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

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dsp-DIF (X = O)
dsp-DIT (X = S)
dsp-DIP-Ph (X = NPh)
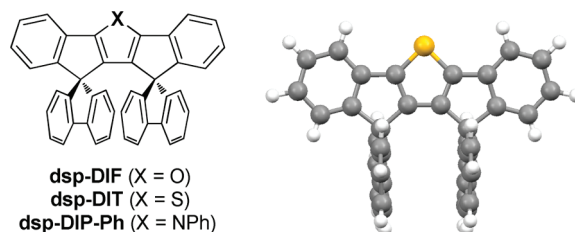
Novel heteroarene-fused dispiro compounds, dispiro[9H-fluorene-9,5′(6′H)-diindeno[1,2-b:2′,1′-d]-furan-6′,9′′-[9H]fluorene] (**dsp-DIF**), dispiro[9H-fluorene-9,5′(6′H)-diindeno[1,2-b:2′,1′-d]thiophene-6′,9′′-[9H]fluorene] (**dsp-DIT**), and 11-phenyldispiro[9H-fluorene-9,5′(6′H)-diindeno[1,2-b:2′,1′-d]pyrrole-6′,9′′-[9H]fluorene] (**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,c,5d,6] or incorporating

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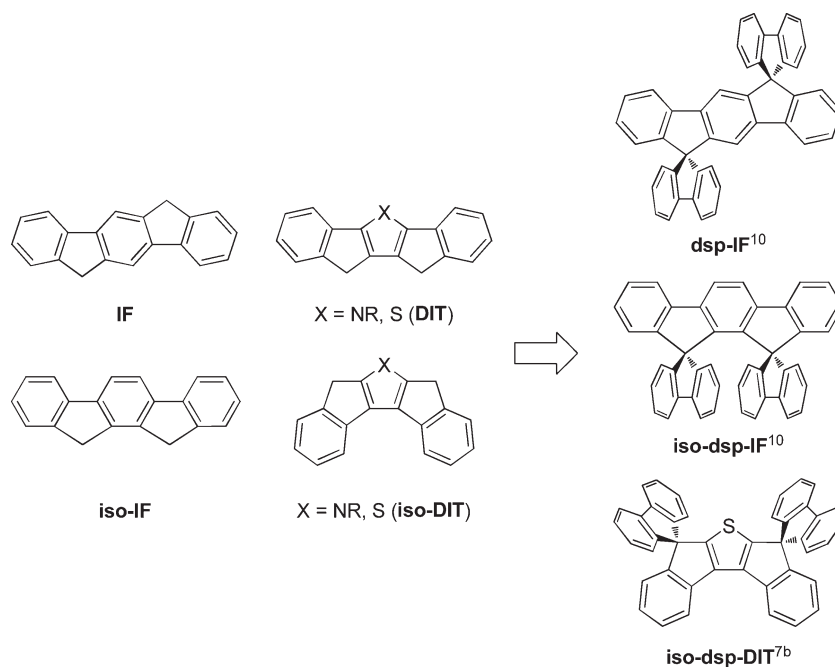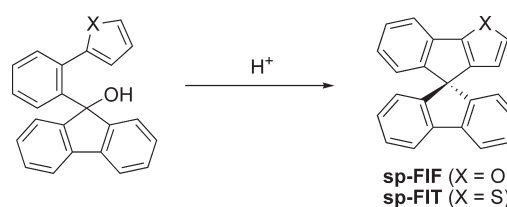
FIGURE 1. Structures of **IF** and **DIT** derivatives and the corresponding dispiro compounds.

heteroarenes directly as components of the π-backbone.[4g,7,8] Indeed, 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, to the best of our knowledge, ladder-type compounds involving both heteroarenes and spiro structures have been less investigated.[7b]

Recently, furan- or thiophene-containing spiro compounds, **sp-FIF** and **sp-FIT**, have been newly synthesized in our laboratory (Scheme 1).[12] Then, we envisioned that novel heteroarene-fused ladder-type compounds could be synthesized

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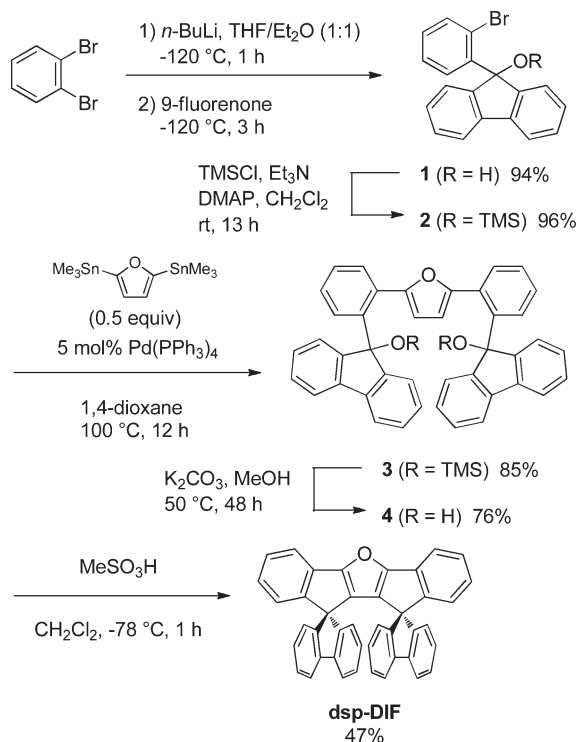
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SCHEME 1. **Synthetic Route to sp-FIF and sp-FIT**

sp-FIF (X = O)
sp-FIT (X = S)

SCHEME 2. **Synthetic Route to Dispiro Compounds**

X = O, NR, S
new targets
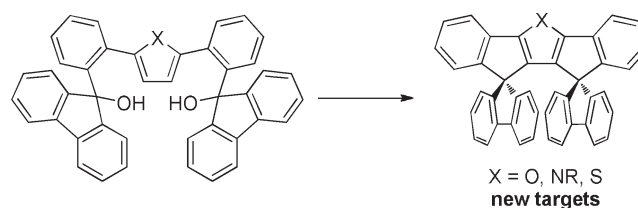
based on an intramolecular Friedel−Crafts-type alkylation. Herein, we report the synthesis, structures, and optical properties of unique dispiro compounds containing heteroles, such as furan, thiophene, or pyrrole (Scheme 2).

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

SCHEME 3. Synthesis of dsp-DIF

1) n-BuLi, THF/Et₂O (1:1)
   -120 °C, 1 h

2) 9-fluorenone
   -120 °C, 3 h

TMSCl, Et₃N
DMAP, CH₂Cl₂
rt, 13 h

1 (R = H) 94%
2 (R = TMS) 96%

(0.5 equiv)
5 mol% Pd(PPh₃)₄

1,4-dioxane
100 °C, 12 h

K₂CO₃, MeOH
50 °C, 48 h

3 (R = TMS) 85%
4 (R = H) 76%

MeSO₃H

CH₂Cl₂, -78 °C, 1 h

dsp-DIF
47%

SCHEME 4. Synthesis of dsp-DIT

1) NaH, THF
   0 °C, 2 h

2) MOMCl
   0 °C, 3 h

1

5
79%

(0.5 equiv)
5 mol% Pd(PPh₃)₄

toluene
110 °C, 87 h

6
33%

10% aq. HCl

AcOH, rt, 1 h

dsp-DIT
46%

spirofluorene skeleton is the acid-promoted Friedel−Crafts reaction.[13] 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.

The synthesis of dispiro[9H-fluorene-9,5′(6′H)-diindeno-[1,2-b:2′,1′-d]thiophene-6′,9″-[9H]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.

To prepare a pyrrole analogue of **dsp-DIF** and **dsp-DIT**, we 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, we 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 to afford **8** in 71% yield in 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-phenyldispiro[9H-fluorene-9,5′(6′H)-diindeno[1,2-b:2′,1′-d]pyrrole-6′,9″-[9H]fluorene] (**dsp-DIP-Ph**) was obtained in 22% yield (in two steps) by acid-promoted intramolecular Friedel−Crafts reaction of the major product, which was produced by copper-catalyzed double hydroamination
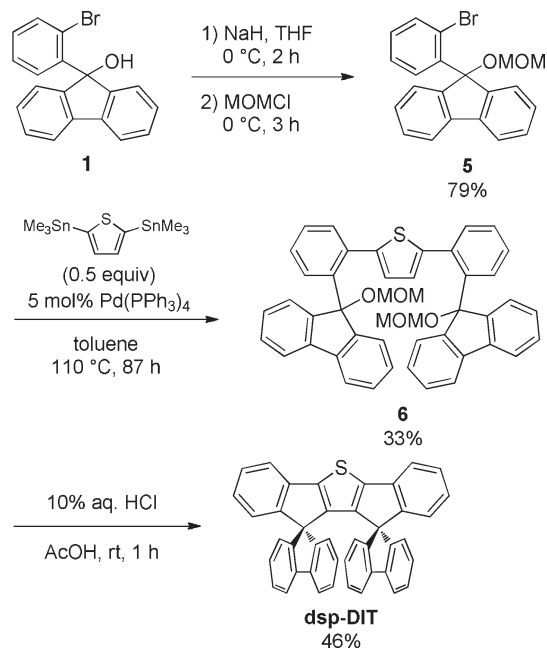
of diyne **10** with aniline. Furthermore, it was possible to transform diyne **10** to thiophene **6**, leading to **dsp-DIT**, by reaction with Na₂S·9H₂O (Scheme 6). This result suggests that diyne **10** has great potential as a key structure to prepare various heteroarene-fused dispiro compounds.

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 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) 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.[14] It is noteworthy that the two fluorene units are completely overlapped in the structure (Figure 2b). Diindenoheteroarene frameworks of three dispiro compounds exhibit nearly planar structures, as found in the small dihedral angles between the mean planes of the two benzene rings (**dsp-DIF**, 1.6°; **dsp-DIT**, 1.2°; **dsp-DIP-Ph**, 2.8°). As a result, highly symmetrical structures of these compounds afforded simple NMR spectra. Furthermore, according to the packing structure, the intermolecular π−π stackings are completely suppressed by the orthogonally arranged spirofluorene structures.[15]
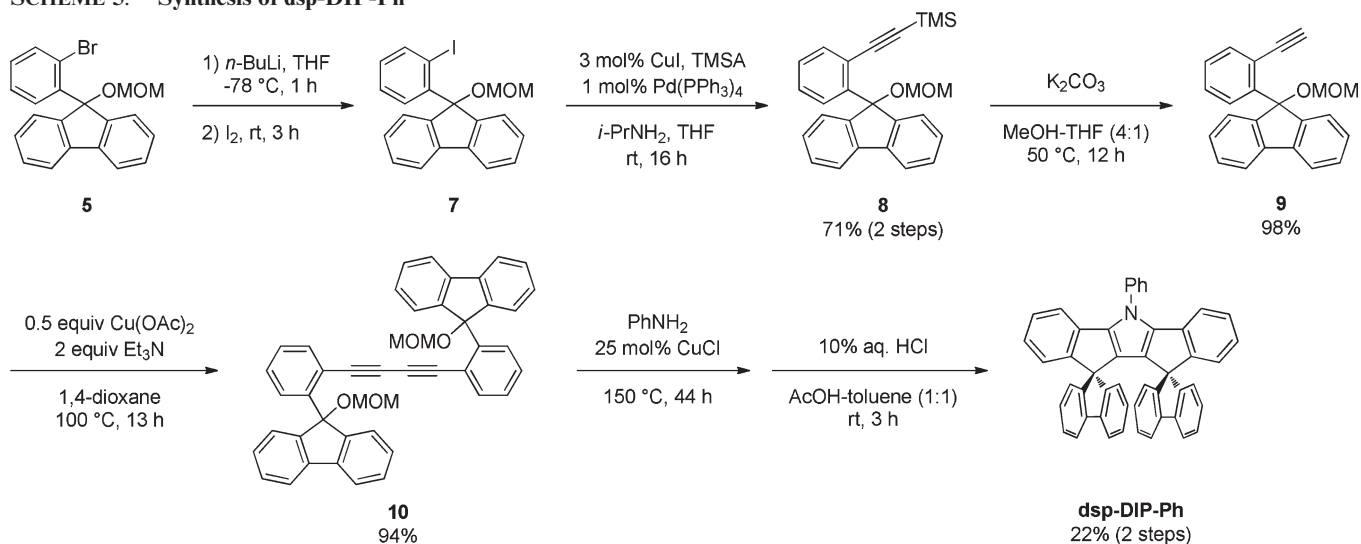
The absorption and emission spectra of dispiro compounds **dsp-DIF**, **dsp-DIT**, and **dsp-DIP-Ph** were measured

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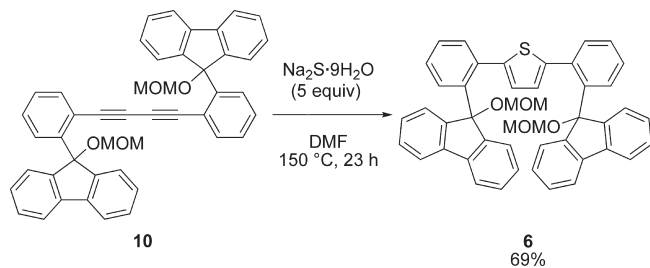
(14) Curtis, M. D.; Cao, J.; Kampf, J. W. J. Am. Chem. Soc. **2004**, 126, 4318.
(15) See the Supporting Information.

SCHEME 5. Synthesis of dsp-DIP-Ph


SCHEME 6. Transformation of 10 to 6

in THF (Figure 3), 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 from 6 to 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.

We next compared the photophysical properties of **dsp-DIT** with those of reference compounds 2,5-diphenylthiophene (**DPT**) and **DIT** (Figure 3, Table 1). The absorption and emission spectra of **DIT** were largely red-shifted, compared with those of **DPT** because of the linking between a thiophene ring and two phenyl groups with methylene chains. 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,[16] thereby extending the π-conjugation and increasing the quantum yield.

(16) Wiesenhofer, H.; Beljonne, D.; Scholes, G. D.; Hennebicq, E.; Brédas, J.-L.; Zojer, E. *Adv. Funct. Mater.* **2005**, *15*, 155.

In addition, **dsp-DIT** showed higher photoluminescence quantum yield in the solid state compared to **DIT** because of the suppression of intermolecular $\pi-\pi$ stackings by
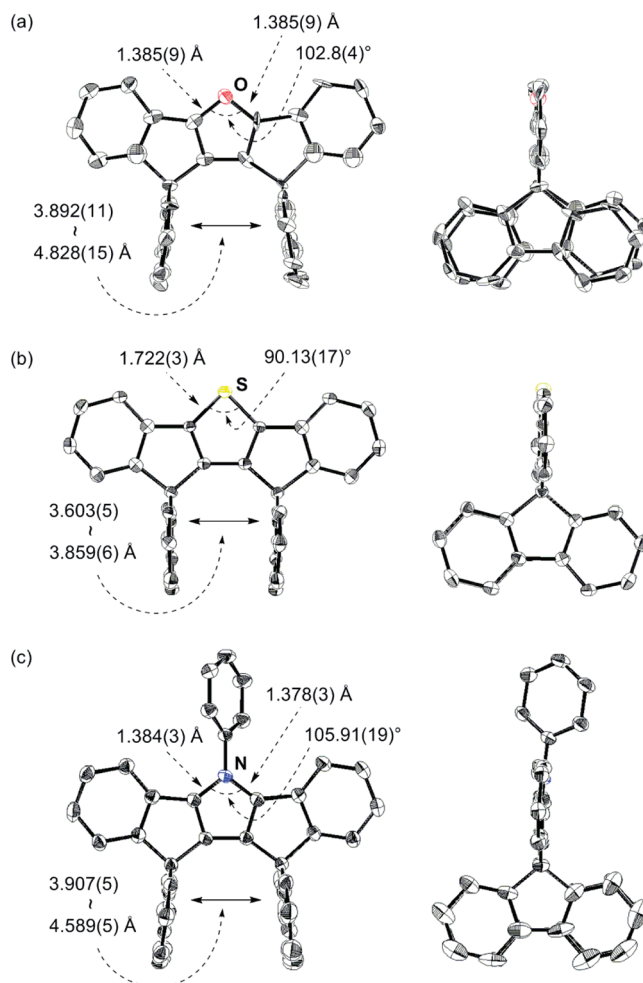
FIGURE 2. X-ray crystal structures of (a) **dsp-DIF**, (b) **dsp-DIT**, and (c) **dsp-DIP-Ph**: (left) top view and (right) side view. All solvent molecules and hydrogen atoms are omitted for clarity.
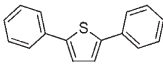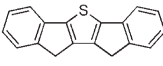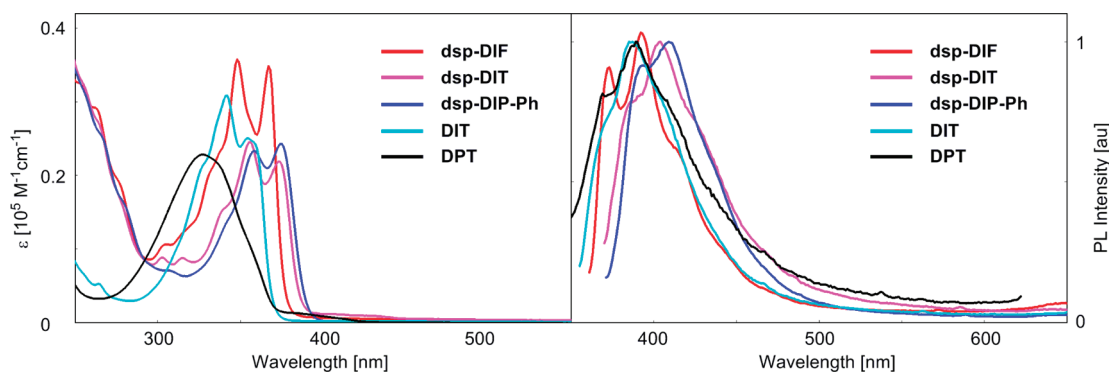
FIGURE 3. Absorption spectra (left) and the emission spectra (right) of dsp compounds and related compounds in THF.

TABLE 1. Optical Properties of dsp Compounds and Related Compounds in THF

compound	λ_{abs} [nm]	ε_{max} [$\times 10^5$ M^{-1}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. $^b\lambda_{ex}$ 350 nm. Relative quantum yield calculated using quinine sulfate in 0.1 M aq H_2SO_4 as a standard.

TABLE 2. Optical Properties of dsp Compounds and DIT in the Solid State

compound	λ_{ex} [nm]	λ_{em} [nm]	$\Phi_{solid}{}^a$
dsp-DIF	348	401, 422	0.089
dsp-DIT	356	492, 522	0.099
dsp-DIP-Ph	358	467	0.040
DIT	342	409	0.017

^{a}Absolute quantum yield determined by a calibrated integrating sphere system.

spirofluorene moieties (Table 2). The bathochromic shifts of absorption and emission maxima of **dsp-DIT** relative to those of **DIT** seem to be also attributed to spiroconjugation[17] between two fluorene moieties and the diindenothiophene skeleton. We then performed a DFT calculation (B3LYP/6-31G(d)) to gain insight into spiroconjugation for **dsp-DIT**. Indeed, the conjugation between two fluorene moieties and the diindenothiophene skeleton was confirmed to exist in the HOMO level (Figure 4).

The oxidation potentials of dsp compounds and related compounds were measured in CH_2Cl_2 (Table 3). The first oxidation potentials of dsp compounds were dependent on the nature of the central heteroarene. Because *N*-phenylpyrrole
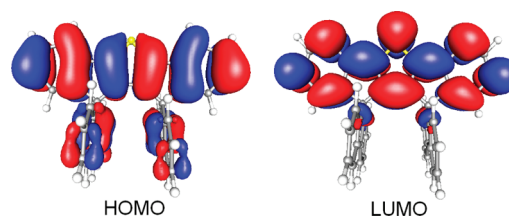
(17) For a recent review, see: Geuenich, D.; Hess, K.; Köhler, F.; Herges, R. *Chem. Rev.* **2005**, *105*, 3758.

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

TABLE 3. Oxidation Potentials of dsp Compounds and Related Compounds in CH_2Cl_2

compound	$E_{1/2\ ox}$ [V]^b
dsp-DIF	0.504, 1.132
dsp-DIT	0.452, 0.596, 0.920
dsp-DIP-Ph	0.272, 1.100
DPT	0.616, 0.932
DIT	0.616

^{a}Absolute quantum yield determined by a calibrated integrating sphere system. ^{b}In CH_2Cl_2 containing 0.10 M Bu$_4$NPF$_6$ vs Fc/Fc$^+$ at 100 mV s^{-1}.

can stabilize the generated radical cation, **dsp-DIP-Ph** shows the lowest oxidation potential. Thiophene compounds **DPT** and **DIT** show their first oxidation potentials with the same value. It is suggested that bridging between the thiophene ring

and two phenyl rings scarcely affects the electronic nature of these compounds. Nevertheless, the first oxidation potential of **dsp-DIT** is much lower than those of **DPT** and **DIT**. It might be due to increase of the HOMO level of **dsp-DIT** by spiroconjugation.

In conclusion, we have 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 elongation 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.

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).[18] To the solution of 1,2-dibromobenzene (2.83 g, 12.0 mmol) in dry THF (20 mL) and dry Et_2O (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/Et_2O (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 NH_4Cl (30 mL) and extracted with Et_2O (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 to give an orange oil. The crude product was purified with column chromatography on SiO_2 (EtOAc−hexane, 1:20) 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}; ^{1}H NMR (300 MHz, CDCl$_3$) 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); ^{13}C NMR (75.5 MHz, CDCl$_3$) 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 the solution of **1** (2.03 g, 6.02 mmol), Et_3N (4.20 mL, 30.1 mmol), and DMAP (73.5 mg, 0.602 mmol) in CH_2Cl_2 (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 (hexane) 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}; ^{1}H 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 $C_{22}H_{21}BrOSi$: C, 64.54; H, 5.17. Found: C, 64.33; H, 5.16.

2,5-Bis(2-(9-(trimethylsilyloxy)-9*H*-fluoren-9-yl)phenyl)furan (3). A flame-dried flask was charged with **2** (15.7 g, 38.3 mmol), 2,5-bis(trimethylstannyl)furan[19] (7.52 g, 19.1 mmol), Pd(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 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}; ^{1}H 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 $C_{48}H_{44}O_3Si_2$: 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 K_2CO_3 (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 Et_2O (3 × 30 mL). The organic layers were combined, washed with brine (3 × 20 mL), and dried over $MgSO_4$. The solvents were removed under reduced pressure, and the residue was purified by washing with Et_2O−hexane (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}; ^{1}H NMR (300 MHz, CDCl$_3$) 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); ^{13}C NMR (75.5 MHz, CDCl$_3$) 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 $C_{42}H_{28}O_3$: C, 86.87; H, 4.86. Found: C, 86.57; H, 4.92.

Dispiro[9*H*-fluorene-9,5′(6′*H*)-diindeno[1,2-*b*:2′,1′-*d*]furan-6′,9″-[9*H*]fluorene] (dsp-DIF). To the solution of **4** (116 mg, 0.199 mmol) in CH_2Cl_2 (15 mL) was added $MeSO_3H$ (114 mg, 1.16 mmol) in CH_2Cl_2 (5 mL) at −78 °C. After stirring for 1 h, the reaction mixture was quenched with water (15 mL) and extracted with CH_2Cl_2 (2 × 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 to give a yellow solid. The crude product was recrystallized from toluene−hexane (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}; ^{1}H NMR (300 MHz, CDCl$_3$) 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,

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J = 7.7 Hz, 2H); ^{13}C NMR (75.5 MHz, CDCl$_3$) δ = 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 C$_{42}$H$_{24}$O: C, 92.62; H, 4.44. Found: C, 92.67; H, 4.61.

9-(2-Bromophenyl)-9-(methoxymethoxy)-9*H*-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 ClCH$_2$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$_2$O (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$_2$ (EtOAc−hexane, 1:20) 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}; ^{1}H NMR (300 MHz, CDCl$_3$) δ = 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$_3$) δ = 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 C$_{21}$H$_{17}$BrO$_2$: C, 66.16; H, 4.49. Found: C, 66.22; H, 4.55.

2,5-Bis(2-(9-(methoxymethoxy)-9*H*-fluoren-9-yl)phenyl)thiophene (6). A flame-dried Schlenk flask was charged with **5** (723 mg, 1.90 mmol), 2,5-bis(trimethylstannyl)thiophene[19] (369 mg, 0.901 mmol), Pd(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 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 SiO$_2$ (EtOAc−hexane, 1:12) 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}; ^{1}H NMR (300 MHz, CDCl$_3$) 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); ^{13}C NMR (75.5 MHz, CDCl$_3$) 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 C$_{46}$H$_{36}$O$_4$S: 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 the 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 NaHCO$_3$ (20 mL) and extracted with EtOAc (3 × 5 mL). The organic layers were combined, washed with saturated aqueous solution of NaHCO$_3$ (3 × 10 mL), and dried over MgSO$_4$. The solvents were removed under reduced pressure to give a yellow solid. The crude product was recrystallized from toluene−hexane (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}; ^{1}H NMR (300 MHz, CDCl$_3$) 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); ^{13}C NMR (75.5 MHz, CDCl$_3$) 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 C$_{42}$H$_{25}$S (M + H$^+$) 561.1677, found 561.1673.

9-(Methoxymethoxy)-9-(2-((trimethylsilyl)ethynyl)phenyl)-9*H*-fluorene (8). 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 °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 × 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 partially purified with column chromatography on SiO$_2$ (EtOAc−hexane, 1:10) 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), Pd(PPh$_3$)$_4$ (7.9 mg, 6.8 × 10^{-3} mmol), *i*-PrNH$_2$ (1.5 mL), dry THF (6 mL), and trimethyl-silylacetylene (0.115 mL, 0.81 mmol) under nitrogen atmosphere. The solution was stirred at room temperature for 16 h. The reaction mixture was cooled to room temperature and filtered through a short Celite pad. After an addition of water (10 mL), the filtrate was 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$_2$ (EtOAc−hexane, 1:40) to give **8** (188 mg, 71% yield based on **5**) as a pale yellow solid.

9-(2-Iodophenyl)-9-(methoxymethoxy)-9*H*-fluorene (7): mp 73.6−74.6 °C; IR (KBr) 732, 752, 762, 915, 1029, 1086, 1149, 1447, 2927 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$) δ = 3.14 (s, 3H), 4.29 (s, 2H), 6.93 (dd, J = 7.7, 7.7 Hz, 1H), 7.10 (d, J = 7.3 Hz, 2H), 7.23 (dd, J = 7.3, 7.7 Hz, 2H), 7.40 (dd, J = 7.7, 7.7 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 C$_{21}$H$_{17}$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}; ^{1}H 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 C$_{26}$H$_{26}$O$_2$Si: C, 78.35; H, 6.58. Found: C, 78.09; H, 6.50.

9-(2-Ethynylphenyl)-9-(methoxymethoxy)-9*H*-fluorene (9). To a solution of **8** (854 mg, 2.14 mmol) in MeOH (20 mL) and THF (5 mL) was added K$_2$CO$_3$ (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$_2$ (EtOAc−hexane, 1:25) 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}; ^{1}H 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 C$_{23}$H$_{18}$O$_2$: C, 84.64; H, 5.56. Found: C, 84.66; H, 5.57.

1,4-Bis(2-(9-(methoxymethoxy)-9*H*-fluoren-9-yl)phenyl)buta-1,3-diyne (10). To a solution of **9** (1.04 g, 3.20 mmol) and Et$_3$N (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 MgSO$_4$. The solvents were removed under reduced pressure, and the residue was purified with column chromatography on SiO$_2$ (EtOAc−hexane, 1:8) 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}; ^{1}H NMR (300 MHz, CDCl$_3$) 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); ^{13}C NMR (75.5 MHz, CDCl$_3$) 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 C$_{46}$H$_{34}$O$_4$: C, 84.90; H, 5.27. Found: C, 84.81; H, 5.15.

11-Phenyldispiro[9*H*-fluorene-9,5′(6′*H*)-diindeno[1,2-*b*:2′,1′-*d*]pyrrole-6′,9″-[9*H*]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 PhNH$_2$ (1.2 mL) under nitrogen atmosphere. The solution was stirred at 150 °C for 44 h. The reaction mixture was cooled 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 NaHCO$_3$ (3 × 10 mL), and brine (10 mL) and dried over MgSO$_4$. The solvents were removed under reduced pressure, and the residue was partially purified with column chromatography on SiO$_2$ (EtOAc−hexane, 1:15) 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 NaHCO$_3$ (15 mL) and extracted with EtOAc (3 × 5 mL). The organic layers were combined, washed with saturated aqueous solution of NaHCO$_3$ (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$_2$ (EtOAc−hexane, 1:20) 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}; ^{1}H NMR (300 MHz, CDCl$_3$) 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); ^{13}C NMR (75.5 MHz, CDCl$_3$) 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 C$_{48}$H$_{30}$N (M + H$^+$) 620.2378, found 620.2362.

Synthesis of 6 from Diyne 10. A flame-dried Schlenk flask was charged with **10** (195 mg, 0.299 mmol), Na$_2$S·9H$_2$O (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 MgSO$_4$. The solvents were removed under reduced pressure, and the residue was purified with column chromatography on SiO$_2$ (EtOAc−hexane, 1:10) to give **6** (142 mg, 69%) as a yellow solid.

Supporting Information Available: Copies of ^{1}H and ^{13}C NMR spectra for all new compounds, X-ray data of **dsp-DIF**, **dsp-DIT**, and **dsp-DIP-Ph**, and DFT calculation data of **dsp-DIT**. This material is available free of charge via the Internet at http://pubs.acs.org.