Thiophene fluorination to enhance photovoltaic performance in low band gap donor –acceptor polymers.

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Experimental section:

General: Reagents and chemicals were purchased from Aldrich and Acros unless otherwise noted. 9-(Bromomethyl)nonadecane **(1)**[1], 3,3'-Dibromo-5,5'-bis(trimethylsilyl)-2,2'-bithiophene (**4**)[2], (5-Bromo-3,4-difluoro-thiophen-2-yl)-trimethyl-silane (**7**)[3] and 4,7-Bis(5-bromo-2-thienyl)-2,1,3-benzothiadiazole (**11**)[4] were synthesized by the reported method. Commercial 2,1,3-benzothiadiazole-4,7-bis(boronic acid pinacol ester) (**8**) was purified by chromatography over silica gel (eluent: 3% ethyl acetate in hexane), followed by recrystallisation from hexane before use.

All reactions were carried out under Ar using solvents and reagents as commercially supplied, unless otherwise stated. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AV-400 (400 MHz), using the residual solvent resonance of $CDCl_3$ or d-1,1,2,2-tetrachloroethane and are given in ppm. Number-average (Mn) and Weight-average (Mw) were determined by Agilent Technologies 1200 series GPC running in chlorobenzene at 80°C, using two PL mixed B columns in series, and calibrated against narrow polydispersity polystyrene standards. Preparative GPC utilised a Shimadzu recycling GPC system running in hexane at 40°C or chlorobenzene at 80°C, using Agilent PLgel 10μm 50A or MIXED-D column, DGU-20A3 Degasser, LC-20A Pump, CTO-20A Column Oven andSPD-20A UV Detector. Electrospray mass spectrometry was performed with a Thermo Electron Corporation DSQII mass spectrometer. UV-vis spectra were recorded on a UV-1601 Shimadzu UV-vis spectrometer. Flash chromatography (FC) was performed on silica gel (Merck Kieselgel 60 F254 230-400 mesh). Photo Electron Spectroscopy in Air (PESA) measurements were recorded with a Riken Keiki AC-2 PESA spectrometer with a power setting of 5nW and a power number of 0.5. Samples for PESA were prepared on glass substrates by spin-coating. Thermogravimetric analysis (TGA) was carried out using a Perkin Elmer Pyris 1 TGA machine, with heating from 100 to 700°C, in dry air, at a heating rate of 10°C/min. Differential scanning calorimetry (DSC) measurements: ~4 mg material was used for the DSC experiments, which was conducted under nitrogen at scan rate of 20 ˚C min^{-1} with a TA DSC-Q20 instrument.

OFET (organic field effect transistors) devices fabrication:

Bottom-gate, bottom-contact OFETs were fabricated on Si/SiO_2 substrates with photolithographically patterned gold electrodes. The electrodes were again treated with the pentafluorobenzene thiol SAM and the SiO_2 was treated with an octadecyltrichlorosilane (OTS) SAM. The channel width and length of the transistors are 1.5 mm and 20 μm, respectively. The polymer was dissolved in dichlorobenzene (5 mg/ml) at 100°C and spin cast to 100 °C substrates before being annealed at 140 °C for 15 min. V_G varied from 0 to -150 V in 1 V steps and V_D set at -10 (linear) and -150 V (saturation).

OPV fabrication and characterization:

All organic photovoltaic devices have a conventional device architecture, ITO/PEDOT: PSS/Polymer:PC71BM/LiF/Al. The precoated ITO glass substrates were cleaned with acetone and isopropyl alcohol under sonification, followed by drying and oxygen plasma treatment. A 30 nm layer of PEDOT:PSS was spin-coated onto the plasma-treated ITO substrate and baked at 150°C for 20 minutes. An 80 nm active layer consisting of 1:1 to 1:4 blend ratios (wt%) of **PGeTFDTBT** or 1:2 blend ratio of **PGeDTBT** and $PC_{71}BM$ was spin-coated on the PEDOT:PSS layer. Active layers were spincoated from o-dichlorobenzene solution containing 12 mg/mL of polymer. The solubility of the polymer was comparatively better in oDCB than in chlorobenzene on heating. Solutions were heated to 90 ^{o}C overnight to ensure full dissolution. Spincoating was performed on substrates at room temperature while solutions were at 60 ^{o}C. The LiF (1 nm)/Al (120 nm) cathode was finally deposited by thermal evaporation under high vacuum (10^{-6} mbar) through a shadow mask. The pixel size, defined by the spatial overlap of the ITO anode and Ca/Al cathode, was 0.045 cm^2.

The device characteristics were obtained using a Xenon lamp at AM1.5 solar illumination (Oriel Instruments). Incident photon conversion efficiency (IPCE) measurements were made using a 100 W tungsten halogen lamp (Bentham IL1 with Bentham 605 stabilized current power supply) coupled to a monochromator with computer-controlled stepper motor (Bentham M300, 300 mm focal length, slit width 3.7 nm, 1800 lines/m grating) The photon flux of light incident on the samples was calibrated using a UV-enhanced silicon photodiode. A 590 nm long-pass glass filter was inserted into the beam at illumination wavelengths longer than 620 nm to remove light from second-order diffraction. Photocurrent was measured using a Keithley 2400 source meter; Measurement duration for a given wavelength was sufficient to ensure the current had stabilized (up to around 5 s under low or zero bias light conditions).

Synthesis of monomer and polymer:

*Diphenybis(2-octyldodecyl) germane (**2**):*

1,2-dichloroethane (1 mL) was added to a dry three neck 500 mL round bottom containing Mg (2.8 g, 117.0 mmol), 9-(bromomethyl)nonadecane (3.4 g, 9.3 mmol) and THF (30 mL). After the reaction was initiated, 9-(bromomethyl)nonadecane (30.3 g, 83.7 mmol) in THF (150 mL) was added dropwise. After complete addition the mixture was refluxed overnight and then cooled to room temperature. The resulting solution of Grignard reagent was then added to a separate flask containing a solution of germanium tetrachloride (5.0 g, 23.3 mmol) in THF (50 mL) at room temperature and the mixture was heated to reflux for 10 h. After cooling to room temperature, phenylmagnesium bromide solution (93 ml of a 1 M solution in THF, 93 mmol) was added dropwise and the resulting mixture was refluxed for 6 h. Then the mixture was cooled to 0 °C and water was added to quench this reaction. Then dilute HCl solution was added and the mixture extracted (3 x 150 mL hexane).Then combined organic phase was washed by saturated $NaHCO_3$ (200 mL) and brine (200 mL). The organics were dried ($MgSO_4$), filtered and the solvent removed solvent under reduced pressure. The residue was purified by silica gel chromatography (eluent: hexane) to afford **2** as a pale yellow oil (12.0 g, yield: 65%). ^{1}H NMR ($CDCl_3$, 400 MHz), δ (ppm): 7.47-7.44 (m, 4H), 7.33-7.30 (m, 6H), 1.52-1.49 (m, 2H), 1.33-1.08 (m, 68H), 0.91-0.87 (m, 12H). ^{13}C NMR ($CDCl_3$, 100 MHz), δ (ppm): 140.1, 134.6, 128.2, 127.8, 36.3, 34.6, 31.9, 31.9, 29.9, 29.7, 29.7, 29.6, 29.4, 26.4, 22.7,19.9, 14.1. HRMS (ESI): [M-H^{+}] Calculated for $C_{52}H_{91}Ge$: 789.6333; found: 789.6331.

*Dibromobis(2-octyldodecyl) germane (**3**)*:

In a 100 mL three neck round bottom flask, diphenylbis(2-octyldodecyl) germane (**2**) (6.0 g, 7.6 mmol) was dissolved in dry 1,2-dichloroethane (30 mL). Bromine (0.82 mL, 16.0 mmol) in 1,2-dichloroethane (15 mL) was added dropwise to the solution in the absence of light. The reaction mixture was heated at reflux for overnight, cooled and the solvent was removed under reduced pressure. The resulting oil was dried under high vacuum to afford **3** as a pale yellow oil (5.92 g, yield: 98%). ^{1}H NMR ($CDCl_3$, 400 MHz), δ (ppm): 1.86-1.81 (m, 6H), 1.35-1.28 (m, 64H), 0.93-0.88 (m, 12H). ^{13}C NMR ($CDCl_3$, 100 MHz), δ (ppm): 35.4, 34.9, 31.9, 29.8, 29.7, 29.6,29.4, 29.3, 26.2, 22.7, 14.1. HRMS (ESI): [M-H^{+}] Calculated for $C_{40}H_{81}Br_2Ge$: 793.3917; found: 793.3897.

*4,4'-Bis(2-octyldodecyl)-dithieno[3,2-b:2',3'-d]germole (**5**):*

A solution of n-BuLi (4.2 mL of a 2.5 M solution in hexanes, 10.5 mmol) was added dropwise to a solution of 3,3'-dibromo-5,5'-bis(trimethylsilyl)-2,2'-bithiophene (**4**) (2.3 g, 4.9 mmol) in THF (20 mL) at -78°C. After stirring for 15 min at -78°C, dibromobis(2-octyldodecyl) germane (**3**) (4.6 g, 5.8 mmol) was added in one portion. The cooling bath was removed and the reactant was allowed to warm to RT, followed by stirring for 0.5 h at RT. Water (40 mL) was added, and the mixture extracted (3 x 30 mL hexane). The combined organics were dried ($MgSO_4$), filtered and concentrated under reduced pressure. The residue was purified by silica gel chromatography (eluent: hexane) to afford a pale yellow oil.

To the resulting oil in ether (100 mL) was added a solution of 37% HCl (Conc, 4 mL) in methanol (40 mL). The mixture was stirred for 1 h at RT, and water (30 mL) was added. Then the mixture was extracted by hexane (3 x 30 mL). The combined organics were dried ($MgSO_4$), filtered and the solvent removed under reduced pressure. The residue was purified by silica gel chromatography (eluent: hexane) to afford **5** as a pale yellow oil (1.67 g, yield: 43%). ^{1}H NMR ($CDCl_3$, 400MHz), δ (ppm): 7.19 (d, J = 4.7, 2H), 7.03 (d, J = 4.7, 2H), 1.52-1.45 (m, 2H), 1.20-1.14 (m, 68H), 0.91-0.87 (m, 12H). ^{13}C NMR ($CDCl_3$, 100MHz), δ (ppm): 146.3, 143.8, 129.8, 124.6, 36.4, 35.6, 31.9, 30.0, 30.0, 30.0, 29.4, 26.7, 22.7, 21.3, 14.1. HRMS (ESI): [M]$^{+}$ Calculated for $C_{48}H_{86}GeS_2$: 800.5383; found: 800.5396.

*4,4'-Bis(2-ethyl-hexyl)-2,6-bis(trimethyltin)-dithieno[3,2-b:2',3'-d]germole (**6**):*

A solution of n-BuLi (1.6 mL of a 2.5 M solution in hexanes, 4.0 mmol) was added dropwise to a solution of 4,4'-bis(2-octyldodecyl)-dithieno[3,2-b:2',3'-d]germole (**5**) (0.8 g, 1.0 mmol) in THF (10 mL) at -78°C. Then the mixture was allowed to warm to 0°C and stirred for 2 h. After cooling to -78°C again, a solution of trimethyltin chloride (4.9 mL of a 1 M solution in THF, 4.9 mmol) was added in one portion. The reactant was allowed to warm to RT, followed by stirring for 0.5 h at RT. Water (10 mL) was added, and the mixture extracted (3 x 20 mL hexane). The combined organics were dried ($MgSO_4$), filtered and concentrated under reduced pressure. The residue was purified by preparative GPC in hexane to afford a pale green oil (0.97 g, yield: 88%). ^{1}H NMR ($CDCl_3$, 400MHz), δ (ppm): 7.07 (s, 2H), 1.53-1.45 (m, 2H), 1.20-1.14 (m, 68H), 0.91-

0.87 (m, 12H). ^{13}C NMR ($CDCl_3$, 100MHz), δ (ppm): 152.2, 145.1, 137.8, 137.1, 36.4, 35.6, 32.0, 30.1, 29.8, 29.7, 29.7, 29.4, 26.8, 22.7, 21.1, 14.1. MS (EI): m/z = 1126.

*4,7-Bis(3,4-difluoro-2-thienyl)-2,1,3-benzothiadiazole (**9**):*
(5-Bromo-3,4-difluoro-thiophen-2-yl)-trimethyl-silane (**7**) (0.70 g, 2.6 mmol), $Pd(PPh_3)_4$ (0.068 g, 0.06 mmol), 2,1,3-benzothiadiazole-4,7-bis(boronic acid pinacol ester) (**8**) (0.46 g, 1.2 mmol) and 2 drops of Aliquot 336 were added to a 20 mL microwave tube. After degassing, pre-degassed toluene (10 mL) and 1 M Na_2CO_3 (3 mL) were added and the mixture was degassed again. Then the mixture was heated to 120 °C (oil bath temperature) and stirred for 1 day. After cooling to room temperature, the mixture was poured into water (20 mL) and extracted by $CHCl_3$ (3 x 50 mL). The combined organics were dried ($MgSO_4$), filtered and the solvent removed under reduced pressure. The residue was purified by silica gel chromatography (eluent: CH_2Cl_2/hexane = 1/2) to afford **9** as a orange solid (0.32 g, yield: 73%). ^{1}H NMR ($CDCl_3$, 400MHz), δ (ppm): 8.18 (s, 2H), 6.93 (dd, J = 4.3, 1.4, 2H). ^{13}C NMR ($CDCl_3$, 100MHz), δ (ppm):151.9, 147.0, 144.6, 127.4, 122.9, 104.9, 90.0. HRMS (ESI): $[M]^+$ Calculated for $C_{14}H_4F_4N_2S_3$: 371.9473; found: 371.9481.

*4,7-Bis(5-bromo-3,4-difluoro-2-thienyl)-2,1,3-benzothiadiazole (**10**):*
4,7-Bis(3,4-difluoro-2-thienyl)-2,1,3-benzothiadiazole (**9**) (0.32 g, 0.86 mmol) was dissolved in a mixture of 50 mL acetic acid and 100 mL $CHCl_3$. Then NBS (0.37 g, 2.1 mmol) was added in one portion in absence of light. The mixture was heated to 60°C and stirred for 1 day. After cooling to RT, water (100 mL) was added to quench the reaction. The organic phase was washed with water (3 x 100 mL) and saturated brine. Then the organic layer was dried ($MgSO_4$), filtered and the solvent removed solvent under reduced pressure. The residue was purified by silica gel chromatography (eluent: $CHCl_3$) and followed by recrystallisation from ethyl acetate to afford **10** as red needles (0.30 g, yield: 66%). ^{1}H NMR (*d*-1,1,2,2-tetrachloroethane, 400MHz, 130ºC), δ (ppm): 8.18 (s, 2H). ^{13}C NMR ($CDCl_3$, 100MHz), δ (ppm):151.7, 143.8, 141.8, 127.2, 122.5, 116.8, 94.4. HRMS (ESI): $[M]^+$ Calculated for $C_{14}H_2Br_2F_4N_2S_3$: 527.7683; found: 527.7681.

Poly[(4,4'-bis(2-octyldodecyl)dithieno[3,2-b:2',3'-d]germole)-2,6-diyl-alt-4,7-bis(3,4-difluoro-2-thienyl)-2,1,3-benzothiadiazole-5,5'-diyl ***(PGeTFDTBT)**:*

To an oven-dried 2 mL high pressure microwave reactor tube equipped with a sealed septum was added the following reagents in a sequential fashion: compound (**10**) (164 mg, 0.31 mmol), compound 6 (349 mg, 0.31 mmol), $Pd_2(dba)_3$ (5.7 mg, 0.006 mmol) and P-(*o*-tol)$_3$ (7.6 mg, 0.025 mmol). The tube was sealed and flushed with Ar, and chlorobenzene (1.0 mL) was added. The solution was thoroughly degassed under Ar, and then the argon inlet was removed. The tube was subjected to the following conditions in a microwave reactor: 120 ºC for 2 min, 140 ºC for 2 min and 180 ºC for 30 min. After cooling to RT, the polymer was precipitated into methanol (100 mL), and filtered through a Soxhlet thimble. The polymer was extracted using Soxhlet apparatus with methanol, acetone, hexane, chloroform and chlorobenzene. The chlorobenzene solution was concentrated and precipitated into methanol, and the precipitant was filtered and dried under vacuum to afford a dark solid (236 mg, yield: 65 %). Then the polymer was purified by preparative GPC column (eluent: chlorobenzene) and **PGeTFDTBT** was obtained (120 mg, yield: 33%, Mn = 37K, PDI = 2.8). ^{1}H NMR (*d*-1,1,2,2-tetrachloroethane, 400MHz, 130 ºC), δ (ppm): 8.24(s, broad, 2H), 7.33 (d, broad, 2H), 1.70-1.33 (m, broad, 70H), 0.95 (m, broad, 12H). Anal. Calcd.: $(C_{62}H_{86}GeF_4N_2S_5)n$: C, 63.74; H, 7.42; N, 2.40. Found: C, 62.39; H, 6.60; N, 2.59.

Poly[(4,4'-bis(2-octyldodecyl)dithieno[3,2-b:2',3'-d]germole)-2,6-diyl-alt-4,7-bis(2-thienyl)-2,1,3-benzothiadiazole-5,5'-diyl *(**PGeDTBT**):*

To an oven-dried 2 mL high pressure microwave reactor tube equipped with a sealed septum was added the following reagents in a sequential fashion: compound (**11**) (131 mg, 0.29 mmol), compound **6**[4] (322 mg, 0.29 mmol), $Pd_2(dba)_3$ (5.3 mg, 0.006 mmol) and P(*o*-tol)$_3$ (7.0 mg, 0.023 mmol). The tube was sealed and flushed with Ar, and chlorobenzene (1.0 mL) was added. The solution was thoroughly degassed under Ar, and then the argon inlet was removed. The tube was subjected to the following conditions in a microwave reactor: 120 ºC for 2 min, 140 ºC for 2 min and 180 ºC for 30 min. After cooling to RT, the polymer was precipitated into methanol (100 mL), and filtered through a Soxhlet thimble. The polymer was extracted using Soxhlet apparatus with methanol, acetone, hexane and chloroform. The chloroform solution was concentrated and precipitated into methanol, and the precipitant was filtered and dried under vacuum to afford a dark solid (180 mg, yield: 57 %). Then the polymer was purified by preparative GPC column (eluent: chlorobenzene) and **PGeTFDTBT** was obtained (88 mg, yield: 28%, Mn = 39K, PDI = 2.5). ^{1}H NMR (*d*-1,1,2,2-tetrachloroethane, 400MHz, 130 ºC), δ (ppm): 8.14(s, broad, 2H), 7.90 (s, broad, 2H), 7.36-7.33 (m, broad, 4H), 1.70-1.66 (m, broad, 2H), 1.45-1.35 (m, broad, 68H), 0.95 (m, broad, 12H). Anal. Calcd.: $(C_{62}H_{90}GeN_2S_5)n$: C, 67.92; H, 8.27; N, 2.56. Found: C, 67.37; H, 8.18; N, 2.80.

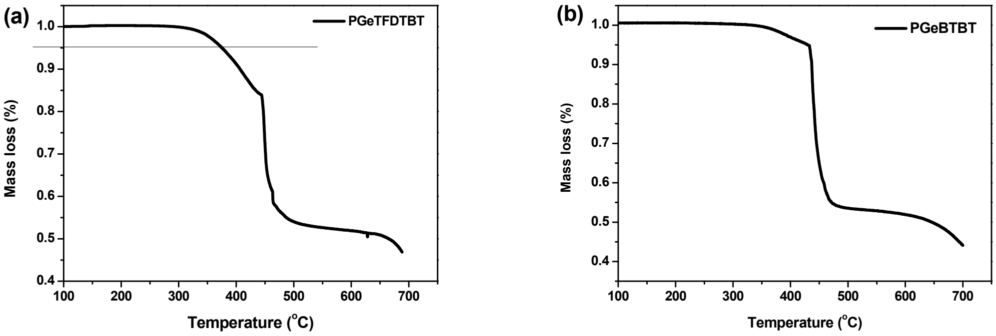

Fig. S1. TGA plots of **PGeTFDTBT** (a) and **PGeDTBT** (b) with a heating rate of 10°C min^{-1} under nitrogen.

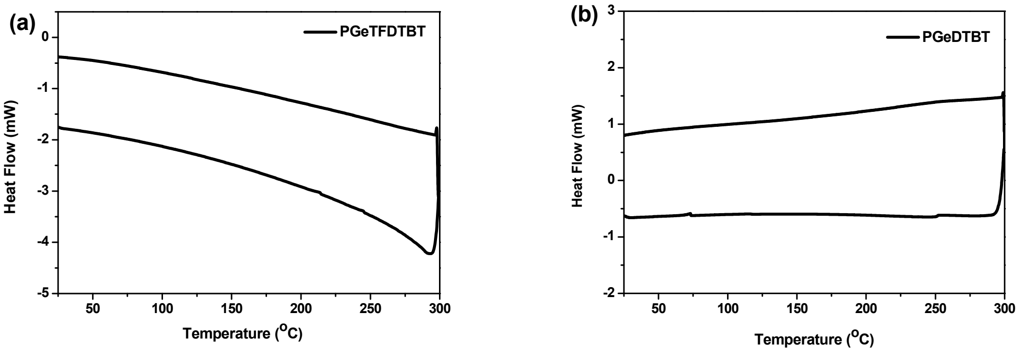

Fig. S2. DSC trace (endo UP) of **PGeTFDTBT** (a) and **PGeDTBT** (b) recorded at a heating, respectively cooling rate of 20°C min^{-1} under N_2.

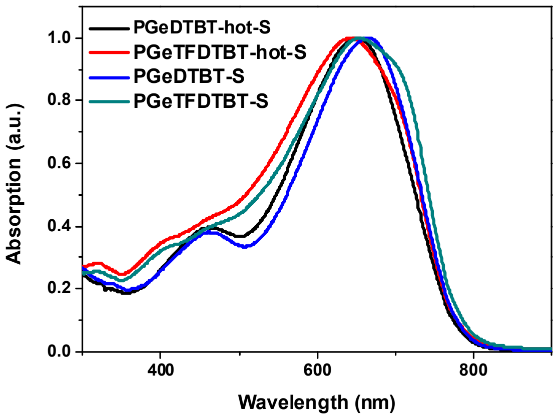

Fig. S3. UV-Vis spectra of **PGeTFDTBT** and **PGeDTBT** in room temperature and hot chlorobenzene.

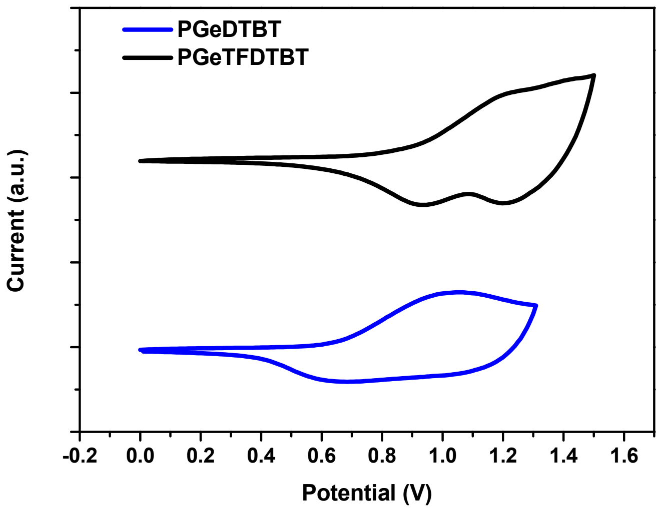

Fig. S4. Cyclic voltammograms of **PGeTFDTBT** and **PGeDTBT** as thin films in 0.1 M Bu4NPF6 solution in acetonitrile at ascan rate of 0.1 V s–1.

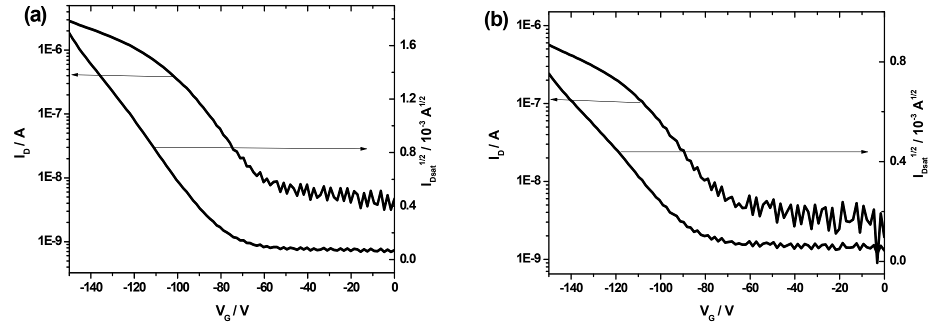

Fig. S5. Transfer characteristics of **PGeTFDTBT** (a) and **PGeDTBT** (b) of bottom-gate, bottom contact organic field-effect transistors (OFET) with channel length = 20 μm and channel width = 1.5 mm at room temperature under N_2.

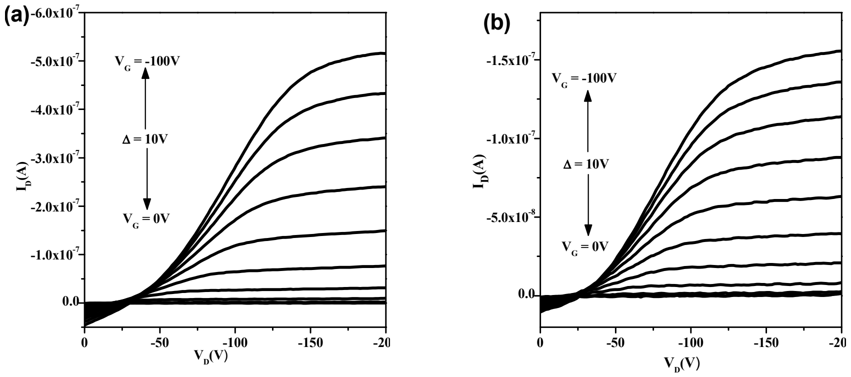

Fig. S6. Output characteristic of **PGeTFDTBT** (a) and **PGeDTBT** (b) of bottom-gate, bottom contact organic field-effect transistors (OFET) with channel length = 20 μm and channel width = 1.5 mm at room temperature under N_2.

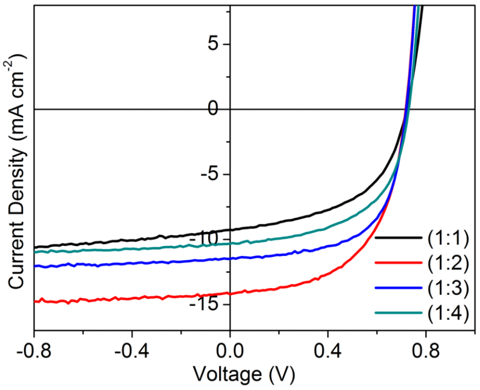

Fig. S7. J-V curves of polymer solar cells based on different blend ratio of **PGeTFDTBT**:$PC_{71}BM$.

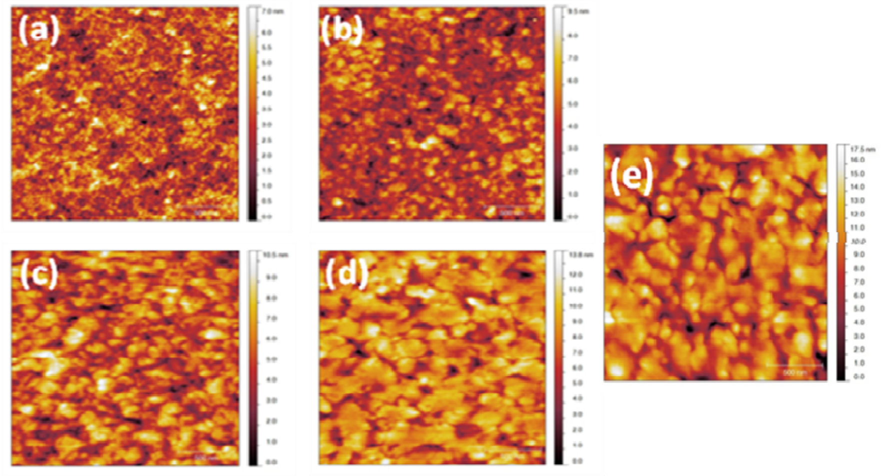

Fig. S8. AFM topography images (2 x 2 μm) of films spin coated from **PGeTFDTBT**/$PC_{71}BM$ with different ratios. (a) 1:1, (b) 1:2, (c) 1:3, (d) 1:4 and spin coated from **PGeDTBT**/$PC_{71}BM$ with 1:2 ratio (e).

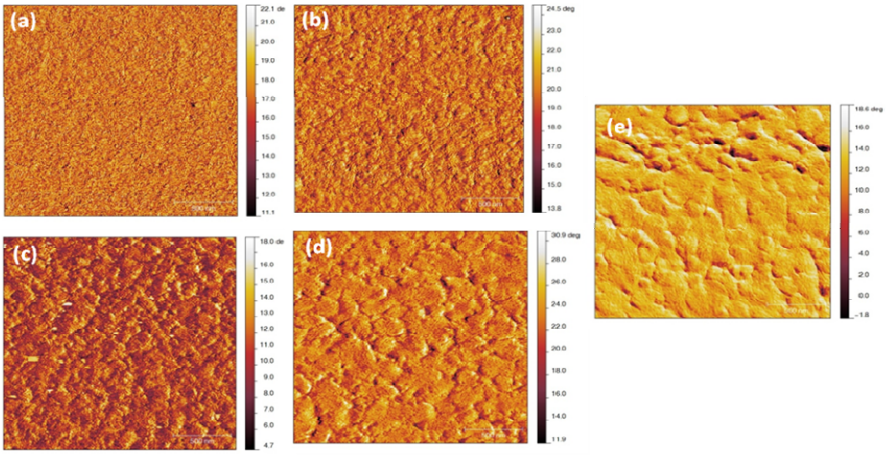

Fig. S9. AFM phase images (2 x 2 μm) of films spin coated from **PGeTFDTBT**/$PC_{71}BM$ with different ratios. (a) 1:1, (b) 1:2, (c) 1:3, (d) 1:4 and spin coated from **PGeDTBT**/$PC_{71}BM$ with 1:2 ratio (e).

Table S1 Summary of photovoltaic device performance of different blend ratios of **PGeTFDTBT**:PC$_{71}$BM.

PGeTFDTBT:PC$_{71}$BM	J_{sc} (mA/cm^2)	V$_{oc}$ (V)	FF	PCE (%)
1:1	9.3	0.72	0.52	3.48
1:2	13.51	0.71	0.57	5.47
1:3	11.5	0.72	0.60	4.97
1:4	10.3	0.72	0.56	4.15

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