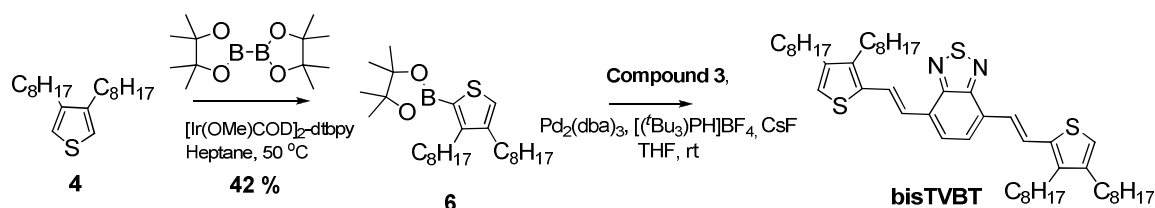


A Facile Approach to Defect-free Vinylene-linked Benzothiadiazole-thiophene Low Bandgap Conjugated Polymers for Organic Solar Cells

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2-(3,4-dioctylthiophen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (6). To a 25 mL two-neck flask charged with 3, 4-octylthiophene (5.0 mmol, 1.37 g). 4,4'-di-tert-butyl-2,2'-bipyridine (3.0 mol %, 40.2 mg) and bis(pinacolato)diboron (2.8 mmol, 711 mg) were added under argon. Three cycles of argon-vacuum were then applied. Subsequently, Degassed heptane (25 ml) was injected. $[\text{Ir}(\text{OMe})(\text{COD})]_2$ (1.5 mol %, 49 mg) was added under argon and the mixture was stirred at 50 °C for 16 h. After cooling down to room temperature, the mixture was filtered and washed with hot hexane. The solvent was removed and the crude oil product was purified by silica gel column chromatography, eluting with $\text{CH}_2\text{Cl}_2/\text{Hexane}$ (3:7) to give colorless oil (917 mg, 42 %). $^1\text{H-NMR}$ (CDCl_3) δ : 7.16 (s, 1H), 2.82 (t, $J =$

7.5 Hz, 2H), 2.54(t, J = 7.2 Hz, 2H), 1.62–1.54 (m, 2H), 1.54–1.45 (m, 2H), 1.32 (s, 12 H), 1.23–1.29 (m, 20H) 0.87 (t, J = 6.3 Hz, 6H); ^{13}C -NMR (CDCl_3) δ : 153.6, 144.1, 127.2, 83.6, 32.2, 32.1, 30.4, 30.0, 29.8, 29.7, 29.65, 29.5, 28.8, 25.0, 22.9, 14.3; HRMS (APCI-TOF) Calculated for $\text{C}_{26}\text{H}_{47}\text{BO}_2\text{S}$ ($\text{M} + \text{H}^+$): 434.3499. Found: m/z 434.3501.

bisTVBT. To a flask charged with 4,7-bis((E)-2-bromovinyl)benzo[c][1,2,5]thiadiazole (1 mmol, 346 mg), $\text{Pd}_2(\text{dba})_3$ (2.5 mmol, 23 mg), $[(^t\text{Bu}_3)\text{PH}]\text{BF}_4$ (7.5 mol %, 22 mg), CsF (6 mmol, 912 mg) under argon atmosphere, 2-(3,4-dioctylthiophen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2.4 mmol) in THF (40 ml) was injected. The resulting mixture was stirred at room temperature for 10 h. Water (100 ml) was added and the organic phase was extracted with diethyl ether (2 x 20 mL). The combined organic phase was dried over MgSO_4 . The solvent was removed and the crude product was purified by silica gel column chromatography, eluting with Dichloromethane/Hexane (15: 85) to yield red solids (689 mg, 86%). ^1H -NMR (CDCl_3) δ : 8.38 (d, J = 16.2 Hz, 2H), 7.50 (s, 2H), 7.29 (d, J = 16.2 Hz, 2H), 6.84 (s, 2H), 2.75 (t, J = 6.6 Hz, 4H), 2.55 (t, J = 7.5 Hz, 4H), 1.70–1.20 (m, 48H), 0.90-0.98 (m, 12H); ^{13}C -NMR (CDCl_3) δ : 154.0, 143.6, 142.0, 137.8, 129.3, 127.4, 126.2, 123.4, 119.4, 32.2., 32.1, 31.3, 30.0., 29.9, 29.8, 29.7, 29.6, 29.56, 29.5, 29.3, 27.3, 22.9, 14.3; HRMS (APCI-TOF) Calculated for $\text{C}_{50}\text{H}_{76}\text{N}_2\text{S}_3$ ($\text{M} + \text{H}^+$): 801.5243. Found: m/z 801.5210. Anal. Calcd for $\text{C}_{50}\text{H}_{76}\text{N}_2\text{S}_3$: C, 74.94; H, 9.56; N, 3.50. Found: C, 75.08; H, 9.56; N, 3.50.

Figure S1. ^1H -NMR spectra of **bisTVBT** in deuterated chloroform (top) at room temperature and **PTVBT** in deuterated tetrachloroethane at 100 $^{\circ}\text{C}$

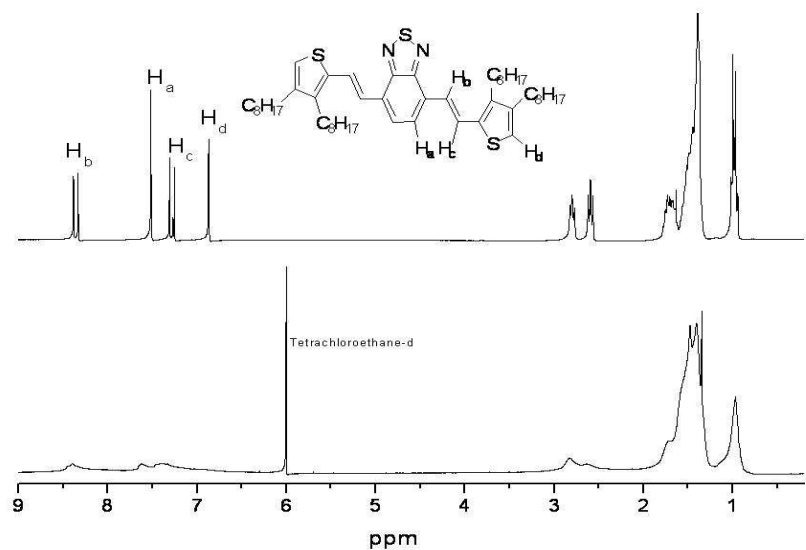


Figure S2. IR spectra of **bisTVBT** and **PTVBT**

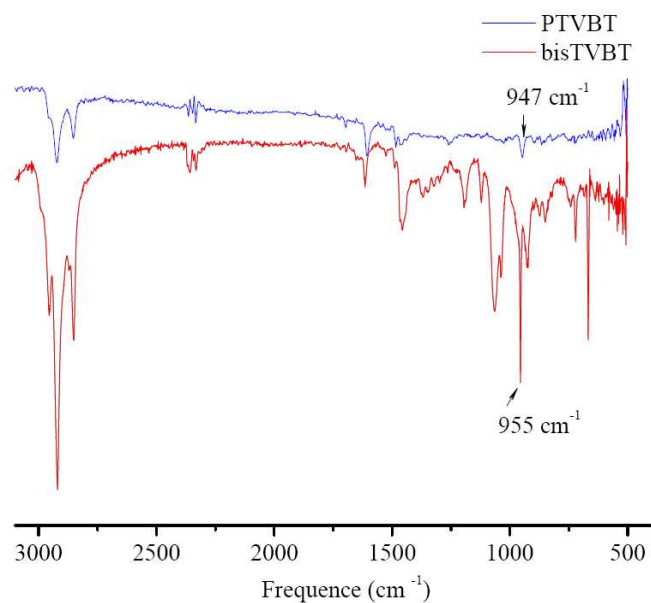


Figure S3. Solid state absorption of PTVBT and PTVBT/PCBM blend on ITO overlaid with the solar simulator spectrum (AM 1.5 conditions, solid line). The Figure shows a great match between the photocurrent spectrum of the blend and the photon emission of the sun.

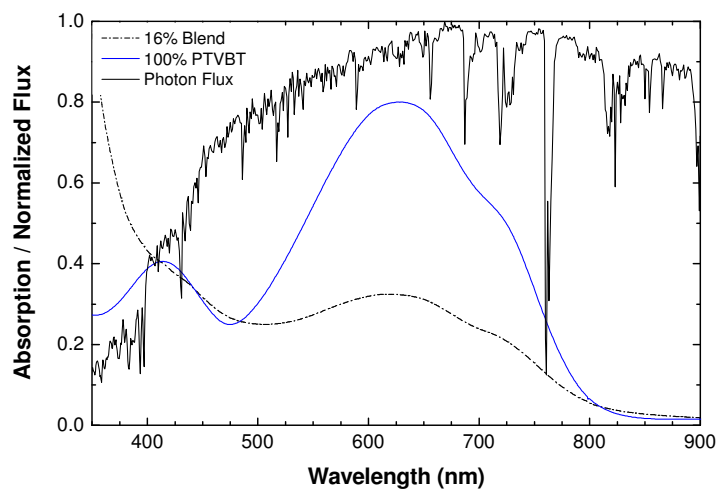


Figure S4. Photoluminescence spectrum of bisTVBT in THF, excited at 470 nm.

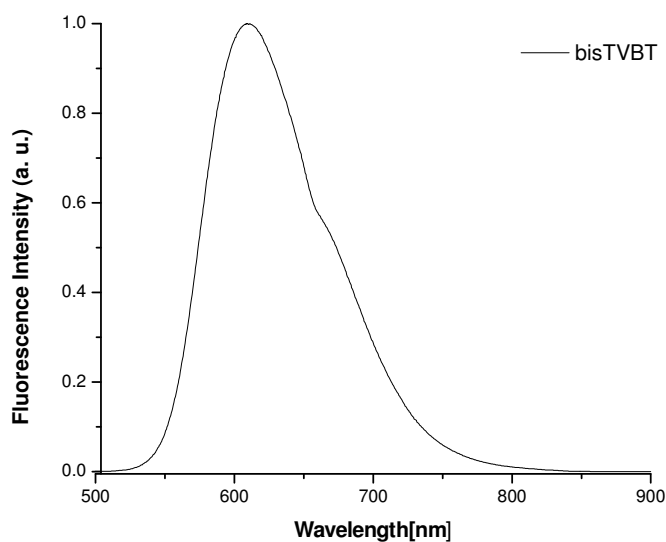


Figure S5. Cyclic voltammetry of PTVBT on a platinum working electrode (0.02 cm^2) in 0.1M TBAP/PC solution at 50 mV s^{-1} .

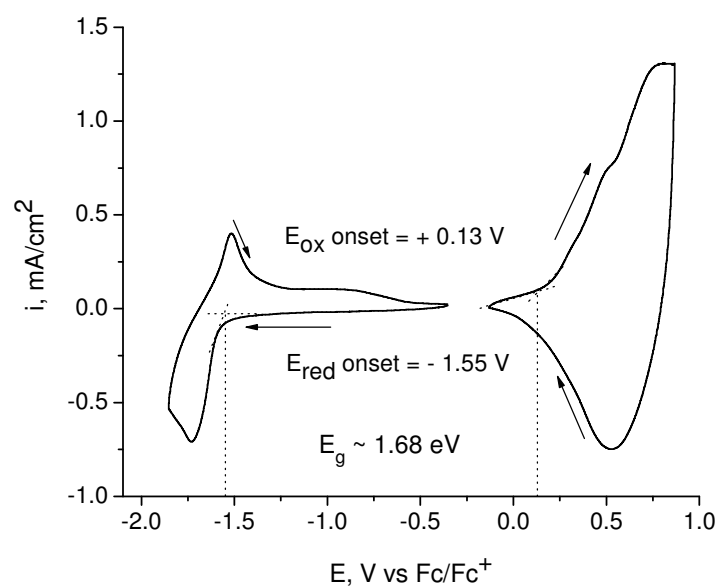


Figure S6. IPCE results for a are displayed for a typical PTVBT cell.

