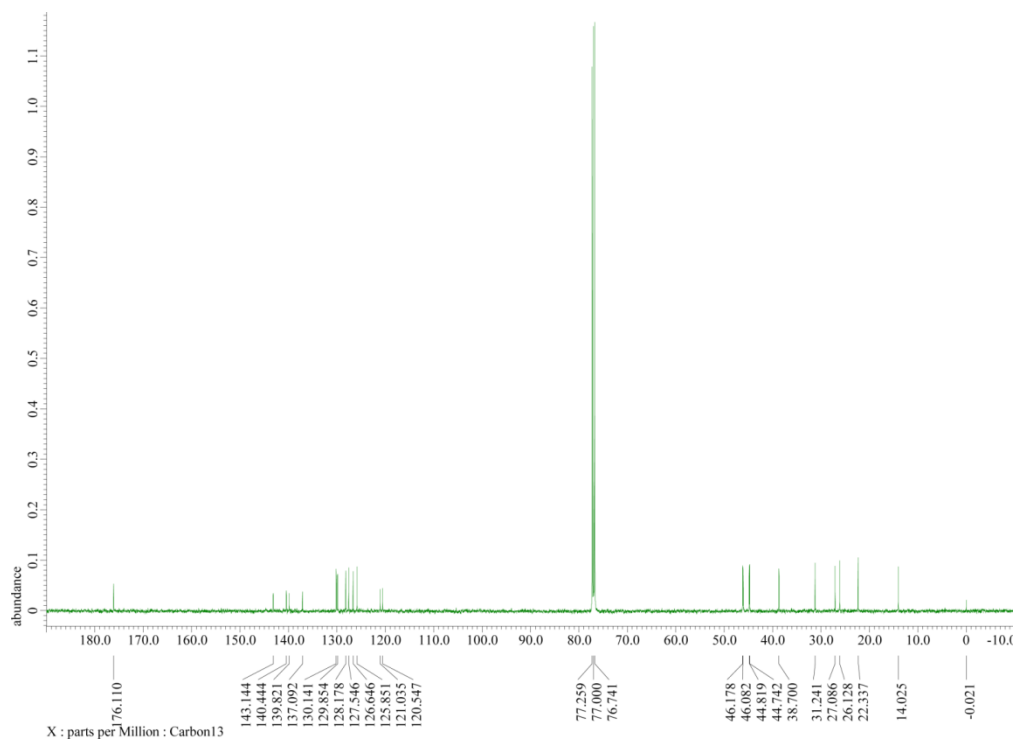


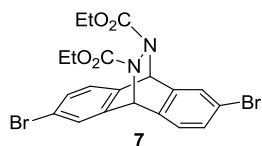


^1H -NMR spectrum (500 MHz, CDCl_3 , Me_4Si)

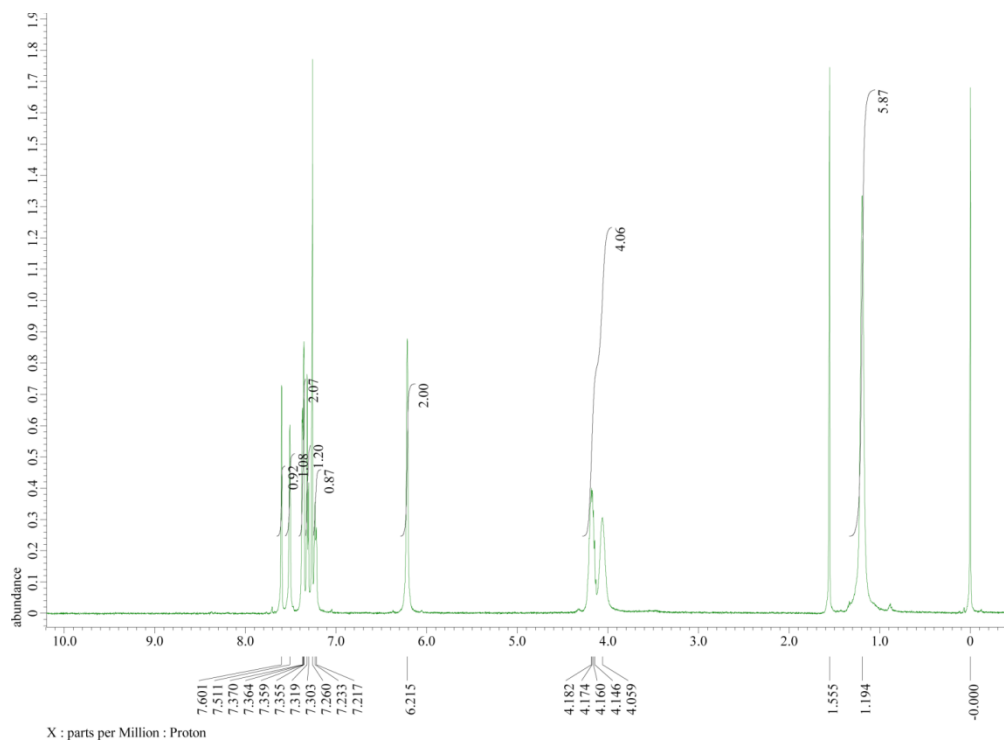


^{13}C -NMR spectrum (125 MHz, CDCl_3 , Me_4Si)

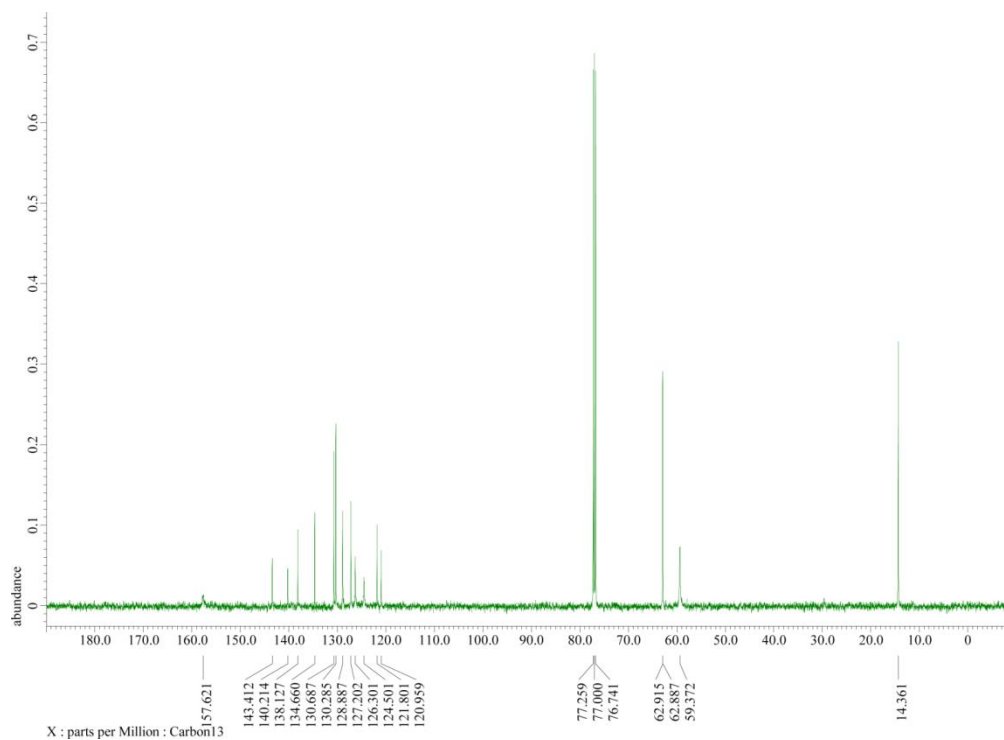


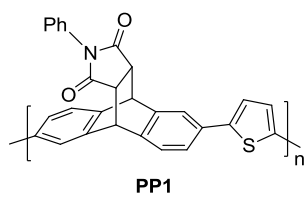


^1H -NMR spectrum (500 MHz, CDCl_3 , Me_4Si)

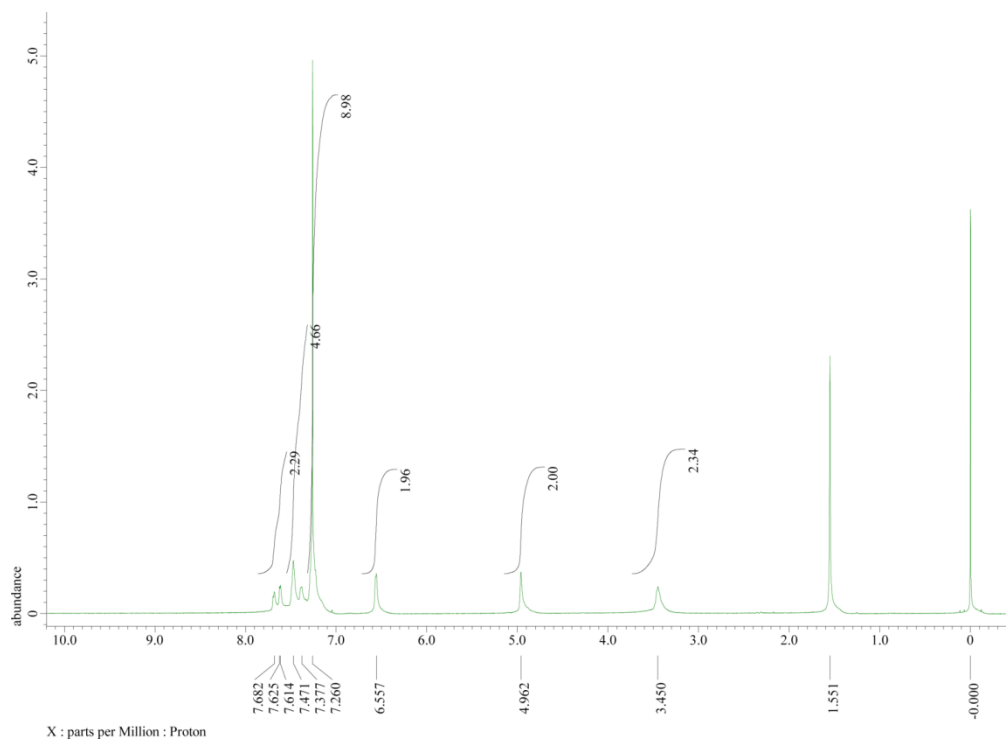


^{13}C -NMR spectrum (125 MHz, CDCl_3 , Me_4Si)

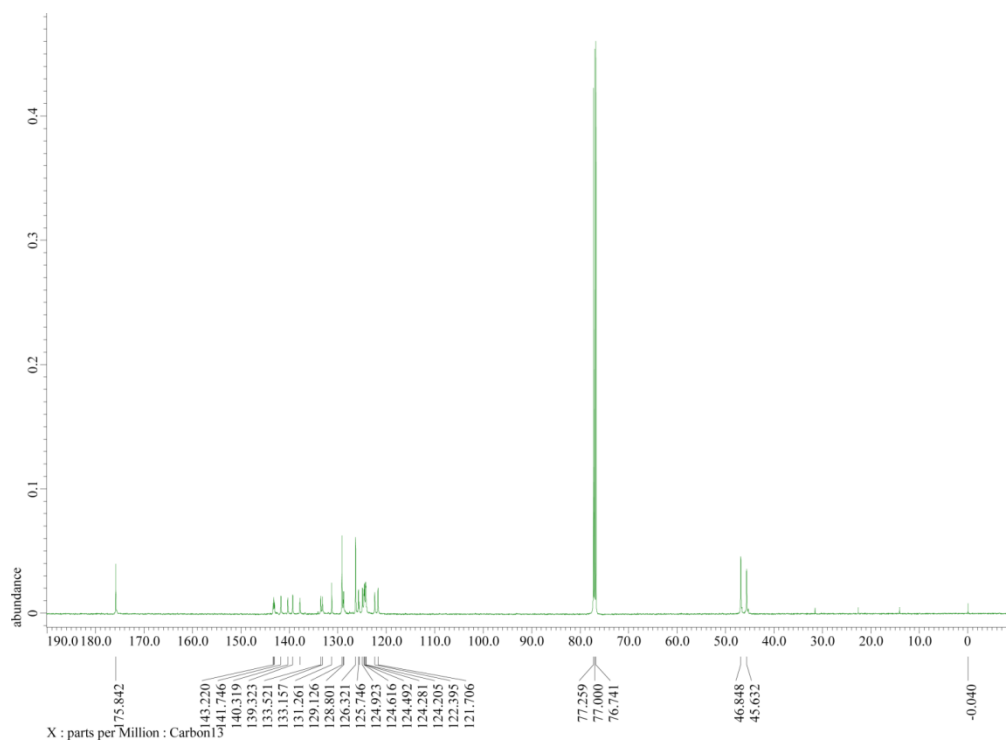


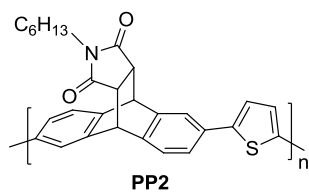


^1H -NMR spectrum (500 MHz, CDCl_3 , Me_4Si)

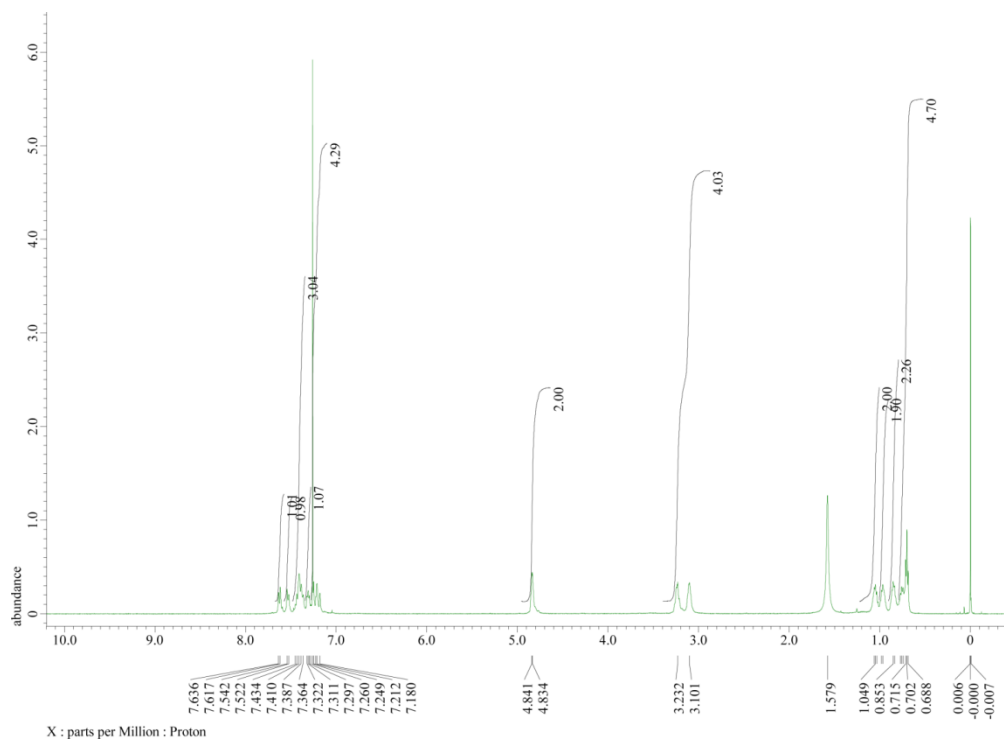


^{13}C -NMR spectrum (125 MHz, CDCl_3 , Me_4Si)

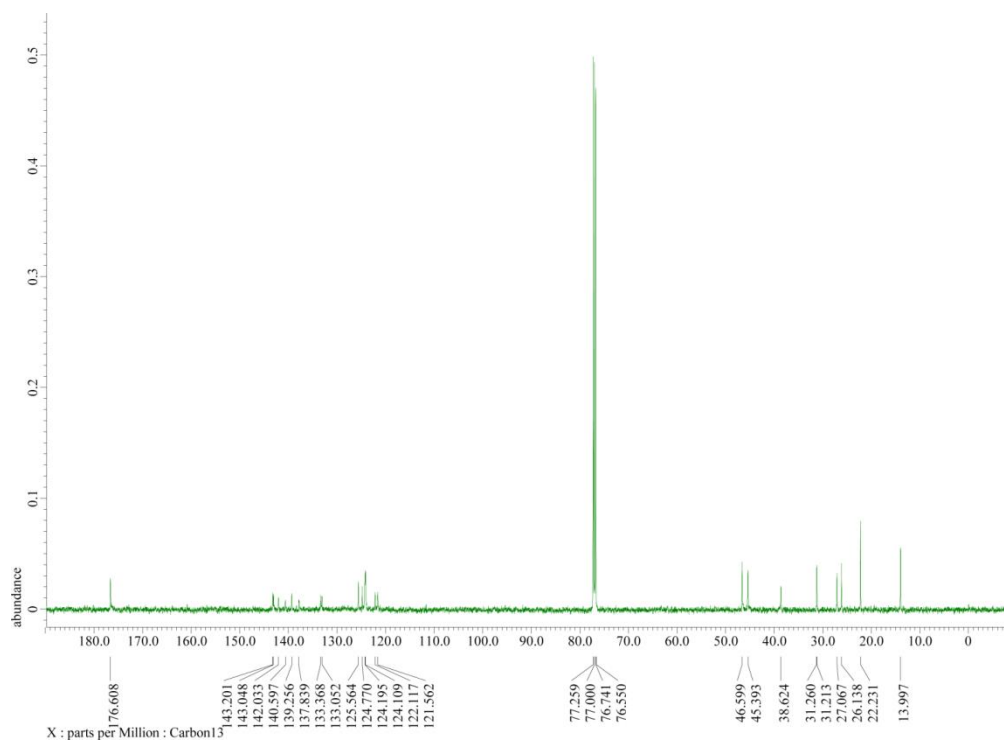


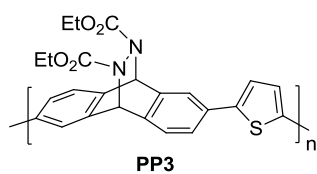


^1H -NMR spectrum (500 MHz, CDCl_3 , Me_4Si)

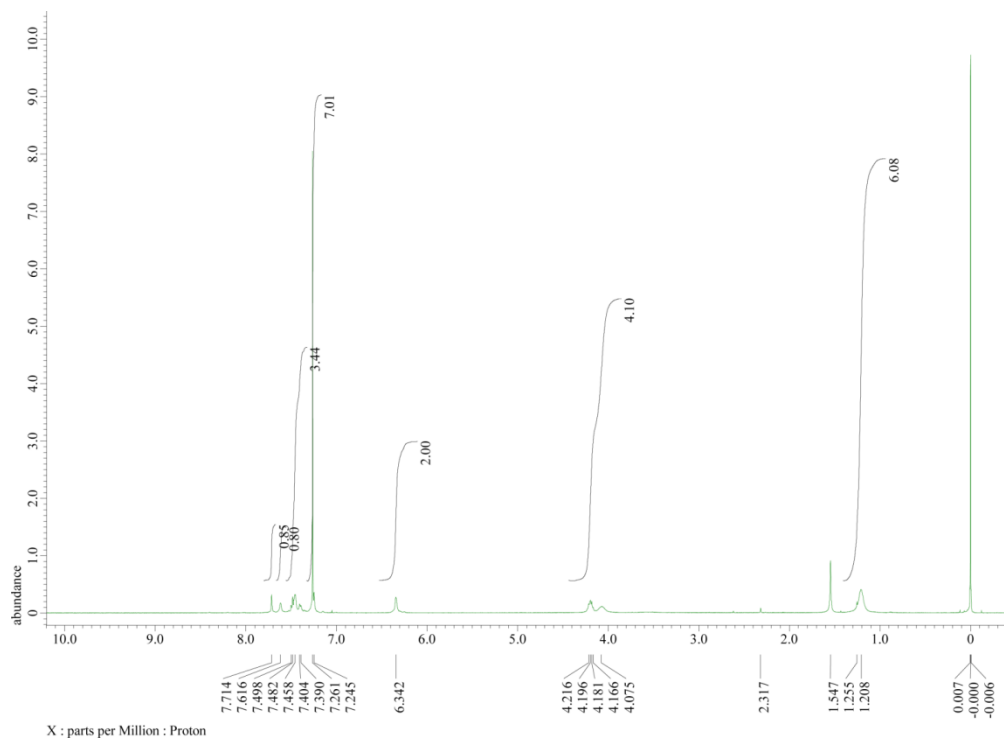


^{13}C -NMR spectrum (125 MHz, CDCl_3 , Me_4Si)

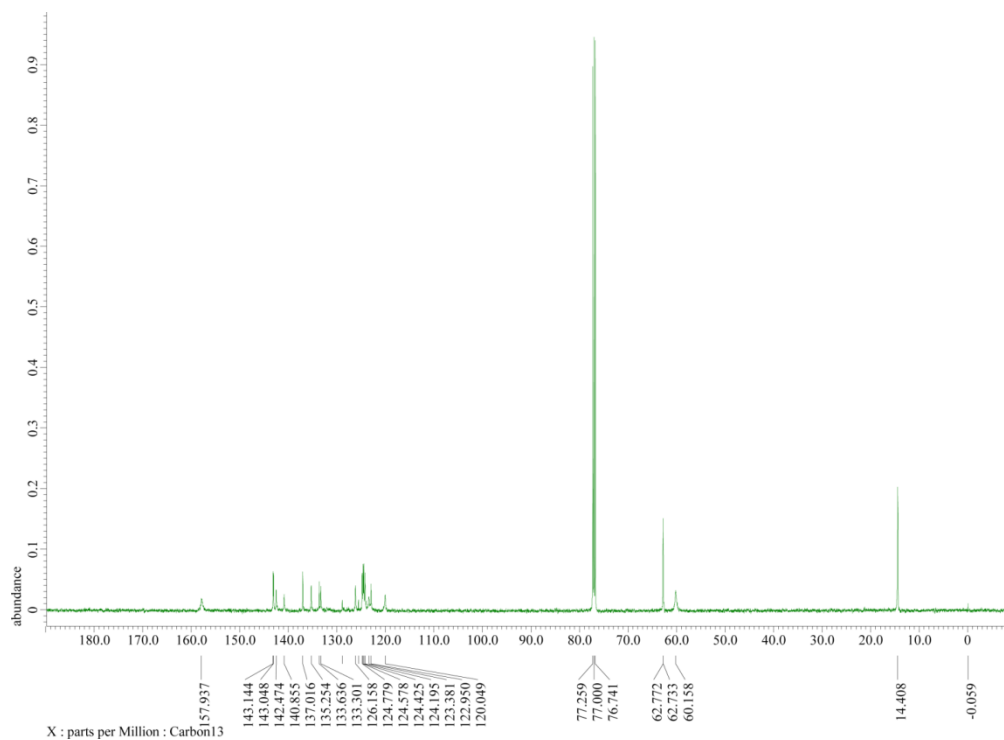


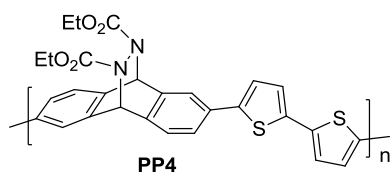


^1H -NMR spectrum (500 MHz, CDCl_3 , Me_4Si)

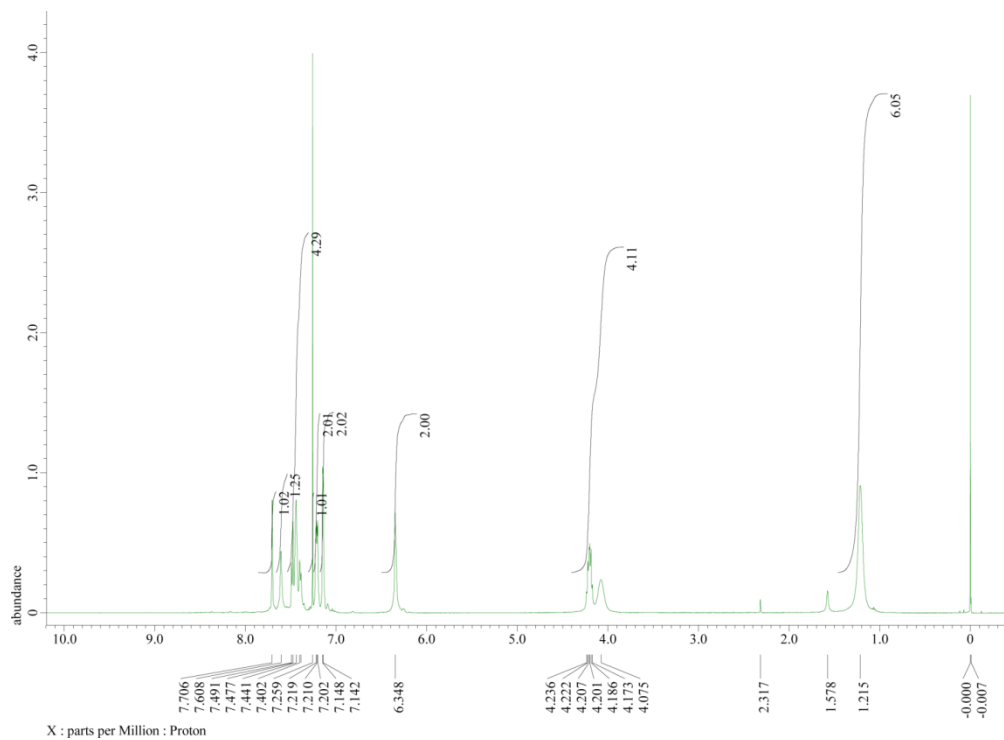


^{13}C -NMR spectrum (125 MHz, CDCl_3 , Me_4Si)

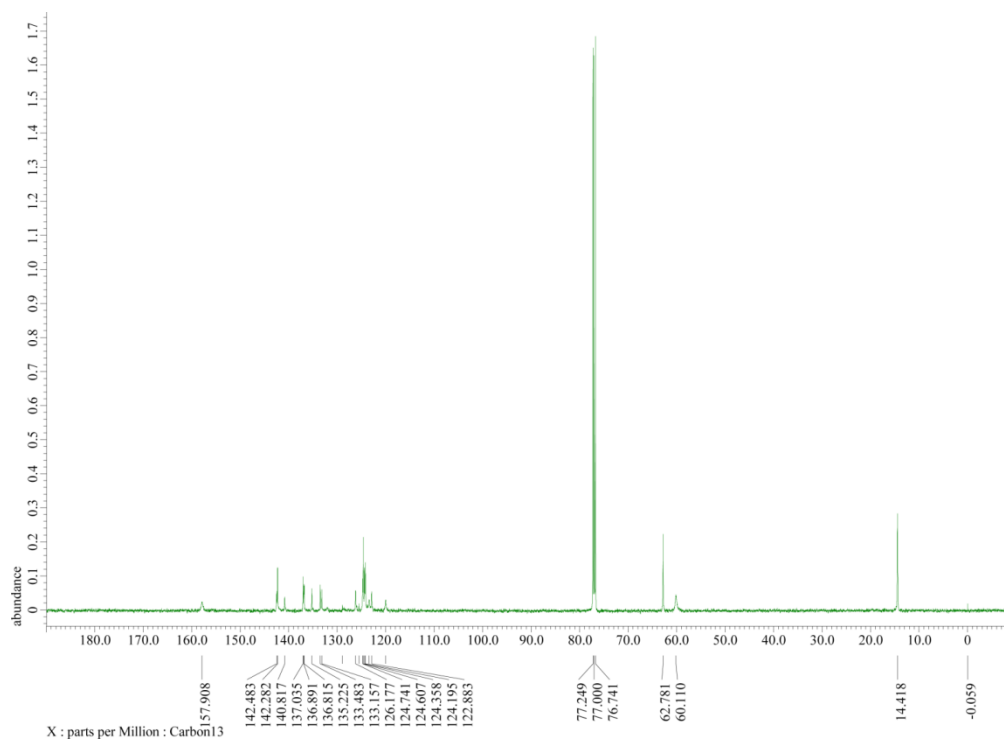




^1H -NMR spectrum (500 MHz, CDCl_3 , Me_4Si)



^{13}C -NMR spectrum (125 MHz, CDCl_3 , Me_4Si)



10. References

1. Ito, K.; Suzuki, T.; Sakamoto, Y.; Kubota, D.; Inoue, Y.; Sato, F.; Tokito, S. *Angew. Chem., Int. Ed.* **2003**, *42*, 1159-1162.
2. Onimura, K.; Matsushima, M.; Yamabuki, K.; Oishi, T. *Polym. J.* **2010**, *42*, 290-297.
3. Jeong, H. G.; Lim, B.; Na, S. I.; Baeg, K. J.; Kim, J.; Yun, J. M.; Kim, D. Y. *Macromol. Chem. Phys.* **2011**, *212*, 2308–2318.
4. Ha, J. S.; Kim, K. H.; Choi, D. H. *J. Am. Chem. Soc.*, **2011**, *133*, 10364-10367.