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# Electronic Modulation of Fused Oligothiophenes by Chemical Oxidation

**Yoshitake Suzuki, Toshihiro Okamoto, Atsushi Wakamiya, and Shigehiro Yamaguchi***

*Department of Chemistry, Graduate School of Science, Nagoya University, Furo, Chikusa, Nagoya 464-8602, Japan*

*yamaguchi@chem.nagoya-u.ac.jp*

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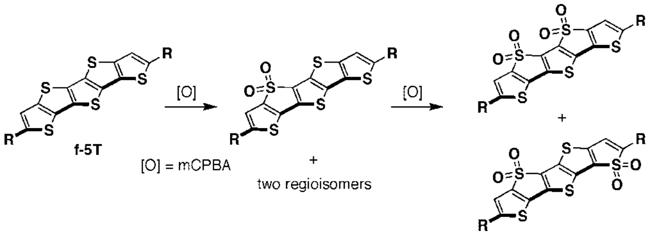
## ABSTRACT



**The reaction of pentathienoacene (f-5T) with mCPBA produced a series of oxidized derivatives containing one or two thiophene-*S*,*S*-dioxide rings. The regioselectivity of the oxidation reflects the aromaticity of each thiophene ring in the f-5T skeleton, and the extent of the oxidation significantly affects the fluorescence and redox properties.**

Fused oligothiophenes[1–6] and related thiophene-containing ladder $\pi$-electron systems[7–12] have recently attracted considerable attention as new materials for organic field-effect transistors (OFETs). They are regarded as the heteroatom analogues of linear acenes, such as pentacene. In contrast to the quinoid nature of the acenes, the fused oligothiophenes maintain a high aromaticity in each thiophene ring (a benzenoid character) and thus have wider HOMO−LUMO gaps with lower-lying HOMOs, which make them promising materials with a high stability.[6,10] In addition, the fused oligothiophenes generally form highly aligned molecular arrays in the crystals.[3a,5b] A weak intermolecular S−S nonbonding interaction has them adopt a face-to-face $\pi$-stacking structure, which is in contrast to the herringbone packing frequently seen in acene derivatives and may be beneficial

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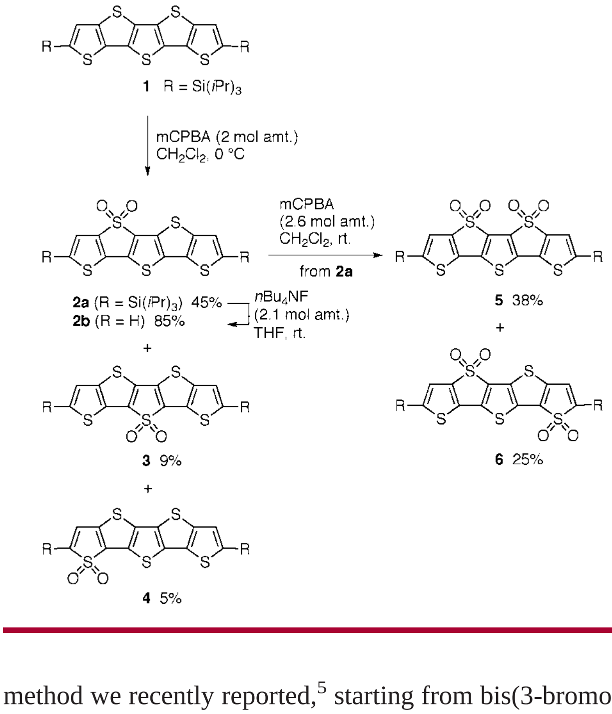
to achieving a high carrier mobility along the $\pi$-stacking direction.[13,14] Recent progress in developing new synthetic methods allows one to produce a series of fascinating derivatives, some of which indeed show a high performance as the stable p-type semiconductors for OFETs, as exemplified by pentathienoacene[6] and benzo-annulated fused oligothiophenes.[9,10]

The next challenge may be the electronic modulation of these fused oligothiophene skeletons from p-type to n-type semiconductors. It is well-established that the chemical oxidation of the thiophene ring to thiophene-*S*,*S*-dioxide is an effective way to alter its nature from electron-donating to electron-accepting.[15–19] Numerous examples of the partial[16–18] or full[19] chemical oxidation of oligothiophenes have demonstrated its effectiveness for tuning electronic structures. We envisioned that this approach would also be applicable to the fused oligothiophenes. In particular, the oxidized fused oligothiophenes would still have a completely flat and rigid structure, which leads to a set of superior properties, such as intense luminescence and high reversibility of the redox processes.[16a] We now report the chemical oxidation of the fused oligothiophenes, particularly focusing on the regioselectivity of the oxidation as well as the effect of the oxidation in terms of the electronic modulation.

An outline of the synthesis is shown in Scheme 1. Pentathienoacene (f-5T) **1**[3a] was prepared according to the method we recently reported,[5] starting from bis(3-bromo-5-triisopropylsilyl-2-thienyl)diacetylene in two steps (see Supporting Information). Triisopropylsilyl groups were introduced at the terminal positions to gain a sufficient solubility. We first examined the reaction of **1** with 2 mol amounts of mCPBA at 0 °C for 48 h. Careful separation of the reaction mixture by silica gel column chromatography gave three monothiophene-*S*,*S*-dioxide products, **2a**, **3**, and **4** in 45, 9, and 5% yields, respectively. Other part of the mixture contained a partially oxidized derivative such as a thiophene-*S*-oxide analogue of **2a** as a byproduct, probably due to the incompleteness of the reaction under this condition. The isolated product **2a** was further treated with 2.6 mol amounts of mCPBA to produce two thiophene ring-oxidized products, **5** and **6**, in 38 and 25% yields, respectively. Interestingly, the reaction of **1** with an excess amount of mCPBA (10 mol amounts) directly produced **5** and **6** in 45 and 27% yields, respectively, together with a trace amount of **3** (4%). Among the oxidized products, the desilylation of **2a** was conducted by the reaction with *n*-$Bu_4NF$ to give **2b** in 85% yield. The structures of these products were verified by NMR spectroscopy as well as mass spectrometry, and, in particular, the regioisomers were unambiguously determined by X-ray crystallography (for **2b**, **5**, and **6**, see Supporting Information).

**Scheme 1.** Stepwise Oxidation of Pentathienoacene **1**



All the oxidized products, except for the desilylated **2b**, maintain a high thermal stability comparable to that of the nonoxidized fused oligothiophene. The TGA measurements showed that the decomposition temperature with a 5% weight loss ($T_{d5}$) exceeds 300 °C even in the case of the doubly oxidized products **5** (373 °C) and **6** (333 °C). However, the desilylation seems to decrease the stability. The $T_{d5}$ for **2b** is 284 °C, which is 50 °C lower than that of **2a** (336 °C). All the silylated derivatives **2a**−**6** have sufficient solubilities in the common organic solvents, such as THF, $CHCl_3$, and toluene (for example, **5**, 9.4 mg/mL in toluene at 25 °C), while the desilylated product **2b** has a poor solubility (0.12 mg/mL in toluene at 25 °C).

It is worth noting that the oxidation of fused oligothiophenes proceeds with a certain regioselectivity. Thus, while f-5T **1** has three environmentally different thiophene rings in its skeleton, its first oxidation produced the three products **2a**, **3**, and **4** in a 76/15/9 ratio (based on the isolated yields). Also, for the oxidation of **2a**, only two products **5** and **6** were obtained in a 60/40 ratio among the possible four doubly oxidized products. To elucidate the origin of the regioselectivity, we carried out the molecular orbital calculations of model compounds **1′** and **2a′** having $SiMe_3$ groups in place of the terminal $Si(iPr)_3$ groups (Figure 1). The NICS (nucleus-independent chemical shifts) calculations[20] at the

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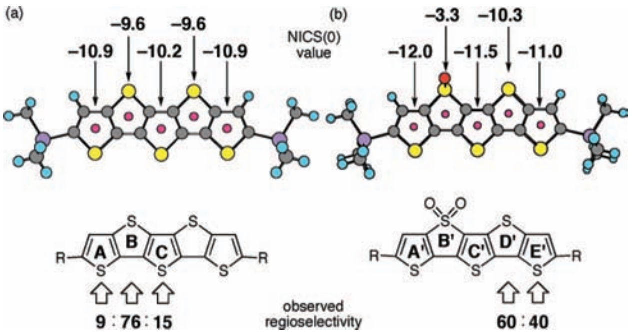

**Figure 1.** NICS(0) value for each thiophene ring in pentathienoacene derivatives (a) **1′** and (b) **2a′** (R = $SiMe_3$) calculated at the HF/6-31+G(d,p)//B3LYP/6-31G(d) level.

HF/6-31+G(d,p)//B3LYP/6-31G(d) level of theory evaluate the aromaticity of each thiophene ring. The fact that all of the three thiophene rings **A**−**C** in **1′** have lower NICS(0) values than that of the parent thiophene (−13.2) indicates the diminished aromaticity in the fused structure. Among the three rings, the ring **B** has the lowest value and that of the central ring **C** is also lower compared to the terminal ring **A**. This result is qualitatively consistent with the fact that the first oxidation occurred dominantly at the ring **B** compared to the rings **A** and **C**. The reduced aromaticity leads to the facile oxidation, and therefore, the ring **B**-oxidized **2a** was obtained as a major product. A similar trend was also observed for the oxidation of **2a**. Thus, the nonaromatic character of the thiophene-*S*,*S*-dioxide ring **B′**, indicated by the NICS(0) value, enhances the aromaticity of the adjacent rings **A′** and **C′**. Consequently, the oxidation occurred at the rings **D′** or **E′**. This trend is in contrast to the case of nonfused oligothiophenes, in which the regioselectivity of the oxidation is highly dependent on the electronic effect of the substituents on the thiophene rings.[18]

To elucidate the effect of the chemical oxidation on the photophysical properties, the UV−vis absorption and fluorescence spectra were measured, the data of which are summarized in Table 1. The fluorescence spectra in THF are shown in Figure S3 (Supporting Information). Some notable points are as follows: (1) Upon the oxidation from **1** to **2a**−**6**, the absorption ($\lambda_{abs}$) and emission maxima ($\lambda_{em}$) are substantially red-shifted by about 40−70 and 95−125 nm, respectively, indicative of the significant perturbation on the electronic structure. The extent of the red shifts is comparable to the shifts observed from the nonfused terthiophenes to their mono- or two-thiophene-oxidized derivatives.[16b–d,18] (2) Among the oxidized products **2a**−**6**, the $\lambda_{abs}$ and $\lambda_{em}$ are not significantly different from one another, despite the difference in the extent of the oxidation or the position of the thiophene-*S*,*S*-dioxide ring. As for the $\lambda_{em}$, the monothiophene-oxidized products tend to have longer maximum wavelengths than the two-thiophene ring-oxidized derivatives. (3) The oxidation of one thiophene ring tends to enhance the fluorescence intensity. In particular, the quantum yields, $\Phi_F$, of **2a** and **3** are 0.76 and 0.66, respectively. In contrast, the doubly oxidized products **5** and **6** only show moderate fluorescences. To elucidate the origin of this difference, the fluorescence lifetime, $\tau_s$, was determined. The radiative and nonradiative rate constants for the decay from the singlet excited state, $k_r$ and $k_{nr}$, are calculated from $\Phi_F$ and $\tau_s$. While the $k_r$ values are comparable to one another in the range of 0.97−5.5 × $10^8$ $s^{-1}$, a large difference exists in the $k_{nr}$. In the monothiophene-oxidized derivatives **2a** and **3**, the $k_{nr}$ is suppressed as about 0.5 × $10^8$ $s^{-1}$, while the $k_{nr}$ values of the doubly oxidized products, **5** and **6**, significantly increase. Although the origin of this difference is unclear at this moment, a slight geometrical change from thiophene to thiophene-*S*,*S*-dioxide in **2a** and **3** (vide infra) may play an important role in releasing the ring strain of this all-five-membered ring-fused skeleton in the excited state.

**Table 1.** Photophysical Data for Pentathienoacene **1** and Its Oxidized Derivatives **2**−**6** in THF

| | absorption | | fluorescence | | | | |
|---|---|---|---|---|---|---|---|
| cmpd | $\lambda_{abs}$[a] [nm] | $\epsilon$ [$M^{-1}$ $cm^{-1}$] | $\lambda_{em}$[b] [nm] | $\Phi_F$ | $\tau_s$[c] [ns] | $k_r$ [$10^8$ $s^{-1}$] | $k_{nr}$ [$10^8$ $s^{-1}$] |
| **1** | 374 | 36300 | 407 | 0.27[d] | 0.49 | 5.5 | 14.9 |
| **2a** | 415 | 23800 | 510 | 0.76[e] | 5.3 | 1.4 | 0.45 |
| **3** | 424 | 20400 | 525 | 0.66[e] | 6.8 | 0.97 | 0.5 |
| **4** | 420 | 23800 | 532 | 0.38[e] | 3.6 | 1.1 | 1.7 |
| **5** | 444 | 31300 | 509 | 0.05[e] | 0.3 | 1.7 | 31.7 |
| **6** | 444 | 31600 | 501 | 0.16[e] | 1.1 | 1.5 | 7.6 |

[a] Only the longest absorption maxima are shown. [b] Emission maxima upon excitation at the absorption maximum wavelengths. [c] Fluorescence lifetimes within ± 0.5 ns error. [d] Determined with pyrene as a standard. [e] Determined with perylene as a standard.

The effect of the chemical oxidation on the redox properties is also an important issue in this chemistry. The electrochemical properties for compounds **1**−**6** were investigated by cyclic voltammetry, the data of which are summarized in Table 2. All the compounds, except for **6**, showed chemically reversible redox processes, demonstrating that the thiophene-*S*,*S*-dioxide rings in the fused skeleton do

**Table 2.** Electrochemical Data for Pentathienoacene **1** and Its Oxidized Derivatives **2**−**6**[a]

| cmpd | oxidation $E_{ox,1/2}$ [V[b]] | reduction $E_{red,1/2}$ [V[b]] |
|---|---|---|
| **1** | +0.63 | |
| **2a** | +0.93 | −1.94 |
| **3** | +0.95 | −1.86 |
| **4** | +0.87 | −1.85 |
| **5** | | −1.66 |
| **6** | | −1.70[c] |

[a] Measurement conditions: $nBu_4PF_6$ (0.1 M) used as an electrolyte in $CH_2Cl_2$. Scan rate 50 mV·$s^{-1}$. [b] versus ferrocene/ferrocenium ion couple (Fc/$Fc^+$). [c] Irreversible peak. A peak potential $E_{pc}$ is reported.

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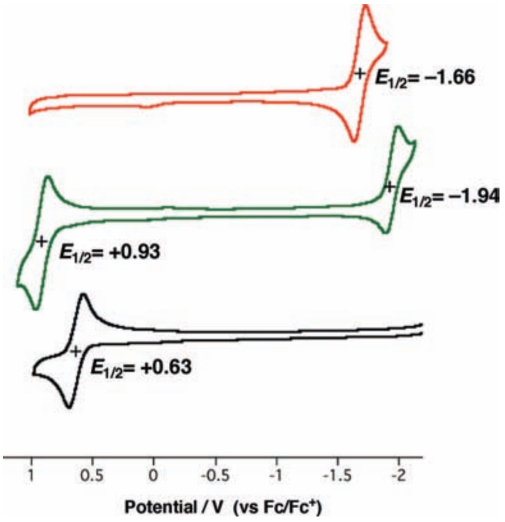

**Figure 2.** Cyclic voltammograms of **1** (black), **2a** (green), and **5** (red).

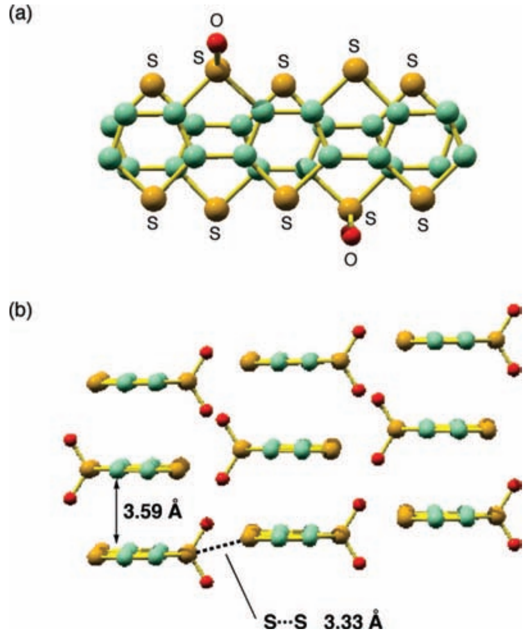

**Figure 3.** Packing structures of **2b**: (a) top view and (b) side view.

not decrease the electrochemical stability. Figure 2 shows the cyclic voltammograms for compounds **1**, **2a**, and **5**, which clearly demonstrates the stepwise electronic tuning dependent on the extent of the oxidation. While **1** shows the oxidation process at $E_{1/2} = +0.63$ V (vs ferrocene/ferrocenium ion couple (Fc/Fc$^+$)), the doubly oxidized **5** shows only the reduction process at $E_{1/2} = -1.66$ V. In the case of the monothiophene-oxidized product **2a**, both the oxidation and reduction processes were observed at $E_{1/2} = +0.93$ and −1.94 V, respectively, indicative of its ambipolar character. These values correspond to the LUMO level of 2.9 eV and the HOMO level of 5.7 eV.[21]

Finally, we succeeded in obtaining a single crystal of the desilylated monothiophene-oxidized product **2b** suitable for X-ray crystallography (Figure 3). The geometry of the thiophene-*S*,*S*-dioxide ring is slightly deviated from the other thiophene rings. The C−S bond (av. 1.77 Å) and C−S−C angle (92.1(9)°) in the thiophene-*S*,*S*-dioxide ring are longer and wider compared to those in the thiophene rings. In the crystal packing, this compound forms face-to-face $\pi$-stacking columns, in which the molecules align in a parallel fashion and completely overlap with the neighboring molecules in an upside-down fashion. The interfacial distance is about 3.59 Å. The nearest intermolecular S−S distance is 3.33 Å, indicative of certain S−S nonbonding interactions. The parallel alignment is rather different from the parent pentathienoacene, which forms the face-to-face $\pi$-stacking, but in a tilted fashion.[3a] This difference is likely due to the favorable stacking in **2b** due to the donor−acceptor interaction between the electron-donating thiophene and electron-accepting thiophene-*S*,*S*-dioxide rings. How these differences in the $\pi$-stacking modes affect the carrier transportation is of interest. We are now investigating the potential applicability of the obtained oxidized fused oligothiophenes to OFETs.

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**Supporting Information Available:** Experimental details, crystallographic data in CIF format and ORTEP drawings, photophysical data, electrochemical data, and results of theoretical calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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