

# Synthesis, characterization and photovoltaic applications of a low band gap polymer based on s-tetrazine and dithienosilole

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## Experimental Section

### Characterization

NMR spectra were recorded in CDCl<sub>3</sub>, or 1,2-dichlorobenzene-d<sub>4</sub> using a Varian Unity Inova spectrometer at a resonance frequency of 399.96 MHz for <sup>1</sup>H and 100.58 MHz for <sup>13</sup>C. UV-vis spectra were measured using a Varian Cary 5000 Spectrometer. Elemental analysis was performed on a TruSpec CHNS Micro Determinators from LECO. Gel permeation chromatography (GPC) (Waters Breeze HPLC system with 1525 Binary HPLC Pump and 2414 Differential Refractometer) was used for measuring the molecular weight and polydispersity index. Chlorobenzene was used as eluent and commercial polystyrenes were used as standard. The differential scanning calorimetry (DSC) analysis was performed under a nitrogen atmosphere (50 mL/min) using a TA Instruments DSC 2920 at a heating rate of 10 °C/min, calibrated with the melting transition of indium. The thermal gravimetric analysis (TGA) was performed using a TA Instruments TGA 2950 at a heating rate of 10 °C/min under a nitrogen atmosphere (60 mL/min). Cyclic voltammetry (CV) measurements were carried out under argon in a three-electrode cell using 0.1 M Bu<sub>4</sub>NPF<sub>6</sub> in anhydrous CH<sub>3</sub>CN as the supporting electrolyte. The polymer was coated on the platinum-working electrode. The CV curves were recorded with reference to an Ag quasi-reference electrode, which was calibrated using a ferrocene/ferrocenium (Fc/Fc<sup>+</sup>) redox couple (4.8 eV below the vacuum level) as an external standard. The E<sub>1/2</sub> of the Fc/Fc<sup>+</sup> redox couple was found to be 0.40 V vs the Ag quasi-reference electrode. Therefore, the HOMO and LUMO energy levels of the copolymers can be estimated using the empirical equation E<sub>HOMO</sub> = -(E<sub>ox</sub><sup>on</sup> + 4.40) eV and E<sub>LUMO</sub> = -(E<sub>red</sub><sup>on</sup> + 4.40) eV, respectively, where E<sub>ox</sub><sup>on</sup> and E<sub>red</sub><sup>on</sup> stand for the onset potentials for oxidation and reduction relative to the Ag quasi-reference electrode, respectively.

### Synthesis

**General:** 4,4'- Bis(2-ethyl-hexyl)-5,5'-bis(trimethylstannyl)-dithieno[3,2-b:2',3'-d]silole<sup>1</sup> was synthesized according to the procedure reported in the literatures.

**4-(2-Ethylhexyl)-2-thiophenecarbaldehyde, 1.** 3-(2-Ethylhexyl)-thiophene (19.6 g, 100 mmol) and anhydrous tetrahydrofuran (250 mL) were charged into a 500 ml flask. The solution was cooled to -78 °C with dry ice/acetone bath. n-butyl lithium (40 mL, 2.5 M in hexane, 100 mmol) was dropped into the solution. After addition, the reaction solution was warmed to room temperature and stirred for 30 min. Then, the solution was cooled to -78 °C again, and was added 1-formylpiperidine (13.6 g, 120 mmol) in one shot. The reaction solution was allowed to warm slowly to room temperature and stirred overnight. The solution was acidified with hydrochloric acid (2 N) and then extracted with ether (2x100 mL). The

organic extracts were combined and washed with distilled water (2x100 mL), dried over anhydrous magnesium sulfate and rotary evaporated to remove the solvent. The residue was purified by silica-gel column using ethyl acetate/hexanes (1/10, v/v, R<sub>f</sub> = 0.3) as the eluent to give a yellow liquid product (18.4 g, 78% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 9.86 (s, 1H), 7.56 (s, 1H), 7.34 (s, 1H), 2.59 (d, 2H, J = 6.8 Hz), 1.58 (m, 1H). 1.18-1.34 (m, 8H), 0.84 (t, 6H, J = 7.2 Hz); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 183.0, 143.5, 143.4, 137.7, 131.2, 40.3, 34.1, 32.3, 28.8, 25.4, 22.9, 14.1, 10.7. (Note: containing about 5% of 3-substituted isomer).

**4-(2-Ethylhexyl)-2-thiophenecarbonitrile, 2.** A mixture of 4-(2-ethylhexyl)-2-thiophenecarbaldehyde (17.3 g, 77.1 mmol) and hydroxylamine hydrochloride salt (8.04 g, 116 mmol) in pyridine/ethanol (40 mL, 1/1, v/v) was refluxed at 85 °C overnight. After cooling down to room temperature, the solvent was removed by rotary evaporator. The residue was taken up with chloroform (100 mL) and washed with distilled water (2x75 mL). After drying over anhydrous magnesium sulfate, the solvent was removed by rotary evaporator to give a yellowish liquid, which was dissolved in acetic anhydride (60 mL). Potassium acetate (0.4 g) was added to the resulting solution. The solution was then heated up to 140 °C and refluxed for 4 h. After cooling, the yellow solution was dropped into 100 mL of 5% NaOH aqueous solution and was extracted with hexane (2x100 mL). The combined organic layers were washed with distilled water and then dried over magnesium sulfate. The solvent was removed by rotary evaporator and the residue was purified by silica-gel column chromatography (EtOAc/Hex = 1/10, v/v, R<sub>f</sub> = 0.5) to yield a light yellow liquid product (15.6 g, 91% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.40 (d, 1H, J=1.2 Hz), 7.15 (d, 1H, J=1.2 Hz), 2.54 (d, 2H, J=6.8 Hz), 1.52 (m, 1H), 1.20-1.29 (m, 8H), 0.86 (m, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 142.8, 138.7, 128.2, 114.5, 109.2, 40.3, 33.9, 32.3, 28.8, 25.4, 22.9, 14.0, 10.7. (Note: the 3-substituted isomer can be removed by silica-gel column chromatography).

**3,6-Bis[4-(2-ethylhexyl)thien-2-yl]-s-tetrazine, 3.** To a solution of 4-(2-ethylhexyl)-2-thiophenecarbonitrile (14.1 g, 63.8 mmol) in ethanol (20 mL) was added hydrazine monohydrate (4.84 g, 95.7 mmol) and sulfur powder (1.02 g, 31.9 mmol). The resulting solution was stirred at room temperature for 10 min and then heated to 90 °C for 1.5 h. After cooling, the solution was rotary evaporated to give a red viscous residue that was dissolved in chloroform (50 mL). To the solution was added isopentyl nitrite (12.0 g, 102 mmol). The solution was stirred at room temperature for 24 h. The solvent was removed by rotary evaporation and the viscous residue was subjected to silica-gel column chromatography (EtOAc/Hex = 1/15, v/v, R<sub>f</sub> = 0.4) to yield the dark red liquid product (5.33 g, 36% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.05 (s, 2H), 2.62 (4H, d, J=7.2 Hz), 1.61 (m, 2H), 1.28-1.37 (m, 16H), 0.90 (m, 12H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 161.6, 144.4, 135.5, 132.6, 128.6, 40.6, 34.6, 32.7, 29.1, 25.8, 23.2, 14.3, 11.1.

**3,6-bis[5-bromo-4-(2-ethylhexyl)thien-2-yl]-s-tetrazine, 4.** To a solution of 3,6-bis[4-(2-ethylhexyl)thien-2-yl]-s-tetrazine (0.6 g, 1.45 mmol) in a mixture of CHCl<sub>3</sub> (15 mL) and glacial acetic acid (10 mL) was added N-bromosuccinimide (0.57 g, 3.18 mmol) at room temperature. The solution was heated and stirred at 50 °C for 4 h and 80 °C for 5h. The solution was subjected to vacuum distillation at about 50 °C to remove solvent completely. The resulting red solid residue was washed with MeOH twice. The product was purified by chromatography through a silica-gel column (CHCl<sub>3</sub>/hex = 2/8, v/v, R<sub>f</sub> = 0.4) to yield the product (red crystal). (1.17 g, 46% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.89 (s, 2H), 2.56 (d, 4H,

$J=7.2$  Hz), 1.65 (m, 2H), 1.25-1.35 (m, 16 H), 0.88 (m, 12 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  160.9, 144.1, 135.0, 132.2, 118.8, 40.1, 34.0, 32.7, 29.0, 25.9, 23.2, 14.3, 11.0.

**poly[(4, 4'-bis(2-ethylhexyl)dithieno[3,2-b:2',3'-d]silole)-5,5'-(3,6-bis[4-(2-ethylhexyl)thienyl-2-yl]-s-tetrazine), PDTSTTz.** To a 25 mL flask was added 4,4'-bis(2-ethylhexyl)-5,5'-bis(trimethylstannyl)-dithieno[3,2-b:2',3'-d]silole (0.3126 g, 0.420 mmol), **4** (0.2514 g, 0.400 mmol) N,N-dimethylformamide (DMF, 0.5 mL) and toluene (8 mL). The system was purged with Ar under vacuum.  $(\text{PPh}_3)_4\text{Pd}(0)$  (0.06 g, 0.006 mmol) was added in a glove box. The solution was stirred and reflux for 24 hr under the protection of Ar. After the solution was cooled down to room temperature, the solution was dropped into acetone to precipitate the copolymer. The copolymer was Soxhlet extracted with n-hexane and acetone, and then collected with hot toluene to obtain 0.32 g copolymer, (yield 91%). GPC:  $M_n = 22,100$  Da,  $M_w = 59,700$  Da, PDI = 2.70.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  8.07 (s, 2H); 7.28 (s, 2H); 2.83 (m, 4H); 1.77 (m, 2H); 1.47 (m, 2H); 1.15-1.44 (m, 32H), 1.03 (m, 4H), 0.89 (m, 12H); 0.82 (m, 12H). Anal. Calcd. For  $\text{C}_{50}\text{H}_{72}\text{N}_4\text{S}_4\text{Si}$  (%): C, 67.82; H, 8.20; N, 6.33; S, 14.48. Found (%): C, 67.53; H, 8.55; N, 6.01; S, 14.53.

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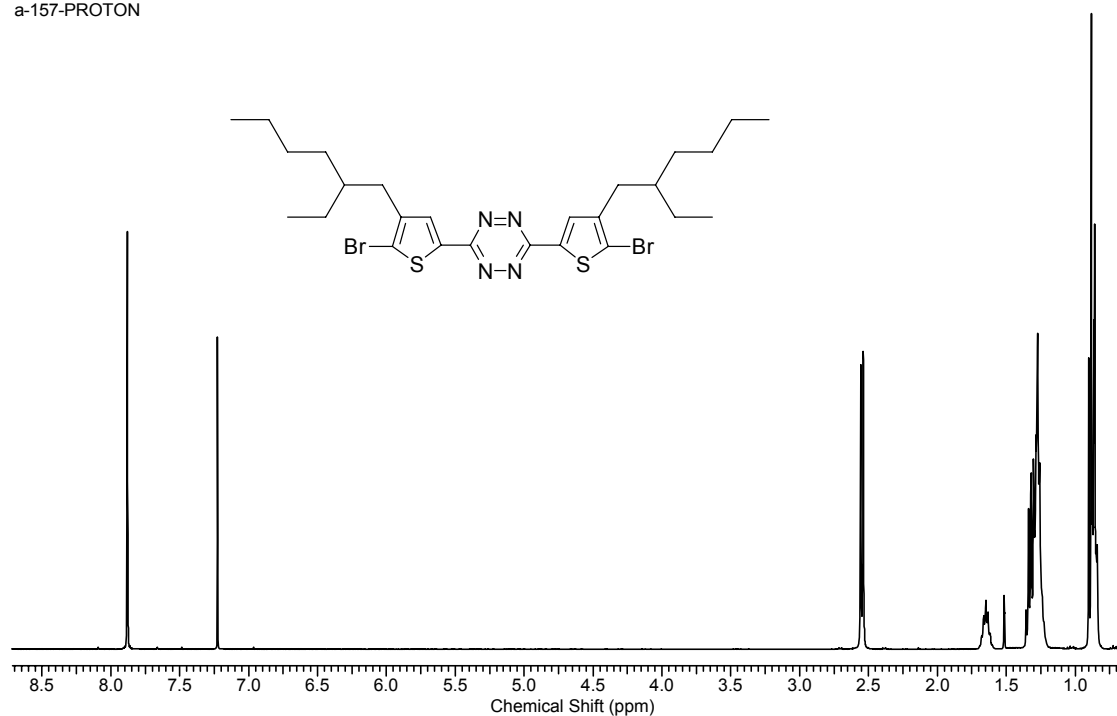


Figure S1.  $^1\text{H}$  NMR Spectrum of 3,6-bis[5-bromo-4-(2-ethylhexyl) thien-2-yl]-s-tetrazine, compound **4**.

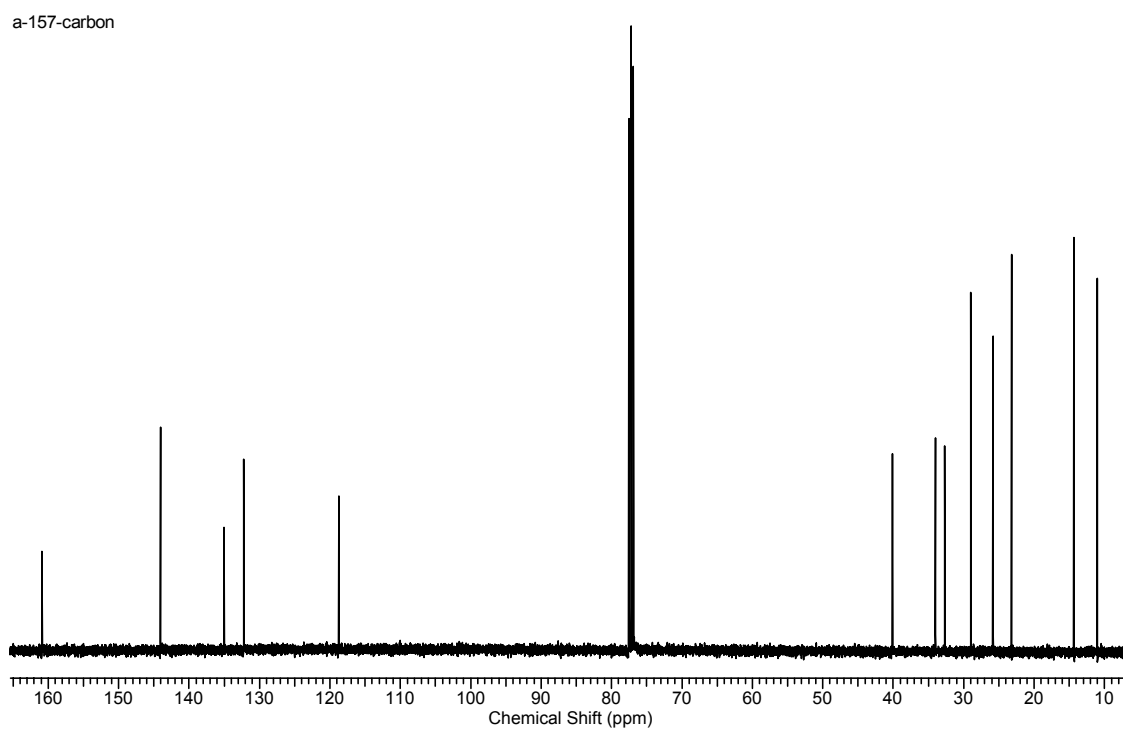


Figure S2.  $^{13}\text{C}$  NMR Spectrum of 3,6-bis[5-bromo-4-(2-ethylhexyl) thien-2-yl]-s-tetrazine, compound **4**.

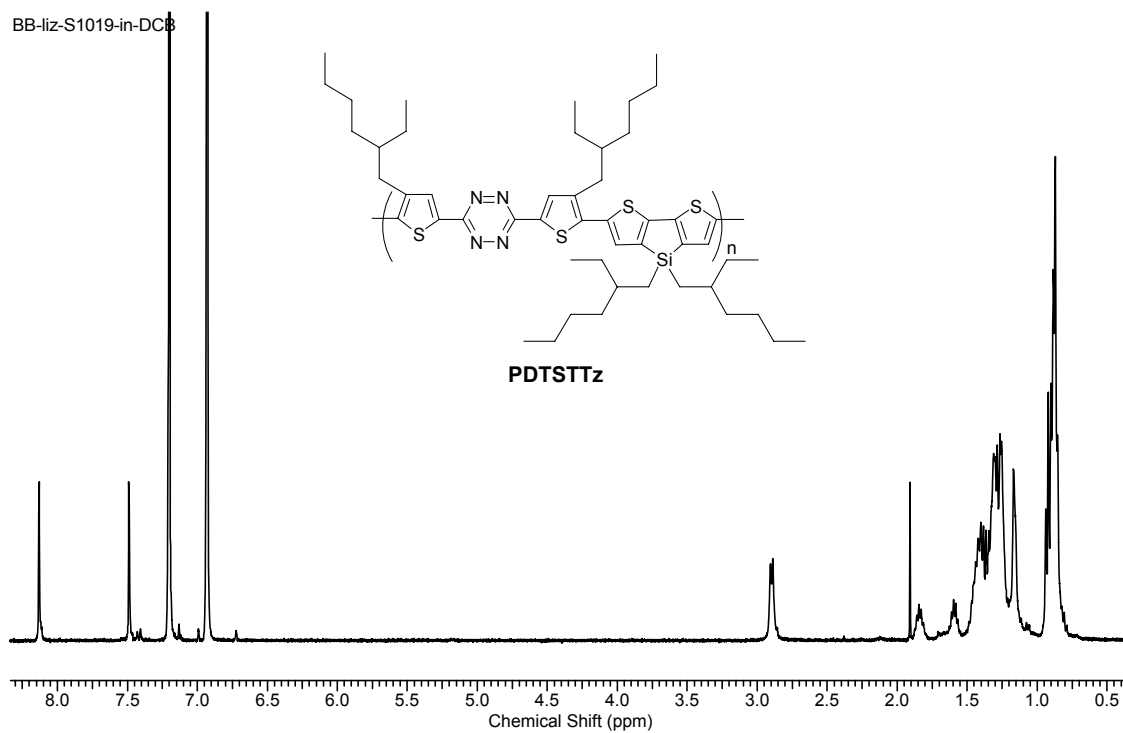


Figure S3.  $^1\text{H}$  NMR Spectrum of **PDTSTtz** in *o*-dichlorobenzene- $d_4$  at 100 °C.

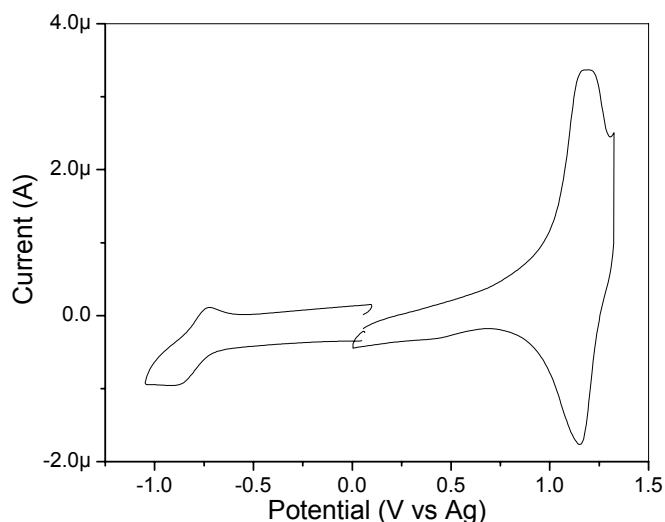


Figure S4. Cyclic voltammogram of PDTSTTz film cast on a platinum electrode in  $\text{Bu}_4\text{NPF}_6/\text{CH}_3\text{CN}$  solution. Fine tuning aa

#### Device fabrication and characterization

Polymer solar cells were fabricated with a general structure of ITO/PEDOT-PSS/PDTSTTz:PC<sub>71</sub>BM/ LiF/Al. Patterned ITO glass substrates were cleaned with detergent before sonicated in CMOS grade acetone and isopropanol for 15 min. The organic residue was further removed by treating with UV-ozone for 10 min. Then a thin layer of PEDOT:PSS (Clevios P, H. C. Starck, 45 nm) was spincoated and dried for 1 h at 120 °C. PDTSTTz and PC<sub>71</sub>BM (ADS) with a designed weight ratio (1:1, 1:2, and 1:3) were dissolved in o-dichlorobenzene containing 2.5% (v/v) diiodooctane at 80 °C. The solution was filtered and spin-coated on the top of PEDOT:PSS layer. The border of the PEDOT:PSS layer and active layer was mechanically removed before 1.0 nm of LiF and 100 nm Al layer were thermally deposited through a shadow mask at a pressure of  $5 \times 10^{-7}$  mbar in a Boc Edwards Auto 500 System. The active area is 50 mm<sup>2</sup>.

The current-voltage (J-V) characteristics were measured with a Keithley 2400 digital source meter under simulated air mass (AM) 1.5 solar irradiation of 100 mW/cm<sup>2</sup> (Sciencetech Inc., SF150). The light intensity was calibrated with a power meter (Gentec Solo PE Laser Power & Energy Meter). The external quantum efficiency (EQE) was performed using a Jobin-Yvon Triax 180 spectrometer, a Jobin-Yvon xenon light source, a Merlin lock-in amplifier, a calibrated Si UV detector, and an SR 570 low noise current amplifier. The reflectance data were collected at 6 degree using a Lambda 950 UV-vis-NIR spectrometer.

#### References:

1. J. Hou, H.-Y. Chen, S. Zhang, G. Li and Y. Yang, *J. Am. Chem. Soc.*, 2008, 130, 16144.