Supporting Information

Efficient bulk heterojunction solar cells based on solution processed small molecules based on same benzo[1,2-b:4, 5-b′]thiophene unit as core donor and different terminal units

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Synthesis and characterization of small molecules DRT3-BDT (1) and DTT3-BDT (2)

Characterization techniques

UV-vis absorption spectra were measured in a 1 cm path-length quartz cell using a Shimadzu model 1700 spectrophotometer. Steady state fluorescence spectra were recorded using a Spex model Fluoromax-3 spectrofluorometer using a 1 cm quartz cell. ^{1}H NMR spectra were recorded at 300 MHz on a Bruker 300Avance NMR spectrometer with X-WIN NMR software. ^{1}H spectra were referenced to tertramethylsilane. ESI mass spectra were recorded on a Water Quattro micro (Water Inc, USA). Cyclic voltammetric experiments were carried out with a PC-controlled CH instruments model CHI620C electrochemical analyzer.Flash column chromatography was carried out using Silica gel 60, 40-63 μm (Panreac Química SLU) as the stationary phase. Size exclusion chromatography was carried out in a large elution column (1000mm x 38 mm) with Biobead SX3 (Bio-Rad Laboratories,

Inc.) as the stationary phase. The eluent was passed through the column under gravity. The elemental analysis was carried aout at the Unidade de Análise Elemental at the University of Santiago de Compostela (USC) using a FISONS model EA1108.

Synthesis and characterization

Synthesis of 3-ethylhexyl rhodanine (2): To a refluxing solution of rhodanine (5.07g,38.07mmol) in ethanol (25mL) was added a hot solution of potassium hydroxide in ethanol (2.22g 39.59 mmol in25 ml ethanol). After additional refluxing for 5 h, the mixture was cooled to 0 °C and the precipitate was filtered and washed with cold ethanol. The obtained potassium salt of rhodanine (1.5 g 8.82 mmol) was refluxed with Ethyl hexyl bromide (10.58g 44.11mmol) in the presence of KI(4.39 g 26.49mmol) in Acetone (15 mL) and DMF (15 mL) for 36 h. After cooling to room temperature and addition of water (40 mL), the crude product was extracted with ethyl acetate, washed with brine, and the crude product purified by flash chromatography on silica gel using a mixture of dichloromethane and hexane as eluent to afford 3-ethyl hexyl rhodanine as dark liquid.^{1}H NMR (500 MHz, Chloroform-*d*) δ4(s,2H), 4.03 – 3.89 (m, 2H), 2.10 – 1.95 (m, 1H), 1.41 – 1.15 (m, 7H), 0.92 (td, *J* = 7.3, 2.8 Hz, 6H) (Figure S1). ^{13}C NMR (126 MHz, $CDCl_3$) (Figure S2) δ 201.64, 174.30, 48.67, 36.73, 35.18, 30.48, 28.42, 23.89, 22.98, 14.12, 14.03, 10.51.MS-ESI (*m/z*): $[M]^+$ calculated for $C_{11}H_{18}NOS_2$: 244.0835; found: 244.0837. HRMS (ESI) spectrum of compound **2** is shown in Figure S3.

Synthesis of 3-ethylhexyl) thiazolidine-2, 4-dione (4): To a refluxing solution of thiazolidine-2, 4-dione (5.0g,43.10m.mol) in ethanol (25mL) was added a hot solution of potassium hydroxide (2.650 g,47.4m mol) in ethanol (25 mL). After additional refluxing for 30 min, the mixture was cooled to 0 °C and the precipitate was filtered and washed with cold ethanol. The obtained potassium salt of thiazolidine-2, 4-dione (3.0 g, 19.4 mmol) was refluxed with Ethyl hexyl bromide (4.11g 21.34 mmol) in DMF (15 mL) for 3−4 h. After cooling to room temperature and addition of water (40 mL), the crude product was extracted with ethyl acetate, washed with brine, and purified by flash chromatography on silica gel using a mixture of dichloromethane and hexane as eluent to afford 3-ethyl hexyl thiazolidine-2, 4-dione as dark liquid.^{1}H NMR (300 MHz, Chloroform-*d*) (Figure S4) δ 3.95 (s, 1H), 3.60 – 3.49 (m, 2H), 1.80 – 1.62 (m, 1H), 1.40 – 1.12 (m, 7H), 0.95 – 0.84 (m, 6H).^{13}C NMR (75 MHz, $CDCl_3$) (Figure S5), δ 171.93, 171.71, 77.45, 77.24, 77.03, 76.61, 45.94, 37.31, 33.60, 30.31, 28.36, 23.70, 22.95, 14.02, 10.33, -1.96.MS-ESI (*m/z*): $[M+Na]^+$ calculated for

$C_{11}H_{19}NNaO_2S$: 252.1029; found: 252.1036. Figure S6 shows the HRMS (ESI) spectrum of compound **4.**

Synthesis of DRT3-BDT (1): 7 (100 mg,0.063 mmol) was dissolved in a solution of dry chloroform (30 mL) and two drops of piperdine and 3-ethylhexyl rhodanine (2) (155mg,0.635 mmol) was added and the resulting solution was heated to reflux and stirred for 12 hours under argon. The reaction mixture was cool to room temperature, then water was added. The crude product was extracted into $CHCl_3$, and the organic layer was dried over Na_2SO_4. The solvent was removed under reduced pressure and the crude product was purified by column chromatography on silica gel using CH_2Cl_2 and hexane (1:1) as eluent and subsequent size exclusion chromatography using THF as eluent to obtain a purple solid (88 mg, 78% yield).^{1}H-NMR (500 MHz, $CDCl_3$) (Figure S7) δ_H 7.7 (s, 2H), 7.57(s, 2H) 7.30(d, J=3.9Hz, 2H),7.16(m, 4H), 7.07(m,4H), 6.93(d, J=3.7Hz,2H), 3.97(d,J=8.5Hz,4H), 2.89(m,4H), 2.80 (m,4H), 2.75 (m,4H), 1.75-1.65 (m,10H), 1.40-1.20(m,72H), 0.98-0.84(m,36H).^{13}C NMR (126 MHz, $CDCl_3$), (Figure S8) δ 192.56, 167.91, 145.93, 140.86, 140.78, 139.41, 138.58, 137.51, 137.29, 137.26, 137.12, 136.83, 135.50, 135.10, 134.69, 130.46, 128.26, 127.86, 127.08, 126.00, 125.48, 124.69, 123.22, 120.28, 119.07, 48.68, 41.51, 37.02, 34.39, 32.58, 31.93, 31.90, 30.54, 30.42, 30.21, 29.81, 29.74, 29.71, 29.61, 29.55, 29.51, 29.47, 29.34, 29.30, 29.00, 28.48, 25.87, 23.95, 23.11, 23.00, 22.71, 22.69, 14.27, 14.14, 14.12, 14.05, 11.02, 10.56.MS (MALDI-TOF) (Figure S9): calcd for [M]+, 2030.8166. Anal. Calcd. For $C_{114}H_{152}N_2O_2S_{14}$ C, 67.40; H, 7.54; N, 1.38; O, 1.58; S, 22.10 Found: C,67.45; H,7.9; N,1.42; S,22.06.

Synthesis of DTT3-BDT (2) : 7 (100 mg,0.063 mmol) was dissolved in a solution of dry chloroform (30 mL) and two drops of piperdine and 3-ethylhexyl thiazolidine-2,4-dione **(4)** (145 mg,0.635 mmol) was added and the resulting solution was heated to reflux and stirred for 48 hours under argon. The reaction mixture was cool to room temperature, then water was added. The crude product was extracted into $CHCl_3$, and the organic layer was dried over Na_2SO_4. The solvent was removed under reduced pressure and the crude product was purified by column chromatography on silica gel using CH_2Cl_2 and hexane (1:1) as eluent and subsequent size exclusion chromatography using THF as eluent to obtain a purple solid (90 mg, 80% yield).^{1}H-NMR (500 MHz, $CDCl_3$) (Figure S10), δ_H ^{1}H-NMR (500 MHz, $CDCl_3$) δ_H 7.9(s,2H), 7.59 (s,2H) 7.30 (d,J=5.1Hz,2H), 7.17(m,4H), 7.10(m,4H), 6.93(d,J=5.1Hz,2H), 3.61(d,J=8.5Hz,4H), 2.88(m,4H), 2.78 (m,4H), 2.74 (m,4H), 1.70-1.65 (m,10H), 1.41-

1.22(m,72H), 0.98-0.84(m,36H).^{13}C NMR (126 MHz, $CDCl_3$) (Figure S11), δ 167.78, 166.60, 146.26, 140.95, 140.81, 138.73, 138.10, 137.47, 137.39, 137.31, 136.81, 136.66, 135.58, 135,04, 134.88, 130.47, 128.38, 127.84, 127.17, 126.22, 125.83, 125.49, 123.38, 119.18, 118.92, 46.12, 41.50, 37.64, 34.40, 32.60, 31.92, 31.90, 30.50, 30.42, 30.34, 29.69, 29.67, 29.55, 29.47, 29.45, 29.30, 29.29, 29.00, 28.44, 25.88, 23.78, 23.78, 23.10, 22.97, 22.70, 14.23, 14.12, 14.05, 11.00, 10.39.MS (MALDI-TOF) (Figure S12): calcd for [M]+, 1998.8049.Anal. Calcd. For $C_{114}H_{152}N_2O_4S_{12}$ C,68.49; H, 7.66; N, 1.40; O, 3.20; S, 19.25 Found: C,68.37;H,8.22; N,1.37; S,18.73.

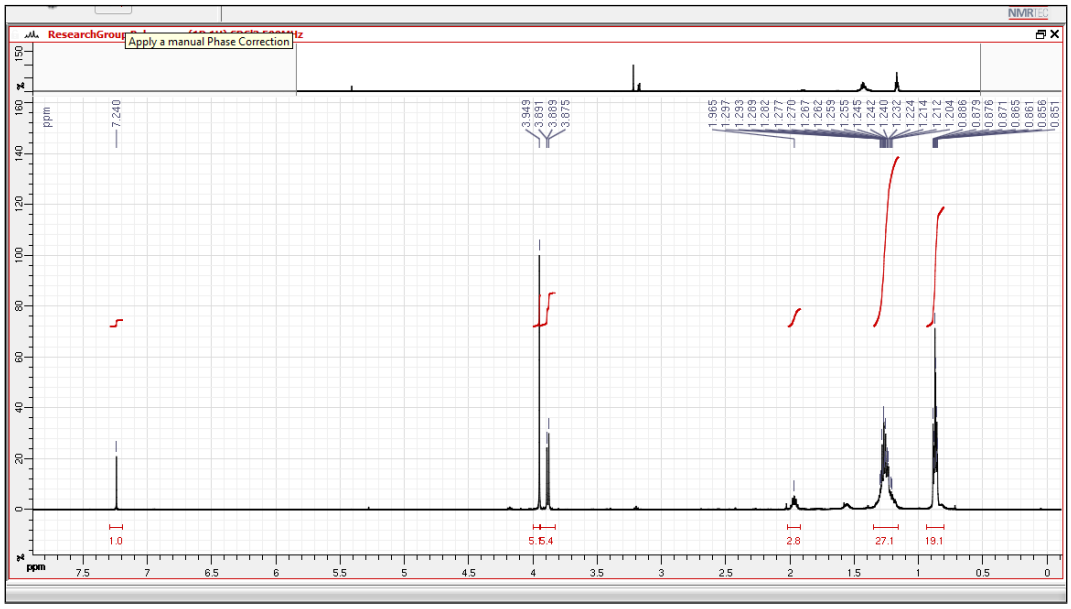

Fig. S 1 ^{1}H NMR spectra of compound **2** recorded in $CDCl_3$.

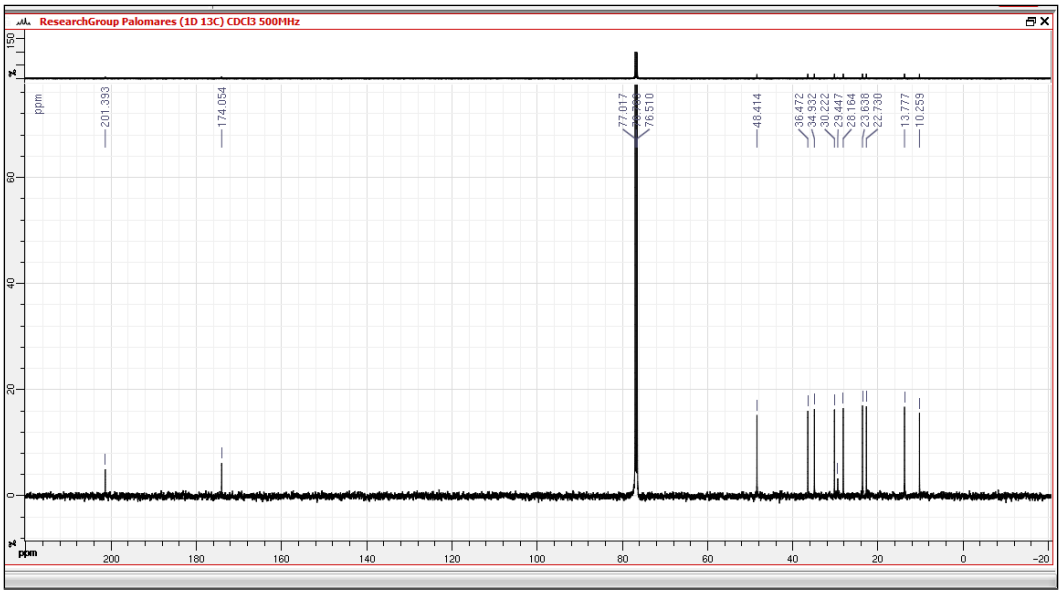

Fig. S2 ^{13}C NMR spectra of compound **2** recorded in $CDCl_3$.

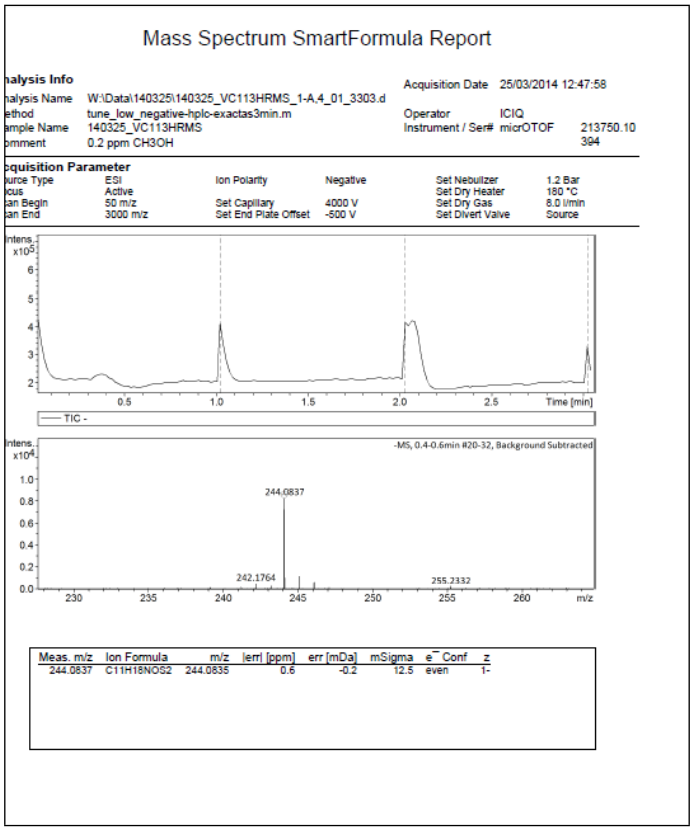

Fig. S3 HRMS (ESI) spectrum of compound **2**.

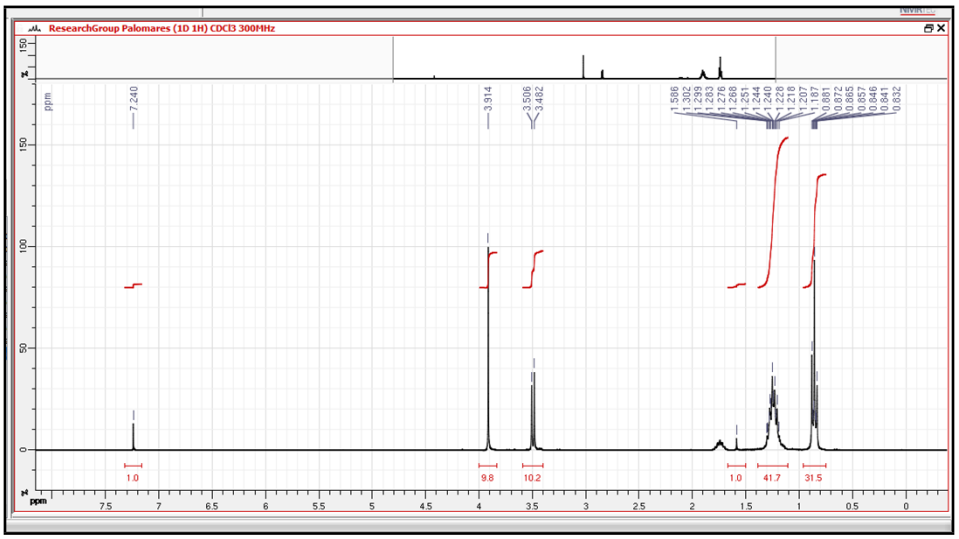

Fig. S 4 ^{1}H NMR spectra of compound **4** recorded in $CDCl_3$.

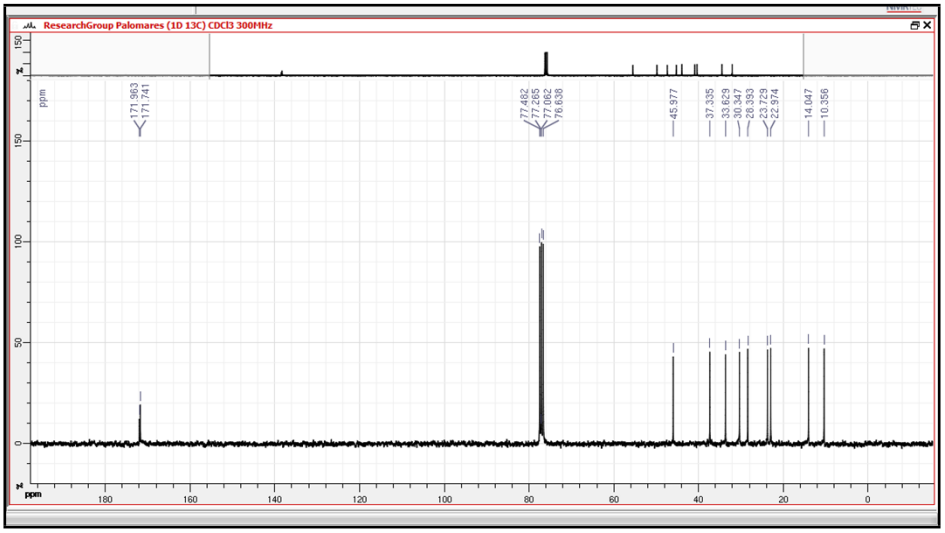

Fig. S5 ^{13}C NMR spectra of compound **4** recorded in $CDCl_3$.

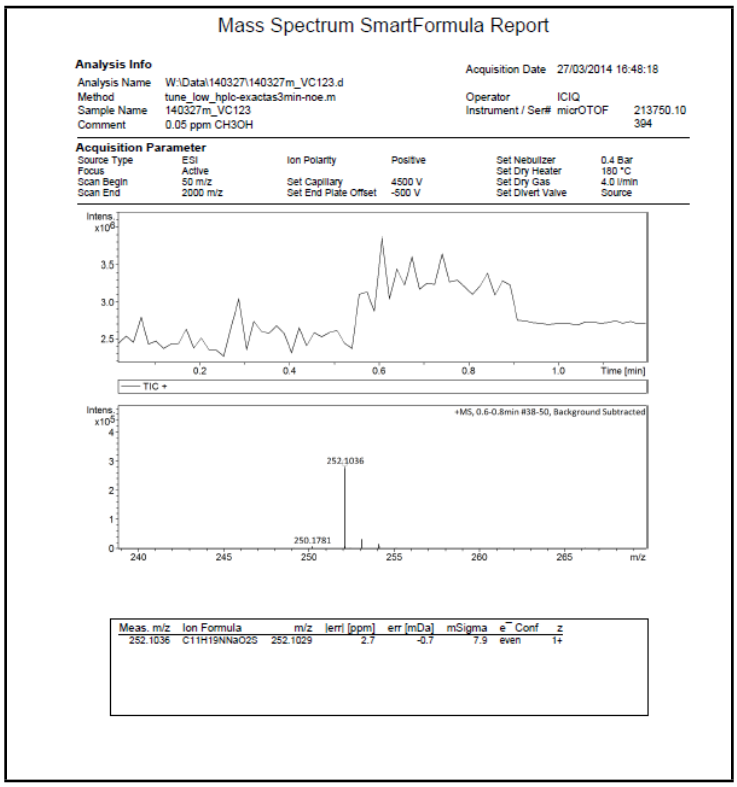

Fig. S6 HRMS (ESI) spectrum of compound **4**.

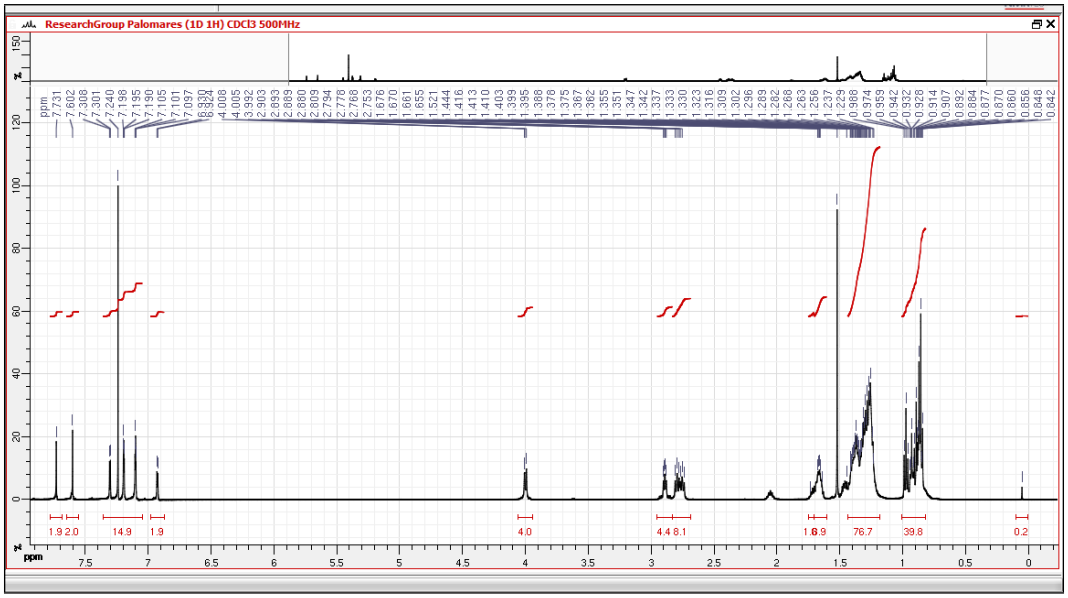

Fig. S7 ^{1}H NMR spectra of compound **DRT3-BDT (1)** recorded in $CDCl_3$.

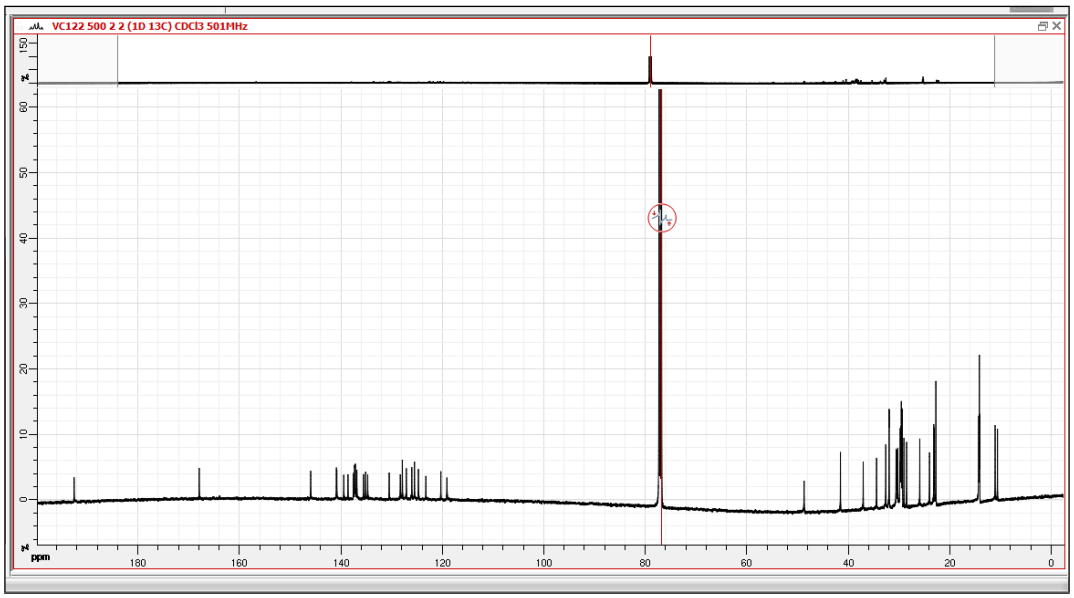

Fig. S8 ^{13}C NMR spectra of compound **DRT3-BDT (1)** recorded in $CDCl_3$.

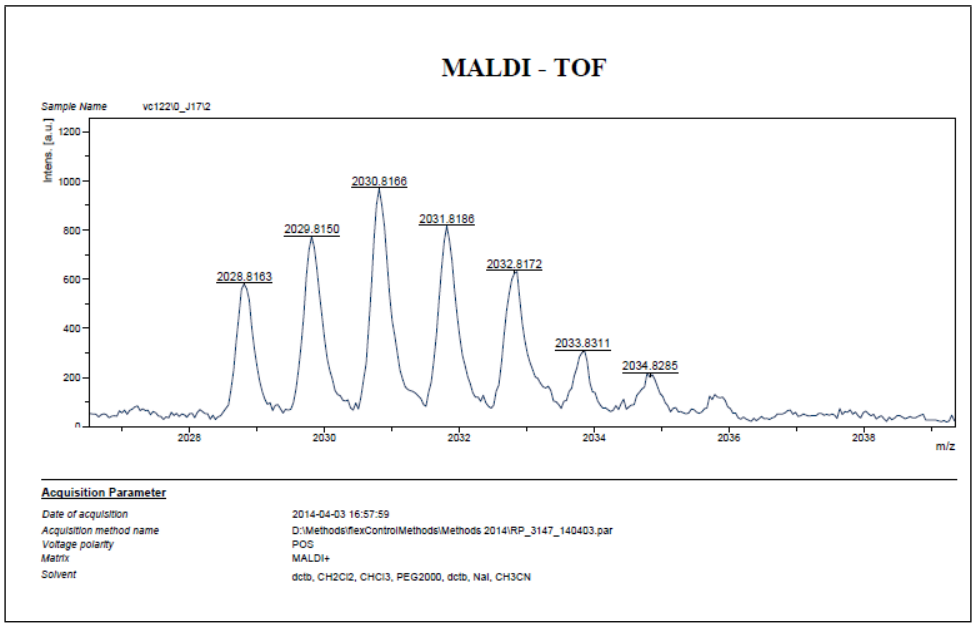

Fig. S9 MALDI-TOF spectra of compound **DRT3-BDT (1)**.

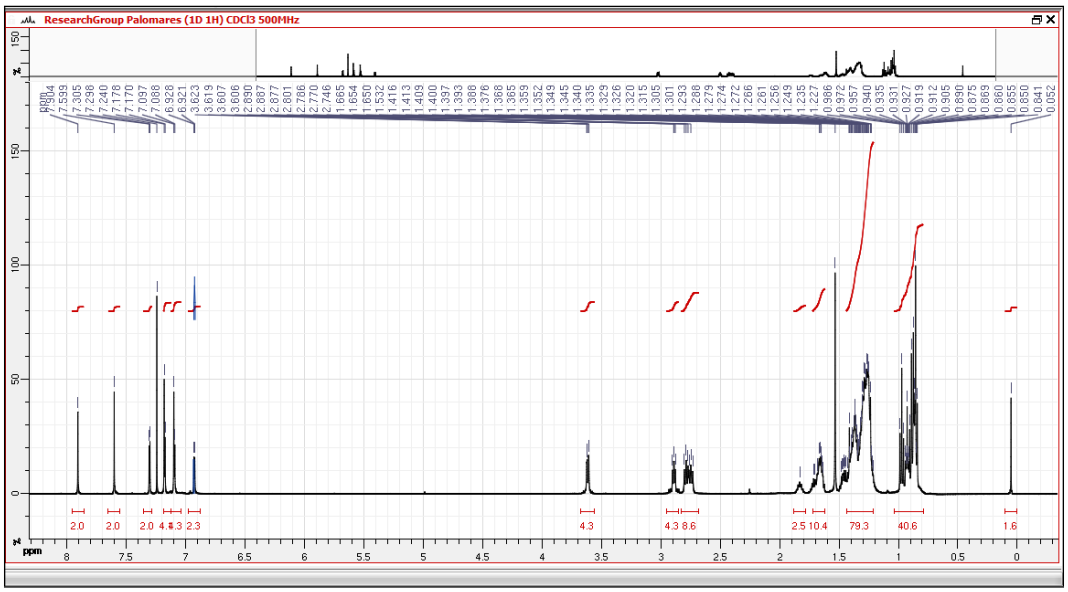

Fig. S 10 ^{1}H NMR spectra of compound **DTT3-BDT (2)** recorded in $CDCl_3$.

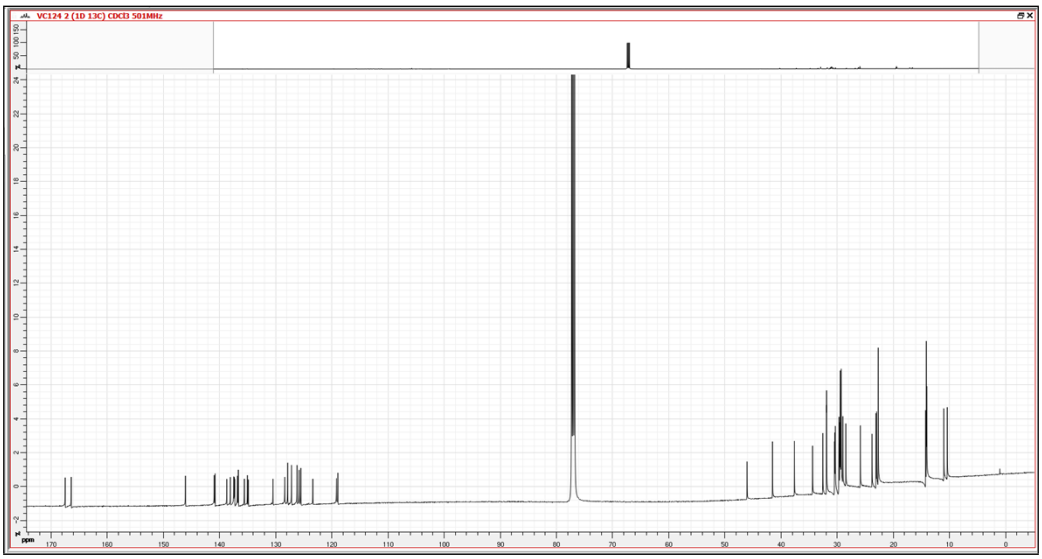

Fig. S11 ^{13}C NMR spectra of compound **DTT3-BDT (2)** recorded in $CDCl_3$.

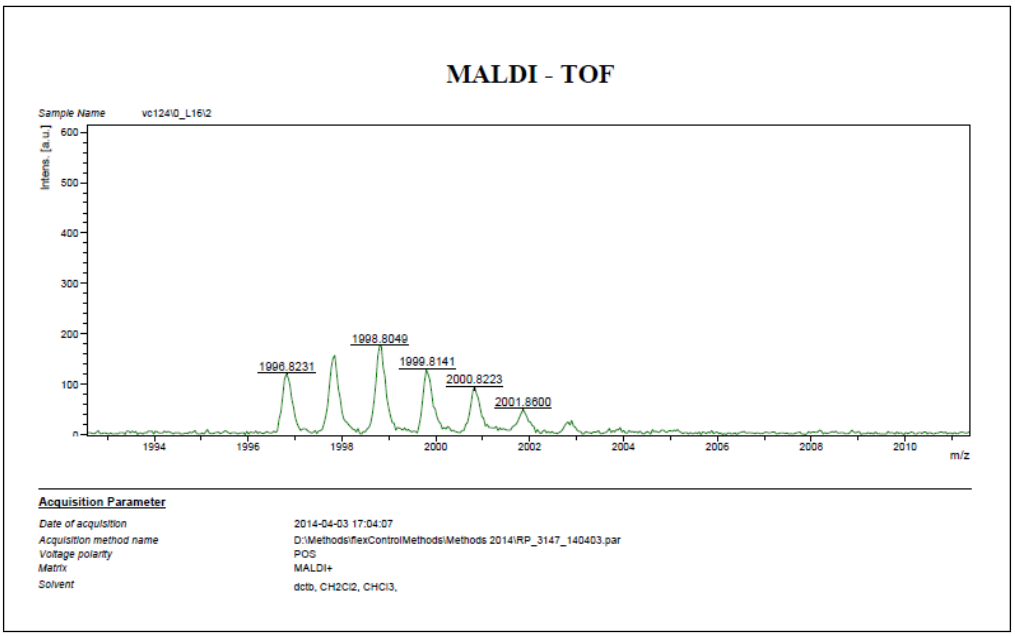

Fig. S12 MALDI-TOF spectra of compound **DTT3-BDT (2)**.

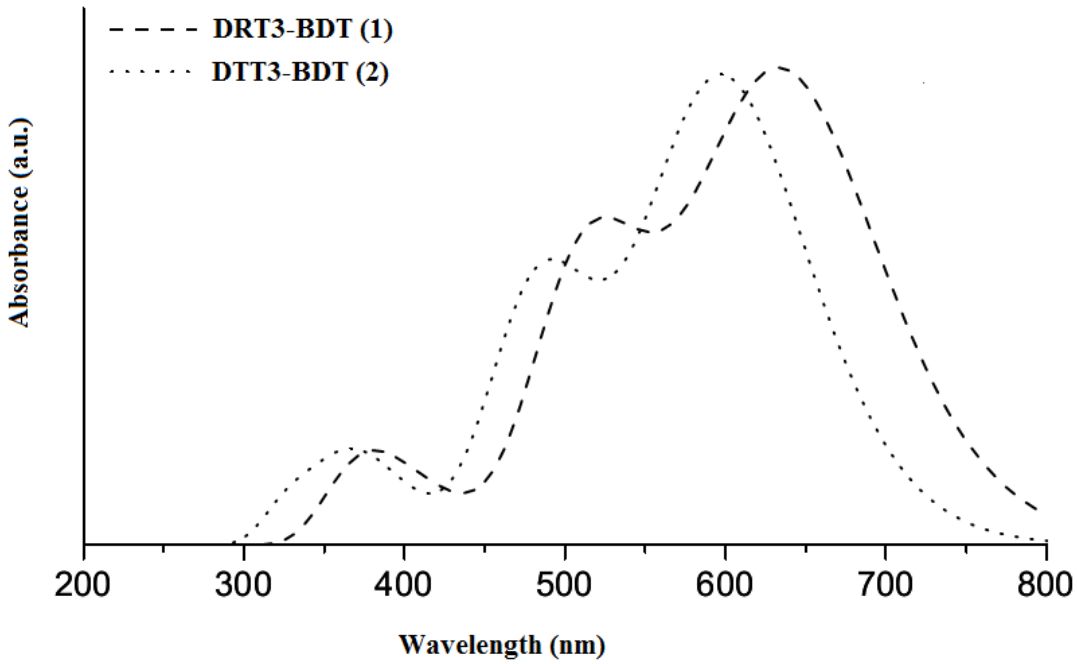

Fig S13. Theoretical UV/Vis absorption spectrum of **DRT3-BDT (1)** and **DTT3-BDT (2)** molecules (calculated using the B3LYP functional)

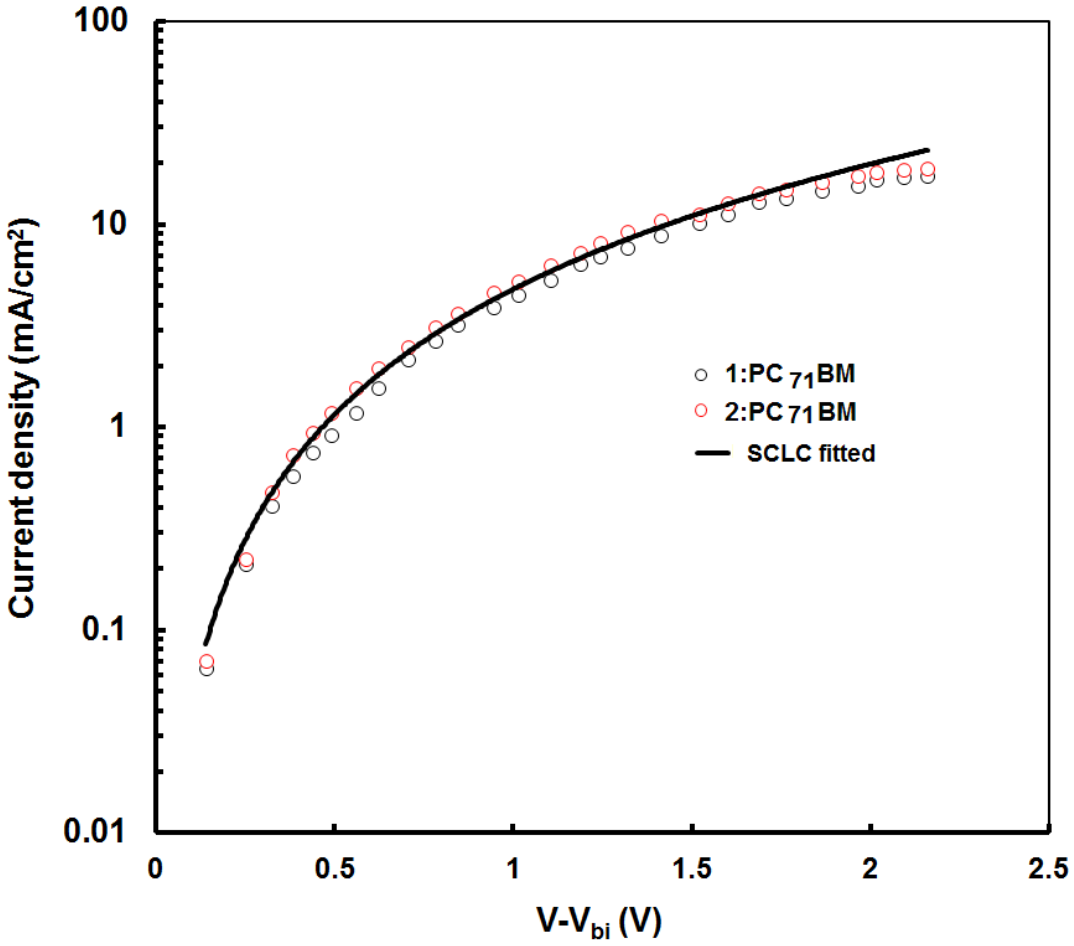

Fig S14 Figure 11 Variation of dark current density with $V-V_{bi}$ for electron only devices. The solid line is SCLC fitted.