

**Studies on Synthesis and Properties of
Heteroarene-Containing π -Conjugated Compounds
Having Spirofluorene Moieties**

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2010

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General Introduction

Recently, π -conjugated compounds have attracted considerable attention in the field of organic functional materials, such as organic light-emitting devices (OLEDs),¹ organic field-effect transistors (OFETs),² organic solar cells,³ ion sensors,⁴ and biological probes.⁵ The following compounds may be mentioned as representative compounds of this class: poly(*p*-phenylene)s, poly(*p*-phenylenevinylene)s, polyfluorenes, oligo- and polythiophenes, oligo-acenes, fullerenes, porphyrins, and so on. Among them, 9,9'-spirobifluorene derivatives have been extensively studied as potential candidates for use in organic electronic devices because of their high morphological stability and higher solubility compared with the corresponding non-spiro-linked parent compounds (Figure 1).⁶ For instance, 2,2',7,7'-tetra-(*N*-phenyl-1-naphthylamine)-9,9'-spirobifluorene (**1**) shows not only higher glass transition temperature by about fifty degrees than *N,N'*-diphenyl-*N,N'*-bis(1-naphthyl)-1,1'-biphenyl-4,4'-diamine (**α -NPB**), which is well-known hole-transport material, but also comparable hole mobility.⁷ In addition, the hole mobility of **1** does not change significantly after being stored in ambient atmosphere for three months, whereas the transistor action of **α -NPB** disappears after being stored for a few days in an ambient atmosphere probably due to the change in the film morphology. In the light of these findings, 9,9'-spirobifluorene derivatives have been successfully applied in organic solar cells,⁸ OLEDs,⁹ OFETs,^{7,10} and lasers.¹¹

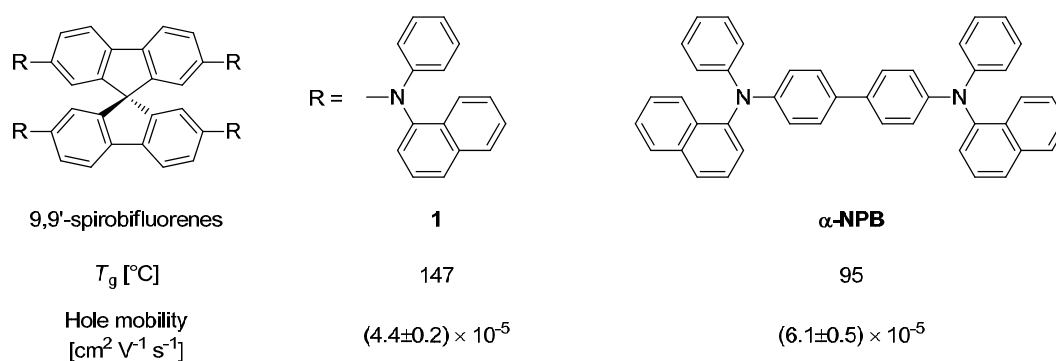


Figure 1. Glass transition temperatures (T_g) and hole mobilities of **1** and **α -NPB**.

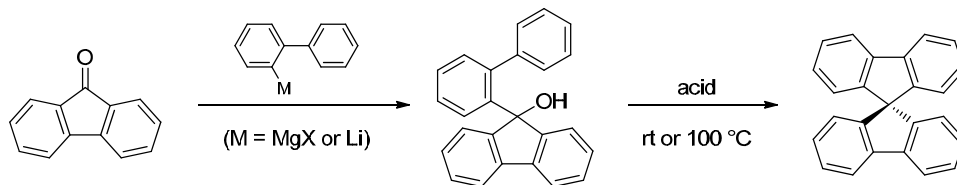
On the other hand, to modulate the electronic properties of π -conjugated compounds such as charge-transporting abilities and/or emission properties, much effort has been made to incorporate heteroarenes directly as components of the π -backbone in the last decade. Spiro compounds bearing pyridine rings^{12–15} or thiophene rings^{16–19} have so far been synthesized and applied into charge-transporting materials and phosphorescent materials.

Construction of spirofluorene moiety

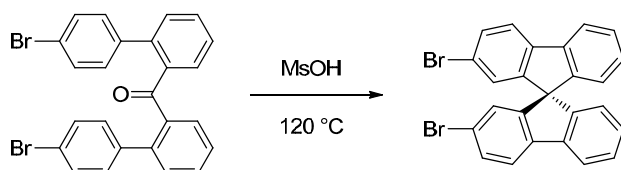
9,9'-Spirobifluorene was first synthesized by Clarkson and Gomberg in 1930 (Scheme 1).²⁰ They started from 2-iodobiphenyl, prepared the Grignard reagent, and reacted it with 9-fluorenone to give 9-(biphenyl-2-yl)-9-fluorenol. Then, acid-promoted Friedel-Crafts type intramolecular alkylation gives 9,9'-spirobifluorene. Since then, this is the standard method for the construction of spirofluorene moieties and has been used by many researchers.^{6a} Several modification, involving other organometallic reagents or acid, have also been reported.

As an alternative method, Zhou et al. have developed the intramolecular double Friedel-Crafts reaction of a benzophenone derivative using methanesulfonic acid (Scheme 2).²¹

Scheme 1

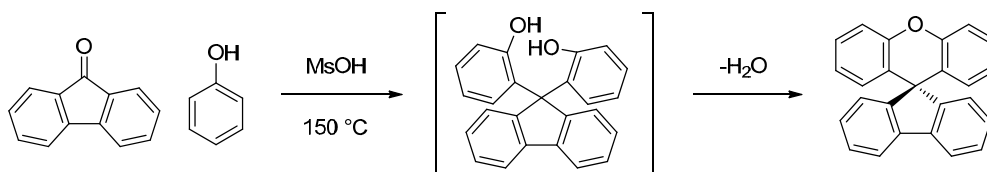


Scheme 2



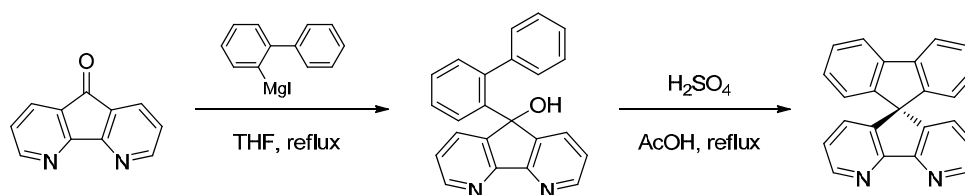
Huang et al. have reported the synthesis of spiro[fluorene-9,9'-xanthene] by the reaction of 9-fluorenone with phenol under acidic condition (Scheme 3). This reaction proceeds via the intermolecular double Friedel-Crafts reaction followed by etherification.²²

Scheme 3



Heteroarene-containing spiro compounds have been synthesized by Friedel-Crafts reaction of the corresponding alcohol precursors in a similar manner to 9,9'-spirobifluorene. As for the synthesis of 4,5-diaza-9,9'-spirobifluorene, 4,5-dazafluorenone is used instead of 9-fluorenone (Scheme 4).¹²

Scheme 4



However, as shown above, all the method of the constructing spirofluorene moieties has been limited to acid-promoted Friedel-Crafts reactions, so that the development of new and efficient synthetic route to spirofluorene compounds remains an important subject to be solved.

Spiroconjugation

It is well-known that spiro compounds, which have two perpendicular π -system linked by a common tetrahedral atom, exhibit through-space interaction, so-called spiroconjugation.²³ From both theoretical and experimental aspects, spiroconjugation has so

far been studied. In the case of spiro[4.4]nonatetraene, for example, the four π orbitals of the two butadiene units interact each other, resulting in increase of HOMO level (Figure 2).^{23a,b,e-g} Similarly in 9,9'-spirobifluorene, evidence for spiroconjugation was obtained by the photoelectron spectroscopy.^{23c}

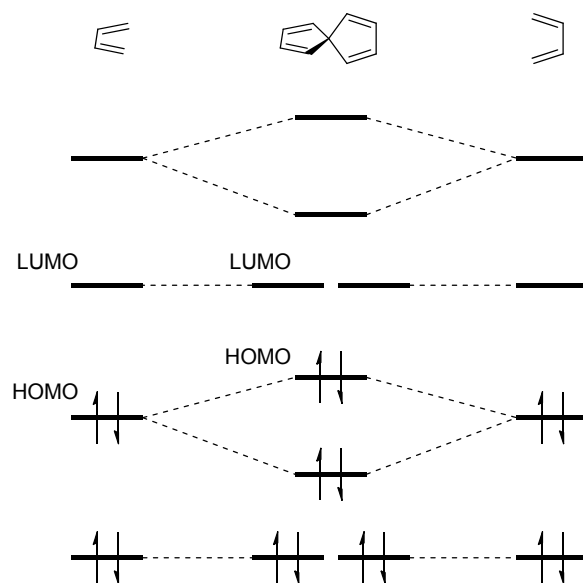


Figure 2. Orbital interaction diagram for spiro[4.4]nonatetraene.

4,5-Diaza-9,9'-spirobifluorene

In 2005, Wong and Wu reported difunctionality of 4,5-diaza-9,9'-spirobifluorene derivative **2** as both hole-transporting material and emitter for an EL device (Figure 3).¹² In

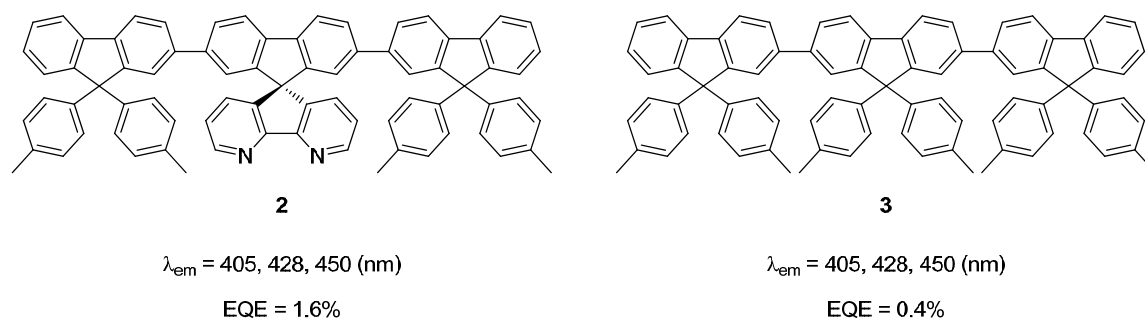


Figure 3. The emission maxima and external quantum efficiencies of compounds **2** and **3**.

most cases, amino groups should be directly introduced to π -frameworks to increase the hole-transporting ability, resulting in the changes of the emission spectra. However, the EL spectrum of **2** was similar to that of terfluorene **3**, indicating that 4,5-diazafluorene moiety could not affect the emitting property of **2**. Furthermore, 4,5-diazafluorene lowered the device voltage and increased the external quantum efficiency (EQE).

In the course of their studies, Wong et al. have demonstrated the photoinduced electron transfer (PeT) in 4,5-diaza-9,9'-spirobifluorenes having diarylamino groups, and evaluated their potential as metal ion sensors (Figure 4).¹³ The absorption spectra of compound **4** in various solvents were identical, but the emission maxima were dependent on solvent polarity. This indicated that PeT occurred from *N,N*-diphenylamino groups to 4,5-diazafluorene unit. In addition, PeT also occurred by an addition of Sr^{2+} ion, leading to significant red shift of the emission maxima and a high degree of a photoluminescence quenching.

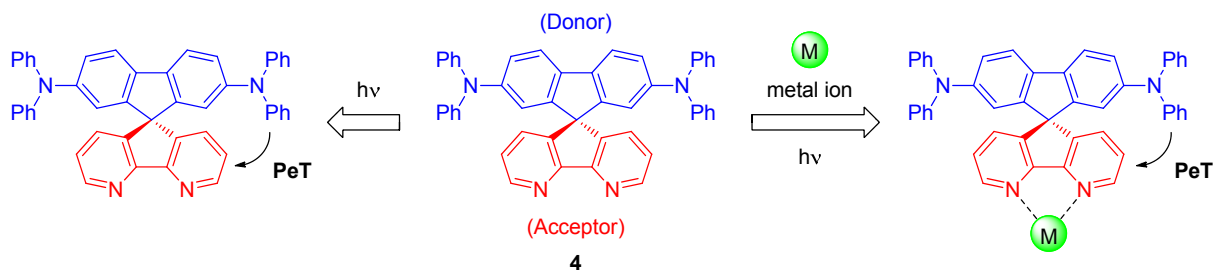


Figure 4. Photoinduced electron transfer sensor based on 4,5-diaza-9,9'-spirobifluorene.

Recently, cationic iridium complexes have been developed employing the chelation of 4,5-diazafluorene unit toward metal ions (Figure 5).¹⁴ Light-emitting electrochemical cells (LECs), which was composed of the iridium complex **5**, exhibited identical emission spectra in acetonitrile solution by virtue of sterically hindered spirofluorene unit ($\lambda_{\text{em}} = 605$ nm in MeCN; $\lambda_{\text{em}} = 593$ nm in neat film). The external quantum efficiency and power efficiency are among the highest reported for solid-state LECs, which indicates that iridium complex **5** is

an excellent candidate for highly efficient solid-state LECs.

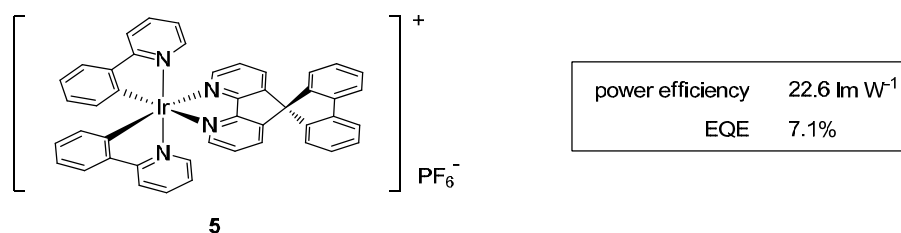


Figure 5. The external quantum efficiency and power efficiency of iridium complex **5**.

4,4'-Spiro[cyclopenta[2,1-*b*;3,4-*b'*]dithiophene] (**6**)

In 2007, Salbeck et al. reported a thiophene analog of 9,9'-spirobifluorene **6**, in which all benzene rings of 9,9'-spirobifluorene are replaced for thiophene rings and they demonstrated FET property of its derivative **7** (Figure 6).^{16a,b} In contrast to no transistor effect of 9,9'-spirobifluorene derivative **8**, **7** exhibited *p*-type transistor characteristics accompanied with lower oxidation potentials, which means that **7** forms a stable radical cation relative to **8**. Furthermore, no significant change in charge carrier mobility and ON/OFF ratios occurred during storage in ambient atmosphere for 10 months.

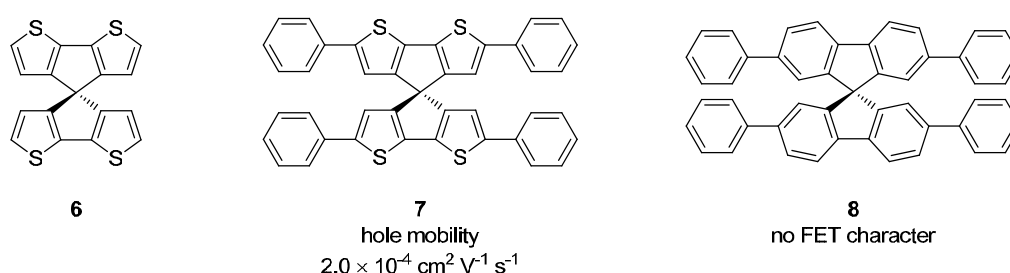


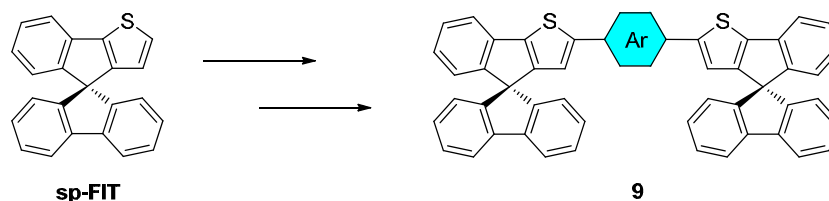
Figure 6. FET properties of spiro compounds **7** and **8**.

Outline of This Thesis

This thesis is composed of chapters 1–5. Chapter 1 describes the synthesis of a new thiophene-containing spiro compound, spiro[fluorene-9,4'-[4*H*]indeno[1,2-*b*]thiophene]

(**sp-FIT**), and the physical properties of its π -extended derivatives **9**, which were prepared using the Stille coupling reaction (Scheme 5). Compounds **9** showed intense fluorescence and extremely high thermal stability because of their highly rigid structures. Furthermore, the derivative having biphenyl linker showed intense fluorescence even in the solid state.

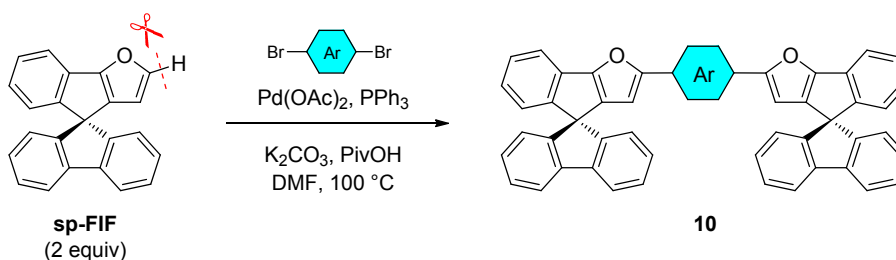
Scheme 5



There remain drawbacks of the use of highly toxic organotin species for the preparation of **9** as well as moderate or low photoluminescence quantum yields of some derivatives. Low quantum yields might be due to the heavy-atom effect of a sulfur atom. Then, chapter 2 describes the synthesis of the furan analogs of thiophene-containing π -conjugated compounds using catalytic direct C–H arylation instead of the Stille coupling reaction (Scheme 6). As expected, the resulting coupling products **10** showed intense fluorescence with higher quantum yields than thiophene analogs and extremely high thermal stability. In addition, the dimeric compound of spiro[fluorene-9,4'-[4H]indeno[1,2-*b*]furan] (**sp-FIF**) showed more intense fluorescence than its thiophene analog, even in the solid state.

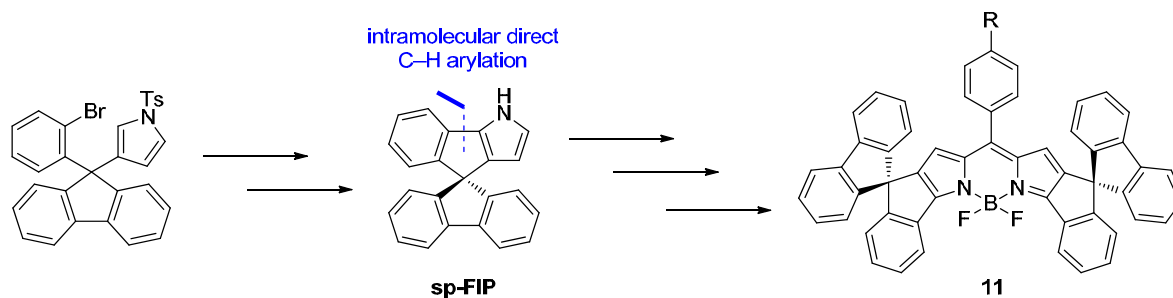
As mentioned above, the methods of the construction of spirofluorene moieties have

Scheme 6



been limited to Friedel-Crafts type reactions. This motivated the author to develop a new method of the construction of a spirofluorene moiety involving pyrrole. Therefore, chapter 3 describes the synthesis of a pyrrole-containing spiro compound 1'*H*-spiro[fluorene-9,4'-indeno[1,2-*b*]pyrrole] (**sp-FIP**) using catalytic intramolecular direct C–H arylation of a pyrrole ring (Scheme 7). In addition, its transformation to structurally constrained boron-dipyrromethene (abbreviated as BODIPY) dyes **11** was demonstrated. These BODIPY dyes exhibited intense bathochromic fluorescence around 670 nm because of their rigid spirofluorene structures. Among them, *N,N*-dimethylaminophenyl-substituted BODIPY dye at 8-position showed solvent-dependent ON/OFF switching of fluorescence.

Scheme 7



In chapter 4, the author describes the synthesis of structurally constrained BODIPY dyes **12** having electron-donating groups at 3,5-positions (Figure 7). The method described in chapter 3 allowed him to prepare **sp-FIP** derivatives having the electron-donating groups, such as MeO or Me₂N. The electron-donating groups caused effective shifts of the emission band of BODIPY dyes to longer-wavelength regions. In particular, the BODIPY dye having Me₂N groups exhibited its emission maxima at near-IR region (741 nm in cyclohexane) and solvatochromism due to intramolecular charge transfer (ICT) process. Furthermore, the ICT process was possible to be modulated by the protonation of amino groups and pH-dependent reversible spectrum changes of BODIPY dye were observed with an addition of trifluoroacetic acid (TFA) and subsequent addition of *i*-Pr₂NEt (Figure 7).

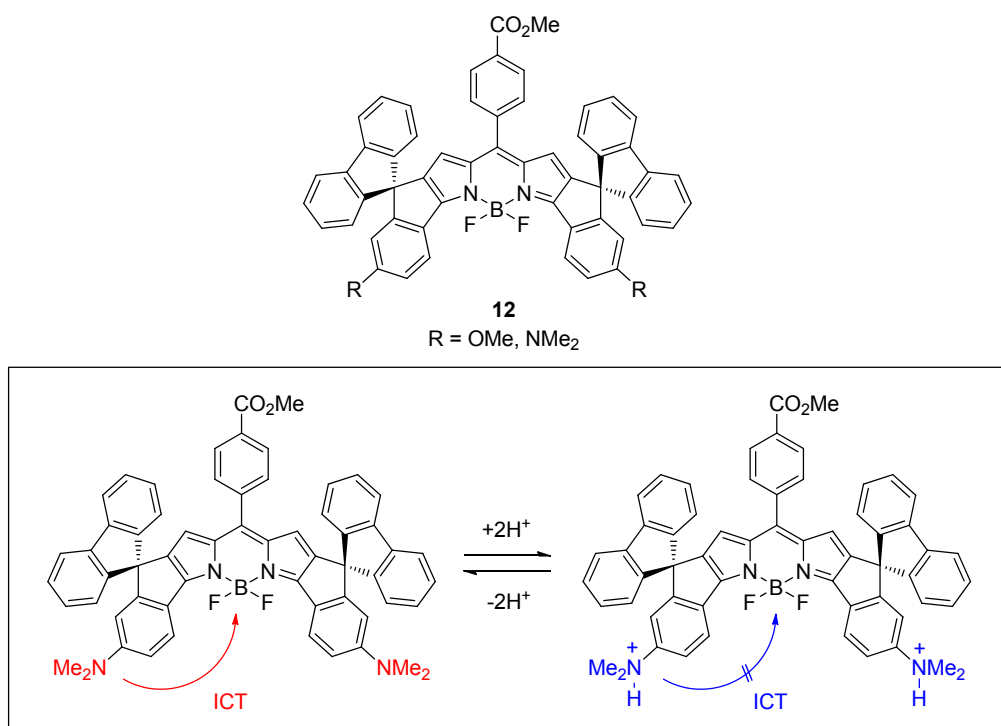


Figure 7. The electron-donor-substituted structurally constrained BODIPY dyes.

The author has dealt with thiophene-, furan-, and pyrrole-containing spiro compounds, **sp-FIT**, **sp-FIF**, and **sp-FIP**, in chapters 1–3. In chapter 5, the author describes the synthesis and structures of ladder-type heteroarene-fused dispiro compounds (Figure 8). Their structures were unambiguously determined by X-ray crystallography. As a result, it was found that two fluorene moieties of thiophene compound **dsp-DIT** were completely over-

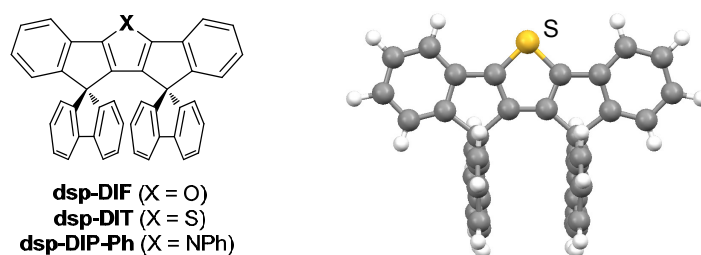


Figure 8. Heteroarene-fused dispiro compounds (left) and the X-ray crystal structure of **dsp-DIT** (right).

lapped with the distance between 3.859(6) Å and 3.603(5) Å. Furthermore, these three dispiro compounds showed blue fluorescence with moderate quantum yields.

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Chapter 1

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

Abstract

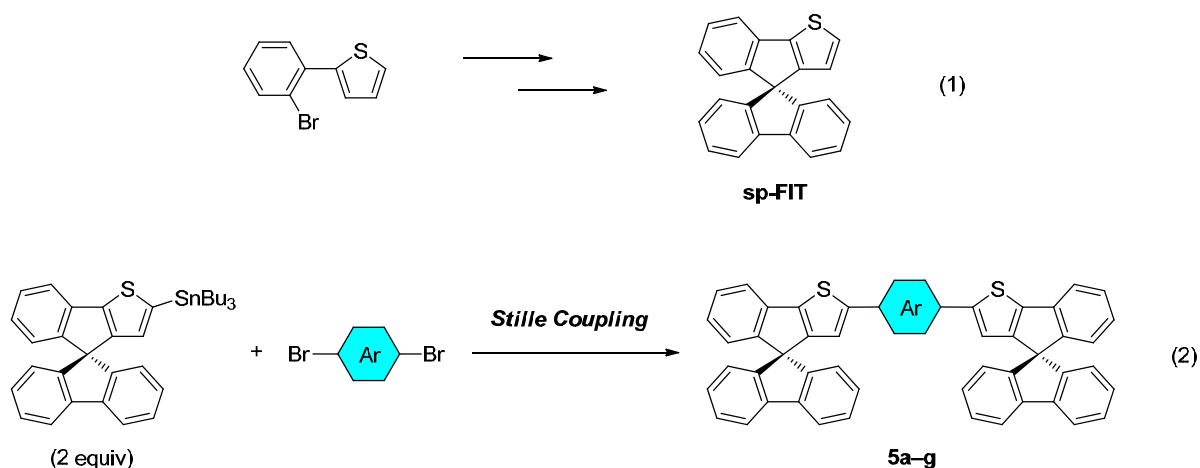
A new thiophene-containing spiro compound, spiro[fluorene-9,4'-[4*H*]-indeno[1,2-*b*]thiophene] (**sp-FIT**), was synthesized. Functionalizations at 2'-position of **sp-FIT**, such as bromination and lithiation followed by quenching with stannyl chloride, smoothly proceeded to afford corresponding derivatives in good yields. The stannyl **sp-FIT** can be employed to the Stille coupling with several dibromoarenes, producing fluorescent coupling products in high yields. Photophysical, electrochemical, and thermal properties of these compounds were investigated. Among them, the derivative having biphenyl linker showed extremely high thermal stability and intense fluorescence even in the solid state.

Introduction

Recently, π -conjugated compounds have received considerable attention in the field of organic electronics, such as organic light-emitting diodes (OLEDs), photovoltaic cell, and organic field-effect transistors (OFETs). 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 OFETs and OLEDs. These oligomers show reversible and higher oxidation potentials than the all-thiophene analogs 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 OFETs, but another type of method to increase the solubility of the materials for OLEDs 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, there are few reports on spiro compounds containing thiophene rings.⁵

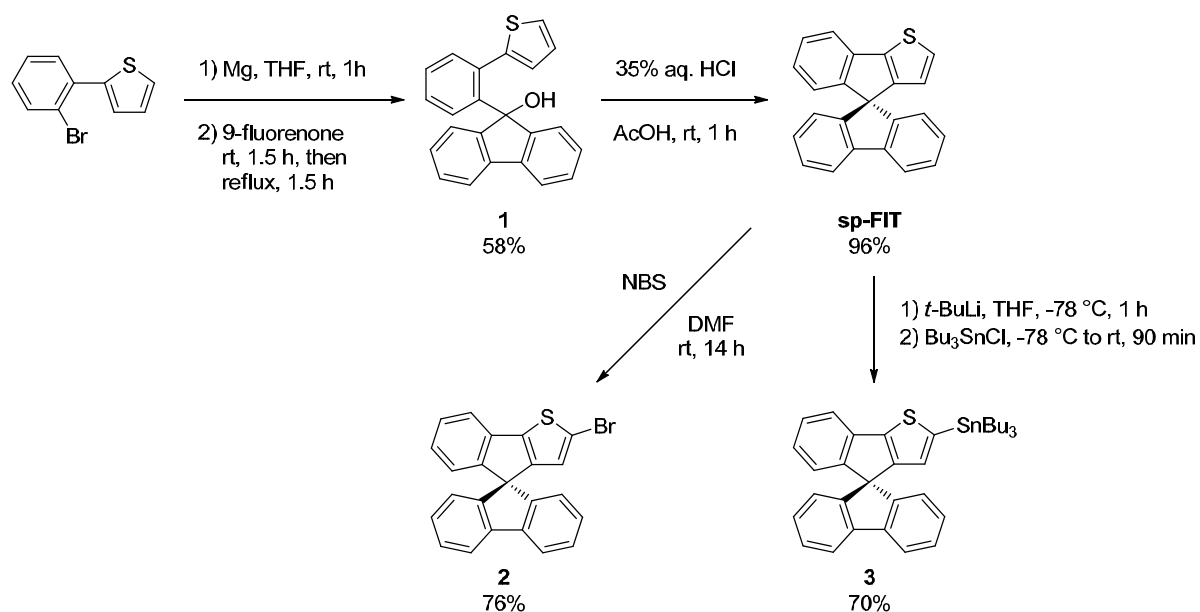
In this chapter, the author describes the synthesis and properties of the thiophene-containing spiro compounds, spiro[fluorene-9,4'-[4*H*]indeno[1,2-*b*]thiophene] (**sp-FIT**) and bis(sp-FIT)arenes **5a–g** (eqs 1 and 2). The optical and electrochemical characteristics of **5a–g** are easily tunable by changing the linking arenes.



Results and Discussion

Scheme 1 depicts the synthesis of **sp-FIT** and its derivatives.^{6a,b} The reaction of 9-fluorenone with the Grignard reagent derived from 1-bromo-2-thienylbenzene afforded

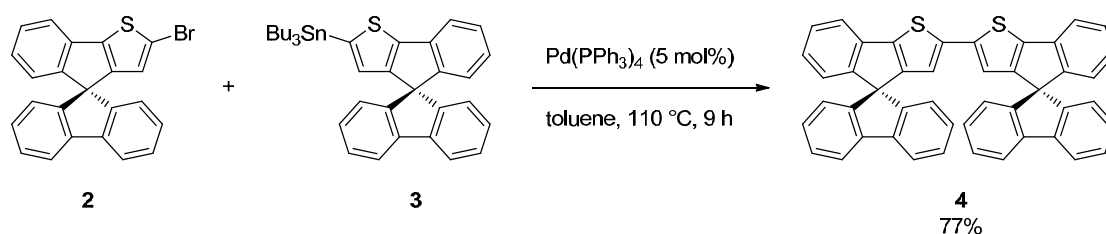
Scheme 1



alcohol **1** in 58% yield. An acid-promoted intramolecular alkylation furnished a thiophene-containing spiro compound **sp-FIT** in 96% yield. Bromination of **sp-FIT** with NBS or lithiation of **sp-FIT** followed by reaction with Bu_3SnCl produced the bromo derivative **2** (76%) or **3** (70%), respectively.

2,2'-Bispiro[fluorene-9,4'-[4*H*]indeno[1,2-*b*]thiophene] (**4**) was synthesized by the Stille coupling reaction of **2** with **3** (Scheme 2). The Stille coupling reaction was also employed for the synthesis of bis(sp-FIT)arenes **5a–g** using several dibromoarenes and two equivalents

Scheme 2

Table 1. Synthesis of **5a–g** using the Stille Coupling

	3 (0.400 mmol)	Br-Ar-Br (0.200 mmol)		
entry	Br-Ar-Br	time [h]	product	yield [%]
1		14	5a	65
2		14	5b	76
3		12	5c	68
4		10	5d	74
5		12	5e	82
6		13	5f	83
7		40	5g	85

of **3** (Table 1).^{6c} Several heteroaromatic rings (entries 4–7) as well as aromatic hydrocarbons (entries 1–3) were successfully introduced. 6,6'-Dibromo-2,2'-bipyridine reacted cleanly to produce the coupling product **5g**, although prolonged reaction time was necessary (entry 7).

As shown in Figure 1, the cyclic voltammogram (CV) for **sp-FIT** in CH₂Cl₂ containing 0.10 M Bu₄NPF₆ showed an irreversible oxidation peak, while that of **4** showed reversible waves. An irreversible peak for **sp-FIT** might be due to rapid oxidative coupling of the radical cation generated in situ on the electrode. Indeed, new oxidation peaks ($E_{1/2 \text{ oxd}} = 0.52$ V and 0.72 V) appears after the second cycle. Oxidation waves of compounds **5a–e** were reversible, while those of compounds **5f** and **5g** were irreversible (Table 2). In comparison with compound **4**, the first oxidation potentials for **5a** and **5b** were more positive with increasing length of the linkers. On the other hand, the second oxidation potentials were less positive. These data suggest that the coulombic repulsion would decrease because of the long distance between both thiophene rings.⁶ Oxidation potentials are also affected by the electronic nature of the linkers. Incorporation of electron-rich heteroarenes, such as thiophene and furan, provides higher HOMO levels (**5d** and **5e**). In contrast, as in the cases of **5f** and **5g**, electron-deficient arenes, such as pyridine and bipyridine, lower their HOMO levels.

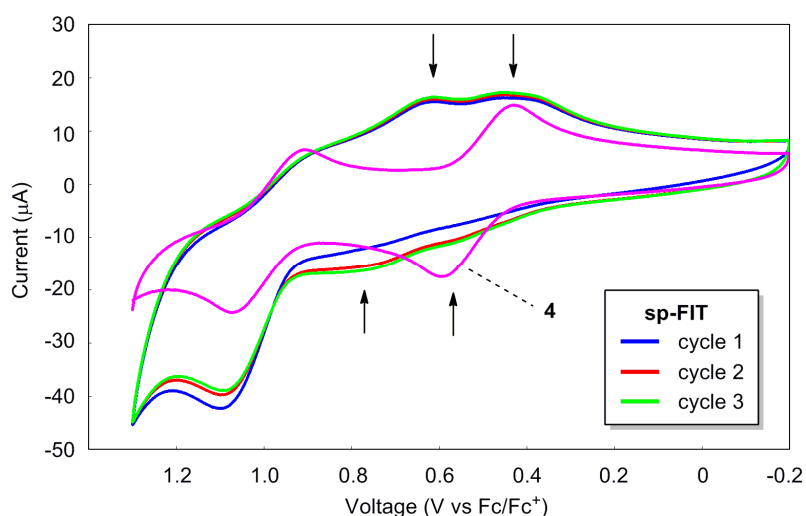


Figure 1. The cyclic voltammograms of **sp-FIT** and **4** in CH₂Cl₂.

Similarly to the results of the CV, the electronic nature of the linkers affects the absorption and emission maxima (Figure 2). Both maxima of **5d** were red shifted relative to **5a**, while those of **5f** were blue shifted. Compared with **4**, the absorption maxima of **5a–c** with aromatic hydrocarbons as the linker were observed at almost the same wavelength, although **5b** exhibited a blue shift because of the slightly twisted biphenyl ring (Table 2). All bis(sp-FIT)arenes showed high quantum yields, and for **4** and **5a,b**, the values of Φ_F are enhanced as the π -framework is extended. Notably, even in the solid state, **5b** shows an intense fluorescence (Table 3).

Table 2. Photophysical, Electrochemical, and Thermal Properties of **4** and **5a–g**

	λ_{abs} (nm) ^a	ε ($\times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$)	λ_{em} (nm) ^b	Φ_F^c	$E_{1/2 \text{ oxd}}$ (V) ^d	T_g (°C) ^e	T_d (°C) ^f
sp-FIT	300, 311	1.53	338, 348	n.d. ^g	0.96	n.d. ^g	n.d. ^g
4	405	3.54	444, 471	0.29	0.50, 0.96	186	391
5a	403	5.49	441, 469	0.78	0.59, 0.84	201	438
5b	389	6.65	436, 462	0.83	0.68, 0.78	209	497
5c	404	6.69	440, 468	0.84	0.57, 0.74	202	398
5d	434	4.41	485, 519	0.29	0.41, 0.72	179	435
5e	425	4.22	465, 498	0.57	0.34, 0.69	160	419
5f	352, 382	3.83, 3.75	412, 433	0.61	0.82 ^h	214	442
5g	365, 379	5.83, 6.00	411, 431	0.55	0.93 ^h	n.d. ^g	456

^a $c = 1.00 \times 10^{-5} \text{ M}$ (in THF). ^b $c = 1.00 \times 10^{-7} \text{ M}$ (in THF). Excited at absorption maxima. ^c Determined by the calibrated integrating sphere system. ^d In CH_2Cl_2 containing 0.10 M Bu_4NPF_6 , V vs Fc/Fc^+ at 100 mV s^{-1} . ^e Glass transition temperature measured by differential scanning calorimetry (DSC) measurement. ^f Decomposition temperature (5% weight loss) obtained from thermogravimetric analysis (TGA). ^g Not determined. ^h Irreversible.

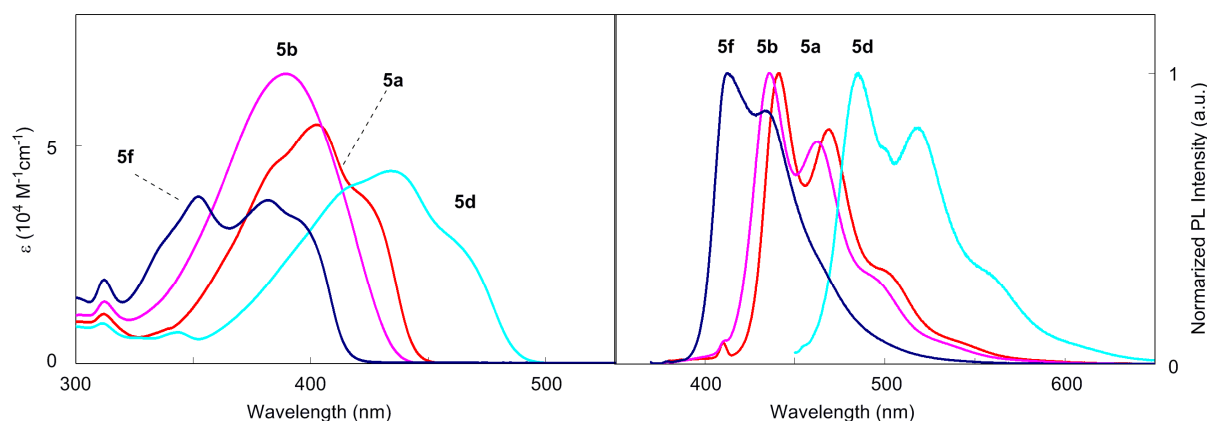


Figure 2. The UV-vis absorption and fluorescence spectra of **5a,b,d,f** in THF.

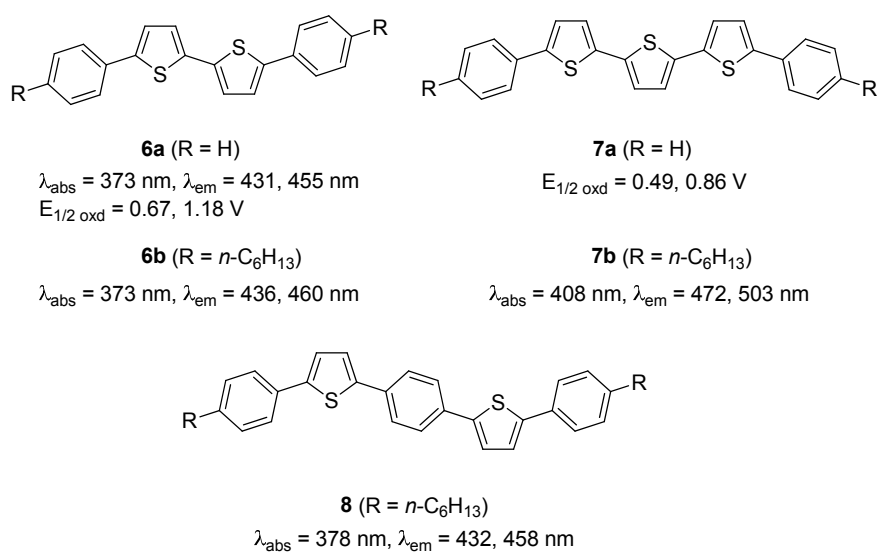
Table 3. Photophysical Properties of **4** and **5a–g** in the solid state

	λ_{ex} (nm) ^a	λ_{em} (nm)	Φ_{F} ^b
4	405	530, 578	0.069
5a	403	496, 525, 562	0.259
5b	389	484, 510, 548	0.585
5c	404	488, 523	0.034
5d	434	563	0.071
5e	425	540	0.037
5f	382	454, 501, 545, 582	0.150
5g	379	430	0.160

^a Excited at the absorption maximum in THF solution.^b Determined by the calibrated integrating sphere system.

The thermal properties of prepared spiro compounds were investigated by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). It is noteworthy that they showed extremely high T_g and T_d up to 214 °C and 497 °C, respectively (Table 2), which are great advantage for practical application in organic electronics devices.

Some similar compounds without a spiro linkage have been reported by other groups (Figure 3).^{2a,7} Both in the absorption and emission spectra, the maximum wavelengths of

**Figure 3.** Photophysical and electrochemical properties of thiophene/phenylene co-oligomers.

spiro compounds **4** and **5a,d** are bathochromic shifted compared with those of similar compounds **6–8** without a spiro linkage. In addition, spiro compounds have lower oxidation potentials than non-spiro 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 conclusion, a new thiophene-containing spiro compound **sp-FIT** has been synthesized. Stille coupling of **3** with **2** or dibromoarenes provided π -extended **4** or bis(sp-FIT)arenes **5a–g**. All of the coupling products showed intense photoluminescence and extremely high thermal stability. Furthermore, **5b** showed intense fluorescence even in the solid state. [4*H*]Indeno[1,2-*b*]thiophenes containing the spirofluorene structure as a building block are expected to find applications in organic functional materials.

Experimental Section

General. Unless otherwise specified, all reagents were purchased from a chemical supplier and used without further purification. Tetrahydrofuran (THF) was distilled over benzophenone ketyl under nitrogen atmosphere. Melting points are uncorrected. ^1H and ^{13}C spectra were recorded on a JEOL AL-300 (300 MHz for ^1H , and 75.5 MHz for ^{13}C) instrument. IR spectra were obtained on a JASCO 460 plus FT/IR spectrometer. Mass spectra were measured with a JEOL JMS-SX102A. Analytical thin-layer chromatography (TLC) was performed on Merck 60F254 silica plates and visualized by UV light. Column chromatography was carried out on Silicycle SilicaFlash F60 60-63 μm (230-400 mesh) silica gel. UV-visible absorption spectra were recorded on a JASCO V-570 UV-vis-NIR spectrometer. Emission spectra were measured with a Jobin Yvon-Horiba FluoroMax-3. Degassed spectral grade solvents were used for the measurements. Absolute fluorescence quantum yields were determined by the calibrated integrating sphere system. Cyclic voltammetry (CV) was performed on a BAS ALS 610C-S electrochemical analyzer. The

CV cell consisted of a glassy carbon electrode, a Pt wire counter electrode, and a Ag/AgNO₃ reference electrode. The measurement was carried out under argon atmosphere using CH₂Cl₂ solutions of samples (1 mM) and 0.1 M tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) as a supporting electrolyte with a scan rate of 100 mV s⁻¹. The redox potentials were calibrated with ferrocene as an internal standard. Differential scanning calorimetry (DSC) was performed on a Rigaku Thermo plus EVO DSC 8230 under nitrogen atmosphere at a heating rate of 20 °C min⁻¹. Thermogravimetric analysis (TGA) was carried out on a Rigaku TG-8120 under nitrogen atmosphere at a heating rate of 10 °C min⁻¹.

9-(2-(2-Thienyl)phenyl)fluoren-9-ol (1): A solution of 2-(2-bromophenyl)thiophene⁸ (18.0 g, 75.4 mmol) in THF (80 mL) was added dropwise to Mg (1.95 g, 80.1 mmol). The mixture was stirred for 1 h at room temperature. To the solution, 9-fluorenone (11.6 g, 63.0 mmol) in THF (75 mL) was added over 15 min and stirred at room temperature for 90 min. Then, the reaction mixture was stirred at 65 °C for 90 min. The reaction mixture was quenched with saturated aqueous solution of NH₄Cl (50 mL) and extracted with EtOAc (3 × 30 mL). The organic layers were combined, washed with brine (3 × 30 mL), and dried over MgSO₄. The solvents were removed under reduced pressure, and the residue was purified with column chromatography on SiO₂ with EtOAc/hexane (v/v = 1/20) as an eluent to give **1** (12.5 g, 58%) as a white solid; mp 144.0–144.2 °C. IR (KBr) 730, 766, 911, 1022, 1158, 1447, 2923, 3060, 3545, cm⁻¹. ¹H NMR (300 MHz, CDCl₃): δ = 2.27 (s, 1H), 5.41 (d, *J* = 2.9 Hz, 1H), 6.30 (dd, *J* = 3.3, 3.7 Hz, 1H), 6.81 (d, *J* = 5.2 Hz, 1H), 7.07 (d, *J* = 7.7 Hz, 1H), 7.19–7.32 (m, 9H), 7.55 (dd, *J* = 7.7, 7.7 Hz, 1H), 8.47 (d, *J* = 8.1 Hz, 1H). ¹³C NMR (75.5 MHz, CDCl₃): δ = 82.4, 120.1, 124.2, 124.9, 125.5, 126.8, 126.9, 128.07, 128.13, 128.8, 132.8, 133.3, 140.2, 140.6, 141.6, 150.7 (two peaks are overlapped). HRMS (FAB): calcd for C₂₃H₁₆OS (M⁺), 340.0922, Found 340.0916.

Spiro[fluorene-9,4'-[4H]indeno[1,2-*b*]thiophene] (sp-FIT): To a solution of **1** (390 mg, 1.14 mmol) in AcOH (30 mL) was added 35% aqueous solution of HCl (1 mL), and the solution was stirred at room temperature for 1 h. After an addition of water (30 mL), precipitate was collected, washed with water, and dissolved in CH₂Cl₂. The CH₂Cl₂ solution was washed with saturated aqueous solution of NaHCO₃ (2 × 20 mL) and brine (2 × 20 mL), and dried over MgSO₄. The solvents were removed under reduced pressure, and the residue was purified with column chromatography on SiO₂ with EtOAc/hexane (v/v = 1/50) as an eluent to give **sp-FIT** (352 mg, 96%) as a white solid; mp 167.0–167.3 °C. IR (KBr) 730, 766, 911, 1022, 1158, 1447, 2923, 3060, 3545 cm⁻¹. ¹H NMR (300 MHz, CDCl₃): δ = 6.47 (d, *J* = 4.7 Hz, 1H), 6.63 (d, *J* = 7.3 Hz, 1H), 6.80 (d, *J* = 7.3 Hz, 2H), 6.98 (dd, *J* = 7.3, 7.7 Hz, 1H), 7.12 (dd, *J* = 7.3, 7.7 Hz, 2H), 7.22 (d, *J* = 4.8 Hz, 1H), 7.28 (dd, *J* = 7.3, 7.7 Hz, 1H), 7.36 (dd, *J* = 7.3, 7.3 Hz, 2H), 7.53 (d, *J* = 7.3 Hz, 1H), 7.82 (d, *J* = 7.7 Hz, 2H). ¹³C NMR (75.5 MHz, CDCl₃): 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 C₂₃H₁₄S: C, 85.68; H, 4.38. Found: C, 85.61; H, 4.18.

2'-Bromospiro[fluorene-9,4'-[4H]indeno[1,2-*b*]thiophene] (2): To a solution of **sp-FIT** (352 mg, 1.09 mmol) in DMF (10 mL) was added NBS (236 mg, 1.31 mmol), and the solution was stirred at room temperature for 14 h. The reaction mixture was quenched with saturated aqueous solution of NaHCO₃ (20 mL) and extracted with EtOAc (3 × 20 mL). The organic layers were combined, washed with brine (2 × 20 mL), and dried over MgSO₄. The solvents were removed under reduced pressure, and the residue was purified with column chromatography on SiO₂ with EtOAc/hexane (v/v = 1/50) as an eluent to give **2** (333 mg, 76%) as a white solid; mp 183.2–183.7 °C. IR (KBr) 680, 741, 827, 906, 955, 1281, 1447, 1600, 2927, 3061 cm⁻¹. ¹H NMR (300 MHz, CDCl₃): δ = 6.48 (s, 1H), 6.63 (d, *J* = 7.7 Hz,

1H), 6.80 (d, $J = 7.3$ Hz, 2H), 6.99 (dd, $J = 7.3, 7.7$ Hz, 1H), 7.12 (dd, $J = 7.3, 7.3$ Hz, 2H), 7.27 (dd, $J = 7.3, 7.7$ Hz, 1H), 7.36 (dd, $J = 7.3, 7.7$ Hz, 2H), 7.46 (d, $J = 7.3$ Hz, 1H), 7.82 (d, $J = 7.7$ Hz, 2H). ^{13}C NMR (75.5 MHz, CDCl_3): $\delta = 64.1, 114.0, 118.9, 120.1, 123.7, 123.8, 124.5, 126.2, 127.8, 128.0, 138.3, 141.7, 143.6, 146.0, 150.5, 150.9$ (two peaks are overlapped). Anal. Calcd for $\text{C}_{23}\text{H}_{13}\text{BrS}$: C, 68.83; H, 3.30. Found: C, 68.59; H, 3.27.

2'-(Tri-*n*-butylstannyl)spiro[fluorene-9,4'-[4*H*]indeno[1,2-*b*]thiophene] (3): To a solution of **sp-FIT** (3.22 g, 10.0 mmol) in dry THF (150 mL) was added *t*-BuLi in pentane (1.5 M, 10.0 mL, 15.0 mmol) at -78°C under N_2 atmosphere. After stirring for 1 h, Bu_3SnCl (4.17 mL, 15.0 mmol) was added and the reaction mixture was stirred at -78°C for 90 min. The reaction mixture was filtered through a short silica gel pad, washed with brine (2×20 mL), and dried over MgSO_4 . The solvents were removed under reduced pressure, and the residue was purified with GPC (CHCl_3) to give **3** (4.28 g, 70%) as a pale brown solid; mp $94.0\text{--}95.0^\circ\text{C}$. IR (KBr) 742, 754, 907, 1280, 1446, 1460, 1600, 2849, 2425, 2955 cm^{-1} . ^1H NMR (300 MHz, CDCl_3): $\delta = 0.84$ (t, $J = 7.3$ Hz, 9H), 1.02–1.06 (m, 6H), 1.25–1.30 (m, 6H), 1.48–1.51 (m, 6H), 6.48 (s, 1H), 6.58 (d, $J = 7.3$ Hz, 1H), 6.81 (d, $J = 7.8$ Hz, 2H), 6.91 (dd, $J = 7.3, 7.3$ Hz, 1H), 7.10 (dd, $J = 7.3, 7.8$ Hz, 2H), 7.23 (dd, $J = 7.3, 7.8$ Hz, 1H), 7.34 (dd, $J = 7.3, 7.8$ Hz, 2H), 7.50 (d, $J = 7.3$ Hz, 1H), 7.81 (d, $J = 7.3$ Hz, 2H). ^{13}C NMR (75.5 MHz, CDCl_3): $\delta = 10.9, 13.6, 27.2, 28.9, 63.0, 119.0, 120.0, 123.7, 123.9, 125.6, 127.5, 127.6, 127.7, 129.2, 138.5, 141.3, 141.7, 147.3, 149.4, 152.2, 153.7$. HRMS (FAB): calcd for $\text{C}_{35}\text{H}_{41}\text{SSn}$ ($\text{M}+\text{H}^+$), 613.1957, Found 613.1964.

A Typical Procedure for Synthesis of 4 and 5: A flame dried Schlenk flask was charged with **3** (245 mg, 0.400 mmol), aryl dibromides (0.200 mmol), $\text{Pd}(\text{PPh}_3)_4$ (11.6 mg, 0.0100 mmol), and dry toluene (2 mL) under nitrogen atmosphere. The solution was stirred at

110 °C for 12 h. After stirring at 110 °C for 12 h, the reaction mixture was cooled, and yellow precipitate was filtered. The precipitate was washed with Et₂O, dissolved in THF, and filtered through Florisil to afford the coupling product **4** or **5**.

2,2'-Bispiro[fluorene-9,4'-[4*H*]indeno[1,2-*b*]thiophene] (4): **2** (0.2 mmol) was used instead of aryl dibromides. A yellow solid (77% yield); mp >300 °C. IR (KBr) 683, 741, 755, 1156, 1281, 1446, 1600, 2954, 3061 cm⁻¹. ¹H NMR (300 MHz, CDCl₃): δ = 6.50 (s, 2H), 6.61 (d, *J* = 7.7 Hz, 2H), 6.79 (d, *J* = 7.7 Hz, 4H), 6.96 (dd, *J* = 7.3, 7.7 Hz, 2H), 7.11 (dd, *J* = 7.3, 7.7 Hz, 4H), 7.23–7.28(m, 2H), 7.35, (dd, *J* = 7.7, 7.7 Hz, 4H), 7.44 (d, *J* = 7.7 Hz, 2H), 7.80 (d, *J* = 7.7 Hz, 4H). ¹³C NMR (75.5 MHz, CDCl₃) : δ 63.7, 117.5, 118.9, 120.1, 123.6, 123.8, 126.0, 127.8, 128.0, 138.5, 141.0, 141.7, 141.9, 146.4, 151.3, 152.7 (two peaks are overlapped). HRMS (FAB): calcd for C₄₆H₂₆S₂ (M⁺), 642.1476, Found 642.1484.

1,4-Bis(spiro[fluorene-9,4'-[4*H*]indeno[1,2-*b*]thien-2-yl])benzene (5a): A yellow solid (65% yield); mp >300 °C. IR (KBr) 744, 819, 1106, 1446, 2919, 3058 cm⁻¹. ¹H NMR (300 MHz, CDCl₃): δ = 6.63 (d, *J* = 7.3 Hz, 2H), 6.71 (s, 2H), 6.85 (d, *J* = 7.7 Hz, 4H), 6.98 (dd, *J* = 7.3, 7.7 Hz, 2H), 7.13 (dd, *J* = 7.3, 7.3 Hz, 4H), 7.29 (dd, *J* = 7.3, 7.9 Hz, 2H), 7.37 (dd, *J* = 7.3, 7.9 Hz, 4H), 7.42 (s, 4H), 7.52 (d, *J* = 7.9 Hz, 2H), 7.83 (d, *J* = 7.3 Hz, 4H). ¹³C NMR (75.5 MHz, CDCl₃): δ = 63.9, 117.3, 118.9, 120.1, 123.6, 123.9, 125.5, 126.0, 127.79, 127.82, 127.9, 133.7, 138.7, 141.7, 142.6, 146.6, 147.1, 151.4, 152.9. HRMS (FAB): calcd for C₅₂H₃₁S₂ (M+H⁺), 719.1867, Found 719.1874.

4,4'-Bis(spiro[fluorene-9,4'-[4*H*]indeno[1,2-*b*]thien-2-yl])biphenyl (5b): A yellow solid (76% yield); mp >300 °C. IR (KBr) 741, 817, 1283, 1446, 1493, 1600, 2919, 3064 cm⁻¹. ¹H NMR (300 MHz, CDCl₃): δ = 6.64 (d, *J* = 7.3 Hz, 2H), 6.76 (s, 2H), 6.87 (d, *J* = 7.0 Hz, 4H),

6.99 (dd, $J = 7.0, 7.7$ Hz, 2H), 7.14 (dd, $J = 7.3, 7.7$ Hz, 4H), 7.30 (dd, $J = 7.3, 7.7$ Hz, 2H), 7.38 (dd, $J = 7.3, 7.7$ Hz, 4H), 7.51–7.57 (m, 10H), 7.85 (d, $J = 8.0$ Hz, 4H). ^{13}C NMR analysis was not possible because of the very limited solubility. HRMS (FAB): calcd for $\text{C}_{58}\text{H}_{34}\text{S}_2$ (M^+), 794.2102, Found 794.2111.

9,9-Dimethyl-2,7-bis(spiro[fluorene-9,4'-[4H]indeno[1,2-*b*]thien-2-yl])fluorene (5c): A yellow solid (68% yield); mp >300 °C. IR (KBr) 683, 741, 818, 1282, 1459, 2960, 3056 cm^{-1} . ^1H NMR (300 MHz, CDCl_3): $\delta = 1.41$ (s, 6H), 6.64 (d, $J = 7.3$ Hz, 2H), 6.78 (s, 2H), 6.88 (d, $J = 7.0$ Hz, 4H), 6.99 (dd, $J = 6.6, 7.7$ Hz, 2H), 7.15 (dd, $J = 7.3, 7.3$ Hz, 4H), 7.30 (dd, $J = 6.6, 7.3$ Hz, 2H), 7.39 (dd, $J = 7.3, 8.0$ Hz, 4H), 7.48–7.60 (m, 8H), 7.86 (d, $J = 7.3$ Hz, 4H). ^{13}C NMR (75.5 MHz, CDCl_3): $\delta = 27.1, 46.9, 63.9, 117.2, 118.9, 119.4, 120.1, 120.3, 123.6, 124.0, 124.6, 126.0, 127.8, 127.86, 127.93, 133.9, 138.2, 138.8, 141.8, 142.3, 146.7, 148.3, 151.4, 152.9, 154.5$. HRMS (FAB): calcd for $\text{C}_{61}\text{H}_{39}\text{S}_2$ ($\text{M}+\text{H}^+$), 835.2493, Found 835.2503.

2,5-Bis(spiro[fluorene-9,4'-[4H]indeno[1,2-*b*]thien-2-yl])thiophene (5d): An yellow solid (74% yield); mp >300 °C. IR (KBr) 683, 743, 776, 1446, 1597, 2924, 3049 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): $\delta = 6.51$ (s, 2H), 6.61 (d, $J = 7.3$ Hz, 2H), 6.84 (d, $J = 7.3$ Hz, 4H), 6.96 (s, 2H), 6.99 (dd, $J = 6.3, 7.8$ Hz, 2H), 7.13 (dd, $J = 6.8, 7.3$ Hz, 4H), 7.28 (dd, $J = 6.3, 7.8$ Hz, 2H), 7.37 (dd, $J = 6.3, 7.4$ Hz, 4H), 7.48 (d, $J = 7.3$ Hz, 2H), 7.83 (d, $J = 7.8$ Hz, 4H). ^{13}C NMR analysis was not possible because of the very limited solubility. HRMS (FAB): calcd for $\text{C}_{50}\text{H}_{29}\text{S}_3$ ($\text{M}+\text{H}^+$), 725.1431, Found 725.1438.

2,5-Bis(spiro[fluorene-9,4'-[4H]indeno[1,2-*b*]thien-2-yl])furan (5e): A yellow solid (82% yield); mp >300 °C. IR (KBr) 681, 743, 791, 1020, 1284, 1446, 1600, 2924, 3058 cm^{-1} . ^1H NMR (300 MHz, CDCl_3): $\delta = 6.39$ (s, 2H), 6.61–6.63 (m, 4H), 6.82 (d, $J = 7.7$ Hz, 4H),

6.97 (dd, $J = 6.6, 7.7$ Hz, 2H), 7.12 (dd, $J = 6.6, 7.3$ Hz, 4H), 7.28 (dd, $J = 6.6, 7.3$ Hz, 2H), 7.37 (dd, $J = 6.6, 7.3$ Hz, 4H), 7.48 (d, $J = 7.7$ Hz, 2H), 7.83 (d, $J = 7.7$ Hz, 4H). ^{13}C NMR (75.5 MHz, CDCl_3): $\delta = 63.7, 107.2, 116.7, 118.8, 120.1, 123.6, 123.8, 126.1, 127.8, 127.9, 136.0, 138.4, 141.7, 142.2, 146.4, 148.5, 151.5, 152.6$ (two peaks are overlapped). Anal. Calcd for $\text{C}_{50}\text{H}_{28}\text{OS}_2$: C, 84.72; H, 3.98. Found: C, 84.45; H, 3.88.

2,6-Bis(spiro[fluorene-9,4'-[4H]indeno[1,2-*b*]thien-2-yl])pyridine (5f): A white solid (83% yield); mp >300 °C. IR (KBr) 681, 745, 796, 1283, 1446, 1561, 2924, 3058 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): $\delta = 6.66$ (d, $J = 7.8$ Hz, 2H), 6.87 (d, $J = 7.8$ Hz, 4H), 6.97 (s, 2H), 7.03 (dd, $J = 7.3$ Hz, 2H), 7.15 (dd, $J = 7.3, 7.8$ Hz, 4H), 7.19 (d, $J = 7.8$ Hz, 2H), 7.34 (dd, $J = 7.3, 7.8$ Hz, 2H), 7.39 (dd, $J = 7.3, 7.8$ Hz, 4H), 7.44 (d, $J = 7.8$ Hz, 1H), 7.65 (d, $J = 7.3$ Hz, 2H), 7.85 (d, $J = 7.8$ Hz, 4H). ^{13}C NMR analysis was not possible because of the very limited solubility. HRMS (FAB): calcd for $\text{C}_{51}\text{H}_{29}\text{NS}_2$ (M^+), 719.1741, Found 719.1732.

6,6'-Bis(spiro[fluorene-9,4'-[4H]indeno[1,2-*b*]thien-2-yl])-2,2'-bipyridine (5g): A white solid (85% yield); mp >300 °C. IR (KBr) 740, 798, 1283, 1438, 1560, 2924, 3058 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): $\delta = 6.66$ (d, $J = 7.3$ Hz, 2H), 6.88 (d, $J = 7.8$ Hz, 4H), 7.00–7.04 (m, 4H), 7.15 (dd, $J = 6.8, 7.3$ Hz, 4H), 7.32 (dd, $J = 7.3, 7.8$ Hz, 2H), 7.40 (dd, $J = 6.8, 7.3$ Hz, 4H), 7.44 (d, $J = 7.4$ Hz, 2H), 7.61 (d, $J = 8.3$ Hz, 2H), 7.74 (dd, $J = 7.3, 7.8$ Hz, 2H), 7.86 (d, $J = 7.8$ Hz, 4H), 8.39 (d, $J = 7.8$ Hz, 2H). ^{13}C NMR (75.5 MHz, CDCl_3): $\delta = 63.9, 118.4, 118.9, 119.2, 119.3, 120.1, 123.7, 123.9, 126.4, 127.86, 127.93, 137.4, 138.7, 141.8, 145.5, 146.7, 148.5, 151.7, 151.8, 152.6, 155.1$ (two peaks are overlapped). HRMS (FAB): calcd for $\text{C}_{56}\text{H}_{33}\text{N}_2\text{S}_2$ ($\text{M}+\text{H}^+$), 797.2085, Found 797.2108.

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Chapter 2

Synthesis and Characterization of Highly Fluorescent and Thermally Stable π -Conjugates involving Spiro[fluorene-9,4'-[4*H*]indeno[1,2-*b*]furan]

Abstract

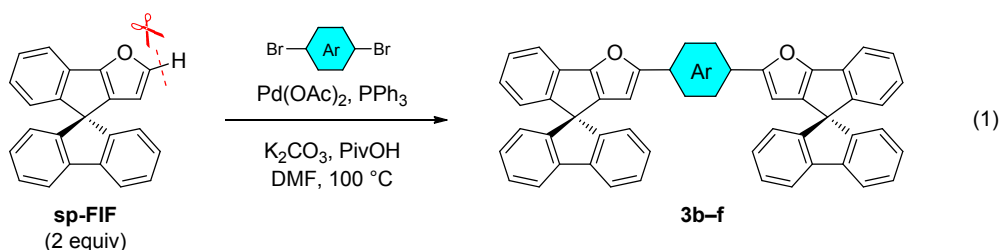
Spiro[fluorene-9,4'-[4*H*]indeno[1,2-*b*]furan] (**sp-FIF**) was synthesized, and its π -conjugation was efficiently elongated using palladium-catalyzed C–H arylation of a furan moiety. The resulting π -conjugated compounds showed intense fluorescence with higher quantum yields than thiophene analogs and extremely high thermal stability. In addition, the dimeric compound of **sp-FIF** showed intense fluorescence even in the solid state.

Introduction

π -Conjugated heterocyclic arene oligomers have been widely investigated for use in organic electronic devices such as organic light-emitting diodes (OLEDs), organic field-effect transistors (OFETs), photovoltaic cells, and nonlinear optical devices.¹ In particular, oligothiophenes^{1,2} and thiophene/phenylene co-oligomers^{1b,3} are of great interest and have been intensively studied because of their excellent optical and electronic properties. However, the corresponding furan-containing π -conjugated compounds have been less explored because of their thermal instability,⁴ although they are expected to have highly fluorescent properties and good hole-transporting abilities.^{4a,c}

In chapter 1, the author described the synthesis of spiro[fluorene-9,4'-[4*H*]indeno[1,2-*b*]thiophene] (**sp-FIT**) and its derivatization by means of the Stille coupling reaction.⁶ The derivatives showed efficient photoluminescence in the blue or bluish green region, and high thermal stability. Although Stille coupling is one of the most powerful tools for the preparation of biaryls involving heteroarenes, the use of highly toxic organotin species is a major drawback. Thus, an alternative method for efficient extension of the π -system is highly desirable. In the past decade, direct arylation has emerged as a useful alternative to conventional methods for the construction of biaryl molecules.⁷⁻¹⁰

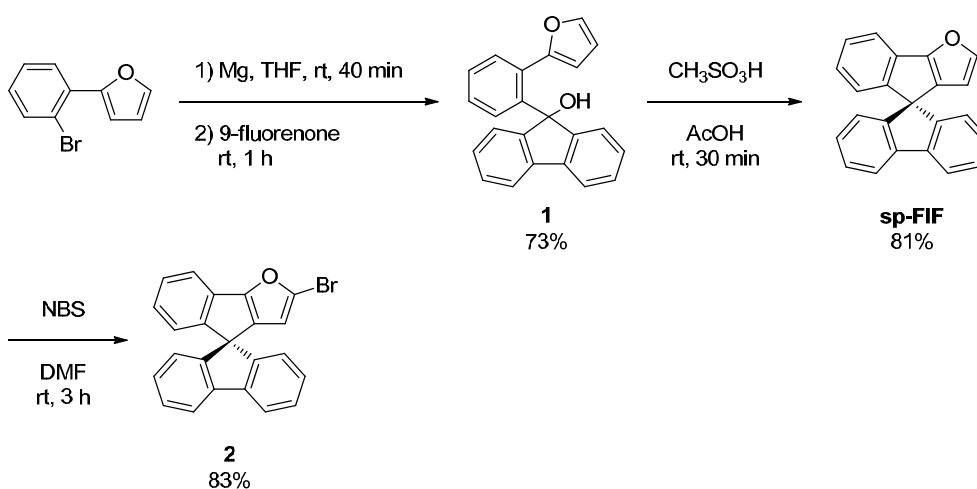
In this chapter, the author describes the first synthesis of furan-containing 9,9'-spirobifluorene analog, spiro[fluorene-9,4'-[4*H*]indeno[1,2-*b*]furan] (**sp-FIF**), and the preparation of its π -extended derivatives via palladium-catalyzed direct arylation, as well as photophysical, electrochemical, and thermal properties of the coupling products.



Results and Discussion

As shown in Scheme 1, **sp-FIF** was prepared in good yield by the two-step conversion of 9-fluorenone as a starting material. The reaction of a Grignard reagent, which was prepared from 1-bromo-2-furylbenzene, and 9-fluorenone gave alcohol **1** in 73% yield. The acid-mediated intramolecular Friedel-Crafts alkylation of **1** afforded **sp-FIF** in 81% yield. The reaction of **sp-FIF** and NBS gave **2** in 83% yield.

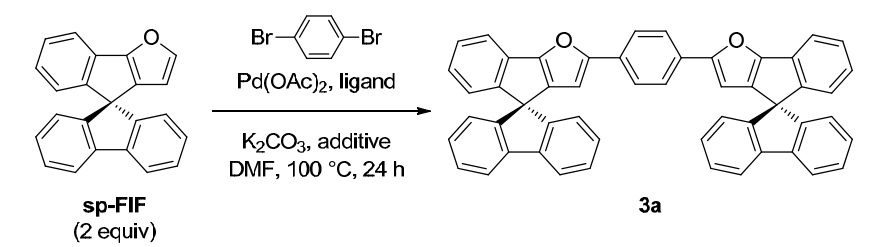
Scheme 1



The author next investigated the direct C–H arylation of a furan moiety of **sp-FIF** with *p*-dibromobenzene to extend the π -conjugation. Results are summarized in Table 1. When **sp-FIF** (0.2 mmol) was treated with *p*-dibromobenzene (0.1 mmol) in the presence of $\text{Pd}(\text{OAc})_2$ (0.01 mmol) and PPh_3 (0.02 mmol) using K_2CO_3 (0.4 mmol) as a base in DMF at 100 °C for 24 h, the coupling product **3a** was obtained in 39% yield with 60% conversion of **sp-FIF** (entry 1). Although the use of PCy_3 as a ligand afforded **3a** in better yield, the selectivity of **3a** was still low. When substoichiometric amounts of pivalic acid,¹⁰ which has been widely used in direct arylation recently, were added to the reaction using PCy_3 (entry 3), the yield was not increased in spite of complete conversion of **sp-FIF**. It was interesting to observe that the use of PPh_3 as a ligand instead of PCy_3 dramatically improved the yield of **3a**

(entry 4). However, the addition of stoichiometric amounts of pivalic acid inhibited the reaction, which indicates that the amount of pivalic acid is important in this cross-coupling reaction (entry 5).

Table 1. The direct arylation of **sp-FIF**^a



entry	ligand	additive	conv. (%) ^b	yield of 3a (%) ^b
1	PPh ₃	—	60	39
2	PCy ₃	—	85	53
3	PCy ₃	PivOH	100	53
4	PPh ₃	PivOH	100	84
5 ^c	PPh ₃	PivOH	4	trace

^a Conditions: **sp-FIF** (0.2 mmol), *p*-dibromobenzene (0.1 mmol), Pd(OAc)₂ (5 mol%), ligand (10 mol%), K₂CO₃ (0.4 mmol), additive (30 mol%), DMF (1 mL). ^b Based on **sp-FIF**. ^c PivOH (100 mol%).

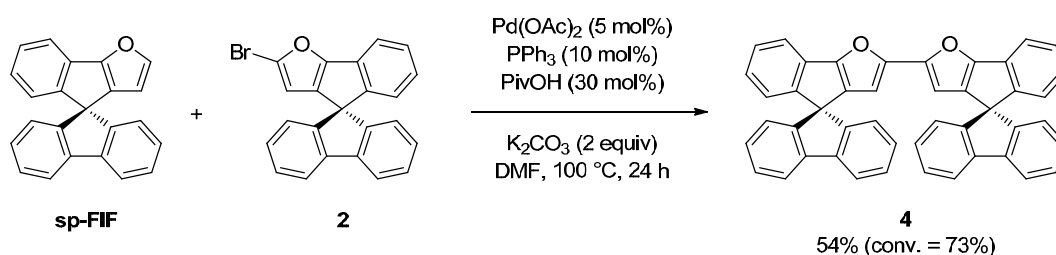
With the optimized conditions, several aryl dibromides were employed to prepare furan-containing π -conjugated compounds bearing various types of linker (Table 2). 4,4'-Dibromobiphenyl and 2,7-dibromo-9,9-dimethylfluorene showed comparable reactivity with *p*-dibromobenzene and produced coupling products **3b** and **3c**, respectively, in good to moderate yield (entries 1 and 2). In contrast, lower yields were observed in the cases of heteroaryl dibromides (entries 3–5). The yield of **3d** was increased to 46% when an excess amount of **sp-FIF** (0.4 mmol) was used (entry 3). Instead of aryl dibromides, employment of an equimolar amount of **2** gave **4** in 54% (Scheme 2).

Table 2. Synthesis of furan-containing π -conjugated compounds **3b–f**

entry	Br-Ar-Br	product	yield (%) ^b
1		3b	82
2		3c	59
3		3d	32 (46) ^c
4		3e	25
5 ^d		3f	21

^a Conditions: **sp-FIF** (0.200 mmol), aryl dibromide (0.100 mmol), Pd(OAc)₂ (5 mol%), PPh₃ (10 mol%), K₂CO₃ (0.400 mmol), PivOH (30 mol%), DMF (1 mL), 100 °C, 24 h.

^b Based on **sp-FIF**. ^c **sp-FIF** (0.400 mmol) was used. ^d 48 h.

Scheme 2

Photophysical, electrochemical, and thermal properties of **3a–f** and **4** are summarized in Table 3. All of the prepared compounds showed intense blue or green fluorescence and high quantum yield (Φ_F) (up to 89%) compared with previously demonstrated thiophene analogs in chapter 1.⁶ In particular, **3a–c** with an aromatic hydrocarbon as a linker showed intense fluorescence at about 430 nm. The low Φ_F of **3d** was because of the internal heavy atom

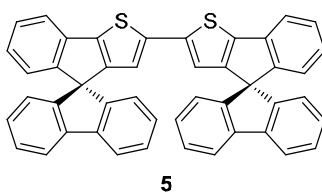
effect of the sulfur atom in thiophene.

Coupling products **3a–d** showed two reversible oxidation potentials in cyclic voltammetry experiments (Table 3). Comparing **3b** with **3a**, oxidation potential increased and the absorption spectrum was broadened and slightly blue-shifted because of the twisted nature of the biphenyl moiety. In the case of dimethylfluorene as a linker, the oxidation potential decreased because of effective elongation of the π -system. On the other hand, introducing five-membered heteroarenes, such as furan and thiophene, resulted in a red shift of absorption and emission spectra, as well as a decrease of oxidation potentials. Compared with thiophene analog **5**, which have been already shown in chapter 1, **4** has blue-shifted emission maxima and lower oxidation potentials. It is noteworthy that Φ_F of **4** is significantly higher than that of **5**. The strong emission was observed even in the solid state (**4**: $\Phi_F = 0.29$; **5**: $\Phi_F = 0.07$). This suggests that furan-containing π -conjugated compounds

Table 3. Photophysical, electrochemical, and thermal properties of **3a–f**

	λ_{abs} (nm) ^a	ϵ ($\times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$)	λ_{em} (nm) ^b	Φ_F^c	$E_{1/2 \text{ oxd}}$ (V) ^d	T_g (°C) ^e	T_d (°C) ^f
3a	396, 420	4.81, 4.02	429, 456	0.87	0.45, 0.71	202	392
3b	390	6.28	432, 459	0.89	0.57, 0.68	182	407
3c	401, 425	7.90, 7.40	434, 462	0.89	0.46, 0.62	191	352
3d	426	5.12	468, 500	0.43	0.31, 0.61	182	383
3e	406, 432	5.36, 3.86	440, 470	0.80	0.30, 0.60	181	380
3f	348, 369	3.56, 4.14	400	0.61	0.89 ^g , 1.09 ^g	n.d. ^h	414
4	382, 407	4.94, 3.97	412, 438	0.79	0.39, 0.78	185	380
5	405	3.54	444, 471	0.29	0.50, 0.96	186	391

^a $c = 1.00 \times 10^{-5} \text{ M}$ (in THF). ^b $c = 1.00 \times 10^{-7} \text{ M}$ (in THF). Excited at absorption maxima. ^c Determined by the calibrated integrating sphere system. ^d In CH_2Cl_2 containing 0.10 M Bu_4NPF_6 , V vs Fc/Fc^+ at 100 mV s^{-1} . ^e Glass transition temperature determined by differential scanning calorimetry (DSC) measurement. ^f Decomposition temperature (5% weight loss) obtained from thermogravimetric analysis (TGA). ^g Irreversible. ^h Not determined.



are superior to thiophene-containing ones as light-emitting materials.

Thermogravimetry analysis and differential scanning calorimetry showed that all compounds **3a–f** possess extremely high thermal stability because of the rigidity of the spirofluorene structures.¹¹ Luh and coauthors reported the most thermally stable furan-containing π -conjugated compounds without spiro linkages (Figure 1).^{4a} The series of compounds **3** in the present study showed higher glass transition temperatures (T_g) and decomposition temperatures (T_d) by about 100 °C. This should be advantageous for application in light-emitting devices.

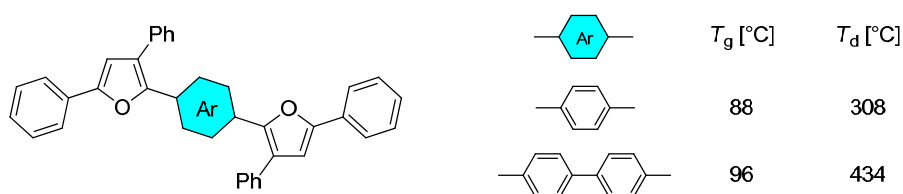


Figure 1. Thermal properties of furan/phenylene co-oligomers.

In conclusion, the author demonstrated the synthesis of the furan-containing spiro compound **sp-FIF** and the efficient palladium-catalyzed direct arylation of **sp-FIF** leading to several π -extended molecules. It is noted that various compounds can be obtained without using organotin compounds. Furthermore, the coupling compounds possess unique properties, such as intense photoluminescence and extremely high thermal stability.

Experimental Section

General. Unless otherwise specified, all reagents were purchased from a chemical supplier and used without further purification. Tetrahydrofuran (THF) was distilled over benzophenone ketyl under nitrogen atmosphere. *N,N*-Dimethylformamide (DMF) was distilled over CaH_2 under nitrogen atmosphere. Melting points are uncorrected. ^1H and ^{13}C spectra were recorded on a JEOL AL-300 (300 MHz for ^1H , and 75.5 MHz for ^{13}C) instrument. IR spectra were obtained on a JASCO 460 plus FT/IR spectrometer. Mass spectra were measured with a JEOL JMS-SX102A. Analytical thin-layer chromatography (TLC) was performed on Merck 60F254 silica plates and visualized by UV light. Column chromatography was carried out on Silicycle SilicaFlash F60 60-63 μm (230-400 mesh) silica gel. UV-visible absorption spectra were recorded on a JASCO V-570 UV-vis-NIR spectrometer. Emission spectra were measured with a Jobin Yvon-Horiba FluoroMax-3. Degassed spectral grade solvents were used for the measurements. Absolute fluorescence quantum yields were determined by the calibrated integrating sphere system. Cyclic voltammetry (CV) was performed on a BAS ALS 610C-S electrochemical analyzer. The CV cell consisted of a glassy carbon electrode, a Pt wire counter electrode, and a Ag/AgNO_3 reference electrode. The measurement was carried out under argon atmosphere using CH_2Cl_2 solutions of samples (1 mM) and 0.1 M tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) as a supporting electrolyte with a scan rate of 100 mV s^{-1} . The redox potentials were calibrated with ferrocene as an internal standard. Differential scanning calorimetry (DSC) was performed on a Rigaku Thermo plus EVO DSC 8230 under nitrogen atmosphere at a heating rate of $20 \text{ }^\circ\text{C min}^{-1}$. Thermogravimetric analysis (TGA) was carried out on a Rigaku TG-8120 under nitrogen atmosphere at a heating rate of $10 \text{ }^\circ\text{C min}^{-1}$.

9-(2-(2-Furyl)phenyl)fluoren-9-ol (1): A solution of 2-(2-Bromophenyl)furan¹² (10.5 g,

47.2 mmol) in THF (50 mL) was added dropwise to Mg (1.15 g, 47.2 mmol). The mixture was stirred for 40 min at room temperature. To the solution, 9-fluorenone (6.54 g, 36.3 mmol) in THF (30 mL) was added over 20 min and stirred at room temperature for 1 h. The reaction mixture was quenched with saturated aqueous solution of NH_4Cl (100 mL) and extracted with EtOAc (3×10 mL). The organic layers were combined, washed with brine (2×50 mL), and dried over MgSO_4 . The solvents were removed under reduced pressure, and the residue was purified with column chromatography on SiO_2 (EtOAc–hexane, 1:20), followed by recrystallization from EtOAc–hexane (1:2) to give **1** (8.65 g, 73%) as a pale yellow solid; mp 114.0–114.8 °C. IR (KBr) 733, 762, 774, 917, 1003, 1020, 1155, 1447, 3016, 2058, 3531 cm^{-1} . ^1H NMR (300 MHz, CDCl_3): δ = 2.42 (s, 1 H), 5.21 (s, 1 H), 5.88 (s, 1 H), 6.78 (s, 1 H), 7.13–7.28 (m, 7 H), 7.32 (dd, J = 7.3, 7.3 Hz, 1H), 7.46 (d, J = 7.7 Hz, 2H), 7.51 (dd, J = 7.3, 7.3 Hz, 1H), 8.24 (d, J = 7.3 Hz, 1H). ^{13}C NMR (75.5 MHz, CDCl_3): δ = 82.8, 108.2, 110.0, 119.9, 124.1, 127.0, 127.3, 128.0, 128.6, 128.8, 129.7, 132.3, 140.0, 141.4, 141.7, 150.6, 152.2. Anal. Calcd for $\text{C}_{23}\text{H}_{16}\text{O}_2$: C, 85.16; H, 4.97. Found: C, 85.19; H, 5.19.

Spiro[fluorene-9,4'-[4H]indeno[1,2-b]furan] (sp-FIF): To a solution of **1** (48.7 mg, 0.150 mmol) in AcOH (4 mL) was added $\text{CH}_3\text{SO}_3\text{H}$ (0.2 mL), and the solution was stirred at room temperature for 30 min. The reaction mixture was quenched with cold saturated aqueous solution of NaHCO_3 (15 mL) and extracted with CHCl_3 (3×5 mL). The organic layers were combined, washed with saturated aqueous solution of NaHCO_3 (2×15 mL) and brine (15 mL), and dried over MgSO_4 . The solvents were removed under reduced pressure, and the residue was purified with column chromatography on SiO_2 (hexane) to give **sp-FIF** (37.3 mg, 81%) as a pale yellow solid; mp 106.7–107.2 °C. IR (KBr) 701, 734, 747, 762, 1443, 3061, 3145 cm^{-1} . ^1H NMR (300 MHz, CDCl_3): δ = 6.09 (d, J = 1.8 Hz, 1H), 6.57 (d, J = 7.7 Hz, 1H), 6.85 (d, J = 7.7 Hz, 2H), 6.92 (dd, J = 7.3, 7.7 Hz, 1H), 7.13 (dd, J = 7.3, 7.7 Hz, 2H), 7.24

(dd, $J = 7.3, 7.7$ Hz, 1H), 7.36 (dd, $J = 7.3, 7.7$ Hz, 2H), 7.47 (d, $J = 1.8$ Hz, 1H), 7.50 (d, $J = 7.7$ Hz, 1H), 7.81 (d, $J = 7.7$ Hz, 2H). ^{13}C NMR (75.5 MHz, CDCl_3): $\delta = 59.4, 107.6, 116.6, 120.0, 123.6, 123.8, 125.6, 127.4, 127.7, 127.8, 132.8, 133.2, 141.8, 146.3, 146.5, 152.5, 160.1$. HRMS (FAB): calcd for $\text{C}_{23}\text{H}_{15}\text{O}$ ($\text{M}+\text{H}^+$), 307.1123, Found 307.1126.

2'-Bromospiro[fluorene-9,4'-[4H]indeno[1,2-*b*]furan] (2): To a solution of **sp-FIF** (460 mg, 1.50 mmol) in DMF (15 mL) was added NBS (281 mg, 1.58 mmol), and the solution was stirred at room temperature for 3 h. The reaction mixture was quenched with saturated aqueous solution of NaHCO_3 (30 mL) and extracted with EtOAc (3×10 mL). The organic layers were combined, washed with brine (2×20 mL), and dried over MgSO_4 . The solvents were removed under reduced pressure, and the residue was purified with column chromatography on SiO_2 (EtOAc–hexane, 1:20) to give **2** (477 mg, 83%) as a colorless solid; mp 173.2 °C (dec.). IR (KBr) 698, 746, 917, 1053, 1380, 1444, 3045 cm^{-1} . ^1H NMR (300 MHz, CDCl_3): $\delta = 6.05$ (s, 1H), 6.57 (d, $J = 7.7$ Hz, 1H), 6.85 (d, $J = 7.7$ Hz, 2H), 6.94 (dd, $J = 7.3, 7.7$ Hz, 1H), 7.14 (dd, $J = 7.3, 7.7$ Hz, 2H), 7.24 (dd, $J = 7.3, 7.7$ Hz, 1H), 7.37 (dd, $J = 7.3, 7.7$ Hz, 2H), 7.48 (d, $J = 7.3$ Hz, 1H), 7.81 (d, $J = 7.3$ Hz, 2H). ^{13}C NMR (75.5 MHz, CDCl_3): $\delta = 59.9, 109.7, 116.6, 120.2, 123.6, 123.9, 124.6, 126.0, 127.6, 127.8, 128.1, 132.7, 134.3, 141.8, 145.5, 151.2, 160.2$. HRMS (FAB): calcd for $\text{C}_{23}\text{H}_{14}^{79}\text{BrO}$ ($\text{M}+\text{H}^+$), 385.0228, Found 385.0218.

A Typical Procedure for Palladium-Catalyzed Direct Arylation of sp-FIF: A flame dried Schlenk flask was charged with phosphines (0.020 mmol), **sp-FIF** (61.3 mg, 0.200 mmol), aryl dibromides (0.100 mmol), $\text{Pd}(\text{OAc})_2$ (2.3 mg, 0.010 mmol), K_2CO_3 (55.3 mg, 0.400 mmol), pivalic acid (6.2 mg, 0.061 mmol), and DMF (1 mL) under nitrogen atmosphere. The solution was stirred at 100 °C for 24 h. The reaction mixture was

cooled down to room temperature, diluted with CHCl_3 , and filtered through a short silica gel pad. The residue was purified with column chromatography on SiO_2 (CHCl_3 –hexane, 1:2) to afford the coupling product **3**.

1,4-Bis(spiro[fluorene-9,4'-[4H]indeno[1,2-*b*]furan-2-yl])benzene (3a): A yellow solid (84% yield); mp >300 °C. IR (KBr) 701, 729, 749, 817, 1283, 1445, 3060 cm^{-1} . ^1H NMR (300 MHz, CDCl_3): δ = 6.41 (s, 2H), 6.60 (d, J = 8.1 Hz, 2H), 6.91 (d, J = 7.3 Hz, 4H), 6.95 (dd, J = 8.1, 8.1 Hz, 2H), 7.15 (dd, J = 7.3, 7.7 Hz, 4H), 7.28 (dd, J = 7.0, 8.1 Hz, 2H), 7.38 (dd, J = 7.3, 7.7 Hz, 4H), 7.56 (d, J = 7.0 Hz, 2H), 7.67 (s, 4H), 7.84 (d, J = 7.7 Hz, 4H). ^{13}C NMR (75.5 MHz, CDCl_3): δ = 59.5, 103.4, 116.6, 120.1, 123.7 (two peaks are overlapped), 123.8, 125.8, 127.6, 127.8, 127.9, 129.8, 133.0, 135.3, 141.9, 146.2, 152.3, 158.1, 159.9. HRMS (FAB): calcd for $\text{C}_{52}\text{H}_{31}\text{O}_2$ ($\text{M}+\text{H}^+$), 687.2324, Found 687.2348.

4,4'-Bis(spiro[fluorene-9,4'-[4H]indeno[1,2-*b*]furan-2-yl])biphenyl (3b): A yellow solid (82% yield); mp >300 °C. IR (KBr) 700, 730, 749, 810, 1105, 1445, 3059 cm^{-1} . ^1H NMR (300 MHz, CDCl_3): δ = 6.44 (s, 2H), 6.60 (d, J = 7.3 Hz, 2H), 6.92 (d, J = 7.3 Hz, 4H), 6.95 (dd, J = 7.0, 7.3 Hz, 2H), 7.16 (dd, J = 7.3, 7.7 Hz, 4H), 7.29 (dd, J = 7.0, 7.3 Hz, 2H), 7.39 (dd, J = 7.3, 7.7 Hz, 4H), 7.58 (d, J = 7.0 Hz, 2H), 7.64 (d, J = 8.4 Hz, 4H), 7.73 (d, J = 8.1 Hz, 4H), 7.84 (d, J = 7.7 Hz, 4H). ^{13}C NMR (75.5 MHz, CDCl_3): δ = 59.6, 103.1, 116.6, 120.1, 123.7, 123.8 (two peaks are overlapped), 125.8, 127.0, 127.6, 127.8, 127.9, 130.2, 133.1, 135.3, 139.0, 141.9, 146.2, 152.3, 158.1, 159.9. HRMS (FAB): calcd for $\text{C}_{58}\text{H}_{35}\text{O}_2$ ($\text{M}+\text{H}^+$), 763.2637, Found 763.2623.

9,9-Dimethyl-2,7-bis(spiro[fluorene-9,4'-[4H]indeno[1,2-*b*]furan-2-yl])fluorene (3c): A yellow solid (59% yield); mp >300 °C. IR (KBr) 701, 748, 817, 1291, 1445, 1464, 2922, 2958,

3059 cm^{-1} . ^1H NMR (300 MHz, CDCl_3): δ = 1.51 (s, 6H), 6.46 (s, 2H), 6.61 (d, J = 7.7 Hz, 2H), 6.92 (d, J = 7.3 Hz, 4H), 6.95 (dd, J = 7.3, 7.7 Hz, 2H), 7.15 (dd, J = 7.3, 7.7 Hz, 4H), 7.29 (dd, J = 7.3, 7.7 Hz, 2H), 7.38 (dd, J = 7.3, 7.7 Hz, 4H), 7.60 (d, J = 7.3 Hz, 2H), 7.65 (d, J = 8.8 Hz, 2H), 7.68 (d, J = 8.4 Hz, 2H), 7.72 (s, 2H), 7.84 (d, J = 7.3 Hz, 4H). ^{13}C NMR (75.5 MHz, CDCl_3): δ = 27.1, 46.9, 59.5, 102.8, 116.6, 117.6, 120.1, 120.3, 122.7, 123.7, 123.8, 125.7, 127.6, 127.8, 127.9, 130.1, 133.2, 135.4, 138.1, 141.9, 146.3, 152.3, 154.4, 158.9, 159.7. HRMS (FAB): calcd for $\text{C}_{61}\text{H}_{39}\text{O}_2$ ($\text{M}+\text{H}^+$), 803.2950, Found 803.2961.

2,5-Bis(spiro[fluorene-9,4'-[4H]indeno[1,2-*b*]furan-2-yl])thiophene (3d): An orange solid (32% yield); mp >300 °C. IR (KBr) 701, 729, 748, 793, 1281, 1445, 3061, 3111 cm^{-1} . ^1H NMR (300 MHz, CDCl_3): δ = 6.21 (s, 2H), 6.58 (d, J = 7.7 Hz, 2H), 6.89 (d, J = 7.3 Hz, 4H), 6.93 (dd, J = 7.3, 7.7 Hz, 2H), 7.15 (s, 2H), 7.14 (dd, J = 7.3, 7.7 Hz, 4H), 7.26 (dd, J = 7.3, 7.7 Hz, 2H), 7.37 (dd, J = 7.3, 7.7 Hz, 4H), 7.53 (d, J = 7.3 Hz, 2H), 7.82 (d, J = 7.7 Hz, 4H). ^{13}C NMR (75.5 MHz, CDCl_3): δ = 59.5, 103.1, 116.7, 120.1, 123.0, 123.7, 123.8, 125.8, 127.6, 127.8, 128.0, 132.3, 132.8, 135.4, 141.9, 146.0, 152.3, 153.3, 159.5. HRMS (FAB): calcd for $\text{C}_{50}\text{H}_{29}\text{O}_2\text{S}$ ($\text{M}+\text{H}^+$), 693.1888, Found 693.1902.

2,5-Bis(spiro[fluorene-9,4'-[4H]indeno[1,2-*b*]furan-2-yl])furan (3e): A yellow solid (25% yield); mp >300 °C. IR (KBr) 701, 728, 747, 778, 944, 1283, 1445, 3058, 3119 cm^{-1} . ^1H NMR (300 MHz, CDCl_3): δ = 6.29 (s, 2H), 6.58 (d, J = 7.3 Hz, 2H), 6.69 (s, 2H), 6.87 (d, J = 7.3 Hz, 4H), 6.93 (dd, J = 7.3, 7.7 Hz, 2H), 7.12 (dd, J = 7.0, 7.0 Hz, 4H), 7.26 (dd, J = 7.3, 7.7 Hz, 2H), 7.36 (dd, J = 7.3, 7.3 Hz, 4H), 7.52 (d, J = 7.7 Hz, 2H), 7.81 (d, J = 7.7 Hz, 4H). ^{13}C NMR (75.5 MHz, CDCl_3): δ = 59.4, 103.3, 107.3, 116.7, 120.1, 123.6, 123.8, 125.8, 127.6, 127.7, 127.9, 132.8, 135.0, 141.9, 145.7, 145.9, 150.1, 152.4, 159.7. HRMS (FAB): calcd for $\text{C}_{50}\text{H}_{28}\text{O}_3$ (M^+), 676.2038, Found 676.2065.

2,6-Bis(spiro[fluorene-9,4'-[4*H*]indeno[1,2-*b*]furan-2-yl])pyridine (3f): A white solid (21% yield); mp >300 °C. IR (KBr) 702, 743, 801, 1281, 1445, 1518, 1566, 3057 cm⁻¹. ¹H NMR (300 MHz, CD₂Cl₂): δ = 6.56 (d, *J* = 7.3 Hz, 2H), 6.72 (s, 2H), 6.82 (d, *J* = 7.7 Hz, 4H), 6.97 (dd, *J* = 7.3, 7.7 Hz, 2H), 7.11 (dd, *J* = 7.3, 7.7 Hz, 4H), 7.30 (dd, *J* = 7.3, 7.7 Hz, 2H), 7.35 (dd, *J* = 7.7, 7.7 Hz, 4H), 7.59 (d, *J* = 8.1 Hz, 2H), 7.60 (d, *J* = 7.3 Hz, 4H), 7.77 (dd, *J* = 7.3, 7.3 Hz, 1H), 7.82 (d, *J* = 7.7 Hz, 4H). ¹³C NMR analysis was not possible because of the very limited solubility. HRMS (FAB): calcd for C₅₁H₂₉NO₂ (M+H⁺), 688.2277, Found 688.2263.

2,2'-Bispiro[fluorene-9,4'-[4*H*]indeno[1,2-*b*]furan] (4): **2** (0.2 mmol) was used instead of aryl dibromides. A yellow solid (54% yield); mp >300 °C. IR (KBr) 699, 727, 746, 1445, 3055 cm⁻¹. ¹H NMR (300 MHz, CDCl₃): δ = 6.37 (s, 2H), 6.58 (d, *J* = 7.3 Hz, 2H), 6.87 (d, *J* = 7.3 Hz, 4H), 6.92 (dd, *J* = 7.3, 7.7 Hz, 2H), 7.14 (dd, *J* = 7.3, 7.7 Hz, 4H), 7.24 (dd, *J* = 7.3, 7.7 Hz, 2H), 7.38 (dd, *J* = 7.3, 7.7 Hz, 4H), 7.46 (d, *J* = 7.3 Hz, 2H), 7.83 (d, *J* = 7.7 Hz, 4H). ¹³C NMR (75.5 MHz, CDCl₃): δ = 59.4, 103.0, 116.6, 120.1, 123.6, 123.8, 125.8, 127.6, 127.7, 128.0, 132.7, 135.0, 141.9, 146.0, 150.5, 152.4, 159.6. HRMS (FAB): calcd for C₄₆H₂₇O₂ (M+H⁺), 611.2011, Found 611.1985.

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Chapter 3

Highly Fluorescent BODIPY Dyes Modulated with Spirofluorene Moieties

Abstract

A new type of structurally constrained BODIPY dye having spirofluorene moieties has been synthesized. These structurally constrained BODIPY dyes with spirofluorene moieties exhibit intense bathochromic fluorescence. The solvent dependence of fluorescence ON/OFF switching of a BODIPY dye having an amino moiety was observed.

Introduction

The technique of visualizing living cells by labeling proteins or DNA with fluorescent dyes is widely applicable to early detection of focus and elucidation of cellular mechanisms.¹ boron-dipyrromethene (BODIPY) dyes are regarded as among the most promising candidates for fluorescent labels and probes.² In general, BODIPY dyes are relatively insensitive to the surrounding environment such as polarity and pH, and have large molar absorption coefficients and high fluorescence quantum yields. Furthermore, their absorption and emission bands are narrow and sharp, and their photophysical properties are readily tunable by modification of the BODIPY core.

Extension of π -conjugated systems in general brings about a bathochromic shift of the emission maxima of fluorophores. However, free rotation between the BODIPY core and π -conjugated groups results in a decrease in quantum yields. Thus, constrained linkage of the BODIPY core with the π -conjugated moieties is essential to obtain efficient bathochromic fluorescence.³ Although structurally constrained BODIPY dyes with moderate quantum yields have been reported so far, only a limited number of studies have appeared.⁴

In this chapter, the author describes the synthesis and photophysical properties of novel BODIPY dyes (**sp-BODIPY**) derived from 1'*H*-spiro[fluorene-9,4'-indeno[1,2-*b*]pyrrole] (**sp-FIP**) (Figure 1). To prepare **sp-FIP** as a key structure, he has explored the palladium-

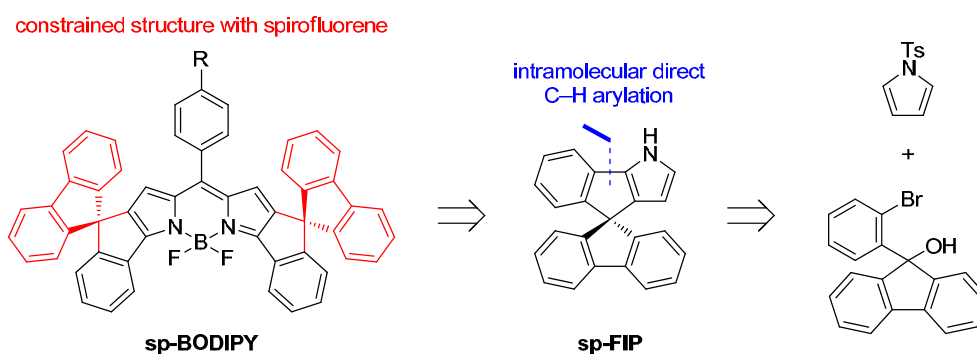


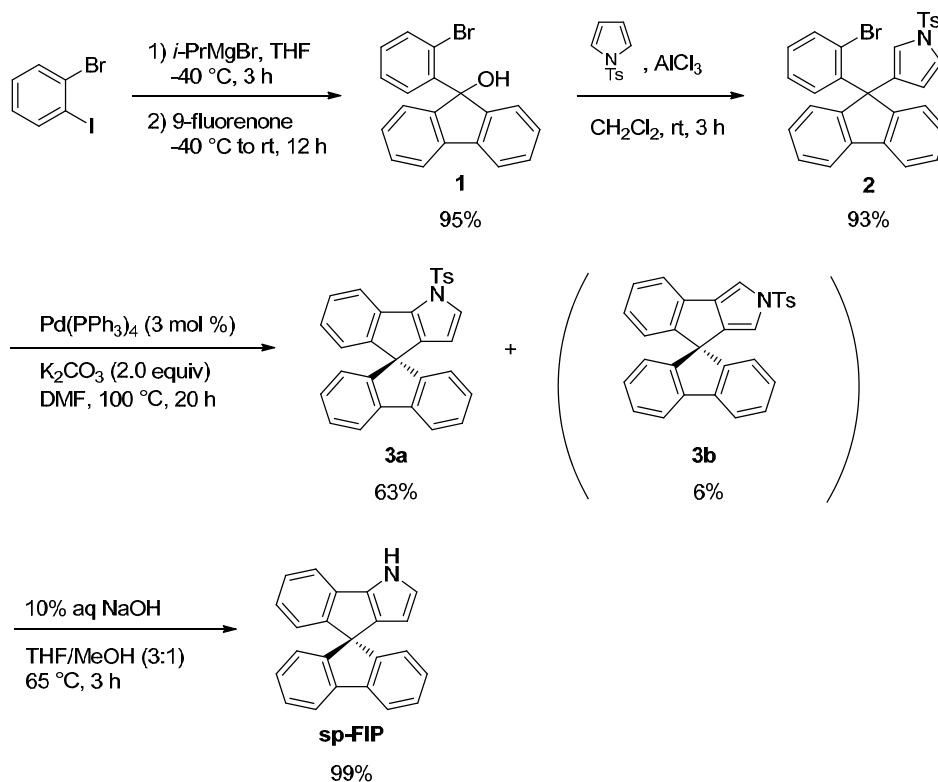
Figure 1. The synthetic route to structurally constrained BODIPY dyes.

catalyzed intramolecular direct C–H arylation of a pyrrole moiety.^{5–7} This approach enabled him to obtain a new type of BODIPY dye. Furthermore, their highly rigid structures reduced nonradiative decay of excited states, resulting in a high photoluminescence quantum yield.

Results and Discussion

The preparation of **sp-FIP** is summarized in Scheme 1. The reaction of 1-bromo-2-iodobenzene with isopropyl Grignard reagent⁸ followed by quenching with 9-fluorenone gave **1** in excellent yield (95%). Friedel-Crafts alkylation of *N*-tosylpyrrole with **1** using AlCl₃ afforded **2** in 93% yield. When the palladium-catalyzed intramolecular direct C–H arylation of **2** was carried out, **3a** and **3b** were isolated in 63% and 6% yields, respectively. The structures of both isomers were determined by X-ray crystallography (see

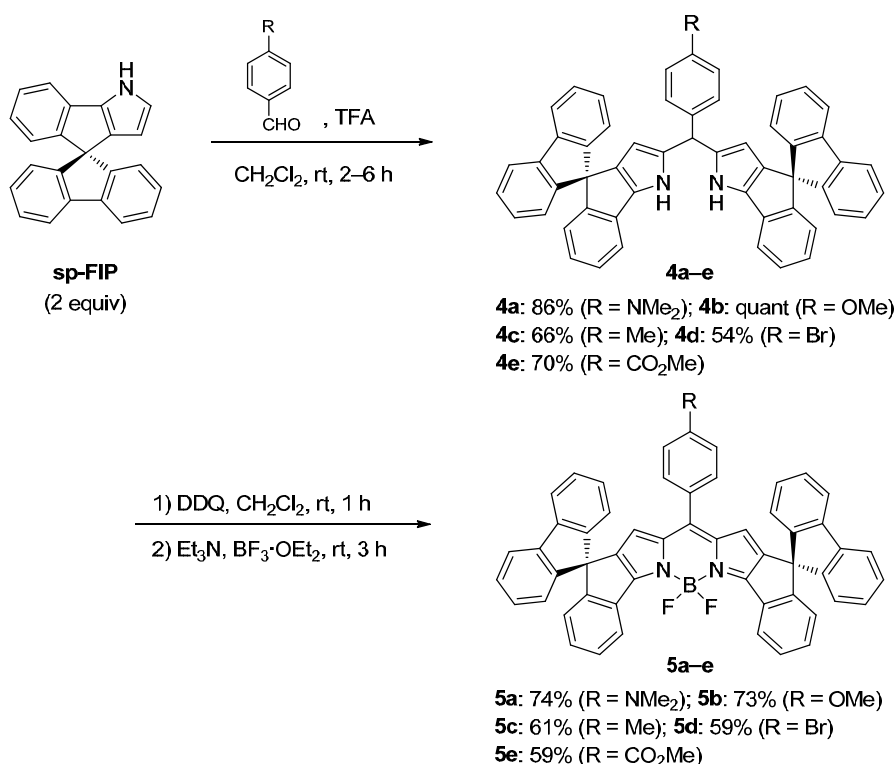
Scheme 1



the Experimental Section). Hydrolysis of the tosyl group of **3a** proceeded smoothly to give **sp-FIP** in quantitative yield (99%).

The author next examined the transformation of **sp-FIP** to BODIPY dyes having various aryl substituents at the meso position (Scheme 2). Several para-substituted aryl aldehydes were reacted with 2 equiv of **sp-FIP** in the presence of catalytic amounts of trifluoroacetic acid (TFA) to afford the corresponding dipyrromethanes **4a–e** in good to excellent yields. Subsequent 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) oxidation and complexation with $\text{BF}_3 \cdot \text{OEt}_2$ led to the formation of BODIPY dyes **5a–e** in good yields. The structure of **5d** was unambiguously determined by X-ray crystallography (see the Experimental Section).

Scheme 2



The absorption and emission spectra of **5a–e** were measured in THF (Table 1). All BODIPY dyes showed an intense, narrow, and sharp absorption band at $\lambda_{\text{abs}} = 627\text{--}641\text{ nm}$ with $\varepsilon = 161,060\text{--}180,700\text{ M}^{-1}\text{cm}^{-1}$. The absorption maxima of **5a–e** were scarcely affected

by the electronic nature of substituents R. Their Stokes shifts are less than 10 nm, while the emission maxima of **5a–e** were observed at 636–652 nm. Furthermore, the emission maxima were also scarcely affected by substituents R. As shown later, it is noteworthy that all BODIPY dyes except **5a** show higher quantum yields in comparison with those reported by Burgess's group.^{4a} This suggests that the constraint of the spirofluorene moieties increases the rigidity of the BODIPY core, thereby reducing the nonradiative decay.

Table 1. Optical Properties of **5a–e** in THF ($c = 1.00 \times 10^{-6}$ M)

compd	λ_{abs} (nm)	ϵ (M ⁻¹ cm ⁻¹)	λ_{ex} (nm)	λ_{em} (nm)	Φ_{F}^a
5a	627	180,700	580	636	0.16
5b	632	178,570	585	640	0.76
5c	634	167,210	585	642	0.67
5d	638	163,890	587	648	0.73
5e	641	161,060	592	652	0.61

^a Determined by the calibrated integrating sphere system.

It is noted that the fluorescence quantum yield of **5a** having an *N,N*-dimethylamino group was exceptionally low relative to the BODIPY dyes **5b–e**. The absorption and emission spectra of **5a** in various solvents with different dielectric constants were measured (Figure 2, Table 2), because photoinduced electron transfer (PeT)⁹ leading to fluorescence quenching was suspected.¹¹ The positions of the absorption maxima and the emission maxima in all solvents were scarcely affected by the dielectric constants of the solvents, whereas the fluorescence quantum yields varied in each solvent. When DMF with a high dielectric constant was used, the quantum yield of **5a** was very low ($\Phi_{\text{F}} = 0.06$). On the other hand, using CHCl₃ and benzene with relatively low dielectric constant as solvents afforded high quantum yields ($\Phi_{\text{F}} = 0.73$ and 0.78, respectively). Because the absorption maxima and the emission maxima of **5a** were not changed by varying the solvent, it was

deduced that in a more polar solvent, such as DMF, PeT from the *N,N*-dimethylaminophenyl group to the BODIPY core readily occurred.

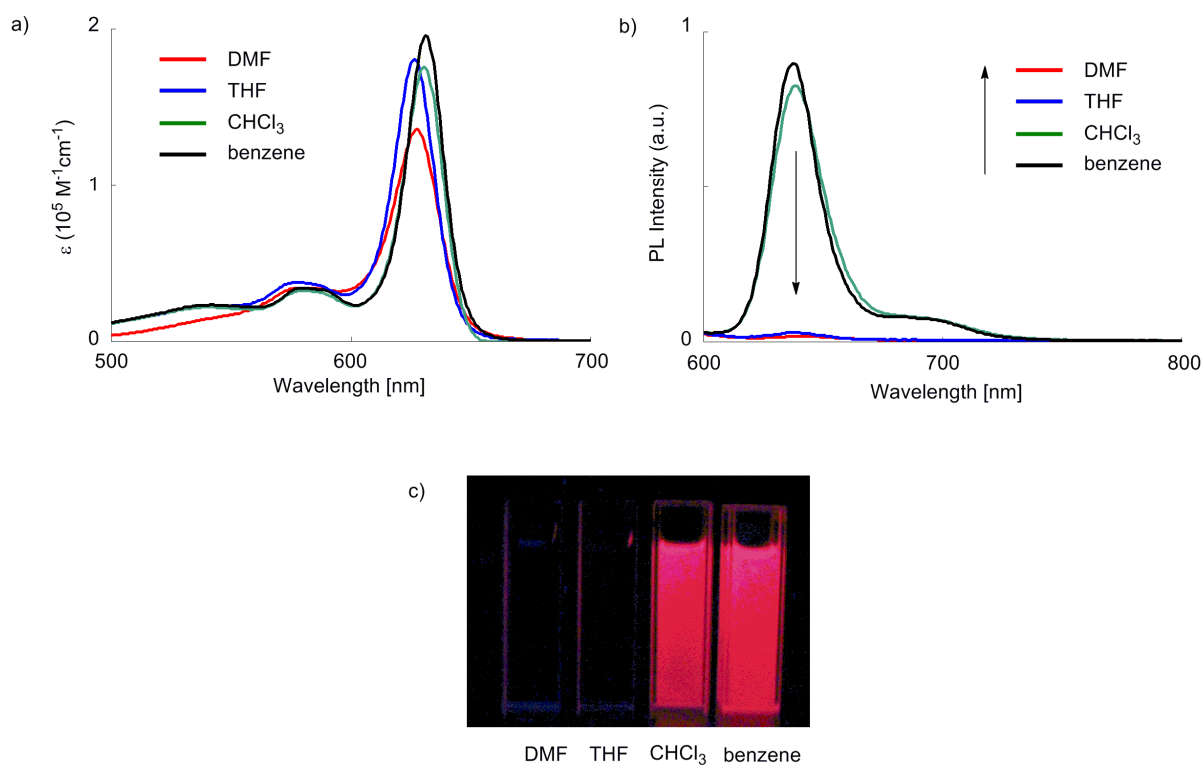


Figure 2. (a) UV-vis absorption and (b) photoluminescence spectra of **5a** in various solvents.

(c) Solvent dependence of fluorescence.

Table 2. Photophysical properties of **5a** in various solvents^a

solvent	λ_{abs} [nm]	λ_{em} [nm]	ϵ_r^b	Φ_F^c
DMF	628	637	36.7	0.06
THF	627	636	7.52	0.16
CHCl ₃	631	639	4.81	0.73
benzene	631	638	2.28	0.78

^a $c = 1.00 \times 10^{-6} \text{ M}$. ^b Relative dielectric constant. ^c Determined by the calibrated integrating sphere system.

The feasibility of electron transfer from the electron donor (*N,N*-dimethylaminophenyl group) to the electron acceptor (BODIPY core) was estimated by the Rehm–Weller equation (eq 1)^{9,11}

$$\Delta G_{\text{ET}} = E_{1/2}(\text{D}^+/\text{D}) - E_{1/2}(\text{A}/\text{A}^-) - \Delta E_{00} - w_{\text{p}} \quad (1)$$

where $E_{1/2}(\text{D}^+/\text{D})$ and $E_{1/2}(\text{A}/\text{A}^-)$ are the ground-state redox potentials of the donor and acceptor moieties, respectively, ΔE_{00} is the singlet excited energy of the fluorophore, and w_{p} is the work term for the charge separation.¹² The relative free energies ($\Delta\Delta G_{\text{ET}}$) of **5a** in various solvents according to Rehm–Weller equation are summarized in Table 3. The *N,N*-dimethylaminophenyl group and BODIPY core are twisted by 79° and conjugately uncoupled according to the result of X-ray analysis.¹³ As shown in Table 3, $\Delta\Delta G_{\text{ET}}$ in various solvents indicates that the electron transfer can take place more easily in following order: in DMF > in THF > in CHCl₃. The emission apparently disappear in THF ($\Phi_{\text{F}} = 0.16$), because fluorescence ON/OFF threshold seems to exist between CHCl₃ and THF (Figure 2c).⁹

Table 3. Relative Free Energies ($\Delta\Delta G_{\text{ET}}$) of **5a** Calculated by Fitting the Data to the Rehm–Weller Equation

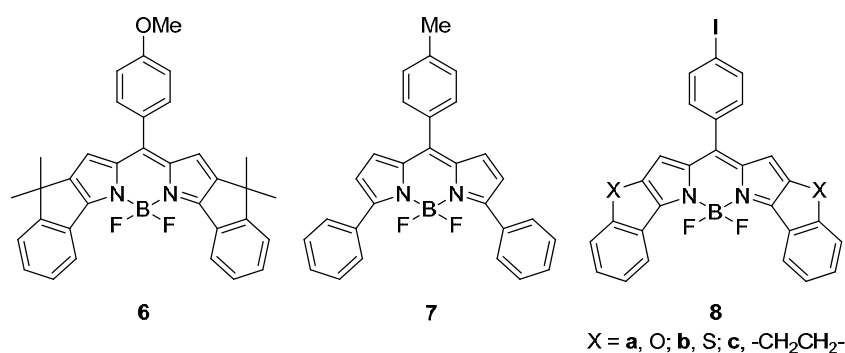
solvent	$E_{1/2}(\text{D}^+/\text{D})$ (V) ^{a,b}	$E_{1/2}(\text{A}/\text{A}^-)$ (V) ^{a,c}	ΔE_{00} (eV) ^d	$\Delta\Delta G_{\text{ET}}$ (eV) ^e
DMF	0.34	-1.19	1.79	-0.29
THF	0.32	-1.44	1.81	-0.08
CHCl ₃	0.34	-1.58	1.89	0

^a Measured by CV with 0.1 M *n*-Bu₄PF₆, V vs Fc/Fc⁺ at 0.1 V s⁻¹. ^b Oxidation potential of *N,N*-dimethylaniline. ^c Reduction potential of **5a**. ^d Estimated by the absorption edge of the UV–vis spectrum. ^e Relative ΔG_{ET} values were calculated with respect to the value in CHCl₃ as a standard.

To reveal the effect of spirofluorene moieties on photophysical properties, the absorption and emission spectra of **5b** were compared with those of BODIPY dyes **6**, **7**, and **8a–c** (Table

4). The absorption and emission maxima of **5b** showed a bathochromic shift in comparison with those of **6** and **7**. On the other hand, compared with both maxima of **8a–c**, a hypsochromic shift of **5b** was observed. However, the photoluminescence quantum yield of **5b** was much higher than those of **6–8**. Compared with **6**, it is obvious that spirofluorene moieties effectively affect the red shift of absorption and emission spectra and increase the quantum yield.

Table 4. Comparison of Optical Properties in THF



compd	λ_{abs} (nm)	λ_{ex} (nm)	λ_{em} (nm)	Φ_{F}^a
5b	632	585	640	0.76
6	623	579	629	0.60
7^a	553	553	586	0.22
8a^b	637		647	0.34
8b^b	658		673	0.05
8c^b	634		647	0.38

^a Reference 14. ^b Reference 4a. in CHCl₃.

To gain insight into the red shift of absorption and emission maxima of **5b** relative to those of **6**, theoretical calculations of model compound **9** were carried out at the B3LYP/6-31G(d) level (Figure 3).^{15,16} A TD-DFT calculation at the B3LYP/6-31G(d) level indicates that the most allowed transition is from HOMO to LUMO and HOMO-2 to LUMO, the oscillator strength being 1.04 (Table 5). HOMO-2 was mainly localized over the two

fluorene moieties, whereas the HOMO and LUMO of **9** were mainly delocalized over the indene-fused BODIPY core. This result implies that an intramolecular charge transfer process might exist in this system. Furthermore, it is noteworthy that the coefficients of the HOMO are slightly delocalized over the fluorene moieties. This phenomenon is well known as spiroconjugation,¹⁷ leading to through-space expansion of the π -system. As a result, it is considered that absorption and emission maxima of **5b** were bathochromically shifted relative to those of **6**.

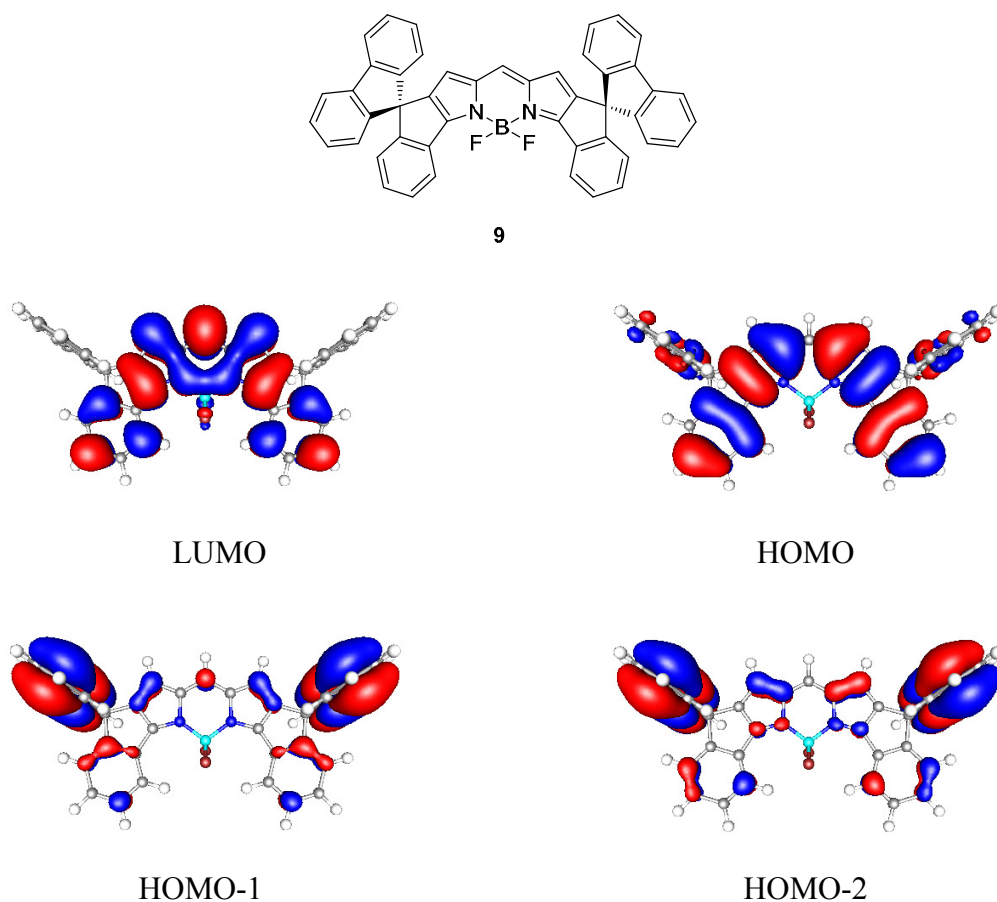


Figure 3. Molecular orbital plots of the frontier orbitals for model compound **9**.

Table 5. Results of TD-DFT calculation for **9** (TD-B3LYP/6-31G(d)//B3LYP/6-31G(d))

λ (nm)	oscillator strength	transition		amplitude
532.00	1.0435	LUMO	← HOMO-2	-0.14168
		LUMO	← HOMO	0.58646
455.34	0.0001	LUMO	← HOMO-1	0.70195
444.47	0.1075	LUMO	← HOMO-2	0.68752

In conclusion, the author has demonstrated that structurally constrained BODIPY dyes based on 1'-*H*-spiro[fluorene-9,4'-indeno[1,2-*b*]pyrrole] exhibit significant increases in the fluorescence quantum yields as well as red shifts of the absorption and emission maxima. Spirofluorene moieties lead to high rigidity and good planarity of the BODIPY core. Furthermore, the fluorescence ON/OFF phenomenon was observed arising from a PeT process from an *N,N*-dimethylaminophenyl unit to the BODIPY core. DFT calculations indicate that the π -system of BODIPY derivatives **5a–d** is extended over the fluorene moieties as well as the BODIPY core because of spiroconjugation.

Experimental Section

General. Unless otherwise specified, all reagents were purchased from a chemical supplier and used without further purification. Tetrahydrofuran (THF) was distilled over benzophenone ketyl under nitrogen atmosphere. *N,N*-Dimethylformamide (DMF) was distilled over CaH₂ under nitrogen atmosphere. CH₂Cl₂ was dried and collected using a Grubbs-type solvent purification system manufactured by Glass Contour. Melting points are uncorrected. ¹H and ¹³C spectra were recorded on a JEOL AL-300 (300 MHz for ¹H, and 75.5 MHz for ¹³C) instrument or a JEOL EX-400 (400 MHz for ¹H, and 100 MHz for ¹³C) instrument. IR spectra were obtained on a JASCO 460 plus FT/IR spectrometer. Mass

spectra were measured with a JEOL JMS-SX102A. Analytical thin-layer chromatography (TLC) was performed on Merck 60F254 silica plates and visualized by UV light. Column chromatography was carried out on Silicycle SilicaFlash F60 60-63 μm (230-400 mesh) silica gel. Preparative HPLC was carried out with a Japan Analytical Industry Co., Ltd, LC-908 chromatograph using a JAIGEL-1H and -2H GPC columns. UV-visible absorption spectra were recorded on a JASCO V-570 UV-vis-NIR spectrometer. Emission spectra were measured with a Jobin Yvon-Horiba FluoroMax-3. Degassed spectral grade solvents were used for the measurements. Absolute fluorescence quantum yields were determined by the calibrated integrating sphere system. Cyclic voltammetry (CV) was performed on a BAS ALS 610C-S electrochemical analyzer. The CV cell consisted of a glassy carbon electrode, a Pt wire counter electrode, and an Ag/AgNO₃ reference electrode. The measurement was carried out under argon atmosphere using solutions of samples (1 mM) and 0.1 M tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) as a supporting electrolyte with a scan rate of 100 mV s⁻¹. The redox potentials were calibrated with ferrocene as an internal standard.

9-(2-Bromophenyl)-9H-fluoren-9-ol (1)¹⁸: The solution of 1-bromo-2-iodobenzene (34.9 g, 124 mmol) in dry THF (120 mL) was cooled to -40 °C. To the solution was added dropwise 1.0 M THF solution of isopropyl magnesium bromide (120 mL), prepared from isopropyl bromide and magnesium turnings. After stirring for 3 h, 9-fluorenone (14.4 g, 80.0 mmol) in dry THF (80 mL) was added over 25 min and stirred at room temperature for 12 h. The reaction mixture was quenched with saturated aqueous solution of NH₄Cl (100 mL) and extracted with EtOAc (3 × 30 mL). The organic layers were combined, washed with brine (2 × 50 mL), and dried over MgSO₄. The solvents were removed under reduced pressure to give a mixture of white solid and yellow oil. The crude product was purified by washing

with hexane and the filtrate was purified with column chromatography on SiO₂ with EtOAc/hexane (v/v = 1/20) as an eluent to give **1** (25.6 g, 95%) as a white solid; mp 145.2–146.0 °C. IR (KBr) 767, 920, 1005, 1157, 1333, 1448, 1604, 3063, 3571 cm⁻¹. ¹H NMR (300 MHz, CDCl₃): δ = 2.39 (br s, 1H), 7.13–7.25 (m, 5H), 7.36–7.47 (m, 4H), 7.67 (d, *J* = 7.7 Hz, 2H), 8.44 (br s, 1H). ¹³C NMR (75.5 MHz, CDCl₃): δ = 83.0, 120.2, 120.9, 123.9, 127.0, 128.3, 129.0, 129.1, 129.2, 134.3, 140.8, 141.3, 148.6.

9-(2-Bromophenyl)-9-(*N*-tosylpyrrol-3-yl)-9*H*-fluorene (2): To a solution of **1** (9.72 g, 28.8 mmol) and *N*-tosylpyrrole (6.94 g, 31.3 mmol) in CH₂Cl₂ (200 mL) was added AlCl₃ (4.39 g, 32.9 mmol) portionwise, and the solution was stirred at room temperature for 3 h. The reaction mixture was quenched with water (60 mL) and extracted with CH₂Cl₂ (3 × 30 mL). The organic layers were combined, washed with saturated aqueous solution of NaHCO₃ (2 × 40 mL) and brine (40 mL), and dried over MgSO₄. The solvents were removed under reduced pressure to give white solid. The crude product was purified by washing with CHCl₃–hexane (1:1) and the filtrate was purified with column chromatography on SiO₂ with EtOAc/hexane (v/v = 1/20) as an eluent to give **2** (14.5 g, 93%) as a white solid; mp 210.2–211.0 °C. IR (KBr) 605, 674, 746, 1065, 1101, 1172, 1253, 1371, 1464, 1596 cm⁻¹. ¹H NMR (300 MHz, CDCl₃): δ = 2.36 (s, 3H), 6.40 (br s, 1H), 6.61 (br s, 1H), 7.01–7.09 (m, 2H), 7.14–7.40 (m, 11H), 7.59 (d, *J* = 8.4 Hz, 2H), 7.71 (d, *J* = 7.7 Hz, 2H). ¹³C NMR (75.5 MHz, CDCl₃): δ = 21.6, 60.4, 115.6, 119.3, 120.4, 121.5, 123.0, 124.7, 126.76, 126.81, 127.4, 127.5, 128.6, 129.9, 131.8, 132.1, 135.4, 136.0, 141.1, 142.1, 144.9, 149.8. HRMS (FAB): calcd for C₃₀H₂₃⁸¹BrNO₂S (M+H⁺), 542.0616, Found 542.0609.

1'-Tosyl-1'*H*-spiro[fluorene-9,4'-indeno[1,2-*b*]pyrrole (3a) and 2'-tosyl-2'*H*-spiro[fluorene-9,4'-indeno[1,2-*c*]pyrrole (3b): A flame dried flask was charged with **2** (14.5 g,

26.8 mmol), K_2CO_3 (7.57 g, 54.8 mmol), $\text{Pd}(\text{PPh}_3)_4$ (930 mg, 0.805 mmol), and dry DMF (200 mL) under nitrogen atmosphere. The solution was stirred at 100 °C for 20 h. The reaction mixture was cooled down to room temperature and filtered through a short silica gel pad. After an addition of water (150 mL), the filtrate was extracted with CH_2Cl_2 (3×30 mL). The organic layers were combined, washed with brine (7×50 mL), and dried over MgSO_4 . The solvents were removed under reduced pressure to give a mixture of white solid and brown oil. The crude product was purified by washing with CHCl_3 /hexane ($v/v = 1/1$) to give **3a** (7.77 g, 63%) as a white solid. The residue was purified with GPC (CHCl_3) to afford **3b** (739 mg, 6%) as a white solid.

3a: A white solid; mp 256.5–257.3 °C. IR (KBr) 670, 699, 749, 1113, 1173, 1192, 1380, 1446, 1462, 1596, 3128 cm^{-1} . ^1H NMR (300 MHz, CDCl_3): δ 2.42 (s, 3H), 5.86 (d, $J = 3.3$ Hz, 1H), 6.52 (d, $J = 7.3$ Hz, 1H), 6.63 (d, $J = 7.7$ Hz, 2H), 6.93 (dd, $J = 7.5, 7.7$ Hz, 1H), 7.07 (dd, $J = 7.3, 7.5$ Hz, 2H), 7.22 (d, $J = 3.3$ Hz, 1H), 7.28–7.36 (m, 5H), 7.78 (d, $J = 7.7$ Hz, 2H), 7.83 (d, $J = 8.4$ Hz, 2H), 8.15 (d, $J = 7.7$ Hz, 1H). ^{13}C NMR (75.5 MHz, CDCl_3): δ 21.6, 60.2, 108.7, 119.5, 120.0, 123.5, 123.6, 125.7, 126.76, 126.81, 127.6, 127.7, 127.8, 130.0, 134.0, 135.9, 138.2, 139.9, 141.8, 145.1, 146.4, 152.5. HRMS (FAB): calcd for $\text{C}_{30}\text{H}_{22}\text{NO}_2\text{S}$ ($\text{M}+\text{H}^+$), 460.1371, Found 460.1364.

3b: A white solid; mp 212.7–213.6 °C. IR (KBr) 673, 752, 1053, 1089, 1166, 1187, 1362, 1446, 1595, 3063 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ 2.39 (s, 3H), 6.49 (d, $J = 7.3$ Hz, 1H), 6.67 (d, $J = 1.5$ Hz, 1H), 6.79 (d, $J = 7.3$ Hz, 2H), 6.97 (dd, $J = 7.3, 7.6$ Hz, 1H), 7.11 (dd, $J = 7.3, 7.3$ Hz, 2H), 7.21–7.26 (m, 3H), 7.32–7.36 (m, 3H), 7.56 (d, $J = 7.8$ Hz, 1H), 7.70 (d, $J = 8.3$ Hz, 2H), 7.78 (d, $J = 7.8$ Hz, 2H). ^{13}C NMR (100 MHz, CDCl_3): δ 21.6, 60.4, 110.0, 113.5, 119.9, 121.4, 124.1, 124.3, 126.8, 127.4, 127.69, 127.72, 127.8, 129.9, 135.3, 135.4, 136.1,

138.7, 140.8, 144.8, 149.6, 153.2. HRMS (FAB): calcd for $C_{30}H_{22}NO_2S$ ($M+H^+$), 460.1371, Found 460.1382.

1'-H-Spiro[fluorene-9,4'-indeno[1,2-*b*]pyrrole (sp-FIP): To a solution of **3a** (7.52 g, 16.4 mmol) in THF (300 mL) and MeOH (100 mL) was added 10% aqueous solution of NaOH (66 mL), and the solution was stirred at 65 °C for 3 h. After cooling to ambient temperature, MeOH was removed under reduced pressure and the residue was extracted with $CHCl_3$ (3 × 20 mL). The organic layers were combined, washed with water (2 × 50 mL) and brine (50 mL), and dried over $MgSO_4$. The solvents were removed under reduced pressure to give brown solid. The crude product was purified by washing with $CHCl_3$ /hexane (v/v = 1/1) and the filtrate was purified with column chromatography on SiO_2 with EtOAc/hexane (v/v = 1/15) as an eluent to give **sp-FIP** (4.96 g, 99%) as a pale blue solid; mp 183.5–184.5 °C. IR (KBr) 748, 1444, 1606, 3060, 3414 cm^{-1} . 1H NMR (300 MHz, $CDCl_3$): δ = 5.79 (dd, J = 1.7, 2.7 Hz, 1H), 6.54 (d, J = 7.7 Hz, 1H), 6.80–6.86 (m, 4H), 7.11 (dd, J = 7.3, 7.3 Hz, 2H), 7.19 (dd, J = 7.3, 7.5 Hz, 1H), 7.31–7.36 (m, 3H), 7.80 (d, J = 7.3 Hz, 2H), 8.41 (br s, 1H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 60.7, 103.9, 115.8, 119.8, 121.9, 123.6, 123.8, 124.3, 127.0, 127.4, 127.5, 133.7, 135.4, 137.8, 141.7, 148.5, 153.0. HRMS (FAB): calcd for $C_{23}H_{16}N$ ($M+H^+$), 306.1283, Found 306.1288.

A Typical Procedure for Synthesis of 4a–e.

To a solution of **sp-FIP** (611 mg, 2.00 mmol) and aldehyde (1.00 mmol) in dry CH_2Cl_2 (20 mL) was added two drops of TFA, and the solution was stirred at room temperature for 2–6 h under nitrogen atmosphere. The reaction mixture was quenched with 5% aqueous solution of $NaHCO_3$ (25 mL) and extracted with $CHCl_3$ (3 × 10 mL). The organic layers were combined, washed with brine (2 × 15 mL), and dried over $MgSO_4$. The solvents were

removed under reduced pressure, and the residue was purified with column chromatography on SiO₂ with EtOAc/hexane (v/v = 1/15) as an eluent to afford **4**.

4a: A purple solid (86% yield); mp >300 °C. IR (KBr) 729, 747, 1280, 1338, 1444, 1474, 1520, 1604, 3059, 3436 cm⁻¹. ¹H NMR (300 MHz, CDCl₃): δ = 2.90 (s, 6H), 5.38 (s, 1H), 5.52 (s, 2H), 6.49 (d, *J* = 7.7 Hz, 2H), 6.65 (d, *J* = 8.8 Hz, 2H), 6.75–6.85 (m, 6H), 7.07–7.19 (m, 10H), 7.32 (dd, *J* = 7.3, 7.3 Hz, 4H), 7.77 (d, *J* = 7.7 Hz, 4H), 8.15 (br s, 2H). ¹³C NMR (75.5 MHz, CDCl₃): δ = 40.5, 44.6, 60.9, 103.1, 112.6, 115.6, 119.8, 123.6, 123.8, 123.9, 126.9, 127.3, 127.5, 129.0, 129.2, 133.6, 135.5, 137.2, 137.7, 141.6, 148.5, 149.5, 152.5. HRMS (FAB): calcd for C₅₅H₄₀N₃ (M+H⁺), 742.3222, Found 742.3237.

4b: A bluish purple solid (quantitative yield); mp >300 °C. IR (KBr) 729, 747, 1031, 1175, 1250, 1445, 1474, 1509, 1605, 3060, 3419 cm⁻¹. ¹H NMR (300 MHz, CDCl₃): δ = 3.76 (s, 3H), 5.44 (s, 1H), 5.51 (s, 2H), 6.48 (d, *J* = 7.7 Hz, 2H), 6.77–6.86 (m, 8H), 7.08–7.21 (m, 10H), 7.32 (dd, *J* = 7.3, 7.7 Hz, 4H), 7.78 (d, *J* = 7.7 Hz, 4H), 8.17 (br s, 2H). ¹³C NMR (75.5 MHz, CDCl₃): δ = 44.8, 55.2, 60.9, 103.3, 114.1, 115.7, 119.8, 123.67, 123.74, 124.1, 127.0, 127.4, 127.5, 129.5, 133.4, 133.7, 135.4, 137.1, 137.4, 141.7, 148.4, 152.6, 158.6. HRMS (FAB): calcd for C₅₄H₃₇N₂O (M+H⁺), 729.2906, Found 729.2916.

4c: A bluish purple solid (66% yield); mp >300 °C. IR (KBr) 728, 746, 1280, 1444, 1474, 1510, 1605, 3058, 3410 cm⁻¹. ¹H NMR (300 MHz, CDCl₃): δ = 2.30 (s, 3H), 5.45 (s, 1H), 5.52 (s, 2H), 6.48 (d, *J* = 7.7 Hz, 2H), 6.77–6.85 (m, 6H), 7.08–7.21 (m, 12H), 7.33 (dd, *J* = 7.3, 7.5 Hz, 4H), 7.78 (d, *J* = 7.3 Hz, 4H), 8.17 (br s, 2H). ¹³C NMR (75.5 MHz, CDCl₃): δ = 21.0, 45.2, 60.9, 103.3, 115.7, 119.8, 123.6, 123.8, 124.1, 127.0, 127.4, 127.5, 128.4, 129.4, 133.6, 135.4, 136.7, 137.0, 137.4, 138.4, 141.7, 148.4, 152.6. HRMS (FAB): calcd for

$C_{54}H_{37}N_2$ ($M+H^+$), 713.2957, Found 713.2977.

4d: A bluish purple solid (54% yield); mp >300 °C. IR (KBr) 728, 746, 1280, 1444, 1486, 1606, 3059, 3411 cm^{-1} . 1H NMR (300 MHz, $CDCl_3$): δ = 5.41 (s, 1H), 5.48 (s, 2H), 6.49 (d, J = 7.3 Hz, 2H), 6.78–6.84 (m, 6H), 7.05–7.37 (m, 16H), 7.78 (d, J = 7.3 Hz, 4H), 8.18 (br s, 2H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 45.0, 60.9, 103.6, 115.8, 119.9, 121.0, 123.6, 123.7, 124.3, 127.0, 127.46, 127.55, 130.2, 131.7, 133.8, 135.3, 136.1, 137.7, 140.4, 141.7, 148.2, 152.6. HRMS (FAB): calcd for $C_{53}H_{33}^{79}BrN_2$ (M^+), 776.1827, Found 776.1838.

4e: A pale purple solid (70% yield); mp >300 °C. IR (KBr) 747, 1104, 1281, 1444, 1608, 1720, 3056, 3415 cm^{-1} . 1H NMR (300 MHz, $CDCl_3$) δ = 3.86 (s, 3H), 5.50 (s, 2H), 5.53 (s, 1H), 6.50 (d, J = 7.3 Hz, 2H), 6.65–6.85 (m, 6H), 7.09–7.14 (m, 6H), 7.22–7.36 (m, 8H), 7.78 (d, J = 7.3 Hz, 4H), 7.92 (d, J = 8.1 Hz, 2H), 8.27 (br s, 2H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 45.6, 52.1, 60.9, 103.7, 115.8, 119.9, 123.6, 123.7, 124.4, 127.1, 127.5, 127.6, 128.5, 129.0, 130.0, 133.8, 135.2, 135.7, 137.8, 141.7, 146.6, 148.2, 152.6, 166.7. HRMS (FAB): calcd for $C_{55}H_{37}O_2N_2$ ($M+H^+$), 757.2855, Found 757.2858.

A Typical Procedure for Synthesis of BODIPY Dyes 5a–e.

To a solution of **4a–e** (0.52 mmol) in dry CH_2Cl_2 (10 mL) was added dropwise DDQ (119 mg, 0.52 mmol) in dry CH_2Cl_2 (10 mL) and the solution was stirred at room temperature for 1 h under nitrogen atmosphere. Et_3N (0.42 mL, 3.01 mmol) was then added, followed by an addition of 47% of $BF_3 \cdot OEt$ (0.83 mL, 3.05 mmol). After stirring for 3 h, the reaction mixture was quenched with water (20 mL). The organic layer was washed with brine (2×20 mL), and dried over Na_2SO_4 . The solvents were removed under reduced pressure, and the residue was purified with column chromatography on SiO_2 with $CHCl_3$ /hexane ($v/v = 1/3$)

as an eluent to afford **5a–e**.

5a: A purple solid (74% yield); mp >300 °C. IR (KBr) 747, 1068, 1098, 1196, 1268, 1338, 1364, 1402, 1464, 1556, 1601 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ = 2.87 (s, 6H), 6.31 (s, 2H), 6.52 (d, J = 8.3 Hz, 2H), 6.63 (d, J = 7.3 Hz, 2H), 6.96 (d, J = 7.3 Hz, 4H), 7.14–7.19 (m, 6H), 7.27 (d, J = 8.8 Hz, 2H), 7.36 (dd, J = 7.3, 7.3 Hz, 4H), 7.49 (dd, J = 7.3, 7.7 Hz, 2H), 7.79 (d, J = 7.8 Hz, 4H), 8.49 (d, J = 7.3 Hz, 2H). ^{13}C NMR (100 MHz, CDCl_3): δ = 40.0, 59.8, 111.3, 120.0, 120.6, 121.9, 124.08, 124.12, 124.2, 127.9 (two peaks are overlapped), 128.6, 129.9, 132.2, 132.9, 140.8, 141.3, 142.5, 143.5, 148.4, 151.6, 156.3, 160.2. HRMS (FAB): calcd for $\text{C}_{55}\text{H}_{36}\text{N}_3\text{F}_2\text{B}$ (M^+), 787.2980, Found 787.2959.

5b: A dark brown solid (73% yield); mp >300 °C. IR (KBr) 756, 1034, 1065, 1096, 1200, 1263, 1334, 1402, 1447, 1469, 1552, 1603 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ = 3.69 (s, 3H), 6.22 (s, 2H), 6.63 (d, J = 7.8 Hz, 2H), 6.75 (d, J = 8.8 Hz, 2H), 6.95 (d, J = 7.8 Hz, 4H), 7.14–7.19 (m, 6H), 7.29 (d, J = 8.8 Hz, 2H), 7.36 (dd, J = 7.6, 7.8 Hz, 4H), 7.50 (dd, J = 7.6, 7.8 Hz, 2H), 7.79 (d, J = 7.3 Hz, 4H), 8.50 (d, J = 7.3 Hz, 2H). ^{13}C NMR (100 MHz, CDCl_3): δ = 55.3, 59.7, 113.7, 120.0, 120.6, 124.17, 124.21, 124.3, 126.5, 127.9, 128.0, 128.7, 130.4, 131.9, 132.6, 141.1, 141.3, 142.1, 142.9, 148.2, 156.6, 161.0, 161.3. HRMS (FAB): calcd for $\text{C}_{54}\text{H}_{34}\text{ON}_2\text{F}_2\text{B}$ ($\text{M}+\text{H}^+$), 775.2741, Found 775.2733.

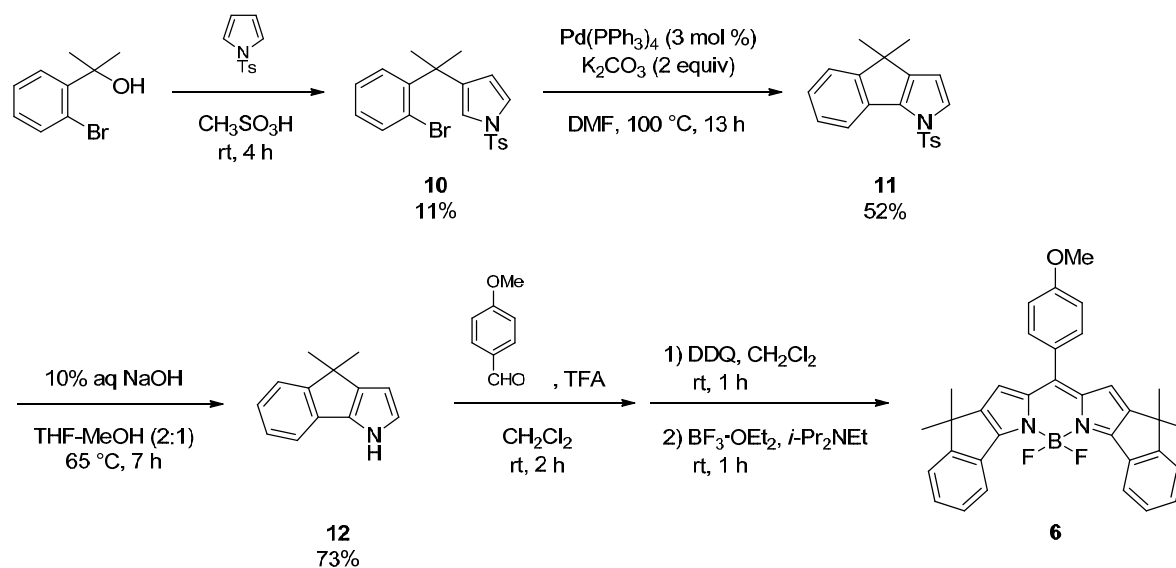
5c: A dark brown solid (61% yield); mp >300 °C. IR (KBr) 756, 1065, 1097, 1200, 1262, 1334, 1402, 1447, 1469, 1553, 1602 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ = 2.24 (s, 3H), 6.20 (s, 2H), 6.64 (d, J = 7.8 Hz, 2H), 6.95 (d, J = 7.8 Hz, 4H), 7.05 (d, J = 7.8 Hz, 2H), 7.15–7.26 (m, 8H), 7.36 (dd, J = 7.3, 7.3 Hz, 4H), 7.51 (dd, J = 7.6, 7.8 Hz, 2H), 7.79 (d, J = 7.8 Hz, 4H), 8.49 (d, J = 7.8 Hz, 2H). ^{13}C NMR (100 MHz, CDCl_3): δ = 21.2, 59.7, 120.0, 120.7,

124.17, 124.23, 124.3, 127.9, 128.0, 128.7, 128.8, 130.3, 130.4, 131.2, 132.5, 140.1, 141.1, 141.3, 142.4, 143.0, 148.2, 156.7, 161.5. HRMS (FAB): calcd for $C_{54}H_{33}N_2F_2B$ (M^+), 758.2714, Found 758.2708.

5d: A dark brown solid (59% yield); mp >300 °C. IR (KBr) 738, 761, 1065, 1096, 1196, 1262, 1333, 1401, 1447, 1469, 1552, 1601 cm^{-1} . 1H NMR (400 MHz, $CDCl_3$): δ = 6.15 (s, 2H), 6.65 (d, J = 7.8 Hz, 2H), 6.95 (d, J = 7.3 Hz, 4H), 7.15–7.26 (m, 8H), 7.37 (dd, J = 7.1, 7.8 Hz, 4H), 7.38 (d, J = 7.8 Hz, 2H), 7.51 (dd, J = 7.3, 7.8 Hz, 2H), 7.79 (d, J = 7.3 Hz, 4H), 8.49 (d, J = 7.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 59.7, 120.1, 120.2, 124.1, 124.2, 124.3, 124.4, 127.9, 128.1, 128.8, 130.8, 131.4, 131.8, 132.3, 132.9, 140.3, 140.8, 141.3, 143.5, 148.1, 156.8, 162.0. HRMS (FAB): calcd for $C_{53}H_{31}N_2^{79}BrF_2B$ ($M+H^+$), 823.1741, Found 823.1718.

5e: A purple solid (59% yield); mp >300 °C. IR (KBr) 758, 1065, 1097, 1268, 1335, 1553, 1726 cm^{-1} . 1H NMR (300 MHz, $CDCl_3$): δ = 3.82 (s, 3H), 6.11 (s, 2H), 6.64 (d, J = 7.7 Hz, 2H), 6.94 (d, J = 7.3 Hz, 4H), 7.13–7.24 (m, 6H), 7.33–7.43 (m, 6H), 7.51 (dd, J = 7.3, 7.7 Hz, 2H), 7.78 (d, J = 7.7 Hz, 4H), 7.89 (d, J = 8.0 Hz, 2H), 8.51 (d, J = 7.7 Hz, 2H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 52.2, 59.7, 120.1, 120.2, 124.1, 124.3, 124.5, 127.9, 128.1, 128.8, 129.3, 130.3, 130.8, 131.1, 132.3, 138.4, 140.3, 140.8, 141.3, 143.6, 148.1, 156.9, 162.2, 166.1. HRMS (FAB): calcd for $C_{55}H_{34}O_2N_2F_2B$ ($M+H^+$), 803.2691, Found 803.2702.

Synthesis of Compound 6.



3-(2-(2-Bromophenyl)propan-2-yl)-*N*-tosylpyrrole (10**):** A solution of *N*-tosylpyrrole (3.32 g, 15.0 mmol) and 2-(2-bromophenyl)propan-2-ol¹⁹ (4.84 g, 22.5 mmol) in $\text{CH}_3\text{SO}_3\text{H}$ (20 mL) was stirred at room temperature for 4 h. The reaction mixture was diluted with cold water (80 mL) and extracted with CH_2Cl_2 (4×15 mL). The organic layers were combined, washed with saturated aqueous solution of NaHCO_3 (2×50 mL) and brine (50 mL), and dried over MgSO_4 . The solvents were removed under reduced pressure, and the residue was purified with GPC (CHCl_3) to afford **10** (666 mg, 11%) as a pale yellow oil; mp 97.8 – 98.7°C . IR (KBr) 589, 681, 803, 1058, 1173, 1357, 1596, 2964 cm^{-1} . ^1H NMR (300 MHz, CDCl_3) δ = 1.67 (s, 6H), 2.40 (s, 3H), 5.91 (dd, J = 1.8, 3.3 Hz, 1H), 6.88 (dd, J = 1.8, 1.8 Hz, 1H), 7.02–7.07 (m, 2H), 7.24–7.29 (m, 3H), 7.44 (dd, J = 1.5, 8.1 Hz, 1H), 7.50 (dd, J = 1.8, 8.1 Hz, 1H), 7.70 (d, J = 8.4 Hz, 2H). ^{13}C NMR (75.5 MHz, CDCl_3) δ = 21.6, 29.7, 40.0, 113.6, 117.5, 120.9, 123.7, 126.7, 127.2, 128.0, 129.7, 135.5, 136.5, 138.3, 144.6, 146.0. HRMS (FAB): calcd for $\text{C}_{20}\text{H}_{21}\text{O}_2\text{N}^{81}\text{BrS}$ ($\text{M}+\text{H}^+$), 420.0457, Found 420.0451.

4,4-Dimethyl-1-tosyl-1,4-dihydroindeno[1,2-*b*]pyrrole (11): A flame dried Schlenk flask was charged with **10** (604 mg, 1.44 mmol), K₂CO₃ (399 mg, 2.88 mmol), Pd(PPh₃)₄ (50.2 mg, 0.0434 mmol), and dry DMF (15 mL) under nitrogen atmosphere. The solution was stirred at 100 °C for 13 h. The reaction mixture was cooled down to room temperature and filtered through a short silica gel pad. After an addition of CH₂Cl₂ (20 mL), the filtrate was washed with 10% aqueous solution of NaCl (5 × 40 mL), and dried over MgSO₄. The solvents were removed under reduced pressure to give a pale brown solid. The crude product was purified by GPC (CHCl₃) to give **11** (254 mg, 52%) as a colorless oil. IR (neat) 539, 768, 1051, 1363, 1597, 2359, 2964 cm⁻¹. ¹H NMR (300 MHz, CDCl₃) δ = 1.36 (s, 6H), 2.34 (s, 3H), 6.31 (d, *J* = 3.3 Hz, 1H), 7.14–7.32, (m, 6H), 7.75 (d, *J* = 8.4 Hz, 2H), 8.03 (d, *J* = 7.3 Hz, 1H). ¹³C NMR (75.5 MHz, CDCl₃) δ = 21.6, 25.8, 42.0, 107.7, 119.4, 122.2, 124.8, 125.9, 126.7, 127.0, 130.0, 132.2, 134.4, 136.1, 144.8, 145.9, 157.1. HRMS (FAB): calcd for C₂₀H₁₉NO₂S (M⁺), 337.1137, Found 337.1130.

4,4-Dimethyl-1,4-dihydroindeno[1,2-*b*]pyrrole (12): To a solution of **11** (253 mg, 0.750 mmol) in THF (7 mL) and MeOH (3.5 mL) was added 10% aqueous solution of NaOH (3 mL), and the solution was stirred at 65 °C for 7 h. After cooling to ambient temperature, the reaction mixture was diluted with cold water (10 mL) and MeOH was removed under reduced pressure. The residue was extracted with EtOAc (3 × 5 mL). The organic layers were combined, washed with brine (2 × 20 mL), and dried over MgSO₄. The solvents were removed under reduced pressure, and the residue was purified with column chromatography on SiO₂ with EtOAc/hexane (v/v = 1/3) as an eluent to afford **12** (101 mg, 73%) as a pale blue solid; mp 130.6–131.3 °C. IR (KBr) 711, 754, 1063, 1454, 1610, 2959, 3370 cm⁻¹. ¹H NMR (300 MHz, CDCl₃) δ = 1.45 (s, 6H), 6.21 (dd, *J* = 1.8, 2.8 Hz, 1H), 6.82 (dd, *J* = 2.4, 2.4 Hz, 1H), 7.06–7.11 (m, 1H), 7.17–7.25 (m, 2H), 7.33 (d, *J* = 7.3 Hz, 1H), 8.22 (br s, 1H). ¹³C

NMR (75.5 MHz, CDCl_3) δ = 26.6, 42.4, 102.9, 115.9, 121.2, 122.5, 123.6, 126.4, 133.5, 134.0, 140.4, 157.5. HRMS (FAB): calcd for $\text{C}_{13}\text{H}_{14}\text{N}$ ($\text{M}+\text{H}^+$), 184.1126, Found 184.1122.

BODIPY Dye 6: To a solution of **12** (94.8 mg, 0.517 mmol) in dry CH_2Cl_2 (6 mL) was added two drops of TFA, and the solution was stirred at room temperature for 2 h under nitrogen atmosphere. The reaction mixture was quenched with saturated aqueous solution of NaHCO_3 (10 mL) and extracted with CH_2Cl_2 (3×5 mL). The organic layers were combined, washed with brine (2×20 mL), and dried over MgSO_4 . The solvents were removed under reduced pressure, and the residue was partially purified with column chromatography on SiO_2 (CH_2Cl_2 –hexane, 4:1) to afford a crude product (49.7 mg) as a blue solid. The crude product was then dissolved in dry CH_2Cl_2 (8 mL). After an addition of DDQ (23.8 mg, 0.105 mmol) in dry CH_2Cl_2 (6 mL), the solution was stirred at room temperature for 1 h under nitrogen atmosphere. $i\text{Pr}_2\text{NEt}_2$ (0.105 mL, 0.603 mmol) and $\text{BF}_3 \cdot \text{OEt}_2$ (0.165 mL, 0.606 mmol) were successively added and after 4 h, the reaction mixture was washed with 10% aqueous solution of NaCl (4×20 mL), and dried over Na_2SO_4 . The solvents were removed under reduced pressure, and the residue was partially purified with column chromatography on SiO_2 with CH_2Cl_2 /hexane ($v/v = 1/3$) as an eluent to afford **6** (30.1 mg, 56%) as a dark brown solid; mp >300 °C. IR (KBr) 759, 1060, 1088, 1278, 1335, 1552, 1603, 2966 cm^{-1} . ^1H NMR (300 MHz, CDCl_3) δ = 1.47 (s, 12H), 3.92 (s, 3H), 6.55 (s, 2H), 7.07 (d, $J = 8.8$ Hz, 2H), 7.38–7.45 (m, 6H), 7.56 (d, $J = 8.4$ Hz, 2H), 8.30 (d, $J = 7.0$ Hz, 2H). ^{13}C NMR (75.5 MHz, CDCl_3) δ = 27.1, 41.9, 55.5, 113.8, 119.3, 122.7, 124.2, 127.2, 127.9, 129.7, 130.8, 132.0, 140.6, 141.1, 148.6, 158.8, 160.87, 160.91. HRMS (FAB): calcd for $\text{C}_{34}\text{H}_{29}\text{ON}_2\text{F}_2\text{B}$ (M^+), 530.2347, Found 530.2351.

X-ray crystallographic analysis of 3a, 3b, and 5d:

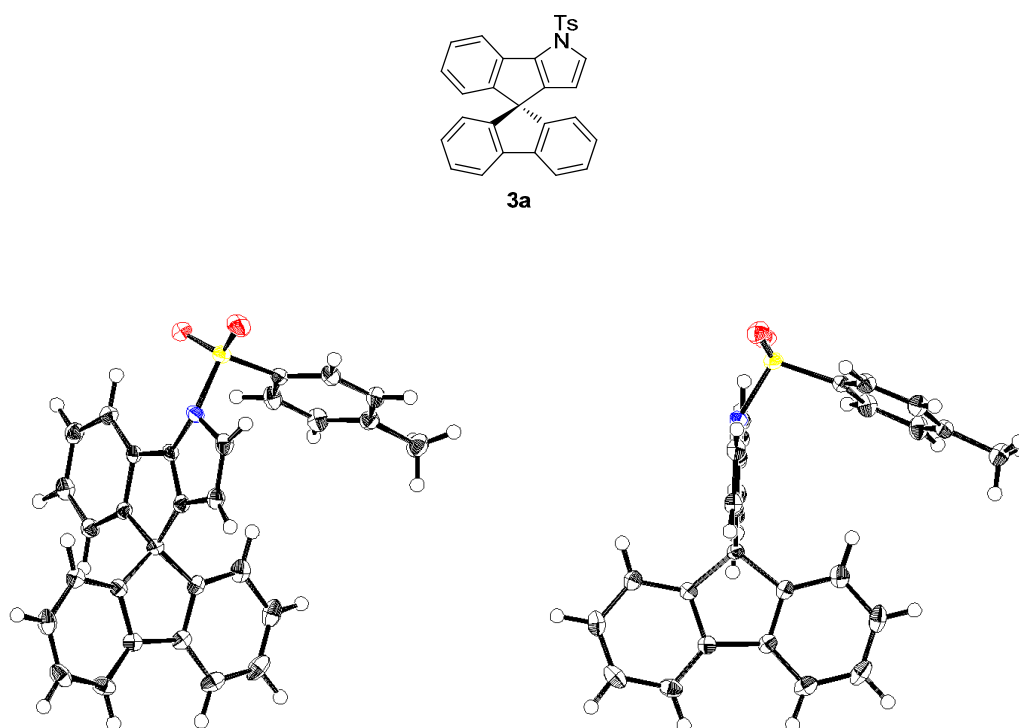


Figure 4. ORTEP drawings of 3a.

Table 6. Crystal data and structure refinement for **3a**

Empirical Formula	C ₃₀ H ₂₁ N O ₂ S
Formula Weight	459.56
Temperature (°C)	−120
Crystal Color, Habit	colorless, block
Crystal Dimensions	0.40 × 0.40 × 0.20 mm
Crystal System	triclinic
Lattice Parameters	$a = 10.327(4) \text{ \AA}$ $\alpha = 75.268(15)^\circ$ $b = 10.808(5) \text{ \AA}$ $\beta = 65.992(11)^\circ$ $c = 11.555(4) \text{ \AA}$ $\gamma = 89.308(19)^\circ$ $V = 1133.3(8) \text{ \AA}^3$
Space Group	<i>P</i> -1 (#2)
Z value	2
D _{calc}	1.347 g/cm ³
F(000)	480.00
μ(MoKα)	1.719 cm ^{−1}
Radiation	MoKα ($\lambda = 0.71070 \text{ \AA}$) graphite monochromated
2θ max	61.8°
No. of Reflections Measured	Total: 10126 Unique: 5815 ($R_{\text{int}} = 0.027$)
Structure Solution	Direct Methods (SIR92)
Refinement	Full-matrix least-squares on F ²
No. Observations (All reflections)	5815
No. Variables	391
Reflection/Parameter Ratio	14.87
Residuals: R_1 ($I > 2.00\sigma(I)$)	0.0470
Residuals: wR_2 (All reflections)	0.0762
Goodness-of-fit on F ²	1.097
Max Shift/Error in Final Cycle	0.000
Maximum peak in Final Diff. Map	0.38 e [−] /Å ³
Minimum peak in Final Diff. Map	−0.60 e [−] /Å ³

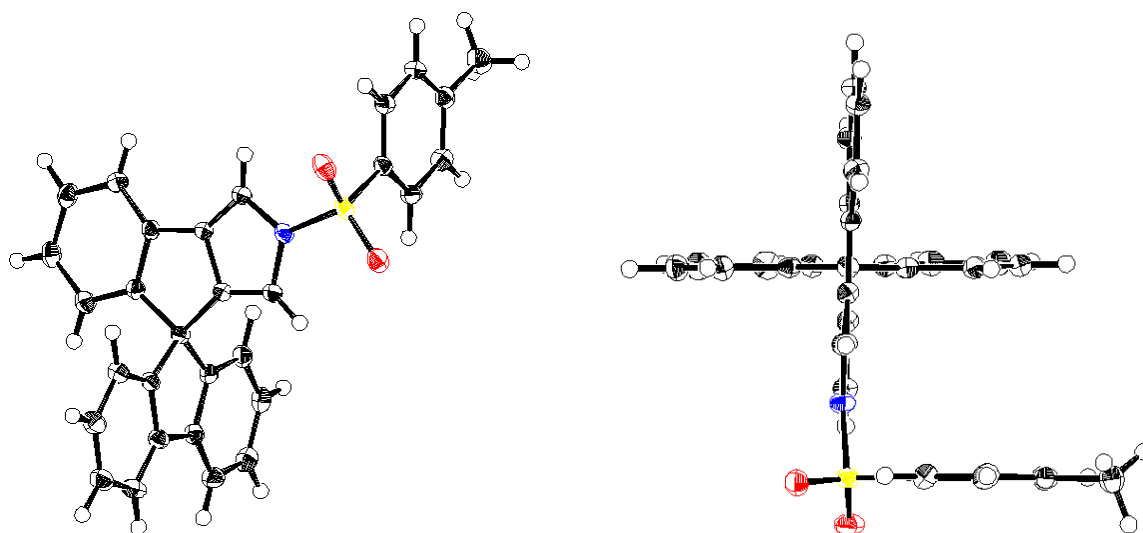
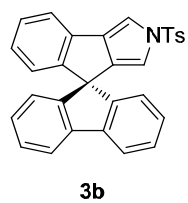
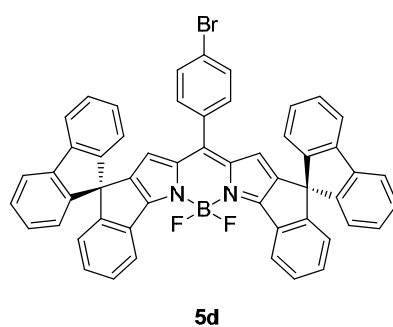


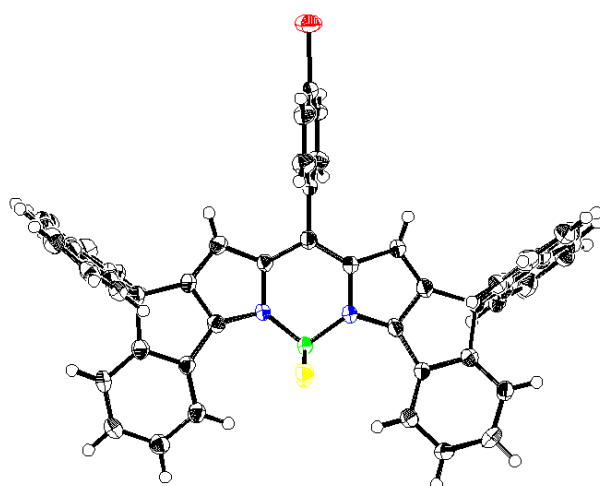
Figure 5. ORTEP drawings of **3b**.

Table 7. Crystal data and structure refinement for **3b**

Empirical Formula	C ₃₀ H ₂₁ N O ₂ S
Formula Weight	459.56
Temperature (°C)	−120
Crystal Color, Habit	colorless, block
Crystal Dimensions	0.20 × 0.20 × 0.20 mm
Crystal System	monoclinic
Lattice Parameters	a = 12.330(4) Å b = 8.447(3) Å β = 95.906(4)° c = 21.697(7) Å V = 2247.6(13) Å ³
Space Group	<i>P</i> 2 ₁ / <i>a</i> (#14)
Z value	4
D _{calc}	1.358 g/cm ³
F(000)	960.00
μ(MoKα)	1.733 cm ^{−1}
Radiation	MoKα (λ = 0.71070 Å) graphite monochromated
2θ max	62.1°
No. of Reflections Measured	Total: 19437 Unique: 6398 (R _{int} = 0.040)
Structure Solution	Direct Methods (SIR92)
Refinement	Full-matrix least-squares on F ²
No. Observations (All reflections)	6398
No. Variables	391
Reflection/Parameter Ratio	16.36
Residuals: R ₁ (I > 2.00σ(I))	0.0475
Residuals: wR ₂ (All reflections)	0.0738
Goodness-of-fit on F ²	1.027
Max Shift/Error in Final Cycle	0.000
Maximum peak in Final Diff. Map	0.47 e [−] /Å ³
Minimum peak in Final Diff. Map	−0.45 e [−] /Å ³



(a)



(b)

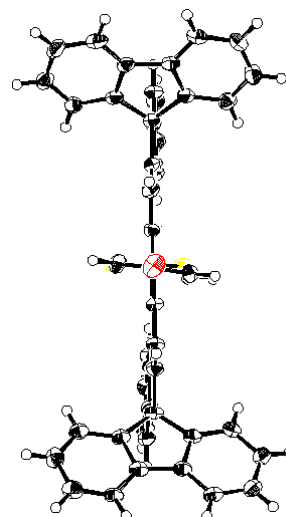


Figure 6. ORTEP drawings of **5d**. (a) Front view; (b) Top view. Solvent molecules have been omitted for clarity.

Table 8. Crystal data and structure refinement for **5d**

Empirical Formula	C ₅₃ H ₃₀ B Br F ₂ N ₂ · C H Cl ₃
Formula Weight	942.92
Temperature (°C)	−120
Crystal Color, Habit	green, block
Crystal Dimensions	0.20 × 0.20 × 0.20 mm
Crystal System	monoclinic
Lattice Parameters	a = 12.794(3) Å b = 17.775(5) Å β = 90.835(4)° c = 18.865(5) Å V = 4289.5(20) Å ³
Space Group	<i>P</i> 2 ₁ / <i>a</i> (#14)
Z value	4
D _{calc}	1.460 g/cm ³
F(000)	1912.00
μ(MoKα)	11.982 cm ^{−1}
Radiation	MoKα (λ = 0.71070 Å) graphite monochromated
2θ max	62.1°
No. of Reflections Measured	Total: 37442 Unique: 11715 (R _{int} = 0.041)
Structure Solution	Direct Methods (SIR92)
Refinement	Full-matrix least-squares on F ²
No. Observations (All reflections)	11715
No. Variables	590
Reflection/Parameter Ratio	19.86
Residuals: R ₁ (I > 2.00σ(I))	0.0801
Residuals: wR ₂ (All reflections)	0.1375
Goodness-of-fit on F ²	1.014
Max Shift/Error in Final Cycle	0.000
Maximum peak in Final Diff. Map	2.06 e [−] /Å ³
Minimum peak in Final Diff. Map	−1.65 e [−] /Å ³

Table 9. Cartesian atomic coordinates for the optimized structure of **9** (B3LYP/6-31G(d)).

atom	x	y	z
C	0.2725108739	-1.0514936071	-1.3249863605
N	-0.6401901250	-0.0098596746	-1.0999803045
B	-0.4617015318	1.0957524529	-0.0054301105
N	0.5516944447	0.5029114922	1.0308337835
C	1.4359503516	-0.5509598336	0.7549765440
C	1.2948244978	-1.2966197104	-0.4122395345
C	-0.0884777679	-1.7437147539	-2.5207715937
F	-1.6820452530	1.3581990334	0.6140226282
C	-1.2187435989	-1.1140435675	-3.0019526871
F	0.0600345121	2.2448207299	-0.5737847811
C	0.9005493991	0.9841479904	2.2359155895
C	2.0062974717	0.2734239698	2.7637238432
C	2.3515983516	-0.6939392826	1.8414990518
C	-1.5285536060	-0.0608878059	-2.1068157682
C	-2.2158260134	-1.1555217286	-4.1439447610
C	-3.1300971042	0.0278168165	-3.7514268712
C	0.4788377045	2.0226488862	3.1529558097
C	1.3548238969	1.9572889617	4.2667245876
C	2.4044906427	0.8322111659	4.1162175282
C	-0.5569069025	2.9623618745	3.1056977806
C	-0.6956464155	3.8469990882	4.1748611698
C	0.1747211520	3.7914205371	5.2705753833
C	1.2032047629	2.8428041311	5.3242643462
C	-2.7100922406	0.6507340099	-2.5482332356
C	-4.2494573212	0.4970019009	-4.4240439994
C	-4.9509186515	1.5863185736	-3.8931249091
C	-4.5406730327	2.1928396122	-2.6993707620
C	-3.4189999008	1.7310682435	-2.0112147571
H	1.9856751600	-2.1119840887	-0.6024569736
H	0.4405400052	-2.5963675261	-2.9263556797
H	3.1375899265	-1.4360297228	1.8952952882
C	-1.5914802841	-1.0050799844	-5.5353533280
C	-2.9692324350	-2.4816459752	-4.2913546089
C	3.8498105465	1.3358777009	4.1925611009
C	2.3757596547	-0.1821680247	5.2643316773

H	-1.2352976818	2.9825398538	2.2606128711
H	-1.4916353795	4.5863094822	4.1585655001
H	0.0483587787	4.4901407627	6.0932208368
H	1.8706665552	2.8007146389	6.1806085133
H	-4.5772829882	0.0267221622	-5.3470658777
H	-5.8281715717	1.9619999243	-4.4129458430
H	-5.1051850995	3.0317432441	-2.3018652148
H	-3.1019999646	2.1794815584	-1.0767491858
C	-0.7770843236	0.0136002176	-6.0144011169
C	-1.9488093821	-2.0895570784	-6.3584762882
C	-3.7335199614	-3.154624609	-3.3461483236
C	-2.8022082410	-3.0045857985	-5.5876398718
C	1.3211526199	-0.9800773871	5.6904717862
C	3.6271432872	-0.2385850353	5.9066515560
C	4.4833241996	2.2767678574	3.3901752141
C	4.5403413411	0.7022017445	5.2427649095
C	-1.4876859483	-2.1565075546	-7.6748846811
C	-3.4056930698	-4.2127903146	-5.9425518242
H	-0.5011368349	0.8499540184	-5.3775451972
C	-0.3161100251	-0.0558612062	-7.3336839692
H	-3.8612086703	-2.7499401742	-2.3455404261
C	-4.3373411139	-4.3650771121	-3.7041415158
C	-4.1739294787	-4.8882654526	-4.9916539131
H	-3.2816276505	-4.6247395713	-6.9408689568
C	-0.6693743899	-1.1319051459	-8.1556819906
H	-1.7580611424	-2.9906582189	-8.3173494788
H	-4.9381122298	-4.9027273290	-2.9756221545
H	-4.6492157264	-5.8296235259	-5.2543700694
H	0.3218286966	0.7331497888	-7.7225187532
H	-0.3030224235	-1.1709964811	-9.1780936122
C	3.8260794283	-1.1015914422	6.9862620992
C	5.8784366737	1.0125617992	5.4942123600
H	0.3556760909	-0.9358340645	5.1932920158
C	1.5228621530	-1.8439940532	6.7725603680
C	2.7651714917	-1.9030091084	7.4138889050
H	4.7891441099	-1.1525790511	7.4878976246
H	2.9061349861	-2.5792597318	8.2528681621
H	0.7073875169	-2.4740371686	7.1172064679

C	6.5143432057	1.9587190159	4.6873546390
H	6.4196284319	0.5275564457	6.3026382260
H	3.9493056423	2.7646655120	2.5790030676
C	5.8241774144	2.5858677812	3.6439455101
H	6.3332691774	3.3194691132	3.0247917941
H	7.5555269021	2.2099694525	4.8714121012

References and Notes

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Chapter 4

Synthesis of Electron-donor-substituted Structurally Constrained BODIPY Dyes and Observation of pH-Dependent ICT Fluorescence

Abstract

New structurally constrained BODIPY dyes having electron-donating substituents were synthesized. As the key compounds for the construction of the BODIPY dyes, 1'*H*-spiro-[fluorene-9,4'-indeno[1,2-*b*]pyrrole] (**sp-FIP**) derivatives with electron-donating groups, such as OMe and NMe₂ at its 6'-position, were prepared using palladium-catalyzed intramolecular direct C–H arylation of a pyrrole moiety. The resulting BODIPY dyes showed bathochromic fluorescence and, in particular, the amino-substituted dye emitted in the near-IR region. Furthermore, pH-dependent reversible spectrum changes of the BODIPY dye were observed with the addition of trifluoroacetic acid (TFA) and subsequent addition of *i*-Pr₂NEt.

Introduction

4,4-Difluoro-4-bora-3a,4a-diaza-*s*-indacenes (BODIPY) are attractive fluorescent dyes because of their remarkable physical properties, such as high photoluminescent quantum yields, large absorption coefficients, narrow emission bands, and high environmental stability.¹ Therefore, they have been widely used in a variety of organic functional materials where biological applications require light-emitting properties in the near-IR or visible red region.² To modulate the optical properties of BODIPY dyes, the following strategies are elaborated: 1) extension of π -conjugation by introducing aryl³ or styryl⁴ substituents at the 3,5-positions; 2) rigidifying the molecular structure to suppress the free rotation of extended substituents and enhance the coplanarity,⁵ and 3) introducing electron-donating groups at the 3,5-positions.⁶⁻⁹ In particular, the third approach is the most effective for the red shift of

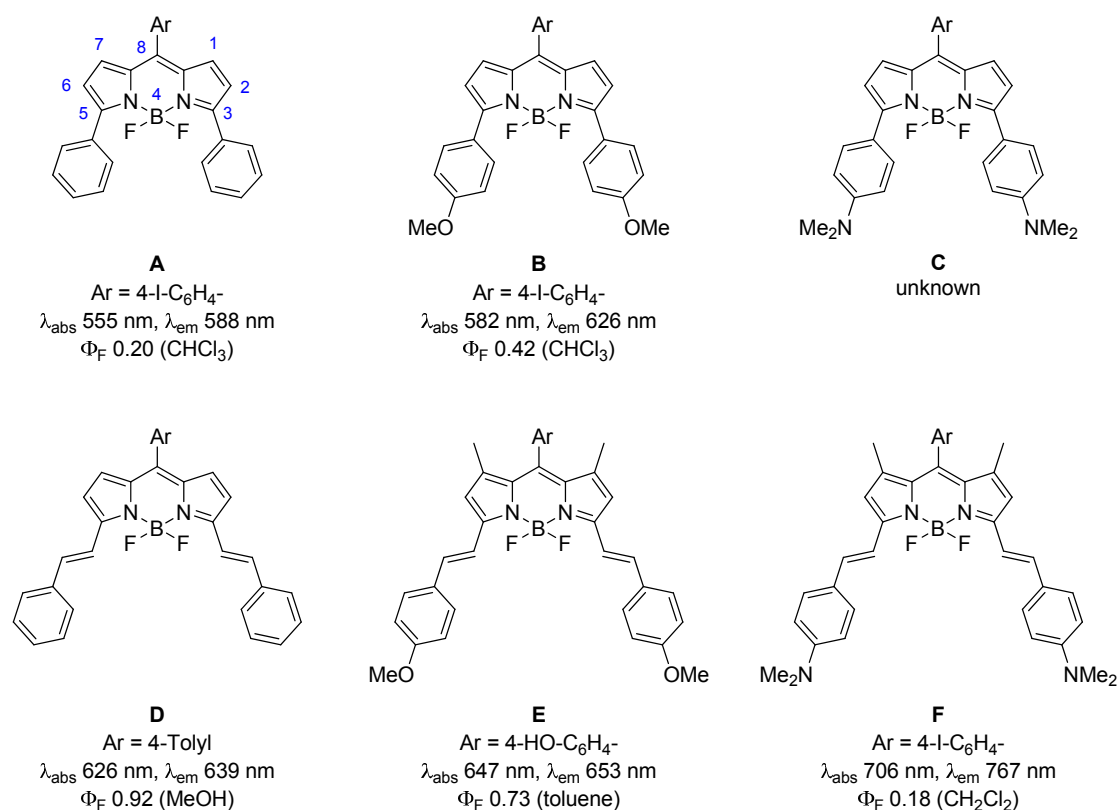


Figure 1. The photophysical properties of 3,5-diaryl or distyryl-substituted BODIPY dyes.

both the absorption and the emission spectra. Burgess et al. investigated the phenyl- or *p*-anisyl-substituted BODIPY dyes (**A** and **B**) and found that the introduction of the electron-donating methoxy groups led to the red shift of the spectra by about 30 nm (Figure 1).^{6a} Similar phenomena have been observed in styryl-substituted BODIPY dyes **D**^{4a} and **E**.^{6b} Ziessel et al. reported that strong electron-donating *p*-aminostyryl groups have great potential to give a bathochromic shift of about 80 nm (Figure 1, **F**).^{6c} In addition, applications in fluorescent sensors of pH⁷ and/or metal ions^{8,9} take advantage of the basicity or coordination of amino groups. However, *p*-aminophenyl-substituted BODIPY dyes (type **C**) have not so far been explored.

In chapter 3, the author has described that structurally constrained BODIPY dyes that were synthesized using the strategies 1 and 2 shown above exhibited intense fluorescence with the emission maxima around 670 nm (Figure 2).¹⁰ He also described solvent-dependent fluorescence of the BODIPY dye with *p*-aminophenyl substituents at the 8-positions, which was caused by photoinduced electron transfer (PeT).^{10,11} He now describes the synthesis of structurally constrained BODIPY dyes with *p*-anisyl or *p*-aminophenyl substituents at the 3,5-positions (types **B** and **C**). Among them, the *p*-aminophenyl-substituted BODIPY dye exhibited solvent-dependent and pH-dependent fluorescence derived from intramolecular charge transfer (ICT).^{7,8,12}

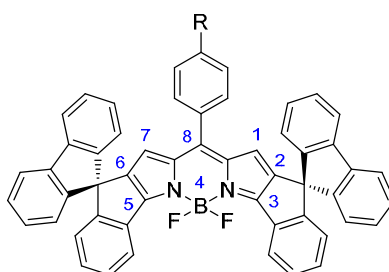
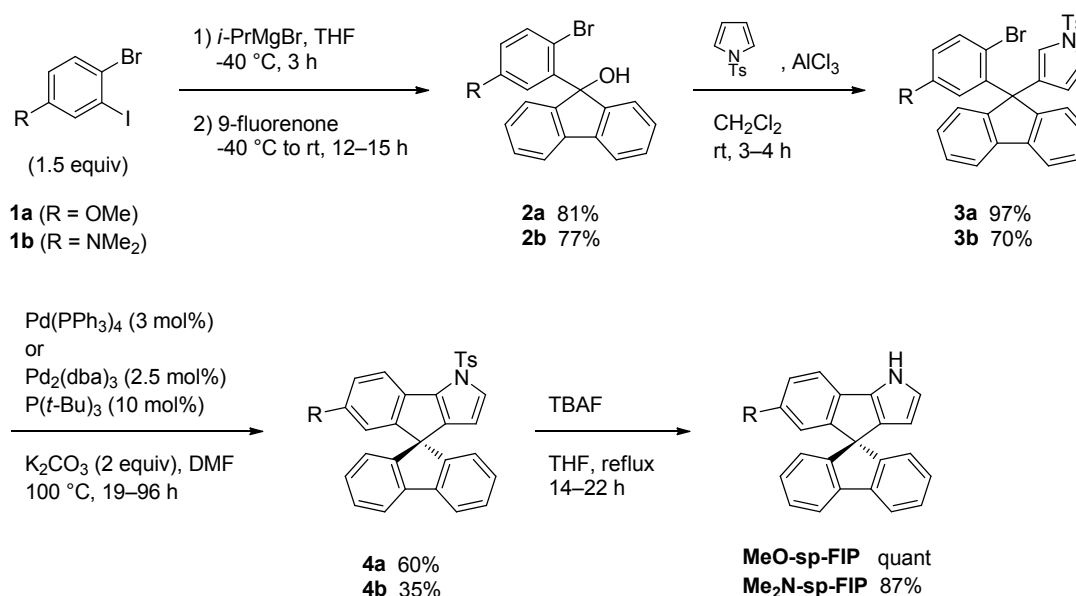


Figure 2. Structurally constrained BODIPY dyes.

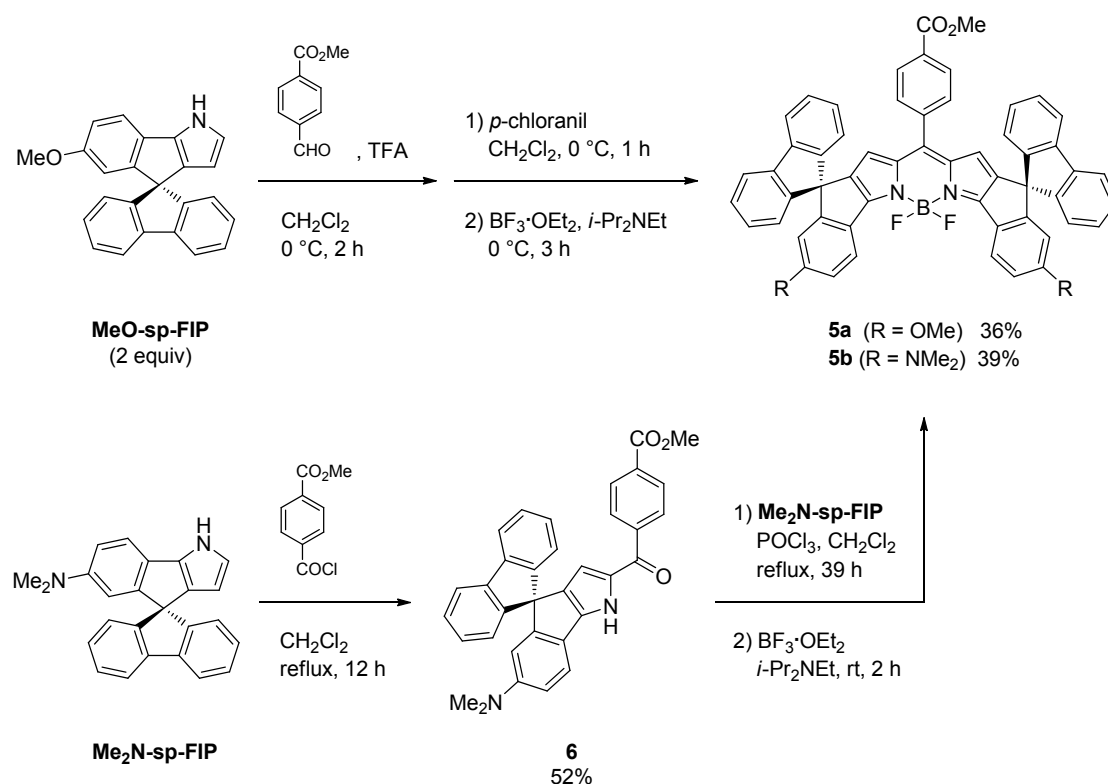
Results and Discussion

The preparations of 6'-methoxy-1'*H*-spiro[fluorene-9,4'-indeno[1,2-*b*]pyrrole] (**MeO-sp-FIP**) and 6'-(*N,N*-dimethylamino)-1'*H*-spiro[fluorene-9,4'-indeno[1,2-*b*]pyrrole] (**Me₂N-sp-FIP**) as key compounds for the synthesis of structurally constrained BODIPY dyes are summarized in Scheme 1. The reaction of 1-bromo-2-iodo-4-methoxybenzene (**1a**) and 4-bromo-3-iodo-*N,N*-dimethylaniline (**1b**) with isopropyl Grignard reagent followed by quenching with 9-fluorenone gave **2a** and **2b** in 81% and 77% yield, respectively. Friedel–Crafts alkylation of *N*-tosylpyrrole with **2a** and **2b** using AlCl₃ afforded **3a** and **3b** in 97% and 70% yield, respectively. The catalytic intramolecular direct C–H arylation^{10,13} of **3a** using Pd(PPh₃)₄ proceeded smoothly to afford **4a** in 60% yield. From **3b**, **4b** was obtained in 35% yield using Pd₂(dba)₃ and P(*t*-Bu)₃ instead of Pd(PPh₃)₄. Detosylation of **4** using tetrabutylammonium fluoride (TBAF) gave **sp-FIP** derivatives, **MeO-sp-FIP** and **Me₂N-sp-FIP**, in excellent yields (quantitative yield and 87%, respectively).

Scheme 1



Scheme 2

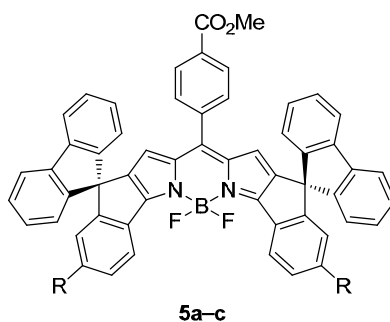


The author next examined the transformation of **sp-FIP** derivatives to BODIPY dyes (Scheme 2). **MeO-sp-FIP** was reacted with methyl 4-formylbenzoate to give dipyrromethane, which was subsequently oxidized and complexed with $\text{BF}_3 \cdot \text{OEt}_2$, leading to the formation of BODIPY dye **5a**. Although he attempted to prepare **5b** using **Me₂N-sp-FIP** in a similar manner, the oxidation using DDQ or *p*-chloranil resulted in decomposition or recovery of the corresponding dipyrromethane. Thus, he changed the synthetic route to **5b**. Acylpyrrole **6** was prepared by the reaction of **Me₂N-sp-FIP** with methyl 4-(chlorocarbonyl)benzoate in 52% yield, and then the condensation of **6** with one equivalent of **Me₂N-sp-FIP**, followed by complexation with $\text{BF}_3 \cdot \text{OEt}_2$ led to the desired BODIPY dye **5b**.

The absorption and emission spectra of **5a** and **5b** were measured in THF (Table 1). The absorption maximum and the emission maximum of **5a** were red-shifted by about 30 nm

compared with those of **5c** without electron-donating groups. Furthermore, **5a** showed intense fluorescence ($\Phi_F = 0.61$) with a small Stokes shift (15 nm) because of its rigid structure. Because of the strong electron-donating ability of *N,N*-dimethylamino groups, **5b** exhibited bathochromic shifts of about 80 nm in both absorption and emission maxima compared with **5c**. However, **5b** showed lower quantum yield ($\Phi_F = 0.30$) with larger Stokes shift (31 nm) than **5a** and **5c**. This indicates the occurrence of intramolecular charge transfer (ICT) in **5b**.

Table 1. Photophysical properties of BODIPY dyes **5a–c** in THF ($c = 1.00 \times 10^{-6}$ M)



BODIPY	R	λ_{abs} [nm]	λ_{ex} [nm]	λ_{em} [nm]	Stokes shift [nm]	Φ_F^a
5a	OMe	666	614	681	15	0.61
5b	NMe ₂	738	676	769	31	0.30
5c^b	H	641	592	652	11	0.67

^a Determined by the calibrated integrating sphere system. ^b Reference 10.

When the absorption spectra of **5b** were measured in various solvents, the positions of the absorption maxima were slightly affected by the solvent polarity (Figure 3, Table 2). In contrast, the features of solvent-dependent fluorescence of **5b** were found in the emission spectra. The emission maximum obviously shifts to a longer wavelength, and the emission spectra were broadened and weakened by going from nonpolar to polar solvents (cyclohexane: 741 nm; DMF: 792 nm). Furthermore, in cyclohexane, **5b** showed sharp and narrow emission spectrum with the highest fluorescence quantum yield ($\Phi_F = 0.51$).

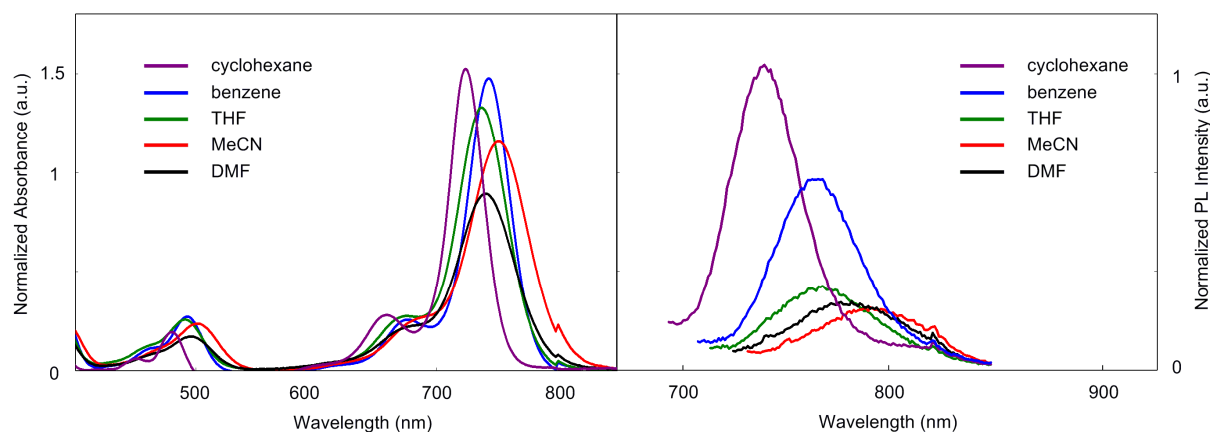


Figure 3. The absorption (left) and emission spectra (right) of **5b** in various solvents.

Table 2. Photophysical properties of BODIPY dyes **5b** in various solvents ($c = 1.00 \times 10^{-6}$ M)

Solvent	λ_{abs} [nm]	λ_{ex} [nm]	λ_{em} [nm]	Stokes shift [nm]	Φ_F^a
cyclohexane	724	659	741	17	0.51
benzene	743	677	769	26	0.42
THF	738	676	769	31	0.30
MeCN	741	676	783	42	0.28
DMF	752	685	792	40	0.23

^a Determined by the calibrated integrating sphere system.

In general, the emission properties of the ICT fluorophores having amino groups can be modulated by cation binding, which reduces the electron-donating ability of the nitrogen atom. As a result, ICT process is prohibited and the inherent sharp emission of the BODIPY dye is restored. The author next titrated **5b** with TFA in acetonitrile solution (Figure 4). In the absorption spectra, the initial absorption band at 741 nm decreased and new absorption bands at 686 nm and 636 nm appeared with addition of TFA ($[\text{TFA}] = 10^{-2}$ M, Figure 4). The peak at 686 nm is anticipated to correspond to **5b-H⁺**. As evidence of this phenomenon, the peak disappeared with additional TFA and a distinctive sharp absorption band of a BODIPY dye appeared at 636 nm, which can correspond to **5b-2H⁺**. The emission spectra showed a

parallel change with the absorption spectra. The original broad fluorescence band of **5b** changed with blue shift as TFA was added, and a sharp and strong emission peak arose at 647 nm when the TFA concentration reached 1 M. Similarly to the absorption spectra, the emission derived from **5b-H⁺** is observed at 721 nm ($[TFA] = 10^{-2}$ M, Figure 4). This indicates that the protonated amino groups no longer act as electron-donors. Then, to prove that the phenomenon is caused by the protonation on amino groups rather than such structural

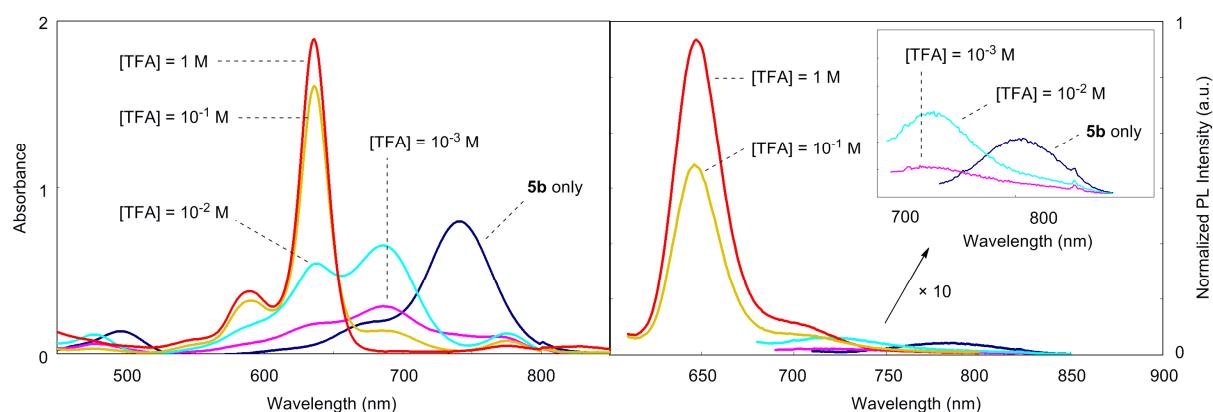


Figure 4. The absorption spectra (left) and the emission spectra (right) of **5b** in the presence of increasing TFA concentrations (0, 10^{-3} , 10^{-2} , 10^{-1} , and 1.0 M) in MeCN (1.00×10^{-6} M).

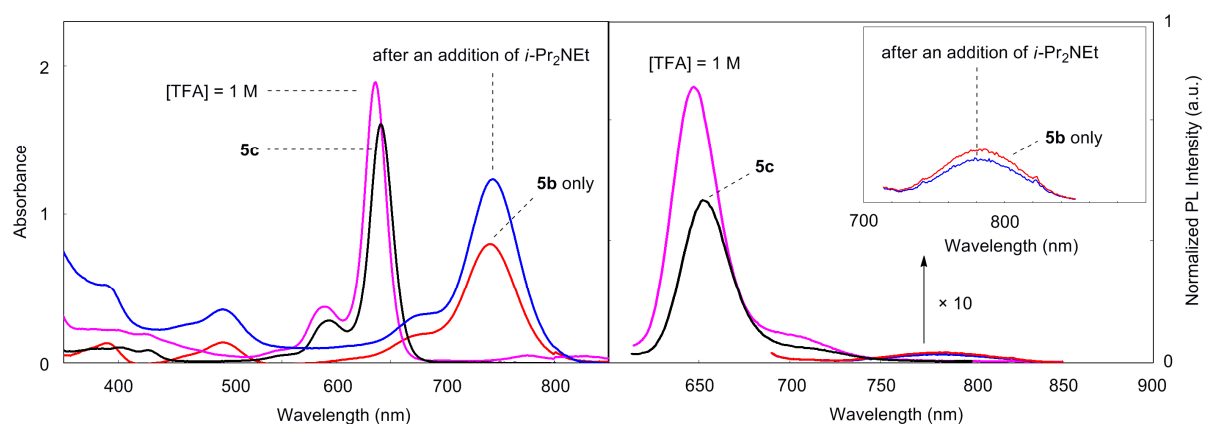


Figure 5. The absorption spectra (left) and the emission spectra (right) of **5b** after an addition of $i\text{-Pr}_2\text{NEt}$.

changes as hydrolysis of the ester group or deboronation, *i*-Pr₂NEt was added to the acidic solution (**5b** with [TFA] = 1 M). As expected, the identical spectra of the original **5b** were restored (Figure 5).

In conclusion, the author has developed structurally constrained BODIPY dyes with electron-donating groups, such as MeO or Me₂N at the para position of phenyl groups substituted at 3,5-positions on the BODIPY core. Palladium-catalyzed intramolecular direct C–H arylation of a pyrrole moiety allowed him to synthesize **sp-FIP** derivatives as the key compounds for the construction of the BODIPY dyes. The emission bands of the resulting BODIPY dyes were shifted bathochromically because of the electron donation from the MeO and Me₂N groups. In addition, amino-substituted BODIPY dye **5b** showed ICT character. The ICT process could be modulated by protonation on amino groups and recovery of original absorption and fluorescence upon deprotonation with an additional base was demonstrated. He envisions the application of **5b** in pH and/or metal ion sensors and further investigations will be reported in due course.

Experimental Section

General. Unless otherwise specified, all reagents were purchased from a chemical supplier and used without further purification. Tetrahydrofuran (THF) was distilled over benzophenone ketyl under nitrogen atmosphere. *N,N*-Dimethylformamide (DMF) was distilled over CaH₂ under nitrogen atmosphere. CH₂Cl₂ was dried and collected using a Grubbs-type solvent purification system manufactured by Glass Contour. Melting points are uncorrected. ¹H and ¹³C spectra were recorded on a JEOL AL-300 (300 MHz for ¹H, and 75.5 MHz for ¹³C) instrument or a JEOL EX-400 (400 MHz for ¹H, and 100 MHz for ¹³C)

instrument. IR spectra were obtained on a JASCO 460 plus FT/IR spectrometer. Mass spectra were measured with a JEOL JMS-SX102A. Analytical thin-layer chromatography (TLC) was performed on Merck 60F254 silica plates and visualized by UV light. Column chromatography was carried out on Silicycle SilicaFlash F60 60-63 μm (230-400 mesh) silica gel. UV-visible absorption spectra were recorded on a JASCO V-570 UV-vis-NIR spectrometer. Emission spectra were measured with a Jobin Yvon-Horiba FluoroMax-3. Degassed spectral grade solvents were used for the measurements. Absolute fluorescence quantum yields were determined by the calibrated integrating sphere system.

4-Bromo-3-iodo-*N,N*-dimethylaniline (1b): To a solution of 4-bromo-3-iodoaniline¹⁴ (12.8 g, 42.9 mmol) in DMF (120 mL) was added K_2CO_3 (23.7 g, 172 mmol) and MeI (6.42 mL, 103 mmol), and the solution was stirred at 70 °C for 13 h. After cooling to ambient temperature, water (180 mL) was added and the solution was extracted with Et_2O (5×40 mL). The organic layers were combined, washed with brine (3×100 mL), and dried over MgSO_4 . The solvents were removed under reduced pressure to give brown solid. The crude product was purified by recrystallization from EtOAc/hexane ($v/v = 1/4$) to give **1b** (10.5 g, 75%) as a pale brown solid; mp 93.8–94.8 °C. IR (KBr) 580, 797, 827, 955, 1231, 1362, 1496, 1582, 2810, 2889 cm^{-1} . ^1H NMR (300 MHz, CDCl_3): $\delta = 2.90$ (s, 6H), 6.54 (dd, $J = 2.9, 8.8$ Hz, 1H), 7.15 (d, $J = 3.3$ Hz, 1H), 7.35 (d, $J = 8.8$ Hz, 1H). ^{13}C NMR (75.5 MHz, CDCl_3): $\delta = 40.3, 101.7, 113.8, 115.1, 123.5, 132.2, 150.0$. Anal. Calcd for $\text{C}_8\text{H}_9\text{NBrI}$: C, 29.48; H, 2.78. Found: C, 29.39; H, 2.51.

9-(2-Bromo-5-methoxyphenyl)-9*H*-fluoren-9-ol (2a): The solution of 1-bromo-2-iodo-4-methoxybenzene (**1a**)¹⁵ (14.1 g, 45.0 mmol) in dry THF (45 mL) was cooled to -40 °C. To the solution was added dropwise 1.0 M THF solution of isopropyl magnesium bromide (45

mL), prepared from isopropyl bromide and magnesium turnings. After stirring for 4 h, 9-fluorenone (6.34 g, 35.2 mmol) in dry THF (35 mL) was added over 15 min and stirred at room temperature for 18 h. The reaction mixture was quenched with saturated aqueous solution of NH_4Cl (100 mL) and extracted with EtOAc (3×30 mL). The organic layers were combined, washed with brine (2×50 mL), and dried over MgSO_4 . The solvents were removed under reduced pressure to give a pale yellow solid. The crude product was purified by washing with CHCl_3 /hexane ($v/v = 1/3$) to give **1a** (10.5 g, 81%) as a white solid; mp 217.8–218.5 °C. IR (KBr) 734, 771, 1009, 1029, 1288, 1462, 1572, 1598, 2939, 3066, 3437 cm^{-1} . ^1H NMR (300 MHz, CDCl_3): $\delta = 2.40$ (br s, 1H), 3.91 (s, 3H), 6.72 (dd, $J = 3.3, 8.8$ Hz, 1H), 7.15–7.30 (m, 5H), 7.39 (dd, $J = 7.3, 7.3$ Hz, 2H), 7.67 (d, $J = 7.7$ Hz, 2H), 8.06 (br s, 1H). ^{13}C NMR (75.5 MHz, CDCl_3): $\delta = 55.5, 111.1, 114.6, 115.1, 120.2, 124.0, 128.4, 129.3, 135.0, 141.4, 141.9, 148.6, 158.8$ (two peaks are overlapped). Anal. Calcd for $\text{C}_{20}\text{H}_{15}\text{O}_2\text{Br}$: C, 65.41; H, 4.12. Found: C, 65.18; H, 3.92.

9-(2-Bromo-5-(dimethylamino)phenyl)-9H-fluoren-9-ol (2b): The solution of **1b** (3.42 g, 10.5 mmol) in dry THF (10 mL) was cooled to -40 °C. To the solution was added dropwise 1.0 M THF solution of isopropyl magnesium bromide (15 mL), prepared from isopropyl bromide and magnesium turnings. After stirring for 4 h, 9-fluorenone (1.26 g, 7.00 mmol) in dry THF (10 mL) was added and stirred at room temperature for 17 h. The reaction mixture was quenched with saturated aqueous solution of NH_4Cl (20 mL) and extracted with EtOAc (3×10 mL). The organic layers were combined, washed with brine (2×30 mL), and dried over MgSO_4 . The solvents were removed under reduced pressure, the residue was purified with column chromatography on SiO_2 with EtOAc/hexane ($v/v = 1/10$) as an eluent to give **2b** (1.91 g, 72%) as a white solid; mp 161.9–162.8 °C. IR (KBr) 733, 746, 770, 1149, 1361, 1446, 1491, 1591, 2808, 2879, 3457 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): $\delta = 2.40$ (br s, 1H), 3.03 (s,

6H), 6.51 (dd, $J = 3.4, 8.8$ Hz, 1H), 7.19–7.25 (m, 5H), 7.37 (dd, $J = 7.3, 8.3$ Hz, 2H), 7.66 (d, $J = 7.3$ Hz, 2H), 7.87 (br s, 1H). ^{13}C NMR (100 MHz, CDCl_3): $\delta = 40.7, 106.9, 113.1, 113.3, 120.1, 124.0, 128.3, 129.1, 134.6, 140.6, 141.3, 149.0, 149.6$ (two peaks are overlapped). HRMS (FAB): calcd for $\text{C}_{21}\text{H}_{18}^{79}\text{BrNO}$ (M^+), 379.0572, Found 379.0564.

3-(9-(2-Bromo-5-methoxyphenyl)-9H-fluoren-9-yl)-N-tosylpyrrole (3a): To a solution of **2a** (372 mg, 1.01 mmol) and *N*-tosylpyrrole (248 g, 1.12 mmol) in CH_2Cl_2 (30 mL) was added AlCl_3 (171 mg, 1.28 mmol) portionwise, and the solution was stirred at room temperature for 3 h. The reaction mixture was quenched with water (20 mL) and extracted with CH_2Cl_2 (3×10 mL). The organic layers were combined, washed with saturated aqueous solution of NaHCO_3 (2×20 mL) and brine (2×20 mL), and dried over MgSO_4 . The solvents were removed under reduced pressure, and the residue was purified with column chromatography on SiO_2 with EtOAc/hexane ($v/v = 1/6$) as an eluent to give **3a** (559 g, 97%) as a white solid; mp 205.8–206.6 °C. IR (KBr) 592, 675, 745, 796, 1067, 1173, 1367, 1465, 1595, 3119, 3134 cm^{-1} . ^1H NMR (300 MHz, CDCl_3): $\delta = 2.37$ (s, 3H), 3.60 (s, 3H), 6.42 (dd, $J = 1.8, 3.3$ Hz, 1H), 6.60–6.63 (m, 2H), 6.85 (br s, 1H), 7.08 (dd, $J = 2.2, 3.3$ Hz, 1H), 7.20–7.40 (m, 9H), 7.61 (d, $J = 8.4$ Hz, 2H), 7.72 (d, $J = 7.3$ Hz, 2H). ^{13}C NMR (75.5 MHz, CDCl_3): $\delta = 21.6, 55.1, 60.4, 113.3, 113.4, 115.6, 118.8, 119.3, 120.4, 121.5, 124.6, 126.8, 127.4, 127.6, 129.9, 131.8, 135.9, 136.0, 141.1, 143.1, 144.8, 149.6, 158.3$. HRMS (FAB): calcd for $\text{C}_{31}\text{H}_{25}^{81}\text{BrNO}_3\text{S}$ ($\text{M}+\text{H}^+$), 572.0722, Found 572.0733.

3-(9-(2-Bromo-5-(dimethylamino)phenyl)-9H-fluoren-9-yl)-N-tosylpyrrole (3b): To a solution of **2b** (188 mg, 0.494 mmol) and *N*-tosylpyrrole (116 mg, 0.525 mmol) in CH_2Cl_2 (5 mL) was added AlCl_3 (90.3 mg, 0.677 mmol) portionwise, and the solution was stirred at room temperature for 4 h. The reaction mixture was quenched with water (20 mL) and

extracted with CH_2Cl_2 (3×5 mL). The organic layers were combined, washed with saturated aqueous solution of NaHCO_3 (2×20 mL) and brine (2×20 mL), and dried over MgSO_4 . The solvents were removed under reduced pressure, and the residue was purified with column chromatography on SiO_2 with EtOAc/hexane ($v/v = 1/2$) as an eluent to give **3b** (199 mg, 70%) as a white solid; mp 216.0–216.8 °C. IR (KBr) 676, 743, 1063, 1173, 1371, 1593 cm^{-1} . ^1H NMR (300 MHz, CDCl_3): δ = 2.38 (s, 3H), 2.68 (s, 6H), 6.41 (dd, $J = 3.3, 8.8$ Hz, 1H), 6.45 (br s, 1H), 6.60 (br s, 1H), 7.08 (dd, $J = 2.6, 2.9$ Hz, 1H), 7.16–7.39 (m, 9H), 7.62 (d, $J = 8.1$ Hz, 2H), 7.72 (d, $J = 7.3$ Hz, 2H). ^{13}C NMR (75.5 MHz, CDCl_3): δ = 21.6, 40.1, 60.6, 109.0, 112.6, 116.0, 116.9, 119.3, 120.3, 121.3, 124.7, 126.7, 127.3, 127.5, 129.8, 132.4, 135.4, 136.2, 141.1, 141.9, 144.7, 149.1, 150.0. HRMS (FAB): calcd for $\text{C}_{32}\text{H}_{28}^{79}\text{BrN}_2\text{O}_2\text{S}$ ($\text{M}+\text{H}^+$), 583.1055, Found 583.1057.

6'-Methoxy-1'-tosyl-1'*H*-spiro[fluorene-9,4'-indeno[1,2-*b*]pyrrole] (4a): A flame dried flask was charged with **3a** (6.85 g, 12.0 mmol), K_2CO_3 (3.32 g, 24.0 mmol), $\text{Pd}(\text{PPh}_3)_4$ (417 mg, 0.361 mmol), and dry DMF (100 mL) under nitrogen atmosphere. The solution was stirred at 100 °C for 13 h. The reaction mixture was cooled down to room temperature and filtered through a short silica gel pad. After an addition of CH_2Cl_2 (100 mL), the filtrate was washed with brine (6×150 mL), and dried over MgSO_4 . The solvents were removed under reduced pressure to give a brown solid. The crude product was purified by washing with CHCl_3 /hexane ($v/v = 1/3$) to give **4a** (3.93 g, 67%) as a pale green solid; mp 211.3–212.0 °C. IR (KBr) 539, 583, 679, 750, 1125, 1171, 1276, 1368, 1586, 3139 cm^{-1} . ^1H NMR (300 MHz, CDCl_3): δ = 2.42 (s, 3H), 3.60 (s, 3H), 5.83 (d, $J = 3.3$ Hz, 1H), 6.09 (d, $J = 2.6$ Hz, 1H), 6.64 (d, $J = 7.7$ Hz, 2H), 6.80 (dd, $J = 2.6, 8.4$ Hz, 1H), 7.08 (dd, $J = 6.6, 7.3$ Hz, 2H), 7.14 (d, $J = 2.9$ Hz, 1H), 7.29–7.35 (m, 4H), 7.78 (d, $J = 7.7$ Hz, 2H), 7.81 (d, $J = 8.4$ Hz, 2H), 8.05 (d, $J = 8.4$ Hz, 1H). ^{13}C NMR (75.5 MHz, CDCl_3): δ = 21.6, 55.3, 60.2, 108.8, 110.7, 112.2, 120.0,

120.1, 123.6, 125.7, 126.7, 127.2, 127.7, 127.8, 130.0, 136.0, 138.2, 138.3, 141.7, 145.0, 146.7, 154.6, 158.2. HRMS (FAB): calcd for $C_{31}H_{24}NO_3S$ ($M+H^+$), 490.1477, Found 490.1494.

6'-(*N,N*-Dimethylamino)-1'-tosyl-1'*H*-spiro[fluorene-9,4'-indeno[1,2-*b*]pyrrole] (4b): A flame dried flask was charged with **3b** (2.93 g, 5.02 mmol), K_2CO_3 (1.38 g, 10.0 mmol), $Pd_2(dba)_3$ (115 mg, 0.126 mmol), $P(t-Bu)_3$ (103 mg, 0.510 mmol), and dry DMF (50 mL) under nitrogen atmosphere. The solution was stirred at 100 °C for 96 h. The reaction mixture was cooled down to room temperature and filtered through a short silica gel pad. After an addition of CH_2Cl_2 (50 mL), the filtrate was washed with brine (6×100 mL), and dried over $MgSO_4$. The solvents were removed under reduced pressure, the residue was purified with column chromatography on SiO_2 with EtOAc/hexane ($v/v = 1/6$) as an eluent to give **4b** (897 mg, 35%) as a greenish brown solid; mp 199.6 °C (dec.). IR (KBr) 576, 679, 743, 1122, 1174, 1371, 1432, 1606, 3130 cm^{-1} . 1H NMR (300 MHz, $CDCl_3$): δ = 2.41 (s, 3H), 2.73 (s, 6H), 5.78 (d, $J = 2.9$ Hz, 1H), 5.91 (d, $J = 2.6$ Hz, 1H), 6.60–6.67 (m, 3H), 7.04–7.09 (m, 3H), 7.25–7.34 (m, 4H), 7.77 (d, $J = 7.3$ Hz, 2H), 7.81 (d, $J = 8.4$ Hz, 2H), 8.00 (d, $J = 8.4$ Hz, 1H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 21.6, 40.6, 60.4, 108.5, 108.8, 111.0, 119.9, 120.0, 123.4, 123.7, 124.7, 126.8, 127.56, 127.61, 129.9, 136.1, 136.9, 138.9, 141.6, 144.7, 147.5, 149.0, 154.3. HRMS (FAB): calcd for $C_{32}H_{26}N_2O_2S$ (M^+), 502.1715, Found 502.1705.

6'-Methoxy-1'*H*-spiro[fluorene-9,4'-indeno[1,2-*b*]pyrrole] (MeO-sp-FIP): To a solution of **4a** (1.96 g, 4.00 mmol) in THF (300 mL) was added 1.0 M THF solution of TBAF (40 mL), and the solution was stirred at 65 °C for 14 h under nitrogen atmosphere. After cooling to ambient temperature, water (40 mL) was added and THF was removed under reduced pressure. The residue was extracted with CH_2Cl_2 (3×15 mL). The organic layers were

combined, washed with brine (2×50 mL), and dried over MgSO_4 . The solvents were removed under reduced pressure, the residue was purified with column chromatography on SiO_2 with $\text{CH}_2\text{Cl}_2/\text{hexane}$ ($v/v = 1/1$) as an eluent to give **MeO-sp-FIP** (1.34 g, quantitative yield) as a pale pink solid; mp $156.9\text{--}157.8$ °C. IR (KBr) 742, 1274, 1444, 1461, 1587, 3063, 3418 cm^{-1} . ^1H NMR (300 MHz, CDCl_3): $\delta = 3.58$ (s, 3H), 5.77 (br s, 1H), 6.13 (d, $J = 2.2$ Hz, 1H), 6.71–6.76 (m, 2H), 6.85 (d, $J = 7.7$ Hz, 2H), 7.11 (dd, $J = 7.3, 7.7$ Hz, 2H), 7.23 (d, $J = 8.4$ Hz, 1H), 7.33 (dd, $J = 7.3, 7.7$ Hz, 2H), 7.80 (d, $J = 7.7$ Hz, 2H), 8.33 (br s, 1H). ^{13}C NMR (75.5 MHz, CDCl_3): $\delta = 55.4, 60.8, 103.9, 111.1, 111.6, 116.1, 119.8, 120.9, 123.8, 127.4, 127.6, 128.7, 132.4, 137.6, 141.6, 148.7, 155.1, 157.3$. HRMS (FAB): calcd for $\text{C}_{24}\text{H}_{18}\text{NO}$ ($\text{M}+\text{H}^+$), 336.1388, Found 336.1371.

6'-(*N,N*-Dimethylamino)-1'*H*-spiro[fluorene-9,4'-indeno[1,2-*b*]pyrrole] (Me₂N-sp-FIP):

To a solution of **4b** (736 mg, 1.46 mmol) in THF (2 mL) was added 1.0 M THF solution of TBAF (14.6 mL), and the solution was stirred at 65 °C for 22 h under nitrogen atmosphere. After cooling to ambient temperature, water (40 mL) was added and THF was removed under reduced pressure. The residue was extracted with CH_2Cl_2 (3×10 mL). The organic layers were combined, washed with brine (2×40 mL), and dried over MgSO_4 . The solvents were removed under reduced pressure, the residue was purified with column chromatography on SiO_2 with $\text{CH}_2\text{Cl}_2/\text{hexane}$ ($v/v = 1/1$) as an eluent to give **Me₂N-sp-FIP** (441 mg, 87%) as a pale green solid; mp 178.2 °C (dec.). IR (KBr) 737, 797, 1440, 1488, 1582, 3396 cm^{-1} . ^1H NMR (300 MHz, CDCl_3): $\delta = 2.71$ (s, 3H), 5.73 (dd, $J = 1.8, 2.6$ Hz, 1H), 6.00 (d, $J = 2.2$ Hz, 1H), 6.56 (dd, $J = 2.2, 8.1$ Hz, 1H), 6.70 (dd, $J = 2.2, 2.6$ Hz, 1H), 6.87 (d, $J = 7.7$ Hz, 2H), 7.11 (dd, $J = 7.3, 7.3$ Hz, 2H), 7.20 (d, $J = 8.4$ Hz, 1H), 7.32 (dd, $J = 7.3, 7.7$ Hz, 2H), 7.80 (d, $J = 7.7$ Hz, 2H), 8.28 (br s, 1H). ^{13}C NMR (75.5 MHz, CDCl_3): $\delta = 41.0, 60.9, 103.7, 109.7, 110.8, 116.2, 119.7, 120.1, 123.9, 125.4, 127.2, 127.5, 131.4, 138.2, 141.5, 148.4, 149.5,$

154.6. HRMS (FAB): calcd for $C_{25}H_{20}N_2$ (M^+), 348.1626, Found 348.1631.

BODIPY dye 5a: To a solution of **MeO-sp-FIP** (336 mg, 1.00 mmol) and methyl 4-formylbenzoate (81.8 mg, 0.50 mmol) in dry CH_2Cl_2 (20 mL) was added two drops of TFA, and the solution was stirred at 0 °C for 2 h under nitrogen atmosphere. The reaction mixture was quenched with saturated aqueous solution of $NaHCO_3$ (20 mL) and extracted with CH_2Cl_2 (3×10 mL). The organic layers were combined, washed with brine (2×25 mL), and dried over $MgSO_4$. The solvents were removed under reduced pressure, and the residue was partially purified with column chromatography on SiO_2 with CH_2Cl_2 as an eluent to afford a crude product (220 mg) as a purple solid. The crude product was then dissolved in dry CH_2Cl_2 (10 mL). After an addition of *p*-chloranil (66.5 mg, 0.270 mmol) in dry CH_2Cl_2 (10 mL), the solution was stirred at 0 °C for 90 min under nitrogen atmosphere. *i*- Pr_2NEt (0.231 mL, 1.33 mmol) and $BF_3 \cdot OEt_2$ (0.360 mL, 1.32 mmol) were successively added and after 2 h, the reaction mixture was washed with 10% aqueous solution of $NaCl$ (3×30 mL), and dried over Na_2SO_4 . The solvents were removed under reduced pressure, and the residue was purified with column chromatography on SiO_2 with CH_2Cl_2 as an eluent to afford **5a** (152 mg, 36% yield based on **MeO-sp-FIP**) as a dark brown solid; mp >300 °C. IR (KBr) 745, 1060, 1176, 1260, 1323, 1548, 1606, 1723, 3062 cm^{-1} . 1H NMR (300 MHz, $CDCl_3$) δ = 3.67 (s, 6H), 3.82 (s, 3H), 6.03 (s, 2H), 6.14 (d, J = 2.2 Hz, 2H), 6.96 (d, J = 7.3 Hz, 4H), 7.04 (dd, J = 2.6, 8.8 Hz, 2H), 7.16 (dd, J = 7.3, 7.7 Hz, 4H), 7.33–7.41 (m, 6H), 7.77 (d, J = 7.3 Hz, 4H), 7.87 (d, J = 8.1 Hz, 2H), 8.40 (d, J = 8.8 Hz, 2H). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ = 52.2, 55.6, 59.8, 109.9, 115.0, 119.3, 120.0, 124.2, 125.47, 125.53, 127.9, 128.0, 129.2, 130.3, 130.8, 138.1, 138.9, 140.2, 141.2, 142.9, 148.2, 159.3, 161.1, 162.2, 166.2. HRMS (FAB): calcd for $C_{57}H_{38}O_4N_2F_2B$ ($M+H^+$), 863.2902, Found 863.2916.

1'-(4-(Methoxycarbonyl)benzoyl)-6'-(*N,N*-dimethylamino)-1'*H*-spiro[fluorene-9,4'-indeno[1,2-*b*]pyrrole] (6): To a solution of **Me₂N-sp-FIP** (108 mg, 0.310 mmol) in dry CH₂Cl₂ (8 mL) was added methyl 4-(chlorocarbonyl)benzoate in dry CH₂Cl₂ (7 mL), and the solution was stirred at 40 °C for 12 h under nitrogen atmosphere. After an addition of water (20 mL), the reaction mixture was extracted with CH₂Cl₂ (3 × 5 mL). The organic layers were combined, washed with brine (2 × 20 mL), and dried over MgSO₄. The solvents were removed under reduced pressure, and the residue was purified with column chromatography on SiO₂ with EtOAc/CH₂Cl₂ (v/v = 1/20) as an eluent to afford **6** (82.6 mg, 52%) as a orange solid; mp 163.5 °C (dec.). IR (KBr) 740, 1279, 1352, 1583, 1725, 3223 cm⁻¹. ¹H NMR (300 MHz, CDCl₃) δ = 2.78 (s, 6H), 3.91 (s, 3H), 5.92 (d, *J* = 2.2 Hz, 1H), 6.37 (s, 1H), 6.60 (dd, *J* = 2.2, 8.4 Hz, 1H), 6.91 (d, *J* = 7.3 Hz, 2H), 7.15 (dd, *J* = 7.3, 7.7 Hz, 2H), 7.36 (dd, *J* = 7.3, 7.7 Hz, 2H), 7.62 (d, *J* = 8.4 Hz, 1H), 7.80 (d, *J* = 7.7 Hz, 2H), 7.86 (d, *J* = 8.1 Hz, 2H), 8.04 (d, *J* = 8.1 Hz, 2H), 11.02 (s, 1H). ¹³C NMR (75.5 MHz, CDCl₃) δ = 40.4, 52.3, 60.6, 107.9, 111.4, 115.9, 119.9, 120.7, 121.2, 124.0, 127.6, 127.8, 128.7, 129.4, 132.0, 134.1, 134.9, 141.4, 143.2, 148.4, 148.8, 150.7, 157.0, 166.5, 182.2. HRMS (FAB): calcd for C₃₄H₂₇O₃N₂ (M+H⁺), 511.2022, Found 511.2018.

BODIPY dye 5b: To a solution of **6** (77.2 mg, 0.151 mmol) and **Me₂N-sp-FIP** (53.1 mg, 0.152 mmol) in CH₂Cl₂ (4 mL) was added POCl₃ (18 μl, 0.197 mmol), and the solution was stirred at 40 °C for 39 h under nitrogen atmosphere. After cooling to ambient temperature, the reaction mixture was quenched with saturated aqueous solution of NaHCO₃ (15 mL) and extracted with CH₂Cl₂ (3 × 5 mL). The organic layers were combined, washed with brine (2 × 25 mL), and dried over Na₂SO₄. The solvents were removed under reduced pressure, and the residue was partially purified with column chromatography on SiO₂ with CH₂Cl₂/EtOAc (v/v = 10/1) as an eluent to afford a crude product (53.8 mg) as a dark green solid. The

crude product was then dissolved in CH₂Cl₂ (8 mL). *i*-Pr₂NEt (0.056 mL, 0.321 mmol) and BF₃•OEt₂ (0.087 mL, 0.320 mmol) were added and the reaction mixture was stirred at room temperature for 2 h. The reaction mixture was washed with 10% aqueous solution of NaCl (3 × 20 mL), and dried over Na₂SO₄. The solvents were removed under reduced pressure, and the residue was partially purified with column chromatography on SiO₂ with CH₂Cl₂/EtOAc (v/v = 40/1) as an eluent to afford **5b** (55.5 mg, 39% yield based on **6**) as a dark brown solid; mp >300 °C. IR (KBr) 1019, 1057, 1276, 1313, 1541, 1602, 1727 cm⁻¹. ¹H NMR (300 MHz, CDCl₃) δ = 2.87 (s, 12H), 3.82 (s, 3H), 5.86 (s, 2H), 5.90 (s, 2H), 6.81 (d, *J* = 8.8 Hz, 2H), 6.99 (d, *J* = 7.7 Hz, 4H), 7.16 (dd, *J* = 7.3, 7.7 Hz, 4H), 7.31–7.40 (m, 6H), 7.76 (d, *J* = 7.7 Hz, 4H), 7.85 (d, *J* = 8.4 Hz, 2H), 8.32 (d, *J* = 8.1 Hz, 2H). ¹³C NMR (75.5 MHz, CDCl₃) δ = 40.4, 52.1, 59.9, 106.7, 112.6, 117.7, 119.8, 121.3, 124.3, 125.2, 127.7, 127.8, 129.1, 130.2, 130.4, 134.4, 139.7, 139.9, 141.2, 142.3, 149.2, 152.0, 159.0, 160.6, 166.4. HRMS (FAB): calcd for C₅₉H₄₃O₂N₄F₂B (M⁺), 888.3457, Found 888.3448.

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Chapter 5

Synthesis, Structures, and Optical Properties of Heteroarene-Fused Dispiro Compounds

Abstract

Novel heteroarene-fused dispiro compounds, dispiro[9*H*-fluorene-9,5'(6'*H*)-diindeno[1,2-*b*:2',1'-*d*]furan-6',9''-[9*H*]fluorene] (**dsp-DIF**), dispiro[9*H*-fluorene-9,5'(6'*H*)-diindeno[1,2-*b*:2',1'-*d*]-thiophene-6',9''-[9*H*]fluorene] (**dsp-DIT**), and 11-phenyl-dispiro[9*H*-fluorene-9,5'(6'*H*)-diindeno[1,2-*b*:2',1'-*d*]pyrrole-6',9''-[9*H*]fluorene] (**dsp-DIP-Ph**) have been synthesized. Their structures were unambiguously determined by X-ray crystallography. These three dispiro compounds showed blue fluorescence with moderate quantum yields.

Introduction

Conjugated polymers and oligomers have attracted considerable attention in recent years as organic semiconductors for application in devices such as organic light-emitting diodes (OLEDs),¹ organic field-effect transistors (OFETs),² and solar cells.³ In particular, ladder-type materials are of great interest as potential components of such organic electronic devices because of their high coplanarity, intense luminescence, and carrier mobility.^{4,5} Since the first synthesis of ladder-type poly(*p*-phenylene)s in 1991,^{4a} there have been many efforts to clarify their structure-property relationships by using structurally defined conjugated oligomers. Among them, 6,12-dihydroindeno[1,2-*b*]fluorene (**IF**) is one of the simplest ladder-type oligomers and regarded as a promising building block for OLEDs and OFETs (Figure 1).⁵ On the other hand, the physical properties of ladder-type compounds can be modulated by incorporating heteroatoms as bridging atoms of the π -backbone^{4b,4c,5d,6} or incorporating heteroarenes directly as components of the π -backbone.^{4g,7,8} Indeed,

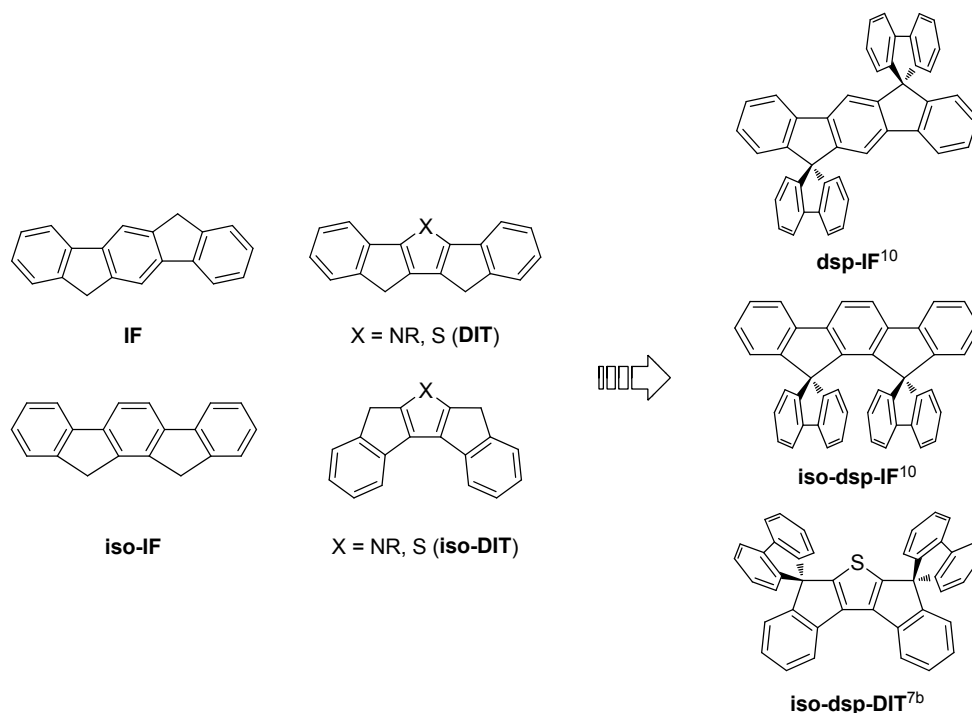


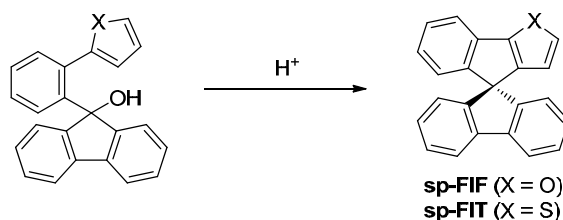
Figure 1. The structures of **IF** and **DIT** derivatives and the corresponding dispiro compounds.

10,11-dihydrodiindeno[1,2-*b*:2',1'-*d*]thiophene (**DIT**) derivatives, in which the central benzene ring of **IF** is replaced by a thiophene ring, show relatively high hole mobilities.^{7c}

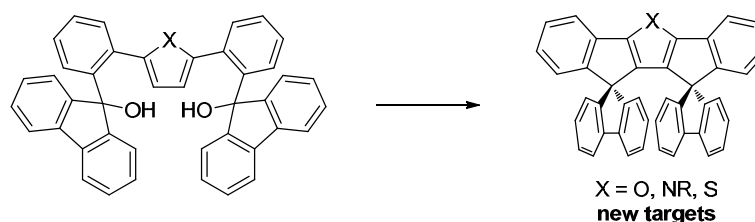
Recently, much attention has been paid to the construction of ladder-type compounds with rigid spiro structures (Figure 1).^{4c,6b,9-11} However, ladder-type compounds involving both heteroarenes and spiro structures have been less investigated.^{7b}

In chapters 1 and 2, the author described the synthesis of furan- or thiophene-containing spiro compounds, **sp-FIF** and **sp-FIT** (Scheme 1). Then, the author envisioned that novel heteroarene-fused ladder-type compounds could be synthesized based on an intramolecular Friedel-Crafts-type alkylation. Herein, he describes the synthesis, structures, and optical properties of unique dispiro compounds containing heteroles, such as furan, thiophene, or pyrrole (Scheme 2).

Scheme 1



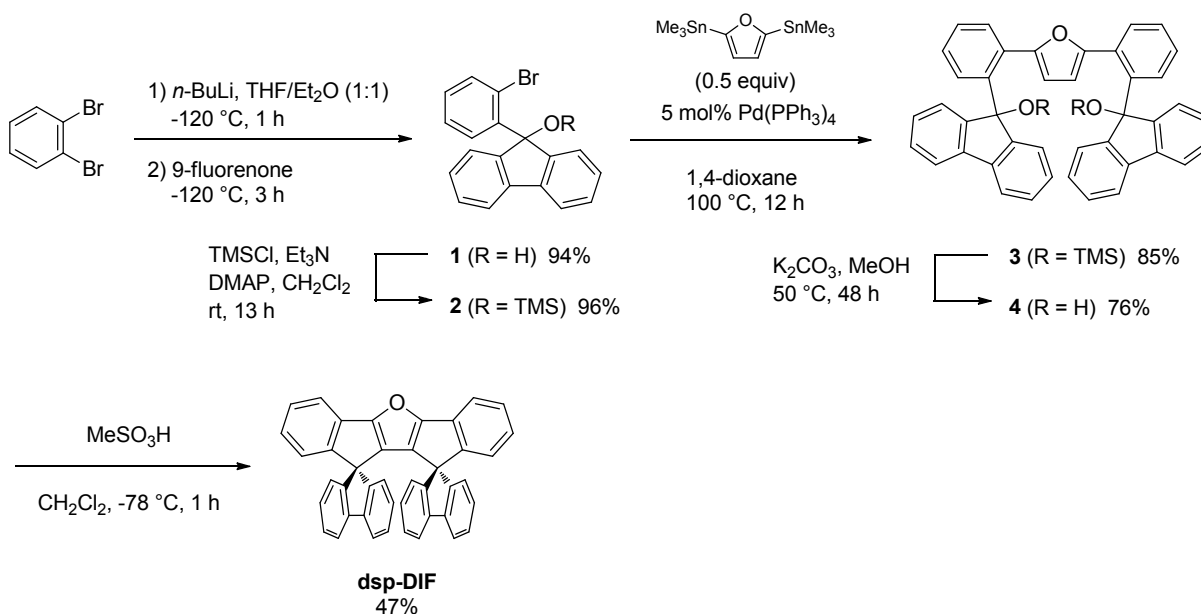
Scheme 2



Results and Discussion

Scheme 3 shows the synthetic route to dispiro[9*H*-fluorene-9,5'-(6'*H*)-diindeno[1,2-*b*:2',1'-*d*]furan-6',9''-[9*H*]fluorene] (**dsp-DIF**). In the first step, lithiation of 1,2-dibromobenzene followed by reaction with 9-fluorenone afforded the alcohol **1** in 94% yield, which was converted to the corresponding silyl ether derivative **2** (96%). The Stille coupling reaction of **2** with 2,5-bis(trimethylstannyl)furan afforded **3** in 85% yield. Deprotection of **3** produced the precursor diol **4** in 76% yield. The conversion of the diol **4** to **dsp-DIF** is sensitive to the reaction conditions. A typical method for constructing the spirofluorene skeleton is the acid-promoted Friedel-Crafts reaction.¹² Although several acids were tested for this reaction at room temperature or 0 °C, only a trace amount of **dsp-DIF** was detected by TLC analysis. Finally, **dsp-DIF** was isolated in 47% yield using methanesulfonic acid in CH₂Cl₂ at -78 °C.

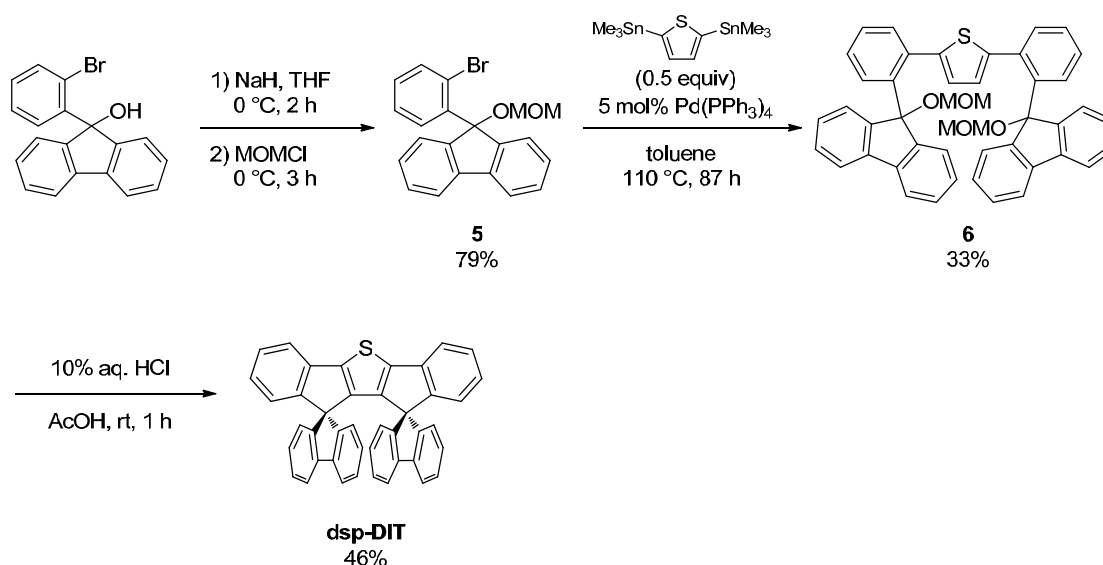
Scheme 3



The synthesis of dispiro[9*H*-fluorene-9,5'-(6'*H*)-diindeno[1,2-*b*:2',1'-*d*]thiophene-6',9''-[9*H*]fluorene] (**dsp-DIT**) is depicted in Scheme 4. The methoxy methyl ether **5** was

obtained in 79% yield through protection of the alcohol **1** with chlorodimethyl ether. The Stille coupling reaction between 2 equiv of **5** and 2,5-bis(trimethylstannyl)thiophene afforded **6** in 33% yield. The reaction of **6** with 10% aq. HCl in acetic acid afforded **dsp-DIT** as a result of the reaction cascade with a deprotection and intramolecular double Friedel-Crafts alkylation.

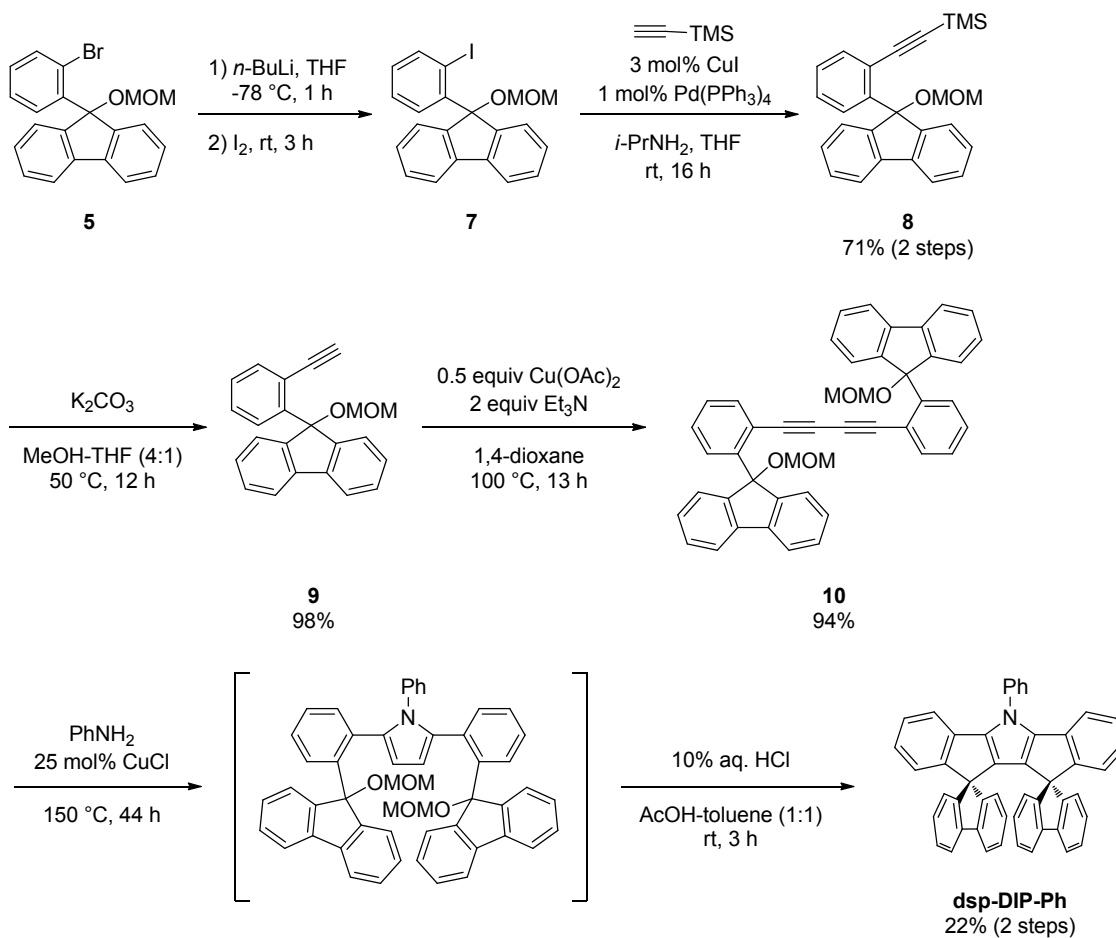
Scheme 4



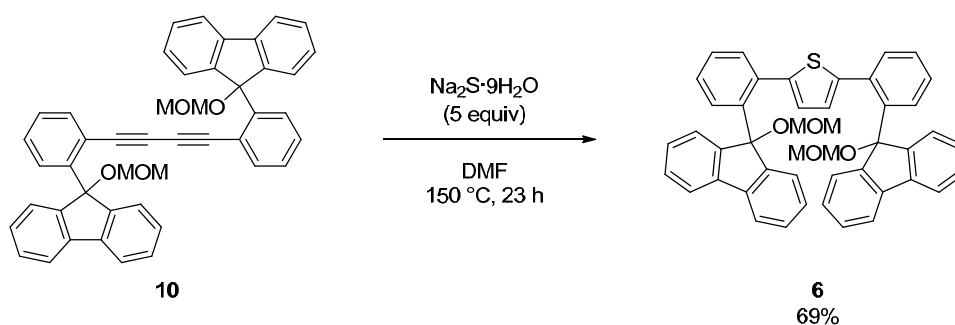
To prepare a pyrrole analog of **dsp-DIF** and **dsp-DIT**, the author first examined the Stille coupling reaction of **5** with *N*-methyl-2,5-bis-(trimethylstannyl)pyrrole according to the synthetic route of **dsp-FIT**. However, the reaction did not proceed at all. Therefore, the author employed another synthetic route based on utilization of copper-catalyzed double hydroamination of a diyne (Scheme 5). The halogen-lithium exchange reaction of **5** followed by quenching with molecular iodine gave **7**, which was subsequently reacted with trimethylsilylacetylene under Sonogashira-coupling condition to afford **8** in 71% yield for two steps. Deprotection of the silyl group of **8** gave alkyne **9** and Glaser coupling gave diyne **10** in excellent yield (98% and 94%, respectively). Finally, 11-phenyl-dispiro[9*H*-fluorene-9,5'-(6'*H*)-diindeno[1,2-*b*:2',1'-*d*]pyrrole-6',9''-[9*H*]fluorene] (**dsp-DIP-Ph**) was obtain-

ed in 22% yield (for two steps) by acid-promoted intramolecular Friedel-Crafts reaction of the major product, which was produced by copper-catalyzed double hydroamination of diyne **10** with aniline. Furthermore, it was possible to transform diyne **10** to thiophene **6**, leading to **dsp-DIT**, by reaction with $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ (Scheme 6). This result suggests that diyne **10** has

Scheme 5



Scheme 6



great potential as a key structure to prepare various heteroarene-fused dispiro compounds.

Single crystals of **dsp-DIF**, **dsp-DIT**, and **dsp-DIP-Ph** were grown by slow evaporation of solution of the compound in CH₂Cl₂/hexane, toluene/hexane, and EtOAc/hexane at room temperature, respectively. X-ray crystal structures of **dsp-DIF**, **dsp-DIT**, and **dsp-DIP-Ph** are shown in Figure 2. For **dsp-DIF** and **dsp-DIP-Ph**, the two fluorene rings are favorably overlapped and fixed closely by the diindenofuran skeleton. The longest distances between

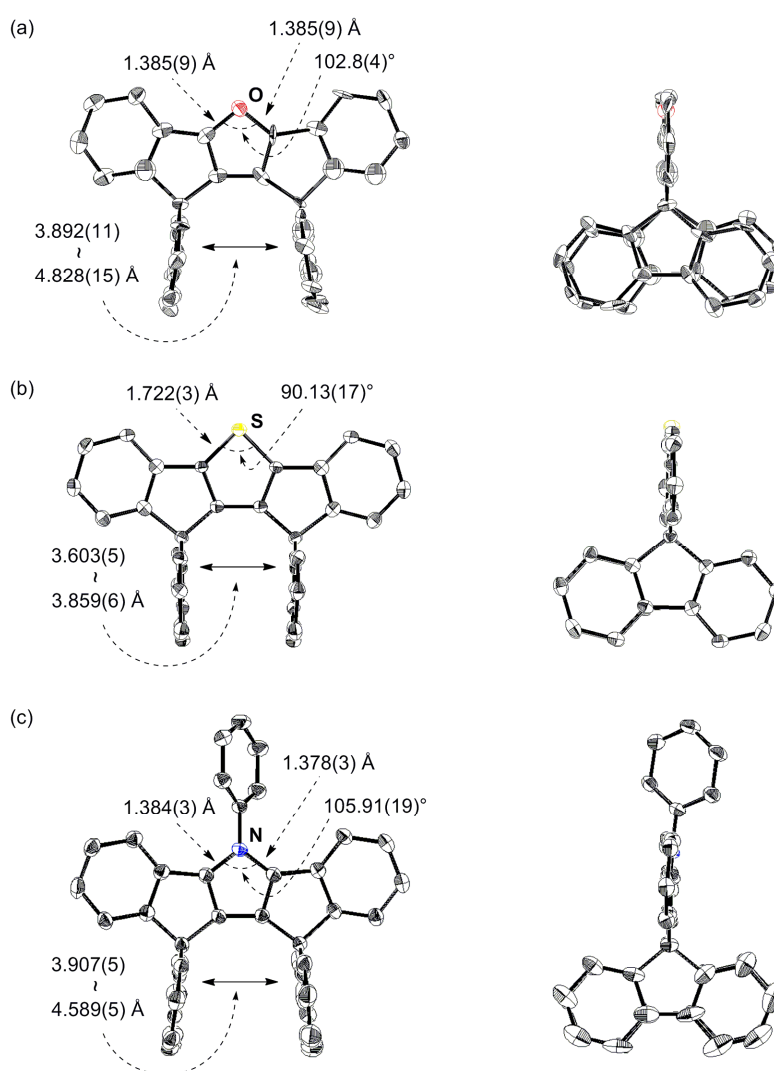


Figure 2. X-ray crystal structures of (a) **dsp-DIF**, (b) **dsp-DIT**, and (c) **dsp-DIP-Ph**: (left) top view and (right) side view. All solvent molecules and hydrogen atoms are omitted for clarity.

the two opposite carbon atoms of each fluorene skeleton are 4.828(15)–4.589(5) Å, while the distances between the two spiro carbon atoms are 3.892(11)–3.831(3) Å. On the other hand, for **dsp-DIT**, the longest and shortest distances between two fluorene rings are 3.859(6) Å and 3.603(5) Å, respectively, and the distance between two spiro carbon atoms is 3.709(4) Å. This shorter distance seems to be due to the longer C–S bond length of **dsp-DIT** by ca. 0.34 Å than the C–O bond length of **dsp-DIF** and the existence of an intramolecular π – π stacking interaction.¹³ It is noteworthy that the two fluorene units are completely overlapped in the structure (Figure 2b). Packing structures of **dsp-DIF**, **dsp-DIT**, and **dsp-DIP-Ph** are shown in Figure 3. It is interesting to find that the intermolecular π – π stackings are completely suppressed by the orthogonally arranged spirofluorene structures.

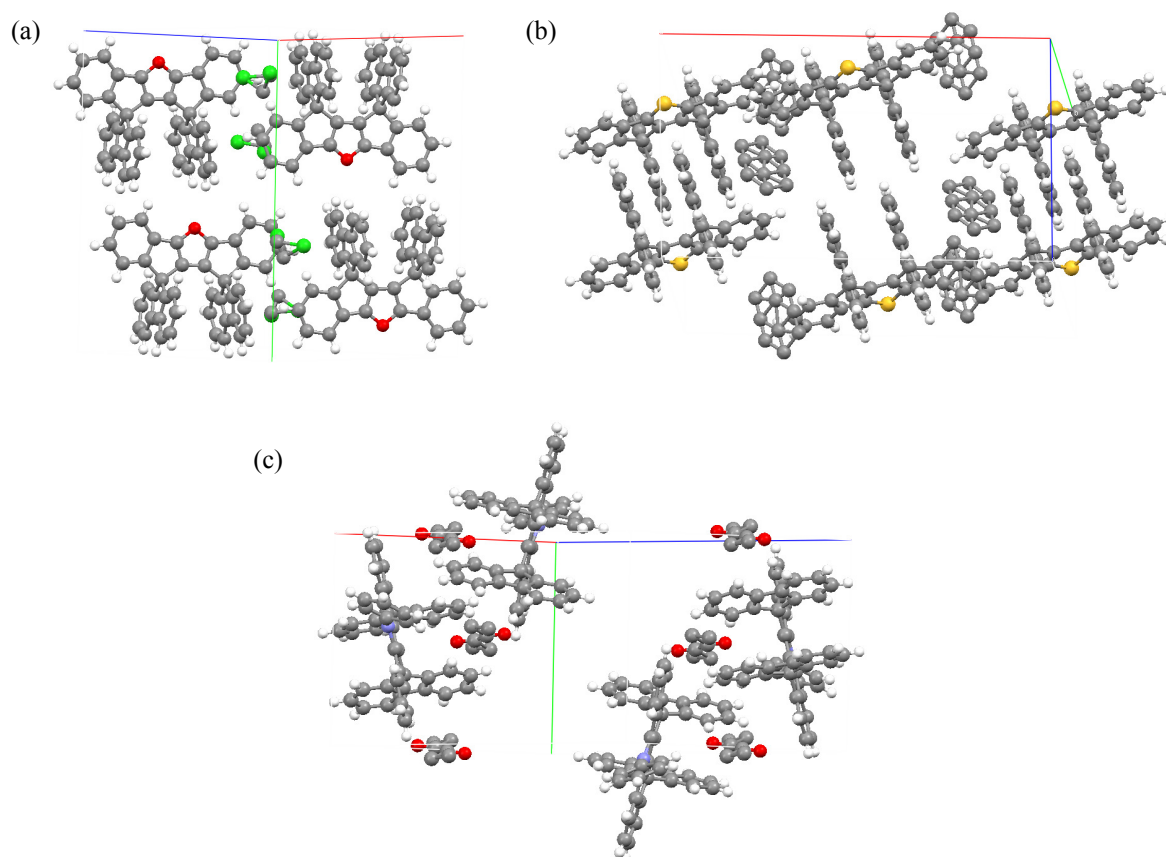
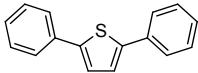
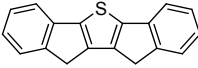


Figure 3. The packing structures of (a) **dsp-DIF**, (b) **dsp-DIT**, and (c) **dsp-DIP-Ph**.

The absorption and emission spectra of dispiro compounds **dsp-DIF**, **dsp-DIT**, and **dsp-DIP-Ph** were measured in THF, and the results are summarized in Table 1. These dispiro compounds exhibited a blue emission in THF solution with moderate quantum efficiency. In the absorption spectra, the absorption maxima of **dsp-DIF** were observed at 348 and 367 nm, while those of **dsp-DIT** and **dsp-DIP-Ph** were slightly red shifted by 6–10 nm. The Stokes shifts were very small (6–18 nm) because of their extremely rigid structure. It is conceivable that both absorption and emission maxima of **dsp-FIP-Ph** were observed more red-shifted, because the π -system is slightly extended due to delocalization of the π electron over the phenyl group on the nitrogen atom.

Table 1. Optical properties of dsp-compounds and related compounds in THF

	λ_{abs} (nm)	ϵ_{max} ($\times 10^5 \text{ M}^{-1}\text{cm}^{-1}$)	λ_{ex} (nm)	λ_{em} (nm)	Φ^a
dsp-DIF	348, 367	3.58	348	373, 393	0.39
dsp-DIT	356, 373	2.46	356	386, 403	0.32
dsp-DIP-Ph	358, 375	2.43	358	393, 408	0.37
 DPT	327, 341	2.28	327	369, 389	0.07 ^b
 DIT	342, 354	3.09	342	374, 385	0.25

^a Absolute quantum yield determined by a calibrated integrating sphere system. ^b λ_{ex} 350 nm. Relative quantum yield calculated by using quinine sulfate in 0.1 M aq. H_2SO_4 as a standard.

The author next compared the photophysical properties of **dsp-DIT** with those of reference compounds 2,5-diphenylthiophene (**DPT**) and **DIT**. The absorption and emission spectra of **DIT** were largely red-shifted, compared with those of **DPT** because of the coplanarity between a thiophene ring and two phenyl groups. The photoluminescence

quantum yield of **DIT** was also increased because of the higher rigidity of its structure. Furthermore, by incorporation of spirofluorene moieties, greater bathochromic shifts were observed in the absorption and emission spectra of **dsp-DIT**, as well as an increase in quantum yield. This suggests that spirofluorene moieties increase the rigidity of the π -backbone and suppress the photo/thermal oxidation of methylene carbon,¹⁴ thereby extending the π -conjugation and increasing the quantum yield. The bathochromic shifts of absorption and emission maxima of **dsp-DIT** relative to those of **DIT** seem to be also attributed to spiroconjugation between two fluorene moieties and the diindenothiophene skeleton. The author then performed a DFT calculation (B3LYP/6-31G(d)) to gain insight into spiroconjugation¹⁵ for **dsp-DIT**. Indeed, the conjugation between two fluorene moieties and the diindenothiophene skeleton was confirmed to exist in the HOMO (Figure 4).

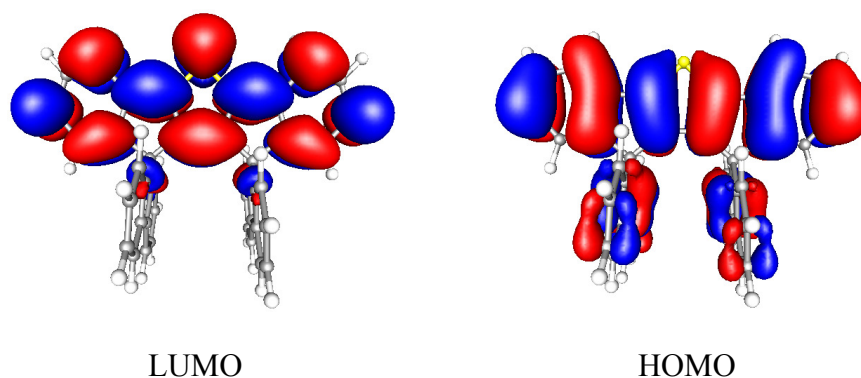


Figure 4. Molecular orbital plots for **dsp-DIT**.

In conclusion, the author has synthesized new types of ladder dispiro compounds **dsp-FIF**, **dsp-FIT**, and **dsp-FIP-Ph**. In the emission spectra, the dispiro compounds showed blue emission with moderate quantum yields, and it was clarified that two spirofluorene moieties could increase the rigidity of the π -frameworks, resulting in an extension of π -conjugation and higher photoluminescence quantum yields. Furthermore, a

DFT calculation supported the suggestion that the bathochromic shifts of the absorption and emission maxima of **dsp-DIT** relative to those of **DIT** were attributed to spiroconjugation between two fluorene moieties and the diindenothiophene skeleton. The structures of all dispiro compounds have been confirmed by X-ray crystallography, and their two fluorene moieties were fixed closely at the same side. In particular, for **dsp-DIT**, two fluorene rings were placed in a parallel fashion and completely overlapped, and their distances from each other were suitable for π - π stacking. Furthermore, as observed from the packing structures, the intermolecular π - π stacking are found to be suppressed by the orthogonality of dsp-structures .

Experimental Section

General. Unless otherwise specified, all reagents were purchased from a chemical supplier and used without further purification. All solvents were dried by the standard method. Melting points are uncorrected. Degassed spectral grade solvents were used for the UV-visible absorption and emission spectra measurements. Absolute fluorescence quantum yields were determined by the calibrated integrating sphere system.

9-(2-Bromophenyl)-9*H*-fluoren-9-ol (1)¹⁶: To a solution of 1,2-dibromobenzene (2.83 g, 12.0 mmol) in dry THF (20 mL) and dry Et₂O (20 mL) was added dropwise 1.55 M hexane solution of *n*-BuLi (7.74 mL, 12.0 mmol) at -120 °C. After stirring for 1 h, 9-fluorenone (1.95 g, 10.8 mmol) in dry THF-Et₂O (15 mL, 1:2) was added over 35 min and stirred at -120 °C for 3 h. The reaction mixture was quenched with saturated aqueous solution of NH₄Cl (30 mL) and extracted with Et₂O (3 × 10 mL). The organic layers were combined, washed with brine (2 × 10 mL), and dried over MgSO₄. The solvents were removed under reduced pressure to give an orange oil. The crude product was purified with column chromatography on SiO₂ with EtOAc/hexane (v/v = 1/20) as an eluent to give **1** (3.41 g, 94%) as a white solid; mp 145.2–146.0 °C. IR (KBr) 767, 920, 1005, 1157, 1333, 1448, 1604, 3063, 3571 cm⁻¹. ¹H NMR (300 MHz, CDCl₃): δ = 2.39 (br s, 1H), 7.13–7.25 (m, 5H), 7.36–7.47 (m, 4H), 7.67 (d, *J* = 7.7 Hz, 2H), 8.44 (br s, 1H). ¹³C NMR (75.5 MHz, CDCl₃): δ = 83.0, 120.2, 120.9, 123.9, 127.0, 128.3, 129.0, 129.1, 129.2, 134.3, 140.8, 141.3, 148.6.

9-(2-Bromophenyl)-9-(trimethylsilyloxy)-9*H*-fluorene (2): To a solution of **1** (2.03 g, 6.02 mmol), Et₃N (4.20 mL, 30.1 mmol), and DMAP (73.5 mg, 0.602 mmol) in CH₂Cl₂ (10 mL) was added chlorotrimethylsilane (1.08 mL, 8.55 mmol), and the solution was stirred at room temperature for 13 h under nitrogen atmosphere. The reaction mixture was quenched with

water (15 mL) and extracted with CH_2Cl_2 (3×10 mL). The organic layers were combined, washed with brine (2×10 mL), and dried over MgSO_4 . The solvents were removed under reduced pressure, and the residue was purified with column chromatography on SiO_2 with hexane as an eluent to give **2** (2.36 g, 96%) as a white solid; mp 129.0–129.8 °C. IR (KBr) 550, 622, 751, 841, 889, 936, 1019, 1066, 1252, 1448, 2947, 3062 cm^{-1} . ^1H NMR (300 MHz, CDCl_3): δ = −0.37 (s, 9H), 7.11 (m, 3H), 7.16 (dd, J = 7.3, 7.7 Hz, 2H), 7.34–7.46 (m, 4H), 7.64 (d, J = 7.3 Hz, 2H), 8.45 (br s, 1H). ^{13}C NMR (75.5 MHz, CDCl_3): δ = 1.0, 84.8, 119.8, 120.5, 125.0, 126.8, 127.9, 128.7, 129.0, 129.6, 134.3, 142.0, 142.7, 148.2. Anal. Calcd. for $\text{C}_{22}\text{H}_{21}\text{BrOSi}$: C, 64.54; H, 5.17. Found: C, 64.33; H, 5.16.

2,5-Bis(2-(9-(trimethylsilyloxy)-9H-fluoren-9-yl)phenyl)furan (3): A flame dried flask was charged with **2** (15.7 g, 38.3 mmol), 2,5-bis(trimethylstannyl)furan¹⁷ (7.52 g, 19.1 mmol), $\text{Pd}(\text{PPh}_3)_4$ (2.19 g, 1.89 mmol), and dry 1,4-dioxane (60 mL) under nitrogen atmosphere. The solution was stirred at 100 °C for 12 h. The reaction mixture was cooled down to room temperature and filtered through a short celite pad. After an addition of water (30 mL), the filtrate was extracted with EtOAc (3×20 mL). The organic layers were combined, washed with brine (2×20 mL), and dried over MgSO_4 . The solvents were removed under reduced pressure to give a yellowish brown solid. The crude product was purified by washing with hexane to give **3** (10.9 g, 85%) as a white solid; mp 232.2–233.0 °C. IR (KBr) 731, 751, 842, 890, 934, 1056, 1251, 1449, 2954, 3061 cm^{-1} . ^1H NMR (300 MHz, CDCl_3): δ = −0.49 (s, 18H), 4.16 (br s, 2H), 6.49 (d, J = 7.3 Hz, 2H), 6.99 (d, J = 7.3 Hz, 4H), 7.09 (dd, J = 7.0, 7.3 Hz, 4H), 7.17 (dd, J = 7.0, 7.7 Hz, 4H), 7.23 (m, 6H), 7.43 (dd, J = 7.7, 7.7 Hz, 2H), 8.26 (br s, 2H). ^{13}C NMR (75.5 MHz, CDCl_3): δ = 0.9, 84.2, 109.1, 119.7, 125.2, 126.2, 127.4, 127.6, 128.0, 128.4, 129.6, 132.2, 140.6, 142.9, 149.8, 150.7. Anal. Calcd. for $\text{C}_{48}\text{H}_{44}\text{O}_3\text{Si}_2$: C, 79.52; H, 6.12. Found: C, 79.48; H, 6.11.

2,5-Bis(2-(9-hydroxy-9-fluorenyl)phenyl)furan (4): To a solution of **3** (10.9 g, 15.3 mmol) in MeOH (200 mL) was added K₂CO₃ (10.3 g, 74.5 mmol), and the solution was stirred at 50 °C for 48 h. After cooling to ambient temperature, the reaction mixture was filtered through a short celite pad, and MeOH was removed under reduced pressure. After an addition of water (80 mL), the residue was extracted with Et₂O (3 × 30 mL). The organic layers were combined, washed with brine (3 × 20 mL), and dried over MgSO₄. The solvents were removed under reduced pressure, and the residue was purified by washing with Et₂O/hexane (v/v = 1/10) to give **4** (6.74 g, 76%) as a white solid; mp 230.1–231.0 °C. IR (KBr) 637, 732, 769, 914, 1013, 1117, 1165, 1448, 3060, 3438, 3532 cm⁻¹. ¹H NMR (300 MHz, CDCl₃): δ = 2.44 (s, 2H), 4.78 (br s, 2H), 6.79 (d, *J* = 7.3 Hz, 2H), 7.06–7.14 (m, 8H), 7.19 (dd, *J* = 7.3, 7.7 Hz, 4H), 7.26 (dd, *J* = 7.3, 7.3 Hz, 2H), 7.34–7.43 (m, 6H), 7.99 (br s, 2H). ¹³C NMR (75.5 MHz, CDCl₃): δ = 83.0, 109.4, 120.0, 124.2, 126.7, 127.3, 128.0, 128.4, 128.6, 129.6, 132.3, 139.8, 141.1, 150.8 (one peak cannot be discriminated due to overlap with another peak). Anal. Calcd. for C₄₂H₂₈O₃: C, 86.87; H, 4.86. Found: C, 86.57; H, 4.92.

Dispiro[9H-fluorene-9,5'(6'H)-diindeno[1,2-b:2',1'-d]furan-6',9''-[9H]fluorene] (dsp-DIF): To a solution of **4** (116 mg, 0.199 mmol) in CH₂Cl₂ (15 mL) was added MeSO₃H (114 mg, 1.16 mmol) in CH₂Cl₂ (5 mL) at -78 °C. After stirring for 1 h, the reaction mixture was quenched with water (15 mL) and extracted with CH₂Cl₂ (2 × 5 mL). The organic layers were combined, washed with brine (2 × 10 mL), and dried over MgSO₄. The solvents were removed under reduced pressure to give a yellow solid. The crude product was recrystallized from toluene/hexane (v/v = 4/1) to give **dsp-DIF** (51.5 mg, 47%) as a white solid; mp 284.4–285.1 °C. IR (KBr) 735, 759, 1446 cm⁻¹. ¹H NMR (300 MHz, CDCl₃): δ = 6.46 (d, *J* = 7.7 Hz, 4H), 6.51 (d, *J* = 7.7 Hz, 2H), 6.71 (dd, *J* = 7.3, 7.7 Hz, 4H), 6.88 (dd, *J* = 7.3, 7.7 Hz, 2H), 7.00 (dd, *J* = 7.3, 7.7 Hz, 4H), 7.26 (dd, *J* = 7.3, 7.7 Hz, 2H), 7.31 (d, *J* = 7.7

Hz, 4H), 7.53 (d, $J = 7.7$ Hz, 2H). ^{13}C NMR (75.5 MHz, CDCl_3): $\delta = 58.4, 116.2, 119.4, 122.9, 124.2, 125.4, 127.1, 127.4, 127.6, 132.3, 134.2, 141.1, 144.1, 150.4, 162.4$. Anal. Calcd. for $\text{C}_{42}\text{H}_{24}\text{O}$: C, 92.62; H, 4.44. Found: C, 92.67; H, 4.61.

9-(2-Bromophenyl)-9-(methoxymethoxy)-9H-fluorene (5): A flame dried flask was charged with NaH (60% dispersion in oil, 73.2 mg, 1.8 mmol) and dry THF (5 mL) under nitrogen atmosphere. A solution of **1** (460 mg, 1.37 mmol) in dry THF (3 mL) was added to the suspension, and the mixture was stirred at 0 °C for 2 h. To the reaction mixture was added $\text{ClCH}_2\text{OCH}_3$ (0.430 mL, 5.70 mmol), and the reaction mixture was stirred at 0 °C for 3 h. After an addition of water (10 mL), the residue was extracted with Et_2O (3×10 mL). The organic layers were combined, washed with brine (3×10 mL), and dried over MgSO_4 . The solvents were removed under reduced pressure, and the residue was purified with column chromatography on SiO_2 with EtOAc /hexane ($v/v = 1/20$) as an eluent to give **5** (412 mg, 79%) as a white solid; mp 73.5–74.4 °C. IR (KBr) 733, 763, 916, 1026, 1039, 1086, 1148, 1269, 1461, 2927 cm^{-1} . ^1H NMR (300 MHz, CDCl_3): $\delta = 3.16$ (s, 3H), 4.29 (s, 2H), 7.10–7.15 (m, 3H), 7.20–7.25 (m, 2H), 7.37–7.47 (m, 4H), 7.66 (d, $J = 7.3$ Hz, 2H), 8.48 (br s, 1H). ^{13}C NMR (75.5 MHz, CDCl_3): $\delta = 55.9, 86.3, 91.5, 119.8, 120.8, 125.0, 126.9, 128.0, 128.8, 129.3, 129.4, 134.7, 141.0, 142.8, 145.3$. Anal. Calcd. for $\text{C}_{21}\text{H}_{17}\text{BrO}_2$: C, 66.16; H, 4.49. Found: C, 66.22; H, 4.55.

2,5-Bis(2-(9-(methoxymethoxy)-9H-fluoren-9-yl)phenyl)thiophene (6): A flame dried Schlenk flask was charged with **5** (723 mg, 1.90 mmol), 2,5-bis(trimethylstannyl)thiophene¹⁷ (369 mg, 0.901 mmol), $\text{Pd}(\text{PPh}_3)_4$ (53.3 mg, 0.046 mmol), and dry toluene (8 mL) under nitrogen atmosphere. The solution was stirred at 100 °C for 87 h. The reaction mixture was cooled down to room temperature and filtered through a short celite pad. The solvents

were removed under reduced pressure, and the residue was purified with column chromatography on SiO₂ with EtOAc/hexane (v/v = 1/12) as an eluent to give **6** (202 mg, 33%) as a yellow solid; mp 210.9–211.8 °C. IR (KBr) 736, 756, 1036, 1152, 1211, 1449, 2924, cm⁻¹. ¹H NMR (300 MHz, CDCl₃): δ = 3.19 (s, 6H), 4.13 (s, 4H), 4.50 (s, 2H), 6.86 (d, *J* = 7.3 Hz, 2H), 7.03–7.10 (m, 8H), 7.15–7.22 (m, 8H), 7.28 (dd, *J* = 7.3, 7.7 Hz, 2H), 7.49 (dd, *J* = 7.3, 7.7 Hz, 2H), 8.43 (d, *J* = 8.0 Hz, 2H). ¹³C NMR (75.5 MHz, CDCl₃): δ = 55.8, 85.8, 91.3, 119.6, 125.0, 125.2, 126.2, 126.9, 127.7, 127.8, 128.7, 132.8, 132.8, 140.1, 141.4, 141.8, 147.3. Anal. Calcd. for C₄₆H₃₆O₄S: C, 80.67; H, 5.30. Found: C, 80.40; H, 5.59.

Dispiro[9*H*-fluorene-9,5'-(6'*H*)-diindeno[1,2-*b*:2',1'-*d*]thiophene-6',9''-[9*H*]fluorene] (dsp-DIT): To a solution of **6** (62.2 mg, 0.091 mmol) in AcOH (5.0 mL) was added 10% aqueous solution of HCl (0.10 mL), and the solution was stirred at room temperature for 1 h. The reaction mixture was poured into saturated aqueous solution of NaHCO₃ (20 mL) and extracted with EtOAc (3 × 5 mL). The organic layers were combined, washed with saturated aqueous solution of NaHCO₃ (3 × 10 mL), and dried over MgSO₄. The solvents were removed under reduced pressure to give a yellow solid. The crude product was recrystallized from toluene/hexane (v/v = 4/1) to give **dsp-DIT** (23.6 mg, 46%) as a yellow solid; mp 276.8–277.5 °C. IR (KBr) 740, 753, 1283, 1447, 1601, 2920 cm⁻¹. ¹H NMR (300 MHz, CDCl₃): δ = 6.30 (d, *J* = 7.3 Hz, 2H), 6.34 (d, *J* = 7.7 Hz, 4H), 6.65 (dd, *J* = 7.3, 7.3 Hz, 4H), 6.83 (dd, *J* = 6.2, 7.7 Hz, 2H), 7.00 (dd, *J* = 7.3, 7.7 Hz, 4H), 7.20 (dd, *J* = 7.3, 7.7 Hz, 2H), 7.25 (d, *J* = 7.3 Hz, 4H), 7.49 (d, *J* = 7.7 Hz, 2H). ¹³C NMR (75.5 MHz, CDCl₃): δ = 62.9, 118.2, 119.7, 123.1, 123.2, 125.8, 127.1, 127.2, 127.4, 138.6, 141.1, 144.2, 145.8, 146.4, 151.8. HRMS (FAB): calcd for C₄₂H₂₅S (M+H⁺), 561.1677, Found 561.1673.

Preparation of 9-(Methoxymethoxy)-9-(2-((trimethylsilyl)ethynyl)phenyl)-9H-fluorene (8) from 5 via Sonogashira-coupling of 9-(2-Iodophenyl)-9-(methoxymethoxy)-9H-fluorene (7): A flame dried flask was charged with **5** (254 mg, 0.666 mmol) and dry THF (7 mL) under nitrogen atmosphere. To the solution was added 1.55 M hexane solution of *n*-BuLi (0.454 mL, 0.704 mmol) at $-78\text{ }^{\circ}\text{C}$. After stirring 1 h, a solution of I_2 (170 mg, 0.671 mmol) in dry THF (3 mL) was added to the solution, and the reaction mixture was stirred at room temperature for 3 h. The reaction mixture was quenched with 10% aqueous solution of NaHSO_3 (10 mL) and extracted with EtOAc ($3 \times 10\text{ mL}$). The organic layers were combined, washed with brine ($2 \times 10\text{ mL}$), and dried over MgSO_4 . The solvents were removed under reduced pressure, and the residue was partially purified with column chromatography on SiO_2 with EtOAc/hexane ($v/v = 1/10$) as an eluent to give **7** (266 mg) as a white solid.

A flame dried Schlenk flask was charged with **7** (266 mg, 1.44 mmol), CuI (3.9 mg, 0.020 mmol), $\text{Pd}(\text{PPh}_3)_4$ (7.9 mg, 6.8×10^{-3} mmol), *i*-PrNH₂ (1.5 mL), dry THF (6 mL), and trimethylsilylacetylene (0.115 mL, 0.81 mmol) under nitrogen atmosphere. The solution was stirred at room temperature for 16 h. The reaction mixture was cooled down to room temperature and filtered through a short celite pad. After an addition of water (10 mL), the filtrate was extracted with EtOAc ($3 \times 5\text{ mL}$). The organic layers were combined, washed with brine ($2 \times 10\text{ mL}$), and dried over MgSO_4 . The solvents were removed under reduced pressure, and the residue was purified with column chromatography on SiO_2 with EtOAc/hexane ($v/v = 1/40$) as an eluent to give **8** (188 mg, 71% yield based on **5**) as a pale yellow solid.

7: mp $73.6\text{--}74.6\text{ }^{\circ}\text{C}$. IR (KBr) 732, 752, 762, 915, 1029, 1086, 1149, 1447, 2927 cm^{-1} . ^1H NMR (300 MHz, CDCl_3): $\delta = 3.14$ (s, 3H), 4.29 (s, 2H), 6.93 (dd, $J = 7.7, 7.7\text{ Hz}$, 1H), 7.10 (d, $J = 7.3\text{ Hz}$, 2H), 7.23 (dd, $J = 7.3, 7.7\text{ Hz}$, 2H), 7.40 (dd, $J = 7.7, 7.7\text{ Hz}$, 2H), 7.51 (dd, $J =$

7.3, 7.3 Hz, 1H), 7.66 (d, J = 7.3 Hz, 2H), 7.76 (d, J = 7.3 Hz, 1H), 8.52 (d, J = 7.7 Hz, 1H).

^{13}C NMR (75.5 MHz, CDCl_3): δ = 55.8, 87.3, 91.6, 119.8, 125.48, 125.45, 127.7, 128.1, 129.0, 129.2, 129.5, 142.2, 143.2, 143.9, 144.8. Anal. Calcd. for $\text{C}_{21}\text{H}_{17}\text{IO}_2$: C, 58.89; H, 4.00. Found: C, 59.15; H, 4.00.

8: mp 47.8–48.8 °C. IR (neat) 751, 766, 838, 859, 1026, 1147, 1246, 1448, 1473, 2155, 2953 cm^{-1} . ^1H NMR (300 MHz, CDCl_3) δ = -0.04 (s, 9H), 3.15 (s, 3H), 4.33 (s, 2H), 7.17–7.26 (m, 5H), 7.34–7.39 (m, 4H), 7.62 (d, J = 7.3 Hz, 2H), 8.16 (br s, 1H). ^{13}C NMR (75.5 MHz, CDCl_3) δ = -0.3, 55.8, 86.5, 91.6, 99.1, 102.6, 119.7, 120.5, 125.3, 126.6, 127.0, 127.8, 128.2, 129.0, 135.8, 142.1, 143.3, 146.4. Anal. Calcd. for $\text{C}_{26}\text{H}_{26}\text{O}_2\text{Si}$: C, 78.35; H, 6.58. Found: C, 78.09; H, 6.50.

9-(2-Ethynylphenyl)-9-(methoxymethoxy)-9H-fluorene (9): To a solution of **8** (854 mg, 2.14 mmol) in MeOH (20 mL) and THF (5 mL) was added K_2CO_3 (443 mg, 3.20 mmol), and the solution was stirred at 50 °C for 12 h. After cooling to ambient temperature, the reaction mixture was quenched with water (10 mL) and extracted with EtOAc (3×5 mL). The organic layers were combined, washed with brine (2×10 mL), and dried over MgSO_4 . The solvents were removed under reduced pressure, and the residue was purified with column chromatography on SiO_2 with EtOAc/hexane (v/v = 1/25) as an eluent to give **9** (682 mg, 98%) as a pale yellow oil; IR (neat) 641, 750, 922, 1026, 1152, 1449, 1474, 2930, 3062, 3293 cm^{-1} . ^1H NMR (300 MHz, CDCl_3): δ = 2.60 (s, 1H), 3.20, (s, 3H), 4.37 (s, 2H), 7.18–7.29 (m, 5H), 7.33–7.41 (m, 4H), 7.61 (d, J = 7.0 Hz, 2H), 8.12 (br s, 1H). ^{13}C NMR (75.5 MHz, CDCl_3): δ = 55.9, 80.8, 81.8, 86.7, 91.8, 119.4, 119.5, 125.4, 126.7, 127.1, 127.8, 128.5, 129.2, 135.3, 142.4, 144.3, 146.3. Anal. Calcd. for $\text{C}_{23}\text{H}_{18}\text{O}_2$: C, 84.64; H, 5.56. Found: C, 84.66; H, 5.57.

1,4-Bis(2-(9-(methoxymethoxy)-9H-fluoren-9-yl)phenyl)buta-1,3-diyne (10): To a solution of **9** (1.04 g, 3.20 mmol) and Et₃N (0.900 mL, 6.46 mmol) in 1,4-dioxane (30 mL) was added Cu(OAc)₂ (291 mg, 1.60 mmol), and the solution was stirred at 100 °C for 13 h. The reaction mixture was cooled down to ambient temperature and filtered through a short celite pad. After an addition of water (30 mL), the residue was extracted with EtOAc (3 × 10 mL). The organic layers were combined, washed with brine (3 × 20 mL), and dried over MgSO₄. The solvents were removed under reduced pressure, and the residue was purified with column chromatography on SiO₂ with EtOAc/hexane (v/v = 1/8) as an eluent to give **10** (979 mg, 94%) as a white solid; mp 172.0–172.7 °C. IR (KBr) 751, 786, 907, 1039, 1093, 1142, 1232, 1450, 2873 cm⁻¹. ¹H NMR (300 MHz, CDCl₃): δ = 3.16 (s, 6H), 4.35, (s, 4H), 7.19–7.38 (m, 18H), 7.58 (d, *J* = 7.0 Hz, 4H), 7.87 (br s, 2H). ¹³C NMR (75.5 MHz, CDCl₃): δ = 56.0, 78.7, 81.1, 87.0, 92.1, 119.7, 119.8, 125.1, 126.7, 127.1, 127.8, 128.6, 129.3, 135.4, 141.8, 145.1, 146.0. Anal. Calcd. for C₄₆H₃₄O₄: C, 84.90; H, 5.27. Found: C, 84.81; H, 5.15.

11-Phenyl-dispiro[9H-fluorene-9,5'(6'H)-diindeno[1,2-b:2',1'-d]pyrrole-6',9''-[9H]fluorene] (dsp-DIP-Ph): A flame dried Schlenk flask was charged with **10** (194 mg, 0.299 mmol), CuCl (7.5 mg, 0.076 mmol), and PhNH₂ (1.2 mL) under nitrogen atmosphere. The solution was stirred at 150 °C for 44 h. The reaction mixture was cooled down to room temperature and filtered through a short celite pad. After an addition of EtOAc (10 mL), the filtrate was washed with 10% aqueous solution of AcOH (5 × 10 mL), saturated aqueous solution of NaHCO₃ (3 × 10 mL), and brine (10 mL), and dried over MgSO₄. The solvents were removed under reduced pressure, and the residue was partially purified with column chromatography on SiO₂ with EtOAc/hexane (v/v = 1/15) as an eluent to give crude product (63.1 mg) as a brown solid.

To the solution of the crude product (63.1 mg) in AcOH (2 mL) and toluene (2 mL) was

added 35% aqueous solution of HCl (0.050 mL), and the solution was stirred at room temperature for 3 h. The reaction mixture was poured into saturated aqueous solution of NaHCO₃ (15 mL) and extracted with EtOAc (3 × 5 mL). The organic layers were combined, washed with saturated aqueous solution of NaHCO₃ (3 × 10 mL), and dried over MgSO₄. The solvents were removed under reduced pressure, and the residue was purified with column chromatography on SiO₂ with EtOAc/hexane (v/v = 1/20) as an eluent to give **dsp-DIP-Ph** (40.0 mg, 22% yield based on **10**) as a pale yellow solid; mp 284.4–285.5 °C. IR (KBr) 727, 737, 1445, 1473, 1508, 1602, 2923 cm⁻¹. ¹H NMR (300 MHz, CDCl₃): δ = 6.40 (d, *J* = 7.3 Hz, 2H), 6.51 (d, *J* = 7.7 Hz, 4H), 6.67–6.75 (m, 6H), 6.96–7.05 (m, 8H), 7.29 (d, *J* = 7.3 Hz, 4H), 7.59 (dd, *J* = 7.3, 7.7 Hz, 1H), 7.71 (dd, *J* = 7.3, 7.7 Hz, 2H), 7.93 (d, *J* = 7.7 Hz, 2H). ¹³C NMR (75.5 MHz, CDCl₃): δ = 59.3, 116.4, 119.3, 123.1, 124.0, 124.3, 126.2, 126.87, 126.94, 127.9, 129.5, 130.9, 135.9, 138.5, 141.0, 141.7, 145.8, 152.0 (one peak cannot be discriminated due to overlap with another peak). HRMS (FAB): calcd for C₄₈H₃₀N (M+H⁺), 620.2378, Found 620.2362.

The Synthesis of 6 from Diyne 10: A flame dried Schlenk flask was charged with **10** (195 mg, 0.299 mmol), Na₂S·9H₂O (361 mg, 1.50 mmol), and dry DMF (5 mL) under nitrogen atmosphere. The solution was stirred at 150 °C for 23 h. After cooling to ambient temperature, water (10 mL) was added to the reaction mixture. The residue was extracted with EtOAc (3 × 5 mL). The organic layers were combined, washed with brine (3 × 10 mL), and dried over MgSO₄. The solvents were removed under reduced pressure, and the residue was purified with column chromatography on SiO₂ with EtOAc/hexane (v/v = 1/10) as an eluent to give **6** (142 mg, 69%) as a yellow solid.

Table 2. Crystal data and structure refinement for **dsp-DIF**

Empirical Formula	$C_{42}H_{24}O \cdot CH_2Cl_2$
Formula Weight	627.57
Temperature (°C)	−120
Crystal Color, Habit	colorless, block
Crystal Dimensions	$0.20 \times 0.20 \times 0.20$ mm
Crystal System	monoclinic
Lattice Parameters	$a = 13.182(7)$ Å $b = 18.871(9)$ Å $c = 13.862(8)$ Å $V = 3193(3)$ Å ³ $\beta = 112.214(3)^\circ$
Space Group	$P2_1/n$ (#14)
Z value	4
D_{calc}	1.306 g/cm ³
F(000)	1296.00
$\mu(\text{MoK}\alpha)$	2.375 cm ^{−1}
Radiation	MoK α ($\lambda = 0.71070$ Å) graphite monochromated
2 θ max	62.1°
No. of Reflections Measured	Total: 20328 Unique: 7863 ($R_{\text{int}} = 0.108$)
Structure Solution	Direct Methods (SIR92)
Refinement	Full-matrix least-squares on F
No. Observations (All reflections)	7863
No. Variables	436
Reflection/Parameter Ratio	18.03
Residuals: R ($I > 2.00\sigma(I)$)	0.1100
Residuals: R_w (All reflections)	0.1799
Goodness-of-fit on F^2	1.023
Max Shift/Error in Final Cycle	0.000
Maximum peak in Final Diff. Map	1.47 e [−] /Å ³
Minimum peak in Final Diff. Map	−2.77 e [−] /Å ³

Table 3. Crystal data and structure refinement for **dsp-DIT**

Empirical Formula	$C_{42}H_{24}S \cdot C_7H_8$
Formula Weight	560.71
Temperature (°C)	−120
Crystal Color, Habit	colorless, block
Crystal Dimensions	$0.20 \times 0.20 \times 0.20$ mm
Crystal System	monoclinic
Lattice Parameters	$a = 23.110(15)$ Å $b = 9.920(6)$ Å $\beta = 95.349(3)^\circ$ $c = 14.678(10)$ Å $V = 3350(4)$ Å ³
Space Group	$C2/c$ (#15)
Z value	4
D_{calc}	1.112 g/cm ³
F(000)	1168.00
$\mu(\text{MoK}\alpha)$	1.229 cm ^{−1}
Radiation	MoK α ($\lambda = 0.71070$ Å) graphite monochromated
2 θ max	61.8°
No. of Reflections Measured	Total: 11967 Unique: 4398 ($R_{\text{int}} = 0.079$)
Structure Solution	Direct Methods (SIR2004)
Refinement	Full-matrix least-squares on F^2
No. Observations (All reflections)	4398
No. Variables	263
Reflection/Parameter Ratio	16.72
Residuals: R_1 ($I > 2.00\sigma(I)$)	0.0622
Residuals: wR_2 (All reflections)	0.1191
Goodness-of-fit on F^2	1.063
Max Shift/Error in Final Cycle	0.000
Maximum peak in Final Diff. Map	2.13 e [−] /Å ³
Minimum peak in Final Diff. Map	−0.80 e [−] /Å ³

Table 4. Crystal data and structure refinement for **dsp-DIP-Ph**

Empirical Formula	$\text{C}_{48}\text{H}_{29}\text{N} \cdot \text{C}_4\text{H}_8\text{O}_2$	
Formula Weight	671.80	
Temperature (°C)	−120	
Crystal Color, Habit	yellow, block	
Crystal Dimensions	0.20 × 0.20 × 0.20 mm	
Crystal System	monoclinic	
Lattice Parameters	$a = 14.490(6) \text{ \AA}$	
	$b = 11.893(4) \text{ \AA}$	$\beta = 108.022(5)^\circ$
	$c = 21.667(8) \text{ \AA}$	
	$V = 3551(2) \text{ \AA}^3$	
Space Group	$P2_1/n$ (#14)	
Z value	4	
D_{calc}	1.257 g/cm ³	
F(000)	1400.00	
$\mu(\text{MoK}\alpha)$	0.739 cm ^{−1}	
Radiation	MoK α ($\lambda = 0.71070 \text{ \AA}$)	
	graphite monochromated	
2 θ max	62.3°	
No. of Reflections Measured	Total: 29735	
	Unique: 9914 ($R_{\text{int}} = 0.048$)	
Structure Solution	Direct Methods (SIR92)	
Refinement	Full-matrix least-squares on F	
No. Observations (All reflections)	9914	
No. Variables	487	
Reflection/Parameter Ratio	20.36	
Residuals: R ($I > 2.00\sigma(I)$)	0.0695	
Residuals: R_w (All reflections)	0.0860	
Goodness-of-fit on F^2	1.028	
Max Shift/Error in Final Cycle	0.000	
Maximum peak in Final Diff. Map	1.10 e [−] /Å ³	
Minimum peak in Final Diff. Map	−0.67 e [−] /Å ³	

Table 5. Cartesian atomic coordinates for the optimized structure of **dsp-DIT** (B3LYP/6-31G(d)).

atom	x	y	z
C	1.2248012437	2.5318022384	0.0281689052
C	0.7113590938	1.2463436701	0.0095904098
C	-0.7113572505	1.2463445729	-0.0096048002
C	-1.2247975664	2.5318036592	-0.0281981807
S	0.0000027204	3.7698439796	-0.0000217903
C	2.6755770858	2.5360189160	0.0705089850
C	3.0815936659	1.1824577958	0.0590986698
C	1.8627161021	0.2409150400	-0.0299002205
C	-1.8627156956	0.2409180408	0.0298974512
C	-3.0815919158	1.1824615164	-0.0591123273
C	-2.6755733993	2.5360219230	-0.0705383067
C	3.6202178267	3.5624731675	0.1241540640
C	4.9751658489	3.2225585661	0.1689769288
C	5.3769843965	1.8835453320	0.1595185219
C	4.4279100604	0.8536861938	0.1023896360
C	-4.4279087788	0.8536913377	-0.1023994739
C	-5.3769816456	1.8835511735	-0.1595402645
C	-4.9751611784	3.2225637224	-0.1690141774
C	-3.6202126686	3.5624769019	-0.1241952635
C	1.9252716328	-0.6067384156	-1.3090756127
C	2.0189786667	-1.9735466019	-0.9899522309
C	1.9836807173	-2.1194245252	0.4715228034
C	1.8678177190	-0.8415053349	1.0514161971
C	-1.9252724836	-0.6067205449	1.3090826259
C	-2.0189816088	-1.9735322695	0.9899750336
C	-1.9836838672	-2.1194271319	-0.4714983098
C	-1.8678188895	-0.8415148208	-1.0514064647
C	-1.9502176195	-0.1809203127	2.6309978221
C	-2.0658827378	-1.1372597897	3.6453008552
C	-2.1571826897	-2.4981668274	3.3331074397
C	-2.1341816651	-2.9261757405	2.0042936787
C	-2.0523379607	-3.2558743191	-1.2794182170
C	-2.0001554272	-3.1017133914	-2.6662897073
C	-1.8812452580	-1.8306517155	-3.2383760250
C	-1.8173568388	-0.6899083949	-2.4311716474

C	2.0523330943	-3.2558624846	1.2794558364
C	2.0001508613	-3.1016854522	2.6663255498
C	1.8812426823	-1.8306169839	3.2383971865
C	1.8173559665	-0.6898828932	2.4311796277
C	1.9502174485	-0.1809534843	-2.6309957276
C	2.0658811258	-1.1373048499	-3.6452877113
C	2.1571789906	-2.4982084208	-3.3330785727
C	2.1341772857	-2.9262019613	-2.0042598765
H	3.3113038046	4.6044554621	0.1334432031
H	5.7235030351	4.0093179663	0.2126731369
H	6.4345517526	1.6373246103	0.1968783403
H	4.7436553215	-0.1861192778	0.0928180104
H	-4.7436555197	-0.1861135742	-0.0928158036
H	-6.4345493554	1.6373315344	-0.1968972182
H	-5.7234972384	4.0093236878	-0.2127194763
H	-3.3112971586	4.6044586438	-0.1334964539
H	-1.8856032942	0.8764120850	2.8742623795
H	-2.0869313590	-0.8194923844	4.6843716503
H	-2.2474370104	-3.2291437115	4.1323241087
H	-2.2060432194	-3.9845544795	1.7670721723
H	-2.1448509049	-4.2458188130	-0.8397903248
H	-2.0508129540	-3.9778048398	-3.3074883356
H	-1.8376405455	-1.7276551770	-4.3191208284
H	-1.7280795410	0.2968284302	-2.8775961404
H	2.1448445081	-4.2458122016	0.8398393806
H	2.0508070733	-3.9777695716	3.3075342976
H	1.8376382288	-1.7276078855	4.3191408034
H	1.7280801941	0.2968592290	2.8775927237
H	1.8856047526	0.8763762057	-2.8742724891
H	2.0869302502	-0.8195494764	-4.6843621745
H	2.2474322039	-3.2291946745	-4.1322867975
H	2.2060372328	-3.9845780705	-1.7670261548

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List of Publications

- Chapter 1 “Synthesis, Characterization, and Photoluminescence of Thiophene-Containing Spiro Compounds”
Toshiyuki Kowada, Yoshio Matsuyama, Kouichi Ohe
Synlett **2008**, 1902.
- Chapter 2 “Synthesis and Characterization of Highly Fluorescent and Thermally Stable π -Conjugates involving Spiro[fluorene-9,4’-[4*H*]indeno[1,2-*b*]furan]”
Toshiyuki Kowada, Kouichi Ohe
Bull. Korean Chem. Soc. in press.
- Chapter 3 “Highly Fluorescent BODIPY Dyes Modulated with Spirofluorene Moieties”
Toshiyuki Kowada, Shuhei Yamaguchi, Kouichi Ohe
Org. Lett. **2010**, 12, 296.
- Chapter 4 “Synthesis of Electron-donor-substituted Structurally Constrained BODIPY Dyes and Observation of pH-Dependent ICT Fluorescence”
Toshiyuki Kowada, Shuhei Yamaguchi, Kouichi Ohe
to be submitted
- Chapter 5 “Synthesis, Structures, and Optical Properties of Heteroarene-Fused Dispiro Compounds”
Toshiyuki Kowada, Toshihisa Kuwabara, Kouichi Ohe
J. Org. Chem. **2010**, 75, 906.

Other Publication

The following publication is not included in this thesis.

“Platinum- and Palladium-Catalyzed Sequential Reactions: Regioselective Synthesis of 9-Fluorenylidenes from 9-Ethynylfluoren-9-yl Carboxylates and Furans”

Koji Miki, Yoshinori Senda, Toshiyuki Kowada, Kouichi Ohe

Synlett **2009**, 1937.

Acknowledgments

The study described in this thesis has been carried out under the direction of Professor Kouichi Ohe at Kyoto University during the period of 5 years from April 2005 to March 2010. The author sincerely thanks Professor Kouichi Ohe for his kind support, valuable suggestions, and constant encouragement during the course of this study.

The author wishes to express his acknowledgment to Lecturer Koji Miki. He also thanks Associate Professor Takao Okazaki for his helpful teaching and advice. He would like to express his gratitude to Assistant Professor Tetsuaki Fujihara and Assistant Professor Kazuhiro Okamoto for their helpful suggestions and discussions.

The author acknowledges his appreciation to Prof. Yasushi Tsuji and Prof. Yasujiro Murata for careful reviewing of this thesis and fruitful comments. The author is deeply grateful to Professor Hironori Kaji and Mr. Tatsuya Fukushima for their assistance with the measurements of photoluminescence quantum yield in the solid state. He is also grateful to Professor Masashi Inoue and Dr. Saburo Hosokawa for assistance with TG analysis.

The author is deeply grateful to Ms. Mayumi Sakamoto and Ms. Akemi Nagano for their kind assistances. He would like to express his sincere thanks to Mr. Toshihisa Kuwabara, Mr. Yoshio Matsuyama, Mr. Shuhei Yamaguchi, and Mr. Hiroki Fujinaga for their collaboration. He sincerely thanks Mr. Masahito Murai for his kind support, helpful discussions, and warm friendship.

The author expresses his appreciation to Messrs. Kosuke Chidate, Bumpei Yoshida, Atsushi Yamamoto, Yoshiaki Kuramochi, Kazuaki Oride, Takahiko Murata, Tomohiro Abo, Hideyuki Matsumoto, Yoshinori Senda, Yuji Ikeda, Yusuke Nakanishi, Motohiro Kaji, Shotaro Yoshida, Shigekazu Kawai, Shin-ichi Nakamura, Tsuyoshi Yorino, Yugo Tai, Sho Kohigashi, Yuki Inoue of Ohe's research group for their warm friendship.

Finally, the author would like to express his sincere gratitude to his parents, Haruhiko Kowada and Ruriko Kowada, for their constant assistance and encouragement.

March, 2010

Toshiyuki Kowada