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SYNTHESIS AND ELECTROCHROMIC PROPERTIES OF BIS(2-TETRATHIAFULVALENYLETHYNYLPHENYL)ETHYNES

Masashi Hasegawa,[#] Yusuke Kobayashi, Kenji Hara, Hideo Enozawa, and Masahiko Iyoda*

Department of Chemistry, Graduate School of Science and Engineering, Tokyo Metropolitan University, Hachioji, Tokyo 192-0397, Japan; iyoda@tmu.ac.jp

Abstract – Bis(2-tetrathiafulvalenylethynylphenyl)ethynes **1a** and **1b** have been synthesized by the Sonogashira coupling reaction of 4-iodotetrathiafulvalenes with bis(2-ethynylphenyl)ethyne. The dimeric TTFs **1a** and **1b** form an open-chain *anti* conformation in the neutral and tetracation states, whereas **1a** and **1b** form a helical *syn* conformation in the mono- and dication states owing to their face-to-face interaction between the two TTF units. Such conformational changes lead to unique electrochromic and on-off switching properties of **1a** and **1b** in UV-vis-NIR spectra.

INTRODUCTION

Large π -conjugated systems with multi-redox sites show various electronic structures that lead to important electrochromic, magnetic, and electroconducting properties.^{1,2} Dimeric and oligomeric tetrathiafulvalenes (TTFs) have been utilized widely as an electroactive unit for designing functional materials in supramolecular chemistry, materials science, and nanoscience.²⁻⁴ Among these oligomers, face-to-face stacked TTFs show various interactions in the neutral and oxidation states, forming weakly interacting neutral (TTF)₂, strongly dimerized mixed-valence (TTF)₂^{•+}, and π -dimer (TTF^{•+})₂.^{5,6} Previously, we reported dimeric TTFs and higher oligomers that show a conformational change between nonhelical and helical structures owing to the strong interaction of TTF units upon oxidation.⁷ With this in mind, we designed a new class of dimeric TTFs, namely, **1a** and **1b**, connected to a phenylene ethynylene scaffold. The dimeric TTFs **1a** and **1b** may show clear electrochromic properties owing to a dynamic conformational change between their open-chain “*anti*” and helical “*syn*” structures depending on the strength of the interaction of their terminal TTF moieties (Figure 1). We report here the unique electrochromic and on-off switching properties of **1a** and **1b** observed in UV-vis-NIR spectra.

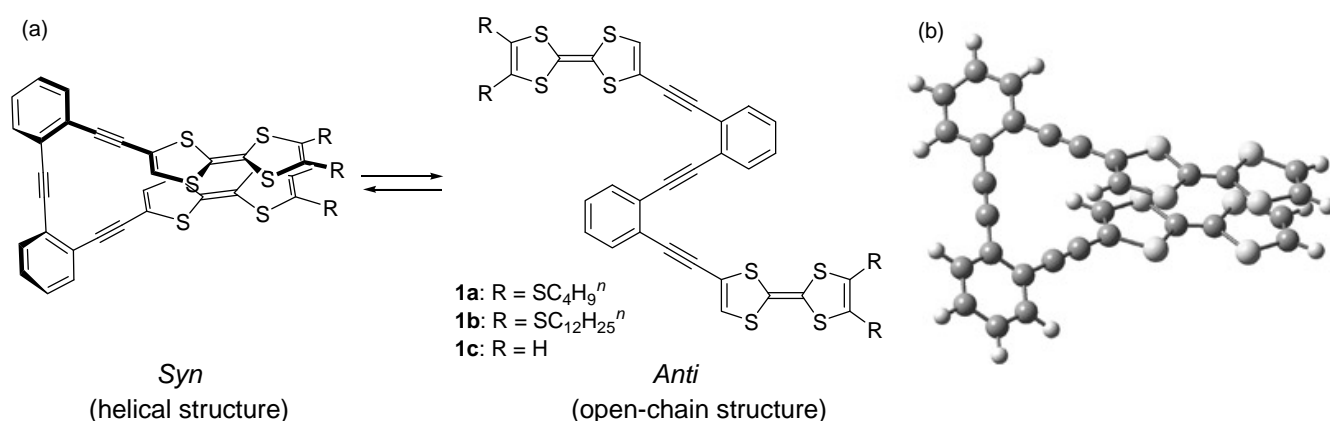
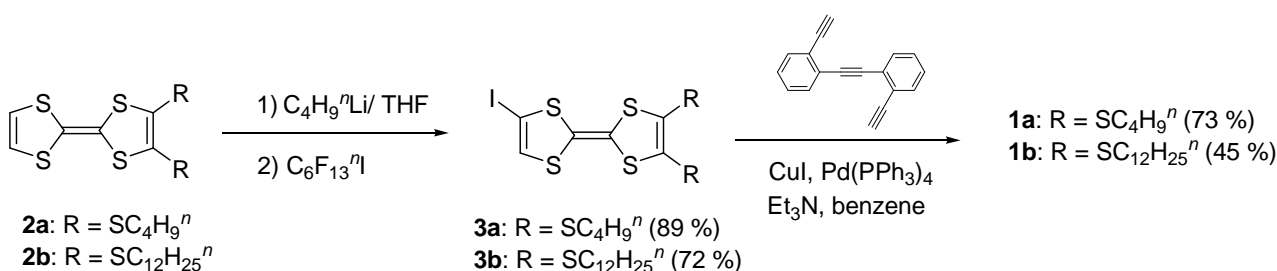


Figure 1. (a) Possible conformational change of **1**. (b) Molecular modeling of the *syn* form of **1c**.

RESULTS AND DISCUSSION

The synthetic route to **1a** and **1b** is depicted in Scheme 1. The treatment of the alkylthio-substituted TTF derivatives **2a** and **2b** with C₄H₉ⁿLi at -90 °C, followed by the addition of C₆F₁₃ⁿI gave 4-iodo-4',5'-bis(alkylthio)tetrathiafulvalenes **3a** and **3b** in good yields. The Sonogashira coupling reaction of **3a** and **3b** with bis(2-ethynylphenyl)ethyne afforded **1a** and **1b** in 73 % and 45 % yields, respectively.^{8,9} The dimeric TTFs **1a** and **1b** are air-stable red crystalline compounds. The chemical shift of the TTF protons of both **1a** and **1b** was similar to those of ethynyl TTF derivatives reported previously.^{4d,10} Since the VT-NMR experiments on **1a** and **1b** in CD₂Cl₂ did not show any spectral change until -90 °C, the predominant conformation of **1a** and **1b** would be the *anti* form in the neutral state (Figure 1).



Scheme 1. Synthetic route to **1a** (R = SC₄H₉ⁿ) and **1b** (R = SC₁₂H₂₅ⁿ)

As shown in Figure 2 and Table 1, the deconvoluted cyclic voltammogram of **1a** in CH₂Cl₂ revealed two one-electron oxidations at 0.03 and 0.05 V (vs. Fc/Fc⁺) and one two-electron oxidation at 0.38 V, corresponding to the formation of **1a**^{•+}, **1a**²⁺, and **1a**⁴⁺, respectively. Similarly, the deconvoluted cyclic voltammogram of **1b** showed sequential oxidation to produce **1b**^{•+}, **1b**²⁺, and **1b**⁴⁺. Since bis(tetrathiafulvalenyl)ethyne and 1,4-bis(tetrathiafulvalenyl)benzene showed only two redox potentials

corresponding to the formation of bis(cation–radical) and bis(dication), the observation of the cation radical $\mathbf{1}^{•+}$ suggests that a face-to-face stacking interaction at the terminal two TTF units produces a mixed-valence (MV) state.¹¹

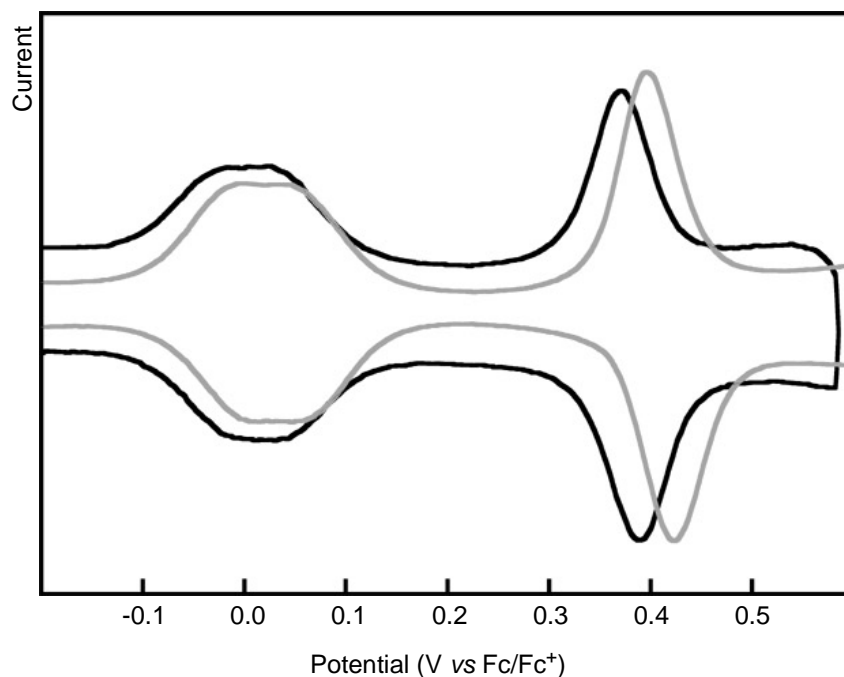


Figure 2. Deconvoluted cyclic voltammograms of **1a** (black line) and **1b** (gray line)

Table 1. Redox potentials of **1a** and **1b**^{a)}

Compd.	$E^1_{1/2}$	$E^2_{1/2}$	$E^3_{1/2}$
1a	0.03 (1 e ⁻)	0.05 (1 e ⁻)	0.38 (2 e ⁻)
1b	0.00 (1 e ⁻)	0.04 (1 e ⁻)	0.41 (2 e ⁻)

^{a)}Conditions: Bu₄ⁿNClO₄, CH₂Cl₂, Pt working electrode and counter-electrode. Potential was measured against a Ag/Ag⁺ electrode and converted to the value vs Fc/Fc⁺.

The dimeric TTFs **1a** and **1b** showed unique electrochromic properties depending on their oxidation state. The chemical oxidation of **1a** or **1b** with *n* equiv. of Fe(ClO₄)₃ in CH₂Cl₂–MeCN (v/v = 4:1) afforded the corresponding cationic species **1a**ⁿ⁺ and **1b**ⁿ⁺ (*n* = 1, 2, and 4), respectively. The solution color of **1a** upon oxidation changed markedly. Thus, the neutral **1a** was yellow, the cation radical **1a**^{•+} was orange, the dication **1a**²⁺ was green, and the tetracation **1a**⁴⁺ was blue. The oxidation of **1b** exhibited similar electrochromism.

The UV–vis–NIR data of the cation radicals, dications, and tetracations derived from **1a** and **1b** are summarized in Table 2. Both the electronic spectra of the cation radicals derived from **1a** and **1b** are very

similar. The electronic spectra of the cation radicals prepared from **1a** or **1b** with 1 equiv. of $\text{Fe}(\text{ClO}_4)_3$ revealed a very broad absorption in the NIR region ($\lambda_{\text{max}} = \text{ca. } 2000 \text{ nm}$) in addition to the absorption at 750 nm (Figure 3). On the basis of results of previous studies, the absorption is assigned to the CT absorption due to the MV state of stacked $(\text{TTF})_2^{+\cdot}$ units.^{6a} Since the spectra were measured under very dilute conditions (10^{-5} M), intermolecular contacts of the $\text{TTF}^{+\cdot}$ can be ruled out.¹² Thus, both **1a** and **1b** adopt a helical *syn* structure in the cation radical state. For the dications **1a**²⁺ and **1b**²⁺, the absorption in the NIR region disappeared and the electronic spectra showed a large split in the $\text{TTF}^{+\cdot}$ transition into blue-shifted absorption and shoulder CT absorption (Figure 3). The pronounced blue shift of the absorptions at 420 and 727 nm is Davydov's blue shift due to the formation of the π -dimer of $\text{TTF}^{+\cdot}$.^{11,13,14} Therefore, the dications **1a**²⁺ and **1b**²⁺ also adopt a helical *syn* structure.¹⁵ However, because of the strong electrostatic repulsion, the electronic spectra of **1a**⁴⁺ and **1b**⁴⁺ showed no stacked absorption.

Table 2. Absorption maxima of **1a**, **1b**, and their cation radicals^{a)}

	Conc. (M)	Color	Wavelength/ nm (ϵ)		
1a	8.2×10^{-5}	yellow	433 (9100)		
1a ⁺	2.7×10^{-5}	orange	436 (12300)	789 (9500)	ca. 2000 (4000)
1a ²⁺	2.4×10^{-5}	green	420 (24800)	727 (20500)	881sh ^{b)} (14500)
1a ⁴⁺	1.2×10^{-5}	blue	667 (35400)		

1b	8.0×10^{-5}	yellow	431 (9800)		
1b ⁺	9.6×10^{-5}	orange	435 (14100)	791 (10800)	ca. 2000 (3900)
1b ²⁺	7.3×10^{-5}	green	420 (27000)	727 (22900)	882sh ^{b)} (16100)
1b ⁴⁺	9.3×10^{-6}	blue	669 (40600)		

a) Measured in CH_2Cl_2 -MeCN (v/v = 4:1) solution at rt. b) sh: shoulder absorption.

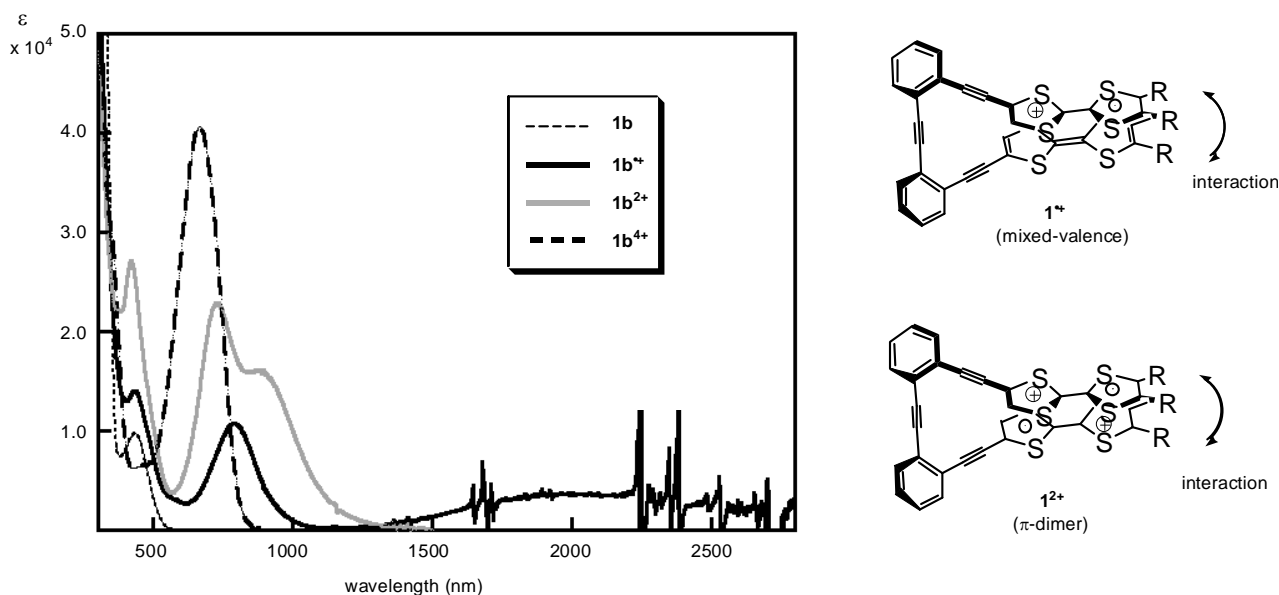


Figure 3. Electronic spectra of **1b** ($\text{R} = \text{S}^n\text{C}_{12}\text{H}_{25}$) and its cationic species **1b**⁺, **1b**²⁺, and **1b**⁴⁺.

In summary, we report here the synthesis of bis(2-tetrathiafulvalenylethynylphenyl)ethynes **1a** and **1b** by the Sonogashira coupling reaction and their electronic properties. The dimeric TTFs **1a** and **1b** showed marked electrochromism depending on the oxidation state, *i.e.*, yellow for **1**, orange for **1**⁺, green for **1**²⁺, and blue for **1**⁴⁺. The remarkable color change is due to the formation of helical structures in the cation–radical and dication states. Furthermore, the cation radicals **1a**^{•+} and **1b**^{•+} showed very wide and intense absorptions in the NIR–IR region, and hence may be a new class of NIR–IR photofilters controlled by redox potentials.

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8. Data for **1a**: red needles, mp 102.5-104 °C; LDI-MS m/z 982 (M^+); 1H NMR (600 MHz, $CDCl_3$) δ 7.65 (dd, $J = 7.6$ and 1.1 Hz, 2H), 7.49 (d, $J = 7.6$ Hz, 2H), 7.36 (td, $J = 7.7$ Hz and 1.2 Hz, 2H), 7.32 (td, $J = 7.7$ and 1.2 Hz, 2H), 6.55 (s, 2H), 2.83-2.80 (m, 8H), 1.65-1.61 (m, 8H), 1.48-1.41 (m, 8H), 0.94-0.92 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.3 (2C, CH), 131.6 (2C, CH), 128.7 (2C), 128.3 (2C, CH), 127.9 (2C), 127.6 (2C), 125.6 (2C), 124.8 (2C), 123.5 (2C), 115.9 (2C), 112.0 (2C), 109.1 (2C), 92.5 (2C, $C\equiv C$), 92.1 (2C, $C\equiv C$), 84.6 (2C, $C\equiv C$), 35.99 (2C, CH_2), 35.96 (2C, CH_2), 31.73 (2C, CH_2), 31.71 (2C, CH_2), 21.63 (2C, CH_2), 21.61 (2C, CH_2), 13.6 (4C, CH_3).
9. Data for **1b**: red fine crystals, mp 85-86.5 °C; LDI-MS m/z 1430 (M^+); 1H NMR (600 MHz, $CDCl_3$) δ 7.65 (dd, $J = 7.7$ and 1.2 Hz, 2H), 7.49 (dd, $J = 7.7$ and 1.2 Hz, 2H), 7.37 (td, $J = 7.7$ and 1.2 Hz, 2H), 7.32 (td, $J = 7.7$ and 1.2 Hz, 2H), 6.57 (s, 2H), 2.83-2.80 (m, 8H), 1.65-1.61 (m, 8H), 1.43-1.38 (m, 8H), 1.32-1.22 (m, 64 H), 0.89-0.86 (m, 12 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 132.38 (2C, CH), 131.71 (2C, CH), 128.73 (2C), 128.34 (2C, CH), 128.01 (2C), 127.76 (2C), 125.70 (2C), 124.81 (2C, CH), 124.55 (2C), 116.03 (2C), 112.57 (2C), 109.21 (2C), 92.54 (2C, $C\equiv C$), 92.19 (2C, $C\equiv C$), 84.63 (2C, $C\equiv C$), 36.40 (2C, CH_2), 36.37 (2C, CH_2), 31.95 (4C, CH_2), 29.79 (2C, CH_2), 29.78 (2C, CH_2), 29.70 (4C, CH_2), 29.68 (4C, CH_2), 39.64 (4C, CH_2), 29.57(2C, CH_2), 29.56 (2C, CH_2), 29.38 (4C, CH_2), 29.18 (2C, CH_2), 29.16 (2C, CH_2), 28.59 (2C, CH_2), 28.57 (2C, CH_2), 22.71 (4C, CH_2), 14.13 (4C, CH_3).
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15. The intensity of the ESR signals of **1a**²⁺ in CH_2Cl_2 -MeCN solution decreased at low temperatures. The solution at -70 °C contains only 10 % unpaired spin compared with the solution at 20 °C.