Synthesis, Characterization, and Photoluminescence of Thiophene-Containing Spiro Compounds

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Abstract: Spiro[fluorene-9,4′-[4*H*]indeno[3,2-*b*]thiophene] (**spiro-FIT**) and bis(spiro-FIT)arenes were synthesized. The UV/vis spectra, emission spectra, and cyclic voltammetry of these compounds are described.

Key words: spiro compounds, Stille reaction, heterocycles, cross-coupling, chromophores

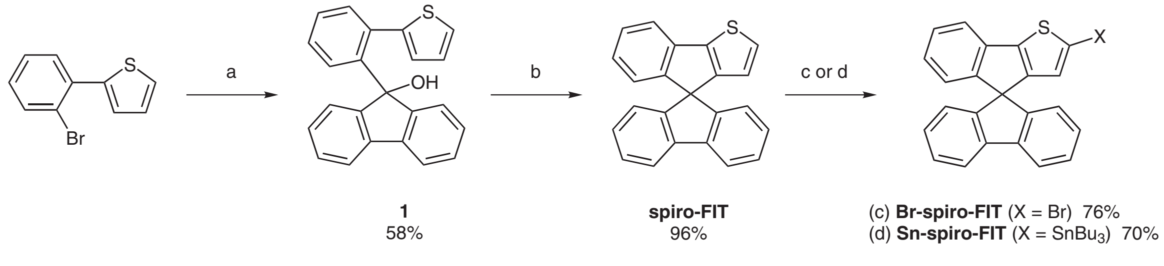
Recently, π-conjugated compounds such as organic light-emitting diodes (OLED), photovoltaic cell, and organic field-effect transistors (OFET) have received considerable attention in the field of organic electronics. In particular, thiophene-based compounds such as poly- and oligothiophenes are among the most studied organic materials because of their charge-transport properties.[1] Thiophene/phenylene[1c,2] and thiophene/fluorene[1c,3] co-oligomers have also been widely studied for applications in OFET and OLED. These oligomers show better oxidative stability than the all-thiophene analogues and are stable in air. However, these thiophene-based compounds often face the problem of limited solubility. The incorporation of alkyl chains into the thiophene backbone results in improved solubility. Their photoluminescence efficiencies (Φ_F) are usually low because of increased nonradiative decay, because the alkylated compounds tend to interact with adjacent molecules in the solid state.[1a] The interchain interaction is effective for applications in OFET, but another type of method to increase the solubility of the materials for OLED is needed.

9,9′-Spirobifluorene derivatives are regarded as the most promising candidates for construction of organic optoelectronics.[4] The rigidity of spiro compounds provides a high glass-transition temperature (T_g) and decomposition temperature (T_d), which are very important for the application of low-molecular-weight compounds to optoelectronic devices. In addition, their solubility is higher than that of the corresponding compounds without a spiro moiety, because their perpendicular conformations based on the spiro linkage efficiently suppress intermolecular interactions between the π-systems. Thus, it is expected that the solubility and Φ_F in the solid state of thiophene-based compounds would be improved by incorporation of a spiro moiety into their framework. However, to the best of our knowledge, there are few reports on spiro compounds containing thiophene rings.[5]

In this paper, we wish to report the synthesis and properties of the thiophene-containing spiro compounds, spiro[fluorene-9,4′-[4*H*]indeno[3,2-*b*]thiophene] (**spiro-FIT**) and bis(spiro-FIT)arenes. The optical and electrochemical characteristics of bis(spiro-FIT)arenes are easily tunable by changing the linking arenes. The Stille coupling reaction can be used for their synthesis, and, thus, desirable materials for practical applications to OLED can be obtained.

Scheme 1 depicts the synthesis of **spiro-FIT** and its derivatives.[6a,b] The reaction of 9-fluorenone with the Grignard reagent derived from 1-bromo-2-thienylbenzene afforded alcohol **1** in 58% yield. An acid-promoted intramolecular alkylation furnished a thiophene-containing spiro compound **spiro-FIT** in 96% yield. Bromination of **spiro-FIT** with NBS or lithiation of **spiro-FIT** followed by reaction with Bu_3SnCl produced the bromo derivative **Br-spiro-FIT** (76%) or **Sn-spiro-FIT** (70%), respectively.

2,2′-Bispiro[fluorene-9,4′-[4*H*]indeno[3,2-*b*]thiophene] (**2**) was synthesized by the Stille coupling reaction of **Br-**



Scheme 1 Synthesis of **spiro-FIT**, **Br-spiro-FIT**, and **Sn-spiro-FIT**. *Reagents and conditions*: (a) (i) Mg, THF, r.t., 1 h; (ii) 9-fluorenone, THF, r.t. to reflux, 3 h; (b) HCl, AcOH, r.t., 1 h; (c) NBS, DMF, r.t., 14 h; (d) (i) *t*-BuLi, THF, –78 °C, 1 h; (ii) Bu_3SnCl, –78 °C to r.t., 90 min.

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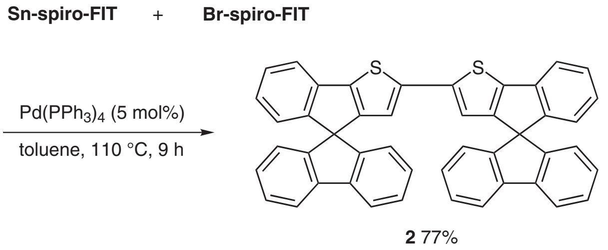


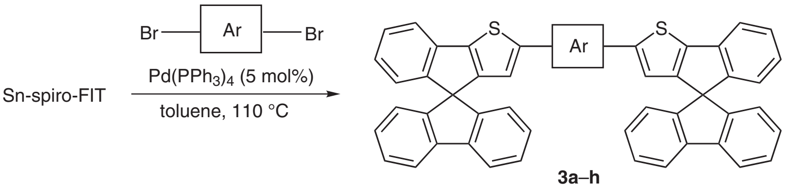
Scheme 2 Synthesis of **2**

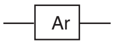
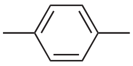
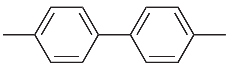
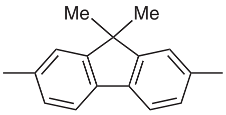
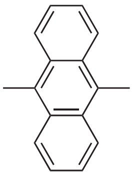
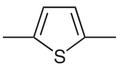
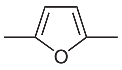
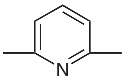
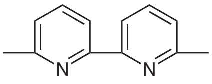
spiro-FIT with **Sn-spiro-FIT** (Scheme 2). The Stille coupling reaction was also employed for the synthesis of bis(spiro-FIT)arenes using several dibromoarenes and two equivalents of **Sn-spiro-FIT** (Table 1).[6c] Several heteroaromatic rings (entries 5–8) as well as aromatic hydrocarbons (entries 1–4) were successfully introduced. Sterically hindered 9,10-dibromoanthracene and 6,6′-dibromo-2,2′-bipyridine reacted cleanly to produce the coupling products **3d** and **3h**, respectively, although prolonged reaction time was necessary (entries 4 and 8).

The thermal properties of prepared spiro compounds were investigated by thermogravimetric analysis (TGA). They showed high T_d up to 442 °C (Table 2).

As shown in Figure 1, the cyclic voltammogram (CV) for **spiro-FIT** in CH_2Cl_2 containing 0.10 M Bu_4NPF_6 showed irreversible oxidation waves, while that of **2** showed reversible waves. Irreversible waves for **spiro-FIT** might be due to in situ electrochemical oxidative coupling of its generated radical cations. Oxidation waves of compounds **3a–f** were reversible, while those of compounds **3g** and **3h** were irreversible (Table 2). In comparison with compound **2**, the first oxidation potentials for **3a** and **3b** increase with increasing length of the linkers. On the other hand, the second oxidation potentials decrease. These data suggest that the coulombic repulsion would decrease because of the long distance between both thiophene rings.[7] Oxidation potentials are also affected by the electronic na-

Table 1 Synthesis of Bis(spiro-FIT)arenes using Stille Coupling[a]



Entry		Time (h)	Product	Yield (%)[b]
1		14	**3a**	65
2		14	**3b**	76
3	 Me Me	12	**3c**	68
4		39	**3d**	77
5	 S	10	**3e**	74
6	 O	12	**3f**	82
7	 N	13	**3g**	83
8	 N N	40	**3h**	85

[a] **Sn-spiro-FIT** (0.400 mmol) and dibromoarenes (0.200 mmol) in toluene (2.0 mL).
[b] Isolated yield.

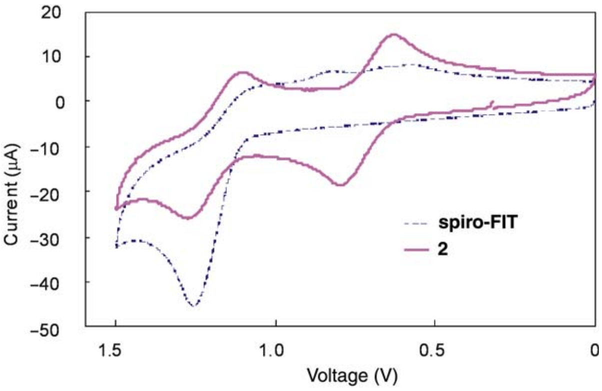


Figure 1 The cyclic voltammograms of **spiro-FIT** and **2** in CH_2Cl_2

ture of the linkers. Incorporation of electron-rich heteroarenes, such as thiophene and furan, provides higher HOMO levels (**3e** and **3f**). In contrast, **3g** and **3h** involving pyridine and bipyridine lower their HOMO levels.

Similarly to the results of the CV, the electronic nature of the linkers affects the absorption and emission maxima (Figure 2). Both maxima of **3e** were red shifted relative to **3a**, while those of **3g** were blue shifted. Compared with **2**, the absorption maxima of **3a–d** with aromatic hydrocarbons as the linker were observed at almost the same wavelength, although **3b** exhibited a blue shift because of the slightly twisted biphenyl ring (Table 2). However, for **2** and **3a**,**b**, the values of Φ_F are enhanced as the π-framework is extended. Except for **3d**, all bis(spiro-FIT)arenes showed relatively high quantum yields.

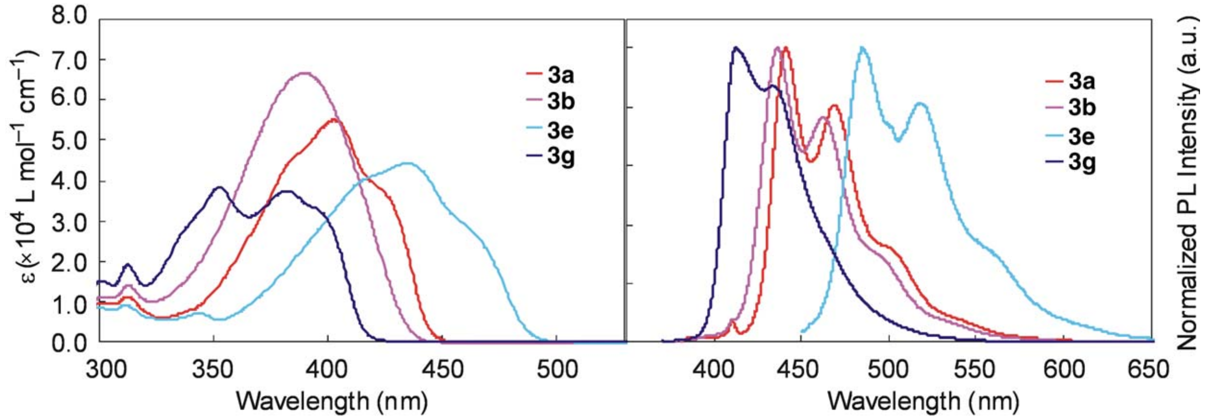


Figure 2 The UV/vis absorption and fluorescence spectra of 3**a**,**b**,**e**,**g** in THF

Table 2 Optical and Electrochemical Properties of **spiro-FIT**, **2**, and **3a**–**h**

	abs λ_{max} (nm)[a]	ε (× 10^4 L mol^{-1} cm^{-1})	PL λ_{max} (nm)[b]	Φ_F[c]	$E_{1/2\ oxd}$ (V)[d]	T_d (°C)[e]
Spiro-FIT	300, 311	1.53	338, 348[f]	<0.01	0.96[h]	217
2	405	3.54	444, 471	0.07	0.50, 0.96	–[i]
3a	403	5.49	441, 469	0.48	0.59, 0.84	438
3b	389	6.65	436, 462	0.71	0.68, 0.78	–[i]
3c	404	6.69	440, 468	0.60	0.57, 0.74	–[i]
3d	403	1.63	439, 466[f]	0.02	0.58	–[i]
3e	434	4.41	485, 519	0.32[g]	0.41, 0.72	435
3f	425	4.22	465, 498	0.81[g]	0.34, 0.69	–[i]
3g	352, 382	3.83, 3.75	412, 433	0.76	0.82[h]	442
3h	365, 379	5.83, 6.00	411, 431	0.53	0.93[h]	–[i]

[a] $c = 1.00 \times 10^{-5}$ mol L^{-1}.
[b] $c = 1.00 \times 10^{-7}$ mol L^{-1}; $\lambda_{ex} = 366$ nm.
[c] Quinine sulfate in 0.1 M aq H_2SO_4 (366 nm, $\Phi_F = 0.55$) as a standard.
[d] In CH_2Cl_2 containing 0.10 M Bu_4NPF_6 vs. Fc/Fc$^+$ at 100 mV s^{-1}.
[e] Decomposition temperature obtained from TGA.
[f] $c = 1.00 \times 10^{-6}$ mol L^{-1}.
[g] Fluorescein in 0.1 M aq NaOH (436 nm, $\Phi_F = 0.90$) as a standard.
[h] Irreversible.
[i] Not determined.

Some similar compounds without a spiro linkage have been reported by other groups (Figure 3).[2a,8]

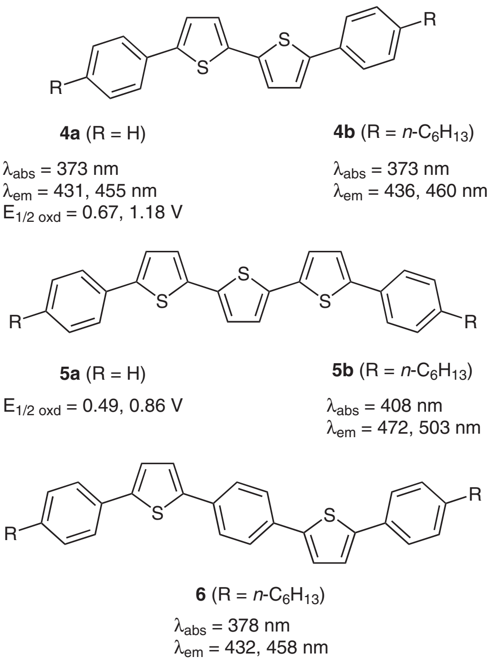


Figure 3 Optical and electrochemical properties of thiophene/phenylene oligomers

Both in the absorption and emission spectra, the maximum wavelengths of spiro compounds **2** and **3a**,**e** are bathochromic shifted compared with those of similar compounds without a spiro linkage. In addition, spiro compounds have lower oxidation potentials than nonspiro compounds. It is considered that these results can be attributed to the increase in planarity of the π-conjugated systems as a result of the spiro linkage.

In summary, a new thiophene-containing spiro compound **spiro-FIT** has been synthesized. Stille coupling between **Sn-spiro-FIT** and dibromoarenes provided π-extended bis(spiro-FIT)arenes. Almost all of the coupling products, except for **3d**, showed efficient photoluminescence. [4*H*]Indeno[3,2-*b*]thiophenes containing the spirofluorene structure as a building block are expected to find applications to organic functional materials.

Acknowledgment

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(6) **Representative Experimental Procedures**
(a) Preparation of Spiro[fluorene-9,4′-[4*H*]indeno[3,2-*b*]thiophene] (spiro-FIT)
To an AcOH solution (30 mL) of 9-(2-thienylphenyl)-fluoren-9-ol (**1**, 390 mg, 1.14 mmol) was added concentrated HCl (1 mL) at r.t., and the mixture was stirred for 1 h. After the addition of H_2O (30 mL), precipitate was collected, washed with H_2O, and dissolved in CH_2Cl_2. The CH_2Cl_2 solution was washed with 5% aq $NaHCO_3$ and brine. The organic layer was dried over $MgSO_4$ and filtered. The solvents were evaporated, and the residue was purified with column chromatography on SiO_2 (EtOAc–hexane, 1:50) to give **spiro-FIT** (352 mg, 96%) as a white solid; mp 167.0–167.3 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 6.47 (d, 1 H, *J* = 4.7 Hz), 6.63 (d, 1 H, *J* = 7.3 Hz), 6.80 (d, 2 H, *J* = 7.3 Hz), 6.98 (dd, 1 H, *J* = 7.3, 7.7 Hz), 7.12 (dd, 2 H, *J* = 7.3, 7.7 Hz), 7.22 (d, 1 H, *J* = 4.8 Hz), 7.28 (dd, 1 H, *J* = 7.3, 7.7 Hz), 7.36 (dd, 2 H, *J* = 7.3, 7.3 Hz), 7.53 (d, 1 H, *J* = 7.3 Hz), 7.82 (d, 2 H, *J* = 7.7 Hz). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 63.5, 118.9, 120.0, 121.4, 123.7, 123.8, 125.9, 127.6, 127.7, 127.8, 128.1, 138.6, 141.7, 143.5, 146.8, 151.8, 152.0. Anal. Calcd for $C_{23}H_{14}S$: C, 85.68; H, 4.38. Found: C, 85.61; H, 4.18.
(b) Preparation of 2-Bromospiro[fluorene-9,4′-[4*H*]indeno[3,2-*b*]thiophene] (Br-spiro-FIT)
To a DMF solution (10 mL) of **spiro-FIT** (352 mg, 1.09 mmol) was added a solution of NBS (236 mg, 1.31 mmol) in DMF (10 mL) in the dark, and the mixture was stirred at r.t. for 14 h. The reaction mixture was poured into brine, extracted with EtOAc, and washed with brine. The organic layer was dried over $MgSO_4$ and filtered. The solvents were evaporated, and the residue was purified with column

chromatography on SiO_2 (EtOAc–hexane, 1:50) to give **Br-spiro-FIT** (333 mg, 76%) as a white solid; mp 183.2–183.7 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 6.48 (s, 1 H), 6.63 (d, 1 H, *J* = 7.7 Hz), 6.80 (d, 2 H, *J* = 7.3 Hz), 6.99 (dd, 1 H, *J* = 7.3, 7.7 Hz), 7.12 (dd, 2 H, *J* = 7.3, 7.3 Hz), 7.27 (dd, 1 H, *J* = 7.3, 7.7 Hz), 7.36 (dd, 2 H, *J* = 7.3, 7.7 Hz), 7.46 (d, 1 H, *J* = 7.3 Hz), 7.82 (d, 2 H, *J* = 7.7 Hz). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 64.1, 114.0, 118.9, 120.1, 123.7, 123.8, 124.5, 126.2, 127.8, 128.0, 138.3, 141.7, 143.6, 146.0, 150.5, 150.9 (one peak cannot be discriminated due to overlap with another peak). Anal. Calcd for $C_{23}H_{13}BrS$: C, 68.83; H, 3.30. Found: C, 68.59; H, 3.27.

(c) Preparation of 2,5-bis{spiro[fluorene-9,4′-[4*H*]indeno[3,2-*b*]thiophen-2-yl]}furan (3f)

Sn-spiro-FIT (245 mg, 0.400 mmol), 2,5-dibromofuran (45.1 mg, 0.200 mmol), $Pd(PPh_3)_4$ (11.6 mg, 0.0100 mmol), and toluene (2 mL) were added to a dry Schlenk flask under N_2. After the mixture was stirred at 110 °C for 12 h in the dark, the reaction mixture was cooled, and yellow precipitate was filtered. The precipitate was washed with Et_2O, dissolved in THF, and filtered by Florisil. The solvents were evaporated to give **3f** (117 mg, 82%) as a yellow solid; mp >300 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 6.39 (s, 2 H), 6.61–6.63 (m, 4 H), 6.82 (d, 4 H, *J* = 7.7 Hz), 6.97 (dd, 2 H, *J* = 6.6, 7.7 Hz), 7.12 (dd, 4 H, *J* = 6.6, 7.3 Hz), 7.28 (dd, 2 H, *J* = 6.6, 7.3 Hz), 7.37 (dd, 4 H, *J* = 6.6, 7.3 Hz), 7.48 (d, 2 H, *J* = 7.7 Hz), 7.83 (d, 4 H, *J* = 7.7 Hz). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 63.7, 107.2, 116.7, 118.8, 120.1, 123.6, 123.8, 126.1, 127.8, 127.9, 136.0, 138.4, 141.7, 142.2, 146.4, 148.5, 151.5, 152.6 (one peak cannot be discriminated due to overlap with another peak). Anal. Calcd for $C_{50}H_{28}OS_2$: C, 84.72; H, 3.98. Found: C, 84.45; H, 3.88.

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