

Systematic Synthesis and Characterization of a Series of Tetra(5-aryl-2-thienyl)thiophenes

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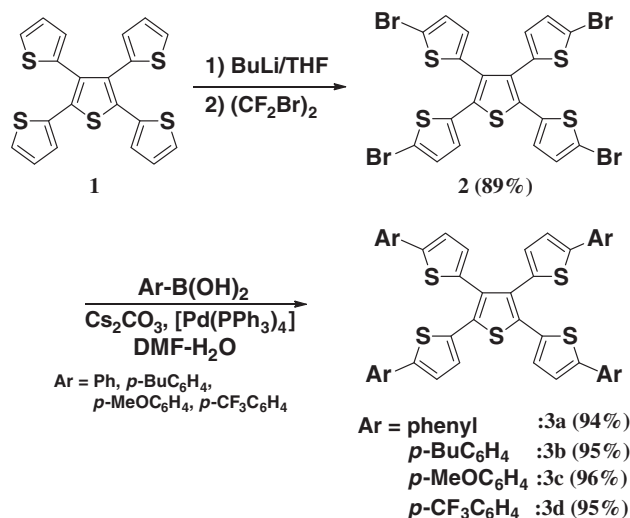
(Received May 27, 2011; CL-110448; E-mail: ogawa@iwate-u.ac.jp)

We have succeeded in the synthesis of a series of tetra(5-aryl-2-thienyl)thiophenes as aryl-functionalized tetrathienylthiophenes. Characterization of these chemicals was performed by physical and spectroscopic means. The electrochemical properties were examined by cyclic voltammetry. The CV of all compounds showed that the redox behavior and potentials were controlled by the electronic effect of the *p*-substituted phenyl groups introduced at the outer α -positions on the four thiophene units linked to the thiophene core.

One-dimensional linear α -oligothiophenes, which possess outstanding thermo- and photostabilities, geometric and electronic structures, and electronic and optical properties, are very useful building segments for designing a wide variety of functional molecules. Molecular modification by regioselective introduction of functional substituents on the thiophene framework can improve their intrinsic electronic and optical properties for use as next generation electronic and optical devices, for example, light-emitting diodes (LEDs) and organic transistors.¹

On the other hand, in recent years, branched 3D oligothiophenes, including α -linkage (connection between the α -position of the thiophenes) and branching α,β -linkage (connection between the α - and β -positions of the thiophenes) within the oligothiophene backbone, have received much attention from the viewpoints of application as a new class of active layers in organic devices due not only to their remarkable solubility, geometric and electronic properties, but also to their electropolymerization ability to prepare 3D polythiophene polymer.² In this research field, our particular interests are the molecular modification of branched oligothiophenes with aryl groups for the construction of functional molecules with a new type of π -electron system as well as investigating the advantage of branched oligothiophenes as a building block. In addition, aryl-introduced oligothiophene derivatives are fundamentally attractive targets for the study of tuning the electronic and optical properties such as the redox activity and luminescence, as a result of controlling the HOMO/LUMO energy levels and their energy gap varied by π -conjugation and the electronic effects of the introduced aryl groups. In this paper, we reported the details of the optical and electrochemical properties of a series of tetra(5-aryl-2-thienyl)thiophenes utilizing tetrathienylthiophene as the key segment, which were designed and synthesized as branched oligothiophenes functionalized by various *p*-substituted phenyl groups.

2,3,4,5-Tetrathienylthiophene (**1**) as a starting material was prepared via the Ni-catalyzed cross-coupling reaction of tetrabromothiophene with 2-thienylmagnesium bromide in ether under reflux conditions based on previous methods.^{2f} The selective bromination of **1** was achieved by selective lithiation at the 5-position of four thiophene branches linked to the thiophene



Scheme 1.

core with a small excess of butyllithium in tetrahydrofuran (THF) at -50°C (Scheme 1), followed by bromination with 1,2-dibromo-1,1,2,2-tetrafluoroethane, which are needed to introduce aryl groups on the terminal thiophene rings via a metal-catalyzed cross-coupling reaction. As a result, the key intermediate, tetra(5-bromo-2-thienyl)thiophene (**2**) was obtained in an 89% yield. The tetra(5-aryl-2-thienyl)thiophenes **3a–3d** have then been systematically synthesized in excellent yields by typical palladium-catalyzed cross-coupling reactions (Suzuki–Miyaura coupling³) of **2** with arylboronic acids (Ar = Ph, *p*-BuC₆H₄, *p*-MeOC₆H₄, and *p*-CF₃C₆H₄) in the presence of cesium carbonate and a catalytic amount of tetrakis(triphenylphosphane)palladium(0), [Pd(PPh₃)₄], in DMF/water at 100°C . The spectral (¹H, ¹³C NMR and FAB-MS) and elemental analysis data for the newly synthesized tetra(5-aryl-2-thienyl)thiophenes **3a–3d** are consistent with the proposed structures.⁴

These compounds are soluble in common organic solvents such as CH₂Cl₂ and THF. Therefore, the electronic properties of **3a–3d** in the solution state were examined by UV–vis absorption spectra and cyclic voltammetry (CV) measurements, and the data are summarized in Table 1.

The UV–vis absorption properties of these compounds were measured at $5 \times 10^{-5} \text{ mol dm}^{-3}$ in dichloromethane, CH₂Cl₂. The maximum wavelengths of the first absorption peaks ($\lambda_{\text{max}}^{\text{ab}}$) assigned to the π – π^* transition within the α -connected linear diarylterthiophene fragment were observed at 404 nm for **3a**, 410 nm for **3b**, 412 nm for **3c**, and 406 nm for **3d**. Their first absorption maxima are red-shifted by about 50 nm in comparison to that of the previously reported tetrathienylthiophene in CH₂Cl₂ ($\lambda_{\text{max}} = 362 \text{ nm}$).^{2a} These results clearly indicated

Table 1. UV-vis^a and electrochemical^b data for compound **3a–3d**

Compd	$\lambda_{\max}^{\text{ab}}$ /nm	$\epsilon/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$	$E_{\text{g}}^{\text{opt}}/\text{eV}^{\text{c}}$	$E_{1/2} (0/+1)/\text{V}^{\text{d}}$	$E_{1/2} (0/-1)/\text{V}^{\text{e}}$	$E_{1/2} (-1/-2)/\text{V}^{\text{e}}$	$E_{\text{g}}^{\text{elec}}/\text{eV}^{\text{f}}$
3a	404	32140	3.07	+0.76	-2.10	-2.29	2.95
3b	410	36480	3.02	+0.69	-2.13	-2.33	2.91
3c	412	41720	3.01	+0.61	-2.19	-2.43	2.90
3d	406	36260	3.05	+0.90	-1.90	-2.05	2.89

^aMeasured in CH_2Cl_2 solution at ambient temperature. ^bAll data collected by cyclic voltammetry technique, redox potentials versus Ag/Ag^+ couple. ^cEstimated by maximum wavelength of the first absorption peaks ($\lambda_{\max}^{\text{ab}}$). ^dMeasured in $0.1 \text{ mol dm}^{-3} [\text{Bu}_4\text{N}][\text{PF}_6]/\text{CH}_2\text{Cl}_2$ solution at ambient temperature. ^eMeasured in $0.1 \text{ mol dm}^{-3} [\text{Bu}_4\text{N}][\text{PF}_6]/\text{THF}$ solution at 260 K. ^fCalculated from the difference between the first oxidation and reduction peak potentials ($E_{\text{p,a}} (0/+1)$, $E_{\text{p,c}} (0/-1)$).

that the introduction of aryl groups effectively elongates the π -conjugation lengths along the α -connected backbone. Unexpectedly, the first absorption maxima of **3a–3d** corresponding to the lowest excitation energy originating from the HOMO–LUMO excitation (π – π^* transition) are almost the same regardless of the expected change to the HOMO–LUMO gap contributing to the electronic effect of substituents (electron-donating of butyl or methoxy groups and electron-withdrawing of trifluoromethyl group) at the *para*-position on the benzene. Actually, the calculated optical HOMO–LUMO energy gap ($E_{\text{g}}^{\text{opt}}$) of **3a–3d** estimated by $\lambda_{\max}^{\text{ab}}$ is very similar, i.e., 3.07 eV for **3a**, 3.02 eV for **3b**, 3.01 eV for **3c**, and 3.05 eV for **3d**.

On the other hand, for compounds **3a–3d**, the maximum wavelengths of the second peaks were observed at about 330 nm. Their second absorption bands could be assigned to the transition within the two arylthienyl branches α,β -linked to the central thiophene core. These assignments are supported by the UV–vis spectra of tetra(α -bithienyl)thiophene corresponding to the previously reported 2-thienyl per-substituted tetrathienylthiophene, which show two absorption peaks with maximum wavelengths at 419 and 345 nm assigned to the transition within the linear α -quinquethiophene fragments and α -bithiophene branches, respectively.^{2c}

The electrochemical properties of **3a–3d** were examined by cyclic voltammetry. In the voltammograms of the anodic scans at a concentration of 1.0 mmol dm^{-3} in $\text{CH}_2\text{Cl}_2/0.1 \text{ mol dm}^{-3} \text{Bu}_4\text{NPF}_6$, the first oxidation waves of all compounds derived from the radical cation species were observed with an electrochemical reversibility, $E_{1/2} (0/+1) = +0.76 \text{ V}$ for **3a**, $+0.69 \text{ V}$ for **3b**, $+0.61 \text{ V}$ for **3c**, and $+0.90 \text{ V}$ for **3d**. In particular, by anodic scanning of compound **3c**, the voltammogram showed a 4-electron, 3-step reversible oxidation wave corresponding to the stepwise oxidations assigned to the 1-, 1-, 2-electron transfer processes based on the differential pulse voltammogram (Figure 1). The reversible electrochemical multistep multielectron oxidation behavior was observed as a unique phenomenon for compound **3c**. This result clearly indicates the formation of the stabilized multiply charged oxidation species produced by the four-electron oxidation of **3c** contributing to the electron-donating effect of the methoxy group on the benzene ring. The first and second oxidations of **3c** were assigned to the stepwise formation of the dication species derived from two-step, two-electron oxidation of the α -connected diarylterthiophene fragment, and then the third oxidation is assigned to the formation of the tetracation diradical species containing two radical cation segments generated by two overlapping one-electron oxidations of two independent *p*-methoxyphenylthienyl branches linked to the central thiophene ring at the same potentials.

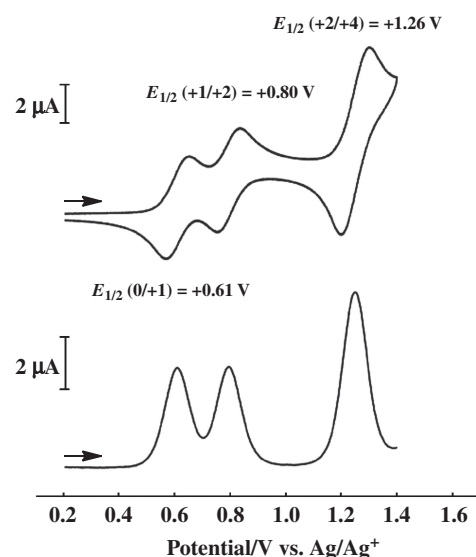


Figure 1. Cyclic voltammogram of compound **3c**. Condition: 1 mmol dm^{-3} sample in $0.1 \text{ mol dm}^{-3} \text{Bu}_4\text{NPF}_6/\text{CH}_2\text{Cl}_2$ solution; scan rate, 200 mV s^{-1} .

On the negative scan of all compounds at the concentration of 1.0 mmol dm^{-3} in $\text{THF}/0.1 \text{ mol dm}^{-3} \text{Bu}_4\text{NPF}_6$, the voltammogram showed two subsequent sets of one-electron reductions with electrochemical reversibility; first reduction ($E_{1/2} (0/-1)$) of -2.10 V for **3a**, -2.13 V for **3b**, -2.19 V for **3c**, -1.90 V for **3d**, and second reduction ($E_{1/2} (-1/-2)$) of -2.29 V for **3a**, -2.33 V for **3b**, -2.43 V for **3c**, -2.05 V for **3d**, which are assigned to the stepwise formation of the dianion species within the α -connected linear diarylterthiophene fragment.

The first oxidation and reduction half-wave potentials clearly indicated that the HOMO level increases in the order of **3c** > **3b** > **3a** > **3d**, and the LUMO level increases in the order of **3d** < **3a** < **3b** < **3c**. These results adequately indicated that the electron-donating or -withdrawing effects of the substituent on the benzene ring can be controlled by the HOMO and the LUMO levels. The electrochemical HOMO–LUMO energy gap ($E_{\text{g}}^{\text{elec}}$) was calculated from the difference between the first oxidation and reduction peak potentials [$E_{\text{p,a}} (0/+1)$, $E_{\text{p,c}} (0/-1)$],⁵ 2.95 eV for **3a**, 2.91 eV for **3b**, 2.90 eV for **3c**, 2.89 eV for **3d**,⁶ which are in good agreement with the optical values ($E_{\text{g}}^{\text{opt}}$, ca. 3.0 eV).

As the results of the experimental observations of the tetra(5-aryl-2-thienyl)thiophenes **3a–3d** in the solution state, although the electronic effect of the substituent on the benzene

ring serves to control the redox behavior attributed to the HOMO and the LUMO energy levels, they have little influence on the HOMO–LUMO energy gap.

We have designed and established a synthetic route to systematically prepare novel tetra(5-aryl-2-thienyl)thiophenes **3a–3d**. The synthetic route would be adapted to the synthesis of varieties aryl-functionalized tetrathienylthiophene series. The optical and electrochemical properties of **3a–3d** were identified by UV–vis spectroscopy and cyclic voltammetric studies. The CV determined the one-step oxidation and two-step reduction in all the compounds, which have redox characteristics controlled by the substitution on the benzene rings. Therefore, we succeeded in establishing a new branched oligothiophene modified by aryl groups with a remarkable molecular electronic structure (π -electron system).

This work was supported by the Ministry of Education, Culture, Sports, Science and Technology Japan (MEXT) and the Japan Science and Technology Agency (JST).

This paper is in celebration of the 2010 Nobel Prize awarded to Professors Richard F. Heck, Akira Suzuki, and Ei-ichi Negishi.

References and Notes

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- Supporting Information is also available electronically on the CSJ-Journal Web site, <http://www.csj.jp/journals/chem-lett/index.html>.
- The first oxidation peak potentials ($E_{p,a}$ (0/+1)) were observed at +0.80 V for **3a**, +0.73 V for **3b**, +0.65 V for **3c**, and +0.94 V for **3d**, and the reduction peak potentials ($E_{p,c}$ (0/–1)) were observed at –2.15 V for **3a**, –2.18 V for **3b**, –2.25 V for **3c**, and –1.95 V for **3d**.
- HOMO^{elec} and LUMO^{elec} energy levels were calculated from the first oxidation and reduction peak potentials according to $E_{HOMO} = -I_p = -(E_{ox} + 4.71)$ eV, $E_{LUMO} = -E_a = -(E_{re} + 4.71)$ eV in which the potential values are relative to the Ag/Ag⁺ reference electrode. M. E. Norako, M. A. Franzman, R. L. Brutchey, *Chem. Mater.* **2009**, *21*, 4299.