

# SYNTHESIS AND CHARACTERIZATION OF COPOLYMERS WITH DIFURODIIKETOPYRROLOPYRROLE (DPP2F) AND THIOPHENE/CYCLOPENTADITHIOPHENE MONOMERS PER ETHYNYLENE SPACERS

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## Abstract

This research investigated the design and synthesis of several copolymers that incorporate difurodioxyppyrrlopyrrole (DPP2F) units coupled via ethynyl (2E) linkages to thiophene (T) or cyclopentadithiophene (CPDT) monomers. These copolymers were prepared via Sonogashira coupling between dibrominated DPP2F monomers with ethynyl thiophene derivatives. PDPP2F-T2E and PDPP2F-CPDT2E polymers were examined by FTIR, UV-vis, <sup>1</sup>H NMR and GPC analysis. The optical band gaps were calculated and compared. We hoped to achieve bandgaps of 1.4 eV or lower, as these copolymers would be useful when incorporated into bulk heterojunction (BHJ) solar cells. The goal of producing copolymers applicable for use in bulk heterojunction (BHJ) solar cells was achieved with band gaps of 1.4 eV and lower.

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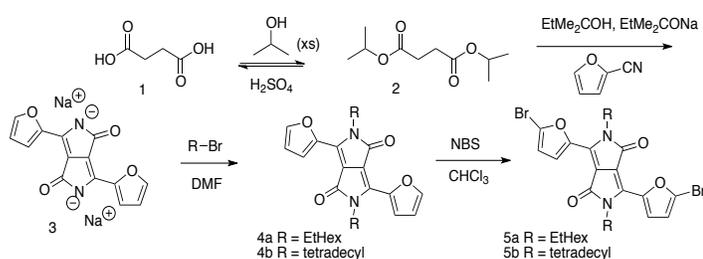
Keywords: organic solar cells, diketopyrrolopyrrole, Sonogashira, cyclopentadithiophene, ethynyl spacer, optical band gap, thiophene

## Introduction

Alternative energy sources are vital not only due to a limited supply of fossil fuels but also because the burning of these fuels have brought about the advent of climate change. One promising source of alternative energy is solar energy. The focus of this research is the synthesis of varying low band gap organic polymers for broad spectrum solar cell applications. Extensive reports in the literature demonstrate that diketopyrrolopyrrole (DPP) and thiophene (T) or cyclopentadithiophene monomers (CPDT) have shown incredible promise in producing low band gap polymers capable of harnessing the energy of a large range of wavelengths and increasing efficiencies.<sup>1,2,3,4,5,6,7,8,9,10,11</sup> The difurodiketopyrrolopyrrole (DP-2F) monomer has alternating furan and thiophene rings which have been shown to increase the solubility of the final polymers in organic solvents.<sup>12</sup> Thus DPP2F-T2E or DPP2F-CPDT2E copolymers would combine these known efficient moieties for solar cell polymers and will couple them together with diethynyl linker arms. The ethynyl spacers are used to reduce steric hindrance and promote a planar polymer backbone.<sup>13</sup>

Scheme 1 demonstrates the synthetic scheme for the production of the DPP2F monomers. This work followed the procedures listed by the Fréchet group with some modifications.<sup>14</sup> Esterification of succinic acid (1) with isopropyl alcohol produced diisopropyl succinate (2). The heterocyclic salt (3) was formed via a mixture of tert-amyl alcohol, alkoxide and 2-cyanofuran. The dialkylated products (4a,b) were formed via a S<sub>N</sub>2 reaction of the salt with the appropriate alkylhalide. Titration of the crude product with cold methanol eased the purification steps. Often mixtures of

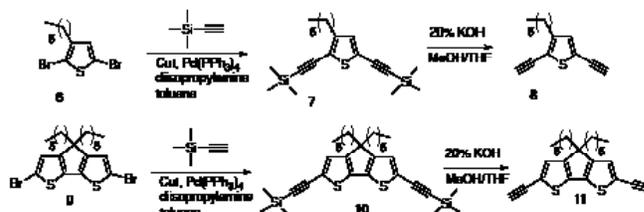
Scheme 1 – Synthetic scheme to produce DPP2F monomer



the N and O alkylated products were observed that required careful separation. The furan rings were then brominated with N-bromosuccinimide to yield the dibromo-DPP2F monomers (5a,b).

Scheme 2 displays the production of the diethynyl-thiophene monomers. 2,5-Dibromo-3-hexylthiophene (6) was reacted with trimethylsilylacetylene under Sonogashira conditions<sup>15</sup> to give the protected diethynylthiophene (7). Deprotection yielded 2,5-diethynyl-3-hexylthiophene (8) based on previous work on acetyl-

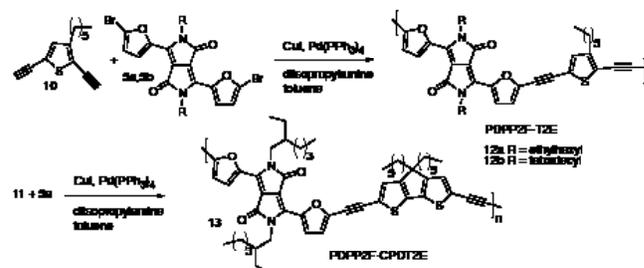
Scheme 2 – Synthetic scheme to produce the diethynyl monomers: T2E and CPDT2E



ed thiophenes by Denise Rutherford.<sup>16</sup> The synthesis of the novel compound, 2,6-diethynyl-4,4-dihexylcyclopentadithiophene (11), followed a similar route. 2,6-Dibromo-4,4-dihexylcyclopentadithiophene (9) was coupled with trimethylsilyl-acetylene, followed by basic silyl cleavage of the resulting diacetylene intermediate (10) to yield the CPDT comonomer (11).

The final polymers were synthesized via Sonogashira coupling between the dibromo-DPP2F and the terminal dialkynylthiophene

Scheme 3 – Formation of PDPP2F-T2E and PDPP2F-CPDT2E copolymers



derivatives as shown in Scheme 3. The PDPP2F-T2E polymers (12a,b) came from the reaction of 2,5-diethynyl-3-hexylthiophene (10) with the appropriate dibromo-DPP2F adduct (5a,b). The 2ECPDT unit (11) was reacted with dibromo-di(2-ethylhexyl)DP-P2F comonomer (5a) to yield the PDPP2F-CPDT2E (13) copolymer.

## Experimental Section

### Physical and Spectra Data

Proton NMR was obtained on a JEOL JNC/ECS Series (400 MHz) spectrometer. Listed proton NMR data are given in the following order: ppm (multiplicity, coupling constants, integrated number of protons and assignment). The chemical shifts were determined as the distance in ppm from TMS.

Infrared spectra were recorded on a Nicolet Avatar 360 FTIR with Gateway 2000 data system. Samples were either run on NaCl plates (liquids) or KBr pellets (solids). FTIR (ATR) spectra were collected on a Thermo Nicolet iS-50 diamond anvil ATR. ATR correction used was angle = 45°, 1 bounce, 1.5 sample refractive index.

An Agiltron PeakSeeker Raman Spectrometer was used to examine Raman data.

UV spectra were obtained using a Shimadzu UV-2450 Spectrometer with an ISR-2200 Integrating Sphere attachment (diffuse reflectance). The polymer sample was mixed with BaSO<sub>4</sub> (Waco spectroscopy grade) and BaSO<sub>4</sub> was used as the reference. The Kubelka-Munk Function was used to allow spectral comparison with the transmission UV. Tauc plots<sup>17</sup> band gap transitions were calculated using energy (hv) in eV on the x axis versus (aE)/r, a is the absorption coefficient, which is the absorbance divided by the thickness of the sample in cm<sup>-1</sup>. A consistent thickness of 1 cm of solid and liquid samples ensured that this was equal to the absorbance. The value r is 1/2 for directly allowed transitions. The resulting plots were extrapolated to find the onset of absorption at the abscissa (or x axis) to give the optical band gap.

GPC data was provided by an Agilent 1260 Infinity GPC/SEC with multiwavelength UV and refractive index detectors. GPC was used to determine the molecular weight range for a solution of this polymer prepared by dissolving 0.003 g of polymer in 3 mL of THF. The mobile phase was HPLC grade THF flowing at 1.00 mL/min. The UV detector was monitored at 254 and 625 nm, and the refractive index detector temperature was set to 35°C. Initially the broad range (200-2,000,000 Da) PLgel 5 μm MIXED-C column (300 x 7.5 mm) was used, and then the range refined using a (200-400,000 Da) ResiPore column (300 x 7.5 mm), both operated at ambient temperature.

### Chromatography

Flash column chromatography refers to the resolution technique of W. Clark Still [*J. Organic Chem.* **1978**, *43*, 2923]. A glass column is filled with a slurry of dry 40-62 m silica gel and solvent. The same solvent is used as an eluent to push a sample through the column, with pressure from a nitrogen inlet to speed the elution to a rate of 2 in./min.

TLC refers to Thin Layer Chromatography, which was done on Sigma Chemical Co. plates made of 250 m silica gel on polyester with a 254 nm fluorescent indicator added. Visualization was performed via iodine chambers or UV lamp.

### Reactions

Concentration under reduced pressure refers to solvent removal using a Büchi RE 011 rotary evaporator connected to a water aspirator and an ethylene glycol cooling system.

Unless otherwise stated, all other solvents and reagents were reagent grade and used without further purification.

### Reagents

2,6-Dibromo-4,4-dihexyl-4H-cyclopenta[1,2-b:5,4-b']dithiophene was purchased from AEchem Scientific Corporations. All other reagents were purchased from Sigma-Aldrich. THF and hexanes were distilled over sodium, stored under nitrogen and 4 Å molecular sieves.

**Diisopropyl succinate (2)**:<sup>18</sup> 31.989 g (0.2709 mol) of succinic acid, 4 mL (0.0736 mol) of concentrated sulfuric acid, 90.00 mL (1.285 mol) of isopropyl alcohol, a stir bar, and molecular sieves were added to a 250 mL round bottom flask equipped with a condenser. The apparatus was purged with nitrogen and allowed to reflux for 24 hours. The solution was extracted with ether (3X), washed with water, and 5% sodium bicarbonate. The organic layer was dried with magnesium sulfate, underwent filtration and the solvent was removed under reduced pressure to yield 15.623g (28.51%) of product. FTIR (neat): [2981,2937 (C-H asym ν), 2880 (C-H sym ν), 1732 (C=O ν), 1469,1456,1342 (C-H δ), 1167 (sp<sup>2</sup>C-O ν), 1108 (COC ν)]; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): [δ= 1.24 ppm (d, J=6.4Hz, 6H, CH<sub>3</sub>), 2.58 (s, 4H, CH<sub>2</sub>), 5.02 (hept, J=6.4Hz, 2H, CH-C=O)]. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): [δ= 21.9 ppm (CH<sub>3</sub>), 29.6 (CH), 68.1 (CH<sub>2</sub>), 171.9 (C=O)].

**3,6-di(furan-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione salt(3)**:<sup>14</sup>

150 mL (1.387 mol) of t-amyl alcohol were added to a two-neck 250 mL round bottom flask equipped with a stir bar and condenser under a nitrogen atmosphere. The temperature was then raised to 60°C and left to stir for an hour. Next 3.458 g (0.1504 mol) of sodium metal pieces were added slowly and then the apparatus reassembled and flushed. The temperature was then gradually increased to 120°C. Twenty hours later, 8.54 mL (0.1504 mol) of 2-furonitrile were added via syringe. Then 10.21 mL (0.05013 mol) of diisopropyl succinate (6) was added drop wise over five minutes, and the temperature was lowered to 90°C. The solution was left to reflux for 2 hours. After reflux, the solution was cooled to room temperature, and the solid was collected. Toluene was used to wash the salt and then it was placed in a drying pistol for four days and then moved to a vacuum oven for 5 days yielding 16.907 g (108%) of product with residual catalyst. FTIR (ATR): [3121 cm<sup>-1</sup> (Ar CH ν), 1652,1623 (C=O ν), 780, 741 (ArCH oop δ)]. <sup>1</sup>H NMR (400 MHz, C<sub>3</sub>D<sub>6</sub>O): [δ = 6.54 ppm (dd, J = 3.6, 2.0 Hz, 1H, =CH), 7.02 (dd, J = 3.6, 1.2 Hz, <sup>1</sup>H, H-C=C-O), 7.63(dd, J = 2.0, 1.2 Hz, 1H, =CH-O)].

### General alkylation procedure (4a,4b)<sup>14</sup>:

A 250 mL two-neck round bottom flask was equipped with a stir bar and condenser. 100 mL of DMF and 3.80 g (12.2 mmol) of the DPP salt (8) were added to the flask and placed under N<sub>2</sub>

atmosphere. The mixture was heated to 120°C and stirred for 30 minutes. Then (35.4 mmol) of the alkyl bromide was added quickly. The apparatus was then purged with nitrogen and the temperature raised to 140°C and left to stir for 20-26 hours. The reaction was followed by TLC with chloroform as the solvent. When the reaction was finished it was then allowed to cool to room temperature. The mixture was stirred with water and chloroform for 24 hours. A fritted glass funnel layered with celite and silica was used to remove the sludge. The organic layer was extracted with chloroform and washed with water, dried with magnesium sulfate, filtered and the solvent removed under reduced pressure. The solid was then purified by trituration with ice-cold methanol, and then vacuum filtration. It was observed that both N and O alkylation were common and needed careful separation. The crude product was then placed through a flash column with chloroform as solvent. If further work was needed, a flash column with 1:6 (EtOAc:hexanes) was employed. The solvent was removed under reduced pressure to give the final product.

**2,5-bis(2-ethylhexyl)-3,6-di(furan-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (4a):**<sup>12</sup> Column chromatography with chloroform as the eluent was used to provide 0.643 g (10.8%) of a very dark green oil ( $R_f$  0.85). FTIR (ATR): [3122  $\text{cm}^{-1}$  (Ar CH  $\nu$ ), 2958, 2928 (CH asym  $\nu$ ), 2873, 2857 CH sym  $\nu$ ), 1662 (C=O  $\nu$ ), 750, 733 (ArCH oop  $\delta$ )]. <sup>1</sup>H NMR (400 MHz,  $\text{CDCl}_3$ ): [ $\delta$  = 0.85-0.95 ppm (m, 12 H), 1.26-1.39(m, 12H), 1.68-1.80(m, 2H), 4.04(d, J = 7.8 Hz, 4H), 6.69(dd, J = 1.7 Hz, 3.6 Hz, 2H), 7.61(d, J = 1.3 Hz, 2H), 8.33(d, J = 3.6 Hz, 2H)].

**2,5-bis(tetradecyl)-3,6-di(furan-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (4b):**<sup>12</sup> Flash column chromatography with chloroform as the eluent ( $R_f$  0.90) and then 1:6 (EtOAc:hexanes) ( $R_f$  0.73) was used to provide 0.927 g (11.6%) of a dark green oil (4b). FTIR (ATR): [3105 $\text{cm}^{-1}$  (Ar CH  $\nu$ ), 2954, 2914 (CH asym  $\nu$ ), 2848 (CH sym  $\nu$ ), 1668 (C=O  $\nu$ ), 1592 (C=C Ar  $\nu$ ), 1479, 1467,1369 (CH  $\delta$ ), 1099 (COC  $\nu$ ), 884, 747(Ar CH oop  $\delta$ )]. <sup>1</sup>H NMR (400 MHz,  $\text{CDCl}_3$ ): [ $\delta$  = 0.88 ppm (t, J= 6.4Hz, 6H,  $\text{CH}_3$ ), 1.34 (m, 4H,  $\text{CH}_2$ ), 3.58 (m, 4H,  $\text{CH}_2$ ), 4.11 (m, 4H, N- $\text{CH}_2$ ), 6.69(d, J = 3.6Hz, 2H, Ar-H), 8.25 (d, J= 3.6 Hz, 2H, Ar-H)].

**General bromination procedure (5a,5b):**<sup>14,19</sup>

The appropriate alkylated DPP2F compound (1.70 mmol) was put into a 100 mL round bottom flask with a stir bar. 50 mL of chloroform were added, and the entire apparatus was placed in a saturated ice bath at 3°C. Recrystallized NBS (0.605 g, 3.40 mmol) was added to the mixture in small portions and the resulting mixture was stirred for 30 minutes under nitrogen. The flask was then warmed to room temperature and stirred until the TLC (chloroform as eluent) showed no sign of the starting material. The organic layer was extracted with chloroform, washed with water, and dried with magnesium sulfate. The solvent was removed under reduced pressure. The crude oil was then placed through a flash column with chloroform as the solvent. Removal of the solvent from the product fractions afforded the dibrominated compound.

**3,6-bis-(5-bromofuran-2-yl)-2,5-bis(2-ethylhexyl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (5a):** Column chromatography was used to separate the components with chloroform as the eluent. The product, a maroon tacky solid, was observed at  $R_f$  of approximately 0.80. All samples with the product were collected and the solvent removed under reduced pressure, yielding 0.349 g (31.8%) of product. FTIR (ATR): [3130 $\text{cm}^{-1}$  (Ar CH  $\nu$ ), 2951, 2917 (CH asym  $\nu$ ), 2846 (CH sym  $\nu$ ), 1664 (C=O  $\nu$ ), 1586  $\text{cm}^{-1}$  (C=C Ar  $\nu$ ), 1476, 1466,1374 (CH  $\delta$ ), 1024 (COC  $\nu$ ), 818, 723

(Ar CH oop  $\delta$ ), 449, 413 (C-Br  $\nu$ )]. <sup>1</sup>H NMR (400 MHz,  $\text{CDCl}_3$ ): [ $\delta$  = 0.88 ppm (t, J = 7.0 Hz, 6 H,  $\text{CH}_3$ ), 0.92(t, J = 7.4 Hz, 6H,  $\text{CH}_3$ ), 1.24-1.39(m, 16H,  $\text{CH}_2$ ), 1.68-1.78(m, 2H,  $\text{CH}_2$ ), 3.99(m, 4H, N- $\text{CH}_2$ ), 6.62(d, J = 3.7 Hz, 2H, Ar-H), 8.30(d, J = 3.7 Hz, 2H, Ar-H)].

**3,6-bis-(5-bromofuran-2-yl)-2,5-bis(tetradecyl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (5b):** Column chromatography was used to separate the components with chloroform as the eluent. The product, a purple tacky solid, was observed at  $R_f$  of approximately 0.80. All samples with the product were collected and the solvent was removed under reduced pressure, yielding 0.772 g (55.8%) of product. FTIR (ATR): [3131 $\text{cm}^{-1}$  (Ar CH  $\nu$ ), 2951, 2918 (CH asym  $\nu$ ), 2847, (CH sym  $\nu$ ), 1667 (C=O  $\nu$ ), 1587  $\text{cm}^{-1}$  (C=C Ar  $\nu$ ), 1477, 1467,1374 (CH  $\delta$ ), 1026 (COC  $\nu$ ), 819, 729(Ar CH oop  $\delta$ ), 449, 418 (C-Br  $\nu$ )]. <sup>1</sup>H NMR (400 MHz,  $\text{CDCl}_3$ ): [ $\delta$  = 0.88 ppm (t, J= 6.8Hz, 6H,  $\text{CH}_3$ ), 1.32 (m, 4H,  $\text{CH}_2$ ), 3.58 (p, J= 6.8Hz, 4H,  $\text{CH}_2$ ), 4.05 (m, 4H, N- $\text{CH}_2$ ), 6.63(dd, J = 3.6, 1.4Hz, 2H, Ar-H), 7.63 (d, J= 1.4 Hz, 2H, Ar-H), 8.31(d, J=3.6Hz, 2H, Ar-H)]

**2,5-bis-(trimethylsilyl)ethynyl)-3-hexylthiophene (7):**<sup>15,16</sup>

0.690 g (3.62 mmol) CuI and 0.115 g (.164 mmol) Pd( $\text{PPh}_3$ )<sub>2</sub>Cl<sub>2</sub> were added to a 100 mL round bottom flask in a glove box with a stir bar and condenser. 1.05 mL (4.90 mmol) 2,5-dibromo-3-hexylthiophene, 1.31 mL (9.35 mmol) trimethylsilylacetylene, 15 mL (107 mmol) diisopropylamine, and 25 mL toluene were also added. The apparatus was wrapped in aluminum foil and purged with nitrogen and then heated to 60°C for 22 hours and followed by TLC, (1:6, EtOAc:hexanes)  $R_f$  =0.75. A plug of silica gel was run after dissolving the dark, black product in ether and using hexane as an eluent. The solvent was then removed under reduced pressure and then high vacuum to yield a black, sticky oil, 2.606 g (117%). A column was then run with the TLC solvent and gave 1.43 g of a dark oil (80.9%). FTIR (ATR): [3050 $\text{cm}^{-1}$  (Ar CH  $\nu$ ), 2964 (CH asym  $\nu$ ), 2858, (CH sym  $\nu$ ), 2068 (CC), 1248 (Si- $\text{CH}_3$   $\nu$ ), 845, 765(Ar CH oop  $\delta$ )]. <sup>1</sup>H NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 0.23 ppm (s, 18H,  $\text{CH}_3$ -Si), 0.87(m, 3H,  $\text{CH}_3$ - $\text{CH}_2$ ), 1.28(m, 2H,  $\text{CH}_2$ ), 1.56(m, 6H,  $\text{CH}_2$ ), 2.56(m, 2H,  $\text{CH}_2$ -Ar), 6.94(s, 1H, Ar-H)]

**2,5-diethynyl-3-hexylthiophene (8):**<sup>16</sup>

1.05 g (2.59 mmol) of the disilylethynylthiophene, 50 mL of methanol, 6 mL of 20% KOH (21.8 mmol), and 100 mL THF were placed in a 500 mL round bottom flask and stirred for four hours. The reaction was followed by TLC (1:6, EtOAc:hexanes) to show the product,  $R_f$  = 0.62. More water was added to the reaction mixture and allowed to stir for 10 minutes. This was then extracted 3x with diethyl ether. The organic layers were then washed with brine and then dried with magnesium sulfate. The solvent was removed under reduced pressure after removing the drying agent. The residual oil was run through a flash column with hexanes as the solvent. The fractions with the correct  $R_f$  were collected and the solvent was removed under reduced pressure to give 0.101 g (18.0 %) of an unstable brown-orange liquid. <sup>1</sup>H NMR (400 MHz,  $\text{CDCl}_3$ ): [ $\delta$  = 0.88 ppm (m, 6H,  $\text{CH}_2$ ), 1.28(m, 6H,  $\text{CH}_2$ ), 1.60(m, 2H,  $\text{CH}_2$ - $\text{CH}_2$ -Ar), 2.64(m, 2H,  $\text{CH}_2$ -Ar), 7.01(s, 1H, Ar-H)].

**2,6-di(trimethylsilyl)-4,4-bis(hexyl)-4H-cyclopenta[1,2-b:5,4-b']dithiophene (10) :**

In a glove bag, 0.3398 g of CuI and 0.1955 g of Pd( $\text{PPh}_3$ )<sub>2</sub>Cl<sub>2</sub> were added to a 100 mL round bottom flask equipped with a stir bar. A condenser was added, and the top capped with a septum and parafilm. Aluminum foil was wrapped around the flask. The apparatus was transferred to a vent hood and purged with nitrogen. 20 mL of toluene, 25 mL of diisopropylamine, 0.181 g (0.00359 mol)

of CPDT and 3 mL (0.0212 mol) of trimethylsilyl acetylene were added via syringe. The system was allowed to reflux overnight. The solution was cooled to room temperature, put through a fritted glass funnel layered with celite and silica and washed with ether and hexanes. The solvent was removed under reduced pressure and placed under vacuum overnight, yielding 0.543 g (285.7%) of a dark brown, heterogenous sludge. FTIR (ATR): [3050cm<sup>-1</sup> (Ar CH v), 2971 (CH asym v), 2855, (CH sym v), 2070 (C≡C), 1246 (Si-CH<sub>3</sub> v), 834, 649(Ar CH oop δ)]. <sup>1</sup>H NMR (400 MHz (CD<sub>3</sub>)<sub>2</sub>CO): [δ (ppm) = 0.18(s, 18H, Si-CH<sub>3</sub>), 0.89(m, 6H, (CH<sub>2</sub>-C), 1.16(m, 12H, CH<sub>2</sub>), 1.76(m, 4H, CH<sub>2</sub>-Ar), 7.21(s, 2H, Ar-H)].

#### 2,6-di(ethynyl)-4,4-bis(hexyl)-4H-cyclopenta[1,2-b:5,4-b'] dithiophene (11):

2.042 g KOH were added to a graduated cylinder and enough water was added to dissolve the salt. Water was then added to the 10 mL mark to make roughly 20% KOH. 1.50 mL (5.46 mmol) of the KOH, 50 mL THF, and 25 mL of MeOH were added to a 1 liter flask containing 0.543 g (0.00351 mol) of the diTMS-CPDT and a stir bar. The reaction was stirred overnight. Diethyl ether and water were added. The reaction mixture was extracted by diethyl ether three times. The organic layers were combined, washed with brine, and dried over magnesium sulfate. The filtrate's solvent was removed under reduced pressure. The dark brown oily organic layer was collected and placed under vacuum for 24 hours, yielding 0.100 g (76.8%) of an unstable dark brown tacky solid. <sup>1</sup>H NMR (400 MHz (CD<sub>3</sub>)<sub>2</sub>CO): [δ (ppm) = 0.89(m, 6H, CH<sub>3</sub>), 1.16(m, 12H, CH<sub>2</sub>), 1.76(m, 4H, CH<sub>2</sub>-Ar), 4.13 (s, 2H, C≡CH), 7.29 (s, 2H, Ar-H)].

#### General synthetic procedure for polymers<sup>15</sup>

In a 100 mL round bottom flask in a glove box was placed 0.400 mmol of the alkylated DFF2F comonomer, 0.400 mmol thiophene monomer, 0.042 g (0.036 mmol) of Pd(PPh<sub>3</sub>)<sub>4</sub>, 0.210 g (2.28 mmol) of CuI, 15 mL diisopropylamine (0.107 mmol) and 25 mL of toluene. A reflux apparatus was assembled, covered in tin foil and purged with nitrogen. The reaction was heated at 60°C for 24 hours. It was then cooled to room temperature and the solvent was removed under reduced pressure. The dark solid was then washed with hot methanol, hot acetone and hot water. After that, the polymer was washed with hexanes using Soxhlet apparatus for about 24 hours and then dried in a 30°C vacuum oven until dry.

**Poly(2,5-(di-2-ethylhexyl)-1,4-dioxo[2H,5H]pyrrolo-[3,4-c] pyrroledifuran-2,5'-diylethynyl-3-hexylthiophene-2,5-diy-lethynylene) PDPP2F(EH)-T(*n*-C<sub>6</sub>)<sub>2</sub>E (12a):** 0.264 g (0.406 mmol) of the 2Br-DPP2F(EH) monomer, 0.086 g (0.398 mmol) of the T(*n*-C<sub>6</sub>)<sub>2</sub>E monomer, 0.042 g (0.078 mmol) Pd(PPh<sub>3</sub>)<sub>4</sub>, and 0.0648 g (0.340 mmol) CuI, 30 mL of toluene and 20 mL of diisopropylamine were used. This gave 11a as a dark red metallic solid, that when dissolved in THF or chloroform, gave a bright blue solution (0.338 g, 97.6%)

UV-vis: [(CHCl<sub>3</sub>), broad peak between 500-700 nm, max at 633 nm, Abs 0.236, ε= 2145); (solid, broad peak 280-800 nm, max at 676 nm)] FTIR (ATR): [3054 cm<sup>-1</sup> (Ar CH v), 2954, 2922 (CH asym v), 2854, (CH sym v), 1663 (C=O v), 1560 cm<sup>-1</sup> (C=C Ar v), 1433, 1378 cm<sup>-1</sup> (CH δ), 1092 (COC v), 780, 723(Ar CH oop δ)]. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): [δ = 0.85-0.96 ppm (m, CH<sub>3</sub>), 1.25-1.64 (m, CH<sub>2</sub>), 2.70 (m, CH<sub>2</sub>-Ar), 4.05 (m, CH<sub>2</sub>-N), 6.91-7.51 (m, Ar-H), 8.43 (m, Ar-H)].

**Poly(2,5-ditetradecyl-1,4-dioxo[2H,5H]pyrrolo-[3,4-c] pyrroledifuran-2,5'-diylethynyl-3-hexylthiophene-2,5-diy-lethynylene) PDPP2F(*n*-C<sub>14</sub>)-T(*n*-C<sub>6</sub>)<sub>2</sub>E (12b):** 0.342g

(0.418mmol) of the 2Br-DPP2F(*n*-C<sub>14</sub>) monomer, 0.144g (0.667mmol) of the T(*n*-C<sub>6</sub>)<sub>2</sub>E monomer, 0.0405 g (0.098 mmol) Pd(PPh<sub>3</sub>)<sub>4</sub>, and 0.0648 g (0.609mmol) CuI, 30 mL of toluene and 20 mL of diisopropylamine were used. The resulting product from this process was a bluish black solid (0.429 g, 99.3%yield). It was not very soluble and produced blue solutions in chloroform or THF. UV-Vis: [(THF), broad peak between 500-700 nm, max at 627 nm, Abs 0.236, ε= 1098); (solid, broad peak 330-800 nm, max at 663 nm)] FTIR: 3127 cm<sup>-1</sup> (ArH v), 2953, 2921 (CH asym v), 2851 (CH sym v), 1666 (C=O v), 1455, 1372 (CH δ), 1099 (COC v), 838, 730 (Ar oop δ)]. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): [δ = 0.88 ppm (m, CH<sub>3</sub>), 1.26-1.79 (m, CH<sub>2</sub>), 2.91 (m, CH<sub>2</sub>-Ar), 4.14 (m, CH<sub>2</sub>-N), 6.93-7.70 (m, Ar-H), 8.40 (m, Ar-H)].

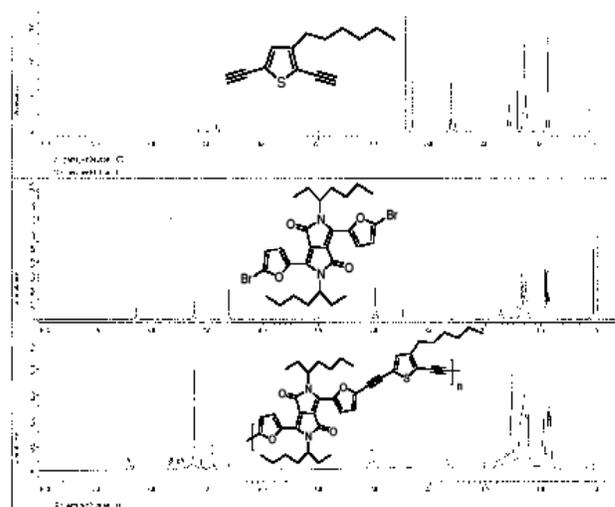
**Poly{2,5-(2-ethylhexyl)-1,4-dioxo[2H,5H]pyrrolo-[3,4-c] pyrroledifuran-2,5'-diylethynyl-4,4-di(2-hexyl)-4H-cyclopenta[2,1-b:3,4-b']dithiophene-2,6-diylethynylene} PDP-P2F(EH)-CPDT(2*n*-C<sub>6</sub>)<sub>2</sub>E (13):** 0.180 g (0.277 mmol) of 2Br-DP-P2F(EH) monomer, 0.100 g (0.270 mmol) of CPDT2E, 0.104 g (0.266 mmol) of Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>, 0.662 g (3.48mmol) of CuI, 20 mL of toluene, and 25 mL of diisopropylamine were used. This yielded 0.243 g (98.4%) of a dark solid that when dissolved in chloroform or THF produced a dark purple solution. UV-Vis: [(CHCl<sub>3</sub>, broad peak between 360-854 nm, max at 512 & 723 nm, 723nm Abs 0.812, ε= 4122); (solid, broad peak 330-800 nm, max at 765 nm)] Raman: [2130 cm<sup>-1</sup> (C≡C v).] ATR IR: [3059 cm<sup>-1</sup> (Ar CH v), 2952, 2926 (CH asym v), 2854 (CH sym v), 1652 (C=O v), 1590 cm<sup>-1</sup> (C=C Ar v), 1455, 14385, 1375 (CH δ), 1095 (CO v), 836,691 (Ar oop δ)]. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): [δ = 0.83 ppm (m, CH<sub>3</sub>), 1.13-1.79 (m, CH<sub>2</sub>), 4.08 (m, CH<sub>2</sub>-N), 6.69-7.66 (m, Ar-H), 8.36-8.48 (m, Ar-H)].

## Results and Discussion

The final polymers were analyzed via <sup>1</sup>H NMR, FTIR, Raman, UV-Vis, and GPC/SEC. <sup>1</sup>H NMR showed the thiophene protons and alkyl chains from the different comonomers. This can be seen in the following Figure 1, which shows the proton NMR for copolymer 12a and its monomers.

UV-vis of the three colorful polymers showed broad absorptions. Table 1 lists the UV-vis data for 12a, 12b and 13 for solu-

Figure 1 – <sup>1</sup>H NMR plots of monomers (8, 5a) and DPP2F(EH)-2E-T (12a) copolymer



tions and solid reflectance spectra. The polymers were dissolved in chloroform or THF to produce the UV-vis solutions. The thiophene polymers were not as soluble as the cyclopentanthiophene version. This is quite apparent as shown in Fig 2, which displays the UV-vis solutions for each polymer ( $\sim 0.03$  g/25 mL). The decreased solubility of the PDPP2F-T2E polymers may explain the observed low absorbances. The solutions of the PDPP2F-T2E polymers were a bright blue while the CPDT polymer solution was a dark purple.

UV-vis spectra of a chloroform solution and the solid copolymer, (PDPP2F(EH)-2ET( $n$ -C<sub>6</sub>)) (12a), are shown in Figure 3. The solid UV spectrum displays a broader absorption range with a  $\lambda_{\max}$  at 676 nm as compared to solution's 633 nm. The other PDPP2F-T2E polymer (12b) had a similar trend, while the CPDT (13) copolymer gave broad absorptions for the solution as well as the solid and the  $\lambda_{\max}$  for the solid came at 765 nm. This resulted in a lower optical band gap for the solid CPDT copolymer (13) 1.0 eV, as compared to either of the thiophenes (12a or 12b) 1.4 eV. The transitions allowed directly from the valence band to the conduction band were calculated with Tauc plots and gave similar results

Figure 2 - UV-vis for PDPP2F(EH)-T2E (12a) & PDPP2F(EH)-CPDT2E (13) polymer solutions in CHCl<sub>3</sub>, and PDPP2F( $n$ -C<sub>14</sub>)-T2E (12b) in THF ( $\sim 0.03$  g in 25 mL of solvent)

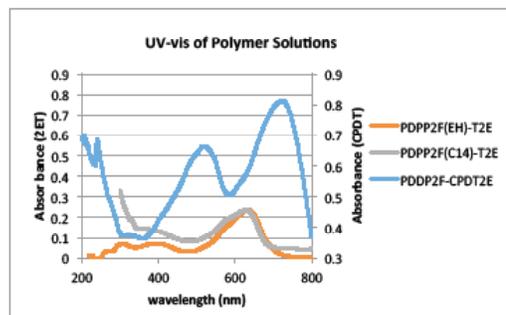


Figure 3 - UV-vis solid and liquid data spectra for PDPP2F(EH)-T( $n$ -C<sub>6</sub>)2E (12a)

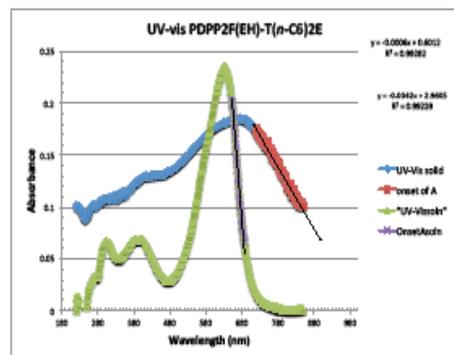


Table 1 - UV-vis Data for polymers

Polymer	$\lambda_{\max}$ (nm) solution	$\epsilon$	$\lambda_{\max}$ (nm) solid	Optical band gap soln (eV)	Optical band gap solid (eV)	Direct transition Tauc <sup>17</sup> (eV)
12a	633	2145	676	1.81	1.43	1.41
12b	627	1098	663	1.99	1.42	1.50
13	723	4122	765	1.45	1.04	1.17

as shown in Table 1.

The polymers were also examined for their molecular weight distributions via gel permeation chromatography (GPC), which are listed in Table 2. Since the molecular weights of the polymers were unknown, the PLgel Mixed C column was used to first determine an average molecular weight and then the ResiPore column was utilized to determine the listed results. The 2-ethylhexyl version of PDPP2F-T2E gave higher molecular weights than the tetradecyl version. The latter however had a narrower molecular weight distribution. It was apparent after the examination of the number average molecular weight (Mn) values, that 12a had the largest polymer chain with 14.5 repeating units. The others were only about 6 monomer units long. The CPDT polymer (13) had an average of 6.9 monomers tethered together and it had a much larger distribution of polymer chain lengths as compared to the T2E versions as shown by the large PDI value (3.7). The Mn values were also used to calculate rough molarities for the UV-vis solutions and obtain approximate molar extinction coefficients, which are reported in Table 1.

Table 2 - GPC data for polymers

Polymer	Acronym	Mw (ResiPore)	Mn (ResiPore)	PDI	Average # of monomers
12a	PDPP2F(EH)-T2E	17681	10231	1.72	14.5
12b	PDPP2F( $n$ -C <sub>14</sub> )-T2E	7537	5609	1.34	6.4
13	PDPP2F-CPDT2E	22451	6091	3.72	6.9

## Conclusions

We have successfully produced and characterized polymers via Sonogashira reactions between dibromo-difuro-diketopyrrolopyrrole (DPP2F) monomers and either diethynyl-thiophene (T2E) or diethynyl-cyclopentadithiophene comonomers (CPDT2E). As predicted the PDPP2F-CPDT2E copolymer (13) was found to have the lowest optical band gap. The onset optical band gaps for the PDPP2F-T2E polymers ranged from 1.8-2eV for the solutions and 1.4 eV for the solid spectra. The onset optical band gaps for the PDPP2F-CPDT2E copolymer were 1.45 eV for the solution and 1.0 eV for the solid. This copolymer was also more soluble in organic solvents than the PDPP2F-T2E polymers, as well as displaying a broader absorption range in the UV-vis. It also gave a higher number average molecular weight (Mn) with a wider molecular weight distribution (PDI) than the PDPP2F-T2E copolymers (12a, 12b). The PDPP( $n$ -C<sub>14</sub>)-T2E and PDPP(EH)-2ECPDT compounds were oligomers of about 6-7 repeating units on average, while the PDPP(EH)-T2E copolymer had a longer chain with approximately 14.5 monomers. The smaller alkyl pendant groups may have made it easier for the monomers to react and thus lead to longer chains.

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