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Syntheses and Properties of Donor–Acceptor-Type 2,5-Diarylthiophene and 2,5-Diarylthiazole

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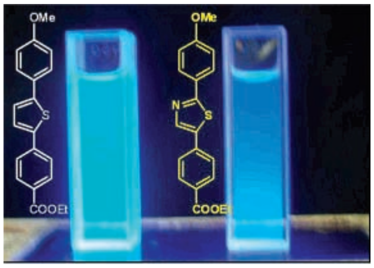
ABSTRACT



Syntheses of differently substituted 2,5-diarylthiophenes and 2,5-diarylthiazoles are carried out with the palladium-catalyzed C–H substitution reaction using AgF as an activator. Remarkably strong photoluminescence is observed in 2,5-diarylthiophene. Differences between the physical properties of liquid crystalline characteristics and cyclic voltammograms of thiophene and thiazole are also studied.

Five-membered heteroaromatics bearing substituents at the 2- and 5-positions have attracted much attention as light-emitting and liquid crystalline materials.[1] These compounds are potentially applied for single-layer electroluminescent devices involving hole-transporting, light-emitting, and electron-transporting characteristics in the same molecule. In particular, unsymmetrical donor−acceptor-type 2,5-diarylated thiophenes that possess both electron-donating and -withdrawing groups are of much interest.[2] However, little has been studied on the characteristics of these molecules because of the lack of practical synthetic methodology.

We have recently reported that the C−H bond at the 2-position of thiazole is efficiently substituted by various aryl groups with a palladium/copper catalyst system and tetrabutylammonium fluoride (TBAF) as an activator to afford the 2-arylated product under extremely mild reaction conditions.[1a] By contrast to the mild substitution at such an electron-deficient C−H bond at a lower temperature, C−H substitution at the electron-enriched carbon atom still requires drastic conditions to achieve the carbon−carbon bond formation.[3] However, our recent studies on C−H homocoupling of heteroaromatic compounds[4] suggest that cross coupling at an electron-enriched C−H of thiophene may also take place at a lower temperature and would be applicable to the diarylthiophene synthesis. We herein report a facile synthesis of 2,5-diarylated thiophene (**1a**) under mild condi-

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(1) (a) Mori, A.; Sekiguchi, A.; Masui, K.; Shimada, T.; Horie, M.; Osakada, K.; Kawamoto, M.; Ikeda, T. *J. Am. Chem. Soc.* **2003**, *125*, 1700. (b) Mochizuki, H.; Hasui, T.; Kawamoto, M.; Shiono, T.; Ikeda, T.; Adachi, C.; Taniguchi, Y.; Shirota, T. *Chem. Commun.* **2000**, 1923. (c) Dölling, K.; Zaschke, H.; Schubert, H. *J. Prakt. Chem.* **1979**, *321*, 643.

(2) (a) Briehn, C. A.; Schiedel, M.-S.; Bonsen, E. M.; Schuhmann, W.; Bäuerle, P. *Angew. Chem., Int. Ed.* **2001**, *40*, 4680. (b) Facchetti, A.; Yoon, M.-H.; Stern, C. L.; Katz, H. E.; Marks, T. J. *Angew. Chem., Int. Ed.* **2003**, *42*, 3900. (c) Yamamoto, T.; Arai, M.; Kokubo, H.; Sasaki, S. *Macromolecules* **2003**, *36*, 7986.

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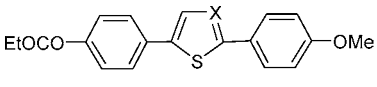
tions utilizing palladium-catalyzed C−H substitution in the presence of AgF. We also apply the method for the preparation of the related thiazole derivative (**1b**), and spectroscopic and thermal properties of these compounds are compared.

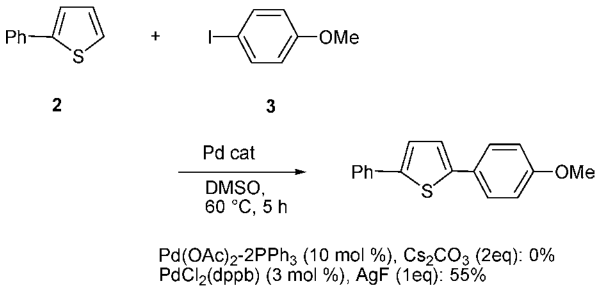


1a (X = CH)
1b (X = N)

Figure 1.

We first examined the reaction of 2-phenylthiophene (**2**), whose carbon atom at the 5-position was electron-enriched, with 4-methoxy-1-iodobenzene (**3**) under several conditions. The reaction did not proceed at 60 °C for 5 h, with 10 mol % of Pd(OAc)$_2$ and 20 mol % of PPh$_3$ in the presence of Cs$_2$CO$_3$, which were the reported conditions that proceeded at 140 °C.[3a,5] By contrast, the C−H substitution reaction was found to take place when AgF was employed as an activator using 3 mol % of PdCl$_2$(dppb) as a catalyst (Scheme 1).

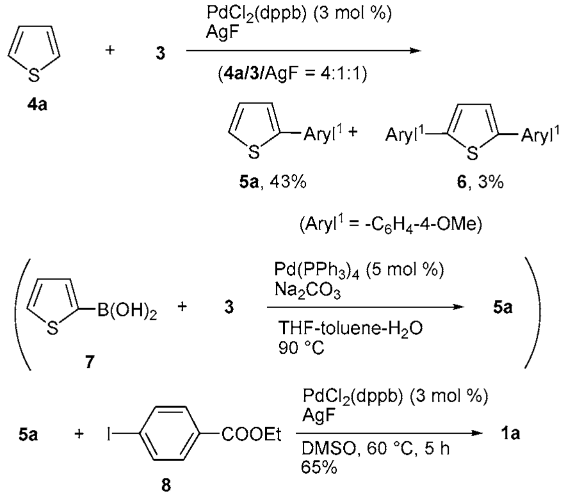
Scheme 1



Although the mechanism of the C−H substitution is not clear, specific interaction of the sulfur atom of **2** with the silver ion would allow the reaction of the electron-enriched heteroaromatic compound to proceed under mild conditions.

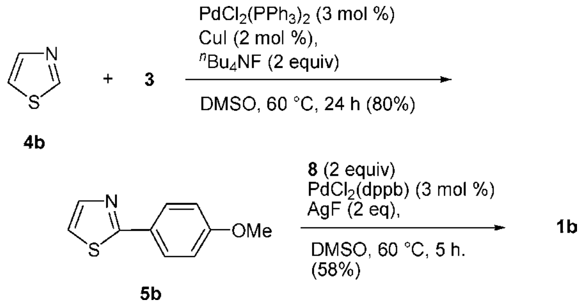
Encouraged by the above results, synthesis of differently substituted 2,5-diarylthiophene **1a** was performed as shown in Scheme 2. The reaction of thiophene (**4a**) with **3** in the presence of AgF, in which 4 equiv of **4a** toward **3** was employed, afforded the 2-arylated product **5a** in 43% yield along with 3% of 2,5-diarylated **6**.[6] Synthesis of **5a** was alternatively carried out with Suzuki−Miyaura coupling[7] of thiophene-2-boronic acid (**7**) with **3**. The palladium-catalyzed reaction of **5a** with ethyl 4-iodobenzoate (**8**) in the presence of AgF also underwent C−H substitution to afford the 2,5-diarylthiophene **1a** in 65% yield.

Scheme 2



Synthesis of 2,5-diarylthiazole (**1b**) was carried out under mild conditions as shown in Scheme 3 by the combination of Pd/Cu/TBAF and Pd/AgF protocols. Substitution at the 2-position of thiazole (**4b**) with **3** proceeded under the conditions as reported previously to give 2-arylated thiazole

Scheme 3



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(3) (a) Pivsa-Art, S.; Satoh, T.; Kawamura, Y.; Miura, M.; Nomura, M. *Bull. Chem. Soc. Jpn.* **1998**, *71*, 467. (b) Yokooji, A.; Okazawa, T.; Satoh, T.; Miura, M.; Nomura, M. *Tetrahedron* **2003**, *59*, 5685. (c) Kondo, Y.; Komine, T. Sakamoto, T. *Org. Lett.* **2000**, *2*, 3111. (d) Sezen, B.; Sames, D. *J. Am. Chem. Soc.* **2003**, *125*, 5274. (e) Sezen, B.; Sames, D. *J. Am. Chem. Soc.* **2003**, *125*, 10580. (f) Sezen, B.; Sames, D. *Org. Lett.* **2003**, *5*, 3607. (g) Lewis, J. C.; Wiedemann, S. H.; Bergman, R. G.; Ellman, J. A. *Org. Lett.* **2004**, *6*, 35. (h) Kamigata, N. Yoshikawa, M. Shimizu, T. *J. Fluorine Chem.* **1998**, *87*, 91. For a review; (i) Miura, M.; Nomura, M. *Top. Curr. Chem.* **2002**, *219*, 211.

(4) Masui, K.; Ikegami, H.; Mori, A. *J. Am. Chem. Soc.* **2004**, *126*, 5074.

(5) Reactions of thiophene derivatives with organic halides: (a) Ohta, A.; Akita, Y.; Ohkkuma, T.; Chiba, M.; Fukunaga, R.; Miyafuji, A.; Nakata, T.; Tani, N.; Aoyagi, Y. *Heterocycles* **1990**, *31*, 1951. (b) Aoyagi, Y.; Inoue, A.; Koizumi, A.; Hashimoto, T.; Tokunaga, K.; Gohma, K.; Komatsu, J.; Sekine, K.; Miyafuji, A.; Kunoh, J.; Honma, R.; Akita, Y.; Ohta, A. *Heterocycles* **1992**, *33*, 257. (c) Gozzi, C.; Lavenot, L.; Ilg, K.; Penalva, V.; Lemaire, M. *Tetrahedron Lett.* **1997**, *38*, 8867. (d) Lavenot, L.; Gozzi, C.; Ilg, K.; Orlova, I.; Penalva, V.; Lemaire, M. *J. Organomet. Chem.* **1998**, *567*, 49.

(6) Diarylated thiophene **6** (37%) and monoarylated **5a** (37%) were obtained when the reaction was carried out with 4 equiv of **3** and 2 equiv of AgF (toward **4a**).

(7) (a) Miyaura, N.; Suzuki, A. *Chem. Rev.* **1995**, *95*, 2457. (b) Suzuki, A. *J. Organomet. Chem.* **1999**, *576*, 147.

5b in 80% yield.[1a] C−H substitution at the 5-position of thiazole was also found to take place similarly to the case of thiophene. The reaction of **5b** with ethyl 4-iodobenzoate (**8**) at 60 °C in the presence of $PdCl_2$(dppb) (3 mol %) and AgF (1 equiv) afforded **1b** in 58%.

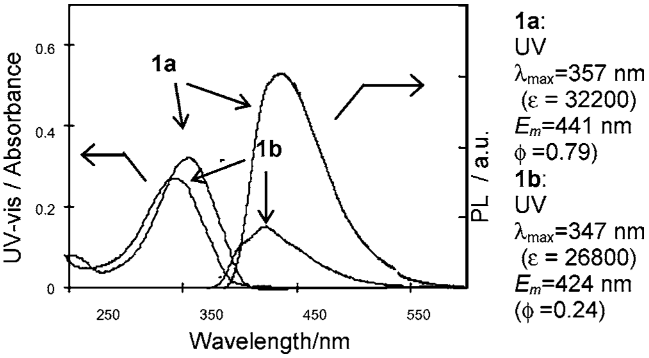

Figure 2. UV−vis absorption (gray) and PL emission (bold) spectra of **1a** and **1b**. The spectra were measured in a chloroform solution (1×10^{-5} and 1×10^{-6} M, respectively).

With differently substituted 2,5-diarylthiophene (**1a**) and -thiazole (**1b**) in hand, we then compared characteristics of these compounds. Figure 2 shows UV−vis absorption and photoluminescent spectra. Both compounds showed similar λ_{max} at ca. 350 nm, and the wavelength of emission was also similar. However, quantum yield (ϕ) of photoluminescence of 2,5-diarylthiophene **1a** was 0.79, which is ca. 3−4 times higher than that of the corresponding thiazole **1b** ($\phi = 0.24$). It should be pointed out that such a strong light emission has not been observed in other thiophene derivatives.[2]

A remarkable difference in thermotropic behaviors of **1a** and **1b** was also observed. Figure 3a shows DSC thermogram on the second cooling. The donor−acceptor-type **1a** exhibited two exothermic peaks at 61.3 and 187.2 °C. The former showed a smaller Δ*H* (0.5 KJ•mol^{-1}), and the latter was a larger Δ*H* (24.5 KJ•mol^{-1}). The behavior was not the typical isotropic-nematic-crystal transition, which was observed in the thermogram of symmetrical 2,5-di(4-methoxyphenyl)-thiophene (**6**)[8] but suggested a higher order mesophase such as a smectic phase. On the other hand, the behavior of donor−acceptor-type thiazole **1b** bearing the same substituents at both 2- and 5-positions of **1a** showed a different thermogram, in which a large Δ*H* of 12.6 KJ•mol^{-1} at 107.1 °C and the smaller Δ*H* of 2.1 KJ•mol^{-1} at 177.0 °C were shown, suggesting a nematic phase. In addition, observation of liquid crystalline texture with a polarizing microscope was also shown in Figure 3b. The results also support the nematic phase of **1b** (ii) and the smectic phase of **1a** (i).[9,10]

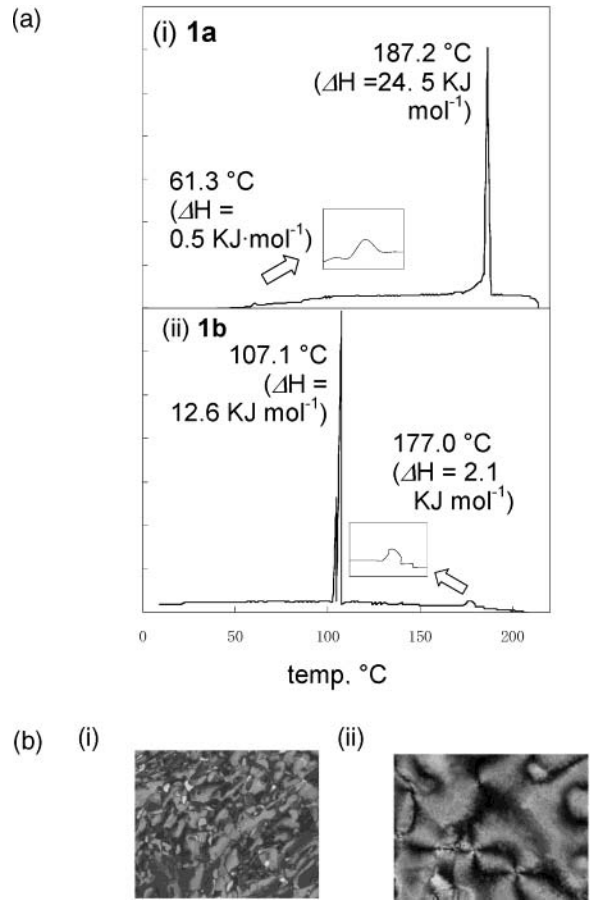

Figure 3. (a) DSC thermogram of **1a** (i) and **1b** (ii) on the second cooling. (b) Liquid crystalline texture of **1a** at 184 °C (i) and **1b** at 177 °C (ii) with a polarizing microscope.

Table 1. Cyclic Voltammogram of **1a** and **1b**[a]

compound	E_{pa} ($E_{1/2}$)/*V* vs Ag^+/Ag^b	E_{pc} ($E_{1/2}$)/*V* vs Ag^+/Ag^b
1a	0.87 (0.84)	
	1.22	
1b	1.13	−2.20 (2.16)

[a] Cyclic voltammogram was measured in an acetonitrile solution of Et_4NBF_4 (0.1 M). Ag^+/Ag was used as reference electrode. [b] Peak potentials are shown: E_{pa} = peak anode potential; E_{pc} = peak cathode potential.

Measurements of cyclic voltammogram of **1a** and **1b** were also carried out.[11] As shown in Table 1, an oxidation wave was observed in the measurement of **1a**, suggesting that 2,5-diarylthiophene potentially involves electron-transporting characteristics as well as light emission in EL and LED devices. On the other hand, **1b** was found to show oxidation

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(8) Kishikawa, K.; Micheke, C. H.; Timothy, M. S. *Chem. Mater.* **1999**, *11*, 867.

(9) *Handbook of Liquid Crystals*; Demus, D., Goodby, J., Gray, G. W., Spiess H.-W., Eds.; Wiley-VCH: Weinheim, 1998.

(10) Further studies on the liquid crystalline characteristics and physical properties of 2,5-diarylthiophenes are under investigation, and details will be described in due course.

(11) Kaifer, A. E.; Gómez-Kaifer, M. *Supramolecular Electrochemistry*; Wiley-VCH: Weinheim, 1999.

and reduction peaks, which suggest both hole and electron transportations leading to a single-layer electroluminescent device.

In conclusion, 2,5-diarylthiazole and -thiophene were synthesized using mild palladium-catalyzed C–H substitution reactions. Since the preparation method is quite simple and practical, it would be suitable for the synthesis of a wide variety of related derivatives in a combinatorial manner. Spectroscopic studies and thermal characterization revealed that the structure of the heteroaromatic moiety largely influences those properties. Further studies on the effect of substituents on physical properties and introduction of these heteroaromatic moieties into a side chain of a polymer for the purpose of preparing thin film on an electrode are under way.

Supporting Information Available: Experimental details and additional data on the characterization of **1a** and **1b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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