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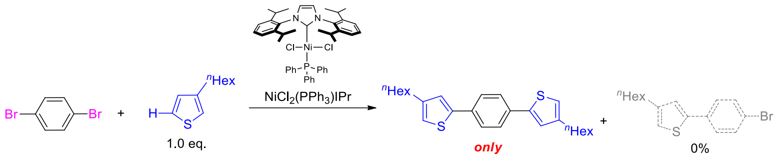

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Studies on the preference of multiple coupling in the introduction of thiophene ring into poly-halogenated aromatic compounds with nickel NHC catalyst

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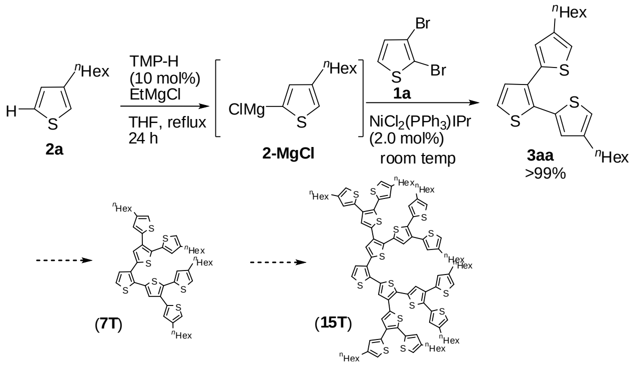
ABSTRACT

Several thiophene derivatives can be deprotonated by the combination of ethyl magnesium chloride (EtMgCl) and a catalytic amount of 2,2,6,6-tetramethylpiperidine (TMP-H). The metalated 3-hexylthiophene reacts with 2,3- and 2,5-dibromothiophenes in the presence of a nickel catalyst bearing NHC ligand (IPr) to afford the di-coupled product exclusively along with recovery of dibromothiophene albeit the equimolar reaction. The 1:1 reaction of 3-hexylthiophene with dibrominated benzene derivatives also gives di-coupled product as a sole product.

1. Introduction

Oligothiophene derivatives have attracted much interest as π-conjugated materials for organic electronic devices.[1] Development of synthetic method of oligothiophenes is a significant issue in organic chemistry, accordingly. In oligothiophene synthesis, cross-coupling reaction of thiophene–metal species with halothiophene has generally been employed to form thiophene–thiophene bond.[2] In addition, coupling reactions at the C–H bond of thiophene have recently reported[3] and applied to the synthesis of organic functional materials bearing thiophene unit.[4] Development of C–H coupling of heteroaromatic compounds with aryl halide has therefore been our major concern[5] and we have recently reported oligothiophene[6] and polythiophene[7] synthesis with deprotonative metalation of thiophene with Knochel-Hauser base (TMPMgCl·LiCl)[8] or the combination of Grignard reagent and a catalytic amount of secondary amine and following nickel-catalyzed cross-coupling reaction with a halide of thiophene. We have also shown that oligothiophene dendrimers are synthesized in a facile manner when regioselective metalation of 3-substituted thiophene and following coupling of 2,3-dibromothiophene in the presence of a nickel catalyst are employed.[9] The reaction affords branched oligothiophene 3-mer and repeating the similar reaction with the thus obtained oligomer leads to oligothiophene dendrimers of higher generations. (Scheme 1)



Scheme 1. Stepwise synthesis of oligothiophene dendrimers by regioselective coupling

During the course of our further studies on oligothiophene dendrimers we have learned that the reaction of 2,3-dibromothiophene (**1a**) with 2.5 equiv. of 3-hexylthiophene (**2a**) proceeds rapidly to give branched oligothiophene 3-mer **3aa** in a quantitative yield after stirring at room temperature for several hours in the presence of 2.0 mol% of a nickel catalyst bearing a *N*-heterocyclic carbenes (NHC) ligand, $NiCl_2(PPh_3)IPr$,[10, 11] while no mono-coupled byproduct **4aa** was observed. Even in the 1:1 reaction of **1a** and **2**, **3aa** was the sole product along with recovery of unreacted 2,3-dibromothiophene. (Scheme 2)

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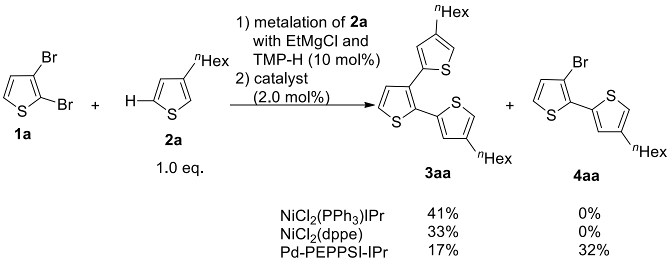


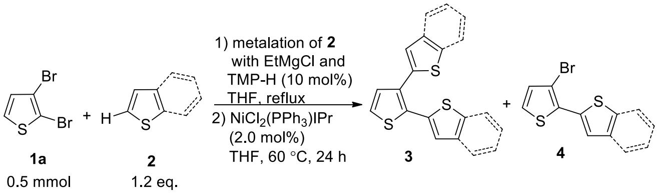
Scheme 2. The 1:1 reaction of **1a** and **2a** with several nickel or palladium catalysts

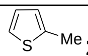
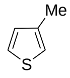
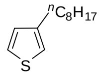
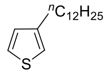
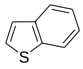
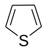
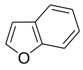
Related unexpected reactivity enhancement in the second cross coupling reaction was recently shown by Larrosa, Goldup, and co-workers with several polyhalogenated aromatic compounds and several organometallic compounds in the presence of palladium catalyst, PEPPSI.[12, 13] It has also been shown by Yokozawa that several cross-coupling polycondensations take place in a catalyst transfer manner to undergo intramolecular migration of a transition-metal catalyst, in which chain-growth polymerization proceeds despite polycondensation,[14, 15] the reaction of which would also be the related enhanced reactivity. However, there is few systematic study on such enhanced multiple coupling related with requirements of substrate and reagent structures as well as ligand and metal species of the catalyst. Herein, we report studies on the preference of enhanced multiple coupling of metalated thiophenes in the presence of a transition-metal-catalyst with poly-halogenated organic electrophiles.

2. Results and Discussion

We first examined the reaction of 2,3-dibromothiophene (**1a**) with a variety of thiophene derivatives **2b-g** (1.2 equiv.) in the presence of 2.0 mol% of NiCl$_2$(PPh$_3$)IPr. Results are summarized in Table 1. In addition to 3-hexylthiophene, the reaction of 2-methylthiophene (**2b**) also took place to afford di-coupled product **3ab** in 34% yield along with 3% of the mono-coupled product **4ab** (entry 1). The reaction of 3-methylthiophene (**3c**) gave **3ac** exclusively in 51% yield. Other 3-alkylated thiophenes, 3-octylthiophene (**2d**) and 3-dodecylthiophene (**2e**), also reacted with **1a** to afford di-coupled product (entries 3 and 4). The reaction of benzo[*b*]thiophene (**2f**) occurred to give **3af** exclusively in 49% yield (entry 5). Unsubstituted thiophene reacted with **1a** to afford **3ag** in 49% yield (entry 6). In addition to thiophene derivatives, the reaction of benzo[*b*]furan (**2h**) was found to react with **1a** to afford **3ah** in 22% yield, while no mono-coupling product was obtained (entry 7).

Table 1. The reaction of 2,3-dibromothiophene (**1a**) with 1.2 equiv. of several thiophene derivatives[a]

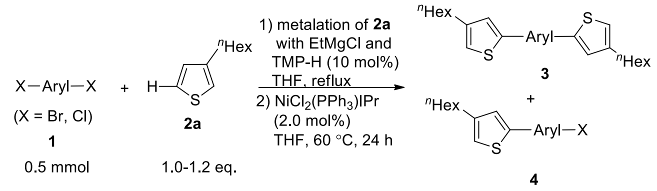


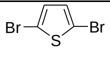
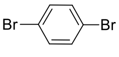
entry	2	yield/%[b]	
		3	4
1	 **2b**	34 (**3ab**)	3[c] (**4ab**)
2	 **2c**	51 (**3ac**)	0
3	 **2d**	56 (**3ad**)	0
4	 **2e**	33 (**3ae**)	0
5	 **2f**	49 (**3af**)	0
6	 **2g**	49 (**3ag**)	0
7	 **2h**	22 (**3ah**)	0

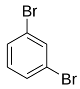
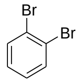
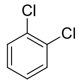
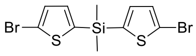
[a] Unless otherwise noted, the reaction was carried out with **2** (0.6 mmol), **1a** (0.5 mmol), and NiCl$_2$(PPh$_3$)IPr (0.01 mmol) in 2.0 mL of THF at 60 ºC for 24 h. [b] Isolated yield. The yield was calculated on the basis of amount of **1a**. [c] The yield was determined by GC analysis.

We next investigated the 1.0-1.2 equiv. reaction of 3-hexylthiophene (**2a**) with a variety of poly-halogenated arenes in the presence of 2.0 mol% of NiCl$_2$(PPh$_3$)IPr. Table 2 summarizes the results. The reaction of **2a** with 2,5-dibromothiophene (**1b**) proceeded smoothly to give terthiophene **3ba** exclusively in 36% yield. In addition to dibromothiophenes, similar effect was observed in the reaction of several bromobenzenes. When 1,4-dibromobenzene (**1d)** was used as a coupling partner, the reaction took place to give di-coupled product **3ca** in 45% yield selectively. The similar trend was also observed in the reaction of 1,3-dibromobenzene (**1d**) and 1,2-dibromobenzene (**1e**) to afford **3da** and **3ea** in 44% and 44% yield, respectively. The reaction of 1,2-chlorobenzene (**1f**) also furnished di-coupled product **3ea** in 36% yield. When dibrominated bithiophene with dimethylsilylene spacer **1g** was employed, the reaction proceeded to afford the mixture of di-coupled product **3ga** and mono-coupled product **4ga** in 27% and 17% yield, respectively.

Table 2. The reaction of 1.0-1.2 equiv. of 3-hexylthiophene (**2a**) with poly-halothiophene derivatives[a]



entry	1	yield/%[b]	
		3	4
1[c]	 **1b**	36 (**3ba**)	0
2[c]	 **1c**	45[d] (**3ca**)	0

3[c]	 **1d**	44 (**3da**)	0
4	 **1e**	44 (**3ea**)	0
5[c]	 **1f**	36 (**3ea**)	0
6[e]	 **1g**	27 (**3ga**)	17 (**4ga**)

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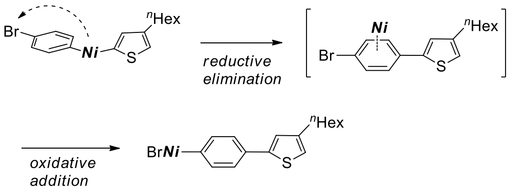
[a] Unless noted, the reaction was performed with **2a** (0.6 mmol), haloarene (0.5 mmol) and $NiCl_2(PPh_3)IPr$ (0.01 mmol) in 2.0 mL of THF. [b] Isolated yield. The yield was calculated on the basis of amount of **1a**. [c] The reaction was carried out with **2a** (0.5 mmol). [d] The yield was estimated by ^1H NMR analysis. [e] The reaction was carried out with 0.254 mmol of **1g**.

Results obtained in Table 1 and 2 shows that multiple coupling of thiophene derivatives with halides of thiophene and benzene ring successfully takes place catalyzed by a nickel complex bearing a NHC ligand despite the use of ca.1:1 metalated thiophene and multiply halogenated substrate. Although details on the preference of multiple coupling have not been clear yet, slower reductive elimination of thiophene–Ni–thiophene due to the electron-donating effect of NHC as well as higher reduction potential of nickel(II) may facilitate intramolecular migration to the second carbon–bromine bond. On the other hand, the reaction with palladium catalyst such as PEPPSI-IPr resulted in giving the mono-coupling product predominantly in the case of thiophene–thiophene coupling (Scheme 2).[9] The remarkable effect of Ni NHC complex as a catalyst seems to be a specific case in the thiophene coupling compared with the related 1:1 reactions of other metallo arenes and alkanes, in which the use of PEPPSI-IPr has effectively underwent multiple coupling.[12] Although we have also examined the multiple coupling reaction of 2,3-dibromothiophene with Grignard reagent PhMgBr in the presence of $NiCl_2(PPh_3)IPr$, mono coupling product was obtained as a major product.[16] These results suggest that preference of the enhanced multiple coupling occurs only when conditions of substrates and the catalyst show a good match whereas a mismatched reaction prefers mono coupling.

The accelerated multiple coupling is suggested to occur in the case of substrates bearing a π-conjugated system. Indeed, the reaction of metalated **1a** with **1g** bearing a dimethylsilylene spacer between bromothiophenes resulted that preferential dicoupling was not observed to afford a mixture of mono- and dicoupled products. The result would closely relate with the catalyst-transfer mechanism in the chain-growth cross-coupling polycondensation of thiophenes proposed by Yokozawa[14, 15], in which intramoleculer transfer of Ni species through the π-conjugated system by reductive elimination and oxidative addition sequence (Scheme 3). It is remarkable that such catalyst-transfer effect would also facilitate the coupling reaction at the second carbon-bromine bond in the π-conjugated system leading to branched oligothiophenes.



Scheme 3. Catalyst transfer through reductive elimination and oxidative addition sequence

3. Conclusion

In conclusion, we have shown that successive multiple coupling reaction of thiophene derivatives with dibrominated thiophene in the presence of nickel NHC catalyst $NiCl_2(PPh_3)IPr$ proceed to give di-coupled product, exclusively despite the use of ca. 1:1 reagent and substrate. This reaction was also shown to be effective for a wide range of poly-halogenated arenes such as 1,4- and 1,2-dihalobenzene.[17]

Acknowledgments

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15. See also: (a) Sheina, E. E.; Liu, J. S.; Iovu, M. C.; Laird, D. W.; McCullough, R. D. *Macromolecules* **2004**, *37*, 3526. (b) Iovu, M. C.; Sheina, E. E.; Gil, R. R.; McCullough, R. D. *Macromolecules* **2005**, *38*, 8649. (c) Tkachov, R.; Senkovskyy, V.; Komber, H.; Sommer, J.-U.; Kiriy, A. *J. Am. Chem. Soc.*, **2010**, *132*, 7803. (d) Beryozkina, T.; Boyko, K.; Khanduyeva, N.; Senkovskyy, V.; Horecha, M.; Oertel, U.; Simon, F.; Stamm, M.; Kiriy, A. *Angew. Chem., Int. Ed.* **2009**, *48*, 2695**.** (e) Tkachov, R.; Senkovskyy, V.; Komber, H.; Kiriy, A. *Macromolecules*, **2011**, *44*, 2006. (f) Huang, W.; Su, L.; Bo, Z. *J. Am. Chem. Soc.* **2009**, *131*, 10348.
16. On the other hand, McCullough et al. have repoted successive coupling of 2,5-dibromothiophene with tolyl magnesium bromide was took place in the presence of NiCl$_2$(dppp) in reference 15a.

17. Representative procedure: To a 20 mL Schlenk tube equipped with a magnetic stirring bar were added 0.99 M EtMgCl (0.505 mL, 0.5 mmol) in THF and TMP-H (0.008 mL, 0.05 mmol). To the solution were added 3-hexylthiophene (**2a**, 0.09 mL, 0.50 mmol) and stirring was continued under reflux for 24 h. Then, 1.4 mL of THF, 1,3-dibromobenzene (**1d**, 118 mg, 0.5 mmol) and NiCl$_2$(PPh$_3$)IPr (7.8 mg, 0.01 mmol) were added successively. The mixture was allowed to stir at 60 °C for 24 h. The mixture was quenched by saturated aqueous solution of ammonium chloride (1.0 mL). The solution was poured into the mixture of diethyl ether/water and two phases were separated. Aqueous was extracted with diethyl ether twice and the combined organic layer was dried over anhydrous sodium sulfate and concentrated under reduced pressure to leave a crude oil, which was purified by column chromatography on silica gel using hexanes as an eluent to afford 89.7 mg 1,3-bis(3-hexylthiophen-5-yl)benzene (**3da**, 44%, pale yellow oil). ^{1}H NMR (CDCl$_3$, 300 MHz) δ 0.90 (t, *J* = 6.8 Hz, 6H), 1.18-1.48 (m, 12H), 1.59-1.75 (m, 4H), 2.63 (t, *J* = 7.7 Hz, 4H), 6.89 (d, *J* = 0.9 Hz, 2H), 7.20 (d, *J* = 1.3 Hz, 2H), 7.31-7.39 (m, 1H), 7.48 (dd, *J* = 1.7, 7.0 Hz, 2H), 7.79 (t, *J* = 1.7 Hz, 1H); ^{13}C NMR (CDCl$_3$, 75 MHz) δ 14.1, 22.6, 29.0, 30.4, 30.6, 31.7, 119.7, 123.1, 124.7, 124.8, 129.3, 135.3, 143.6, 144.3; IR (ATR) 2954, 2926, 2854, 1600, 1577, 1559, 1549, 1489, 1465, 1458, 1377, 1261, 1204, 1088, 1025, 880, 837, 787, 729, 687, 668, 652, 633 cm^{-1}; HRMS (DART-ESI+) Calcd for $C_{26}H_{35}S_2$ [M+H]$^+$:411.2180; found: m/z 411.2164.

2,3-bis(3-methylthiophen-5-yl)thiophene (**3ac**)
^{1}H NMR (CDCl$_3$, 300 MHz) δ 2.23 (d, *J* = 0.9 Hz, 3H), 2.25 (d, *J* = 0.9 Hz, 3H), 6.82-6.86 (m, 1H), 6.89-6.91 (m, 2H), 6.95 (d, *J* = 1.3 Hz, 1H), 7.12 (d, *J* = 5.3 Hz, 1H), 7.23 (d, *J* = 5.3 Hz, 1H); ^{13}C NMR (CDCl$_3$, 75 MHz) δ 15.65, 15.69, 120.7, 120.8, 122.0, 122.1, 124.1, 124.2, 128.7, 129.7, 130.1, 131.6, 132.1, 134.6, 137.2, 137.5, 137.6; IR (ATR) 1551, 1523, 1444, 1399, 1380, 1253, 1201, 142, 1090, 1031, 991, 875, 837, 797, 779, 737, 693, 645 cm^{-1}; HRMS (DART-ESI+) Calcd for $C_{14}H_{13}S_3$ [M+H]$^+$:277.0179; found: m/z 277.0188.

2,3-bis(3-octylthiophen-5-yl)thiophene (**3ad**)
^{1}H NMR (CDCl$_3$, 300 MHz) δ 0.88 (t, *J* = 6.6 Hz, 6H), 1.11-1.42 (m, 20H), 1.47-1.68 (m, 4H), 2.47-2.63 (m, 4H), 6.83 (s, 1H), 6.87-6.92 (m, 2H), 6.96 (d, *J* = 1.3 Hz, 1H), 7.13 (d, *J* = 5.3 Hz, 1H), 7.23 (d, *J* = 5.3 Hz, 1H); ^{13}C NMR (CDCl$_3$, 75 MHz) δ 14.1, 22.7, 29.3, 29.41, 29.43, 30.40, 30.43, 31.9, 119.9, 121.2, 124.1, 127.7, 129.1, 129.6, 131.7, 132.2, 134.6, 137.1, 143.2, 143.3; IR (ATR) 2955, 2924, 2854, 1462, 1378, 1256, 1201, 1045, 840, 797, 725, 695, 645 cm^{-1}; HRMS (DART-ESI+) Calcd for $C_{28}H_{41}S_3$ [M+H]$^+$:473.2370; found: m/z 473.2358.

2,3-bis(3-dodecylthiophen-5-yl)thiophene (**3ae**)
^{1}H NMR (CDCl$_3$, 300 MHz) δ 0.88 (t, *J* = 6.6 Hz, 6H), 1.61-1.41 (m, 36H), 1.50-1.64 (m, 4H), 2.49-2.61 (m, 4H), 6.83 (s, 1H), 6.87-6.91 (m, 2H), 6.96 (d, *J* = 1.3 Hz, 1H), 7.13 (d, *J* = 5.3 Hz, 1H), 7.23 (d, *J* = 5.3 Hz, 1H); ^{13}C NMR (CDCl$_3$, 75 MHz) δ 14.1, 22.7, 29.3, 29.4, 29.48, 29.5, 29.63, 29.66, 29.70, 30.44, 30.45, 30.5, 31.9, 119.9, 121.2, 124.0, 127.8, 129.2, 129.7, 131.7, 132.2, 134.6, 137.2, 143.2, 143.3; IR (ATR) 2954, 2916, 2872, 2849, 1466, 871, 847, 736, 722, 712, 700, 645 cm^{-1}; HRMS (DART-ESI+) Calcd for $C_{36}H_{57}S_3$ [M+H]$^+$:585.3622; found: m/z 585.3608.

2,3-bis(benzo[*b*]thiophen-2-yl)thiophene (**3af**)
^{1}H NMR (CDCl$_3$, 300 MHz) δ 7.28 (d, *J* = 5.3 Hz, 1H), 7.27-7.37 (m, 5H), 7.39 (d, *J* = 5.3 Hz, 1H), 7.42 (s, 1H), 7.69-7.80 (m, 4H); ^{13}C NMR (CDCl$_3$, 75 MHz) δ 122.1 (×2), 123.4, 123.6, 123.7, 124.31, 124.33, 124.46, 124.48, 124.7, 125.6, 130.3, 132.66, 132.68, 135.1, 137.4, 139.6, 139.9, 140.1, 140.6; IR (ATR) 1260, 1155, 1091, 1020, 862, 798, 744, 724, 709, 696, 685 cm^{-1}; HRMS (DART-ESI+) Calcd for $C_{20}H_{13}S_3$ [M+H]$^+$:349.0179; found: m/z 349.0165.

2,3-bis(benzo[*b*]furan-2-yl)thiophene (**3ah**)
^{1}H NMR (CDCl$_3$, 300 MHz) δ 6.99 (s, 1H), 7.08 (s, 1H), 7.21-7.36 (m, 4H), 7.43 (d, *J* = 5.3 Hz, 1H), 7.48 (d, *J* = 5.3 Hz, 1H), 7.50 (d, *J* = 3.5 Hz, 1H), 7.53 (d, *J* = 3.5 Hz, 1H), 7.57 (s, 1H), 7.59 (s, 1H); ^{13}C NMR (CDCl$_3$, 75 MHz) δ 104.6, 105.3, 111.15, 111.19, 121.0, 121.1, 123.0, 123.2, 124.5, 124.8, 126.2, 128.81, 128.84, 128.9, 129.0, 129.1, 149.6, 151.5, 154.4, 154.6; IR (ATR) 1450, 1257, 1170, 1160, 1144, 1110, 1098, 1066, 1011, 946, 882, 863, 810, 799, 751, 739, 670, 660 cm^{-1}; HRMS (DART-ESI+) Calcd for $C_{20}H_{13}O_2S$ [M+H]$^+$:317.0636; found: m/z 317.0642.

1,2-bis(3-hexylthiophen-5-yl)benzene (**3ea**)
^{1}H NMR (CDCl$_3$, 300 MHz) δ 0.89 (t, *J* = 6.7 Hz, 6H), 1.19-1.43 (m, 12H), 1.46-1.63 (m, 4H), 2.52 (t, *J* = 7.5 Hz, 4H), 6.70 (d, *J* = 1.3 Hz, 2H), 6.84 (d, *J* = 1.3 Hz, 2H), 7.32 (dd, *J* = 3.4, 5.8 Hz, 2H), 7.48 (dd, *J* = 3.4, 5.8 Hz, 2H); ^{13}C NMR (CDCl$_3$, 75 MHz) δ 14.1, 22.6, 28.9, 30.4, 30.5, 31.7, 120.4, 127.6, 128.5, 130.7, 134.0, 142.3, 143.1; IR (ATR) 2955, 2926, 2855, 1490, 1465, 1377, 1200, 1105, 1048, 984, 843, 760, 726, 651, 634 cm^{-1}; HRMS (DART-ESI+) Calcd for $C_{26}H_{35}S_2$ [M+H]$^+$:411.2180; found: m/z 411.2187.

Bis(3'-hexyl-2,2'-bithiophen-5-yl)dimethylsilane (**3ga**)
^{1}H NMR (CDCl$_3$, 300 MHz) δ 0.64 (s, 6H), 0.88 (t, *J* = 6.6 Hz, 6H), 1.21-1.41 (m, 12H), 1.53-1.72 (m, 4H), 2.56 (t, *J* = 7.6 Hz, 4H), 6.80 (d, *J* = 1.3 Hz, 2H), 7.03 (d, *J* = 1.3 Hz, 2H), 7.21 (s, 4H); ^{13}C NMR (CDCl$_3$, 75 MHz) δ -0.29, 14.1, 22.6, 29.0, 30.3, 30.5, 31.7, 119.3, 124.8, 125.5, 136.16, 136.22, 136.7, 144.0, 144.1; IR (ATR) 2955, 2926, 2855, 1461, 1453, 1416, 1252, 1215, 1191, 1071, 995, 854, 832, 799, 779, 738, 697, 676, 642 cm^{-1}; HRMS (DART-ESI+) Calcd for $C_{30}H_{41}S_4Si$ [M+H]$^+$:557.1860; found: m/z 557.1875.

(5-bromothiophen-2-yl)-(5'-hexyl-2,2'-bithiophen-5-yl)dimethylsilane (**4ga**)
^{1}H NMR (CDCl$_3$, 300 MHz) δ 0.62 (s, 6H), 0.89 (t, *J* = 6.7 Hz, 3H), 1.21-1.39 (m, 6H), 1.56-1.69 (m, 2H), 2.57 (t, *J* = 7.6 Hz, 2H), 6.81 (d, *J* = 1.3 Hz, 1H), 7.03 (d, *J* = 1.3 Hz, 1H), 7.06 (d, *J* = 3.5 Hz, 1H), 7.11 (d, *J* = 3.5 Hz, 1H), 7.18 (d, *J* = 3.5 Hz, 1H), 7.21 (d, *J* = 3.5 Hz, 1H)