Enhanced Device Performance of Organic Solar Cells via Reduction of the Crystallinity in the Donor Polymer

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Supporting Information

1. Cyclic Voltammogram

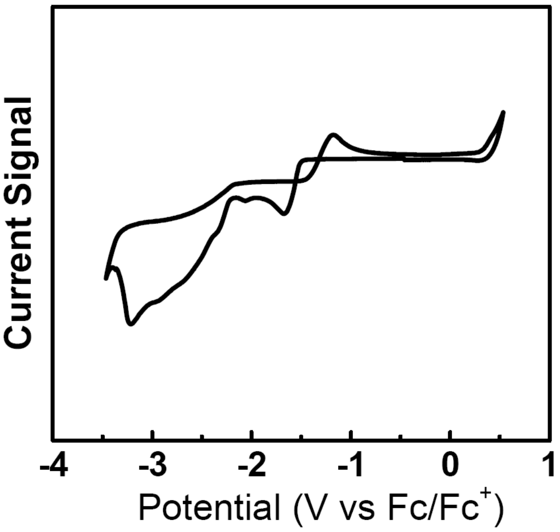

Figure S1. Cyclic Voltammograms of PPVQT-C8

2. Synthesis

4-octylthiophene-2-boronic acid pinacol ester (1)

3-Octylthiophene (5.3 g, 30 mmole) in THF was slowly added to the premixed solution of n-butyllithium (14 mL, 2.5 M in THF) and tetramethylethylene-diamine (5.4 mL, 36 mmole) in THF at -78°C. After stirring for 4 hr, the mixture was added isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (7.4 mL. 36 mmole) and then slowly warmed to room temperature overnight. The mixture was diluted with chloroform and washed with water and brine. The organic layer was separated and dried over MgSO4, and then concentrated under reduced pressure. The desired product **compound (1)** was obtained by column chromatography (silica gel, hexane-chloroform (20:1) as eluent) as a colorless oil. 1H NMR (300 MHz, CDCl3) 7.47 (d, 1H), 7.21 (d, 1H), 2.62 (t, 2H), 1.61 (m, 2H), 1.28 (m, 10H), 0.88 (t, 3H). (Fig. S3)

3,3‴-dialkylquarterthiophene (2)

Compound (1) (2.1 g, 6.5 mmole) and 5,5'-dibromo-2,2'-bithiophene (1.0 g, 3.1 mmole) were dissolved in 100 mL of toluene with stirring. After adding K2CO3 solution (4.5 g in 10 mL of water) and palladium complex (750 mg, 5 mol% vs. **compound (1)**), Pd(PPh3)4, the reaction mixture was stirred at 90°C for overnight. After the reaction was completed, the reaction mixture was cooled to room temperature and filtered through a Celite pad, then concentrated under reduced pressure. The residue was dissolved in chloroform and washed with a saturated ammonium chloride solution and brine. The organic layer was separated and dried over MgSO4, then condensed to brown solid under vacuum. The solid was purified by column chromatography (silica gel, hexane as eluent) to yield the desired product (**compound (2)**); yield= 81%, 1H NMR (300 MHz, CDCl3) 7.04 (s, 2H), 7.03 (s, 2H), 7.01 (d, 2H), 6.81 (d, 2H), 2.58 (t, 4H), 1.62 (m, 4H), 1.32 (m, 20H), 0.89 (m, 6H). 13C NMR (75 MHz, CDCl3) 144.2, 136.7, 136.6, 135.7, 125.1, 124.1, 124.0, 119.2, 31.9, 30.5, 30.4, 29.4, 29.3, 29.3, 22.7, 14.1. Maldi-TOF MS calcd for C32H42S4 554.2169, found 554.209. (Fig S4-S6)

Compound (3).

Compound (2) (2.15 g, 4.06 mmole) was dissolved in 100 mL of anhydrous ethyl ether under nitrogen atmosphere and added BuLi solution (3.6 mL, 2.5M in tetrahydrofuran). The reaction mixture was stirred for 4 hr at room temperature, and then chilled to -78°C with acetone-liquid nitrogen bath. After addition of dimethylformamide (700μL, 9mmole), the reaction solution was warmed to room temperature for overnight and diluted with chloroform, then washed with water and brine. The organic layer was separated and dried over MgSO4, then condensed to a dark-red solid under vacuum. The solid was purified by column chromatography (silica gel, hexane-chloroform (1:1 to 1:4) as eluent) to yield the desired product (**compound (3)**); yield= 76%, 1H NMR (300 MHz, CDCl3) 9.99 (s, 2H), 7.26 (d, 2H), 7.16 (d, 2H), 7.07 (d, 2H), 2.93 (t, 4H), 1.71 (m, 4H), 1.32 (m, 20H), 0.89 (m, 6H). 13C NMR (75 MHz, CDCl3) 181.5, 153.9, 145.2, 137.8, 136.1, 135.7, 126.8, 126.7, 125.3, 31.8, 31.4, 29.3, 29.2, 28.6, 22.6, 14.1 Maldi-TOF MS calcd C34H42O2S4 610.2068, found 610.226 (Fig S7-S9)

1,4-Bis(diethyl-phosphonate-methyl)-2,5-di(octyloxy)-benzene(compound (4))

Compound (4) was prepared by a reported method, Hou1, J.; Yang, C.; Qiao, J.; Li, Y. Synth. Met. 2005, 150, 297–304. 1H NMR (300MHz, CDCl3) 6.92 (d, 2H), 4.02 (m, 8H), 3.91 (t, 4H), 3.25 (s, 2H), 3.19 (s, 2H), 1.76 (m, 4H), 1.43 (m, 4H), 1.29 (m, 16H), 1.23 (t, 12H), 0.89 (m, 6H). 13C NMR (75MHz, CDCl3) 150.4 (d), 119.5 (t), 114.9, 69.0, 61.9 (t), 31.8, 29.5, 29.4, 29.3, 27.2, 26.1, 25.3, 22.7, 16.4 (t), 14.1. HRMS calcd for C32H60O8P2 635.3842, found 635.3820. (Fig. S10-S12)

PPVQT-C8.

Compound (3) (183 mg, 0.3 mmole) and **compound (4)** (191 mg, 0.3 mmole) were dissolved in 3 mL of anhydrous tetrahydrofuran under nitrogen atmosphere. The reaction mixture was warmed to 60°C, and then potassium tert-butoxide solution (1 mL, 1.0 M in tetrahydrofuran) was added dropwise. The reaction solution was stirred at 60°C for 12 h under nitrogen atmosphere and chilled to room temperature and then was condensed to a dark-red polymer. The obtained polymer solid was extracted with soxhlet with acetone, methanol, and chloroform, subsequently. The chloroform extract was condensed under vacuum to give a film-like dark-red polymer solid; yield= 55%; Mn = 20,205, 1H NMR (300 MHz, CDCl3) 7.43~6.90 (m, 10H), 4.06 (m, 4H), 2.68 (m, 4H), 1.91 (m, 4H), 1.55 (m, 22H), 1.27 (m, 22H), 0.89 (m, 12H). (Fig S13)

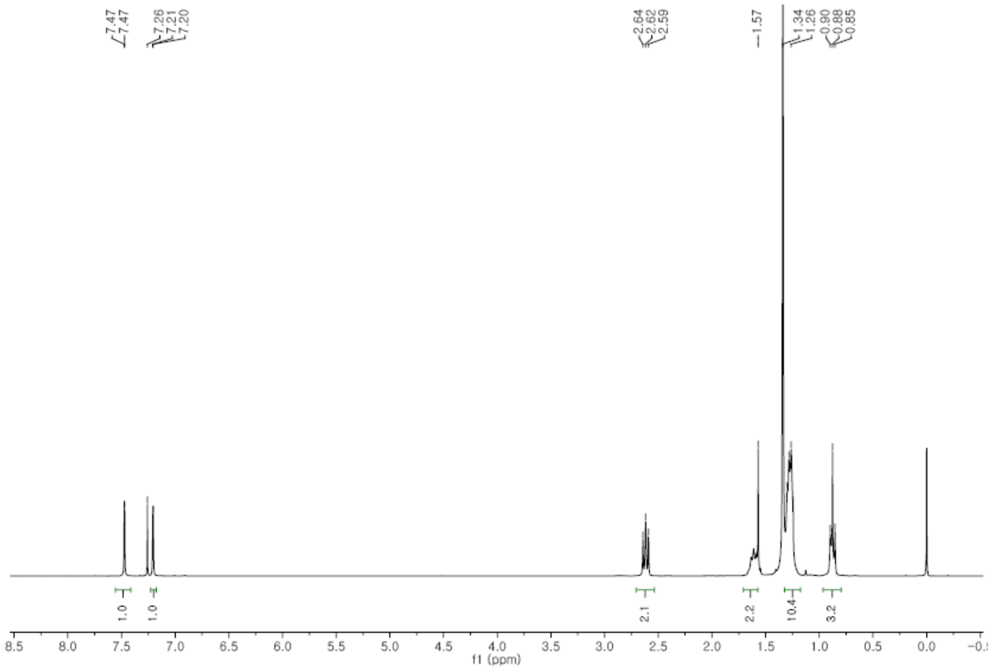

Figure S2. ^{1}H NMR spectrum of **compound (1)** in $CDCl_3$

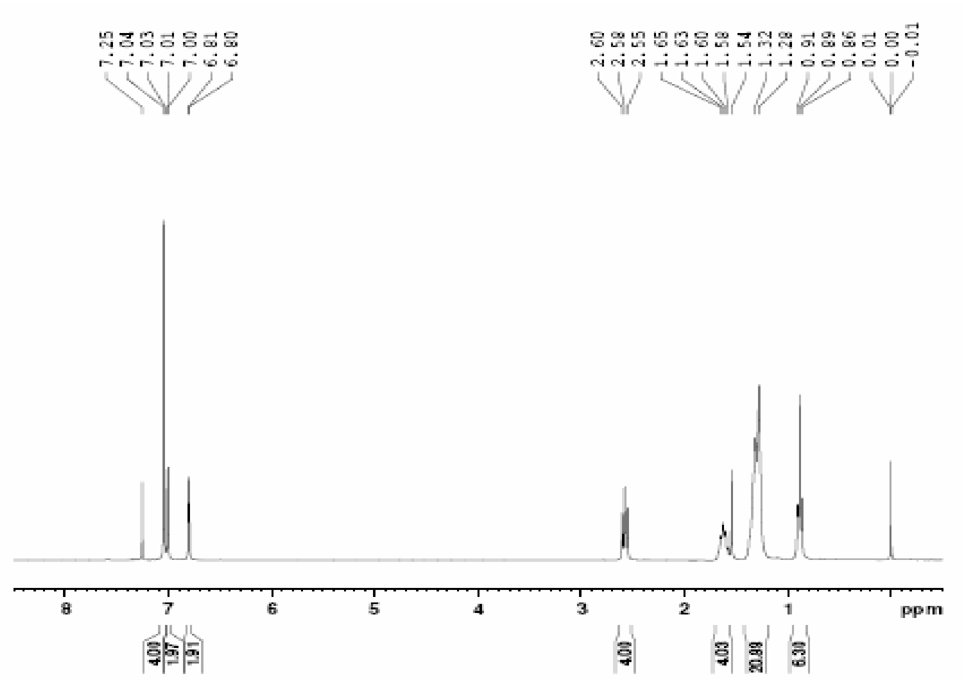

Figure S3. ^{1}H NMR spectrum of **compound (2)** in $CDCl_3$

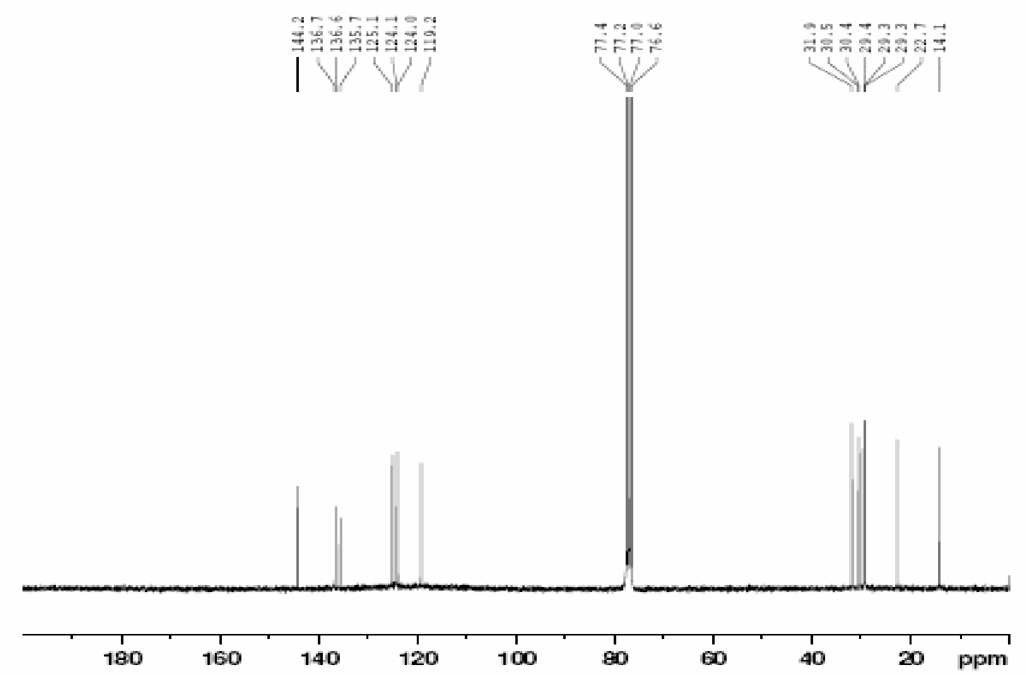

Figure S4. ^{13}C NMR spectrum of **compound (2)** in $CDCl_3$

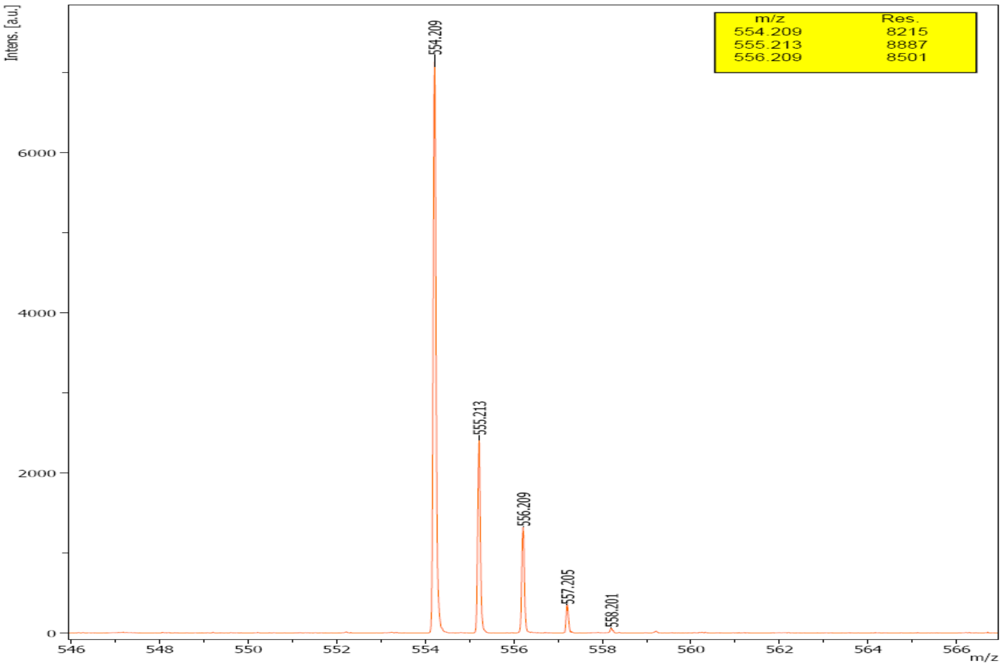

Figure S5. Maldi-TOF Mass spectrum of **compound (2)** in $CDCl_3$

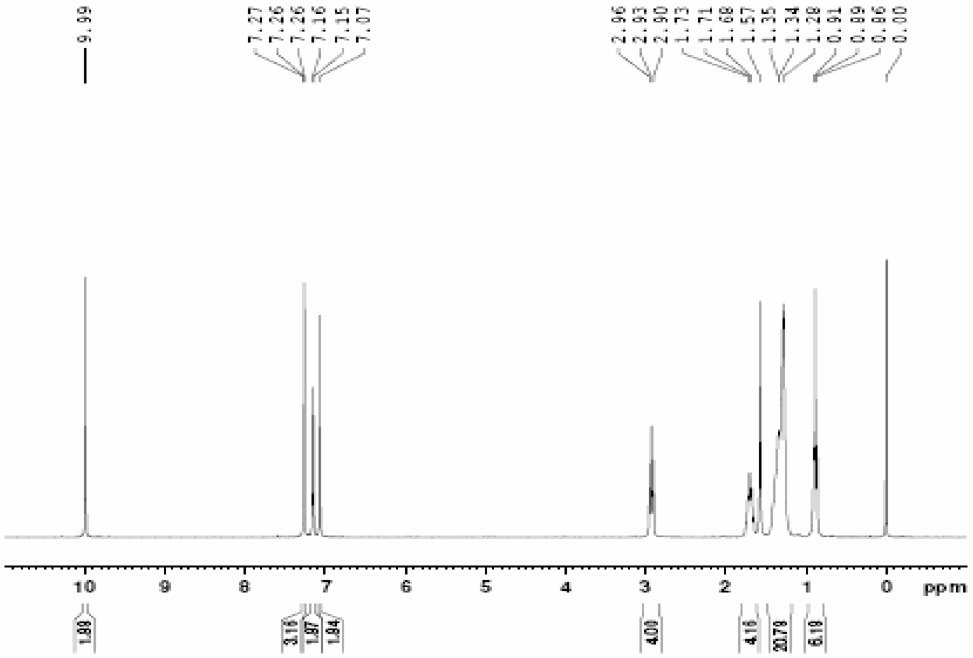

Figure S6. ^1H NMR spectrum of **compound (3)** in $CDCl_3$

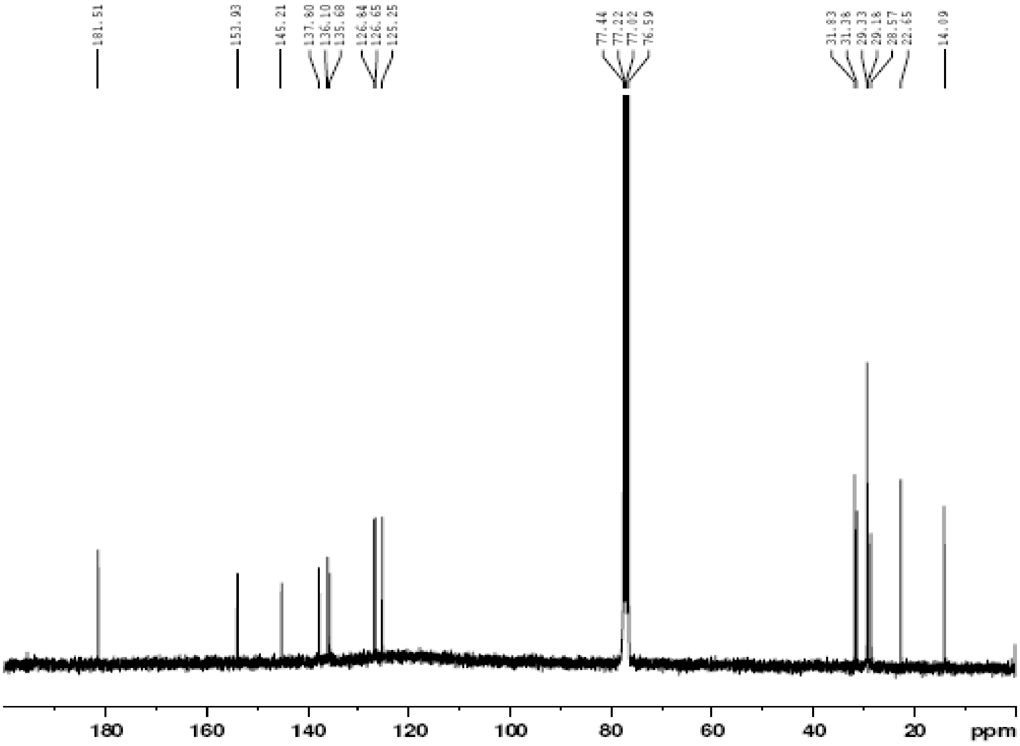

Figure S7. ^{13}C NMR spectrum of **compound (3)** in $CDCl_3$

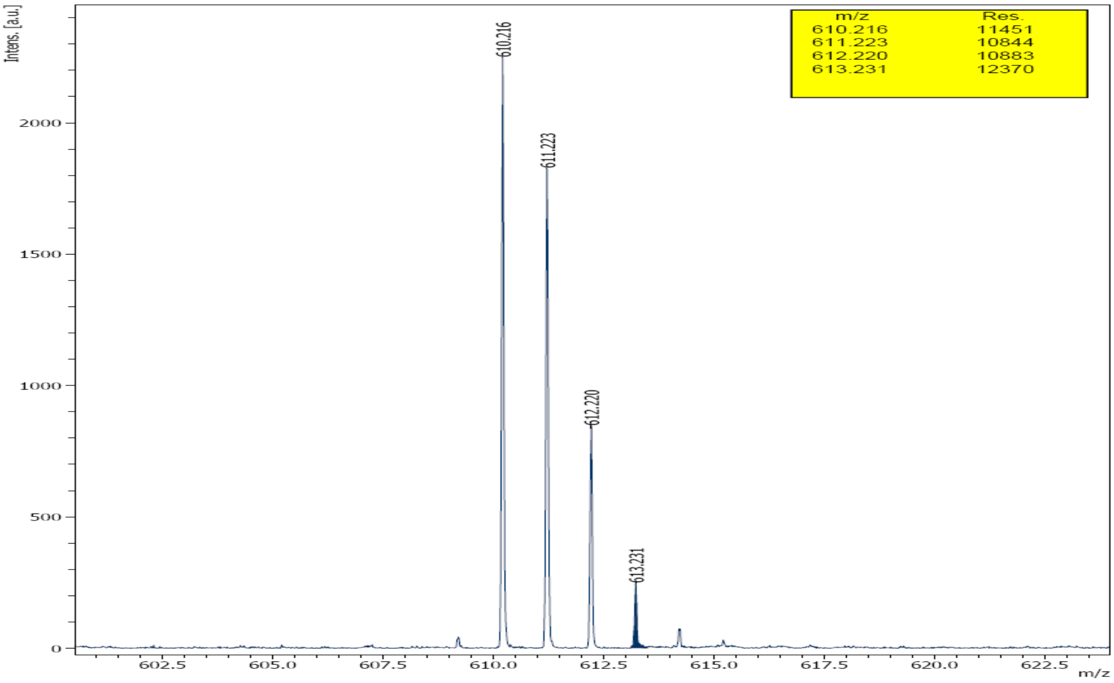

Figure S8. Maldi-TOF Mass spectrum of **compound (3)** in $CDCl_3$

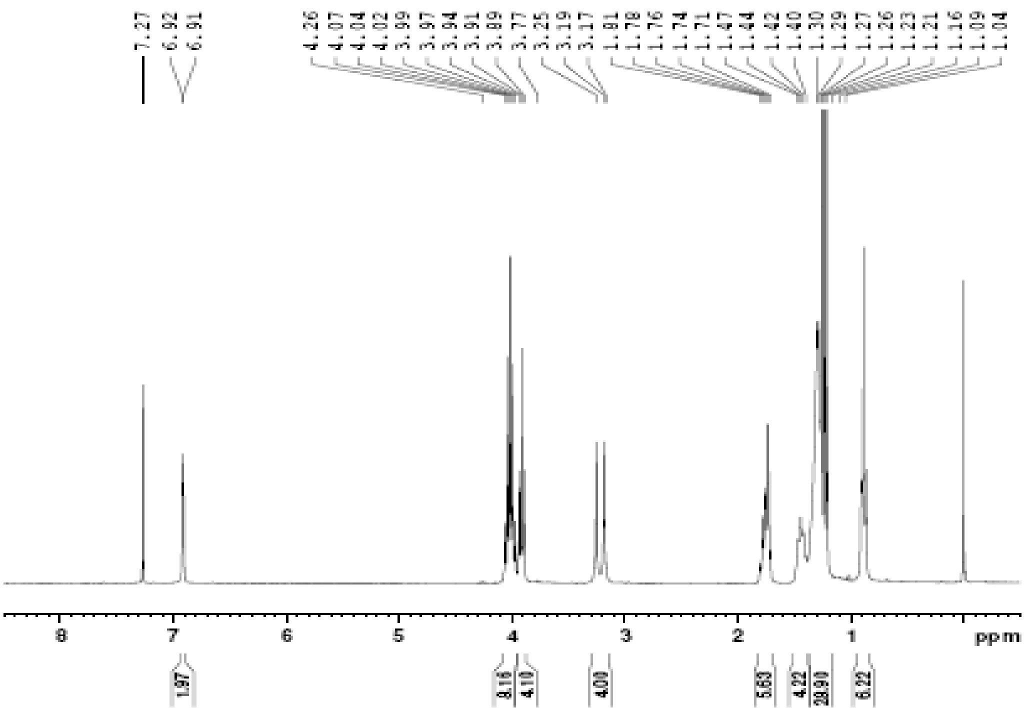

Figure S9. ^{1}H NMR spectrum of **compound (4)** in $CDCl_3$

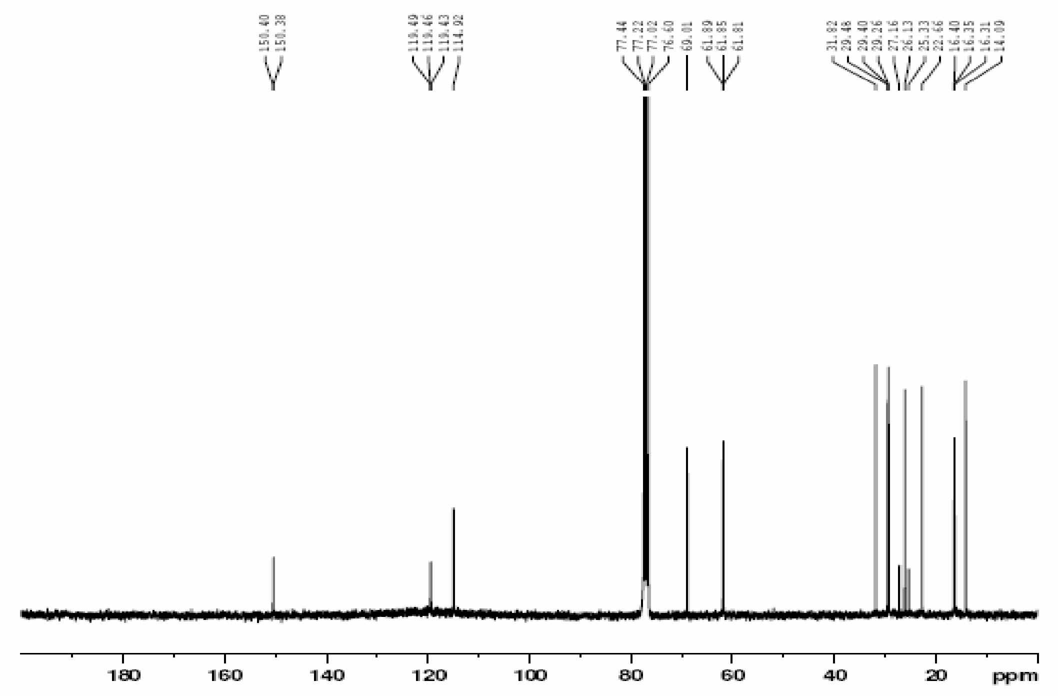

Figure S10. ^{13}C NMR spectrum of **compound (4)** in $CDCl_3$

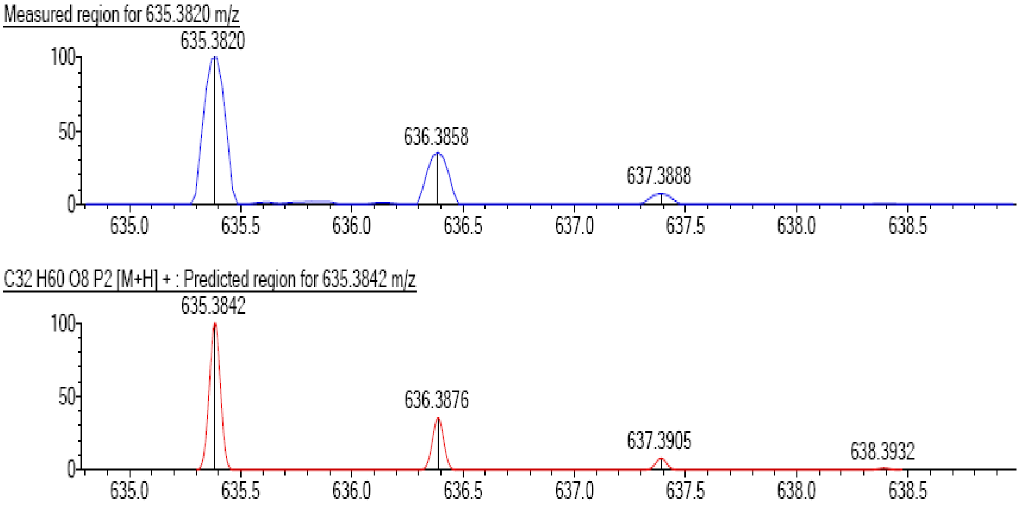

Figure S11. Maldi-TOF Mass spectrum of **compound (4)** in CDCl$_3$

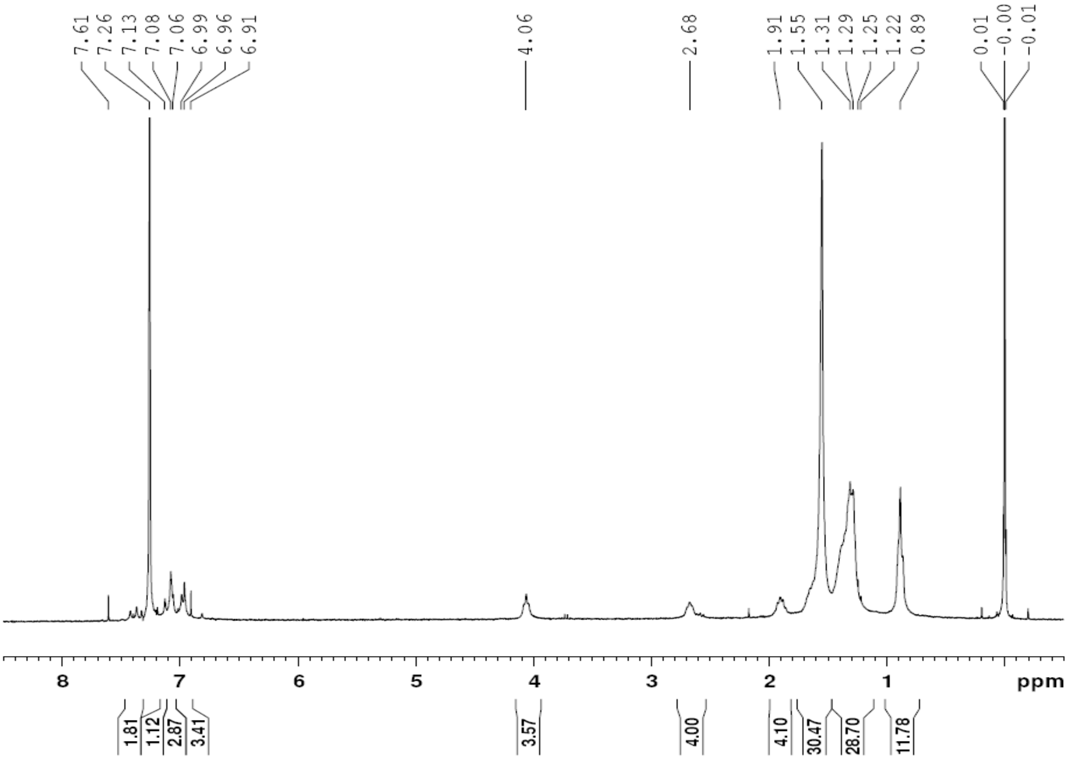

Figure S12. ^{1}H NMR spectrum of **PPVQT-C8** in CDCl$_3$