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Tetradecafluorosexithiophene: The First Perfluorinated Oligothiophene

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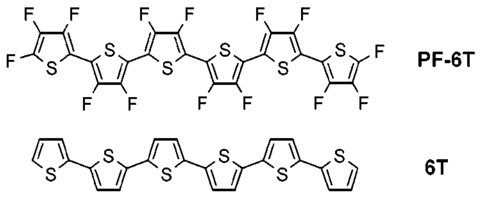
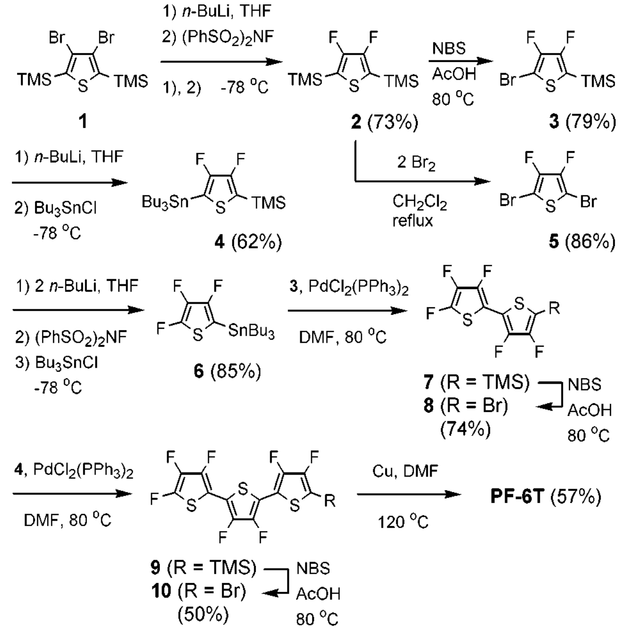
Organic semiconductors have attained much attention because of the recent progress of organic light-emitting diodes (OLEDs) and field-effect transistors (FETs). It was impressive that FETs based on organic single crystals exhibited superconductivity,[1] lasing,[2] and quantum Hall effect.[3] In the last paper, we reported that perfluorinated oligo(*p*-phenylene)s, such as perfluoro-*p*-sexiphenyl ($C_{36}F_{26}$), were efficient n-type semiconductors for the electron-transport layer of OLEDs.[4a] Molecular design of organic semiconductors for FETs should be different from that for OLEDs. A FET requires planar and crystalline materials for high carrier mobility. On the other hand, an OLED prefers nonplanar and amorphous materials. We designed tetradecafluorosexithiophene (perfluoro-α-sexithiophene; **PF-6T**) as a potential n-type semiconductor for FETs for the following reasons: (1) The dihedral angles of perfluorinated oligothiophenes would be much smaller than those of perfluorinated oligophenylenes[5] if thiophene rings have an *all-trans* conformation.[6] (See Chart 1.) (2) α-Sexithiophene (**6T**) is an excellent p-type semiconductor with high hole mobility.[7] (3) Perfluorination is an effective way to convert a p-type organic semiconductor to an n-type one.[4,8,9] We report herein the synthesis and X-ray structure of **PF-6T**. Absorption and emission spectra as well as thermal and electrochemical properties are also presented in comparison with **6T**.

Although tetrafluorothiophene has been prepared by fluorination of thiophene over $KCoF_4$ and subsequent dehydrofluorination,[10] any perfluorinated oligothiophenes (**PF-*n*T**: $n > 1$) have not yet been reported. To introduce fluorine atoms to a thiophene ring, the reaction of thienyllithiums[11] with several F^+ reagents[12] was examined. We found that *N*-fluoro-*N*-(phenylsulfonyl)-benzenesulfonamide, $(PhSO_2)_2NF$, gave the most satisfactory result.[13] As shown in Scheme 1, lithiation of TMS-protected 3,4-dibromothiophene **1** with an equivalent of *n*-BuLi followed by treatment with $(PhSO_2)_2NF$ provided a mixture of **1** and 3,4-difluoro-2,5-bis(trimethylsilyl)thiophene (**2**).[14] Further lithiation and fluorination were repeated without isolating the mixture to afford **2** in 73%. Bromination of **2** with *N*-bromosuccinimide (NBS) yielded monobromothiophene **3** in 79%. Tributyltin derivative **4** was obtained in 62% by lithiation of **3** and quenching with Bu_3SnCl. Dibromide **5**, which was prepared by the reaction of **2** with bromine in 86%, was allowed to react with 2 equiv of *n*-BuLi, $(PhSO_2)_2NF$, and Bu_3SnCl to give stannylated trifluorothiophene **6** in 85%. The Stille coupling of **3** and **6** in the presence of $PdCl_2(PPh_3)_2$ afforded bithiophene **7**. This was treated with NBS without purification to give perfluoro-5-bromobithiophene (**8**) in 74%. Similarly, the coupling reaction of **4** and **8** followed by bromination yielded perfluoro-5-bromoterthiophene (**10**) in 50%. The Ullmann coupling of **10** in DMF provided **PF-6T** in 57%.

Chart 1



Scheme 1



PF-6T was purified by train sublimation[15] and used for characterization. It is an orange crystalline solid and slightly soluble in $CHCl_3$ and aromatic solvents such as toluene. Its structure was determined by EI-MS, elemental analysis, and X-ray crystallography.[13] **PF-6T** exhibits bluish-green photoluminescence in solution and an orange emission in the solid state. Figure 1 shows the absorption and emission spectra of **PF-6T** and **6T** in $CHCl_3$. The shapes of the spectra are almost identical. The absorption and emission maxima of **PF-6T** (421 and 471 nm, respectively) shifted to higher energies relative to those of **6T** (435 and 508 nm, respectively).

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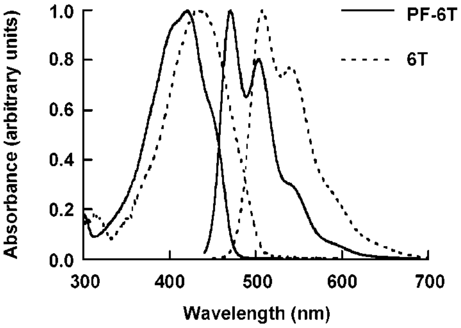

Figure 1. Absorption and emission spectra of **PF-6T** and **6T** in $CHCl_3$.

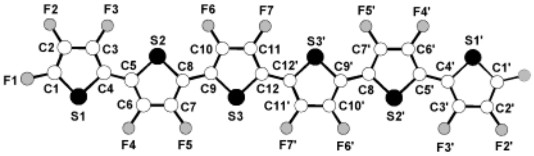

Figure 2. Molecular structure and labeling of **PF-6T**.

The thermal properties were investigated by differential scanning calorimetry (DSC). The DSC trace of **PF-6T** exhibited a sharp melting endotherm at 286 °C.[13] On the second heating, a lower melting endotherm due to a different crystalline phase was observed at 258 °C, which was followed by immediate crystallization at 262 °C to the high-temperature phase (T_m = 286 °C).[16] The electrochemical measurements on **PF-6T** and **6T** were performed in 1,2-dichlorobenzene at 50 °C.[13] The differential pulse voltammogram (DPV) of **6T** showed a reduction peak at −2.31 V and two oxidation peaks at 0.41 and 0.63 V (vs Fc/Fc^+). As expected, the redox potentials of **PF-6T** shifted positively relative to **6T**: Two reduction peaks at −1.86 and −2.05 V as well as an oxidation peak at 0.95 V were observed.[17] The potential differences between the first reduction and oxidation peaks are 2.72 V for **6T** and 2.81 V for **PF-6T**. This result is in agreement with a blue shift in absorption spectra, suggesting that the HOMO−LUMO gap of **PF-6T** is larger than that of **6T** in solution.

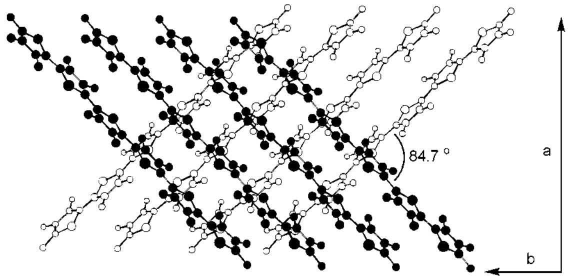

Figure 3. Molecular packing diagram of **PF-6T** with a view down the *c* axis.

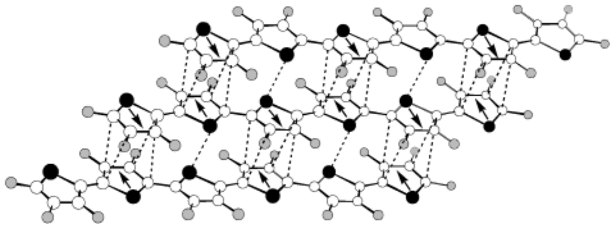

Figure 4. The short C−C (3.53−3.68 Å) and S−S contacts (3.65 Å) in the same stack (dotted lines). Dipole moments induced by fluorine atoms are indicated by arrows.

Single crystals of **PF-6T** were successfully grown by slow sublimation at 270 °C under a flow of 1 atm of argon.[18] An orange plate was used for X-ray crystallography.[13,19] The structure of **PF-6T** is *all-trans* and planar as observed for **6T** (Figure 2).[16] The dihedral angles between the adjacent thiophene rings are 0.7 (S1−C4−C5−C6), 1.5 (S2−C8−C9−C10), and 0.8° (S3−C12−C12′-C11′). The C−C bond distances are 1.33−1.39 Å in the thiophene rings (**6T**: 1.34−1.42 Å) and 1.43−1.44 Å between the rings (**6T**: 1.44 Å).[16a] The C−S bond distances range from 1.70 to 1.73 Å (**6T**: 1.71−1.74 Å). Interestingly, the C−C and C−S bonds in **PF-6T** are slightly shorter than the corresponding bonds in **6T**. This is probably because the inductive effect of fluorine lowers the energy levels of π-bonding orbitals. Figure 3 shows a crystal packing view of **PF-6T** along the *c* axis. **PF-6T** adopts a π-stack structure with face-to-face molecules.[20] This is quite different from the herringbone structure of **6T**,[16] in which $\pi-\pi$ interactions between neighboring molecules are minimized to reduce the repulsion between π-orbitals. The molecules in the adjacent stack are tilted at an angle of 84.7°. In Figure 4, the short C−C (3.53−3.68 Å) and S−S contacts (3.65 Å) in the same stack are shown. The next molecule slides along the long molecular axis by a thiophene unit to cancel dipole moments induced by fluorine atoms. We speculate that the dipole−dipole interactions between neighboring molecules overcome the $\pi-\pi$ repulsions and are responsible for the π-stack structure rather than the herringbone structure.

In conclusion, we have shown the synthetic method to obtain perfluorinated oligothiophenes. The X-ray structure of **PF-6T** suggests high electron mobility along the $\pi-\pi$ stacking direction (the *b* axis). Fabrication of n-type FETs with this new material is currently underway and will be reported elsewhere.

Acknowledgment. This paper is dedicated to Professor Fred Wudl on the occasion of his 60th birthday. We thank Prof. K. Inoue for the use of his X-ray diffractometer and Dr. M. Akita for help in X-ray structural determination. This work was supported by Japan Society for the Promotion of Science (Grant-in-Aid for Scientific Research B-12554027 and Encouragement of Young Scientists 12740391).

Supporting Information Available: Experimental details, DSC traces, DPVs, and X-ray structural determination (PDF); an X-ray crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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