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Design of Medium Band gap Random Terpolymers Containing Fluorene Linked Diketopyrrolopyrrole and Thiophene Co-monomers: an Experimental and Theoretical Study

B. Sambath Kumar,[ab] E. Varathan,[abc] S. J. Ananthakrishnan, [ab] V. Subramanian *[abc] and N. Somanathan *[ab]

[a] Council of Scientific and Industrial Research (CSIR)-CLRI,Adyar, Chennai – 600 020, Fax: +91-044-24911589; Tel: +91-044-24437189; Email: nsomanathan@rediffmail.com, somanathan@clri.res.in.

[b] CSIR-Network of Institutes for Solar Energy, India.

[c] Academy of Scientific and Innovative Research (AcSIR), Anusandhan Bahavan, 2 Rafi Marg, New Delhi 110001, India.

1. Synthetic procedures

Synthesis of 3,6-di(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (1).

In a two-necked round-bottom flask, 11.2 g (100 mmol) *t*-BuOK was taken. To this 6.54 g (60 mmol) 2-thiophene carbonitrile in 50 mL *t*-amyl alcohol was added. The reaction mixture was heated to 110 ºC. 2.92 g (20 mmol) dimethyl succinate in 16 ml *t*-amyl alcohol was added dropwise over a period of two hours at 110 ºC. Then it was continued for another 2 hours at 110 ºC. Then it was cooled to 65 ºC and diluted with 100 mL of methanol. The reaction mixture was neutralized with glacial acetic acid, filtered and washed with methanol and warm water. A dark purple solid was obtained with 52% yield and it was used directly for next step without further purification.

Synthesis of 2,5-dioctyl-3,6-di(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (2).

2.0 g (50 mmol) of **3**,6-di(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione and 5.0 g (100 mmol) of potassium carbonate were dissolved in 50 mL of DMF. The reaction mixture was heated to 110 ºC . To this 5.21 g (10 mmol) of bromooctane was added drop by drop. Then the reaction mixture was continued for 24 hours at 110 ºC. Then it was cooled poured into 200 ml of water and extracted with chloroform. The organic layer was dried with $MgSO_4$, filtered and concentrated. Then it was purified by column chromatograpy using hexane/chloroform (5:5) gave a purple solid with yield (40%).^{1}H NMR (400 MHz, *CDCl3*) δ 8.93-8.92 (dd, 2H, *J* 3.8, 0.8) 7.77 – 7.42 (2 H, m), 7.27 (2 H, m), 4.05 (4 H, t, *J* 7.5), 1.78 – 1.67 (4 H, m), 1.45 – 1.18 (20 H, m), 0.87 (6 H, m). ; ^{13}C NMR (100 MHz, *CDCl3*) δ 161.32, 139.98, 135.27, 130.66, 129.78, 128.59, 107.66, 42.22, 31.77, 29.95, 29.21, 29.20, 26.88, 22.63, 14.10. Elemental

Analysis, Calculated (%):C, 68.66; H, 7.68; N, 5.34; S, 12.22 Found: C, 68.81; H, 7.58; N, 5.69; S, 12.08.

Synthesis of 3,6-bis(5-bromothiophen-2-yl)-2,5-dioctylpyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (M7).

In a single neck 100 ml round-bottom flask 1.0 g (5 mmol) of **2** was taken and it was dissolved in 50 mL of $CHCl_3$. To this 345 mg (10.5 mmol) of NBS was added in one portion. The reaction mixture was stirred in dark for 48 hours. Then it was poured in water and extracted in chloroform. The crude product was purified by column chromatography using hexane/chloroform (3:7) as an eluent give purple product with 60% yield. ^{1}H NMR (400 MHz, *CDCl3*) δ 8.68 (d, 2H, J 4.2), 7.25(d, 2H, J 4.2), 4.27-3.79 (m, 4H), 1.71 (m, 4H), 1.47 – 1.20 (m, 20H), 0.88 (m, 6H). Elemental Analysis, Calculated (%):C, 52.79; H, 5.61; N, 4.10; S, 9.40 Found: C, 52.61; H, 5.81; N, 4.29; S, 9.28.

Synthesis of 2,5-dibromothiophene-3-carbaldehyde (3).

To a two-necked round-bottom flask 5.0 g (45 mmol) of 3-thiophenecarboxaldehyde was taken with 50 mL of DMF. 17.45 g (98 mmol) of NBS was added portion wise over a period of 15 minutes. Then it was allowed to stirred at room temperature for 24 hours. After that the reaction mixture was poured in water and extracted in DCM. The organic layer was dried with $MgSO_4$, filtered and concentrated. Then it was purified by column chromatograpy using hexane/chloroform (9:1) gave a white solid. (yield 80%). ^{1}H NMR (400 MHz, *CDCl3*) δ 9.78 (s,1H), 7.34-7.27 (s, 1H); ^{13}C NMR (100 MHz, *CDCl3*) δ 183.22, 139.28, 128.66, 124.34, 113.41. Elemental Analysis, Calculated (%): C, 22.25; H, 0.75; S, 11.88. Found: C, 22.58; H, 0.89; S, 11.67.

Synthesis of 2-((2,5-dibromothiophen-3-yl)methylene)malononitrile (M4)

In a single neck round bottom flask 1.0 g (3.7 mmol) of **3,** 0.367 g (5.5 mmol) of malonitrile was taken it was dissolved in 50 mL of methanol. To this 0.456 g (5.5 mmol) of piperidene was added. The reaction mixture was stirred at room temperature for 24 hours. The red solid was filtered off and recrystallised in ethanol gives (yield 75%).^{1}H NMR (400 MHz, *CDCl3*) δ 7.70 (s, 1H), 7.90 (s, 1H); ^{13}C NMR (100 MHz, *CDCl3*) δ 148.56, 133.67, 127.41, 126.58, 115.05, 113.39, 112.16, 83.04. Elemental Analysis, Calculated C, 30.22; H, 0.63; N, 8.81; S, 10.08. Found: C, 30.37; H, 0.71; N, 8.69; S, 10.17. EI mass: 317.9880 (calcd for $C_8H_2Br_2N_2S$: 317.9879)

Synthesis of (E)-ethyl 2-cyano-3-(2,5-dibromothiophen-3-yl)acrylate. (M5)

In a single neck round bottom flask 1.0 g (3.7 mmol) of **3,** 0.627 g (5.5 mmol) of ethyl cyanoacetate was taken and it was dissolved in 50 mL of methanol. To this 0.456 g (5.5 mmol) of piperidene was added. The reaction mixture was stirred at room temperature for 24 hours. The pale red solid was filtered off and recrystallised in ethanol gives (yield 69%).^{1}H NMR (400 MHz, *CDCl3*) δ 8.16 (1 H, s), 8.01 (1 H, s), 4.39 (1 H, d, *J* 7.1), 1.40 (1 H, t, *J* 7.1).; ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.17, 143.93, 134.09, 128.15, 125.04, 115.03, 114.01, 103.43, 63.02, 14.17. Elemental Analysis, Calculated (%):C, 32.90; H, 1.93; N, 3.84; S, 8.78 Found: C, 33.01; H, 2.09;N,3.76; S, 8.97. EI mass: 365.0411 (calcd for $C_{10}H_7Br_2NO_2S$: 365.0411)

Synthesis of (E)-3-(2,5-dibromothiophen-3-yl)-2-(thiophen-2-yl)acrylonitrile (M6)

In a single neck round bottom flask 1.0 g (3.7 mmol) of **3,** 0.678 g (5.5 mmol) 2-thiopheneacetonitrile of was taken and it was dissolved in 50 mL of methanol. To this 0.456 g

(5.5 mmol) of piperidene was added. The reaction mixture was stirred at room temperature for 24 hours. The green solid was filtered off and recrystallised in ethanol gives (yield 71%).^{1}H NMR (400 MHz, *CDCl3*) δ 7.93 (s, 1H), 7.40 (d, 1H, J 3.6), 7.35 (d, 1H, *J* 5.0), 7.26 (s, 1H), 7.09-7.07 (t, 1H); ^{13}C NMR (100 MHz, *CDCl3*) δ 138.55, 135.19, 129.41, 128.36, 127.86, 127.02, 117.96, 116.29, 113.10, 106.88. Elemental Analysis, Calculated (%):C, 35.22; H, 1.34; N, 3.73; S, 17.10. Found: C, 35.41; H, 1.21; N, 3.69; S, 17.28. EI mass: 375.1022 (calcd for $C_{11}H_5Br_2NS_2$: 375.1021)

General Procedure for Polymerization

Six random copolymers were synthesized using Suzuki coupling polymerization. 9,9-dihexylfluorene-2,7-diboronic acid bis(1,3-propanediol) ester (1 eq), equimolar amount of 3,6-bis(5-bromothiophen-2-yl)-2,5-dihexylpyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione(M7) (0.5 eq) and variable thiophene comonomer M1, M2, M3, M4, M5, and M6 (0.05 eq) was taken in 100 ml round-bottom flask. To this 2 M aqueous K_2CO_3 (5 mL), tetrakis(triphenylphosphine)palladium (0.01 eq) and Aliquat 336 three drops in 10 mL of anhydrous toluene was stirred at 90^{o}C for 48 hours under N_2 atmosphere. The reaction mixture was cooled to room temperature and poured in 200 mL methanol. The polymer was filtered off and it was further purified by Soxhlet extractions with methanol, acetone, hexane, and $CHCl_3$. The $CHCl_3$ fraction was concentrated and reprecipit ation in methanol gives dark green solid.

Synthesis of PTFDPP (P1)

9,9-dihexylfluorene-2,7-diboronic acid bis(1,3-propanediol) ester, M7 and M1, tetrakis(triphenylphosphine)palladium (3.0 mg, 2.6 μmol), and toluene (10 mL) for this polymerization. ^{1}H NMR (CDCl3, ppm): δ 9.02 (br, 2H), 7.76−7.47 (br, 14H), 7.25 (br, 2H),

4.18 (br, 4H), 2.03−1.83 (br, 12H), 1.39−0.90 (br, 52H), 0.77-0.71 (br, 18H). Elemental Analysis, Calculated (%):C, 79.32; H, 8.40; N, 2.20; S, 7.56 Found: C, 79.81; H, 8.72; N, 2.59; S, 7.88.

Synthesis of PBTFDPP (P2)

9,9-dihexylfluorene-2,7-diboronic acid bis(1,3-propanediol) ester, M7 and M2, tetrakis(triphenylphosphine)palladium (3.0 mg, 2.6 μmol), and toluene (10 mL) for this polymerization. ^{1}H-NMR (CDCl3, 400 MHz): δ (ppm) 9.02 (br, 2H), 7.72−7.59 (br, 14H), 7.36 (br, 2H), 7.26 (br, 2H), 4.19 (br, 4H), 2.06−1.86 (br, 12H), 1.40−1.10 (br, 52H), 0.95-0.77 (br, 18H). Elemental Analysis, Calculated (%): C, 78.06; H, 8.04; N, 2.07; S, 9.47 Found: C, 78.61; H, 8.57; N, 2.57; S, 9.76.

Synthesis of PTTFDPP (P3)

9,9-dihexylfluorene-2,7-diboronic acid bis(1,3-propanediol) ester, M7 and M3, tetrakis(triphenylphosphine)palladium (3.0 mg, 2.6 μmol), and toluene (10 mL) for this polymerization. ^{1}H NMR (CDCl3, ppm): δ δ 9.02 (br, 2H), 7.76−7.58 (br, 14H), 7.34 (br, 2H), 7.21−7.17 (br, 2H), 4.18 (br, 4H), 2.06−1.85 (br, 12H), 1.61−1.39 (br, 22H), 1.09−0.93 (br, 30H), 0.77-0.75 (br, 18H). Elemental Analysis, Calculated (%):C, 76.94; H, 7.72; N, 1.95; S, 11.16. Found: C, 77.38; H, 8.04; N, 2.19; S, 11.45.

Synthesis of PTDCNFDPP (P4)

9,9-dihexylfluorene-2,7-diboronic acid bis(1,3-propanediol) ester, M7 and M4, tetrakis(triphenylphosphine)palladium (3.0 mg, 2.6 μmol), and toluene (10 mL) for this polymerization. ^{1}H NMR (CDCl3, ppm): δ 9.02 (br, 2H), 7.89−7.26 (br, 15H), 6.87 (br, 1H),

4.14 (br, 4H), 2.07−1.86 (br, 12H), 1.51−1.10 (br, 52H), 0.93-0.77(br, 18H). Elemental Analysis, Calculated (%): C, 78.41; H, 7.93; N, 4.16; S, 7.14. Found: C, 78.98; H, 8.17; N, 4.73; S, 7.33

Synthesis of PTCNEFDPP (P5)

9,9-dihexylfluorene-2,7-diboronic acid bis(1,3-propanediol) ester, M7 and M5, tetrakis(triphenylphosphine)palladium (3.0 mg, 2.6 μmol), and toluene (10 mL) for this polymerization. ^{1}H NMR (CDCl3, ppm): δ 8.94 (br, 2H), 7.82−7.42 (br, 16H), 4.11 (br, 4H), 3.68 (br, 2H), 2.08 (br, 12H), 1.44−1.27 (br, 22H), 1.11-0.94 (br, 30H), 0.78 (br, 21H). Elemental Analysis, Calculated (%):C, 77.49; H, 8.02; N, 3.01; S, 6.90. Found: C, 77.96; H, 8.63; N, 3.56; S, 7.21.

Synthesis of PTPTFDPP (P6)

9,9-dihexylfluorene-2,7-diboronic acid bis(1,3-propanediol) ester, M7 and M6, tetrakis(triphenylphosphine)palladium (3.0 mg, 2.6 μmol), and toluene (10 mL) for this polymerization. ^{1}H NMR (CDCl3, ppm): δ δ 9.03 (br, 2H), 7.76−7.73 (br, 4H), 7.70−7.54 (br, 8H), 7.49−7.41 (br, 4H), 7.24 (br, 2H), 7.10 (br, 1H), 4.19 (br, 4H), 2.08−1.85 (br, 12H), 1.63−1.52 (br, 6H), 1.39−1.24 (br, 16H), 1.10 (br, 30H), 0.95-0.77 (br, 18H). Elemental Analysis, Calculated (%):C, 77.79; H, 7.82; N, 2.99; O, 2.28; S, 9.13. Found: C, 78.07; H, 8.11; N, 3.12; S, 9.48.

2. ^{1} H-NMR and ^{13}C-NMR spectra

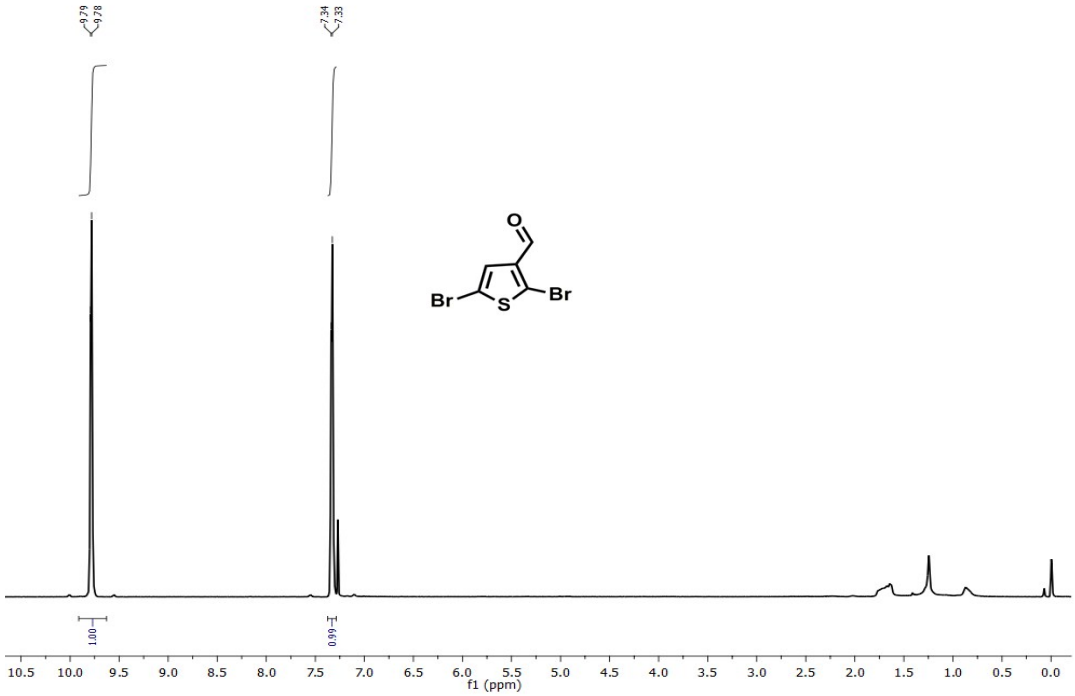


Fig. S1 ^{1} H-NMR of compound 3 in $CDCl_3$.

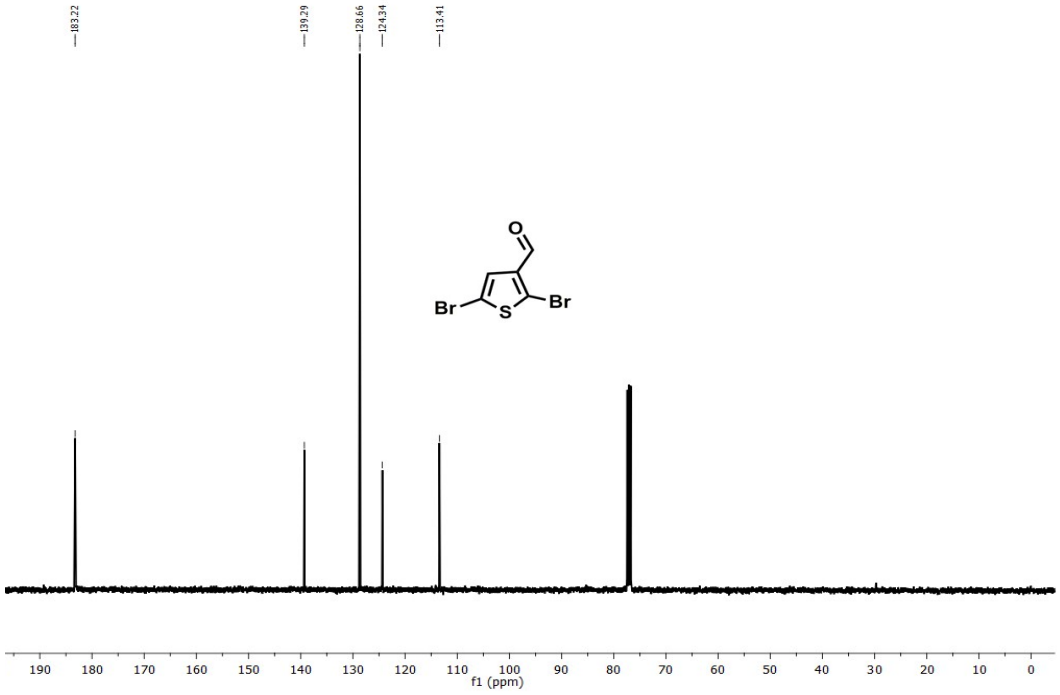


Fig. S2 ^{13} C-NMR of compound 3 in $CDCl_3$.

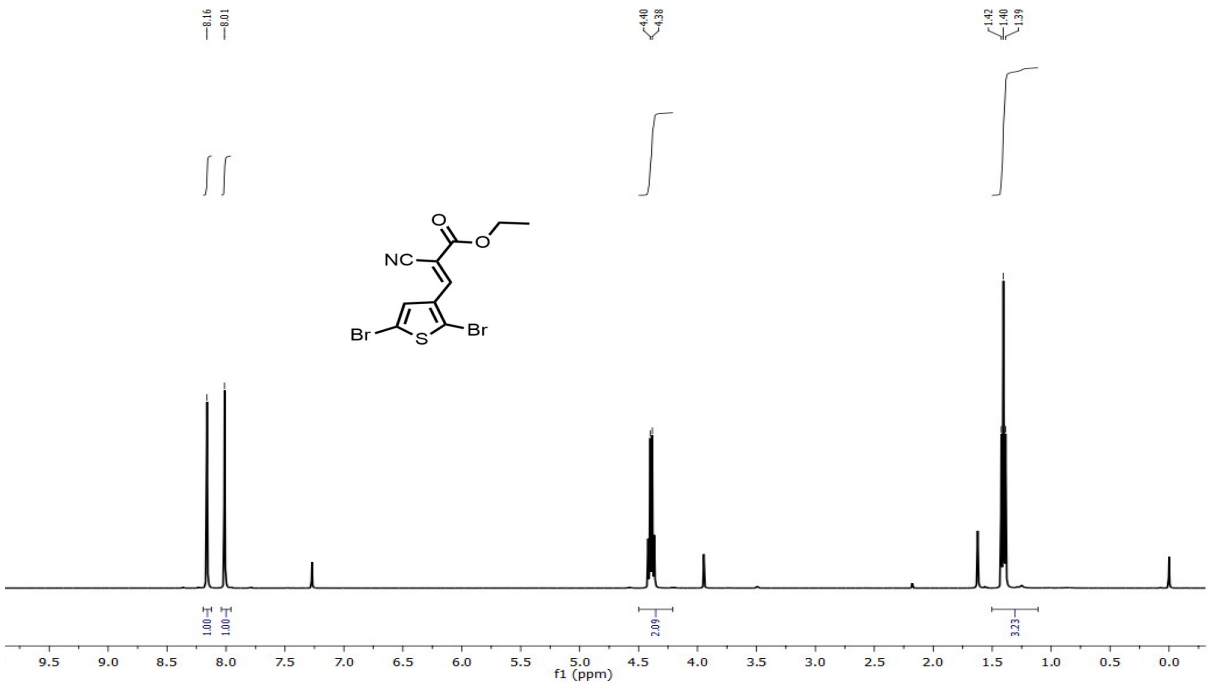


Fig. S3 [1] H-NMR of compound M5 in $CDCl_3$.

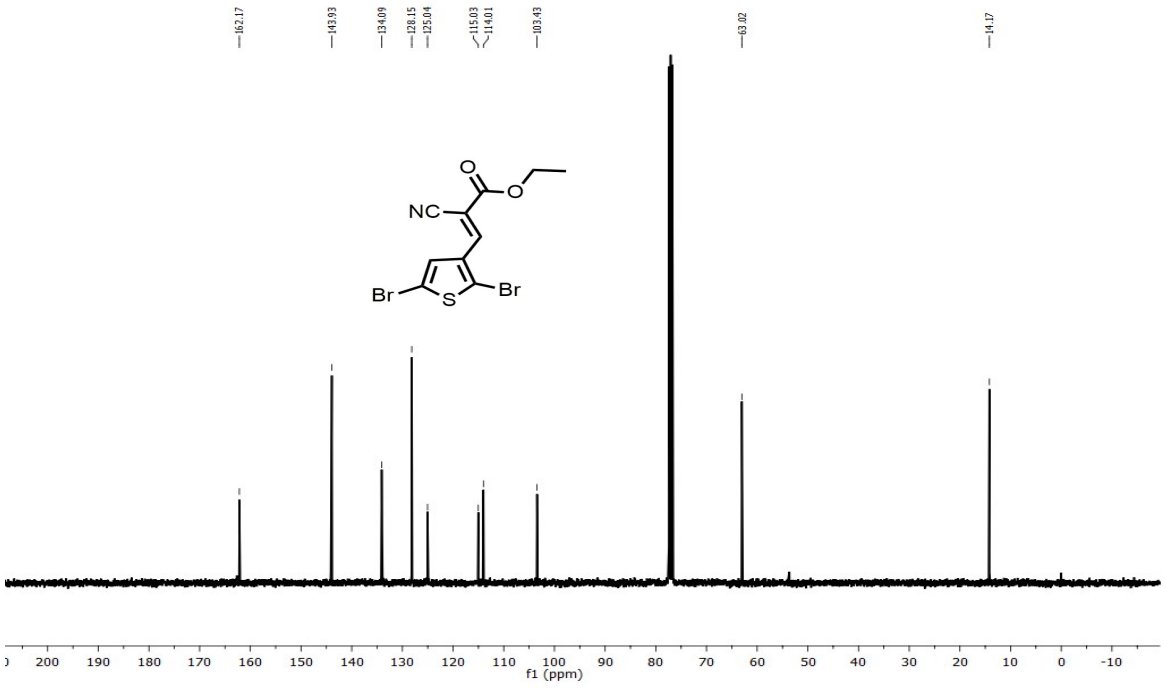


Fig. S4 [13] C-NMR of compound M5 in $CDCl_3$.

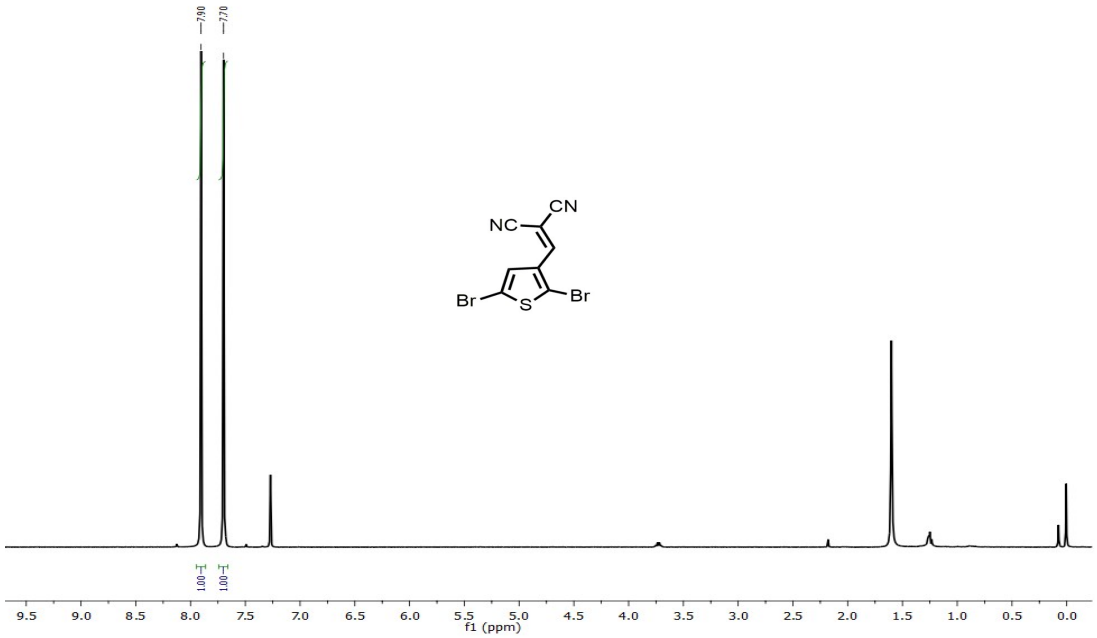


Fig. S5 [1] H-NMR of compound M4 in $CDCl_3$.

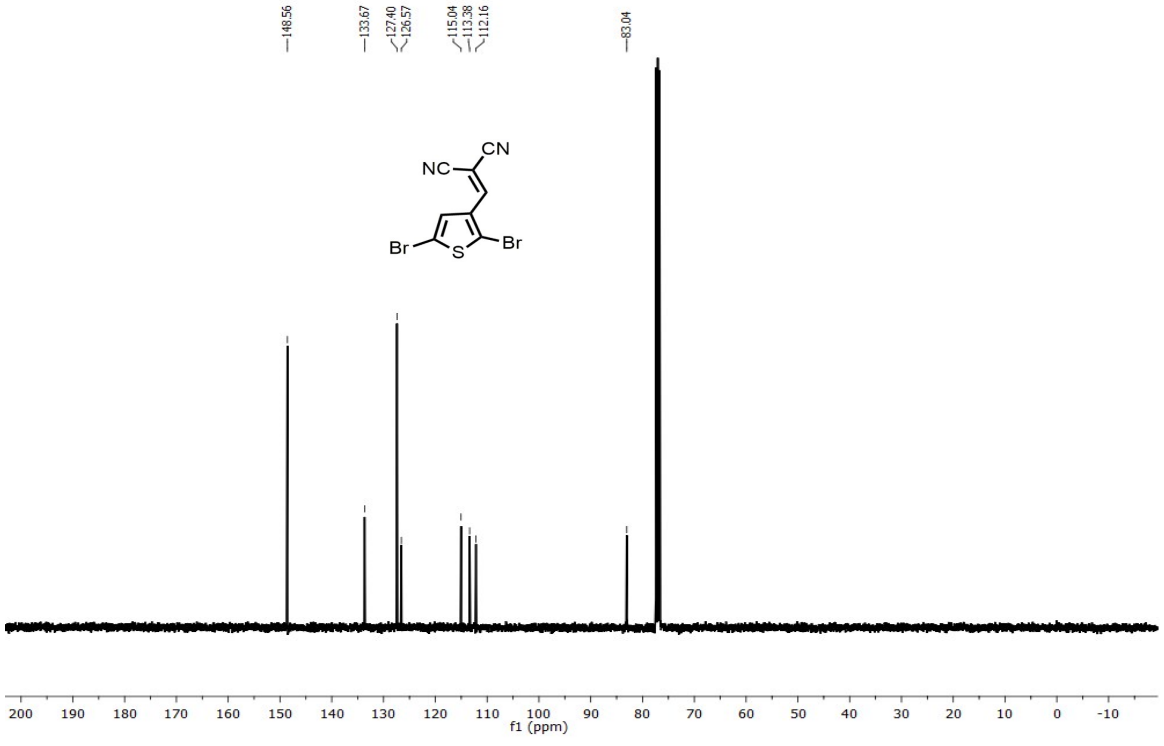


Fig. S6 [13] C-NMR of compound M4 in $CDCl_3$.

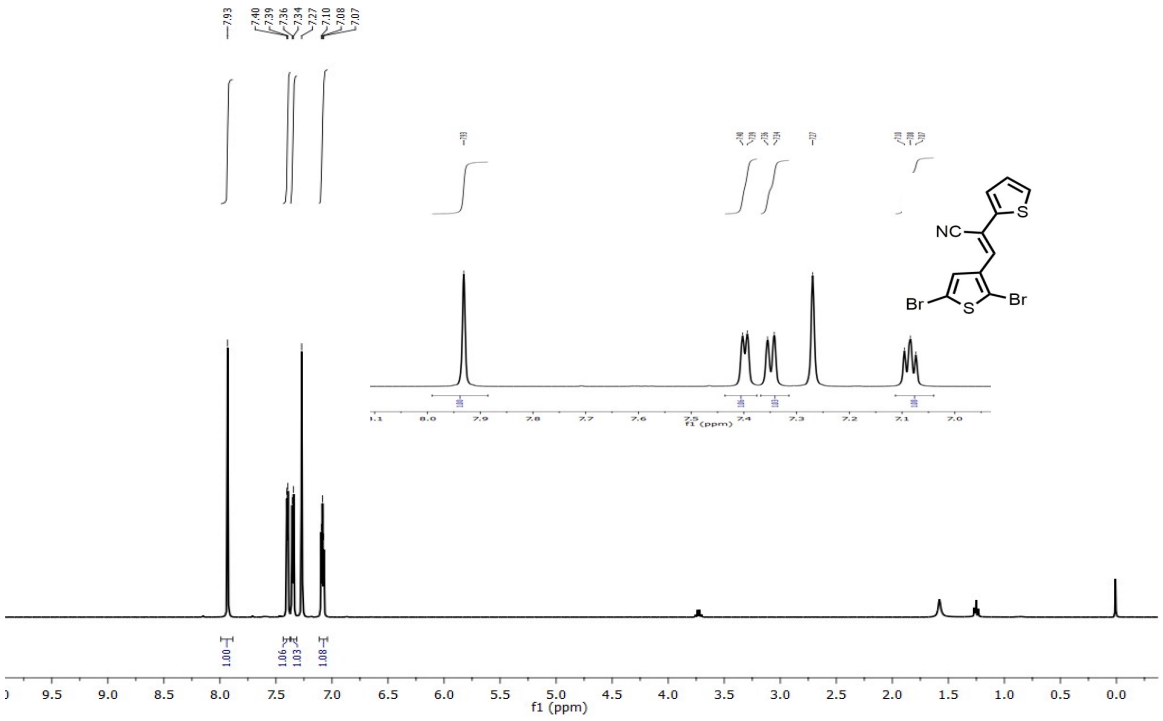


Fig. S7 [1] H-NMR of compound M6 in $CDCl_3$.

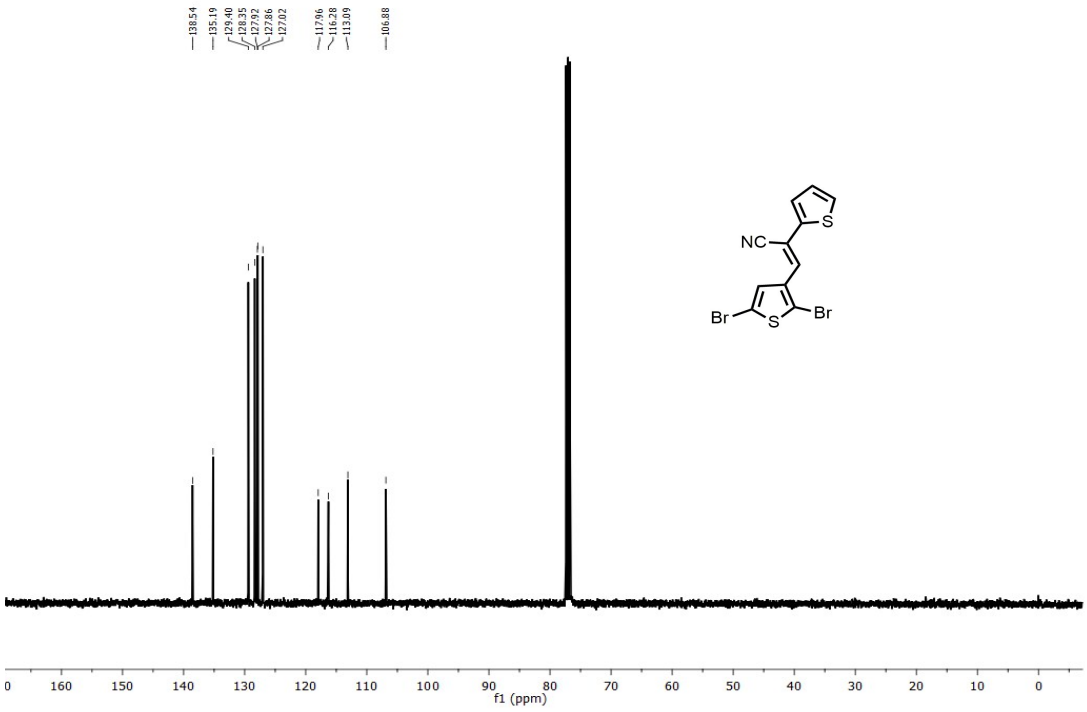


Fig. S8 [13] C-NMR of compound M6 in $CDCl_3$.

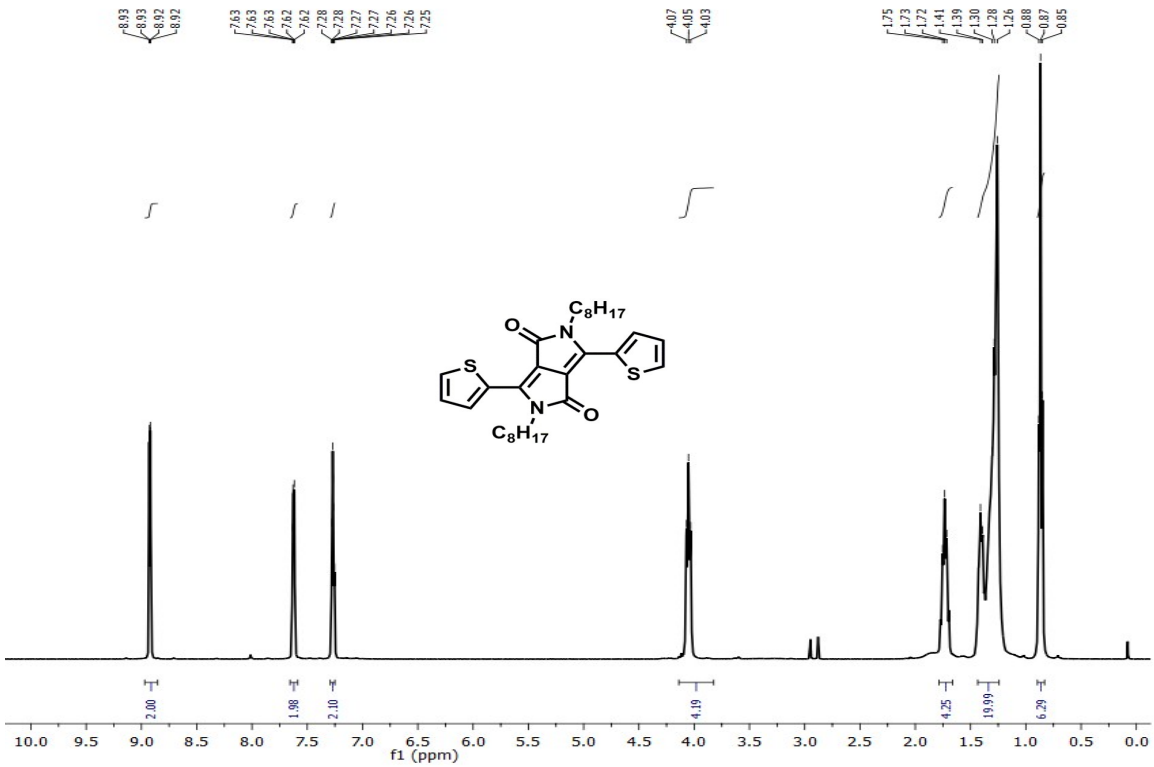


Fig. S9 [1] H-NMR of compound 2 in $CDCl_3$.

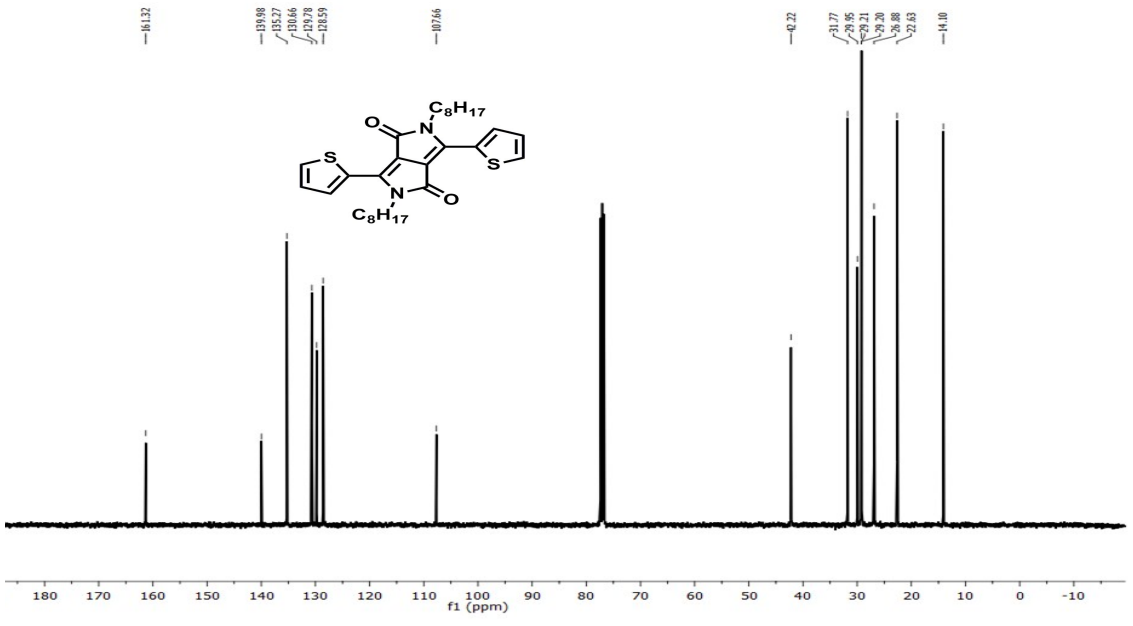


Fig. S10 [13] C-NMR of compound 2 in $CDCl_3$.

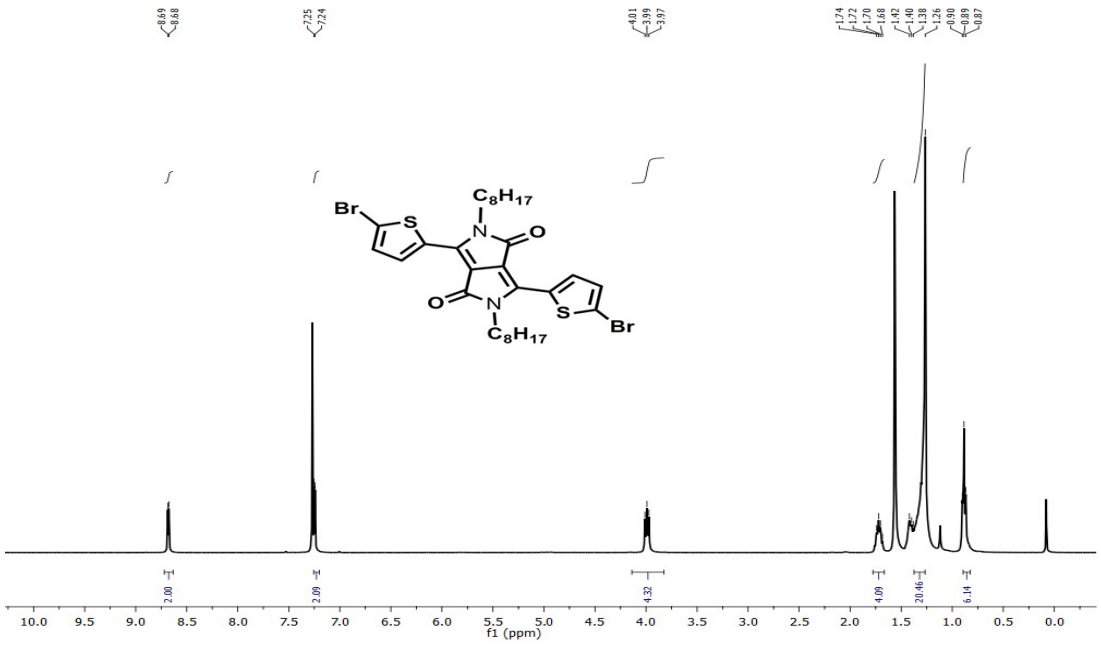


Fig. S11 [1] H-NMR of compound M7 in $CDCl_3$.

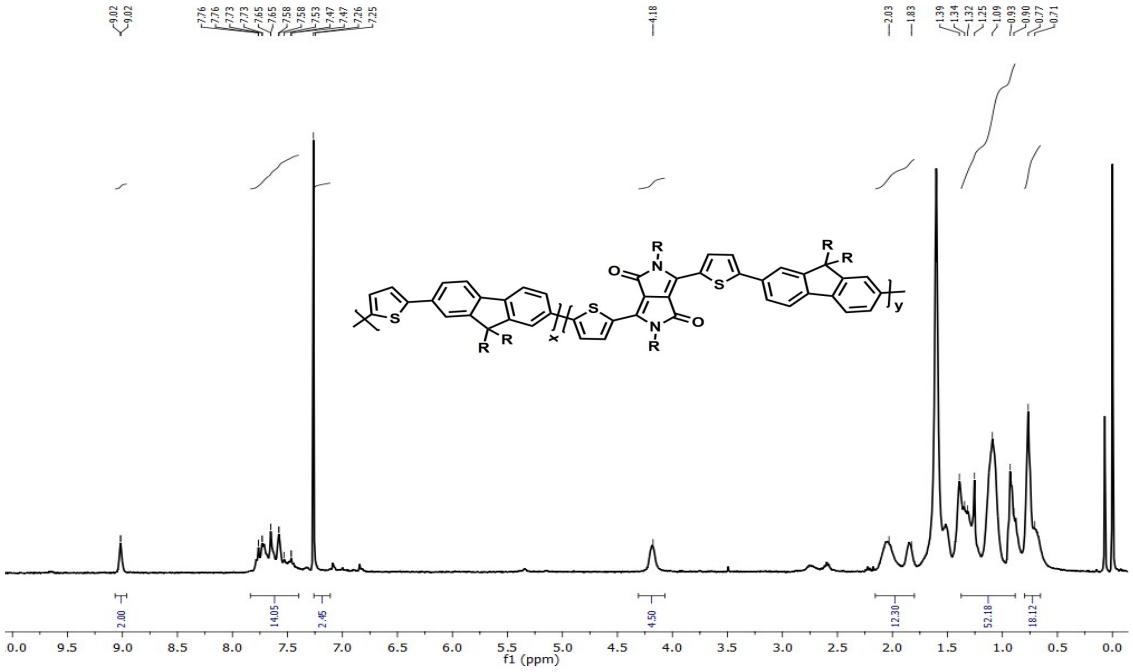


Fig. S12 [1] H-NMR of Polymer P1 in $CDCl_3$.

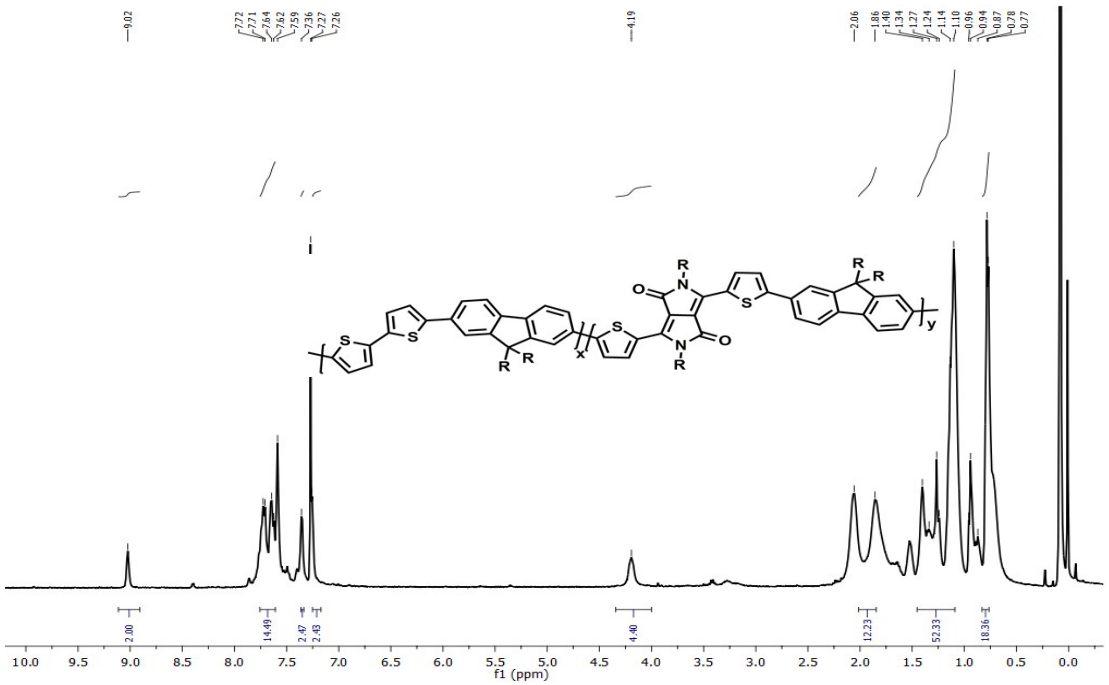


Fig. S13 [1] H-NMR of Polymer P2 in $CDCl_3$.

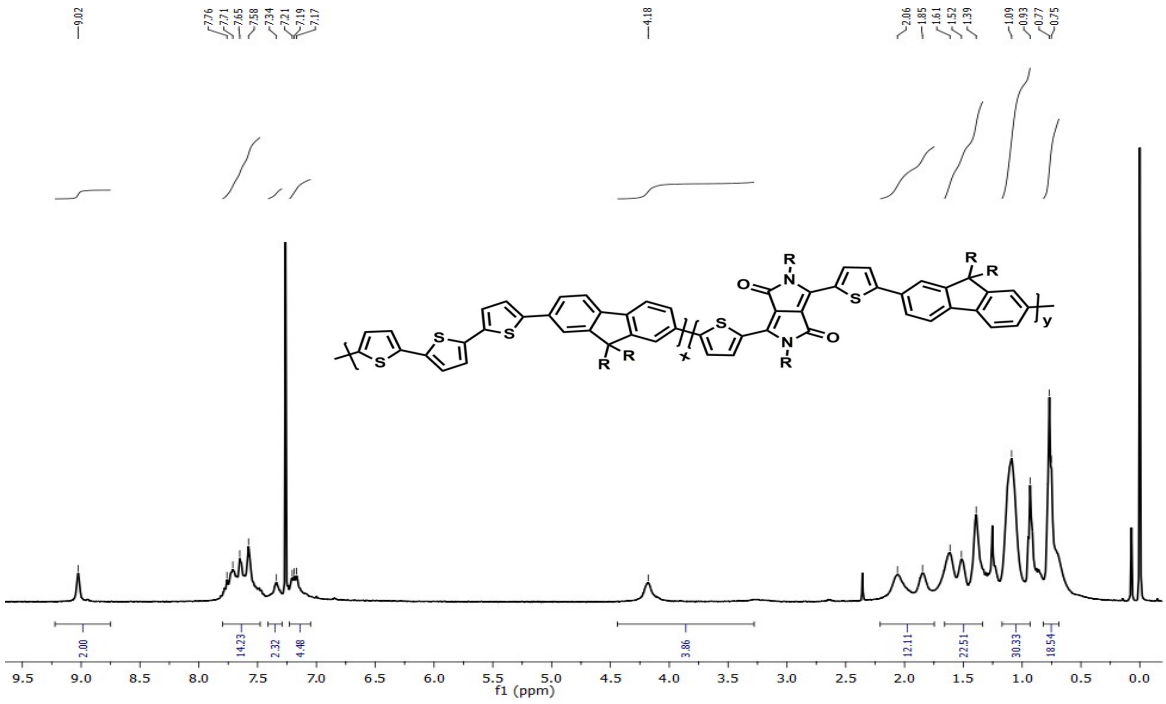


Fig. S14 [1] H-NMR of Polymer P3 in $CDCl_3$.

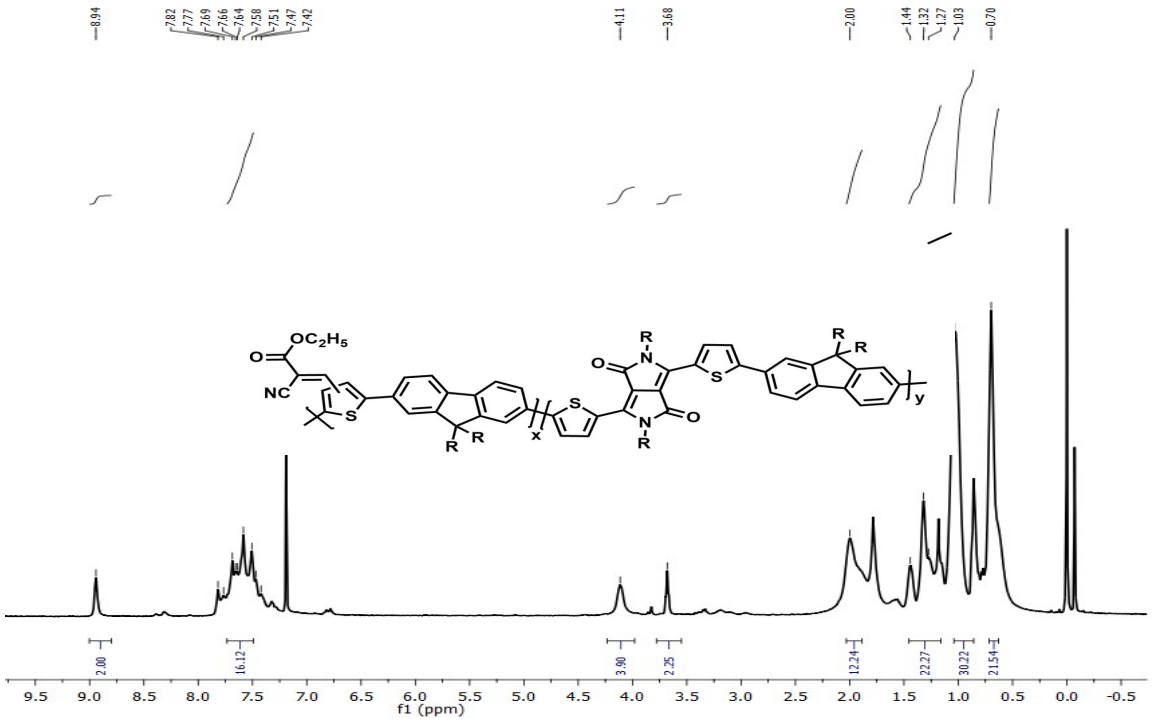


Fig. S15 [1] H-NMR of Polymer P5 in $CDCl_3$.

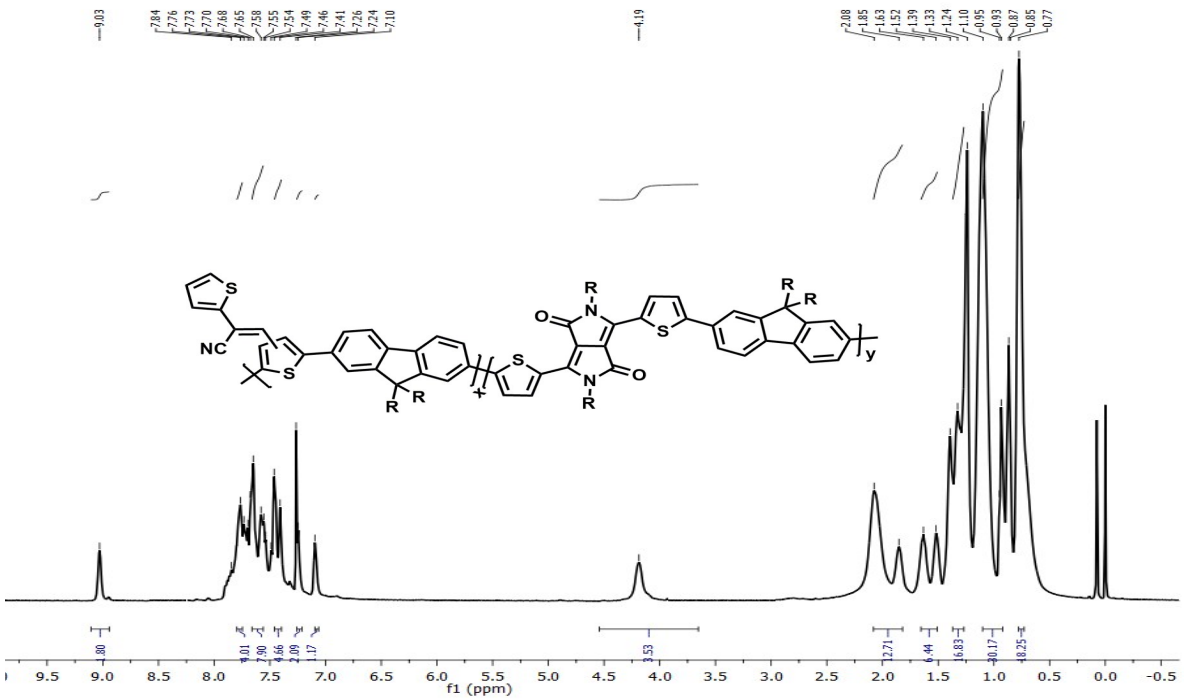


Fig. S16 [1] H-NMR of Polymer P6 in $CDCl_3$.

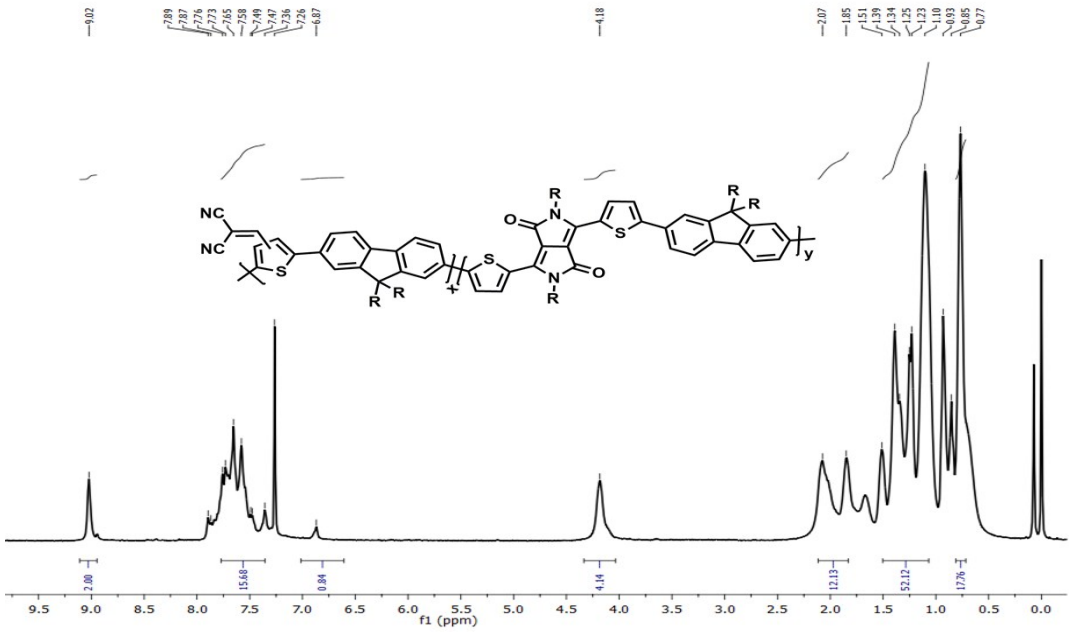


Fig. S17 [1] H-NMR of Polymer P4 in $CDCl_3$.

3. FT-IR spectra

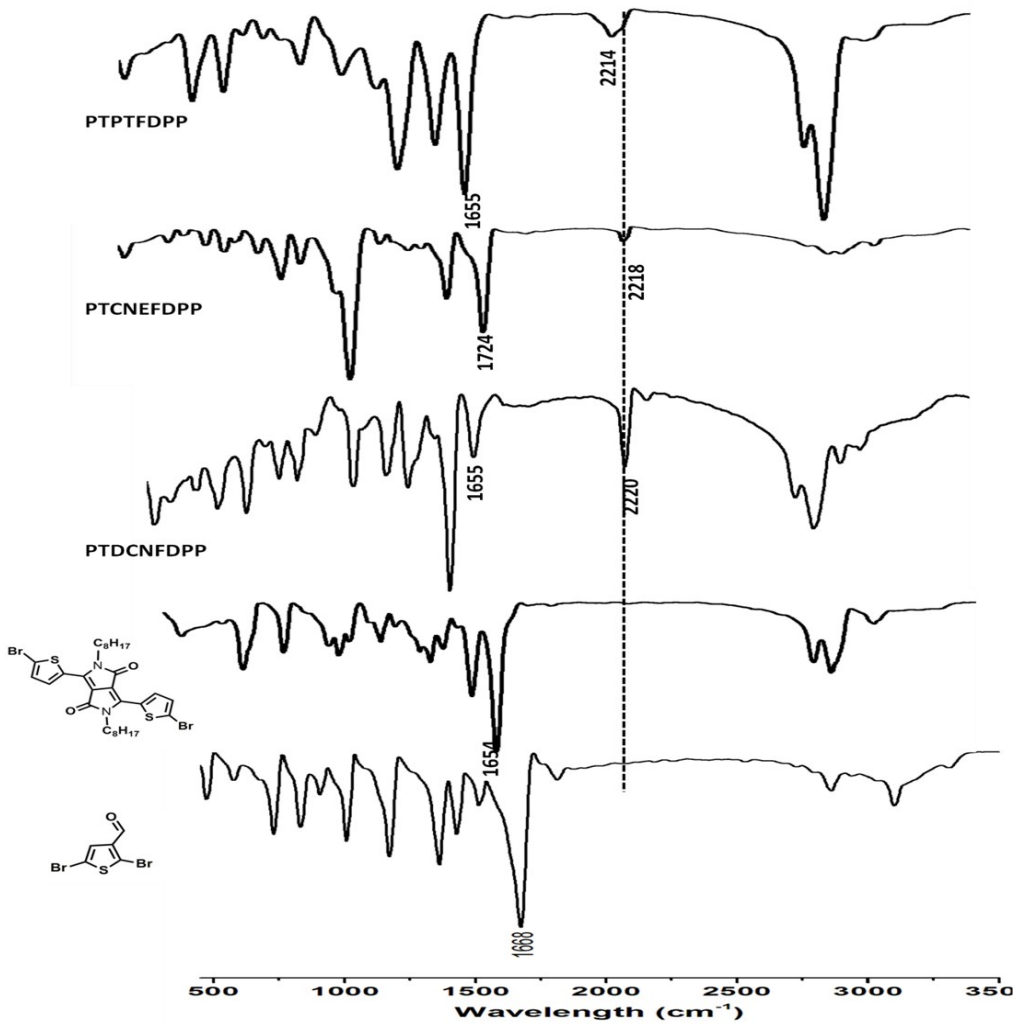


Fig. S18 FT-IR spectra of the monomers (3 & M7) and copolymers (P4, P5 & P6)

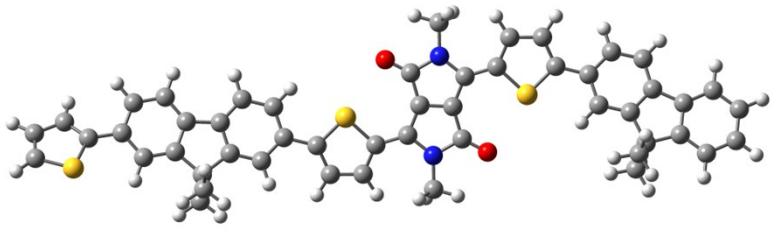
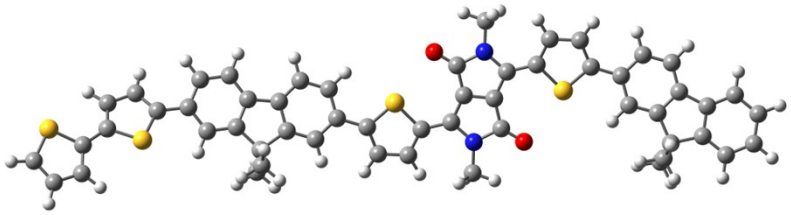
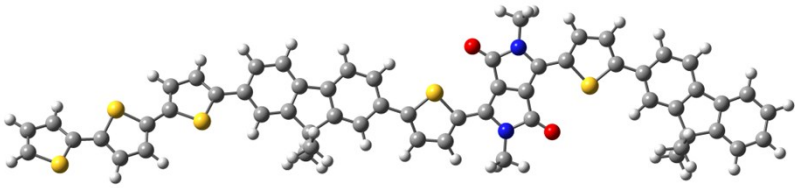
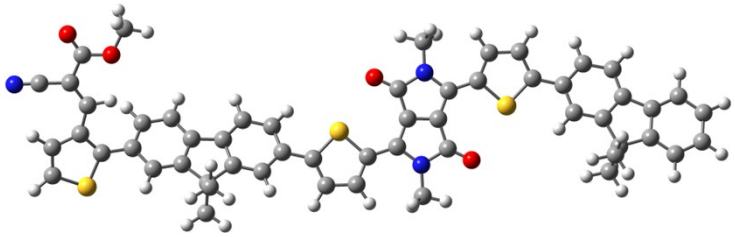
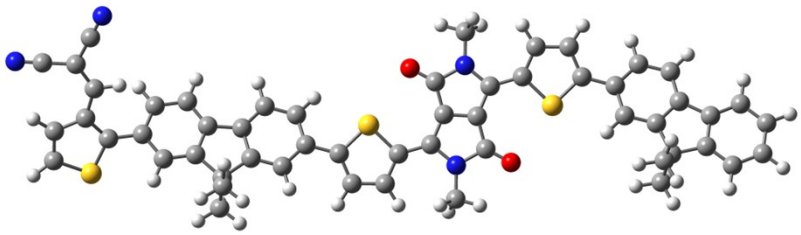
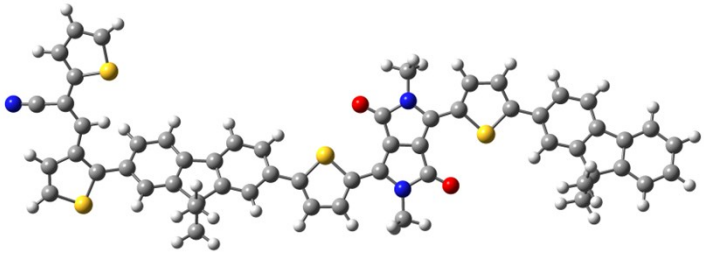
Polymer	
PTFDPP	
PBTFDPP	
PTTFDPP	
PTCNEFDPP	
PTDCNFDPP	
PTPTFDPP	

Fig. S19. Optimized geometries at B3LYP/6-31G* method.

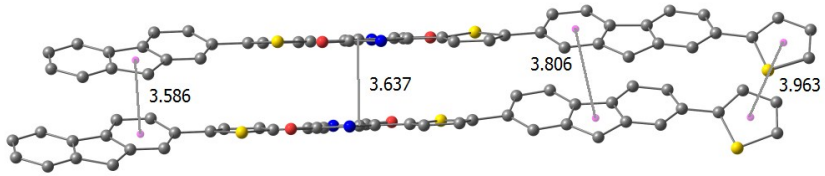
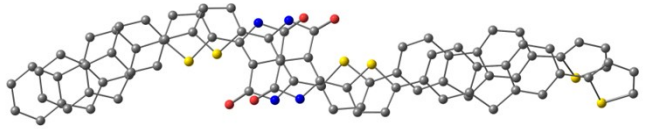
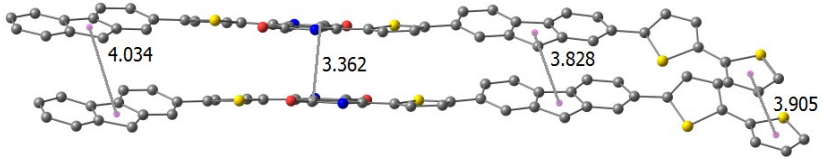
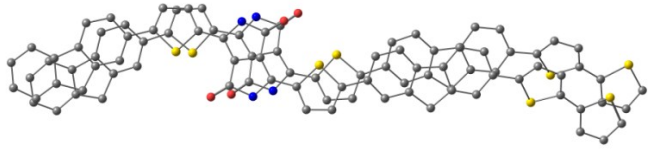
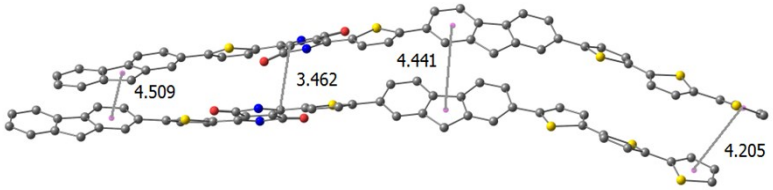
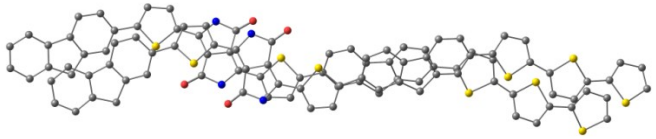
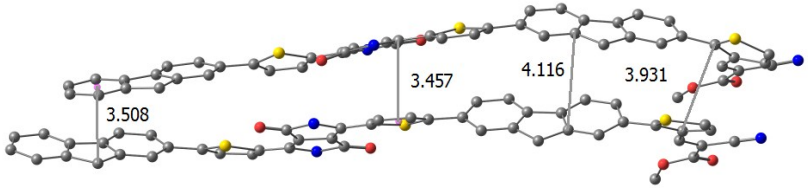
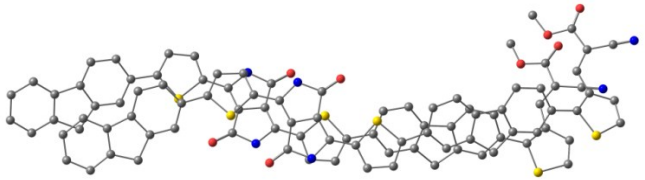
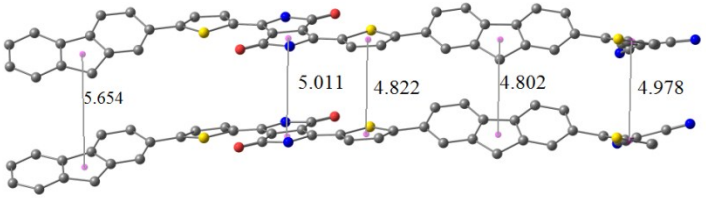
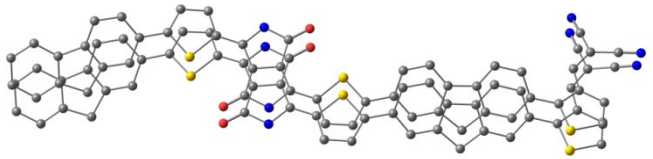
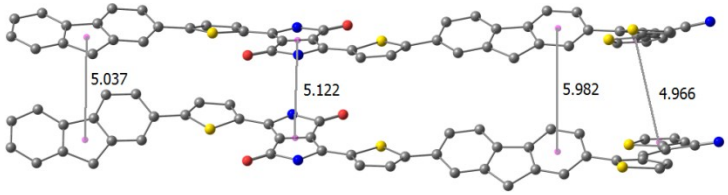
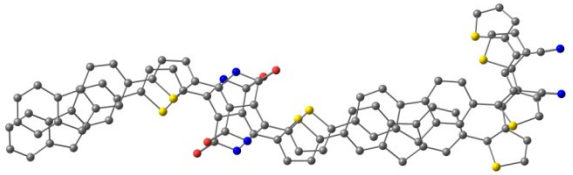
Polymer	Side face	Front face
PTFDPP		
PBTFDPP		
PTTFDPP		
PTCNEFDPP		
PTDCNFDPP		
PTPTFDPP		

Fig. S20. Optimized dimer molecules at M05-2X/6-31G* level

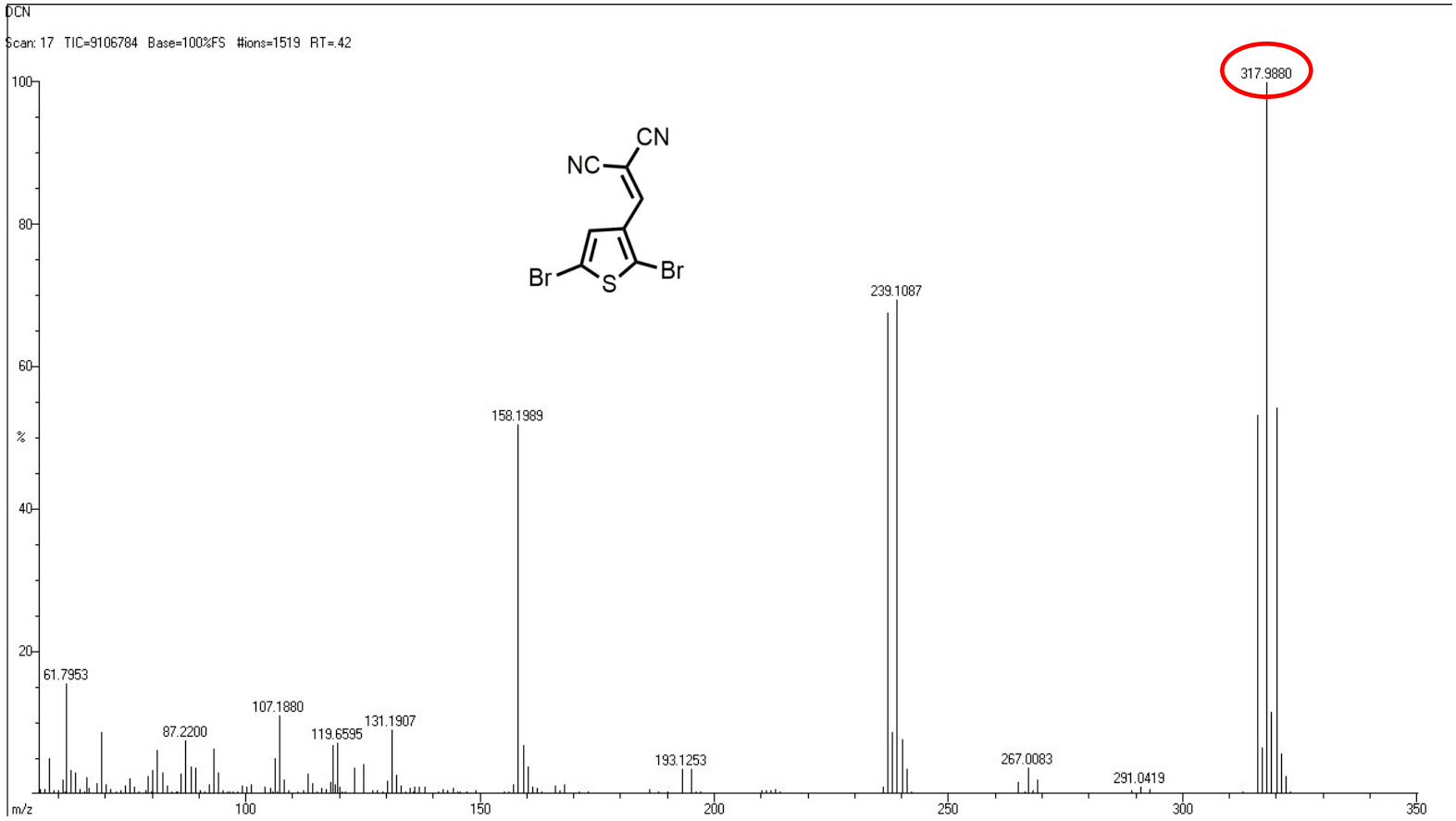


Fig. S21. Electron ionization spectrum of monomer M4.

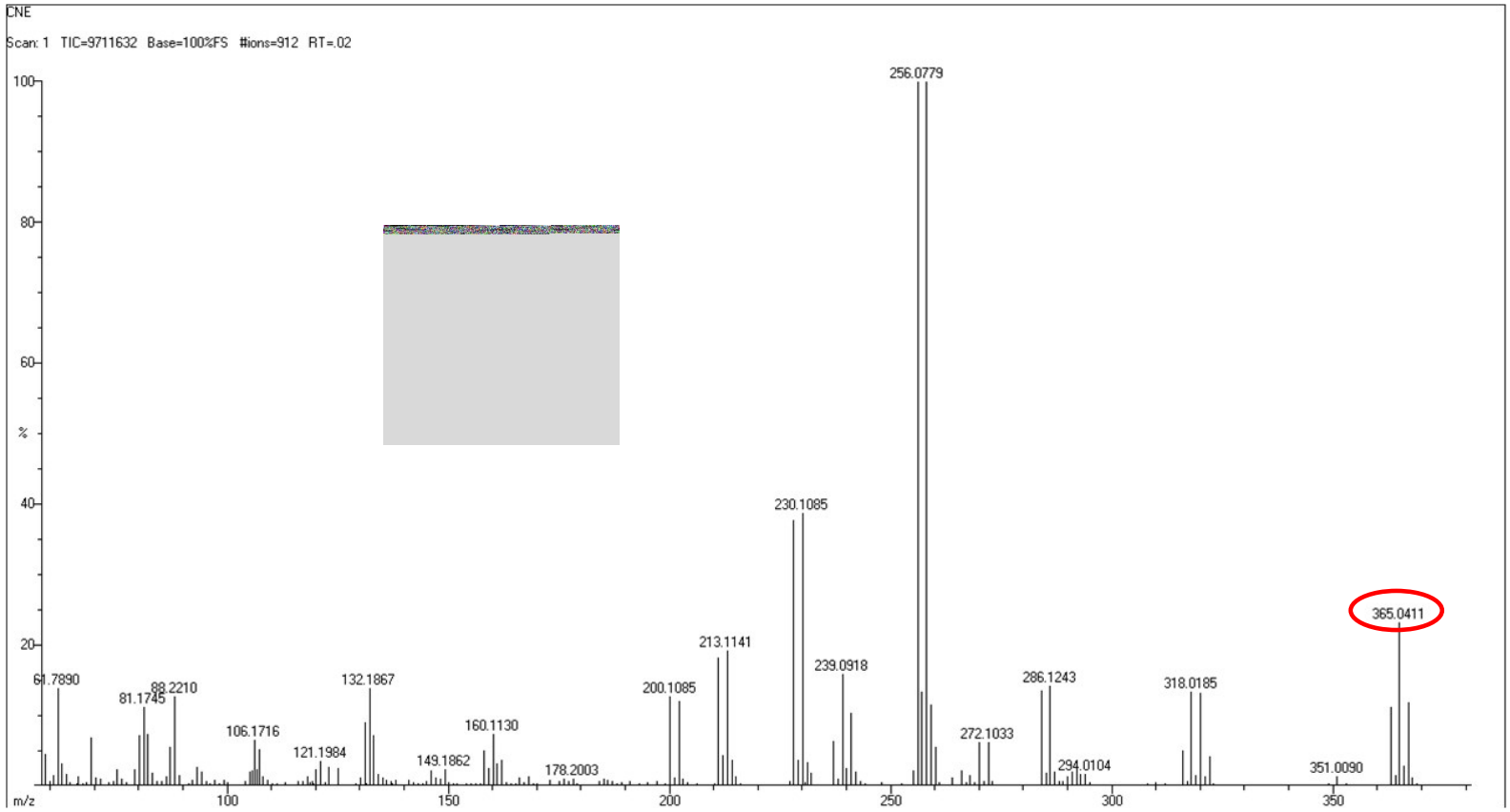


Fig. S22. Electron ionization spectrum of monomer M5.

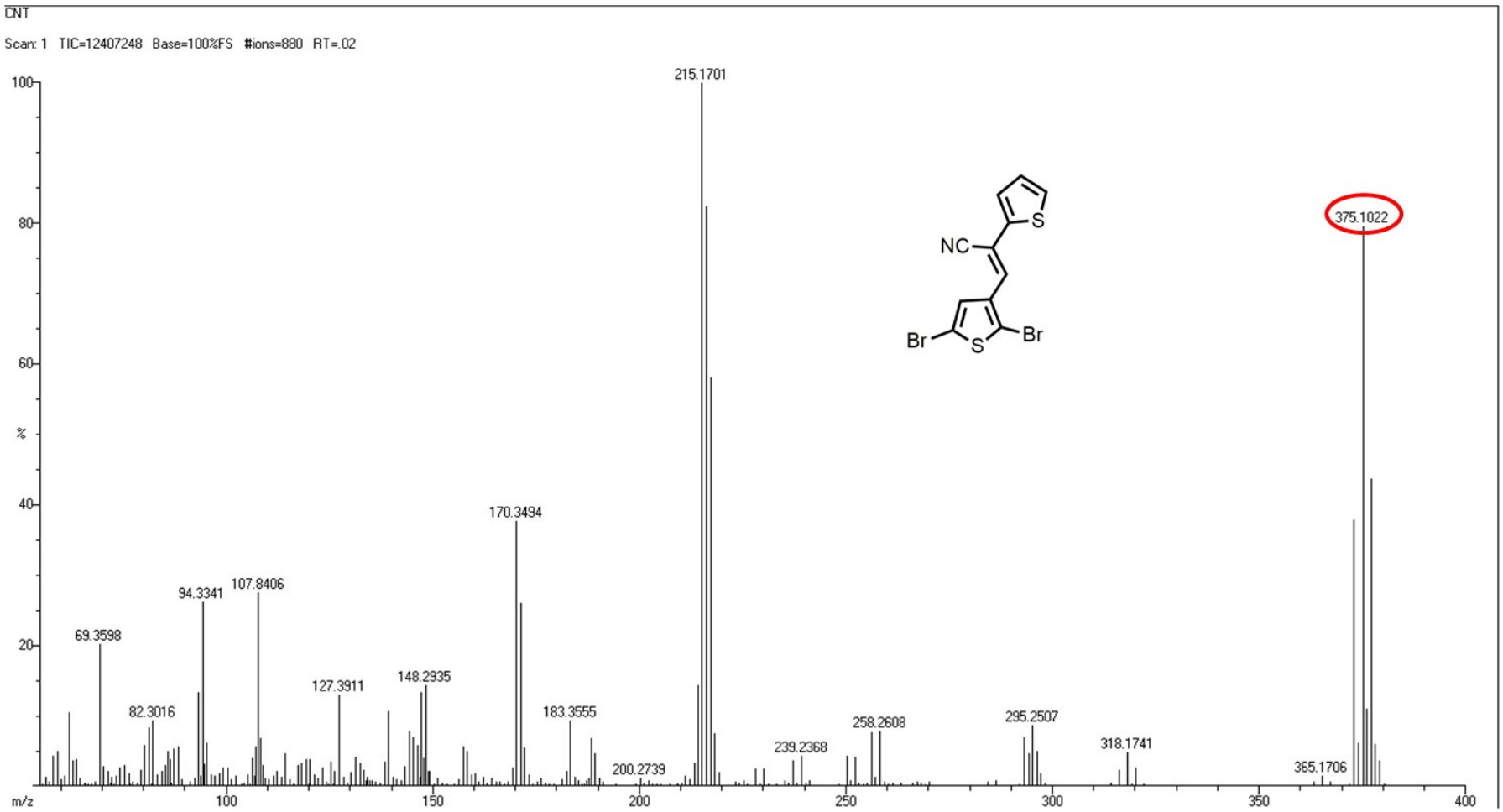


Fig. S23 Electron ionization spectrum of monomer M6.