

## Theory Guided Systematic Molecular Design of Benzothiadiazole-Phenazine Based Self-Assembling Electron-Acceptors

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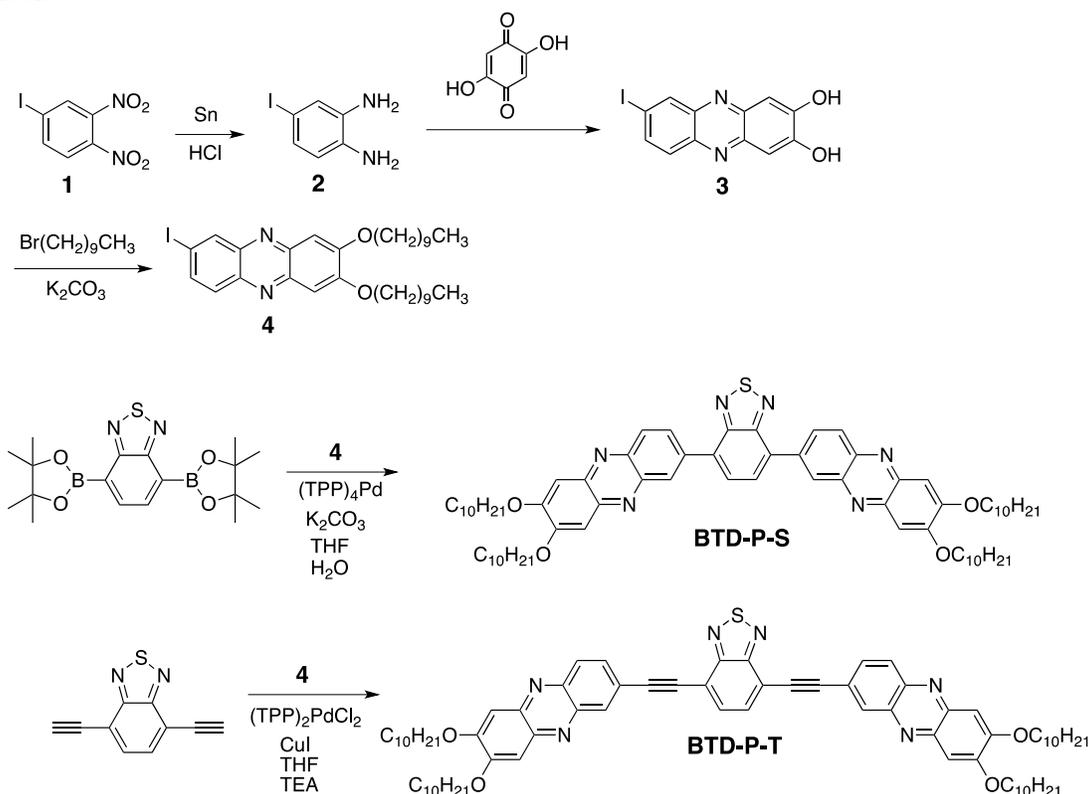
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### General Characterization

Nuclear magnetic resonance (NMR) spectra were obtained with a Varian Gemini 400 MHz NMR spectrometer at room temperature. Deuterated chloroform (CDCl<sub>3</sub>) containing tetramethylsilane (TMS) as an internal reference was used as the solvent for both <sup>1</sup>H NMR and <sup>13</sup>C NMR. Mass spectra were collected at the University of Texas at Arlington. Optical properties of the molecules were obtained with a Shimadzu UV-2600 UV-visible spectrophotometer and Horiba Fluorimeter using a xenon lamp excitation source for absorption and fluorescence emission, respectively. Electrochemistry measurements were performed with CV on a CH instrument 660D with a three electrode configuration, with a cell equipped with a platinum plate as the counter electrode, a platinum disc as the working electrode (2 mm diameter), and a non-aqueous Ag/Ag<sup>+</sup> electrode (Ag in 10 mM AgNO<sub>3</sub> solution in anhydrous acetonitrile) as the reference electrode. CV measurements for all compounds were recorded in a methylene chloride solution containing 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF<sub>6</sub>) as the supporting electrolyte. All solutions were purged with Ar for 20-30 min before each experiment, and a positive pressure of Ar was maintained over the sample solution during the experiments. The scan rate was  $v = 100$  mV/s for all experiments. All potentials are reported versus the ferrocene/ferrocenium (Fc/Fc<sup>+</sup>) redox couple which was used as an internal standard (6-10 drops of an 8 mM solution in methylene chloride).

## Synthesis



Scheme S1. Synthetic routes to **BTD-P-S** and **BTD-P-T**.

All chemicals were purchased from commercial sources and used as received without further purification.

### 1,2-diamino-4-iodobenzene (2)

Ethanol (50 mL) was added to a round bottom flask containing 4-iodo-1,2-dinitrobenzene<sup>1</sup> (**1**) (1.80 g, 6.10 mmol) followed by Tin metal (2.50 g, 20.74 mmol). Hydrochloric Acid (14 mL) was slowly added to the slurry. The solution was stirred at room temperature for 1 hour, and then at 65°C for 4 hours. Once cooled to room temperature, the solution was poured into a beaker containing 375 mL of ether. 55 mL of 0.5M Na<sub>2</sub>S was added followed by 55 mL of a saturated NaHCO<sub>3</sub> solution. This solution was filtered, and the filtrate was washed with 0.5M Na<sub>2</sub>S, and the crude product was extracted into ethyl acetate. The organic extract was dried over sodium sulfate, filtered and evaporated to give the crude product in 90 % yield. <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>, ppm) δ 7.00-6.96 (2H, overlapping peaks), 6.46 (1H, d, *J* = 7.6 Hz), 3.38 (4H, broad singlet).

### 2,3-dihydroxy-7-iodo-phenazine (3)

To a flask containing 1,2-diamino-4-iodo-benzene (1.30 g, 5.6 mmol), 2,5-dihydroxyquinone (778 mg, 5.6 mmol), 98 mL ethanol was added. The mixture was stirred at 80°C for 24 hours. The solvent was evaporated and the resulting solid was used for ether synthesis without further characterization or purification.

### 2,3-Bis-decyloxy-7-iodophenazine (4)

Bromodecane (3.50 mL, 16.8 mmol), potassium carbonate (2.70 g, 19.5 mmol), and 20 mL of dimethylformamide were added to a round bottom flask containing 2,3-dihydroxy-7-iodophenazine (5.60 mmol). The reaction mixture was stirred at 60°C for 24 hours. An additional 2.3 mL of bromodecane (11.2 mmol) and 1.9 g of potassium carbonate were added (13.7 mmol), and the mixture was stirred an additional 24 hours at 60°C. The resulting solution was cooled to room temperature, and poured into 100 mL of water. The red precipitates were filtered and purified by silica gel column chromatography (1/1 CH<sub>2</sub>Cl<sub>2</sub>/Hexane) providing a yield of 42%. <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>, ppm) δ 8.57 (1H, d, *J* = 1.6 Hz), 7.95 (1H, dd, *J* = 9.2, 2.0 Hz), 7.85 (1H, d, *J* = 8.8 Hz), 7.30 (2H, s), 4.22 (4H, m), 1.95 (4H, m), 1.54 (4H, m), 1.40-1.28 (24H, overlapping peaks), 0.88 (6H, t, *J* = 6.8 Hz); <sup>13</sup>C (100 MHz, CDCl<sub>3</sub>, ppm): 154.98, 154.82, 142.40, 142.18, 142.11, 140.68, 140.68, 137.76, 137.30, 129.94, 105.42, 94.47, 69.33, 31.89, 29.58, 29.53, 29.32, 28.68, 25.99, 22.66, 14.09 (one aliphatic peak was not observed due to overlapping).

### **BTD-P-S**

2,3-Bis-decyloxy-7-iodophenazine (525 mg, 0.849 mmol), 2,1,3-benzothiadiazole-4,7-bis(boronic acid pinacol ester) (Aldrich, 150 mg, 0.387 mmol), tetrakis(triphenylphosphine)palladium(0) (20.0 mg, 0.0155 mmol), and potassium carbonate (320 mg, 2.32 mmol) were added to a reaction flask. 30 mL tetrahydrofuran (degassed with Argon for 40 minutes) and 15 mL deionized water (degassed with Argon for 60 minutes) were added via syringe. The reaction mixture was stirred at 65°C overnight and then let cool to room temperature. The resulting precipitates were filtered and washed with methanol. The pure product was obtained by silica gel column chromatography (1% methanol/ CH<sub>2</sub>Cl<sub>2</sub>) followed by basic alumina column chromatography (1/99 methanol/ CH<sub>2</sub>Cl<sub>2</sub>) and reprecipitation from CHCl<sub>3</sub> into methanol in 37% yield. <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>, ppm) δ 8.89 (2H, d, *J* = 2.0 Hz), 8.45 (2H, dd, *J* = 8.8 Hz, 2.0 Hz), 8.31 (2H, d, *J* = 8.8 Hz), 8.11 (2H, s), 7.39 (4H, d, *J* = 2.0 Hz), 4.26 (8H, m, two overlapped triplets), 1.98 (8H, m), 1.57 (8H, m, overlapped with H<sub>2</sub>O), 1.44-1.29 (48H, overlapping peaks), 0.89 (12H, m, two overlapped triplets). <sup>13</sup>C (100 MHz, CDCl<sub>3</sub>, ppm) δ 154.68, 154.60, 154.11, 142.48, 142.26, 141.76, 141.68, 137.35, 132.77, 129.98, 129.23, 128.87, 128.71, 105.63, 69.34, 31.94, 29.65, 29.60, 29.40, 29.37, 28.77, 26.07, 22.71, 14.13 (one aromatic peak was not observed due to overlapping). HRMS (ESI) *m/z* [M+H]<sup>+</sup> calcd for C<sub>70</sub>H<sub>97</sub>N<sub>6</sub>O<sub>4</sub>S, 1117.7287, found 1117.7297.

### **BTD-P-T**

To a solution of 2,3-bis-decyloxy-7-iodophenazine (1.8 g, 2.91 mmol), Bis(triphenylphosphine)palladium(II) dichloride (10.0 mg, 0.0147 mmol) in 40 mL of tetrahydrofuran and 12.5 mL of triethylamine (both degassed with Ar), 4,7-diethynyl-2,1,3-benzothiadiazole<sup>2</sup> (270 mg, 1.47 mmol) in 10 mL of degassed THF was added via syringe, followed by CuI (3.0 mg, 0.00147 mmol). The reaction mixture was refluxed for 5 hours and then let cool to room temperature. The resulting precipitates were filtered and washed with methanol. The pure product was obtained by silica gel column chromatography (5% Ethyl Acetate/CHCl<sub>3</sub>) followed by basic alumina chromatography (5/95 Ethyl Acetate/CHCl<sub>3</sub>) in 44% yield. <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>, ppm) δ 8.47 (2H, d, *J* = 2 Hz), 8.14 (2H, d, *J* = 9.2 Hz), 7.95 (2H, dd, *J* = 8.8, 1.6 Hz), 7.93, (2H, s), 7.35 (4H, d, *J* = 4.4 Hz), 4.25 (8H, two overlapped triplets, *J* = 6.8 Hz), 1.97 (8H, m), 1.55 (8H, m, overlapped with H<sub>2</sub>O), 1.42-1.29 (48H, overlapping peaks) 0.89 (12H, t, *J* = 6.8 Hz). <sup>13</sup>C (100 MHz, CDCl<sub>3</sub>, ppm) δ 154.97, 154.78,

154.40, 142.71, 142.31, 141.75, 141.34, 132.69, 131.34, 129.05, 122.73, 117.24, 105.62, 105.52, 97.49 ( $C_{sp}$ ), 87.83 ( $C_{sp}$ ), 69.38, 31.91, 29.60, 29.57, 29.36, 29.34, 28.73, 26.02, 22.68, 14.10 (one aromatic peak was not observed due to overlapping); HRMS (ESI)  $m/z$   $[M+H]^+$  calcd for  $C_{74}H_{97}N_6O_4S$  1165.7287, found 1165.7304.

### **BHJ OSC fabrication**

An indium tin oxide (ITO) coated glass was cleaned by ultrasonic treatment in acetone, DI water, and isopropyl alcohol and dried by using nitrogen gas. A ZnO solution was prepared by dissolving zinc acetate dihydrate ( $Zn(CH_3COO)_2 \cdot 2H_2O$ , 1.0 g) and ethanolamine ( $NH_2CH_2CH_2OH$ , 0.28 g) in 2-methoxyethanol ( $CH_3OCH_2CH_2OH$ , 10 mL) under vigorous stirring for 24 hr. The cleaned ITO coated glass was treated in an UV/ $O_3$  chamber for 20 min and immediately spin-coated with the ZnO solution. Then, the ZnO coated ITO substrate was annealed on a hot plate for 60 min at 200 °C. The thickness of ZnO layer was approximately 40 nm. Poly(3-hexylthiophene) (P3HT) and BTD-P, which were blended in different weight ratio, were dissolved in chlorobenzene with 3 vol % DIO. Next, the P3HT:BT-D-P solution was spin-coated on top of the ZnO layer and annealed for 10 min at 160 °C in a  $N_2$  purged glove box to form a photoactive layer with a thickness of 100 nm. Finally, an anode layer composed of a  $MoO_3$  layer (10 nm) and an Ag layer (100 nm) was deposited by thermal evaporation with the shadow mask in a high vacuum thermal evaporator. Therefore, we fabricated the organic solar cell devices with ITO/ZnO (40 nm)/P3HT:BT-D-P (100 nm)/  $MoO_3$  (10 nm)/Ag(100 nm) configuration.



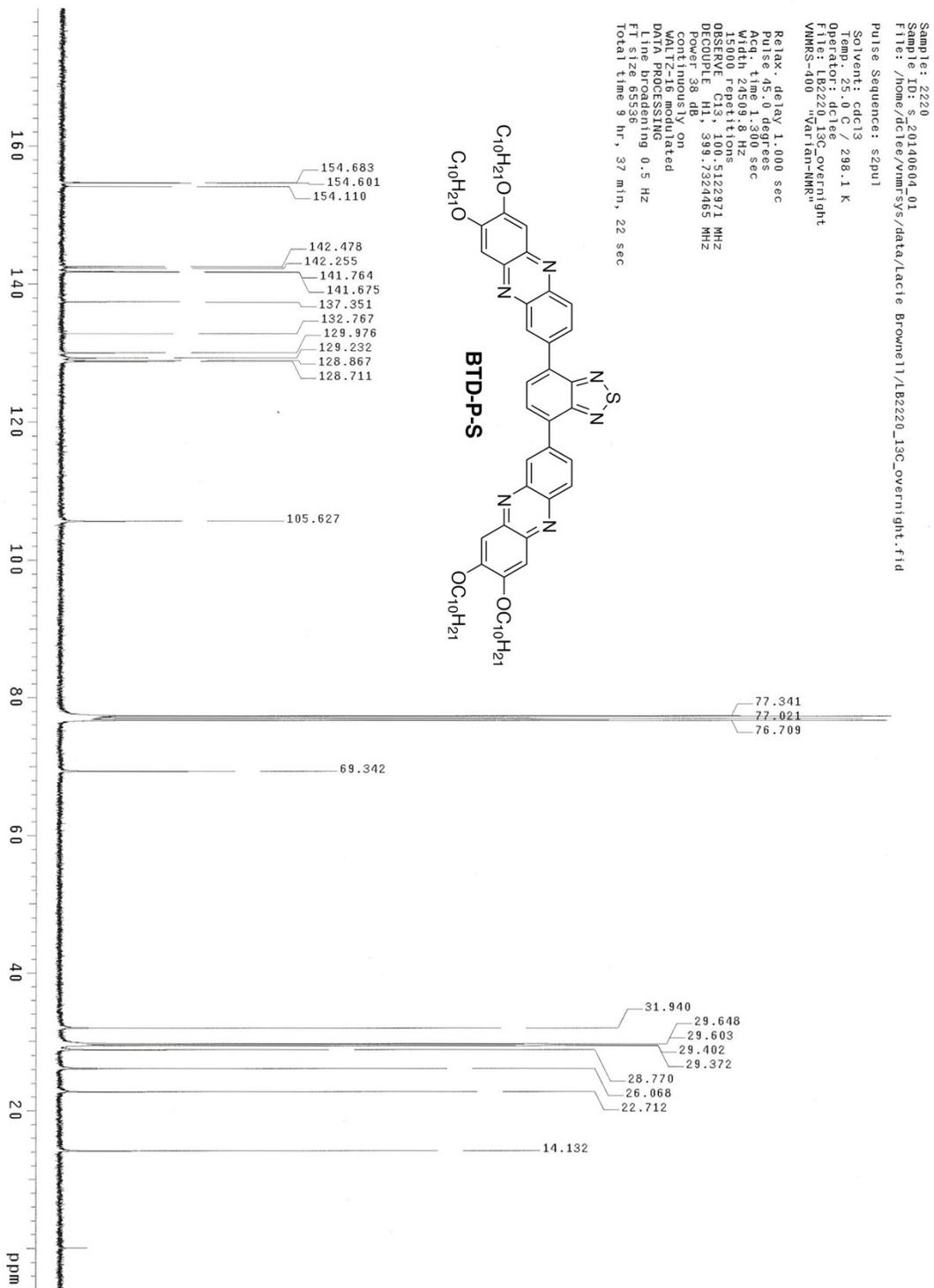


Figure S2.  $^{13}C$  NMR spectrum of **BTD-P-S** ( $CDCl_3$ ).

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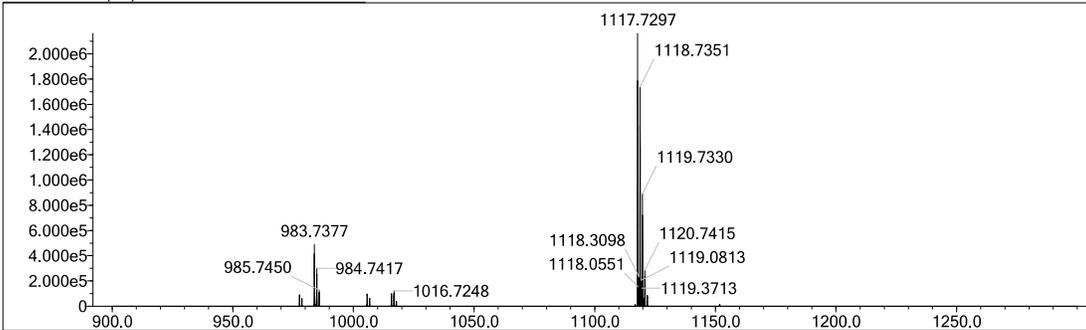
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C	4	0	70	F	1	0	0					Na
N	3	0	6	S	2	0	1					

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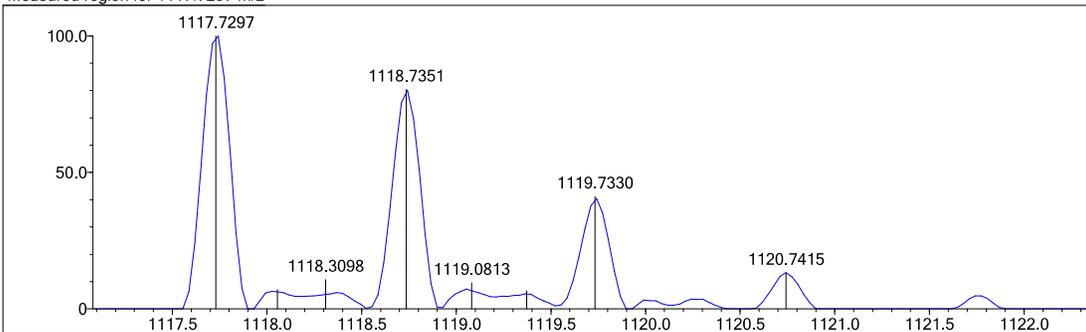
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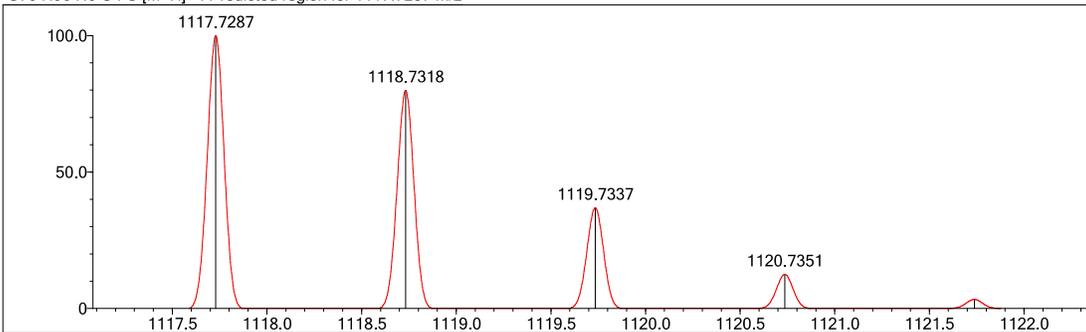
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Measured region for 1117.7297 m/z



C70 H96 N6 O4 S [M+H]<sup>+</sup> : Predicted region for 1117.7287 m/z



Rank	Score	Formula (M)	Ion	Meas. m/z	Pred. m/z	Df. (mDa)	Df. (ppm)	Iso	DBE
1	89.72	C70 H96 N6 O4 S	[M+H] <sup>+</sup>	1117.7297	1117.7287	1.0	0.89	89.72	26.0

Figure S3. High Resolution Mass-Spectrum of **BTD-P-S**.

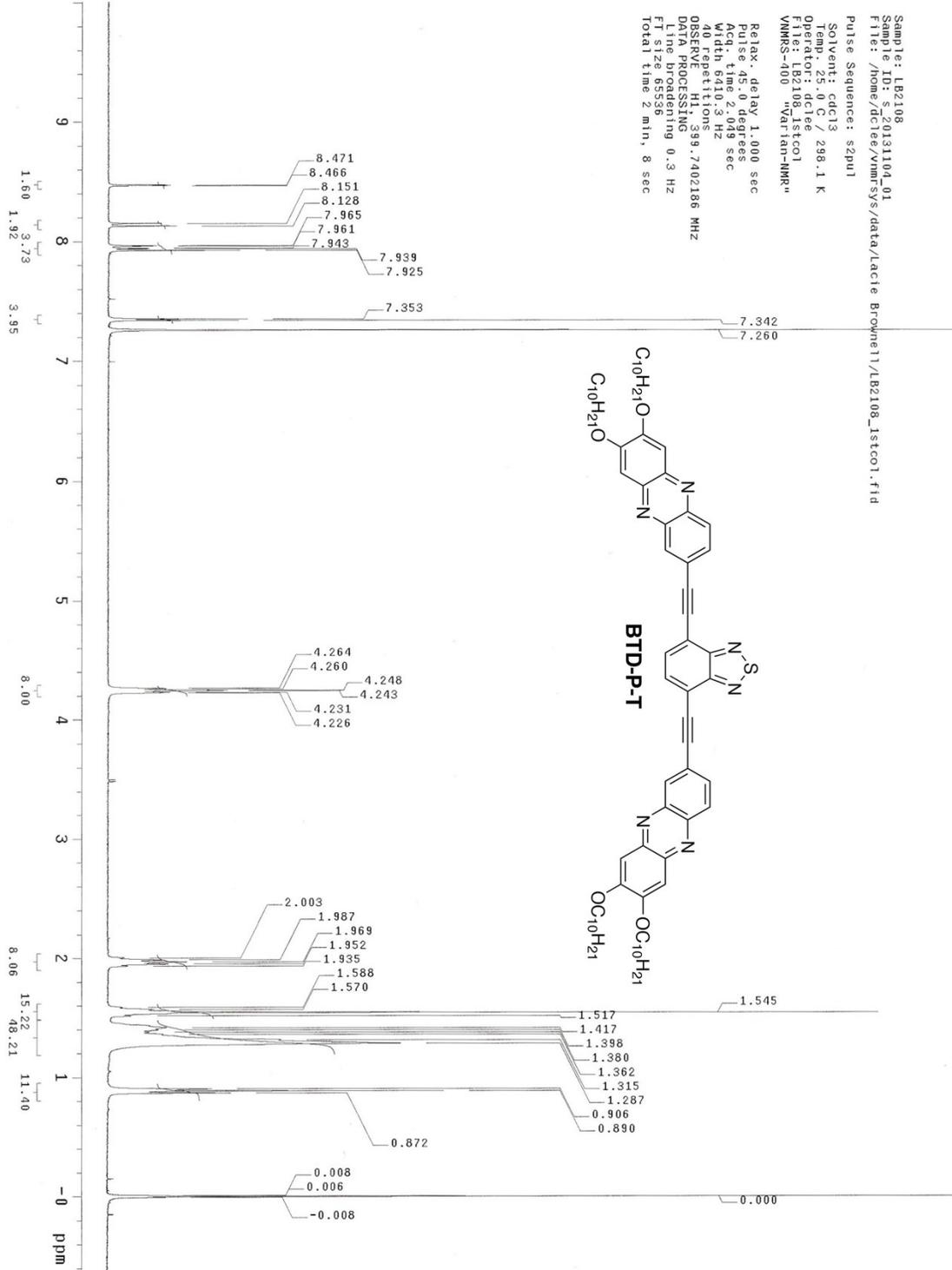


Figure S4.  $^1\text{H}$  NMR spectrum of **BT-D-P-T** ( $\text{CDCl}_3$ ).

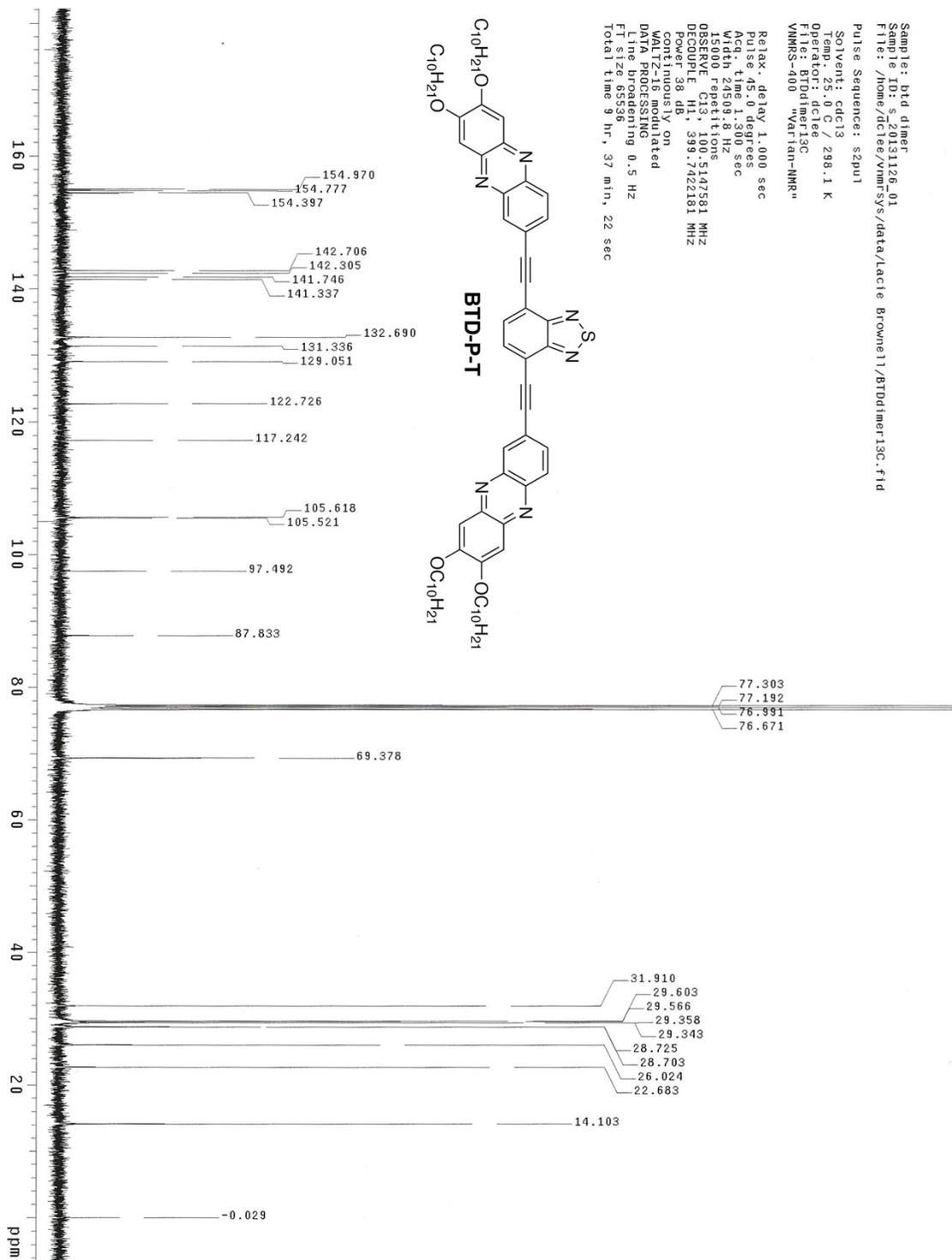


Figure S5. <sup>13</sup>C NMR spectrum of **BT-D-P-T** (CDCl<sub>3</sub>).

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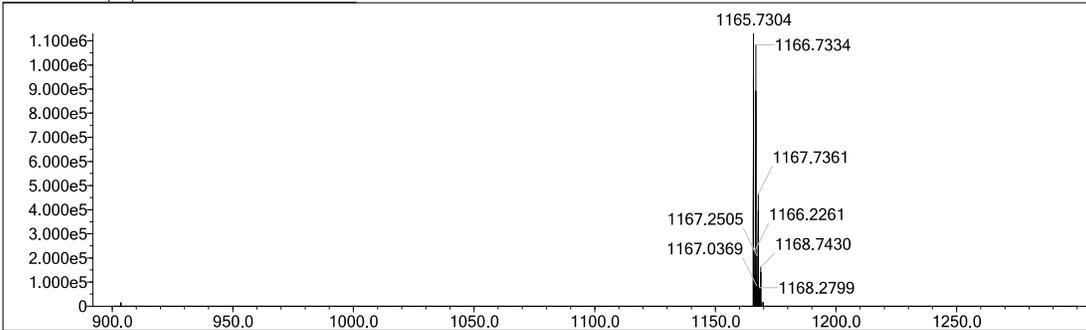
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C	4	74	74	F	1	0	0					Na
N	3	0	6	S	2	0	1					

Error Margin (ppm): 10  
 HC Ratio: unlimited  
 Max Isotopes: all  
 MSn Iso RI (%): 75.00

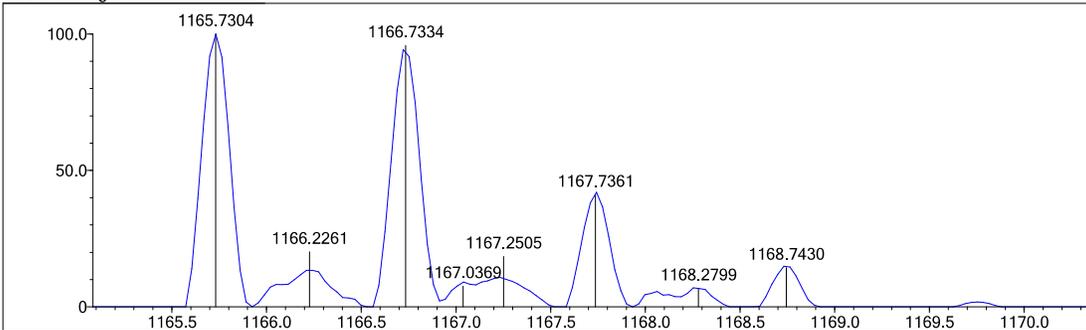
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 MSn Logic Mode: OR

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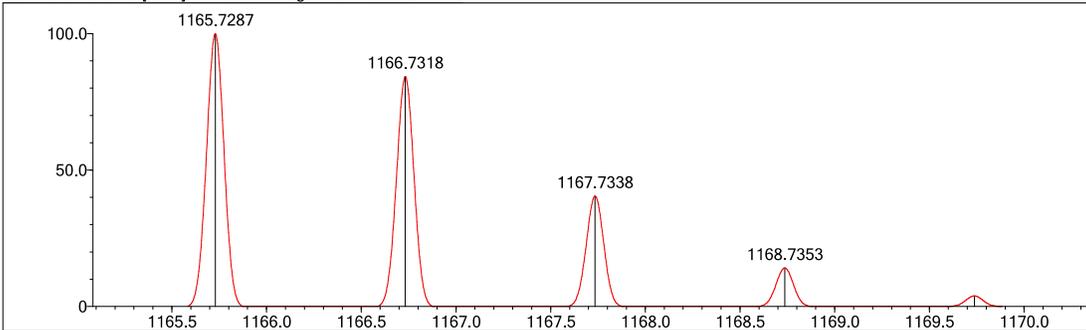
Event#: 1 MS(E+) Ret. Time : 0.063 Scan# : 9



Measured region for 1165.7304 m/z



C74 H96 N6 O4 S [M+H]<sup>+</sup> : Predicted region for 1165.7287 m/z



Rank	Score	Formula (M)	Ion	Meas. m/z	Pred. m/z	Df. (mDa)	Df. (ppm)	Iso	DBE
1	75.42	C74 H96 N6 O4 S	[M+H] <sup>+</sup>	1165.7304	1165.7287	1.7	1.46	76.29	30.0

Figure S6. High Resolution Mass-Spectrum of **BTD-P-T**.

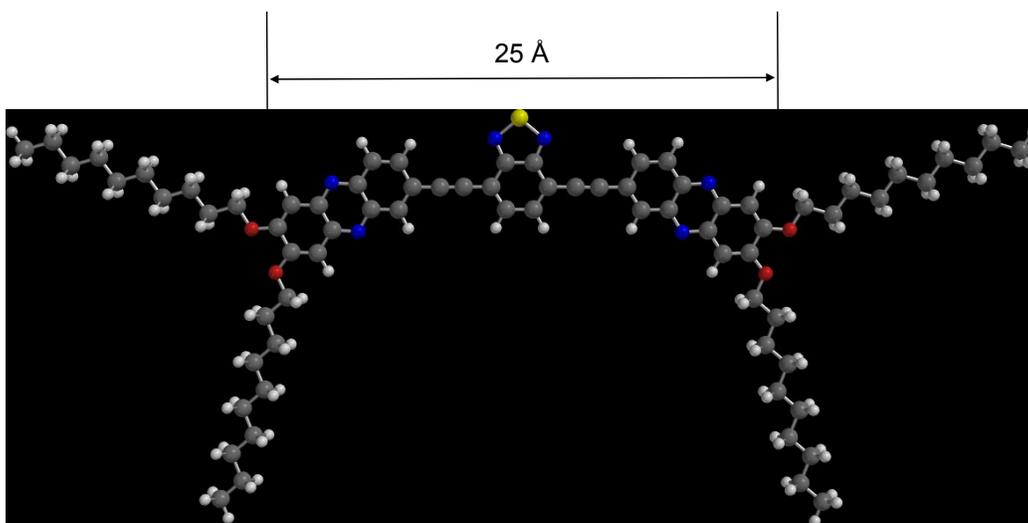


Figure S7. Molecular length of **BTD-P-T**.

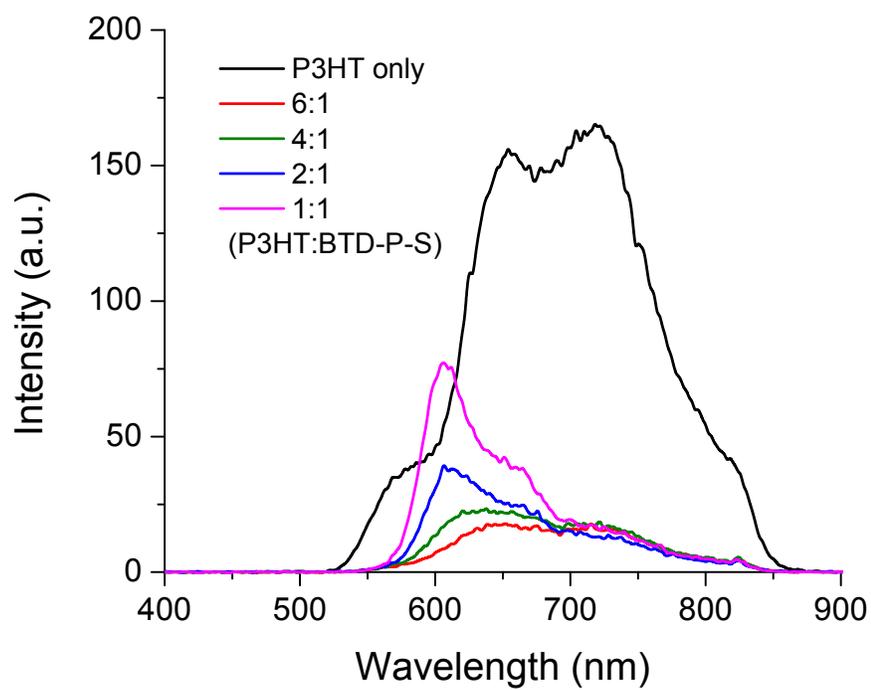


Figure S8. FL spectra of P3HT and P3HT:**BTD-P-S** blend film.

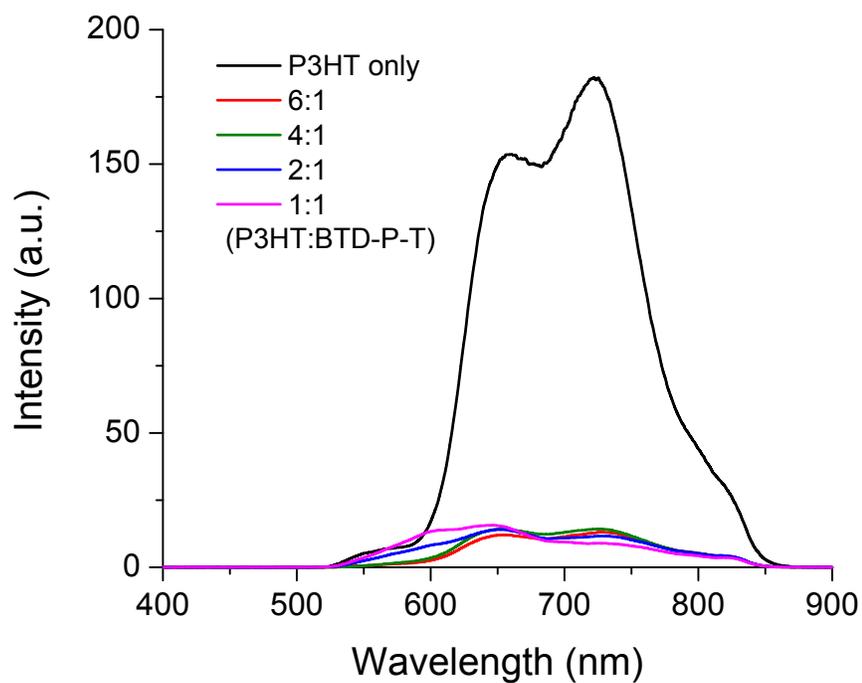


Figure S9. FL spectra of P3HT and P3HT:**BTD-P-T** blend films.

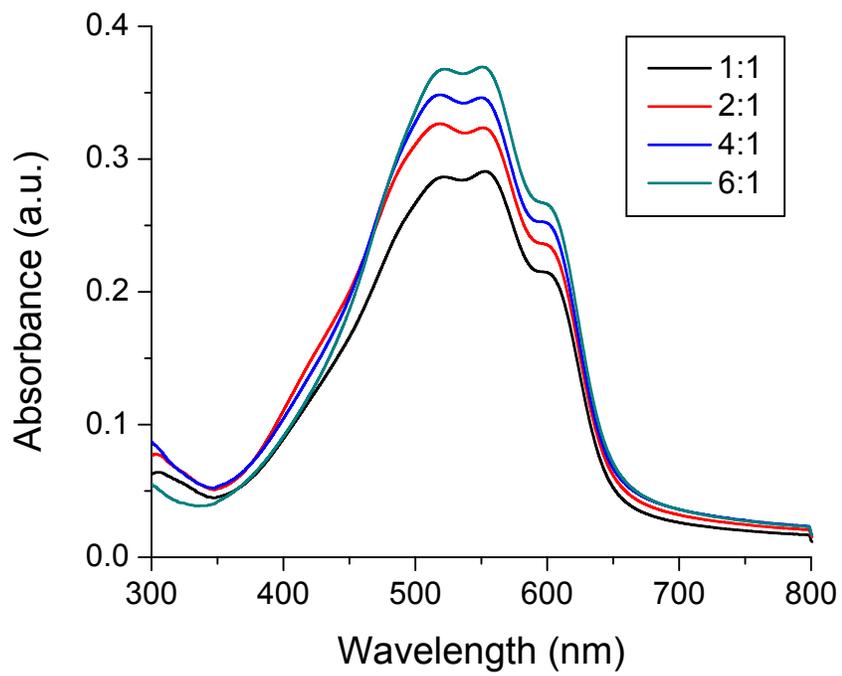


Figure S10. UV-vis absorption of P3HT:**BTD-P-T** at different ratios.

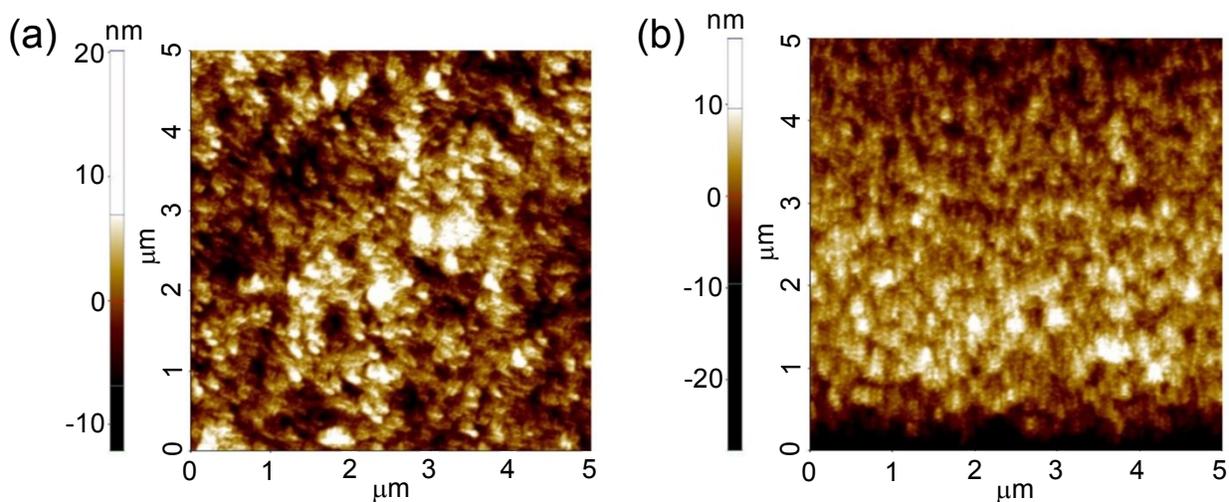


Figure S11. AFM images of P3HT:BTDP-T blend at the ratio of (a) 1:1 and (b) 6:1.

Table S1. Molar absorptivity ( $\epsilon$ ) and fluorescence quantum yield ( $\Phi_F$ ) of BTDP compounds in dichloromethane.

	$\epsilon$	$\Phi_F$
<b>BTDP-S</b>	76725 (426 nm)	58%
<b>BTDP-T</b>	86127 (446 nm)	66%

References:

1. Kapil, R. S. "Nitration of *m*-Iodonitrobenzene" *J. Chem. Soc.* **1959**, 4127-4128.
2. Susumu, K.; Fisher, J. A. N.; Zheng, J.; Beratan, D. N.; Yodh, A. G.; Therien, M. J. "Two-Photon Absorption Properties of Proquinoidal D-A-D and A-D-A Quadrupolar Chromophores" *J. Phys. Chem. A* **2011**, *115*, 5525-5539.