

## Supporting Information

### **Poly[3-(5-octyl-thienylene-vinyl)-thiophene]: A Side-chain Conjugated Polymer with Very Broad Absorption Band**

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#### **Experimental details:**

**Reagents** n-Butyllithium 2.88 M in hexane, methylmagnesium bromide, were purchased from Alfa Asia Chemical Co., and Ni(dppp)Cl<sub>2</sub> was purchased from Aldrich Chemical Co., and used as received. Tetrahydrofuran was dried over Na/benzophenone ketyl and freshly distilled prior to use. N,N-Dimethyl-formamide, 1-bromo-octane, thiophene, and 3-methylthiophene were dried over molecular sieves and freshly distilled prior to use. The other materials were common commercial chemicals and used as received.

**Instruments and measurements** <sup>1</sup>H (300MHz) NMR spectra were measured on a Bruker DMX-300 spectrometer. Absorption spectra were taken on a Hitachi U-3010 UV-Vis spectrophotometer. Photoluminescence spectra were measured using a Hitachi F-4500 spectrophotometer. *M<sub>n</sub>* molecular weight of polymers was measured

by GPC method, and polystyrene was used as a standard. TGA measurement was performed on a Perkin-Elmer TGA-7. X-ray diffraction (XRD) patterns were recorded by a Rigaku D/max-2500 diffractometer operated at 40 kV voltage and a 200 mA current with Cu K $\alpha$  radiation. Samples for XRD measurements are solid powder prepared by drying the purified product under vacuum. Electrochemical cyclic voltammetry was conducted on a Zahner IM6e Electrochemical Workstation with Pt disc (0.06 cm<sup>2</sup>), Pt plate, and Ag/Ag<sup>+</sup> (0.01M) as working electrode, counter electrode and reference electrode respectively in a 0.1 M tetrabutylammonium hexafluorophosphate (Bu<sub>4</sub>NPF<sub>6</sub>) acetonitrile solution. The molecular weight of polymers was measured by GPC method, and polystyrene was used as a standard. The thickness of different layers in the photovoltaic devices was measured on an Ambios Tech. XP-2 profilometer. The carrier collection efficiency was measured using a Keithley 196 System DMM coupled with monochromator and 500 W Xenon lamp. The light intensity at each wavelength was calibrated with a standard single-crystal Si photovoltaic cell.

### Synthesis section

**2-octyl-thiophene.** Thiophene (8.4 g, 0.10 mol) was dissolved in 60 ml THF in a well-dried flask under the protection of N<sub>2</sub> flow. The solution was placed in a liquid nitrogen/acetone cooling bath, and n-butyl lithium (35 ml, 0.10 mol, 2.88 M in hexane) was added dropwise. The cooling bath was removed, and the solution was warmed to room temperature. 1-bromo-octane (19.3 g, 0.10 mol) was added in one portion. After 6 h, the solution was poured into 200 ml cool water. The organic layer was separated, and the aqua layer was extracted by ether. The organic layers were collected, washed with water, and dried over anhydrous MgSO<sub>4</sub> and the removal of solvent gave a crude product. Distillation under vacuum gave 13.9g (0.071mol, yield 71%) of 2-octyl-thiophene was obtained. <sup>1</sup>H NMR ( $\delta$ , CDCl<sub>3</sub>): 6.91 (d, 1H), 6.72(t, 1H), 6.60 (d, 1H), 2.55 (t, 2H), 1.62 (p, 2H), 1.20 (m, 10H), 0.93 (t, 3H).

**5-Octyl-thiophene-2-carbaldehyde.** 5-octyl-thiophene-2-carbaldehyde was prepared by the same procedure to make 2-octyl-thiophene, but N-carbaldehyde-piperidine (22.6g, 0.20mol) was used instead of 1-bromo-octane.

Distillation under vacuum gave 14.5 g (0.065mol, yield 65%) of colorless 5-Octyl-thiophene-2-carbaldehyde.  $^1\text{H}$  NMR ( $\delta$ ,  $\text{CDCl}_3$ ): 9.86 (s, 1H), 7.37 (d, 1H), 6.70 (d, 1H), 2.60 (t, 2H), 1.65 (p, 2H), 1.23 (m, 10H), 0.98 (t, 3H).  
Calculated for  $\text{C}_{13}\text{H}_{20}\text{OS}$ : C = 69.59; H = 8.98; S = 14.29; found: C = 69.78; H = 9.00; S = 14.31.

**2,5-Dibromo-3-methyl-thiophene.** 3-methyl-thiophene (10.78g, 0.11 mol) was dissolved in THF and acetic acid (80 mL:80 mL/v:v) in a 500 ml one necked flask equipped for stirring. n-Bromosuccinimide (39.16g, 0.22 mol) was added to the solution in one portion, and the solution was stirred for 1 h. Then the solution was extracted with ether; the organic extracts were washed with water three times and  $\text{NaHCO}_3$  (aq) twice. The organic layer was dried over anhydrous  $\text{Na}_2\text{SO}_4$  and the removal of solvent gave a crude product. Distillation under vacuum gave 24.0 g (0.94 mol, yield 85%) of colorless 2,5-dibromo-3-methyl-thiophene.  $^1\text{H}$  NMR ( $\delta$ ,  $\text{CDCl}_3$ ): 6.78 (s, 1H), 2.51 (s, 3H). Calculated for  $\text{C}_5\text{H}_4\text{Br}_2\text{S}$ : C = 23.46; H = 1.58; Br = 62.44; S = 12.53; found: C = 23.40; H = 1.60; Br = 62.30; S = 12.63.

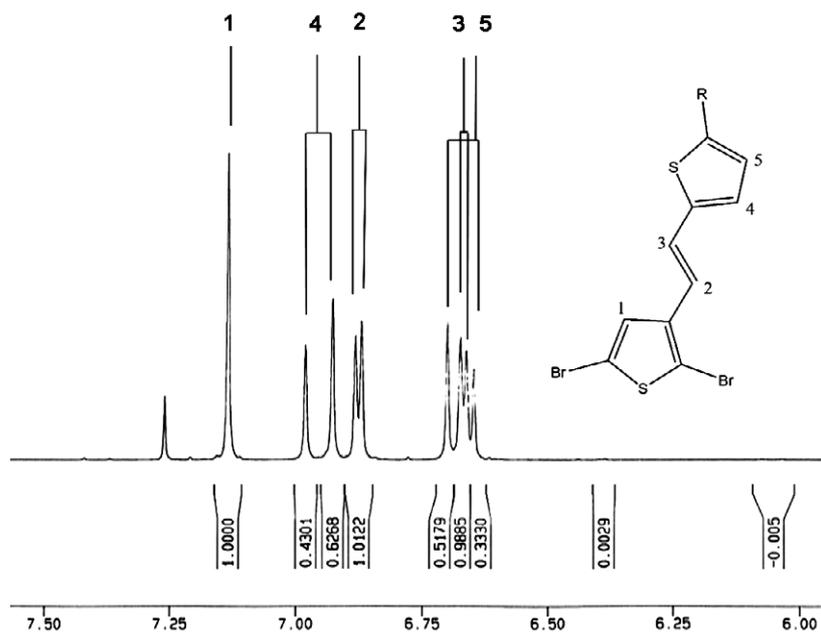
**2,5-Dibromo-3-bromomethyl-thiophene.** 2,5-Dibromo-3-bromomethyl-thiophene was prepared by reacting 2,5-dibromo-3-methyl-thiophene (12.8 g, 50 mmol) with N-bromosuccinimide (8.9 g, 50 mmol) in 100 mL of carbon tetrachloride ( $\text{CCl}_4$ ). A small amount of benzoyl peroxide was added as an initiator. The mixture was refluxed for 3 h under nitrogen atmosphere. The completion of the reaction was indicated by the appearance of succinimide on the surface of the solution. The organic layer was washed with water and dried over anhydrous  $\text{MgSO}_4$ . Distillation under vacuum gave 13.9 g (41 mmol, yield 83%) of colorless 2,5-dibromo-3-bromomethyl-thiophene.  $^1\text{H}$  NMR ( $\delta$ ,  $\text{CDCl}_3$ ): 6.42 (s, 1H), 4.56 (s, 2H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 300 MHz,  $\delta$ /ppm): 142.71, 134.53, 115.12, 113.12, 21.44.

**2,5-Dibromo-3-(5-octyl-thienylene-vinyl)-thiophene.** 2,5-dibromo-3-bromomethyl-thiophene (3.35 g, 10 mmol) and Phosphorous acid triethyl ester (1.66 g, 10 mmol) were put in a flask, and heated to  $160^\circ\text{C}$  for 2 h. This product of (2,5-Dibromo-thiophen-3-ylmethyl)-phosphonic acid diethyl ester was obtained and used directly without any purification.

(2,5-Dibromo-thiophen-3-ylmethyl)-phosphonic acid diethyl ester was dissolved in 20 ml DMF. Under an

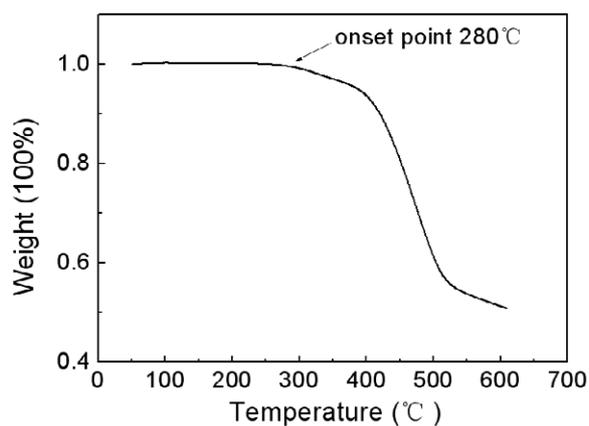
ice-water bath,  $\text{NaOCH}_3$  (0.6 g in 10 ml DMF) was added into the solution. Then 5-Octyl-thiophene-2-carbaldehyde (0.01 mol) was added dropwise to the solution. After 30 min, the solution was poured into cold water, and extracted with ether. The organic layer was washed with water and then dried over anhydrous  $\text{MgSO}_4$ , filtered, and concentrated. Purification was carried out via silica gel column chromatography, using petroleum ether as the eluent. After concentration, 2,5-Dibromo-3-[2-(5-octyl-thienyl)-vinyl]-thiophene was obtained as pale yellow oil (2.82g, yield 61%).  $^1\text{H NMR}$  ( $\delta$ ,  $\text{CDCl}_3$ ): 7.17 (s, 1H), 7.02 (d, 1H), 6.92 (d, 1H), 6.74 (d, 1H), 6.70 (d, 1H), 2.85 (t, 2H), 1.75 (p, 2H), 1.37 (m, 10H), 0.96 (t, 3H). Calculated for  $\text{C}_{18}\text{H}_{22}\text{Br}_2\text{S}_2$ : C, 46.76; H, 4.80; Br, 34.57; S, 13.87; found: C, 46.70; H, 4.77; Br, 34.63; S, 13.77.

**The synthesis of POTVT using Grignard Metathesis method.** At the protection of per-purified nitrogen atmosphere, the monomer, 2,5-Dibromo-3-(5-octyl-thienylene-vinyl)-thiophene, (3 mmol) was dissolved in fresh distilled THF (20 ml, resulting in a 0.15 M solution). To this solution was added methylmagnesium bromide (1.67 ml, 1.8 M in THF). The mixture was heated to reflux for 1 hour and at the same time  $\text{Ni}(\text{dppp})\text{Cl}_2$  (16 mg, 1 mol%) was added. After 45min at reflux, another  $\text{Ni}(\text{dppp})\text{Cl}_2$  (16 mg, 1mol%) was added again. After 30 min, the reaction was poured over 100 ml of methanol and then filtered through a Soxhlet thimble, which was then subjected to Soxhlet extraction with methanol, hexane, and THF. The polymer was recovered from the THF fraction by rotary evaporation. The solid was dried under vacuum for 1 day. After dried, 0.50 g (yield 55%) polymer of POTVT was obtained. Calcd. for  $\text{C}_{18}\text{H}_{22}\text{S}_2$ : C=71.47; H=7.33; S=21.20. Found: C=70.70 ; H=7.29; S=20.68; Br $\leq$ 0.30.



**Figure S1** <sup>1</sup>H NMR spectra of 2,5-Dibromo-3-(5-octyl-thienylene-vinyl)-thiophene (Compound 5)

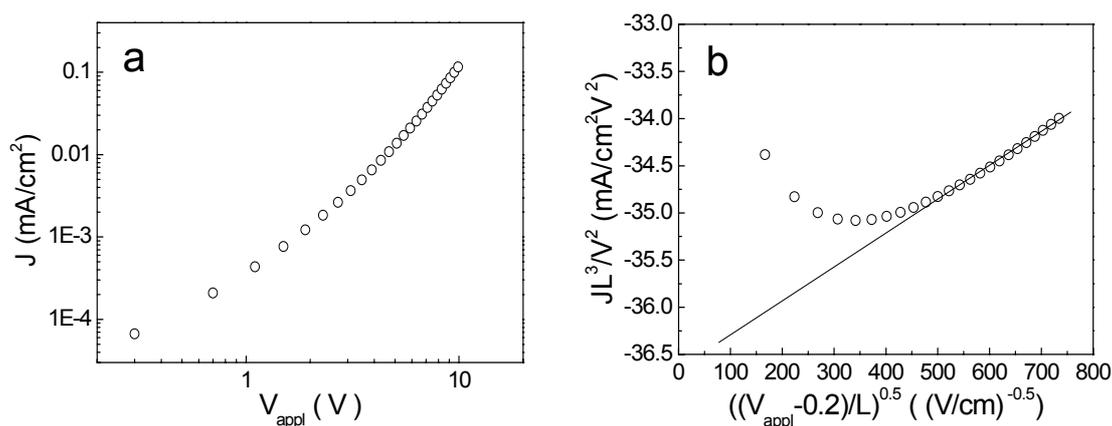
**Thermal stability.** TGA measurement was performed on a Perkin-Elmer TGA-7, and a sample of approximate 2.5 mg was temperature-equilibrated to 50~500°C, as a heating rate of 10°C/min.



**Figure S2.** TGA plot of POTVT.

**Measurement of hole mobility by space-charge limited current model.** We fabricated and characterized devices as reported by Malliaras. In Figure S2 (b), the current-voltage data was corrected for the built-in potential,

which was established from difference between the work functions of the anode (PEDOT:PSS) and the cathode (Au), and was shown as the logarithm of  $JL_3/V_2$  versus the square root of the mean electric field. The slope of a line in this plot gives the characteristic field  $E_0$  and the intercept, the zero-field mobility  $\mu_0$ . A fit yields  $\mu_0 = 3.7 \times 10^{-4} \text{ cm}^2/\text{Vs}$  and  $E_0 = 59 \text{ kV/cm}$  for the hole mobility.



**Figure S3.** (a) Current-voltage data from devices with Au cathodes and ITO/PEDOT:PSS anodes, and the structure of device was ITO/PEDOT:PSS(30nm)/POTVT(180nm)/Au,  $V_{\text{appl}}$  is the applied bias; (b)  $JL_3/V_2$  vs.  $((V_{\text{appl}} - 0.2)/L)^{0.5}$  plot, where  $V_{\text{appl}}$  was corrected by subtracting the work function difference (0.2) between the anode and the cathode.

### Fabrication of photovoltaic cells

Polymer photovoltaic cells were fabricated with ITO glass as an anode, Ca/Al as a cathode and the blend film of the polymer/PCBM in between as a photosensitive layer. The ITO glass was pre-cleaned and modified by a thin layer of PEDOT-PSS (Bayer) which was spin-cast from a PEDOT-PSS aqueous solution on the ITO substrate, and the thickness of PEDOT: PSS is about 50 nm. The photosensitive layer was prepared by spin-coating a blend solution of POTVT or P3HT and PCBM with a weight ratio of 1:1 in chlorobenzene at 1500 rpm on the ITO/PEDOT:PSS electrode. Then a metal cathode, which was made up of Ca and Al, was deposited on the polymer layer by vacuum evaporation under  $3 \times 10^{-4}$  Pa. The thickness of the photosensitive layer was measured to be ca.

160 nm. The effective area of one cell is about 10 mm<sup>2</sup>.

The  $I$ - $V$  curves of the PSCs based on POTVT and P3HT were shown in Figure S4 and S5. The short circuit current ( $I_{sc}$ ), open circuit voltage ( $V_{oc}$ ), power conversion efficiency (PCE) and fill factor (FF) of the PSC based on POTVT were 6.07 mA/cm<sup>2</sup>, 0.5 V, 1.30% and 36.4% under the illumination of AM1.5, 80 mW/cm<sup>2</sup>. For the PSC based on P3HT, these data were 4.06 mA/cm<sup>2</sup>, 0.6 V, 1.24% and 43.2% respectively.

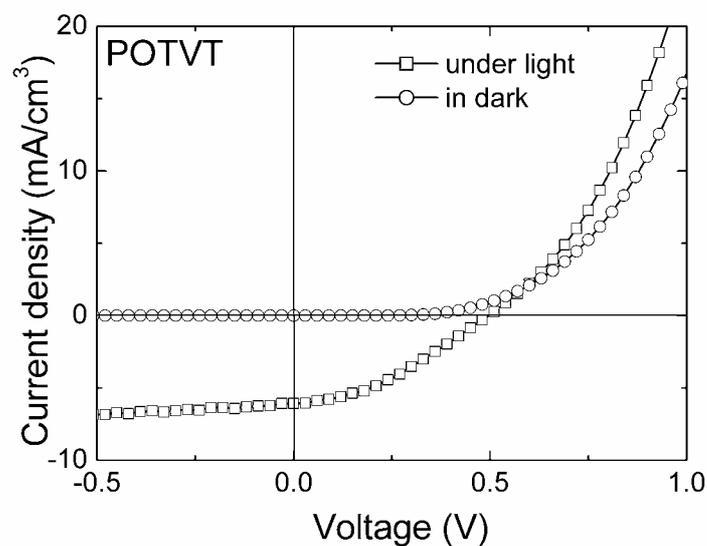


Figure S4.  $I$ - $V$  curves of the polymer solar cell based on the blend of POTVT and PCBM (1:1 w/w).

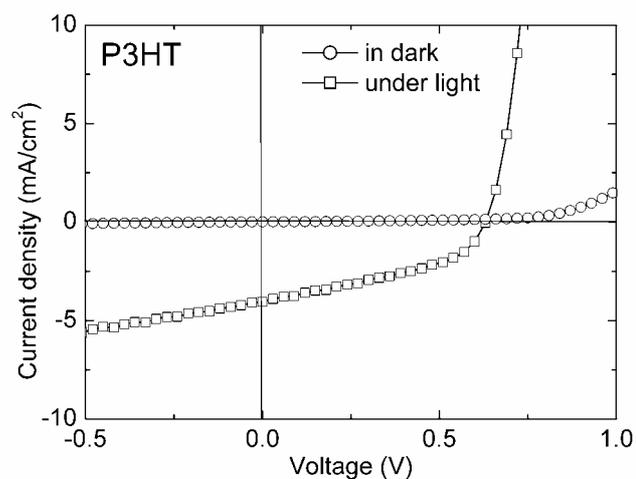


Figure S5.  $I$ - $V$  curves of the polymer solar cell based on the blend of P3HT and PCBM (1:1 w/w).

