Electronic Supplementary Information

for

Carbazole-based BODIPYs with ethynyl substituents at the boron center:
solid-state excimer fluorescence in the VIS/NIR region

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Table of Contents

[A] Experimental Procedures and Compound Data…………………………………… S2
[B] Reference……………………………………………………………………………… S11
[C] NMR Spectra……………………………………………………………………… S12
[D] UV/vis Absorption and Fluorescence Spectra……………………………… S34
[E] Fluorescence Lifetime…………………………………………………………… S35
[F] X-ray Crystal Structures………………………………………………………… S37

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Experimental Procedures and Compound Data

Synthesis of 2. A solution of 7a<sup>S1</sup> (41.2 mg, 100 µmol), BPh<sub>3</sub> (93.0 mg, 384 µmol), and iPr<sub>2</sub>NEt (0.33 mL, 1.9 mmol) in dry toluene (2.0 mL) was heated at reflux for 48 h under N<sub>2</sub>. After cooling to rt, the mixture was evaporated. The residue was purified by silica gel chromatography with CHCl<sub>3</sub>/hexane to give 2 as an orange solid (36.2 mg, 62.8 µmol, 63%).

<sup>1</sup>H NMR (CDCl<sub>3</sub>) δ = 8.34 (d, J = 1.2 Hz, 1H, H<sup>i</sup>), 8.05 (d, J = 2.0 Hz, 1H, H<sup>j</sup>), 7.81 (dd, J = 0.8, 7.2 Hz, 1H, H<sup>k</sup>), 7.73 (d, J = 2.0 Hz, 1H, H<sup>j</sup>), 7.64 (d, J = 8.8 Hz, 1H, H<sup>i</sup>), 7.46–7.43 (m, 4H, oPh), 7.34 (t, J = 2.0 Hz, 1H, H<sup>j</sup>), 7.25–7.16 (m, 8H, H<sup>j</sup>, H<sup>k</sup>, mPh, oPh), 6.78 (d, J = 8.8 Hz, 1H, H<sup>i</sup>), 1.51 (s, 9H, tBu), and 1.38 ppm (s, 9H, tBu); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ = 168.85, 146.55, 143.79, 141.82, 141.09, 140.35, 133.95, 130.22, 127.65, 127.34, 126.65, 125.90, 125.40, 124.63, 124.40, 123.99, 122.53, 122.02, 119.41, 116.43, 114.21, 109.46, 35.00, 34.72, 32.15, and 32.08 ppm; HR-MS (APCI): m/z = 576.2790. calcd for C<sub>39</sub>H<sub>37</sub>N<sub>2</sub>B<sub>1</sub>S<sub>1</sub>: 576.2783 [M]; UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>) λ<sub>max</sub> (ε) = 310 (9470), 339 (9300), and 505 nm (7520 mol<sup>-1</sup> dm<sup>3</sup> cm<sup>-1</sup>).

Synthesis of 3a. To a solution of phenylacetylene (0.20 mL 1.8 mmol) in dry THF (2.0 mL) was added EtMgBr (1 M in hexane, 2.0 mL, 2.0 mmol) under N<sub>2</sub>, and the mixture was heated at 60 °C for 2 h. A solution of 1a<sup>S1</sup> (54.8 mg, 119 µmol) in dry THF (5.0 mL) was added, and the mixture was heated at reflux for 24 h. After cooling to rt, water was added, and organic products were extracted with CHCl<sub>3</sub>. The extracts were dried over Na<sub>2</sub>SO<sub>4</sub> and evaporated. The residue was purified by silica gel chromatography with CHCl<sub>3</sub>/hexane to give 3a as an orange solid (56.3 mg, 90.1 µmol, 76%).

Scheme S1 Synthesis of 2–6.
1H NMR (CDCl3, 400 MHz) δ = 9.20 (d, J = 8.4 Hz, 1H, Hf), 8.34 (d, J = 1.2 Hz, 1H, Hg), 8.17 (d, J = 8.8 Hz, 1H, Hh), 8.14 (d, J = 2.0 Hz, 1H, Hi), 7.92 (d, J = 7.6 Hz, 1H, Hj), 7.73 (t, J = 8.0 Hz, 1H, Hk), 7.71 (d, J = 1.6 Hz, 1H, Hl), 7.65 (dd, J = 2.0, 8.8 Hz, 1H, Hm), 7.55 (t, J = 7.6 Hz, 1H, Hn), 7.33–7.30 (m, 4H, oPh), 7.19–7.16 (m, 6H, mPh, pPh), 1.50 (s, 9H, tBu), and 1.49 ppm (s, 9H, tBu); 13C NMR (CDCl3, 100 MHz) δ = 167.48, 145.37, 142.58, 141.22, 138.49, 131.78, 129.83, 128.01, 127.65, 127.36, 126.64, 125.43, 125.05, 124.66, 123.98, 122.64, 121.90, 119.27, 116.62, 114.28, 108.08, 98.11, 35.02, 34.94, 32.24, and 32.15 ppm; HR-MS (APCI): m/z = 624.2755. calcd for C43H37N2B3S1: 624.2783 [M]+; UV/Vis (CH2Cl2) λmax (ε) = 307 (14700), 329 (13600), and 499 nm (12500 mol⁻¹dm³cm⁻¹).

**Synthesis of 4.** To a solution of 1a (50.4 mg 110 µmol) in dry CH2Cl2 (7.0 mL) was added trimethylsilyl cyanide (0.27 mL, 2.2 mmol) and BF3·OEt2 (0.14 mL, 1.1 mmol) under N2, and the mixture was heated at reflux for 2 h. After cooling to r.t., water was added, and the organic layer was dried over Na2SO4 and evaporated. The residue was purified by silica gel chromatography with CHCl3 to give 4 as an orange solid (45.7 mg, 96.4 µmol, 88%).

1H NMR (CDCl3, 400 MHz) δ = 8.63 (d, J = 8.8 Hz, 1H, H1), 8.42 (d, J = 2.0 Hz, 1H, H4), 8.15 (d, J = 1.2 Hz, 1H, H3), 8.02 (d, J = 8.0 Hz, 1H, H5), 7.91 (d, J = 8.8 Hz, 1H, H6), 7.87 (d, J = 8.4 Hz, 1H, H7), 7.76 (d, J = 1.6 Hz, 1H, H8), 7.74 (dd, J = 1.8, 8.6 Hz, 1H, H9), 7.68 (t, J = 7.2 Hz, 1H, H10), 1.51 ppm (s, 9H, tBu), and 1.49 ppm (s, 9H, tBu); 13C NMR (CDCl3) δ = 169.37, 144.99, 143.75, 143.16, 140.94, 137.82, 129.65, 128.98, 127.98, 127.11, 126.11, 125.97, 124.39, 122.83, 119.76, 119.68, 117.44, 112.72, 107.17, 35.21, 35.04, 32.06, and 31.96 ppm; HR-MS (APCI): m/z = 474.2028. calcd for C29H27N4B3S1: 474.2049 [M]+; UV/Vis (CH2Cl2) λmax (ε) = 304 (12200), 332 (14000), 343 (14000), and 499 nm (14600 mol⁻¹dm³cm⁻¹).

**Synthesis of 5.** To a solution of 1a (72.7 mg 163 µmol) in dry CH2Cl2 (10 mL) was added EtMgBr (1 M in hexane, 0.50 mL, 0.5 mmol) under N2, and the mixture was stirred at r.t. for 30 min. Water was added, and organic products were extracted with CHCl3. The extracts were dried over Na2SO4 and evaporated. The residue was purified by silica gel chromatography with CHCl3/hexane to give 5 as a red solid (23.4 mg, 50.4 µmol, 31%).

1H NMR (CDCl3) δ = 8.49 (d, J = 8.8 Hz, 1H, H3), 8.26 (d, J = 2.0 Hz, 1H, H4), 8.12 (d, J = 2.0 Hz, 1H, H5), 7.89 (dd, J = 0.8, 8.0 Hz, 1H, H6), 7.70 (d, J = 8.8 Hz, 1H, H7), 7.60 (d, J = 1.6 Hz, 1H, H8), 7.58 (t, J = 8.0 Hz, 1H, H9), 7.51 (dd, J = 2.0, 8.8 Hz, 1H, H10), 7.49 (t, J = 7.0 Hz, 1H, H11), 1.50 (s, 9H, tBu), 1.48 (s, 9H, tBu), 1.30 ppm (q, J = 7.6 Hz, 4H, CH2), and 0.37 ppm (t, J = 7.8 Hz, 6H,
CH$_3$; $^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$ = 169.16, 145.86, 142.30, 141.24, 140.73, 139.83, 130.05, 127.52, 126.13, 124.37, 124.28, 123.69, 122.31, 121.04, 119.35, 116.58, 113.59, 108.99, 34.87, 34.79, 32.21, 32.15, 14.83, and 9.65 ppm; HR-MS (APCI): $m/z = 480.2760$. calcd for C$_{31}$H$_{37}$N$_2$B$_3$S$_1$: 480.2782 [M$^+$]; UV/Vis (CH$_2$Cl$_2$) $\lambda_{max}$ ($\varepsilon$) = 313 (22600), 331 (19500), and 515 nm (14100 mol$^{-1}$dm$^3$cm$^{-1}$).

**Synthesis of 6.** A flask containing 1a (52.0 mg, 113 µmol) and AlCl$_3$ (25.4 mg, 191 µmol) was purged with N$_2$, charged with dry CH$_2$Cl$_2$ (10 mL), and heated at reflux for 10 min. After cooling to rt, dry MeOH (3.0 mL, 74 mmol) was added, and the mixture was stirred at rt for 30 min. The mixture was passed through basic alumina and evaporated. The residue was purified by silica gel chromatography with CHCl$_3$ to give 6 as a yellow solid (29.9 mg, 61.8 µmol, 55%).

$^1$H NMR (CDCl$_3$) $\delta$ = 8.91 (d, $J = 8.4$ Hz, 1H, H$^1$), 8.39 (d, $J = 1.6$ Hz, 1H, H$^4$), 8.14 (d, $J = 2.0$ Hz, 1H, H$^5$), 7.92 (d, $J = 8.4$ Hz, 1H, H$^6$), 7.91 (d, $J = 7.6$ Hz, 1H, H$^7$), 7.80 (d, $J = 1.2$ Hz, 1H, H$^8$), 7.64 (t, $J = 7.2$ Hz, 1H, H$^9$), 7.60 (dd, $J = 2.0$, 8.8 Hz, 1H, H$^b$), 7.53 (t, $J = 7.6$ Hz, 1H, H$^i$), 2.90 (s, 6H, OMe), 1.54 (s, 9H, tBu), and 1.49 ppm (s, 9H, tBu); $^{13}$C NMR (CDCl$_3$) $\delta$ = 168.85, 145.63, 143.16, 142.45, 141.52, 140.43, 129.75, 128.24, 126.59, 125.55, 125.13, 124.21, 123.72, 122.28, 121.85, 119.34, 116.60, 114.01, 108.70, 50.09, 35.08, 34.95, and 32.19 ppm; HR-MS (APCI): $m/z = 484.2352$. calcd for C$_{29}$H$_{33}$N$_2$O$_2$B$_3$S$_1$: 484.2355 [M$^+$]; UV/Vis (CH$_2$Cl$_2$) $\lambda_{max}$ ($\varepsilon$) = 301 (14000), 324 (16800), and 462 nm (14800 mol$^{-1}$dm$^3$cm$^{-1}$).

![Scheme S2](image)

**Scheme S2** Synthesis of 3b–f.

**Synthesis of 3b.** 3b (Orange solid, 63.4 mg, 124 µmol, 82%) was synthesized from 1b$^{[S1]}$ (53.0 mg, 152 µmol) via a method similar to the synthesis of 3a.

$^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ = 9.23 (d, $J = 8.8$ Hz, 1H, H$^1$), 8.33 (d, $J = 8.0$ Hz, 1H, H$^4$), 8.27 (d, $J = 7.2$ Hz, 1H, H$^5$), 8.14 (d, $J = 8.0$ Hz, 1H, H$^d$), 7.94 (d, $J = 8.4$ Hz, 1H, H$^h$), 7.76 (t, $J = 7.2$ Hz,
1H, H\text{I}), 7.75 (d, J = 7.2 Hz, 1H, H\text{II}), 7.61 (t, J = 8.0 Hz, 1H, H\text{III}), 7.59 (t, J = 8.4 Hz, 1H, H\text{IV}), 7.36–7.31 (m, 5H, H\text{V}, oPh), and 7.23–7.17 ppm (m, 7H, H\text{VI}, mPh, pPh); \text{^{13}C} \text{NMR} (\text{CDCl}_{3}, 100 MHz) \delta = 167.22, 145.23, 144.02, 139.33, 131.74, 129.92, 128.07, 127.75, 127.49, 126.84, 126.65, 125.15, 124.88, 124.25, 122.79, 122.65, 121.99, 120.65, 119.93, 118.01, 115.07, 108.98, and 98.37 ppm; HR-MS (APCI): m/z = 512.1525. calcld for C\text{_{35}H}_{\text{21}N}_{\text{2}B}_{\text{3}S}_{\text{1}}: 512.1530 [M]\text{^+}; \text{UV/Vis} (\text{CH}_{\text{2}Cl}_{\text{2}}) \lambda_{\text{max}} (\epsilon) = 301 (17000), 324 (15900), and 482 nm (14400 \text{ mol}^{-1} \text{ dm}^{3} \text{ cm}^{-1}).

**Synthesis of 3c.** 3c (purple solid, 56.0 mg, 97.9 \text{ \mu mol}, 82%) was synthesized from 1c\text{[SI]} (48.6 mg, 119 \text{ \mu mol}) via a method similar to the synthesis of 3a.

\text{^1H} \text{NMR} (\text{CDCl}_{3}, 400 MHz) \delta = 9.20 (d, J = 8.4 Hz, 1H, H\text{I}), 8.19 (d, J = 8.8 Hz, 1H, H\text{II}), 7.84 (d, J = 7.6 Hz, 1H, H\text{III}), 7.79 (d, J = 2.4 Hz, 1H, H\text{IV}), 7.73 (t, J = 8.0 Hz, 1H, H\text{V}), 7.54 (d, J = 2.0 Hz, 1H, H\text{VI}), 7.51 (t, J = 7.6 Hz, 1H, H\text{VII}), 7.35–7.33 (m, 4H, oPh), 7.23 (dd, J = 2.2, 9.0 Hz, 1H, H\text{VIII}), 7.21–7.18 (m, 7H, H\text{IX}, mPh, pPh), 3.92 (s, 3H, OMe), and 3.86 ppm (s, 3H, OMe); \text{^{13}C} \text{NMR} (\text{CDCl}_{3}, 100 MHz) \delta = 166.51, 154.00, 152.48, 145.26, 139.66, 135.79, 131.72, 129.93, 128.09, 127.71, 127.48, 126.74, 125.69, 124.92, 124.22, 124.54, 121.98, 116.14, 115.48, 114.25, 108.62, 108.27, 103.58, 98.29, 56.80, and 56.18 ppm; HR-MS (APCI): m/z = 572.1756. calcld for C\text{_{37}H}_{\text{25}N}_{\text{2}O}_{\text{2}B}_{\text{3}S}_{\text{1}}: 572.1742 [M]\text{^+}; \text{UV/Vis} (\text{CH}_{\text{2}Cl}_{\text{2}}) \lambda_{\text{max}} (\epsilon) = 319 (16600), 348 (14400), and 534 nm (11600 \text{ mol}^{-1} \text{ dm}^{3} \text{ cm}^{-1}).

**Synthesis of 3d.** 3d (red solid, 37.5 mg, 56.4 \text{ \mu mol}, 56%) was synthesized from 1d\text{[SI]} (50.4 mg, 101 \text{ \mu mol}) via a method similar to the synthesis of 3a.

\text{^1H} \text{NMR} (\text{CDCl}_{3}, 400 MHz) \delta = 9.24 (d, J = 8.8 Hz, 1H, H\text{I}), 8.49 (d, J = 1.2 Hz, 1H, H\text{II}), 8.39 (d, J = 8.0 Hz, 1H, H\text{III}), 8.34 (d, J = 1.6 Hz, 1H, H\text{IV}), 7.91 (d, J = 7.6 Hz, 1H, H\text{V}), 7.88 (d, J = 1.6 Hz, 1H, H\text{VI}), 7.87 (dd, J = 1.6, 8.4 Hz, 1H, H\text{VII}), 7.78–7.74 (m, 3H, H\text{VIII}, oPh), 7.69 (d, J = 7.2 Hz, 2H, oPh), 7.55 (t, J = 7.4 Hz, 1H, H\text{IX}), 7.51–7.46 (m, 4H, mPh), 7.38–7.33 (m, 6H, pPh, oPh), and 7.23–7.18 ppm (m, 6H, mPh, pPh); \text{^{13}C} \text{NMR} (\text{CDCl}_{3}, 100 MHz) \delta = 167.05, 145.26, 143.98, 142.40, 141.23, 139.29, 133.50, 132.19, 131.77, 129.94, 129.09, 128.86, 128.12, 127.85, 127.57, 127.54, 127.31, 127.10, 126.95, 126.61, 126.55, 126.50, 125.86, 124.96, 124.82, 122.66, 122.08, 121.81, 119.34, 115.19, 109.26, and 98.54 ppm; HR-MS (APCI): m/z = 665.2195. calcld for C\text{_{47}H}_{\text{30}N}_{\text{2}B}_{\text{3}S}_{\text{1}}: 665.2225 [M+H]\text{^+}; \text{UV/Vis} (\text{CH}_{\text{2}Cl}_{\text{2}}) \lambda_{\text{max}} (\epsilon) = 255 (55100), 311 (32900), and 503 nm (12400 \text{ mol}^{-1} \text{ dm}^{3} \text{ cm}^{-1}).
Synthesis of 3e. 3e (Orange solid, 53.8 mg, 71.8 µmol, 80%) was synthesized from 1e\(^{[61]}\) (52.8 mg, 90.3 µmol) via a method similar to the synthesis of 3a.

\(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta = 9.25\) (d, \(J = 8.8\) Hz, 1H, H\(^a\)), 8.34 (d, \(J = 8.8\) Hz, 1H, H\(^b\)), 7.98 (d, \(J = 0.8\) Hz, 1H, H\(^c\)), 7.95 (d, \(J = 7.6\) Hz, 1H, H\(^d\)), 7.84 (d, \(J = 0.8\) Hz, 1H, H\(^e\)), 7.77 (t, \(J = 8.8\) Hz, 1H, H\(^f\)), 7.59 (t, \(J = 8.4\) Hz, 1H, H\(^g\)), 7.54 (d, \(J = 1.2\) Hz, 1H, H\(^h\)), 7.38–7.35 (m, 5H, H, Ph), 7.21–7.19 (m, 6H, mPh, pPh), 7.03 (s, 2H, Mes), 7.00 (s, 2H, Mes), 2.38 (s, 3H, Me), 2.37 (s, 3H, Me), 2.114 (s, 1H, NH), 1.10 g, 2.03 mmol) and evaporated. The residue was purified by silica gel chromatography with EtOAc column and evaporated. The residue was purified by silica gel chromatography with CHCl\(_3\)/hexane to give the desired product as a white solid (1.21 g, 2.24 mmol, 88%).

Synthesis of 3,6-bis(3,5-di-tert-butylphenyl)carbazole. A solution of 3,6-dibromocarbazole (825 mg, 2.54 mmol), 3,5-di-tert-butylphenylboronic acid (2.39 g, 10.2 mmol), Pd(PPh\(_3\))\(_4\) (194 mg, 168 µmol), and NaHCO\(_3\) (2.12 g, 25.2 mmol) in toluene/EtOH/H\(_2\)O (18/12/12 mL) was degassed and heated at 100 °C for 12 h under N\(_2\). After cooling to rt, organic products were extracted with EtOAc, and the extracts were passed through a silica gel column with EtOAc and evaporated. The residue was purified by silica gel chromatography with CHCl\(_3\)/hexane to give the desired product as a white solid (1.21 g, 2.24 mmol, 88%).

\(^1\)H NMR (CDCl\(_3\)) \(\delta = 8.43\) (d, \(J = 1.2\) Hz, 1H, H\(^a\)), 8.02 (s, 1H, NH), 7.77 (dd, \(J = 1.6\) Hz, 8H, 2H, H\(^e\)), 7.65 (d, \(J = 1.6\) Hz, 4H, Ar), 7.55 (t, \(J = 1.6\) Hz, 2H, Ar), 7.50 (d, \(J = 8.8\) Hz, 1H, H\(^h\)), and 1.53 ppm (s, 36H, \(t\)Bu); \(^{13}\)C NMR (CDCl\(_3\)) \(\delta = 151.21, 141.74, 139.39, 134.68, 126.19, 124.01, 122.18, 120.90, 119.31, 110.95, 35.17, and 31.77 ppm. HR-MS (APCI): \(m/z = 544.3911\). calcd for C\(_{40}\)H\(_{50}\)N\(_1\): 544.3938 [M+H]

Synthesis of 3,6-bis(3,5-di-tert-butylphenyl)-1-bromocarbazole. To a solution of 3,6-bis(3,5-di-tert-butylphenyl)carbazole (1.10 g, 2.03 mmol) was added NBS (365 mg, 2.05 mmol) at 0 °C, and the mixture was stirred at 0 °C for 3 h in the dark. The mixture was evaporated, and the residue was purified by silica gel chromatography with CHCl\(_3\)/hexane to give the desired product as a white solid (1.12 g, 1.80 mmol, 89%).

\(^1\)H NMR (CDCl\(_3\)) \(\delta = 8.42\) (d, \(J = 1.6\) Hz, 1H, H\(^a\)), 8.37 (d, \(J = 0.8\) Hz, 1H, H\(^b\)), 8.35 (s, 1H, NH), 7.94 (d, \(J = 1.2\) Hz, 1H, H\(^c\)), 7.84 (dd, \(J = 1.4\) Hz, 8H, 1H, H\(^d\)), 7.66 (d, \(J = 1.6\) Hz, 2H, Ar), 7.63 (d, \(J = 8.4\) Hz, 1H, H\(^e\)), 7.62 (d, \(J = 1.6\) Hz, 2H, Ar), 7.59 (t, \(J = 1.6\) Hz, 1H, Ar), 7.58 (t, \(J = 1.6\) Hz,
1H, Ar), 1.549 (s, 18H, tBu), and 1.545 ppm (s, 18H, tBu); 13C NMR (CDCl3) δ = 151.39, 151.27, 141.47, 140.62, 139.00, 137.92, 136.25, 135.34, 128.05, 126.92, 125.18, 124.45, 122.16, 121.34, 121.06, 119.78, 118.47, 111.37, 104.41, 35.18, and 31.77 ppm; HR-MS (APCI): m/z = 622.2889. calcd for C40H47N3Br1: 622.2880 [M–H]–.

Synthesis of 7f. A suspension of 3,6-bis(3,5-di-tert-butylphenyl)-1-bromocarbazole (1.09 g, 1.75 mmol), benzothiazole (0.58 mL, 5.4 mmol), Pd(OAc)2 (29.7 mg, 132 μmol), Cu(OAc)2·H2O (73.2 mg, 366 μmol), PPh3 (248 mg, 946 μmol), and K2CO3 (521 mg, 3.78 mmol) in dry toluene (3.0 mL) was degassed and heated at reflux for 15 h under N2. After the solvent was removed, the residue was purified by silica gel chromatography with CHCl3/hexane to give 7f as a yellow solid (511 mg, 755 μmol, 43%). 1H NMR (CDCl3) δ = 11.05 (s, 1H, NH), 8.45 (d, J = 1.2 Hz, 1H, Hα or Hβ), 8.38 (s, 1H, Hβ), 8.23 (d, J = 8.0 Hz, 1H, Hγ or Hδ), 8.16 (d, J = 1.2 Hz, 1H, Hδ or Hγ), 7.97 (d, J = 7.6 Hz, 1H, Hγ or Hδ), 7.78 (dd, J = 1.6, 8.0 Hz, 1H, Hβ), 7.73 (d, J = 8.0 Hz, 1H, Hγ), 7.59 (d, J = 1.2 Hz, 2H, Ar), 7.57–7.55 (m, 3H, H6 or H7 and Ar), 7.52 (t, J = 1.8 Hz, 1H, Ar), 7.47 (t, J = 1.6 Hz, 1H, Ar), 7.45 (t, J = 8.4 Hz, 1H, Hγ or Hδ), 1.47 (s, 18H, tBu), and 1.45 ppm (s, 18H, tBu); 13C NMR (CDCl3) δ = 168.04, 154.15, 151.50, 151.23, 141.64, 141.20, 139.76, 137.27, 135.05, 134.56, 133.90, 126.83, 126.53, 125.50, 125.42, 125.38, 123.43, 122.97, 122.43, 122.30, 122.19, 121.79, 121.38, 120.98, 119.52, 115.98, 111.71, 35.23, 35.18, and 31.78 ppm; HR-MS (APCI): m/z = 675.3801. calcd for C41H51N2S1: 675.3778 [M–H]–.

Synthesis of 1f. 7f (536 mg, 792 μmol) was dissolved in dry toluene (10 mL). tPr2NEt (1.0 mL, 5.8 mmol) and then BF3·OEt2 (0.24 mL, 1.9 mmol) were added, and the mixture was heated at 100 °C for 1 h under N2. After the solvents were removed, the residue was purified by silica gel chromatography with CHCl3/hexane to give 1f as a yellow solid (530 mg, 731 μmol, 92%). 1H NMR (CDCl3) δ = 8.66 (d, J = 8.0 Hz, 1H, Hβ), 8.56 (s, 1H, Hδ), 8.36 (s, 1H, Hδ), 8.07 (d, J = 8.0 Hz, 1H, Hα), 8.03 (s, 1H, Hγ), 7.94 (d, J = 8.0 Hz, 1H, Hδ), 7.85 (dd, J = 1.4, 8.0 Hz, 1H, Hβ), 7.74 (t, J = 7.6 Hz, 1H, Hβ), 7.59 (t, J = 7.6 Hz, 1H, Hδ), 7.57 (d, J = 2.0 Hz, 2H, Ar), 7.54–7.53 (m, 3H, Ar), 7.47 (s, 1H, Ar), 1.46 (s, 18H, tBu), and 1.44 ppm (s, 18H, tBu); 13C NMR (CDCl3) δ = 168.28, 151.70, 151.24, 144.36, 143.16, 141.60, 140.72, 139.99, 136.04, 134.80, 129.44, 128.84, 127.63, 127.28, 127.23, 126.10, 124.82, 122.45, 122.32, 122.24, 121.69, 121.06, 119.94, 114.46, 108.93, 35.24, 35.18, and 31.77 ppm; HR-MS (APCI): m/z = 725.3881. calcd for C42H52N2S1Br2F2: 725.3915 [M+H]++; UV/Vis (CH2Cl2) λmax (ε) = 328 (21900), 341 (22100), and 470 nm (17400 mol–1 dm3 cm–1).
Synthesis of 3f. 3f (red solid, 60.5 mg, 71.8 µmol, 60%) was synthesized from 1f (82.0 mg, 113 µmol) via a method similar to the synthesis of 3a. 1H NMR (CDCl3) δ = 9.26 (d, J = 8.0 Hz, 1H, H1), 8.51 (d, J = 1.2 Hz, 1H, H3), 8.39 (d, J = 8.8 Hz, 1H, H5), 8.37 (d, J = 1.2 Hz, 1H, H6), 7.96 (d, J = 8.4 Hz, 1H, H4), 7.94 (d, J = 1.2 Hz, 1H, H8), 7.86 (dd, J = 1.6, 8.8 Hz, 1H, H8), 7.78 (t, J = 7.2 Hz, 1H, Hb), 7.60 (t, J = 7.6 Hz, 1H, Hf), 7.59 (d, J = 1.6 Hz, 2H, Ar), 7.53 (d, J = 2.0 Hz, 2H, Ar), 7.51 (t, J = 2.0 Hz, 1H, Ar), 7.44 (t, J = 2.0 Hz, 1H, Ar), 7.37–7.35 (m, 4H, oPh), 7.20–7.19 (m, 6H, mPh, pPh), 1.45 (s, 18H, tBu), and 1.44 ppm (s, 18H, tBu); 13C NMR (CDCl3) δ = 167.20, 151.59, 151.11, 145.37, 143.87, 142.00, 141.07, 139.26, 134.97, 133.69, 131.80, 130.01, 128.08, 127.88, 127.51, 127.21, 127.01, 125.82, 124.90, 124.85, 122.74, 122.32, 122.13, 122.04, 121.45, 120.76, 119.57, 115.11, 109.14, 98.46, 35.23, 35.18, 31.79, and 31.77 ppm; HR-MS (APCI): m/z = 889.4740. calcd for C63H62N2B1S1: 889.4732 [M+H]+; UV/Vis (CH2Cl2) λmax (ε) = 306 (33000), 345 (18000), and 507 nm (12700 mol⁻¹dm³cm⁻¹).

Scheme S3  Synthesis of 3g–n.

Synthesis of 3g. 3g (red solid, 47.3 mg, 72.5 µmol, 76%) was synthesized from 1e (55.5 mg, 94.9 µmol) with 2-ethynyltoluene via a method similar to the synthesis of 3a. 1H NMR (CDCl3) δ = 9.31 (d, J = 8.4 Hz, 1H, H1), 8.41 (d, J = 8.0 Hz, 1H, H3), 8.00 (s, 1H, H5), 7.95 (d, J = 7.6 Hz, 1H, H4), 7.86 (s, 1H, H6), 7.75 (t, J = 7.8 Hz, 1H, H8), 7.60 (t, J = 7.6 Hz, 1H, Hf), 7.55 (s, 1H, Hb), 7.36 (d, J = 8.4 Hz, 1H, H8), 7.29 (d, J = 7.6 Hz, 2H, o-tolyl), 7.12–7.10 (m, 4H, o-tolyl), 7.04–7.01 (m, 6H, o-tolyl, Mes), 2.39 (s, 3H, Me), 2.38 (s, 9H, Me), 2.13 (s, 6H, Me), and 2.11 ppm (s, 6H, Me); 13C NMR (CDCl3) δ = 167.23, 145.27, 143.05, 140.28, 140.64, 138.72, 138.60, 137.22, 136.98, 136.90, 136.42, 132.74, 131.92, 130.95, 129.96, 129.29, 128.67, 128.41, 128.21, 128.14, 127.69, 127.54, 126.95, 125.69, 125.30, 124.66, 124.38, 123.43, 122.92, 122.01, 121.11, 115.16, 109.06, 97.48, 21.28, 21.24, and 21.08 ppm; HR-MS (APCI): m/z = 776.3429. calcd for C53H45N2B1S1: 776.3411 [M]+; UV/Vis (CH2Cl2) λmax (ε) = 308 (18600), 329 (15700), and 498 nm (12700 mol⁻¹dm³cm⁻¹).
Synthesis of 3h.  3h (Orange solid, 38.5 mg, 60.0 µmol, 58%) was synthesized from 1e (60.4 mg, 103 µmol) with 3-ethynyltoluene via a method similar to the synthesis of 3a.

\(^1\)H NMR (CDCl\(_3\)) \(\delta = 9.24\) (d, \(J = 8.0\) Hz, 1H, \(H^f\)), 8.34 (d, \(J = 8.8\) Hz, 1H, H\(^g\)), 7.98 (d, \(J = 0.8\) Hz, 1H, H\(^i\)), 7.94 (d, \(J = 8.0\) Hz, 1H, H\(^i\)), 7.84 (d, \(J = 0.8\) Hz, 1H, H\(^i\)), 7.77 (t, \(J = 7.6\) Hz, 1H, H\(^b\)), 7.59 (t, \(J = 7.6\) Hz, 1H, H\(^b\)), 7.53 (d, \(J = 0.8\) Hz, 1H, H\(^i\)), 7.37 (dd, \(J = 1.6, 8.0\) Hz, 1H, H\(^b\)), 7.20 (s, 2H, m-tolyl), 7.17 (d, \(J = 8.0\) Hz, 2H, m-tolyl), 7.09 (t, \(J = 7.6\) Hz, 2H, m-tolyl), 7.03 (s, 2H, Mes), 7.01 (d, \(J = 7.6\) Hz, 2H, m-tolyl), 7.00 (s, 2H, Mes), 2.38 (s, 3H, Me), 2.37 (s, 3H, Me), 2.24 (s, 6H, Me), 2.113 (s, 6H, Me), and 2.110 ppm (s, 6H, Me); \(^{13}\)C NMR (CDCl\(_3\)) \(\delta = 167.14, 145.38, 143.15, 140.07, 138.71, 138.63, 137.69, 137.21, 136.97, 136.40, 132.68, 132.42, 130.92, 129.97, 128.85, 128.60, 128.40, 128.14, 128.00, 127.84, 126.90, 125.71, 124.74, 124.38, 123.37, 122.79, 121.96, 121.11, 114.97, 109.07, 98.54, 21.32, and 21.26 ppm; HR-MS (APCI): \(m/z = 776.3424\). caleld for \(C_{55}H_{45}N_2B_3Si\): 776.3411 \([M]\); UV/Vis (CH\(_2\)Cl\(_2\)) \(\lambda_{max} (\varepsilon) = 308\) (19000), 329 (15900), and 497 nm (13500 mol\(^{-1}\) dm\(^3\) cm\(^{-1}\)).

Synthesis of 3i.  3i (Orange solid, 54.7 mg, 70.4 µmol, 70%) was synthesized from 1e (58.5 mg, 100 µmol) with 4-ethynyltoluene via a method similar to the synthesis of 3a.

\(^1\)H NMR (CDCl\(_3\)) \(\delta = 9.26\) (d, \(J = 8.4\) Hz, 1H, H\(^i\)), 8.35 (d, \(J = 8.4\) Hz, 1H, H\(^g\)), 7.98 (d, \(J = 1.2\) Hz, 1H, H\(^i\)), 7.93 (d, \(J = 7.6\) Hz, 1H, H\(^i\)), 7.84 (d, \(J = 1.2\) Hz, 1H, H\(^i\)), 7.76 (t, \(J = 7.2\) Hz, 1H, H\(^b\)), 7.57 (t, \(J = 8.4\) Hz, 1H, H\(^b\)), 7.53 (d, \(J = 1.2\) Hz, 1H, H\(^i\)), 7.37 (dd, \(J = 1.6, 8.4\) Hz, 1H, H\(^b\)), 7.26 (d, \(J = 8.0\) Hz, 4H, p-tolyl), 7.03 (s, 2H, Mes), 7.01 (d, \(J = 8.0\) Hz, 4H, p-tolyl), 7.00 (s, 2H, Mes), 2.39 (s, 3H, Me), 2.37 (s, 3H, Me), 2.28 (s, 6H, Me), and 2.12 ppm (s, 12H, Me); \(^{13}\)C NMR (CDCl\(_3\)) \(\delta = 167.08, 145.40, 143.16, 140.08, 138.70, 138.64, 137.43, 137.19, 136.96, 136.38, 132.65, 131.67, 130.88, 129.98, 128.84, 128.55, 128.40, 128.35, 128.13, 127.77, 126.87, 125.70, 124.37, 123.37, 122.84, 121.94, 121.90, 121.10, 114.97, 109.09, 98.51, 21.53, 21.33, 21.26, and 21.23 ppm; HR-MS (APCI): \(m/z = 776.3418\). caleld for \(C_{55}H_{45}N_2B_3Si\): 776.3411 \([M]\); UV/Vis (CH\(_2\)Cl\(_2\)) \(\lambda_{max} (\varepsilon) = 308\) (16500), 329 (16100), and 497 nm (13300 mol\(^{-1}\) dm\(^3\) cm\(^{-1}\)).

Synthesis of 3j.  3j (Orange solid, 31.4 mg, 37.6 µmol, 36%) was synthesized from 1e (60.9 mg, 104 µmol) with 2-ethynyl-1,3,5-trimethylbenzene via a method similar to the synthesis of 3a.

\(^1\)H NMR (CDCl\(_3\)) \(\delta = 9.36\) (d, \(J = 8.0\) Hz, 1H, H\(^i\)), 8.45 (d, \(J = 8.0\) Hz, 1H, H\(^i\)), 7.98 (s, 1H, H\(^d\)), 7.94 (d, \(J = 7.6\) Hz, 1H, H\(^i\)), 7.83 (s, 1H, H\(^i\)), 7.71 (t, \(J = 8.0\) Hz, 1H, H\(^b\)), 7.58 (t, \(J = 7.8\) Hz, 1H,
H), 7.54 (s, 1H, Hf), 7.32 (d, J = 8.4 Hz, 1H, Hb), 7.03 (s, 2H, Mes), 7.00 (s, 2H, Mes), 6.74 (s, 4H, Mes), 2.39 (s, 3H, Me), 2.37 (s, 3H, Me), 2.23 (s, 12H, Me), 2.20 (s, 6H, Me), 2.13 (s, 6H, Me), and 2.08 ppm (s, 6H, Me); 13C NMR (CDCl3) δ = 167.15, 145.24, 142.99, 140.11, 138.74, 138.67, 137.19, 137.03, 136.88, 136.76, 136.40, 132.63, 130.80, 129.90, 128.65, 128.39, 128.12, 127.92, 127.38, 126.95, 125.66, 124.27, 123.39, 123.33, 121.90, 121.63, 120.93, 115.64, 109.06, 96.46, 21.35, 21.30, 21.22, and 21.11 ppm; HR-MS (APCI): m/z = 832.4047. calcd for C_{59}H_{53}N_2B_{3}S_1: 832.4038 [M]⁺; UV/Vis (CH_2Cl_2) λ_max (ε) = 308 (18400), 330 (15700), and 499 nm (12900 mol⁻¹dm³cm⁻¹).

**Synthesis of 3k.** 3k (Orange solid, 105 mg, 138 µmol, 90%) was synthesized from 1e (89.5 mg, 153 µmol) with cyclohexylacetylene via a method similar to the synthesis of 3a.

1H NMR (CDCl3) δ = 9.22 (d, J = 8.4 Hz, 1H, Hf), 8.26 (d, J = 8.4 Hz, 1H, Ha), 7.94 (d, J = 1.2 Hz, 1H, Hb), 7.87 (d, J = 7.6 Hz, 1H, Hg), 7.80 (d, J = 0.8 Hz, 1H, Hc), 7.68 (t, J = 8.0 Hz, 1H, Hc), 7.53 (t, J = 7.6 Hz, 1H, Hg), 7.47 (s, 1H, Hc), 7.31 (dd, J = 1.6, 8.0 Hz, 1H, Hc), 7.02 (s, 2H, Mes), 6.99 (s, 2H, Mes), 2.44–2.37 (m, 2H, c-hex), 2.38 (s, 3H, Me), 2.37 (s, 3H, Me), 2.11 (s, 12H, Me), 1.75–1.67 (m, 8H, c-hex), 1.49–1.41 (m, 6H, c-hex), and 1.38–1.24 ppm (m, 6H, c-hex); 13C NMR (CDCl3) δ = 166.72, 145.44, 143.14, 140.21, 138.78, 138.68, 137.09, 136.99, 136.94, 136.29, 132.24, 130.44, 130.01, 128.36, 128.26, 128.11, 127.88, 127.14, 126.65, 125.60, 124.27, 123.43, 123.16, 121.69, 120.89, 115.23, 109.12, 103.28, 32.96, 29.91, 26.27, 24.72, 21.25, and 21.22 ppm; HR-MS (APCI): m/z = 760.4030. calcd for C_{53}H_{53}N_2B_{3}S_1: 760.4037 [M]⁺; UV/Vis (CH_2Cl_2) λ_max (ε) = 309 (16500), 340 (16100), and 497 nm (13300 mol⁻¹dm³cm⁻¹).

**Synthesis of 3l.** 3l (Orange solid, 51.4 mg, 70.1 µmol, 69%) was synthesized from 1e (59.2 mg, 101 µmol) with cyclopentylacetylene via a method similar to the synthesis of 3a.

1H NMR (CDCl3) δ = 9.11 (d, J = 8.8 Hz, 1H, Hf), 8.19 (d, J = 8.0 Hz, 1H, Hc), 7.92 (d, J = 0.8 Hz, 1H, Hb), 7.89 (d, J = 8.4 Hz, 1H, Hc), 7.79 (d, J = 0.8 Hz, 1H, Hc), 7.69 (t, J = 7.4 Hz, 1H, Hb), 7.54 (t, J = 7.4 Hz, 1H, Hc), 7.47 (d, J = 0.8 Hz, 1H, Hc), 7.31 (dd, J = 1.4, 8.0 Hz, 1H, Hb), 7.02 (s, 2H, Mes), 6.99 (s, 2H, Mes), 2.60 (quin, J = 7.1 Hz, 2H, c-pent), 2.38 (s, 3H, Me), 2.36 (s, 3H, Me), 2.10 (s, 6H, Me), 2.09 (s, 6H, Me), 1.79–1.75 (m, 4H, c-pent), and 1.67–1.44 ppm (m, 12H, c-pent); 13C NMR (CDCl3) δ = 166.68, 145.47, 143.16, 140.21, 138.77, 138.66, 137.10, 137.00, 136.95, 136.30, 132.24, 130.44, 130.01, 128.36, 128.25, 128.12, 127.91, 127.17, 126.64, 125.57, 124.25, 123.27, 123.17, 121.69, 120.90, 115.10, 109.12, 103.48, 34.21, 34.17, 31.44, 24.95, 21.28,
21.25, and 21.22 ppm; HR-MS (APCI): \( m/z = 732.3740 \). calcld for C_{51}H_{49}N_{2}B_{1}S_{1}: 732.3724 [M];
UV/Vis (CH_{2}Cl_{2}) \( \lambda_{\text{max}} (\varepsilon) = 309 \) (16200), 338 (15900), and 496 nm (13600 mol^{-1}dm^{3}cm^{-1}).

**Synthesis of 3m.** 3m (Orange solid, 35.8 mg, 47.1 \( \mu \)mol, 45%) was synthesized from 1e (60.6 mg, 104 \( \mu \)mol) with 3-ethylthiophene via a method similar to the synthesis of 3a.

\(^1\)H NMR (CDCl_{3}) \( \delta = 9.20 \) (d, \( J = 8.4 \) Hz, 1H, \( H^f \)), 8.30 (d, \( J = 8.4 \) Hz, 1H, \( H^a \)), 7.98 (s, 1H, \( H^d \)), 7.94 (d, \( J = 8.0 \) Hz, 1H, \( H^f \)), 7.84 (s, 1H, \( H^e \)), 7.76 (t, \( J = 7.6 \) Hz, 1H, \( H^b \)), 7.58 (t, \( J = 7.8 \) Hz, 1H, \( H^b \)), 7.54 (s, 1H, \( H^e \)), 7.36 (d, \( J = 8.4 \) Hz, 1H, \( H^b \)), 7.30 (d, \( J = 2.8 \) Hz, 2H, thiophene), 7.15 (dd, \( J = 3.2 \), 5.2 Hz, 2H, thiophene), 7.04 (d, \( J = 4.4 \) Hz, 2H, thiophene), 7.03 (s, 2H, Mes), 7.00 (s, 2H, Mes), 2.39 (s, 3H, Me), 2.37 (s, 3H, Me), and 2.08 ppm (s, 12H, Me); \(^{13}\)C NMR (CDCl_{3}) \( \delta = 167.14, 145.32, 143.08, 140.00, 138.65, 138.56, 137.23, 136.94, 136.42, 132.78, 131.00, 130.38, 129.97, 128.64, 128.41, 128.15, 127.93, 127.82, 126.92, 125.69, 124.74, 124.38, 124.00, 123.41, 122.67, 122.02, 121.16, 114.84, 109.04, 93.24, 21.33, and 21.24 ppm; HR-MS (APCI): \( m/z = 760.2244 \). calcld for C_{49}H_{37}N_{2}B_{1}S_{3}: 760.2226 [M]; UV/Vis (CH_{2}Cl_{2}) \( \lambda_{\text{max}} (\varepsilon) = 308 \) (19000), 329 (16500), and 496 nm (14000 mol^{-1}dm^{3}cm^{-1}).

**Synthesis of 3n.** 3n (red solid, 19.4 mg, 25.5 \( \mu \)mol, 25%) was synthesized from 1e (59.0 mg, 101 \( \mu \)mol) with 2-ethylthiophene via a method similar to the synthesis of 3a.

\(^1\)H NMR (CDCl_{3}) \( \delta = 9.12 \) (d, \( J = 8.8 \) Hz, 1H, \( H^i \)), 8.25 (d, \( J = 8.0 \) Hz, 1H, \( H^a \)), 7.98 (d, \( J = 0.8 \) Hz, 1H, \( H^d \)), 7.94 (d, \( J = 7.6 \) Hz, 1H, \( H^f \)), 7.83 (s, 1H, \( H^e \)), 7.77 (t, \( J = 7.4 \) Hz, 1H, \( H^h \)), 7.59 (t, \( J = 7.6 \) Hz, 1H, \( H^b \)), 7.54 (d, \( J = 0.8 \) Hz, 1H, \( H^e \)), 7.36 (dd, \( J = 1.6 \), 8.4 Hz, 1H, \( H^b \)), 7.12 (d, \( J = 5.2 \) Hz, 2H, thiophene), 7.09 (d, \( J = 3.6 \) Hz, 2H, thiophene), 7.03 (s, 2H, Mes), 6.99 (s, 2H, Mes), 6.87 (dd, \( J = 3.8 \), 5.0 Hz, 2H, thiophene), 2.38 (s, 3H, Me), 2.36 (s, 3H, Me), 2.11 (s, 6H, Me), and 2.10 ppm (s, 6H, Me); \(^{13}\)C NMR couldn’t detect peaks for 3n because of the unstability; HR-MS (APCI): \( m/z = 760.2236 \). calcld for C_{49}H_{37}N_{2}B_{1}S_{3}: 760.2226 [M]; UV/Vis (CH_{2}Cl_{2}) \( \lambda_{\text{max}} (\varepsilon) = 331 \) (15100), 370 (4100), and 508 nm (9500 mol^{-1}dm^{3}cm^{-1}).

[B] Reference

[C] NMR spectra

1H NMR spectrum of 2 in CDCl₃

13C NMR spectrum of 2 in CDCl₃
1H NMR spectrum of 3a in CDCl₃

13C NMR spectrum of 3a in CDCl₃
$^1$H NMR spectrum of 4 in CDCl$_3$

$^{13}$C NMR spectrum of 4 in CDCl$_3$
$^1$H NMR spectrum of 5 in CDCl$_3$

$^{13}$C NMR spectrum of 5 in CDCl$_3$
$^1$H NMR spectrum of 6 in CDCl$_3$

$^{13}$C NMR spectrum of 6 in CDCl$_3$
$^{1}$H NMR spectrum of 3b in CDCl$_3$

$^{13}$C NMR spectrum of 3b in CDCl$_3$
$^1$H NMR spectrum of 3c in CDCl$_3$

$^{13}$C NMR spectrum of 3c in CDCl$_3$
S19

$^1$H NMR spectrum of 3d in CDCl$_3$

$^{13}$C NMR spectrum of 3d in CDCl$_3$
$^1$H NMR spectrum of 3e in CDCl$_3$

$^{13}$C NMR spectrum of 3e in CDCl$_3$
$^1$H NMR spectrum of 3,6-bis(3,5-di-tert-butylphenyl)carbazole in CDCl$_3$

$^{13}$C NMR spectrum of 3,6-bis(3,5-di-tert-butylphenyl)carbazole in CDCl$_3$
$^1$H NMR spectrum of 3,6-bis(3,5-di-tert-butylphenyl)-1-bromocarbazole in CDCl$_3$

$^{13}$C NMR spectrum of 3,6-bis(3,5-di-tert-butylphenyl)-1-bromocarbazole in CDCl$_3$
$^1$H NMR spectrum of 7f in CDCl$_3$

$^{13}$C NMR spectrum of 7f in CDCl$_3$
$^1$H NMR spectrum of 1f in CDCl$_3$

$^{13}$C NMR spectrum of 1f in CDCl$_3$
$^1$H NMR spectrum of 3f in CDCl$_3$

$^{13}$C NMR spectrum of 3f in CDCl$_3$
$^1$H NMR spectrum of 3g in CDCl$_3$

$^{13}$C NMR spectrum of 3g in CDCl$_3$
$^1$H NMR spectrum of $3h$ in CDCl$_3$
H NMR spectrum of 3i in CDCl₃

^{13}C NMR spectrum of 3i in CDCl₃
$^1$H NMR spectrum of $\textbf{3j}$ in CDCl$_3$

$^{13}$C NMR spectrum of $\textbf{3j}$ in CDCl$_3$
$^1$H NMR spectrum of 3k in CDCl$_3$

$^{13}$C NMR spectrum of 3k in CDCl$_3$
$^{1}$H NMR spectrum of 3m in CDCl$_3$

$^{13}$C NMR spectrum of 3m in CDCl$_3$
$^1$H NMR spectrum of 3n in CDCl$_3$
Fig. S1  UV/vis absorption (in CH$_2$Cl$_2$) and fluorescence (in CH$_2$Cl$_2$: dotted line, in the solid state: solid line) spectra of (a) 1–6, (b) 3a–f, (c) 3g–j and (d) 3k–n. Photographic images of the powdered compounds under black light ($\lambda = 365$ nm) are shown.
[E] Fluorescence Lifetime

(a)

(b)

(c)
Fig. S2  Fluorescence decay analyses of (a) 1a, (b) 2, (c) 3a, (d) 4, (e) 5 and (f) 6 in CH₂Cl₂ (left) and in the solid state (right)
[F] X-ray Crystal Structures

Single crystals of 2, 3a, 4, 3b, 3e and 3f were obtained by the vapor diffusion method (CH$_2$Cl$_2$/hexane for 2 and 3b, CH$_2$Cl$_2$/octane for 3a, CH$_2$Cl$_2$/MeOH for 4 and 3e, and CHCl$_3$/hexane for 3f). X-ray data at 93 K were taken on a Rigaku-Raxis-RAPIID imaging plate system with Cu-K$_\alpha$ radiation ($\lambda = 1.54187$ Å), and structures were processed and refined by CrystalStructure and Yadokari. All non-hydrogen atoms were refined anisotropically and the hydrogen atoms were calculated in ideal positions.

Crystallographic data for 2: formula: C$_{30}$H$_{37}$N$_2$S$_2$B$_1$:C$_6$H$_{14}$, $M_w$ = 662.74, monoclinic, space group $P2_1/a$, $a = 10.337(2)$, $b = 25.595(5)$, $c = 14.097(3)$ Å, $\beta = 97.574(5)^\circ$, $V = 3697.2(13)$ Å$^3$, $Z = 4$, $\rho_{calcd} = 1.191$ gcm$^{-3}$, $T = -180$ °C, 23880 measured reflections, 6549 unique reflections ($R_{int} = 0.0336$), $R_1 = 0.0568$ ($I > 2\sigma(I)$), $wR_2 = 0.1593$ (all data), GOF = 1.048.

Crystallographic data for 3a: formula: C$_{43}$H$_{52}$N$_2$S$_2$:CH$_2$Cl$_2$, $M_w$ = 709.54, triclinic, space group $P\overline{1}$, $a = 12.213(4)$, $b = 13.215(7)$, $c = 13.236(9)$ Å, $\alpha = 119.751(18)$, $\beta = 96.382(14)$, $\gamma = 91.1942(13)^\circ$, $V = 1836.0(17)$ Å$^3$, $Z = 2$, $\rho_{calcd} = 1.283$ gcm$^{-3}$, $T = -180$ °C, 22400 measured reflections, 5715 unique reflections ($R_{int} = 0.0695$), $R_1 = 0.0451$ ($I > 2\sigma(I)$), $wR_2 = 0.1261$ (all data), GOF = 1.056.

Crystallographic data for 4: formula: C$_{26}$H$_{27}$N$_4$S$_2$B$_1$, $M_w$ = 474.41, monoclinic, space group $P2_1/a$, $a = 11.733(3)$, $b = 9.921(2)$, $c = 21.775(5)$ Å, $\beta = 94.847(9)^\circ$, $V = 2525.6(10)$ Å$^3$, $Z = 4$, $\rho_{calcd} = 1.248$ gcm$^{-3}$, $T = -180$ °C, 24175 measured reflections, 4480 unique reflections ($R_{int} = 0.0465$), $R_1 = 0.0348$ ($I > 2\sigma(I)$), $wR_2 = 0.0997$ (all data), GOF = 1.041.

Crystallographic data for 3b: formula: C$_{35}$H$_{32}$N$_2$S$_2$:CH$_2$Cl$_2$, $M_w$ = 597.33, triclinic, space group $P\overline{1}$, $a = 10.523(3)$, $b = 11.578(3)$, $c = 12.402(6)$ Å, $\alpha = 97.230(11)$, $\beta = 102.026(15)$, $\gamma = 100.544(3)^\circ$, $V = 1431.6(9)$ Å$^3$, $Z = 2$, $\rho_{calcd} = 1.386$ gcm$^{-3}$, $T = -180$ °C, 17192 measured reflections, 4602 unique reflections ($R_{int} = 0.0406$), $R_1 = 0.0351$ ($I > 2\sigma(I)$), $wR_2 = 0.0929$ (all data), GOF = 1.051.

Crystallographic data for 3e: formula: C$_{33}$H$_{41}$N$_2$S$_3$B$_1$:CO, $M_w$ = 776.76, triclinic, space group $P\overline{1}$, $a = 11.071(3)$, $b = 12.310(4)$, $c = 15.729(5)$ Å, $\alpha = 99.083(14)$, $\beta = 96.913(9)$, $\gamma = 99.963(9)^\circ$, $V = 2060.7(11)$ Å$^3$, $Z = 2$, $\rho_{calcd} = 1.252$ gcm$^{-3}$, $T = -180$ °C, 26226 measured reflections, 6989 unique reflections ($R_{int} = 0.0285$), $R_1 = 0.0649$ ($I > 2\sigma(I)$), $wR_2 = 0.1792$ (all data), GOF = 1.074.

Crystallographic data for 3f: formula: C$_{65}$H$_{61}$N$_2$S$_4$B$_1$:2(CHCl$_3$), $M_w$ = 1127.74, triclinic, space group $P\overline{1}$, $a = 11.908(4)$, $b = 13.971(6)$, $c = 17.856(7)$ Å, $\alpha = 100.643(12)$, $\beta = 92.2079(10)$, $\gamma = 92.499(16)^\circ$, $V = 2913(2)$ Å$^3$, $Z = 2$, $\rho_{calcd} = 1.286$ gcm$^{-3}$, $T = -180$ °C, 35282 measured reflections, 9820 unique reflections ($R_{int} = 0.0702$), $R_1 = 0.0619$ ($I > 2\sigma(I)$), $wR_2 = 0.1859$ (all data), GOF = 1.009.

CCDC 1536630 (2), 1536632 (3a), 1536633 (4), 1536631 (3b), 1536634 (3e) and 1536635 (3f) contains the supplementary crystallographic data for this paper.
Fig. S3  Crystal structures of (a) 2, (b) 3a, (c) 4, (d) 3b, (e) 3e and (f) 3f. Hydrogen atoms are omitted for clarity. The thermal ellipsoids are drawn at the 50% probability level. Selected bond distances (Å) are shown. Mean plane deviations are calculated for the atoms excluding the peripheral substituents.
Fig. S4  Crystal packing of (a) 3a, (b) 3b, (c) 3e and (d) 3f. Hydrogen atoms are omitted for clarity. The thermal ellipsoids are drawn at the 50% probability level. Intermolecular distances are shown between the mean planes of the molecules, excluding the peripheral substituents.