Supporting Information for

Increased Open Circuit Voltage in Fluorinated Benzothiadiazole-Based Alternating Conjugated Polymers

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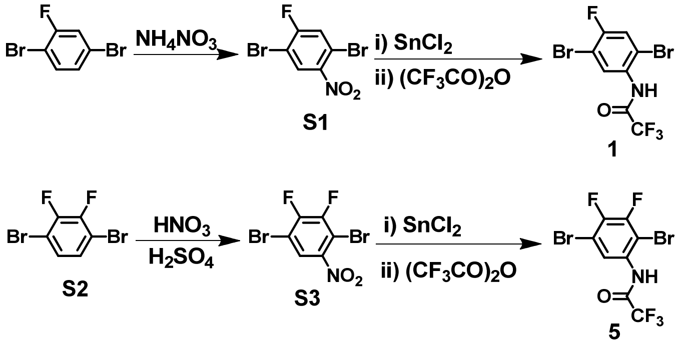

Scheme S1. Synthesis of compounds 1 and 5.

Experimental details

Materials synthesis

All chemicals, unless otherwise specified, were purchased from Aldrich and used as received.

*Synthesis of 2,5-dibromo-4-fluoro-nitrobenzene (**S1**).*

To a solution of 1,4-dibromo-2-fluorobenzene (5.0 g, 19.7 mmol) in dichloromethane (16 mL), trifluoroacetic acid (8 mL), and trifluoroacetic anhydride (16 mL) at 0^{o}C was added NH_4NO_3 (2 g, 25 mmol), the mixture was then stirred at room temperature overnight. After that, the mixture was poured into water and the aqueous solution was extracted with dichloromethane twice. The combined organic phase was dried over Na_2SO_4. After removing the solvent, the crude compound was purified by silica column to give off-white solid (5.0g, 85%). ^{1}H NMR ($CDCl_3$, ppm): 8.21 (d, J = 6.36 Hz, 1H), 7.57 (d, J = 7.41 Hz, 1H).GC-MS (M^+, $C_6H_2Br_2FNO_2$), calcd, 298.9; found: 299.

Synthesis of N-(2’,5’-dibromo-4’-fluorophenyl)-2,2,2-trifluoroacetamide(**1**)**.**

To a solution of compound **S1** (5.0 g, 16.7 mmol) in ethanol (16 mL) and conc. HCl (14 mL) at 0 ^{o}C was added $SnCl_2{\bullet}2H_2O$ (20 g, 88 mmol) in several portions. After addition, the mixture was heated to reflux for 45 min and then stirred at room temperature overnight. Aqueous KOH solution was added to adjust the pH value to ~9. Then, the mixture was extracted with dichloromethane three times. The combined organic phases were washed with water twice and dried over anhydrous Na_2SO_4. After removing the solvent, the crude product was dissolved into chloroform (250 mL). The trifluoroacetic anhydride (19 mL) was added into the mixture slowly and the resulting mixture was stirred at room temperature for 2 hours. The saturated aqueous $NaHCO_3$ was then added into the mixture, and the organic phase was separated and dried over Na2SO4. After removing solvent, the crude product was purified by silica column to give a yellow solid (4.1 g, 61%). ^{1}H NMR ($CDCl_3$, ppm): 8.62 (d, J = 6.66 Hz, 1H), 8.31 (s, 1H), 7.45 (d, J = 7.32 Hz, 1H). GC-MS(M^+, $C_8H_3Br_2F_2NO$), cacld, 364.9; found: 365.

Synthesis of N-(2',5'-dibromo-4'-fluoro-6'-nitrophenyl)-2,2,2-trifluoroacetamide(**2**).

To a solution of conc. H_2SO_4 (40 mL) and HNO_3 (20 mL) was added compound 1 (3.8 g, 9.3 mmol) very slowly at -10 ^{o}C. The mixture was stirred at this temperature for 2 hours and then poured into ice. The resulting solid was recovered and purified by a short flash column using dichloromethane to give a white solid (3.6 g, 85%). ^{1}H NMR ($CDCl_3$, ppm): 7.84 (s, 1H), 7.71 (d, J = 7.11 Hz, 1H).GC-MS(M^+, $C_8H_2Br_2F_4N_2O_3$), cacld, 409.9; found: 410.

Synthesis of 2,5-dibromo-4-fluoro-6-nitroaniline (**3**).

In a 100-mL single neck flask, the mixture solution of compound 2 (2 g, 4.9 mmol) in conc. H_2SO_4 (15 mL) and H_2O (50 mL) was refluxed for 3 hours. Then, the mixture was slowly added into aqueous KOH, the pH value was then adjusted to ~8-9. The mixture was extracted with ethyl acetate twice. The organic phase was dried over anhydrous

Na_2SO_4. After removing the solvent, the crude product was dried under vacuum and used directly without further purification (1.2 g, 78%). ^{1}H NMR ($CDCl_3$, ppm): 7.49 (d, J = 7.29 Hz, 1H), 5.05 (s, 2H).^{19}F NMR ($CDCl_3$, ppm): -115.59, -115.62.GC-MS: (M^+, $C_6H_3Br_2FN_2O_2$), cacld, 313.9; found: 314.

Synthesis of 2,5-dibromo-4-fluoro-5,6-benzenediamine (**4**).

To a solution of compound 3 (1.2 g, 3.8 mmol) in ethanol (15 mL) and conc. HCl (10 mL) was added $SnCl_2$•$2H_2O$ (6 g, 26 mmol) in several portions. The mixture was refluxed for 1 hour and stirred overnightat room temperature. Then, pH value of the mixture was adjusted to ~8-9 by adding aqueous KOH solution, and then the mixture was extracted with ethyl acetate three times. The combined organic phases were dried over anhydrous Na_2SO_4. Further purification was run by silica column to give an off-white solid (1.0 g, 72%). ^{1}H NMR ($CDCl_3$, ppm): 6.84 (d, J = 8.01 Hz, 1H), 4.15 (s, 2H), 3.65 (s, 2H).^{13}C NMR ($CDCl_3$, ppm): 154.33, 152.41, 135.93 (d, J = 3.27 Hz), 128.92 (d, J = 2.59 Hz), 109.61 (d, J = 11.35 Hz), 109.01 (d, J = 26.38 Hz), 96.95 (d, J = 24.14 Hz).^{19}F NMR ($CDCl_3$, ppm): -116.06, -116.09. GC-MS (M^+, $C_6H_5Br_2FN_2$), cacld, 283.9; found: 284.

Synthesis of 4,7-dibromo-5-fluoro-[2,1,3]benzothiadiazole (**FBT**).

To a solution of compound 4 (0.6 g, 2.1 mmol) in pyridine (10 mL) was added $SOCl_2$ (1.2 mL) slowly at 0 °C. After the addition, the mixture was stirred at room temperature for 3 days. Then, the mixture was poured into ice, and extracted with dichloromethane. The organic phase was dried over anhydrous Na_2SO_4. After removing the solvent, the crude product was purified by silica column to give a white solid (0.58 g, 88%).^{1}H NMR

($CDCl_3$, ppm): 7.83 (d, J = 8.31 Hz, 1H). ^{19}F NMR ($CDCl_3$, ppm): -103.10 (d, J = 1.27 Hz), -103.13 (d, J = 1.21 Hz). GC-MS (M^+, $C_6HBr_2FN_2S$), cacld, 311.9; found: 312.

Synthesis of 1,4-dibromo-2,3-difluorobenzene (**S2**).[1]

To a solution of LDA (prepared from *n*-BuLi (48 mL, 2.5 M in hexane) and diisopropylamine (18 mL)) at -78 °C was added the mixture of 1,2-difluorobenzene (6.2 g, 54.4 mmol) and trimethylsilyl chloride (13.4 g, 123 mmol). After addition, the mixture was stirred at -78 °C for 1 hour and at room temperature for 1 hour.Then, the mixture was poured into water and was extracted with dichloromethane three times. The organic phase was then dried over Na_2SO_4. After removing the solvent, the crude product was run a short flash column using hexane as the eluent to give a white solid (~13g). The white solid was then dissolved into dichloromethane (40 mL), and bromine (20 mL)in dichloromethane (20 mL) was added slowly. Then, the mixture was heated to reflux until there was no starting material found (monitored by GC-MS). After cooling to room temperature, the mixture was poured into aqueous Na_2SO_3 solution. The aqueous phase was extracted with dichloromethane twice. The combined organic phases were dried over anhydrous Na_2SO_4. After removing the solvent, the crude product was purified by distillation to give a colorless liquid (12.6 g, 85%). GC-MS (M^+, $C_6H_2Br_2F_2$), cacld, 271.9; found: 272.

Synthesis of 2,5-dibromo-3,4-difluoro-1-nitrobenzene(**S3**).

To a solution of conc. H_2SO_4 (100 mL) and HNO_3 (50 mL) was added compound S2 (9.8 g, 36 mmol) very slowly at -10 °C. The mixture was stirred at this temperature for 2 hours and then poured into ice. The resulting solid was recovered and purified by a short flash column using dichloromethane (10.2 g, 89%).GC-MS (ESI): (M^+, $C_6HBr_2F_2NO_2$), cacld, 316.9; found: 317.

Synthesis of N-(2',5'-dibromo-3',4'-difluorophenyl)-2,2,2-trifluoroacetamide(**5**).

The compound 5 was synthesized by following similar procedure of compound 1.^{1}H NMR ($CDCl_3$, ppm): 8.46-8.43 (q, 1H), 8.33 (s, 1H).^{13}C NMR ($CDCl_3$, ppm): 154.25 (q), 149.61 (d, J = 15.78 Hz), 147.47 (t), 145.46 (d, J = 14.72 Hz), 130.57, 120.59 (d, J = 3.58 Hz), 116.67, 114.38, 110.43 (d, J = 19.39 Hz), 102.75 (d, J = 21.16 Hz).GC-MS: (M^+, $C_8H_2Br_2F_5NO$), cacld, 382.9; found: 383.

Synthesis of N-(2',5'-dibromo-3',4'-difluoro-6'-nitrophenyl)-2,2,2-trifluoroacetamide(**6**).

The compound 6 was synthesized by following similar procedure of compound 2.^{1}H NMR ($CDCl_3$, ppm): 8.03 (s, 1H). GC-MS (M^+, $C_8HBr_2F_5N_2O_3$), cacld, 427.9; found: 428.

Synthesis of 2,5-dibromo-3,4-difluoro-6-nitroaniline (**7**).

The compound 7 was synthesized by following similar procedure of compound 3.^{1}H NMR ($CDCl_3$, ppm): 5.43 (s, 2H).^{19}F NMR ($CDCl_3$, ppm): -115.99, -116.08, -135.83, -135.92. GC-MS: (M^+, $C_6H_2Br_2F_2N_2O_2$), cacld, 331.9; found: 332.

Synthesis of 2,5-dibromo-3,4-difluoro-5,6-benzenediamine (**8**).

The compound 8 was synthesized by following similar procedure of compound 4. ^{1}H NMR ($CDCl_3$, ppm): 3.85 (s, 4H). ^{13}C NMR ($CDCl_3$, ppm): 142.99 (d, J = 18.11 Hz), 141.06 (d, J = 17.65 Hz), 129.78, 98.39 (t). ^{19}F NMR ($CDCl_3$, ppm): -139.02. GC-MS (M^+, $C_6H_4Br_2F_2N_2$), cacld, 301.9; found: 302.

Synthesis of 4,7-dibromo-5,6-difluoro-[2,1,3]benzothiadiazole (**DFBT**).

The compound DFBT was synthesized by following similar procedure of compound FBT. ^{13}C NMR ($CDCl_3$, ppm): 153.15, 152.98, 151.07, 149.07, 99.67. ^{19}F NMR ($CDCl_3$, ppm): -119.38. GC-MS (M^+, $C_6Br_2F_2N_2S$), cacld, 329.9; found: 330.

Synthesis of PIDT-FBT: Compound 9 (327 mg, 0.27 mmol) and FBT (78 mg, 0.25 mmol) were charged in a 25 mL flask under N_2 protection. After the additionof toluene (3 mL), the mixture was degassed by following the addition of $Pd_2(dba)_3$ (7 mg) and P(*o*-tol)$_3$ (21 mg). Then, the mixture was heated up to 120 °C for 3 days. After cooling to room temperature, the mixture was poured into acetone. The precipitate was collected and dissolved into a small amount of chloroform and passed through a short silica column. After removing most of chloroform, the chloroform solution was poured into hexane, and the solid was collected and dried overnight under vacuum (220 mg, 83%). ^{1}H NMR ($CDCl_3$, ppm): 8.25 (br, 2H), 8.04 (br, 1H), 7.57 (m, 2H), 7.26 (m, 8H), 7.12 (m, 8H), 2.59 (br, 8H), 1.58 (m, 8H), 1.35 (m, 24H), 0.89 (m, 12H). Molecular weight: M_n = 32.9 k, PDI = 3.70.

Synthesis of PIDT-DFBT: Compound 9 (321 mg, 0.27 mmol) and DFBT (82 mg, 0.25 mmol) were charged in a 25 mL flask under N_2 protection. After the additionof toluene (3 mL), the mixture was degassed by following the addition of $Pd_2(dba)_3$ (7 mg) and P(*o*-tol)$_3$ (25 mg). Then, the mixture was heated up to 120 °C for 3 days. After cooling to room temperature, the mixture was poured into acetone. The precipitate was collected and dissolved into a small amount of chloroform and passed through a short silica column. After removing most of chloroform, the chloroform solution was poured into hexane, and the solid was collected and dried overnight under vacuum (240 mg, 90%).^{1}H NMR ($CDCl_3$, ppm): 8.26 (s, 2H), 7.60 (s, 2H), 7.26 (br, 8H), 7.13 (br, 8H), 2.60 (br, 8H), 1.62 (m, 8H), 1.31 (m, 24H), 0.89 (m, 12H). Molecular weight: M_n = 61.4 k, PDI = 3.04.

General characterization methods

UV-Vis spectra were measured using a Perkin-Elmer Lambda-9 spectrophotometer. The ^{1}H and ^{13}C NMR spectra were collected on a Bruker AV 300 and 500 spectrameter operating at 300 and 125 MHz in deuterated chloroform solution with TMS as reference, respectively.Cyclic voltammetry of polymer film was conducted in acetonitrile with 0.1 M of tetrabutylammonium hexafluorophosphate using a scan rate of 100 mV s^{-1}. ITO, Ag/AgCl and Pt mesh were used as working electrode, reference electrode and counter electrode, respectively. AFM images under tapping mode were taken on a Veeco multimode AFM with a Nanoscope III controller.

Device fabrication: To fabricate the conventional solar cells, ITO-coated glass substrates (15 Ω/sq.) were cleaned with detergent, de-ionized water, acetone, and isopropyl alcohol. A thin layer (ca. 40 nm) of PEDOT:PSS (Baytron® P VP AI 4083, filtered at 0.45 μm) was first spin-coated on the pre-cleaned ITO-coated glass substrates at 5,000 rpm and baked at 140°C for 10 minutes under ambient conditions. The substrates were then transferred into an argon-filled glove-box. Subsequently, the polymer : $PC_{71}BM$ active layer (1:3 wt, ~70-100 nm, prepared by dissolving the polymer in o-dichlorobenzene and filtered with a 0.2 μm PTFE filter) was spin-coated on the PEDOT:PSS layer from a homogeneously blended solution.The substrates were annealed at 110 °C for 10 minutes prior to electrode deposition. At the final stage, the substrates were pumped down to high vacuum ($< 2 \times 10^{-6}$ Torr), and calcium (30 nm) topped with aluminum (100 nm) was thermally evaporated onto the active layer through shadow masks to define the active area (10.08×10^{-2} cm^2) of the devices. More than 10 devices were fabricated for each polymer. The hole-only devices for space charge limited current (SCLC) mobilities were fabricated with same procedure, except the evaporationof MoO_3(10 nm) instead of Ca.The SCLC model was employed to extract the vertical hole mobility with the equation, $J = 9\varepsilon_0\varepsilon_r\mu V^2/8L^3$, where J is the current density, $\varepsilon_0\varepsilon_r$ is the permittivity of the polymer, μ is the carrier mobility, and L is the active layer thickness.

Device characterization: The current-voltage (I-V) characteristics of unencapsulated photovoltaic devices were measured under ambient using a Keithley 2400 source-measurement unit. An Oriel xenon lamp (450 Watt) with an AM1.5 G filter was used as the solar simulator. A Hamamatsu silicon solar cell with a KG5 color filter, which is traced to the National Renewable Energy Laboratory (NREL), was used as the reference cell. To calibrate the light intensity of the solar simulator, the power of the xenon lamp was adjusted to make the short-circuit current (*ISC*) of the reference cell under simulated sun light as high as it was under the calibration condition. The spectral mismatches resulting from the test cells, the reference cell, the solar simulator, and the AM1.5 were calibrated with mismatch factors (*M*). According to Shrotriya et al.[2] the mismatch factor is defined as

$$M = \frac{\int_{\lambda_1}^{\lambda_2} E_{\mathrm{Ref}}(\lambda)S_R(\lambda)d\lambda \int_{\lambda_1}^{\lambda_2} E_S(\lambda)S_T(\lambda)d\lambda}{\int_{\lambda_1}^{\lambda_2} E_{\mathrm{Ref}}(\lambda)S_T(\lambda)d\lambda \int_{\lambda_1}^{\lambda_2} E_S(\lambda)S_R(\lambda)d\lambda}$$

where $E_{\mathrm{Ref}}(\lambda)$is the reference spectral irradiance (AM1.5), $E_S(\lambda)$ is the source spectral irradiance, $S_R(\lambda)$ is the spectral responsivity of the reference cell, and $S_T(\lambda)$ is the spectral responsivity of the test cell, each as a function of wavelength (λ). The spectral responsivities of the test cells and the reference cell were calculated from the corresponding external quantum efficiencies (EQE) by the relationship

$$S(\lambda) = \frac{q\lambda}{hc} EQE(\lambda),$$

where the constant term *q/hc* equals 8.0655 × $10^5$for wavelength in units of meters and $S(\lambda)$ in units of AW^{-1}. The Hamamatsu solar cell was also used as the detector for determining the spectral irradiance of the solar simulator. To minimize the spectral transformation, theirradiance spectrum has been calibrated with the spectral responsively of the Hamamatsu cell and the grating efficiency curve of the monochromator (Oriel Cornerstone 130). It should be noted that the spectral irradiance of the solar simulator and the EQE were only recorded between 350 nm to 800 nm because of the limitation of the calibrated region of the Hamamatsu cell. The slight extend in the EQE response compared to the absorption of polymer film is a common phenomenon in the polymer photovoltaic cells. The reason is coming from either the charge-transfer absorption between polymer and acceptor (PCBM) or the absorption of PCBM at the interface or in the polymer rich phase. This phenomenon has been reported and discussed in literature.[3]

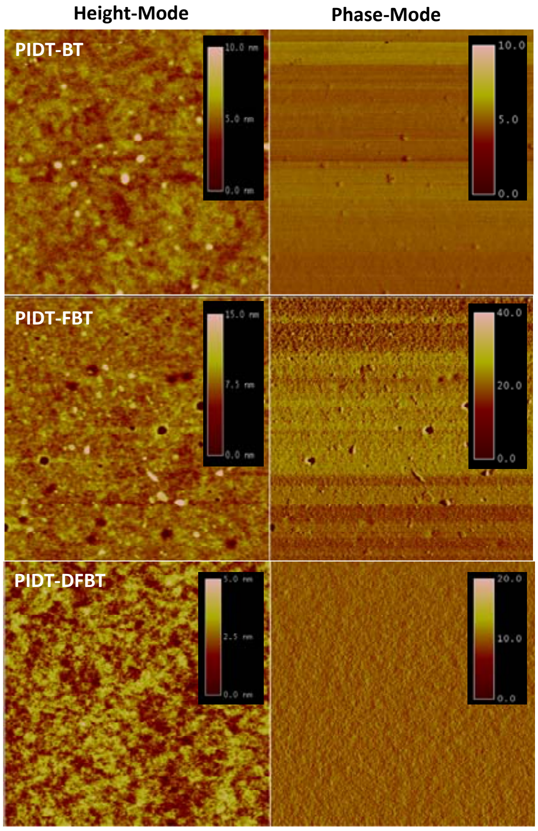

Figure S1. AFM morphologies (height-mode and phase-mode, 5 µm x 5 µm) of photoactive layer with one p-type polymer and $PC_{71}BM$.

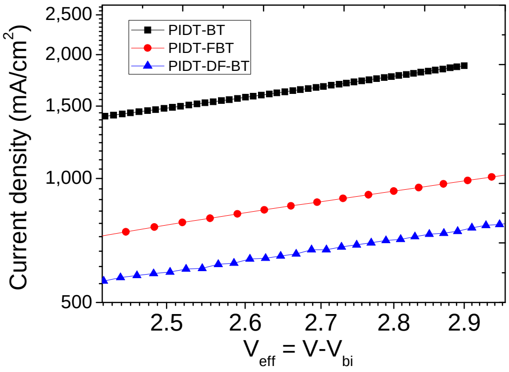

Figure S2. The SCLC curves of PIDT-BT, PIDT-FBT and PIDT-DFBT-based hole-only devices.

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3. (a) M. Presselt,M. Bärenklau, R. Rösch, W. J. D. Beenken, E. Runge, S. Shokhovets, H. Hoppe, G. Gobsch,*Appl. Phys. Lett*. 2010, **97**, 253302. (b)J. J. Benson-Smith, L. Goris, K. Vandewal,K. Haenen, J. V. Manca, D. Vanderzande, D. D. C. Bradley, J. Nelson,*Adv. Funct. Mater.* 2007, **17**, 451