

Supporting Information

Utilizing Difluorinated Thiophene Units to Improve Performance of Polymer Solar Cells

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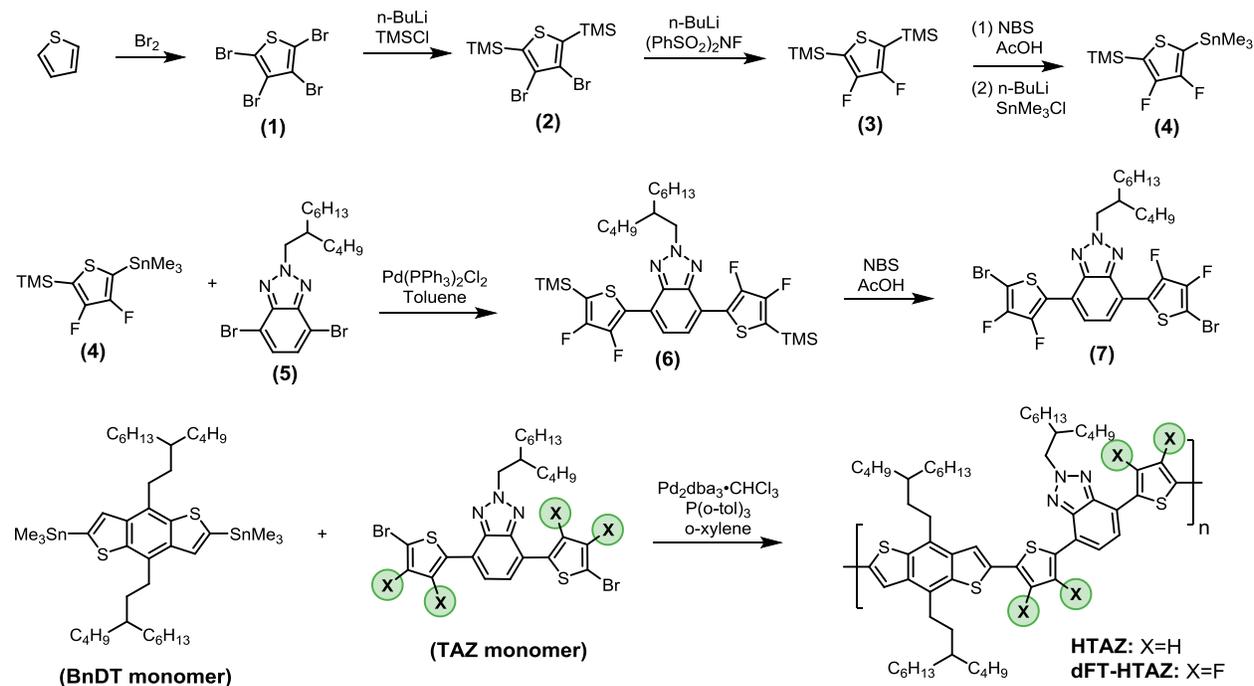
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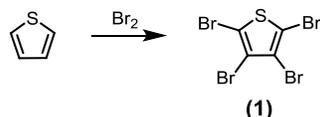
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Synthesis:

All chemicals were purchased from commercial source (Sigma-Aldrich, Fisher, Acros, etc.) and were used as received except when specified. THF was distilled over sodium and benzophenone before use. For reactions under argon, the reaction flask was evacuated and refilled with argon for three times.

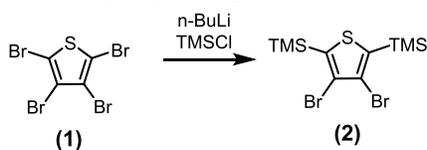


Synthesis of 2,3,4,5-Tetrabromothiophene (**1**):



First a solution of chloroform (20 mL) and thiophene (5.0 g, 0.06 mol, 1 eq.) was prepared and cooled to 0 °C with an ice/water bath. Then, via addition funnel, a solution of chloroform (10 mL) and liquid bromine (5.4 mL, 0.21 mol, 3.5 eq.) was added dropwise slowly over the course of 4 hours. After that time period, the reaction mixture was allowed to warm to room temperature by removal the ice/water bath. An additional aliquot of liquid bromine (1.1 mL, 0.042 mol, 0.7 eq.) was added, and the reaction mixture was subsequently stirred under reflux for 4 hours. To remove any excess liquid bromine, a saturated aqueous solution of NaOH was added to quench the mixture. The reaction mixture continued to stir under reflux for one additional hour. To workup the reaction, the mixture was first extracted with dichloromethane (x3) and the combined organic portions were dried over magnesium sulfate. After filtration, the organic solution was concentrated under reduced pressure/rotovap. Finally, the crude solid was recrystallized from a 1:1 solution (by volume) of chloroform:ethanol to provide pure (**1**) as long colorless needlelike crystals (21.11 g, 88% yield).

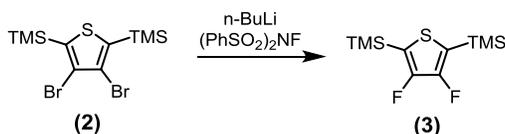
Synthesis of 3,4-Dibromo-2,5-bis(trimethylsilyl)thiophene (**2**):



2,3,4,5-Tetrabromothiophene (**1**) (15 g, 37.5 mmol, 1 eq.) was added to a 250 mL three-necked flask which was sequentially evacuated and refilled with argon three times. The starting material was then dissolved in anhydrous THF (80 mL) which was distilled over sodium and benzophenone (via THF still) under the protection of argon. The solution was cooled to $-78\text{ }^{\circ}\text{C}$ with dry ice/acetone bath. After cooling for 30 minutes, a solution of n-BuLi (2.5 M in hexanes, 15 mL, 37.5 mmol, 1 eq.) was slowly added in a dropwise fashion over the course of 15 minutes. After the final drops of n-BuLi were added, the mixture was stirred for 30 minutes. While the reaction flask was still at $-78\text{ }^{\circ}\text{C}$, a solution of chlorotrimethylsilane (4.76 mL, 37.5 mmol, 1 eq.) was then added in one portion and stirring was maintained for 90 minutes. An additional 1 equivalent of n-BuLi (2.5 M in hexanes, 15 mL, 37.5 mmol, 1 eq.) was added dropwise to the reaction mixture, and after the solution was stirred for a further 30 minutes, a second portion of chlorotrimethylsilane (4.76 mL, 37.5 mmol, 1 eq.) was added. The reaction mixture was then stirred for 30 minutes at $-78\text{ }^{\circ}\text{C}$. After this time, the reaction mixture was allowed to slowly warm to room temperature and left to stir overnight. To workup the reaction mixture, first a saturated ammonium chloride solution (100 mL) was prepared. The reaction mixture was quenched with water, opened to air, and then poured into the ammonium chloride solution. The organic components of the mixture were extracted with dichloromethane (x3), and the combined organic phases were washed with water (x3). After being dried over MgSO_4 , the organic phase was filtered and the resulting filtrate was concentrated under reduced pressure/rotovap. The resulting colorless oil was purified by vacuum distillation to give (**2**) (11.84 g, 82%).

^1H (400 MHz, CDCl_3): δ 0.39 (18H, s).

Synthesis of 3,4-Difluoro-2,5-bis(trimethylsilyl)thiophene (**3**):



3,4-Dibromo-2,5-bis(trimethylsilyl)thiophene (**2**) (10.9 g, 28.22 mmol, 1 eq.) was added to a multineck round bottom flask, which was then evacuated and refilled with an argon atmosphere three times. The starting material was dissolved in 150 mL dry tetrahydrofuran (from still) and cooled to $-78\text{ }^{\circ}\text{C}$ in a dry ice/acetone bath. Then n-BuLi (2.5 M in hexane) and N-fluoro-N-(phenylsulfonyl)benzenesulfonamide (herein abbreviated NFSI), which was dissolved in dry THF, were added at $-78\text{ }^{\circ}\text{C}$ alternately in the following portions:

- i) n-BuLi (11.74 mL, 29.35 mmol, 1.04 eq.), stir for 30 min, then NFSI (9.25 g, 29.35 mmol, 1.04 eq.) dissolved in 50 mL THF, stir for an additional 30 min.

- ii) n-BuLi (5.87 mL, 14.67 mmol, 0.52 eq.), stir for 30 min, then NFSI (4.63 g, 14.67 mmol, 0.52 eq.) dissolved in 20 mL THF, stir for an additional 30 min.
- iii) n-BuLi (2.94 mL, 7.34 mmol, 0.26 eq.), stir for 30 min, then NFSI (2.31 g, 7.34 mmol, 0.26 eq.) dissolved in 15 mL THF, stir for an additional 30 min.
- iv) n-BuLi (1.47 mL, 3.67 mmol, 0.13 eq.), stir for 30 min, then NFSI (1.16 g, 3.67 mmol, 0.13 eq.) dissolved in 10 mL THF, stir for an additional 30 min.
- v) n-BuLi (1.47 mL, 3.67 mmol, 0.13 eq.), stir for 30 min, then NFSI (1.78 g, 5.64 mmol, 0.20 eq.) dissolved in 20 mL THF, stir for an additional 30 min.

The dry ice/acetone bath was removed and the mixture was stirred at room temperature overnight. To workup the reaction mixture, first the flask was quenched with water. This was followed with 200 mL of 1 M HCl being added to the suspension. The organic layer was separated, washed with brine (x3), and dried over magnesium sulfate. After filtration, the solution was concentrated under reduced pressure/rotovap and run through a silica gel plug using hexane as eluent. After removing the hexane under reduced pressure/rotovap, the resulting oil was purified via vacuum distillation and yielded (**3**) (3.06 g, 41%) as a colorless oil.

¹⁹F (376 MHz, CDCl₃): δ -130.5 (s, 2F).

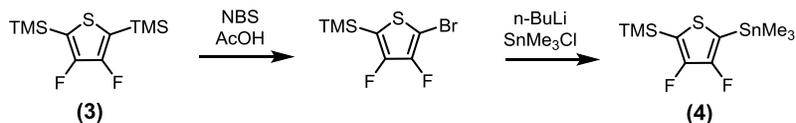
¹H (400 MHz, CDCl₃): δ 0.32 (s, 18H).

Alternatively, we have also tried a different approach where the order of addition for n-BuLi and NFSI was changed: First, 3,4-Dibromo-2,5-bis(trimethylsilyl)thiophene (**2**) (24.60 g, 63.7 mmol, 1 eq.) and NFSI (36.15 g, 114.6 mmol, 1.8 eq.) were added to a multineck round bottom flask which was evacuated and refilled with argon three times. The starting material and NFSI were then dissolved in dry tetrahydrofuran (from still) and cooled to -78 °C in a dry ice/acetone bath. Then n-BuLi (2.5 M in hexane) and NFSI were added at -78 °C in the following portions:

- i) n-BuLi (17.8 mL, 44.60 mmol, 0.7 eq.), stir for 1 h,
- ii) n-BuLi (17.8 mL, 44.60 mmol, 0.7 eq.), stir for 1 h,
- iii) n-BuLi (17.8 mL, 44.60 mmol, 0.7 eq.), stir for 1 h,
- iv) NFSI (24.10 g, 76.4 mmol, 1.2 eq.) dissolved in dry THF, stir for 30 min,
- v) n-BuLi (30.6 mL, 76.4 mmol, 1.2 eq.), stir for 1 h,
- vi) NFSI (20.08 g, 63.7 mmol, 1 eq.) dissolved in dry THF, stir for 30 min,
- vii) n-BuLi (25.5 mL, 63.7 mmol, 1 eq.), stir for 1 h,

The dry ice/acetone bath was then removed and the mixture was stirred at room temperature overnight. The mixture was quenched with water, and the workup began with extracting the organic layer with ethyl acetate. After being washed with brine (x2) and water (x2), and dried over magnesium sulfate, the organic phase was filtered and the resulting solution was concentrated under reduced pressure and run through a silica gel plug using hexane as eluent. After removing the hexane under reduced pressure/rotovap, vacuum distillation yielded (**3**) (6.74 g, 40%) as a colorless oil. Interestingly, both procedures produced nearly identical yields. In previous reports, when synthesizing a mono-fluorinated thiophene unit, the yields for the different protocols varied largely.

Synthesis of 3,4-Difluoro-2-trimethylsilyl-5-(trimethylstannyl)thiophene (**4**):



A mixture of 3,4-Difluoro-2,5-bis(trimethylsilyl)thiophene (**3**) (6.4 g, 24.2 mmol, 1 eq.) and NBS (*N*-bromosuccinimide) (4.73 g, 26.6 mmol, 1.1 eq.) in acetic acid was stirred at 80 °C overnight. The reaction mixture was wrapped in aluminum foil to minimize light exposure, and the reaction proceeded under a normal air atmosphere. The resulting mixture was purified using the following protocol: first, the reaction mixture was poured into water and extracted with ethyl acetate. The resulting organic layer was washed with 1 M NaOH, brine, and water (x1 each), then dried with magnesium sulfate. After filtration, the filtrate was concentrated under reduced pressure/rotovap. The resulting residue was purified through silica gel column (hexanes eluent), to yield the intermediate (3.64 g, 56%). Warning, the intermediate is very low boiling point and can be pulled off at low temperatures on the rotovap.

^{19}F (376 MHz, CDCl_3): δ -125.4 (d, $J=14.4$ Hz, 1F), -134.5 (d, $J=14.1$ Hz, 1F).

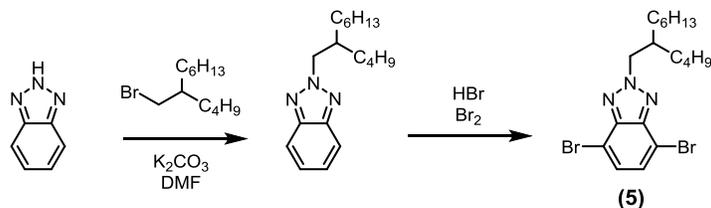
^1H (400 MHz, CDCl_3): δ 0.32 (s, 9H).

The resulting brominated material (2.98 g, 10.99 mmol, 1 eq.) was added to a flask which was then evacuated and refilled with argon three times. The oil was solubilized in dry THF (30 mL) from the still, and the mixture was cooled with a dry ice/acetone bath. Next, 2.5 M *n*-BuLi in hexanes (4.6 mL, 11.54 mmol, 1.05 eq.) was added to the flask, still at -78 °C and under argon. The mixture was stirred at -78 °C for 30 minutes. A 1 M solution of Me_3SnCl in hexanes (12.1 mL, 12.09 mmol, 1.1 eq.) was added dropwise, and the resulting solution was stirred at -78 °C for 1 hour. The reaction mixture was allowed to warm to room temperature for 45 minutes and was then quenched with water. After extraction with hexanes, the organic layer was washed with brine (x3), dried with magnesium sulfate, filtered, and concentrated under reduced pressure/rotovap to give (**4**) as a faint yellow oil (3.63 g, 93%). Note: there were trace impurities on the ^{19}F NMR spectra, but the ^1H NMR spectra was clean.

^{19}F (376 MHz, CDCl_3): δ -131.1 (d, $J=16.6$ Hz, 1F), -131.8 (d, $J=16.8$ Hz, 1F).

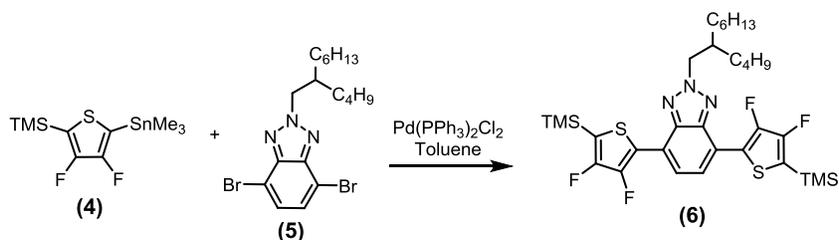
^1H (400 MHz, CDCl_3): δ 0.40 (s, 9H), 0.31 (s, 9H).

Synthesis of 4,7-dibromo-2-(2-butyloctyl)-2H-benzo[d][1,2,3]triazole (**5**):



4,7-dibromo-2-(2-butyloctyl)-2H-benzo[d][1,2,3]triazole (**5**) was synthesized according to previously literature reports. (doi.org/10.1021/cm802937x)

Synthesis of 2-(2-butyloctyl)-4,7-bis(3,4-difluoro-5-(trimethylsilyl)thiophen-2-yl)-2H-benzo[d][1,2,3]triazole (**6**):

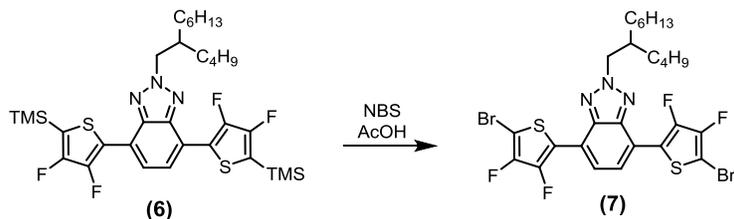


Both (**4**) (3.6 g, 10.2 mmol, 2.5 eq.) and (**5**) (1.8 g, 4.05 mmol, 1.0 eq.) were added to a multineck round bottom flask fitted with a condensing column. The flask was evacuated and refilled with an argon atmosphere three times. The starting materials were dissolved by the addition of anhydrous toluene. Finally, bis(triphenylphosphine)palladium (II) dichloride (86 mg, 0.12 mmol, 0.03 eq.) was added under argon stream. The reaction mixture was purged with argon for 30 minutes, which was then refluxed for 50 hours. Toluene was removed under reduced pressure/rotovap, and the reaction mixture was purified through silica gel column (9:1 hexanes:dichloromethane eluent), to yield (**6**) as a yellow oil (1.15 g, 43%).

^{19}F (376 MHz, CDCl_3): δ -128.4 (d, $J=15.6$ Hz, 2F), -133.8 (d, $J=15.3$ Hz, 2F).

^1H (400 MHz, CDCl_3): δ 7.89 (s, 2H), 4.79 (d, $J=4.24$ Hz, 2H), 2.28 (m, 1H), 1.19-1.49 (m, 16H), 0.80-0.94 (m, 6H), 0.32 (s, 18H).

Synthesis of 4,7-bis(5-bromo-3,4-difluorothiophen-2-yl)-2-(2-butyloctyl)-2H-benzo[d][1,2,3]triazole (**7**):



The starting material (**6**) (1.15 g, 1.71 mmol, 1.0 eq.) was added to a flask which was then evacuated and refilled with argon three times. The starting material was then dissolved in a mixture of dichloromethane:acetic acid = 10:1 (33 mL) which was purged with argon gas for 1 hour. NBS (630 mg, 3.54 mmol, 2.05 eq.) was then added under a stream of argon, and the reaction mixture was stirred in dark at ambient temperatures (under argon) for 75 hours. To workup the reaction, the reaction mixture was first poured into a mixture of water and ethyl acetate (1:1). The organic layer was extracted with ethyl acetate (x2), and the combined organic layer was washed with water and brine (x2). The organic solution was dried over magnesium sulfate, filtered, and concentrated under reduced pressure/rotovap. The crude product was purified through silica gel column (20:1 hexanes:dichloromethane eluent), and (**7**) was further recrystallized in ethanol multiple times. The resulting yellow crystalline powder was the product (520 mg, 46%). Overall reaction scheme yield: 2.5%.

^{19}F (376 MHz, CDCl_3): δ -130.7 (d, $J=12.9$ Hz, 2F), -134.1 (d, $J=12.9$ Hz, 2F).

^1H (400 MHz, CDCl_3): δ 7.92 (s, 2H), 4.75 (d, $J=6.34$ Hz, 2H), 2.26 (m, 1H), 1.28-1.51 (m, 16H), 0.92 (t, $J=7.22$ Hz, 3H), 0.87 (t, $J=6.63$ Hz, 3H).

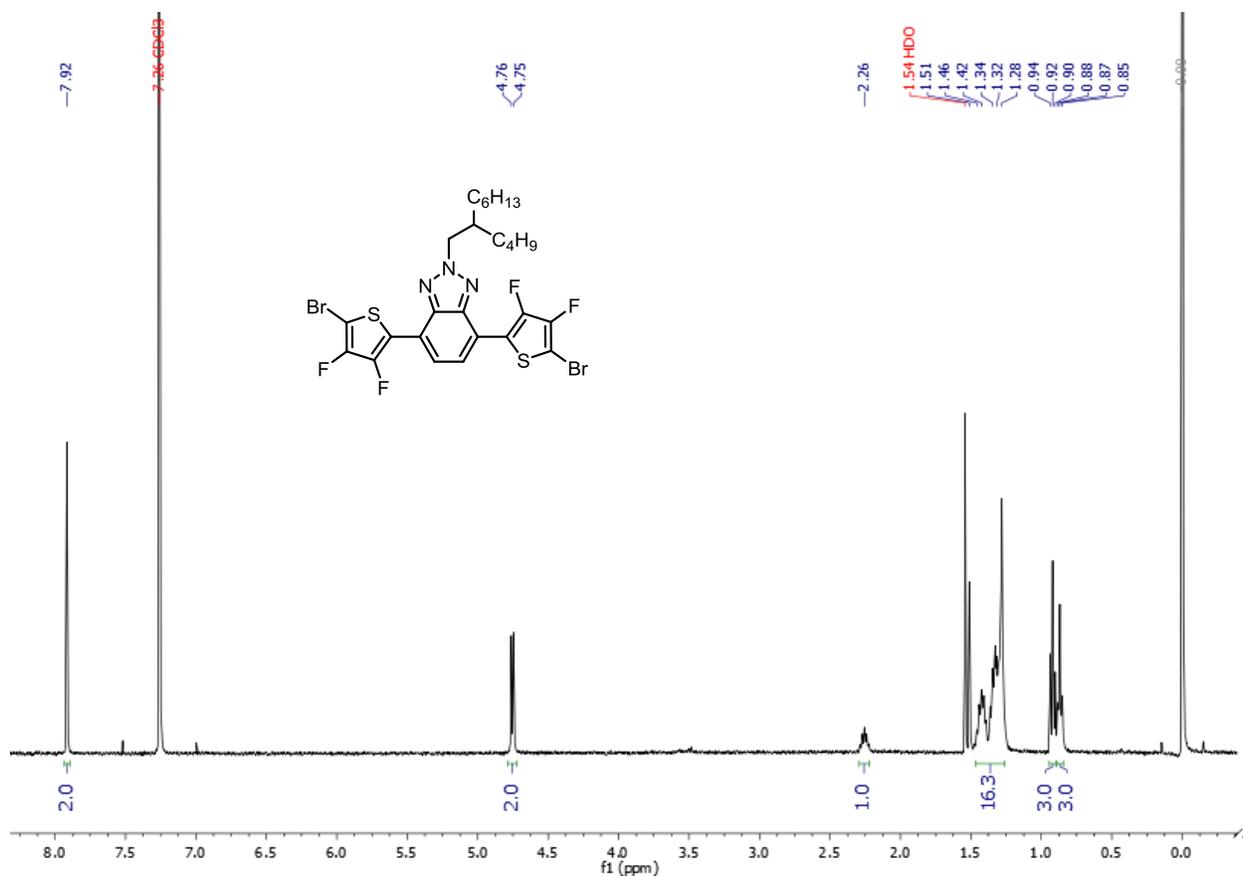
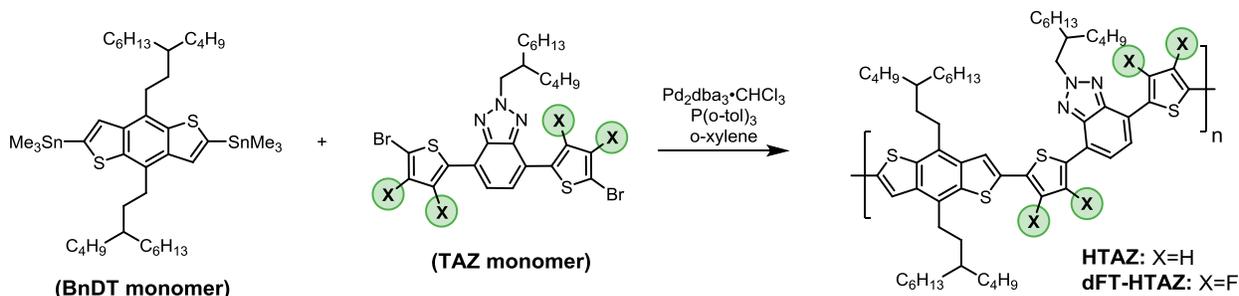


Figure S1 – ^1H NMR for dFT-HTAZ monomer

Polymerization of HTAZ and dFT-HTAZ:



BnDT monomer (0.100 mmol, 1 eq.), TAZ monomer (0.100 mmol, 1 eq.), $\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$ (0.002 mmol, 0.02 eq.) and $\text{P}(\text{o-tol})_3$ (0.016 mmol, 0.16 eq.) were charged into a 10 mL vial designed for microwave reactor. The mixture was evacuated and refilled with argon for three cycles before addition of anhydrous o-xylene under an argon stream. The reaction was heated up to 200 °C and held at that temperature for 10 min in a CEM microwave reactor. After the

polymerization, the crude polymer was dissolved in hot chlorobenzene and precipitated into stirring methanol. The collected polymer was extracted via a Soxhlet extractor with ethyl acetate, hexanes, and chloroform. The polymer solution in chloroform was concentrated under reduced pressure/rotavap, and the polymer was redissolved into a minimal amount of hot chlorobenzene and precipitated into methanol. The polymer was then collected via vacuum filtration and formed a thin metallic golden colored film, which was then dried under vacuum. Note: the molecular weight of the polymer can be controlled by tuning the ratio of the BnDT and TAZ monomers.

^{19}F NMR Spectra:

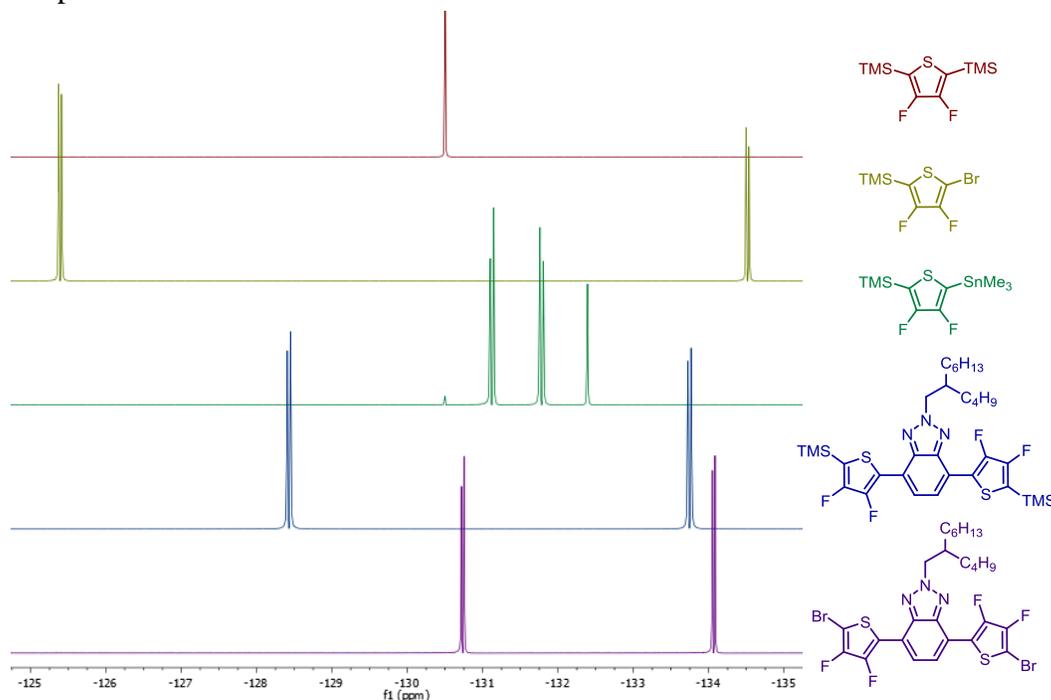


Figure S2 – ^{19}F NMR for dFT-HTAZ monomer and various precursors

Characterization Methods:

^1H and ^{19}F nuclear magnetic resonance (NMR) measurements were recorded with Bruker DRX spectrometer (400 MHz). UV-Visible absorption spectra were obtained with a Shimadzu UV-2600 spectrophotometer. CV measurements were carried out on thin films using a Bioanalytical Systems (BAS) Epsilon potentiostat with a standard three-electrode configuration. A three electrode cell of a glassy carbon working electrode, Ag/Ag^+ reference electrode, and Pt counter electrode were used. Films of the FREAs were drop-cast onto the glassy carbon electrode from hot chloroform solution (2 mg/mL, with tetrabutylammonium hexafluorophosphate added at 100 wt%) and dried using a heat gun. 0.1 M solution of tetrabutylammonium hexafluorophosphate in anhydrous acetonitrile was used as a supporting electrolyte. Scans were carried out under argon atmosphere at a scan rate of 100 mV/s. The reference electrode was calibrated using a ferrocene/ferrocenium redox couple. Solar cell devices were tested under AM 1.5G irradiation

calibrated with an NREL certified standard silicon solar cell. Current density-voltage curves were measured via a Keithley 2400 digital source meter. GIWAXS measurements were performed at beamline 7.3.3 (DOI: 10.1088/1742-6596/247/1/012007) at the ALS. The 10 KeV X-ray beam was incident at a grazing angle of 0.13 degree. The scattered X-rays were detected using a 2D area detector (Pilatus 1M). All measurements were conducted under He atmosphere to reduce air scattering.

SCLC mobility was acquired through the hole-only devices with a configuration of ITO/PEDOT:PSS/active layer/MoO₃/Al. The experimental dark current densities J were measured by Keithley 2400. The applied voltage V was corrected from the voltage drop V_{rs} due to the series resistance and contact resistance, which were found from a reference device without the active layer, and the build-in potential, which are estimated from the V_{OC} of corresponding hole-only devices under 1 sun condition. From the plots of $J^{0.5}$ vs V , hole mobilities of polymers were deduced from the Mott-Gurneys law:

$$J = \frac{9}{8} \varepsilon_r \varepsilon_0 \mu_h \frac{V^2}{L^3}$$

where ε_0 is the permittivity of free space, ε_r is the dielectric constant of the polymer which is assumed to be around 3, μ_h is the hole mobility, V is the voltage drop across the device, and L is the film thickness of the active layer.

Device Fabrication:

Glass substrates coated with patterned indium doped tin oxide (ITO) were purchased from Thin Film Devices, Inc. About 150 nm sputtered ITO pattern had a resistivity of 20 Ω /sq. Prior to use, the substrates were ultrasonicated in deionized water, acetone, and then 2-propanol for 15 min each. The substrates were dried under a stream of nitrogen gas and subjected to the treatment of UV–ozone for 15 min. The devices were made by the following methods:

(1) Polymer:PCBM blends with device stack: ITO/HTL/polymer:PCBM/Ca/Al.

For devices with PEDOT:PSS as the hole transport layer, a filtered dispersion of PEDOT:PSS in water (Clevios PH500 from Heraeus) was then spun cast onto cleaned ITO substrates at 4000 rpm for 60 s and then baked at 130 °C for 15 min in air to give a thin film with a thickness of about 40 nm. For devices with CuSCN as the hole transport layer, the CuSCN was dissolved in diethylsulfide with the concentration 22.7 mg/mL under stirring for 1 h. Then the CuSCN solution was filtered by 0.2 μ m poly(tetrafluoroethylene) (PTFE) filter and spun-cast on the cleaned ITO substrates at 7000 rpm for 60 s and then baked at 100 °C for 10 min in air to give a thin film with a thickness of about 40 nm. Then blends of polymer:PC₆₁BM (1:2 w/w) were dissolved in chlorobenzene and 3% 1,8-diiodooctane with heating at 130 °C for 6 h. All the solutions were filtered through a 5.0 μ m PTFE filter and spun-cast at an optimized rpm for 60 s onto the PEDOT:PSS or CuSCN layer. The devices were finished for measurement after thermal

deposition of a 30 nm film of calcium and a 70 nm aluminum film as the cathode for a conventional structure at a base pressure of 2×10^{-6} mbar. There are 8 devices per substrate, with an active area of 13 mm^2 per device.

(2) Polymer:ITIC/ITIC-Th1 blends with device stack: ITO/ZnO/polymer:acceptor/MoO₃/Al.

The ZnO precursor solution was prepared by dissolving 1 g zinc acetate dihydrate and 0.28 g ethanolamine in 10 mL of 2-methoxyethanol. The solution was stirred overnight, then spun cast onto the cleaned ITO slides at 4,000 rpm for 30 s and baked for 30 min at 150 °C in air. The substrates were then transferred to a nitrogen filled glovebox for active layer deposition. For polymer:ITIC and polymer:ITIC-Th1 devices, the polymers:acceptor (1:1 w/w) were dissolved in toluene with heating at 80 °C for 6 h. The active layer solutions were then spun-cast atop the ZnO layer at an optimized RPM for 60 s, followed by thermal annealing at 150 °C for 15 min. The devices were finished by evaporation of 10 nm of MoO₃ and 70 nm of aluminum. These blends also have 8 devices per substrate, with an active area of 13 mm^2 per device.

Table S1 – Optimization of dFT-HTAZ:PCBM blends with different conditions

Solvent (+ Additives)	Hole Transport Layer	J_{sc} (mA/cm ²)	V_{oc} (V)	FF (%)	PCE (%)
CB + 3% DIO	CuSCN	9.74 ± 0.33	0.989 ± 0.002	61.9 ± 1.4	5.97 ± 0.28
CB + 3% DPE	CuSCN	8.30 ± 0.35	0.983 ± 0.002	67.3 ± 0.7	5.49 ± 0.23
CB + 3% CN	CuSCN	7.95 ± 0.38	0.986 ± 0.001	60.9 ± 0.9	4.77 ± 0.21
TCB	CuSCN	6.93 ± 0.56	0.978 ± 0.002	66.5 ± 0.6	4.51 ± 0.34
CB + 3% DIO	PEDOT:PSS	8.84 ± 0.17	0.951 ± 0.011	41.7 ± 2.1	3.51 ± 0.26
TCB	PEDOT:PSS	4.18 ± 1.46	0.931 ± 0.019	28.7 ± 1.2	1.12 ± 0.40

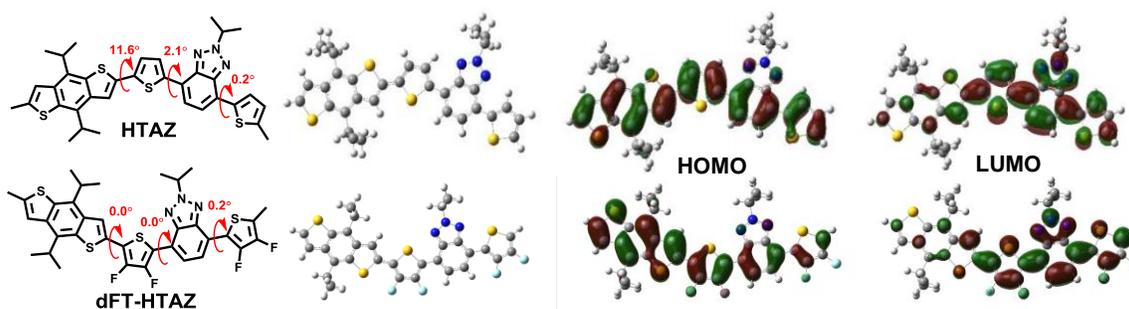


Figure S3 – Chemical structures of HTAZ and dFT-HTAZ with optimized conformation per repeat unit with calculated dihedral angles shown on the structures. Also HOMO and LUMO distributions structures for each polymer are shown.

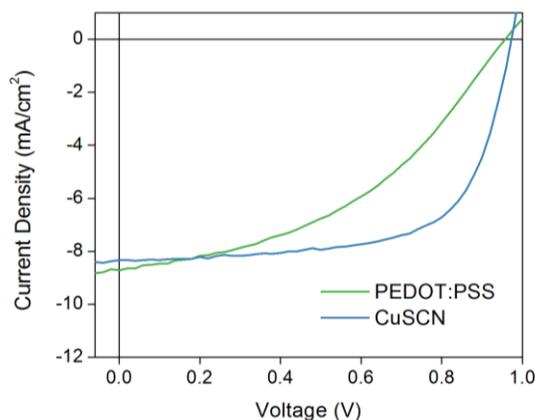


Figure S4 – Representative J - V curves of dFT:HTAZ-PCBM blends with different hole transport layers of PEDOT:PSS and CuSCN

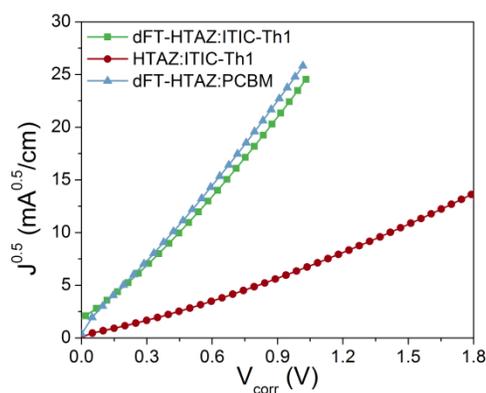


Figure S5 – SCLC hole mobility curves for various active layers

Table S2 – Mobility Values for key blends

Active Layer	Thickness	Hole Mobility ($\times 10^{-4} \text{ cm}^2/\text{Vs}$)
HTAZ:PCBM [α]	249	1.7
dFT-HTAZ:PCBM	191	15.5 ± 5.3
HTAZ:ITIC-Th1	162	6.27 ± 0.59
dFT-HTAZ:ITIC-Th1	153	1.09 ± 0.22

[α] previously reported in Q. Zhang, L. Yan, X. Jiao, Z. Peng, S. Liu, J. J. Rech, E. Klump, H. Ade, F. So and W. You, Fluorinated Thiophene Units Improve Photovoltaic Device Performance of Donor–Acceptor Copolymers, *Chem. Mater.*, 2017, **29**, 5990–6002.

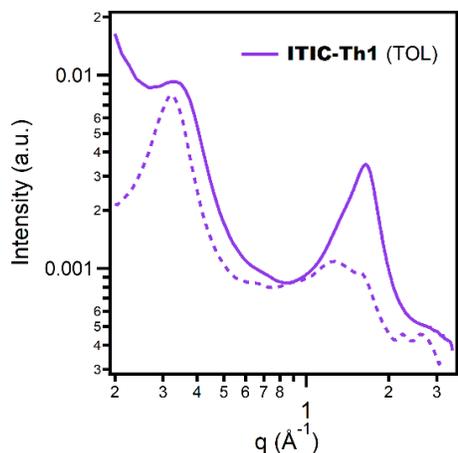


Figure S6 – 1D GIWAXS profile for neat ITIC-Th1; 1D profile has both in-plane q_{xy} (dotted line) and out-of-plane q_z (solid line) directions shown.

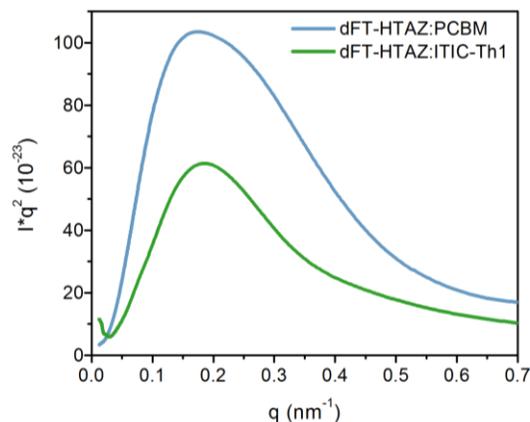


Figure S7 – Lorentz-corrected RSoXS profiles of dFT-HTAZ:PCBM and dFT-HTAZ:ITIC-Th1 blend films

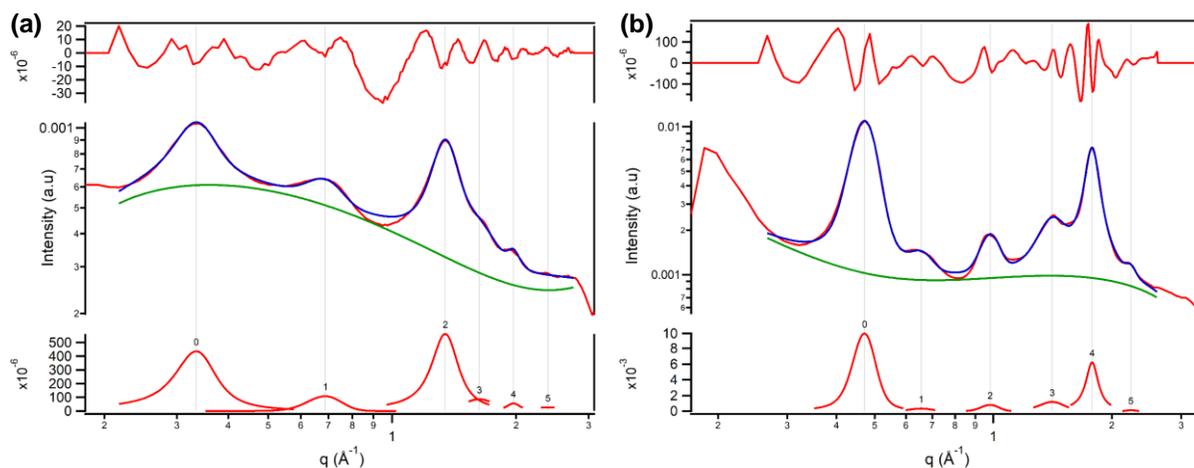


Figure S8 – Diffraction profiles cut along the $\sim q_z$ axis of the 2D GIWAXS images for (a) dFT-HTAZ:PCBM and (b) dFT-HTAZ:ITIC-Th1 blend films (blue line), their fits (red line) fitted to pseudo-Voigt functions