Supporting Information

For

Bithiopheneimide-Dithienosilole/Dithienogermole Copolymers for Efficient Solar Cells: Information from Structure-Property–Device Performance Correlations and Comparison to Thieno[3,4-*c*]pyrrole-4,6-dione Analogues

Xugang Guo,[†] Nanjia Zhou,[‡] Sylvia J. Lou,[†] Jonathan W. Hennek,[†] Rocío Ponce Ortiz,[†,§] Melanie R. Butler,[†] Pierre-Luc T. Boudreault,[†] Joseph Strzalka,[□] Pierre-Olivier Morin,[#] Mario Leclerc,[#] Juan T. López Navarrete,[§] Mark A. Ratner,[*,†] Lin X. Chen,[*,†] Robert P. H. Chang,[*,‡] Antonio Facchetti,[*,†,‡,⊥] and Tobin J. Marks[*,†,‡]

[†]Department of Chemistry and the Materials Research Center, the Argonne-Northwestern Solar Energy Research Center, Northwestern University, 2145 Sheridan Road, Evanston, Illinois 60208, USA

[‡]Department of Materials Science and Engineering and the Materials Research Center, the Argonne-Northwestern Solar Energy Research Center, Northwestern University, 2145 Sheridan Road, Evanston, Illinois, 60208, USA

[§]Department of Physical Chemistry, University of Málaga, Campus de Teatinos s/n, Málaga 29071, Spain

[□]X-ray Sciences Division, Argonne National Laboratory, Argonne, Illinois, 60439, USA

[#]Département de Chimie, Université Laval, Quebec City, Quebec, G1V 0A6, Canada

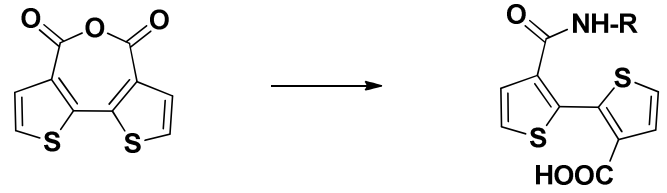
[⊥]Polyera Corporation, 8045 Lamon Avenue, Skokie, Illinois 60077, USA

E-mail: ratner@chem.northwestern.edu (M.A.R.); lchen@anl.gov (L.X.C.); r-chang@northwestern.edu (R.P.H.C.); a-facchetti@northwestern.edu (A.F.); t-marks@northwestern.edu (T.J.M.)

Materials and Methods

All reagents are commercially available and were used without further purification unless otherwise stated. Anhydrous dichloromethane was distilled from CaH_2; THF and toluene were distilled from Na/benzophenone. Monomers 2,2'-bithiophene-3,3'-dicarboxylic anhydride,[1] 4,4-Bis(2-ethyl-hexyl)-2,6-bis(trimethyltin)-dithieno[3,2-*b*:2',3'-*d*]silole,[2] 4,4-Bis(2-ethyl-hexyl)-2,6-bis(trimethyltin)-dithieno[3,2-*b*:2',3'-*d*]germole,[3] and polymer **PTPDSi-C8**[4] were prepared following published procedures. Unless otherwise stated, all reactions were carried out under inert atmosphere using standard Schlenk line techniques. UV-Vis spectra were recorded on a Varian Cary 50 Scan UV-Vis spectrophotometer. The solution absorption spectra of polymers were recorded on 10^{-5} M (based on repeating units) *orth*-dichlorobenzene (DCB) solutions, and the polymer film absorption spectra were recorded from films cast from 1 mg/mL dichlorobenzene solutions. Differential scanning calorimetry (DSC) was performed on a TA model DSC 2920 with a heating ramp of 10 °C/min. NMR spectra were recorded on Varian Unity Plus 500 (500 MHz, room temperature) or Mercury (400 MHz, high temperature) spectrometers, and chemical shifts are referenced to residual protio-solvent signals. Elemental analyses (EA) of monomers and polymer samples were performed by Midwest Microlab (Indianapolis, IN). The electrochemical properties of the polymers were investigated as thin films in anhydrous acetonitrile under N_2 at a scan rate of 50 mV/s using 0.1 M tetrakis(*n*-butyl)ammonium hexafluorophosphate ($(n\text{-Bu})_4NPF_6$) as the supporting electrolyte. Pt electrodes were used as both the working and counter electrodes, and an Ag wire was used as the pseudoreference electrode. Polymer films were drop-cast onto the Pt working electrode from a 0.2% (w/w) chlorobenzene (CB) solution. Polymer molecular weights were determined on a Polymer Laboratories PL-GPC 220 using trichlorobenzene as eluent at 170 ºC vs polystyrene standards. AFM measurements were performed by using a Dimension Icon Scanning Probe Microscope (Veeco) in tapping mode. XRD measurements were performed on an 18 kW Rigaku ATXG diffractometer using a multilayer parabolic mirror, a NaI scintillation detector, and X-rays of wavelength λ = 1.541 Å. TEM specimens were prepared following identical conditions as the actual devices, but were drop cast onto 2 mm × 2 mm NaCl (100) polished substrates (MTI Corp.). After drying, substrates were transferred to deionized water and the floated films were transferred to TEM grids (Ted Pella, Inc.). TEM images were obtained on JEOL JEM-2100F TEM. The device cross-sectional structure was characterized using a Hitachi S4800-II SEM. Grazing incidence x-ray scattering measurements were performed at Beamline 8ID[5] of the Advanced Photon Source at Argonne National Laboratory. An x-ray wavelength of λ = 1.6868 Å was used and data were collected using a 30 s exposure at a sample-detector distance of 204 mm with a Pilatus photodiode array.

Synthesis of monomers

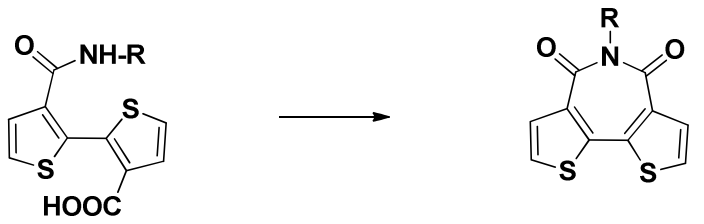


1a: R = *n*-hexyl
1b: R = *n*-octyl
1c: R = 2-ethylhexyl

Synthesis of 3-(*n*-hexyl)carbamoyl-3'-carboxylic acid-2,2'-bithiophene 1a. A solution of *n*-hexylamine solution (0.81 g, 8 mmol) in 60 mL of dichloromethane was added dropwise to the solution of 2,2'-bithiophene-3,3'-dicarboxylic anhydride (1.89 g, 8 mmol) in 100 mL of dichloromethane. After addition, the reaction was stirred under reflux for 2h. Upon removal of solvent, the residue oil was purified by column chromatography using ethyl acetate as eluent to give a white solid as the product (2.54 g, 94% yield). ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 7.47 (d, 1H), 7.39 (d, 1H), 7.37 (d, 1H), 7.27 (d, 1H), 6.02 (s, 1H), 3.25 (m, 2H), 1.40 (m, 2H), 1.24 (m, 6H), 0.85 (t, 3H).

Synthesis of 3-(*n*-octyl)carbamoyl-3'-carboxylic acid-2,2'-bithiophene 1b. This material was synthesized following the same procedure for **1a** from 2,2'-bithiophene-3,3'-dicarboxylic anhydride and *n*-octylamine. After purification by column chromatography using ethyl acetate as eluent, the product was obtained as a white solid as the product (1.34 g, 93%). ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 7.50 (d, 1H), 7.42 (d, 1H), 7.39 (d, 1H), 7.30 (d, 1H), 6.12 (s, 1H), 3.29 (m, 2H), 1.43 (m, 2H), 1.26 (m, 10H), 0.88 (t, 3H).

Synthesis of 3-(2-ethylhexyl)carbamoyl-3'-carboxylic acid-2,2'-bithiophene 1c. This material was synthesized following the same procedure for **1a** from 2,2'-bithiophene-3,3'-dicarboxylic anhydride and 2-ethylhexylamine. After purification by column chromatography using ethyl acetate as eluent, the product was obtained as a colorless oil as the product (1.77 g, 91%). ^{1}H NMR (500 MHz, CDCl$_3$, ppm): δ 7.52 (d, 1H), 7.41 (d, 1H), 7.38 (d, 1H), 7.31 (d, 1H), 6.10 (s, 1H), 3.24 (m, 2H), 1.50 (m, 1H), 1.29 (m, 8H), 0.88 (m, 6H).



1a: R = *n*-hexyl
1b: R = *n*-octyl
1c: R = 2-ethylhexyl

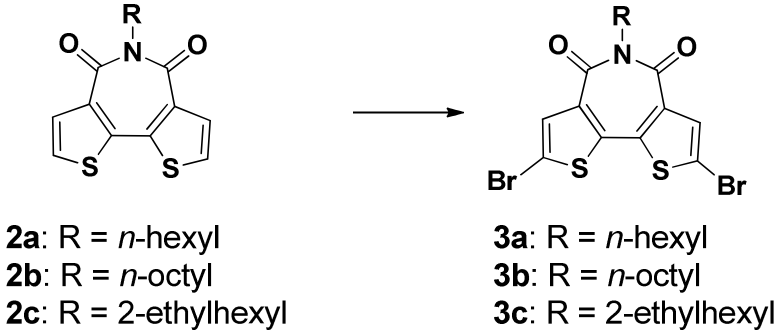
2a: R = *n*-hexyl
2b: R = *n*-octyl
2c: R = 2-ethylhexyl

Synthesis of Synthesis of *N*-(*n*-hexyl)-2,2'-bithiophene-3,3'-dicarboximide 2a. A solution of **1a** (1.69 g, 5 mmol) in 30 mL of thionyl chloride was refluxed for 2h. Then all thionyl chloride was removed under vaccum. The residual oil was purified by column chromatography using dichloromethane:hexane (1:1) as eluent to provide a white solid as the product (1.42 g, 89%). ^{1}H NMR (500 MHz, CDCl$_3$, ppm): δ 7.74 (d, 2H), 7.25 (d, 2H), 4.20 (m, 2H), 1.71 (m, 2H), 1.31 (m, 6H), 0.89 (t, 3H). ^{13}C NMR (125 MHz, CDCl$_3$, ppm): δ 161.89, 137.74, 133.45, 133.14, 124.32, 46.41, 31.68, 27.70, 26.97, 22.70, 14.19.

Synthesis of *N*-(*n*-octyl)-2,2'-bithiophene-3,3'-dicarboximide 2b. This material was synthesized following the same procedure for **2a**. After purification over column chromatography using dichloromethane:hexane (1:1) as eluent, the product was obtained as a white solid (1.34 g, 91% yield)

^{1}H NMR (500 MHz, CDCl$_3$, ppm): δ 7.74 (d, 2H), 7.22 (d, 2H), 4.19 (t, 2H), 1.69 (m, 2H), 1.35 (m, 10H), 0.89 (t, 3H). ^{13}C NMR (125 MHz, CDCl$_3$, ppm): δ 161.92, 137.81, 133.50, 133.13, 124.38, 46.34, 32.01, 29.53, 29.47, 27.96, 27.45, 22.84, 14.29.

Synthesis of *N*-(2-ethylhexyl)-2,2'-bithiophene-3,3'-dicarboximide 2c. This material was synthesized following the same procedure for **2a**. After purification over column chromatography using dichloromethane:hexane (1:1) as eluent, the product was obtained as a white solid (1.76 g, 90% yield) ^{1}H NMR (500 MHz, CDCl$_3$, ppm): δ 7.71 (d, 2H), 7.23 (d, 2H), 4.24 (m, 2H), 1.86 (m, 1H), 1.32 (m, 8H), 0.89 (m, 6H). ^{13}C NMR (125 MHz, CDCl$_3$, ppm): δ 162.46, 137.59, 133.49, 133.22, 124.40, 49.25, 37.95, 30.89, 28.81, 24.21, 23.31, 14.27, 10.89.



Synthesis of *N*-(*n*-hexyl)-5,5'-dibromo-2,2'-bithiophene-3,3'-dicarboximide 3a.[1] This material was synthesized following the published procedure[1] from **2a**. After purification by column chromatography over silica gel with hexane:dichloromethane (1:1) as eluent, a pale yellow solid was obtained as the desired product (96% yield). ^{1}H NMR (500 MHz, CDCl$_3$, ppm): δ 7.69 (s, 2H), 4.15 (t, 2H), 1.67 (m, 2H), 1.36 (m, 6H), 0.90 (t, 3H). ^{13}C NMR (125 MHz, CDCl$_3$, ppm): δ 160.53, 137.80, 135.74, 133.51, 112.73, 46.61, 31.72, 27.79, 27.02, 22.80, 14.25. Anal. Calcd for $C_{16}H_{15}Br_2NO_2S_2$ (%): C, 40.27; H, 3.17; N, 2.93. Found (%), C, 40.22; H, 3.23; N, 2.77.

Synthesis of *N*-(*n*-octyl)-5,5'-dibromo-2,2'-bithiophene-3,3'-dicarboximide 3b.[1] This material was synthesized following the published procedure[1] from **2b**. After purification by column chromatography over silica gel with hexane:dichloromethane (1:1) as eluent, a pale yellow solid was obtained as the desired product (97% yield). ^{1}H NMR (500 MHz, CDCl$_3$, ppm): δ 7.69 (s, 2H), 4.14 (t, 2H), 1.64 (m, 2H), 1.30 (m, 10H), 0.88 (t, 3H). ^{13}C NMR (125 MHz, CDCl$_3$, ppm): δ 160.48, 137.77, 135.73, 133.47, 112.73, 46.61, 32.02, 29.50, 29.45, 27.83, 27.36, 22.86, 14.32. Anal. Calcd for $C_{18}H_{19}Br_2NO_2S_2$ (%): C, 42.79; H, 3.79; N, 2.77. Found (%), C, 42.83; H, 3.83; N, 2.80.

Synthesis of *N*-(2-ethylhexyl)-5,5'-dibromo-2,2'-bithiophene-3,3'-dicarboximide 3c.[1] This material was synthesized following the published procedure[1] from **2c**. After purification by column chromatography over silica gel with hexane:dichloromethane (1:1) as eluent, a pale yellow solid was obtained as the desired product (95% yield). ^{1}H NMR (500 MHz, CDCl$_3$, ppm): δ 7.66 (s, 2H), 4.18 (m, 2H), 1.81 (m, 1H), 1.29 (m, 8H), 0.89 (m, 6H). ^{13}C NMR (125 MHz, CDCl$_3$, ppm): δ 160.93, 137.56, 135.73, 133.50, 112.71, 49.49, 37.86, 30.83, 28.77, 24.14, 23.30, 14.31, 10.84. Anal. Calcd for $C_{18}H_{19}Br_2NO_2S_2$ (%): C, 42.79; H, 3.79; N, 2.77. Found (%), C, 42.84; H, 3.73; N, 2.93.

Synthesis of 4,4'-bis(2-ethylhexyl)-5,5'-bis(trimethyltin)-dithieno[3,2-b:2',3'-d]silole.[2] This material was synthesized following the published procedure[2] from 3,3'5,5'-tetrabromo-2,2'-bithiophene. After purification by column chromatography over basic aluminum oxide as the stationary phase with hexane/triethyl amine (95%/5%) as eluent,[6] a light yellow oil was obtained as the desired product. ^{1}H NMR (500 MHz, CDCl$_3$, ppm): δ 7.08 (s, 2H), 1.44 (m, 2H), 1.27(m, 4H), 1.16 (m, 12H), 0.94 (m, 4H), 0.84 (m, 6H), 0.79 (m, 6H), 0.38 (s, 18H). ^{13}C NMR (125 MHz, CDCl$_3$, ppm): δ 154.86, 144.10, 138.10, 137.60, 36.11, 35.81, 29.17, 29.09, 23.23, 18.01, 14.42, 11.06, -7.96. Anal. Calcd for $C_{30}H_{54}S_2SiSn_2$ (%): C, 48.41; H, 7.31; N, 0. Found (%), C, 48.70; H, 7.67; N, none found.

Synthesis of 4,4'-bis(2-ethylhexyl)-5,5'-bis(trimethyltin)-dithieno[3,2-b:2',3'-d]germole.[3] This materials was synthesized following the published procedure[3] from 3,3'5,5'-tetrabromo-2,2'-bithiophene. After workup, a pale yellow liquid was obtained as the product with high purity (> 95%)

based on ^{1}H NMR spectrum. Further purification using basic column chromatography leads to the monomer decomposition. ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 7.09 (s, 2H), 1.50 (m, 2H), 1.32 (m, 4H), 1.23 (m, 16H), 0.84 (t, 6H), 0.81 (t, 6H), 0.39 (s, 18H). ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 152.39, 145.26, 138.01, 137.38, 37.18, 35.65, 29.13, 28.99, 23.26, 20.85, 14.42, 11.12, -7.95. Anal. Calcd for $C_{30}H_{54}GeS_2Sn_2$ (%): C, 45.67; H, 6.90; N, 0. Found (%), C, 46.93; H, 6.88; N, none found.

General Procedure for polymer synthesis: An air-free flask was charged with the two monomers (0.2 mmol each), $Pd_2(dba)_3$, and $P(o\text{-tolyl})_3$ (1:8, $Pd_2(dba)_3$:$P(o\text{-tolyl})_3$ molar ratio; Pd loading = 0.03 equiv.). The flask and its contents were subjected to 3 pump/purge cycles with argon, followed by addition of 8 mL anhydrous toluene. The sealed reaction flask was then stirred at 110 ºC for 72 h. Then, 0.1 mL 2-(tributylstanny)thiophene was added and the reaction mixture was stirred at 110 ºC for another 12 h. Finally, 0.2 mL 2-bromothiophene was added and the reaction mixture was stirred for another 12 h. After cooling to room temperature, the reaction mixture was dripped into 100 mL of methanol (containing 5 mL 12 N HCl) with vigorous stirring. After 4 h stirring, the polymer was transferred to a thimble. After drying, the crude product was subjected to sequential Soxhlet extraction. After a final extraction with chloroform, the polymer solution was then precipitated in 100 mL of methanol with vigorous stirring. The polymer was collected by filtration and dried to afford purple solid as the product.

PBTISi-C6. This product was obtained as blue solid after Soxhlet extraction with methanol, acetone, hexane, dichloromethane, and chloroform (98 mg, 67% yield). ^{1}H NMR (400 MHz, $C_2D_2Cl_4$, 130 ºC, ppm): δ 7.81 (br, 2H), 7.32 (br, 2H), 4.30 (br, 2H), 1.83 (br, 2H), 1.44-1.13 (m, 28H), 1.01 (b, 15H). Anal. Calcd for $C_{42}H_{55}NO_2S_4Si$ (%): C, 65.44; H, 7.00; N, 1.91. Found (%): C, 65.21; H, 7.22; N, 1.76. M_n = 29 kDa, PDI = 3.3.

PBTISi-C8. This product was obtained as blue solid after Soxhlet extraction with methanol, acetone, hexane, dichloromethane, and chloroform (91 mg, 60% yield). ^{1}H NMR (400 MHz, $C_2D_2Cl_4$, 130 ºC, ppm): δ 7.83 (br, 2H), 7.33 (br, 2H), 4.32 (br, 2H), 1.85 (br, 2H), 1.45-1.15 (m, 32H), 1.01 (b, 15H). Anal. Calcd for $C_{42}H_{55}NO_2S_4Si$ (%): C, 66.18; H, 7.27; N, 1.84. Found (%): C, 66.27; H, 7.21; N, 1.91. M_n = 30 kDa, PDI = 3.1.

PBTISi-EH. This product was obtained as blue solid after Soxhlet extraction with methanol, acetone, hexane, and chloroform (145 mg, 95% yield). ^1H NMR (400 MHz, $C_2D_2Cl_4$, 130 ºC, ppm): δ 7.86 (br, 2H), 7.33 (br, 2H), 4.35 (br, 2H), 2.01 (br, 1H), 1.45-1.15 (m, 30H), 1.02 (18H). Anal. Calcd for $C_{42}H_{55}NO_2S_4Si$ (%): C, 66.18; H, 7.27; N, 1.84. Found (%): C, 66.22; H, 7.33; N, 1.91. M_n = 26 kDa, PDI = 2.8.

PBTIGe-C6. This product was obtained as blue solid after Soxhlet extraction with methanol, acetone, hexane, dichloromethane, and chloroform (102 mg, 65% yield). ^1H NMR (400 MHz, $C_2D_2Cl_4$, 130 ºC, ppm): δ 7.80 (br, 2H), 7.33 (br, 2H), 4.39 (br, 2H), 1.83 (br, 2H), 1.44-1.10 (m, 28H), 0.99 (b, 15H). Anal. Calcd for $C_{40}H_{51}GeNO_2S_4$ (%): C, 61.69; H, 6.60; N, 1.80. Found (%): C, 62.01; H, 6.77; N, 1.92. M_n = 27 kDa, PDI = 2.9.

PBTIGe-C8. This product was obtained as blue solid after Soxhlet extraction with methanol, acetone, hexane, dichloromethane, and chloroform (86 mg, 53% yield). ^1H NMR (400 MHz, $C_2D_2Cl_4$, 130 ºC, ppm): δ 7.83 (br, 2H), 7.33 (br, 2H), 4.32 (br, 2H), 1.85 (br, 2H), 1.45-1.15 (m, 32H), 1.01 (b, 15H). Anal. Calcd for $C_{42}H_{55}GeNO_2S_4$ (%): C, 62.53; H, 6.87; N, 1.74. Found (%): C, 62.52; H, 6.93; N, 1.77. M_n = 25 kDa, PDI = 2.7.

PBTIGe-EH. This product was obtained as blue solid after Soxhlet extraction with methanol, acetone, hexane, and chloroform (145 mg, 95% yield). ^1H NMR (400 MHz, $C_2D_2Cl_4$, 130 ºC, ppm): δ 7.86 (br, 2H), 7.33 (br, 2H), 4.35 (br, 2H), 2.01 (br, 4H), 1.45-1.15 (m, 30H), 1.02 (18H). Anal. Calcd for $C_{42}H_{55}GeNO_2S_4$ (%): C, 62.53; H, 6.87; N, 1.74. Found (%): C, 63.39; H, 7.16; N, 1.82. M_n = 18 kDa, PDI = 2.3.

PTPDSi-C8: This product was obtained by following published procedure[4] after Soxhlet with methanol, acetone, hexane, dichloromethane, and chloroform (145 mg, 95% yield). ^{1}H NMR (400 MHz, $C_2D_2Cl_4$, 130 ºC, ppm): δ 7.56 (br, 2H), 3.45 (br, 2H), 2.10-1.10 (m, 34H), 0.90 (15H). Anal. Calcd for $C_{38}H_{53}NO_2S_3Si$ (%): C, 67.11; H, 7.85; N, 2.06. Found (%): C, 67.55; H, 8.12; N, 1.98. M_n = 29 kDa, PDI = 1.8.

OTFT Fabrication and Characterization

Bottom-gate/top-contact (BGTC) OTFTs were fabricated to investigate the charge transport properties of the BTI-based polymers. For the BGTC devices, the semiconductor layer was deposited by spin-coating a 10 mg/mL polymer solution in $CHCl_3$ under ambient conditions on octadecyltrichlorosilane (OTS)-treated, p-doped Si (100) wafers having a 300 nm thermally grown SiO_2 dielectric layer. The capacitance of the 300 nm SiO_2 gate insulator is ~11 nFcm^{-2}. Prior to OTS deposition, the wafers were solvent-cleaned by immersion in ethanol with sonication, and were then dried in a filtered stream of N_2, followed by 5 min plasma cleaning. Alkylsilation of the Si/SiO_2 surface was carried out by submerging the silicon wafers in a 0.5 M solution of OTS in hexanes at 55-60% relative humidity. OTFT devices were completed by vapor deposition of gold source and drain electrodes through a shadow mask to define devices with channel a length of 100 μm and width of 5000 μm. Device characterization was performed under ambient conditions in a probe station with a Keithley 6430 subfemtoamp meter (drain) and a Keithley 2400 (gate) source meter, operated by a locally written Labview program.

OPV Fabrication and Characterization

Pre-patterned ITO-coated glass (Thin Film Devices, Inc.) with a sheet resistance of ~8Ω/□ was used as the substrate. It was cleaned by sequential sonication in hexane, DI water, methanol, isopropanol, and acetone. After UV/ozone treatment (Jelight Co.) for 30 min, the ZnO electron transport/hole blocking layer was prepared by spin-coating at 5000 rpm from a ZnO precursor solution prepared from 0.5 M zinc acetate dehydrate in 0.5 M monoethanolamine and 2-methoxyethanol under N_2. After cleaning the electrical contacts, substrates were immediately baked in air for 5 min. The films were then rinsed with DI water, isopropanol, and acetone, and then dried in a glovebox. Active layer solutions were prepared in DCB or DCB/DIO with various ratios (polymer concentration: 10 mg/mL). For optimum performance devices, active layers were both spin-coated 1000 rpm to obtain thicknesses of ~100 nm. Thin layers of 10 nm MoO_x and 100 nm of Ag were then thermally evaporated through a shadow mask at ~10^{-6} Torr. Device I-V characteristics measured under AM1.5G light (100 mW/cm^2) using the Xe arc lamp of a Spectra-Nova Class A solar simulator. The light intensity was calibrated using an NREL-certified monocrystalline Si diode coupled to a KG3 filter to bring spectral mismatch to unity. Four-point contact measurements were performed and electrical characterizations were measured with a Keithley 2400 unit. The area of all devices was 6 mm^2, and an aperture was used on top of cells during measurements. EQEs were characterized using an Oriel model QE-PV-SI instrument equipped with an NIST-certified Si diode. Monochromatic light was generated from an Oriel 300W lamp source.

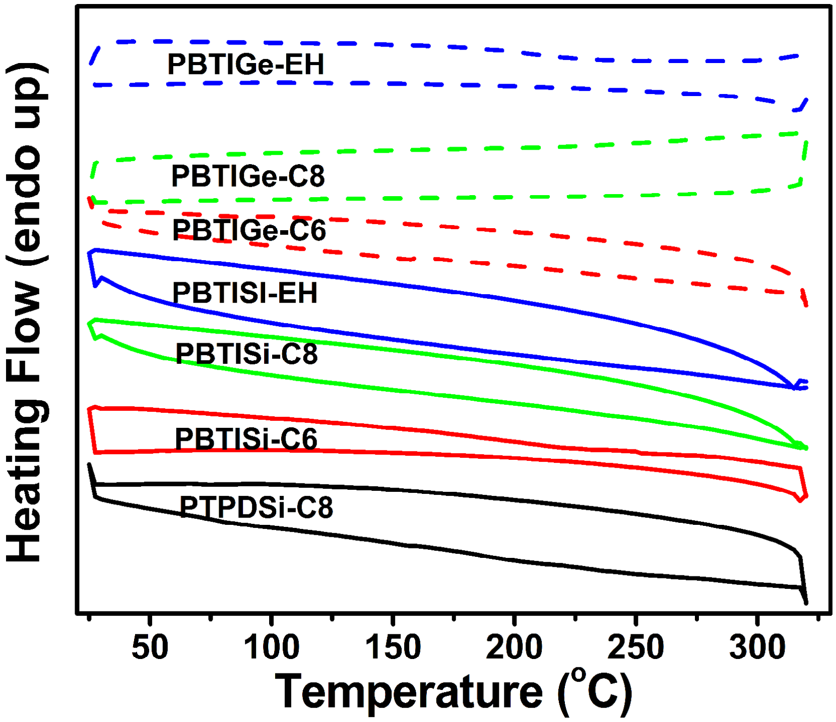


Figure S1. DSC thermograms of polymers **PBTISi**, **PBTIGe**, and **PTPDSi-C8** during first cooling and second heating scans (heating ramp: 10 ºC/min). The lower line is first cooling scan and the upper line is second heating scan.

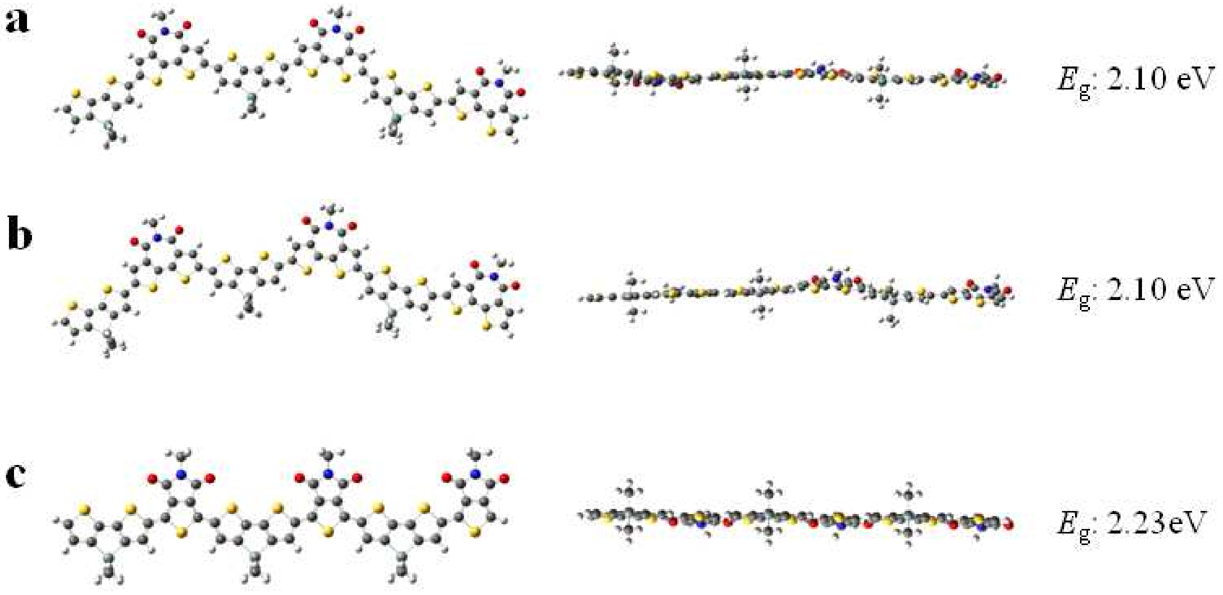


Figure S2. Computed optimized geometry and E_gs for the trimers: (a) **BTIDTG** trimer, (b) **BTIDTS** trimer, and (c) **TPDDTS** trimer. The calculations were carried out at the DFT//B3LYP/6-31G** level, alkyl chains are replaced here by methyl groups to simplify the calculation.

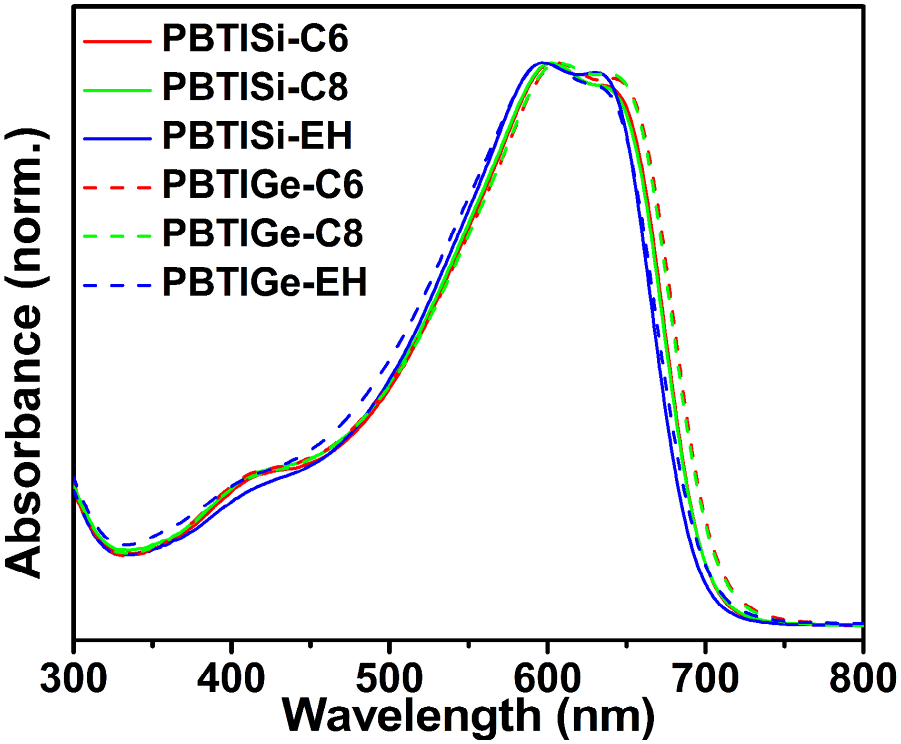


Figure S3. Optical absorption spectra of polymers **PBTISi**, **PBTIGe**, and **PTPDSi-S8** solutions in DCB at room temperature (1 × 10^{-5} M, based on polymer repeat unit).

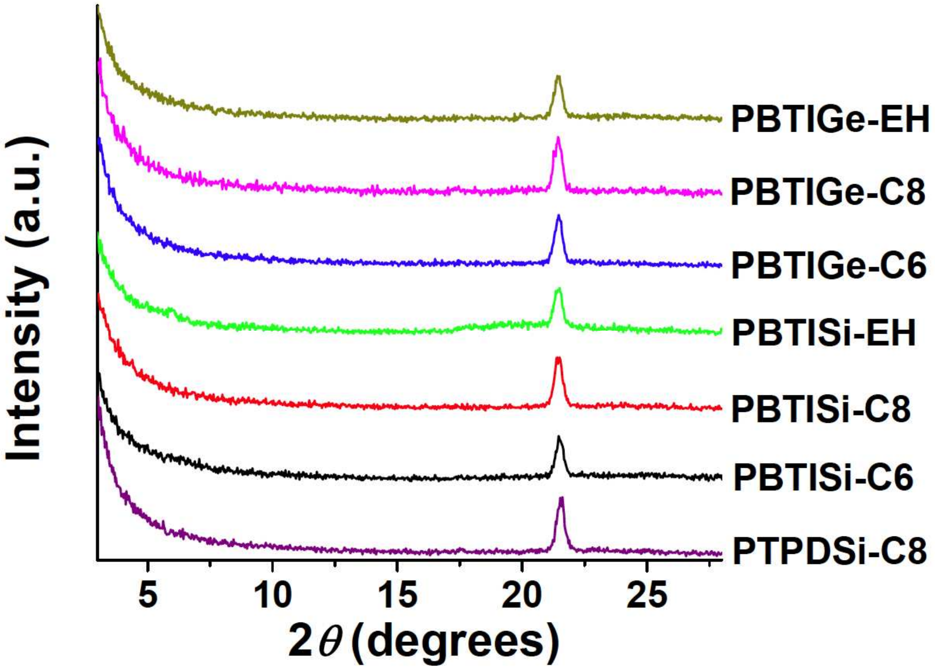


Figure S4. X-ray diffraction (XRD) scattering patterns of films of polymers **PBTISi**, **PBTIGe**, and **PTPDSi-C8** produced by spinning coating polymer solutions onto ITO-coated glass substrates.

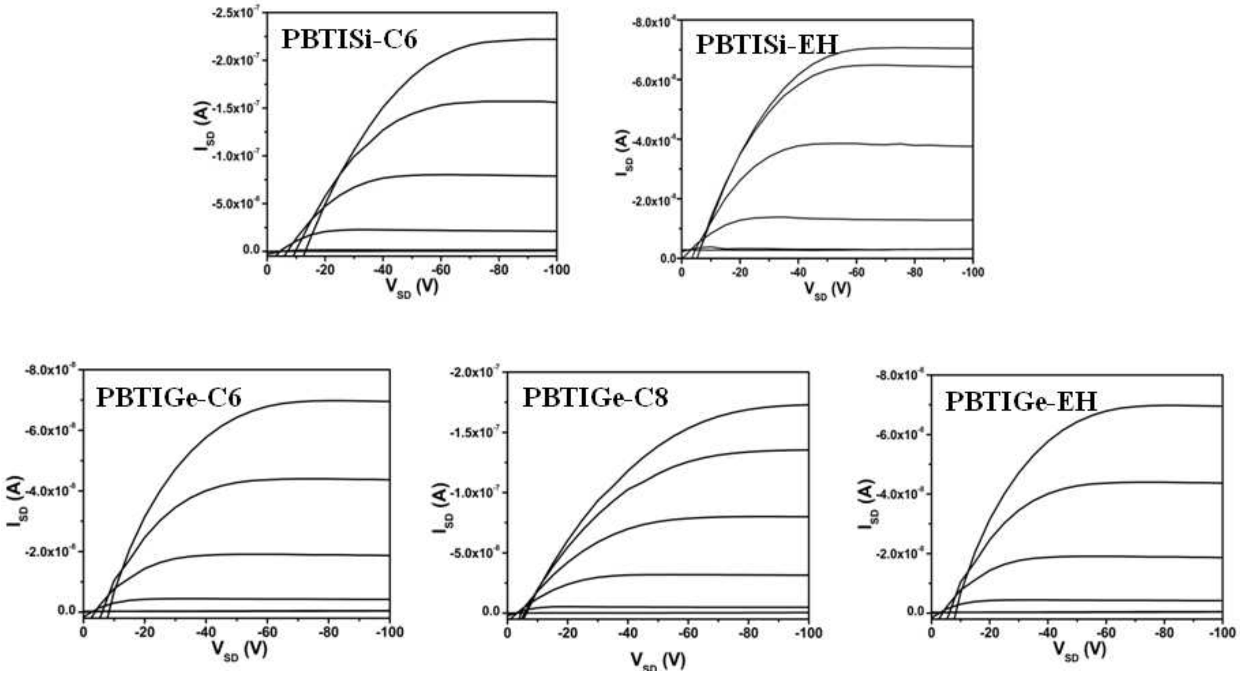


Figure S5. OTFT output characteristics for polymers **PBTISi-C6**, **PBTISi-EH**, **PBTIGe-C8**, **PBTIGe-C8**, and **PBTIGe-EH**-based bottom-gate/top-contact OTFTs annealed at 150 °C measured in air. The gate voltage varies from 20 to -100 V (channel width: 5000 μm, channel length: 100 μm).

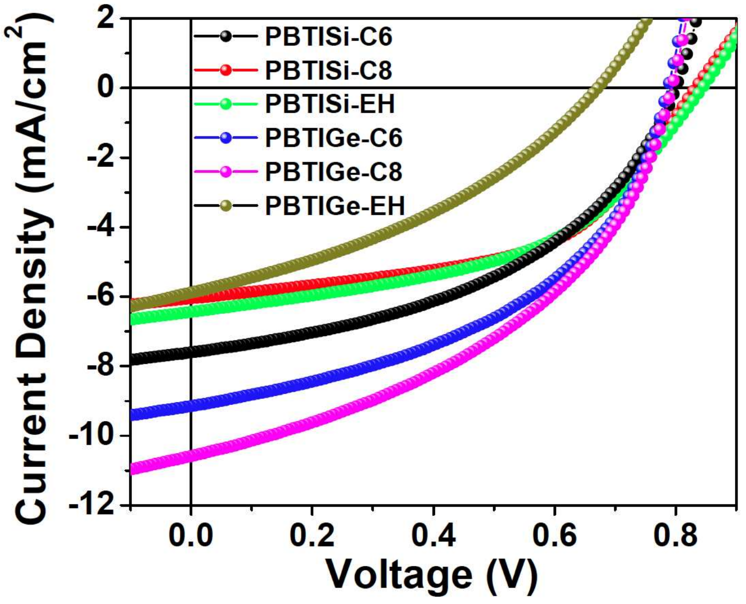


Figure S6. *J*-*V* characteristics of Polymer:$PC_{71}BM$ (1:1, w/w) solar cells fabricated with the indicated polymers using *ortho*-dichlorobenzene as the solvent without diiodooctane (DIO) as the processing additive.

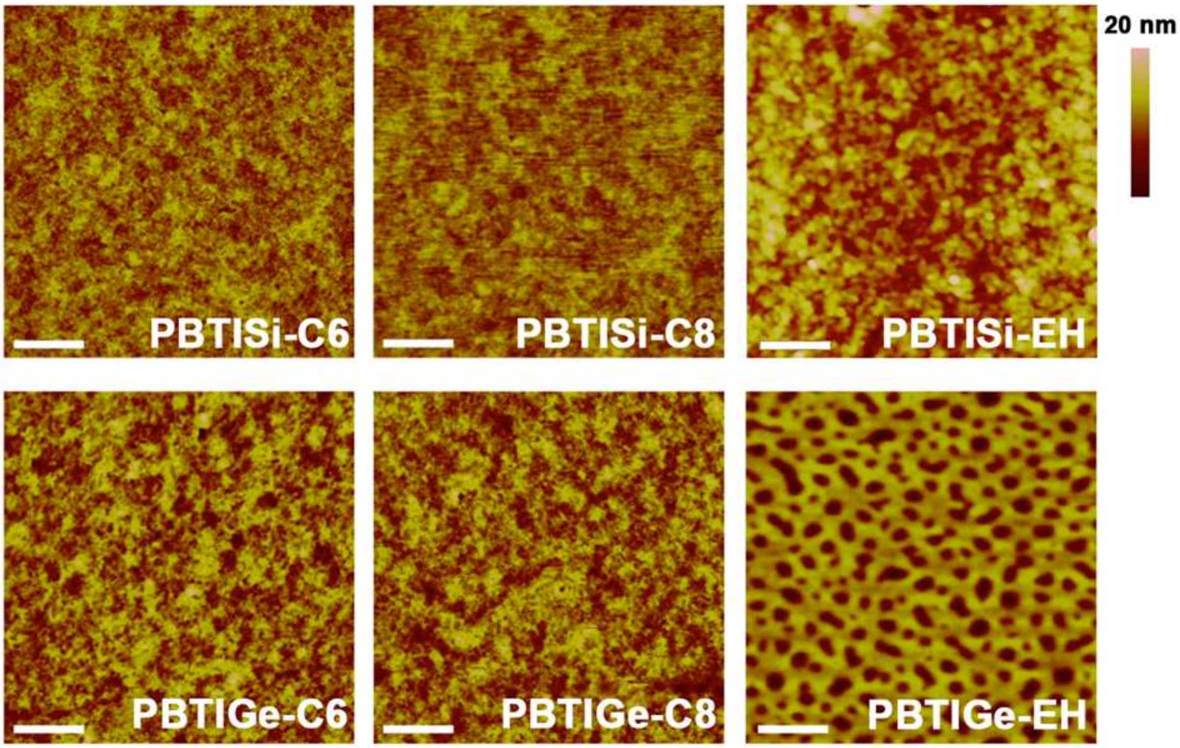


Figure S7. AFM topographical images of the indicated polymer/PC$_{71}$BM (1:1) blend films fabricated with the indicated polymers using *ortho*-dichlorobenzene as the solvent without diiodooctane (DIO) as the processing additive. AFM scale bars are 1 μm.

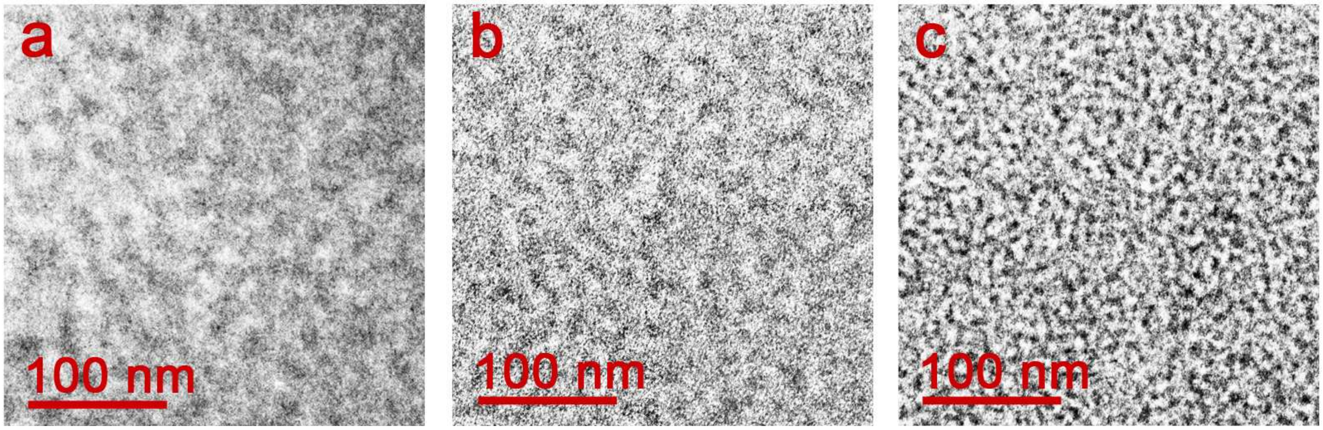


Figure S8. TEM images of **PBTISi-C8** with different D/A ratios: (a) **PBTISi-C8**:PC$_{71}$BM (1:1), (b) **PBTISi-C8**:PC$_{71}$BM (1:1.5), and (c) **PBTISi-C8**:PC$_{71}$BM (1:2) blend films processed in DIO (DCB:DIO = 98:2; v/v as the solvent) .

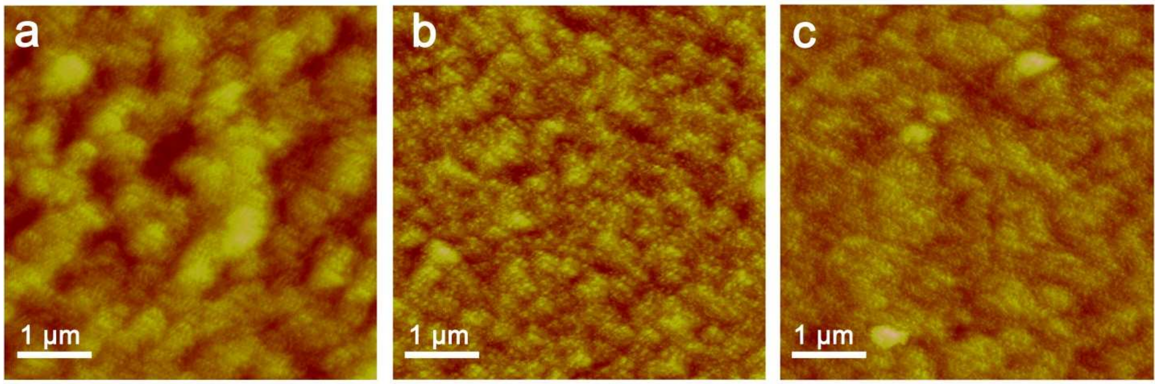


Figure S9. Tapping-mode AFM images for **PBTISi-C8**:$PC_{71}BM$ (1:1) solar cells fabricated using DCB/DIO as solvent with varying v/v ratios: (a) 98.5%/1.5%; (b) 97.5%:2.5%; (c) 97%:3.0%. (AFM scan area: 5 µm × 5 µm)

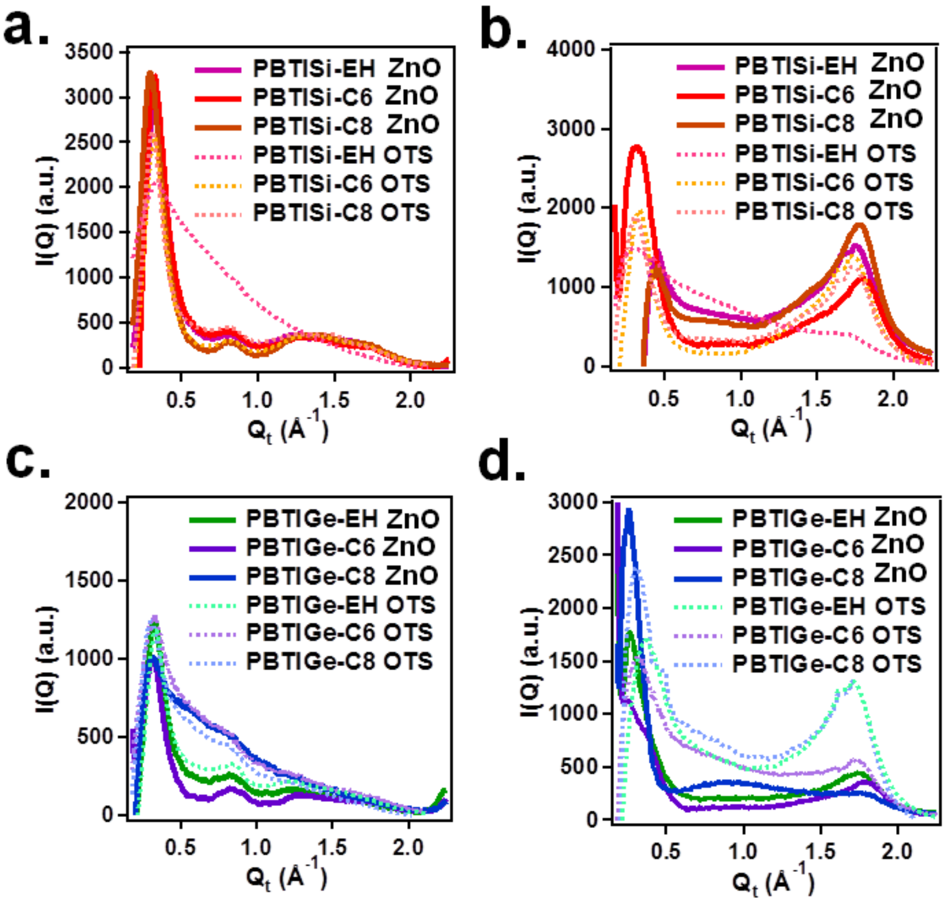


Figure S10. (a) in-plan linecuts of 2D GIWAXS of **PBTISi** polymers on ZnO and OTS substrates; and (b) out-of-plane linecuts of 2D GIWAXS of **PBTISi** polymers on ZnO and OTS substrates; (c) in-plan linecuts of 2D GIWAXS of **PBTIGe** polymers on ZnO and OTS substrates; and (d) out-of-plane linecuts of 2D GIWAXS of **PBTIGe** polymers on ZnO and OTS substrates;

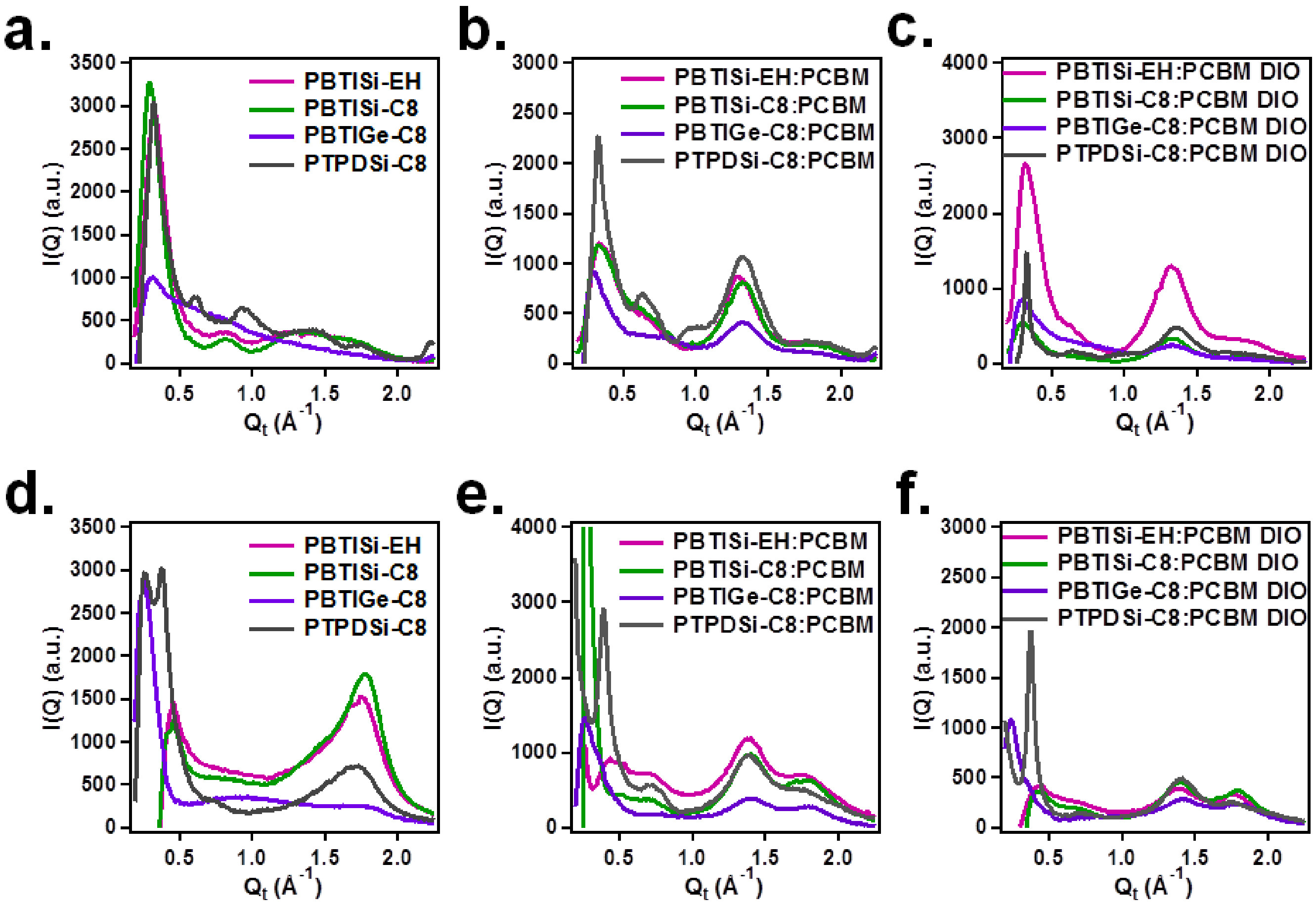


Figure 11. (a) In-plan linecuts of 2D GIWAXS of neat polymer films. (b) In-plan linecuts of polymer/$PC_{71}BM$ blend films without DIO. (c) In-plan linecuts of polymer/$PC_{71}BM$ blend films with DIO as processing addative. (d) Out-of-plane linecuts of neat polymer films; (e) Out-of-plane linecuts of polymer/$PC_{71}BM$ blend films without DIO; (f) Out-of-plane linecuts of polymer/$PC_{71}BM$ blend films with DIO as processing addative. The films are deposited on ZnO coated ITO substrate and the polymer/$PC_{71}BM$ ratios and DIO percentages are used for device fabrications yielding the best-performing solar cells.

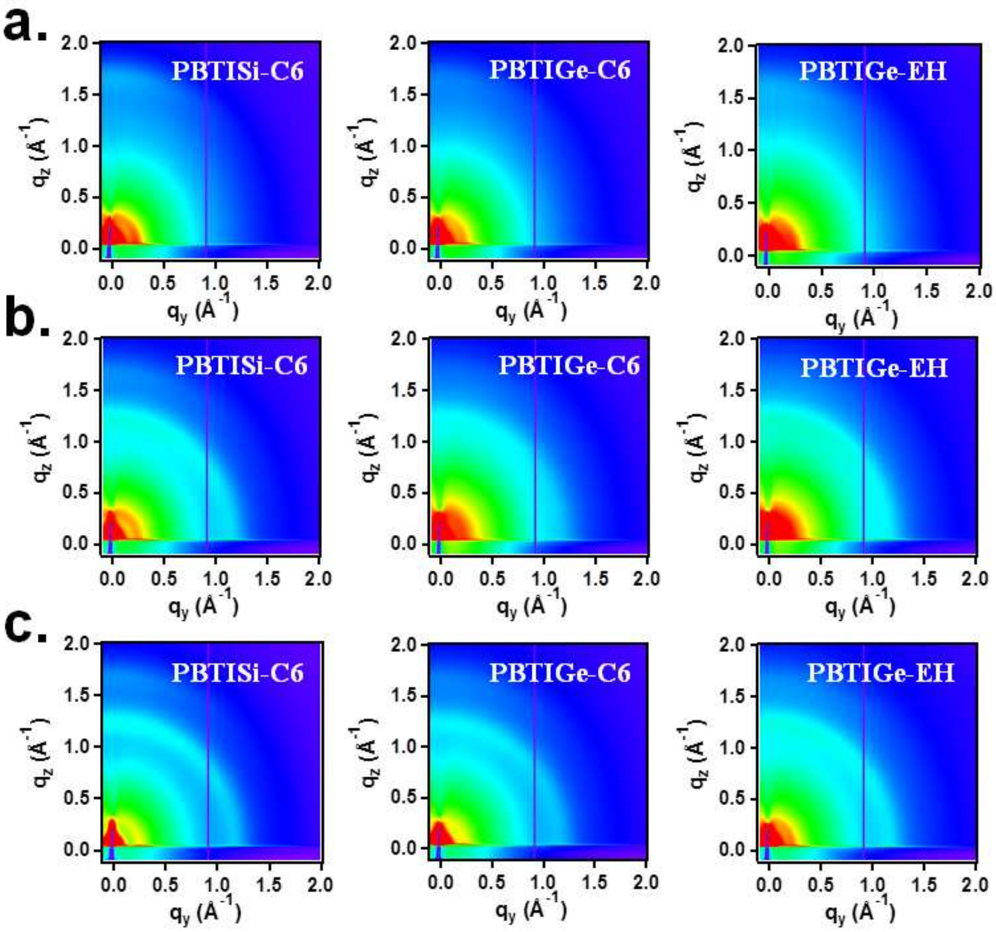


Figure 12. (a) 2D GIWAXS image of neat polymer films; (b) polymer:$PC_{71}BM$ blend films without DIO; and (c) polymer:$PC_{71}BM$ (1:1) blend film with DIO as the processing additive. The films are deposited on ZnO coated ITO substrate and the polymer/$PC_{71}BM$ ratios and DIO percentages are used for device fabrications yielding the best-performing solar cells.

Table S1. Photovoltaic parameters for polymer:$PC_{71}BM$ (1:1; w/w) inverted solar cells fabricated using DCB/DIO as the processing solvent with varying v/v ratios.

polymer	DCB:DIO (%:%)	V_{oc} (V)	J_{sc} (mA/cm^2)	*FF* (%)	PCE (%)
PBTISi-C6	100:0	0.800	7.61	45.0	2.74
PBTISi-C8	100:0	0.838	6.06	52.6	2.67
PBTISi-C8	98.5:1.5	0.815	11.77	53.2	5.10
PBTISi-C8	98:2	0.803	12.81	62.3	6.41
PBTISi-C8	97.5:2.5	0.791	12.49	56.4	5.57
PBTISi-C8	97:3	0.775	11.59	58.3	5.23
PBTISi-EH	100:0	0.847	6.46	48.4	2.65
PBTISi-EH	98:2	0.834	12.51	53.1	5.54
PBTIGe-C6	100:0	0.785	9.15	46.8	3.36
PBTIGe-C8	100:0	0.792	10.59	43.3	3.63
PBTIGe-EH	100:0	0.671	5.88	36.2	1.43

References:

(1) Letizia, J. A.; Salata, M. R.; Tribout, C. M.; Facchetti, A.; Ratner, M. A.; Marks, T. J. *J. Am. Chem. Soc.* **2008**, *130*, 9679.

(2) Hou, J.; Chen, H.-Y.; Zhang, S.; Li, G.; Yang, Y. *J. Am. Chem. Soc.* **2008**, *130*, 16144.

(3) Gendron, D.; Morin, P.-O.; Berrouard, P.; Allard, N.; Aïch, B. R.; Garon, C. N.; Tao, Y.; Leclerc, M. *Macromolecules* **2011**, *44*, 7188-7193.

(4) Chu, T. Y.; Lu, J. P.; Beaupré, S.; Zhang, Y. G.; Pouliot, J. R.; Wakim, S.; Zhou, J. Y.; Leclerc, M.; Li, Z.; Ding, J. F.; Tao, Y. *J. Am. Chem. Soc.* **2011**, *133*, 4250-4253.

(5) Jiang, Z.; Li, X.; Strzalka, J.; Sprung, M.; Sun, T.; Sandy, A. R.; Narayanan, S.; Lee, D. R.; Wang, J. *J. Synchrotron Rad.* **2012**, *19*, 627-636.

(6) Guo, X.; Watson, M. D. *Org. Lett.* **2008**, *10*, 5333-5336.