Synthesis and Characterization of Poly(3,5-didodecyl-cyclopenta[2,1-b;3,4-b']dithiophen-4-one)

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Abstract

Different methods have been explored to synthesize the first soluble cyclopenta[2,1-b;3,4-b']dithiophen-4-one (CPDTO) homopolymer, poly(3,5-didodecylCPDTO), **C₁₂-PCPDTO**. Oxidation of the monomer **C₁₂-CPDTO** by FeCl₃ only gave oligomers. Elemental and NMR analyses indicated that oligomers were chlorinated at the both ends. A mechanism is proposed to explain why chlorination is so problematic for oxidation polymerization of **C₁₂-CPDTO** in comparison to 3-alkylthiophene. Dedoping of the oligomers was also investigated. Pd-catalyzed reaction of dibromo monomer and hexamethylditin yielded **C₁₂-PCPDTO-Sn** with an M_w of 22,816. This polymer exhibits a bimodal distribution of molecular weight, which is rationalized by an analysis of relative reactivities of species present in the polymerization process. The optical bandgap is 1.85 eV in both chloroform solution and film, much larger than that of electrochemically synthesized unalkylated PCPDTO film. This is explained by poor backbone planarity as predicted by DFT calculation of C₂-CPDTO oligomers. The efficient synthesis of the monomer and the polymer paves the way for future synthesis of soluble planar CPDTO homopolymers with alternating alkylated and non-alkylated CPDTO units.

Key words: CPDTO, dedoping, Stille reaction, bimodal molecular weight distribution, band gap, extinction coefficient.

Introduction

In the past decade, many conjugated polymers have been designed and synthesized for photovoltaic (PV) applications [1-4]. Narrow optical bandgap is a critical property for PV polymers, which allows more efficiently absorption of sunlight. Among many aromatic structural units used for low bandgap polymers [1,3,5,6], 4H-cyclopenta[2,1-b;3,4-b']dithiophene-4-one (CPDTO) [7-9] is one of a few monomers that can produce homopolymers with very low bandgaps (1.1-1.2 eV) [10,11]. In CPDTO, two thiophene units are locked into a planar structure by a carbonyl group. Effective D-A interaction between the sulfur atoms

(donors) and the carbonyl group (acceptor) gives rise to its red color and a λ_{max} of 472 nm [12], even longer than that of regioregular poly(3-hexylthiophene) (P3HT, 456 nm) [13].

Unsubstituted CPDTo has been widely incorporated as an acceptor unit in many donor-acceptor type copolymers [14-18] and small molecules or oligomers [19-22]. Bandgaps of these polymers are typically in the range of 1.7- 2.0 eV, much larger than that of PCPDTo. Alkylated CPDTo derivatives, 2,6-dibromo-3,5-bis(2-ethylhexyl)-cyclopenta[2,1-b:3,4-b']dithiophen-4-one, where alkyl = n-dodecyl or 2-ethylhexyl, has been used to prepare soluble CPDTo-vinylene copolymers [23], however, synthesis of soluble CPDTo homopolymer has not been reported.

Synthesis of homopolymer of dialkylated CPDTo is much more challenging than the synthesis of poly(3-alkylthiophene) as CPDTo is more difficult to oxidize and the carbonyl group does not allow lithiation or preparation of Grignard reagent from CPDTo or its brominated compounds. We wish to report a more effective synthesis of 2,6-dibromo-3,5-bis-n-dodecyl-cyclopenta[2,1-b:3,4-b']dithiophen-4-one, C_{12} -diBrCPDTo, and study of different polymerization reactions of C_{12} -CPDTo and C_{12} -diBrCPDTo, including oxidation of C_{12} -CPDTo by FeCl_3 , Ullmann coupling of C_{12} -diBrCPDTo, and palladium-catalyzed Stille polymerization of C_{12} -diBrCPDTo and hexamethylditin. It was found that only the third method gave a polymer product. Results of physical, optical, thermal and electrochemical characterization show that the new polymer is very soluble and non-aggregating or crystalline in the solid state. Due to the large dihedral angles between neighboring CPDTo units (calculated by the DFT method), the polymer is highly nonplanar, and therefore was not further investigated for photovoltaic application, but the efficient synthesis of the monomer and the polymer paves the way for future synthesis of soluble planar CPDTo homopolymers with alternating alkylated and non-alkylated CPDTo units.

2. Experimental Section

NMR experiments were conducted on a Bruker 400MHz NMR spectrometer unless otherwise noted. Molecular weight of polymers were measured on an Agilent 1100 series HPLC system with ChemStation B.04.03 and GPC Data Analysis B.01.02, equipped with two serial GPC columns (PL1110-6500: PLGel 5 mm MIXED-C 7.5×300 mm). The following polystyrene standards from Polymer Standards Services-USA, Inc. were used for GPC calibration: 1) $\text{Mp/Mw/Mn}=6520/6480/6240$, $\text{Mw/Mn} = 1.04$, 2) $9890/9000/9590$, 1.07 , 3) $44200/42300/41400$, 1.02 , 4) $120\text{K}/115\text{K}/109\text{K}$, 1.05 , and 5) $184\text{K}/184\text{K}/180\text{K}$, 1.02 . UV-vis absorption spectra were obtained on an Agilent 8453 photodiode array UV-vis absorption spectrometer. Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) are performed simultaneously on a Seiko TG/DTA 220 thermal analysis system with a N_2 flow rate of 20 mL/minute. Mass characterization was performed on a Thermoquest Finnigan LCQ Deca Mass Spectrometer at the

Chemistry Instrumentation Center, SUNY at Buffalo. Elemental analysis was performed at Atlantic Microlab, Inc., Norcross, GA.

Cyclovoltammetry. Cyclovoltammetric measurements were performed on an eDAQ Potentiostat System (ER466 plus software EChem 2.1.5) equipped with platinum auxiliary and working electrodes and a silver reference electrode in a CH₃CN solution of AgNO₃ (0.01 M) and tetrabutylammonium hexafluorophosphate, TBA-HFP (0.1 M). The polymer samples were dissolved in chloroform and then dip coated onto the Pt working electrode. The electrodes are housed in an 8-mL vial half-filled with TBA-HFP/acetonitrile solution (0.1 M). The solution was N₂-purged and a scan rate of 100mV/s was used. Between measurements, the surface of the electrodes were cleaned or polished. Ferrocene (2 mM in the electrolyte solution) was used as an internal reference standard and its HOMO level of –5.10 eV [24] was used in calculations.

3,5,3',5'-Tetrabromo-4,4'-didodecyl-[2,2']bithiophenyl (2). A 100-mL round bottom flask was flushed with nitrogen gas, and charged with **1** [25,26] (4.89g, 10 mmol) and diethyl ether (20 mL). The flask was cooled in a –70 °C bath. When the solution started to turn cloudy, 2.5M BuLi (4 mL) was added via a syringe over 1 to 2 minutes. With no delay, CuCl₂ powder (1.68 g, 12.5 mmol) was added over 2 minutes. The cold bath was then removed and the mixture was stirred vigorously for 40 h. The mixture was filtered to remove solid. The solution was condensed to give the crude product which was purified by silica gel chromatography and vacuum distillation (to remove mono thiophene species) to afford 1.96 g light yellow solid. Yield: 48%. ¹H NMR (CDCl₃): δ 0.88 (t, 6H, J=7.0Hz), 1.2-1.7 (m, 40H), 2.66 (t, 4H, J=7.9Hz). ¹³C NMR (CDCl₃): δ 14.15, 22.71, 28.47, 29.22 (multiple Cs), 29.70 (multiple Cs), 31.94, 111.04, 114.57, 128.55, 140.88 ppm. Anal. calcd. for C₃₂H₅₀Br₄S₂: 814.008; found: 814.008.

3,3'-Dibromo-4,4'-didodecyl-[2,2']bithiophenyl (3). A 250-mL round bottom flask was flushed with nitrogen gas, and charged with **2** (15.225g, 18.6 mmol) and diethyl ether (150 mL). The flask was cooled in a –30 °C bath. When the solution started to turn cloudy, BuLi (2.5M, 14.9 mL, 37.2 mmol) was added via a syringe over 5 minutes. With no delay, water (2 mL) was added. The solution was transferred to a separation funnel, and washed with brine (50 mL). The organic phase was dried with MgSO₄, condensed, and vacuum dried to afford 12.28 g liquid product with >98% purity by ¹H and ¹³C NMR. Yield: Quantitative. ¹H NMR (CDCl₃): δ 0.88 (t, 6H, J=7.0Hz), 1.2-1.7 (m, 40H), 2.62 (t, 4H, J=7.9Hz), 7.11 (s, 2H). ¹³C NMR (CDCl₃): δ 14.14, 22.71, 28.59, 29.45 (multiple Cs), 29.61 (multiple Cs), 30.80, 32.16, 115.45 121.71, 129.34, 142.28 ppm. Anal. calcd. for C₃₂H₅₂Br₂S₂: 658.187; found: 658.186.

3,5-Didodecyl-cyclopenta[2,1-b;3,4-b']dithiophen-4-one (4). To a solution of **3** (12.28g, 18.59 mmol) and diethyl ether (100 mL) cooled in –40 °C bath, BuLi (2.5 M, 16.4 mL, 41 mmol) was added over 5

minutes. Five minutes later, dimethylcarbamoyl chloride (2.799 g, 26.03 mmol) was added via a syringe. The solution was stirred for 20 minutes. Then, 2 N HCl (15 mL) was added to acidify the solution. The organic layer was separated out, washed with brine (10 mL×2), dried with MgSO₄, and condensed by rotary evaporation. The crude product was purified with a silica gel (1 L) column using hexanes as the eluent. Yield of the pure product: 3.89 g, 39.6%. ¹H NMR (CDCl₃): δ 0.88 (t, 6H, J=7.0Hz), 1.2-1.7 (m, 40H), 2.65 (t, 4H, J=7.7Hz), 6.61 (s, 2H). ¹³C NMR (CDCl₃): δ 14.15, 22.72, 28.16, 29.39 (multiple Cs), 29.71 (multiple Cs), 31.95, 122.07, 140.24, 140.52, 149.13, 184.12 ppm. Anal. calcd. for C₃₃H₅₂OS₂: 528.3460; found: 529.3466.

2,6-Dibromo-3,5-didodecyl-cyclopenta[2,1-b;3,4-b']dithiophen-4-one (5). A 100-mL round-bottom flask, charged with a solution of **4** (5.29 g, 10.0 mmol) in CHCl₃ (50 mL), was cooled in an ice water bath and wrapped with black plastic film to block light. N-bromosuccinimide (NBS) powder (3.65 g, 20.5 mmol) was added in small portions over 30 minutes. The ice bath was removed after the addition and the solution was stirred for 24 h. Then, the solvent was removed by rotary evaporation. Water (100 mL) was added to the flask, and the mixture was sonicated for 30 minutes. Water along with succinimide was removed by filtration. The succinimide removal process was repeated one time. ¹H NMR spectrum showed no succinimide or any other impurity. The yield was quantitative. ¹H NMR (CDCl₃): δ 0.88 (t, 6H, J=7.0Hz), 1.2-1.7 (m, 40H), 2.64 (t, 4H, J=7.7Hz). ¹³C NMR (CDCl₃): δ 14.14, 22.71, 26.93, 29.02, 29.29, 29.38 (two Cs), 29.59, 29.66, 29.70 (two Cs), 31.94, 110.85, 137.13, 139.64, 147.25, 182.28 ppm. Anal. calcd. for C₃₃H₅₀OS₂: 684.167. Found: 684.167.

C₁₂-PCPDTO-Fe-3h. In a glovebox, chloroform (1.5 mL) and iron (III) chloride (6 mol. eq., 92 mg, 0.227 mmol) were added to **4** (50 mg, 0.0945 mmol) in a 4-mL vial. The solution turn green in 5 minutes. The mixture was stirred at RT for 3 hours. Then, one drop of the mixture was sandwiched between two glass slides for UV-vis absorption measurement. The reaction was quenched by mixing with 2 N HCl (2 mL). One drop of the CHCl₃ solution was used for UV-vis absorption measurement. A few drops were treated with concentrated HCl (12 N) and absorption spectrum was recorded. The remaining mixture was washed with 2 N HCl until the aqueous phase became colorless. After washing with water, the organic phase was condensed and vacuumed. Yield: 49.1 mg, 98.2%. Anal. found: C 71.62, H 8.97, Cl 4.27.

C₁₂-PCPDTO-Fe-20h & 48h. In a glovebox, chloroform (0.26 mL) and iron (III) chloride (6 mol. eq., 36.8 mg, 0.227 mmol) were added to **4** (20 mg, 0.0378 mmol) in a 4-mL vial. The mixture was stirred at RT for 20 hours. A small amount of solution was taken out for TLC, GPC and UV-vis absorption measurements. The reaction was continued for additional 28 hours, followed by addition of a mixture of hexanes and chloroform (4 mL, v:v = 3:1) and 2 N HCl (2 mL). After being stirred vigorously for 5

minutes, the water phase was taken out using a pipette. Washing with 2 N HCl (2 mL) was repeated two times. After washing with Na₂CO₃ solution, the organic solution was dried with MgSO₄, and condensed to 0.5 mL. MeOH (2 mL) was added to precipitate the polymer - a viscous oil. MeOH was removed using a pipette. Fresh MeOH (2 mL) was added, followed by sonication to remove any soluble impurities. The purple solution was transferred into a separation funnel, washed with 2 N HCl (2 mL) until the water phase is no longer yellow. The chloroform solution was condensed and dropped into methanol. Yield: 19.5 mg oil, 98.0%. ¹H NMR (CDCl₃, 600 MHz): δ 0.88 (s, br, 6H), 1.2-1.7 (m, 40H), 2.62 (s, br, 4H, with a shoulder peak at 2.68), no aromatic peak. ¹³C NMR spectrum was not collected since the product is a mixture of low oligomers.

C₁₂-PCPDTO-Cu-Fe. In a glovebox, compound **5** (444 mg, 0.647 mmol), copper powder (164 mg, 2.59 mmol), DMF (2 mL) and a stirring magnet were added into an 8-mL vial. The vial, tightly closed with a Teflon-lined cap, was heated with stirring in a 158 °C oil bath in a fume hood for 18 hours. ¹H NMR spectrum of the reaction mixture indicated the absence of **5** and the presence of fully and partially debrominated products of **5**. The solution in the mixture was filtered into stirred MeOH. Product was collected by filtration and dried in vacuum to yield 239 mg of sticky solid - **C₁₂-PCPDTO-Cu**. ¹H NMR spectrum of the solid (in SI) shows a peak at 6.66 ppm. From the integration ratio of this and Th-CH₂ peak, the degree of polymerization is estimated to be 4. In a glovebox, chloroform (4 mL) and iron (III) chloride (220 mg, 1.36 mmol) were added to **C₁₂-PCPDTO-Cu** (239 mg, 0.454 mmol). The mixture was stirred at RT for 2 hours 15 minutes. The reaction was then quenched with 2 N HCl. The purple solution was transferred into a separation funnel, washed with 2 N HCl (~ 2 mL a time) until the water phase is no longer yellow. The chloroform solution was condensed and dropped into methanol. The solid polymer **C₁₂-PCPDTO-Cu-Fe** was collected by filtration and washed with methanol. Yield: 230 mg, 67%. ¹H NMR (CDCl₃): δ 0.88 (s, br, 6H), 1.2-1.7 (m, 40H), 2.63 (s, br, 4H), no aromatic peak. ¹³C NMR (CDCl₃): δ 14.10, 22.83, 29.51, 29.57, 29.78, 29.86 (multiple Cs), 30.24, 131.60, 141.03, 141.79, 149.81, 184.32 ppm.

Poly(3,5-didodecyl-cyclopenta[2,1-b;3,4-b']dithiophen-4-one), C₁₂-PCPDTO-Sn. In a glovebox, compound **5** (47.8 mg, 0.0696 mmol), hexamethylditin (22.8 mg, 0.0696 mmol), Pd(PPh₃)₄ (2.24 mg, 0.00209 mmol), toluene (0.25 mL) and a stirring magnet were added into a 4-mL vial. The vial, closed with a Teflon-lined cap, was heated with stirring in a 140 °C oil bath in a fume hood. At 2.5 h, the vial was brought into the glovebox to withdraw sample for thin-layer chromatography (TLC), which showed no trace of the monomer. After an additional 4 hours 40 minutes of reaction, MeOH (2mL) was added. The mixture was sonicated for 10 minutes. The solvent, which was nearly colorless, was decanted. 37 mg of dried polymer was obtained with a yield of 100%. ¹H NMR (CDCl₃, 600 MHz): δ 0.88 (s, br, 6H), 1.2-

1.7 (m, 40H), 2.62 (s, br, 4H), no aromatic peak. ^{13}C NMR (CDCl_3 , 600 MHz): δ 14.14, 22.74, 27.01, 29.38, 29.42, 29.63, 29.66, 29.68, 29.70, 29.72, 30.13, 31.95, 130.75, 140.14, 140.96, 149.11, 183.79 ppm. Anal. found: C 74.45, H 9.57, Cl 0.36.

3. Results and Discussion

3.1 Synthesis of monomers

The synthetic steps for **C₁₂-CPDTO (4)** and its dibromo compound (**5**) are shown in Scheme 1. Upon addition of n-BuLi to **1** [25,26], metal-halogen exchange happened at the position 2, allowing the desired 2,2'-coupling reaction to happen in the presence of CuCl_2 [27] and give compound **2** in 48% yield. Treatment of **2** with n-BuLi and then water removed two bromo groups at the 5,5'-positions and gave compound **3** quantitatively. Dilithiate of compound **3** was reacted with dimethylcarbamoyl chloride, in a manner similar to the synthesis of CPDTO [8], to give **4** in 40% yield. ^1H NMR spectra of synthesized compounds **1**, **2**, **3**, and **4** are shown in Figure S1 in Supporting Information. A blown-up ^1H NMR spectrum and a photo of crystals of **4** is shown in Figure S2 to show its purity ($\geq 99\%$). Compounds **1** and **2** have nearly identical proton spectra, but rather different ^{13}C peak positions in the aromatic region (Figure S3). Compound **5** was obtained in quantitative yield from dibromination of **4** with NBS. This compound has appeared in the literature [23], but with no characterization data. Its ^1H NMR spectrum in Figure S4 shows a high purity ($>99\%$). The overall yield of our route to **C₁₂-diBr-CPDTO** is 19%, better than the 12% in the literature [23].

Scheme 1. Synthesis of **C₁₂-PCPDTO**.

3.2 Oxidation polymerization of C₁₂-CPD₂O: Dedoping of product

Since chemical oxidation with FeCl₃ has been widely used to synthesize polymers with high molecular weight from thiophene-based monomers [28-31], this method was investigated first to polymerize compound **4** using the following general procedure of reaction, workup and dedoping: **C₁₂-CPD₂O**, chloroform and FeCl₃ are mixed in a vial in a N₂ glovebox at RT (21 °C). In 5 minutes, the color of the solution changed from light brown to green. The reaction was run for varied amount of time. Dilute HCl (2 N) was added to quench the reaction. The color changed immediately from green to purple. The chloroform solution was washed two more times with 2 N HCl, and with water (1 mL×3). It was then condensed and precipitated in MeOH. No further color change was observed.

Washing with MeOH has been used as a method for dedoping poly(3-hexylthiophene)s (P3HT) prepared by oxidation with FeCl₃ [32]. Since **C₁₂-PCPD₂O** is less electron rich due to the presence of carbonyl groups, its dedoping should be easier than P3HT. The color change was an indication to us that dedoping happened immediately when 2 N HCl was added to quench the reaction. To substantiate this view and to obtain more knowledge about the doped product, a 3-hour reaction was run and UV-vis absorption spectra were recorded for the product chloroform solutions at different stages of workup: 1) the reaction mixture at the end of reaction – **Rxn_mix-doped**, 2) the reaction mixture after quenching with 2 N HCl, prior to washing with additional 2 N HCl – **Rxn_mix-Fe, 2N HCl**, 3) the reaction mixture washed with 2 N HCl twice to remove Fe³⁺, then treated with concentrated HCl – **Rxn_mix-12N HCl**, and 4) the product obtained after washing with water three times - **C₁₂-PCPD₂O-Fe-3h**.

UV-vis absorption spectra of the four samples are shown in Figure 1. **Rxn_mix-doped** shows absorption over the whole range of wavelength, clearly not a behavior of a neutral polymer. The spectrum of **Rxn_mix-Fe, 2N HCl** is totally different from that of **Rxn_mix-doped**, but same as those of the last two samples, except that the peak at 309 nm was weaker; this was presumably caused by interactions of the product with Fe³⁺, not proton, as the 309 nm peak in the spectrum of **Rxn_mix-12N HCl** is nearly as strong as that of the cleaned product, **C₁₂-PCPD₂O-Fe-3h**. So, dedoping of **C₁₂-PCPD₂O** did happen immediately when doped product was brought into contact with water (even though it is highly acidic!). Treatment of undoped **C₁₂-PCPD₂O** with concentrated HCl (12 N) did not bring any notable change to the absorption spectrum, suggesting that doping of **C₁₂-PCPD₂O** was caused by Fe³⁺, not HCl generated in the reaction.

Figure 1. UV-vis spectra of **C₁₂-PCPDTO** oxidative polymerization product chromophore at different stages of workup and purification.

3.3 Oxidation polymerization of **C₁₂-PCPDTO**: Reaction time, molecular weight (MW) and chlorination

C₁₂-PCPDTO-Fe-3h was a viscous oil, a sign of low MW. Normalized GPC elugrams of **C₁₂-PCPDTO-Fe-3h** and other **C₁₂-PCPDTOs** are shown in Figure 2. Peaks of monomer, dimer, and oligomers up to hexamers are identified. As **C₁₂-PCPDTO-Fe-3h** was only cleaned by washing with water, any unreacted monomer and other monomeric species (e.g., chlorinated) were retained. The GPC elugram only shows a trace amount of monomeric species at 17.07 minutes. However, the number average MW (M_n) is only 2493, corresponding to a degree of polymerization (DP) of 4.73. It is well known that GPC overestimates the MWs of rigid-rod polymers. A calibration curve of GPC M_n vs MALDI-TOF M_n has been obtained for P3HT [33]. Assuming that the calibration applies to **C₁₂-PCPDTO**, overestimation factors are obtained for the GPC M_n s of the **C₁₂-PCPDTOs** in Table 1 and listed in the table. Corrected M_n s and DPs are also calculated and listed in the table. The corrected DP of **C₁₂-PCPDTO-Fe-3h** is 3.53. The proton NMR spectrum is shown in Figure S5. No aromatic protons are detected. Since chlorination of product has been observed for oxidative polymerization of thiophene derivatives [32], the disappearance of aromatic protons was likely due to chlorination. This is confirmed by the result of elemental analysis (C 71.62, H 8.97, Cl 4.27) which matches the calculated element contents (C 71.83, H 9.13, Cl 4.52) of $M_{3.53}Cl_{2.5}$, where **M** is **C₁₂-PCPDTO**, suggesting that an average oligomer contains about 2.5 Cl atoms.

To study the effect of reaction time on MW, another reaction was performed and samples (**C₁₂-PCPDTO-Fe-20h** and **-48h**) were collected at 20 hours and 48 hours for GPC measurement. The results (Figure 2 and Table 1) show that M_n only increased by 12% when the reaction time was increased from 3 hours to

48 hours, but polydispersity increased from 2.16 to 4.14. In the proton NMR spectrum of **C₁₂-PCPDTO-Fe-48h** (Figure S5), aromatic protons are again absent.

Figure 2. Normalized gel permeation chromatograms of **C₁₂-PCPDTOs** prepared by different methods.

Table 1. Summary of GPC results of **C₁₂-PCPDTOs** prepared by different methods. M_p is the MW at the highest peak.

	M_w	M_n and DP (correction: factor, M_n and DP)	M_p	PD
C₁₂-PCPDTO-Fe-3h	5381	2493, 4.73 (1.34, 1860, 3.53)	2647	2.16
C₁₂-PCPDTO-Fe-20h	11472	2761, 5.24 (1.39, 1986, 3.77)	2658	4.15
C₁₂-PCPDTO-Fe-48h	11567	2793, 5.30 (1.39, 2009, 3.81)	2656	4.14
C₁₂-PCPDTO-Cu-Fe (2h15m)	6469	3271, 6.21 (1.47, 2225, 4.23)	4278	1.98
C₁₂-PCPDTO-Sn	22816	8925, 16.9 (2.19, 4075, 7.72)	13979	2.56

3.3 Oxidation polymerization of oligomers

C₁₂-PCPDTO oligomeric product was obtained from an Ullmann coupling reaction of monomer **5** in presence of copper powder. The product, **C₁₂-PCPDTO-Cu**, was a sticky solid, a tetramer on average by analysis of the ¹H NMR spectrum (Figure S5). The low DP was due to debromination of **5** and oligomers during the reaction. The side reaction has been observed in the Ullmann reaction of 3-alkoxycarbonyl-2,5-dibromothiophene [34]. **C₁₂-PCPDTO-Cu** chloroform solution was then treated with FeCl₃ for 2 hours 15 minutes. M_n of the product, **C₁₂-PCPDTO-Cu-Fe**, (3271, DP = 6.21, Table 1) was only slightly higher than that of **C₁₂-PCPDTO-Fe-48h**. In its ¹H NMR spectrum (Figure S5), no aromatic protons were detected either. Since DP only increased from 4 (based on NMR analysis) to 6.21 (by GPC) after FeCl₃ treatment, one can conclude that chlorination was the dominating reaction in the oxidation of tetramer by FeCl₃. ¹³C spectrum of **C₁₂-PCPDTO-Cu-Fe** is given in Figure S6. Only four atomic carbon peaks are

seen, consistent with the fact that halogens do not usually exert a strong electronic substituent effect [35]. Some minor aliphatic carbon peaks are seen, two of them at 30.24 and 27.27 ppm. They are not from impurities, and their intensities decrease with increasing MW (see CNMR of **C₁₂-PCPDTO-Sn**). So, they are assigned to the side chain on the two terminal thiophene moieties. The peak height at 30.24 ppm is 1/3.6 of the height of the peak at 32.14 ppm, matching pretty well the ratio of the numbers of terminal and internal dodecyl groups, 1/3.28, as calculated from the corrected DP of **C₁₂-PCPDTO-Cu-Fe**.

3.4 Oxidation polymerization of **C₁₂-CPDPTO**: Mechanism

Low MWs of **C₁₂-PCPDTOs** from oxidative polymerization by FeCl₃ were likely a consequence of chlorination of terminal thiophene units of the monomer and oligomers. To substantiate this view, let us first review the mechanism of oxidative polymerization of 3-alkylthiophene proposed by Y. Wei et al. [36] (Scheme 2 top). This mechanism was a correction of the previously proposed mechanism which consisted of a series of radical coupling reactions [36]. The key step in Wei's mechanism is electrophilic substitution of 3-alkylthiophene by an oxidized 3-alkylthiophene (a radical cation). Chlorination by combination of thiophene radical cation and chloride anion (in FeCl₃⁻ or other iron complexes) is not competitive or does not affect polymerization, since high molecular weight can be obtained (e.g., M_n 49,000 [32]).

Oxidation polymerization of 3-alkylthiophene:

Oxidation polymerization of **C₁₂-CPDPTO**:

Scheme 2. Proposed mechanism of oxidative polymerization of **C₁₂-PCPDTO** and dedoping.

Now let us try to formulate a mechanism for oxidation polymerization of **C₁₂-CPD₂O**. (Scheme 2). The reaction starts with oxidation of the monomer (**M**) to form a monomeric radical cation **M^{•+}**, which may undergo three reactions: **A** - electrophilic substitution of **M** by **M^{•+}**, **B** - combination with **Cl⁻** in **FeCl₃⁻** or other iron complexes, and **C** - radical coupling of **M^{•+}**. **C** may be ruled out as the reaction rate is highly dependent on the radical cation concentration which is expected to be low as the standard **Fe³⁺/Fe²⁺** potential (0.77 V vs SHE, standard hydrogen electrode) is significantly lower than the oxidation onset potential of **C₁₂-CPD₂O**, which is not measured as its film on the working electrode is easily dissolved by the solvent used in CV, but is expected to be higher than that of its oligomers [36] which is 0.9V above the potential of **Ag⁺/Ag** (0.7996 V vs SHE) (See cyclovoltammetry results). Also, the positive charge in **M^{•+}** is more located on the α -carbon for stabilization by resonance with the sulfur atom, and the radical is more located on the tertiary β -carbon. This further disfavors **C**. So, in Scheme 2, only **A** and **B** are shown. Presence of the carbonyl group in **C₁₂-CPD₂O** reduces its reactivity for reaction **A**, without affecting (if not boosting) the reactivity of **M^{•+}** for **B**. So, we can conclude that chlorination reaction is made competitive by the electron-withdrawing carbonyl group in **C₁₂-CPD₂O**.

The product distribution suggests that reaction rates of **A** and **B** are comparable. In this case, sizes of reactants can affect competitiveness of **A** and **B**. Activation energies are needed for both reactions, and come from kinetic energies of the reactants involved. Larger molecules are slower in motion at a given temperature. For **B**, one participant is a small molecule (**FeCl₃⁻** or **FeCl₃**), which has a kinetic energy that does not change as polymerization proceeds. For **A**, kinetic energies of all reactants decrease as PD increases. When monomers with no or mono chlorine are present, their dimerization is preferred than their coupling with dimers. This explains the observation that the trimer peak is smaller than the dimer peak for all **C₁₂-PCPD₂O-Fe** products, unusual for step polymerization reactions. This also explains why oxidation polymerization of **C₁₂-PCPD₂O-Cu** (tetramer on average) was less effective than polymerization of the monomer. The DP only increased from 4 to 6.21; this is because mainly the lightest components in **C₁₂-PCPD₂O-Cu** (dimers and trimers) contributed to MW increase, while the higher oligomers moved too slowly to activate reaction **A**, yielding the dominance to **B**.

One resonance structure of oxidized dichlorinated oligomer, **Cl₂M_n^{•+}**, is shown in Scheme 2. The **C⁺** is stabilized by resonance with both sulfur and chlorine, making **Cl₂M_n^{•+}** more stable than **M_n^{•+}**. Given the lower aggressiveness of **Cl₂M_n^{•+}**, and the lower reactivity of **Cl₂M_n** for electrophilic substitution (due to deactivation by chlorine), polymerization become extremely slow after all oligomers are dichlorinated. **Cl₂M_n^{•+}** were likely the species that gave the persistent green color observed in the reactions. Some **Cl₂M_n^{•+}** may be further chlorinated, leading to > 2 chlorine atoms per oligomer, as suggested by the elemental analysis of **C₁₂-PCPD₂O-Fe-3h**. As soon as water (in 2 N HCl) was added, hydration

stabilizes Fe^{3+} and allow $\text{Cl}_2\text{M}_n^{++}$ to be reduced (dedoped) by Fe^{2+} . The dedoping is fast as **C₁₂-PCPDTO** has a high oxidation potential.

3.5 Polymerization of **C₁₂-diBrCPDTo** using hexamethylditin

Polymerization of **5** in presence of hexamethylditin and $\text{Pd}(\text{PPh}_3)_4$ was identified to be a more effective polymerization method. The reaction has been used by Jenekhe [37] to polymerize a thiophene-based dibromo compound. In this type of reaction, a dibromo compound first reacts with hexamethylditin to undergo a metal-halogen exchange [38] to give an difunctional intermediate, which polymerizes via the Stille coupling reaction [37]. The resulting polymer, **C₁₂-PCPDTo-Sn**, has an M_n of 8925, corresponding to a DP of 16.9, and an M_w of 22816. The corrected M_n and DP are 4075 and 7.72. The elemental analysis of the polymer for C, H, and Br shows a composition of 74.45, 9.57 and 0.36, respectively. The result is satisfactory for a polymer with a formula of $\text{M}_{7.72}\text{Br}_{0.31}$ (C 74.74, H 9.55, Br, 0.61), where **M** is the monomer. So the polymer is likely ended with 0.31 bromine per polymer molecule. No trace of trimethyltin was detected in the NMR experiment.

It is noted that the GPC elugram (Figure 2) shows a bimodal MW distribution for **C₁₂-PCPDTo-Sn**. To find a reason for this behavior, literature search was done on this issue for conjugated polymers synthesized via the Stille reaction. However, no literature on this topic has been found, and MW distribution curves are usually not presented in published papers. One paper studied the homo-coupling issue in a Stille co-polymerization using different catalysts [39]. Multimodal distribution was observed in MALDI-TOF analysis of certain polymers, and was attributed to homocoupling - a common side reaction in Stille reactions [39]. However, in the polymerization for **C₁₂-PCPDTo-Sn**, there is only one monomeric unit (**C₁₂-CPDTo**), thus homocoupling is not an issue.

To develop an explanation for the bimodal MW distribution, let us try to understand the reaction process. The first step in the reaction was Br - SnMe_3 exchange. This produces two new monomeric species. So, three monomeric compounds were present at the early stage of the reaction: **Br-M-Br**, **Br-M-Sn**, **Sn-M-Sn**, where Sn is SnMe_3 . **Br-M-Sn** is the product of the exchange reaction and is certainly more stable than the other two due to a nice combination of e-rich Sn and electronegative atom Br. Coupling of these species gave **Br-M₂-Br**, **Br-M₂-Sn**, and **Sn-M₂-Sn**. Coupling would continue to produce oligomeric species: **Br-M_n-Br**, **Br-M_n-Sn**, and **Sn-M_n-Sn**. Among them, **Br-M_n-Br** and **Sn-M_n-Sn** are more reactive as **Br-M_n-Sn** is more stable. They would mostly react with the major species **Br-M_n-Sn** to produce **Br-M_n-Br** and **Sn-M_n-Sn** again, but with higher MWs. As a result, the fraction of the highest molecular weight was produced from the reactions involving **Br-M_n-Br** and **Sn-M_n-Sn**. Since they were the minor species from the beginning and their percentage kept dropping due to reactions between themselves (**Br-M_n-Br** and **Sn-**

M_n -Sn), the highest MW fraction is very small, shown as a shoulder peak on the high MW slope of the main GPC peak of **C₁₂-PCPDTO-Sn**. Indeed, the area of the shoulder peak is estimated to be only 8.5% of the total area.

In the ^1H NMR spectrum (Figure 3), the aromatic proton peak can hardly be seen and Me_3Sn signal (at 0.3 ppm) is not detected at all. ^{13}C NMR spectrum shows only five aromatic carbon peaks (Figure 4) as expected, with a peak pattern same as that of **C₁₂-PCPDTO-Cu-Fe** but with small differences in the chemical shifts presumably due to difference in the terminal functionalities of the two polymers. Again, minor peaks are seen at 30.14 and 27.02 ppm and are attributed to the side chains on the two terminal thiophene moieties. The peak height at 30.14 ppm is 1/6.37 of the height of the peak at 31.96 ppm, matching well with the ratio of the numbers of terminal and internal dodecyl groups, 1/6.72, as calculated from the corrected DP of 7.72. **C₁₂-PCPDTO-Sn** was soluble in common organic solvents such as THF, chloroform, etc. In chloroform, the solubility is greater than 40 mg/mL.

Figure 3. ^1H NMR (CDCl_3 , 600 MHz) spectrum of **C₁₂-PCPDTO-Sn**.

Figure 4. ^{13}C NMR (CDCl_3 , 600 MHz) spectrum of **C₁₂-PCPDTO-Sn**.

3.6 Thermal and electrochemical properties

No melting peak was detected in the DTA thermogram of **C₁₂-PCPDTO-Sn** (Figure 5), indicating an amorphous nature of the polymer, which explains its unusually high solubility. An exothermic process of the polymer occurred at 242 °C, but 5% weight loss did not happen until 372 °C. This suggests that the initial decomposition was of a type of addition reaction involving unsaturated carbons. The polymer has an oxidation potential of -5.98 eV and a reduction potential of -3.52 eV and electrochemical energy gap (E_g^{EC}) of 2.46 eV, as measured by a cyclovoltammeter (Figure 5). The CV curves of **C₁₂-PCPDTO-Cu-Fe** are essentially same. CV of **C₁₂-PCPDTO-Fe-48h** was not performed as it was an oil and its film can be easily dissolved by the CV solvent MeCN. The E_g^{EC} of **C₁₂-PCPDTO-Sn** is greater than the measured optical bandgap (E_g^{opt} , in next section) by 0.61 eV, much larger than the commonly observed difference of 0.1-0.2 eV between the two methods [40,41], indicating the presence of large over-potentials in the electrochemical redox reactions. Similar differences (up to 0.55 eV) have been reported for polythiophenes with bulky alkyl side chains [41]. Over-potential was also found in oxidative polymerization of 3-substituted thiophene [42,43] and dithieno[3,2-b:2,3-d]pyrroles [44] to increase with increasing alkyl chain length. For **C₁₂-PCPDTO**, the exceptionally large difference between E_g^{EC} and E_g^{opt} , is due to both the length of the alkyl chains and the highly nonplanar nature (see the calculation section) of the polymer backbone which makes close contact of π -conjugated system with electrode surface physically impossible.

Figure 5. DTA, TGA and cyclovoltammograph of **C₁₂-PCPDTO-Sn**.

3.7 Optical properties

UV-vis absorption spectra of chloroform solutions of **4**, **5**, **C₁₂-PCPDTO-Sn** and a film of the polymer, as well as a photograph of the solutions, are shown in Figure 6. The chloroform solution of monomer **4** is already pink-colored and has an absorption peak wavelength of 499 nm, longer than that of regioregular poly(3-hexylthiophene) (456 nm) [13]. Substitution by two bromo groups at 2,6-positions of **C₁₂-CPDTO** causes a red shift in λ_{max} by 32 nm. The polymer solution has an absorption peak at 552 nm and an optical bandgap of 1.85 eV, much greater than the optical bandgap reported for the film of unalkylated PCPDTO [10]. From **C₁₂-CPDTO** to **C₁₂-PCPDTO**, the absorption peak wavelength red-shifts by only 53 nm (0.24 eV). The small red shift is partially due to twisting of neighboring aromatic rings caused by head-to-head side chains. This is a common reason for reduced λ_{max} of polymer optical absorption. For example, regiorandom P3HT, which contains head-to-head linkages, exhibits a UV-vis absorption λ_{max} 22 nm shorter than that of regioregular P3HT [13]. More reduction in λ_{max} is expected for **C₁₂-PCPDTO** since every linkage is head-to-head. As will be shown later, DFT-calculated dihedral angles for dialkylated CPDTO oligomers are close to 90°. UV-vis absorption spectrum of the film shows no red shift in peak wavelength (Figure 6), indicating the lack of strong interchain interaction in the solid state. Such interaction in regioregular (RR) P3HT caused a reduction of 0.40 eV in bandgap from its chloroform solution to film [13].

UV-vis absorption spectra of chloroform solutions of **C₁₂-PCPDTO-Cu**, **-Cu-Fe**, and **Fe** are presented in Figure S7. Peak wavelengths, absorption cutoff wavelengths, bandgaps, molar extinction coefficients and intensities at the long wavelength peak (λ_{max}) relative to the short wavelength peaks are listed in Table 2. Except **C₁₂-PCPDTO-Cu**, which has a DP = 4 and thus slightly blue-shifted, all **C₁₂-PCPDTOs**, have essentially the same λ_{max} and bandgap (550-552 nm, 1.85 eV). **C₁₂-PCPDTO-Sn** and **-Fe-48h** have very similar molar extinction coefficient (ϵ), indicating that ϵ is nearly saturated at the pentamer level. All **C₁₂-PCPDTOs** have relatively weaker absorption for the long wavelength peak, and its extinction coefficient is much lower than that of regioregular P3HT (Table 2). It is worth noting that the film of **C₁₂-PCPDTO-Sn** showed significant improvement in absorption at the long wavelength peak. A more pronounced preferential enhancement of the long wavelength absorption in solid state is found for PCPDTO film which shows an absorbance ratio of 1:2 for the long and short wavelength peaks [10], as compared to the ratio of 1:3.52 for the film of weakly interacting **C₁₂-PCPDTO-Sn**.

Figure 6. UV-vis absorption spectra of **4**, **5** and **C₁₂-PCPDPTO-Sn**. Intensities at the long wavelength peak wavelengths are normalized.

Table 2. Peak wavelengths, absorption cutoff wavelengths, bandgaps, molar extinction coefficients and intensities at the long wavelength peak (λ_{max}) relative to the short wavelength peaks.

Chloroform solutions	$\lambda_{\text{max}}/\text{nm}$	$\lambda_{\text{cutoff}}/\text{nm}$	E_g/eV	$\epsilon, \text{L/mol.cm}$	Rel. intensity at λ_{max}
C₁₂-CPDPTO	499	617	2.01	1370	1:2.88
C₁₂-diBrCPDPTO	531	655	1.89	2065	---
C₁₂-PCPDPTO-Fe 20h	550	670	1.85	---	1:5.84
C₁₂-PCPDPTO-Fe 48h	552	670	1.85	3748	1:5.54
C₁₂-PCPDPTO-Cu	539	660	1.88	---	---
C₁₂-PCPDPTO-Cu-Fe	552	670	1.85	---	1:5.23
C₁₂-PCPDPTO-Sn film	552	670	1.85	3800	1:5.40
	550	670	1.85		1:3.52
P3HT (Aldrich)	446	552	2.24	8070	

3.8 Density functional theory (DFT) Calculation

To confirm the influence of side chains on coplanarity and bandgap of alkylated PCPDPTO, structural optimization was implemented in Gaussian09.21 for oligomers of alkylated CDPTO up to 6 repeat units (Figure 7) using the B3LYP functional and standard split valence plus polarization basis set 6-31G(d, p) in the DFT formalism. Methyl groups are commonly used [45-47] as the side groups in such calculations to save computation time. Use of side chains longer than three carbons is not necessary as has been shown in the calculation of head-to-head alkylthiophene oligomers [48]. In this work, ethyl groups were chosen to provide good representation of long alkyl chains and to avoid frequent failure in computation associated with larger structures. A rough estimate of theoretical E_g is the energy difference between the HOMO and LUMO energies obtained from DFT calculations [49,50].

The calculated values of HOMO/LUMO energy and dihedral angles are presented in Table 3. The E_g values are plotted in Figure 7 as functions of $1/n$. E_g of polymer C_2 -PCPDTO was obtained to be 2.10 eV as the intercept of the linear fit of the data points according to the free-electron molecular orbital model (FEMO) [51]. The dihedral angle between two central CPDTO units in each oligomer is 106.6° for the dimer, indicating that two CPDTO units are nearly perpendicular. The angle increases as the oligomer gets longer, but remains highly non-planar even for the hexamer.

Table 3. DFT calculation results for four series of oligomers. The dihedral angle is the angle between two central CPDTO units in each oligomer.

	HOMO (eV)	LUMO (eV)	E_g (eV)	Dihedral angle
C_2 -(CPDTO) $_n$				
n=1	5.83	2.71	3.12	
n=2	5.73	2.90	2.83	106.6
n=3	5.53	3.10	2.43	118.4
n=4	5.50	3.16	2.34	119.9
n=5	5.51	3.20	2.31	119.6
n=6	5.47	3.23	2.24	121.9
n= ∞			2.10	

Figure 7. Structures of C_2 -CPDTO oligomers used in the computational study, and plots of calculated energy gaps of $(C_2\text{-CPDTO})_n$ versus $1/n$, where n is the number of repeat units and linear fitting of the data points of each series.

4. Conclusions

We have explored different methods for the synthesis of the first soluble CPDTO homopolymer, poly(3,5-didodecyl-cyclopenta[2,1-b;3,4-b']dithiophen-4-one) or **C₁₂-PCPDTO** via chemical oxidation, Ullmann coupling and Stille reaction. It is found that high molecular weight could not be achieved by oxidation of **C₁₂-CPDTO** using FeCl₃, in contrary to oxidation of 3-alkylthiophene. Chlorination of oligomers happened during the oxidation polymerization and caused the polymerization to practically terminate. A mechanism is proposed and described in detail to provide rationales for low MW, worse performance of oligomers in oxidation polymerization, and ease of dedoping. Dibromo C₁₂-CPDTO was effectively polymerized in presence of hexylmethylditin and Pd⁰ catalyst via a Stille reaction. The polymer was found to have an optical bandgap as high as 1.80 eV in chloroform solution, as well as in film. DFT calculation was conducted to estimate the dihedral angles in C₂-CPDTO oligomers. The dihedral angles are closer to 90° than to 180°, suggesting that the polymer is highly nonplanar. As a result, side chains on the polymer are sticking out in all directions, making it impossible for polymer chains to interact with electrode surface in the electrochemical measurement or π -stack in the film. Consequently, an exceptionally large difference between electrochemical bandgap and optical bandgap was observed, and the optical bandgap of **C₁₂-PCPDTO** in solution and film is substantially greater than that of electrochemically synthesized unalkylated PCPDTO film.

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GRAPHICAL ABSTRACT

Synthesis and Characterization of Poly(3,5-didodecyl-cyclopenta[2,1-b;3,4-b']dithiophen-4-one)

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Different methods have been explored to synthesize the first soluble CPDТО homopolymer, poly(3,5-didodecyl-cyclopenta[2,1-b;3,4-b']dithiophen-4-one), C₁₂-PCPDТО. Chemical oxidation of monomer by FeCl₃ only gave oligomers, but Pd-catalyzed reaction of dibromo monomer and hexamethylditin yielded C₁₂-PCPDТО with a M_w of 22,816 and a polydispersity of 2.56. The polymer was characterized by ¹H and ¹³C NMR spectroscopy, gel permeation chromatography, differential thermal analysis, cyclovoltammetry, and UV-vis absorption.