**Electronic Supporting Information (ESI) for**

**A boron-doped helicene as highly soluble, benchtop-stable green emitter**

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1. Experimental section

1.1. Materials

Unless otherwise specified, all reactions were carried out under an atmosphere of dry N₂ or Ar using carefully dried and degassed solvents, flame-dried glassware, and Schlenk or glovebox techniques. Et₂O and THF were distilled from Na/benzophenone immediately prior to use. CHCl₃ and Me₃SiCl were freshly distilled from CaH₂; CDCl₃ was distilled from CaH₂ and stored over molecular sieves (3 Å). n-BuLi (ca. 1.6 M in n-hexane; Rockwood Lithium) and t-BuLi (ca. 1.9 M in n-hexane; Rockwood Lithium) were used as received. Column chromatography was performed by using silica gel 60 (Macherey–Nagel). 1,8-Diodonaphthalene¹ (note: we found it essential to purify the commercial starting material 1,8-diaminonaphthalene (99%; Sigma–Aldrich) by distillation from zinc dust and recrystallisation from hot hexane (colourless needles) prior to use), 1-bromo-8-iodonaphthalene,² (2,6-dibromophenyl)dimethylboronate³ and potassium (2,6-difluorophenyl)trifluoroborate⁴ were synthesised according to literature procedures.

1.2. General characterisation methods

NMR spectra were recorded at 300 K using the following spectrometers: Bruker Avance-300, Avance-400 or Avance-500. Chemical shifts are referenced to (residual) solvent signals (¹H,¹³C {¹H}; CDCl₃, δ = 7.26/77.0 ppm; CD₂CN, δ = 1.94/1.3 ppm, pyridine-d₅, δ = 7.22/123.9 ppm) or external BF₃·Et₂O (¹¹B, δ = 0.00 ppm) and CFCl₃ (¹⁹F, δ = 0.00 ppm). Abbreviations: s = singlet, d = doublet, dd = doublet of doublets, ddd = doublet of doublets of doublets, t = triplet, vt = virtual triplet, td = triplet of doublets, q = quartet, m = multiplet, br. = broad, n.o. = signal not observed. In most cases, signals of boron-bonded carbon atoms were broadened beyond detection in the ¹³C {¹H} NMR spectra due to the fast quadrupolar relaxation of boron; whenever possible, their chemical shift values were determined using the cross peaks in the HMBC spectra.

UV/vis absorption and emission spectra were recorded at room temperature with a Varian Cary 50 Scan UV/vis spectrophotometer; the extinction coefficients (ε) were determined by serial dilution. Photoluminescence (PL) spectra were recorded at room temperature using a Jasco FP-8300 spectrofluorometer; the fluorescence quantum yields (QY) were determined by using a calibrated integrating sphere (ILF-835 100 mm diameter Integrating Sphere; Jasco), a quantum-yield calculation program (FWQE-880; Jasco), and highly diluted samples of at least five different concentrations (range between 10⁻⁵ and 10⁻⁷ mol L⁻¹) in each measurement. Each sample was carefully degassed with Ar using an injection needle and a septum-capped cuvette. Under these conditions, the QY of the fluorescence standard, 9,10-diphenylanthracene, was determined as 94% (lit.: 97%). Solvents used for UV/vis spectroscopic measurements (cyclohexane, C₆H₁₂, CHCl₃) were purchased as spectroscopic grade.

Electrochemical measurements (cyclic voltammetry, CV) were performed at room temperature by using an EG&G Princeton Applied Research 263A potentiostat with a platinum disk working electrode (2.00 mm diameter) and a platinum wire counter electrode. The reference electrode was a silver wire on which AgCl had been deposited by immersing the wire into HCl/HNO₃ (3:1). The solvent (o-dichlorobenzene) was dried over CaH₂ as described above and degassed with Ar and a final freeze–pump–thaw cycle. [nBu₃N][PF₆] (0.1 mol L⁻¹) was employed as the supporting electrolyte. All potential values are referenced against the FeH/FeH⁺ redox couple (FeH = ferrocene; E₁/₂ = 0 V). Scan rates were varied between 50 and 400 mV s⁻¹.
High resolution mass spectra were recorded in positive mode with a Thermo Fisher Scientific MALDI LTQ Orbitrap XL spectrometer (matrices: 2,5-dihydroxybenzoic acid (1) and 4-chloro-α-cyanocinnamic acid (1Br)). Exact masses were calculated based on the predominant combination of natural isotopes. Combustion analyses were performed by the microanalytical laboratory of the Goethe-University Frankfurt. HPLC analyses were performed using a Sykam system equipped with an S1121 solvent delivery system, an S3310 UV/vis detector, and a RI2000 refractive index detector. A ReproSil-Pur C18-AQ (10 μm, 250 × 20 mm; Dr. Maisch HPLC GmbH) column was used with a flow rate of 3 mL min⁻¹.

2. IUPAC nomenclature and NMR numbering scheme

According to the IUPAC recommendations and preferred names of 2013, compound 1 is a boron-containing derivative of 9bH-naphtho[1,8-ab]perylene; its systematic name is therefore 9b-bora-naphtho[1,8-ab]perylene (see Figure below; left). For clarity reasons, our assignment of chemical shifts follows a numbering scheme different from the IUPAC rules, in order to take into account the symmetry elements of the molecular structure (see Figure below; right).

![IUPAC nomenclature and NMR numbering scheme](attachment:image.png)
3. Syntheses, purification methods and analytical data

3.1. Synthesis of potassium (2,6-dibromophenyl)trifluoroborate (4):

(2,6-Dibromophenyl)dimethylboronate (1.91 g, 6.21 mmol) was dissolved in non-dried MeOH (30 mL), treated with neat solid KHF$_2$ (0.969 g, 12.4 mmol) at room temperature and stirred for 24 h. The solvent was evaporated to dryness and the white solid residue was washed with CHCl$_3$ (2 × 10 mL) and cold H$_2$O (5 mL; 0 °C) to give 4 as a colourless microcrystalline solid. Yield: 1.8 g (5.27 mmol; 85% assuming non-solvated K$^+$ ions).

$^1$H NMR (500.2 MHz, CD$_3$CN): δ = 6.82 (1H, t, $^3$J$_{HH}$ = 7.9 Hz, H-4), 7.43 (2H, d, $^3$J$_{HH}$ = 7.9 Hz, H-3).

$^{11}$B NMR (96.3 MHz, CD$_3$CN): δ = 1.9 (q, $^1$J$_{BF}$ = 47 Hz).

$^{13}$C($^1$H) NMR (75.4 MHz, CD$_3$CN): δ = 129.3 (C-4), 129.4 (C-2), 133.3 (C-3), 148.5 (C-1; detected through a crosspeak in the HMBC spectrum).

$^{19}$F NMR (470.6 MHz, CD$_3$CN): δ = −134.8 (q, $^1$J$_{FB}$ = 47 Hz).

EA (%): found: C, 20.75; H, 0.8. C$_6$H$_3$BBr$_2$F$_3$K [341.80] requires C, 21.1; H, 0.9.
3.2. Synthesis of bis(8-iodonaphth-1’-yl)(2,6-difluorophenyl)borane (5):

\[ \text{Synthesis of bis(8-iodonaphth-1’-yl)(2,6-difluorophenyl)borane (5):} \]

\[ n-\text{BuLi in } n\text{-hexane (1.56 M, 0.72 mL, 1.12 mmol) was added dropwise with stirring at 0 °C to a} \]
\[ \text{solution of 1,8-diodonaphthalene (0.432 g, 1.14 mmol) in Et}_2\text{O (20 mL). Stirring was continued for} \]
\[ 10 \text{ min before the reaction mixture was warmed to room temperature within 1 h. The resulting solution} \]
\[ \text{was again cooled to 0 °C and neat } 3 \text{ (0.100 g, 0.46 mmol) was added in one portion. The reaction} \]
\[ \text{mixture was allowed to warm to room temperature overnight and stirred for another 3 d. The resulting} \]
\[ \text{yellow suspension was treated with neat } \text{Me}_3\text{SiCl (0.18 mL, 0.15 g, 1.38 mmol) at room temperature} \]
\[ \text{and stirred for another 24 h. All volatiles were removed under reduced pressure. The sticky, orange-} \]
\[ \text{coloured crude product was purified by column chromatography to obtain 5 as a yellow solid (silica} \]
\[ \text{gel; first cyclohexane, then stepwise increasing the polarity of the eluent by the addition of CHCl}_3 \text{ up} \]
\[ \text{to a ratio cyclohexane:CHCl}_3 = 2:1; R_f = 0.44 (cyclohexane:CHCl}_3 = 2:1). Yield: 0.140 g (0.22 mmol;} \]
\[ 49\%). Single crystals suitable for X-ray crystallography were obtained by slow evaporation of a} \]
\[ \text{saturated solution of 5 in MeOH:CHCl}_3 = 1:1.} \]

**1H NMR (500.2 MHz, CDCl3):** \( \delta = 6.47−6.50 \) (2H, m, PhH-3), 7.16−7.19 (2H, m, H-6), 7.21−7.25
\( (1H, m, PhH-4), 7.50 (2H, dd, ^3J_{HH} = 7.9 \text{ Hz, } ^1J_{HH} = 7.0 \text{ Hz, H-3}), 7.94 (2H, dd, ^3J_{HH} = 7.9 \text{ Hz,} \]
\( ^4J_{HH} = 1.1 \text{ Hz, H-4}), 7.96 (2H, dd, ^1J_{HH} = 8.1 \text{ Hz, } ^4J_{HH} = 1.0 \text{ Hz, H-5}), 8.04 (2H, dd, ^1J_{HH} = 7.3 \text{ Hz,} \]
\( ^4J_{HH} = 1.0 \text{ Hz, H-7}), 8.59 (2H, br. d, H-2). \)

**11B NMR (160.5 MHz, CDCl3):** \( \delta = 59 (h_{\text{vib}} \approx 1080 \text{ Hz}). \)

**13C{1H} NMR (125.8 MHz, CDCl3):** \( \delta = 99.0 \) (C-8), 111.2 (m, PhC-3), 125.2 (C-3), 127.0 (C-6),
\( 129.7 \) (C-5), 132.5 (C-4), 133.2 (t, \( ^3J_{CF} = 11.5 \text{ Hz, PhC-4}), 135.0 \) (C-4a), 139.2 (C-7), 139.7 (C-2),
\( 140.2 \) (d, \( ^3J_{CF} = 2.7 \text{ Hz, C-8a}), 148.5 \) (C-1), 164.0 (dd, \( ^1J_{CF} = 251.1 \text{ Hz, } ^3J_{CF} = 11.4 \text{ Hz, PhC-2}), \text{n.o.} \)
\( \text{(PhC-1).} \)

**19F NMR (470.6 MHz, CDCl3):** \( \delta = -97.7 \) (m).

**EA (%):** found: C, 49.9; H, 2.45. C_{26}H_{15}BF_{2}I_{2} [630.01] requires C, 49.6; H, 2.4.
3.3. Synthesis of bis(8-bromonaphth-1-yl)(2,6-dibromophenyl)borane (6):

\[
\text{\begin{center}
\begin{tikzpicture}
\end{tikzpicture}
\end{center}
}
\]

\textit{n-BuLi} in \textit{n}-hexane (1.56 m, 1.85 mL, 2.88 mmol) was added dropwise with stirring at 0 °C to a solution of 1-bromo-8-iodonaphthalene (0.916 g, 2.75 mmol) in EtO (40 mL). Stirring was continued for 30 min before the reaction mixture was warmed to room temperature within 1 h. The resulting yellow solution was again cooled to 0 °C and neat 4 (0.427 g, 1.25 mmol) was added. The reaction mixture was allowed to warm to room temperature overnight and stirred for 3 d. The resulting orange-coloured suspension was treated with neat MeSiCl (0.48 mL, 0.41 g, 3.8 mmol) at room temperature and stirred for another 24 h. All volatiles were removed under reduced pressure. The brown crude product was purified by column chromatography to obtain 6 as a pale yellow solid. (silica gel; first cyclohexane:CHCl\textsubscript{3} = 10:1, then cyclohexane:CHCl\textsubscript{3} = 5:1 and finally cyclohexane:CHCl\textsubscript{3} = 1:1; \textit{Rf} = 0.43 (cyclohexane:CHCl\textsubscript{3} = 5:1)) Yield: 0.48 g (0.73 mmol; 58%). Single crystals of 6 suitable for X-ray crystallography were obtained by slow evaporation of a saturated solution in \textit{n}-hexane:CHCl\textsubscript{3} = 1:1.

\textbf{\textit{1H} NMR (500.2 MHz, CDCl\textsubscript{3})}: \(\delta = 6.81\) (1H, t, \(\text{i}_{\text{HH}} = 7.9\) Hz, PhH-4), 7.30 (2H, d, \(\text{i}_{\text{HH}} = 7.9\) Hz, PhH-3), 7.32 (2H, dd, \(\text{i}_{\text{HH}} = 8.1\) Hz, \(\text{i}_{\text{HH}} = 7.4\) Hz, H-6), 7.49 (2H, dd, \(\text{i}_{\text{HH}} = 8.0\) Hz, \(\text{i}_{\text{HH}} = 7.0\) Hz, H-3), 7.67 (2H, dd, \(\text{i}_{\text{HH}} = 7.4\) Hz, \(\text{i}_{\text{HH}} = 1.1\) Hz, H-7), 7.89 (2H, dd, \(\text{i}_{\text{HH}} = 8.1\) Hz, \(\text{i}_{\text{HH}} = 1.1\) Hz, H-5), 7.99 (2H, dd, \(\text{i}_{\text{HH}} = 8.0\) Hz, \(\text{i}_{\text{HH}} = 1.1\) Hz, H-4), 8.41 (2H, dd, \(\text{i}_{\text{HH}} = 7.0\) Hz, \(\text{i}_{\text{HH}} = 1.1\) Hz, H-2).

\textbf{\textit{1B} NMR (160.5 MHz, CDCl\textsubscript{3})}: \(\delta = 64\) \(J_{\text{B}H} \approx 1000\) Hz).

\textbf{\textit{13C}({\textit{1H}}) NMR (125.8 MHz, CDCl\textsubscript{3})}: \(\delta = 123.6\) (C-8), 126.2 (C-3), 126.3 (C-6), 128.6 (C-5), 130.8 (PhC-4), 130.9 (PhC-2), 131.0 (C-7), 132.5 (C-4), 133.6 (PhC-3), 135.5 (C-4a), 137.3 (C-8a), 140.0 (C-2), 146.0 (PhC-1; detected through a crosspeak in the HMBC spectrum), 146.7 (C-1).

\textbf{EA (%):} found: C, 47.6; H, 2.3. C\textsubscript{26}H\textsubscript{18}BBr\textsubscript{4} \(\textit{[657.83]}\) requires C, 47.5; H, 2.3.

Note: Even the analytically pure, single crystalline material gave rise to a second set of resonances in the \textit{1H} and \textit{13C}({\textit{1H}}) NMR spectra (approximately 15% according to \textit{1H} integral ratios). Moreover, NMR control spectra taken at different stages of the workup procedure always showed the same ratio between the major and the minor component. We therefore assume that the minor component is not an impurity, but a \textit{C\textsubscript{1}}-symmetric rotamer of the highly congested compound 6 (we do not observe the phenomenon in the case of 5, which carries two small fluorine atoms instead of two bulky bromine atoms).

\textbf{\textit{1H} NMR (500.2 MHz, CDCl\textsubscript{3})}: \(\delta = 6.63\) (1H, dd), 7.02 (1H, t), 7.04 (1H, vt), 7.29 (1H, vt), 7.35 (1H, dd), 7.36–7.42 (3H, m), 7.62 (1H, dd), 7.78–7.81 (4H, m), 7.93 (1H, dd), 7.98 (1H, dd).

\textbf{\textit{13C}({\textit{1H}}) NMR (125.8 MHz, CDCl\textsubscript{3})}: \(\delta = 125.4, 125.9, 126.9, 129.0, 129.2, 131.0\) (x2), 132.0, 132.1, 132.5, 132.9, 133.2, 133.3, 135.3, 139.6, n.o. (quaternary carbon atoms).
3.4. Synthesis of 9b-boranaphtho[1,8-ab]perylene (1):

6 (0.172 g, 0.26 mmol) and 2,2′-bipyridyl (0.163 g, 1.05 mmol) were dissolved in THF (200 mL) and the yellow solution was degassed for 20 min by bubbling Ar through it. Neat COD (0.10 mL, 0.088 g, 0.81 mmol) and solid Ni(COD)₂ (0.288 mg, 1.05 mmol) were added, whereupon the mixture slowly turned dark. The solution was stirred for 16 h at room temperature and subsequently quenched with non-dried cyclohexane/CHCl₃ (1:1; 20 mL). A grey precipitate formed and the supernatant turned orange. The suspension was filtered over a pad of silica gel and rinsed with cyclohexane/CHCl₃ (1:1) until the silica gel was no longer green fluorescent. All volatiles were removed from the filtrate under dynamic vacuum to obtain an orange solid, which showed an intense green fluorescence in solution (λ<sub>ex</sub> = 366 nm). The crude product was further purified by column chromatography (silica gel; first cyclohexane to remove COD and bpy and then cyclohexane:CHCl₃ = 5:1 to elute analytically pure 1; R<sub>f</sub> = 0.29 (cyclohexane:CHCl₃ = 5:1)). 1 is a bright orange solid, which shows green fluorescence in hexane solution and orange fluorescence in the solid state (λ<sub>ex</sub> = 366 nm). Yield: 0.076 g (0.225 mmol; 86%). Single crystals of 1 suitable for X-ray crystallography were grown by layering a concentrated solution in CHCl₃ with MeOH. Crystalline material used for the photophysical and electrochemical investigations was obtained by slow evaporation of a concentrated solution of 1 in C₆H₆.

^1H NMR (500.2 MHz, CDCl₃): δ = 7.75 (2H, vt, H-6), 7.84–7.89 (3H, m, H-3, PhH-4), 8.06 (2H, d, ^3J_HH = 7.9 Hz, H-5), 8.25 (2H, d, ^3J_HH = 7.9 Hz, H-4), 8.48 (2H, d, ^3J_HH = 7.9 Hz, PhH-3), 8.70 (2H, d, ^3J_HH = 7.9 Hz, H-7), 8.79 (2H, br. d, H-2).

^11B NMR (160.5 MHz, CDCl₃): δ = 50 (ν<sub>β</sub> ≈ 740 Hz).

^13C[^1]H NMR (125.8 MHz, CDCl₃): δ = 122.8 (PhC-3), 125.2 (C-7), 126.1 (C-6), 126.2 (C-3), 130.4 (C-5), 132.4 (PhC-4), 132.6 (C-8a), 133.1 (C-8), 133.5 (C-4a), 134.3 (C-4), 134.7 (C-1), 135.4 (PhC-1), 140.7 (C-2), 140.8 (PhC-2).

HRMS (MALDI): calcd. for C₂₆H₁₂B (M⁺), 338.12659; found 338.12655.

UV/vis (cyclohexane): λ<sub>max</sub> (ε / M⁻¹ cm⁻¹) = 462 (17700), 324 (17000) nm.

Fluorescence (cyclohexane): λ<sub>em</sub> (λ<sub>ex</sub> = 440 nm) = 485 nm; QY = 0.81.

Cyclic voltammetry (o-dichlorobenzene, [nBu₄N][PF₆], 0.1 M, 200 mV s⁻¹, vs. FeH/FeH⁺):

E<sub>cb</sub> = −1.91 V.
3.5. Formation of the Lewis adduct 1·py:

1 was dissolved in non-dried toluene and treated with pyridine until the intense green fluorescent solution turned pale yellow. Single crystals of 1·py suitable for X-ray crystallography were obtained by gas-phase diffusion of n-heptane into the toluene/pyridine solution.

\[ \text{\textsuperscript{1}H NMR (500.2 MHz, pyridine-d\textsubscript{5}}) : \delta = 7.62 (2H, vt, H-6), 7.65 (1H, vt, PhH-4), 7.76 (2H, dd, \textsuperscript{3}J_{HH} = 8.0 \text{ Hz}, \textsuperscript{4}J_{HH} = 6.8 \text{ Hz}, H-3), 7.98–8.00 (4H, m, H-4,5), 8.34 (2H, d, \textsuperscript{1}J_{HH} = 7.9 \text{ Hz}, PhH-3), 8.39 (2H, dd, \textsuperscript{3}J_{HH} = 6.8 \text{ Hz}, \textsuperscript{4}J_{HH} = 0.9 \text{ Hz}, H-2), 8.49 (2H, dd, \textsuperscript{3}J_{HH} = 7.4 \text{ Hz}, \textsuperscript{4}J_{HH} = 0.8 \text{ Hz}, H-7). \]

\[ \text{\textsuperscript{11}B NMR (160.5 MHz, pyridine-d\textsubscript{5}}) : \delta = -2 (\text{h\textsubscript{11} \approx 300 Hz}). \]

\[ \text{\textsuperscript{13}C\textsuperscript{\textsuperscript{1}}H NMR (125.8 MHz, pyridine-d\textsubscript{5}}) : \delta = 122.1 (C-7), 124.4 (PhC-3), 126.3 (C-6), 126.6 (C-3), 127.7 (C-4), 128.5 (PhC-4), 129.4 (C-5), 133.5 (C-2), 134.2 (C-8a), 135.0 (C-4a), 136.2 (C-8), 140.1 (PhC-2), 145.2 (C-1, PhC-1). \]
3.6. Synthesis of 1-bromo-9b-boranaphtho[1,8-ab]perylene (1Br)

1 (21.6 mg, 0.064 mmol) and N-bromosuccinimide (17.1 mg, 0.096 mmol) were dissolved in CHCl₃ (2 mL) and stirred at room temperature for 2 d. The yellow solution was purified by column chromatography (silica gel; first cyclohexane and then cyclohexane:CHCl₃ = 5:1; Rf = 0.43 (cyclohexane:CHCl₃ = 5:1)). A sample of pure 1Br was obtained by analytical scale HPLC (eluent: MeOH:MeOt-Bu = 4:1; flow rate: 3 mL min⁻¹; detection: UV/vis (440 nm); tᵣ = 41 min). 1Br is a bright yellow solid which is non-fluorescent, both in solution and in the solid state.

¹H NMR (500.2 MHz, CDCl₃): δ = 7.73 (1H, t, ¹JHH = 7.8 Hz, H-6'), 7.77 (1H, t, ¹JHH = 7.8 Hz, H-6), 7.83-7.87 (2H, m, H-3,3'), 8.07 (1H, br. d, ¹JHH = 8.7 Hz, PhH-4), 8.27 (2×1H, 2×dd, ¹JHH = 8.0 Hz, ³JHH = 0.9 Hz, H-4,4'), 8.35 (1H, d, ³JHH = 8.7 Hz, PhH-3), 8.58 (1H, dd, ¹JHH = 6.9 Hz, ³JHH = 0.9 Hz, H-2), 8.67 (1H, dd, ³JHH = 6.9 Hz, ⁴JHH = 0.9 Hz, H-2'), 8.72 (1H, br. d, H-7), 9.30 (1H, dd, ³JHH = 7.8 Hz, ⁴JHH = 0.9 Hz, H-7').

¹¹B NMR (160.5 MHz, CDCl₃): δ = 50 (h½ ≈ 760 Hz).

¹³C{¹H} NMR (125.8 MHz, CDCl₃): δ = 120.7 (PhC-3'), 123.7 (PhC-3), 124.8 (C-6'), 125.5 (C-7), 125.9 (C-6), 126.2 (C-3 or C-3'), 126.4 (C-3 or C-3'), 129.2 (C-7'), 130.2 (C-5'), 130.5 (C-5'), 130.9 (C-5), 131.9 (C-8'), 132.2 (C-8), 132.2 (C-4a'), 132.8 (C-8a), 132.9 (C-8a'), 133.3 (C-4a), 134.3 (C-4'), 134.5 (C-4), 139.2 (PhC-1), 139.5 (PhC-4), 139.5 (PhC-2), 139.6 (C-2'), 140.4 (PhC-2'), 141.9 (C-2), n.o. (C-1,1').

HRMS (MALDI): calcd. for C₂₆H₁₄BBr (M⁺), 416.03665; found 416.03719.
4. UV/vis absorption and emission spectra of 1

**Figure S1:** Normalised UV/vis absorption spectra of 1 in three different solvents (CHCl₃, C₆H₆, cyclohexane).

**Figure S2:** Normalised emission spectra of 1 ($\lambda_{ex} = 440$ nm) in three different solvents (cyclohexane, C₆H₆, CHCl₃).
Figure S3: Normalised UV/vis absorption and emission spectra of 1 in cyclohexane.

Table S1: UV/vis absorption and emission data of 1 in three different solvents.

<table>
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<tr>
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<th>cyclohexane</th>
<th>C₆H₆</th>
<th>CHCl₃</th>
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<td>λ&lt;sub&gt;abs&lt;/sub&gt; / nm</td>
<td>462 (19200)</td>
<td>466 (17700)</td>
<td>464 (21000)</td>
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<tr>
<td>(ε / M&lt;sup&gt;-1&lt;/sup&gt; cm&lt;sup&gt;-1&lt;/sup&gt;)</td>
<td>324 (17600)</td>
<td>327 (17000)</td>
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<tr>
<td>QY</td>
<td>81</td>
<td>75</td>
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</tr>
</tbody>
</table>
5. Cyclic voltammogram of 1

**Figure S4**: Top: Cathodic scan of the cyclic voltammogram of 1 in o-dichlorobenzene showing a reversible redox transition at $E_{1/2} = -1.91$ V. Bottom: Anodic scan showing an irreversible redox transition at $E_{pa} = 1.14$ V. Conditions: room temperature, supporting electrolyte: $[n$Bu$_4$N][PF$_6$] (0.1 M), scan rate 200 mV s$^{-1}$. 
6. X-ray crystal structure analyses of 5, 6, 1 and 1·py

The reflection data for all structures were collected on a STOE IPDS II two-circle diffractometer with a Genix Microfocus tube with mirror optics using MoKα radiation (\(\lambda = 0.71073\) Å) and were scaled using the frame-scaling procedure in the X-AREA\(^6\) program system.

The structures were solved by direct methods using the program SHELXS\(^7\) and refined against \(F^2\) with full-matrix least-squares techniques using the program SHELXL.\(^8\) The H atoms were assigned to idealised geometric positions.

5 is a non-merohedral twin with a fractional contribution of 0.2479(16) for the minor domain. Due to the absence of anomalous scatterers, the absolute configuration of 1 and 1·py could not be determined. In 1·py, the contribution of disordered solvent molecules was subtracted from the reflection data using the SQUEEZE routine in PLATON.\(^9\)

Crystallographic data have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-1420444 (5), CCDC-1420445 (6), CCDC-1420446 (1), CCDC-1420447 (1·py). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

**Crystal data of 5:** \(\text{C}_{26}\text{H}_{15}\text{BF}_3\text{I}_2\), \(M_r = 629.99\) g mol\(^{-1}\), yellow plate, 0.28×0.16×0.04 mm\(^3\), monoclinic, space group \(C2/c\), \(a = 20.082(3)\) Å, \(b = 9.3614(8)\) Å, \(c = 14.7770(18)\) Å, \(\beta = 126.854(8)\)\(^\circ\), \(V = 2222.9(5)\) Å\(^3\), \(Z = 4\), \(\rho_{calcd} = 1.882\) g cm\(^{-3}\), \(\mu = 2.857\) mm\(^{-1}\), \(F(000) = 1200\), \(T = 173(2)\) K, \(R_1 = 0.0594\), \(wR_2 = 0.1555\) (all data), \(15809\) reflections measured, 9924 unique and 143 parameters \((R_{int} = 0.055)\), which were used in all calculations.

**Crystal data of 6:** \(\text{C}_{26}\text{H}_{15}\text{BBr}_4\), \(M_r = 657.83\) g mol\(^{-1}\), colourless plate, 0.19×0.17×0.07 mm\(^3\), monoclinic, space group \(P2_1/c\), \(a = 12.6333(9)\) Å, \(b = 14.6789(7)\) Å, \(c = 12.1639(8)\) Å, \(\beta = 94.908(6)\)\(^\circ\), \(V = 2247.4(2)\) Å\(^3\), \(Z = 4\), \(\rho_{calcd} = 1.944\) g cm\(^{-3}\), \(\mu = 7.175\) mm\(^{-1}\), \(F(000) = 1264\), \(T = 173(2)\) K, \(R_1 = 0.0457\), \(wR_2 = 0.0971\) (all data), \(29288\) reflections measured, 4584 unique and 280 parameters \((R_{int} = 0.0759)\), which were used in all calculations.

**Crystal data of 1:** \(\text{C}_{26}\text{H}_{15}\text{B}\), \(M_r = 338.19\) g mol\(^{-1}\), yellow plate, 0.17×0.09×0.01 mm\(^3\), orthorhombic, space group \(P2_12_12_1\), \(a = 3.9791(12)\) Å, \(b = 19.948(6)\) Å, \(c = 20.208(5)\) Å, \(V = 1604.0(8)\) Å\(^3\), \(Z = 4\), \(\rho_{calcd} = 1.400\) g cm\(^{-3}\), \(\mu = 0.079\) mm\(^{-1}\), \(F(000) = 704\), \(T = 173(2)\) K, \(R_1 = 0.0677\), \(wR_2 = 0.1360\) (all data), \(7082\) reflections measured, 2966 unique and 245 parameters \((R_{int} = 0.1333)\), which were used in all calculations.

**Crystal data of 1·py:** \(\text{C}_3\text{H}_{20}\text{BN}\), \(M_r = 417.29\) g mol\(^{-1}\), colourless block, 0.24×0.24×0.16 mm\(^3\), cubic, space group \(F\bar{4}3c\), \(a = 48.2907(17)\) Å, \(V = 112614(12)\) Å\(^3\), \(Z = 192\), \(\rho_{calcd} = 1.181\) g cm\(^{-3}\), \(\mu = 0.067\) mm\(^{-1}\), \(F(000) = 41856\), \(T = 173(2)\) K, \(R_1 = 0.0654\), \(wR_2 = 0.1311\) (all data), \(66865\) reflections measured, 8695 unique and 595 parameters \((R_{int} = 0.1275)\), which were used in all calculations.
**Figure S5:** Molecular structure and numbering scheme of compound 5 in the solid state (50% probability for thermal ellipsoids); hydrogen atoms are omitted for clarity. Selected bond lengths [Å], atom···atom distances [Å] and torsion angles [°]: B(1)−C(1) = 1.582(15), B(1)−C(11) = 1.572(10), F(1)−C(2) = 1.351(10), I(1)−C(13) = 2.115(9); B(1)···F(1) = 2.914(9), B(1)···I(1) = 3.295(3); C(1)−B(1)−C(11) = 121.9(5), C(11#)−B(1)−C(11) = 116.1(9), C(1)−B(1)−C(11#) = 121.9(5); C(1)−B(1)−C(11)−C(20) = 123.2(5). Symmetry transformation used to generate equivalent atoms: #1: -x+1,y,-z+3/2.

**Figure S6:** Molecular structure and numbering scheme of compound 6 in the solid state (50% probability for thermal ellipsoids); hydrogen atoms are omitted for clarity. Selected bond lengths [Å], atom···atom distances [Å] and torsion angles [°]: B(1)−C(1) = 1.598(7), B(1)−C(11) = 1.575(7), B(1)−C(21) = 1.572(7), Br(1)−C(2) = 1.917(5), Br(2)−C(6) = 1.923(5), Br(3)−C(13) = 1.907(5), Br(4)−C(23) = 1.902(5); B(1)···Br(1) = 3.335(5), B(1)···Br(2) = 3.312(5), B(1)···Br(3) = 3.178(5), B(1)···Br(4) = 3.1823(5); C(1)−B(1)−C(11) = 121.6(4), C(1)−B(1)−C(21) = 120.0(4), C(11)−B(1)−C(21) = 118.4(4); C(1)−B(1)−C(11)−C(20) = 126.0(5), C(1)−B(1)−C(21)−C(30) = 128.5(4).
**Figure S7:** Molecular structure and numbering scheme of compound 1 in the solid state (50% probability for thermal ellipsoids): *Left:* top view. *Right:* side view. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å], bond angles [°] and torsion angles [°]: B(1)−C(1) = 1.538(12), B(1)−C(11) = 1.532(13), B(1)−C(21) = 1.576(11); C(1)−B(1)−C(11) = 117.1(7), C(1)−B(1)−C(21) = 116.2(8), C(11)−B(1)−C(21) = 126.6(8); C(11)−B(1)−C(21)−C(30) = 11.4(13), C(20)−C(11)−B(1)−C(21) = 13.9(14). The central boron atom adopts a trigonal-planar coordination (sum of the three C−B−C bond angles = 359.9°).

**Figure S8:** Crystal packing of 1: *Left:* View along the a-axis. *Right:* View along the c-axis.
**Figure S9:** Molecular structure and numbering scheme of compound 1·py in the solid state (50% probability for thermal ellipsoids); hydrogen atoms are omitted for clarity. The unit cell contains two crystallographically independent molecules (1·py and 1·pyA). Selected bond lengths [Å], bond angles [°] and torsion angles [°]: B(1)–C(1) = 1.594(8), B(1)–C(11) = 1.616(8), B(1)–C(21) = 1.613(9), B(1)–N(31) = 1.695(7); C(1)–B(1)–C(11) = 108.1(4), C(1)–(B1)–C(21) = 112.8(5), C(11)–B(1)–C(21) = 119.4(5), C(1)–(B1)–N(31) = 105.9(4); C(11)–B(1)–C(21)–C(30) = –56.1(7), C(20)–C(11)–B(1)–C(21) = 12.1(8); B(1A)–C(1A) = 1.586(9), B(1A)–C(11A) = 1.623(8), B(1A)–C(21A) = 1.603(9), B(1A)–N(31A) = 1.693(7); C(1A)–B(1A)–C(11A) = 108.6(5), C(1A)–B(1A)–C(21A) = 112.4(5), C(11A)–B(1A)–C(21A) = 119.4(5), C(1A)–B(1A)–N(31A) = 103.9(4); C(11A)–B(1A)–C(21A)–C(30A) = –48.4(7), C(20A)–C(11A)–B(1A)–C(21A) = 11.5(8). The sum of the three C–B–C bond angles are 340.3° (1·py) and 340.4° (1·pyA), respectively.
7. Plots of $^1$H, $^{11}$B, $^{13}$C{$^1$H} and $^{19}$F NMR spectra of all new compounds

Figure S10: $^1$H NMR (500.2 MHz) spectrum of compound 4 in CD$_3$CN.

Figure S11: $^{13}$C{$^1$H} NMR (75.4 MHz) spectrum of compound 4 in CD$_3$CN.
Figure S12: $^1$H NMR (500.2 MHz) spectrum of compound 5 in CDCl$_3$.

Figure S13: $^{13}$C{$^1$H} NMR (125.8 MHz) spectrum of compound 5 in CDCl$_3$. 
Figure S14: $^{19}$F NMR (470.6 MHz) spectrum of compound 5 in CDCl$_3$.

Figure S15: $^1$H NMR (500.2 MHz) spectrum of compound 6 in CDCl$_3$. 
Figure S16: $^{13}$C ($^1$H) NMR (125.8 MHz) spectrum of compound 6 in CDCl$_3$.

Figure S17: $^1$H NMR (500.2 MHz) spectrum of the C$_1$-symmetric rotamer of 6 in CDCl$_3$. 
**Figure S18:** $^{13}$C ($^{1}$H) NMR (125.8 MHz) spectrum of the C$_{1}$-symmetric rotamer of 6 in CDCl$_{3}$.

**Figure S19:** $^{1}$H NMR (500.2 MHz) spectrum of compound 1 in CDCl$_{3}$.
Figure S20: $^{13}$C{\textsuperscript{1}H} NMR (125.8 MHz) spectrum of compound 1 in CDCl\textsubscript{3}.

Figure S21: $^{11}$B NMR (160.5 MHz) spectrum of compound 1 in CDCl\textsubscript{3}. Note: A baseline correction has not been performed.
**Figure S22:** $^1$H NMR (500.2 MHz) spectrum of compound 1·py in pyridine-$d_5$.

**Figure S23:** $^{13}$C{$^1$H} NMR (125.8 MHz) spectrum of compound 1·py in pyridine-$d_5$. 
Figure S24: $^{11}$B NMR (160.5 MHz) spectrum of compound 1·py in pyridine-$d_5$.

Figure S25: $^1$H NMR (500.2 MHz) spectrum of compound 1Br in CDCl$_3$. 
Figure S26: 13C (1H) NMR (125.8 MHz) spectrum of compound 1Br in CDCl₃.
8. References