One-Pot Synthesis of Boron-Doped Polycyclic Aromatic Hydrocarbons via 1,4-Boron Migration

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1. Materials and Methods

General methods and materials: 2,4,6-tri-tert-butylpyridine, boron tribromide (BBr₃) anhydrous trichlorobenzene were purchased from Aldrich, Acros Organics, the catalysts were sourced from Strem. All those chemicals were used as received without further purification. Anhydrous toluene and tetrahydrofuran were obtained from MBRAUN MB-SPS-5 solvent purification system. All the sensitive reactions were performed using standard vacuum-line and Schlenk techniques. Thin layer chromatography (TLC) was performed on silica-coated aluminum sheets with a fluorescence indicator (TLC silica gel 60 F254, purchased from Merck KGaA). Column chromatography was performed on silica (SiO₂, particle size 0.063-0.200 mm, purchased from VWR). NMR spectra were recorded on a Bruker AV-II 300 spectrometer operating at 300 MHz for ¹H, 75 MHz for ¹³C and 96 MHz for ¹¹B. ¹¹B NMR chemical shifts were referenced to the external standard boron signal of BF₃•Et₂O (δ = 0 ppm). CD₂Cl₂ (¹H, δ = 5.32 ppm, ¹³C, δ = 53.8 ppm) or C₂D₂Cl₄ (¹H, δ = 5.98 ppm; ¹³C, δ = 74.4 ppm) were used as solvent and TMS (δTMS = 0.00) was used as internal standard. The following abbreviations are used to describe peak patterns as appropriate: s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet. Dichloromethane-d₂ (99.9 atom% D) was purchased from Euriso-top. The high-resolution mass spectrometry (HRMS) analyses were performed by using Agilent Q-TOF (APCI mode using acetonitrile as solvent) instruments. UV-visible spectra were measured on an Agilent Cary 5000 UV-vis-NIR spectrophotometer by using 10 mm optical-path quartz cell at room temperature. Fluorescence spectra were recorded at room temperature on a Perkin-Elmer Fluorescence Spectrometer LS 55 using a 10 mm fluorescence quartz cell. Cyclic voltammetry (CV) was carried out on a PARSTAT4000 potentiostat (Princeton Applied Research, Ametek, Germany) in a three-electrode cell in degassed dry dichloromethane solution containing 0.1 M of tetra-n-butylammonium hexafluorophosphate (n-Bu₄NPF₆) at different scan rates at room temperature. A Pt wire, silver chloride-coated silver wire, and Pt disc electrode were used as the working electrode, the reference electrode, and the counter electrode, respectively. Ferrocene as the reference redox system (−4.8 eV) was used. Photoluminescence quantum yields (PLQYs) of thin films were measured on a Hamamatsu C9920-03 Absolute PLQY Measurement System. Excited-state lifetimes of thin films were measured on a Hamamatsu C11367-34 Quantaurus-Tau Fluorescence lifetime spectrometer.
2. Synthetic procedures

2a, 2c-2f, 2h-2j\textsuperscript{1-5} and 2p\textsuperscript{3} were synthesized according to the reported literature.

Synthesis of 2-((2-chlorophenyl)ethynyl)-1,1'-biphenyl (2b)

\[
\text{Br-} \begin{array}{c} \text{Cl} \\ \text{C} \end{array} + \text{B(OH)}_2 \xrightarrow{\text{Pd(PPh}_3)_4, \text{K}_2\text{CO}_3} \text{Br-} \begin{array}{c} \text{Cl} \\ \text{O} \end{array}
\]

A flask was charged with 1-bromo-2-((2-chlorophenyl)ethynyl)benzene\textsuperscript{6} (1.65 g, 5 mmol), phenylboronic acid (1.22 g, 10 mmol), and potassium carbonate (K\textsubscript{2}CO\textsubscript{3}) (2.7 g, 20 mmol) along with toluene (20 mL), ethanol (EtOH) (10 mL) and water (10 mL). The mixture was degassed by argon (Ar) bubbling for 30 mins and then tetrakis(triphenylphosphine)palladium(0) (Pd(PPh\textsubscript{3})\textsubscript{4}) (287 mg, 0.25 mmol) was added. The mixture was refluxed for 24 hours. The resulting crude precipitate was extracted with ethyl acetate and purified by silica gel column chromatography with iso-hexane/ dichloromethane (CH\textsubscript{2}Cl\textsubscript{2}) (10:1) as eluent to afford 2b as colorless oil (1.18 g, 82%).

\(^1\text{H} \text{NMR (300 MHz, CD}_2\text{Cl}_2): \delta 7.77 - 7.69 (m, 3H), 7.53 - 7.37 (m, 8H), 7.29 - 7.19 (m, 2H).\)

\(^{13}\text{C} \text{NMR (75 MHz, CD}_2\text{Cl}_2): \delta 144.24, 140.70, 135.92, 133.68, 133.59, 129.96, 129.74, 129.68, 129.58, 129.41, 128.42, 127.92, 127.53, 126.87, 123.55, 121.46, 94.59, 89.22. \text{HRMS (ACPI, m/z): calcd for C}_{20}\text{H}_{13}\text{Cl, 288.0706; observed 288.0701.}\)

Synthesis of 2-((2-chlorophenyl)ethynyl)-1,1'-biphenyl (2g)
A flask was charged with 2-bromo-3-(phenylethynyl)naphthalene (0.612 g, 2 mmol), phenylboronic acid (0.61 g, 5 mmol), and K$_2$CO$_3$ (1.08 g, 8 mmol) along with toluene (10 mL), EtOH (5 mL) and water (5 mL). The mixture was degassed by Ar bubbling for 30 mins and then Pd(PPh$_3$)$_4$ (110 mg, 0.1 mmol) was added. The mixture was refluxed for 24 hours. The resulting crude precipitate was extracted with ethyl acetate and purified by silica gel column chromatography with iso-hexane/ CH$_2$Cl$_2$ (10:1) as eluent to afford 2g as pale-yellow solid (0.52 g, 86%).

$^1$H NMR (300 MHz, CD$_2$Cl$_2$): $\delta$ 8.21 (s, 1H), 7.91 - 7.86 (m, 3H), 7.80 - 7.73 (m, 2H), 7.56 - 7.44 (m, 5H), 7.40 - 7.31 (m, 5H).

$^{13}$C NMR (75 MHz, CD$_2$Cl$_2$): $\delta$ 140.91, 140.84, 133.45, 133.11, 132.49, 131.61, 129.99, 128.72, 128.66, 128.27, 128.22, 127.91, 127.72, 127.50, 126.98, 123.65, 120.28, 92.89, 89.89.

HRMS (ACPI, m/z): calcd for C$_{24}$H$_{16}$, 304.1252; observed 304.1248.

**Synthesis of 2',5'-bis((4-(tert-butyl)phenyl)ethynyl)-1,1':4',1''-terphenyl (2k)**
A flask was charged with 4,4'-(2,5-dibromo-1,4-phenylene)bis(ethyne-2,1-diyl))bis(tert-buty1benzene) (1.65 g, 3 mmol), phenylboronic acid (1.83 g, 15 mmol), and K$_2$CO$_3$ (3.3 g, 24 mmol) along with toluene (20 mL), EtOH (10 mL) and water (10 mL). The mixture was degassed by Ar bubbling for 30 mins and then (Pd(PPh$_3$)$_4$) (345 mg, 0.3 mmol) was added. The mixture was refluxed for 24 hours. The resulting crude precipitate was extracted with ethyl acetate and purified by silica gel column chromatography with iso-hexane/CH$_2$Cl$_2$ (10:1) as eluent to afford 2k as white solid (1.3 g, 80%).

$^1$H NMR (300 MHz, CD$_2$Cl$_2$): δ 7.80 - 7.70 (m, 6H), 7.57 - 7.40 (m, 6H), 7.38 - 7.26 (m, 8H), 1.30 (s, 18H).

$^{13}$C NMR (75 MHz, CD$_2$Cl$_2$): δ 151.96, 142.30, 139.46, 133.65, 131.02, 129.28, 128.01, 127.80, 125.42, 121.71, 119.96, 34.70, 30.84. HRMS (ACPI, m/z): calcd for C$_{42}$H$_{38}$, 542.2974; observed 542.2965.

**Synthesis of 1,1'-(2,5-bis(4-(tert-butyl)phenyl)ethynyl)-1,4-phenylene)dinaphthalene (2l)**

A flask was charged with 4,4'-(2,5-dibromo-1,4-phenylene)bis(ethyne-2,1-diyl))bis(tert-buty1benzene) (1.65 g, 3 mmol), naphthalen-1-ylboronic acid (706 mg, 9 mmol), and K$_2$CO$_3$ (3.3 g, 24 mmol) along with toluene (20 mL), EtOH (10 mL) and water (10 mL). The mixture was degassed by Ar bubbling for 30 mins and then Pd(PPh$_3$)$_4$ (345 mg, 0.3 mmol) was added. The mixture was refluxed for 24 hours under Ar. The resulting crude precipitate was extracted with ethyl acetate and purified by silica gel column chromatography with iso-hexane/CH$_2$Cl$_2$ (10:1) as eluent to afford 2l as white powder (1.2 g, 62%).
$^1$H NMR (300 MHz, CD$_2$Cl$_2$): $\delta$ 8.09 - 7.97 (m, 4H), 7.92 (dddd, $J = 16.4$, 8.8, 2.0, 0.8 Hz, 2H), 7.79 (d, $J = 1.2$ Hz, 2H), 7.73 - 7.62 (m, 4H), 7.62 - 7.45 (m, 4H), 7.19 - 7.10 (m, 4H), 6.76 - 6.66 (m, 4H), 1.22 (s, 18H).

$^{13}$C NMR (75 MHz, CD$_2$Cl$_2$): $\delta$ 152.11, 142.55, 138.33, 134.13, 134.00, 131.18, 128.57, 127.94, 126.76, 126.40, 126.37, 126.23, 126.20, 125.61, 125.53, 119.97, 95.10, 34.96, 31.15. HRMS (ACPI, m/z): calcd for C$_{50}$H$_{42}$, 642.3287; observed 642.3284.

**Synthesis of 4,4'-(4,6-dibromo-1,3-phenylene)bis(ethyne-2,1-diyl))bis(tert-butylbenzene) (5)**

![Chemical structure](image)

To a mixture of 1,5-dibromo-2,4-diiodobenzene (2.4 g, 5mmol), bis(triphenylphosphine)palladium chloride (Pd(PPh$_3$)$_2$Cl$_2$) (350 mg, 0.5 mmol) and copper iodide (CuI) (52.5 mg, 0.25 mmol) was added dry tetrahydrofuran and triethylamine (Et$_3$N), 1-(tert-butyl)-4-ethynylbenzene (790 mg, 5 mmol) was added under argon flow. The mixture was reacted under room temperature for 4 hours. The resulting crude precipitate was extracted with ethyl acetate and purified by silica gel column chromatography with iso-hexane/CH$_2$Cl$_2$ (10:1) as eluent to afford 5 as pale yellow solid (2.43 g, 90%).

$^1$H NMR (300 MHz, CD$_2$Cl$_2$): $\delta$ 7.78 (s, 1H), 7.60 (s, 1H), 7.53 - 7.36 (m, 4H), 7.36 - 7.24 (m, 4H), 1.22 (s, 18H).

$^{13}$C NMR (75 MHz, CD$_2$Cl$_2$): $\delta$ 152.99, 136.70, 136.08, 131.8, 125.94, 125.35, 119.68, 95.92, 86.41, 35.18, 31.28. HRMS (ACPI, m/z): calcd for C$_{30}$H$_{28}$Br$_2$, 546.0558; observed 546.0557.

**Synthesis of 4',6'-(4-(tert-butyl)phenyl)ethynyl)-1,1':3',1''-terphenyl (2m)**
A flask was charged with 5 (546 mg, 1 mmol), phenylboronic acid (610 mg, 5 mmol), and K₂CO₃ (1.1 g, 8 mmol) along with toluene (10 mL), EtOH (5 mL) and water (5 mL). The mixture was degassed by Ar bubbling for 30 mins and then Pd(PPh₃)₄ (55 mg, 0.05 mmol) was added. The mixture was refluxed for 24 hours under Ar. The resulting crude precipitate was extracted with ethyl acetate and purified by silica gel column chromatography with isohexane/CH₂Cl₂ (10:1) as eluent to afford 2m as white solid (466 mg, 86%).

\[ \text{1H NMR (300 MHz, CD₂Cl₂): } \delta 7.82 \text{ (s, 1H), 7.65 (d, } J = 1.7 \text{ Hz, 2H), 7.63 (t, } J = 1.5 \text{ Hz, 2H), 7.43 - 7.31 \text{ (m, 7H), 7.27 - 7.19 (m, 8H), 1.20 (s, 18H).} \]

\[ \text{13C NMR (75 MHz, CD₂Cl₂): } \delta 152.28, 143.77, 140.22, 137.40, 131.45, 131.06, 129.67, 128.40, 128.26, 125.82, 121.14, 120.44, 88.16, 35.10, 31.29. \]

HRMS (ACPI, m/z): calcd for C₄₂H₃₈,542.2974; observed 542.2965.

**Synthesis of 2,7-dibromo-3,6-bis((4-((tert-butyl)phenyl)ethynyl)naphthalene (6)**

To a mixture of 3,6-dibromonaphthalene-2,7-diyl bis(trifluoromethanesulfonate)⁹ (1.16 g, 2 mmol), Pd(PPh₃)₂Cl₂ (0.2 mmol, 140 mg) and CuI (0.1 mmol, 21 mg) was added dry tetrahydrofuran and Et₃N, 1-((tert-butyl)-4-ethynylbenzene (316 mg, 2 mmol) was added under argon flow. The mixture was heated to 60 °C for 6 hours. The resulting crude precipitate was extracted with ethyl acetate and purified by silica gel column chromatography with iso-
hexane/CH\textsubscript{2}Cl\textsubscript{2} (10:1) as eluent to afford 6 as white pale yellow solid (1.14 g, 96%).

\(^1\)H NMR (300 MHz, CD\textsubscript{2}Cl\textsubscript{2}): \(\delta\) 7.83 (d, \(J = 1.8\) Hz, 4H), 7.44 (d, \(J = 8.5\) Hz, 4H), 7.31 (d, \(J = 8.5\) Hz, 4H), 1.23 (s, 18H).

\(^{13}\)C NMR (75 MHz, CD\textsubscript{2}Cl\textsubscript{2}): \(\delta\) 152.82, 133.48, 132.45, 131.81, 130.56, 130.24, 125.97, 125.93, 124.31, 124.18, 119.93, 95.20, 87.68, 35.17, 31.28. HRMS (ACPI, m/z): calcd for C\textsubscript{34}H\textsubscript{30}Br\textsubscript{2}, 596.0714; observed 596.0713.

**Synthesis of 2,7-bis((4-(tert-butyl)phenyl)ethynyl)-3,6-diphenylnaphthalene (2n)**

A flask was charged with 6 (596 mg, 1 mmol), phenylboronic acid (610 mg, 5 mmol), and K\textsubscript{2}CO\textsubscript{3} (1.1 g, 8 mmol) along with toluene (10 mL), EtOH (5 mL) and water (5 mL). The mixture was degassed by Ar bubbling for 30 mins and then Pd(PPh\textsubscript{3})\textsubscript{4} (0.5 mmol, 550 mg) was added. The mixture was refluxed for 24 hours under Ar. The resulting crude precipitate was extracted with ethyl acetate and purified by silica gel column chromatography with isohexane/CH\textsubscript{2}Cl\textsubscript{2} (10:1) as eluent to afford 2n as white solid (485 mg, 82%).

\(^1\)H NMR (300 MHz, CD\textsubscript{2}Cl\textsubscript{2}): \(\delta\) 8.01 (s, 2H), 7.73 (s, 2H), 7.64 (dt, \(J = 6.0, 1.5\) Hz, 4H), 7.42 - 7.31 (m, 6H), 7.26 - 7.17 (m, 8H), 1.19 (s, 18H).

\(^{13}\)C NMR (75 MHz, CD\textsubscript{2}Cl\textsubscript{2}): \(\delta\) 151.86, 141.63, 140.32, 131.97, 131.07, 129.64, 128.26, 127.96, 127.70, 125.46, 120.92, 120.16, 88.83, 34.74, 30.94. HRMS (ACPI, m/z): calcd for C\textsubscript{46}H\textsubscript{40}, 592.3130; observed 592.3140.

**Synthesis of 1,1’-(4,6-bis((4-(tert-butyl)phenyl)ethynyl)-1,3-phenylene)dinaphthalene (2o)**
A flask was charged with 5 (546 mg, 1 mmol), naphthalen-1-ylboronic acid (516 mg, 3 mmol), and K$_2$CO$_3$ (1.1 g, 8 mmol) along with toluene (10 mL), EtOH (5 mL) and water (5 mL). The mixture was degassed by Ar bubbling for 30 mins and then Pd(PPh$_3$)$_4$ (55 mg, 0.05 mmol) was added. The mixture was refluxed for 24 hours under Ar. The resulting crude precipitate was extracted with ethyl acetate and purified by silica gel column chromatography with iso-hexane/CH$_2$Cl$_2$ (10:1) as eluent to afford 2o as white solid (526 mg, 82%).

$^1$H NMR (300 MHz, CD$_2$Cl$_2$): $\delta$ 8.01 (d, $J = 1.3$ Hz, 1H), 7.99 - 7.91 (m, 5H), 7.67 - 7.45 (m, 10H), 7.23 - 7.15 (m, 4H), 6.84 - 6.73 (m, 4H), 1.25 (s, 18H).

$^{13}$C NMR (75 MHz, CD$_2$Cl$_2$): $\delta$ 152.09, 143.00, 133.97, 133.28, 132.08, 131.22, 128.56, 127.92, 126.72, 126.67, 126.39, 126.16, 125.54, 123.63, 120.03, 87.92, 34.98, 31.17. HRMS (ACPI, m/z): calcd for C$_{50}$H$_{42}$, 642.3287; observed 642.3283.
Mechanism investigation:

In a 25 mL two-necked Schlenk flask, 2-(phenylethynyl)-1,1'-biphenyl (2a) (0.2 mmol, 49 mg) and 2,4,6-tri-tert-butylpyridine (TBP) (0.3 mmol, 73.2 mg) were charged under the protection of argon. After adding 2 mL anhydrous 1,2,4-trichlorobenzene (TCB) and boron tribromide (BBr$_3$) (0.4 mmol), the mixture was heated to 80 °C and stirred for 12 hours. After cooling to room temperature, pinacol (0.8 mmol, 94.4 mg) which dissolved in Et$_3$N was added to the mixture and stirred for a further 1 hour under room temperature. Then all volatiles were removed under reduced pressure, the crude product was purified by flash chromatography on silica gel using iso-hexane/CH$_2$Cl$_2$ (5:1) as eluent to get 4,4,5,5-tetramethyl-2-(10-phenylphenanthren-9-yl)-1,3,2-dioxaborolane (3) as white solid (34 mg, 45%).

$^1$H NMR (300 MHz, CD$_2$Cl$_2$): δ 8.81 - 8.73 (m, 2H), 8.05 -7.98 (m, 1H), 7.71 - 7.62 (m, 3H), 7.57 - 7.40 (m, 7H), 1.13 (s, 12H).

$^{13}$C NMR (75 MHz, CD$_2$Cl$_2$): δ 144.21, 141.39, 133.76, 131.64, 131.17, 130.97, 129.68, 129.21, 128.99, 128.26, 127.76, 127.63, 127.09, 126.69, 126.59, 123.07, 122.86, 84.31, 24.97. The NMR spectra are consistent with the reported literature.$^{10}$
In a 25 mL two-necked Schlenk flask, compound 3’,5’-dimethyl-2-(phenylethynyl)-1,1’-biphenyl (2p) (0.2 mmol, 56.4 mg) and TBP (0.3 mmol, 73.2 mg) were charged under the protection of argon. After adding 2 mL anhydrous TCB and BBr$_3$ (0.4 mmol), the mixture was heated to 200 °C and stirred for 12 hours. After cooling to room temperature, pinacol (0.8 mmol, 94.4 mg) which dissolved in Et$_3$N was added to the mixture and stirred for a further 1 hour at room temperature. Then all volatiles were removed under reduced pressure, the crude product was purified by flash chromatography on silica gel using iso-hexane/CH$_2$Cl$_2$ (5:1) as eluent to get 2-(2-(6,8-dimethylphenanthren-9-yl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (4) as pale solid (36 mg, 44%).

$^1$H NMR (300 MHz, CD$_2$Cl$_2$): $\delta$ 8.71 (dd, $J = 8.4, 1.3$ Hz, 1H), 8.54 (s, 1H), 7.94 - 7.82 (m, 2H), 7.72 - 7.44 (m, 7H), 2.54 (s, 3H), 2.36 (d, $J = 0.8$ Hz, 3H), 0.91 (s, 6H), 0.81 (s, 6H).

$^{13}$C NMR (75 MHz, CD$_2$Cl$_2$): $\delta$ 146.40, 139.95, 136.15, 135.90, 134.72, 131.74, 131.06, 130.57, 130.50, 130.03, 129.03, 128.79, 127.35, 126.89, 126.82, 126.46, 126.35, 123.42, 122.59, 83.64, 24.49, 24.35, 20.50, 20.19. HRMS (ACPI, m/z): calcd for C$_{28}$H$_{29}$BO$_2$, 408.2261; observed 408.2235.
General procedure A for the synthesis of mono B-doped PAHs 1a-1h:

In a 25 mL two-necked Schlenk flask, corresponding compound 2 (1.0 equiv), TBP (1.5 equiv) were charged under the protection of argon. After adding anhydrous TCB (1 mL/mmol) and BBr₃ (2.0 equiv), the mixture was heated to 200 °C and stirred for 12 hours. After cooling to room temperature, mesitylmagnesium bromide (MesMgBr) (2.0 equiv) was used for work-up and stirred for a further 1 hour. Then all volatiles were removed under reduced pressure, the crude product was purified by flash chromatography on silica gel.

General procedure B for the synthesis of dual B-doped PAHs 1k-1o:

In a 25 mL two-necked Schlenk flask, corresponding compound 2 (1.0 equiv), TBP (3.0 equiv) were charged under the protection of argon. After adding anhydrous TCB (1 mL/mmol) and BBr₃ (4.0 equiv), the mixture was heated to 200 °C and stirred for 12 hours. After cooling to room temperature, MesMgBr (4.0 equiv) was used for work-up and stirred for a further 1 hour. Then all volatiles were removed under reduced pressure, the crude product was purified by flash chromatography on silica gel.

8-Mesityl-8H-benzo[e]phenanthro[1,10-bc]borinine (1a). This reaction was carried out in a 0.2 mmol scale for 2a. Following the general procedure A, the crude product was purified by flash chromatography on silica gel using iso-hexane to iso-hexane:CH₂Cl₂ (10:1) as eluent to give 1a as yellow powder (33 mg, 43%).

¹H NMR (300 MHz, CD₂Cl₂): δ 9.17 (dd, J = 8.5, 1.4 Hz, 1H), 9.11 (s, 1H), 8.88 - 8.80 (m, 1H), 8.80 - 8.70 (m, 1H), 8.16 (dd, J = 8.4, 7.2, 1.6 Hz, 2H), 7.87 - 7.69 (m, 5H), 7.48 - 7.41 (m, 1H), 6.98 (q, J = 0.8 Hz, 2H), 2.42 (s, 3H), 2.00 (s, 6H).
13C NMR (75 MHz, CD$_2$Cl$_2$): $\delta$ 142.22, 140.51, 138.97, 138.59, 137.16, 133.83, 132.32, 132.01, 131.54, 130.83, 130.18, 130.16, 129.96, 128.37, 127.96, 127.65, 127.46, 127.23, 126.88, 124.08, 122.96, 23.22, 21.38. The spectra of 1a are consistent with the reported literature.$^{11}$

12-Chloro-8-mesityl-8H-benzo[e]phenanthro[1,10-bc]borinine (1b). This reaction was carried out in a 0.2 mmol scale for 2b. Following the general procedure A, the crude product was purified by flash chromatography on silica gel using iso-hexane to iso-hexane:CH$_2$Cl$_2$ (10:1) as eluent to give 1b as pale-yellow solid (32 mg, 38%).

$^1$H NMR (300 MHz, CD$_2$Cl$_2$): $\delta$ 9.74 (s, 1H), 9.04 (dd, $J = 8.5$, 1.4 Hz, 1H), 8.69 (ddd, $J = 8.2$, 1.3, 0.7 Hz, 1H), 8.10 - 7.91 (m, 2H), 7.81 - 7.54 (m, 5H), 7.24 (dd, $J = 7.8$, 7.2 Hz, 1H), 6.85 (q, $J = 0.8$ Hz, 2H), 2.29 (s, 3H), 1.86 (s, 6H).

13C NMR (75 MHz, CD$_2$Cl$_2$): $\delta$ 140.47, 140.14, 138.92, 137.55, 137.52, 137.37, 133.45, 132.89, 132.69, 131.37, 131.30, 130.46, 130.37, 129.85, 129.10, 128.87, 128.00, 127.48, 127.31, 126.63, 122.78, 23.16, 21.37. $^{11}$B NMR (96 MHz, CD$_2$Cl$_2$): $\delta$ = 66.93 (br.). HRMS (ACPI, m/z): calcd for C$_{29}$H$_{22}$BCl, 416.1503; observed 416.1498.
10-(Tert-butyl)-8-mesityl-8H-benzo[e]phenanthro[1,10-bc]borinine (1c). This reaction was carried out in a 0.2 mmol scale for 2c. Following the general procedure A, the crude product was purified by flash chromatography on silica gel using iso-hexane to iso-hexane:CH$_2$Cl$_2$ (10:1) as eluent to give 1c as yellow powder (41 mg, 46 %).

$^1$H NMR (300 MHz, CD$_2$Cl$_2$): $\delta$ 9.15 (dd, $J = 8.4, 1.4$ Hz, 1H), 9.06 (s, 1H), 8.84 - 8.79 (m, 1H), 8.67 (d, $J = 9.3$ Hz, 1H), 8.14 (ddd, $J = 14.4, 7.2, 1.6$ Hz, 2H), 7.92 - 7.86 (m, 2H), 7.86 - 7.68 (m, 3H), 6.98 (s, 2H), 2.42 (s, 3H), 2.00 (s, 6H), 1.33 (s, 9H).

$^{13}$C NMR (75 MHz, CD$_2$Cl$_2$): $\delta$ 150.39, 140.37, 139.61, 138.92, 136.99, 135.08, 132.30, 132.12, 131.39, 131.27, 130.93, 130.11, 130.04, 129.76, 128.12, 127.38, 127.22, 126.81, 123.92, 122.95, 34.80, 31.31, 23.27, 21.42. $^{11}$B NMR not observed. HRMS (ACP1, m/z): calcd for C$_{33}$H$_{31}$B, 438.2519; observed 438.2511.

8-Mesityl-8H-phenanthro[10',1'-4,5,6]borinino[3,2-b]thiophene (1d). This reaction was carried out in a 0.2 mmol scale for 2d. Following the general procedure A, the crude product was purified by flash chromatography on silica gel using iso-hexane to iso-hexane:CH$_2$Cl$_2$ (10:1) as eluent to give 1d as yellow powder (35 mg, 45 %).

$^1$H NMR (300 MHz, CD$_2$Cl$_2$): $\delta$ 9.08 (dd, $J = 8.3, 1.4$ Hz, 1H), 8.81 (d, $J = 8.2$ Hz, 1H), 8.74 (s, 1H), 8.12 (ddd, $J = 11.0, 7.4, 1.4$ Hz, 2H), 7.86 - 7.63 (m, 3H), 7.39 (d, $J = 5.0$ Hz, 1H), 7.26 (d, $J = 5.0$ Hz, 1H), 6.95 (s, 2H), 2.39 (s, 3H), 2.04 (s, 6H).

$^{13}$C NMR (75 MHz, CD$_2$Cl$_2$): $\delta$ 157.34, 141.15, 138.85, 137.19, 133.96, 131.93, 131.75, 130.98, 129.81, 129.70, 129.06, 129.05, 128.75, 128.58, 127.59, 127.30, 127.27, 124.86, 123.24, 54.52, 54.16, 53.80, 53.44, 53.08, 23.21, 21.36. $^{11}$B NMR (96 MHz, CD$_2$Cl$_2$): $\delta =$ 60.65 (br.). HRMS (ACP1, m/z): calcd for C$_{27}$H$_{21}$BS, 388.1457; observed 388.1470.
7-Chloro-8-mesityl-8H-benzo[e]phenanthro[1,10-bc]borinine (1e). This reaction was carried out in a 0.2 mmol scale for 2e. Following the general procedure A, the crude product was purified by flash chromatography on silica gel using iso-hexane to iso-hexane:CH₂Cl₂ (10:1) as eluent to give 1e as pale yellow oil (23 mg, 28%).

¹H NMR (300 MHz, CD₂Cl₂): δ 9.10 (dd, J = 8.5, 1.4 Hz, 1H), 9.00 (s, 1H), 8.81 - 8.68 (m, 2H), 8.19 - 8.10 (m, 2H), 7.89 - 7.79 (m, 3H), 7.75 - 7.66 (m, 1H), 7.50 - 7.43 (m, 1H), 6.97 (s, 2H), 2.41 (s, 3H), 1.98 (s, 6H).

¹³C NMR (75 MHz, CD₂Cl₂): δ 141.42, 140.39, 138.56, 138.31, 137.40, 136.87, 133.59, 132.69, 131.79, 131.24, 129.52, 129.44, 128.44, 128.19, 127.67, 127.50, 126.92, 126.87, 126.17, 124.44, 123.83, 22.81, 20.98. ¹¹B NMR not observed. HRMS (ACPI, m/z): calcd for C₂₉H₂₂BCl, 416.1503; observed 416.1523.

8-Mesityl-5-phenyl-8H-benzo[e]phenanthro[1,10-bc]borinine (1f). This reaction was carried out in a 0.2 mmol scale for 2f. Following the general procedure A, the crude product was purified by flash chromatography on silica gel using iso-hexane to iso-hexane:CH₂Cl₂ (10:1) as eluent to give 1f as yellow powder (40 mg, 44%).
$^1$H NMR (300 MHz, CD$_2$Cl$_2$): $\delta$ 9.10 (s, 1H), 8.75 (d, $J = 8.1$ Hz, 1H), 8.10 (dd, $J = 7.5$, 2.4 Hz, 2H), 7.91 - 7.71 (m, 3H), 7.65 (d, $J = 7.2$ Hz, 1H), 7.58 - 7.38 (m, 7H), 7.16 (dd, $J = 8.7$, 6.9 Hz, 1H), 6.97 (s, 2H), 2.41 (s, 3H), 2.02 (s, 6H).

$^{13}$C NMR (75 MHz, CD$_2$Cl$_2$): $\delta$ 147.30, 145.44, 142.21, 138.92, 138.62, 137.92, 136.77, 133.64, 133.43, 132.84, 131.10, 130.62, 130.31, 129.50, 129.09, 128.96, 128.84, 128.55, 127.46, 127.22, 126.87, 126.39, 125.81, 123.93, 22.85, 20.99. $^{11}$B NMR (96 MHz, CD$_2$Cl$_2$): $\delta$ = 68.47 (br.). HRMS (ACPI, m/z): calcd for C$_{35}$H$_{27}$B, 458.2206; observed 458.2227.

4-Mesityl-4H-benzo[e]tetrapheno[4,5-be]borinine (1g). This reaction was carried out in a 0.2 mmol scale for 2g. Following the general procedure A, the crude product was purified by flash chromatography on silica gel using iso-hexane to iso-hexane:CH$_2$Cl$_2$ (10:1) as eluent to give 1g as pale yellow solid (40 mg, 46%).

$^1$H NMR (300 MHz, CD$_2$Cl$_2$): $\delta$ 9.29 - 9.20 (m, 2H), 9.13 (s, 1H), 8.77 - 8.70 (m, 1H), 8.62 (s, 1H), 8.14 (ddt, $J = 13.9$, 7.1, 2.2 Hz, 3H), 7.83 (ddd, $J = 7.1$, 4.8, 3.1 Hz, 3H), 7.65 - 7.56 (m, 2H), 7.47 (td, $J = 7.3$, 0.9 Hz, 1H), 7.00 (d, $J = 1.1$ Hz, 2H), 2.43 (s, 3H), 2.03 (s, 6H).

$^{13}$C NMR (75 MHz, CD$_2$Cl$_2$): $\delta$ 142.15, 139.88, 138.93, 138.55, 137.17, 133.78, 133.20, 133.17, 132.61, 130.92, 130.54, 130.48, 129.59, 129.47, 128.96, 128.86, 128.74, 128.28, 127.72, 127.27, 127.05, 126.82, 126.52, 124.12, 121.88, 23.19, 21.39. $^{11}$B NMR (96 MHz, CD$_2$Cl$_2$): $\delta$ = 65.59 (br.). HRMS (ACPI, m/z): calcd for C$_{33}$H$_{25}$B, 432.2049; observed 432.2046.
3-Chloro-8-mesityl-8H-benzo[e]phenanthro[1,10-be]borinine (1h). This reaction was carried out in a 0.2 mmol scale for 2h. Following the general procedure A, the crude product was purified by flash chromatography on silica gel using iso-hexane to iso-hexane:CH₂Cl₂ (10:1) as eluent to give 1h as pale yellow solid (35 mg, 42%).

¹H NMR (300 MHz, CD₂Cl₂): δ 9.05 (dd, J = 8.4, 1.4 Hz, 1H), 8.95 (s, 1H), 8.73 - 8.62 (m, 2H), 8.18 - 8.04 (m, 2H), 7.87 - 7.78 (m, 3H), 7.68 (dd, J = 8.9, 2.2 Hz, 1H), 7.47 (td, J = 7.3, 0.9 Hz, 1H), 7.04 - 6.95 (m, 2H), 2.42 (s, 3H), 2.00 (s, 6H).

¹³C NMR (75 MHz, CD₂Cl₂): δ 141.79, 140.76, 138.94, 138.68, 137.26, 133.96, 133.04, 133.02, 132.19, 132.13, 129.88, 129.77, 129.76, 128.78, 128.53, 128.04, 127.27, 126.52, 124.76, 124.21, 23.22, 21.38. ¹¹B NMR (96 MHz, CD₂Cl₂): δ = 66.97 (br.). HRMS (ACPI, m/z): calcd for C₂₉H₂₂BCl, 416.1503; observed 416.1519.

Synthesis of 1k. This reaction was carried out in a 0.2 mmol scale for 2k. Following the general procedure B, the crude product was purified by flash chromatography on silica gel
using iso-hexane to iso-hexane:CH₂Cl₂ (10:1) as eluent to give 1k as orange powder (62 mg, 40%).

¹H NMR (300 MHz, CD₂Cl₂): δ 9.49 (s, 1H), 9.37 (dd, J = 8.4, 1.4 Hz, 1H), 9.31 (s, 1H), 8.76 (d, J = 8.3 Hz, 1H), 8.15 (dd, J = 7.0, 1.3 Hz, 1H), 7.92 (dd, J = 8.8, 2.4 Hz, 1H), 7.91 (s, 2H), 7.00 (s, 2H), 2.44 (s, 3H), 2.04 (s, 6H), 1.35 (s, 9H).

¹³C NMR (75 MHz, CD₂Cl₂): δ 150.69, 140.26, 139.50, 138.91, 137.06, 135.54, 135.18, 131.75, 131.37, 130.12, 129.61, 128.05, 127.26, 127.19, 124.11, 123.91, 34.86, 31.32, 23.27, 21.43, peaks corresponding to B-C could not be observed. ¹¹B NMR not observed. HRMS (ACPI, m/z): calcd for C₆₀H₅₆B₂, 798.4568; observed 798.4561.

Synthesis of 1l. This reaction was carried out in a 0.2 mmol scale for 2l. Following the general procedure B, the crude product was purified by flash chromatography on silica gel using iso-hexane to iso-hexane:CH₂Cl₂ (10:1) as eluent to give 1l as red powder (40 mg, 22%).

¹H NMR (300 MHz, CD₂Cl₂): δ 9.76 (s, 1H), 9.44 (d, J = 8.6 Hz, 1H), 9.22 (s, 1H), 8.67 (d, J = 8.5 Hz, 1H), 8.51 (s, 1H), 8.11 (dd, J = 8.2, 1.4 Hz, 1H), 7.90 (ddd, J = 8.5, 6.8, 1.4 Hz, 1H), 7.85 -7.77 (m, 2H), 7.68 (ddd, J = 8.0, 6.9, 1.0 Hz, 1H), 6.95 (s, 2H), 2.38 (s, 3H), 1.98 (s, 6H), 1.25 (s, 9H).

¹³C NMR (75 MHz, CD₂Cl₂): δ 150.55, 143.30, 140.29, 139.08, 137.10, 135.25, 133.65, 132.93, 131.93, 131.76, 131.61, 130.72, 129.50, 129.39, 129.06, 128.77, 127.88, 127.34, 127.02, 126.64, 124.46, 34.82, 31.29, 23.32, 21.48, peaks corresponding to B-C could not be
observed. $^{11}$B NMR not observed. HRMS (ACPI, m/z): calcd for C$_{60}$H$_{60}$B$_2$, 898.4881; observed 898.4873.

**Synthesis of 1m.** This reaction was carried out in a 0.2 mmol scale for 2m. Following the general procedure B, the crude product was purified by flash chromatography on silica gel using iso-hexane to iso-hexane:CH$_2$Cl$_2$ (10:1) as eluent to give 1m as pale-yellow powder (28 mg, 18%).

$^1$H NMR (300 MHz, CD$_2$Cl$_2$): $\delta$ 10.13 (s, 1H), 9.39 (dd, $J = 8.5$, 1.4 Hz, 2H), 9.18 (s, 2H), 8.79 (s, 1H), 8.67 (d, $J = 8.4$ Hz, 2H), 8.07 (dd, $J = 7.0$, 1.3 Hz, 2H), 7.91 - 7.76 (m, 5H), 7.05 - 6.73 (m, 4H), 2.35 (s, 6H), 1.96 (s, 12H), 1.27 (s, 18H).

$^{13}$C NMR (75 MHz, CD$_2$Cl$_2$): $\delta$ 150.66, 140.33, 139.50, 138.91, 137.06, 135.13, 133.22, 131.53, 131.35, 131.24, 130.52, 129.65, 127.42, 127.26, 127.12, 124.09, 116.74, 34.86, 31.32, 31.27, 21.44, peaks corresponding to B-C could not be observed. $^{11}$B NMR not observed. HRMS (ACPI, m/z): calcd for C$_{60}$H$_{60}$B$_2$, 798.4568; observed 798.4564.
**Synthesis of 1n.** This reaction was carried out in a 0.2 mmol scale for 2n. Following the general procedure B, the crude product was purified by flash chromatography on silica gel using iso-hexane to iso-hexane:CH₂Cl₂ (5:1) as eluent to give 1n as orange powder (41 mg, 24%).

¹H NMR (300 MHz, C₂D₂Cl₄): δ 9.48 (s, 2H), 9.26 (dd, J = 8.4, 1.4 Hz, 2H), 9.07 (s, 2H), 8.82 (s, 2H), 8.66 (d, J = 8.5 Hz, 2H), 8.15 (dd, J = 7.1, 1.2 Hz, 2H), 7.91 - 7.79 (m, 6H), 6.98 (s, 4H), 2.45 (s, 6H), 2.06 (s, 12H), 1.34 (s, 18H).

¹³C NMR (75 MHz, C₂D₂Cl₄): δ 150.68, 140.73, 140.17, 139.30, 139.02, 136.90, 136.67, 135.71, 135.46, 133.64, 131.61, 131.21, 131.16, 130.43, 129.88, 129.44, 128.83, 128.15, 127.45, 127.33, 124.10, 122.58, 35.00, 31.76, 23.77, 22.03; peaks corresponding to B-C could not be observed. ¹¹B NMR not observed. HRMS (ACPI, m/z): calcd for C₆₄H₅₈B₂, 848.4725; observed 848.4725.
**Synthesis of 1o.** This reaction was carried out in a 0.2 mmol scale for 2o. Following the general procedure B, the crude product was purified by flash chromatography on silica gel using iso-hexane to iso-hexane:CH2Cl2 (5:1) as eluent to give 1o as red powder (45 mg, 25%).

1H NMR (300 MHz, CD2Cl2): \(\delta\) 9.32 (s, 2H), 9.13 (d, \(J = 8.4\) Hz, 2H), 9.05 (s, 1H), 8.78 (d, \(J = 8.6\) Hz, 2H), 8.56 (s, 2H), 8.13 (dd, \(J = 8.0, 1.5\) Hz, 2H), 7.94 (dd, \(J = 8.5, 2.4\) Hz, 2H), 7.89 (d, \(J = 2.3\) Hz, 2H), 7.75 (ddd, \(J = 8.5, 6.8, 1.5\) Hz, 2H), 7.65 (ddd, \(J = 7.9, 6.9, 1.1\) Hz, 2H), 7.06 - 6.99 (m, 4H), 2.47 (s, 6H), 2.07 (s, 12H), 1.36 (s, 18H).

13C NMR (75 MHz, CD2Cl2): \(\delta\) 150.60, 143.09, 139.06, 137.11, 135.19, 133.34, 132.97, 131.76, 131.71, 130.55, 128.91, 128.89, 128.85, 128.72, 128.38, 127.34, 126.54, 126.11, 124.52, 34.84, 31.32, 23.32, 21.49, peaks corresponding to B-C could not be observed. 11B NMR not observed. HRMS (ACPI, m/z): calcd for C68H60B2, 898.4881; observed 898.4890.
3. NMR Spectra

Figure S1: $^1$H NMR spectrum of 2b (300 MHz, CD$_2$Cl$_2$, room temperature).

Figure S2: $^{13}$C NMR spectrum of 2b (75 MHz, CD$_2$Cl$_2$, room temperature).
Figure S3: $^1$H NMR spectrum of 2g (300 MHz, CD$_2$Cl$_2$, room temperature).

Figure S4: $^{13}$C NMR spectrum of 2g (75 MHz, CD$_2$Cl$_2$, room temperature).
Figure S5: $^1$H NMR spectrum of 2k (300 MHz, CD$_2$Cl$_2$, room temperature).

Figure S6: $^{13}$C NMR spectrum of 2k (75 MHz, CD$_2$Cl$_2$, room temperature).
Figure S7: $^1$H NMR spectrum of 2l (300 MHz, CD$_2$Cl$_2$, room temperature).

Figure S8: $^{13}$C NMR spectrum of 2l (75 MHz, CD$_2$Cl$_2$, room temperature).
Figure S9: $^1$H NMR spectrum of 5 (300 MHz, CD$_2$Cl$_2$, room temperature).

Figure S10: $^{13}$C NMR spectrum of 5 (75 MHz, CD$_2$Cl$_2$, room temperature).
Figure S11: $^1$H NMR spectrum of 2m (300 MHz, CD$_2$Cl$_2$, room temperature).

Figure S12: $^{13}$C NMR spectrum of 2m (75 MHz, CD$_2$Cl$_2$, room temperature).
Figure S13: $^1$H NMR spectrum of 6 (300 MHz, CD$_2$Cl$_2$, room temperature).

Figure S14: $^{13}$C NMR spectrum of 6 (75 MHz, CD$_2$Cl$_2$, room temperature).
Figure S15: $^1$H NMR spectrum of 2n (300 MHz, CD$_2$Cl$_2$, room temperature).

Figure S16: $^{13}$C NMR spectrum of 2n (75 MHz, CD$_2$Cl$_2$, room temperature).
Figure S17: $^1$H NMR spectrum of 2o (300 MHz, CD$_2$Cl$_2$, room temperature).

Figure S18: $^{13}$C NMR spectrum of 2o (75 MHz, CD$_2$Cl$_2$, room temperature).
Figure S19: $^1$H NMR spectrum of 3 (300 MHz, CD$_2$Cl$_2$, room temperature).

Figure S20: $^{13}$C NMR spectrum of 3 (75 MHz, CD$_2$Cl$_2$, room temperature).
Figure S21: $^1$H NMR spectrum of 4 (300 MHz, CD$_2$Cl$_2$, room temperature).

Figure S22: $^{13}$C NMR spectrum of 4 (75 MHz, CD$_2$Cl$_2$, room temperature).
Figure S23: $^1$H NMR spectrum of 1a (300 MHz, CD$_2$Cl$_2$, room temperature).

Figure S24: $^{13}$C NMR spectrum of 1a (75 MHz, CD$_2$Cl$_2$, room temperature).
Figure S25: $^1$H NMR spectrum of 1b (300 MHz, CD$_2$Cl$_2$, room temperature).

Figure S26: $^{13}$C NMR spectrum of 1b (75 MHz, CD$_2$Cl$_2$, room temperature).
Figure S27: $^{11}$B NMR spectrum of 1b (96 MHz, CD$_2$Cl$_2$, room temperature).
Figure S28: $^1$H NMR spectrum of 1c (300 MHz, CD$_2$Cl$_2$, room temperature).

Figure S29: $^{13}$C NMR spectrum of 1c (75 MHz, CD$_2$Cl$_2$, room temperature).
Figure S30: $^1$H NMR spectrum of 1d (300 MHz, CD$_2$Cl$_2$, room temperature).

Figure S31: $^{13}$C NMR spectrum of 1d (75 MHz, CD$_2$Cl$_2$, room temperature).
Figure S32: $^{11}$B NMR spectrum of 1d (96 MHz, CD$_2$Cl$_2$, room temperature).
Figure S33: $^1$H NMR spectrum of 1e (300 MHz, CD$_2$Cl$_2$, room temperature).

Figure S34: $^{13}$C NMR spectrum of 1e (75 MHz, CD$_2$Cl$_2$, room temperature).
Figure S35: $^1$H NMR spectrum of If (96 MHz, CD$_2$Cl$_2$, room temperature).

Figure S36: $^{13}$C NMR spectrum of If (75 MHz, CD$_2$Cl$_2$, room temperature).
Figure S37: $^{11}$B NMR spectrum of 1f (96 MHz, CD$_2$Cl$_2$, room temperature).
Figure S38: $^1$H NMR spectrum of 1g (300 MHz, CD$_2$Cl$_2$, room temperature).

Figure S39: $^{13}$C NMR spectrum of 1g (75 MHz, CD$_2$Cl$_2$, room temperature).
Figure S40: $^{11}$B NMR spectrum of 1g (96 MHz, CD$_2$Cl$_2$, room temperature).
Figure S41: $^1$H NMR spectrum of 1h (300 MHz, CD$_2$Cl$_2$, room temperature).

Figure S42: $^{13}$C NMR spectrum of 1h (75 MHz, CD$_2$Cl$_2$, room temperature).
Figure S43: $^{11}$B NMR spectrum of 1h (96 MHz, CD$_2$Cl$_2$, room temperature).
Figure S44: $^1$H NMR spectrum of 1k (300 MHz, CD$_2$Cl$_2$, room temperature).

Figure S45: $^{13}$C NMR spectrum of 1k (75 MHz, CD$_2$Cl$_2$, room temperature).
Figure S46: $^1$H NMR spectrum of II (300 MHz, CD$_2$Cl$_2$, room temperature).

Figure S47: $^{13}$C NMR spectrum of II (75 MHz, CD$_2$Cl$_2$, room temperature).
Figure S48: $^1$H NMR spectrum of 1m (300 MHz, CD$_2$Cl$_2$, room temperature).

Figure S49: $^{13}$C NMR spectrum of 1m (75 MHz, CD$_2$Cl$_2$, room temperature).
Figure S50: $^1$H NMR spectrum of 1n (300 MHz, C$_2$D$_2$Cl$_4$, room temperature).

Figure S51: $^{13}$C NMR spectrum of 1n (75 MHz, C$_2$D$_2$Cl$_4$, room temperature).
Figure S52: $^1$H NMR spectrum of 1o (300 MHz, CD$_2$Cl$_2$, room temperature).

Figure S53: $^{13}$C NMR spectrum of 1o (75 MHz, CD$_2$Cl$_2$, room temperature).
4. Cyclic Voltammetry

Figure S54. Cyclic voltammogram of 1b-1o (−10⁻⁴ M, 0.1 M n-Bu₄NPF₆ in CH₂Cl₂, vs. Fc⁺/₀, 298 K).
Table S1. Optical and electrochemical properties of 1b-1o.

| Compound | λ<sub>abs</sub> [nm] | λ<sub>em</sub> [nm] | Stokes shift [cm<sup>-1</sup>] | Φ<sub>PL</sub> | First reduction wave (V) | Second reduction wave (V) | LUMO (eV) | HOMO (eV) | ΔE<sub>opt</sub> (eV) |
|----------|----------------------|-------------------|-------------------------------|------------|------------------------|--------------------------|---------|---------|-------------|
| 1b       | 404 (4.4), 386 (3.5) | 456               | 2823                          | 0.06       | −2.15                  | −                        | −2.65   | −       | 2.91        |
| 1c       | 406 (5.0), 388 (3.7) | 433               | 1536                          | 0.57       | −2.13                  | −                        | −2.67   | −       | 2.90        |
| 1d       | 404 (3.2)            | 462               | 3107                          | 0.18       | −2.03                  | −                        | −2.77   | −       | 2.78        |
| 1e       | 398 (4.0), 380 (3.3) | 424               | 1541                          | 0.38       | −2.03                  | −                        | −2.77   | −       | 2.98        |
| 1f       | 408 (4.8), 387 (4.1) | 437               | 1626                          | 0.52       | −1.98                  | −                        | −2.82   | −       | 2.66        |
| 1g       | 443 (2.8), 419 (2.2) | 469               | 1251                          | 0.97       | −2.04                  | −                        | −2.76   | −5.64  | 2.68        |
| 1h       | 397 (4.5), 379 ()    | 418               | 1265                          | 0.70       | −2.06                  | −                        | −2.74   | −       | 3.0         |
| 1k       | 476 (1.9), 446 (1.1), | 488              | 516                           | 0.71       | −1.92                  | −2.05                    | −2.88   | −5.6   | 2.48        |
|          | 426 (1.4)            |                  |                               |            |                        |                          |         |         |             |
| 1l       | 515 (0.5), 481 (0.4), | 530              | 550                           | 0.45       | −1.96                  | −2.09                    | −2.84   | −5.45  | 2.30        |
|          |                      |                  |                               |            |                        |                          |         |         |             |
| 1m       | 467 (0.55), 438 (0.55), | 470              | 137                           | 0.62       | −2.01                  | −2.18                    | −2.79   | −5.75  | 2.57        |
|          |                      |                  |                               |            |                        |                          |         |         |             |
| 1n       | 504 (0.6), 471 (0.6), | 514              | 386                           | 0.68       | −1.97                  | −2.17                    | −2.82   | −5.42  | 2.36        |

**Notes:**
- λ<sub>abs</sub>: absorption wavelength
- λ<sub>em</sub>: emission wavelength
- Φ<sub>PL</sub>: photoluminescence quantum yield
- ΔE<sub>opt</sub>: optical energy gap
Optical measurements carried out at 298 K in CH₂Cl₂ (10⁻⁶ M). Fluorescence quantum yield values measured using quinine hemisulfate salt monohydrate as reference for 1b-1f, and 1h, fluorescein acid as reference for 1g, and 1k-1o. Measured in CH₂Cl₂ with [nBu₄N][PF₆] (0.1 M) as the supporting electrolyte at a scan rate of 100 mV s⁻¹, electrochemical reduction potentials were calibrated with ferrocene as an internal standard and are referenced vs Fc⁺⁻. LUMO energy calculated from the onsets of the first reduction waves using \( E_{\text{LUMO}} = -E_{\text{red}} - 4.80 \text{ eV} \), HOMO energy calculated from the onsets of the first oxidation waves using \( E_{\text{HOMO}} = -E_{\text{ox}} - 4.80 \text{ eV} \). Optical band gap obtained from the onset of absorption. Fluorescence quantum yield of thin films.
5. X-ray Crystallography

Single crystals suitable for X-ray crystallography were obtained by slow diffusion of \( n \)-hexane (1b) and \( iso \)-hexane (1k) in the respective CH\(_2\)Cl\(_2\) solution of the compounds. The crystal of 1b was coated with Paratone-N oil, mounted using a nylon loop and frozen in the cold nitrogen stream. Data were collected at 100 K on a Rigaku Oxford Diffraction SuperNova system with an AtlasS2 detector using Cu Ka radiation (\( \lambda = 1.54184 \) Å) generated by a Nova micro-focus X-ray source. Single-crystal X-ray data of 1k are collected on Bruker D8 VENTURE MetalJet Photon II CPAD X-Ray Diffractometer, using Ga Ka, radiation (1.34138 Å) at 173K. Data collection was done using APEX3 v2018.7-2 (Bruker-AXS, 2018) program. Cell refinement and data reduction are done using SAINT V8.38A (Bruker AXS Inc., 2017) program. The structures are solved using SHELXT 2014/5 (Sheldrick, 2014) program and refined by SHELXL2018/3 (Sheldrick, 2018) program. All e.s.d.'s are estimated using the full covariance matrix. Yawing disorder of the terminal 2,4,6-trimethylphenyl groups were treated into disordered parts. Suitable geometrical restraints were applied on the disordered parts to achieve a stable and chemically sensible model. Crystal and data collection details for both compounds are given in Table S2. In case of 1b data reduction and absorption correction was performed with CrysalisPro\(^{[12]}\). Using Olex2\(^{[13]}\), the structures were solved with SHELXT\(^{[14]}\) by direct methods and refined with SHELXL\(^{[15]}\) by least-square minimization against F2 using first isotropic and later anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms bonded to carbon atoms were added to the structure models on calculated positions using the riding model. Images of the structures were produced with Olex2\(^{[13]}\) software. The X-ray crystallographic coordinates for structures reported in this article have been deposited at the Cambridge Crystallographic Data Centre (CCDC), under deposition number, CCDC 2020106 (for 1b) CCDC 1950988 (for 1k). These data can be obtained free of charge from CCDC via https://www.ccdc.cam.ac.uk/structures/.

Table S2. Crystallographic data and details of the structure refinements of 1b and 1k.

|          | 1b          | 1k          |
|----------|-------------|-------------|
| Empirical formula | C\(_{29}\)H\(_{22}\)BCl | C\(_{60}\)H\(_{54}\)B\(_2\) |
| Property                        | Value 1                  | Value 2                  |
|--------------------------------|--------------------------|--------------------------|
| Formula weight                 | 416.72                   | 798.66                   |
| Temperature/K                  | 100.0(1)                 | 173(2)                   |
| Crystal system                 | triclinic                | monoclinic               |
| Space group                    | $P\bar{1}$               | $P_2_1$                  |
| $a$/Å                          | 9.4715(3)                | 13.6737(18)              |
| $b$/Å                          | 10.3376(4)               | 27.143(3)                |
| $c$/Å                          | 12.1585(4)               | 25.118(3)                |
| $\alpha$/°                     | 67.247(3)                | 90                       |
| $\beta$/°                      | 78.303(3)                | 96.675(5)                |
| $\gamma$/°                     | 73.715(3)                | 90                       |
| Volume/Å³                      | 1047.79(7)               | 9259.2(19)               |
| $Z$                            | 2                        | 8                        |
| $\rho_{\text{calc}}$/g/Å³      | 1.321                    | 1.146                    |
| $\mu$/mm$^{-1}$                | 1.699                    | 0.304                    |
| $F(000)$                       | 436.0                    | 3408.0                   |
| Crystal size/mm$^3$            | $0.342 \times 0.24 \times 0.065$ | $0.081 \times 0.037 \times 0.021$ |
| Radiation                      | CuKα ($\lambda = 1.54184$) | GaKα ($\lambda = 1.34138$) |
| $2\Theta$ range for data collection/° | 7.93 to 136.486         | 5.662 to 123.886         |
| Index ranges                   | -9 ≤ h ≤ 11, -12 ≤ k ≤ 10, -17 ≤ h ≤ 17, -35 ≤ k ≤ 35, -29 ≤ l ≤ 32 |
| Reflections collected          | 8833                     | 125588                   |
| Independent reflections        | 3834 [R(int) = 0.0207, R(sigma) = 0.0245] | 42885 [R(int) = 0.0077, R(sigma) = 0.0069] |
| Data[I>2σ(I)] restraints/parameters | 3834/0/283               | 31344/422/2359           |
| Goodness-of-fit on F$^2$        | 1.130                    | 1.044                    |
| Final R indexes [F$^2$ > 2σ (F$^2$)] | $R_1 = 0.0472$, $wR_2 = 0.1330$ | $R_1 = 0.0519$, $wR_2 = 0.1236$ |
| Final R indexes [all data]     | $R_1 = 0.494$, $wR_2 = 0.1345$ | $R_1 = 0.0768$, $wR_2 = 0.1376$ |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.49/-0.35             | 0.29/-0.24               |
| CCDC                           | 2020106                  | 1950988                  |
6. DFT Calculation Details

All density functional theory (DFT) calculations were performed using the Gaussian 09 program. The geometry optimization in the ground state was used the RB3LYP functional with the 6-31G(d) basis set. All geometry optimization was done in the gas phase. In order to simulate the UV-Vis spectra of the molecules, TD-DFT calculations using B3LYP functional and 6-31G(d) basis set were used. For better comparison to the experimental absorption spectra the polarity of the solvent dichloromethane was added. AICD plot was calculated by using the method developed by Herges based on the optimized ground-state geometries at a RB3LYP/6-31G(d) level of theory.

Nucleus independent chemical shifts (NICS) values were calculated using the standard gauge invariant atomic orbital (GIAO) method at B3LYP functional. The 6-311+G(d,2p) basis set was used for the C, and H atoms. All NICS values were averaged by two positions (above and below the plane) of each molecule.

For transition state (TS) calculation, all the structures were optimized in gas phase by using RB3LYP level of density functional theory with the 6-31G(d) basis. To confirm the accuracy of the transition state, frequency calculation was performed. The Gibbs free energies of reaction ($\Delta_r G^\circ$) at room temperature (298 K) can be calculated by the following equations

$$H_{corr} = E_{tot} + kBT$$

$$G_{corr} = H_{corr} - TS_{tot}$$

$$\Delta r G^\circ (T) = \sum (\varepsilon_0 + G_{corr})_{products} - \sum (\varepsilon_0 + G_{corr})_{reactants}$$

where $H_{corr}$ is the thermal correction to Enthalpy; $E_{tot}$ is the correction to the internal thermal energy; $k_B$ is the Boltzmann constant; $T$ is the temperature; $G_{corr}$ is the thermal correction to Gibbs free energy (thermal Free Energies); $S_{tot}$ is the correction to the internal Entropy; $\varepsilon_0$ is the total electronic energy. In our case, the product is the transition state and the reactant are the starting state.
Optimized structure and HOMO/LUMO energy level of 1b-1d

Figure S55. Optimized structure and calculated HOMO/LUMO energy of 1b.

Figure S56. Optimized structure and calculated HOMO/LUMO energy of 1c.

Figure S57. Optimized structure and calculated HOMO/LUMO energy of 1d.
Figure S58. Optimized structure and calculated HOMO/LUMO energy of 1e.

Figure S59. Optimized structure and calculated HOMO/LUMO energy of 1f.

Figure S60. Optimized structure and calculated HOMO/LUMO energy of 1g.
Figure S61. Optimized structure and calculated HOMO/LUMO energy of $1$h.

Figure S62. Optimized structure and calculated HOMO/LUMO energy of $1$k.

Figure S63. Optimized structure and calculated HOMO/LUMO energy of $1$l.
Figure S64. Optimized structure and calculated HOMO/LUMO energy of 1m.

Figure S65. Optimized structure and calculated HOMO/LUMO energy of 1n.

Figure S66. Optimized structure and calculated HOMO/LUMO energy of 1o.
Calculated ACID Plots and NICS

For ACID calculations, the direction of magnetic field is orthogonal to the XY plane and points upward. The clockwise (diamagnetic) and counterclockwise (paramagnetic) current flows are indicated by the red and black arrows, respectively.

Figure S67. ACID plots (left) and NICS (1zz, avg) (right) values of 1b.

Figure S68. ACID plots (left) and NICS (1zz, avg) (right) values of 1c.
Figure S69. ACID plots (left) and NICS (1zz, avg) (right) values of 1d.

Figure S70. ACID plots (left) and NICS (1zz, avg) (right) values of 1e.
Figure S71. ACID plots (left) and NICS (1zz, avg) (right) values of 1f.

Figure S72. ACID plots (left) and NICS (1zz, avg) (right) values of 1g.
Figure S73. ACID plots (left) and NICS (1zz, avg) (right) values of 1h.

Figure S74. ACID plots (left) and NICS (1zz, avg) (right) values of 1k.

Figure S75. ACID plots (left) and NICS (1zz, avg) (right) values of 1l.
Figure S76. ACID plots (left) and NICS (1zz, avg) (right) values of 1m.

Figure S77. ACID plots (left) and NICS (1zz, avg) (right) values of 1n.

Figure S78. ACID plots (left) and NICS (1zz, avg) (right) values of 1o.
Figure S79. Comparison the ACID plots of B-PAH 1k (left) and its pristine carbon framework-zetherene derivatives (right).

Figure S80. Calculated energy barrier of 1,4-boron migration process in vacuum (black) and in 1,2,4-trichlorobenzene (red). Unit: kcal/mol.
7. Organic Light-emitting Diodes Devices

*Table S3.* Key parameters of the vacuum-deposited OLEDs based on 1f and 1k.

| Compound | Conc. [v/v%] | CE[a] [cd A⁻¹] | PE[b] [lm W⁻¹] | EQE[c] [%] | λ_max[d] [nm] | CIE[e] [x, y] |
|----------|--------------|----------------|----------------|-----------|-------------|-------------|
| 1f       | 11           | 2.3            | 2.1            | 3.5       | 456         | 0.14, 0.11  |
| 1k       | 11           | 10.7           | 8.4            | 3.2       | 516         | 0.30, 0.62  |

[a] CE represents maximum current efficiency.  
[b] PE represents maximum power efficiency.  
[c] EQE represents maximum external quantum efficiency.  
[d] λ_max represents peak maximum.  
[e] CIE coordinates are taken at a luminance of 100 cd m⁻².
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