

Supporting Information

Fluorine Substituted Conjugated Polymer of Medium Band Gap Yields 7% Efficiency in Polymer-Fullerene Solar Cells

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Reagents. All solvents are ACS grade unless otherwise noted. Anhydrous THF was obtained by distillation from sodium/benzophenone prior to use. Diisopropylamine was distilled from potassium hydroxide prior to use. 4,7-dibromo-2-(2-butyloctyl)-2H-benzo[d][1,2,3]triazole,^{1,2} 2,6-Bis(trimethyltin)-4,8-(3-butylnonyl)benzo[1,2-b:4,5-b']dithiophene,³ 2-butyloctylbromide,⁴ and 5,6-difluoro-1H-benzo[d][1,2,3]triazole⁵ were prepared according to modified literature procedures. All reagents were purchased from VWR, Fisher Scientific, Dynamic Absorbents, Silicycle, Accela ChemBio Inc., and were used without further purification.

4,7-bis(5-bromothiophen-2-yl)-2-(2-butyloctyl)-2H-benzo[d][1,2,3]triazole (HTAZ). Thiophene (3.01 g, 2.5 eq) was dissolved in dry THF (40 mL) in a flame dried flask under argon. The mixture was cooled to 0°C in an ice bath, and 1.6M n-BuLi in hexanes (22.8 mL, 2.55 eq) was added dropwise over 3 minutes. The solution was stirred for 35 min maintaining the temperature at 0°C, and then anhydrous ZnCl₂ (5.07 g, 2.6 eq) was added as a solution in 40 mL dry THF. The reaction was stirred for 5 min at 0°C, and then Pd(PPh₃)₂Cl₂ (602 mg, 6 mol %) was added in one portion. 4,7-dibromo-2-(2-butyloctyl)-2H-benzo[d][1,2,3]triazole (6.39 g, 1.0 eq) was then added via cannula as a solution in 20 mL of dry THF. The reaction mixture was then heated to reflux, and stirred for 16 h. The reaction mixture was then poured into water and extracted with ethyl acetate. The organic layer was then washed with water (3x), dried (MgSO₄), filtered, concentrated in vacuo, and purified by column chromatography on silica gel using 4:1 hexanes:CH₂Cl₂ as the eluent. The resulting fluorescent yellow solid was then dissolved into THF (80 mL), and N-bromosuccinimide (2.89 g, 2.0 eq) was added in one portion. The reaction mixture was stirred for 3.5 h, and then poured into saturated NaHCO₃ solution and extracted with ethyl acetate. The organic phase was then washed with water (3 ×), dried (MgSO₄), filtered, and

concentrated in vacuo. The material was then purified by column chromatography on silica gel, using 3:1 hexanes:chloroform as the eluent. The resulting yellow solid (HTAZ) was then recrystallized twice from isopropanol to yield a yellow powder. Yield (2 steps): 2.79 g (32%). Fluorescent yellow solid; mp 70°C. ^1H NMR (CDCl_3 , 400 MHz, δ): 7.76 (d, $^3J_{\text{HH}} = 3.6$ Hz, 2H), 7.46 (s, 2H), 7.10 (d, $^3J_{\text{HH}} = 4$ Hz, 2H), 4.71 (d, $^3J_{\text{HH}} = 6.4$ Hz, 2H), 2.27 (m, 1H), 1.26 (m, 16H), 0.90 (t, $^3J_{\text{HH}} = 7.2$ Hz, 3H), 0.86 (t, $^3J_{\text{HH}} = 6$ Hz, 3H). ^{13}C NMR (CDCl_3 , 100 MHz, δ): 141.55, 141.24, 130.80, 126.81, 122.90, 122.01, 113.16, 59.88, 39.09, 31.82, 31.38, 31.15, 29.56, 28.45, 26.17, 22.96, 22.65, 14.09. Anal. Calcd for $\text{C}_{26}\text{H}_{31}\text{Br}_2\text{N}_3\text{S}_2$: C, 51.24; H, 5.13; N, 6.89. Found: C, 51.52; H, 4.95; N, 6.88.

Polymerization of PBnDT-HTAZ. 2,6-Bis(trimethyltin)-4,8-(3-butylonyl)benzo[1,2-b:4,5-b']dithiophene (132 mg, 1.0 eq), HTAZ (91.4 mg, 1.0 eq), $\text{Pd}_2(\text{dba})_3$ (2.8 mg, 0.02 eq), and tri(*o*-tolyl)phosphine (7.2 mg, 0.16 eq) were combined in a dry microwave vial. The vial was sealed with a septum cap, and then evacuated and refilled with argon three times. Dry, oxygen free *o*-xylene (0.75 mL) was added. The mixture was then reacted in a microwave reactor for 20 min, at 200°C (at 300W), and then cooled to room temperature. The reaction mixture was diluted with chlorobenzene (3 mL), and then the polymer solution was precipitated into methanol (100 mL) at room temperature. The resulting purple-black solid was filtered into a Soxhlet thimble, and extracted with methanol, ethyl acetate, hexanes, and chloroform until the wash from each extraction was colorless. When there was no solid remaining in the thimble, the chloroform fraction was concentrated, and chlorobenzene was added (5 mL). The polymer solution was then precipitated into methanol at room temperature, filtered, and dried under vacuum at 0.5 mmHg. Yield: 143 mg (95%). Purple metallic solid. ^1H NMR @ 400K ($\text{C}_2\text{D}_2\text{Cl}_4$, 400 MHz, δ): 7.86,

7.23, 4.87, 3.14, 2.41, 1.87, 1.50, 1.08. GPC (1,2,4-trichlorobenzene at 135°C): $M_n = 47.6$ kg/mol, $M_w = 133.4$ kg/mol, PDI = 2.57.

2-(2-butyloctyl)-5,6-difluoro-2H-benzo[d][1,2,3]triazole (2). 5,6-difluoro-1H-benzo[d][1,2,3]triazole (8.04 g, 1.0 eq), potassium tert-butoxide (5.87 g, 1.01 eq), and 2-butyloctylbromide (13.04 g, 1.01 eq) were dissolved in 130 mL of methanol. The reaction was heated to reflux for 17 h. The reaction mixture was then poured into saturated NH_4Cl solution, and extracted with ethyl acetate. The organic layer was washed with water (2x), dried (Na_2SO_4), filtered, concentrated in vacuo, and purified by column chromatography on silica gel using 10:1 hexanes:ethyl acetate as the eluent. Yield: 2.88 g (17%). Colorless oil. ^1H NMR (CDCl_3 , 400 MHz, δ): 7.59 (t, $^3J_{\text{HF}} = 8.4$ Hz, 2H), 4.58 (d, $^3J_{\text{HH}} = 6.8$ Hz, 2H), 2.22 (m, 1H), 1.28 (m, 16H), 0.86 (t, $^3J_{\text{HH}} = 5.6$ Hz, 6H).

4,7-dibromo-2-(2-butyloctyl)-5,6-difluoro-2H-benzo[d][1,2,3]triazole (3). 1.6M n-BuLi in hexanes (12.5 mL, 2.25 eq) was added dropwise over 3 min to a solution of diisopropylamine (3.10 mL, 2.5 eq) and dry THF (90 mL) under argon at -78°C . The solution was stirred for 15 min, and then a solution of Compound **2** (2.88 g, 1.0 eq) and trimethylsilyl chloride (3.1 mL, 2.75 eq) in dry THF (35 mL) was added dropwise over 10 minutes at -78°C . -78°C was maintained while the reaction was stirred for 3 h, and then the reaction was quenched with 10 mL of saturated NH_4Cl . The reaction was warmed to room temperature and poured into saturated NH_4Cl . The mixture was extracted with ethyl acetate, washed with water (3x), dried (MgSO_4), and concentrated in vacuo. The residue was then dissolved into CHCl_3 (30 mL), and bromine (3.6 mL, 8.0 eq) was added in one portion, and the reaction was stirred for 16 h at room temperature, shielded from light. The reaction was then poured into a mixture of 10% NaOH and ice, and extracted with methylene chloride. The organic layer was washed with brine, dried

(MgSO₄), and purified by column chromatography on silica gel using 4:1 hexanes:methylene chloride as the eluent. Yield (2 steps): 2.28 g (53%). Colorless oil. ¹H NMR (CDCl₃, 300 MHz, δ): 4.65 (d, ³J_{HH} = 7.2 Hz, 2H), 2.31 (m, 1H), 1.24 (m, 16H), 0.87 (m, 6H). ¹³C NMR (CDCl₃, 100 MHz, δ): 149.07 (dd, ¹J_{CF} = 253 Hz, ²J_{CF} = 20 Hz), 138.86 (t, ^{3,4}J_{CF} = 2.5 Hz), 96.10 (dd, ²J_{CF} = 15 Hz, ³J_{CF} = 9 Hz), 61.11, 38.98, 31.64, 31.08, 30.79, 29.40, 28.18, 25.93, 22.81, 22.57, 14.05, 13.92.

2-(2-butyloctyl)-5,6-difluoro-4,7-di(thiophen-2-yl)-2H-benzo[d][1,2,3]triazole (4).

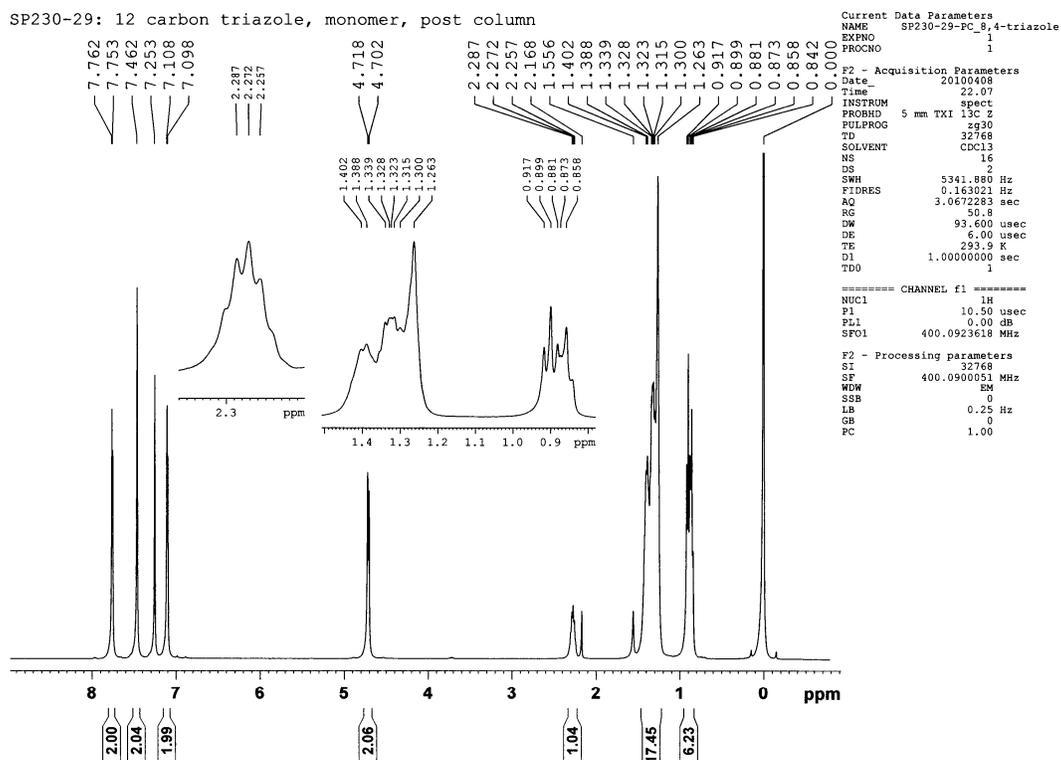
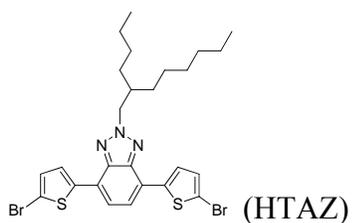
Thiophene (0.87 g, 2.25 eq) was dissolved into dry THF (20 mL), and cooled to 0°C under argon. 1.6M n-BuLi in hexanes (6.6 mL, 2.3 eq) was added dropwise over 3 min. The reaction was allowed to stir at 0°C for 35 min, and then a solution of anhydrous ZnCl₂ (1.47 g, 2.35 eq) in dry THF (20mL) was added via syringe at 0°C. After 5 min, Pd(PPh₃)₂Cl₂ (193 mg, 6 mol %) was added in one portion at 0°C. Then compound **3** (2.21 g, 1.0 eq) was added via syringe as a solution in dry THF (15 mL). The reaction mixture was then heated to reflux, and stirred for 16 h. The reaction was then poured into water, and extracted with ethyl acetate. The organic layer was washed with water (3x), dried (MgSO₄), filtered, concentrated in vacuo, and purified by column chromatography on silica gel using 4:1 hexanes:methylene chloride as the eluent. Yield: 1.99 g (89%). Fluorescent yellow solid. ¹H NMR (CDCl₃, 300 MHz, δ): 8.33 (dd, ³J_{HH} = 3.9 Hz, ⁴J_{HH} = 0.9 Hz, 2H), 7.55 (dd, ³J_{HH} = 5.1 Hz, ⁴J_{HH} = 1.2 Hz, 2H), 7.24 (m, 2H), 4.73 (d, ³J_{HH} = 6.6 Hz, 2H), 2.86 (m, 1H), 1.26 (m, 16H), 0.89 (m, 6H).

4,7-bis(5-bromothiophen-2-yl)-2-(2-butyloctyl)-5,6-difluoro-2H-benzo[d][1,2,3]triazole (FTAZ). Combine **4** (1.99 g, 1.0 eq), *N*-bromosuccinimide (1.46 g, 2.0 eq), and THF (75 mL). Stir for 20 hours at room temperature, and then pour the reaction mixture into a saturated solution of sodium bicarbonate. Extract with methylene chloride, dried (MgSO₄), filtered, and

then silica gel was added. The slurry was concentrated in vacuo, and the resulting solid purified by column chromatography on silica gel using 10:1 hexanes:methylene chloride as the eluent. After repeating the chromatography step a second time, a fluorescent yellow solid was obtained in purity sufficient for polymerization. Yield: 1.87 g (71%). Fluorescent yellow solid; mp 76°C. ^1H NMR (CDCl_3 , 400 MHz, δ): 7.97 (d, $^3J_{\text{HH}} = 4$ Hz, 2H), 7.13 (d, $^3J_{\text{HH}} = 4$ Hz, 2H), 4.68 (d, $^3J_{\text{HH}} = 6.4$ Hz, 2H), 2.23 (m, 1H), 1.40 (m, 4H), 1.27 (m, 12H), 0.91 (t, $^3J_{\text{HH}} = 7.2$ Hz, 3H), 0.86 (t, $^3J_{\text{HH}} = 6.8$ Hz, 3H). ^{13}C NMR (CDCl_3 , 100 MHz, δ): 146.89 (dd, $^1J_{\text{CF}} = 252$ Hz, $^2J_{\text{CF}} = 19$ Hz), 137.01 (t, $^{3,4}J_{\text{CF}} = 4.2$ Hz), 133.76, 130.26 (m), 130.19, 115.92 (m), 109.29 (dd, $^3J_{\text{CF}} = 9.5$ Hz, $^4J_{\text{CF}} = 4.4$ Hz), 59.84, 39.10, 31.84, 31.41, 31.17, 29.57, 28.47, 26.20, 22.97, 22.66, 14.09. Anal. Calcd for $\text{C}_{26}\text{H}_{29}\text{Br}_2\text{F}_2\text{N}_3\text{S}_2$: C, 48.38; H, 4.53; N, 6.51. Found: C, 48.20; H, 4.55; N, 6.62.

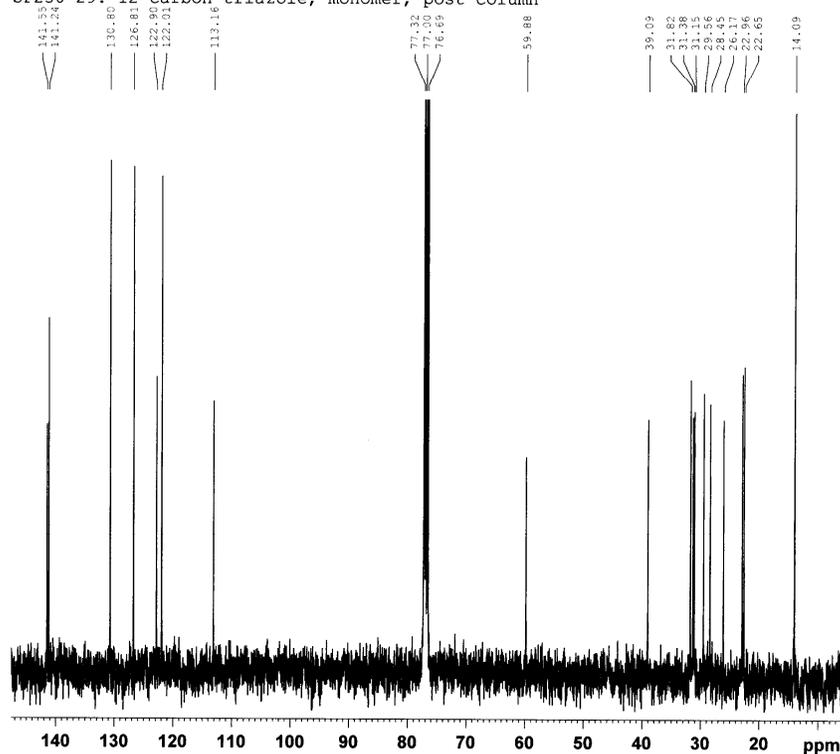
Polymerization of PBnDT-FTAZ. 2,6-Bis(trimethyltin)-4,8-(3-butylnonyl)benzo[1,2-b:4,5-b']dithiophene (132 mg, 1.0 eq), FTAZ (97 mg, 1.0 eq), $\text{Pd}_2(\text{dba})_3$ (2.8 mg, 0.02 eq), and tri(*o*-tolyl)phosphine (7.2 mg, 0.16 eq) were combined in a dry microwave vial. The vial was then sealed with a septum cap, and then evacuated and refilled with argon three times. Dry, oxygen free *o*-xylene (0.75 mL) was added. The mixture was then reacted in a microwave reactor for 20 min, at 200°C (at 300W), and then cooled to room temperature. The reaction mixture was then diluted with chlorobenzene (3 mL), and then the polymer solution was precipitated into methanol (100 mL) at room temperature. The resulting purple-black solid was filtered into a Soxhlet thimble, and extracted with methanol, ethyl acetate, hexanes, and chloroform until the wash from each extraction was colorless. When there was no solid remaining in the Soxhlet thimble, the chloroform fraction was then concentrated, and chlorobenzene was added (5 mL). The polymer solution was then precipitated into methanol at room temperature, filtered, and dried under vacuum at 0.5 mmHg. Yield: 153 mg (98%). Purple

metallic solid. ^1H NMR @ 400K ($\text{C}_2\text{D}_2\text{Cl}_4$, 400 MHz, δ): 8.20, 7.26, 4.84, 3.07, 2.46, 1.51, 1.14,
1.05. GPC (1,2,4-trichlorobenzene at 135°C): $M_n = 42.2$ kg/mol, $M_w = 99.9$ kg/mol, PDI = 2.36.



^1H NMR (CDCl_3 , 400 MHz, δ): 7.76 (d, $^3J_{\text{HH}} = 3.6$ Hz, 2H), 7.46 (s, 2H), 7.10 (d, $^3J_{\text{HH}} = 4$ Hz, 2H), 4.71 (d, $^3J_{\text{HH}} = 6.4$ Hz, 2H), 2.27 (m, 1H), 1.26 (m, 16H), 0.90 (t, $^3J_{\text{HH}} = 7.2$ Hz, 3H), 0.86 (t, $^3J_{\text{HH}} = 6$ Hz, 3H).

SP230-29: 12 carbon triazole, monomer, post column



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PROCNO   1

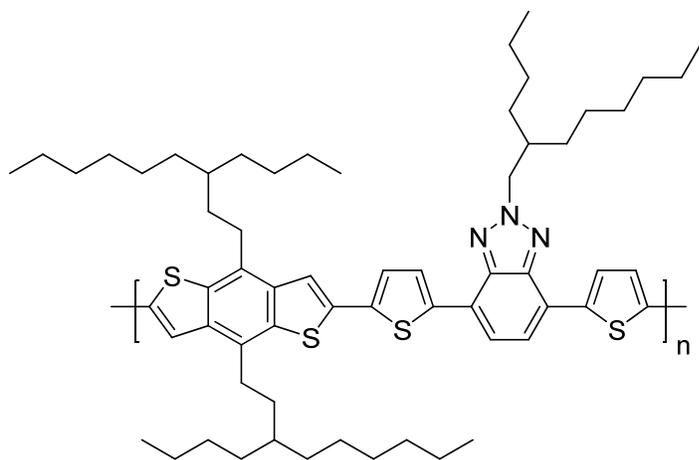
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TDO      1

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PL1      0.00 dB
SFO1    100.6137773 MHz

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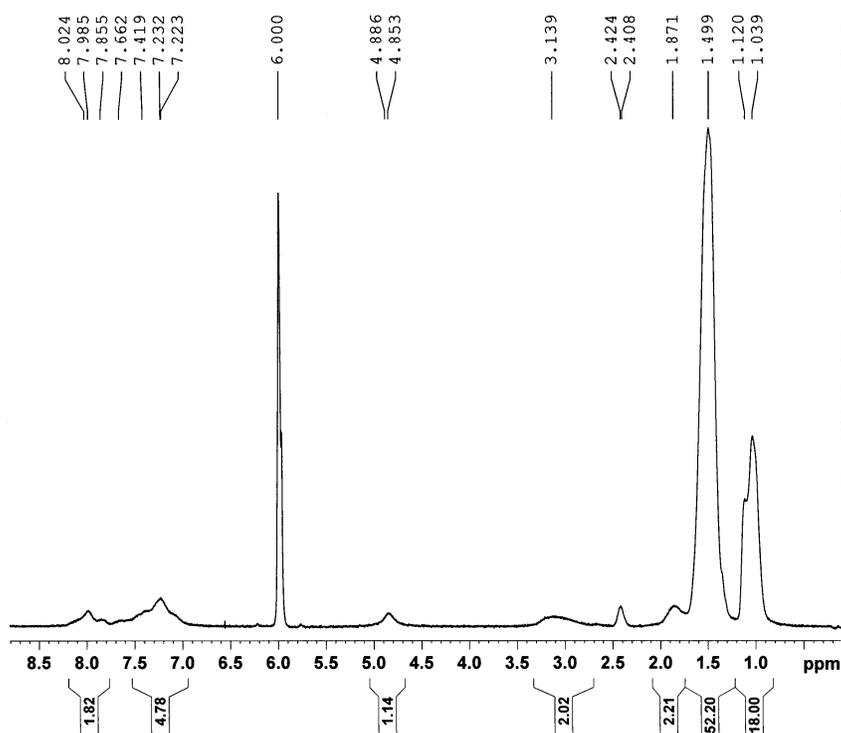
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^{13}C NMR (CDCl_3 , 100 MHz, δ): 141.55, 141.24, 130.80, 126.81, 122.90, 122.01, 113.16, 59.88, 39.09, 31.82, 31.38, 31.15, 29.56, 28.45, 26.17, 22.96, 22.65, 14.09.



PBnDT-HTAZ

SP232-33-3: No Fluorines, 3rd Batch



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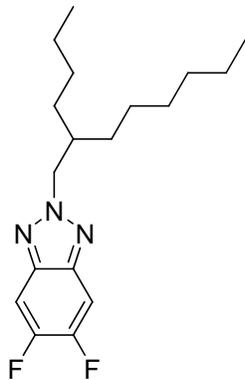
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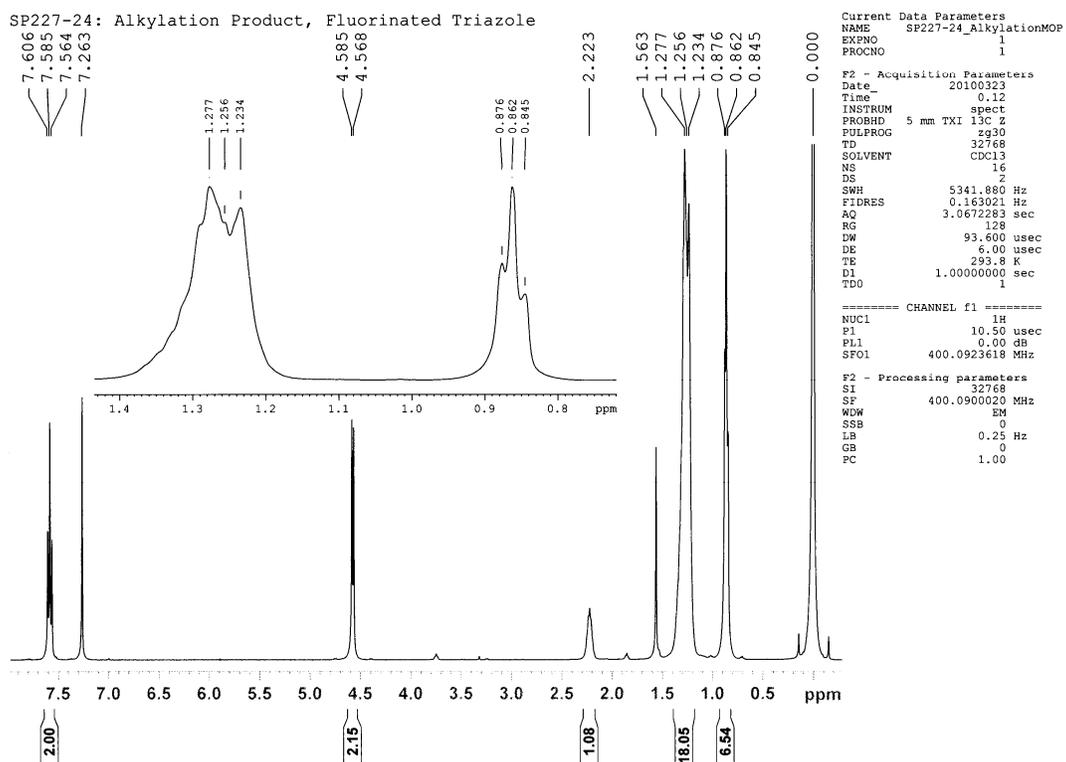
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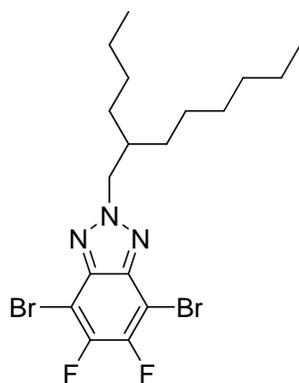
$^1\text{H NMR}$ @ 400K ($\text{C}_2\text{D}_2\text{Cl}_4$, 400 MHz, δ): 7.86, 7.23, 4.87, 3.14, 2.41, 1.87, 1.50, 1.08.



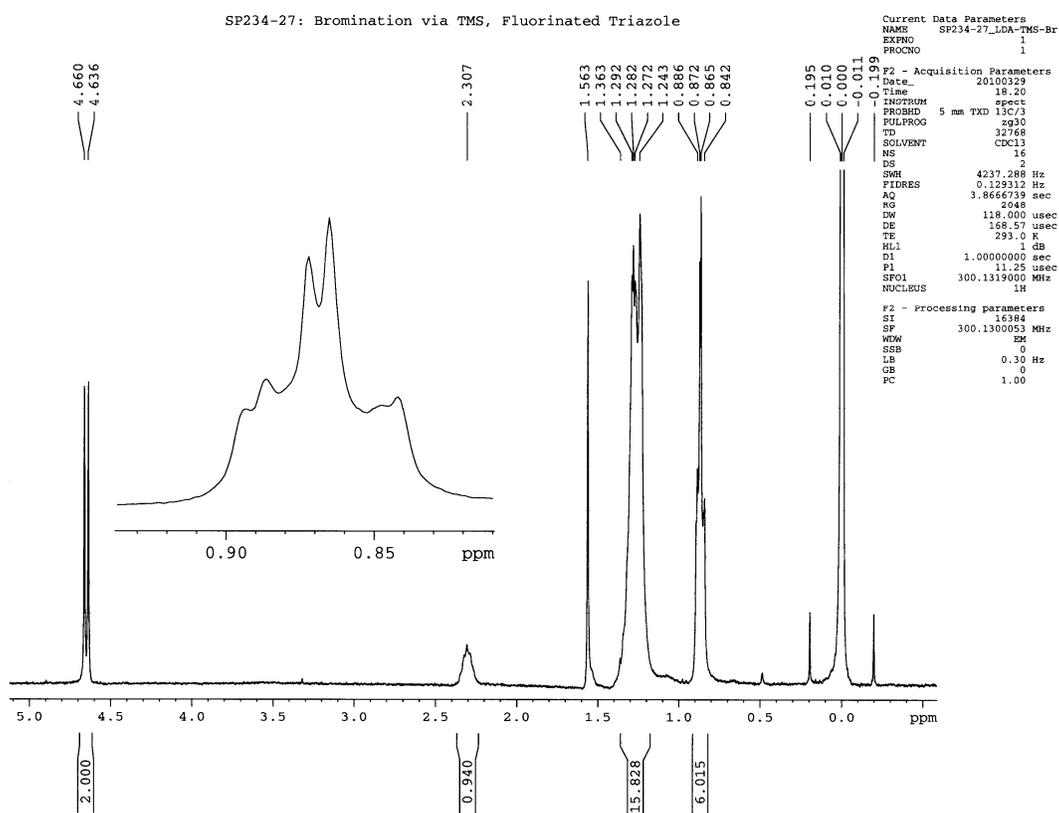
Compound 2



^1H NMR (CDCl_3 , 400 MHz, δ): 7.59 (t, $^3J_{\text{HF}} = 8.4$ Hz, 2H), 4.58 (d, $^3J_{\text{HH}} = 6.8$ Hz, 2H), 2.22 (m, 1H), 1.28 (m, 16H), 0.86 (t, $^3J_{\text{HH}} = 5.6$ Hz, 6H).

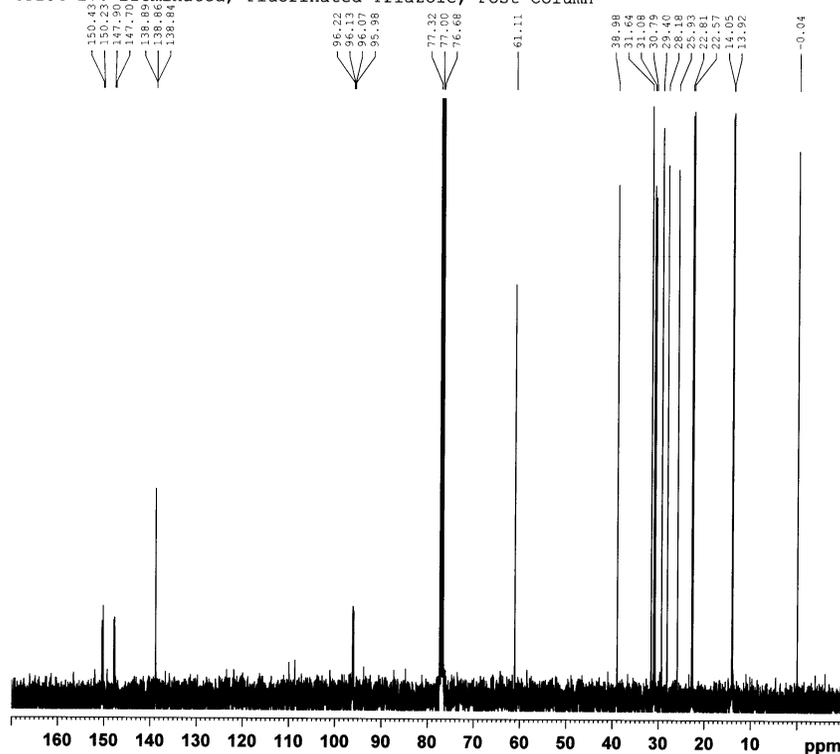


Compound 3



^1H NMR (CDCl_3 , 300 MHz, δ): 4.65 (d, $^3J_{\text{HH}} = 7.2$ Hz, 2H), 2.31 (m, 1H), 1.24 (m, 16H), 0.87 (m, 6H).

SP234-27: Brominated, Fluorinated Triazole, Post Column



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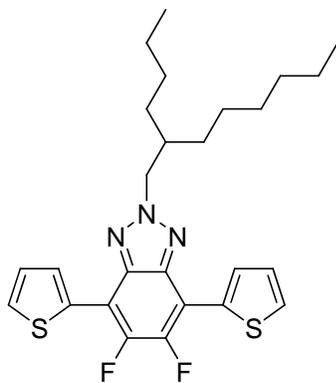
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 AQ 0.6816452 sec
 RG 3649.1
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 DE 6.00 usec
 FE 294.9 K
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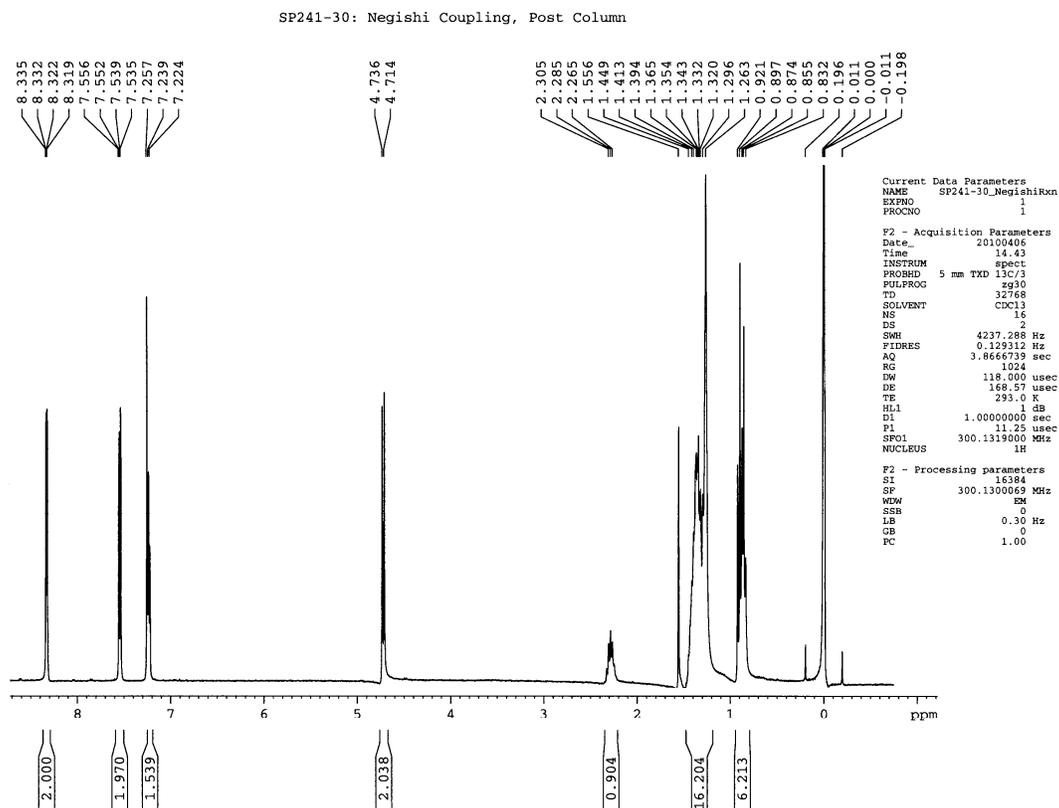
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F2 - Processing parameters
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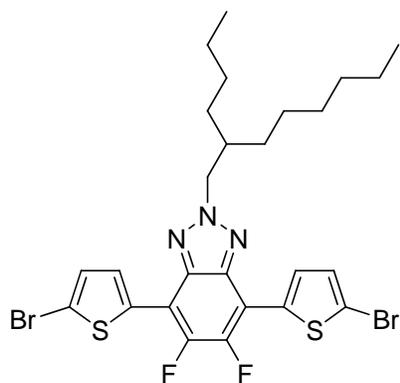
^{13}C NMR (CDCl_3 , 100 MHz, δ): 149.07 (dd, $^1J_{\text{CF}} = 253$ Hz, $^2J_{\text{CF}} = 20$ Hz), 138.86 (t, $^3,4J_{\text{CF}} = 2.5$ Hz), 96.10 (dd, $^2J_{\text{CF}} = 15$ Hz, $^3J_{\text{CF}} = 9$ Hz), 61.11, 38.98, 31.64, 31.08, 30.79, 29.40, 28.18, 25.93, 22.81, 22.57, 14.05, 13.92.



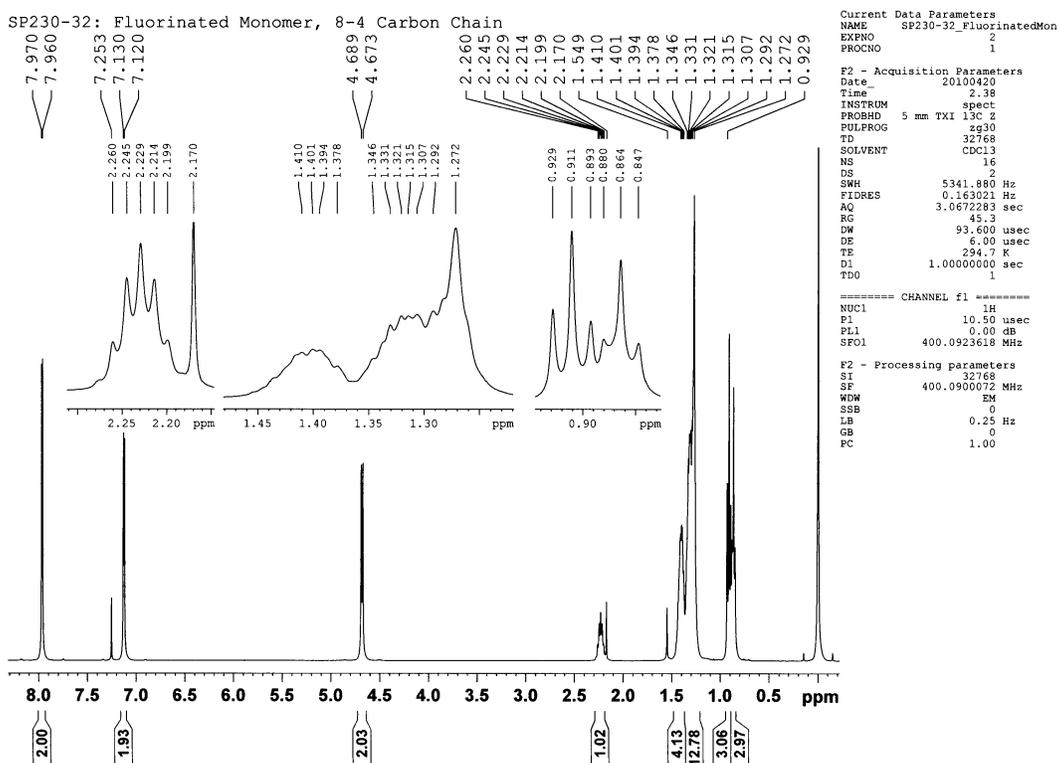
Compound 4



^1H NMR (CDCl_3 , 300 MHz, δ): 8.33 (dd, $^3J_{\text{HH}} = 3.9$ Hz, $^4J_{\text{HH}} = 0.9$ Hz, 2H), 7.55 (dd, $^3J_{\text{HH}} = 5.1$ Hz, $^4J_{\text{HH}} = 1.2$ Hz, 2H), 7.24 (m, 2H), 4.73 (d, $^3J_{\text{HH}} = 6.6$ Hz, 2H), 2.86 (m, 1H), 1.26 (m, 16H), 0.89 (m, 6H).

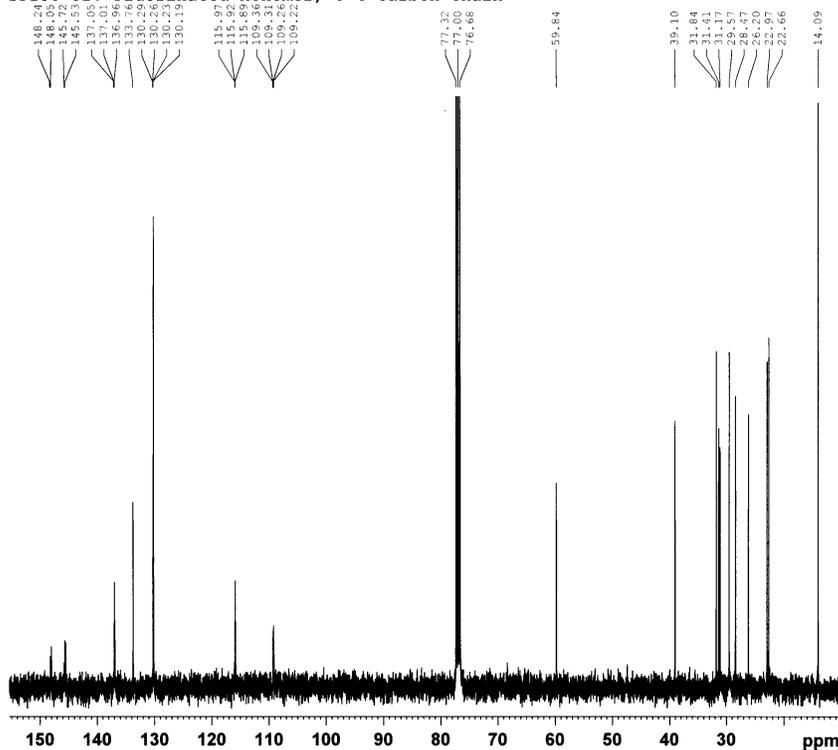


FTAZ



^1H NMR (CDCl_3 , 400 MHz, δ): 7.97 (d, $^3J_{\text{HH}} = 4$ Hz, 2H), 7.13 (d, $^3J_{\text{HH}} = 4$ Hz, 2H), 4.68 (d, $^3J_{\text{HH}} = 6.4$ Hz, 2H), 2.23 (m, 1H), 1.40 (m, 4H), 1.27 (m, 12H), 0.91 (t, $^3J_{\text{HH}} = 7.2$ Hz, 3H), 0.86 (t, $^3J_{\text{HH}} = 6.8$ Hz, 3H).

SP230-32: Fluorinated Monomer, 8-4 Carbon Chain



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PROCNO    1

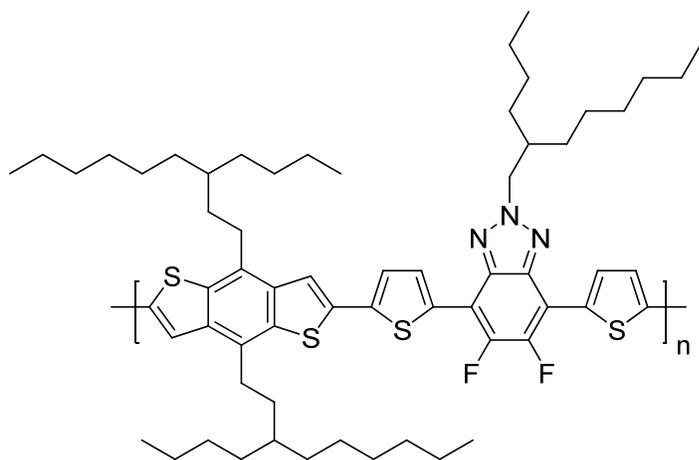
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DELTA     4.9000010 sec
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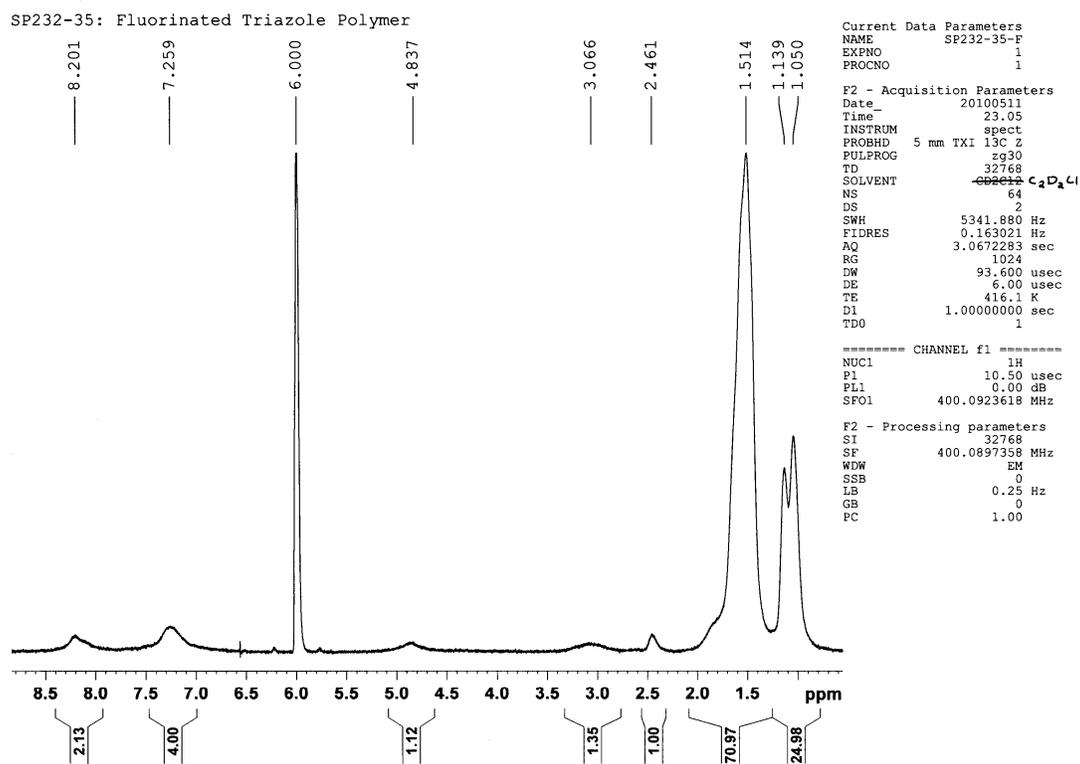
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PL13       23.00 dB
SFO2       400.0916004 MHz

F2 - Processing parameters
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WDW        EM
SSB        0
LB         1.00 Hz
GB         0
PC         1.40
    
```

^{13}C NMR (CDCl_3 , 100 MHz, δ): 146.89 (dd, $^1J_{\text{CF}} = 252$ Hz, $^2J_{\text{CF}} = 19$ Hz), 137.01 (t, $^3,4J_{\text{CF}} = 4.2$ Hz), 133.76, 130.26 (m), 130.19, 115.92 (m), 109.29 (dd, $^3J_{\text{CF}} = 9.5$ Hz, $^4J_{\text{CF}} = 4.4$ Hz), 59.84, 39.10, 31.84, 31.41, 31.17, 29.57, 28.47, 26.20, 22.97, 22.66, 14.09.



PBnDT-FTAZ



¹H NMR @ 400K (C₂D₂Cl₄, 400 MHz, δ): 8.20, 7.26, 4.84, 3.07, 2.46, 1.51, 1.14, 1.05.

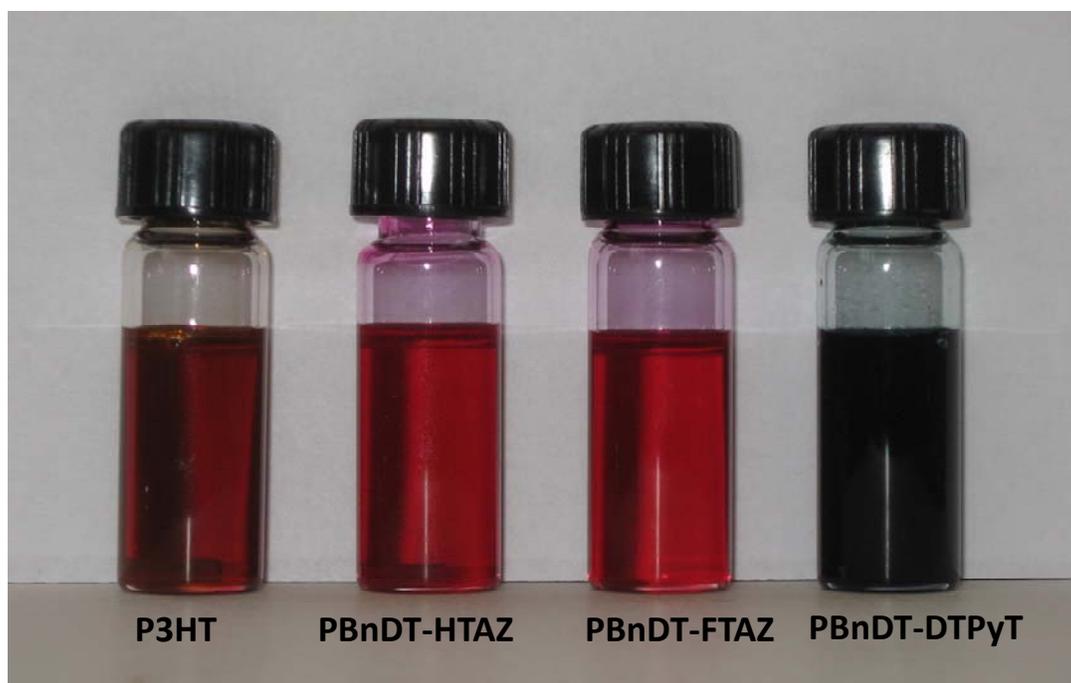


Figure S1. Polymer solutions, 0.75 mg/mL in dichlorobenzene. P3HT and low band gap copolymer PBnDT-DTPyT (*Angew. Chem., Int. Ed.* **2010**, *49*, 7992) included as a reference.

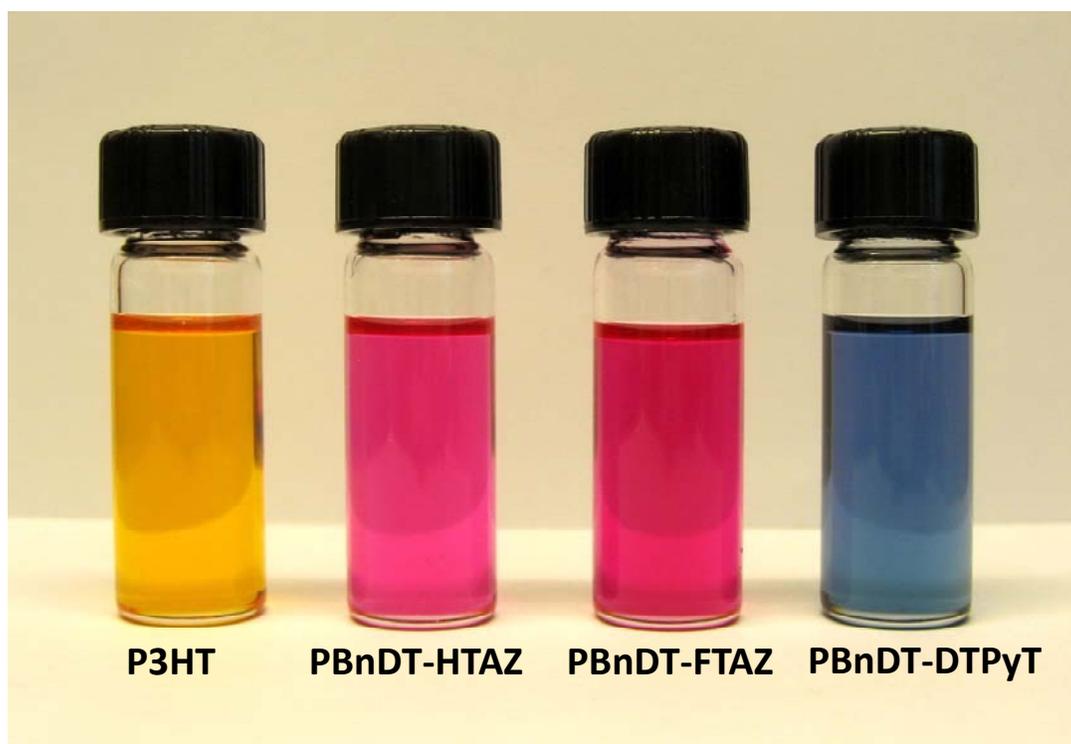


Figure S2. Polymer solutions, 0.025 mg/mL in dichlorobenzene. P3HT and low band gap copolymer PBnDT-DTPyT included as a reference.

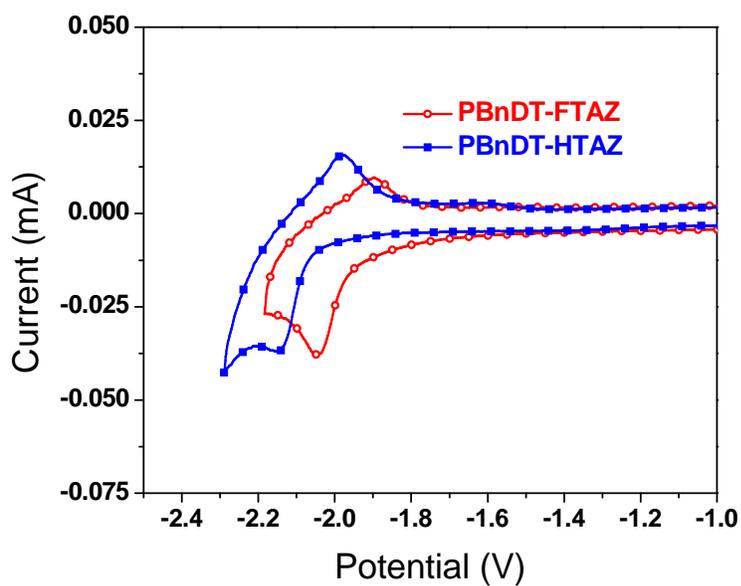


Figure S3. Cyclic voltammetry curves for the reduction of the two polymers. LUMOs for PBnDT-FTAZ and PBnDT-HTAZ are -3.05 eV and -2.87 eV, respectively.

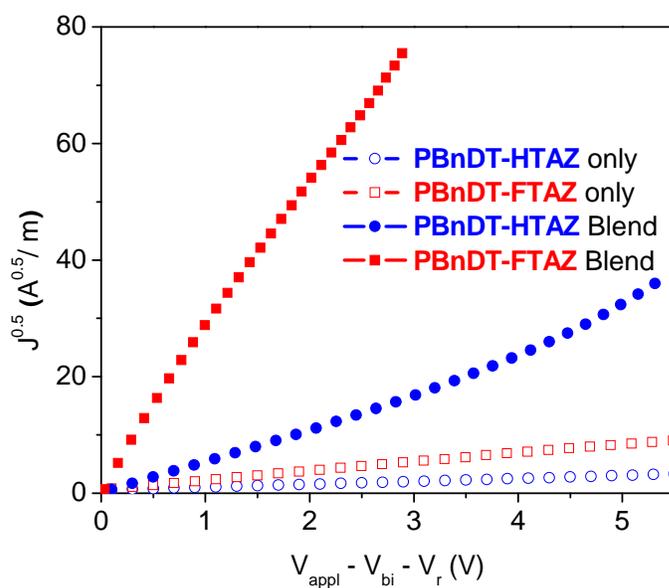


Figure S4. SCLC hole mobility measurements for each polymer, and 1:2 polymer:PC₆₁BM blend.

XRD Spectroscopy

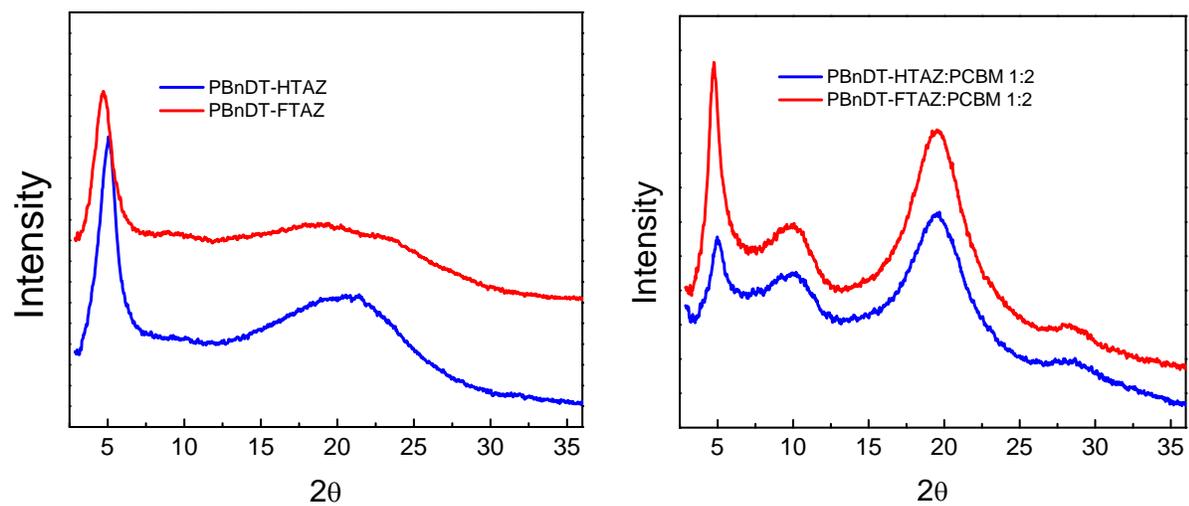


Figure S5: XRD spectra of the polymer-only films (left) and polymer/PC₆₁BM blend films (right).

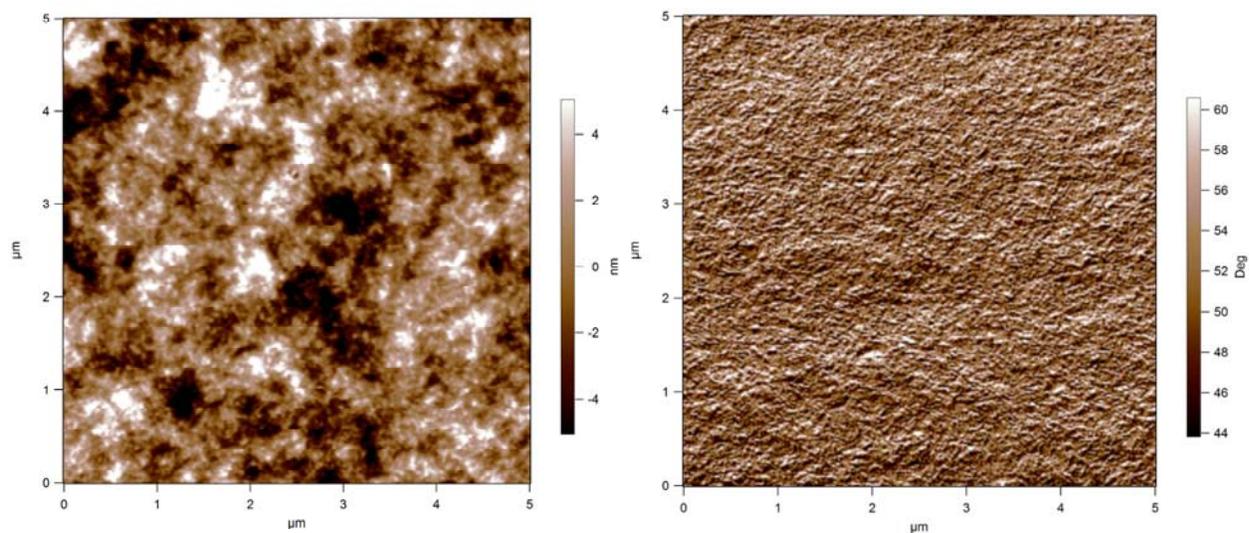


Figure S6. AFM images of PBnDT-HTAZ:PC₆₁BM film in a 1:2 ratio blend. (left: height image; right: phase image).

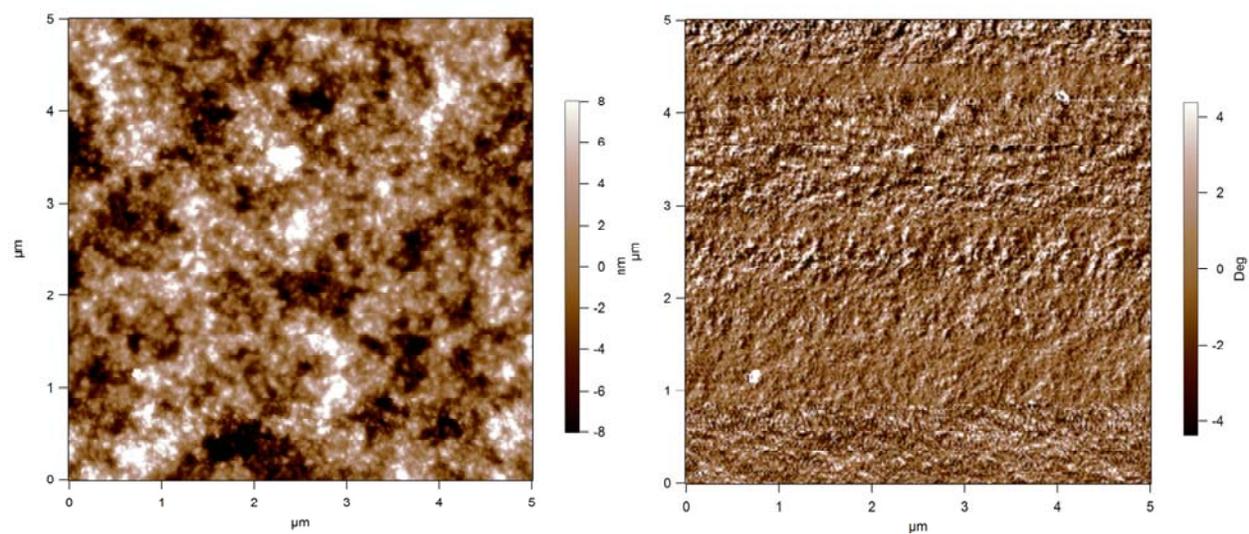


Figure S7. AFM images of PBnDT-FTAZ:PC₆₁BM film in a 1:2 ratio blend. (left: height image; right: phase image). The PBnDT-FTAZ blend yielded slightly rougher films on a consistent basis.

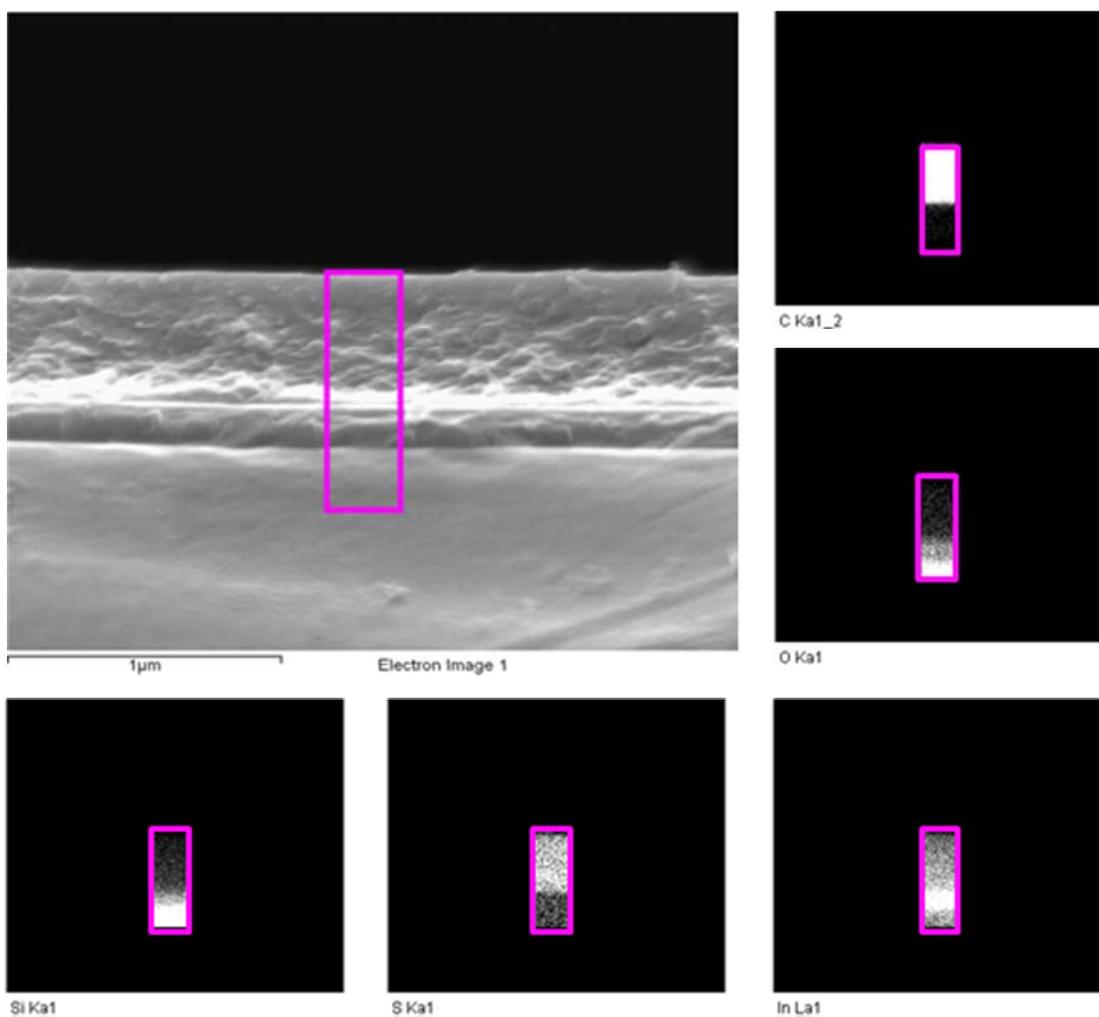


Figure S8. Energy dispersive spectroscopy confirms the elemental composition of the photovoltaic cell. No metal anode was evaporated on top. The small images, clockwise from the top are carbon, oxygen, indium, sulfur, and silicon. White color represents a high concentration of the atom. Indium measurement has a low signal to noise ratio, however, the highest concentration of indium is observed in the ITO layer.

Device Film Thickness Measurements (via SEM)

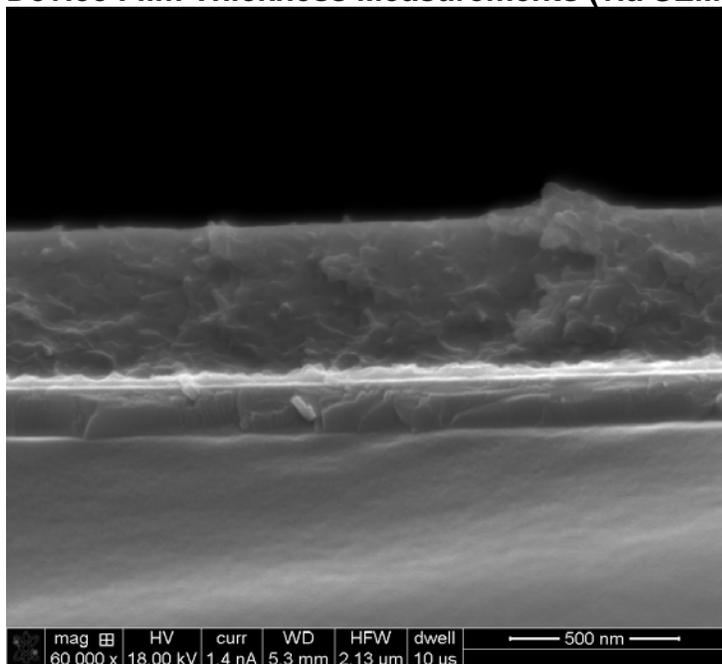


Figure S9. 400 nm PBnDT-FTAZ:PC₆₁BM 1:2. In order from top to bottom, active layer, PEDOT:PSS, ITO, glass.

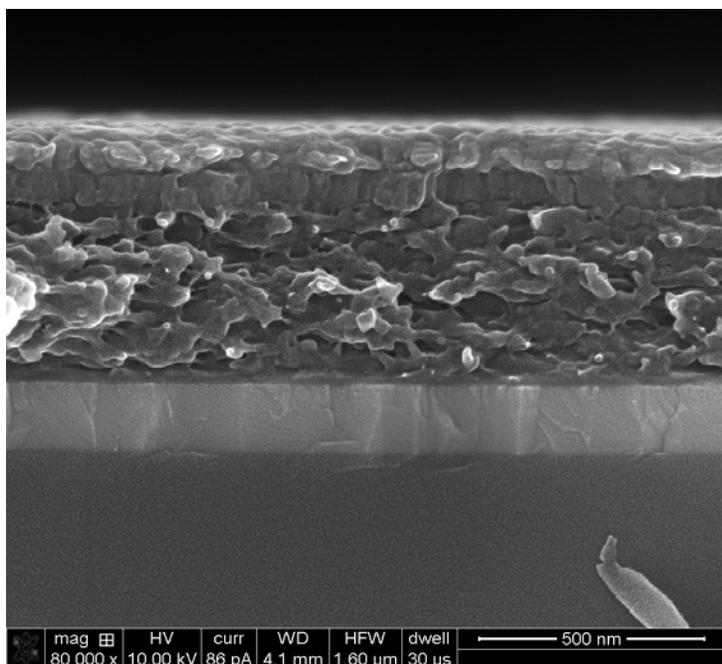


Figure S10. 310 nm PBnDT-FTAZ:PC₆₁BM 1:2. In order from top to bottom, Aluminum/Calcium, active layer, PEDOT:PSS, ITO, glass.

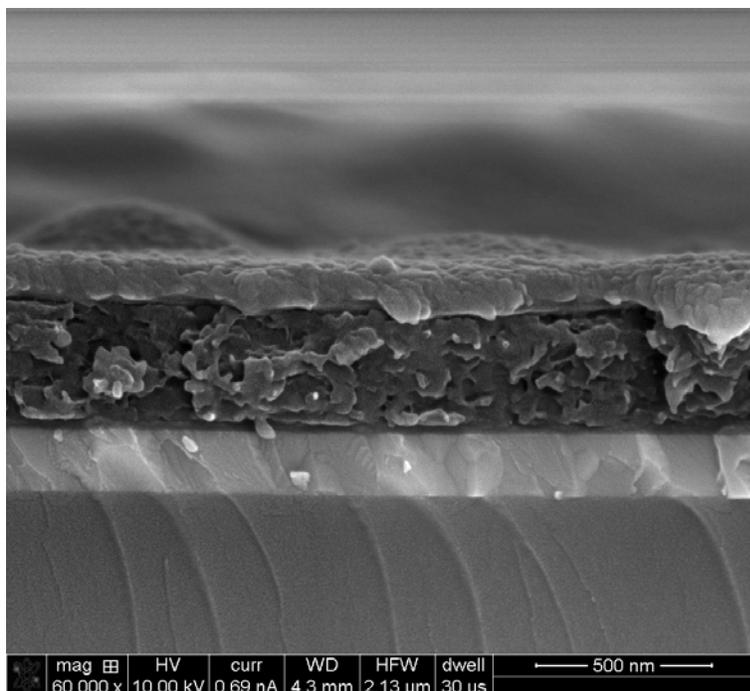


Figure S11. 250 nm PBDT-FTAZ:PC₆₁BM 1:2. In order from top to bottom, Aluminum/Calcium, active layer, PEDOT:PSS, ITO, glass.

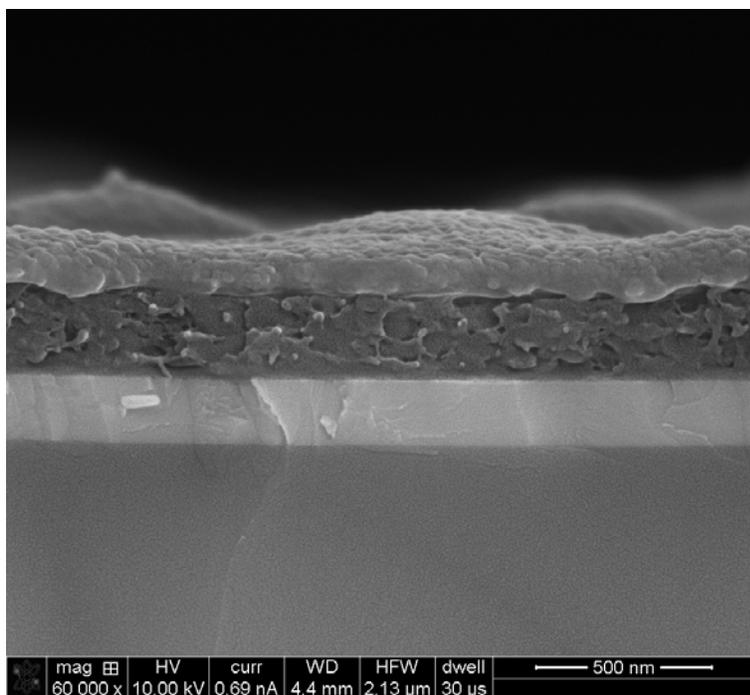


Figure S12. 160 nm PBDT-FTAZ:PC₆₁BM 1:2. In order from top to bottom, Aluminum/Calcium, active layer, PEDOT:PSS, ITO, glass.

References:

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