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Studies on synthesis of 5,5'-distyryl-2,2'-bithiophene derivatives and their optical and electrochemical properties

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π-Conjugated bithiophene derivatives are expected to show remarkable optical and electrochemical properties owing to the characteristic electronic state. Recently, we reported that Pd-catalyzed C–H homocoupling of thiophene derivatives smoothly occurred in the presence of $AgNO_3$ and KF, and the corresponding bithiophene derivatives were obtained in high yields. In this study, the π-conjugated bithiophene derivatives having aryl groups symmetrically through carbon–carbon double bonds were synthesized by the C–H homocoupling reaction and Wittig reaction. In order to clarify the influence of terminal functional groups to physical properties, energy gaps were estimated from the onset of absorption in the UV-vis spectrum and quantum yields of fluorescence were calculated on the basis of fluorescence spectra. Furthermore, standard oxidation potentials were determined by cyclic voltammetry and the electron properties were calculated by density functional theory method.

Key words: bitiophene, homocoupling, energy gap, standard oxidation potential, fluorescence

1. INTRODUCTION

Oligothiophenes consist of covalently-bonded thiophene rings and have remarkable optical and electrochemical properties owing to the characteristic π-conjugated system. Therefore, they are expected to be utilized as organic semiconductors for thin film field effect transistors (FETs),[1] electroluminescence device (EL),[2] photoelectrical conversion element.[3] and so on. Among oligothiophene, we focus on bithiophene skeleton, one of oligothiophenes, and attempt to construct the novel π-conjugated system that two aryl groups bond with the bithiophene unit symmetrically through unsaturated bonds.

Bithiophene derivatives can be synthesized from the corresponding thiophenes. Kirsch et al. reported that thienyl bromides reacted with thienylstannanes to form asymmetric bithiophene derivatives by Stille coupling reaction.[4] Vollmer and his co-workers also synthesized asymmetric bithiophene derivatives by Suzuki coupling reaction using thienyl bromides and organoboron derivatives.[5] On the other hand, Tian et al. reported that symmetric bithiophene derivatives were obtained by homocoupling reaction of thienyl bromides in the presence of $NiCl_2$, Zn, and PPh_3.[6] However, these methods were required to prepare halogenated thiophenes as the starting materials and halogenation of thiophene derivative was difficult depending on its functional group. Therefore, the total yields of bithiophene derivatives from the corresponding thiophenes were not necessarily high.

In our previous paper, we reported that Pd-catalyzed C–H homocoupling reaction occurred smoothly in the presence of AgF, and bithiophene derivatives with various functional groups were synthesized in high yields[7]. Using the obtained bithiophenes as the starting materials, the novel π-conjugated system as shown in Figure 1 could be constructed easily.

In this study, we synthesized the novel bithiophene derivatives **1** that π-conjugated system of the bithiophene skeleton was extended by the substituted styryl groups. The substituent (X) was the electron donating group (EDG: -^{t}Bu, -CH_3), the electron withdrawing group (EWG: -$COOCH_3$), or H. The two hexyl groups were introduced to improve the solubility of the materials in organic solvents.

In order to clarify the influence of terminal functional groups to the physical properties, energy gaps were estimated from the onset of absorption in the UV-vis spectrum and quantum yields of fluorescence were calculated on the basis of fluorescence spectra. Furthermore, standard oxidation potentials were determined by cyclic voltammetry and the electron properties were calculated by density functional theory method.

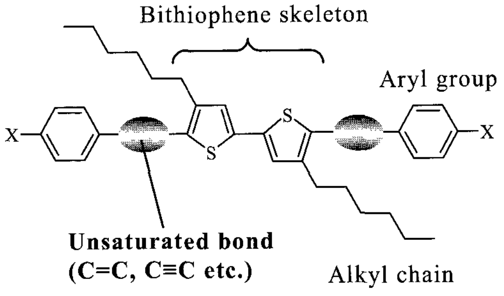
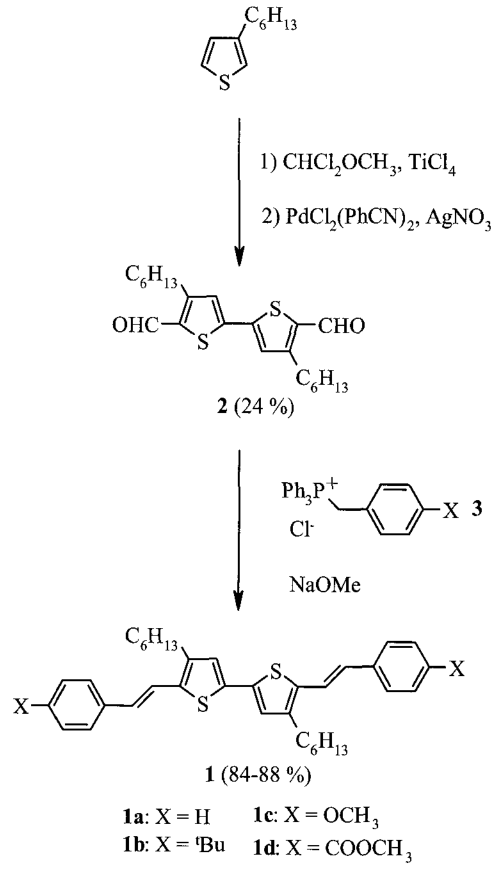


Figure 1 Chemical structure of bithiophene derivatives.

2. EXPERIMENTAL

2.1 The distyrylbithiophene derivatives **1** were synthesized by the combination of the homocoupling reaction and Wittig reaction (Scheme 1).



Scheme 1 Synthetic route of distyrylbithiophene derivatives **1**.

All the reagents were used without further purification.

Infrared absorption measurements were carried out with JASCO FT/IR-620 and ^1H NMR spectra were measured using JEOL AL-400.

2.2 Preparation of 4,4'-dihexyl-5,5'-diformyl-2,2'-bithiophene **2**

A solution of 3-hexylthiophene (15.3 g, 90.7 mmol) and $CHCl_2OCH_3$ (10.5 g, 90.7 mmol) in CH_2Cl_2 (75 ml) was stirred and cooled to −12 °C. After cooling, a solution of $TiCl_4$ (34.4 g, 181 mmol) in CH_2Cl_2 (75 ml) was added to the solution and stirred at −12 °C for 2 h. The reaction mixture was quenched with H_2O and washed with 100 ml of 10 wt% K_2CO_3, 100 ml of H_2O and 100 ml of brine. After dried over Na_2SO_4, the solvent was removed and the obtained crude product was dissolved in DMSO (150 ml) without purification. Subsequently, KF (10.4 g, 181 mmol), $PdCl_2(PhCN)_2$ (0.70 g, 1.80 mmol) and $AgNO_3$ (30.1 g, 181 mmol) were added to the solution and stirred at 60 °C for 24 h. The reaction mixture was diluted with 200 ml of CH_2Cl_2 and filtrated. The filtrate was washed with 300 ml of H_2O and 200 ml of brine. After dried over Na_2SO_4, the residue was purified by a silica gel column chromatography (eluent: CH_2Cl_2) and recrystallized from the mixed solvent of CH_2Cl_2 and hexane (1/1, v/v) to give a yellow solid **2** (4.32 g, 24 %). ^1H NMR (400 MHz, $CDCl_3$): δ 10.0 (s, 2 H, CHO), 7.20 (s, 2 H, thiophene), 2.94 (t, 4 H, CH_2), 1.72-1.60 (m, 4 H, CH_2), 1.40-1.30 (m, 12 H, CH_2), 0.88 (t, 6 H, CH_3). IR (KBr): 3273, 2956, 2925, 2855, 1647, 1437, 1206, 830, 659 cm^{-1}.

2.3 Preparation of 4,4-dihexyl-5,5'-distyryl-2,2'-bithiophene **1a**.

NaOMe (234 mg, 4.40 mmol) was added to a solution of benzylphosphonium chloride **3a** (858 mg, 2.20 mmol) in MeOH (50 ml). After stirred at room temperature for 15 min, diformylbithiophene **2** (195 mg, 0.499 mmol) was added to the mixture and refluxed for 24 h. Subsequently, the reaction mixture was cooled to room temperature and filtrated. After washed with MeOH several times, the residue was purified by a silica gel column chromatography (eluent: CH_2Cl_2) and recrystallized from the mixed solvent of CH_2Cl_2 and MeOH (1/1, v/v) to give a orange solid **1a** (230 mg, 85 %). ^1H NMR (400 MHz, $CDCl_3$): δ 7.46 (d, 4 H, Ph, J=7.6 Hz), 7.35 (t, 4 H, Ph, J=7.6 Hz), 7.24 (t, 2 H, Ph, J=7.6 Hz) 7.20 (d, 2 H, olefin, J=16 Hz), 6.95 (s, 2 H, thiophene), 6.86 (d, 2 H, olefin, J=16 Hz), 2.66 (t, 4 H, CH_2), 1.63-1.59 (m, 4 H, CH_2), 1.41-1.30 (m, 12 H, CH_2), 0.90 (t, 6 H, CH_3). IR (KBr): 3026, 2926, 2857, 1597, 1516, 1187, 951, 820, 745, 687, 519 cm^{-1}.

The other distyrylbithiophene derivatives **1b**, **1c**, and **1d** were also synthesized in a manner similar to **1a**. The reaction yields of the bithiophene derivatives were 87 %, 88 %, and 84 %, respectively. The ^1H NMR and IR data are described below.

Distyrylbithiophene **1b**
^1H NMR (400 MHz, $CDCl_3$): δ 7.39 (q, 8 H, J=6.4 Hz), 7.16 (d, 2 H, olefin, J=16 Hz), 6.93 (s, 2 H, thiophene), 6.85 (d, 2 H, olefin, J=16 Hz), 2.65 (t, 4 H, CH_2), 1.64-1.59 (m, 4 H, CH_2), 1.40-1.30 (m, 30 H, CH_2 and ᵗBu), 0.90 (t, 6 H, CH_3). IR (KBr): 3024, 2959, 2926, 2855, 1615, 1524, 1524, 1461, 1362, 1270, 1108, 938, 812, 557 cm^{-1}.

Distyrylbithiophene **1c**
^1H NMR (400 MHz, $CDCl_3$): δ 7.40 (d, 4 H, J=8.4 Hz), 7.06 (d, 2 H, olefin, J=16 Hz), 6.92 (s, 2 H, thiophene), 6.90 (d, 4 H, J=8.4 Hz), 6.81 (d, 2 H, olefin, J=16 Hz), 3.83 (t, 6 H, OCH_3), 2.64 (t, 4 H, CH_2), 1.65-1.58 (m, 4 H, CH_2), 1.40-1.30 (m, 12 H, CH_2), 0.90 (t, 6 H, CH_3). IR (KBr): 2925, 1604, 1507, 1246, 1173, 1032, 934, 810, 529 cm^{-1}.

Distyrylbithiophene **1d**
^1H NMR (400 MHz, $CDCl_3$): δ 8.00 (d, 4 H, J=8.0 Hz), 7.52 (d, 4 H, J=8.0 Hz), 7.27 (d, 2 H, olefin, J=16 Hz), 6.98 (s, 2 H, thiophene), 6.86 (d, 2 H, olefin, J=16 Hz), 3.93 (s, 6 H, $COOCH_3$), 2.68 (t, 4 H, CH_2), 1.66-1.59 (m, 4 H, CH_2), 1.42-1.27 (m, 12 H, CH_2), 0.89 (t, 6 H, CH_3). IR (KBr): 2927, 1715, 1598, 1435, 1281, 1177, 1108, 764 cm^{-1}.

2.4 Measurements of optical and electrochemical properties of bithiophene derivatives 1

UV-vis absorption spectra were measured with Shimadzu MultiSpec-1500 spectrophotometer. Fluorescence measurement was performed with HITACHI F-2500 spectrophotometer. Cyclic voltammetry was carried out using a potentiostat (HOKUTO DENKO HA-1510) and a function generator (HOKUTO DENKO HB-105).

2.5 Quantum chemical calculation of bithiophene derivatives 1

Ground-state geometry optimization and electron properties were computed by density functional theory method using PC GAMESS program[8]. All calculations were performed using the B3LYP hybrid functional[9] and 6-31G(d) basis set[10]. Figure 2 shows the HOMO and LUMO of the bithiophene derivative **1a**.

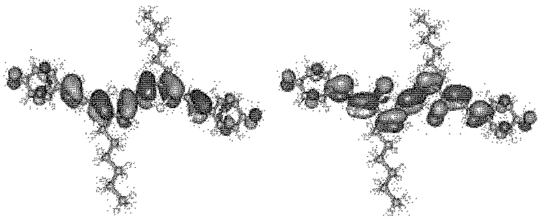


Figure 2 HOMO (left) and LUMO (right) of bithiophene derivative **1a**.

3. RESULT AND DISCUSSION

3.1 Optical properties of bithiophene derivatives 1

Figure 3 shows the UV-vis absorption spectra of the bithiophene derivatives **1** in $CHCl_3$ solutions. Since the conjugation lengths of the terminal-subsutituted bithiophene derivatives **1b-d** were longer than that of the non-substituted bithiophene derivative **1a**, the absorption bands and the absorption maxima (λ_{abs}) in the UV-vis spectra slightly red-shifted. λ_{abs} of the substituted bithiophene derivatives **1b** and **1c** had a little red-shift of 3 nm and 6 nm compared to that of non-substituted bithiophene **1a**, respectively. Since the π-conjugated system of **1d** was extended by the two ester carbonyl groups, the shift (18 nm) became larger than that of **1b** and **1c**.

The energy gaps (E_g) corresponding to π–π* transition were estimated from the onset of absorption in the UV-vis spectrum, and the energy gaps (calcd E_g) were obtained using the B3LYP/ 6-31G(d). The results are summarized in Table 1. In each case, the difference between E_g and calcd E_g. was estimated about 0.2 eV .

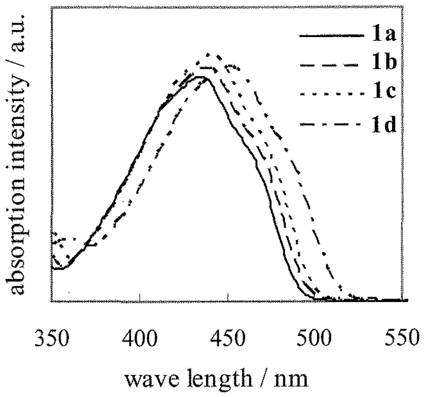


Figure 3 UV-vis absorption spectra of bithiophene derivatives **1**.

The fluorescence spectra of the bithiophene derivatives **1** in $CHCl_3$ are shown in Figure 4. According to formula (1), the fluorescence quantum yields (Φ_F) of the bithiophene derivatives **1** at room temperature were determined using 1 N H_2SO_4 solution of quinine sulfate as a standard substance (std). In order to correct the error induced by the difference of refractive index between the standard solution and the bithiophene solution, the term of $(n/n_{std})^2$ was introduced.

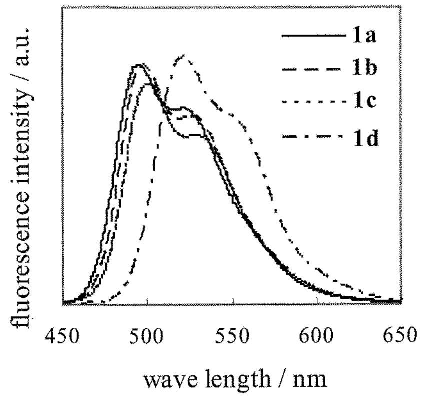


Figure 4 Fluorescence spectra of bithiophene derivatives **1**.

$$\Phi_F = \Phi_{std} \times (I / I_{std}) \times (A_{std} / A) \times (n / n_{std})^2 \quad (1)$$

Absorbance: A
Peak area of fluorescence spectra: I
Refractive index of solvent: n

Table 1 Optical and electrochemical properties of the bithiophene derivatives **1**

Bithiophene 1	λ_{abs} /nm	λ_{em} /nm	Φ_F[a] /-	E_g[b] /eV	calcd E_g[c] /eV	$E_{1/2}$ vs SCE /V	HOMO[c] /eV	LUMO[c] /eV
1a	434	495	0.053	2.48	2.66	0.78	−4.69	−2.02
1b	437	498	0.060	2.46	2.65	0.75	−4.60	−1.95
1c	440	501	0.056	2.44	2.62	0.71	−4.46	−1.84
1d	452	523	0.060	2.38	2.54	0.85	−4.95	−2.41

a Determined by comparison of quinine sulfate (Φ=0.546).
b Estimated from the onset of absorption in the UV-vis spectrum.
c Calculated by B3LYP/6-31G(d).

As shown in Table 1, the Φ_F of the bithiophene derivatives **1** were 0.053-0.060. These results indicate that the optical properties of the bithiophene derivatives **1** depend on their conjugation lengths irrespective of the terminal substituents.

3.2 Electrochemical properties of bithiophene derivatives 1

The standard oxidation potentials ($E_{1/2}$) of the bithiophene derivatives **1** were measured with a three-electrode system using a glassy carbon working electrode, a platinum wire counter electrode and a SCE reference electrode in CH_2Cl_2 containing 0.1 M tetrabutylammonium hexafluorophosphate (n-Bu_4NPF_6) as a supporting electrolyte at scan rate of 50 mV/s under N_2.

The cyclic voltammograms are shown in Figure 5 and the standard oxidation potentials ($E_{1/2}$) of bitihophene derivatives **1** are described in Table 1.

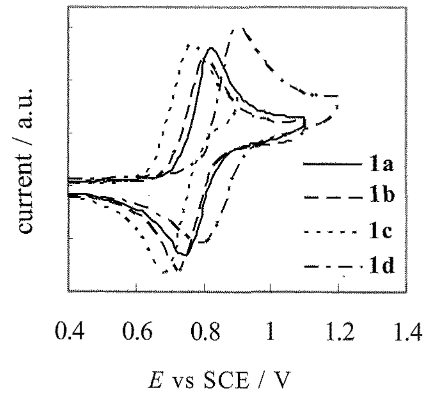


Figure 5 Cyclic voltammograms of bithiophene derivatives **1** in 0.1 M n-Bu_4NPF_6 $CHCl_3$ solution under N_2.

The HOMO levels of the bithiophene derivatives **1** were calculated by B3LYP/6-31G(d). As shown in Table 1, the HOMO levels of the EDG-substituted bithiophene derivatives **1b** and **1c** shifted to higher energy in comparison with that of the non-substituted bithiophene derivative **1a**. On the other hand, the HOMO levels of the EWG-substituted bithiophene derivative **1d** shifted to lower energy.

Figure 6 shows the graph relating calculated HOMO levels of bithiophene derivatives **1** to the $E_{1/2}$ values. Since the $E_{1/2}$ value corresponds to the energy necessary to remove one electron from HOMO level, the $E_{1/2}$ values correlated strongly with the calculated HOMO levels and R^2 value was 0.997. These results suggest that the HOMO levels of the bithiophene derivatives **1** can be controlled by the terminal substituents. When EDG-substituents are introduced into the conjugated system, the $E_{1/2}$ value shifts to lower energy. On the other hand, in the cases of EWG-substituents, the $E_{1/2}$ value shifts to higher energy.

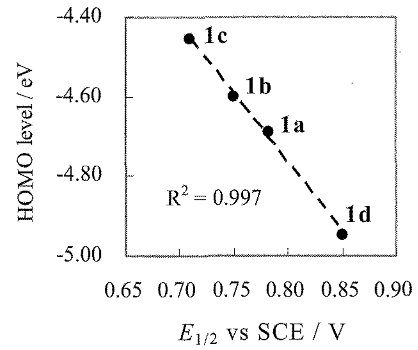


Figure 6 Graph relating HOMO levels of bithiophene derivatives to $E_{1/2}$ **1a**:X=H, **1b**:X=^{t}Bu (EDG), **1c**:X=OCH_3 (EDG), and **1d**:X=$COOCH_3$ (EWG).

4. CONCLUSION

The π-conjugated bithiophene derivatives **1** having aryl groups symmetrically through carbon–carbon double bonds were synthesized by the Pd-catalyzed C–H homocoupling reaction and Wittig reaction, and their optical and electrochemical properties were evaluated.

All of the absorption bands in the UV-vis spectra slightly red-shifted regardless of the terminal substituents (X). Furthermore, there was a little difference in the fluorescence quantum yields (Φ_F) irrespective of the terminal substituents. These results indicate that the optical properties of the bithiophene derivatives **1** depended on their conjugation lengths irrespective of the terminal substituents. On the other hand, since the HOMO levels of the bithiophene derivative **1** correlated strongly with terminal substituents, it is suggested that the electrochemical properties of the bithiophene derivatives **1** can be controlled by changing the terminal functional groups.

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