

Supporting Information

***Tert*-Butylated Spirofluorene Derivatives with Arylamine Groups for Highly Efficient Blue Organic Light Emitting Diodes**

Kum Hee Lee,^a Seul Ong Kim,^a Jae Nam You,^a Sunwoo Kang,^a Jin Yong Lee,^a Kyoung Soo Yook,^b Soon Ok Jeon,^b Jun Yeob Lee,^{*b} and Seung Soo Yoon^{*a}

^a Department of Chemistry, Sungkyunkwan University, Suwon, 440-746, Korea. Fax: 82 31 290 7075; Tel: 82 31 290 7071; E-mail: ssyoon@skku.edu

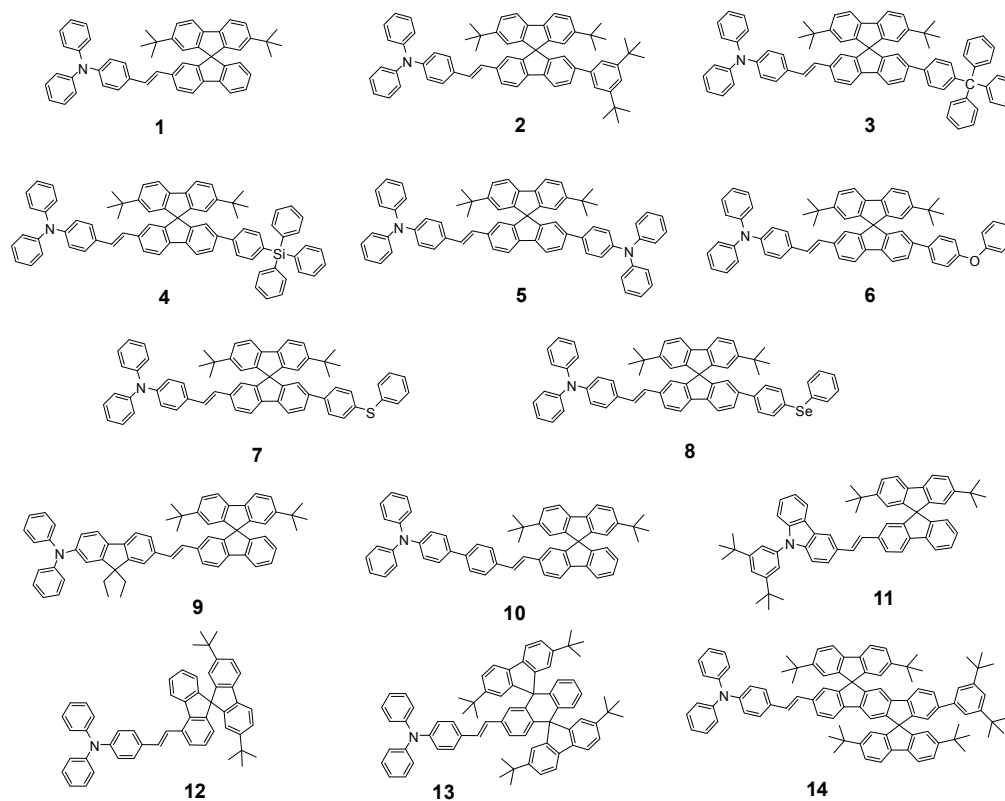
^b Department of Polymer Science and Engineering, Dankook University, Yongin, 448-701, Korea. Fax: 82 31 8021 7218; Tel: 82 31 8005 3585; E-mail: leej17@dankook.ac.kr

General information

The ¹H and ¹³C NMR spectra were recorded on a Varian (Unity Inova 300Nb) spectrometer using CDCl₃ as the solvent. The FT-IR spectra were recorded using a Bruker VERTEX70 FT-IR spectrometer. The low- and high-resolution mass spectra were measured using a Jeol JMS-AX505WA spectrometer in FAB mode or Jeol JMS-600 spectrometer in EI mode. The UV-vis absorption measurements of these blue emitting materials in dichloromethane (10⁻⁵ M) were acquired using a Sinco S-3100 in a quartz cuvette (1.0 cm path). The photoluminescence spectra were measured on an Amincobrowman series 2 luminescence spectrometer. The fluorescence quantum yield of the blue materials were determined in dichloromethane at 293 K using BDAVBi as a reference ($\Phi = 86\%$).¹⁰ The HOMO energy levels were determined with a low energy photoelectron spectrometer (Riken-Keiki, AC-2). The energy band gaps were determined from the intersection of the absorption and photoluminescence spectra. The LUMO energy levels were calculated by subtracting the corresponding optical band gap energies from the HOMO energy values.

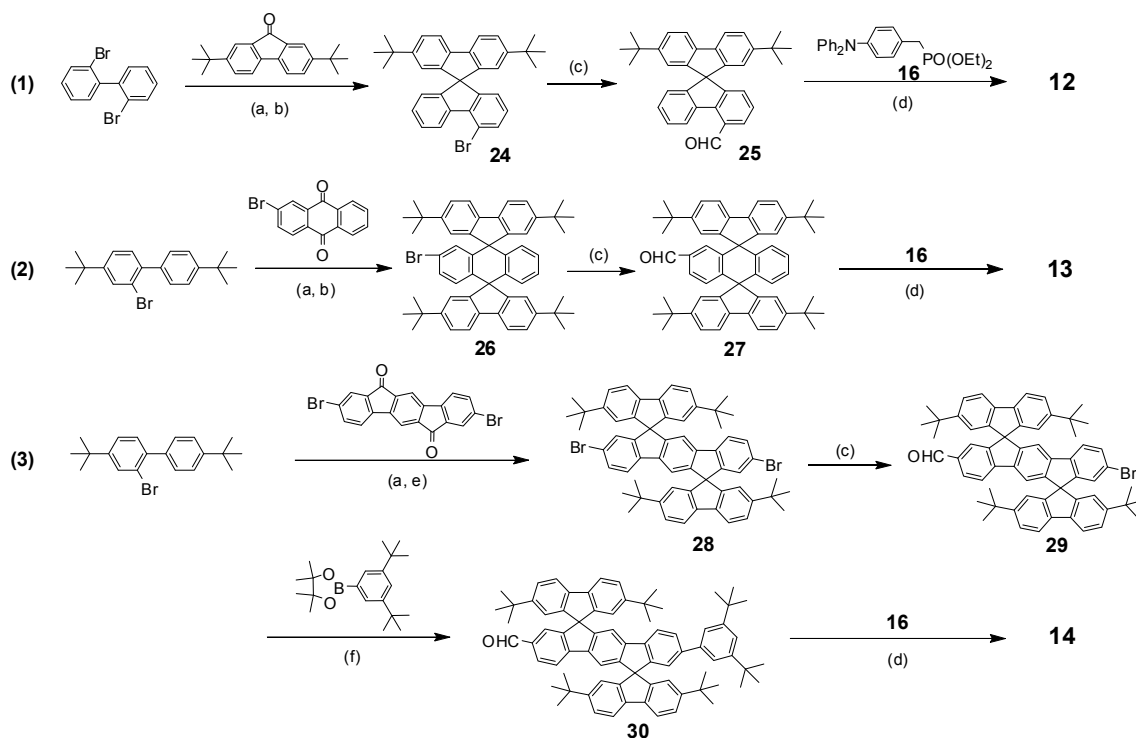
n-Butyllithium (1.6 M) in hexane, *N,N*-dimethylformamide, potassium *tert*-butoxide, 4-bromotriphenylamine, 4-bromodiphenyl ether, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, tetrakis(triphenylphosphine)palladium(0), aliquat 336, sodium borohydride, triethyl phosphite, and iodine were obtained from Aldrich Chemical Co. and used as received. 2-Bromoanthraquinone was obtained from TCI Co. THF was dried over the sodium benzophenone ketyl anion radical and distilled under a dry nitrogen atmosphere immediately before use. 2-Bromo-4,4'-di-*tert*-butylbiphenyl,²⁸ 2-bromo-(2',7'-di-*tert*-butyl)-9,9'-spirobifluorene,²⁸ 2,7-dibromo-2',7'-di-*tert*-butyl-9,9'-spirobifluorene,²⁹ diethyl 4-(diphenylamino)benzylphosphonate (16),³⁰ 2-(3,5-di-*tert*-butylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane,³¹ *p*-bromo-tetraphenylmethane,³² 4-bromotriphenylsilylbenzene,³³ 4-bromophenyl phenyl sulfide,³⁴ 4-bromophenyl phenyl selenide,³⁵ 4'-(diphenylamino)biphenyl-4-carbaldehyde,³⁶ diethyl (7-

(diphenylamino)-9,9-diethylfluoren-2-yl)methylphosphonate,¹⁰ 2,8-dibromo-indeno[1,2-b]fluorene-6,12-dione,³⁷ 9-(3,5-di-*tert*-butylphenyl)-9*H*-carbazole-3-carbaldehyde,³⁸ (9-(3,5-di-*tert*-butylphenyl)-9*H*-carbazol-3-yl)methanol (22),³⁹ and diethyl 9-(3,5-di-*tert*-butylphenyl)-9*H*-carbazoylphosphonate (23)³⁹ were prepared as previously reported.



Scheme 1. Structures of targeted *tert*-butylated spirofluorene cored derivatives (**1-14**).

General Procedure for the Horner-Wadsworth-Emmons Reaction. Synthesis of **1**, **9-14**, and **18**: A 1.0 M potassium *tert*-butoxide (1.70 mL, 1.70 mmol) solution in THF under N₂ was added dropwise to a mixture of compound **15** (676 mg, 1.48 mmol) and compound **16** (585 mg, 1.48 mmol) in 35 mL of anhydrous THF at 0 °C. The reaction mixture was stirred for 10 min at 0 °C followed by 1 h at room temperature and quenched with water. The solution mixture was extracted with ethyl acetate, and washed with water. The combined organic layer was dried with anhydrous MgSO₄, filtered and evaporated to dryness. The crude product was purified by silica gel column chromatography using dichloromethane/hexane (1/5, v/v) as the eluent.



Scheme 3. Synthesis of **12-14**. Conditions: (a) *n*-BuLi, THF, -78°C to room temperature; (b) acetic acid, H_2SO_4 ; (c) *n*-BuLi, DMF, THF, -78°C , 2h; (d) *t*-BuOK (1.2 eq), THF, 0°C to room temperature, 1h; (e) H_2SO_4 , dichloromethane; (f) $\text{Pd}(\text{PPh}_3)_4$, Aliquat 336, K_2CO_3 , toluene, 120°C . See the Experimental section for full details.

2-(4-Diphenylaminostyryl)-2',7'-di-*tert*-butyl-9,9'-spirobifluorene (1): Yellow solid. Yield: 75 %. ^1H NMR (300 MHz, CDCl_3 , δ): 7.82 (dd, $J = 7.8, 2.5$ Hz, 1H), 7.73 (d, $J = 8.0$ Hz, 1H), 7.51 (dd, $J = 7.9, 1.4$ Hz, 1H), 7.39 (dd, $J = 7.9, 1.6$ Hz, 2H), 7.34 (d, $J = 7.3$ Hz, 1H), 7.29-7.21 (m, 10H), 7.10-6.96 (m, 8H), 6.87 (d, $J = 3.3$ Hz, 2H), 6.85 (s, 1H), 6.71-6.68 (m, 2H), 1.16 (s, 18H); ^{13}C NMR (75 MHz, CDCl_3 , δ): 151.0, 150.2, 150.1, 149.1, 147.7, 147.3, 141.6, 141.3, 139.4, 137.4, 131.7, 129.5, 127.8, 127.6, 127.4, 126.1, 125.0, 124.7, 124.4, 123.7, 123.2, 122.2, 120.9, 120.3, 119.9, 119.2, 66.4, 35.0, 31.7; FT-IR (ATR, cm^{-1}): $\nu = 3028, 2958, 2868, 1590, 1508, 1493, 1460, 1329, 1279, 1253, 962, 893, 821, 753, 735, 696$; HRMS (FAB, m/z): $[\text{M}^+\text{H}]$ calcd for $\text{C}_{53}\text{H}_{48}\text{N}$, 698.3787; found, 698.3758.

2-(2-(7-Diphenylamino-9,9-diethyl-fluoren-2-yl)vinyl)-2',7'-di-*tert*-butyl-9,9'-spirobifluorene (9): Yellow solid. Yield: 93 %. ^1H NMR (300 MHz, CDCl_3 , δ): 7.83 (dd, $J = 7.7, 2.4$ Hz, 2H), 7.74 (d, $J = 7.9$ Hz, 2H), 7.52 (d, $J = 7.9$ Hz, 1H), 7.40 (dd, $J = 8.0, 1.7$ Hz, 2H), 7.34 (d, $J = 7.5$ Hz, 1H), 7.29-7.21 (m, 7H), 7.10-6.94 (m, 10H), 6.89-6.82 (m, 4H), 6.72-6.68 (m, 2H), 1.94-1.80 (m, 4H), 1.15 (s, 18H), 0.30 (t, $J = 7.1$ Hz, 6H); ^{13}C NMR (75 MHz, CDCl_3 , δ): 151.8, 151.0, 150.5, 150.3, 150.1, 149.1, 148.2, 147.3, 141.4, 141.2, 139.5, 137.4, 135.8, 129.4, 128.8, 128.0, 127.9, 127.7, 126.2, 126.0, 125.1, 124.5, 124.0, 122.7, 122.4, 120.9, 120.5, 120.3,

120.0, 119.4, 119.3, 66.4, 56.2, 35.1, 32.9, 31.7, 8.7; FT-IR (ATR, cm^{-1}): $\nu = 3032, 2963, 2873, 1590, 1492, 1466, 1345, 1277, 1253, 961, 820, 769, 753, 737$; HRMS (FAB, m/z): $[\text{M}^+\text{H}]$ calcd for $\text{C}_{64}\text{H}_{60}\text{N}$, 842.4725; found, 842.4693.

2-(2-(4-Diphenylaminobiphenyl-4'-yl)vinyl)-2',7'-di-tert-butyl-9,9'-spirobifluorene (10): Yellow solid. Yield: 40 %. ^1H NMR (300 MHz, CDCl_3 , δ): 7.83 (d, $J = 7.7$ Hz, 1H), 7.74 (d, $J = 8.0$ Hz, 2H), 7.60-7.33 (m, 11H), 7.28-7.16 (m, 5H), 7.12-6.89 (m, 12H), 6.72-6.68 (m, 2H), 1.15 (s, 18H); ^{13}C NMR (75 MHz, CDCl_3 , δ): 161.5, 151.0, 150.2, 150.1, 149.1, 147.8, 147.4, 141.7, 141.6, 139.6, 139.4, 137.2, 136.1, 134.6, 129.5, 128.7, 127.7, 127.6, 127.0, 126.9, 126.4, 125.0, 124.6, 124.4, 124.0, 123.1, 122.4, 122.3, 120.9, 120.3, 120.0, 119.2, 35.0, 31.6; FT-IR (ATR, cm^{-1}): $\nu = 3028, 2960, 2867, 1591, 1492, 1460, 1363, 1326, 1278, 1254, 1004, 963, 821, 770, 753, 737$; HRMS (FAB, m/z): $[\text{M}^+\text{H}]$ calcd for $\text{C}_{59}\text{H}_{52}\text{N}$, 774.4099; found, 774.4051.

2',7'-Di-tert-butyl-2-[9-(3,5-di-tert-butylphenyl)carbazol-3-ylethenyl]-spirobifluorene (11): Yield: 68%. ^1H NMR (300 MHz, CDCl_3 , δ): 8.16 (s, 1H), 8.09 (d, $J = 7.6$ Hz, 1H), 7.84 (d, $J = 7.9$ Hz, 2H), 7.75 (d, $J = 8.0$ Hz, 2H), 7.57 (d, $J = 7.9$ Hz, 1H), 7.53-7.17 (m, 11H), 7.15 (s, 1H), 7.09-7.00 (m, 2H), 6.94 (s, 1H), 6.79-6.71 (m, 3H), 1.37 (s, 20H), 1.15 (s, 16H); ^{13}C NMR (75 MHz, CDCl_3 , δ): 152.8, 151.0, 150.3, 149.2, 141.5, 139.5, 137.7, 137.0, 129.1, 127.7, 126.7, 126.2, 125.1, 124.7, 123.8, 121.4, 121.3, 120.9, 120.5, 120.3, 120.1, 119.9, 119.3, 110.3, 35.3, 35.1, 31.7; FT-IR (ATR, cm^{-1}): 2964, 2904, 2867, 1595, 1489, 1476, 1460, 1362, 1252, 1232, 1204, 959, 820, 767, 743, 728; (FAB, m/z): $[\text{M}^+\text{H}]$ calcd for $\text{C}_{61}\text{H}_{62}\text{N}$: 808.4882 $[\text{M}^+]$, found: 808.4859.

4-(4-Diphenylaminostyryl)-2',7'-di-tert-butyl-9,9'-spirobifluorene (12): Yellow solid. Yield: 91 %. ^1H NMR (300 MHz, CDCl_3 , δ): 8.03 (d, $J = 7.9$ Hz, 1H), 7.94 (d, $J = 16.1$ Hz, 1H), 7.71 (d, $J = 7.9$ Hz, 2H), 7.56-7.49 (m, 3H), 7.39-7.26 (m, 7H), 7.19-7.00 (m, 12H), 6.73 (d, $J = 7.1$ Hz, 1H), 6.67-6.61 (m, 2H), 1.15 (s, 18H); ^{13}C NMR (75 MHz, CDCl_3 , δ): 151.0, 150.4, 150.2, 149.4, 147.8, 142.4, 139.5, 139.1, 134.2, 131.9, 131.2, 129.6, 127.9, 127.8, 127.7, 127.6, 126.0, 125.7, 125.0, 124.9, 124.6, 123.8, 123.6, 123.4, 120.9, 119.3, 66.3, 35.1, 31.7; FT-IR (ATR, cm^{-1}): $\nu = 3035, 2969, 2868, 1590, 1509, 1494, 1326, 1314, 1286, 1252, 1179, 961, 820, 750, 736, 695$; HRMS (FAB, m/z): $[\text{M}^+\text{H}]$ calcd for $\text{C}_{53}\text{H}_{48}\text{N}$, 698.3786; found, 698.3759.

2-(4-Diphenylaminostyryl)-2',2'',7',7''-tetra-tert-butyl-dispiro(fluorene-9,9'-anthracene-10,9''-fluorene) (13): Yellow solid. Yield: 80 %. ^1H NMR (300 MHz, CDCl_3 , δ): 7.80 (d, $J = 8.0$ Hz, 2H), 7.44 (d, $J = 8.0$ Hz, 4H), 7.26-7.13 (m, 9H), 7.05-6.96 (m, 7H), 6.92 (d, $J = 8.5$ Hz, 3H), 6.78-6.71 (m, 3H), 6.66-6.52 (m, 4H), 6.41-6.34 (m, 3H), 1.21 (s, 36H); ^{13}C NMR (75 MHz, CDCl_3 , δ): 158.1, 157.9, 151.4, 147.7, 147.1, 138.4, 138.3, 137.3, 137.2, 137.0, 136.5, 135.5, 131.9, 129.5, 129.4, 129.1, 127.6, 127.3, 127.1, 126.6, 124.6, 124.5, 123.8, 123.4, 123.1, 122.5, 119.2, 58.7, 35.2, 32.0, 31.1; FT-IR (ATR, cm^{-1}): $\nu = 3026, 2968, 2903, 2868, 1591, 1508, 1492, 1363, 1278, 1253, 1217, 959, 875, 819, 753, 729, 696$; HRMS (FAB, m/z): $[\text{M}^+\text{H}]$ calcd for $\text{C}_{74}\text{H}_{72}\text{N}$, 974.5664; found, 974.5624.

2-(3,5-Di-*tert*-butylphenyl)-8-(4-diphenylaminostyryl)-2',2'',7',7''-tetra-*tert*-butyl-dispiro (fluorene-9',6-indeno[1,2-*b*]fluorene-12,9''-fluorene) (14): Yellow solid. Yield: 54 %. ¹H NMR (300 MHz, CDCl₃, δ): 7.79 (t, *J* = 7.5 Hz, 5H), 7.54 (d, *J* = 7.9 Hz, 1H), 7.47-7.41 (m, 6H), 7.25-7.19 (m, 7H), 7.16-7.11 (m, 3H), 7.05 (d, *J* = 7.6 Hz, 5H), 6.99-6.94 (m, 5H), 6.83-6.79 (m, 3H), 6.76-6.74 (m, 2H), 6.72-6.70 (m, 2H), 1.18-1.16 (m, 54H); ¹³C NMR (75 MHz, CDCl₃, δ): 152.1, 151.3, 151.2, 151.1, 151.0, 150.6, 150.1, 149.7, 149.4, 149.3, 148.5, 147.7, 147.4, 140.9, 139.5, 139.4, 131.7, 131.0, 130.7, 129.5, 127.5, 127.4, 126.1, 125.5, 125.2, 125.1, 124.7, 123.7, 123.2, 122.0, 121.7, 121.2, 121.0, 120.5, 119.6, 119.4, 115.8, 66.3, 35.1, 35.0, 31.7; FT-IR (ATR, cm⁻¹): ν = 2969, 1591, 1508, 1493, 1459, 1363, 1277, 1253, 960, 821, 752, 696, 664. FABMS (*m/z*): 1236 (M⁺). HRMS (FAB, *m/z*): [M⁺] calcd for C₉₄H₉₃N, 1235.7308; found 1235.7301.

2-Bromo-7-(4-diphenylaminostyryl)-2',7'-di-*tert*-butyl-9,9'-spirobifluorene (18): Yellow solid. Yield: 92 %. ¹H NMR (300 MHz, CDCl₃, δ): 7.81-7.68 (m, 4H), 7.52 (d, *J* = 7.9 Hz, 1H), 7.48 (dd, *J* = 8.2, 1.8 Hz, 1H), 7.42 (dd, *J* = 8.0, 1.7 Hz, 2H), 7.29-7.21 (m, 6H), 7.01-6.94 (m, 8H), 6.87 (d, *J* = 7.3 Hz, 2H), 6.83-6.81 (m, 2H), 6.67 (s, 2H), 1.17 (s, 18H); ¹³C NMR (75 MHz, CDCl₃, δ): 152.1, 151.2, 150.0, 148.3, 147.7, 147.5, 140.7, 140.1, 139.4, 138.0, 131.5, 130.9, 129.5, 128.1, 127.5, 127.4, 127.1, 126.3, 125.4, 124.7, 123.6, 123.2, 122.3, 121.4, 121.3, 120.8, 120.4, 119.5, 66.3, 35.1, 31.7; FT-IR (ATR, cm⁻¹): ν = 3028, 2964, 2868, 1590, 1507, 1492, 1455, 1328, 1314, 1280, 1253, 1176, 1059, 1032, 961, 819, 753, 733, 695; FABMS (*m/z*): 777 [M⁺].

General Procedure for the Suzuki Reaction, Synthesis of 2-8, and 30: A solution of compound **19** (1.07 g, 1.30 mmol), 2-(3,5-di-*tert*-butylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (497 mg, 1.56 mmol), tetrakis(triphenylphosphine)palladium (60.0 mg, 0.05 mmol), Aliquat 336 (0.06 mL, 0.13 mmol), and aqueous K₂CO₃ (2.0 M, 6.5 mL) in toluene (40.0 mL) were heated at 120 °C under N₂ for 4 h. After cooling the solution, the product was extracted with CH₂Cl₂, washed with brine and H₂O, and dried (MgSO₄). The solvent was evaporated and the residue was purified by silica gel column chromatography using EtOAc/hexane.

2-(3,5-Di-*tert*-butylphenyl)-7-(4-diphenylaminostyryl)-2',7'-di-*tert*-butyl-9,9'-spirobifluorene (2): Yellow solid. Yield: 91 %. ¹H NMR (300 MHz, CDCl₃, δ): 7.87 (d, *J* = 7.9 Hz, 2H), 7.83 (d, *J* = 7.9 Hz, 2H), 7.73 (d, *J* = 8.0 Hz, 2H), 7.58 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.52 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.40 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.33-7.18 (m, 9H), 7.08-6.94 (m, 8H), 6.90-6.82 (m, 4H), 6.73 (s, 1H), 1.27 (s, 18H), 1.15 (s, 18H); ¹³C NMR (75 MHz, CDCl₃, δ): 151.2, 151.0, 150.8, 150.7, 149.2, 147.8, 147.4, 142.3, 141.1, 141.0, 140.8, 139.5, 137.4, 131.8, 129.5, 127.7, 127.4, 126.2, 125.1, 124.7, 123.7, 123.4, 123.2, 122.3, 121.7, 121.6, 121.0, 120.3, 120.1, 119.3, 66.6, 35.1, 31.7, 31.2; FT-IR (ATR, cm⁻¹): ν = 3030, 2967, 2904, 2868, 1591, 1536, 1509, 1493, 1362, 1326, 1279, 1253, 966, 820, 753, 732, 697; HRMS (FAB, *m/z*): [M⁺+H] calcd for C₆₇H₆₈N, 886.5351; found, 886.5316.

2-(*p*-Triphenylmethylphenyl)-7-(4-diphenylaminostyryl)-2',7'-di-*tert*-butyl-9,9'-spirobifluorene (3): Bright green solid. Yield: 66 %. ^1H NMR (300 MHz, CDCl_3 , δ): 7.86 (d, $J = 8.1$ Hz, 1H), 7.83 (d, $J = 7.9$ Hz, 1H), 7.72 (d, $J = 8.1$ Hz, 2H), 7.60 (dd, $J = 8.0, 1.6$ Hz, 1H), 7.52 (d, $J = 8.0$ Hz, 1H), 7.38 (dd, $J = 8.1, 1.7$ Hz, 2H), 7.33-6.85 (m, 38H), 6.70 (s, 1H), 1.14 (s, 18H); ^{13}C NMR (75 MHz, CDCl_3 , δ): 151.0, 150.5, 149.1, 147.7, 146.9, 146.0, 140.1, 139.5, 137.4, 131.6, 131.3, 129.5, 127.7, 127.4, 126.7, 126.1, 125.2, 124.7, 123.7, 123.2, 122.7, 122.3, 120.9, 120.3, 119.3, 64.9, 35.1, 31.7; FT-IR (ATR, cm^{-1}): $\nu = 3016, 2970, 2948, 1590, 1422, 1365, 1228, 1216, 1050, 1033, 818, 750, 699$; FABMS (m/z): 1015 [M^+]; HRMS (FAB, m/z): [M^+] calcd for $\text{C}_{78}\text{H}_{65}\text{N}$, 1015.5117; found, 1015.5092.

2-(*p*-Triphenylsilylphenyl)-7-(4-diphenylaminostyryl)-2',7'-di-*tert*-butyl-9,9'-spirobifluorene (4): Bright green solid. Yield: 54 %. ^1H NMR (300 MHz, CDCl_3 , δ): 7.78 (d, $J = 7.9$ Hz, 1H), 7.83 (d, $J = 7.9$ Hz, 1H), 7.72 (d, $J = 8.0$ Hz, 1H), 7.63 (dd, $J = 8.0, 1.5$ Hz, 1H), 7.54-7.19 (m, 30H), 7.08-6.86 (m, 12H), 6.71 (s, 1H), 1.14 (s, 18H); ^{13}C NMR (75 MHz, CDCl_3 , δ): 151.0, 150.9, 150.6, 149.0, 147.7, 142.3, 141.2, 140.9, 140.4, 139.4, 137.5, 136.9, 136.5, 134.3, 129.8, 129.4, 128.1, 127.8, 127.4, 126.8, 126.6, 126.2, 125.1, 124.7, 123.7, 123.2, 122.9, 122.2, 120.9, 120.3, 119.3, 66.4, 35.0, 31.6; FT-IR (ATR, cm^{-1}): $\nu = 3015, 2970, 2948, 1590, 1427, 1365, 1228, 1216, 1110, 1051, 1033, 818, 753, 728, 696$; FABMS (m/z): 1031 [M^+]; HRMS (FAB, m/z): [M^+] calcd for $\text{C}_{77}\text{H}_{65}\text{NSi}$, 1031.4886; found, 1031.4879.

2-(*p*-Diphenylaminophenyl)-7-(4-diphenylaminostyryl)-2',7'-di-*tert*-butyl-9,9'-spirobifluorene (5): Yellow solid. Yield: 46 %. ^1H NMR (300 MHz, CDCl_3 , δ): 7.86 (d, $J = 7.9$ Hz, 1H), 7.82 (d, $J = 8.0$ Hz, 1H), 7.73 (d, $J = 7.9$ Hz, 2H), 7.58 (dd, $J = 7.9, 1.6$ Hz, 1H), 7.52 (d, $J = 8.0$ Hz, 1H), 7.39 (dd, $J = 8.0, 1.7$ Hz, 2H), 7.32-7.18 (m, 15H), 7.08-6.96 (m, 15H), 6.88-6.83 (m, 3H), 6.72 (s, 1H), 1.15 (s, 18H); ^{13}C NMR (75 MHz, CDCl_3 , δ): 151.1, 150.9, 150.6, 149.2, 147.8, 147.7, 147.4, 147.2, 141.1, 140.6, 140.2, 139.5, 137.4, 135.3, 131.8, 129.6, 129.5, 127.9, 127.7, 127.4, 126.4, 125.2, 124.7, 124.5, 124.1, 123.7, 123.2, 123.1, 122.4, 122.3, 121.0, 120.3, 119.3, 66.5, 35.1, 31.7; FT-IR (ATR, cm^{-1}): $\nu = 3015, 2970, 1590, 1492, 1365, 1252, 1228, 1216, 1051, 1033, 819, 752, 695$; HRMS (FAB, m/z): [M^+H] calcd for $\text{C}_{71}\text{H}_{61}\text{N}_2$, 941.4834; found, 941.4810.

2-(*p*-Phenoxyphenyl)-7-(4-diphenylaminostyryl)-2',7'-di-*tert*-butyl-9,9'-spirobifluorene (6): Yellow solid. Yield: 62 %. ^1H NMR (300 MHz, CDCl_3 , δ): 7.87 (d, $J = 7.9$ Hz, 1H), 7.83 (d, $J = 7.9$ Hz, 1H), 7.74 (d, $J = 8.0$ Hz, 2H), 7.58 (dd, $J = 7.9, 1.6$ Hz, 1H), 7.53 (d, $J = 7.9$ Hz, 1H), 7.42-7.37 (m, 4H), 7.33-7.20 (m, 9H), 7.10-6.82 (m, 17H), 6.72 (s, 1H), 1.15 (s, 18H); ^{13}C NMR (75 MHz, CDCl_3 , δ): 157.4, 156.8, 151.1, 150.9, 150.6, 149.2, 147.8, 147.4, 141.0, 140.8, 140.1, 139.5, 137.5, 136.4, 131.7, 130.0, 129.5, 128.5, 127.8, 127.5, 127.4, 126.7, 126.3, 125.2, 124.7, 123.7, 123.5, 123.2, 122.6, 122.4, 121.0, 120.4, 119.4, 119.3, 119.0, 66.6, 35.1, 31.7; FT-IR (ATR, cm^{-1}): $\nu = 3015, 2970, 1590, 1489, 1365, 1229, 1216, 1051, 1033, 821, 750, 69$; HRMS (FAB, m/z): [M^+H] calcd for $\text{C}_{65}\text{H}_{56}\text{NO}$, 866.4361; found, 866.4337.

2-(*p*-Phenylthiophenyl)-7-(4-diphenylaminostyryl)-2',7'-di-*tert*-butyl-9,9'-spirobifluorene (7): Yellow solid. Yield: 44 %. ^1H NMR (300 MHz, CDCl_3 , δ): 7.88 (d, $J = 8.1$ Hz, 1H), 7.83 (d, $J = 8.0$ Hz, 1H), 7.73 (d, $J = 8.0$ Hz, 2H), 7.59 (dd, $J = 7.9, 1.6$ Hz, 1H), 7.52 (d, $J = 8.0$ Hz, 1H), 7.42-7.35 (m, 4H), 7.32-7.20 (m, 15H), 7.08-6.96 (m, 8H), 6.88-6.83 (m, 3H), 6.71 (s, 1H), 1.15 (s, 18H); ^{13}C NMR (75 MHz, CDCl_3 , δ): 151.1, 151.0, 150.6, 149.0, 147.7, 147.4, 141.3, 140.8, 140.1, 139.8, 139.5, 137.6, 134.7, 131.6, 131.1, 129.5, 129.4, 127.9, 127.4, 127.3, 127.2, 126.8, 126.3, 125.2, 124.7, 123.7, 123.2, 122.7, 122.3, 121.0, 120.4, 119.4, 66.5, 35.1, 35.0, 31.7; FT-IR (ATR, cm^{-1}): $\nu = 3015, 2970, 1590, 1492, 1365, 1252, 1228, 1216, 1051, 1033, 818, 751, 695$; HRMS (FAB, m/z): $[\text{M}^+\text{H}]$ calcd for $\text{C}_{65}\text{H}_{56}\text{NS}$, 882.4133; found, 882.4107.

2-(*p*-Phenylselanylphenyl)-7-(4-diphenylaminostyryl)-2',7'-di-*tert*-butyl-9,9'-spirobifluorene (8): Yellow solid. Yield: 35 %. ^1H NMR (300 MHz, CDCl_3 , δ): 7.88 (d, $J = 7.9$ Hz, 1H), 7.83 (d, $J = 7.9$ Hz, 1H), 7.76-7.67 (m, 3H), 7.63-7.51 (m, 3H), 7.47-7.40 (m, 4H), 7.34-7.20 (m, 10H), 7.12-6.94 (m, 9H), 6.91-6.83 (m, 4H), 6.72-6.63 (m, 2H); ^{13}C NMR (75 MHz, CDCl_3 , δ): 151.1, 148.9, 147.7, 139.4, 137.7, 131.8, 129.4, 128.8, 127.9, 127.4, 126.2, 125.2, 124.7, 123.6, 123.2, 122.6, 122.2, 120.9, 120.4, 119.3, 35.0, 31.6; FT-IR (ATR, cm^{-1}): $\nu = 3015, 2970, 2948, 1590, 1440, 1365, 1228, 1216, 1050, 1033, 895, 817, 753, 668$; HRMS (FAB, m/z): $[\text{M}^+\text{H}]$ calcd for $\text{C}_{65}\text{H}_{56}\text{NSe}$, 930.3577; found, 929.3541.

2-(3,5-Di-*tert*-butylphenyl)-8-formyl-2',2'',7',7''-tetra-*tert*-butyl-dispiro (fluorene-9',6-indeno[1,2-*b*]fluorene-12,9''-fluorene) (30): Yellow solid. Yield: 78 %. ^1H NMR (300 MHz, CDCl_3 , δ): 9.74 (s, 1H), 7.81-7.78 (m, 4H), 7.69 (d, $J = 6.7$ Hz, 2H), 7.65-7.57 (m, 2H), 7.50-7.42 (m, 4H), 7.39-7.22 (m, 5H), 7.20-6.98 (m, 1H), 6.87-6.79 (m, 1H), 6.72-6.68 (m, 4H), 1.34 (s, 18H), 1.16 (s, 36H); ^{13}C NMR (75 MHz, CDCl_3 , δ): 192.3, 152.8, 151.3, 151.2, 151.1, 151.0, 150.6, 150.3, 150.2, 149.0, 148.1, 141.3, 140.1, 139.6, 139.5, 135.7, 130.4, 128.3, 127.7, 125.5, 125.2, 124.3, 121.7, 121.0, 120.8, 120.6, 119.7, 119.5, 117.0, 116.1, 115.0, 109.9, 66.2, 35.1, 31.7, 31.6, 30.0, 25.1; FT-IR (ATR, cm^{-1}): $\nu = 2963, 2867, 1603, 1476, 1461, 1393, 1253, 1202, 1185, 890, 823, 736, 725, 709, 675$. FABMS (m/z): 995 $[\text{M}^+]$.

General procedure for the synthesis of compounds 15, 17, 25, 27, and 29: *n*-Butyllithium (1.70 mL of a 1.6 M solution in hexane, 2.66 mmol) dropwise was added to a THF (35 mL) solution of 2-bromo-2',7'-di-*tert*-butyl-9,9'-spirobifluorene (900 mg, 1.70 mmol) at -78 °C, and the mixture was stirred at this temperature for 1 h before adding dimethylformamide (0.21 mL, 2.66 mmol). After stirring for 1 h at -78 °C, the residue was extracted with ethyl acetate, and washed with water. The combined organic layer was dried with anhydrous MgSO_4 , filtered and evaporated to dryness. Chromatography (hexane:EtOAc = 20: 1) afforded the desired product.

2-Formyl-2',7'-di-*tert*-butyl-9,9'-spirobifluorene (15): White solid. Yield: 40 %. ^1H NMR (300 MHz, CDCl_3 , δ): 9.83 (s, 1H), 7.99 (d, $J = 7.7$ Hz, 1H), 7.95-7.90 (m, 2H), 7.72 (d, $J = 8.0$ Hz, 2H), 7.44-7.38 (m, 3H), 7.19 (t, J

= 7.6 Hz, 2H), 6.78 (d, $J = 7.6$ Hz, 1H), 6.60 (s, 2H), 1.13 (s, 18H); ^{13}C NMR (75 MHz, CDCl_3 , δ): 192.3, 151.2, 151.1, 150.7, 148.2, 147.8, 140.3, 139.5, 136.1, 130.2, 129.7, 128.2, 128.0, 125.8, 125.4, 124.8, 121.2, 120.6, 120.5, 119.9, 119.5, 66.2, 35.0, 31.7, 31.6, 31.3; FT-IR (ATR, cm^{-1}): $\nu = 3015, 2970, 2948, 1738, 1441, 1365, 1228, 1216, 1050, 1033, 832, 735$; EIMS (m/z): 456 [M^+].

2-Bromo-7-formyl-2',7'-di-*tert*-butyl-9,9'-spirobifluorene (17): White solid. Yield: 71 %. ^1H NMR (300 MHz, CDCl_3 , δ): 9.83 (s, 1H), 7.99-7.91 (m, 1H), 7.80 (d, $J = 8.1$ Hz, 1H), 7.73 (d, $J = 8.1$ Hz, 1H), 7.55 (dd, $J = 7.9, 1.6$ Hz, 1H), 7.42 (dd, $J = 8.0, 1.7$ Hz, 1H), 7.28-7.24 (m, 5H), 6.91 (s, 1H), 6.60 (s, 1H), 1.16 (s, 18H); ^{13}C NMR (75 MHz, CDCl_3 , δ): 192.0, 153.1, 151.4, 150.5, 147.0, 146.9, 139.5, 139.3, 136.4, 131.4, 130.4, 127.9, 125.9, 125.8, 123.6, 122.6, 120.7, 120.5, 119.7, 66.1, 35.1, 31.6; FT-IR (ATR, cm^{-1}): $\nu = 2970, 1738, 1696, 1605, 1476, 1453, 1365, 1229, 1216, 1204, 1057, 1033, 891, 818, 735$; EIMS (m/z): 537 [M^+].

4-Formyl-2',7'-di-*tert*-butyl-9,9'-spirobifluorene (25): White solid. Yield: 93 %. ^1H NMR (300 MHz, CDCl_3 , δ): 10.7 (s, 1H), 8.67 (d, $J = 7.9$ Hz, 1H), 7.88 (dd, $J = 7.8, 1.1$ Hz, 1H), 7.72 (d, $J = 8.0$ Hz, 2H), 7.45-7.37 (m, 3H), 7.27-7.17 (m, 2H), 6.94 (dd, $J = 8.0, 1.1$ Hz, 1H), 6.77 (d, $J = 7.5$ Hz, 1H), 6.62 (s, 2H), 1.14 (s, 18H); ^{13}C NMR (75 MHz, CDCl_3 , δ): 192.4, 151.9, 151.2, 150.6, 148.4, 142.7, 140.5, 139.5, 132.7, 132.1, 130.1, 129.4, 128.2, 127.7, 125.9, 125.3, 124.6, 120.7, 119.5, 66.2, 35.1, 31.6, 31.4; FT-IR (ATR, cm^{-1}): $\nu = 2970, 1594, 1566, 1477, 1454, 1365, 1228, 1216, 1204, 1052, 1033, 814, 733$; EIMS (m/z): 457 [M^+].

2-Formyl-2',2'',7',7''-tetra-*tert*-butyl-dispiro(fluorene-9,9'-anthracene-10,9''-fluorene) (27): White solid. Yield: 78 %. ^1H NMR (300 MHz, CDCl_3 , δ): 9.54 (s, 1H), 7.84-7.76 (m, 4H), 7.47 (d, $J = 6.4$ Hz, 4H), 7.32-7.16 (m, 5H), 6.87 (s, 1H), 6.80-6.72 (m, 2H), 6.53 (d, $J = 8.2$ Hz, 1H), 6.43-6.30 (m, 2H), 1.27 (s, 36 H); ^{13}C NMR (75 MHz, CDCl_3 , δ): 192.4, 157.5, 157.4, 151.7, 144.4, 138.4, 138.3, 138.2, 136.5, 136.2, 135.1, 133.8, 130.3, 129.0, 127.0, 125.4, 125.0, 122.5, 122.4, 119.5, 119.4, 58.5, 35.2, 32.0; FT-IR (ATR, cm^{-1}): $\nu = 2968, 2869, 1738, 1702, 1606, 1563, 1474, 1362, 1252, 1216, 875, 755, 729, 648$; FABMS (m/z): 732 [M^+].

2-Bromo-8-formyl-2',2'',7',7''-tetra-*tert*-butyl-dispiro(fluorene-9',6-indeno[1,2-b]fluorene-12,9''-fluorene) (29): Pale yellow solid. Yield: 27 %. ^1H NMR (300 MHz, CDCl_3 , δ): 9.77 (s, 1H), 7.81-7.70 (m, 6H), 7.61 (d, $J = 7.5$ Hz, 1H), 7.47-7.43 (m, 4H), 7.21 (d, $J = 9.1$ Hz, 3H), 7.04 (t, $J = 7.3$ Hz, 1H), 6.70 (d, $J = 8.4$ Hz, 5H), 1.16 (s, 36H); ^{13}C NMR (75 MHz, CDCl_3 , δ): 192.3, 151.3, 151.2, 151.1, 150.1, 149.0, 148.2, 148.1, 139.6, 139.5, 139.4, 135.7, 130.4, 128.3, 127.6, 125.6, 125.5, 125.3, 125.2, 121.0, 120.8, 120.6, 119.6, 119.4, 116.1, 35.1, 31.7; FT-IR (ATR, cm^{-1}): $\nu = 2959, 2868, 1698, 1605, 1476, 1461, 1412, 1363, 1254, 1185, 890, 821, 737, 646$; FABMS (m/z): 885 [M^+].

2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolanyl)-7-(4-diphenylamino-styryl)-2',7'-di-*tert*-butyl-9,9'-spirobifluorene (19): To a solution of 18 (1.0 g, 1.29 mmol) in THF (10 ml) was added *n*-BuLi (1.2 ml, 1.6 M in hexane, 1.93

mmol) dropwise at $-78\text{ }^{\circ}\text{C}$. After stirring for 1 hour at $-78\text{ }^{\circ}\text{C}$, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.39 ml, 1.93 mmol) was added in one portion. The resulting mixture was stirred for another 3 hours at $-78\text{ }^{\circ}\text{C}$ and warmed gradually to room temperature. The reaction was quenched with water and extracted with dichloromethane. The crude product was purified by column chromatography on silica gel using 1:3 EtOAc/hexane as the eluent. Yellow solid. Yield: 92%. ^1H NMR (300 MHz, CDCl_3 , δ): 7.88-7.81 (m, 3H), 7.72 (d, $J = 7.9\text{ Hz}$, 2H), 7.51 (d, $J = 8.0\text{ Hz}$, 1H), 7.38 (dd, $J = 8.0, 1.7\text{ Hz}$, 2H), 7.28- 7.20 (m, 6H), 7.16 (s, 1H), 7.08-6.92 (m, 8H), 6.86 (d, $J = 6.4\text{ Hz}$, 2H), 6.81-6.77 (m, 1H), 6.70-6.65 (m, 2H), 1.26 (s, 12H), 1.14 (s, 18H); ^{13}C NMR (75 MHz, CDCl_3 , δ): 151.3, 151.0, 149.3, 149.1, 149.0, 147.7, 147.4, 145.0, 140.9, 139.7, 138.1, 134.9, 131.7, 130.6, 129.5, 128.0, 127.5, 127.4, 126.0, 125.2, 124.7, 124.4, 123.7, 123.3, 122.3, 121.1, 120.8, 119.4, 83.9, 66.5, 35.1, 32.0, 31.7, 30.0, 25.1; FT-IR (ATR, cm^{-1}): $\nu = 2968, 2868, 1590, 1508, 1493, 1356, 1314, 1279, 1253, 1232, 1144, 1032, 961, 857, 822, 752, 696$; FABMS (m/z): 823 [M^+].

(4'-(Diphenylamino)biphenyl-4-yl)methanol (**20**): Ethanol (20 mL) was added to a mixture of 4'-(diphenylamino)biphenyl-4-carbaldehyde (440 mg, 1.25 mmol) and sodium borohydride (189 mg, 5.00 mmol) in a two-neck round-bottomed flask, and heated under reflux at $78\text{ }^{\circ}\text{C}$ for 2 h. The reaction mixture poured into ice water, extracted with diethyl ether, and washed with water. The combined organic layer was dried with anhydrous MgSO_4 , filtered, evaporated to dryness, and the crude product was purified by silica gel column chromatography using EtOAc/Hexane (1/5, v/v) eluent to produce a yellow oil. Yield: 95 %. ^1H NMR (300 MHz, CDCl_3 , δ): 7.53 (d, $J = 8.2\text{ Hz}$, 2H), 7.44 (d, $J = 8.5\text{ Hz}$, 4H), 7.36 (d, $J = 8.0\text{ Hz}$, 2H), 7.26-7.19 (m, 2H), 7.11 (d, $J = 8.5\text{ Hz}$, 6H), 7.00 (t, $J = 7.8\text{ Hz}$, 2H), 5.23 (s, 1H), 4.65 (s, 2H); ^{13}C NMR (75 MHz, CDCl_3 , δ): 147.9, 147.5, 140.2, 139.6, 134.9, 129.5, 127.9, 127.7, 127.0, 124.7, 124.1, 123.2, 65.3; IR (ATR, cm^{-1}): $\nu = 3037, 2921, 1590, 1528, 1490, 1327, 1287, 1270, 1075, 1050, 1023, 1010, 850, 838, 810, 758, 747, 734, 694$; EIMS (m/z): 351 [M^+].

Diethyl (4'-(diphenylamino)biphenyl-4-yl)methylphosphonate (**21**): Triethylphosphite (0.36 mL, excess) was added to compound **20** (377 mg, 1.07 mmol) charged with nitrogen. Iodine (272 mg, 1.07 mmol) was then added at all once at $0\text{ }^{\circ}\text{C}$, stirred for 30 min, warmed to room temperature, and stirred for 12 h. The excess triethylphosphite was removed by distillation. The residue extracted with EtOAc, washed with water, and the combined organic layer was dried with anhydrous MgSO_4 , filtered and evaporated to dryness. The crude product was purified by silica gel column chromatography using EtOAc/Hexane (1/2, v/v) as the eluent to produce yellow oil. Yield: 46%. ^1H NMR (300 MHz, CDCl_3 , δ): 7.52 (d, $J = 7.9\text{ Hz}$, 2H), 7.46 (d, $J = 8.4\text{ Hz}$, 2H), 7.34 (dd, $J = 8.1, 2.2\text{ Hz}$, 2H), 7.28-7.23 (m, 4H), 7.12 (d, $J = 8.0\text{ Hz}$, 6H), 7.02 (t, $J = 7.4\text{ Hz}$, 2H), 4.16-4.01 (m, 4H), 3.22 (s, 1H), 3.11 (s, 1H), 1.39-1.23 (m, 6H); ^{13}C NMR (75 MHz, CDCl_3 , δ): 147.9, 147.4, 139.4 (d, $J_{pc} = 3.7\text{ Hz}$), 134.8, 130.4 (d, $J_{pc} = 6.6\text{ Hz}$), 129.5, 128.7 (d, $J_{pc} = 9.4\text{ Hz}$), 127.8, 126.9 (d, $J_{pc} = 3.3\text{ Hz}$), 124.6, 124.1, 123.2, 62.4 (d, $J_{pc} = 6.6\text{ Hz}$), 33.6 (d, $J_{pc} = 139.7\text{ Hz}$), 16.6 (d, $J_{pc} = 6.1\text{ Hz}$); FT-IR (ATR, cm^{-1}): $\nu = 2983, 2908, 1592, 1493, 1442, 1326, 1271, 1027, 969, 822, 754, 696$; EIMS (m/z): 471 [M^+].

General procedure for the synthesis of **24**, **26** and **28**: *n*-BuLi (2,80 mL of a 1.6M solution in hexane, 4.48 mmol) was added to 2,2'-dibromobiphenyl (1.44 g, 4.93 mmol) in anhydrous THF (30 mL) within 30 min at -78 °C. The reaction mixture was stirred for 1h before adding 1.40 g (4.48 mmol) of 2,7-di-*tert*-butyl-9*H*-fluoren-9-one. After stirring for 3 h at room temperature, the residue extracted with EtOAc, and washed with water. The combined organic layer was dried with anhydrous MgSO₄, filtered, and evaporated to dryness. The mixture was added to AcOH (5 mL) and heated under refluxed at 130 °C for 1 h. The mixture was then added to HCl (5 mL). The solid filter with water was extracted with CH₂Cl₂. The crude product was purified by silica gel column chromatography using EtOAc/Hexane (1/20, v/v) as the eluent.

4-Bromo-2',7'-di-*tert*-butyl-9,9'-spirobifluorene (**24**): Yellow solid. Yield: 88 %. ¹H NMR (300 MHz, CDCl₃, δ): 8.67 (d, *J* = 7.7 Hz, 1H), 7.69 (d, *J* = 8.0 Hz, 2H), 7.46 (d, *J* = 7.2 Hz, 1H), 7.39-7.34 (m, 3H), 7.10 (t, *J* = 7.5 Hz, 1H), 6.85 (t, *J* = 7.7 Hz, 1H), 6.72-6.61 (m, 4H), 1.12 (s, 18H); ¹³C NMR (75 MHz, CDCl₃, δ): 152.7, 151.2, 150.0, 148.8, 141.1, 140.1, 139.5, 132.7, 128.8, 128.7, 127.5, 125.2, 124.4, 123.6, 123.5, 120.9, 119.4, 116.8, 66.5, 35.1, 31.7; FT-IR (ATR, cm⁻¹): ν = 2965, 2868, 1475, 1440, 1420, 1362, 1251, 1075, 880, 823, 815, 773, 730, 694, 635; EIMS (*m/z*): 508 [M⁺].

2-Bromo-2',2'',7',7''-tetra-*tert*-butyl-dispiro(fluorene-9,9'-anthracene-10,9''-fluorene) (**26**): Yellow solid. Yield: 22 %. ¹H NMR (300 MHz, CDCl₃, δ): 7.78 (d, *J* = 7.9 Hz, 4H), 7.46-7.42 (m, 3H), 7.21 (s, 4H), 6.84 (dd, *J* = 8.6, 2.2 Hz, 2H), 6.74-6.69 (m, 2H), 6.50 (s, 1H), 6.36-6.30 (m, 2H), 6.27-6.24 (d, *J* = 8.6 Hz, 1H), 1.27 (s, 36H); ¹³C-NMR (75 MHz, CDCl₃, δ): 157.6, 157.4, 151.7, 151.6, 139.6, 138.2, 136.7, 136.6, 136.4, 131.5, 131.2, 130.2, 128.9, 126.,7 124.8, 124.7, 122.5, 122.4, 120.3, 119.4, 119.3, 58.4, 35.2, 32.0; FT-IR (ATR, cm⁻¹): ν = 2965, 1588, 1475, 1361, 1251, 1164, 1142, 959, 875, 818, 754, 729, 648; FABMS (*m/z*): 784 [M⁺].

2,8-Dibromo-2',2'',7',7''-tetra-*tert*-butyl-dispiro(fluorene-9',6-indeno[1,2-b]fluorene-12,9''-fluorene) (**28**): Brown solid. Yield: 53%. ¹H NMR (300 MHz, CDCl₃, δ): 7.78 (d, *J* = 8.1 Hz, 4H), 7.47-7.42 (m, 6H), 7.35 (dd, *J* = 1.8, 8.1 Hz, 2H), 7.13 (s, 2H), 6.80 (d, *J* = 1.6 Hz, 2H), 6.69 (d, *J* = 1.6 Hz, 4H), 1.79 (s, 36H); ¹³C-NMR (75 MHz, CDCl₃, δ): 152.1, 151.2, 149.7, 148.3, 141.1, 140.6, 139.4, 130.7, 127.3, 125.4, 121.7, 121.4, 120.9, 119.5, 115.9, 66.2, 35.1, 31.7; FT-IR (ATR, cm⁻¹): ν = 2964, 2869, 1476, 1458, 1421, 1253, 1060, 819, 750, 723, 675; FABMS (*m/z*):936 [M⁺].

Device Fabrication and Characterization

The device configuration of the blue devices was indium tin oxide (ITO, 150 nm)/*N,N'*-diphenyl-*N,N'*-bis-[4-(phenyl-*m*-tolyl-amino)-phenyl]-biphenyl-4,4'-diamine (DNTPD, 60 nm)/*N,N'*-di(1-naphthyl)-*N,N'*-

diphenylbenzidine(NPB, 30 nm)/MADN:dopants (30 nm)/tris(8-hydroxyquinoline) aluminium(Alq_3 , 20 nm)/LiF(1.0 nm)/Al(200 nm). DNTPD and NPB were hole injection and hole transport materials, respectively. Alq_3 was used as an electron transport layer and LiF/Al as a cathode. All organic materials except for dopants were deposited at a deposition rate of 1 Å/s. Current (I)-voltage (V)-luminance (L) characteristics and electroluminescence (EL) spectra of the devices were measured with a Keithley 2400 source measurement unit and CS 1000A spectrophotometer.

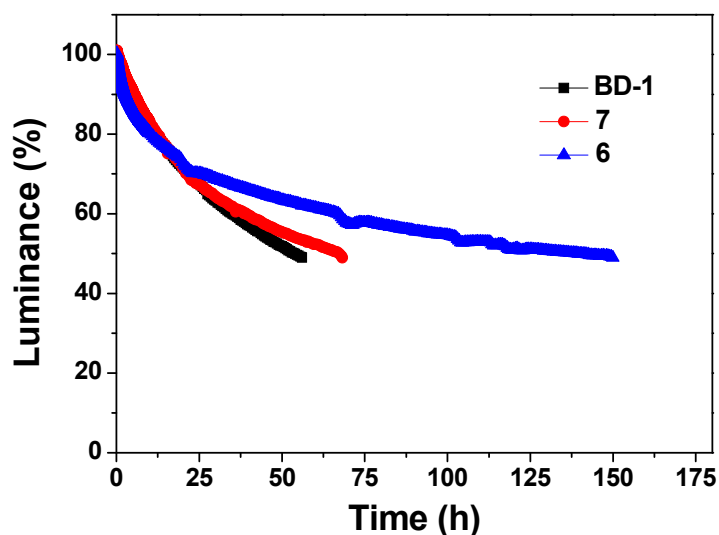


Figure S1. Operation lifetime test for the blue devices.