

Development of a New s-Tetrazine Based Copolymer for Efficient Solar Cells

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Experimental Section

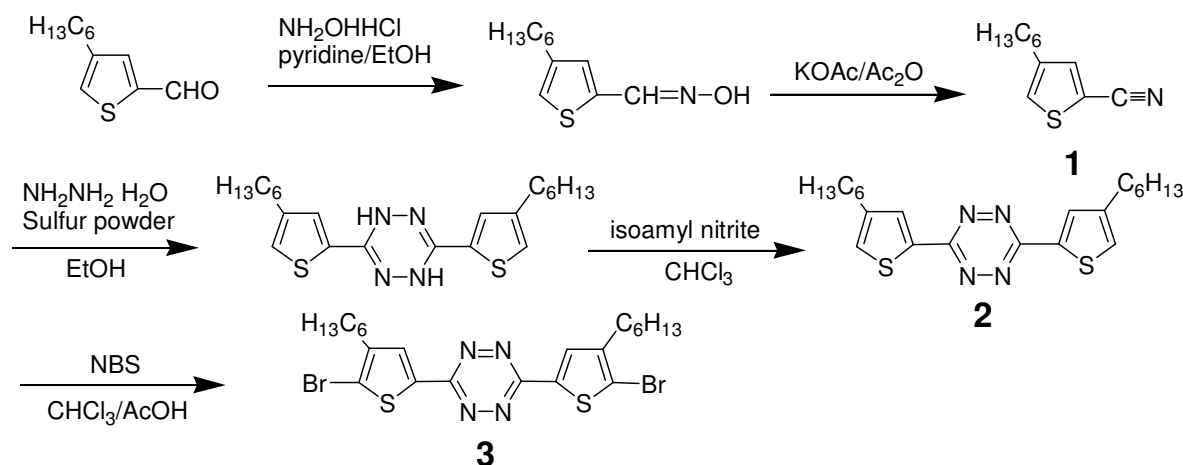
Characterization

NMR spectra were recorded in CDCl₃, or 1,2-dichlorobenzene-d₄ using a Varian Unity Inova spectrometer at a resonance frequency of 399.96 MHz for ¹H and 100.58 MHz for ¹³C. UV-vis spectra were measured using a Varian Cary 5000 Spectrometer. The onset values and optical band gap were estimated using the method of Tauc plot.¹ 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 standards. 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 Bu₄NPF₆ in anhydrous CH₃CN as the supporting electrolyte. The polymer was coated on the platinum-working electrode from a 1,2-dichlorobenzene solution. The CV curves were recorded referenced to an Ag quasi-reference electrode, which was calibrated using a ferrocene/ferrocenium (Fc/Fc⁺) redox couple (4.8 eV below the vacuum level) as an external standard. The half wave potential (E_{1/2}) of the Fc/Fc⁺ 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_{HOMO} = -(E_{1/2}^{ox} + 4.40) eV and E_{LUMO} = -(E_{1/2}^{red} + 4.40) eV, respectively, where E_{1/2}^{ox} and E_{1/2}^{red} stand for the half wave potentials of the oxidation and reduction couples relative to the Ag quasi-reference electrode, respectively. High-resolution mass spectrum was measured with Kratos Concept 1S Mass Spectrometry.

Synthesis

General: 4-hexylthiophene-2-carbaldehyde² and 4,4-dihexyl-2,6-bis(trimethylstannanyl)-4H-cyclopenta[2,1-b:3,4-b']dithiophene³ were synthesized according to the procedure reported in the literatures.

Scheme S1. Synthesis of the tetrazine monomer



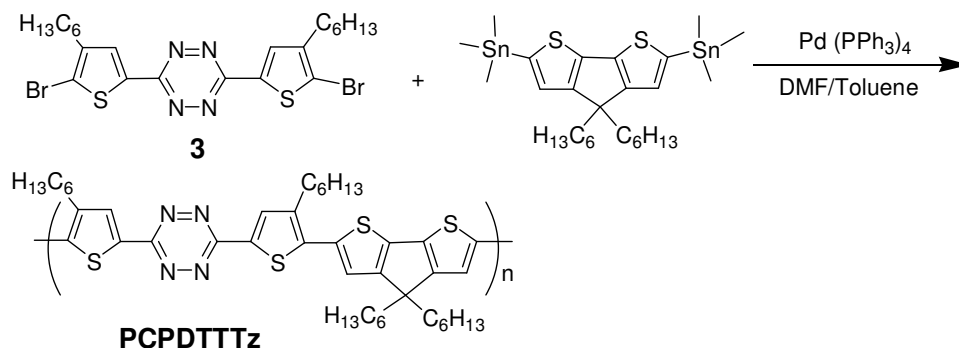
4-hexylthiophene-2-carbonitrile (1): A mixture solution of 4-hexylthiophene-2-carbaldehyde (11.8 g, 60.0 mmol) and hydroxylamine hydrochloride salt (6.3 g, 90 mmol) in pyridine/ethanol (60 mL, 1/1 v/v) was stirred at 80 °C overnight. Then the solvent was removed using a rotary evaporator. The residue was dissolved in chloroform (100 mL), and the solution was washed with distilled water (2 x 50 mL) and dried over anhydrous magnesium sulphate. The solvent was removed under vacuum, and the viscous liquid residue was dissolved in acetic anhydride (30 mL) containing potassium acetate (0.2 g) and then refluxed for 3 hours. The mixture was poured into distilled water (100 mL) and extracted with hexanes (3 x 50 mL). The organic phase was washed with 5% aqueous sodium hydroxide solution and then water, dried over anhydrous magnesium sulphate before the solvent was removed by a rotate evaporator. The yellow liquid residue was purified by silica-gel column chromatograph (EtOAc/hexane=7/93, v/v, Rf=0.4) to yield a clear light yellow liquid product. (9.8 g, 84.5% yield). ^1H NMR (400 MHz, CDCl_3): δ 7.43 (d, 1H, $J=1.4$ Hz); 7.17 (d, 1H, $J=1.4$ Hz); 2.60 (t, 2H, $J=8.0$ Hz); 1.59 (m, 2H); 1.22-1.36 (m, 6H); 0.87 (m, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 144.04, 138.22, 127.41, 114.48, 109.28, 31.45, 30.18, 29.86, 28.67, 22.46, 13.96. HRMS EI calcd for $\text{C}_{11}\text{H}_{15}\text{S}$ 193.0925, found 193.0915.

3,6-bis(4-hexyl-2-thienyl)-1,2,4,5-tetrazine (2): To a mixture of compound **1** (4.6 g, 23.8 mmol) and sulphur (0.53 g, 16.7 mmol) in anhydrous ethanol (15 mL) was slowly added fresh hydrazine monohydrate (1.8 g, 35.7 mmol) at room temperature. The solution turned into yellow and large amount of gas evolved. The solution was heated up to reflux and stirred for 2h. Then was cold down to room temperature with crystal formed in solution. The crystal was collected by filtration and rinsed with cold ethanol before dried under vacuum. To a chloroform solution (50 mL) of the obtained solid, isoamyl nitrite (5.58 g, 47.6 mmol) was added and the solution was stirred at room temperature overnight. The solvent was removed and the resulting red solid was washed with methanol twice before purified by silica-gel column chromatography (CHCl_3 /Hexane=4/6, v/v, Rf=0.5) to yield red needle-like crystal (2.0 g, yield: 40.5%). ^1H NMR (400 MHz, CDCl_3): δ 8.07 (d, 2H, $J=1.6$ Hz); 7.26 (d, 2H, $J=1.6$ Hz); 2.68 (t, 4H, $J=7.6$ Hz); 1.63-1.71 (m, 4H); 1.29-1.40 (m, 12H); 0.89 (m, 6H). ^{13}C NMR (100 MHz, CDCl_3): δ 161.35, 145.46, 135.48, 131.88, 127.57, 31.62, 30.37, 30.34, 28.87, 22.58, 14.08. HRMS EI calcd for $\text{C}_{22}\text{H}_{30}\text{N}_4\text{S}_2$ 414.1912, found 414.1895.

3,6-bis(5-bromo-4-hexyl-2-thienyl)-1,2,4,5-tetrazine (3): To a suspension solution of compound **2** (0.9 g, 1.8 mmol) in chloroform (20 mL) and acetic acid (20 mL) was added N-

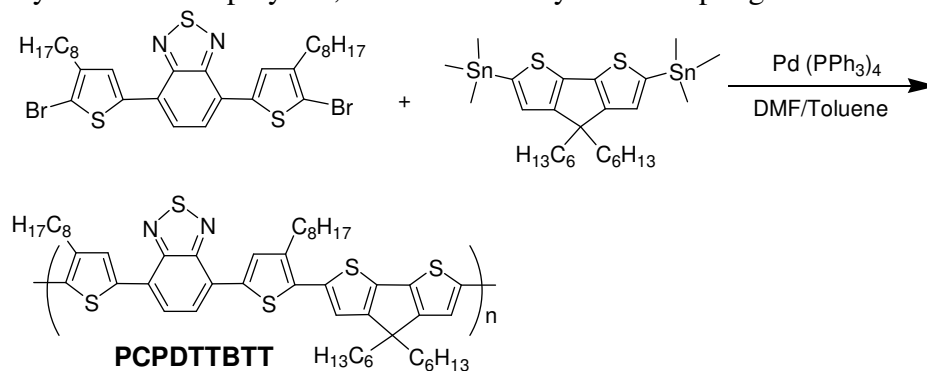
bromosuccinimide (0.32 g, 1.8 mmol) at room temperature. The mixture was stirred at RT under dark for 1h before heated at 80 °C for 5h. Then the solution was poured into distilled water (100 mL) and extracted with chloroform (3 X 30 mL). The organic phase was washed with water, dried over anhydrous magnesium sulphate. The solvent was removed by a rotate evaporator and the residue was purified by silica-gel chromatography (CHCl₃/hexane=1/2, v/v, R_f=0.5) to yield the product (0.9 g, yield 87%). ¹H NMR (400 MHz, CDCl₃): δ 7.93 (s, 2H); 2.63 (t, 4H, J=7.6 Hz); 1.65 (m, 4H); 1.28-1.40 (m, 12H); 0.89 (m, 6H). ¹³C NMR (100 MHz, CDCl₃): δ 160.67, 144.59, 134.95, 131.47, 117.94, 31.56, 29.57, 29.45, 28.82, 22.56, 14.06. HRMS EI calcd for C₂₂H₂₈N₄Br₂S₂ 570.0122, found 570.0127.

Scheme S2. Synthesis of the polymer, PCPDTTTz by Stille coupling reaction



PCPDTTTz: 4,4-dihexyl-2,6-bis(trimethylstannanyl)-4H-cyclopenta[2,1-b:3,4-b']dithiophene (0.2756 g, 0.410 mmol) and compound 3 (0.2290 g, 0.400 mmol) were dissolved in a mixture of 8 mL of toluene and 0.8 mL of N,N-dimethyl formamide (DMF). The mixture were purged with argon under vacuum for 3 times before 6 mg of Pd(PPh₃)₄ was added in a glove box. Then the solution was stirred and refluxed for 24 hours under argon before was cooled to room temperature and precipitated into acetone. The resulted polymer was further purified by Soxhlet extraction with hexanes, acetone and toluene. The polymer recovered from dichlorobenzene was precipitated in acetone and dried under vacuum for 16 hours to get PCPDTTTz as dark solid (110 mg, yield: 36%). GPC: M_n=20.0K, M_w=28.2K, PDI=1.41. ¹H NMR (1,2-dichlorobenzene-d₄, 100°C): δ 8.11 (s, 2H); 7.37 (s, 2H); 2.91(t, 4H); 2.05(br, 4H); 1.78 (m, 4H); 1.46(m, 4H); 1.10-1.40(m, 24H), 0.89(t, 6H); 0.82(t, 6H).

Scheme S3. Synthesis of the polymer, PCPDTTBTT by Stille coupling reaction



PCPFTTBTT, poly(2,6-(4,4-dihexyl-4H-cyclopenta[2,1-b:3,4-b']dithiophene)-alt-5,5'-(4,7-bis(4-octylthienyl-2-yl)-2,1,3-benzothiadiazole: 4,4-dihexyl-2,6-bis(trimethylstannanyl)-4H-cyclopenta[2,1-b:3,4-b']dithiophene (0.1378 g, 0.205 mmol) and 4,7-bis(5-bromo-4-octyl-2-thienyl)-2,1,3-benzothiadiazole⁴ (0.1365 g, 0.200 mmol) were dissolved in a mixture of 5 mL of toluene and 0.5 mL of DMF. The mixture were purged with argon under vacuum for 3 times before 3 mg of Pd(PPh₃)₄ was added in a glove box. Then the solution was stirred and refluxed for 24 hours under argon before was cooled to room temperature and precipitated into MeOH. The resulted polymer (0.168 g) was further purified by Soxhlet extraction with acetone, hexanes and dichloromethane. The polymer recovered from chloroform was precipitated in methanol and dried under vacuum for 16 hours, to get PCPDTTZ as dark solid (70 mg, yield: 40%). GPC: M_n=40.7K, M_w=68.3K, PDI=1.68. ¹H NMR (1,2-dichlorobenzene-d₄, 100 °C): δ 8.11 (s, 2H); 7.74 (s, 2H); 7.33 (s, 2H); 2.97 (br, 4H); 2.04(br, 4H); 1.85 (br, 4H); 1.50 (br, 4H); 1.04-1.40 (m, 28H), 0.86-0.98 (m, 10H); 0.82(br, 6H).

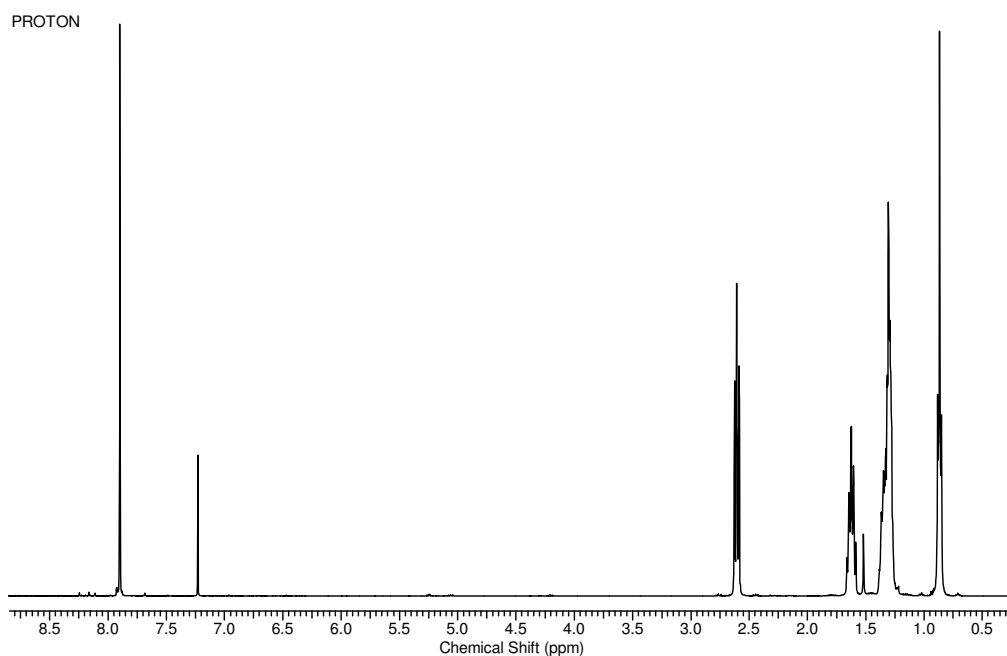


Figure S1. ¹H NMR spectrum of 3,6-bis(5-bromo-4-hexyl-2-thienyl)-1,2,4,5-tetrazine, compound **3**.

ID-Liz-S1040-C

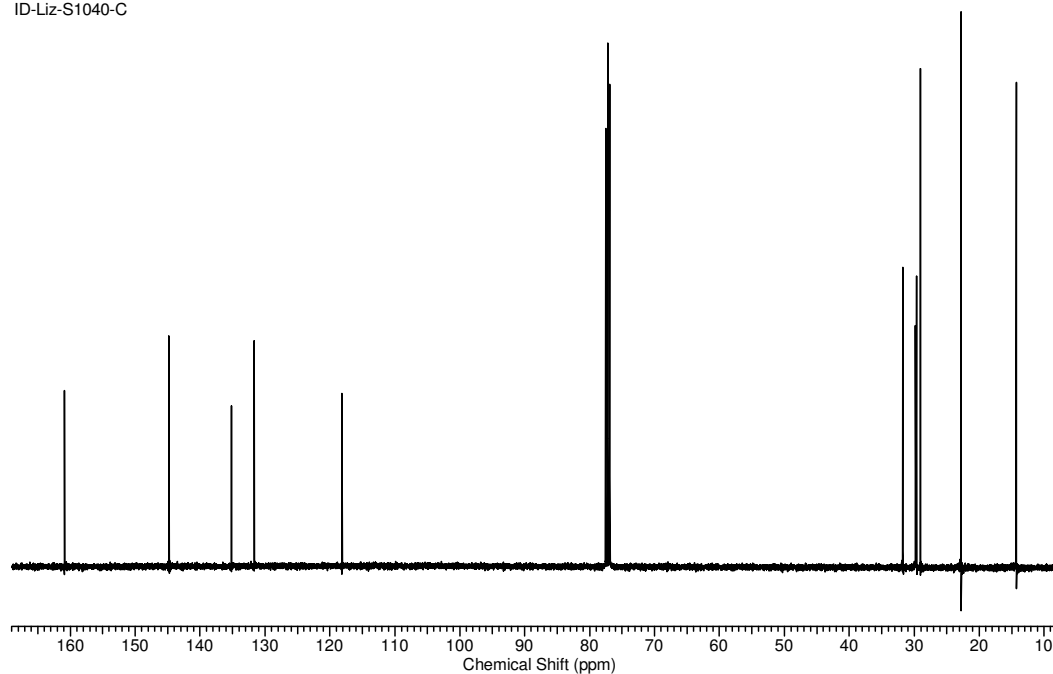


Figure S2. ^{13}C NMR spectrum of 3,6-bis(5-bromo-4-hexyl-2-thienyl)-1,2,4,5-tetrazine, compound **3**.

BB-liz-S1047-in-DCB

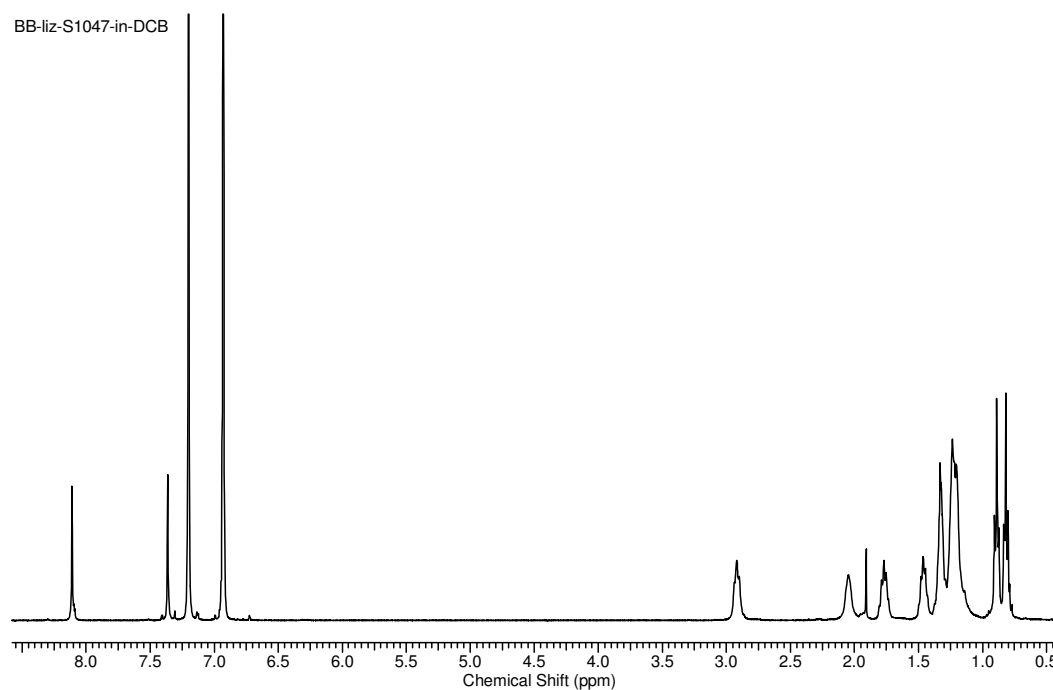


Figure S3. ^1H NMR Spectrum of the polymer, PCPDTTz in 1,2-dichlorobenzene- d_4 at 100 $^\circ\text{C}$.

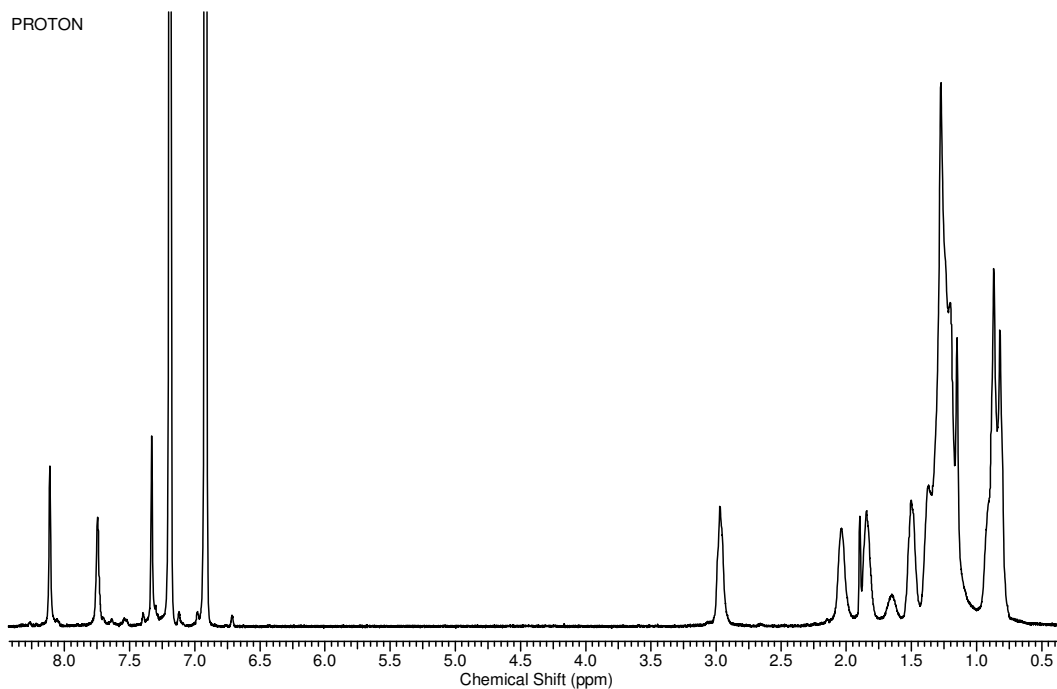


Figure S4. ^1H NMR Spectrum of the polymer, PCPDTTBTT in 1,2-dichlorobenzene- d_4 at 100 $^\circ\text{C}$.

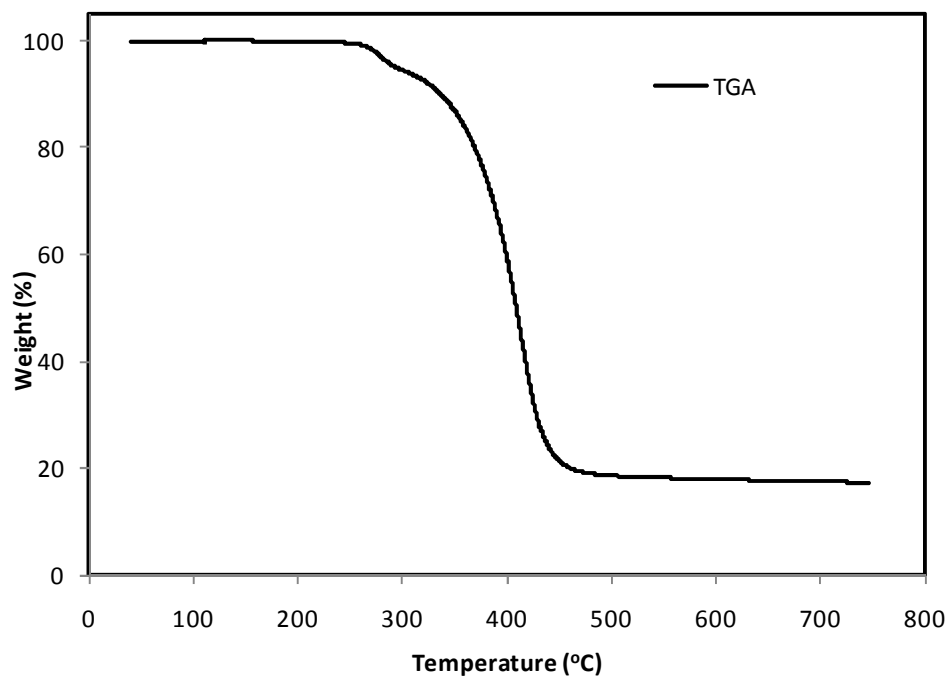


Figure S5. TGA curve of PCPDTTTz collected under N_2 at a heating rate of 10 $^\circ\text{C}/\text{min}$.

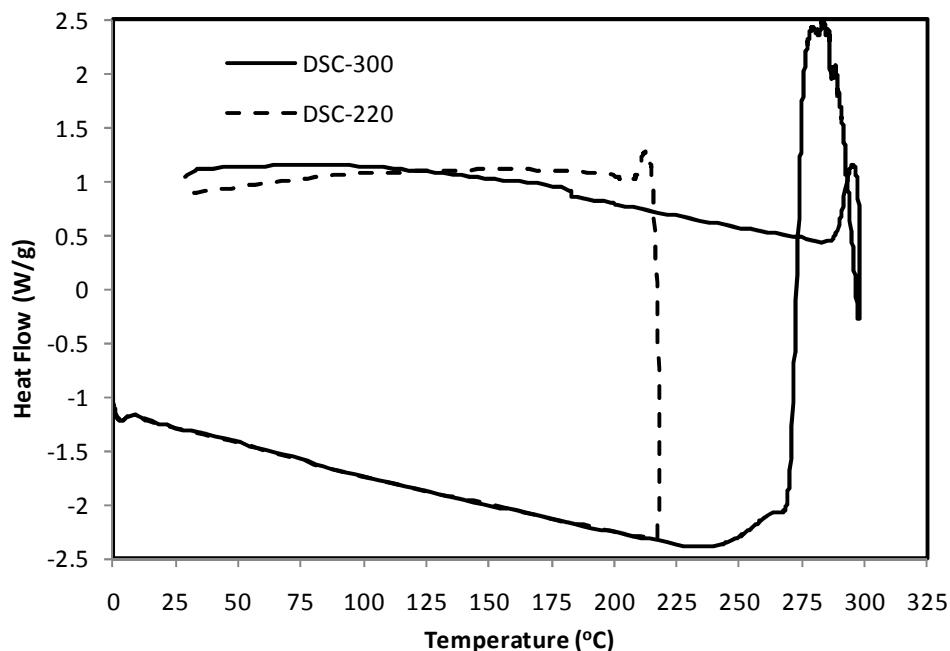


Figure S6. DSC curve of PCPDTTTz collected under N₂ at a scanning rate of 10°C/min (dashed line: 0 to 220°C cycle; solid line: 0 to 300°C cycle).

Device fabrication and characterization

Polymer solar cells were fabricated with a general structure of ITO/PEDOT:PSS/PCPDTTTz:PC₇₁BM/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. PCPDTTZ and PC₇₁BM (ADS) (1:2 weight ratio) was dissolved in a mixture of o-dichlorobenzene and diiodooctane (2.5% v/v) at 100 °C. The solution was filtered and spincoated 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 5×10^{-7} mbar in a Boc Edwards Auto 500 System. The active area is 50 mm².

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 100mW/cm² (Sciencetech Inc., SF150). The light intensity was calibrated with a power meter (Gentec Solo PE Laser Power & Energy Meter). The external quantum efficiency (EQE) curve was measured using a Jobin-Yvon Triax 180 spectrometer, a Jobin-Yvon xenon light source, a Merlin lock-in amplifier, a calibrated Si UV detector, and a SR 570 low noise current amplifier. The reflectance data were collected at 6 degree using a Lambda 950 UV-vis-NIR spectrometer.

Comparison with benzothiathiazole based polymers

In order to evaluate the electron deficient property of the tetrazine unit in the tetrazine polymer, PCPDTTTz, we attempt to compare its cyclic voltammetry (CV) behavior with one of its closest benzothiadiazole analogue. Therefore, poly(2,6-(4,4-dihexyl-4H-cyclopenta[2,1-b:3,4-b'] dithiophene)-alt-5,5'-(4,7-bis(4-octylthienyl-2-yl)-2,1,3-benzothiadiazole), PCPFTTBTT has been prepared. This polymer has the same main chain structure of the polymer reported in literature,⁵ while with an octyl group attached on the thiophene ring at the 4-position to make it comparable with PCPDTTTz. The CV measurements of these two polymers were conducted at the same condition.

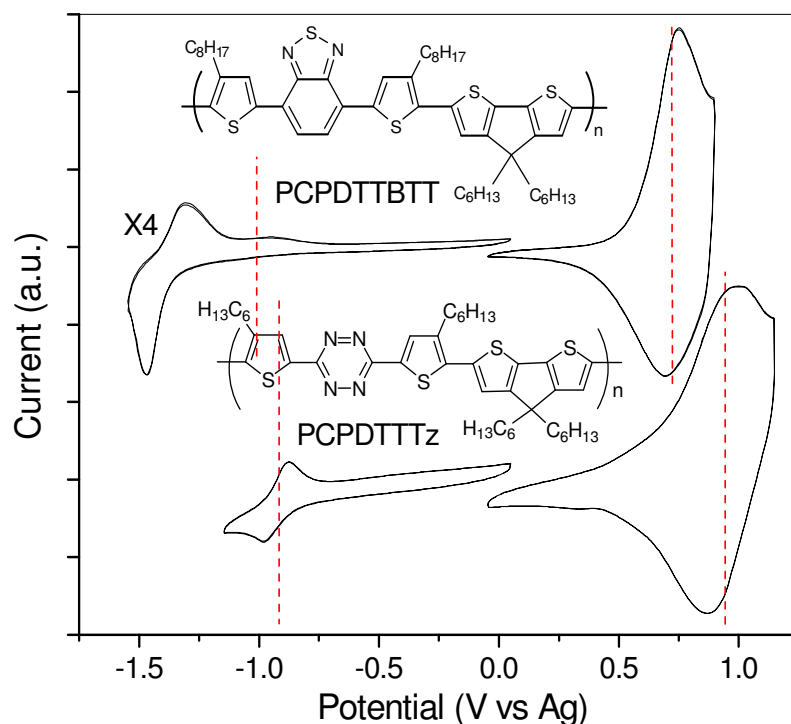


Figure S7. Cyclic voltammogram of PCPDTTBTT and PCPDTTTz film cast on a platinum electrode in 0.1 M Bu₄NPF₆/CH₃CN solution.

Table S1. Energy levels and band gap of PCPDTTBTT and PCPDTTTz.

Polymer	Half wave potentials (eV)		HOMO (eV)	LUMO (eV)	Egap (eV)
	Eox	Ered			
PCPDTTBTT	0.72	-1.01	-5.12	-3.39	1.73
PCPDTTTz	0.94	-0.92	-5.34	-3.48	1.86

Figure S7 and Table S1 showed PCPDTTTz has lower LUMO and HOMO energy levels than its benzothiadiazole analogue, PCPDTTBTT, although the latter has a narrower band gap. This

result indicates tetrazine unit in the polymer main chain has a higher electron deficient effect than benzothiadiazole unit. The lower HOMO energy level of the tetrazine polymer (0.22 eV lower) also explains why the device from PCPDTTz show a higher V_{oc} (0.75 V) than PCPDTTBTT (V_{oc} =0.60 V).⁵

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