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Synthesis and Photophysical Properties of 1,3-Di(oligothienyl)propane

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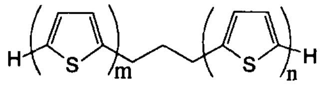
Abstract: Three kinds of 1,3-di(oligothienyl)propanes were synthesized. Two of them are homogeneous dimers composed of bithienyls or terthienyls and the third, a heterogeneous dimer in which bithienyl and terthienyl units are linked. It has been found that in the homogeneous dimers there is little electronic interaction between two oligothienyl units both in the ground and the singlet excited states. On the other hand, it has become clear that in the heterogeneous dimer an effective energy transfer from the bithienyl to the terthienyl unit takes place. © 1997 Elsevier Science Ltd.

In the last decade, various oligothiophenes have been widely studied as the model compounds for polythiophene, one of typical conjugated polymer[1-4]. Most of these studies were carried out in highly dilute solution in order to suppress any intermolecular interaction. However, in conjugated polymers intermolecular processes are important in such phenomena as charge transport and relaxation of the photo-excited state which are much affected by their higher-order structure. These processes should involve a combination of the intra- and intermolecular electron transfer and the electronic excitation transfer processes. By linking two oligothiophenes it will become possible to observe the intermolecular process between them. The dimer composed of two oligothiophenes has already been synthesized by Diaz et al[5]. However, in these molecules two oligothienyl components are fused orthogonally based on Aviram's hypothetical structure[6], between which there is little electronic interaction. Moreover, the heterogeneous dimer composed of two oligothienyls of different conjugation lengths has not yet been synthesized.

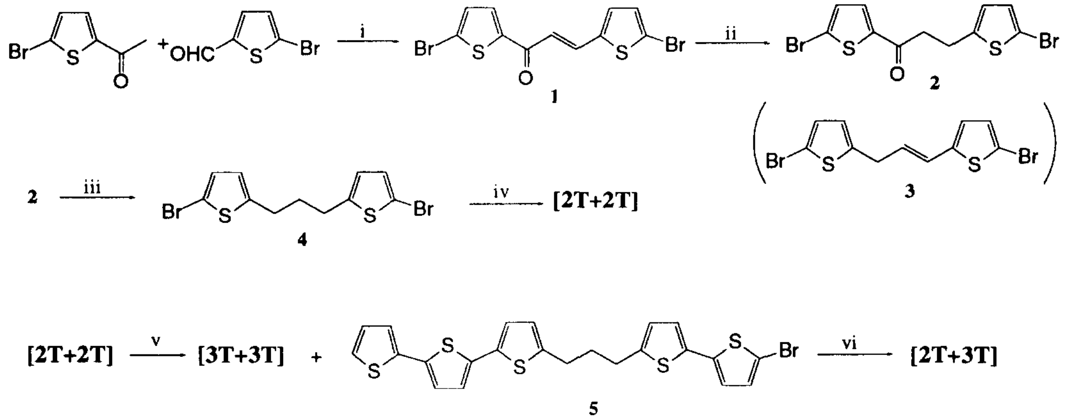
In this letter, we report the first synthesis of three kinds of novel oligothiophene dimers. Two of them are homogeneous dimers composed of bithienyls (**[2T+2T]**) or terthienyls (**[3T+3T]**) and the third, a heterogeneous dimer in which bithienyl and terthienyl units are linked (**[2T+3T]**). Intramolecular bichromophoric compounds, in particular, compounds in which two aromatic chromophores are connected by trimethylene, have been used to study the formation of the intramolecular excimer[7] and dimer radical cation[8]. These oligothiophene dimers can possibly have a stacked conformation so that the overlap of the π-orbitals of the two chromophores may be maximized. The photophysical properties of these dimers will also be reported.



m=n=2 **[2T+2T]**
m=2, n=3 **[2T+3T]**
m=n=3 **[3T+3T]**

Oligothiophene dimers were synthesized following Scheme I. In order to avoid the problem of solubility, 1,3-di(5-bromo-2-thienyl)propane **4** was synthesized and followed by the stepwise addition of the thiophene rings by a Grignard coupling reaction[9]. In this synthesis, hydrogenation of chalcone-like compound **1** using Pd-C was unsuccessful, presumably because of catalytic poisoning by thiophene[10]. Hence 1,3-di(5-bromo-2-thienyl)propane **4** was prepared by reduction of **1** with $LiAlH_4/AlCl_3$. The details of the procedure are described

Scheme I



Reagents and conditions: i) NaOH, ethanol ii) $LiAlH_4/AlCl_3$, THF iii) $LiAlH_4/AlCl_3$, ether iv) Thienyl magnesium bromide, $[NiCl_2(dppp)]$, ether v) NBS, $CH_3COOH/CHCl_3=1/1$; Thienyl magnesium bromide, $[NiCl_2(dppp)]$, ether vi) *n*-BuLi, ether; H_2O

below.

2-Bromo-5-acetylthiophene (4.8 g, 24 mmol) and 2-bromo-5-thiophenecarboxyaldehyde (4.9 g, 25.4 mmol) were stirred for 3 hours in 110 mL of a 1:1 mixture of ethanol and 1 N NaOH aqueous solution. Yellow precipitates appeared immediately. After stirring, an excess amount of water was added to the reaction mixture and then filtrated. 7.06 g of **1** was obtained as needle-like crystals by recrystallization from hot ethanol (Yield : 79.2 %)[11].

1 was reduced using $LiAlH_4/AlCl_3$ in dry THF: Under N_2 atmosphere, 0.70 g of $LiAlH_4$ was suspended in 50 mL of dry THF. 45 mL of dry THF solution of anhydrous $AlCl_3$ (2.5 g) was added to the suspension. **1** (7.0 g, 18.5 mmol) was dissolved in 70 mL of dry THF and added to the suspension dropwise at room temperature. After stirring for 1 hour, THF saturated by water was added until excessive $LiAlH_4/AlCl_3$ turned into gray coagulates. After filtration, ether was added to the filtrate and then the crude product was extracted from water. The yellow oil obtained was applied to column chromatography on SiO_2 using *n*-hexane/ethyl acetate = 9/1 as eluent. 2.7 g of **2**[11] was obtained as a light-yellow oil (Yield: 38.4 %). In this step, **3**[11] was obtained as a major byproduct (Yield: 20.5 %).

2 was reduced by $LiAlH_4/AlCl_3$ following the same procedure as for the reduction of **1**. In this step, dry ether was used as solvent instead of dry THF. Purification by column chromatography on SiO_2 (eluent : *n*-hexane/ethyl acetate = 9/1), afforded **4**[11] (Yield : 63.0 %).

Two thiophene molecules were further added to each thiophene bromide unit of **4** by a Grignard coupling reaction. 15 mmol of thienyl magnesium bromide in 5 mL of dry ether was added to 20 mL of an ether solution containing 1.8 g of **4** (4.5 mmol) and 0.11 g of $[NiCl_2(dppp)]$ under reflux. The mixture was stirred under reflux for 24 hours. After hydrolysis the product was extracted with ether. The crude product obtained was applied to column chromatography on SiO_2 (eluent : *n*-hexane/ethyl acetate = 9/1) followed by MPLC on SiO_2 (eluent : *n*-hexane/ethyl acetate = 50/1) giving 1.24 g of **[2T+2T]**[12] (Yield : 74.5 %).

Bromination of the α positions of **[2T+2T]** using *N*-bromosuccinimide(NBS) in a 1:1 mixture of chloroform and acetic acid[13] afforded the brominated product quantitatively. The product was applied to the Grignard coupling with the same procedure as that for **[2T+2T]**. In this case, an ether solution of thienyl magnesium bromide was added at room temperature. Purification by column chromatography on SiO_2 followed by MPLC on SiO_2 afforded **[3T+3T]**[12] (Yield: 7.1 %) and **5** (Yield : 16.3 %).

0.047g of **5** was suspended in 25 mL of dry ether, lithiated at room temperature with 0.05 mL of *n*-butyl lithium solution (1.6 N in *n*-hexane), and then hydrolyzed. Purification by column chromatography on SiO_2 (eluent : *n*-hexane/toluene = 8/2) afforded **[2T+3T]**[12] in 75.4 % yield.

Table 1. Absorption and fluorescence data of oligothiophenes and oligothiophene dimers

	2T	**[2T+2T]**	**3T**	**[3T+3T]**	**[2T+3T]**
Absorption					
λ_{max} / nm	302	311	351	363	324, 339, 357
ε_{max} / 10^4L mol^{-1}cm^{-1}	1.26	2.53	2.38	—[b]	1.92, 2.03, 2.08
Fluorescence					
λ_{max} / nm	376	375	429	437	437
Q. Y.[a]	0.013	0.021	0.059	0.071	0.064

[a]Quantum yields were determined using quinine sulfate in 1N H_2SO_4*aq*. as a standard. [b]Unestimated because of extremely low solubility for acetonitrile.

The absorption and fluorescence spectra of the oligothiophene dimers were observed and compared with the corresponding unsubstituted oligothiophenes, bithiophene (**2T**) and terthiophene (**3T**). All the data were obtained at 20 °C in dilute acetonitrile solution(10^{-5} – 10^{-6} M). The absorption band maxima (λ_{max}) are listed in Table 1. In the homogeneous dimers, **[2T+2T]** and **[3T+3T]**, the band maxima shifted to longer wavelength in comparison with those of **2T** and **3T**, respectively. These shifts are due to alkyl substitution on the α position of the thiophene ring[4]. The molar extinction coefficient of **[2T+2T]** was almost twice as large as that of **2T**. Changes in the absorption band such as broadening and appearance of additional absorption bands due to stacked conformation were not observed. Hence, it can be concluded the electronic interaction between two oligothienyl units was negligible in the ground state. In the heterogeneous dimer, **[2T+3T]**, a broad absorption band consisting of three peaks was observed; the shape of this band bears a close resemblance to that of the summation of the spectra of **2T** and **3T** as seen from Fig. 1. Slight disagreement between them could be ascribed to the difference in the effect of alkyl-substitution on **2T** and **3T**. However, it is also pointed out that the interaction between these two oligothienyl units is negligible and that these units independently absorb the light.

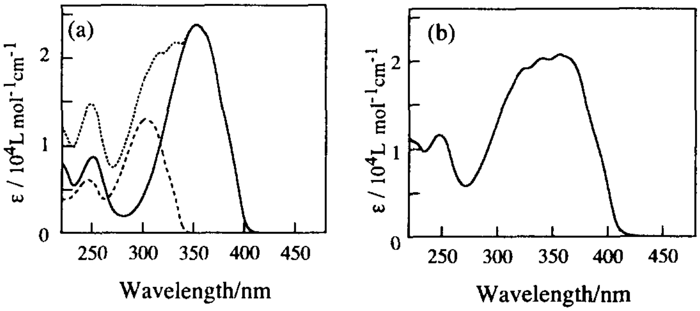


Fig. 1 Absorption spectra of (a) **2T** (solid line), **3T** (broken line), their summation (dotted line), and (b) **[2T+3T]**.

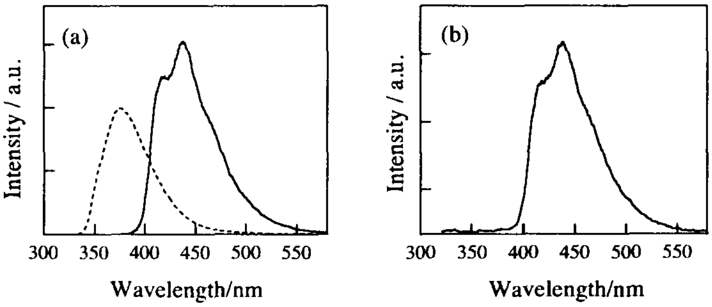


Fig. 2 Fluorescence spectra of (a) **[2T+2T]** (broken line), **[3T+3T]** (solid line), and (b) **[2T+3T]**. The excitation wavelength was 300 nm.

In the fluorescence spectra of **[2T+2T]** and **[3T+3T]**, the emission derived from the excimer state was unobservable under the present condition. Moreover, the quantum yields did not decrease compared with those of **2T** and **3T**, confirming that there was no additional nonradiative transition due to the stacked conformation. In these homogeneous dimers, the electronic interaction between two oligothienyl units was, thus, also negligible in the singlet excited state.

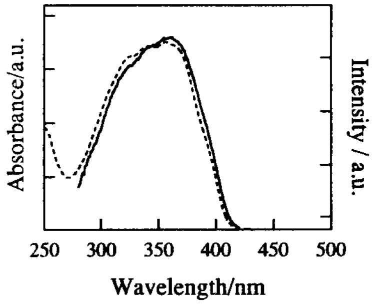


Fig. 3 Fluorescence excitation spectrum (solid line) monitored at 430 nm, and absorption spectrum (broken line) of **[2T+3T]**.

In **[2T+3T]**, on the other hand, only the emission from the terthienyl unit was observed as shown in Fig. 2. It was found that ca. 80 % of light was absorbed by the bithienyl unit when pumped at 300 nm, while the terthienyl unit was selectively pumped at 365 nm. The same spectra were observed by pumping at these different wavelengths and their quantum yields were identical. The fluorescence excitation spectrum monitored at 430 nm was superimposable on its absorption spectrum (Fig. 3) and showed that the excitation of the bithienyl unit contributed to the emission of the terthienyl unit. This result strongly suggests that the electronic excitation energy in the bithienyl unit was completely transferred to the terthienyl unit. Although the details of this excitation transfer are currently not known, the emission from bithiophene was also observed in the equivalent mixture of bithiophene and terthiophene. Based on these results, it can be concluded that intramolecular energy transfer takes place in **[2T+3T]** and that the electronic excitation state of the bithienyl unit transfers to the terthienyl unit within the lifetime of the singlet excited state of bithiophene (46 ps)[14]. These findings also imply that in a conjugated polymer film the electronic excitation transfer effectively occurs between two segments with different effective conjugation lengths.

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11. ^{1}H-NMR (400 MHz, $CDCl_3$) **1**: δ 6.99 (1H, d, J = 15 Hz), 7.06 (1H, d, J = 3-4 Hz), 7.11 (1H, d, J = 3-4 Hz), 7.15 (1H, d, J = 3-4 Hz), 7.55 (1H, d, J = 3-4 Hz), 7.81 (1H, d, J = 15 Hz). **2**: δ 3.16 (4H, s), 6.59 (1H, d, J = 3-4 Hz), 6.83 (1H, d, J = 3-4 Hz), 7.08 (1H, d, J = 3-4 Hz), 7.42 (1H, d, J = 3-4 Hz). **3**: δ 3.57 (2H, d, J = 7 Hz), 6.03 (1H, td, J = 7, 16 Hz), 6.47 (1H, d, J = 16 Hz), 6.58 (1H, d, J = 3-4 Hz), 6.64 (1H, d, J = 3-4 Hz), 6.87 (1H, d, J = 3-4 Hz), 6.88 (1H, d, J = 3-4 Hz). **4**: δ 1.94 (2H, m, J = 7-8 Hz), 2.77 (4H, t, J = 7-8 Hz), 6.52 (2H, d, J = 3-4 Hz), 6.83 (2H, d, J = 3-4 Hz).
12. ^{1}H-NMR (400 MHz, $CDCl_3$) **[2T+2T]**: δ 2.04 (2H, m, J = 7-8 Hz), 2.84 (4H, t, J = 7-8 Hz), 6.67 (2H, d, J = 3-4 Hz), 6.96 (2H, dd, J = 3-4, 5 Hz), 6.97 (2H, d, J = 3-4 Hz), 7.08 (2H, dd, J = 3-4, 1 Hz), 7.13 (2H, dd, J = 5, 1 Hz). EIMS: m/z; 372(M^+). Anal. Calcd. for $C_{19}H_{16}S_4$: C, 61.25; H, 4.33; S, 34.42. Found: C, 61.26; H, 4.17; S, 34.41. **[3T+3T]**: δ 2.08 (2H, m, J = 7-8 Hz), 2.89 (4H, t, J = 7-8 Hz), 6.72 (2H, d, J = 3-4 Hz), 6.99-7.02 (6H, m), 7.06 (2H, d, J = 3-4 Hz), 7.16 (2H, dd, J = 3-4, 1 Hz), 7.20 (2H, dd, J = 5, 1 Hz). EIMS: m/z; 536 (M^+). **[2T+3T]**: δ 2.08 (2H, m, J = 7-8 Hz), 2.88 (4H, t, J = 6-7 Hz), 6.72 (2H, d, J = 3-4 Hz), 6.96-7.02 (5H, m), 7.06 (1H, d, J = 3-4 Hz), 7.11 (1H, d, J = 3-4 Hz), 7.16 (1H, d, J = 3-4 Hz), 7.17 (1H, dd, J = 1,5 Hz), 7.20 (1H, dd, J = 1,5 Hz). EIMS: m/z; 454 (M^+).
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