Towards conjugated polymers with low exciton binding energy

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Chapter 4

Synthesis of thieno[3,4-b]thiophene-based 2-D conjugated polymers featuring a donor backbone and pendant acceptor groups

ABSTRACT Control of the chemical quality of conjugated polymers offers fundamental support for the development of photovoltaic materials. The successful utilization of new design/synthesis strategies may need dedicated chemistry exploration. This chapter discusses the synthesis of a two-dimensional conjugated polymer comprising a polythiophene backbone, a pendant thieno[2,3-c]pyrrole-4,6-dione acceptor, and a thieno[3,4-b]thiophene bridge. 2,5,8,11-Tetraoxadodecyl (TEG) side-groups are used as solubilizing side chains. It is found that in spite of efficient chain growth, the as-presented one-pot Suzuki-Miyaura homopolymerization (see Chapter 2) persistently introduces unassignable impurities to the polymer (P1). Although an exact explanation is not pursued, it is hypothesized that the oxygen atoms in the TEG chains chelate the boron atoms in the reaction system of Suzuki-Miyaura homopolymerization. This hypothesis is supported by an experiment with a control polymer (P2) where alkyl chains were employed as solubilizing side chains, where the problem with P1 was well eliminated, as evidenced by our mass spectra analysis. Stille copolymerization is used to yield the desired 2-D conjugated polymer (CC1). The present work hints to important aspects of bis(pinacolato)diboron-promoted homopolymerization regarding its potential drawbacks, which might limit its application scope.
4.1 Introduction

Two-dimensional (2-D) conjugated polymers have been studied as candidates for organic photovoltaics in the past two decades, alternative to one-dimensional donor-acceptor conjugated polymers. In these 2-D polymers, the acceptors are configured perpendicularly to the donor backbone. On the basis of precedent developments, 2-D photovoltaic polymers may fall into the following categories (for examples of structures, see Figure 6 in Chapter 1 and Figure 1 in Chapter 3): (i) Polythiophene backbones with pendant groups ranging from thiophenic or phenyl moieties,\(^1,2,3\) with an ethylenic linker between the backbone and the pendant groups. (ii) Polythiophene backbones with pendant groups such as phenanthrenyl-imidazole, with the pendant groups directly installed on the 3-position of the backbone thiophenes;\(^4,5,6,7,8\) (iii) Fluorene and triphenylamine based backbones with various pendant acceptors,\(^9,10,11,12,13,14\) where an ethylenic linker is used as the backbone-pendant group bridge; (iv) A backbone based on more extensively conjugated moieties (e.g. benzothiadiazole) in conjugation to ethylenic linker bridged acceptors on thiophene units.\(^15,16,17,18,19\) The synthesis of these polymers is generally done by Suzuki or Stille cross-coupling promoted copolymerization of two bifunctional monomers. In cases where acceptors such as malononitrile were employed,\(^10\) authors take the advantage of Knoevenagel condensation by preparing a polymer precursor, which is then functionalized with the corresponding acceptors.

The present chapter discusses the design and synthesis of a two-dimensional conjugated polymer based on a thieno[3,4-b]thiophene bridge between a polythiophene backbone and a thieno[2,3-b]pyrrole-4,6-dione acceptor, as shown in the following figure:

![Figure 1](image)

**Figure 1.** Chemical structure of polymer CC1 comprising a polythiophene backbone, thieno[2,3-c]pyrrole-4,6-dione acceptor, and a thieno[3,4-b]thiophene bridge.

Originally, the pursued structure was one similar to CC1, but absent of the thiophene ring on the right side of the repeating unit. It starts with the convergent synthesis of the monomer with cross-conjugated thieno[3,4-b]thiophene and thieno[2,3-b]pyrrole-4,6-dione. Motivated by the work presented in Chapter 2, a homopolymerization of the cross-conjugated monomer was conducted. Structural characterization of the polymer indicated the problem of bis(pinacolato)diboron-promoted homopolymerization of
monomers containing TEG side chains being hindered by these substituents. Although polymers of improved chemical integrity are attainable with Stille copolymerization, the presented synthetic work provides strong evidence that the application of bis(pinacolato)diboron promoted homopolymerization might be side-chain sensitive. To this end, we proposed and executed the strategy which used one extra thiophene to furnish a Stille cross-coupling polycondensation, yielding CC1 with decent chemical quality.

4.2 Synthesis

4.2.1 Monomer synthesis

Scheme 1 presents the synthesis of the monomer for the construction of the two-dimensional conjugated polymers.
Intermediate 4 was synthesized in four steps from 3,4-dibromothiophene. Compound 2 was found to be rather susceptible to oxidation, even at low temperatures. Therefore, double TMS protection (3) was necessary before further chemical manipulation. Compound 3 was obtained through a one-pot reaction, without removal of the possible mono TMS-protected impurity. In the last step, compound 3 was converted to the target compound 4 by lithiation and subsequent quenching with trimethyltin chloride. The acceptor unit 8 was synthesized according to literature methods, starting from 2,3-dibromothiophene. While compound 11 appeared to be fairly stable to ambient conditions and normal purification processes, the resulting key intermediate 12 turned out to be quite unstable, making it impossible to purify it by column chromatography (both silica and Al₂O₃ were tried as stationary phases).

In the case of brominating 11 with N-bromosuccinimide (NBS), compound 12 was formed in high yield, but the removal of succinimide residue proved to be rather difficult as a result of the incompatibility of 12 with column chromatography. We also found that these succinimide residues tend to adversely affect the subsequent Stille cross-coupling between 12 and 10, which gave 13 only in extremely low yields. Fortunately, switching from NBS to bromine for the bromination of 11 afforded high quality of 12 in good yield, using a simple water-washing procedure and eliminating the need for any other purification procedure. Compound 13 was thus synthesized from the cross-coupling of 10 and 12 in a decent yield. Compound 13 was readily converted into the final target monomer 14 by double bromination with NBS.
4.2.2 Synthesis of 2-D conjugated polymers

The successful one-pot homopolymerization of dibrominated monomers in Chapter 2 offered a motivation to synthesize a homopolymer with bis(pinacolato)diboron as the condensation reagent, as shown in Scheme 2.

Scheme 2. One-pot Suzuki-Miyaura homopolymerization of monomer 14 to polymer P1.

The above polymerization proceeded overnight at toluene/DMF refluxing temperature to yield a purple-blue viscous solution. Soxhlet extraction with methanol, acetone and then hexane removed low-molecular weight fractions and impurities. Finally, soxhlet extraction with chloroform yielded a deep purple product showing an exceptional solubility, not only in chloroform, but also in less polar solvents such as THF. This solubility feature is likely to be caused by the installation of TEG chains. The UV-vis absorption spectrum of a solution of P1 in chloroform is shown in Figure 2.

Figure 2. UV-vis absorption spectrum of the homopolymerization result from monomer 14.
Different from a typical donor-acceptor alternating conjugated polymer, the as-obtained 2-D polymer showed a strong and broad absorption covering the entire visible spectrum from 400 to 700 nm, with an optical bandgap of 1.69 eV. Note that other 2-D conjugated polymers were reported to show narrower absorptions but similarly possess strong absorptions in the visible region. Furthermore, a HOMO energy level of −5.0 eV was derived from cyclic voltammetry measurements (Figure 3). In conjunction with the optical bandgap, this yields a LUMO energy level of −3.31 eV. These preliminary results indicated that this material has the right frontier orbital energies for application in polymer solar cells with fullerene derivatives as the electron acceptor.

**Figure 3.** Cyclic voltammogram (oxidative cycle) of polymer P1 as a drop-cast film. The film was dropcast from a THF solution (~1 mg/mL). A 0.1 M solution of tetrabutylammonium hexafluorophosphate in anhydrous acetonitrile was used as the electrolyte. Scan rate: 50 mV/s.
One of the major advantages of the bis(pinacolato)diboron promoted homopolymerization is that it can generate high quality polymers with well-controlled end groups. In order to check whether such a clean homopolymerization had also occurred for polymer P1, we performed MALDI-TOF experiments on the as-obtained polymer, with 2-((4-hydroxyphenyl)diazenyl)benzoic acid as the matrix. The spectrum is shown in Figure 4.

![Figure 4. MALDI-TOF spectrum of homopolymer P1. with 2-((4-hydroxyphenyl)diazenyl)benzoic acid as the matrix. Peaks 1-6 refer to oligomers comprising 3-8 repeating units.](image)

Figure 4 reveals a number of things regarding the bis(pinacolato)diboron-mediated homopolymerization: (i) The polymerization has proceeded successfully; (ii) There are clearly “regularly repeating” peaks (1 – 6), suggesting oligomers of different lengths; (iii) Most importantly, all sets of peaks appear as a cluster of peaks absent of sufficient peak-to-peak resolution, notably different from what one would expect from a normal mass spectrum; (iv) the resolution of each peak is different from each other, i.e., the first peak is resolvable in terms of the multiple side peaks, but as soon the molecular weight increases, the limited resolution tends to diminish further; (v) the width of a set of peaks can be as wide as 700 Da (peak 4), (vi) assuming each broad set of peaks is based on one oligomer, for example, peak 1 contains multiple peaks, and each of these peaks is a trimer attached with a different amount of exotic species. Then, as the molecular weight increases, the deviation between the center of the broad peak and the expected molecular weight of the corresponding oligomer keeps increasing.

The MALDI-TOF measurements suggest a successful polymerization with efficient chain growth, which indicates the backbone growth has been proceeding as expected. The results also reveal a complex situation regarding the chemical quality of the polymer obtained by this method. It is speculated that TEG chains are attracting a species from the reaction medium. With a longer polymer chain, the presence
of increasingly more TEG chains in a single polymer is able to attract more of this species. The exact identity of this species is unknown within the current study scope, but it should be either potassium ions, or the boronate side product which is produced within each Suzuki cycle. The first possibility with K$^+$ may be eliminated based on the simple isotope composition of potassium, thus not expected to create such a broad cluster of peaks (Figure 4). Also note that by treating the polymer with crown ether 18-crown-6, no change to the quality of the polymer sample was observed. This further puts the second possibility of binding with boronate to the front. This may be plausible with an oxygen–boron interaction. We did not design further experiments to prove if these broad clusters of peaks are caused by the adsorption of boronate species by the oxygen atoms in the TEG chains.

Nevertheless, the MALDI-TOF results tend to suggest that the as-presented homopolymerization is unfortunately not compatible with monomers containing TEG chains. In order to get evidence for this hypothesis, we designed a control polymer P2, which was obtained from the homopolymerization of a similar monomer with the same backbone of 14, but all TEG chains are replaced with alkyl chains. Scheme 3 shows the synthetic details of P2:


The synthesis of P2 started from obtaining the key intermediate 18. Compound 18 was synthesized with 3 steps starting from 3-bromo thiophene (15), which was first transformed to 3-decyl thiophene (16) by coupling with the corresponding Grignard reagent. 16 was then brominated into 17, which offered selective lithiation for the generation of 18. Compound 18 was then coupled with 12 with the same procedures used for the synthesis of compound 14, and this eventually led to the synthesis of dibrominated monomer 20. Finally, 20 was subjected to a bis(pinacolato)diboron-mediated homopolymerization, giving the homopolymer P2. P2 was purified by a conventional Soxhlet extraction procedure, in which methanol and acetone were first used as extraction solvents to remove low-
molecular weight fractions, and then hexane and chloroform were used in sequence to collect samples for mass spectra characterization. The MALDI-TOF spectrum of P2 is presented in Figure 5.

![MALDI-TOF spectrum](image)

**Figure 5.** MALDI-TOF spectrum of homopolymer P2 (chloroform fraction), with trans-3-indoleacrylic acid as the matrix.

As shown in Figure 5, the employment of alkyl chains immediately eliminated the peak broadening phenomenon in Figure 4, despite the presence of other minor impurities. This contrast suggests that TEG chains can be problematic for bis(pinacolato)diboron mediated polymerizations, at least with the given structure design. To this end, Stille copolymerization was brought forward, in order to obtain the 2-D polymer with decent chemical purity. To do this, we polymerized monomer 14 with one thiophene unit, as shown in Scheme 4.

![Scheme 4](image)

**Scheme 4.** Copolymerization of monomer 14 and bis-stannylated thiophene to copolymer CC1.
This copolymerization gave polymer CC1 as a deep-purple solid in a decent yield of 85%. As mentioned before, homopolymer P1 from the homopolymerization showed a remarkable solubility in THF at room temperature. It is worth noting that adding one repeating thiophene unit into the backbone with Stille cross-coupling copolymerization, however, has completely eliminated the THF-solubility of the polymer, even at elevated temperatures. This observation might serve as an indirect proof that the impurity in Figure 4 is related to boronate species, which would confer many more methyl groups for better solubility. The copolymer resulted from the above polymerization is characterized with MALDI-TOF for chemical integrity, as shown in Figure 6 (top).

![Figure 6](image.png)

**Figure 6.** MALDI-TOF spectrum (top) of CC1 synthesized from Stille copolymerization and a zoom-in of peak 1 (bottom). The peak sets A–D represents oligomers based on sequentially increasing numbers of repeating unit 13 (see Scheme 1). The highest peaks in all peak sets are assigned to oligomers end-capped with a thiophene on each side, based on the m/z values. The other side peaks represent oligomers of various end-cappings, such as Br, SnMe3, and/or thiophene on one side. Dithranol was used as the matrix (top).
The spectrum of the resulting copolymer is clearly free of broadened peaks. Each set of peaks consists of 3 peaks (for example, the first set of peaks contains 1, 2 and 3, the second set of peaks contains 4, 5 and 6.). A, B, C and D are regular repetitions after the first two sets of peaks. While Stille polymerization is known for its poor control of end groups, peaks 1-6 are readily assigned to oligomers of different end groups including hydrogen and bromine atoms and trimethyltin groups. Note that methyl transfer is also observed (Figure 6, bottom), in good accordance with the observation described in Chapter 2.

4.3 Discussion

Thieno[3,4-b]thiophene has been employed as the bridge between the acceptor and donor segments in the conjugated polymer CC1. Such a design is less likely to cause notable backbone torsion in comparison to the installation of acceptor moieties directly on the third position of thiophene units, as seen in previous reports on 2-D conjugated polymers. While bis(pinacolato)diboron promoted polycondensation has enabled an efficient polymerization of a dibrominated monomer, it unfortunately yielded a polymer with unassignable impurities, as discussed in previous paragraphs. Although the detailed mechanism of the peak broadening in Figure 3 is not scrutinized, one plausible reason is that TEG chains have adsorbed some boronate species from the reaction medium. It would be interesting to precisely understand the chemistry involved here in the future. We would like to note that despite its well-known problem of poor-end group control, Stille copolymerization has proven to be a preferable synthetic route for conjugated polymers featuring TEG chains.
4.4 Conclusions

A complete understanding of a new design/synthetic strategy, both on its upside and downside, is highly valuable to the progress of material evolution. Here, we have studied the synthetic challenges when bis(pinacolato)diboron-mediated homopolymerization meets TEG chains. The unique merits brought by installing TEG chains on molecules have now been well seen and widely applied. In our design of a 2-D conjugated polymer, TEG chains are included as solubilizing side chains. While bis(pinacolato)diboron has promoted an effective polycondensation of the macromonomers, we also spotted unassignable impurities. The apparent existence of these impurities was visualized by the unusually broad peaks in MALDI-TOF spectra of the as-obtained polymer. While the exact nature of the impurities is not clear yet, we postulate that it has likely originated from the oxygen-boron interaction between TEG chains and boronates. This postulate is supported by a control experiment where peak-broadening is completely eliminated, when TEG chains were replaced with conventional alkyl chains. In this sense, conventional Stille copolymerization was employed to produce the 2-D conjugated polymer, with slight structure modification to the originally designed polymer structure.
4.5 Experimental

Materials and methods

All reagents and solvents were purchased from commercial sources and used without further purification, unless otherwise indicated. UV/Vis measurements were carried out on a Jenway 6715 spectrometer in 1-cm fused quartz cuvettes with concentrations of 0.03–0.1 mg/mL in CHCl₃. MALDI-TOF spectra were taken on a Biosystems Voyager apparatus. Samples were prepared by mixing the matrix (~10 mg/mL in THF) and polymer sample (~1 mg/mL in THF or CHCl₃) at room temperature in a 3:1 volume ratio. All measurements were performed in positive ion mode. NMR spectra were measured using a Varian AMX400 (400 MHz) instrument at 25 °C. Cyclic voltammetry measurements were carried out with an Autolab PGSTAT100 potentiostat in a three-electrode configuration. The working electrode was a glass carbon electrode, the counter electrode was a platinum wire, and the pseudoreference was an Ag/AgCl wire externally calibrated against ferrocene (Fc/Fc⁺). Polymer films were dropcast from a THF solution at a concentration of ~1 mg/mL on the working electrode and allowed to dry.

Synthesis

((4-Bromothiophen-3-yl)ethynyl)trimethylsilane (1) A flame-dried, 250-mL, three-neck flask equipped with a water cooler was loaded with Pd(PPh₃)₄ (500 mg, 0.43 mmol) and CuI (150 mg), followed by sufficient degassing. Dry THF (100 mL) and distilled triethylamine were mixed with 3,4-dibromothiophene (7 mL, 63 mmol) and trimethylsilylacetylene (11 mL, 72 mmol) in a separate Schlenk flask, which was briefly degassed at −20 °C. After warming up to room temperature, the as-degassed solvent/reactant mixture was transferred into the three-neck flask via cannula. The reaction was then allowed to slowly warmed up to 80 °C and stirred overnight. After cooling down to room temperature, the solvent was removed under reduced pressure and the oil-like residue was dissolved in diethyl ether (250 mL) and washed with water (250 mL). The organic phase was collected and concentrated, and the residue was subjected to silica gel chromatography with pentane as eluent, yielding ((4-bromothiophen-3-yl)ethynyl)trimethylsilane (1) as a colorless oil (10 g, 67% yield). ¹H NMR (400 MHz, CDCl₃) δ 7.46 (d, J = 4 Hz, 1H), 7.21 (d, J = 4 Hz, 1H), 0.26 (s, 9H).

Thieno[3,4-b]thiophene (2) A 250 mL, three-neck Schlenk flask was flamed, and equipped with a solid-addition arm charged with elemental sulfur (0.789 g, 24.61 mmol). Compound 1 (5.8 g, 22.37 mmol) was then added to the flask, followed by the transfer of dry diethyl ether (100 mL). The system was then allowed to cool down in an ethanol/liquid nitrogen cold bath, after which the system was briefly degassed. n-BuLi (24.61 mmol, 10 mL) was then added dropwise into the reaction flask. The sulfur was poured into the reaction system 1 hour after the addition of n-BuLi. The reaction was maintained in the cold bath for 70 min, during which period the cold bath slowly warmed up to 30 °C. The reaction
mixture was then poured into a separation funnel with ice-cooled brine (200 mL). After a quick washing, the aqueous phase was collected and placed on a heater at 70 °C for 1 h. This aqueous system was then extracted with diethyl ether (250 mL), and the organic phase was collected and concentrated. The residue was purified with silica gel chromatography (pentane as eluent) to yield thieno[3,4-b]thiophene as a colorless oil (3.14 g, 82%). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.34 ($d$, 8 Hz, 1 H), 7.33 ($s$, 1 H), 7.25 ($dd$, 8 Hz, 1 H), 6.93 ($dd$, 8 Hz, 1 H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 147.59, 139.32, 132.38, 116.75, 111.59, 110.57.

(Thieno[3,4-b]thiophene-4,6-diyl)bis(trimethylsilane) (3) A flame-dried, 100 mL, three-neck flask was charged with thieno[3,4-b]thiophene (1.25 g, 8.91 mmol) and dry THF (50 mL). The reaction flask was then cooled down to −80 °C using an ethanol/liquid N$_2$ cold bath. n-BuLi (2.5 M, 3.92 mL) was then added dropwise. The reaction was kept below −50 °C for 1 h, afterwards chlorotrimethylsilane (1.25 mL) was added all at once. The cold bath was then removed. After 1 h, the reaction mixture was poured into water (250 mL) and extracted with diethyl ether (200 mL). The organic phase was collected and thoroughly concentrated to give a yellowish oil, which was further purified by silica gel chromatography, affording the product as a colorless oil (1.8 g, 71%). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.44 ($d$, 8 Hz, 1H), 7.03 ($d$, 8 Hz, 1H), 0.41 ($s$, 9H), 0.40 ($s$, 9H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 137.88, 132.52, 129.08, 128.28, 125.36, 117.52, 0.22, −0.51.

(2-(Trimethylstannyl)thieno[3,4-b]thiophene-4,6-diyl)bis(trimethylsilane) (4) (Thieno[3,4-b]thiophene-4,6-diyl)bis(trimethylsilane) (0.853 g, 3 mmol) was transferred into a flame-dried, 100 mL, three-neck flask, which was connected to a nitrogen Schlenk line. Dry THF (50 mL) was then added via a cannula into the reaction flask. An ethanol/liquid nitrogen cold bath was used to cool down the reaction system to −80 °C. n-BuLi (3.3 mmol) was then added dropwise. After 15 min, chlorotrimethylstannane (3.3 mmol) was added into the reaction flask via a syringe, after which the cold bath was removed. After 15 min, the reaction mixture was poured into water (200 mL), and washed with diethyl ether (250 mL). The organic phase was collected and dried over Na$_2$SO$_4$. After filtering, the filtrate was concentrated under vacuum to yield (1.34 g, 97% yield) 4 as yellow oil. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.03 (s, 1H), 0.40 (s, 9H), 0.39 (s, 9H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 157.47, 152.68, 148.15, 130.20, 128.00, 124.79, 0.27, −0.51, −8.53.

Thiophene-2,3-dicarboxylic acid (5) 2,3-Dibromothiophene (5 g, 20.67 mmol) and dry THF (50 mL) were loaded into a flame-dried, 250-mL, three-neck flask, which was then cooled to −80 °C with an ethanol/liquid N$_2$ cold bath. Two balloons filled with dry CO$_2$ (2 L, 1 atm) were sealed and connected to the reaction flask. n-BuLi (12.92 mL, 20.67 mmol) was then added dropwise within 3 min. After 40 min, CO$_2$ was released into the reaction flask. The cold bath was then removed. After 1 h, the reaction mixture was poured into water with an excess of aqueous HCl. The mixture was then extracted with diethyl ether (250 mL). The organic phase was collected and dried over Na$_2$SO$_4$. The ether solution was
filtered and thoroughly concentrated under vacuum. The as-obtained white solid (4.25 g, yield 99%) was immediately transferred into a flame-dried, 250 mL, three-neck flask. Following the same protocol as above except for the usage of 2.2 equivalents of n-BuLi, the intermediate was lithiated at – 80 °C for 40 min, and quenched with CO2 (2 L, 1 atm). After 1 h, the resulting reaction mixture was worked-up in the same way as described above, yielding 2,3-dicarboxylic acid thiophene (5) as a white solid (3.5 g, 95% yield), which is used without further purification.

5-Decyl-4-H-thieno[2,3-c]pyrrole-4,6(5-H)-dione (7) A flame-dried, 100-mL, three-neck flask was charged with 5 (3.5 g, 20.33 mmol), followed by the addition of dry toluene (20 mL) and 0.05 mL of DMF. Oxalyl chloride (8.13 mL, 81 mmol) was added under vigorous stirring. Afterwards the reaction was set at 100 °C. After 50 min, the solvent in the reaction flask was removed with a strong N2 flow. The intermediate compound 6 was then obtained as a brown oil. Decylamine (4.06 mL, 20.33 mmol) was then added all at once. The reaction was then stirred at 100 °C overnight. The resulting brown mixture was then poured into water (150 mL) and extracted with dichloromethane (200 mL). The as-obtained solid was subjected to silica gel chromatography using an eluent of dichloromethane/hexane (v/v = 1:2), affording 7 as a colorless oil (3.2 g, 55% yield). 1H NMR (400 MHz, CDCl3) δ 7.74 (d, J = 4 Hz, 1H), 7.29 (d, J = 4 Hz, 1H), 3.58 (t, J = 8 Hz, 2H), 3.56 (q, J = 8 Hz, 2H), 1.62 (t, J = 8 Hz, 2H), 1.30–1.25 (m, 14H), 0.86(t, J = 8 Hz, 3H). 13C NMR (101 MHz, CDCl3) δ 163.91, 162.71, 144.66, 140.81, 137.23, 121.04, 38.46, 31.84, 29.46, 29.47, 29.26, 29.17, 28.79, 26.78, 22.65, 14.10.

2-Bromo-5-decyl-4H-thieno[2,3-c]pyrrole-4,6(5H)-dione (8) Compound 7 (2 g, 6.8 mmol) was dissolved in CF3COOH (20 mL). NBS (1.24 g, 7 mmol) was then added, followed by the addition of concentrated H2SO4 (2 mL). After stirring at room temperature for 7 h, the mixture was poured into water (150 mL) and extracted with CH2Cl2 (200 mL). The organic phase was collected and concentrated under reduced pressure to afford a brown solid, which was subjected to silica gel chromatography with CH2Cl2/hexane (v/v = 1:1) as eluent, yielding product 8 as a yellow solid (2.4 g, 95% yield). 1H NMR (400 MHz, CDCl3) δ 7.30 (s, 1H), 3.57 (t, J = 8 Hz, 2H), 1.62 (t, J = 8 Hz, 2H), 1.30–1.25 (m, 14H), 0.87 (t, J = 8 Hz, 3H). 13C NMR (101 MHz, CDCl3) δ 162.80, 161.80, 143.69, 140.27, 125.22, 123.64, 38.53, 31.72, 29.36, 29.34, 29.13, 29.01, 28.56, 26.62, 22.53, 13.98.

1-(Thiophen-3-yl)-2,5,8,11-tetraoxadodecane (9) A 100-mL, three-neck flask equipped with water cooler was flame-dried and charged with NaH (1.471 g, 36.8 mmol, 60%wt in mineral oil). Dry THF (50 mL) was then introduced via a cannula. 3-Thienylmethanol (2.1 g, 18.39 mmol) was then added into the NaH suspension dropwise. As soon as the H2 evolution ended, diethylene glycol 2-bromoethyl methyl ether (5.01 g, 22.07 mmol) was added via syringe, all at once. The reaction mixture was then gently refluxed overnight. After cooling to room temperature, the resulting solution was poured into water (150 mL) and extracted with dichloromethane (200 mL). The organic phase was collected and
concentrated, and the residue was subjected to silica gel chromatography with dichloromethane as eluent. The product 9 was obtained as a colorless oil (3.1 g, 65% yield). 1H NMR (400 MHz, CDCl3) δ 7.29–7.27 (m, 1 H), 7.22–7.21 (m, 1 H), 7.08–7.06 (m, 1 H), 4.57 (s, 2 H), 3.66–3.62 (m, 10 H), 3.56–3.53 (m, 2 H), 3.37 (s, 3 H). 13C NMR (101 MHz, CDCl3) δ 139.39, 127.28, 125.81, 122.72, 71.86, 70.56, 70.54, 70.44, 69.24, 68.35, 58.91.

(3-(2,5,8,11-Tetraoxadodecyl)thiophen-2-yl)trimethylstannane (10) A flame-dried, 100-mL, three-neck flask was charged with 1-(thiophen-3-yl)-2,5,8,11-tetraoxadodecane (0.6 g, 2.305 mmol), followed by the transfer of dry diethyl ether. The reaction system was cooled down using an ethanol/liquid nitrogen bath. n-BuLi (1.584 mL, 2.54 mmol) was then added dropwise. After keeping the reaction mixture at −80 °C for 40 min, chlorotrimethylstannane (2.76 mmol, 1 M THF solution) was added into the reaction mixture all at once. The cooling bath was then removed, and the solution was stirred for 3 h. The resulting solution was poured into water (150 mL), and extracted with diethyl ether (200 mL). The organic phase was collected and concentrated under vacuum to give a brown residue, which was further subjected to silica gel chromatography with dichloromethane as eluent. No further purification was processed. 1H NMR (400 MHz, CDCl3) δ 7.54 (d, J = 4 Hz, 1H), 7.16 (d, J = 4 Hz, 1H), 4.58 (m, 2H), 3.65 (m, 12H), 3.37 (s, 3H), 0.36 (s, 9H). 13C NMR (101 MHz, CDCl3) δ 146.46, 135.04, 130.68, 128.93, 71.86, 70.59, 70.55, 70.51, 70.08, 69.52, 59.01, −7.59.

2-(4,6-Bis(trimethylsilyl)thieno[3,4-b]thiophen-2-yl)-5-decyl-4H-thieno[2,3-c]pyrrole-4,6(5H)-dione (11) To a flame-dried, 100-mL, three-neck flask was added 2-(trimethylstannyl)thieno[3,4-b]thiophene-4,6-diy)bis(trimethylsilane) (0.75 g, 1.676 mmol), 2-bromo-5-decyl-4-H-thieno[2,3-c]pyrrole-4,6(5-H)-dione (0.624 g, 1.676 mmol) and Pd(PPh3)4 (97 mg, 0.084 mmol). Degassed toluene (20 mL) and DMF (7 mL) were subsequently transferred via a cannula into the reaction flask. The reaction system was set at 100 °C and stirred overnight. After cooling down to room temperature, the resulting mixture was poured into water (100 mL) and extracted with ethyl acetate (150 mL). The organic phase was collected and concentrated under vacuum to give a brown residue, which was further subjected to silica gel column chromatography with toluene/hexanes (1/2, v/v), yielding 0.56 g of 11 as yellow solid (560 mg, yield 58%). 1H NMR (400 MHz, CDCl3) δ 7.40 (s, 1H), 7.25 (s, 1H), 3.60 (2J = 8 Hz, 2H), 1.64 (m, 2H), 1.32-1.25 (m, 14H), 0.87 (t, J = 4 Hz, 3H), 0.43 (d, J = 4 Hz, 18H). 13C NMR (101 MHz, CDCl3) δ 163.62, 162.49, 153.70, 150.59, 146.17, 144.83, 140.36, 137.98, 135.24, 130.02, 117.15, 115.81, 38.47, 31.91, 29.56, 29.54, 29.33, 29.20, 28.80, 26.84, 22.72, 14.17, 0.23, −0.62.

5-Decyl-2-(4,6-dibromothieno[3,4-b]thiophen-2-yl)-4H-thieno[2,3-c]pyrrole-4,6(5H)-dione (12) 2-(4,6-Bis(trimethylsilyl)thieno[3,4-b]thiophen-2-yl)-5-decyl-4-H-thieno[2,3-c]pyrrole-4,6(5-H)-dione (0.424 g, 0.736 mmol) was dissolved in 5 mL of CHCl3. Bromine (0.083 mL, 1.62 mmol) was then added via a syringe. The mixture was stirred at room temperature for 30 min, after which the solution was poured into water (100 mL) and extracted with CHCl3 (150 mL). The organic phase was collected
and concentrated under vacuum to yield a yellow solid (0.434 g, 95% yield). No further purification was processed. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.37 (s, 1H), 7.04 (s, 1H), 3.60 (t, $J = 8$ Hz, 2H), 1.64 (t, $J = 8$ Hz, 2H), 1.32−1.25 (m, 14H), 0.87 (t, $J = 8$ Hz, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 163.35, 162.24, 148.77, 146.08, 144.78, 141.57, 139.31, 138.23, 118.25, 114.76, 38.73, 31.89, 29.55, 29.31, 28.81, 28.75, 26.86, 22.71, 14.17.

2-(4,6-Bis(3-(2,5,8,11-tetraoxadodecyl)thiophen-2-yl)thieno[3,4-b]thiophen-2-yl)-5-decyl-4H-thieno[2,3-c]pyrrole-4,6(5H)-dione (13) Compound 10 (0.323 g, 0.76 mmol) and 12 (0.15 g, 0.25 mmol) were charged into a dry, 25 mL of CHCl$_3$, followed by the addition of ca. 20 g of dry silica gel. NBS (32 mg, 0.18 mmol) was then added via syringe. The reaction was then set at 80 °C and stirred overnight. After cooling down to room temperature, the reaction mixture was poured into water (100 mL) and extracted with ethyl acetate (150 mL). The organic phase was collected and concentrated to give a red oil, which was then purified on silica gel column with a eluent of ethyl acetate/isopropyl alcohol (v/v = 10/1). Compound 13 was obtained as a red oil (0.13 g, 65%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.40 (s, 1H), 7.39 (s, 1H), 7.37 (d, $J = 4$ Hz, 1H), 7.36 (d, $J = 4$ Hz, 1H), 7.23 (d, $J = 4$ Hz, 1H), 7.21 (d, $J = 4$ Hz, 1H), 4.69 (s, 2H), 4.62 (s, 2H), 3.67−3.58 (m, 24H), 3.49 (m, 2H), 3.33 (s, 6H), 1.61 (t, $J = 8$ Hz, 2H), 1.29−1.23 (m, 14H), 0.85 (t, $J = 8$ Hz, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 165.93, 164.83, 152.22, 147.42, 146.61, 143.22, 141.09, 139.21, 138.78, 138.28, 133.96, 132.82, 131.37, 128.84, 128.39, 127.51, 126.89, 124.66, 120.39, 118.47, 74.50, 73.21, 73.07, 72.37, 69.78, 69.48, 61.51, 34.44, 32.10, 31.86, 31.76, 31.37, 29.40, 25.26, 16.74.

2-(4,6-Bis(5-bromo-3-(2,5,8,11-tetraoxadodecyl)thiophen-2-yl)thieno[3,4-b]thiophen-2-yl)-5-decyl-4H-thieno[2,3-c]pyrrole-4,6(5H)-dione (14) Compound 13 (58 mg, 0.061 mmol) was dissolved in 10 mL of CHCl$_3$, followed by the addition of ca. 20 g of dry silica gel. NBS (32 mg, 0.18 mmol) was then added. After stirring at room temperature for 30 min, the mixture was filtered on a glass filter. The filtrated silica gel was thoroughly washed with ethyl acetate/methanol (50 mL, v/v=20/1). The filtrate was collected and concentrated to give a red oil, which was then purified on silica gel column with a eluent of ethyl acetate/isopropyl alcohol (v/v = 10/1) to afford the monomeric compound 14 as a viscous red oil (45 mg, 70% yield). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.42 (s, 1H), 7.36 (s, 1H), 7.22 (s, 1H), 7.19 (s, 1H), 4.61 (s, 2H), 4.56 (s, 2H), 3.68−3.62 (m, 24H), 3.53 (m, 2H), 3.36 (s, 3H), 3.36 (s, 3H), 1.63 (t, $J = 8$ Hz, 2H), 1.31−1.25 (m, 14H), 0.87 (t, $J = 8$ Hz, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 163.45, 162.35, 149.31, 144.93, 144.56, 141.31, 138.99, 137.55, 137.27, 136.48, 132.88, 132.71, 132.44, 132.08, 123.13, 121.12, 118.15, 115.45, 112.86, 112.41, 71.88, 70.64, 70.58, 70.56, 70.51, 70.50, 69.89, 66.83, 66.54, 59.00, 38.65, 31.85, 29.51, 29.27, 28.77, 26.80, 22.66, 14.12.

2-(4,6-bis(3-decythiophen-2-yl)thieno[3,4-b]thiophen-2-yl)-5-decyl-4H-thieno[2,3-c]pyrrole-4,6(5H)-dione (19) Compounds 18$^{b0}$ (380 mg, 0.98 mmol) and 12 (176 mg, 0.3 mmol) were charged into a dry,
25-mL, three-neck flask, followed by the addition of Pd\textsubscript{2}(dba\textsubscript{3})-CHCl\textsubscript{3} (12 mg, 0.011 mmol) and P(o-tol\textsubscript{3}) (16 mg, 0.05 mmol). Degassed toluene (10 mL) was then added via syringe. The reaction was then set at 80 °C and stirred overnight. After cooling down to room temperature, the reaction mixture was poured into water (100 mL) and extracted with ethyl acetate (150 mL). The organic phase was collected and concentrated to give a brown oil, which was then purified on a silica gel column with an eluent of ethyl acetate/toluene (v/v = 1/5). Compound 19 was obtained as a reddish oil (0.16 g, 60%). \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \( \delta \) 7.41 (s, 1H), 7.39 (s, 1H), 7.37 (d, \( J = 4 \) Hz, 1H), 7.36 (d, \( J = 4 \) Hz, 1H), 7.21 (d, \( J = 4 \) Hz, 1H), 7.19 (d, \( J = 4 \) Hz, 1H), 3.48 (m, 2H), 1.58 (m, 4H), 1.29–1.23 (m, 51H), 0.84 (m, 9H).

2-(4,6-bis(5-bromo-3-decylthiophen-2-yl)thieno[3,4-b]thiophen-2-yl)-5-decyl-4H-thieno[2,3-c]pyrrole-4,6(5H)-dione (20) Compound 19 (160 mg, 0.18 mmol) was dissolved in 10 mL of CHCl\textsubscript{3}, followed by the addition of ca. 5 g of dry silica gel. NBS (64 mg, 0.36 mmol) was then added. After stirring at room temperature for 30 min, the mixture was filtered on a glass filter. The filtrated silica gel was thoroughly washed with ethyl acetate/toluene (v/v = 1/7, 50 mL). The filtrated was collected and concentrated to give a red oil, which was then purified on silica gel column, with an eluent of ethyl acetate/toluene (v/v = 1/6), to afford the monomeric compound 20 as a viscous reddish oil (140 mg, 70% yield). \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \( \delta \) 7.44 (s, 1H), 7.37 (s, 1H), 7.24 (s, 1H), 7.21 (s, 1H), 3.49 (m, 2H), 1.58 (m, 4H), 1.29–1.23 (m, 51H), 0.84 (m, 9H).

General procedure of bis(pinacolato)diboron-mediated homopolymerization (P1 and P2). A 25 mL, flame-dried two neck flask, filled with dry N\textsubscript{2}, was charged with the dibrominated macromonomer (0.05 mmol), Pd(dppf)Cl\textsubscript{2} (CH\textsubscript{2}Cl\textsubscript{2} adduct) (3 mg), K\textsubscript{3}PO\textsubscript{4} (50 mg) and bis(pinacolato)diboron (26 mg). Degassed toluene/DMF (v/v = 4/1) (6 mL) was introduced into the reaction flask via a syringe. The reaction was set at 110 °C overnight. Afterwards, the reaction mixture was cooled to room temperature, and added dropwise into 500 mL of methanol. The precipitate was collected with a cellulose thimble, which was subjected to Soxhlet extraction with methanol for 24 h, acetone for 8 h, hexane for 5 h, and CHCl\textsubscript{3} for 5 h, respectively. The chloroform fraction was obtained as a purple solid. P1 (30 mg, ~60% yield) \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \( \delta \) 7.72–6.64 (4 H, br), 4.61–4.19 (4 H, br), 4.18–2.98 (17 H, br), 1.83–0.71 (br). P2 (20 mg, ~40% yield) \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \( \delta \) 7.72–6.64 (4 H, br), 4.2–3.2 (2 H, br), 1.83–0.71 (br).

Synthesis of CC1. A 25 mL, flame-dried two neck flask, filled with dry N\textsubscript{2}, was charged with 14 (100 mg, 0.09 mmol) and bis(trimethylstannyl)thiophene (38 mg, 0.09 mmol), followed by the addition of Pd\textsubscript{2}(dba\textsubscript{3}) (CHCl\textsubscript{3} adduct, recrystallized from acetone) (3 mg) and P(o-tol\textsubscript{3}) (12 mg). Degassed dry toluene (5 mL) was then introduced into the reaction flask via a cannula. The reaction was then set at 100 °C for 24 h. Afterwards, the reaction mixture was allowed to cool to room temperature, and added dropwise into 500 mL of methanol. The precipitate was collected with a cellulose thimble, which was then subjected to Soxhlet extraction with methanol for 24 h, acetone for 7 h, hexane for 5 h, and CHCl\textsubscript{3}.
for 3 h, respectively. The chloroform fraction was obtained as a purple-blue solid after precipitation in methanol (80 mg, ~85%). $^1$H NMR (400 MHz, CDCl$_3$). $\delta$ 7.72–6.7 (6 H, br), 4.61–4.19 (4 H, br), 4.18–2.98 (17 H, br), 1.83–0.71 (br).
4.6 References

14 Li, W.; Li, Q.; Liu, S.; Duan, C.; Ying, L.; Huang, F.; Cao, Y. Sci. China Chem. 2015, 58 (2), 257–266.