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(Citation)
Synthesis-Stuttgart,49(6):1285-1294

(Issue Date)
2017-03

(Resource Type)
journal article

(Version)
Accepted Manuscript

A Step-Efficient Pathway to Chlorine-Functionalized Thiophene Oligomers by Palladium-Catalyzed Deprotonative Coupling of Chlorothiophenes

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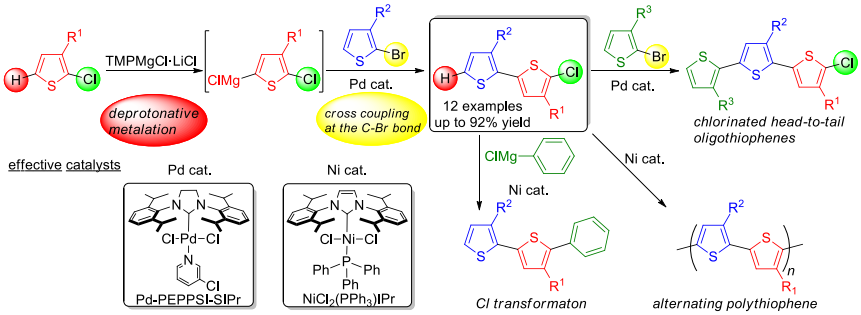
This paper is dedicated to Professor Tamejiro Hiyama on the occasion of his 70th birthday.

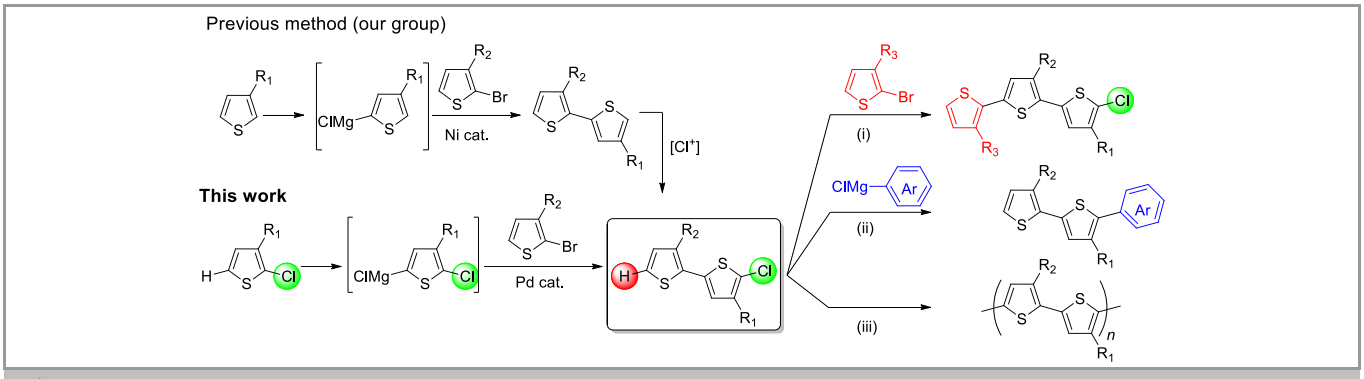


Received:
Accepted:
Published online:
DOI:

Abstract Deprotonative metalation of 2-chloro-3-substituted thiophene at the 5-position of the thiophene ring is performed by a bulky magnesium amide 2,2,6,6-tetramethylpiperidin-1-yl magnesium chloride lithium chloride salt (TMPMgCl·LiCl). The obtained metallic species reacts with bromothiophene to afford the regioregular head-to-tail-type chlorobithiophene, which is subjected to further end functionalization by the coupling reaction with C-Cl bond. Deprotonative C-H coupling polycondensation of differently-substituted chlorobithiophene gives polythiophene of the formal alternating copolymer.

Key words Thiophene oligomer, palladium catalyst, chlorothiophene, Knochel-Hauser base, alternating copolymer

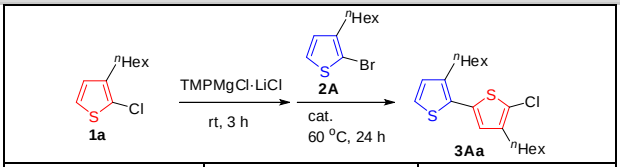
Development of preparative method for oligothiophenes with well-defined structures has been of great interest in materials science.[1] Considerable efforts have been paid for the practical synthesis of oligothiophenes, in which control of the regioregularity to the head-to-tail (HT) manner is particularly important to induce high performances as electronic materials.[2] In conjunction with the formation of a thiophene-thiophene bond cross-coupling strategy involving the reaction of a metalated thiophene with a thienyl halide has been a method of choice using a transition metal complex as a catalyst. Stepwise preparation of oligothiophene with a well-defined structure has been performed employing such cross-coupling strategies.[3] We have been engaged in designing preparative protocols of HT-regioregular oligothiophenes and polythiophenes. We have shown that C-H functionalization reactions of thiophenes also serve as an effective tool for the oligothiophene synthesis.[4,5] Regioselective deprotonation of 3-substituted thiophene at the 5-position and following coupling of 2-halothiophene have been, indeed, shown as stepwise synthesis of regioregular oligothiophenes, in which each extension of the thiophene unit proceeds in a single step (Scheme 1).[6] Our concern is turned to the application of the thus obtained well-defined oligothiophenes to the introduction of additional functionalities. In addition, the oligothiophene can also be a monomer of a formal alternating copolymer when a differently substituted oligothiophene is employed. We envisaged that coupling of a 5-metalated 2-chloro-3-substituted thiophene with another 2-halothiophenes bearing a substituent at the 3-position would form the thiophene-thiophene bond to give the corresponding HT-type chlorobithiophene. Although we have previously reported that such a metalated chlorothiophene reacts with several aryl bromides to undergo arylation,[7] the reaction has not been employed for the preparation of bithiophene because of difficulties of cross coupling with highly electron-enriched (unactivated) organic electrophiles such as 2-halothiophene. However, it is intriguing if such a coupling is successfully applied for the HT-type oligothiophene synthesis. Since the preparation protocol to give halobithiophene can also omit additional halogenation from the coupling-halogenation sequence, the process may enhance the step efficiency. Subsequently, the obtained chlorobithiophene would be employed for (i) further extension of a thiophene unit by a coupling reaction at the C-H bond, (ii) cross coupling as an electrophile with a variety of organometallic species,[8] and (iii) cross-coupling polymerization leading to polythiophene.[9,10] We herein report that deprotonative coupling of chlorothiophene at the C-H bond with bromothiophenes forms the chlorinated bithiophene when a palladium complex is employed as a catalyst.



Scheme 1 Step-efficient preparation and synthetic utilization of chlorobithiophene

Deprotonative metalation at the C-H bond of chlorothiophene **1** followed by coupling with bromothiophene **2** was examined with nickel(II) NHC (*N*-heterocyclic carbene) complex,[11] which has been shown as a catalyst for the reaction forming thiophene-thiophene bond.[6] Deprotonation of chlorothiophene **1a** was carried out with 1.2 equiv of Knochel-Hauser base (TMPMgCl·LiCl, TMP: 2,2,6,6-tetramethylpiperidin-1-yl)[12] at room temperature for 3 h to generate the metalated thiophene at the 5-position. Following addition of 2-bromo-3-hexylthiophene (**2A**) and a nickel catalyst bearing a NHC ligand $NiCl_2(PPh_3)IPr$ (1.0 mol %) as a catalyst showed color change to dark purple suggesting polymerization of the metalated chlorothiophene itself whereas formation of the desired head-to-tail bithiophene **3Aa** was observed in a poor yield after stirring at 60 °C for 24 h. The use of nickel(0) catalysts formed by the reaction of $Ni(cod)_2$ with NHC ligand such as IPr and SIPr also resulted in poor yields. The reaction of **1a** and **2A** with several nickel(II) catalysts bearing bidentate diphosphines DPPP and DPPF was ineffective albeit little polymerization and yields of the coupling product **3Aa** were moderate to low. No reaction took place using a ubiquitous nickel complex $NiCl_2(PPh_3)_2$. Although the reaction with $PdCl_2(PPh_3)_2$ and $PdCl_2$dppf did not afford the coupling product **3Aa**, a slightly higher yield was observed in the reaction of $PdCl_2$(dppe) (21%). A remarkable improvement of the yield of **3Aa** was achieved in the reaction with $Pd(^tBu_3P)_2$ (78% yield). It was also found that use of Pd-PEPPSI-IPr,[13] which is a palladium complex bearing *N*-heterocyclic carbene ligand, afforded the thiophene-thiophene coupling product in 41% yield. Use of Pd-PEPPSI-SIPr resulted in a higher yield (77%). Little polymerization was observed in the coupling reaction with above palladium catalysts in the presence of bromothiophene as a coupling partner in the reaction mixture. In addition to the deprotonative metalation with the Knochel-Hauser base (TMPMgCl·LiCl) at room temperature for 3 h, it was also found that the metalation with EtMgCl/10 mol % TMPH (66 °C, 5 h for the deprotonation) or EtMgCl/10 mol % DMPH: *cis*-2,6-dimethylpiperidine (room temperature, 3 h) similarly afforded the corresponding coupling product in 82% and 80% yields, respectively. These results are summarized in Table 1.

Table 1 Deprotonation of chlorothiophene **1a** and coupling with 2-bromo-3-hexylthiophene (**2A**)[a]

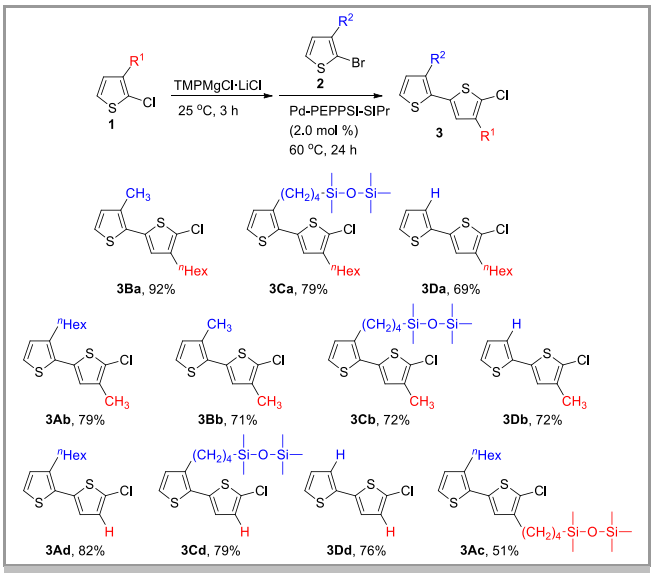


entry	catalyst	yield[b], %
1	$NiCl_2(PPh_3)IPr$[c]	12
2	$Ni(cod)_2$+IPr	14
3	$Ni(cod)_2$ +SIPr[c]	9
4	$NiCl_2$dppf[d]	22
5	$NiCl_2$dppp[d]	38
6	$NiCl_2(PPh_3)_2$	0
7	$PdCl_2(PPh_3)_2$	0
8	$PdCl_2$dppf	0
9	$PdCl_2$dppe[d]	21
10	$Pd(^tBu_3P)_2$	78
11	Pd-PEPPSI-IPr	41
12	Pd-PEPPSI-SIPr	77
13[e]	Pd-PEPPSI-SIPr	82
14[f]	Pd-PEPPSI-SIPr	80

[a]Unless noted, the deprotonation reaction was carried out with 1a (0.5 mmol) and TMPMgCl·LiCl (1.2 eq) at room temperature for 3 h under nitrogen atmosphere. The coupling reaction was performed with 2A (0.6 mmol) in 5 mL of THF in the presence of a 2 mol % catalyst. [b]Isolated yield. [c]IPr: 1,3-Bis(2,6-diisopropylphenyl)-1,3-dihydro-2*H*-imidazol-2-ylidene, SIPr: 1,3-Bis(2,6-diisopropylphenyl)imidazolidin-2-ylidene, [d]dppe: 1,2-Bis(diphenylphosphino)ethane; dppp: 1,3-Bis(diphenylphosphino)propane; dppf: 1,1'-Bis(diphenylphosphino)ferrocene. [e]Deprotonation with EtMgCl/10 mol % TMPH (2,2,6,6-tetramethylpiperidine) at 66 °C for 5 h. [f]Deprotonation with EtMgCl/10 mol % DMPH (*cis*-2,6-dimethylpiperidine) at room temperature for 3 h.

With the optimized conditions for the coupling reaction to form head-to-tail (HT) type bithiophene **3Aa**, synthesis of several bithiophene derivatives bearing different substituents was examined. As shown in Scheme 2, after deprotonation with TMPMgCl·LiCl at room temperature, metalated **1a** reacted with 2-bromo-3-methylthiophene (**2B**) in the presence of Pd-PEPPSI-SIPr (2.0 mol %) gave the corresponding bithiophene **3Ba** in 92% yield. The reaction of **1a** with bromothiophene bearing a disiloxane moiety **2C**[14] similarly led to the formation of **3Ca** in 79% yield. The reaction of 2-chloro-3-methylthiophene (**1b**) with **2A** (R^2 = hexyl) and **2B** (R^2 = CH_3) afforded the bithiophene **3Ab** (79%) and **3Bb** (71%), respectively. Siloxanes bearing bromothiophene **2C** and unsubstituted thiophene **2D** also led to the corresponding bithiophenes. Most of the coupling reaction with various 3-

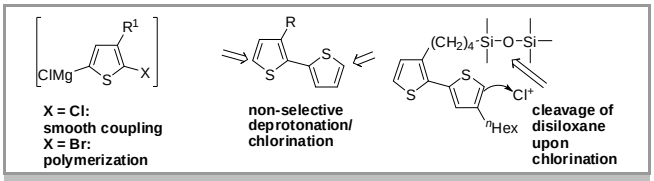
substituted chloro- and bromothiophenes proceeded smoothly showing that a variety of head-to-tail-type chlorinated bithiophenes **3** are readily available and the thus obtained **3** can be subjected to reactions at the C-H bond of the 5'-position as an organometallic nucleophile after deprotonative metalation as well as substrates as organic electrophiles at the C-Cl bond at the 2-position.



Scheme 2 Synthesis of differently-substituted chlorobithiophenes

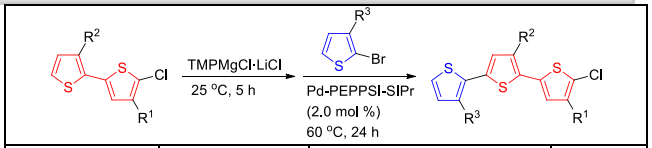
The obtained chlorobithiophene **3Aa** was found to further react with bromothiophene **2A** and bromobithiophene **4** under similar conditions to afford terthiophene **5** and quaterthiophene **6** as shown in Table 2. Unsubstituted chlorobithiophene **3Dd** reacted with 2-bromothiophene (**2D**) to give chloroterthiophene **7** in 91% yield. Bithiophene bearing a different substituent **3Ba** also reacted with **2A** and **2B** to furnish terthiophene **8** (71%) and **9** (88%), respectively. Chlorinated oligothiophene bearing a branched structure[6b] was employed as a metalated thiophene dendrimer **3T-2Cl** to react with **2a** affording the corresponding coupling product **10** in 87% yield.

Deprotonative metalation of chlorothiophene followed by palladium-catalyzed cross coupling was shown to afford the chlorinated oligomer successfully. The deprotonation conditions are relatively smooth compared with the case of the regioselective deprotonation protocol of a 3-substituted thiophene[6a] due to the electronegative effect of the chlorine atom as a substituent. The coupling reaction of thus metalated chlorothiophene **1** with bromothiophene **2** was shown to proceed much smoothly otherwise deprotonation with catalytic secondary amines such as DMPH or dicyclohexylamine combined with a Grignard reagent would not be achieved in the absence of chlorine atom on bithiophene under such a mild conditions at room temperature within several hours (See entry 13 and 14 of Table 1). The chlorine atom may also serve as a class of a protective group at the 2-position of bithiophene. When the deprotonative metalation was carried out with non-chlorinated thiophene derivatives with less bulky magnesium amide, non-regioselective deprotonation would take place. In addition, use of metalated bromothiophene instead of the chloro analog may cause coupling at the carbon-bromine bond after the formation of the thus coupled bromobithiophene. Furthermore, considering the following transformation reactions utilizing the C-Cl bond, facile formation of chlorinated oligothiophenes would allow to skip the post halogenation reaction. It should also be pointed out that chlorobithiophene **3Ad**, which is the coupling product of **1d** and **2A** shown in Scheme 2, cannot be obtained regioselectively by the post halogenation pathway because of difficulties of the controlled chlorination with NCS. It is also shown that halogenation of thiophene derivatives bearing a disiloxane-containing substituent at the 3-position has been difficult.[14] Preparation of **3Ca**, **3Cb**, **3Cd,** and **3Ac** through the regiocontrolled chlorination of the corresponding non-halogenated bithiophene with NCS or NBS would not be achieved by the post halogenation, accordingly (Scheme 3).



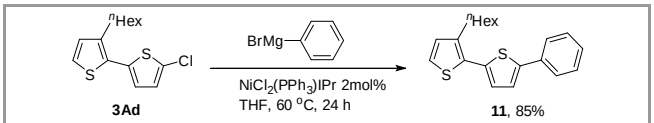
Scheme 3 Synthetic disadvantages in the use of non-chlorinated thiophenes

Table 2 Syntheses of terthiophene and quaterthiophene



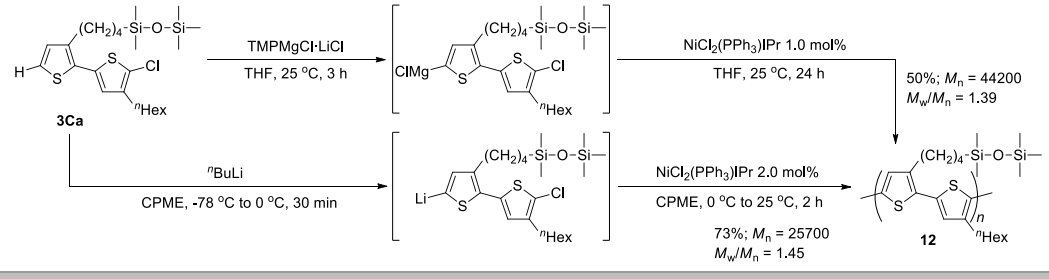
chloride	bromide	product	yield[b], %
3Aa	2A	5	55
3Aa	4	6	50
3Dd	2D	7	91
3Ba	2A	8	71
3Ba	2B	9	88
3T-2Cl	2A	10	87

[a]Unless noted, the reaction was carried out with chlorothiophene 3 (0.5 mmol) in 5 mL of THF under nitrogen atmosphere. The coupling reaction was performed with heteroaryl bromide (0.75 mmol). [b]Isolated yield.



Scheme 4 Cross coupling of chlorobithiophene with phenyl Grignard reagent

Chlorobithiophenes **3** can also be employed as an organic electrophile by the cross-coupling reaction with an organometallic nucleophile catalyzed by a transition metal complex. The reaction of chlorobithiophene **3Ad** underwent the cross-coupling reaction with phenyl Grignard reagent in the presence of nickel catalyst to afford **11** in 85% yield (Scheme 4).[8]



Scheme 5 Deprotonative cross-coupling polymerization of differently-substituted chlorobithiophene leading to formal alternating copolymer

The obtained oligothiophenes bearing different substituents were found to be employed as monomers for polythiophenes, which are recognized as formal alternating copolymer of different thiophenes as shown in Scheme 5.[15] The reaction of chlorobithiophene bearing hexyl and disiloxane substituents at the 3- and 3'-positions, respectively, **3Ca** was subjected to polymerization by treatment of the Knochel-Hauser base and following addition of 1.0 mol % $NiCl_2(PPh_3)IPr$. The corresponding polymer **12** was obtained in 50% yield with M_n of 44200 (M_w/M_n = 1.39). The reaction by Murahashi coupling polymerization with ^{n}BuLi as a deprotonating agent[16] also proceeded to afford **12** in 73% yield (M_n = 25700; M_w/M_n = 1.45) as summarized in Scheme 5. MALDI-TOF mass spectrum of the obtained polymer **12** indicated clear repeating of 451 Da suggesting that the polymer was composed of bithiophene with *n*-hexyl and disiloxane-containing alkylene substituents (See Supporting Information).

In summary, we have shown that deprotonative C-H coupling of thiophenes bearing chlorine atom with thienyl bromide proceeds with a palladium catalyst forming chlorinated bithiophene, which allows further coupling reaction to extend the thiophene unit leading up to chlorinated quaterthiophene. The obtained chloro-oligothiophenes were found also to be subjected to C-H coupling polymerization. The formal alternative copolymer was synthesized when a differently-substituted chlorobithiophene is employed as a monomer.

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General. All the reactions were carried out under nitrogen atmosphere. ^{1}H NMR (500 or 400 MHz) and ^{13}C NMR (125 or 100 MHz) spectra were measured on BRUKER Avance-500 and JEOL ECZ400 as a $CDCl_3$ solution unless noted. The chemical shifts were expressed in ppm with $CHCl_3$ (7.26 ppm for ^{1}H) or $CDCl_3$ (77.16 ppm for ^{13}C) as internal standards. IR spectra were recorded on Bruker Alpha with an ATR attachment (Ge). High resolution mass spectra (HRMS) were measured by JEOL JMS-T100LP AccuTOF LC-Plus (ESI) with a JEOL MS-5414DART attachment. For thin layer chromatography (TLC) analyses throughout this work, Merck precoated TLC plates (silica gel 60 F_{254}) were used. Purification by HPLC with preparative SEC column (JAI-GEL-2H) was performed by JAI LC-9201. SEC analyses were carried out with a standard HPLC system equipped with a UV detector at 40 °C using $CHCl_3$ as an eluent with Shodex KF-806L. Molecular weights and molecular weight distributions were estimated on the basis of the calibration curve obtained by 6 standard polystyrenes. MALDI-TOF mass spectra were measured by Bruker Daltonics Flexscan ultrafleXtreme.

Procedures

2-Chloro-3-hexyl-5-(3-hexylthiophen-2-yl)thiophene[17] **(3Aa)**: To 20 mL Schlenk tube equipped with a magnetic stirring bar were added 2-chloro-3-hexylthiophene (**1a**: 65 µL, 0.30 mmol) and a 1 M THF solution of TMPMgCl·LiCl (0.36 mL, 0.36 mmol) at room temperature under a nitrogen atmosphere. After stirring at room temperature for 3 h, 2-bromo-3-hexylthiophene (**2A**: 72 µL, 0.36 mmol), Pd-PEPPSI-SIPr (4.1 mg, 6 µmol) and THF (3.0 mL) were added successively. The resulting solution was stirred at 60 °C for 24 h. After cooling the resulting mixture to room temperature, the reaction was terminated by pouring the mixture to 1 M HCl_{aq} and chloroform to observe separation into two phases. The aqueous layer was extracted twice with chloroform and the combined organic extracts were dried over anhydrous sodium sulfate. After removal of the solvent, the residual crude oil was purified by column chromatography (hexanes) on silica gel to afford 79.7 mg of 2-chloro-3-hexyl-5-(3-hexylthiophen-2-yl)thiophene (**3Aa**) in 77% yield as a light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.83-0.95 (m, 6H), 1.22-1.42 (m, 12H), 1.56-1.65 (m, 4H), 2.56 (t, *J* = 7.5 Hz, 2H), 2.70 (t, *J* = 7.8 Hz, 2H), 6.78 (s, 1H), 6.91 (d, *J* = 5.0 Hz, 1H), 7.15 (d, *J* = 5.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.2, 22.8, 28.2, 29.1, 29.2, 29.3, 29.7, 30.9, 31.7, 31.8, 123.9, 124.1, 126.6, 130.0, 130.1, 132.7, 139.7, 139.9.

Preparation of 3Aa through the deprotonation with a catalytic amount of TMPH or *cis*-2,6-dimethylpiperidine and EtMgCl: To 20 mL Schlenk tube equipped with a magnetic stirring bar were added 2-chloro-3-hexylthiophene (**1a**: 0.105 g, 0.52 mmol) and a 1 M THF solution of EtMgCl (0.62 mL, 0.62 mmol) at room temperature under a nitrogen atmosphere followed by addition of 2,2,6,6-teteramethylpiperidine (8.8µL, 0.05 mmol). The resulting solution was stirred under reflux for 5 h. After cooling the mixture to room temperature, the solution was diluted with THF (5.0 mL). Then, **2A** (0.154 g, 0.62 mmol) and Pd-PEPPSI-SIPr (71 mg, 0.10 mmol) were added. The mixture was stirred at 60 °C for 21 h. Isolation of the product was carried out in a similar manner to afford 158 mg of **3Aa**. (82% yield). Deprotonation with *cis*-2,6-dimethylpiperidine (0.1 equiv to **1a**) and EtMgCl (1.0 equiv) was performed at room temperature for 3 h (80% yield).

2-Chloro-3-hexyl-5-(3-methylthiophen-2-yl)thiophene (3Ba): Synthesis of **3Ba** was carried out in a similar manner to the synthesis of **3Aa** from 2-chloro-3-hexylthiophene (**1a**, 1.0 mL, 5.2 mmol), TMPMgCl·LiCl (6.3 mL, 6.3 mmol, 1 M in THF), 2-bromo-3-methylthiophene (**2B**, 1.1 g, 6.3 mmol), and Pd-PEPPSI-SIPr (70 mg, 0.1 mmol) in THF (35 mL) at 60 °C for 24 h (light yellow oil, 92%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.92 (t, *J* = 7.5 Hz, 3H), 1.31-1.43 (m, 6H), 1.58-1.67 (m, 2H), 2.37 (s, 3H), 2.59 (t, *J* = 7.5 Hz, 2H), 6.83 (s, 1H), 6.87 (d, *J* = 5.0 Hz, 1H), 7.14 (d, *J* = 5.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.2, 15.3, 22.8, 28.2, 29.1, 29.7, 31.8, 123.5, 124.0, 126.2, 130.6, 131.4, 133.1, 134.2, 139.8. IR (ATR) 2954, 2926, 2856, 1463, 1199, 1042, 830, 705, 617 cm^{-1}. HRMS (DART-ESI$^+$) calcd for $C_{15}H_{20}{}^{35}ClS_2$: 299.0695; found *m/z* 299.0687.

2-Chloro-3-hexyl-5-(3-(4-(1,1,3,3,3-pentamethyldisiloxan-1-yl)butan-1-yl)thiophen-2-yl)thiophene (3Ca): Synthesis of **3Ca** was carried out in a similar manner to the synthesis of **3Aa** from 2-chloro-3-hexylthiophene (**1a**, 298 mg, 1.46 mmol), TMPMgCl·LiCl (1.75 mL, 1.75 mmol, 1 M in THF), 2-bromo-3-(4-(1,1,3,3,3-pentamethyldisiloxan-1-yl)butan-1-yl)thiophene[14] (**2C**, 640 mg, 1.75 mmol) and Pd-PEPPSI-SIPr (19 mg, 0.03 mmol) in THF (5.0 mL) at 60 °C for 24 h (light yellow oil, 79%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.03 (s, 6H), 0.05 (s, 9H), 0.51-0.56 (m, 2H), 0.87-0.91 (m, 3H), 1.24-1.43 (m, 8H), 1.55-1.68 (m, 4H), 2.56 (t, *J* = 7.8 Hz, 2H), 2.71 (t, *J* = 7.8 Hz, 2H), 6.78 (s, 1H), 6.90 (d, *J* = 5.0 Hz, 1H), 7.15 (d, *J* = 5.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 0.5, 2.1, 14.2, 18.4, 22.8, 23.4, 28.2, 29.0, 29.1, 29.7, 31.8, 34.5, 124.0, 124.1, 126.7, 130.0, 130.1, 132.7, 139.7, 139.9. IR (ATR) 2955, 2926, 2857, 1459, 1413, 1252, 1053, 841, 807, 783, 753 cm^{-1}. HRMS (DART-ESI$^+$) calcd for $C_{23}H_{40}{}^{35}ClOS_2Si_2$: 487.1748; found *m/z* 487.1728.

2-Chloro-3-hexyl-5-(thiophen-2-yl)thiophene (3Da): Synthesis of **3Da** was carried out in a similar manner to the synthesis of **3Aa** from 2-chloro-3-hexylthiophene (**1a**, 94 mg, 0.47 mmol), TMPMgCl·LiCl (0.76 mL, 0.76 mmol, 1 M in THF), 2-bromothiophene (**2D**, 93 mg, 0.57 mmol) and Pd-PEPPSI-SIPr (6.5 mg, 9.4 μmol) in THF (5.0 mL) at 60 °C for 24 h (light yellow oil, 69%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.89 (t, *J* = 7.1 Hz, 3H), 1.27-1.39 (m, 6H), 1.54-1.64 (m, 2H), 2.54 (t, *J* = 7.8 Hz, 2H), 6.86 (s, 1H), 7.00 (dd, *J* = 3.7, 5.0 Hz, 1H), 7.08 (dd, *J* = 1.4, 3.7 Hz, 1H), 7.20 (dd, *J* = 1.4, 5.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 22.7, 28.2, 29.0, 29.7, 31.7, 123.2, 123.7, 124.3, 124.9, 127.9, 133.8, 136.9, 140.2. IR (ATR) 2955, 2926, 2856, 1522, 1457, 1419, 1042, 833, 816, 691 cm^{-1}. HRMS (DART-ESI$^+$) calcd for $C_{14}H_{18}{}^{35}ClS_2$: 285.0538; found *m/z* 285.0548.

2-Chloro-3-methyl-5-(3-hexylthiophen-2-yl)thiophene (3Ab): Synthesis of **3Ab** was carried out in a similar manner to the synthesis of **3Aa** from 2-chloro-3-methylthiophene (**1b**, 84.7 mg, 0.64 mmol), TMPMgCl·LiCl (0.77 mL, 0.77 mmol, 1 M in THF), 2-bromo-3-hexylthiophene (**2A**, 190 mg, 0.77 mmol) and Pd-PEPPSI-SIPr (8.7 mg, 13 μmol) in THF (5.0 mL) at 60 °C for 24 h (light yellow oil, 79%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, *J* = 6.9 Hz, 3H), 1.25-1.40 (m, 6H), 1.55-1.65 (m, 2H), 2.19 (s, 3H), 2.70 (t, *J* = 8.0 Hz, 2H), 6.77 (s, 1H), 6.91 (d, *J* = 5.0 Hz, 1H), 7.16 (d, *J* = 5.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.6, 14.2, 22.8, 29.2, 29.3, 30.8, 31.8, 124.0, 124.5, 127.6, 130.0x2, 132.6, 134.7, 140.0. IR (ATR) 2955, 2926, 2856, 1566, 1536, 1465, 1412, 1378, 1194, 1085, 1047, 1007, 876, 831, 723, 686, 651 cm^{-1}. HRMS (DART-ESI$^+$) calcd for $C_{15}H_{20}{}^{35}ClS_2$: 299.0695; found *m/z* 299.0704.

2-Chloro-3-methyl-5-(3-methylthiophen-2-yl)thiophene (3Bb): Synthesis of **3Bb** was carried out in a similar manner to the synthesis of **3Aa** from 2-chloro-3-methylthiophene (**1b**, 76.4 mg, 0.58 mmol), TMPMgCl·LiCl (0.69 mL, 0.69 mmol, 1 M in THF), 2-bromo-3-methylthiophene (**2B**, 122 mg, 0.69 mmol) and Pd-PEPPSI-SIPr (7.9 mg, 12 μmol) in THF (5.0 mL) at 60 °C for 24 h (light yellow oil, 71%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.20 (s, 3H), 2.35 (s, 3H), 6.79 (s, 1H), 6.86 (d, *J* = 5.0 Hz, 1H), 7.13 (d, *J* = 5.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.7, 15.3, 123.5, 124.4, 127.1, 130.5, 131.4, 132.9, 134.3, 134.8. IR (ATR) 1566, 1537, 1448, 1407, 1380, 1198, 1047, 927, 830, 706, 618 cm^{-1}. HRMS (DART-ESI$^+$) calcd for $C_{10}H_{10}{}^{35}ClS_2$: 228.9912; found *m/z* 228.9918.

2-Chloro-3-methyl-5-(3-(4-(1,1,3,3,3-pentamethyldisiloxan-1-yl)butan-1-yl)thiophen-2-yl)thiophene (3Cb): Synthesis of **3Cb** was carried out in a similar manner to the synthesis of **3Aa** from 2-chloro-3-methylthiophene (**1b**, 137 mg, 1.0 mmol), TMPMgCl·LiCl (1.2 mL, 1.2 mmol, 1 M in THF), 2-bromo-3-(4-(1,1,3,3,3-pentamethyldisiloxan-1-yl)butan-1-yl)thiophene (**2C**, 439 mg, 1.2 mmol) and Pd-PEPPSI-SIPr (13.6 mg, 0.02 mmol) in THF (10 mL) at 60 °C for 24 h (light yellow oil, 72%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.03 (s, 6H), 0.05 (s, 9H), 0.50-0.57 (m, 2H), 1.33-1.44 (m, 2H), 1.58-1.68 (m, 2H), 2.19 (s, 3H), 2.70 (t, *J* = 7.8 Hz, 2H), 6.77 (s, 1H), 6.90 (d, *J* = 5.2 Hz, 1H), 7.15 (d, *J* = 5.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 0.5, 2.1, 13.7, 18.4, 23.3, 29.0, 34.5, 124.0, 124.6, 127.6, 129.9, 130.0, 132.6, 134.7, 139.9. IR (ATR) 2955, 2924, 2858, 1567, 1411, 1252, 1194, 1051, 840, 807, 783, 753, 687, 651, 625 cm^{-1}. HRMS (DART-ESI$^+$) calcd for $C_{18}H_{30}{}^{35}ClS_2Si_2$: 417.0951; found *m/z* 417.0979.

2-Chloro-3-methyl-5-(thiophen-2-yl)thiophene (3Db): Synthesis of **3Db** was carried out in a similar manner to the synthesis of **3Aa** from 2-chloro-3-methylthiophene (**1b**, 73.5 mg, 0.55 mmol), TMPMgCl·LiCl (0.67 mL, 0.67 mmol, 1 M in THF), 2-bromothiophene (**2D**, 109 mg, 0.67 mmol) and Pd-PEPPSI-SIPr (7.6 mg, 11 μmol) in THF (5.0 mL) at 60 °C for 24 h (light yellow solid, 72%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.18 (s, 3H), 6.85 (s, 1H), 6.98-7.03 (m, 1H), 7.08 (d, *J* = 3.7 Hz, 1H), 7.20 (d, *J* = 5.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.7, 123.6, 123.8, 124.6, 125.3, 127.9, 133.7, 135.2, 136.9. IR (ATR) 1566, 1521, 1459, 1416, 1241, 1225, 1186, 1075, 1045, 835, 814, 689 cm^{-1}. HRMS (DART-ESI$^+$) calcd for $C_9H_8{}^{35}ClS_2$: 214.9756; found *m/z* 214.9756.

2-Chloro-3-(4-(1,1,3,3,3-pentamethyldisiloxan-1-yl)butan-1-yl)-5-(3-hexylthiophen-2-yl)thiophene (3Ac): Synthesis of **3Ac** was carried out in a similar manner to the synthesis of **3Aa** from 2-chloro-3-(4-(1,1,3,3,3-pentamethyldisiloxan-1-yl)butan-1-yl)thiophene[2b] (**1c**, 112 mg, 0.35 mmol), TMPMgCl·LiCl (0.42 mL, 0.42 mmol, 1 M in THF), 2-bromo-3-hexylthiophene (**2A**, 104 mg, 0.42 mmol) and Pd-PEPPSI-SIPr (4.8 mg, 7.0 μmol) in THF (3.5 mL) at 60 °C for 24 h (light yellow oil, 51%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.04 (s, 6H), 0.05 (s, 9H), 0.53-0.59 (m, 2H), 0.88 (t, *J* = 6.9 Hz, 3H), 1.26-1.43 (m, 8H), 1.56-1.67 (m, 4H), 2.57 (t, *J* = 7.6 Hz, 2H), 2.70 (t, *J* = 7.8 Hz, 2H), 6.78 (s, 1H), 6.91 (d, *J* = 5.3 Hz, 1H), 7.15 (d, *J* = 5.3 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 0.5, 2.2, 14.2, 18.3, 22.8, 23.1, 27.9, 29.2, 29.3, 30.9, 31.8, 33.4, 124.0, 124.1, 126.7, 130.0, 130.1, 132.7, 139.7, 140.0. IR (ATR) 2955, 2927, 2857, 1461, 1414, 1252, 1054, 841, 807, 783, 753, 688, 649 cm^{-1}. HRMS (DART-ESI$^+$) calcd for $C_{23}H_{40}{}^{35}ClOS_2Si_2$: 487.1748; found *m/z* 487.1732.

2-Chloro-5-(3-hexylthiophen-2-yl)thiophene (3Ad): Synthesis of **3Ad** was carried out in a similar manner to the synthesis of **3Aa** from 2-chlorothiophene (**1d**, 64.8 mg, 0.55 mmol), TMPMgCl·LiCl (0.66 mL, 0.66 mmol, 1 M in THF), 2-bromo-3-hexylthiophene (**2A**, 163 mg, 0.66 mmol) and Pd-PEPPSI-SIPr (7.4 mg, 11 μmol) in THF (5.4 mL) at 60 °C for 24 h (light yellow oil, 82%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.85-0.91 (t, *J* = 7.2 Hz, 3H), 1.26-1.39 (m, 6H), 1.56-1.65 (m, 2H), 2.67-2.73 (t, *J* = 7.8 Hz, 2H), 6.86 (d, *J* = 4.1 Hz, 1H), 6.87 (d, *J* = 4.1 Hz, 1H), 6.92 (d, *J* = 5.0 Hz, 1H), 7.18 (d, *J* = 5.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 22.7, 29.2, 29.3, 30.9, 31.8, 124.3, 125.3, 126.5, 129.6, 129.7, 130.0, 135.0, 140.3. IR (ATR) 2955, 2927, 2856, 1514, 1455, 1417, 1377, 1066, 999, 834, 791, 722, 693, 671, 648 cm^{-1}. HRMS (DART-ESI$^+$) calcd for $C_{14}H_{18}{}^{35}ClS_2$: 285.0538; found *m/z* 285.0528.

2-Chloro-5-(3-(4-(1,1,3,3,3-pentamethyldisiloxan-1-yl)butan-1-yl)thiophen-2-yl)thiophene (3Cd): Synthesis of **3Cd** was carried out in a similar manner to the synthesis of **3Aa** from 2-chlorothiophene (**1d**, 60.5 mg, 0.51 mmol), TMPMgCl·LiCl (0.61 mL, 0.61 mmol, 1 M in THF), 2-bromo-3-(4-(1,1,3,3,3-pentamethyldisiloxan-1-yl)butan-1-yl)thiophene (**2C**, 222 mg, 0.61 mmol) and Pd-PEPPSI-SIPr (7.0 mg, 10 μmol) in THF (5.1 mL) at 60 °C for 24 h (light yellow oil, 79%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.03 (s, 6H), 0.05 (s, 9H), 0.50-0.56 (m, 2H), 1.32-1.42 (m, 2H), 1.58-1.68 (m, 2H), 2.70 (t, *J* = 7.6 Hz, 2H), 6.86 (d, *J* = 3.7 Hz, 1H), 6.87 (d, *J* = 3.7 Hz, 1H), 6.92 (d, *J* = 5.0 Hz, 1H), 7.18 (d, *J* = 5.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 0.5, 2.1, 18.3, 23.3, 29.0, 34.6, 124.3, 125.4, 126.5, 129.6, 129.7, 130.0, 135.0, 140.3. IR (ATR) 2956, 2925, 2858, 1514, 1454, 1416, 1252, 1054, 1000, 840, 791, 753, 726, 690, 649, 627 cm^{-1}. HRMS (DART-ESI$^+$) calcd for $C_{17}H_{28}{}^{35}ClOS_2Si_2$: 403.0809; found *m/z* 403.0804.

2-Chloro-5-(thiophen-2-yl)thiophene (3Dd): Synthesis of **3Dd** was carried out in a similar manner to the synthesis of **3Aa** from 2-chlorothiophene (**1d**, 2.58 g, 21.8 mmol), TMPMgCl·LiCl (26.1 mL, 26.1 mmol, 1 M in THF), 2-bromothiophene (**2D**, 2.50 mL, 26.1 mmol) and Pd-PEPPSI-SIPr (0.11 mg, 0.16 mmol) in THF (50 mL) at 60 °C for 24 h (light yellow solid, 76%), whose ^{1}H NMR spectrum was identical to that

reported in the literature.[18] ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.83 (d, *J* = 4.1 Hz, 1H), 6.93 (d, *J* = 4.1 Hz, 1H), 7.01 (dd, *J* = 3.7, 5.0 Hz ,1H), 7.10 (dd, *J* = 0.9, 3.7 Hz, 1H), 7.22 (dd, *J* = 1.4, 5.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 123.0, 124.0, 124.9, 127.0, 128.0, 128.8, 136.1, 136.6.

2-Chloro-3-hexyl-5-(5-(3-hexylthiophen-2-yl)-3-hexylthiophen-2-yl)thiophene[17] **(5)**: To chlorobithiophene **3Aa** (111 mg, 0.30 mmol) was added a 0.75 M THF solution of TMPMgCl·LiCl (0.60 mL, 0.45 mmol) at room temperature under nitrogen atmosphere. After stirring for 3 h, 2-bromo-3-hexylthiophene (**2A**: 133 mg, 0.54 mmol), Pd-PEPPSI-SIPr (4.1 mg, 6 μmol) and THF (0.45 mL) were added successively. The resulting solution was stirred at 60 °C for 24 h. After cooling the resulting mixture to room temperature, the reaction was terminated by pouring the mixture to 1 M HCl_{aq} and chloroform to separate into two phases. The aqueous layer was extracted twice with chloroform and the combined organic extracts were dried over anhydrous sodium sulfate. Removal of the solvent left a crude oil, which was purified by column chromatography (hexanes) on silica gel to afford 101 mg of **5** in 59% yield as a light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.86-0.94 (m, 9H), 1.28-1.42 (m, 18H), 1.56-1.70 (m, 6H), 2.57 (t, *J* = 7.8 Hz, 2H), 2.70 (t, *J* = 7.8 Hz, 2H), 2.76 (t, *J* = 7.8 Hz, 2H), 6.81 (s, 1H), 6.91 (s, 1H), 6.92 (d, *J* = 5.2 Hz, 1H), 7.16 (d, *J* = 5.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 22.8, 28.2, 29.1, 29.4, 29.7, 30.7, 30.8, 31.8, 123.8, 124.2, 126.4, 128.7, 129.9, 130.2, 130.5, 132.4, 134.5, 139.7, 139.8, 140.1.

2-Chloro-3-hexyl-5-(5-(5-(3-hexylthiophen-2-yl)-3-hexylthiophen-2-yl)-3-hexylthiophen-2-yl)thiophene (6): The reaction was carried out in a similar manner to the synthesis of **5** from 2-chloro-3-hexyl-5-(3-hexylthiophen-2-yl)thiophene (**3Aa**, 111 mg, 0.30 mmol), TMPMgCl·LiCl (0.60 mL, 0.45 mmol, 0.75 M in THF), 2-bromo-3-hexyl-5-(3-hexylthiophen-2-yl)thiophene (**4**)[6a] (223 mg, 0.54 mmol) and Pd-PEPPSI-SIPr (4.1 mg, 6 μmol) in THF (0.45 mL) to afford **6** as a light yellow oil (50%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.86-0.92 (m, 12H), 1.28-1.43 (m, 24H), 1.56-1.71 (m, 8H), 2.57 (t, *J* = 7.8 Hz, 2H), 2.71 (t, *J* = 7.8 Hz, 2H), 2.76 (t, *J* = 7.8 Hz, 2H), 2.78 (t, *J* = 8.0 Hz, 2H), 6.82 (s, 1H), 6.91-6.94 (m, 3H), 7.16 (d, *J* = 5.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 22.8, 28.2, 29.1, 29.3, 29.4, 29.5, 29.7, 30.6, 30.7, 30.8, 31.7, 31.8, 123.7, 124.2, 126.4, 128.5, 128.8, 130.0, 130.2, 130.3, 130.6, 132.4, 134.2, 134.3, 139.8, 139.9, 140.0, 140.2. IR (ATR) 2955, 2926, 2856, 1731, 1537, 1464, 1377, 1196, 1093, 1043, 832, 726, 689, 650 cm^{-1}. HRMS (DART-ESI$^+$) calcd for $C_{40}H_{58}{}^{35}ClS_4$: 701.3109; found *m/z* 701.3112.

2-Chloro-5-(5-(thiophen-2-yl)thiophen-2-yl)thiophene[19] **(7)**: The reaction was carried out in a similar manner to the synthesis of **5** from **3Dd**, TMPMgCl·LiCl (3.5 mL, 3.5 mmol, 1 M in THF), **2D** (865 mg, 3.5 mmol) and Pd-PEPPSI-SIPr (32 mg, 0.047 mmol) to afford **7** in 91% yield as a colorless solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.84 (d, *J* = 4.1 Hz, 1H), 6.93 (d, *J* = 4.1 Hz, 1H), 7.00 (d, *J* = 4.1 Hz, 1H), 7.03 (dd, *J* = 3.7, 5.0 Hz, 1H), 7.07 (d, *J* = 4.1 Hz, 1H), 7.17 (dd, *J* = 0.9, 3.7 Hz, 1H), 7.23 (dd, *J* = 1.4, 5.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 122.8, 124.0, 124.4, 124.5, 124.8, 127.1, 128.0, 128.9, 135.3, 135.9, 136.7, 137.0.

2-Chloro-3-hexyl-(5-(3-hexylthiophen-2-yl)-3-methylthiophen-2-yl)thiophene (8): The reaction was carried out in a similar manner to the synthesis of **5** from 2-chloro-3-hexyl-5-(3-methylthiophen-2-yl)thiophene (**3Ba**, 704 mg, 2.35 mmol), TMPMgCl·LiCl (3.5 mL, 3.5 mmol, 1 M in THF), **2A** (865 mg, 3.5 mmol) and Pd-PEPPSI-SIPr (32 mg, 0.047 mmol) in THF (3.1 mL) at 60 °C for 24 h to afford 71% of **8** as a light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.86-0.93 (m, 6H), 1.27-1.40 (m, 12H), 1.58-1.68 (m, 4H), 2.36 (s, 3H), 2.57 (t, *J* = 7.5 Hz, 2H), 2.76 (t, *J* = 7.8 Hz, 2H), 6.82 (s, 1H), 6.87 (s, 1H), 6.92 (d, *J* = 5.0 Hz, 1H), 7.16 (d, *J* = 5.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 15.5, 22.7, 28.2, 29.1, 29.3, 29.4, 29.7, 30.7, 31.7, 31.8, 123.8, 124.1, 125.9, 130.0, 130.2, 130.3, 130.4, 132.8, 134.1, 134.3, 139.8, 139.9. IR (ATR) 2955, 2926, 2856, 1546, 1456, 1378, 1090, 1043, 832, 727, 651, 620 cm^{-1}. HRMS (DART-ESI$^+$) calcd for $C_{25}H_{34}{}^{35}ClS_3$: 465.1511; found *m/z* 465.1532.

2-Chloro-3-hexyl-(5-(3-methylthiophen-2-yl)-3-methylthiophen-2-yl)thiophene (9): The reaction was carried out in a similar manner to the synthesis of **5** from 2-chloro-3-hexyl-5-(3-methylthiophen-2-yl)thiophene (**3Ba**, 660 mg, 2.21 mmol), TMPMgCl·LiCl (3.3 mL, 3.3 mmol, 1 M in THF), **2B** (584 mg, 3.3 mmol) and Pd-PEPPSI-SIPr (30 mg, 0.044 mmol) in THF (2.9 mL) at 60 °C for 24 h to afford 88% of **9** as a light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.90 (t, *J* = 7.1 Hz, 3H), 1.29-1.40 (m, 6H), 1.56-1.65 (m, 2H), 2.36 (s, 3H), 2.41 (s, 3H), 2.57 (t, *J* = 7.8 Hz, 2H), 6.83 (s, 1H), 6.88 (d, *J* = 5.2 Hz, 1H), 6.90 (s, 1H), 7.13 (d, *J* = 5.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 15.5, 15.6, 22.7, 28.2, 29.1, 29.7, 31.7, 123.3, 124.0, 125.9, 129.5, 130.2, 130.9, 131.6, 132.8x2, 134.1, 134.4, 139.9. IR (ATR) 2925, 2856, 1454, 1378, 1043, 927, 830, 704, 617 cm^{-1}. HRMS (DART-ESI$^+$) calcd for $C_{20}H_{24}{}^{35}ClS_3$: 395.0729; found *m/z* 395.0719.

2-Chloro-3-hexyl-5-(3-(3-hexyl-2-chlorothiophen-5-yl)-5-(3-hexylthiophen-2-yl)thiophen-2-yl)thiophene (10): The reaction was carried out in a similar manner to the synthesis of **5** from **3T-2Cl**[20] (216 mg, 0.445 mmol), TMPMgCl·LiCl (0.67 mL, 0.67 mmol, 1 M in THF), **2A** (166 mg, 0.67 mmol), and Pd-PEPPSI-SIPr (6 mg, 9 μmol) in THF (5.0 mL) at 60 °C for 24 h to afford **10** as a light yellow oil (87%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.86-0.93 (m, 9H), 1.27-1.41 (m, 18H), 1.54-1.69 (m, 6H), 2.55 (t, *J* = 7.5 Hz, 4H), 2.77 (t, *J* = 7.8 Hz, 2H), 6.81 (s, 1H), 6.87 (s, 1H), 6.94 (d, *J* = 5.4 Hz, 1H), 7.05 (s, 1H), 7.20 (d, *J* = 5.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 22.7, 28.1, 29.0, 29.3, 29.4, 29.6, 29.7, 30.8, 31.8, 124.4, 124.9, 125.9, 127.7, 127.8, 128.6, 129.5, 130.2, 130.9x2, 131.7, 133.3, 135.5, 139.6, 139.7, 140.5. IR (ATR) 2955, 2926, 2856, 1549, 1521, 1464, 1377, 1201, 1034, 834, 725, 640 cm^{-1}. HRMS (DART-ESI$^+$) calcd for $C_{34}H_{45}{}^{35}Cl_2S_4$: 651.1781; found *m/z* 651.1778.

2-(3-Hexylthiophen-2-yl)-5-phenylthiophene (11): To chlorobithiophene **3Ad** (73.1 mg, 0.256 mmol) and $NiCl_2(PPh_3)IPr$ (4.0 mg, 5.1 μmol) in THF (0.33 mL) was added a 1.02 M THF solution of phenylmagnesium bromide (0.30 mL, 0.31 mmol) dropwise at room temperature under a nitrogen atmosphere. The resulting mixture was stirred at 60 °C for 24 h. After cooling the reaction mixture to room temperature, the solution was poured into a mixture of chloroform and 1 M hydrochloric acid to separate into two phases. The aqueous layer was extracted with chloroform twice. The combined organic layer was dried over anhydrous sodium sulfate and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel using hexanes as an eluent to afford 71.1 mg of **11** (85%). ^{1}H NMR (400 MHz, $(CD_3)_2CO$) δ 0.90 (t, *J* = 6.9 Hz, 3H), 1.29-1.47 (m, 6H), 1.64-1.75 (m, 2H), 2.85 (t, *J* = 8.0 Hz, 2H), 7.06 (d, *J* = 5.0 Hz, 1H), 7.18 (d, *J* = 4.1 Hz, 1H), 7.35 (t, *J* = 7.3 Hz, 1H), 7.39 (d, *J* = 5.0 Hz, 1H), 7.45 (t, *J* = 7.8 Hz, 2H), 7.49 (d, *J* = 3.7 Hz, 1H), 7.71 (dd, *J* = 1.1, 8.5 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 22.8, 29.3, 29.4, 30.8, 31.8, 123.5, 123.8, 125.7, 126.9, 127.6, 129.1, 130.2, 130.7, 134.3, 135.8, 139.8, 144.0. IR (ATR) 2953, 2926, 2855, 1599, 1493, 1463, 1377, 1261, 1073, 1030, 906, 834, 800, 754, 723, 689, 655, 639, 627 cm^{-1}. HRMS (DART-ESI$^+$) calcd for $C_{20}H_{23}S_2$: 327.1241; found *m/z* 327.1247.

Polymerization of chlorobithiophene 3Ca leading to poly(3-(4-(1,1,3,3,3-pentamethyldisiloxan-1-yl)butan-1-yl)-thiophen-2,5-diyl)-*alt*-poly(3-hexylthiophen-2,5-diyl) (12): To 20 mL Schlenk tube equipped with a magnetic stirring bar were added **3Ca** (355 mg, 0.73 mmol) and 1 M THF solution of TMPMgCl·LiCl (0.87 mL, 0.87 mmol) was added at room temperature. After stirring at room temperature for 3 h, THF (7.2 mL) and $NiCl_2(PPh_3)IPr$ (5.7 mg, 7.3 μmol) was then added to initiate polymerization. The color of the solution was turned to light orange. After stirring at room temperature for 24 h, 1 M HCl_{aq} (2 mL) was added to terminate the polymerization to separate into two phases. Aqueous was extracted with chloroform and the combined organic extracts were concentrated under reduced pressure to leave crude oil still containing organic solvent, which was poured into methanol to form precipitates. The mixture was filtered off and the residue was washed with methanol and hexanes to afford 165 mg of **12** (50 %). The head-to-tail (HT) regioregularity was confirmed by ^{1}H NMR analysis (HT: 2.80; TT: 2.60 ppm, respectively) and the molecular weight (M_n) and the molecular

weight distribution (M_w/M_n) was estimated by SEC analysis. HT>99%, M_n = 44200, M_w = 61600, M_w/M_n = 1.39. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.06 (s, 15H), 0.57-0.64 (m, 2H), 0.92 (brt, *J* = 6.9 Hz, 3H), 1.32-1.40 (m, 4H), 1.40-1.52 (m, 4H), 1.66-1.79 (m, 4H), 2.81 (brt, *J* = 6.9 Hz, 4H), 6.979 (s, 1H), 6.982 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 0.5, 2.2, 14.3, 18.4, 22.8, 23.5, 29.4, 29.6, 30.7, 31.9, 34.4, 128.8, 130.7, 133.9, 139.9, 140.0. IR (ATR) 2955, 2926, 2857, 1509, 1252, 1056, 841, 805, 781, 754 cm^{-1}.

Synthesis of polythiophene 12 by Murahashi coupling polymerization with *n*-BuLi: To a solution of **3Ca** (54 mg, 0.11 mmol) in 1.6 mL of cyclopentyl methyl ether (CPME) was added a hexane solution of 1.6 M *n*-butyllithium (70.0 μL, 0.11 mmol) at -78 °C and the resulting mixture was stirred with raising the temperature to 0 °C over 30 min. Then, $NiCl_2(PPh_3)IPr$ (1.7 mg, 2.2 μmol) was added and further stirring was continued for 2 h. The reaction mixture was poured into a mixture of 1 M HCl_{aq} (2.0 mL) and methanol to form a precipitate, which was filtered off to leave a dark purple solid. After washing with methanol repeatedly, the solid was dried under reduced pressure to afford 35 mg of **12** (73% isolated yield). Molecular weight and molecular weight distribution were estimated by SEC analysis (eluent: $CHCl_3$) using polystyrene standards. SEC analysis showed M_n = 25700, M_w = 37300, M_w/M_n = 1.45. The regioregularity was estimated by ^{1}H NMR analysis (thienyl-CH_2- signals) at δ 2.80 (HT) and 2.60 (TT) signals. (HT regioregularity = 98%).

Acknowledgment

This work was supported by Kakenhi B (No. 25288049) by JSPS and by Special Coordination Funds for Promoting Science and Technology, Creation of Innovation Centers for Advanced Interdisciplinary Research Areas (Innovative Bioproduction Kobe) by MEXT.

Supporting Information

YES (this text will be updated with links prior to publication)

Primary Data

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