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# Synthesis and Properties of 2,2′-Di(heteroaryl)-9,9′-spirobifluorenes

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A series of 2,2′-di(heteroaryl)-9,9′-spirobifluorenes were prepared by employing Friedländer reaction of 2,2′-diacetyl-9,9′-spirodifluorene with a series of *ortho*-aminoarenecarbaldehydes. The compound 2,2′-di(benzo[*b*]-1,10-phenanthrolin-2-yl)-9,9′-spirofluorene (**4e**) showed a green light emission at 500 nm upon the excitation of the absorption at 374 nm while 2,2′-di(benzo[*h*]quinolin-2-yl)-9,9′-spirofluorene (**4c**), 2,2′-di(1,10-phenanthrolin-2-yl)-9,9′-spirofluorene (**4d**), 2-(benzo[*h*]quinolin-2-yl)-2′-(benzo[*b*]-1,10-phenanthrolin-2-yl)-9,9′-spirofluorene (**4g**), and 2-(1,10-phenanthrolin-2-yl)-2′-(benzo[*b*]-1,10-phenanthrolin-2-yl)-9,9′-spirofluorene (**4h**) showed emissions at 413, 465, 442, and 442 nm upon excitation of the absorption at 370, 362, 370, and 363 nm, respectively, thus having potential for OLED applications.

The 9,9′-spirobifluorene (9,9′-spirobi[9*H*-fluorene] ([5,5]-spirobifluorylidene, **1**), as well as its derivatives have been attractive due to the characteristic structure since its first preparation in 1930.[1] Early studies on this molecule were focused on the molecular recognition of various $\alpha$-amino-alcohols by 9,9′-spirobifluorene-based crown ethers,[2–10] and monosaccharides by dendritic cleft receptors,[11–20] as well as by inclusion compounds with hydrocarbons,[4,21,22] carbohydrate,[23,24] and $\alpha$-hydroxycarboxylates.[25] However, focus of studies on compounds with 9,9′-spirobifluorene especially 9,9′-spirobifluorene-based oligomers as well as polymers has been switched to applications in molecular electronic devices for light-emitting devices.[26–33]

Although a few pyridine-derived monomeric 2,2′-di(heteroaryl)-9,9′-spirobifluorenes such as 2,2′-di(benzo[*h*]quinolin-2-yl)-9,9′-spirobifluorene (**4c**),[34] 2,2′-di(1,10-phenanthrolin-2-yl)-9,9′-spirobifluorene (**4d**),[35–37] and 2,2′,7,7′-tetra(benzo[*h*]-quinolin-2-yl)-9,9′-spirobifluorene[38] have been reported to show promising photophysical properties for OLED applications, systematic approaches either for the preparation or for the examination of their properties of systems with heteroaromatics have not yet been pursued.[39,40] Additionally, benzo[*b*]-1,10-phenanthroline (bphen) and related compounds show promising light emission with improved stability.[41]

Our interest in the preparation and properties of bphen[42,43] and related polydentates[44] spurred us to study a series of 9,9′-spirobifluorene-derived *N*-heterocycles.

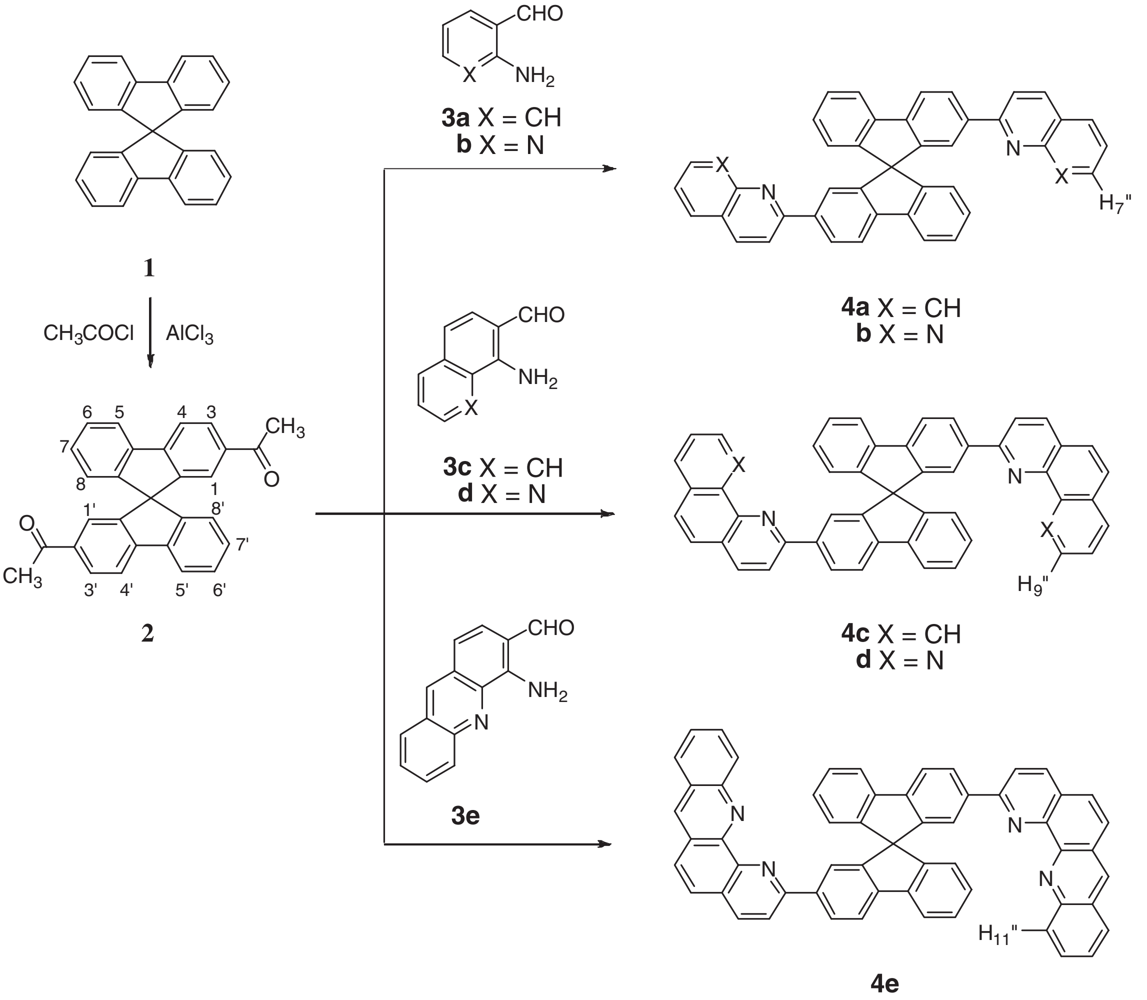
## Results and Discussion

Synthesis of the pyridine-derived 2,2′-di(heteroaryl)-9,9′-spirobifluorenes was straightforward as shown in Scheme 1. The Friedländer condensation of 2,2′-diacetyl-9,9′-spirobifluorene (**2**)[2] with a series of *o*-aminoarenecarbaldehydes (**3**)[45–49] afforded a series of heteroaromatics with 9,9′-spirobifluorene skeleton in 82–99% yields. The starting 2,2′-diacetyl-9,9′-spirobifluorene was prepared in 51% yield by Friedel–Craft acylation of 9,9′-spirobifluorene. Prerequisite 9,9′-spirobifluorene was readily prepared in 3 steps from commercially available 2-bromobiphenyl and fluorenone in 35% overall yield.[1,4,50,51]

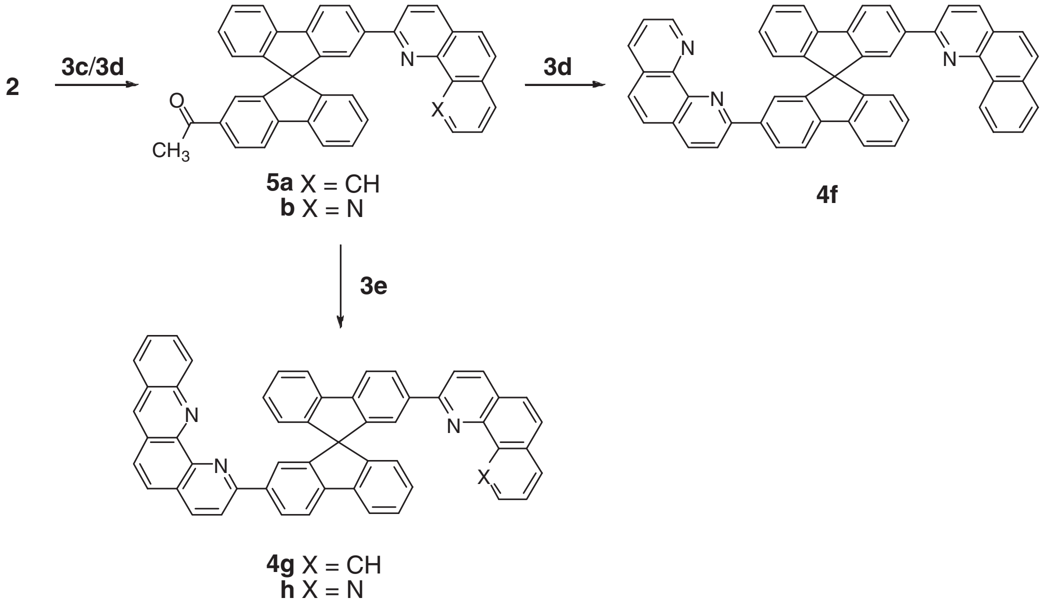
Some proton resonances of the products were characteristic enough to afford probes for the structure suggested. The protons adjacent to nitrogen such as H7″ of **4b** and H9″ of **4d** are the those of characteristic chemical shifts ($\delta$ 8.99 and 9.14, respectively) with relatively small $^3J$ coupling constant (4.3 Hz).[52] In addition, the resonances of H1 of 9,9′-spirobifluorene moiety generally appeared in the region of $\delta$ 7.48–7.80 with a characteristic *meta*-coupling constant ($^4J = 1.4$–$1.8$ Hz). The protons H8, H1′, and H8′ of the 9,9′-spirobifluorene moiety are the most upfield-shifted due to the anisotropic effect of the neighboring two phenyl groups, thus were resonated in the range of $\delta$ 6.80–6.71. Additionally, the protons at the *peri*-position of **4a** and **4e** (H8″ of **4a**, H11″ of **4e**) were resonated at $\delta$ 8.30 and 8.70, respectively, and H10″ of the benzo[*h*]-quinoline moiety of **4c** was resonated at $\delta$ 9.36 as a doublet of doublet ($^3J = 9.0$ Hz and $^4J = 1.2$ Hz), which experienced the anisotropic effect of neighboring pyridine as well as the electronic effects of lone pair electrons on N1″ most seriously.

The same Friedländer reaction of **2** with one equivalent of **3c** afforded mono-condensed products **5a** in 89% yield along with a trace of doubly condensed **4c**, which were readily separable (Scheme 2). Consecutive condensation of **5a** with second *o*-aminoaldehydes **3d** and **3e** afforded **4f** and **4g** in 92% and 95% yield, respectively. However, a reaction of **2** with **3d** afforded an inseparable mixture of **2**, **5b**, and **4d**. The three component mixture thus was subjected to second condensation reaction with **3e** to lead to three expected compounds **4e**, **4h**, and **4d** in a ratio of 1:5:2 which were separated by column chromatography on silica gel eluting with $CH_2Cl_2$:$CH_3OH$ (97:3).

Since 2,2′-disubstituted 9,9′-spirobifluorenes are chiral, the compounds prepared can be considered to have an additional chiral axis through the aryl–aryl bond. When free rotation of the two aryl–aryl bonds of **4** is restricted, such conformational rigidity may lead to two rotameric diastereomers. However, the energy barrier between the two rotamers is not expected to be high enough leading to a separation of the two rotamers at room temperature. $^1$H NMR spectra of all the mixed heterocycles (**4f**, **4g**, and **4h**) showed only one set of each proton resonance implying that the aryl–aryl bond is free to rotate in each case.



**Scheme 1.** Synthesis of symmetric 2,2′-di(heteroaryl)-9,9′-spirobifluorenes.



**Scheme 2.** Synthesis of unsymmetric 2,2′-di(heteroaryl)-9,9′-spirobifluorenes.

**Table 1.** UV Absorption and Emission Spectral Data of **1** and 2,2′-Heteroaryl-9,9′-spirobifluorenes

| Compd | $\lambda_{abs}$/nm (log $\varepsilon$) | $\lambda_{excit}$/nm | $\lambda_{em}$/nm |
|---|---|---|---|
| **1** | 223 (4.65), 239 (4.40), 272 (4.29), 296 (3.92), 308 (4.11) | 308 | 388 |
| **4a** | 222 (4.55), 253 (4.30), 281 (4.37), 341 (4.39), 351 (4.34) | 351 | 391 |
| **4b** | 223 (4.50), 256 (4.24), 275 (4.20), 298 (4.15), 348 (4.42) | 350 | 382, 398 |
| **4c** | 230 (4.58), 302 (4.38), 331 (4.35), 351 (4.18), 370 (4.17) | 370 | 397, 413 |
| **4d** | 232 (4.61), 267 (4.28), 299 (4.33), 331 (4.36), 344 (4.27), 362 (4.17) | 362 | 442, 465, 498 |
| **4e** | 227 (4.72), 255 (4.83), 285 (4.02), 336 (4.67), 357 (4.52), 373 (4.39) | 373 | 500 |
| **4f** | 233 (4.62), 333 (4.40), 350 (4.27), 365 (4.23) | 365 | 378, 396 |
| **4g** | 235 (4.71), 252 (4.67), 335 (4.59), 353 (4.23), 370 (4.39) | 370 | 442 |
| **4h** | 234 (4.72), 255 (4.65), 334 (4.63), 363 (4.44) | 363 | 442 |

To our surprise, an additional compound ($R_f = 0.25$, $CH_2Cl_2$) was isolated from the reaction mixture along with the compound **4f** ($R_f = 0.28$, $CH_2Cl_2$), by preparative TLC. Although the $^1$H NMR spectrum of this species was very similar to that of **4f**, the region $\delta$ 7.88–7.58 is significantly different (see Supporting Information). The major difference lay in the resonances of H1 and H1′. H1 and H1′ of the less polar compound resonate at $\delta$ 7.56 and $\delta$ 7.53 (could be reversed) while these protons of the more polar compound resonate at $\delta$ 7.71. Although $^{13}$C NMR spectrum of the less polar compound showed 50 carbon resonances corresponding to the structure, we failed to get good $^{13}$C NMR spectrum due to instability of the corresponding rotamer. Although attempts to measure the energy barrier by $^1$H NMR temperature variation were not successful due to rapid conversion of one to another at the temperature of 35–50 °C, the energy barrier range between the two rotamers was calculated by using a previously reported equation[53] to give 16.5–17.6 kcal mol$^{-1}$. Even though the restricted rotation of aryl–aryl bonds in **4f** may result in rotational isomerism, we cannot explain why only **4f** has such a high energy barrier compared to the other congeners. Such an immature premise may not rule out the possible presence of as yet unidentified intermediates based on the broadening of the peaks at $\delta$ 9.19, 8.65, and 8.23 in the $^1$H NMR spectrum. It should be noted that attempts to resolve the enantiomers of **4** by conventional methods have not been successful as of yet.

UV absorption spectra of **4**, bphen, and the parent 9,9′-spirobifluorene (**1**) were taken in EtOH ($1.21 \times 10^{-5}$ M) and are summarized in Table 1. Three major absorption maxima originating from the $\pi$–$\pi^*$ transition were observed in the regions of 224–233, 255–267, 276–293, 330–339, and 350–374 nm. The absorptions in the range of 330–370 nm were not observed in the parent compound 9,9′-spirobifluorene, thus such absorptions were from $\pi$–$\pi^*$ transition of the heterocyclic rings of the system. Two rotamers of **4f** showed the same absorption as expected. The absorption maximum is highly dependent on the nature of the heterocycles attached to 9,9′-spirobifluorene. Annulation of an additional benzene ring (**4d** vs. **4e**) not only led to bathochromic shift of the absorptions at 331, 344, and 362 nm to 336, 357, and 373 nm, respectively, but also increased corresponding intensity due to the expansion of conjugated $\pi$-bonds.

The photoluminescence (PL) of **1**, **4**, and bphen was studied in EtOH ($1.21 \times 10^{-5}$ M) to evaluate their potentials as a key structure for further OLED applications and are presented in Figure 1. All the ligands could be well excited by 365–405 nm light to show emissions in the range of 398–500 nm. The observed emission wavelength (Table 1) is highly dependent on the heterocycles on 9,9′-spirobifluorene and is bathochromatically shifted from 388 nm for 9,9′-spirobifluorene to 400–500 nm. The compound **4e** showed a green light emission at 500 nm upon the excitation of the absorption at 374 nm while **4c**, **4d**, **4g**, and **4h** showed emissions at 413, 465, 442, and 442 nm upon excitation of the absorption at 370, 362, 370, and 363 nm, respectively, thus to have a potential for OLED applications. The emission wavelength ($\lambda_{em} = 388$ nm) of bphen is coincidently matched to that of 9,9′-spirobifluorene.

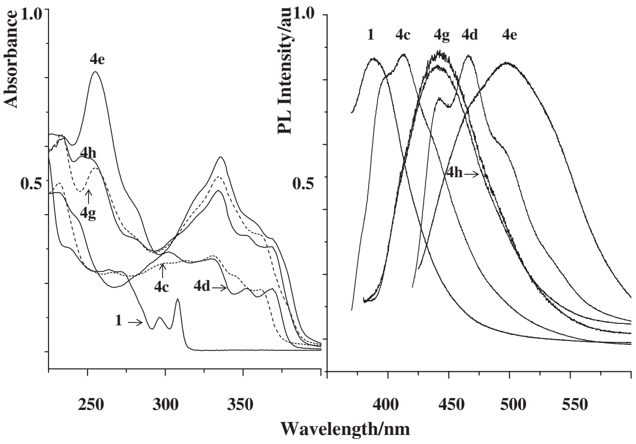


**Figure 1.** Absorption and photoluminescence (PL) spectra of 9,9′-spirobifluorene (**1**) and selected 2,2′-di(heteroaryl)-9,9′-spirobifluorenes **4** in EtOH ($1.21 \times 10^{-5}$ M) at 298 K.

In conclusion, a series of 9,9′-spirobifluorene-derived heterocycles were prepared by employing Friedländer reaction of 2,2′-diacetyl-9,9′-spirobifluorene with a series of *ortho*-aminoaldehydes. The compound, 2,2′-di(benzo[*b*]-1,10-phenanthrolin-2-yl)-9,9′-spirofluorene (**4e**) showed a green light emission at 500 nm upon the excitation of the absorption at 374 nm while **4c**, **4d**, **4g**, and **4h** showed emissions at 413, 465, 442, and 442 nm upon excitation of the absorption at 370, 362, 370, and 363 nm, respectively, thus to have potential for OLED applications. Studies on asymmetric synthesis of the ligands employing optically active 2,2-diacetyl-9,9′-spirobifluorene as well as metal complex chemistry of the ligands are in progress, which will be due in the future.

## Experimental

Melting points were determined using a Fischer–Jones melting point apparatus and are not corrected. UV spectra were recorded on a JASCO-V550 spectrophotometer and emission spectra on a F-4500 Fluorescence Spectrophotometer, Rigong International, Japan. FT-IR spectra were recorded on a JASCO FT-IR 300E spectrophotometer. The NMR spectra were recorded on a Bruker-250 spectrometer 250, 300, or 600 MHz for $^{1}$H NMR and 62.5 MHz for $^{13}$C NMR and are reported as parts per million (ppm) from the internal standard tetramethylsilane (TMS). The starting 9,9′-spirobifluorene,[1,50–51] 2,2′-diacetyl-9,9′-spirobifluorene,[2] *o*-aminobenzaldehyde,[45] 2-aminonicotinaldehyde,[46] 1-aminonaphthalene-2-carbaldehyde,[48] 8-aminoquinoline-7-carbaldehyde,[47,48] and 4-aminoacridine-3-carbaldehyde[49] were prepared by employing previously reported methods. Chemicals and solvents were commercial reagent grade and used without further purification. Electrospray ionization mass spectrometry (MS/ESI) experiments were performed on a LCQ advantage-trap mass spectrometer (Thermo Finnigan, San Jose, CA, USA). Elemental analyses were taken on a Hewlett-Packard Model 185B elemental analyzer. Abbreviations q, naph, bq, and phen were introduced for quinoline, 1,8-naphthyridine, benzo[*h*]quinoline, and 1,10-phenanthroline, respectively.

**2,2′-Di(quinolin-2-yl)-9,9′-spirobifluorene (4a) (General Procedure).** A mixture of 2-aminobenzaldehyde (190 mg, 1.57 mmol) and 2,2′-diacetyl-9,9′-spirobifluorene (400 mg, 0.63 mmol) in absolute EtOH (20 mL) with saturated alcoholic KOH (1 mL) was refluxed for 5 h. Upon cooling the reaction mixture solid was formed, which was collected as a pure product (300 mg, 83%) as yellow solid, mp 302 °C. $^{1}$H NMR (250 MHz, CDCl$_3$): $\delta$ 8.30 (2H, dd, $J = 8.6$, 1.6 Hz, H8 of q), 8.05–8.00 (6H, m, H4, H5 of q, H3 and H3′), 7.93 (2H, d, $J = 7.7$ Hz, H3 of q), 7.70 (2H, dd, $J = 7.5$, 1.2 Hz, H4 and H4′), 7.65 (2H, d, $J = 8.6$ Hz, H5 and H5′), 7.64 (2H, td, $J = 8.6$, 1.5 Hz, H7 of q), 7.51 (2H, d, $J = 1.5$ Hz, H1 and H1′), 7.42 (2H, td, $J = 7.5$, 1.5 Hz, H6 of q), 7.37 (2H, t, $J = 7.5$ Hz, H6 and H6′), 7.13 (2H, td, $J = 8.6$, 1.5 Hz, H7 and H7′), 6.78 (2H, d, $J = 7.5$ Hz, H8 and H8′). $^{13}$C NMR (62.5 MHz, CDCl$_3$): $\delta$ 157.03, 149.35, 148.97, 148.10, 143.20, 141.20, 139.48, 136.49, 129.56, 129.51, 128.29, 127.87, 127.81, 127.32, 127.01, 126.11, 124.21, 123.32, 120.53, 120.45, 119.15, 66.18. MS (ESI): $m/z = 571$ [M + H]$^+$. Anal. Calcd for C$_{43}$H$_{26}$N$_2$ (570.7): C, 90.50; H, 4.59; N, 4.91%. Found: C, 90.50; H, 4.62; N, 4.88%.

**2,2′-Di(1,8-naphthyridin-2-yl)-9,9′-spirobifluorene (4b).** Yellow crystalline solid (82%), mp > 315 °C. $^{1}$H NMR (250 MHz, CDCl$_3$): $\delta$ 8.99 (2H, dd, $J = 4.3$, 1.8 Hz, H7 of naph), 8.36 (2H, dd, $J = 8.1$, 1.5 Hz, H5 and H5′), 8.06 (2H, d, $J = 8.6$ Hz, H4 of naph), 8.04 (2H, dd, $J = 8.6$, 1.8 Hz, H5 of naph), 8.02 (2H, d, $J = 8.4$ Hz, H3 of naph), 7.92 (2H, d, $J = 7.8$ Hz, H4 and H4′), 7.84 (2H, d, $J = 8.6$ Hz, H5 and H5′), 7.80 (2H, d, $J = 1.2$ Hz, H1 and H1′), 7.38 (2H, td, $J = 7.5$, 1.2 Hz, H6 and H6′), 7.33 (2H, dd, $J = 8.1$, 4.3 Hz, H6 of naph), 7.11 (2H, td, $J = 7.5$, 1.2 Hz, H7 and H7′), 6.76 (2H, d, $J = 7.6$ Hz, H8 and H8′). $^{13}$C NMR (62.5 MHz, CDCl$_3$): $\delta$ 160.01, 155.88, 153.56, 149.42, 149.02, 144.24, 141.03, 138.04, 137.37, 136.64, 128.47, 128.03, 120.45, 119.88, 66.16. MS (ESI): $m/z = 573$ [M + H]$^+$. Anal. Calcd for C$_{41}$H$_{24}$N$_4$ (572.7): C, 85.99; H, 4.23; N, 9.78%. Found: C, 86.00; H, 4.20; N, 9.80%.

**2,2′-Di(benzo[*h*]quinolin-2-yl)-9,9′-spirobifluorene (4c).** Yellow crystalline solid (86%): Unreported physical and spectral data are as follows, mp > 300 °C. $^{1}$H NMR (250 MHz, CDCl$_3$): $\delta$ 9.36 (2H, dd, $J = 9.0$, 1.2 Hz, H10 of bq), 8.62 (2H, dd, $J = 8.0$, 1.2 Hz, H4 of bq), 8.10 (2H, d, $J = 8.0$ Hz, H3 of bq), 8.04 (2H, d, $J = 8.5$ Hz, H5/H6), 7.98 (2H, d, $J = 7.5$ Hz, H5 and H5′), 7.83 (2H, dd, $J = 8.2$, 1.5 Hz, H4 and H4′), 7.76 (2H, d, $J = 8.5$ Hz, H6/H5), 7.70 (2H, d, $J = 8.5$ Hz, H8 of bq), 7.66 (2H, ddd, $J = 8.5$, 7.5, 1.2 Hz, H6 and H6′), 7.59 (2H, d, $J = 9.0$ Hz, H7 of bq), 7.56 (2H, d, $J = 1.7$ Hz, H1 and H1′), 7.22 (2H, td, $J = 7.5$, 1.0 Hz, H7 and H7′), 6.82 (2H, d, $J = 7.5$ Hz, H8 and H8′). $^{13}$C NMR (62.5 MHz, CDCl$_3$): $\delta_{\mathrm{C}}$ 155.29, 149.40, 146.08, 143.10, 141.29, 139.63, 136.27, 133.78, 131.63, 128.25, 128.05, 127.96, 127.90, 127.70, 127.30, 126.81, 125.01, 124.63, 124.21, 122.91, 120.64, 120.44, 119.16, 66.23. MS (ESI): $m/z = 671$ [M + H]$^+$.

**2,2′-Di(1,10-phenanthrolin-2-yl)-9,9′-spirobifluorene (4d).** Yellow crystalline solid (82%), mp > 300 °C. (lit.[35] mp > 300 °C). $^{1}$H NMR (250 MHz, CDCl$_3$): $\delta$ 9.14 (2H, dd, $J = 4.3$, 1.5 Hz, H9 of phen), 8.60 (2H, dd, $J = 8.0$, 1.2 Hz, H4 of phen), 8.17 (2H, dd, $J = 7.9$, 1.7 Hz, H7 of phen), 8.12 (2H, d, $J = 8.4$ Hz, H8 and H8′ of phen), 8.06 (2H, d, $J = 8.1$ Hz, H4 and H4′), 7.93 (2H, d, $J = 7.8$ Hz, H5 and H5′), 7.83 (2H, d, $J = 8.3$ Hz, H3 and H3′), 7.68 (4H, AB quartet, H5 and H6 of phen), 7.57 (2H, dd, $J = 8.0$, 4.3 Hz, H8 of phen), 7.48 (2H, d, $J = 1.3$ Hz, H1 and H1′), 7.38 (2H, td, $J = 6.8$, 1.0 Hz, H6 and H6′), 7.11 (2H, td, $J = 7.5$, 1.8 Hz, H7 and H7′), 6.77 (2H, d, $J = 7.5$ Hz, H8 and H8′). MS (ESI): $m/z = 673$ [M + H]$^+$.

**2,2′-Di(benzo[*b*]-1,10-phenanthrolin-2-yl)-9,9′-spirofluorene (4e).** Yellow crystalline solid (99%), mp 280–282 °C. $^{1}$H NMR (250 MHz, CDCl$_3$): $\delta$ 8.70 (2H, dd, $J = 8.0$, 1.5 Hz, H11 of bphen), 8.66 (2H, s, H7 of bphen), 8.56 (2H, d, $J = 8.7$ Hz, H4 of bphen), 8.14 (2H, d, $J = 8.1$ Hz, H8 of bphen), 8.07 (2H, d, $J = 8.4$ Hz, H5/H6 of bphen), 7.99 (2H, d, $J = 7.5$ Hz, H3 of bphen), 7.97 (2H, d, $J = 7.2$ Hz, H3 and H3′), 7.87 (2H, d, $J = 8.4$ Hz, H6/H5 of bphen), 7.83 (2H, ddd, $J = 8.4$, 7.8, 1.2 Hz, H10 of bphen), 7.73 (2H, d, $J = 9.0$ Hz, H5 and H5′), 7.60 (2H, td, $J = 7.2$, 1.2 Hz, H9 of bphen), 7.57 (2H, d, $J = 9.0$ Hz, H4 and H4′), 7.55 (2H, d, $J = 1.2$ Hz, H1 and H1′), 7.41 (2H, td, $J = 7.2$, 1.2 Hz, H6 and H6′), 7.14 (2H, td, $J = 7.2$, 0.6 Hz, H7 and H7′), 6.80 (2H, td, $J = 7.5$ Hz, H8 and H8′). $^{13}$C NMR (62.5 MHz, CDCl$_3$): $\delta$ 157.11, 149.47, 148.87, 148.11, 146.82, 146.20, 143.22, 141.32, 139.67, 136.50, 135.81, 130.85, 130.00, 128.85, 128.23, 127.97, 127.85, 127.52, 127.23, 126.94, 126.69, 126.48, 125.71, 124.15, 123.30, 121.39, 120.70, 120.49, 66.21. MS (ESI): $m/z = 773$ [M + H]$^+$. Anal. Calcd for C$_{57}$H$_{32}$N$_4$ (772.9): C, 88.58; H, 4.17; N, 7.25%. Found: C, 88.62; H, 4.14; N, 7.24%.

**2-Acetyl-2′-(benzo[*h*]quinolin-2-yl)-9,9′-spirobifluorene (5a).** Yellow crystalline solid (92%), mp > 300 °C. IR (KBr) $\nu$ 1710 cm$^{-1}$. $^{1}$H NMR (600 MHz, CDCl$_3$): $\delta$ 9.33 (1H, d, $J = 7.2$ Hz, H10 of bq), 8.55 (1H, d, $J = 7.8$ Hz, H4 of bq), 8.08–8.02 (3H, m, H3, H5/H6, H7 of bq), 7.98–7.93 (3H, m, H3 of bq, H5 and H5′), 7.86 (1H, dd, $J = 7.2$, 2.0 Hz, H4), 7.74 (1H, d, $J = 8.5$ Hz, H4′), 7.73 (1H, d, $J = 9.6$ Hz, H6/H5 of bq), 7.70 (1H, t, $J = 7.2$ Hz, H9 of bq), 7.67 (1H, t, $J = 7.2$ Hz, H8 of bq), 7.62 (1H, d, $J = 8.4$ Hz, H3′), 7.49 (1H, d, $J = 0.8$ Hz, H1′), 7.43 (2H, overlapped t, $J = 7.6$ Hz, H6 and H6′), 7.39

(1H, d, $J = 0.8$ Hz, H1), 7.20 (1H, td, $J = 7.6$, 1.0 Hz, H7), 7.15 (1H, td, $J = 7.6$, 1.0 Hz, H7′), 6.83 (1H, d, $J = 7.6$ Hz, H8), 6.72 (1H, d, $J = 7.6$ Hz, H8′), 2.44 (3H, s). $^{13}$C NMR (62.5 MHz, $\mathrm{CDCl_3}$): $\delta$ 197.62, 155.23, 149.94, 148.97, 148.55, 148.26, 146.66, 146.08, 143.05, 141.32, 140.38, 139.68, 136.71, 136.31, 133.78, 131.57, 129.26, 128.82, 128.25, 128.09 (two carbons), 128.07 (two carbons), 127.73, 127.38, 126.82, 125.01, 124.97, 124.55, 124.40, 124.20, 123.93, 122.71, 121.02, 120.71, 120.58, 120.01, 119.06, 66.24, 29.69. MS (ESI): $m/z = 536$ $[\mathrm{M + H}]^+$. Anal. Calcd for $\mathrm{C_{40}H_{25}NO}$ (535.6): C, 89.69; H, 4.70; N, 2.61%. Found: C, 89.71; H, 4.69; N, 2.60%.

**2-(Benzo[*h*]quinolin-2-yl)-2′-(1,10-phenanthrolin-2-yl)-9,9′-spirobifluorene (4f).** The more polar compound (19%) ($R_f = 0.25$, $\mathrm{CH_2Cl_2}$): Yellow crystalline solid, mp > 300 °C. $^1$H NMR (600 MHz, $\mathrm{CDCl_3}$): $\delta$ 9.38 (1H, d, $J = 8.1$ Hz), 9.19 (1H, br s), 8.70–8.65 (1H, m), 8.62 (1H, dd, $J = 8.4$, 1.8 Hz), 8.23 (1H, d, $J = 7.8$ Hz), 8.14 (1H, d, $J = 8.4$ Hz), 8.12 (1H, d, $J = 8.4$ Hz), 8.10 (1H, d, $J = 8.4$ Hz), 8.07 (1H, d, $J = 8.4$ Hz), 7.98 (1H, dd, $J = 7.2$, 1.2 Hz), 7.97 (1H, d, $J = 7.2$ Hz), 7.88 (1H, d, $J = 8.4$ Hz), 7.86 (1H, dd, $J = 7.8$, 1.3 Hz), 7.78 (1H, d, $J = 9.0$ Hz), 7.74–7.70 (4H, m), 7.66 (1H, td, $J = 7.8$, 1.8 Hz), 7.62 (2H, d, $J = 9.0$ Hz), 7.56 (1H, d, $J = 1.2$ Hz, H1/H1′), 7.53 (1H, d, $J = 1.2$ Hz, H1′/H1), 7.42 (2H, td, $J = 7.2$, 1.0 Hz), 7.16 (1H, td, $J = 7.2$, 1.0 Hz), 7.15 (1H, d, $J = 7.2$ Hz), 6.81 (2H, td, $J = 7.2$, 1.0 Hz). MS (ESI): $m/z = 672$ $[\mathrm{M + H}]^+$. Anal. Calcd for $\mathrm{C_{50}H_{29}N_3}$ (671.8): C, 89.39; H, 4.35; N, 6.26%. Found: C, 89.42; H, 4.33; N, 6.25%. The less polar compound (76%) ($R_f = 0.28$, $\mathrm{CH_2Cl_2}$): Yellow crystalline solid, mp > 300 °C. $^1$H NMR (600 MHz, $\mathrm{CDCl_3}$): $\delta$ 9.35 (1H, d, $J = 7.8$ Hz, H10 of bq), 9.15 (1H, d, $J = 4.2$ Hz, H9 of phen), 8.64 (1H, dd, $J = 7.8$, 1.5 Hz, H4 of bq), 8.61 (1H, dd, $J = 7.2$, 1.5 Hz, H4 of phen), 8.21 (1H, dd, $J = 8.1$, 2.0 Hz, H7 of phen), 8.14 (1H, d, $J = 8.1$ Hz, H7 of bq), 8.12 (1H, d, $J = 8.1$ Hz, H3 of bq), 8.10 (1H, d, $J = 8.4$ Hz, H3 of phen), 8.07 (1H, d, $J = 8.4$ Hz, H5/H6 of bq), 7.98 (1H, d, $J = 7.5$ Hz, H5/H5′), 7.97 (1H, d, $J = 7.5$ Hz, H5′/H5), 7.88 (1H, d, $J = 9.0$ Hz, H5/H6 of bq), 7.87 (1H, t, $J = 8.4$ Hz, H8 of bq), 7.78 (1H, d, $J = 8.4$ Hz, H6/H5 of phen), 7.72–7.70 (4H, m, H9 of bq, H4, H3′, H4′), 7.66 (1H, td, $J = 8.1$, 0.6 Hz, H8 of bq), 7.61 (1H, d, $J = 9.0$ Hz, H6/H5 of phen), 7.60 (1H, dd, $J = 7.5$, 4.2 Hz, H3 of phen), 7.54 (1H, d, $J = 1.3$ Hz, H1/H1′), 7.51 (1H, d, $J = 1.3$ Hz, H1′/H1), 7.42 (2H, td, $J = 7.5$, 1.5 Hz, H6 and H6′), 7.16 (1H, td, $J = 7.2$, 1.2 Hz, H7/H7′), 7.15 (1H, td, $J = 7.2$, 1.2 Hz, H7′/H7), 6.81 (2H, dd, $J = 7.5$, 1.8 Hz, H8 and H8′). $^{13}$C NMR (62.5 MHz, $\mathrm{CDCl_3}$): $\delta$ 157.56, 155.30, 150.13, 149.45, 149.41, 149.01, 148.73, 146.04, 145.76, 143.23, 143.10, 141.29, 141.25, 139.71, 139.63, 136.55, 136.29, 136.19, 133.75, 131.63, 128.97, 128.95, 128.25, 128.20, 128.02, 127.93, 127.86 (three carbons), 127.67, 127.37, 127.24, 126.81, 126.35, 126.01, 125.02, 125.00, 124.62, 124.24, 124.11, 123.24, 122.96, 122.81, 121.11, 120.74, 120.59, 120.52, 120.40, 119.18, 66.21. MS (ESI): $m/z = 672$ $[\mathrm{M + H^+}]$. Anal. Calcd for $\mathrm{C_{50}H_{29}N_3}$ (671.8): C, 89.39; H, 4.35; N, 6.26%. Found: C, 89.40; H, 4.32; N, 6.28%.

**2-(Benzo[*h*]quinolin-2-yl)-2′-(benzo[*b*]-1,10-phenanthrolin-2-yl)-9,9′-spirobifluorene (4g).** Pale yellow crystalline solid, mp 244 °C. $^1$H NMR (600 MHz, $\mathrm{CDCl_3}$): $\delta$ 9.38 (1H, dd, $J = 8.0$, 1.8 Hz), 8.71 (1H, dd, $J = 8.0$, 1.8 Hz), 8.69 (1H, s), 8.63 (1H, dd, $J = 8.4$, 1.8 Hz), 8.57 (1H, d, $J = 8.6$ Hz), 8.16 (1H, d, $J = 8.4$ Hz), 8.11 (1H, d, $J = 8.4$ Hz), 8.09 (1H, d, $J = 8.4$ Hz), 8.05 (1H, d, $J = 8.0$ Hz), 8.02 (1H, d, $J = 8.0$ Hz), 8.00 (1H, d, $J = 8.4$ Hz), 7.98 (1H, d, $J = 8.4$ Hz), 7.89 (1H, d, $J = 8.4$ Hz), 7.85 (1H, td, $J = 8.4$, 1.2 Hz), 7.84 (1H, d, $J = 8.4$ Hz), 7.78 (1H, d, $J = 8.4$ Hz), 7.77 (1H, d, $J = 9.0$ Hz), 7.71 (1H, td, $J = 8.4$, 1.2 Hz), 7.70 (1H, d, $J = 8.4$ Hz), 7.65 (1H, td, $J = 8.4$, 1.2 Hz), 7.63 (1H, t, $J = 8.4$ Hz), 7.61–7.58 (4H, m), 7.43 (2H, overlapped td, $J = 8.4$, 1.2 Hz), 7.16 (1H, t, $J = 8.4$ Hz), 7.15 (1H, t, $J = 8.4$ Hz), 6.83 (1H, d, $J = 8.4$ Hz), 6.82 (1H, d, $J = 8.4$ Hz). $^{13}$C NMR (62.5 MHz, $\mathrm{CDCl_3}$): $\delta$ 157.21, 155.35, 149.50, 149.48, 149.06, 148.92, 148.36, 147.04, 146.56, 146.09, 143.23, 143.15, 141.35, 141.33, 139.79, 139.67, 136.53, 136.28, 135.70, 133.78, 131.68, 131.06, 129.94, 128.86, 128.26, 128.22, 128.02 (two carbons), 127.95, 127.88 (two carbons), 127.67, 127.54, 127.33, 127.24, 127.05, 126.81, 126.73, 126.63, 125.74, 125.02 (two carbons), 124.70, 124.25, 124.16, 123.32, 123.00, 121.41, 120.71, 120.59, 120.52, 120.41, 119.18, 66.28. MS (ESI): $m/z = 722$ $[\mathrm{M + H}]^+$. Anal. Calcd for $\mathrm{C_{54}H_{31}N_3}$ (721.8): C, 89.85; H, 4.33; N, 5.82%. Found: C, 89.78; H, 4.32; N, 5.84%.

**2-(Benzo[*b*]-1,10-phenanthrolin-2-yl)-2′-(1,10-phenanthrolin-2-yl)-9,9′-spirobifluorene (4h).** Pale yellow needles [$R_f = 0.4$ ($\mathrm{CH_2Cl_2{:}CH_3OH} = 97{:}3$), $R_f$ values of **4d** and **4e** are 0.1 and 0.7, respectively], mp 235 °C. $^1$H NMR (600 MHz, $\mathrm{CDCl_3}$): $\delta$ 9.17 (1H, dd, $J = 4.8$, 1.8 Hz, H9 of phen), 8.70 (1H, dd, $J = 8.4$, 1.8 Hz, H11 of bphen), 8.68 (1H, s, H7 of bphen), 8.66 (1H, dd, $J = 8.4$, 1.8 Hz, H4 of bphen), 8.57 (1H, d, $J = 8.5$ Hz, H4 of phen), 8.18 (1H, dd, $J = 8.0$, 1.8 Hz, H7 of phen), 8.14 (1H, d, $J = 8.4$ Hz, H3 of bphen), 8.115 (1H, d, $J = 8.4$ Hz), 8.110 (1H, d, $J = 8.4$ Hz), 8.087 (1H, d, $J = 8.4$ Hz), 8.02 (1H, dd, $J = 8.4$, 0.6 Hz), 7.98 (1H, d, $J = 8.4$ Hz), 7.97 (1H, d, $J = 8.4$ Hz), 7.88 (1H, d, $J = 8.4$ Hz), 7.852 (1H, td, $J = 8.4$, 1.8 Hz), 7.847 (1H, d, $J = 8.4$ Hz), 7.76 (1H, d, $J = 9.0$ Hz), 7.68 (2H, AB quartet), 7.62 (1H, td, $J = 8.4$, 1.2 Hz), 7.59 (1H, d, $J = 8.4$ Hz), 7.58 (1H, d, $J = 8.4$, 4.2 Hz), 7.56 (1H, d, $J = 1.8$ Hz), 7.52 (1H, d, $J = 1.8$ Hz), 7.42 (1H, td, $J = 8.4$, 0.6 Hz, H6/H6′), 7.41 (1H, td, $J = 8.4$, 0.6 Hz, H6′/H6), 7.16 (1H, td, $J = 8.4$, 1.2 Hz, H7/H7′), 7.15 (1H, td, $J = 8.4$, 1.2 Hz, H7′/H7), 6.81 (2H, d, $J = 8.3$ Hz, H8 and H8′). $^{13}$C NMR (62.5 MHz, $\mathrm{CDCl_3}$): $\delta$ 157.82, 157.48, 150.44 (two carbons), 149.75, 149.74, 149.17, 149.05, 148.59, 147.30, 146.77, 146.48, 146.13, 143.49, 143.46, 141.58, 141.57, 136.80 (two carbons), 136.28, 135.93, 131.28, 130.19, 129.20, 129.16, 126.09, 128.48 (two carbons), 128.26, 128.09 (two carbons), 127.78, 127.62, 127.56, 127.29, 126.96, 126.82, 126.57 (two carbons), 126.24, 126.01, 124.43, 124.41, 123.60, 123.56, 123.03, 121.70, 121.33, 120.95, 120.93, 120.73 (two carbons), 66.50. MS (ESI): $m/z = 723$ $[\mathrm{M + H}]^+$. Anal. Calcd for $\mathrm{C_{53}H_{30}N_4}$ (722.8): C, 88.07; H, 4.18; N, 7.75%. Found: C, 88.14; H, 4.16; N, 7.68%.

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## Supporting Information

$^1$H NMR spectra of the two diastereomers of **4f** are available. This material is available free of charge on the web at http://www.csj.jp/journals/bcsj/.

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