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Electronegative Oligothiophenes Fully Annelated with Hexafluorocyclopentene: Synthesis, Properties, and Intrinsic Electron Mobility

Yoshikazu Umemoto, Yutaka Ie, Akinori Saeki, Shu Seki, Seiichi Tagawa, and Yoshio Aso*

The Institute of Scientific and Industrial Research, Osaka University, 8-1, Mihogaoka, Ibaraki, Osaka 567-0047, Japan

aso@sanken.osaka-u.ac.jp

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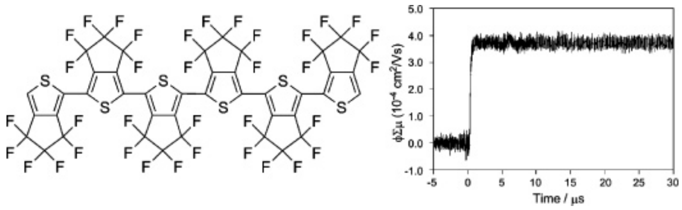
ABSTRACT



Synthesis of hexafluorocyclopenta[*c*]thiophene-repeated oligothiophenes up to 6-mer has been accomplished. The photophysical and electrochemical properties of these oligomers unambiguously exemplify marked electronegative character without disrupting the effective conjugation. The combination of time-resolved microwave conductivity and transient optical spectroscopy measurements of the 6-mer revealed the intrinsic electron mobility to be as high as 2.0×10^{-1} cm^2 V^{-1} s^{-1}.

Thiophene-based oligomers and polymers have good electron-donating properties and inherently low electron affinities, and they therefore have widespread applications as hole-transporting materials to various electronics such as organic light-emitting diodes, organic field-effect transistors (OFETs), and organic solar cells.[1] A critical objective for the continued advancement in the field of organic electronics is the development of electronegative conjugated oligomers that enable the invention of novel electron-transporting materials.[2] In this context, oligothiophenes bearing fluoro or perfluoroalkyl groups have inspired growing research efforts due to their potential in the field of n-type OFETs.[3−8] Recently, we have reported that the hexafluorocyclopenta[*c*]thiophene unit

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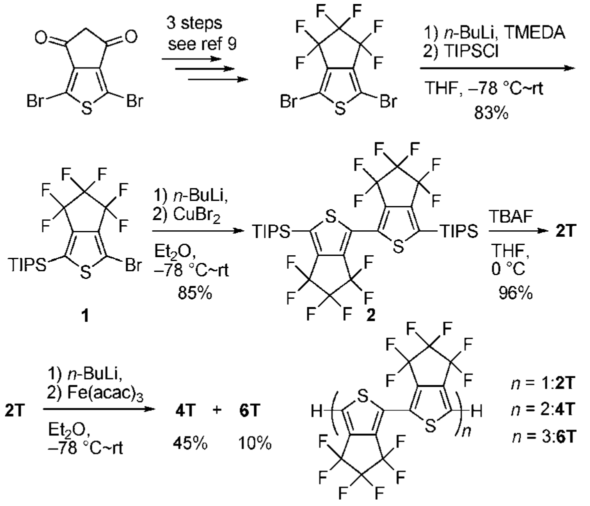
incorporated into thiophene oligomers induces electronegative character without disrupting the effective conjugation in spite of the presence of perfluoroalkyl groups at both the β-positions.[9] Stimulated by this result, we have concentrated our efforts on synthesizing it-repeated homo-oligomers, which should exhibit higher electronegativity while keeping the effective conjugation. This would constitute a novel electron-transporting conjugated system. Here we report on the synthesis of hexafluorocyclopenta[*c*]thiophene homo-oligomers **2T**−**6T**, their electronic properties, and the intrinsic electron mobility of **6T**.

Scheme 1. Synthesis of Hexafluorocyclopenta[*c*]thiophene Oligomers



The synthetic route to the oligomers **2T**−**6T** is outlined in Scheme 1. As conventional transition-metal-catalyzed cross-coupling reactions including the Stille, Negishi, and Suzuki reactions failed to obtain the desired oligomers due to low stability and/or reactivity of the organometallic derivatives, we carried out oxidative coupling reactions of lithiated species. Thus, conversion to a dimer derivative **2** was accomplished by lithiation of **1** with *n*-BuLi followed by oxidative coupling with $CuBr_2$. The dimer **2T** was readily obtained after protodesilylation of **2** using TBAF. Subsequent $Fe(acac)_3$-mediated oxidative coupling of lithiated **2T** directly provided a mixture of **4T** and **6T**, which were separated and purified by column chromatography on silica gel. Further purification of **4T** and **6T** for elemental analysis and spectroscopic and physical measurements was performed by gradient sublimation under high vacuum. The synthetic details and the compound-identification data are described in the Supporting Information. It is worth mentioning that, while the molecular weights of the hexafluorocyclopenta[*c*]thiophene-containing mixed-oligothiophenes were easily characterized by MALDI-TOF mass measurement in a positive ionization mode,[9] we did not observe any $[M]^+$ signals of **4T** or **6T** under this mode. Instead, the negative-mode ionization of **4T** and **6T** resulted in the clear detection of their $[M]^-$ ions, showing that the formation of the molecular anions becomes easier owing to the increased number of electronegative repeating units.

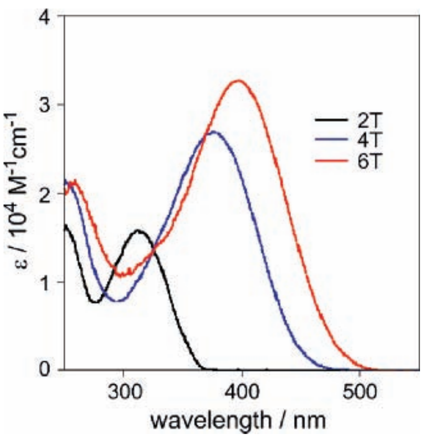


Figure 1. UV−vis absorption spectra of **2T**−**6T** in THF.

The UV−vis absorption spectra of **2T**−**6T** are shown in Figure 1, and the absorption maxima are tabulated in Table 1. As the number of thiophene unit was increased, a marked red-shift of the absorption maximum together with an increase in the molar extinction coefficient was observed. This result clearly indicates that the annelation of hexafluorocyclopentene at all the thiophene rings has little effect on the effective conjugation.[10]

Table 1. Spectroscopic and CV Data for the Oligomers

compd	abs_{max}[a]/nm	$E_{p.a.}$[b]/V	$E_{p.c.}$[b]/V
2T	312	not observed	−1.80[c]
4T	376	not observed	−1.27
6T	398	not observed	−1.03, −1.27

[a] In THF. [b] In C_6H_5F, 0.1 M *n*-Bu_4NPF_6, V vs Fc/Fc^+. [c] Irreversible.

Cyclic voltammetry (CV) measurements of **2T**−**6T** showed distinct reduction waves on a cathodic scan (Figure 2 and Table 1), while no oxidation wave was observed within the range of potential measured for all the oligomers (Figure S2 in the Supporting Information). Their reduction potentials, on going from 2-mer to 6-mer, are markedly shifted to more positive values with the improvement of reversibility, and **6T** exhibits even a quasi-reversible second reduction wave. The high potential and good reversibility of the reduction waves of **6T** indicate the formation of stable anionic species in solution.

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(10) The $\pi-\pi^*$ transition energies (eV) of these oligomers showed linear relation against the inverse thiophene-ring numbers, and the coefficient of its linear relation (2.61) is smaller than that of nonsubstituted oligothiophenes (3.68) in THF (Figure S1 in the Supporting Information).

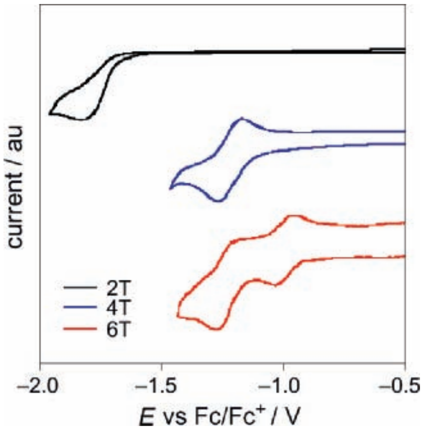

Figure 2. Cyclic voltammograms of **2T**−**6T** in C_6H_5F containing 0.1 M $TBAPF_6$, 100 mV s^{-1}.

In order to get further insight into the properties of the reduced species, chemical reduction of **6T** was performed by using elemental sodium in dry THF under degassed conditions. The neutral $\pi-\pi^*$ transition band of **6T** was bleached, and instead two optical transitions appeared in the UV−vis−NIR spectrum as shown in Figure 3, which was attributed to the formation of a radical anion.[11]

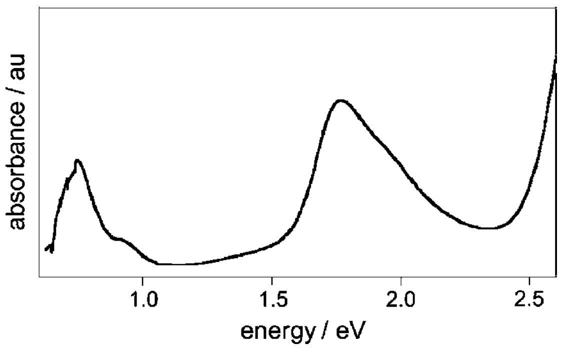

Figure 3. UV−vis−NIR spectrum of chemically reduced **6T** in THF.

The observed transition energies of 0.75 and 1.77 eV are well reproduced by TD−DFT calculations (B3LYP/6-31G(d,p)) and correspond to the excitations from the SOMO to LUMO level and from the SOMO to LUMO+2 level, respectively, both partially mixed with the HOMO−SOMO transition (see the Supporting Information).

It has been well-known that field-effect mobility is strongly affected by, in addition to the electronic properties and packing structures of organic molecules, the morphology of organic films at the interface with gate dielectrics and metal electrodes, which are normally tuned by varied terminal groups in oligomers and device fabrication conditions. For the evaluation of rather intrinsic electron mobility of **6T**, we have utilized the combination of time-resolved microwave conductivity (TRMC) and transient optical spectroscopy (TOS) measurements as an electrodeless method.[12] The film of **6T** was prepared by drop cast from a THF solution. The electronic absorption of **6T** film has the onset at 545 nm, and the spectrum displays a broad shoulder as compared to the solution spectrum, indicating some intermolecular interaction in the film (Figure S3 in the Supporting Information).[13] To generate charge carriers by photoinduced electron transfer, 3.6 mol % of *N*,*N*,*N*′,*N*′-tetramethyl-*p*-phenylenediamine was doped as an electron donor to the **6T** film. Upon laser excitation at 355 nm, the absorption of the **6T** radical anion at 710 nm was observed in the TOS measurement, and the product of electron mobility and photoinduced charge separation yield ($\phi\Sigma\mu$) of 4.2 × 10^{-4} cm^2 V^{-1} s^{-1} was obtained (Figure 4). Based on the ϕ value of 2.1 × 10^{-3} estimated by the TOS, the electron mobility of **6T** was found to be 2.0 × 10^{-1} cm^2 V^{-1} s^{-1}.

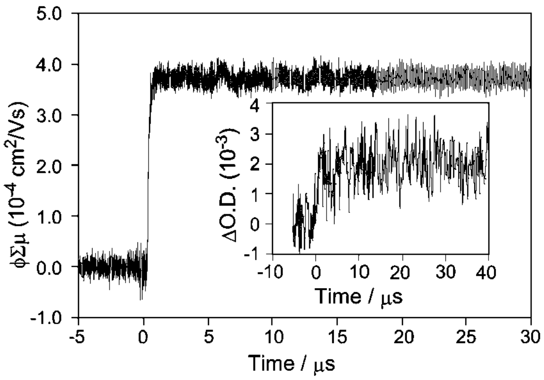

Figure 4. Kinetic traces of microwave conductivity transients and transient absorption (inset) of **6T** film upon 355 nm irradiation.

This high electron mobility of the long-lived radical anion might be attributable to the following reasons. First, lowering the LUMO level leads to the efficient electron injection into the conjugated system. Second, delocalization of the LUMO orbital over the whole conjugated system of the **6T** molecule suppresses the charge recombination, which allows long-lived anion species and facilitates the moving of electrons along the intramolecular and intermolecular backbones. Little changes between the SOMO orbital of the radical anion and the LUMO orbital of the adjacent neutral molecule support the ease of intermolecular electron migration (Figure 5).

In conclusion, we have successfully synthesized novel electronegative oligothiophenes annelated with hexafluoro-

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(13) This film did not show any peaks on X-ray diffraction measurement, and no FET behavior was observed on a bottom-contact OFET setup.

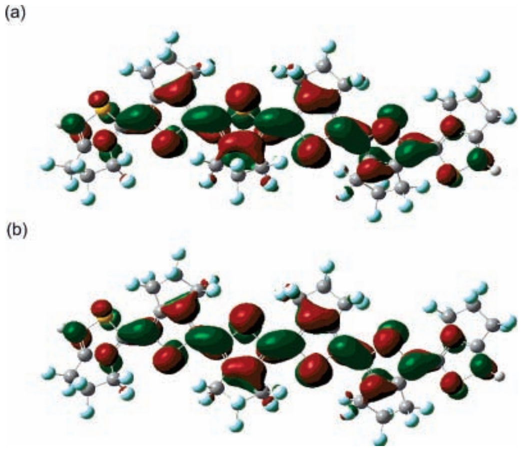

Figure 5. Calculated LUMO (a) of **6T** and SOMO (b) of **6T** radical anion.

cyclopentene at *all* the β-positions and established the strong influence of the hexafluorocyclopentene moiety on their electronic and electrochemical properties. The combination of TRMC and TOS techniques revealed the intrinsic electron mobility to be as high as 2.0 × 10^{-1} cm^2 V^{-1} s^{-1}. Further studies on application to FET devices as well as the comparison of TRMC and field-effect electron mobility will be reported in due course.

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Supporting Information Available: Detailed experimental procedures and characterization data of all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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