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Synthesis of 3,4′-Diaryl- and 4,4′-Diaryl-2,2′-bithienyls from 2,5-Dichlorothiophene[1)]

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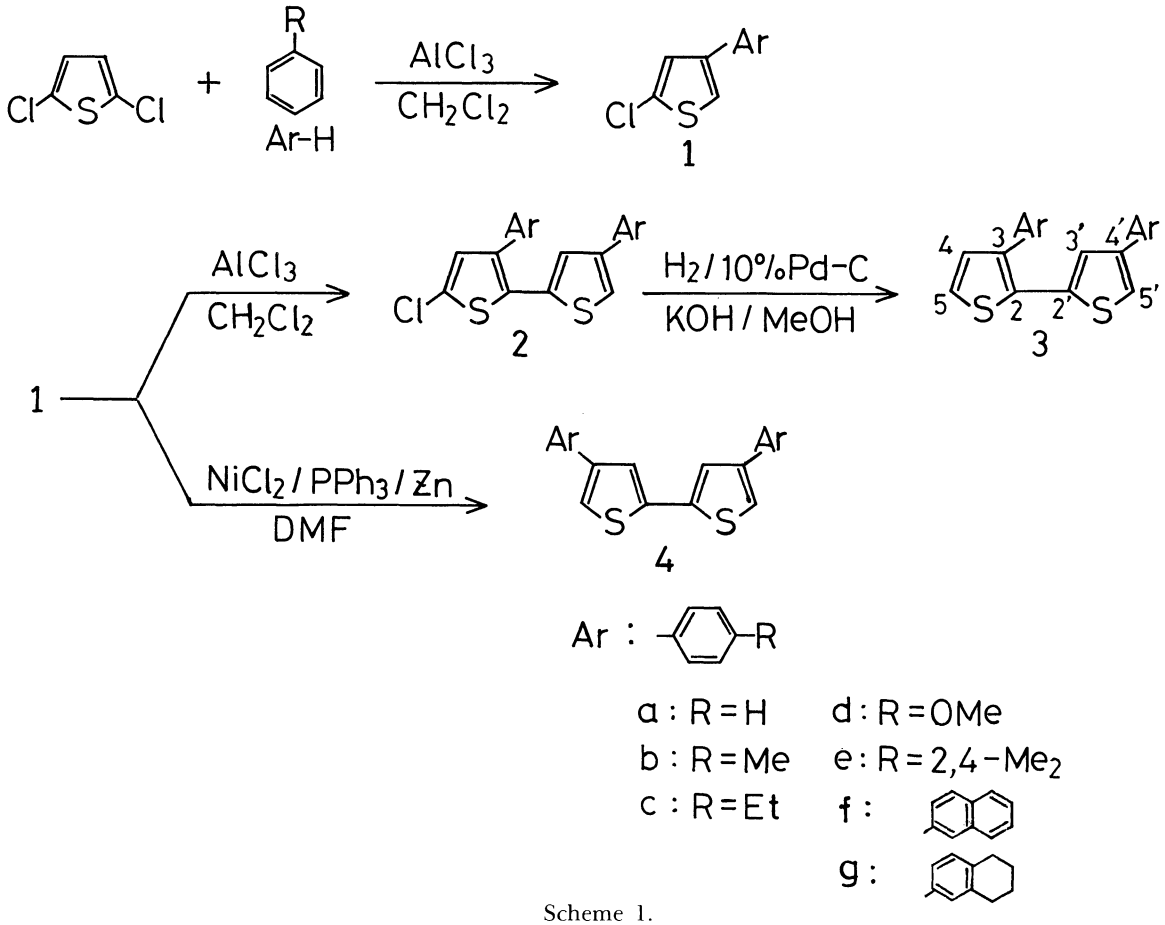
3,4′-Diaryl-, and 4,4′-diaryl-2,2′-bithienyls, new classes of mixed thiophene–arene oligomers, were synthesized from 2,5-dichlorothiophene via 4-aryl-2-chlorothiophene in three and two steps, respectively. Namely, a Friedel–Crafts type self-condensation of 4-aryl-2-chlorothiophene, followed by catalytic dechlorination, yielded unsymmetrical bithienyls. Homocoupling of 4-aryl-2-chlorothiophene using a nickel–phosphine catalyst gave symmetrical bithienyls.

Although the syntheses and properties of oligophenylenes have been systematically investigated, the chemistry of their thiophene analogues, thiophene oligomers and mixed thiophene–arene oligomers, has not yet been fully explored. Oligomers with definite structure, corresponding to quaterphenyl or its higher homologues, are rather limited in number; only a few of those containing 2,3′-bithienyl or 3-arylthiophene unit have been known.[2–5)] As for diarylbithienyls, one of the simplest classes of oligomers, for example, only two (5,5′-diaryl-[3)] and 3,3′-diphenyl-2,2′-bithienyl[4)]) have been reported. We have reported the synthesis of a series of unsymmetrical 5,5′-diaryl-2,3′-bithienyls by acid-catalyzed coupling of 2-arylthiophenes.[5)] Some of the oligomers have recently attracted attention in connection with their potential electric conductivity.[6)]

During the course of the studies on the acid-catalyzed reactions of thiophene nuclei, we found that, in the presence of $AlCl_3$, the chlorine atom of chlorothiophenes was sufficiently reactive; 2-chlorothiophene gave the corresponding 2-arylthiophenes with some aromatic compounds,[7)] while 2, 5-dichlorothiophene gave 4-aryl-2-chlorothiophenes (**1**) unexpectedly.[8)] These findings suggest a simple route to certain arylthiophenes starting from readily available chlorothiophenes. As an extension of the studies,



Scheme 1.

we found a convenient method for the synthesis of unsymmetrical 3,4′-diaryl-2,2′-bithienyls (**3**) from **1**. Furthermore, a series of symmetrical 4,4′-diaryl-2,2′-bithienyls (**4**) has been synthesized by homo-coupling of **1** using a nickel-phosphine catalyst. Besides forming new classes of mixed thiophene-arene oligomers, these compounds are interesting as potential key building blocks for well-ordered β-arylthiophene oligomers from the viewpoint of electrochemical properties.

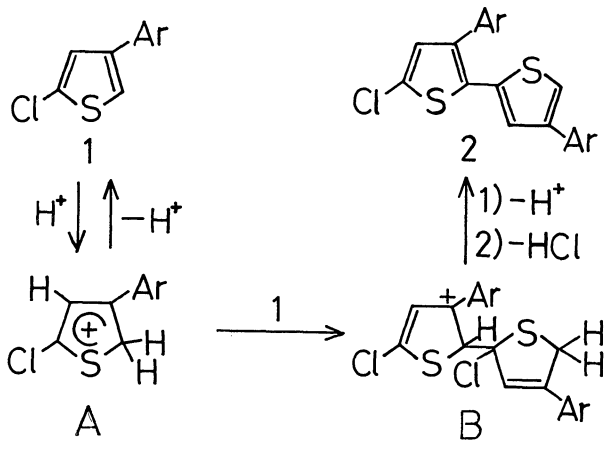
Results and Discussion

In order to find a simple route to 2,4-diarylthiophenes which were not easily accessible by traditional methods, the Friedel-Crafts type reaction of **1** with aromatic compounds was investigated. When reacted with such an active compound as anisole, however, **1** were found to undergo self-condensation with the elimination of HCl to give, instead of the expected product, 5-chloro-3,4′-diaryl-2,2′-bithienyls (**2**). This prompted us to apply the procedure for the synthesis of the unsymmetrical bithienyls, **3**. Self-condensation products, **2**, precursors of **3**, could be synthesized by this procedure in satisfactory yields. The results are summarized in Table 1.

The procedure of the Friedel-Crafts type reaction is simple; a mixture of **1** and an equimolar amount of $AlCl_3$ in CH_2Cl_2 or in CH_2Cl_2-benzene was stirred below 40 °C for a total of 2 h.

The assignment of the 3,4′-diaryl-2,2′-bithienyl structure is based on the NMR spectra of the self-condensation products, **2**, and those of the dechlorination products, **3**. The AB quartets with coupling constants J=1.3—1.7 Hz, observed in the aromatic region of the spectra of **2**, indicate the presence of a 2,4- disubstituted thiophene ring in the molecules. Moreover, the two sets of coupling constants, 1.5—1.6 and 5.0—5.3 Hz, observed in the aromatic region of the spectra of **3** are apparently derived from 2,4-di- and 2,3-disubstituted thiophene ring protons, respectively.[9]

The probable mechanism for self-condensation is shown in Scheme 2; this requires an initial protonation of **1** to form the thiophenium ion **A** as the electrophile. It is generally accepted that $AlCl_3$, when coming into contact with H_2O in moist air or HCl, produces a hypothetical species, such as $[H]^+[AlCl_3OH]^-$ or $[H]^+[AlCl_4]^-$ which acts as a proton source. Once the reaction occurs, it can provide HCl, which, together with $AlCl_3$, stimulates a further reaction. The existence of such a protonated species as **A** was confirmed by a direct NMR spectroscopic observation;[10] the spectrum of the thiophenium ion (**A**, **Ar**=Ph) produced from 2-chloro-4-phenylthiophene (**1a**) in HSO_3F at 32 °C shows, in addition to signals at 7.7—8.4 ppm due to the phenyl protons, two signals at 5.82 and 8.32 ppm with a relative intensity of 2:1. An attack of the thiophenium ion, **A** on the 5-position of **1**, followed by elimination of a proton and a HCl molecule, yields the self-condensation product, **2**.



Scheme 2.

The chlorine atom of the self-condensation products, **2**, could be easily removed by catalytic hydrogenation under atmospheric pressure using 10% Pd-C as a catalyst to give the unsymmetrical bithienyls, **3**, in satisfactory yields. The results are summarized in Table 1.

Symmetrical diarylbithienyls can be obtained by homo-coupling of the corresponding aryl-substituted halothiophenes. 3,3′-Diphenyl-2,2′-bithienyl was prepared by a Ullmann reaction of 3-phenyl-2-iodothiophene, though in low yield.[4] Efficient methods for

Table 1. Friedel-Crafts Type Self-Condensation of 4-Aryl-2-chlorothiophenes (**1**) and Catalytic Dechlorination of the Products (**2**)

1 Ar	**2** Yield[a]/%	**2** Mp (θ_m/°C)	**3** Yield[a]/%	**3** Mp (θ_m/°C)
a R=H	59	69—70 (hex)[b]	86	113—114 (hex-chl)
b R=Me	63	101—102 (hex)	90	161—162 (hex-chl)
c R=Et	69	Oil	75	Oil
d R=OMe	68	103—104 (ac-MeOH)	71	92—93 (MeOH)
f 2-Naphthyl	65	151—152 (hex-chl)	77	155—156 (hex-chl)

a) Isolated yields based on **1** or **2** used. b) Solvent for recrystallization: hex=hexane, ac=acetone, chl=chloroform, MeOH=methanol.

Table 2. Coupling of 4-Aryl-2-chlorothiophenes (**1**)

1 Ar	4 Yield[a]/%	4 Mp (θ_m/°C)
a R=H	63	224—225 (ben)[b]
b R=Me	75	220—221 (chl)
c R=Et	65	181—182 (hex-ben)
d R=OMe	65	289—291[d]
e R=2,4-Me_2	59	101—102 (hex)
f 2-Naphthyl	82	268—269 (chl)
g 2-Tetrahydro-2-naphthyl[c]	85	151—152 (hex-ben)

a) Isolated yields based on **1** used. b) Solvent for recrystallization: hex=hexane, ben=benzene, chl=chloroform. c) 5,6,7,8-Tetrahydro2-naphthyl. d) Purified by sublimation under reduced pressure (240 °C/1 mmHg).

coupling aryl halides have recently been developed using zerovalent nickel complexes. This method was applied to **1** for the synthesis of the symmetrical bithienyls, **4**. The nature of the zerovalent nickel complex used has been known to play an important role in nickel-mediated coupling. In addition, the amount of nickel complexes used is dependent upon the situation; in catalytic or stoichiometric amount. 4-Aryl-2-chlorothiophenes **1** were successfully coupled to **4** by using stoichiometric amounts of the nickel–phosphine complex prepared in situ from $NiCl_2$/PPh_3/Zn at a molar ratio of 1/4/1 in *N*,*N*-dimethylformamide (DMF) at 50 °C.[11] The results are summarized in Table 2. It has been reported that aryl chlorides, which tend to give unsatisfactory results in nickel-mediated reactions, can be efficiently coupled to diaryls by using catalytic amounts of the nickel complex in the presence of excess zinc.[12] Application of the catalytic method, however, led to the dechlorination of **1** in preference to coupling.

The structures of symmetrical bithienyls, **4**, were confirmed by their ^{1}H NMR spectra, which showed in the aromatic region an AB quartet with a coupling constant, J=1.4—1.5 Hz, characteristic of 2,4-dosibstituted thiophenes.[9]

Under the conditions employed for the synthesis of the symmetrical bithienyls, **4**, the nickel-mediated coupling of 2,5-dichloro-3-phenylthiophene was slow, affording 5-chloro-4,4′-diphenyl-2,2′-bithienyl (15%) together with the starting substance (25%) and 2-chloro-3-phenylthiophene (30%) instead of the expepcted 5,5′-dichloro-3,3′-diphenyl-2,2′-bithienyl, a precursor of the isomeric 3,3′-diphenyl-2,2′-bithienyls, in a prolonged reaction (12 h). A similar reaction (5 h) of 2-chloro-3-phenylthiophene did not give the desired 3,3′-diphenyl-2,2′-bithienyl, either, but yielded 3-phenylthiophene (25%) along with the starting substance (ca. 40%). These results indicate that steric hindrance plays an important role in nickel-mediated coupling.

In summary, we could synthesize 3,4′-diaryl-(**3**) and 4,4′-diaryl-2,2′-bithienyls (**4**), new classes of mixed thiophene–arene oligomers, which would be accessible only through many steps by other routes, in good yields in 3 and 2 steps, respectively, from readily available 2,5-dichlorothiophene. 4-Aryl-2-chlorothiophenes, **1**, which are obtained in one step from 2,5-dichlorothiophene by the Friedel–Crafts type reaction, serves as the key intermediates, suggesting the synthetic versatility of **1**.

Experimental

All of the melting and boiling points are uncorrected. The UV and MS spectra were obtained on a Hitachi 228A and a Hitachi RMU-6M (70 eV, unless otherwise noted), respectively. The ^{1}H NMR spectra were recorded on a Hitachi R-90H (90 MHz) or a Varian XL-200 (200 MHz) spectrometer using TMS as an internal reference.

4-Aryl-2-chlorothiophenes (**1**) were prepared from 2,5-dichlorothiophene by a previously described method.[8] Commercial $AlCl_3$ was used without special precautions against moisture.

Self-Condensation of 4-Aryl-2-chlorothiophene (1). Pulverized $AlCl_3$ (1.38 g, 10 mmol) was added in portions to an ice-cooled solution of **1** (10 mmol) in CH_2Cl_2 (10 ml) over ca. 5 min periods. The solution developed a dark-brown color. The reaction mixture was stirred in an ice-bath for 30 min, then at room temperature for 60 min, and finally at the reflux temperature of the solvent for an additional 30 min. The reaction mixture was poured into ice water (ca. 40 ml) and extracted with $CHCl_3$ (10 ml×3). The extracts were combined, washed successively with water, 5% $NaHCO_3$ solution, and water and dried. After removing the solvent, the residue was chromatographed (silica gel/hexane or hexane–$CHCl_3$) to afford, together with a small amount of unreacted **1**, 5-chloro-3,4′-diaryl-2,2′-bithienyl (**2**). In reactions with **1a** and **1f**, which are less soluble in CH_2Cl_2 under cooling, a mixture of CH_2Cl_2 (10 ml) and benzene (3—8 ml) was used as the solvent. In the case of **1d**, the reaction was carried out for 1 h in a mixed solvent of CH_2Cl_2 (10 ml) and anisole (10 ml) at room temperature, and then at ca. 40 °C for 30 min. Analytical samples were purified by recrystallization or chromatography.

5-Chloro-3,4′-diphenyl-2,2′-bithienyl (2a). UV (MeOH) 235 (log ε 4.44), 243 (sh, 4.43), 266 (sh, 4.36), and 320 nm (3.94); ^{1}H NMR (90 MHz; acetone-d_6) δ=7.06 (1H, s, 4-H), 7.28 (1H, d, J=1.7 Hz, 3′-H), and 7.3—7.65 (11H, m including d at 7.53, J=1.7 Hz, phenyl and 5′-H); MS *m/z* (rel intensity) 352 (M^+, 100). Found: C, 68.18; H, 3.58%. Calcd for $C_{20}H_{13}ClS_2$: C, 68.07; H, 3.71%.

5-Chloro-3,4′-di-*p*-tolyl-2,2′-bithienyl (2b). UV (MeOH) 240 (log ε 4.45), 247 (4.45), 271 (sh, 4.36), and 325 nm (3.91); ^{1}H NMR (90 MHz; acetone-d_6) δ=2.26 and 2.27 (6H, s each, CH_3), 7.00 (1H, s, 4-H), 7.09 and 7.18 (4H, AA′BB′m, *p*-phenyl), 7.20 and 7.29 (2H, AA′BB′m, *p*-phenyl), 7.33 (1H, d, J=1.3 Hz, 3′-H), and 7.4—7.5 (3H, m consisting of AA′BB′m at 7.40 and 7.49, and d at 7.50, J=1.3 Hz, *p*-phenyl and 5′-H); MS *m/z* (rel intensity) 380 (M^+, 100). Found: C, 69.40; H, 4.20%. Calcd for $C_{22}H_{17}ClS_2$: C, 69.36; H, 4.50%.

5-Chloro-3,4′-bis(*p*-ethylphenyl)-2,2′-bithienyl (2c). UV (MeOH) 244 (log ε 4.27), 271 (sh, 4.36), and 325 nm (3.73);

^{1}H NMR (90 MHz; $CDCl_3$) δ=1.19 (6H, t, J=6.8 Hz, CH_2CH_3), 2.64 (4H, q, J=6.8 Hz, CH_2CH_3), 6.90 (1H, s, 4-H), and 7.05—7.65 (10H, m, p-phenyl, 3′-H, and 5′-H); MS m/z (rel intensity) 408 (M^+, 100). Found: C, 70.22; H, 5.08%. Calcd for $C_{24}H_{21}ClS_2$: C, 70.48; H, 5.18%.

5-Chloro-3,4′-bis(p-methoxyphenyl)-2,2′-bithienyl (2d). UV (MeOH) 245 (sh, log ε 4.40), 254 (4.43), 273 (4.42), and 318—331 nm (3.89); ^{1}H NMR (90 MHz; acetone-d_6) δ=3.77 (6H, s, OCH_3), 6.85 and 6.95 (4H, AA′BB′m, p-phenyl), 7.02 (1H, s, 4-H), and 7.2—7.6 (6H, m including AA′BB′m at 7.24 and 7.34, and 7.47 and 7.57, p-phenyl, 3′-H and 5′-H); MS m/z (rel intensity) 412 (M^+, 100). Found: C, 63.99; H, 4.11%. Calcd for $C_{22}H_{17}ClO_2S_2$: C, 63.99; H, 4.15%.

5-Chloro-3,4′-di(2-naphthyl)-2,2′-bithienyl (2f). UV (MeOH) 222 (log ε 4.72), 243 (4.71), 290 (4.35), and 301 nm (sh, 4.29); ^{1}H NMR (90 MHz; $CDCl_3$) δ=7.00 (1H, s, 4-H) and 7.2—7.9 (16H, m, naphthyl, 3′-H, and 5′-H); MS m/z (rel intensity) 452 (M^+, 100). Found: C, 74.17; H, 3.59%. Calcd for $C_{28}H_{17}ClS_2$: C, 74.27; H, 3.78%.

Catalytic Dechlorination of 5-Chloro-3,4′-diaryl-2,2′-bithienyls (2). A mixture of **2** (3 mmol), KOH (1.5 g), 10% Pd–C (0.6 g), and MeOH (50 ml; MeOH (25 ml) and dioxane (50 ml) in the case of **2b** and **2d**) was stirred at room tempeprature under an atmosphere of H_2 in an atmospheric-pressure hydrogenation apparatus. After the calculated amount of H_2 was taken up (usually within 1 h), the catalyst was removed by filtration and washed with MeOH (20 ml; dioxane (20 ml) in the case of **2b** and **2d**). The combined filtrate and washings were evaporated to ca. 20 ml. Water (40 ml) was added to the residue and the resulting crystalline materials were removed by filtration, washed with a little water, dried, and chromatographed (silica gel/hexane–$CHCl_3$) to give 3,4′-diaryl-2,2′-bithienyls (**3**). The analytical sample was purified by recrystallization, sublimation under reduced pressure, or chromatography.

3,4′-Diphenyl-2,2′-bithienyl (3a). UV (MeOH) 249 (sh, log ε 4.42), 263 (4.48), and 318 nm (sh, 3.87); ^{1}H NMR (200 MHz; acetone-d_6) δ=7.17 (1H, d, J=5.2 Hz, 4-H), and 7.25—7.7 (13H, m including d at 7.53, J=5.2 Hz, 3′-H, 5′-H, 5-H, and p-phenyl); MS m/z (rel intensity) 318 (M^+, 100). Found: C, 75.16 H, 4.48%. Calcd for $C_{20}H_{14}S_2$: C, 75.43; H, 4.43%.

3,4′-Di-p-tolyl-2,2′-bithienyl (3b). UV (MeOH) 250 (sh, log ε 4.19), 265 (4.26), and 320 nm (sh, 3.74); ^{1}H NMR (200 MHz; acetone-d_6) δ=2.33 and 2.35 (6H, s each, CH_3), 7.15 (1H, d, J=5.2 Hz, 4-H), 7.19 and 7.23 (4H, AA′BB′m, p-phenyl), 7.29 and 7.33 (2H, AA′BB′m, p-phenyl), 7.39 (1H, d, J=1.5 Hz, 3′-H), 7.5—7.55 (3H, m including d at 7.52, J=5.2 Hz, and AA′BB′m at 7.53, 5-H and p-phenyl), and 7.58 (1H, d, J=1.5 Hz, 5′-H); MS m/z (rel intensity) 346 (M^+, 100). Found: C, 75.96; H, 5.15%. Calcd for $C_{22}H_{18}S_2$: C, 76.26; H, 5.24%.

3,4′-Bis(p-ethylphenyl)-2,2′-bithienyl (3c). UV (MeOH) 250 (sh, log ε 4.47), 266 (4.51), and 320 nm (sh, 3.84); ^{1}H NMR (200 MHz; acetone-d_6) δ=1.20 and 1.22 (6H, t each, J=7.6 Hz, CH_2CH_3), 2.62 and 2.64 (4H, q each, J=7.6 Hz, CH_2CH_3), 7.13 (1H, d, J=5.3 Hz, 4-H), 7.19 and 7.23 (4H, AA′BB′m, p-phenyl), 7.25—7.45 (3H, m, 3′-H and p-phenyl), and 7.5—7.7 (4H, m, 5-H, 5′-H, and p-phenyl); MS m/z (rel intensity) 374 (M^+, 100). Found: C, 76.81; H, 5.92%. Calcd for $C_{24}H_{22}S_2$: C, 76.96; H, 5.92%.

3,4′-Bis(p-methoxyphenyl)-2,2′-bithienyl (3d). UV (MeOH) 232 (sh, log ε 4.38), 250 (4.42), 272 (4.48), and 333 nm (sh, 3.76); ^{1}H NMR (200 MHz; acetone-d_6) δ=3.79 and 3.80 (6H, s each, OCH_3), 6.91 and 6.96 (4H, AA′BB′m, p-phenyl), 7.12 (1H, d, J=5.0 Hz, 4-H), 7.31 and 7.35 (2H, AA′BB′m, p-phenyl), 7.37 (1H, d, J=1.6 Hz, 3′-H), 7.46 and 7.47 (2H, d each, J=1.6 Hz, J=5.0 Hz, 5′-H and 5-H), and 7.53 and 7.57 (2H, AA′BB′m, p-phenyl); MS m/z (rel intensity) 378 (M^+, 100). Found: C, 69.87; H, 4.72%. Calcd for $C_{22}H_{18}O_2S_2$: C, 69.81; H, 4.79%.

3,4′-Di(2-naphthyl)-2,2′-bithienyl (3f). UV (MeOH) 222 (log ε 4.79), 244 (sh, 4.71), 263 (sh, 4.63), and 290 nm (sh, 4.45); ^{1}H NMR (200 MHz; acetone-d_6) δ=7.33 (1H, d, J=5.2 Hz, 4-H), 7.45—7.6 (4H, m, naphthyl), 7.62 (1H, d, J=5.2 Hz, 5-H), 7.66 (1H, d, J=1.6 Hz, 3′-H), 7.77 (1H, d, J=1.6 Hz, 5′-H), 7.8—8.2 (10H, m, naphthyl); MS m/z (rel intensity) 418 (M^+, 100). Found: C, 80.07; H, 4.17%. Calcd for $C_{28}H_{18}S_2$: C, 80.34 H, 4.33%.

Coupling of 4-Aryl-2-chlorothiophenes (1). The procedure is a modification of the one described by Tiecco et al.[11] for the preparation of bipyridyls, in which $NiCl_2$ is used instead of $NiCl_2 \cdot 6H_2O$. To a solution of $NiCl_2$ (0.65 g, 5 mmol) and PPh_3 (5.2 g, 20 mmol) in N,N-dimethylformamide (25 ml), Zn powder (0.32 g, 5 mmol) was added under an N_2 atmosphere. The mixture was stirred at 50 °C for 1 h. 4-Aryl-2-chlorothiophene (**1**; 5 mmol) was added to the resulting red brown solution. After stirring for 30 min, the mixture was poured into H_2O (50 ml). The precipitate was filtered, washed with H_2O (20 ml), and dried.

(a) When the coupling product was soluble in $CHCl_3$, as were the cases with **4e** and **4g**, the precipitate was directly chromatographed (silica gel/hexane–$CHCl_3$ (3:2)), giving **4e** or **4g** together with PPh_3 and a small amount of the dechlorination product of **1e** or **1g**. (b) When the coupling product was less soluble in $CHCl_3$ (**4d** and **4f**), the precipitate was washed with the solvent (20 ml×2) and the PPh_3-free residue was then sublimed under reduced pressure (230 °C (bath)/1 mmHg; 1 mmHg=133.322 Pa) or treated with hot 10% HCl (20 ml) and washed with H_2O to give **4d** or **4f**. (c) In the cases with **1a**, **1b**, and **1c**, the precipitate was extracted with $CHCl_3$ (20 ml×2). The undissolved solid was recrystallized from $CHCl_3$ to yield the coupling product. Evaporation of the combined extracts followed by column chromatography (silica gel/hexane–$CHCl_3$ (3: 1—2)) gave another crop of the product.

The analytical samples were purified by recrystallization.

4,4′-Diphenyl-2,2′-bithienyl (4a). UV (MeOH) 258 (log ε 4.74) and 323 nm (4.06); ^{1}H NMR (90 MHz, $CDCl_3$); δ=7.2—7.7 (m, phenyl, 3-H, 3′-H, 5-H, and 5′-H); MS m/z (rel intensity) 318 (M^+, 100). Found: C, 75.51; H, 4.27%. Calcd for $C_{20}H_{14}S_2$: C, 75.43; H, 4.43%.

4,4′-Di-p-tolyl-2,2′-bithienyl (4b). UV (MeOH) 261 (log ε 4.71) and 325 nm (3.96); ^{1}H NMR (90 MHz, $CDCl_3$) δ=2.38 (6H, s, CH_3), 7.1—7.3 (6H, m including AA′BB′m at 7.16 and 7.25, and d at 7.28, J=1.6 Hz, p-phenyl, 3-H, and 3′-H), and 7.3—7.55 (6H, m including AA′BB′m at 7.46 and 7.55, p-phenyl, 5-H, and 5′-H); MS m/z (rel intensity) 346 (M^+, 100). Found: C, 76.23; H, 5.24%. Calcd for $C_{22}H_{18}S_2$: C, 76.26; H, 5.24%.

4,4′-Bis(p-ethylphenyl)-2,2′-bithienyl (4c). UV (MeOH) 260 (log ε 4.78) and 325 nm (4.02); ^{1}H NMR (90 MHz, $CDCl_3$) δ=1.26 (6H, t, J=7.6 Hz, CH_2CH_3), 2.67 (4H, q, J=7.6 Hz, CH_2CH_3), 7.05—7.3 (6H, m including AA′BB′m at 7.17 and

7.27, and d at 7.28, J=1.5 Hz, p-phenyl, 3-H, and 3′-H), and 7.35—7.65 (6H, m including d at 7.46, J=1.5 Hz, and AA′BB′m at 7.47 and 7.57, 5-H, 5′-H, and p-phenyl); MS m/z (rel intensity) 374 (M^+, 100). Found: C, 77.16; H, 5.86%. Calcd for $C_{24}H_{22}S_2$: C, 77.16; H, 5.92%.

4,4′-Bis(*p*-methoxyphenyl)-2,2′-bithienyl (4d). UV (MeOH; molar extinction coefficients were not determined because of low solubility) 265 and 302 nm (sh); ^{1}H NMR (90 MHz, pyridine-d_5 peak intensities were not determined because of low solubility) δ=3.75 (s, OCH_3), 7.09 and 7.18 (AA′BB′m p-phenyl), 7.76 and 7.85 (AA′BB′m, p-phenyl), 7.77 (d, J=1.4 Hz, 3-H and 3′-H), and 7.90 (d, J=1.4 Hz, 5-H and 5′-H); MS m/z (rel intensity) 378 (M^+, 100). Found: 69.95; H, 4.67%. Calcd for $C_{22}H_{18}O_2S_2$: C, 69.81; H, 4.67%.

4,4′-Bis(2,4-dimethylphenyl)-2,2′-bithienyl (4e). UV (MeOH) 253 (log ε 4.45) and 322 nm (4.20); ^{1}H NMR (90 MHz, $CDCl_3$) δ=1.50 (12H, s, CH_3), 6.85—7.4 (10H, m including d at 7.03 and 7.21, J=1.4 Hz, 3-H, 3′-H, 5-H, 5′-H, and trisubstituted phenyl); MS m/z (rel intensity) 374 (M^+, 100). Found: C, 77.26; H, 5.92%. Calcd for $C_{24}H_{22}S_2$: C, 76.96; H, 5.92%.

4,4′-Di(2-naphthyl)-2,2′-bithienyl (4f). UV (MeOH; molar extinction coefficients were not determined because of low solubility) 257, 290, and 306 nm (sh); ^{1}H NMR (90 MHz, pyridine-d_5; peak intensities were not determined because of low solubility) δ=7.4—8.4 (m including d at 7.87 and 8.08, J=1.5 Hz each, naphthyl, 3-H, 3′-H, 5-H, and 5′-H); MS m/z (rel intensity) 418 (M^+, 100). Found: C, 80.47; H, 4.12%. Calcd for $C_{28}H_{18}S_2$: C, 80.34; H, 4.33%.

4,4′-Bis(5,6,7,8-tetrahydro-2-naphthyl)-2,2′-bithienyl (4g). UV (MeOH) 252 (sh, log ε 4.61), 258 (sh, 4.75), 264 (4.75), and 326 nm (4.00); ^{1}H NMR (90 MHz, $CDCl_3$) δ=1.6—1.95 (8H, m, $PhCH_2CH_2$), 2.78 (8H, br s, $PhCH_2$), 6.9—7.35 (8H, m including d at 7.24, J=1.5 Hz, 3-H, 3′-H, and trisubstituted phenyl), and 7.43 (2H, d, J=1.5 Hz, 5-H and 5′-H); MS m/z (rel intensity) 426 (M^+, 100). Found: C, 79.09; H, 6.09%. Calcd for $C_{28}H_{26}S_2$: C, 78.83; H, 6.14%.

2,5-Dichloro-3-phenylthiophene. Sulfonyl chloride (8.1 g, 60 mmol) was added to a stirred solution of **1** (7.8 g, 40 mmol) in CCl_4 (60 ml) over ca. 5 min period and the mixture refluxed for 60 h. The reaction mixture was poured into ice water (ca. 40 ml) and extracted with CCl_4 (15 ml×3). The extracts were combined, washed successively with water, 5% $NaHCO_3$ solution, and water again, and dried. After evaporating the solvent, the residue was chromatographed (silica gel/hexane) to afford 2,5-dichloro-3-phenylthiophene (4.6 g, 50%) as an oil. UV (MeOH) 233 (log ε 4.33) and 260 nm (3.92); ^{1}H NMR (90 MHz, CCl_4) δ=6.83 (1H, s, 4-H), 7.21—7.49 (5H, m, phenyl); MS m/z (rel intensity) 230 (M^++2, 69), 228 (M^+, 100). Found: C, 52.45; H, 2.50%. Calcd for $C_{10}H_6Cl_2S$: C, 52.42; H, 2.64%.

Coupling of 2,5-Dichloro-3-phenylthiophene. 2,5-Dichloro-3-phenylthiophene (0.8 g, 3.5 mmol) was subjected to coupling under the conditions described above, except for the reaction period (12 h instead of 1 h). A work-up and repeated chromatography (silica gel/hexane) of the reaction mixture gave 5-chloro-4,4′-diphenyl-2,2′-bithienyl (0.1 g, 15%) together with 2,5-dichloro-3-phenylthiopheene (0.2 g, 25%) and 2-chloro-3-phenylthiophene (0.2 g, 30%). The structure of the 5-chloro-4,4′-diphenyl-2,2′-bithienyl was confirmed by its catalytic dechlorination, which gave the known 4,4′-diphenyl-2,2′-bithienyl.

5-Chloro-4,4′-diphenyl-2,2′-bithienyl. Pale yellow needles, mp 144—145 °C (hexane–$CHCl_3$); UV (MeOH) 254 (log ε 4.63), 328 (4.11), and 351 nm (sh, 3.78); ^{1}H NMR (90 MHz, $CDCl_3$) δ=7.23 (1H, s, 3-H), 7.35—7.8 (12H, m including d at 7.48 and 7.63, J=1.7 Hz each, phenyl, 3′-H, and 5′-H); MS m/z (rel intensity) 354 (M^++2, 40), 352 (M^+, 100). Found: C, 68.07; H, 3.48%. Calcd for $C_{20}H_{13}ClS_2$; C, 68.07; H, 3.71%.

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