Supporting Information

A Modular Cascade Synthetic Strategy Toward Structurally Constrained Boron-Doped Polycyclic Aromatic Hydrocarbons

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1. Experimental details

**General methods and materials**: 2,4,6-tri-tert-butylpyridine (TBP), boron tribromide (BBr₃) and anhydrous trichlorobenzene (TCB) 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 (δₜ₆MS = 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 on a Bruker Autoflex Speed MALDI TOF MS (Bruker Daltonics, Bremen, Germany) using dithranol or trans-2-[3-(4-tert-Butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) as matrix. 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.
2. Synthetic procedures

**General procedure A for the synthesis of starting materials 2a-2m:**

A flask was charged with 3 (1.0 equiv), (4-(naphthalen-1-yl)phenyl)boronic acid (1.5 equiv), and potassium carbonate (K₂CO₃) (4.0 equiv) along with toluene : ethanol (EtOH) : water = (2:1:1). The mixture was degassed by argon (Ar) bubbling for 30 mins and then tetrakis(triphenylphosphine)palladium(0) (Pd(PPh₃)₄) (5%) was added. The mixture was refluxed for 12-24 hours. The resulting crude precipitate was extracted with ethyl acetate and purified by silica gel column chromatography to afford corresponding compound.

**General procedure B for the synthesis of starting materials 2n-2v:**

A flask was charged with 3 (1.0 equiv), (4-(diphenylamino)phenyl)boronic acid (1.5 equiv), and K₂CO₃ (4.0 equiv) along with toluene : EtOH : water = (2:1:1). The mixture was degassed by Ar bubbling for 30 mins and then Pd(PPh₃)₄ (10%) was added. The mixture was refluxed for 12-24 hours. The resulting crude precipitate was extracted with ethyl acetate and purified by silica gel column chromatography to afford corresponding compound.

**General procedure C for the synthesis of B-doped [4]helicene (1a-1i) and BN-doped [4]helicene (1n-1t):**

In a 25 mL two-necked Schlenk flask, the corresponding compound 2 (1.0 equiv), TBP (1.5 equiv) were charged under the protection of argon. After adding anhydrous TCB (10 mL/mmol) and BBr₃ (2.0 equiv), the mixture was heated to 200 °C and stirred for 12 hours. After cooling to room temperature, all volatiles were removed under reduced pressure, the crude product was purified by flash chromatography on silica gel, pure hexane was used to remove the TCB before increasing the polarity of eluent gradually.

**General procedure D for the synthesis of BN-doped double [4]helicene (1u and 1v):**

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 (10 mL/mmol) and BBr₃ (4.0 equiv), the mixture
was heated to 200 °C and stirred for 12 hours. After cooling to room temperature, all volatiles were removed under reduced pressure, the crude product was purified by flash chromatography on silica gel, pure hexane was used to remove the TCB before increasing the polarity of eluent gradually.

**The synthesis of 1-(2'-(phenylethynyl)-[1,1'-biphenyl]-4-yl)naphthalene (2a)**

This reaction was carried out in a 2 mmol scale for 3a. 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 2a as colorless oil (547 mg, 72%).

¹H NMR (300 MHz, CD₂Cl₂): δ 8.19 - 8.09 (m, 1H), 8.09 - 7.89 (m, 4H), 7.85 - 7.78 (m, 1H), 7.74 - 7.68 (m, 2H), 7.66 - 7.49 (m, 8H), 7.49 - 7.36 (m, 4H).

¹³C NMR (76 MHz, CD₂Cl₂): δ 143.99, 140.35, 140.32, 139.93, 134.33, 133.26, 132.02, 131.71, 130.66, 129.89, 129.75, 129.15, 128.80, 128.71, 128.68, 128.10, 127.67, 127.43, 126.52, 126.31, 126.24, 125.87, 123.79, 121.97, 92.80, 89.94.

HRMS (MALDI): calcd for C₃₀H₂₀ [M]⁺, 380.1560, observed 380.1567.

**The synthesis of 2-(4-(naphthalen-1-yl)phenyl)-3-(phenylethynyl)naphthalene (2b)**

This reaction was carried out in a 2 mmol scale for 3b. 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 2b as pale-yellow solid (560 mg, 65%).

¹H NMR (300 MHz, CDCl₃): δ 8.06 (s, 1H), 7.91 (dd, J = 8.5, 1.4 Hz, 1H), 7.82 - 7.66 (m, 7H), 7.51 - 7.44 (m, 2H), 7.41 - 7.24 (m, 8H), 7.13 (dt, J = 4.5, 2.7 Hz, 3H).
^{13}C NMR (76 MHz, CDCl\textsubscript{3}): \(\delta\) 140.36, 140.00, 139.83, 139.46, 133.84, 133.03, 132.75, 132.14, 131.65, 131.33, 129.57, 128.31, 128.24, 128.17, 127.89, 127.69, 127.42, 127.05, 126.96, 126.55, 126.05, 126.04, 125.79, 125.42, 123.45, 120.06, 89.87.

HRMS (MALDI): calcd for C\textsubscript{34}H\textsubscript{22}[M]^+, 430.1716, observed 430.1727.

The synthesis of 3-(4-(naphthalen-1-yl)phenyl)-2-(phenylethynyl)thiophene (2d)

This reaction was carried out in a 2 mmol scale for 3d. Following the general procedure A, the crude product was purified by flash chromatography on silica gel using iso-hexane to iso-hexane:CH\textsubscript{2}Cl\textsubscript{2} (10:1) as eluent to give 2d as solid (478 mg, 62%).

^{1}H NMR (300 MHz, CD\textsubscript{2}Cl\textsubscript{2}): \(\delta\) 8.12 - 8.02 (m, 3H), 8.02 - 7.90 (m, 2H), 7.69 - 7.64 (m, 2H), 7.62 - 7.48 (m, 6H), 7.44 - 7.34 (m, 5H).

^{13}C NMR (76 MHz, CD\textsubscript{2}Cl\textsubscript{2}): \(\delta\) 144.78, 140.51, 140.15, 134.66, 134.28, 131.89, 131.59, 130.59, 128.88, 128.68, 128.41, 128.12, 127.38, 127.25, 126.52, 126.23, 125.83, 123.36, 95.79, 83.77.

HRMS (MALDI): calcd for C\textsubscript{28}H\textsubscript{18}S[M]^+, 386.1124, observed 386.1125.

The synthesis of 1-(2'-(2-chlorophenyl)ethynyl)-[1,1'-biphenyl]-4-yl)naphthalene (2e)

This reaction was carried out in a 2 mmol scale for 3e. Following the general procedure A, the crude product was purified by flash chromatography on silica gel using iso-hexane to iso-hexane:CH\textsubscript{2}Cl\textsubscript{2} (10:1) as eluent to give 2e as solid (563 mg, 68%).

^{1}H NMR (300 MHz, CD\textsubscript{2}Cl\textsubscript{2}): \(\delta\) 8.07 (dd, \(J = 8.5, 1.4\) Hz, 1H), 8.00 - 7.84 (m, 4H), 7.80 (dd, \(J = 7.5, 1.5\) Hz, 1H), 7.68 - 7.39 (m, 11H), 7.30 - 7.19 (m, 2H)).

^{13}C NMR (76 MHz, CD\textsubscript{2}Cl\textsubscript{2}): \(\delta\) 142.99, 139.35, 139.31, 138.70, 133.29, 132.78, 132.68, 130.99, 129.17,
128.97, 128.72, 128.64, 128.51, 127.66, 127.06, 126.65, 126.38, 125.92, 125.47, 125.34, 125.20, 124.84, 120.59, 93.74, 88.52.

HRMS (MALDI): calcd for C_{30}H_{19}Cl [M]^+, 414.1170, observed 414.1174.

The synthesis of 2-((4'-(naphthalen-1-yl)-[1,1'-biphenyl]-2-yl)ethynyl)thiophene (2g)

This reaction was carried out in a 2 mmol scale for 3g. 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 2g as pale-yellow oil (663 mg, 86%).

$^1$H NMR (300 MHz, CD_{2}Cl_{2}): $\delta$ 8.08 (ddt, $J = 8.2, 1.7, 0.8$ Hz, 1H), 8.02 - 7.90 (m, 2H), 7.87 - 7.81 (m, 2H), 7.75 - 7.62 (m, 3H), 7.62 - 7.37 (m, 7H), 7.30 (dd, $J = 5.2, 1.1$ Hz, 1H), 7.24 (dd, $J = 3.6, 1.2$ Hz, 1H), 7.01 (dd, $J = 5.1, 3.7$ Hz, 1H).

$^{13}$C NMR (76 MHz, CD_{2}Cl_{2}): $\delta$ 143.72, 140.37, 140.29, 139.70, 134.28, 132.83, 132.00, 131.98, 130.12, 129.87, 129.59, 129.23, 128.66, 128.07, 127.86, 127.65, 127.55, 127.38, 126.46, 126.37, 126.21, 125.84, 121.64, 93.64, 86.15.

HRMS (MALDI): calcd for C_{28}H_{18}S [M]^+, 386.1124, observed 386.1122.

The synthesis of 1-(2'-(4-(tert-butyl)phenyl)ethynyl)-[1,1'-biphenyl]-4-yl)naphthalene (2h)

This reaction was carried out in a 2 mmol scale for 3h. 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 2h as solid (592 mg, 68%).
\(^1\)H NMR (300 MHz, CD\(_2\)Cl\(_2\)): \(\delta\) 8.11 - 8.03 (m, 1H), 8.00 - 7.90 (m, 2H), 7.89 - 7.84 (m, 2H), 7.75 - 7.70 (m, 1H), 7.68 - 7.62 (m, 2H), 7.61 - 7.36 (m, 11H), 1.33 (s, 9H).

\(^{13}\)C NMR (76 MHz, CD\(_2\)Cl\(_2\)): \(\delta\) 143.87, 140.36, 140.29, 139.98, 134.31, 133.14, 132.02, 131.41, 130.02, 129.85, 129.73, 128.94, 128.69, 128.07, 127.64, 127.41, 126.49, 126.34, 126.21, 125.85, 125.83, 122.17, 120.69, 92.97, 89.21, 35.06, 31.28.

HRMS (MALDI): calcd for C\(_{34}\)H\(_{28}\) [M]+, 436.2186, observed 436.2189.

The synthesis of 4-((4′-(naphthalen-1-yl)-[1,1′-biphenyl]-2-yl)ethynyl)benzonitrile (2i)

This reaction was carried out in a 2 mmol scale for 3i. Following the general procedure A, the crude product was purified by flash chromatography on silica gel using iso-hexane to iso-hexane:ethyl acetate (20:1) as eluent to give 2i as white solid (648 mg, 80%).

\(^1\)H NMR (300 MHz, CD\(_2\)Cl\(_2\)): \(\delta\) 8.06 - 7.89 (m, 3H), 7.84 - 7.77 (m, 2H), 7.74 (dd, \(J = 7.6, 1.4\) Hz, 1H), 7.68 - 7.40 (m, 13H).

\(^{13}\)C NMR (76 MHz, CD\(_2\)Cl\(_2\)): \(\delta\) 144.43, 140.52, 139.60, 134.27, 133.46, 132.43, 132.07, 131.91, 130.07, 129.94, 129.92, 129.63, 128.72, 128.52, 128.14, 127.73, 127.36, 126.47, 126.25, 126.11, 125.83, 121.00, 111.78, 94.14, 91.04.

HRMS (MALDI): calcd for C\(_{31}\)H\(_{19}\)N [M]+, 405.1506, observed 405.1506.

The synthesis of N,N-dimethyl-4-((4′-(naphthalen-1-yl)-[1,1′-biphenyl]-2-yl)ethynyl)aniline (2j)

This reaction was carried out in a 2 mmol scale for 3j. 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 2j as pale-yellow solid (710 mg, 84%).

1H NMR (300 MHz, CD₂Cl₂): δ 8.09 - 8.01 (m, 1H), 7.99 - 7.88 (m, 2H), 7.88 - 7.82 (m, 2H), 7.69 - 7.33 (m, 10H), 7.31 - 7.24 (m, 2H), 6.67 - 6.58 (m, 2H), 2.96 (s, 6H).

13C NMR (76 MHz, CD₂Cl₂): δ 150.63, 143.19, 140.40, 140.15, 140.13, 134.28, 132.72, 132.67, 132.00, 129.94, 129.75, 129.71, 128.63, 128.19, 127.99, 127.56, 127.39, 126.45, 126.36, 126.16, 125.82, 122.83, 112.11, 110.15, 94.20, 87.70, 40.30.

HRMS (MALDI): calcd for C₃₂H₂₅N[M]⁺, 423.1982, observed 423.1985.

The synthesis of 1-(2'-(phenylethynyl)-5'-(trifluoromethyl)-[1,1'-biphenyl]-4-yl)naphthalene (2m)

This reaction was carried out in a 2 mmol scale for 3m. Following the general procedure A, the crude product was purified by flash chromatography on silica gel using iso-hexane:ethyl acetate (20:1) as eluent to give 2m as white solid (644 mg, 72%).

1H NMR (300 MHz, CD₂Cl₂): δ 8.04 - 7.89 (m, 4H), 7.87 - 7.82 (m, 2H), 7.72 - 7.64 (m, 4H), 7.62 - 7.43 (m, 6H), 7.37 - 7.32 (m, 3H).

13C NMR (76 MHz, CD₂Cl₂): δ 147.24, 141.15, 140.05, 138.58, 134.29, 131.92, 131.80, 130.43, 130.21, 130.06, 130.01, 129.97, 129.61, 129.54, 129.14, 128.85, 128.71, 128.22, 127.40, 126.55, 126.25, 126.16, 125.83, 125.46, 125.41, 123.10, 122.91, 94.05, 88.35.

HRMS (MALDI): calcd for C₃₁H₁₉F₃ [M]⁺, 448.1433, observed 448.1439.

The synthesis of N,N-diphenyl-2'-(phenylethynyl)-[1,1'-biphenyl]-4-amine (2n)
This reaction was carried out in a 2 mmol scale for 3n. 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 2n as white solid (715 mg, 85%).

H NMR (300 MHz, CD₂Cl₂): \( \delta \) 7.66 (dd, \( J = 7.5, 1.5 \) Hz, 1H), 7.64 - 7.57 (m, 2H), 7.51 - 7.27 (m, 12H), 7.18 (dd, \( J = 8.6, 1.6 \) Hz, 6H), 7.12 - 7.03 (m, 2H).

C NMR (76 MHz, CD₂Cl₂): \( \delta \) 148.13, 147.75, 143.92, 134.87, 133.13, 131.61, 130.63, 129.67, 129.56, 129.05, 128.74, 128.60, 127.20, 124.82, 123.81, 123.37, 123.36, 121.65, 92.51, 91.03.

HRMS (MALDI): calcd for C₃₂H₂₃N \([M]^+\), 421.1825, observed 421.1826.

The synthesis of N,N-diphenyl-4-(3-(phenylethynyl)naphthalen-2-yl)aniline (2o)

This reaction was carried out in a 2 mmol scale for 3o. 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 2o as pale-yellow solid (612 mg, 65%).

H NMR (300 MHz, CD₂Cl₂): \( \delta \) 8.20 (s, 1H), 7.95 - 7.81 (m, 3H), 7.73 - 7.65 (m, 2H), 7.58 - 7.49 (m, 2H), 7.47 - 7.41 (m, 2H), 7.40 - 7.27 (m, 7H), 7.21 (ddt, \( J = 8.5, 3.5, 2.5 \) Hz, 6H), 7.13 - 7.04 (m, 2H).

C NMR (76 MHz, CD₂Cl₂): \( \delta \) 148.16, 147.76, 140.57, 134.85, 133.53, 133.05, 132.35, 131.62, 130.90, 129.67, 128.77, 128.66, 128.21, 128.17, 127.73, 127.47, 126.83, 124.79, 123.79, 123.44, 123.35, 120.29, 93.01, 90.25.

HRMS (MALDI): calcd for C₃₆H₂₅N \([M]^+\), 471.1982, observed 471.1985.

The synthesis of 5'-(9H-carbazol-9-yl)-N,N-diphenyl-2'-(phenylethynyl)-[1,1'-biphenyl]-4-amine (2p)
This reaction was carried out in a 2 mmol scale for 3p. 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 2p as pale-yellow solid (504 mg, 43%).

\(^1\)H NMR (300 MHz, CD₂Cl₂): \(\delta\) 8.15 (dt, \(J = 7.7, 1.0 \text{ Hz}, 2\text{H}), 7.87 (d, \(J = 8.2 \text{ Hz}, 1\text{H}), 7.71 - 7.62 (m, 3\text{H}), 7.58 - 7.51 (m, 3\text{H}), 7.49 - 7.39 (m, 4\text{H}), 7.38 - 7.24 (m, 9\text{H}), 7.19 - 7.12 (m, 6\text{H}), 7.09 - 7.02 (m, 2\text{H}).

\(^{13}\)C NMR (76 MHz, CD₂Cl₂): \(\delta\) 148.19, 147.99, 145.64, 140.91, 138.18, 134.65, 133.74, 131.67, 130.59, 129.67, 128.80, 128.78, 127.59, 126.45, 125.31, 124.98, 123.90, 123.63, 123.54, 123.07, 120.65, 120.59, 120.51, 110.25, 93.18, 89.47.

HRMS (MALDI): calcd for C₄₄H₃₀N₂ \([M]^+\), 586.2404, observed 586.2410.

The synthesis of 9-(2'-(phenylethynyl)-[1,1'-biphenyl]-4-yl)-9H-carbazole (2r)

This reaction was carried out in a 2 mmol scale for 3r. 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 2r as pale-yellow solid (320 mg, 38%).

\(^1\)H NMR (300 MHz, CD₂Cl₂): \(\delta\) 8.20 (dt, \(J = 7.7, 1.0 \text{ Hz}, 2\text{H}), 8.00 - 7.87 (m, 2\text{H}), 7.78 - 7.65 (m, 3\text{H}), 7.61 - 7.39 (m, 9\text{H}), 7.38 - 7.30 (m, 5\text{H}).

\(^{13}\)C NMR (76 MHz, CD₂Cl₂): \(\delta\) 143.50, 141.23, 140.04, 137.34, 133.15, 131.66, 131.29, 129.77, 129.16,
The synthesis of N-(naphthalen-2-yl)-N-(2'-(phenylethynyl)-[1,1'-biphenyl]-4-yl)naphthalen-2-amine (2t)

This reaction was carried out in a 0.5 mmol scale for 3t. 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 2t as pale-yellow solid (220 mg, 85%).

¹H NMR (300 MHz, CD₂Cl₂): δ 7.81 (dd, 8.9, 5.0 Hz, 4H), 7.70 - 7.54 (m, 7H), 7.52 - 7.25 (m, 16H).

¹³C NMR (76 MHz, CD₂Cl₂): δ 147.58, 145.72, 143.73, 135.42, 134.89, 133.23, 131.59, 130.76, 130.70, 129.58, 129.35, 129.07, 128.78, 128.60, 127.91, 127.32, 127.26, 126.72, 125.07, 124.99, 123.93, 123.78, 121.62, 121.16, 92.51, 89.91.

HRMS (MALDI): calcd for C₄₀H₂₇N [M⁺], 521.2138, observed 521.2142.

The synthesis of 2',5'-bis((4-(tert-butyl)phenyl)ethynyl)-N₄,N₄',N₄'',N₄'''-tetraphenyl-[1,1':4',1''-terphenyl]-4,4''-diamine (2u)
This reaction was carried out in a 1 mmol scale for 3u. 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 2u as orange solid (753 mg, 86%).

$^1$H NMR (300 MHz, CD₂Cl₂): $\delta$ 7.71 (s, 2H), 7.68 - 7.62 (m, 4H), 7.36 - 7.27 (m, 16H), 7.20 - 7.15 (m, 12H), 7.10 - 7.04 (m, 4H), 1.33 (s, 18H)

$^{13}$C NMR (76 MHz, CD₂Cl₂): $\delta$ 152.28, 148.09, 147.95, 141.97, 133.71, 133.61, 131.39, 130.53, 129.67, 125.82, 124.89, 123.41, 123.28, 121.88, 120.49, 94.31, 89.21, 35.09, 31.25.

HRMS (MALDI): calcd for C₆₆H₅₆N₂ [M$^+$], 876.4438, observed 876.4439.

The synthesis of 4',6'-bis((4-(tert-butyl)phenyl)ethynyl)-N$^4$,N$^4$,N$^{4''}$,N$^{4''}$-tetraphenyl-[1,1':3',1''-terphenyl]-4,4''-diamine (2v)

This reaction was carried out in a 1 mmol scale for 3v. 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 2v as yellow solid (736 mg, 84%).
$^1$H NMR (300 MHz, CD$_2$Cl$_2$): $\delta$ 7.88 (s, 1H), 7.68 - 7.63 (m, 4H), 7.54 (s, 1H), 7.39 - 7.27 (m, 16H), 7.19 - 7.14 (m, 12H), 7.10 - 7.05 (m, 4H), 1.34 (s, 18H).

$^{13}$C NMR (76 MHz, CD$_2$Cl$_2$): $\delta$ 152.19, 148.04, 143.43, 137.24, 134.03, 131.37, 130.52, 130.26, 129.67, 129.61, 125.81, 124.94, 124.66, 123.47, 123.13, 120.56, 120.42, 93.38, 88.57, 35.09, 31.27.

HRMS (MALDI): calcd for C$_{66}$H$_{56}$N$_2$ [M]$^+$, 876.4438, observed 876.4448.

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**The synthesis of 3b-boratribenzo[de,h,rst]pentaphene (1a)**

This reaction was carried out in a 0.3 mmol scale for 2a. Following the general procedure C, the crude product was purified by flash chromatography on silica gel with hexane to hexane: CH$_2$Cl$_2$ (10:1) as eluent to afford 1a as yellow powder (33 mg, 28%).

$^1$H NMR (300 MHz, C$_2$D$_2$Cl$_4$): $\delta$ 9.19 (d, $J = 9.0$ Hz, 1H), 9.10 (dd, $J = 7.0$, 1.3 Hz, 1H), 9.06 (s, 1H), 8.94 - 8.80 (m, 3H), 8.73 (dd, $J = 18.8$, 7.8 Hz, 2H), 8.34 (dd, $J = 8.1$, 1.3 Hz, 1H), 8.21 - 8.15 (m, 2H), 7.93 (dd, $J = 8.1$, 7.0 Hz, 1H), 7.88 - 7.81 (m, 2H), 7.80 - 7.64 (m, 3H).

$^{13}$C NMR (76 MHz, C$_2$D$_2$Cl$_4$): $\delta$ 142.59, 140.93, 138.45, 135.37, 133.36, 132.77, 132.17, 132.10, 131.20, 130.22, 128.66, 128.16, 127.50, 127.05, 126.97, 126.70, 126.66, 125.21, 123.28, 123.14, 120.80, peaks corresponding to B-C could not be observed. Note: due to the low solubility, the record of $^{11}$B NMR is not successful.

HRMS (MALDI): calcd for C$_{30}$H$_{17}$B [M]$^+$, 388.1418, observed 388.1424.
The synthesis of 3b-boratribenzo[de,h,vwx]hexaphene (1b)

This reaction was carried out in a 0.3 mmol scale for 2b. Following the general procedure A, the crude product was purified by flash chromatography on silica gel with hexane to hexane: CH₂Cl₂ (10:1) as eluent to afford 1b as yellow powder (24 mg, 18%).

¹H NMR (300 MHz, C₂D₂Cl₄): δ 9.28 (d, J = 9.6 Hz, 2H), 9.12 - 9.02 (m, 2H), 8.85 (t, J = 8.2 Hz, 2H), 8.74 (d, J = 8.2 Hz, 1H), 8.69 - 8.61 (m, 2H), 8.33 (dd, J = 8.2, 1.2 Hz, 1H), 8.23 - 8.10 (m, 3H), 7.91 (dd, J = 8.0, 7.0 Hz, 1H), 7.87 - 7.80 (m, 2H), 7.71 - 7.59 (m, 3H).

¹³C NMR (76 MHz, C₂D₂Cl₄): δ 142.55, 141.03, 140.77, 138.41, 135.29, 133.41, 132.91, 132.52, 132.15, 131.81, 131.50, 129.07, 128.93, 128.50, 127.70, 127.64, 126.90, 126.66, 125.22, 123.34, 121.97, 120.80, peaks corresponding to B-C could not be observed.

HRMS (MALDI): calcd for C₃₄H₁₉B [M]⁺, 438.1574, observed 438.1582.

The synthesis of 10-chloro-3b-boratribenzo[de,h,rst]pentaphene (1c)

This reaction was carried out in a 0.3 mmol scale for 2c. Following the general procedure A, the crude product was purified by flash chromatography on silica gel with hexane to hexane: CH₂Cl₂ (10:1) as eluent to afford 1c as yellow powder (44 mg, 35%).

¹H NMR (300 MHz, C₂D₂Cl₄): δ 9.04 (d, J = 7.0 Hz, 1H), 8.96 (d, J = 8.8 Hz, 1H), 8.79 (d, J = 6.6 Hz, 2H), 8.72 (d, J = 8.8 Hz, 1H), 8.63 (d, J = 7.5 Hz, 3H), 8.32 (d, J = 8.0 Hz, 1H), 8.15 (d, J = 8.0 Hz, 1H), 8.03 (s, 1H), 7.90 (t, J = 7.5 Hz, 1H), 7.80 (dt, J = 8.1, 5.2 Hz, 2H), 7.64 (t, J = 7.4 Hz, 2H).
$^{13}$C NMR (76 MHz, C$_2$D$_2$Cl$_4$): $\delta$ 142.10, 141.48, 141.01, 138.47, 135.47, 133.31, 133.26, 133.00, 132.88, 132.53, 132.21, 129.29, 128.77, 128.41, 128.29, 128.18, 127.75, 127.04, 126.69, 126.62, 125.55, 125.24, 124.80, 123.56, 120.80, peaks corresponding to B-C could not be observed.

HRMS (MALDI): calcd for C$_{30}$H$_{16}$BCl $[M]^+$, 422.1028, observed 422.1024.

The synthesis of 9-thia-3b-borabenzo[a]inden[6,5,4-cd]perylene (1d)

This reaction was carried out in a 0.3 mmol scale for 2d. Following the general procedure A, the crude product was purified by flash chromatography on silica gel with hexane to hexane: CH$_2$Cl$_2$ (10:1)) as eluent to afford 1d as pale-yellow powder (30 mg, 25%).

$^1$H NMR (300 MHz, C$_2$D$_2$Cl$_4$): $\delta$ 9.19 (s, 1H), 9.14 (dd, $J = 6.9$, 1.4 Hz, 1H), 8.89 (dd, $J = 7.5$, 1.1 Hz, 1H), 8.82 (s, 2H), 8.76 - 8.64 (m, 2H), 8.34 (dd, $J = 8.1$, 1.3 Hz, 1H), 8.21 - 8.12 (m, 2H), 7.93 (dd, $J = 8.0$, 7.0 Hz, 1H), 7.88 - 7.75 (m, 3H), 7.64 (td, $J = 7.4$, 1.0 Hz, 1H).

$^{13}$C NMR (76 MHz, C$_2$D$_2$Cl$_4$) $\delta$ 142.76, 141.17, 140.97, 138.59, 138.44, 135.32, 133.37, 132.88, 132.15, 132.07, 130.06, 128.54, 127.62, 127.12, 127.00, 126.63, 126.56, 124.88, 123.24, 122.71, 120.8, 120.34, peaks corresponding to B-C could not be observed.

HRMS (MALDI): calcd for C$_{28}$H$_{15}$BS $[M]^+$, 394.0982, observed 394.0982.

The synthesis of 7-chloro-3b-boratribenzo[de,h,rst]pentaphene (1e)

This reaction was carried out in a 0.3 mmol scale for 2e. Following the general procedure A, the crude product was purified by flash chromatography on silica gel with hexane to hexane: CH$_2$Cl$_2$ (10:1)) as eluent to afford
**1e** as pale-yellow powder (32 mg, 25%).

\[^1\text{H} \text{NMR} \ (300 \text{ MHz, } \text{C}_2\text{D}_2\text{Cl}_4) : \delta 9.62 \ (s, 1\text{H}), 9.13 \ (d, J = 8.9 \text{ Hz, } 1\text{H}), 8.97 \ (d, J = 6.9 \text{ Hz, } 1\text{H}), 8.87 - 8.71 \ (m, 3\text{H}), 8.48 \ (d, J = 7.3 \text{ Hz, } 1\text{H}), 8.32 \ (d, J = 8.0 \text{ Hz, } 1\text{H}), 8.14 \ (t, J = 8.6 \text{ Hz, } 2\text{H}), 7.90 \ (t, J = 7.5 \text{ Hz, } 1\text{H}), 7.86 - 7.75 \ (m, 3\text{H}), 7.71 \ (t, J = 7.3 \text{ Hz, } 1\text{H}), 7.53 \ (t, J = 7.6 \text{ Hz, } 1\text{H}).\]

\[^{13}\text{C} \text{NMR} \ (75 \text{ MHz, } \text{C}_2\text{D}_2\text{Cl}_4) : \delta 140.51, 140.10, 137.71, 135.26, 135.12, 133.19, 132.90, 132.60, 132.28, 131.66, 130.68, 130.55, 130.07, 129.22, 128.38, 128.16, 127.76, 127.61, 127.02, 126.48, 126.24, 122.63, 122.46, 120.34, \text{peaks corresponding to B-C could not be observed.}\]

HRMS (MALDI): calcd for C\text{_{30}H}_{16}\text{BCl} \ [M]^+, 422.1028, observed 422.1031.

**The synthesis of 7-bromo-3b-boratribenzo[de,hrst]pentaphene (1f)**

![Chemical Structure Image]

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 with hexane to hexane: CH\text{\textsubscript{2}}Cl\text{\textsubscript{2}} (10:1) as eluent to afford 1f as pale-yellow powder (15 mg, 18%).

\[^1\text{H} \text{NMR} \ (300 \text{ MHz, } \text{C}_2\text{D}_2\text{Cl}_4) : \delta 9.62 \ (s, 1\text{H}), 9.14 \ (d, J = 8.9 \text{ Hz, } 1\text{H}), 9.00 \ (d, J = 6.9 \text{ Hz, } 1\text{H}), 8.89 - 8.71 \ (m, 3\text{H}), 8.54 \ (d, J = 7.2 \text{ Hz, } 1\text{H}), 8.33 \ (d, J = 8.0 \text{ Hz, } 1\text{H}), 8.14 \ (t, J = 8.0 \text{ Hz, } 2\text{H}), 8.10 - 8.04 \ (m, 1\text{H}), 7.85 \ (d, J = 23.1, 7.6 \text{ Hz, } 3\text{H}), 7.71 \ (t, J = 7.3 \text{ Hz, } 1\text{H}), 7.45 \ (t, J = 7.6 \text{ Hz, } 1\text{H}).\]

\[^{13}\text{C} \text{NMR} \ (75 \text{ MHz, } \text{C}_2\text{D}_2\text{Cl}_4) : \delta 142.31, 141.00, 140.52, 139.22, 138.64, 135.64, 133.39, 133.83, 132.83, 132.75, 132.15, 131.43, 131.17, 131.11, 130.51, 130.42, 128.85, 128.65, 128.54, 128.01, 127.52, 126.97, 126.75, 126.70, 123.16, 122.97, \text{peaks corresponding to B-C could not be observed.}\]

HRMS (MALDI): calcd for C\text{_{30}H}_{16}\text{BB} \ [M]^+, 466.0523, observed 466.0531.

**The synthesis of 6-thia-3b-boradibenzo[de,hrst]cyclopenta[h]pentaphene (1g)**

S15
This reaction was carried out in a 0.3 mmol scale for 2g. Following the general procedure A, the crude product was purified by flash chromatography on silica gel with hexane to hexane: CH$_2$Cl$_2$ (10:1) as eluent to afford 1g as yellow powder (47 mg, 40%).

$^1$H NMR (300 MHz, C$_2$D$_2$Cl$_4$): $\delta$ 9.32 (dd, $J = 7.0$, 1.3 Hz, 1H), 9.15 (d, $J = 9.0$ Hz, 1H), 8.97 - 8.89 (m, 2H), 8.84 (d, $J = 8.2$ Hz, 1H), 8.72 (s, 1H), 8.39 (d, $J = 5.2$ Hz, 1H), 8.33 (dd, $J = 7.8$, 1.3 Hz, 1H), 8.14 (dd, $J = 16.3$, 7.8 Hz, 2H), 7.92 (dd, $J = 8.1$, 6.9 Hz, 1H), 7.88 - 7.68 (m, 3H), 7.62 (d, $J = 5.1$ Hz, 1H).

$^{13}$C NMR (75 MHz, C$_2$D$_2$Cl$_4$): $\delta$ 143.12, 140.14, 135.44, 133.43, 132.10, 131.95, 129.67, 128.67, 128.16, 128.07, 127.97, 127.37, 127.13, 126.56, 126.44, 125.12, 123.51, 123.29, peaks corresponding to B-C could not be observed.

HRMS (MALDI): calcd for C$_{28}$H$_{15}$BS [M]$^+$, 394.0982, observed 394.0990.

The synthesis of 5-(tert-butyl)-3b-boratribenzo[de,h,rst]pentaphene (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 with hexane to hexane: CH$_2$Cl$_2$ (10:1) as eluent to afford 1h as yellow powder (35 mg, 39%).

$^1$H NMR (300 MHz, C$_2$D$_2$Cl$_4$): $\delta$ 9.17 (d, $J = 9.0$ Hz, 1H), 9.08 (dd, $J = 7.0$, 1.3 Hz, 1H), 9.02 (s, 1H), 8.92 - 8.80 (m, 3H), 8.73 - 8.65 (m, 2H), 8.35 (dd, $J = 8.2$, 1.2 Hz, 1H), 8.17 (dd, $J = 7.2$, 6.1, 1.3 Hz, 2H), 7.96 (dd, $J = 8.0$, 7.0 Hz, 1H), 7.91 - 7.84 (m, 2H), 7.80 - 7.69 (m, 2H), 1.53 (s, 9H).

$^{13}$C NMR (75 MHz, C$_2$D$_2$Cl$_4$): $\delta$ 149.55, 140.87, 140.31, 139.46, 134.79, 134.61, 132.97, 132.44, 131.77,
131.64, 131.58, 130.84, 130.64, 130.55, 129.71, 129.29, 128.23, 128.16, 127.52, 127.02, 126.50, 126.32, 126.27, 126.16, 124.58, 122.80, 122.72, 120.38, 34.86, 31.55, peaks corresponding to B-C could not be observed.

HRMS (MALDI): calcd for C_{34}H_{23}B [M]^+, 444.2044, observed 444.2039.

The synthesis of 3b-boratribenzo[de,h,rst]pentaphene-5-carbonitrile (1i)

This reaction was carried out in a 0.2 mmol scale for 2i. Following the general procedure A, the crude product was purified by flash chromatography on silica gel with hexane to hexane: ethyl acetate (20:1)) as eluent to afford 1i as yellow powder (22 mg, 27%).

$^1$H NMR (300 MHz, C$_2$D$_2$Cl$_4$): $\delta$ 8.96 (d, $J = 9.0$ Hz, 1H), 8.78 (d, $J = 7.3$ Hz, 2H), 8.75 - 8.59 (m, 4H), 8.54 (d, $J = 8.7$ Hz, 1H), 8.32 (dd, $J = 8.2$, 1.3 Hz, 1H), 8.15 (d, $J = 7.9$ Hz, 1H), 8.04 (dd, $J = 7.9$, 1.5 Hz, 1H), 7.89 - 7.74 (m, 4H), 7.69 (td, $J = 7.4$, 6.9, 1.2 Hz, 1H).

$^{13}$C NMR (75 MHz, C$_2$D$_2$Cl$_4$): $\delta$ 145.54, 141.53, 141.21, 140.13, 135.58, 133.20, 132.82, 132.11, 131.80, 131.09, 131.05, 130.39, 130.06, 129.64, 128.55, 128.42, 127.95, 127.23, 126.97, 126.31, 125.06, 122.89, 122.64, 120.38, 120.04, 109.58, peaks corresponding to B-C could not be observed.

HRMS (MALDI): calcd for C$_{31}$H$_{16}$BN [M]$^+$, 413.1370, observed 413.1365.

The synthesis of 7-phenyl-7H-7-aza-11b-boratribenzo[cf,pqr]tetraphene (1n)
This reaction was carried out in a 0.2 mmol scale for 2n. Following the general procedure A, the crude product was purified by flash chromatography on silica gel with hexane: CH₂Cl₂ (10:1) as eluent to afford 1n as orange powder (50 mg, 58%).

\(^1\)H NMR (300 MHz, CD₂Cl₂): \(\delta 9.31 (s, 1H), 9.22 (dd, J = 7.8, 1.7 Hz, 1H), 9.12 (dd, J = 7.6, 1.5 Hz, 1H), 9.03 (d, J = 9.6 Hz, 1H), 8.95 (dd, J = 8.2, 1.1 Hz, 1H), 8.81 - 8.74 (m, 1H), 8.25 (dd, J = 7.7, 1.6 Hz, 1H), 7.91 - 7.61 (m, 8H), 7.49 (dd, J = 7.9, 3.1, 1.1 Hz, 3H), 7.33 (d, J = 9.5 Hz, 1H), 7.13 (dd, J = 8.8, 1.0 Hz, 1H).

\(^{13}\)C NMR (75 MHz, CD₂Cl₂): \(\delta 146.39, 145.81, 142.14, 141.41, 136.30, 135.50, 131.48, 131.37, 130.99, 130.65, 130.57, 130.28, 129.84, 129.53, 128.86, 127.40, 126.97, 126.21, 126.01, 124.91, 123.05, 122.29, 120.96, 118.27, 117.38, \) peaks corresponding to B-C could not be observed.

HRMS (MALDI): calcd for C\(_{32}\)H\(_{20}\)BN [M\(^+\)], 429.1683, observed 429.1691.

**The synthesis of 18-phenyl-18H-18-aza-4b-boraanthra[9,1,2-cde]benzo[a]tetracene (1o)**

This reaction was carried out in a 0.2 mmol scale for 2o. Following the general procedure A, the crude product was purified by flash chromatography on silica gel with hexane: CH₂Cl₂ (10:1) as eluent to afford 1o as orange powder (70 mg, 73%).

\(^1\)H NMR (300 MHz, CD₂Cl₂): \(\delta 9.15 (s, 1H), 9.04 (d, J = 11.3 Hz, 2H), 8.94 (dd, J = 11.2, 8.4 Hz, 2H), 8.76 (d, J = 8.2 Hz, 1H), 8.57 (s, 1H), 8.09 - 7.98 (m, 2H), 7.66 (ddq, J = 21.9, 14.9, 7.4 Hz, 5H), 7.55 - 7.40 (m, 3H), 7.35 (dd, J = 7.5, 5.4 Hz, 3H), 7.15 (d, J = 9.3 Hz, 1H), 6.97 (d, J = 8.7 Hz, 1H).

\(^{13}\)C NMR (75 MHz, CD₂Cl₂): \(\delta 142.12, 141.45, 136.33, 135.62, 132.60, 131.74, 131.68, 131.38, 130.71, 130.69, 129.96, 129.47, 128.96, 128.63, 128.61, 128.24, 128.23, 127.13, 126.72, 126.20, 125.71, 124.97, 120.84, 120.63, 118.12, 116.93, \) peaks corresponding to B-C could not be observed.

\(^{11}\)B NMR (96 MHz, CD₂Cl₂): \(\delta = 41.3\) (br.).

HRMS (MALDI, m/z): calcd for C\(_{36}\)H\(_{22}\)BN [M\(^+\)], 479.1840, observed 479.1853.
The synthesis of 3-(9H-carbazol-9-yl)-7-phenyl-7H-7-aza-11b-boratribenzo[c,f,pqr]tetraphene (1p)

This reaction was carried out in a 0.2 mmol scale for 2p. Following the general procedure A, the crude product was purified by flash chromatography on silica gel with hexane: CH$_2$Cl$_2$ (5:1) as eluent to afford 1p as orange powder (92 mg, 76%).

$^1$H NMR (300 MHz, CD$_2$Cl$_2$): $\delta$ 9.39 (s, 1H), 9.23 (dd, $J = 7.9$, 1.7 Hz, 1H), 9.14 (dd, $J = 7.6$, 1.5 Hz, 1H), 9.01 - 8.87 (m, 3H), 8.46 (d, $J = 8.5$ Hz, 1H), 8.21 (ddd, $J = 7.7$, 1.3, 0.7 Hz, 2H), 7.93 - 7.83 (m, 2H), 7.80 - 7.56 (m, 7H), 7.53 - 7.40 (m, 5H), 7.36 - 7.28 (m, 3H), 7.13 (dd, $J = 8.7$, 1.0 Hz, 1H).

$^{13}$C NMR (75 MHz, CD$_2$Cl$_2$): $\delta$ 146.39, 146.04, 142.00, 141.49, 141.23, 136.62, 136.36, 135.51, 131.94, 131.68, 131.59, 131.47, 131.38, 130.73, 130.70, 130.55, 129.92, 129.58, 128.83, 127.18, 126.47, 125.68, 125.00, 124.98, 123.83, 122.81, 121.12, 120.66, 120.48, 120.35, 118.33, 117.69, 110.24, peaks corresponding to B-C could not be observed.

HRMS (MALDI): calcd for C$_{44}$H$_{27}$BN$_2$ [M]$^+$, 594.2262, observed 594.2270.

The synthesis of 13-(tert-butyl)-5-(9H-carbazol-9-yl)-7-phenyl-7H-7-aza-11b-boratribenzo[c,f,pqr]tetraphene (1q)
This reaction was carried out in a 0.1 mmol scale for 2q. Following the general procedure A, the crude product was purified by flash chromatography on silica gel with hexane: CH₂Cl₂ (5:1) as eluent to afford 1p as orange powder (36 mg, 56%).

\(^1\)H NMR (300 MHz, CD₂Cl₂): \(\delta\) 9.34 (s, 1H), 9.21 (dd, \(J = 7.8, 1.7\) Hz, 1H), 9.11 (d, \(J = 2.3\) Hz, 1H), 8.90 (d, \(J = 8.7\) Hz, 1H), 8.21 - 8.15 (m, 3H), 7.98 (dd, \(J = 8.6, 2.3\) Hz, 1H), 7.70 - 7.65 (m, 3H), 7.58 - 7.50 (m, 4H), 7.42 - 7.38 (m, 1H), 7.36 (s, 1H), 7.24 (td, \(J = 7.4, 1.5\) Hz, 4H), 7.12 (d, \(J = 8.6\) Hz, 1H), 6.97 - 6.93 (m, 3H), 6.88 (dd, \(J = 6.8, 1.6\) Hz, 1H), 1.61 (s, 9H).

\(^13\)C NMR (75 MHz, CD₂Cl₂): \(\delta\) 146.64, 141.68, 140.62, 139.09, 135.68, 132.72, 131.87, 131.65, 131.41, 130.37, 129.70, 128.59, 127.71, 127.13, 126.38, 126.01, 125.05, 124.55, 124.17, 121.49, 120.66, 120.58, 118.73, 118.23, 110.66, 32.31, 30.07, peaks corresponding to B-C could not be observed.

HRMS (MALDI): calcd for C₄₈H₃₅BN₂ \([M]^{+}\), 650.2888, observed 650.2886.

The synthesis of 16b-aza-9b-boradibenzo[f,pqr]fluoreno[9,1-bc]tetraphene (1r)

This reaction was carried out in a 0.3 mmol scale for 2r. Following the general procedure A, the crude product was purified by flash chromatography on silica gel with hexane: CH₂Cl₂ (5:1) as eluent to afford 1r as yellow powder (10 mg, 8%).

\(^1\)H NMR (300 MHz, C₂D₂Cl₄): \(\delta\) 9.31 (d, \(J = 9.4\) Hz, 1H), 9.19 (s, 1H), 9.15 - 9.05 (m, 2H), 9.00 (d, \(J = 9.3\) Hz, 1H), 8.83 (t, \(J = 7.4\) Hz, 2H), 8.59 - 8.47 (m, 2H), 8.32 - 8.27 (m, 1H), 8.25 - 8.18 (m, 1H), 7.89 - 7.79 (m, 3H), 7.77 - 7.65 (m, 3H), 7.53 (t, \(J = 7.4\) Hz, 1H).

\(^13\)C NMR (75 MHz, C₂D₂Cl₄): \(\delta\) 142.66, 141.59, 140.29, 137.31, 134.16, 131.72, 131.54, 131.45, 131.13, 130.75, 130.12, 129.98, 128.13, 127.86, 127.77, 127.46, 126.90, 124.91, 124.48, 124.19, 123.75, 123.17, 122.75, 121.84, 120.80, 115.65, 115.53, peaks corresponding to B-C could not be observed.

HRMS (MALDI): calcd for C₃₂H₁₅BN \([M]^{+}\), 427.1527, observed 427.1534.

The synthesis of 13-oxa-17b-aza-9b-boratetrabenzo[a,de,h,rst]pentaphene (1s)
This reaction was carried out in a 0.2 mmol scale for 2s. Following the general procedure A, the crude product was purified by flash chromatography on silica gel with hexane: CH₂Cl₂ (5:1) as eluent to afford 1s as yellow powder (9 mg, 10%).

¹H NMR (300 MHz, CD₂Cl₂): δ 9.24 (s, 1H), 9.15 (d, J = 9.6 Hz, 1H), 8.86 (t, J = 9.4 Hz, 3H), 8.57 - 8.50 (m, 1H), 8.48 - 8.39 (m, 1H), 8.25 (d, J = 7.9 Hz, 1H), 7.84 (dt, J = 19.1, 7.7 Hz, 2H), 7.76 - 7.60 (m, 3H), 7.43 - 7.35 (m, 1H), 7.31 (d, J = 8.0 Hz, 1H), 7.27 - 7.17 (m, 2H), 7.11 (t, J = 7.4 Hz, 1H).

¹³C NMR (75 MHz, CD₂Cl₂): δ 149.54, 141.66, 136.07, 131.53, 131.31, 130.71, 129.01, 129.12, 128.45, 127.79, 127.24, 126.74, 126.52, 126.47, 124.82, 123.97, 123.65, 122.46, 120.45, 118.01, 117.86, 116.67, peaks corresponding to B-C could not be observed.

HRMS (MALDI): calcd for C₃₂H₁₂BNO [M]⁺, 443.1476, observed 443.1479.

**The synthesis of 18-(naphthalen-2-yl)-18H-18-aza-6c-boradibenzo[c,m]naphtho[1,2,3,4-pqr]tetraphene (1t)**

This reaction was carried out in a 0.2 mmol scale for 2t. Following the general procedure A, the crude product was purified by flash chromatography on silica gel with hexane: CH₂Cl₂ (5:1) as eluent to afford 1t as orange powder (11 mg, 10%).

¹H NMR (300 MHz, CD₂Cl₂): δ 9.80 (s, 1H), 9.34 (s, 1H), 9.26 (dd, J = 7.5, 1.6 Hz, 1H), 9.00 (dd, J = 8.7, 2.6 Hz, 2H), 8.75 (d, J = 8.1 Hz, 1H), 8.35 (d, J = 8.6 Hz, 1H), 8.26 (ddd, J = 7.1, 5.4, 2.1 Hz, 2H), 8.18 (d, J
= 8.1 Hz, 1H), 8.12 (d, \(J = 2.0\) Hz, 1H), 8.02 (d, \(J = 8.0\) Hz, 1H), 7.93 (ddd, \(J = 8.4, 7.1, 1.6\) Hz, 1H), 7.82 (dd, \(J = 7.4, 1.2\) Hz, 1H), 7.73 (ddddd, \(J = 16.4, 10.8, 4.1, 2.4\) Hz, 5H), 7.63 (dd, \(J = 8.6, 2.1\) Hz, 1H), 7.53 - 7.45 (m, 3H), 7.33 (d, \(J = 9.4\) Hz, 1H).

\(^{13}\)C NMR (75 MHz, CD\(_2\)Cl\(_2\)): \(\delta\) 147.50, 144.33, 141.76, 139.64, 137.22, 136.51, 135.21, 135.18, 133.79, 131.87, 131.20, 131.08, 130.94, 130.80, 130.55, 129.93, 129.90, 129.70, 129.28, 128.71, 128.48, 128.41, 127.76, 127.67, 127.60, 127.39, 127.34, 127.17, 126.79, 125.99, 125.00, 124.18, 122.85, 122.23, 117.26, 113.72, peaks corresponding to B-C could not be observed.

HRMS (MALDI): calcd for C\(_{40}\)H\(_{24}\)BN\([M]^+\), 529.1996, observed 529.2006.

The synthesis of 1u

This reaction was carried out in a 0.15 mmol scale for 2s. Following the general procedure A, the crude product was purified by flash chromatography on silica gel with hexane to hexane: CH\(_2\)Cl\(_2\) (5:1)) as eluent to afford 1s as orange powder (80 mg, 60%).

\(^{1}\)H NMR (300 MHz, C\(_2\)D\(_2\)Cl\(_4\)): \(\delta\) 9.41 (s, 4H), 9.25 - 9.04 (m, 6H), 8.93 (d, \(J = 8.7\) Hz, 2H), 7.96 (dd, \(J = 8.7, 2.1\) Hz, 2H), 7.78 (q, \(J = 8.0, 7.4\) Hz, 6H), 7.63 (d, \(J = 7.8\) Hz, 2H), 7.48 (dd, \(J = 21.3, 7.3\) Hz, 6H), 7.27 (d, \(J = 9.2\) Hz, 2H), 7.09 (d, \(J = 8.7\) Hz, 2H), 1.60 (s, 18H).

\(^{13}\)C NMR (75 MHz, C\(_2\)D\(_2\)Cl\(_4\)): \(\delta\) 149.85, 146.84, 145.87, 142.43, 139.11, 135.69, 133.11, 132.26, 131.65, 131.38, 130.88, 130.60, 129.50, 128.82, 128.71, 128.33, 126.50, 125.07, 123.03, 122.33, 121.05, 118.23, 117.01, 35.34, 32.1 peaks corresponding to B-C could not be observed.

HRMS (MALDI): calcd for C\(_{66}\)H\(_{50}\)B\(_2\)N\(_2\)\([M]^+\), 892.4155, observed 892.4164.

The synthesis of 1v
This reaction was carried out in a 0.15 mmol scale for 2t. Following the general procedure A, the crude product was purified by flash chromatography on silica gel with hexane to hexane: CH$_2$Cl$_2$ (5:1) as eluent to afford 1t as orange powder (74 mg, 55%).

$^1$H NMR (300 MHz, C$_2$D$_2$Cl$_4$): $\delta$ 10.07 (s, 1H), 9.40 (s, 2H), 9.29 (d, $J$ = 9.6 Hz, 2H), 9.23 - 9.19 (m, 2H), 9.13 (d, $J$ = 2.2 Hz, 2H), 8.99 (s, 1H), 8.90 (d, $J$ = 8.8 Hz, 2H), 7.96 (dd, $J$ = 8.6, 2.3 Hz, 2H), 7.82 - 7.77 (m, 4H), 7.69 - 7.64 (m, 2H), 7.55 - 7.53 (m, 2H), 7.52 (d, $J$ = 1.5 Hz, 2H), 7.50 (d, $J$ = 2.4 Hz, 2H), 7.41 - 7.39 (s, 1H), 7.33 (d, $J$ = 9.4 Hz, 2H), 7.24 - 7.24 (s, $J$ = 2.4 Hz, 1H), 7.14 (dd, $J$ = 8.8, 1.0 Hz, 2H), 1.65 (s, 18H).

$^{13}$C NMR (75 MHz, C$_2$D$_2$Cl$_4$): $\delta$ 149.81, 146.84, 146.01, 142.46, 139.10, 135.77, 133.04, 131.89, 131.68, 131.58, 131.38, 130.89, 130.76, 129.82, 129.49, 129.45, 128.79, 128.48, 128.38, 126.09, 125.07, 123.37, 121.13, 120.82, 118.23, 116.97, 114.74, 35.32, 32.10, peaks corresponding to B-C could not be observed.

HRMS (MALDI): calcd for C$_{66}$H$_{50}$B$_2$N$_2$[M]$^+$, 892.4155, observed 892.4158.
3. NMR spectra

3.1 NMR spectrum of starting materials 2a-2v

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

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

Figure S4. $^{13}$C NMR spectrum of 2b (300 MHz, CD$_2$Cl$_2$, room temperature).
**Figure S5.** $^1$H NMR spectrum of 2d (300 MHz, CD$_2$Cl$_2$, room temperature).

**Figure S6.** $^{13}$C NMR spectrum of 2d (300 MHz, CD$_2$Cl$_2$, room temperature).
Figure S7. $^1$H NMR spectrum of 2e (300 MHz, CD$_2$Cl$_2$, room temperature).

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

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

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

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

Figure S16. $^{13}$C NMR spectrum of 2i (300 MHz, CD$_2$Cl$_2$, room temperature).
**Figure S17.** $^1$H NMR spectrum of 2m (300 MHz, CD$_2$Cl$_2$, room temperature).

**Figure S18.** $^{13}$C NMR spectrum of 2m (300 MHz, CD$_2$Cl$_2$, room temperature).
**Figure S19.** $^1$H NMR spectrum of 2n (300 MHz, CD$_2$Cl$_2$, room temperature).

**Figure S20.** $^{13}$C NMR spectrum of 2n (300 MHz, CD$_2$Cl$_2$, room temperature).
Figure S21. $^1$H NMR spectrum of 2o (300 MHz, CD$_2$Cl$_2$, room temperature).

Figure S22. $^{13}$C NMR spectrum of 2o (300 MHz, CD$_2$Cl$_2$, room temperature).
Figure S23. $^1$H NMR spectrum of 2p (300 MHz, CD$_2$Cl$_2$, room temperature).

Figure S24. $^{13}$C NMR spectrum of 2p (300 MHz, CD$_2$Cl$_2$, room temperature).
Figure S25. $^1$H NMR spectrum of 2r (300 MHz, CD$_2$Cl$_2$, room temperature).

Figure S26. $^{13}$C NMR spectrum of 2r (300 MHz, CD$_2$Cl$_2$, room temperature).
Figure S27. $^1$H NMR spectrum of 2t (300 MHz, CD$_2$Cl$_2$, room temperature).

Figure S28. $^{13}$C NMR spectrum of 2t (300 MHz, CD$_2$Cl$_2$, room temperature).
Figure S29. $^1$H NMR spectrum of 2u (300 MHz, CD$_2$Cl$_2$, room temperature).

Figure S30. $^{13}$C NMR spectrum of 2u (300 MHz, CD$_2$Cl$_2$, room temperature).
Figure S31. $^1$H NMR spectrum of 2v (300 MHz, CD$_2$Cl$_2$, room temperature).

Figure S32. $^{13}$C NMR spectrum of 2v (300 MHz, CD$_2$Cl$_2$, room temperature).
3.2 NMR spectrum of compounds 1a-1v

**Figure S33.** $^1$H NMR spectrum of 1a (300 MHz, C$_2$D$_2$Cl$_4$, room temperature).

**Figure S34.** $^{13}$C NMR spectrum of 1a (300 MHz, C$_2$D$_2$Cl$_4$, room temperature).
Figure S35. $^1$H NMR spectrum of 1b (300 MHz, C$_2$D$_2$Cl$_4$, room temperature).

Figure S36. $^{13}$C NMR spectrum of 1b (300 MHz, C$_2$D$_2$Cl$_4$, room temperature).
Figure S37. $^1$H NMR spectrum of 1c (300 MHz, C$_2$D$_2$Cl$_4$, room temperature).

Figure S38. $^{13}$C NMR spectrum of 1c (300 MHz, C$_2$D$_2$Cl$_4$, room temperature).
Figure S39. $^1$H NMR spectrum of 1d (300 MHz, C$_2$D$_2$Cl$_4$, room temperature).

Figure S40. $^{13}$C NMR spectrum of 1d (300 MHz, C$_2$D$_2$Cl$_4$, room temperature).
Figure S41. $^1$H NMR spectrum of 1e (300 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$, room temperature).

Figure S42. $^{13}$C NMR spectrum of 1e (300 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$, room temperature).
Figure S43. $^1$H NMR spectrum of 1f (300 MHz, C$_2$D$_2$Cl$_4$, room temperature).

Figure S44. $^{13}$C NMR spectrum of 1f (300 MHz, C$_2$D$_2$Cl$_4$, room temperature).
Figure S45. $^1$H NMR spectrum of 1g (300 MHz, C$_2$D$_2$Cl$_4$, room temperature).

Figure S46. $^1$H NMR spectrum of 1g (300 MHz, C$_2$D$_2$Cl$_4$, room temperature).
Figure S47. $^1$H NMR spectrum of 1h (300 MHz, C$_2$D$_2$Cl$_4$, room temperature).

Figure S48. $^{13}$C NMR spectrum of 1h (300 MHz, C$_2$D$_2$Cl$_4$, room temperature).
Figure S49. $^1$H NMR spectrum of 1i (300 MHz, C$_2$D$_2$Cl$_4$, room temperature).

Figure S50. $^{13}$C NMR spectrum of 1i (300 MHz, C$_2$D$_2$Cl$_4$, room temperature).
Figure S51. $^1$H NMR spectrum of 1n (300 MHz, CD$_2$Cl$_2$, room temperature).

Figure S52. $^{13}$C NMR spectrum of 1n (300 MHz, CD$_2$Cl$_2$, room temperature).
Figure S53. $^1$H NMR spectrum of 1o (300 MHz, CD$_2$Cl$_2$, room temperature).

Figure S54. $^{13}$C NMR spectrum of 1o (300 MHz, CD$_2$Cl$_2$, room temperature).
Figure S55. $^{11}$B NMR spectrum of 1o (300 MHz, CD$_2$Cl$_2$, room temperature).
Figure S56. $^1$H NMR spectrum of 1p (300 MHz, CD$_2$Cl$_2$, room temperature).

Figure S57. $^{13}$C NMR spectrum of 1p (300 MHz, CD$_2$Cl$_2$, room temperature).
Figure S58. $^1$H NMR spectrum of $1q$ (300 MHz, CD$_2$Cl$_2$, room temperature).

Figure S59. $^{13}$C NMR spectrum of $1q$ (300 MHz, CD$_2$Cl$_2$, room temperature).
Figure S60. $^1$H NMR spectrum of 1r (300 MHz, C$_2$D$_2$Cl$_4$, room temperature).

Figure S61. $^{13}$C NMR spectrum of 1r (300 MHz, C$_2$D$_2$Cl$_4$, room temperature).
Figure S62. $^1$H NMR spectrum of 1s (300 MHz, CD$_2$Cl$_2$, room temperature).

Figure S63. $^{13}$C NMR spectrum of 1s (300 MHz, CD$_2$Cl$_2$, room temperature).
Figure S64. $^1$H NMR spectrum of 1t (300 MHz, CD$_2$Cl$_2$, room temperature).

Figure S65. $^{13}$C NMR spectrum of 1t (300 MHz, CD$_2$Cl$_2$, room temperature).
Figure S66. COSY spectrum of 1t (500 MHz, C$_2$D$_2$Cl$_4$, 30 °C).

Figure S67. NOESY spectrum of 1t (500 MHz, C$_2$D$_2$Cl$_4$, 30 °C).
Figure S68. HSQC spectrum of 1t (500 MHz, C2D2Cl4, 30 °C).

Figure S69. HMBC spectrum of 1t (500 MHz, C2D2Cl4, 30 °C).
Figure S70. Structure verification of 1t.
Figure S71. $^1$H NMR spectrum of 1u (300 MHz, C$_2$D$_2$Cl$_4$, room temperature).

Figure S72. $^{13}$C NMR spectrum of 1u (300 MHz, C$_2$D$_2$Cl$_4$, room temperature).
Figure S73. $^1$H NMR spectrum of 1v (300 MHz, C$_2$D$_2$Cl$_4$, room temperature).

Figure S74. $^{13}$C NMR spectrum of 1v (300 MHz, C$_2$D$_2$Cl$_4$, room temperature).
4. Optical and electrochemical properties

Table S1. Optical and electrochemical properties of 1a-1v.

| Comp. | $\lambda_{\text{abs}}$ [nm] | $\lambda_{\text{em}}$ [nm]$^a$ | Stokes shift [cm$^{-1}$] | $\Phi_{\text{PL}}$$^b$ | $\Delta E_{\text{opt}}$ (eV)$^c$ |
|-------|---------------------|---------------------|-----------------|----------------|---------------------|
| 1a    | 455 (0.89), 433 (0.64) | 481                | 1188            | 0.62           | 2.60                |
| 1b    | 490 (0.85), 464 (0.61) | 533                | 1647            | 0.53           | 2.38                |
| 1c    | 453 (0.49), 430 (0.37) | 474                | 978             | 0.46           | 2.61                |
| 1d    | 448 (1.37), 366 (0.77) | 525                | 3274            | 0.09           | 2.58                |
| 1e    | 457 (1.52), 444 (1.23) | 488                | 1626            | 0.13           | 2.57                |
| 1f    | 458 (1.63), 363 (1.42) | 481                | 1044            | 0.01           | 2.56                |
| 1g    | 466 (1.57), 443 (1.09) | 518                | 1265            | 0.11           | 2.54                |
| 1h    | 456 (1.92), 366 (1.47) | 504                | 2154            | 0.24           | 2.58                |
| 1i    | 462 (0.91), 438 (0.71) | 463                | 47              | 0.85           | 2.56                |
| 1n    | 440 (1.52), 417 (1.04) | 449                | 456             | 0.58           | 2.73                |
| 1o    | 476 (1.44), 449 (1.14) | 490                | 600             | 0.25           | 2.52                |
| 1p    | 440 (1.68), 416 (1.84) | 451                | 554             | 0.62           | 2.72                |
| 1q    | 444 (1.3), 395 (1.56)  | 456                | 593             | 0.64           | 2.68                |
| 1r    | 446 (2.2), 425 (1.17)  | 461                | 729             | 0.35           | 2.67                |
The electrochemical properties of represented compounds were elucidated by cyclic voltammetry (CV). The B-doped [4]helicene compounds 1a and 1g presented a single reversible reduction wave at −1.75 V and −1.77 V (vs. Fc+/0), respectively. In stark contrast, the BN-[4]helicene compound 1n displayed a reversible oxidative peak at 0.87 V and no reduction wave was observed in the cathode region. Besides, carbazole containing compound 1p could be reversibly oxidized at potentials of 0.62 and 0.80 V. These results demonstrate the significant effect of nitrogen incorporation on the redox behavior of sc-B-PAHs. Furthermore, for the double helicenes compounds 1u and 1v, both the single reductive peak and the four oxidative peaks are irreversible.
5. X-ray crystallographic analysis

Single crystal of compounds 1e, 1o and 1n were obtained by slow diffusion of methanol into their dichloromethane solution, respectively

Table S2. Crystallographic data and details of the structure refinements of 1e, 1o and 1n.

|            | 1e                | 1o                | 1n                |
|------------|-------------------|-------------------|-------------------|
| Empirical formula | C_{30}H_{16}BCl   | 2(C_{60}H_{50}B_{2}N_{2}) | 1.5(C_{60}H_{50}B_{2}N_{2})/CH_{2}Cl_{2}/CH_{3}OH |
| Formula weight | 422.69            | 958.71            | 1456.01           |
| Temperature/K | 100               | 100               | 100               |
| Crystal system  | monoclinic       | triclinic         | triclinic         |
| Space group    | P2_1/n            | P\overline{1}     | P\overline{1}     |
| a/Å            | 3.8600(8)         | 10.680(2)         | 14.660(3)         |
| b/Å            | 25.430(5)         | 15.230(3)         | 16.210(3)         |
| c/Å            | 19.170(4)         | 16.150(3)         | 18.070(4)         |
| \(\alpha/\)  | 90                | 73.55(3)          | 64.71(3)          |
| \(\beta/\)   | 91.70(3)          | 85.17(3)          | 79.40(3)          |
| \(\gamma/\)  | 90                | 72.50(3)          | 88.03(3)          |
| Volume/Å³     | 1880.9(7)         | 2402.8(10)        | 3811.6(16)        |
| Z             | 4                 | 2                 | 2                 |
| \(\rho_{calc}/\)g/cm³ | 1.493        | 1.325            | 1.269            |
| \(\mu/\)mm⁻¹ | 0.282             | 0.092             | 0.177             |
| F(000)        | 872               | 1000             | 1530             |
| Crystal size/mm³ | 0.2*0.08*0.08 | 0.2*0.05*0.05 | 0.2*0.05*0.05 |
| Radiation     | 0.77977           | 0.77977           | 0.77977           |
| 2\(\Theta\) range for data collection/° | 2.96-73.388 | 2.884-73.682 | 3.052-73.69 |
| Index ranges  | -5 ≤ h ≤ 5, -38 ≤ k ≤ 38, -29 ≤ l ≤ 29 | -16 ≤ h ≤ 15, -21 ≤ k ≤ 22, -23 ≤ l ≤ 23 | -22 ≤ h ≤ 22, -24 ≤ k ≤ 24, -24 ≤ l ≤ 24 |
| Reflections collected | 32123     | 48833            | 76415            |
| Independent reflections | 5920      | 14212            | 22422            |
| Data/[\(F^{2} > 2\sigma(F^{2})\)] / restraints/parameters | 5040/0/289 | 12209/0/685 | 16314/36/1064 |
| Goodness-of-fit on \(F^{2}\) | 1.047  | 1.028           | 1.024           |
| Final R indexes \([F^{2} > 2\sigma(F^{2})]\) | 0.0621 | 0.0515         | 0.0992          |
| Final R indexes [all data] | 0.0727 | 0.0585          | 0.1253          |
| Largest diff. peak/hole / e Å⁻³ | 2.115 / -0.420 | 0.659 / -0.265 | 2.624 / -1.258 |
| C-B bonds length | C₁-B₁ (1.548 Å), C₂-B₂ (1.555 Å) | C₁-B₁ (1.536 Å), C₂-B₂ (1.546 Å) | C₁-B₁ (1.535 Å), C₂-B₂ (1.553 Å) |
| CCDC     | C₃-B₁(1.527 Å) | C₃-B₁(1.516 Å) | C₃-B₁(1.513 Å) |
|----------|----------------|----------------|----------------|
| 2087046  |                 | 2087048        | 2087049        |

6. DFT calculations

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.

**Optimized structure and HOMO/LUMO energy level of 1a-1i, 1n-1v.**

![Optimized structure and calculated HOMO/LUMO energy of 1a](image1.png)

**Figure S76.** Optimized structure and calculated HOMO/LUMO energy of 1a.

![Optimized structure and calculated HOMO/LUMO energy of 1b](image2.png)

**Figure S77.** Optimized structure and calculated HOMO/LUMO energy of 1b.
Figure S78. Optimized structure and calculated HOMO/LUMO energy of 1c.

Figure S79. Optimized structure and calculated HOMO/LUMO energy of 1d.

Figure S80. Optimized structure and calculated HOMO/LUMO energy of 1e.

Figure S81. Optimized structure and calculated HOMO/LUMO energy of 1f.
Figure S82. Optimized structure and calculated HOMO/LUMO energy of 1g.

Figure S83. Optimized structure and calculated HOMO/LUMO energy of 1h.

Figure S84. Optimized structure and calculated HOMO/LUMO energy of 1i.

Figure S85. Optimized structure and calculated HOMO/LUMO energy of 1n.
Figure S86. Optimized structure and calculated HOMO/LUMO energy of 1o.

Figure S87. Optimized structure and calculated HOMO/LUMO energy of 1p.

Figure S88. Optimized structure and calculated HOMO/LUMO energy of 1q.

Figure S89. Optimized structure and calculated HOMO/LUMO energy of 1r.
Figure S90. Optimized structure and calculated HOMO/LUMO energy of 1s.

Figure S91. Optimized structure and calculated HOMO/LUMO energy of 1t.

Figure S92. Optimized structure and calculated HOMO/LUMO energy of 1u.

Figure S93. Optimized structure and calculated HOMO/LUMO energy of 1v.
Figure S94. NICS(0)zz values of 1g, 1p, 1u and 1v.

Figure S95. a) Chemical structures of the represented sc-B-PAHs 1a and 1n in this work and their all-C analogues 1a’, 1n’, b) calculated molecular orbitals and energy diagrams of 1a, 1a’, 1n and 1n’.

As shown in Figure S95, we drawn the all-C analogues of 1a and 1n, respectively. Compared with the all-
C PAHs 1a’ and 1n’, the main advantage of 1a and 1n is the drastically improved photoluminescence quantum yields because of their sp² hybridized trigonal planar geometry resulting in less nonradiative decay. Besides, the resultant sc-B-PAHs also exhibit Lewis acid character of boron center. Most importantly, for compound 1a, the boron incorporation lowers the LUMO energy significantly from -1.53 eV (1a’) to -2.33 eV (1a) while slightly changes its HOMO energy level, therefore the energy gap of 1a is lower than that of all-C analogues 1a’. However, for B/N co-doped compound 1n, the LUMO energy is higher and the HOMO energy is lower than that of 1n’, thus exhibiting a larger energy gap correspondingly.

7. Mechanism investigation for the cascade reaction

Figure S96. Proposed mechanism for the synthesis of sc-B-PAHs 1a.

By using compound 1a as an example, Figure S96 presents the detail of the proposed mechanism in this work. Firstly, the intermediate A is formed through 6-endo-dig borylative cyclization of alkyne 2a in the presence of BBr₃. Subsequently, the resultant intermediate A undergoes 1,4-boron migration to afford Aryl-BBr₂ intermediate B. Finally, sc-B-PAHs 1a is achieved after two times electrophilic borylation.
Figure S97. Mechanism of 6-endo-dig cyclization process and haloboration process.

The haloboration of triple bond in dialkynes will provide two structural isomers of the corresponding vinyl bromides. But in our case, the ortho position of diarylalkynes is substituted with another aromatic ring; BBr₃ will therefore initiate 6-endo-dig cyclization reaction, which is more favorable than haloboration process. On the other hand, we didn’t observe haloboration byproduct (4c) after the reaction, which suggests that arylBBr₂ species are formed via 6-endo-dig cyclization reaction rather the haloboration process.

8. References

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