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Electronegative Oligothiophenes Based on a Hexafluorocyclopentene-Annelated Thiophene Unit

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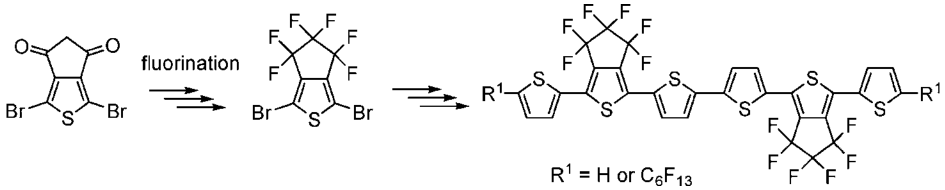
ABSTRACT



The synthesis of hexafluorocyclopenta[*c*]thiophene and its based oligothiophenes is described. The effectiveness of a hexafluorocyclopentene unit to lower the LUMO level without disturbing the effective conjugation could be unambiguously clarified by spectroscopic measurements and X-ray analysis.

Thiophene-based linear π-conjugated oligomers and polymers are intensively investigated as organic electronic materials.[1] A large number of substituted oligothiophene derivatives have been synthesized and investigated as active materials in organic field-effect transistors (OFETs), light-emitting didodes (OLEDs), and photovoltaic devices (solar cells). The vast majority of them exhibits hole-transporting (p-type) FET activity. On the other hand, electron-transporting (n-type) oligothiophenes have been of great interest for organic electronics[2] because n-type organic semiconductors are relatively rare and oligothiophenes possess promising physical properties. It has been known that the introduction of electron-withdrawing groups into π-conjugated systems stabilizes the LUMO energy, which facilitates electron injection, leading to an increasing n-type character. In this context, oligothiophenes introduced cyano,[3] nitro,[4] fluoro,[5] dicyanomethylene,[4b,6] ester,[7] perfluoroalkyl,[8,9] perfluoroaryl,[10] or perfluoroalkylphenyl[11] groups that have been prepared and some of them revealed n-type FET activity. Among them, the perfluoroalkyl group has emerged as a leading candidate because of its stability, large electron-withdrawing nature, and solubility effect.

In general, the oligothiophenes bearing perfluoroalkyl groups can be classified into two types depending on the position: (i) terminal α,ω-positions of the backbone and (ii)

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β-positions in the thiophene rings. Marks et al. have recently reported systematical studies of oligothiophenes bearing perfluorohexyl groups at the terminal α,*ω*-positions (**A**) as well as at the lateral *β*,*β′*-positions (**B**) (Figure 1).[9] They concluded that the substitution patterns, in most of the cases, have little effect on their electronic properties, and lateral substitution of the thiophene oligomer does not necessarily inhibit FET performance. Therefore, further introduction of perfluoroalkyl groups to oligothiophene *β*-positions is expected to increase the electronegativity of oligothiophene. However, such chemical modification might cause severe inhibition of the degree of backbone conjugation because it was speculated that *β*-perfluoroalkyl groups will have significantly greater steric constraints than the corresponding alkyl substituents.[9]

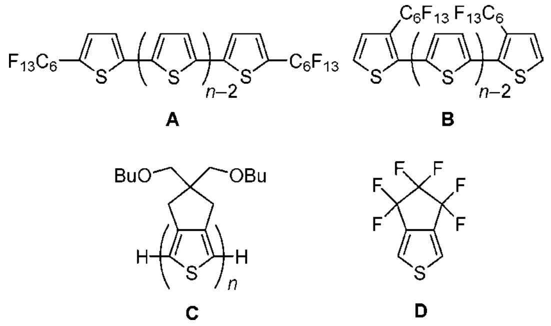

Figure 1. Perfluoroalkyl-substituted oligothiophenes (**A** and **B**), cyclopenta[*c*]thiophene oligomer (**C**), and hexafluorocyclopenta[*c*]thiophene (**D**).

Recently, we have reported on the synthesis and properties of soluble long oligothiophenes (**C**) up to 96-mer, in which *β*-positions of all thiophenes are completely blocked by annelation with the cyclopentene ring.[12] The spectroscopic measurements of this series of oligomers revealed that the effective conjugation is maintained by fastening alkyl groups at every *β*-position as the cyclopentene ring fusions. In line with this investigation, we anticipated that the ring fusion of hexafluorocyclopentene to both *β*-sites of the thiophene ring (**D**) contributes to not only lowering the LUMO level but also keeping the conjugation between consecutive thiophene rings in its based oligomers. In this communication, we report the synthesis of the hexafluorocyclopenta[*c*]thiophene unit as a novel electronegative thiophene building block and properties of its based oligothiophenes for n-type organic semiconductors.

Because the conventional Cu-mediated perfluoroalkylation of halogenated arenes[13] cannot be applied to the synthesis of hexafluorocyclopenta[*c*]thiophene (**D**) due to the difficulty of obtaining 1,3-dihalohexafluoropropane,[14] we have designed a unique route based on a combination of two types of fluorination reactions as shown in Scheme 1. First, fluorination of cyclopenta[*c*]thiophene-4,6-dione (**1**)[15] was carried out by the treatment with *N*-fluoro-6-(trifluoromethyl)pyridinium-2-sulfonate (MEC-04B)[16] in ethyl acetate to give 5,5-difluorocyclopenta[*c*]thiophene-4,6-dione (**2**) in 84% yield. Then, conversion of the two carbonyl groups to difluoromethylene groups was accomplished via the formation of bis-1,3-dithiolane derivative **3** followed by desulfurative fluorination with HF•pyridine and dibromatin[17] in dichloromethane to afford 1,3-dibromohexafluorocyclopenta[*c*]thiophene (**4**) in 73% two-step yield.[18]

The hexafluorocyclopenta[*c*]thiophene-based terthiophenes **$\mathrm{R_f}$-TFT-$\mathrm{R_f}$**, **TFT**, and **5** were synthesized by Stille coupling reactions (Scheme 1). The treatment of **4** with 3 equiv of 2-perfluorohexyl-5-tributylstanylthiophene[9a] afforded **$\mathrm{R_f}$-TFT−$\mathrm{R_f}$** in 81% yield. This double-coupling reaction proceeds very effectively, and the sole product was **$\mathrm{R_f}$-TFT-$\mathrm{R_f}$** even if the reaction was carried out in a 1:1 molar ratio. On the other hand, a three-component coupling of **4** with 1.0 equiv of 2-perfluorohexyl-5-tributylstanylthiophene and 3.0 equiv of 2-tributylstanylthiophene gave a mixtute of **TFT** and **5**, which was successfully separated by silica-gel column chromatography to give the pure products in 49 and 41% yields, respectively. The terthiophenes **TFT** and **5** were then iodinated by PhI•$(\mathrm{OCOCF_3})_2$−$\mathrm{I_2}$ to smoothly give rise to **6** (61%) and **7** (98%), respectively. Finally, the Pd-promoted

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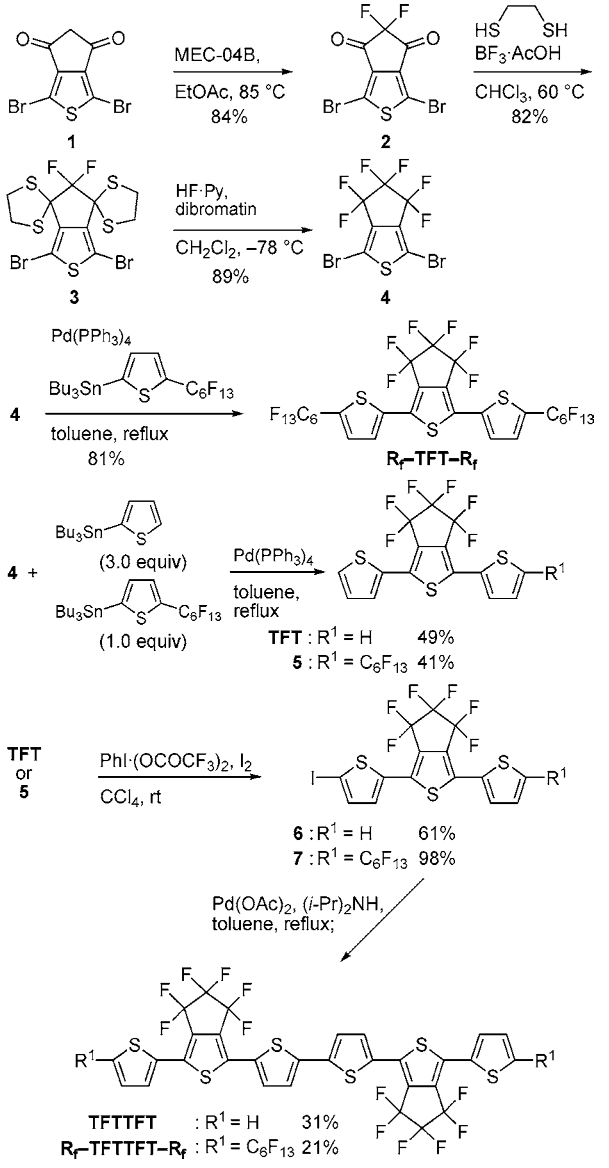
(18) All new compounds were fully characterized by spectroscopic measurements and elemental analyses; see Supporting Information.

Scheme 1. Synthetic Routes of **TFTTFT** and **R$_\mathrm{f}$-TFTTFT-R$_\mathrm{f}$**



reductive coupling of **6** or **7** yielded **TFTTFT** or **R$_\mathrm{f}$-TFTTFT-R$_\mathrm{f}$** in moderate yields.

Single crystals of **TFT** and **TFTTFT** were grown from a CHCl$_3$ or hexane−EtOAc solution by slow evaporation and were subjected to X-ray analyses.[19] Although positional disorder of the sulfur atoms was observed in the terminal two thiophene rings, the **TFT** molecule exhibits mainly a syn−syn conformation regarding the interring single bonds as shown in the Supporting Information Figure S01.[20] The dihedral angles between the adjacent thiophene rings are 31.9 and 27.4°. The **TFTTFT** molecule is located on a crystallographic inversion center and exhibits a syn−syn−anti conformation (from terminal thiophene to central) with dihedral angles 25.6, 22.1, and 180.0°, respectively (Figure 2). These syn conformations might be ascribed to cancel the dipole interaction between the thiophene and hexafluorocyclopenta[*c*]thiophene units. The dihedral angles observed in the syn conformations are much smaller than the corresponding angles reported for the β-perfluorohexyl-substituted oligothiophenes.[9a] This result clearly indicates that the hexafluorocyclopentene unit contributes to effective conjugation of the backbone π-system. Unlike perfluoroalkyl-containing oligomers, the slipped-stacking structure without segregation of hexafluorocyclopentene units is observed (Figure 3). The minimum interplanar distance between the backbones is found to be 3.55 Å, typical values of oligothiophenes.

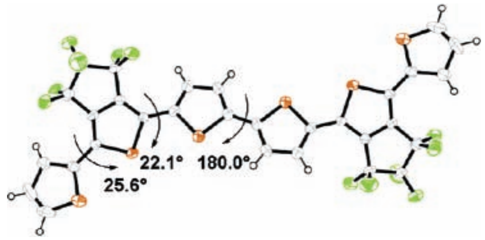


Figure 2. Molecular structure of **TFTTFT**.

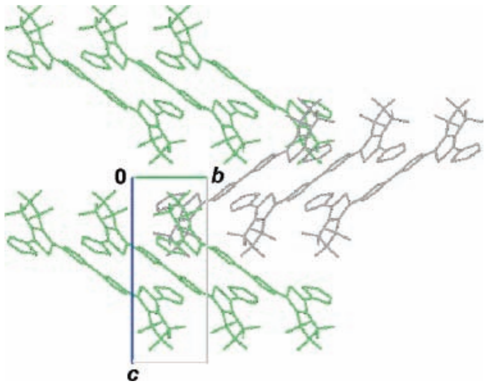


Figure 3. Crystal packing of **TFTTFT**.

The UV−vis absorption, fluorescence, and cyclic voltammetry (CV) data of the hexafluorocyclopenta[*c*]thiophene-based oligothiophenes were summarized in Table 1 together with the corresponding data for **3T** and **3T(β-R$_\mathrm{f}$)** for comparison. Compared with those of **3T(β-R$_\mathrm{f}$)**, the absorption and emission maxima of **TFT** and **R$_\mathrm{f}$-TFT-R$_\mathrm{f}$** are largely red shifted and much closer to those observed for **3T**. On

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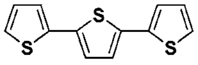
(19) Crystal Data for **TFT**: C$_{15}$H$_6$F$_6$S$_3$, $M = 396.38$, monoclinic, space group $P2_1/a$ (No. 14), $a = 15.461(1)$, $b = 5.7223(3)$, $c = 17.076(1)$ Å, $\beta = 96.684(2)^\circ$, $V = 1500.5(2)$ Å^3, $Z = 4$, $D_\mathrm{calcd} = 1.755$ g cm^{-3}, $F_{(000)} = 792.00$, $\mu = 5.55$ cm^{-1} (Mo Kα; $\lambda = 0.71069$ Å), 13 591 reflections measured, 3410 unique, $R = 0.047$ for $I > 2\sigma(I)$, $wR = 0.1170$ for all data. Crystal Data for **TFTTFT**: C$_{30}$H$_{10}$F$_{12}$S$_6$, $M = 790.8$, monoclinic, space group $C2/c$ (No. 15), $a = 34.977(2)$, $b = 5.7994(3)$, $c = 15.474(1)$ Å, $\beta = 110.238(2)^\circ$, $V = 2944.9(3)$ Å^3, $Z = 4$, $D_\mathrm{calcd} = 1.519$ g cm^{-3}, $F_{(000)} = 813.74$, $\mu = 5.55$ cm^{-1} (Mo Kα; $\lambda = 0.71069$ Å), 12 751 reflections measured, 3368 unique, $R = 0.083$ for $I > 2\sigma(I)$, $wR = 0.2449$ for all data.

(20) The contributions of anti conformations owing to disorder of the terminal thiophenes are 20 and 30%.

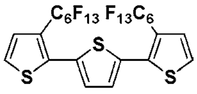
Table 1. Spectroscopic Data for the Oligomers

compound	abs$_{max}$/nm[a]	flu$_{max}$/nm[a]	$E_{p.a.}$/V[b]	$E_{p.c.}$/V[b]
R$_f$-TFT-R$_f$	364	428, 449	nd (>2.00)	−1.57[c]
TFT	373	436, 452	+1.63[c]	−1.72[c]
TFTTFT	450	534, 570	+0.88	−1.55[c]
R$_f$-TFT-R$_f$	452	538, 575	+1.00	−1.55[c]
3T	354	406, 430	+1.15[c]	nd (<−2.00)
3T(β-R$_f$)[d]	304	429, 446	+2.01	−2.23

[a] In CH_2Cl_2. [b] In C_6H_5F, 0.1 M $TBAPF_6$, V vs Fc/Fc^+. [c] Irreversible. [d] In THF; see ref 9a.



3T



3T(β-R$_f$)

CV measurements, **TFT** showed both irreversible oxidation and reduction peaks, the potentials of which are much higher than those of **3T**. It is important to note that the reduction potential of **TFT** is also positively shifted compared with that of **3T(β-R$_f$)**, indicating that the hexafluorocyclopenta-[*c*]thiophene unit effectively enhances the electronegativity of oligothiophenes. These results indicate that, as we expected, the introduction of the hexafluorocyclopentene unit does not break the conjugation between thiophene units, which is consistent with the above-mentioned X-ray molecular structure but does influence both the HOMO and LUMO levels. The introduction of the electron-withdrawing perfluorohexyl groups to the terminal α,ω-positions of **TFT** causes further positive shifts of both the reduction and oxidation potentials. The extension of the π-conjugation on going from **TFT** to **TFTTFT** shifts the absorption band to lower energy by 77 nm as well as the reduction potential to a more positive value by 0.17 V. Notably, the reduction potential of **TFTTFT** is the same as that of **R$_f$-TFTTFT-R$_f$** indicating that the terminal perfluoroalkyl groups have little influence on the LUMO level unlike **TFT**. The HOMO−LUMO gaps obtained from the redox peak potentials are 2.43 eV for **TFTTFT** and 2.55 eV for **R$_f$-TFTTFT-R$_f$**. DFT calculations are in agreement with the experimental results; the HOMO−LUMO gaps calculated at the B3LYP/6-31G(d,p) level are 2.64 eV for **TFTTFT**.[21] These are a little smaller than those of most organic semiconductors used in n-type OFETs.[9a]

In conclusion, we clearly demonstrated a novel synthetic route to hexafluorocyclopentene-fused thiophene and its based oligomers. The effectiveness of introducing the hexafluorocyclopentene unit into oligomers could be unambiguously elucidated by spectroscopic measurements and X-ray analysis. This molecular design enabled us to open a clue for the development of new materials for n-type OFETs. Further modification of the structure to allow a better understanding of the structure−property relationship and studies of charge-carrier mobilities of these oligomers will be forthcoming.

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Supporting Information Available: Synthesis and characterization of all compounds as well as crystallographic CIF files of **TFT** and **TFTTFT**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(21) The geometries were optimized with the restricted Becke hybrid (B3LYP) at 6-31 G(d, p) level. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A. Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Oritz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A.; *Gaussian 03*, Revision B.04; Gaussian, Inc., P.