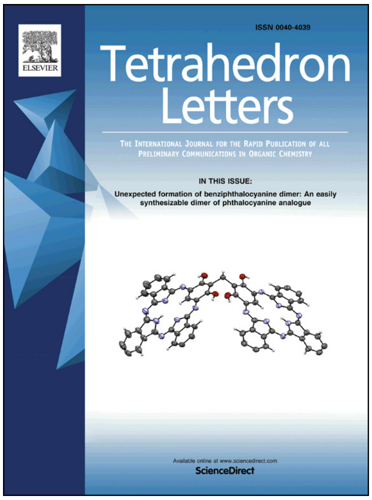

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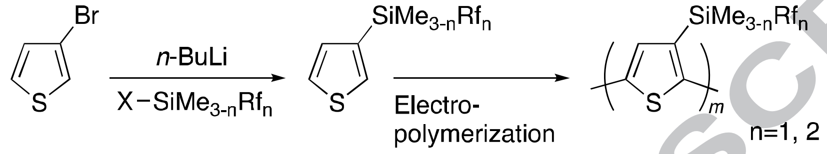

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Synthesis and Utility of 3-Silylthiophenes Having Perfluoroalkyl Groups

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ABSTRACT

The synthesis of a novel class of 3-silyl substituted thiophenes possessing perfluoroalkyl groups on the silicon atom was investigated. The treatment of 3-bromothiophene with *n*-butyllithium followed by the reaction with halosilanes proceeded to afford the corresponding 3-silyl substituted thiophenes **1** in good yields. The chemical polymerization of the resulting **1** did not work well. However, the electropolymerization of 3-silylthiophenes **1a** and **1b** provided the corresponding polymers **5a** and **5b** with head-to-tail regioregularity. The cyclic voltammogram of the resulting polymers **5a** and **5b** indicated both n- and p-doping properties.

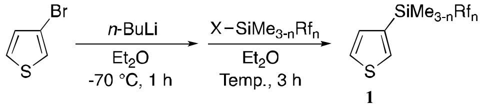
Introduction

Polythiophene has been well-known as one of the most favorable conjugated conducting polymers,[1] and expected as materials for organic solar cell[2] and liquid crystal device.[3] There has been growing interest due to its high conductivity, environmental and thermal stability. However, unsubstituted polythiophene is intractable and soluble only in solutions like mixtures of arsenic trifluoride and arsenic pentafluoride.[4] To improve solubility in organic solvents and workability, substituted polythiophenes with flexible side chains have been synthesized in the 1980s.[5] Notably, Hotta *et al.* prepared substituted thiophene having a *n*-hexyl chain at the 3-position, and polymerized it electrochemically and chemically, and characterized the obtained polymer in solution, and formed into films.[6] Thenceforth, poly(3-hexylthiophene) has been used for preparation of electronic devices as organic photovoltaics and so on.[7] Besides, 3-silyl substituted thiophenes are expected to improve in conductive performance of polymerized thiophenes by using steric and electrically positive properties of silyl group. Unfortunately, a few reports have been known to synthesize poly(3-trimethylsilylthiophene) and measure its electrochemical properties.[8] On the other hand, polythiophenes containing perfluoroalkyl groups are also interested, because their amphiphilic properties, low surface energy and the electron withdrawing nature of the fluorinated alkyl chains, and large dipole moments induced by polar C–F bonds have powerful effects on the structural order and the orientation of organic semiconducting polymers in thin films.[9] However, there is little information about poly(thiophene) having the properties of both silyl groups and perfluoroalkyl groups mentioned above. In this paper, we describe the convenient synthetic methods of 3-silylthiophenes possessing perfluoroalkyl groups or other hydrocarbon groups on the silicon atom and their polymerization.

Results and discussion

Initially the synthesis of 3-silyl substituted thiophenes **1** possessing perfluoroalkyl groups on the silicon atom was carried out. The results are shown in Table 1. According to the literature, bromosilane derivatives including two or three 1H,1H,2H,2H-tridecafluorooctyl groups were prepared as silylation reagents.[10] Then the treatment of 3-bromothiophene with *n*-butyllithium and the following reaction with halosilanes afforded the corresponding 3-silyl substituted thiophenes **1** in good yields, independent of the number of perfluoroalkyl groups on the silicon atom.

Table 1. Synthesis of 3-silyl substituted thiophenes **1** possessing perfluoroalkyl groups

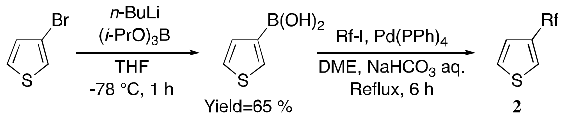


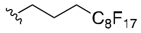
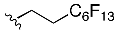
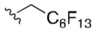
Entry	X	n	Temp. (°C)	Product	Yield[a] (%)
1	Cl	1	-70	**1a**	93
2	Br	2	0	**1b**	84
3	Br	3	0	**1c**	87

$Rf=CH_2CH_2C_6F_{13}$
[a] Isolated yield.

To compare the properties of the obtained thiophenes **1** to other substituted thiophenes, perfluoroalkyl substituted thiophenes without silicon atom were synthesized (Table 2). 3-

Table 2. Synthesis of 3-perfluoroalkyl substituted thiophenes **2**



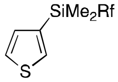
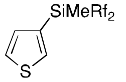
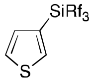
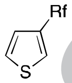
Entry	Rf	Product	Yield^a (%)
1		**2a**	58
2		**2b**	65
3		**2c**	No reaction

^{a} Isolated yield.

Lithiothiophene prepared by the reaction of 3-bromothiophene with *n*-butyllithium reacted with triisopropyl borate in THF to form 3-thienylboronic acid. The reaction of resulted boronic acid with perfluoroalkyl iodide in the presence of palladium catalyst gave the corresponding 3-perfluoroalkyl substituted thiophenes **2**. The reaction of perfluoroalkyl iodide including two or three methylene spacers provided the desired products in good yields (Entries 1 and 2). Though, 1H,1H-tridecafluoroheptyl iodide did not react at all under the same conditions (Entry 3).

To quantify the fluorophilicity (*f*=ln *P*)[11] of the obtained 3-substituted thiophenes **1** and **2** possessing perfluoroalkyl groups, selected perfluorohexane (FC-72)/ethyl acetate and FC-72/CH_2Cl_2 partition coefficients[12] were measured. The data are summarized in Table 3. In the case of **1a** and **2b** having a 1H,1H,2H,2H-tridecafluorooctyl group, the thiophenes respectively contain 51 and 57 wt.% fluorine and exhibited low fluorophilicity with slightly positive *f* values.[11] The thiophenes **1b** and **1c** possessing two or three perfluoroalkyl groups contain >60 wt.% fluorine and indicated higher fluorophilicity than **1a** and **2b**. Especially, **1c** exhibited a significant fluorophilicity (*f* >3) in FC-72/CH_2Cl_2.

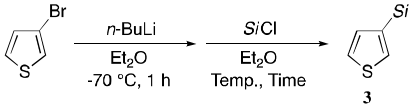
Table 3. Fluorophilicity of 3-substituted thiophenes possessing perfluoroalkyl groups

3-Substituted thiophene^a	Fluorine weight ratio (%)	$P_{FC72/EtOAc}$	$f_{FC72/EtOAc}$	P_{FC72/CH_2Cl_2}	f_{FC72/CH_2Cl_2}
1a 	50.6	1.51	0.41	1.46	0.58
1b 	60.2	2.10	0.74	2.10	0.74
1c 	64.3	3.28	1.19	29.0	3.37
2b 	57.4	1.22	0.20	1.30	0.26

^{a} Rf=$CH_2CH_2C_6F_{13}$.

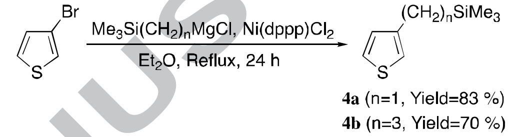
Additionally, the synthesis of 3-silylthiophenes possessing other hydrocarbon groups on the silicon atom and 3-substituted thiophenes having methylene spacers between the silyl group and the thiophene ring was examined. These results are summarized in Table 4 and Scheme 1 respectively. The direct silylated thiophenes **3** having different silyl groups were synthesized by a similar reaction to obtain 3-silyl substituted thiophenes **1**. In these reactions, the yields were affected by the kind of silyl groups. The reaction using sterically bulky silylation reagent did not proceed well (Entries 3 and 6), however, other reactions gave the target products in good yields. On the other hand, silylmethylmagnesium chloride or silylpropylmagnesium chloride reacted with 3-bromothiophene in the presence of nickel catalyst to afford the corresponding 3-silylalkyl substituted thiophenes **4** in good yields (Scheme 1).[13]

Table 4. Synthesis of 3-silylthiophenes **3** possessing hydrocarbon groups



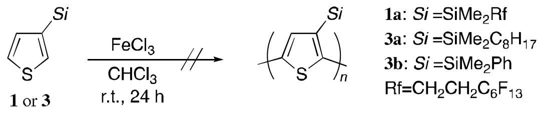
Entry	*Si*	Temp. (°C)	Time (h)	Product	Yield^a (%)
1	$SiMe_2C_8H_{17}$	-20	3	**3a**	91
2	$SiMe_2Ph$	-20	1	**3b**	84
3	$SiMe_2$(*t*-Bu)	r.t.	3	**3c**	12
4	$SiMe_2(CH_2)_2CF_3$	-70	3	**3d**	75
5	$SiEt_3$	-20	2	**3e**	84
6	Si(*i*-Pr)$_3$	-20	3	**3f**	No reaction

^{a} Isolated yield.

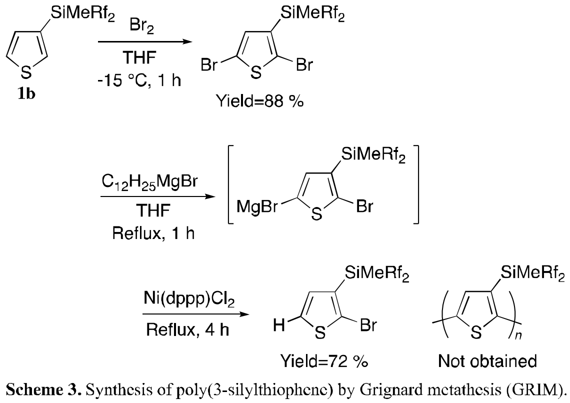


Scheme 1. Synthesis of 3-silylalkyl substituted thiophenes **4**.

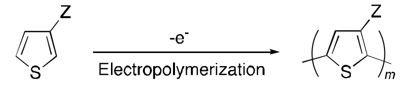
Next, the polymer synthesis using the resulting 3-substituted thiophenes was investigated. Initially oxidative polymerization of 3-silylthiophenes **1** or **3** with $FeCl_3$ catalyst was attempted (Scheme 2).[14] In these reactions, desired polythiophenes were not obtained, since desilylation was proceeded almost entirely during a polymerization. Then, synthesis of polythiophene known as the Grignard metathesis (GRIM) method was examined (Scheme 3).[15] The starting material, 2,5-dibromo-3-silylthiophene was prepared by the treatment of **1b** with bromine in good yield. The resulted 2,5-dibromo-3-silylthiophene was treated with Grignard reagent to form an intermediate 2-bromo-5-bromomagnesio-3-silylthiophene. To polymerize this intermediate, cross-coupling reaction using a catalytic amount of Ni(dppp)Cl_2 was carried out. However, the reaction proceeded to afford 2-bromo-3-silylthiophene exclusively as hydrolysate, and the desired polymer was not obtained at all.



Scheme 2. Oxidative polymerization of 3-silylthiophenes with $FeCl_3$ catalyst.



Scheme 3. Synthesis of poly(3-silylthiophene) by Grignard metathesis (GRIM).



1-4 **5-8**

1 and **5**: Z=SiMe$_{3-n}$Rf$_n$ (Rf=(CH$_2$)$_2$C$_6$F$_{13}$, n=1-3)
2 and **6**: Z=(CH$_2$)$_3$C$_8$F$_{17}$, (CH$_2$)$_2$C$_6$F$_{13}$
3 and **7**: Z=SiMe$_2$R (R=C$_8$H$_{17}$, Ph, *t*-Bu, (CH$_2$)$_2$CF$_3$)
4 and **8**: Z=CH$_2$SiMe$_3$, (CH$_2$)$_3$SiMe$_3$

Scheme 4. Electropolymerization of 3-substituted thiophenes.

Then the monomers **1-4** were then polymerized by electrochemical technique (Scheme 4). The corresponding polymers **5-8** were electrolytically deposited on glassy carbon (GC) from a 0.1 M Bu$_4$NPF$_6$ / nitrobenzene solution containing 10 mM monomers **1-4**, respectively. The potential of the working electrode was repetitively cycled from the negative potential where the electrolytic reaction did not occur to the potential where the monomer oxidized at a scan rate of 100 mVs^{-1}. All electrode potentials were referred to an Ag | 0.01 M AgClO$_4$ in the experimental electrolyte solution electrode. Figure 1 illustrates the linear sweep voltammograms of 10 mM monomer **1a** and **1b** in a 0.1M Bu$_4$NPF$_6$ /nitrobenzene solution as an example. Since the anode current started to increase at about +1.1 V with either monomer, this response is due to the oxidation of thiophene. Figure 2 and 3 show the repetitive cyclic voltammograms during the electropolymerization process of **1a** and **1b**. New oxidation-reduction wave appeared from -0.5 V to +0.8 V which did not appear in the oxidation of the monomer in Figure 1. These waves are found to be derived from polymers because they have grown by repeating cycles. Unfortunately, 3-silylthiophene **1c** was insoluble in nitrobenzene, therefore the polymerization of **1c** was not achieved. The resulting polymers **5-8** were insoluble in any organic solvents. After polymerization, the coated electrodes were transferred into acetonitrile solution containing only 0.1 M Bu$_4$NPF$_6$. Figure 4 shows a cyclic voltammogram of polymer **5a** over the whole potential range. The onset of polymer **5a** oxidation occurs at +0.2 V and a set of anodic and cathodic peaks are observed at +0.65 V and +0.55 V, respectively. On the other hand, the onset of polymer **5a** reduction occurs around -1.5 V and a set of cathodic anodic peaks are observed at -2.2 V and -1.8 V. The small anodic peak at *ca.* -1.6 V is attributable to the formation *trapped* cations.[16] A similar result was observed in a cyclic voltammogram of polymer **5b** (Figure 5). These results clearly indicate both n- and p-dopable nature of poly(3-silylthiophenes) possessing perfluoroalkyl groups on the silicon atom, and suggest the possibility of materials for supercapacitors (type III),[17] although the polymers **6-8** did not show apparent n-doping process. It is noteworthy that the ratio of n- and p-doping charge was polymer **5b** higher than polymer **5a**. Though, it is unclear at present why polythiophenes having a fluorous silyl group revealed both n- and p-doping properties.

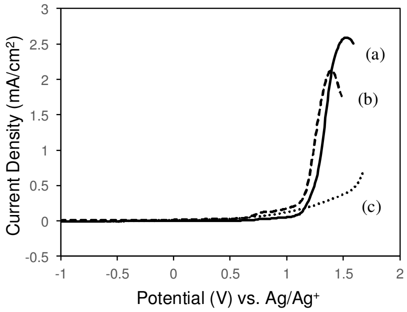


Figure 1. Linear sweep voltammograms of monomer **1a** (a) and **1b** (b). Potential sweep 100mV/s. (c); Monomer free solution

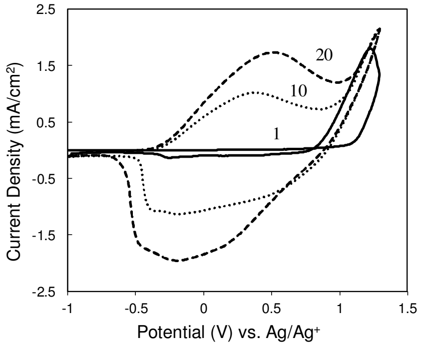


Figure 2. Electropolymerization of 10 mM monomer **1a** in a 0.1M Bu$_4$NPF$_6$ /nitrobenzene solution. Numerical values in the figure exhibit cycle number.

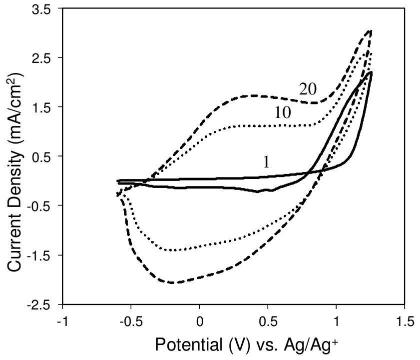


Figure 3. Electropolymerization of 10 mM monomer **1b** in a 0.1M Bu$_4$NPF$_6$ /nitrobenzene solution. Numerical values in the figure exhibit cycle number.

To clarify the regioregularity of resulted poly(3-silylthiopenes) **5**, regioselective synthesis of bithiophenes and the following electropolymerization of them were investigated (Scheme 5). Firstly, the head-to-tail (HT) dimers **9** were prepared

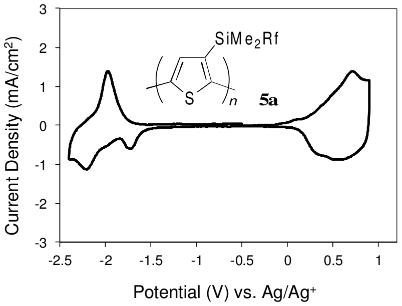


Figure 4. Cyclic voltammogram of **5a** in 0.1 M Bu$_4$NPF$_6$/acetonitrile solution with a scan rate of 100 mV/s.

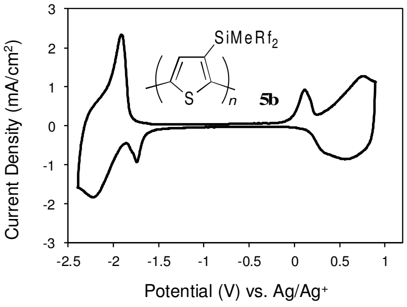
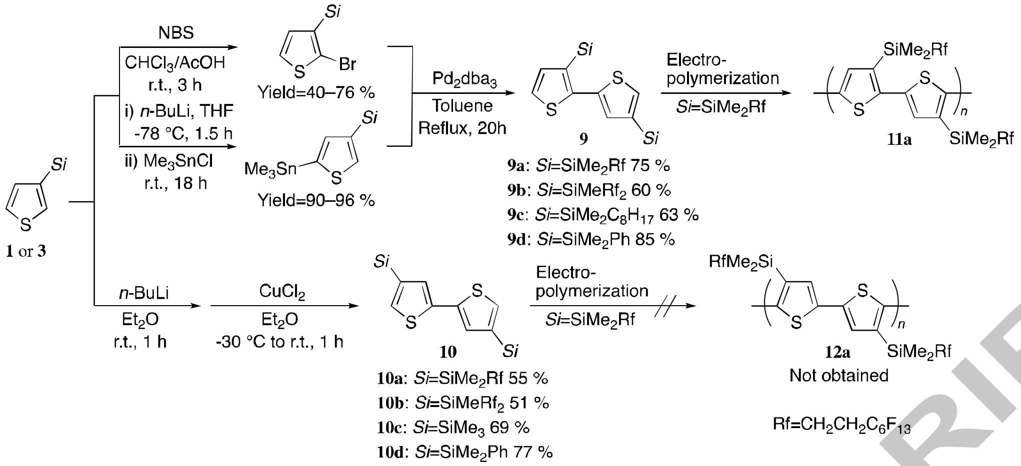


Figure 5. Cyclic voltammogram of **5b** in 0.1 M Bu$_4$NPF$_6$/acetonitrile solution with a scan rate of 100 mV/s.



Scheme 5. Regioselective synthesis of bithiophenes and their polymerization.

as follows. The treatment of 3-silylthiophenes **1** or **3** with NBS afforded 2-bromo-3-silylthiophenes,[18] and then the treatment of **1** or **3** with *n*-butyllithium followed by an addition of trimethyltin chloride gave 4-silyl-2-stannylthiophenes.[19] The still coupling of the resulting thienyl bromides with thienylstannanes provided the corresponding 2,5'-bithiophenes **9** in good yields.[19] On the other hand, self-coupling of thienyllithium derived from the reaction of **1** or **3** with *n*-butyllithium in the presence of Cu catalyst yielded 5,5'-bithiophenes **10**.[20] The electropolymerization of **9a** under the same condition of polymerization of **1** gave polymer films **11a** on GC, and the cyclic voltammogram of the polymer **11a** indicated both n- and p-dopable nature. However, the electropolymerization of bithiophene **10a** under the same condition did not proceed well. The self-coupling reaction of **10a** will be extremely difficult, because the bulky silyl groups near the reaction point have to be close together to react intermolecularly. As a consequence, these results suggest that the electropolymerization of **1** proceeded to produce the polymer **5** with HT regioregularity.

Conclusion

In conclusion, synthesis of 3-silyl substituted thiophenes **1** possessing perfluoroalkyl groups on the silicon atom has been described. To compare the effect of substituent groups on conductive properties of polythiophene derivatives, 3-perfluoroalkyl substituted thiophenes **2**, 3-silylated thiophenes **3** having different silyl groups, and 3-silylalkyl substituted thiophenes **4** having methylene spacers were also prepared. The chemical polymerization of the resulting substituted thiophenes **1** by oxidative polymerization using ferric chloride, and Grignard metathesis method did not proceed to afford the desired polythiophenes. On the other hand, the corresponding polymer films **5** were yielded by electrochemical oxidation. The resulting polymers **5** indicate both n- and p-doping properties, so they have the possibility of materials for supercapacitors. Further studies aimed at interpretation of effect of perfluoroalkylsilyl group on both n- and p-doping properties and application of the resulting polymer films into supercapacitors are now in progress in our laboratory. The results will be reported in due course.

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References and notes

1. For reviews on polythiophene, see: (a) Handbook of Thiophene-Based Materials; Perepichka, I. F.; Perepichka, D. F., Eds.; Wiley-VCH: Chichester, U.K., **2009**. (b)Street, G. B.; Clarke, T. C. *IBM J. Res. Dev.* **1981**, *25*, 51–57; (c) Reddinger, J. L.; Reynolds, J. R. *Adv. Polym. Sci.* **1999**, *145*, 57–122; (d) McQuade, D. T.; Pullen, A. E.; Swager, T. M. *Chem. Rev.* **2000**, *100*, 2537–2574.
2. For recent reviews on polythiophene based organic solar cells, see: (a) Mehmood, U.; Al-Ahmed, A.; Hussein, I. A. *Renewable Sustainable Energy Rev.* **2016**, *57*, 550−561; (b) Lu, L.; Zheng, T.; Wu, Q.; Schneider, A. M.; Zhao, D., Yu, L. *Chem. Rev.* **2015**, *115*, 12666–12731; (c) Wang, H.-J.; Chen, C.-P.; Jeng, R.-J. *Materials* **2014**, *7*, 2411–2439; (d) Kim, Y.; Lim, E. *Polymers* **2014**, *6*, 382–407.
3. For reviews on polythiophene based liquid crystalline, see: (a) Iino, H.; Hanna, J.-I. *Polym. J.* **2017**, *49*, 23–30; (b) Xiao, Y.; Zeng, D.; Mazur, L. M.; Castiglione, A.; Lacaze, E.; Heinrich, B.; Donnio, B.; Kreher, D.; Attias, A.-J.; Ribierre, J.-C.; Mathevet, F. *Polym. J.* **2017**, *49*, 31–39; (c) Watanabe, M.; Tsuchiya, K.; Shinnai, T.; Kijima, M. *Macromolecules* **2012**, *45*, 1825–1832; (d) Goto, H.; Dai, X.; Narihiro, H.; Akagi, K. *Macromolecules* **2004**, *37*, 2353–2362; (e) Kijima, M.; Setoh, K.; Shirakawa, H. *Chem. Lett.* **2000**, *29*, 936–937; (f) Hong, X. M.; Collard, D. M. *Macromolecules* **2000**, *33*, 6916–6917.
4. Frommer, J. E. *Acc. Chem. Res.* **1986**, *19*, 2–9.
5. (a) Yamamoto, T.; Sanechika, K.; Yamamoto, A. *J. Polym. Sci., Polym. Lett. Ed.* **1980**, *18*, 9–12; (b) Sugimoto, R.; Takeda, S.; Gu, H. B.; Yoshino, K. *Chem. Express.* **1986**, *1*, 635–638.
6. (a) Hotta, S.; Rughooputh, S. D. D. V.; Heeger, A. J.; Wudl, F. *Macromolecules* **1987**, *20*, 212–215; (b) Hotta, S.; Soga, M.; Sonoda, N. *Synth. Met.* **1988**, *26*, 267–279; (c) Hotta, S. *Synth. Met.* **1987**, *22*, 103–113; (d) Hotta, S.; Rughooputh, S. D. D. V.; Heeger, A. J. *Synth. Met.* **1987**, *22*, 79–87.
7. (a) P3HT Revisited - From Molecular Scale to Solar Cell Devices; Ludwigs, S., Ed.; Springer: Berlin, **2014**; (b) Bhatt, M. P.; Magurudeniya, H. D.; Rainbolt, E. A.; Huang, P.; Dissanayake, D. S.; Biewer, M. C.; Stefan, M. C. *J. Nanosci. Nanotechnol.* **2014**, *14*, 10331050; (c) Yu, J.; Zheng, Y.; Huang, J. *Polymers* **2014**, *6*, 2473-2509. (d) Handa, N. V.; Serrano, A. V.; Robb, M. J.; Hawker. C. J. *J. Polym. Sci. Part A: Polym. Chem.* **2015**, *53*, 831–841; (e) Kim, D. H.; Han, J. T.; Park, Y. D.; Jang, Y.; Cho, J. H.; Hwang, M.; Cho, K. *Adv. Mater.* **2006**, *18*, 719–723.
8. (a) Lère-Porte, J.-P.; Moreau, J. J. E.; Sauvajol, J.-L. *J. Organomet. Chem.* **1996**, *521*, 11–19; (b) Sauvajol, J.-L.; Chorro, C.; Lère-Porte, J.-P.; Corriu, R. J. P.; Moreau, J. J. E.; Thépot, P.; Man, M. W. C. *Synth. Met.* **1994**, *62*, 233–244; (c) Adebimpe, D.; Kathirgamanathan, P.; Shepherd, M. *J. Electroanal. Chem.* **1993**,

348, 447–450; (d) Ritter, S. K.; Noftel, R. E. *Inorg. Chim. Acta* **1999**, *287*, 232–237.

9. (a) Geng, Y.; Tajima, K.; Hashimoto, K. *Macromol. Rapid Commun.* **2011**, *32*, 1478–1483; (b) Li, L.; Counts, K. E.; Kurosawa, S.; Teja, A. S.; Collard, D. M. *Adv. Mater.* **2004**, *16*, 180–183; (c) Büchner, W.; Garreau, R.; Lemaire, M.; Roncali, J.; Garnier, F. *J. Electroanal. Chem.* **1990**, *277*, 355–358.
10. Schwinn, D.; Bannwarth, W. *Helv. Chim. Acta* **2002**, *85*, 255–264.
11. (a) Kiss, L. E.; Kövesdi, I.; Rábai, J. *J. Fluor. Chem.* **2001**, *193*, 67–72; (b) Jbeily, M.; Kressler, J. *J. Fluor. Chem.* **2017**, *108*, 95–109.
12. (a) Horvath, I. T.; Rabai, J. *Science* **1994**. *266*, 72–75; (b) Emnet, C.; Weber, K. M.; Vidal, J. A.; Consorti, C. S.; Stuart, A. M.; Gladysz, J. A. *Adv. Synth. Catal.* **2006**, *348*, 1625–134.
13. Tamao, K.; Kodama, S.; Nakajima, I.; Kumada, M.; Minato, A.; Suzuki, K. *Tetrahedron* **1982**, *38*, 3347–3354.
14. (a) Amou, A.; Haba, O.; Shirato, K.; Hayakawa, T.; Ueda, M.; Takeuchi,K.; Asai, M. *J. Polym. Sci., Part A: Polym. Chem.* **1999**, *37*, 1943–1948; (b) Sugimoto, R.; Taketa, S.; Gu, H. B.; Yoshino, K. *Chem. Express* **1986**, *1*, 635–638.
15. (a) Osaka, I.; McCullough, R. D. *Acc. Chem. Res.* **2008**, *41*, 1202–1214; (b) Chen, T. A.; Rieke, R. D. *J. Am. Chem. Soc.* **1992**, *114*, 10087–10088; (c) Loewe, R. S.; Ewbank, E. C.; Liu, J.; Zhai, L.; McCullough, R. D. *Macromolecules* **2001**, *34*, 4324–4333.
16. Fletcher, S. *J. Chem. Soc., Faraday Trans.*, **1993**, *89*, 311–320.
17. Rudge, A.; Davey, J.; Gottesfeld, S.; Ferraris, J. P. *Proc. Electrochem. Soc.*, **1993**, *93–23*, 74–85.
18. Yagai, S.; Suzuki, M.; Lin, X.; Gushiken, M.; Noguchi, T.; Karatsu, T.; Kitamura, A.; Saeki, A.; Seki, S.; Kikkawa, Y.; Tani, Y.; Nakayama, K.-I. *Chem. Eur. J.* **2014**, *20*, 16128–16137.
19. Bundgaard, E.; Hagemann, O.; Bjerring, M.; Nielsen, N. C.; Andreasen, J. W.; Andreasen, B.; Krebs, F. C. *Macromolecules* **2012**, *45*, 3644–3646.
20. Lukevics, E.; Arsenyan, P.; Belyakov, S.; Popelis, J.; Pudova, O. *Organometallics* **2001**, *20*, 2487–2491.

Highlights

- Synthesis of 3-silylthiophenes possessing perfluoroalkyl groups on silicon atom.
- Electropolymerization of 3-silylthiophenes with head-to-tail regioregularity.
- Cyclic voltammogram of the polymers indicated both n- and p-doping properties.