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A formal preparation of regioregular and alternating thiophene−thiophene copolymers bearing different substituents

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Abstract

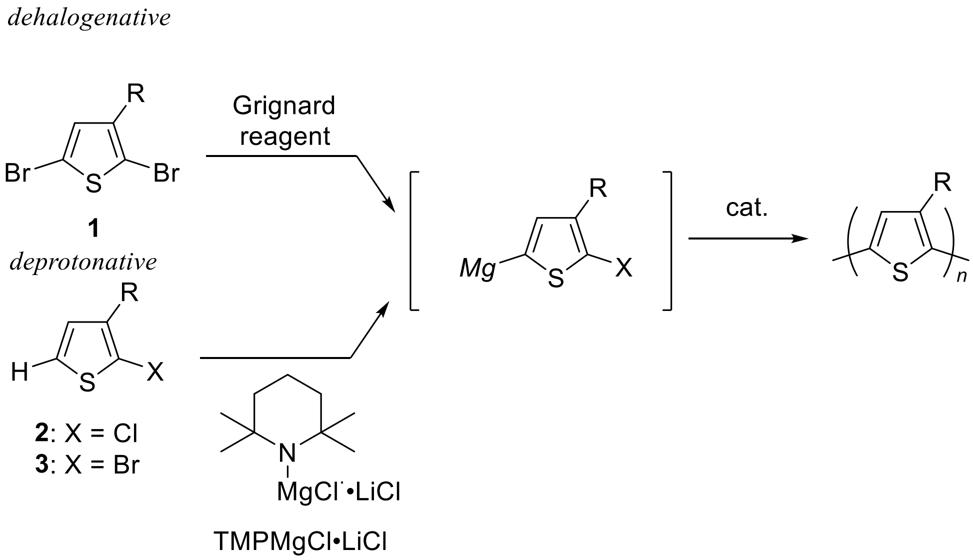
Differently substituted thiophene−thiophene alternating copolymer was formally synthesized employing a halobithiophene as a monomer. Nickel-catalyzed polymerization of bithiophene, which substituent at the 3-position involves alkyl, fluoroalkyl, or oligosiloxane containing alkyl group, afforded the corresponding copolymer in good to excellent yield. The solubility test to organic solvents was performed to reveal several copolymers show a superior solubility. X-ray diffraction analysis of the thin film of the alternating copolymer composed of methyl and branched oligosiloxane substituents was also performed and found that the film suggested formation of dual-layered structure.

Keywords

regioregular polythiophene; alternating copolymer; nickel(II) catalyst; solubility; oligosiloxane

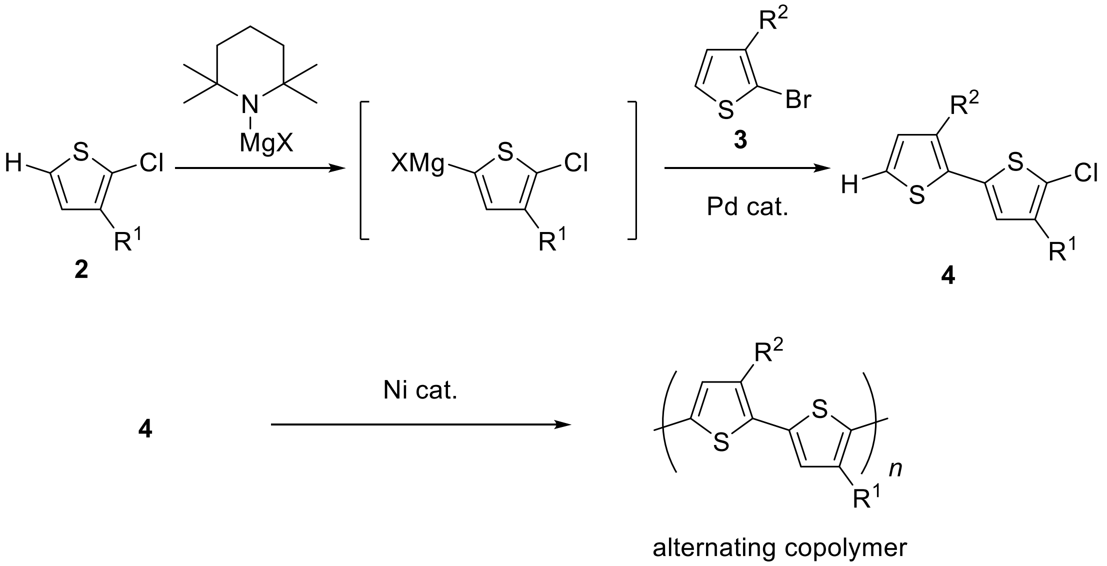
Introduction

Polythiophenes attract much attention in materials science because of their extended π-conjugation, which is applied for a wide range of electronic materials. In particular, the regioregular polymers with head-to-tail (HT) orientation by the substituent at the 3-position are extensively studied to date since those generally show superior performances as material.[1-6] Cross-coupling polymerization catalyzed by a transition metal complex has been recognized as an effective tool to afford the regioregular polythiophene, in which 2,5-dihalo-3-substituted thiophene **1** is employed as a monomer precursor converting to the corresponding organometallic monomer by the halogen−magnesium exchange reaction with a Grignard reagent. Employment of **1** leading to polythiophene is shown to proceed in a dehalogenative manner.[3] We have recently shown that generation of the organometallic monomer species can also be achieved alternatively by a deprotonative method with 2-halo-3-substituted thiophene **2** and **3** with a bulky magnesium amide Knochel-Hauser base (TMPMgCl·LiCl)[7] and following polymerization catalyzed by a nickel complex leads to the regioregular HT-polythiophene.[8,9] An additional remark of the deprotonative protocol for polythiophene is the use of chlorothiophene **3**, in which the use of a nickel NHC (N-heterocyclic carbene) complex has found effective.[10,11] We have also engaged in the design of the side chain of polythiophenes and several functionalities have been successfuly introduced.[12-14] Our further concern is turned to the copolymerization of thiophene employing differently substituted thiophene monomers, with which several copolymerizations are plausible to give thiophene/thiophene copolymers of random[15] (statistical), gradient,[16,17] block,[18,19] alternating,[20-23] etc.[24,25] We are thus interested in the preparation of alternating polythiophene bearing two kinds of different substituent. We envisaged that such an alternating copolymer in the perfect regularity is achieved by deprotonative polymerization employing a bithiophene with different substituents at the 3,3'-positions.



Scheme 1: Cross-coupling polymerization of thiophene

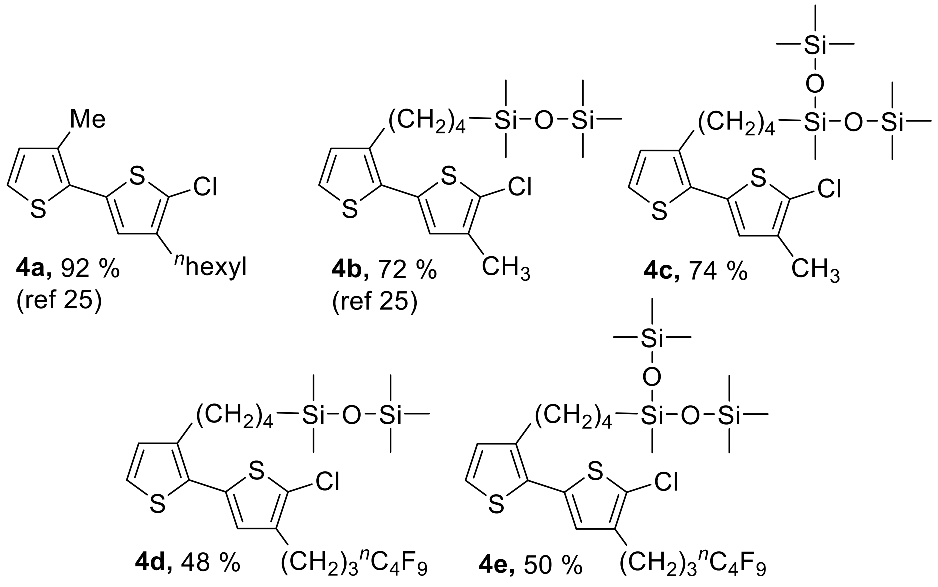
We have recently shown that the coupling of 2-chloro-3-substituted thiophene **2** with 2-bromo-3-substituted thiophene **3**.[25] The use of a palladium catalyst [26] efficiently surpressed the undesired polymerization to afford the HT halobithiophene with different substituents. Polymerization of **4** (R^1 = ^{n}hexyl; $R^2 = (CH_2)_4Si(Me_2)OSiMe_3$) was also examined preliminary and it was confirmed that the formal alternating copolymer was obtained with extremely high regularity. We herein wish to study polymerization of bithiophene **4**, which possesses several kinds of substituents with a variety of functionalities. Since a part of homopolymer is well-recognized as rather insoluble in most of organic solvents, the improved solubility in the related alternating copolymer is discussed.



Scheme 2: polymerization of bithiophene

Results and Discussion

Synthesis of chlorobithiophenes with different substitents at the 3,3'-positions were carried out in a manner as we described previously.[25] We chose five kinds of chlorobithiophenes as a monomer precursor for the alternating copolymer as summarized in Scheme 3. Cross coupling proceeded smoothly as shown in Scheme 2 to afford bithiophene **4** in 48-92% yield.



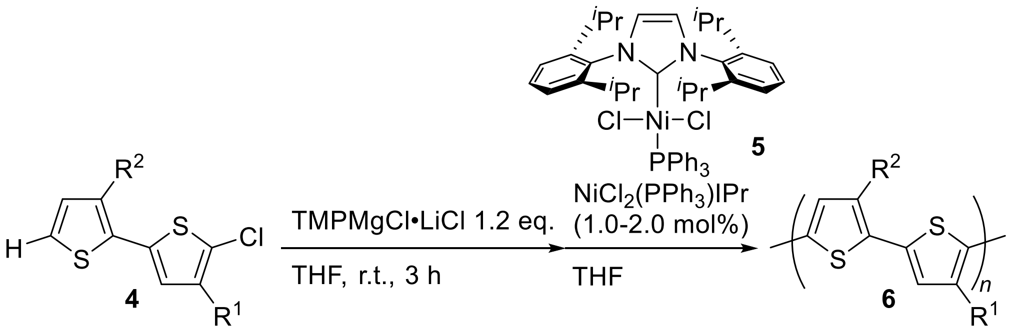
Scheme 3: Preparation of chlorobithiophenes

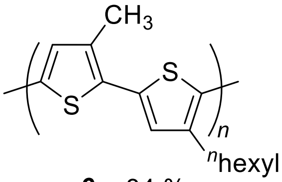
The formal synthesis of alternating copolymer was carried out with monomer precursor **4** by deprotonation with Knochel−Hauser base followed by addition of nickel catalyst NiCl$_2$(PPh$_3$)IPr to initiate the polymerization of bithiophene.

We first carried out the polymerization of chlorobithiophene **4a** bearing hexyl and methyl substituents at the 3- and 3'-positions, respectively. Although the polymerization took place in a slightly low yield (34%) indeed, formation of hardly soluble precipitates was observed during the reaction and the thus obtaind solid was found to fail to dissolve in any of organic solvents. As studied in references on the regioregular polythiophene synthesis, P3HT (poly-3-hexylthiophene) can be smoothly dissolved in several organic solvents. In contrast, there has been few reports on the preparation of regioregular polythiophene bearing a methyl group at the 3-position.[27] Incorpration of the alternating methyl substituent would resulted in much inferior solubility of the alternating copolymer, accordingly. Several kinds of chlorobithiophene **4** was then subjected to the polymerization in a similar manner.

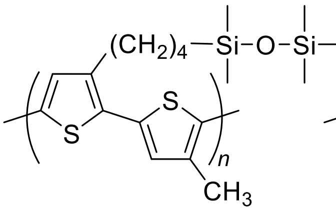
The result concerning the formal alternating copolymerization is summarized in Table 1. The deprotonation by the Knochel−Hauser base was carried out at room temperature for 3 h. Addition of the nickel catalyst **5** and further stirring at room temperature followed. The reaction proceeded smoothly to afford the corresponding formal alternating copolymers in 48-84% yields.[28] The molecular weight was found controllable based on the ratio of monomer/catalyst feed ratio and the molecular weight distributions were relatively narrow.

Table 1: Polymerization of chlorobithiophenes

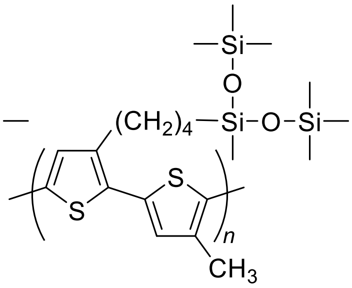




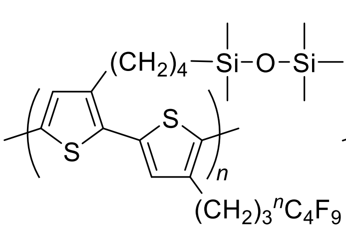
6a, 34 %
(2.0 mol%, 60 °C, 20 h)
Low solubility



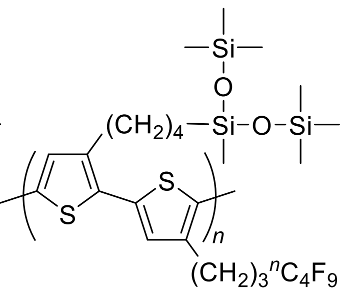
6b, 84%
(2.0 mol%, r.t., 24 h)
M_n=10400, M_w/M_n=1.62



6c, 84%
(1.0 mol%, r.t., 18 h)
M_n=70100, M_w/M_n=1.38



6d, 48%
(1.0 mol%, r.t., 1 h)
M_n=68600, M_w/M_n=1.15



6e, 58%
(1.0 mol%, r.t., 1 h)
M_n=33200, M_w/M_n=1.07

Solubility tests of the obtained polymer was studied as summarized in Figure 1. Although the alternating copolymer composed of methyl and C4 alkyl with terminal pentamethyldisiloxane group **6b** was obtained with slightly low molecular weight suggesting improved solubility compared with **6a** (R^2 = Me; R^1 = ^{n}hexyl), attempted dissolution of the obtained polythiophene **6b** to chloroform was found unsuccessful. Switching the oligosiloxane moiety to the branched derivative (R^2 = $(CH_2)_4Si(Me)(OSiMe_3)_2$) remarkably improved the solubility and the copolymer **6c** was soluble in chloroform whereas dissolution to hexane was unsuccessful. Copolymers bearing a fluoroalkyl substituent ($(CH_2)_3{}^nC_4F_9$), whose solubility of the corresponding homopolymer was relatively worse than that of the long-chained alkyl derivative, was then examined. The alternating copolymer **6d** bearing fluoroalkyl and non-branched disiloxane, respectively, was nicely dissolved in chloroform, while attempted dissolution of **6e** in hexanes was shown to be unsuccessful. Remarkable solubility in hexanes concerning copolymer bearing a partial substituent of the fluoroalkyl group was achieved when copolymer composed of branched oligosiloxane **6e** was employed.

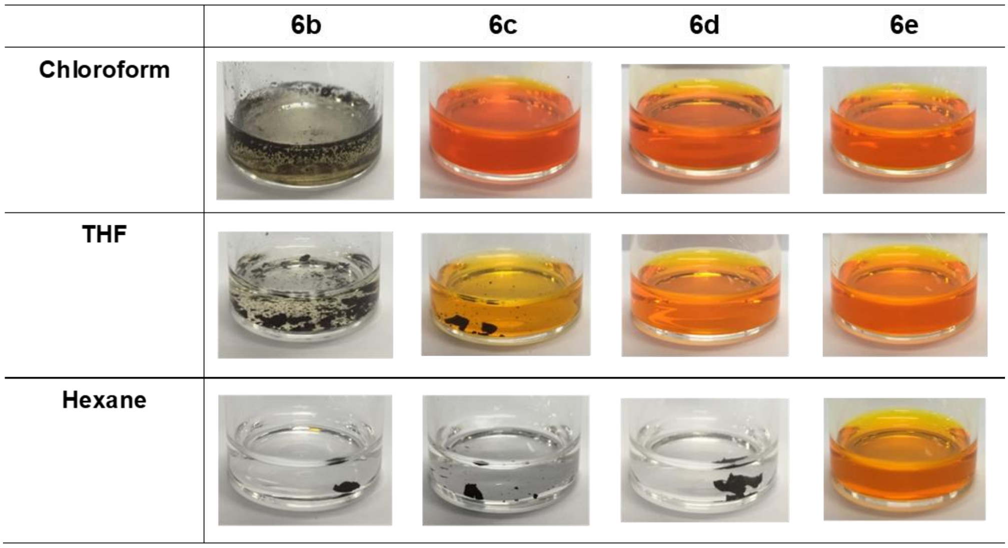
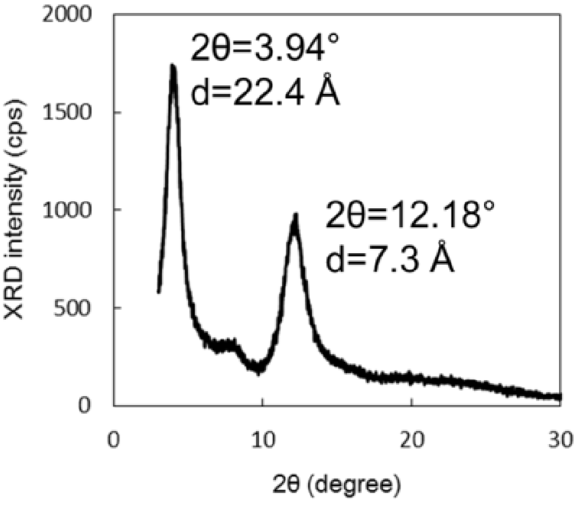


Figure 1: Solubility tests of alternating copolymer **6** (1 mg dissolved in 1 mL of the solvent)

XRD analysis of the copolymer **6c** bearing a branched oligosiloxane and methyl groups was carried out. Two remarkable peaks were observed in 2θ = 3.94° and 12.18°, respectively, as shown in Fig 2 (a). The result suggests that the thin film of the alternating copolymer **6c** shows bilayer lamellar structure involving 7.3 Å and 22.4 Å distances, respectively,[13,29,30] (Fig 2(b)) The molecular modeling of the alternating copolymer **6c** suggests the chain lengths of 11.6 Å and 2.2 Å, respectively. The values of the observed layer distances of copolymer **6c** closely corresponds to the twice values 11.6 x 2 and 2.2 x 2 (Fig 2(c)), in which conformation of the carbon−carbon single bond between thiophene rings is anti. The proposed layer distances of regiorandom poly(3-methylthiophene) of 7.7 Å reported by Yan and co-workers also suggested the close value of our result from the XRD analysis (7.3 Å) on the layer distance corresponding to the aggregation of the alternating methyl substituent.[27]

(a)



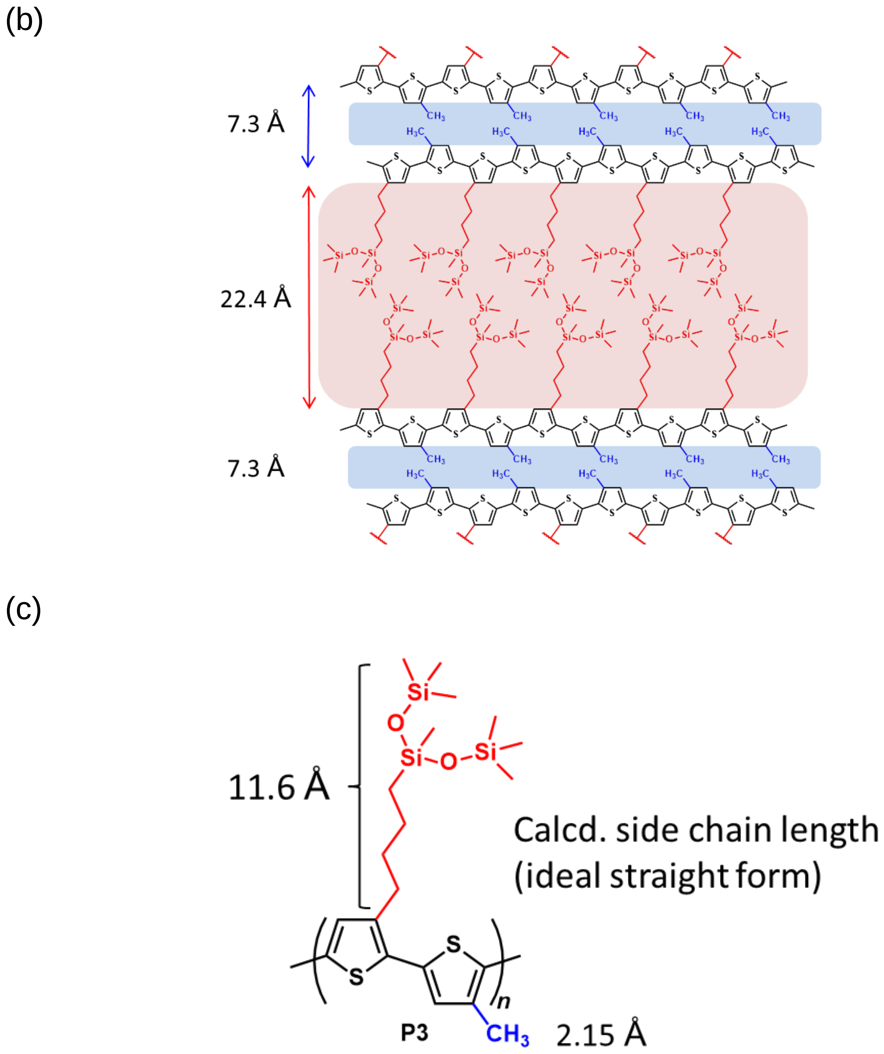


Figure 2: XRD measurement and prediction of bilayer lamellar structure of polymer **6c**

In summary, we have shown that formal alternating thiophene–thiophene copolymers were synthesized when a differently-substituted halobithiophene was employed as a monomer by nickel-catalyzed deprotonative polymerization was applied. Introduction of oligosiloxane containing at the side chain revealed improve solubilities in organic solvents, by which several components bearing a less soluble by itself could be incorporated into the copolymer. Measurement of X-ray diffraction revealed that the alternating copolymer bearing different chain lengths at the side chain revealed to show the structure of dual layer distances in the thin-film state.

Experimental.

General. Polymerization was carried out with standard Schlenk technique under a nitrogen or argon atmosphere. ^1H NMR (400 MHz), ^{19}F NMR (376 MHz) and $^{13}C\{^1H\}$ NMR (100 MHz) spectra were measured on JEOL ECZ400 as a $CDCl_3$ solution unless noted. The chemical shifts were expressed in ppm with $CHCl_3$ (7.26 ppm for ^1H), C_6F_6 (−164.9 ppm for ^{19}F) 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-1H and 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-402HQ and KF-404HQ. Molecular weights and molecular weight distributions were estimated on the basis of the calibration curve obtained by 6 standard polystyrenes. UV-vis absorption spectra of the polymer films were measured with Shimadzu UV-3150. XRD analysis was carried out with Rigaku RINT-2000(CuKα). Concerning the solvent of the nickel and palladium-catalyzed reactions THF (anhydrous grade) was purchased from Kanto Chemical. Co. Ltd. and passed through alumina and copper column (Nikko Hansen & Co. Ltd.) or distilled from sodium dispersion in a mineral oil/benzophenone ketyl[31] prior to use. Knochel-Hauser base (TMPMgCl·LiCl) was purchased from Sigma-Aldrich Co. Ltd. as a 1 M

THF solution. $NiCl_2(IPr)PPh_3$ (**5**) was purchased from TCI Co. Ltd. Other chemicals were purchased and used without further purification. Preparation of chlorobithiophene **4a** and **4b** was performed in a manner reported previously.[25] Results on the synthesis and characteristics of the obtained **4c-4e** were summarized in Supporting Information.

General procedure for the polymerization of chlorobithiophene representative as the reaction of 4b leading to poly(3-(4-(1,1,3,3,3-pentamethyldisiloxy)butan-3-yl)thiophen-2,5-diyl)-*alt*-poly(3-methylthiophen-2,5-diyl) (6b): To 20 mL Schlenk tube equipped with a magnetic stirring bar were added **4b** (104 mg, 0.25 mmol) and 1 M THF solution of TMPMgCl·LiCl (0.3 mL, 0.3 mmol) was added at room temperature. After stirring at room temperature for 3 h, THF (2.5 mL) and $NiCl_2(PPh_3)IPr$ (**5**, 3.9 mg, 6.0 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, the reaction mixture was poured into a mixture of hydrochloric acid (1.0 M, 2 mL) and methanol (10 mL) to form a precipitate, which was filtered off to leave a dark purple solid. After washing with methanol and hexanes repeatedly, the solid was dried under reduced pressure to afford 79.6 mg of **6b** (84% isolated yield). The head-to-tail (HT) regioregularity was confirmed by ^1H NMR analysis and the molecular weight (M_n) and the molecular weight distribution (M_w/M_n) was estimated by SEC analysis. HT=98%, $M_n = 10400$, $M_w = 16900$, $M_w/M_n = 1.62$. ^1H NMR (400 MHz, $CDCl_3$) δ 0.02-0.08 (br, 15H), 0.50-0.63 (m, 2H), 1.41-1.52 (m, 2H), 1.64-1.78 (m, 2H), 2.44 (s, 3H), 2.75-2.85 (m, 2H), 6.95 (s, 1H), 6.99 (s, 1H). IR (ATR) 2956, 2925, 2855, 1728, 1445, 1252, 1057, 841, 806, 782, 753 cm^{-1}.

Other polymers **6c-6e** were synthesized in a similar manner. Properties and spectroscopic data were summarized below.

Poly(3-(4-bistrimethylsiloxysilylbutan-1-yl)thiophen-2,5-diyl)-*alt*-poly(3-methylthiophen-2,5-diyl) (6c): 84% yield. M_n = 70100, M_w/M_n = 1.38. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.03 (s, 3H), 0.09 (s, 18H), 0.43-0.65 (m, 2H), 1.35-1.55 (m, 2H), 1.63-1.85 (m, 2H), 2.44 (s, 3H), 2.71-2.92 (m, 2H), 6.95 (s, 1H), 7.00 (s, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ -0.1, 2.1, 15.9, 17.7, 23.3, 29.4, 34.2, 128.3, 130.0, 130.4, 131.0, 133.5, 134.3, 134.4, 140.0. IR (ATR) 2957, 2926, 2858, 1511, 1449, 1256, 1046, 841, 802, 782, 754, 668 cm^{-1}.

Poly(3-(4-(1,1,3,3,3-pentamethyldisiloxy)butan-3-yl)thiophen-2,5-diyl)-*alt*-poly(3-(4,4,5,5,6,6,7,7,7-nonafluoroheptyl)thiophen-2,5-diyl) (6d): 48% yield. M_n = 68600, M_w/M_n = 1.15. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.06 (s, 15H), 0.55-0.66 (m, 2H), 1.41-1.55 (m, 2H), 1.67-1.83 (m, 2H), 1.97-2.12 (m, 2H), 2.12-2.30 (m, 2H), 2.73-2.88 (m, 2H), 2.88-3.01 (m, 2H), 7.00 (br, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 0.5, 2.1, 18.4, 21.3 (br), 23.5, 28.7, 29.4, 30.6 (t, J = 22 Hz), 34.4, 128.2, 129.3, 130.7, 131.6, 133.3, 134.4, 137.8, 140.4. IR (ATR) 2957, 2925, 1452, 1356, 1252, 1232, 1169, 1134, 1059, 879, 842, 807, 783, 752, 720, 701 cm^{-1}.

Poly(3-(4-bistrimethylsiloxysilylbutan-1-yl)thiophen-2,5-diyl)-*alt*-poly(3-(4,4,5,5,6,6,7,7,7-nonafluoroheptyl)thiophen-2,5-diyl) (6e): 58% yield. SEC analysis showed M_n = 33200, M_w/M_n = 1.07. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.03 (s, 3H), 0.09 (s, 18H), 0.44-0.66 (m, 2H), 1.37-1.60 (m, 2H), 1.60-1.86 (m, 2H), 1.94-2.33 (m, 4H), 2.63-3.11 (m, 4H), 7.00 (br, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ -0.2, 2.0, 17.7, 21.3, 23.3, 28.7, 29.4, 30.6 (t, J = 22 Hz), 34.2, 128.2, 129.3, 130.7, 131.6, 133.3, 134.5, 137.8, 140.4. IR (ATR) 2957, 1455, 1356, 1251, 1233, 1134, 1052, 840, 801, 773, 754, 720, 700 cm^{-1}.

Supporting Information

Synthesis of chlorobithiophene **4** was carried out in a manner as shown our previous report. Spectroscopic properties and analytical data for **4** were summarized below.

2-Chloro-3-hexyl-5-(3-methylthiophen-2-yl)thiophene (4a):[25] 92% yield as a light yellow oil. ^{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{^{1}H} NMR (100 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-methyl-5-(3-(4-pentamethyldisiloxybutan-1-yl)thiophen-2-yl)thiophene (4b):[25] 72% yield as a light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.0 (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), 2.67-2.74 (m, 2H), 6.77 (s, 1H), 6.90 (d, *J* = 5.0 Hz, 1H), 7.15 (d, *J* = 5.0 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 0.5, 2.2, 13.7, 18.4, 23.3, 29.0, 34.5, 124.0, 124.6, 127.6, 128.4, 130.0, 132.7, 134.7, 140.0. 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-(3-(4-bistrimethylsiloxysilylbutan-1-yl)thiophen-2-yl)thiophene (4c): 74% yield as a light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.0 (s, 3H), 0.07 (s, 18H), 0.44-0.51 (m, 2H), 1.33-1.42 (m, 2H), 1.58-1.67 (m, 2H), 2.19 (s, 3H), 2.67-2.73 (m, 2H), 6.77 (s, 1H), 6.90 (d, *J* = 5.0 Hz, 1H), 7.15 (d, *J* = 5.0 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ -0.1, 2.0, 13.7, 17.6, 23.1, 28.9, 34.4, 124.1, 124.5, 127.6, 130.0, 130.1, 132.6, 134.7, 140.0. IR (ATR) 2957, 1411, 1256, 1045, 840, 799, 783, 754, 688, 651 cm^{-1}. HRMS (DART-ESI$^+$) calcd for $C_{20}H_{35}{}^{35}ClO_2S_2Si_3$: 491.1153; found *m/z* 491.1177.

2-Chloro-3-(4,4,5,5,6,6,7,7,7-nonafluoroheptyl)-5-(3-(4-pentamethyldisiloxybutan-1-yl)thiophen-2-yl)thiophene (4d): 46% yield as a light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.0 (s, 6H), 0.05 (s, 9H), 0.50-0.57 (m, 2H), 1.33-1.43 (m, 2H), 1.58-1.69 (m, 2H), 1.89-1.99 (m, 2H), 2.05-2.21 (m, 2H), 2.69 (t, *J* = 7.3 Hz, 2H), 2.71 (t, *J* = 7.3 Hz, 2H), 6.79 (s, 1H), 6.91 (d, *J* = 5.0 Hz, 1H), 7.17 (d, *J* = 5.0 Hz, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 0.4, 2.1, 18.3, 20.5 (br), 23.4, 27.4, 29.0, 30.4 (t, *J* = 22 Hz), 34.5, 124.3, 125.1, 126.0, 129.7, 130.2, 133.6, 137.6, 140.3. ^{19}F NMR (376 MHz, C_6F_6) δ -129.2, -127.6, -117.6, -84.2. IR (ATR) 2957, 1252, 1232, 1167, 1133, 1101, 1057, 1013, 879, 842, 807, 784, 752, 736, 719, 689, 651 cm^{-1}. HRMS (DART-ESI$^+$) calcd for $C_{24}H_{33}{}^{35}ClF_9OS_2Si_2$: 663.1056; found *m/z* 663.1050.

2-Chloro-3-(4,4,5,5,6,6,7,7,7-nonafluoroheptyl)-5-(3-(4-bistrimethylsiloxysilylbutan-1-yl)thiophen-2-yl)thiophene (4e): 50% yield as a light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.0 (s, 3H), 0.07 (s, 18H), 0.44-0.52 (m, 2H), 1.32-1.43 (m, 2H), 1.58-1.68 (m, 2H), 1.89-1.99 (m, 2H), 2.04-2.21 (m, 2H), 2.68 (t, *J* = 7.8 Hz, 2H), 2.70 (t, *J* = 7.8 Hz, 2H), 6.79 (s, 1H), 6.91 (d, *J* = 5.0 Hz, 1H), 7.17 (d, *J* = 5.0 Hz, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ -0.2, 2.0, 17.6, 20.5(br), 23.1, 27.4, 29.0, 30.4 (t, *J* = 22 Hz), 34.3, 124.3, 125.1, 126.0, 129.7, 130.2, 133.6, 137.6, 140.2. ^{19}F NMR (376 MHz, C_6F_6) δ -129.2, -127.6, -117.6, -84.2. IR (ATR) 2958, 1252, 1233, 1167, 1134, 1046, 870, 841, 800, 783, 754, 719, 689, 651 cm^{-1}. HRMS (DART-ESI$^+$) calcd for $C_{27}H_{43}{}^{35}ClF_9OS_2Si_3$: 737.1608; found *m/z* 737.1611.

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