Synthesis of Luminescent 2-(2’-Hydroxyphenyl) benzoxazole (HBO) Borate Complexes

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1) General Methods

All reactions were performed under a dry atmosphere of argon. All chemicals were received from commercial sources (Aldrich, Alfa Aesar or ABCR) and used without further purification. 1,2-dichloroethane and dichloromethane were distilled over P₂O₅ under an argon atmosphere. Thin layer chromatography (TLC) was performed on silica gel or aluminium oxide (Al₂O₃) plates coated with fluorescent indicator. Chromatographic purifications were conducted using 40-63 μm silica gel or basic aluminium oxide. All mixtures of solvents are given in v/v ratio. BODIPY dye 22¹ and methyl 3-amino-4-hydroxybenzoate 1b² were prepared according to reported procedures.

The 200 (¹H), 300 (¹H), 400 (¹H), 50.3 (¹³C), 75.46 (¹³C), 100.3 (¹³C) MHz NMR spectra were recorded at room temperature with perdeuterated solvents with residual protonated solvent signals as internal references. The 128 (¹¹B) MHz NMR spectra were recorded at room temperature with borosilicate glass as reference. UV-Vis spectra were recorded using a dual-beam grating spectrophotometer with a 1 cm quartz cell. All fluorescence spectra were corrected. The fluorescence quantum yield (Φexp) was calculated from eq (1).

\[
\Phi_{\text{exp}} = \Phi_{\text{ref}} \frac{F [1 - \exp(-A_{\text{ref}} \ln 10)] \eta^2}{F_{\text{ref}} [1 - \exp(-A \ln 10)] \eta^2_{\text{ref}}} \quad \text{(eq 1)}
\]

Here, \( F \) denotes the integral of the corrected fluorescence spectrum, \( A \) is the absorbance at the excitation wavelength, and \( n \) is the refractive index of the medium. The reference systems were: Quinine \( \Phi = 0.55 \) in H₂SO₄ 1N, \( \lambda_{\text{ex}} = 366 \) nm for dyes emitting below 480 nm, Rhodamine 6G, \( \Phi = 0.88 \) in ethanol \( \lambda_{\text{ex}} = 488 \) nm for dyes emitting between 480 and 570 nm and cresyl violet, \( \Phi = 0.55 \lambda_{\text{ex}} = 546 \) nm in ethanol for dyes emitting above 570 nm.³

Luminescence lifetimes were measured on an Edimburgh Instruments spectrofluorimeter equipped with a R928 photomultiplier and a PicoQuant PDL 800-D pulsed diode connected to a GwInstect GFG-8015G delay generator. No filter was used for the excitation. Lifetimes were deconvoluted with FS-900 software using a light-scattering solution (LUDOX) for instrument response.
2) Experimental

2.1) Synthesis of HBO derivatives 1-9

**Route A**

To a solution of 2-aminophenol I ($R_1 = H$, Ia or $R_1 = CO_2Me$, Ib) in absolute ethanol was added 1 equivalent of 2-hydroxybenzaldehyde II ($R_2 = H$, IIa; $R_2 = 3,5^tBu$, IIb; $R_2 = 4-$OMe, IIc; $R_2, R_3 =$ Naphtyl, IId). The mixture was stirred at 90°C for an hour until an orange to red precipitate formed. After cooling down, the precipitate was filtered and washed with ethanol. It was then redissolved in dry dichloromethane and 1.2 equivalent of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) was added as a concentrated dichloromethane solution. The resulting dark mixture was stirred at RT overnight. After solvent evaporation, the crude residue was purified by silica gel chromatography eluting with CH$_2$Cl$_2$/Pet. Ether 1:1 to CH$_2$Cl$_2$ 100% leading to HBO 1-6 as beige to white powders.

**Route B**

To a solution of 2-aminophenol I ($R_1 = H$, Ia or $R_1 = NO_2$, Ic) in methanol was added 1 equivalent of 2-hydroxybenzaldehyde II ($R_2 = 3,5^tBu$, IIb or $R_2 = NEt_2$, IIf), 1 equivalent of phenylboronic acid and 3 equivalents of potassium cyanide. The mixture was stirred for 24 hours at RT. After solvent evaporation, the crude residue was purified by silica gel chromatography eluting with CH$_2$Cl$_2$/Pet. Ether 7:3 to CH$_2$Cl$_2$ 100% leading to HBO 7-9 as yellow to white powders.

**HBO 1**

![Route A](image)

**Route A.** Beige powder. 60%. $^1$H NMR (200MHz, CDCl$_3$) $\delta$ (ppm) : 11.50 (s, 1H, OH), 8.04 (dd, 1H, CH Ar, J = 8Hz), 7.70-7.76 (m, 1H, CH Ar), 7.58-7.64 (m, 1H, CH Ar), 7.35-7.50 (m, 3H, CH Ar), 7.14 (d, 1H, CH Ar, J = 8Hz), 6.98-7.06 (m, 1H, CH Ar). $^{13}$C NMR (75MHz, CDCl$_3$) $\delta$ (ppm) : 162.9, 158.8, 149.1, 140.0, 133.6, 127.1, 125.2, 125.0, 119.6, 119.3, 117.3, 110.7, 110.6.
HBO 2

**Route A.** White powder. 75%. $^1$H NMR (200MHz, CDCl$_3$) δ (ppm): 11.93 (s, 1H, OH), 7.93 (m, 1H, CH Ar), 7.70-7.93 (m, 1H, CH Ar), 7.60-7.70 (m, 1H, CH Ar), 7.53 (m, 1H, CH Ar), 7.33-7.40 (m, 2H, CH Ar), 1.51 (s, 9H, CH$_3$), 1.40 (s, 9H, CH$_3$). $^{13}$C NMR (75MHz, CDCl$_3$) δ (ppm): 164.2, 156.0, 149.3, 141.3, 140.2, 137.4, 128.6, 125.2, 125.0, 121.4, 119.2, 110.7, 109.9, 35.4, 34.6, 31.7, 29.6. Anal. Calculated for C$_{21}$H$_{25}$NO$_2$: C, 77.98; H, 7.79; N, 4.33; Found C, 77.74; H, 7.55; N, 4.09. EI-MS (m/z): 324.2 (100).

HBO 3

**Route A.** White powder. 35%. $^1$H NMR (200MHz, CDCl$_3$) δ (ppm): 11.66 (s, 1H, OH), 7.91 (d, 1H, CH Ar, J = 8.4 Hz), 7.66-7.71 (m, 1H, CH Ar), 7.55-7.60 (m, 1H, CH Ar), 7.32-7.37 (m, 2H, CH Ar), 6.56-6.64 (m, 2H, CH Ar), 3.86 (s, 3H, CH$_3$). $^{13}$C NMR (75MHz, CDCl$_3$) δ (ppm): 164.2, 163.1, 160.8, 149.0, 140.0, 128.3, 124.9, 124.8, 118.8, 110.5, 107.8, 103.7, 101.2, 55.5.

HBO 4

**Route A.** Off-white powder. 44%. $^1$H NMR (300MHz, CDCl$_3$) δ (ppm): 13.21 (br.s., 1H, OH), 9.06 (d, 1H, CH Ar, J = 8.7 Hz), 7.63-7.89 (m, 5H, CH Ar), 7.26-7.44 (m, 4H, CH Ar). $^{13}$C NMR (75MHz, CDCl$_3$) δ (ppm): 164.8, 161.1, 148.8, 138.3, 134.8, 130.9, 129.1, 128.5, 128.4, 125.2, 125.1, 124.5, 123.7, 119.4, 118.7, 110.7, 102.3.

HBO 5

**Route A.** White powder. 75%. $^1$H NMR (300MHz, CDCl$_3$) δ (ppm): 11.09 (br.s., 1H, OH), 8.34 (s, 1H, CH Ar), 8.08 (d, 1H, CH Ar, J = 9 Hz), 7.88 (d, 1H, CH Ar, J = 8.7 Hz), 7.58 (d, 1H, CH Ar, J = 8.4 Hz), 6.56-6.61 (m, 2H, CH Ar), 3.96 (s, 3H, CH$_3$), 3.86 (s, 3H, CH$_3$). $^{13}$C NMR (75MHz, CDCl$_3$) δ (ppm): 168.5, 165.3, 162.9, 162.6, 150.9, 130.9, 129.6, 128.7, 126.8, 117.8, 111.2, 111.0, 102.4, 98.5, 55.9, 52.7. Anal. Calculated for
C\textsubscript{16}H\textsubscript{13}NO\textsubscript{5}: C, 64.21; H, 4.38; N, 4.68; Found: C, 63.94; H, 4.12; N, 4.37. EI-MS (m/z) : 300.0 (100).

**HBO 6**

**Route A.** Off-white powder. 50%. \textsuperscript{1}H NMR (200MHz, CDCl\textsubscript{3}) \(\delta\) (ppm): 11.68 (br.s., 1H, OH), 8.39 (s, 1H, CH Ar), 8.12 (d, 1H, CH Ar, J = 8.6 Hz), 7.90 (s, 1H, CH Ar), 7.65 (d, 1H, CH Ar, J = 8.6 Hz), 7.54 (s, 1H, CH Ar), 3.97 (s, 3H, CH\textsubscript{3}), 1.52 (s, 9H, CH\textsubscript{3}), 1.40 (s, 9H, CH\textsubscript{3}). \textsuperscript{13}C NMR (75MHz, CDCl\textsubscript{3}) \(\delta\) (ppm): 166.4, 165.4, 155.9, 151.9, 141.2, 140.3, 137.3, 129.0, 127.4, 127.0, 121.3, 120.8, 110.3, 109.3, 52.4, 35.2, 34.2, 31.5, 29.5. Anal. Calculated for C\textsubscript{23}H\textsubscript{27}NO\textsubscript{4}: C, 72.42; H, 7.13; N, 3.67; Found: C, 72.18; H, 6.81; N, 3.43. EI-MS (m/z) : 382.2 (100).

**HBO 7**

**Route B.** Off-yellow powder. 20%. \textsuperscript{1}H NMR (200MHz, CDCl\textsubscript{3}) \(\delta\) (ppm): 11.45 (br.s., 1H, OH), 8.59 (s, 1H, CH Ar), 8.35 (d, 1H, CH Ar, J = 10 Hz), 7.90 (s, 1H, CH Ar), 7.72 (d, 1H, CH Ar, J = 10 Hz), 7.59 (d, 1H, CH Ar, J = 10 Hz), 1.50 (s, 9H, CH\textsubscript{3}), 1.39 (s, 9H, CH\textsubscript{3}). \textsuperscript{13}C NMR (75MHz, CDCl\textsubscript{3}) \(\delta\) (ppm): 167.0, 156.4, 152.6, 145.6, 141.7, 140.7, 137.7, 129.9, 121.4, 121.1, 115.1, 110.3, 108.7, 35.4, 34.5, 31.5, 29.4. Anal. Calculated for C\textsubscript{21}H\textsubscript{24}N\textsubscript{2}O\textsubscript{4}: C, 68.46; H, 6.57; N, 7.60. Found C, 68.24; H, 6.38; N, 7.27. EI-MS (m/z) : 369.2 (100).

**HBO 8**

**Route B.** Off-yellow powder. 18%. \textsuperscript{1}H NMR (300MHz, CDCl\textsubscript{3}) \(\delta\) (ppm): 11.45 (s., 1H, OH), 7.80 (d, 1H, CH Ar, J = 9 Hz), 7.60-7.64 (m, 1H, CH Ar), 7.51-7.54 (m, 1H, CH Ar), 7.24-7.34 (m, 2H, CH Ar), 6.31-6.36 (m, 2H, CH Ar), 3.42 (q, 4H, CH\textsubscript{2}, J = 7.2 Hz), 1.22 (t, 6H, CH\textsubscript{3}, J = 7.2 Hz). \textsuperscript{13}C NMR (75MHz, CDCl\textsubscript{3}) \(\delta\) (ppm): 164.0, 160.5, 152.0, 148.9, 140.7, 128.3, 124.4, 123.8, 118.2, 110.1, 104.2, 98.6, 97.9, 44.6, 12.7.
HBO 9

Route B. Off-yellow powder. 23%. $^1$H NMR (300MHz, CDCl$_3$) δ (ppm): 10.95 (s, 1H, OH), 8.44 (s, 1H, CH Ar), 8.21 (d, 1H, CH Ar, J = 9.5 Hz), 7.75 (d, 1H, CH Ar, J = 9 Hz), 7.57 (d, 1H, J = 9 Hz), 6.28-6.35 (m, 2H, CH Ar), 3.42 (q, 4H, CH$_2$, J = 7.2 Hz), 1.23 (t, 3H, CH$_3$, J = 6.9 Hz). $^{13}$C NMR (75MHz, CDCl$_3$) δ (ppm): 166.7, 160.9, 152.9, 152.7, 145.3, 141.5, 128.5, 119.9, 113.8, 109.8, 104.7, 97.7, 97.3, 44.7, 12.7. Anal. Calculated for C$_{17}$H$_{17}$N$_3$O$_4$: C, 62.38; H, 5.23; N, 12.84. Found C, 62.17; H, 4.91; N, 12.57. EI-MS (m/z) : 328.1 (100).

2.2) Synthesis of HBO.BF$_2$ complexes 10-20

General Procedure

To a stirred solution of HBO 1-9 in freshly distilled 1,2-dichloroethane (0.1 mL/mg), BF$_3$.Et$_2$O (6 eqts) was syringed under argon. After 5 minutes, N,N-Diisopropylethylamine (DIEA) (6 eqts) was added and the resulting mixture stirred at 40°C for 1 hour. The crude solution was filtered through a column of basic Al$_2$O$_3$, eluting with CH$_2$Cl$_2$, to afford clean HBO.BF$_2$ complexes 10-18 as yellow to white powders after evaporation of the solvents in vacuo.

HBO.BF$_2$ 10

Off-white powder. 70%. $^1$H NMR (300MHz, CDCl$_3$) δ (ppm): 7.94-7.99 (m, 2H, CH Ar), 7.73-7.78 (m, 1H, CH Ar), 4-55-7.72 (m, 3H, CH Ar), 7.23-7.27 (m, 1H, CH Ar), 7.05-7.12 (m, 1H, CH Ar). $^{13}$C NMR (50MHz, CDCl$_3$) δ (ppm): 162.6, 158.5, 148.9, 139.8, 133.3, 126.7, 125.1, 124.8, 119.3, 119.0, 117.2, 110.4, 110.3. $^{11}$B NMR (128 MHz, CDCl$_3$) δ (ppm): 1.44 (J$_{BF}$ = 10.63 Hz). Anal. Calculated for C$_{13}$H$_8$BF$_2$NO$_2$: C, 60.28; H, 3.11; N, 5.41; Found C, 59.96; H, 2.79; N, 5.19. EI-MS (m/z) : 259.0 (100), 240.0 (15).
**HBO.BF$_2$ 11**

White powder. 97%. $^1$H NMR (300MHz, CDCl$_3$) δ (ppm): 7.95-8.00 (m, 1H, CH Ar), 7.71-7.79 (m, 3H, CH Ar), 7.53-7.58 (m, 2H, CH Ar), 1.52 (s, 9H, CH$_3$), 1.38 (s, 9H, CH$_3$). $^{13}$C NMR (75MHz, CDCl$_3$) δ (ppm): 162.8, 156.8, 148.7, 142.5, 140.0, 132.9, 130.9, 127.2, 127.1, 119.1, 116.9, 111.5, 105.6, 35.4, 35.5, 31.3, 29.4. $^{11}$B NMR (128 MHz, CDCl$_3$) δ (ppm): 1.45 ($J_{BF} = 8.45$ Hz). Anal. Calculated for C$_{21}$H$_{24}$BF$_2$NO$_2$; C, 67.94; H, 6.52; N, 3.77; Found C, 67.69; H, 6.44; N, 3.66. EI-MS (m/z) : 371.1 (100), 352.1 (20).

**HBO.BF$_2$ 12**

White powder. 88%. $^1$H NMR (300MHz, CDCl$_3$) δ (ppm): 7.89-7.92 (m, 1H, CH Ar), 7.82-7.84 (m, 1H, CH Ar), 7.66-7.69 (m, 1H, CH Ar), 7.49-7.54 (m, 2H, CH Ar), 6.65-6.69 (m, 2H, CH Ar), 3.90 (s, 3H, CH$_3$). $^{13}$C NMR (75MHz, CDCl$_3$) δ (ppm): 167.9, 162.3, 161.8, 148.3, 130.6, 127.1, 126.8, 126.7, 116.3, 111.2, 110.4, 102.5, 99.1, 55.8. $^{11}$B NMR (128 MHz, CDCl$_3$) δ (ppm): 1.40 ($J_{BF} = 10.88$ Hz). Anal. Calculated for C$_{14}$H$_{10}$BF$_2$NO$_3$; C, 58.17; H, 3.49; N, 4.85; Found C, 57.84; H, 3.15; N, 4.60. EI-MS (m/z) : 289.0 (100), 270.0 (10).

**HBO.BF$_2$ 13**

White powder. 89%. $^1$H NMR (200MHz, CDCl$_3$) δ (ppm): 8.88 (d, 1H, CH Ar, $J = 8.8$ Hz), 8.00-8.10 (m, 2H, CH Ar), 7.82-7.88 (m, 3H, CH Ar), 7.48-7.77 (m, 3H, CH Ar), 7.37 (d, 1H, CH Ar, $J = 9.2$ Hz). $^{13}$C NMR (75MHz, CDCl$_3$) δ (ppm): 162.9, 162.6, 148.6, 139.5, 130.1, 129.8, 129.6, 129.3, 128.4, 127.5, 127.1, 125.1, 123.6, 121.1, 116.7, 111.6, 98.8. $^{11}$B NMR (128 MHz, CDCl$_3$) δ (ppm): 1.51 ($J_{BF} = 10.63$ Hz). Anal. Calculated for C$_{17}$H$_{10}$BF$_2$NO$_2$; C, 66.06; H, 3.26; N, 4.53; Found C, 65.83; H, 3.09; N, 4.28. EI-MS (m/z) : 309.0 (100), 290.0 (25).
HBO.BF$_2$ 14

Beige powder. 76%. $^1$H NMR (300MHz, CDCl$_3$) δ (ppm): 8.54 (s, 1H, CH Ar), 8.24 (d, 1H, CH Ar, J = 8.9 Hz), 7.82 (d, 1H, CH Ar, J = 9.3 Hz), 7.72 (d, 1H, CH Ar, J = 8.7 Hz), 6.65-6.69 (m, 2H, CH Ar), 3.98 (s, 3H, CH$_3$), 3.90 (s, 3H, CH$_3$). $^{13}$C NMR (75MHz, CDCl$_3$) δ (ppm): 166.5, 165.3, 163.0, 162.7, 151.0, 131.1, 129.6, 128.7, 126.9, 118.0, 111.3, 111.0, 102.5, 98.6, 55.9, 52.7. Anal. Calculated for C$_{16}$H$_{12}$BF$_2$NO$_5$; C, 55.37; H, 3.48; N, 4.04. Found C, 55.28; H, 3.17; N, 3.79. EI-MS (m/z) : 347.0 (100), 328.0 (20).

HBO.BF$_2$ 15

White powder. 89%. $^1$H NMR (200MHz, CDCl$_3$) δ (ppm): 8.60 (s, 1H, CH Ar), 8.28 (d, 1H, CH Ar, J = 8.6 Hz), 7.75-7.79 (m, 3H, CH Ar), 3.99 (s, 3H, CH$_3$), 1.51 (s, 9H, CH$_3$), 1.37 (s, 3H, CH$_3$). $^{13}$C NMR (75MHz, CDCl$_3$) δ (ppm): 165.3, 164.0, 157.2, 142.7, 140.0, 133.5, 131.0, 129.4, 128.6, 119.1, 118.2, 111.2, 105.1, 52.8, 35.2, 34.5, 31.1, 29.4. $^{11}$B NMR (128 MHz, CDCl$_3$) δ (ppm): 1.45 (J$_{BF}$ = 8.45Hz). Anal. Calculated for C$_{23}$H$_{26}$BF$_2$NO$_4$; C, 64.35; H, 6.10; N, 3.26. Found C, 64.17; H, 5.79; N, 3.04. EI-MS (m/z) : 429.1 (100), 410.1 (10).

HBO.BF$_2$ 16

Off-white powder. 90%. $^1$H NMR (200MHz, CDCl$_3$) δ (ppm): 8.80 (s, 1H, CH Ar), 8.49 (d, 1H, J = 9 Hz), 7.88 (d, 1H, CH Ar, J = 9.2 Hz), 7.78 (s, 2H, CH Ar), 1.51 (s, 9H, CH$_3$), 1.38 (s, 3H, CH$_3$). $^{13}$C NMR (75MHz, CDCl$_3$) δ (ppm): 165.6, 157.8, 151.6, 146.8, 143.2, 140.5, 134.6, 131.7, 122.9, 119.2, 113.1, 112.1, 104.8, 35.5, 34.6, 31.2, 29.3. Anal. Calculated for C$_{21}$H$_{23}$BF$_2$N$_2$O$_4$; C, 60.60; H, 5.57; N, 6.73; Found C, 60.50; H, 5.29; N, 6.47. EI-MS (m/z) : 416.1 (100), 397.1 (20).
HBO.BF$_2$ 17

Yellow powder. 80%. $^1$H NMR (200MHz, CDCl$_3$) $\delta$ (ppm): 7.74-7.78 (m, 1H, CH Ar), 7.52-7.65 (m, 2H, CH Ar), 7.26-7.45 (m, 2H, CH Ar), 6.26-3.37 (m, 2H, CH Ar), 3.38 (q, 4H, CH$_2$, $J = 7$ Hz), 1.19 (t, 6H, CH$_3$, $J = 7$Hz). $^{13}$C NMR (75MHz, CDCl$_3$) $\delta$ (ppm): 161.9, 161.5, 155.3, 148.5, 131.4, 127.1, 126.6, 125.6, 115.7, 111.1, 106.3, 99.0, 93.9, 45.0, 12.7. $^{11}$B NMR (128 MHz, CDCl$_3$) $\delta$ (ppm): 1.36 ($J_{BF} = 12.67$ Hz). Anal. Calculated for C$_{17}$H$_{17}$BF$_2$N$_2$O$_2$; C, 61.85; H, 5.19; N, 8.49. Found C, 61.66; H, 4.84; N, 8.21. EI-MS (m/z) : 330.1 (100), 311.1 (20).

HBO.BF$_2$ 18

Yellow powder. 64%. $^1$H NMR (200MHz, CDCl$_3$) $\delta$ (ppm): 8.63 (s, 1H, CH Ar), 8.33 (d, 1H, CH Ar, $J = 8.7$ Hz), 7.66-7.70 (m, 2H, CH Ar), 6.44 (d, 1H, CH Ar, $J = 10.2$ Hz), 6.33 (s, 1H, CH Ar), 3.46 (q, 4H, CH$_2$, $J = 7.2$ Hz), 1.26 (t, 6H, CH$_3$, $J = 5.1$ Hz). $^{13}$C NMR (75MHz, CDCl$_3$) $\delta$ (ppm): 164.0, 162.3, 156.2, 151.6, 146.5, 132.5, 127.3, 121.5, 111.6, 111.1, 107.1, 99.1, 93.2, 42.2, 12.7. Anal. Calculated for C$_{17}$H$_{16}$BF$_2$N$_3$O$_4$; C, 54.43; H, 4.30; N, 11.20. Found C, 54.32; H, 4.21; N, 11.12. EI-MS (m/z) : 375.1 (100), 356.1 (25).

2.3) Synthesis of HBO 19 and BODIPY dyes 21-22

HBO 19

To a solution of HBO 6 (230 mg; 0.6 mmol) in THF (10mL), 1mL of a solution of NaOH 3M was added dropwise at 0°C. The resulting mixture was further stirred at 50°C overnight. After cooling down, the solvent were evaporated. The residue was taken up in 50 mL of ethyl acetate, washed successively with H$_2$O and HCl 1M until neutral pH of the aqueous phase, dried (MgSO$_4$) and the solvents were evaporated in vacuo. HBO 19 (215 mg, 97%) was obtained pure as a white powder.
1H NMR (200MHz, DMSO-d6) δ (ppm): 11.8 (s, 1H, OH), 8.36 (s, 1H, CH Ar), 7.87-8.06 (m, 3H, CH Ar), 7.54 (s, 1H, CH Ar), 1.45 (s, 9H, CH3), 1.34 (s, 9H, CH3). 13C NMR (75MHz, DMSO-d6) δ (ppm): 166.5, 164.3, 154.9, 151.5, 141.1, 139.1, 136.7, 128.4, 127.0, 120.8, 120.0, 111.1, 108.9, 34.7, 33.8, 31.2, 29.2. Anal. Calculated for C22H25NO4; C, 71.91; H, 6.86; N, 3.81. Found C, 71.82; H, 6.54; N, 3.66. EI-MS (m/z) : 367.1 (100).

BODIPY 21

To a solution of HBO 19 (63 mg; 0.16 mmol) in 10 mL of distilled CH2Cl2 was added BODIPY 20 (59 mg; 0.16 mmol), 4-Dimethylaminopyridine (DMAP) (20 mg; 0.16 mmol) and 1-(3-Dimethylaminopropl)-3-ethylcarbo-diimide hydro chloride (EDCl.HCl) (25 mg; 0.16 mmol). The resulting mixture was stirred at RT overnight before it was diluted with 30 mL of CH2Cl2, washed with water, dried (MgSO4) and the solvents evaporated in vacuo. Purification by SiO2 column chromatography (CH2Cl2 100%) afforded BODIPY 21 as a red powder (100 mg, 84%).

1H NMR (300MHz, CDCl3) δ (ppm): 11.67 (s, 1H, OH), 8.23 (s, 1H, CH Ar), 8.11 (s, 1H, CH Ar), 7.84-8.00 (m, 4H, CH Ar), 7.71 (d, 1H, CH Ar, J = 8.4 Hz), 7.56 (s, 1H, CH Ar), 7.26-7.33 (m, 1H, CH Ar), 2.54 (s, 6H, CH3), 2.31 (q, 4H, CH2, J= 7 Hz), 1.51 (s, 9H, CH3), 1.39 (s, 9H, CH3), 1.37 (s, 6H, CH3), 99 (t, 6H, CH3, J = 7 Hz). 13C NMR (75MHz, CDCl3) δ (ppm): 165.7, 165.4, 156.2, 153.9, 151.3, 141.5, 140.6, 139.6, 138.6, 138.4, 137.5, 132.9, 132.2, 132.0, 131.0, 129.3, 124.8, 121.4, 120.4, 117.8, 111.0, 109.2, 35.4, 34.5, 31.5, 29.5, 17.1, 14.7, 12.6, 12.0. Anal. Calculated for C45H51BF2N4O3; C, 72.58; H, 6.90; N, 7.52. Found C, 72.39; H, 6.76; N, 7.28. EI-MS (m/z) : 744.4 (100), 725.4 (25).
BODIPY 22

To a stirred solution of BODIPY 21 (30 mg, 0.04 mmol) in 4 mL of distilled 1,2-dichloroethane, BF₃·Et₂O (30 µL, 0.24 mmol) was syringed under argon. After 5 minutes, N,N-Diisopropylethylamine (DIEA) (42 µL, 0.24 mmol) was added and the resulting mixture stirred at 40°C for 1 hour. The crude solution was filtered through a pad of basic Al₂O₃, eluting with CH₂Cl₂, to afford clean BODIPY 22 as a red powder (28 mg, 88%) after evaporation of the solvents in vacuo.

¹H NMR (300MHz, CDCl₃) δ (ppm): 8.39 (br.s., 1H, NH), 8.32 (s, 1H, CH Ar), 8.25 (d, 1H, CH Ar, J = 8.7 Hz), 7.84-7.91 (m, 3H, CH Ar), 7.79 (d, 2H, CH Ar, J = 8.1 Hz), 7.33 (d, 2H, J = 8.7 Hz), 2.54 (s, 6H, CH₃), 2.32 (q, 4H, CH₂, J = 8 Hz), 1.51 (s, 9H, CH₃), 1.38 (s, 15H, CH₃), 1.00 (t, 6H, CH₃, J = 7.8 Hz). ¹³C NMR (75MHz, CDCl₃) δ (ppm): 163.2, 162.9, 156.2, 152.8, 149.5, 142.1, 139.2, 138.5, 137.3, 137.3; 133.4, 132.9, 131.8, 131.3, 130.1, 129.9, 128.3, 126.9, 119.6, 118.2, 113.5, 111.2, 104.2, 34.4, 33.5, 28.4, 16.1, 13.6, 11.5, 10.9. Anal. Calculated for C₄₅H₅₀B₂F₄N₄O₃; C, 68.20; H, 6.36; N, 7.07. Found C, 67.94; H, 6.09; N, 6.82. EI-MS (m/z) : 792.4 (100), 754.4 (15).

2.4) Synthesis of HBO 23-24 and dye 25

HBO 23

A solution of HBO 9 (40 mg, 0.12 mmol) in toluene (5 ml) was degassed with argon. After addition of Pd/C (10%), H₂ gas was bubbled through the solution. It was then stirred under an hydrogen atmosphere at room temperature for 20h. A filtration over Celite® enables to obtain 23 a pale brown powder. Yield 94%.

¹H NMR (200 MHz, CDCl₃) δ (ppm): 13.38 (1H, s, OH), 8.36 (1H, s, CH Imine), 7.75 (1H, d, J = 9.6 Hz, CH Ar.), 7.28 (1H, d, J = 8.4 Hz, CH Ar.), 6.92 (1H, d, J = 2.0 Hz, CH Ar.), 6.62
(1H, dd, \( J_1 = 8.4 \) Hz, \( J_2 = 2.2 \) Hz, CH Ar.), 6.32 (2H, m, CH Ar.) 3;40 (1H, q, \( J = 7.0 \) Hz, \( \text{CH}_2 \text{NEt}_2 \)), 1.21 (6H, t, \( J = 7.0 \) Hz, \( \text{CH}_3 \text{NEt}_2 \)); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) δ (ppm): 164.6, 160.6, 152.0, 143.9, 143.2, 141.9, 126.4, 112.3, 110.3, 104.4, 104.1, 99.2, 98.1, 44.8, 12.9; Anal. Calculated for \( \text{C}_{17}\text{H}_{19}\text{N}_{3}\text{O}_{2} \): C, 68.67; H, 6.44; N, 14.13; Found: C, 68.47; H, 6.27; N, 13.92; EI-MS (m/z) : 297.1 (100).

**HBO 24**

To a solution HBO 23 (60 mg, 0.2 mmol) and pTsOH (one crystal) in dry ethanol was added 4-(Diethylamino)salicyaldehyde (40 mg, 0.2 mmol). The resulting solution was refluxed overnight. After cooling down, an orange powder precipitates. It was then centrifugated, washed with ethanol, pentane and dried under vacuum. Yield 81%.

\(^1\)H NMR (200 MHz, Acetone-d\(_6\)) δ (ppm): 13.32 (1H, s, OH), 11.25 (1H, s, OH), 8.73 (1H, s, CH Imine), 7.72 (3H, m, CH Ar.), 7.33 (2H, m, CH Ar.), 6.43 (2H, m, CH Ar.), 6.28 (1H, d, \( J = 2.4 \) Hz, CH Ar.), 6.18 (1H, s, CH Ar.), 3.50 (8H, m, \( \text{CH}_2 \text{NEt}_2 \)), 1.21 (12H, m, \( \text{CH}_3 \text{NEt}_2 \)); \(^{13}\)C NMR (100 MHz, Acetone-d\(_6\)) δ (ppm): 166.0, 164.5, 162.8, 161.7, 153.4, 153.1, 148.0, 142.6, 135.3, 129.2, 119.4, 111.3, 110.0, 109.9, 105.6, 105.5, 104.9, 98.8, 98.4, 98.2, 45.21, 45.19, 44.8, 13.0; Anal. Calculated for \( \text{C}_{28}\text{H}_{32}\text{N}_{4}\text{O}_{3} \): C, 71.16; H, 6.83; N, 11.86; Found: C, 69.82; H, 6.61; N, 11.62; EI-MS (m/z) : 472.1 (100).

**Dye 25**

To a solution of HBO 24 (26 mg, 0.055 mmol) in 1,2- dichloroethane was added BF\(_3\).OEt\(_2\) (6 eq.). and DIEA (6 eq.). The resulting mixture was stirred at 85°C for 30 min. After cooling down, the reaction mixture was filtered over a column of basic Al\(_2\)O\(_3\). The residue is then precipitated by a slow diffusion of pentane in a solution of THF to obtain a yellow powder. Yield 93%.
$^1$H NMR (200 MHz, CDCl$_3$) δ (ppm): 8.15 (1H, s, CH Imine), 7.86 (1H, d, $J = 8.6$ Hz, CH Ar.), 7.65 (3H, m, CH Ar.), 7.28 (2H, m, CH Ar.), 6.43 (2H, m, CH Ar.), 6.34 (1H, d, $J = 2.2$ Hz), 6.24 (1H, d, $J = 2.2$ Hz), 3.47 (8H, m, CH$_2$NEt$_2$), 1.26 (12H, m, CH$_3$NEt$_2$) ; $^{13}$C NMR (100 MHz, CDCl$_3$) δ (ppm): 162.4, 161.9, 158.5, 157.0, 155.8, 155.7, 147.5, 142.4, 134.5, 122.3, 111.6, 109.3, 107.4, 106.7, 99.3, 98.3, 88.7, 45.5, 45.3, 12.9, 12.8 ; $^{11}$B NMR (128MHz, CDCl$_3$) δ (ppm): 1.32 (br.s, BF$_2$ HBO) 0.98 (t, $J = 16.6$ Hz, BF$_2$ Boranil) ; Anal. Calculated for C$_{28}$H$_{30}$B$_2$F$_4$N$_4$O$_3$: C, 59.19; H, 5.32; N, 9.86; Found : C, 58.87; H, 5.04; N, 9.59; EI-MS (m/z) 549.2 (100); 519.2(35).
3) $^1H, ^{13}C$ Spectra
10
Acetone

25
5) Spectroscopic Data
5) Crystallographic Data

The structures presented herein were solved from colourless single crystals grown obtained by slow diffusion of pentane in a dichloromethane solution at room temperature. X-ray diffraction data were collected using a Rigaku MM007 HF copper rotating-anode generator with Osmic confocal optics and a rapid II Curved Image Plate at room temperature for compound 12 and at 200 (2) K for compound 13.

A total of 70 images for 12 (195 for 13) with 5° rotation per image and 30 second exposure per degree of oscillation were measured according to a w-scan profile data strategy derived by the CrystalClear software package.\textsuperscript{S1} Intensities were reduced and merged after empirical absorption correction using CrystalClear. Both structures were solved by direct methods (SHELXS-97)\textsuperscript{S2} and refined on $F^2$ by means of full-matrix least-squares methods (SHELXL-97).\textsuperscript{S2} All non-hydrogen atoms were refined anisotropically whereas hydrogen atoms were placed at the calculated positions and refined using a riding model. ORTEP drawings were made using ORTEP3\textsuperscript{S3} as implemented within PLATON\textsuperscript{S4} and packing studies were carried out using MERCURY.\textsuperscript{S6}

Results for 12: C$_{14}$H$_{10}$B$_2$F$_2$N$_2$O$_3$, Mr= 289.04, T= 293(2) K, colourless block, 0.45 x 0.21 x 0.18 mm, monoclinic, space group P 2$_1$/c (n° 14), a= 8.2999(4) Å, b= 8.6119(3) Å, c= 18.3770(15) Å, $\beta$= 107.826(6) °, V= 1250.49(13) Å$^3$, Z= 4, $r_{\text{calc}}$= 1.535 g.cm$^{-3}$, $2\theta_{\text{max}}$ = 136.4 °, F(000) = 592 e-, 5541 measured reflections, 2162 independent, -8 ≤ h ≤ 9, -10 ≤ k ≤ 4, -19 ≤ l ≤ 22, R(int)= 0.025, $\mu$= 1.084 mm$^{-1}$, multi-scan absorption correction, relative $T_{\text{min}}$= 0.811 and $T_{\text{max}}$= 1.0, 192 parameters were refined against all reflections, R$_1$= 0.0693, wR$_2$= 0.1182 (using all 2152 data) based on observed $F$ values, R$_1$= 0.0404, wR$_2$= 0.0966 (1418 reflections with $I$>2$s$(I)), Extinction coefficient 0.0013(3), Dr$_{\text{min}}$ and r$_{\text{max}}$ = -0.194 and 0.189 e.Å$^{-3}$, GOF=1.071 based on $F^2$.

Results for 13: C$_{17}$H$_{10}$B$_2$F$_2$N$_2$O$_2$, Mr= 309.07, T= 200(2) K, colourless parallelepiped stick, 0.55 x 0.30 x 0.18 mm, triclinic, space group P -1 (n° 2), a= 8.9782(6) Å, b= 8.8759(3) Å, c= 10.0346(7) Å, $\alpha$= 105.033(7) °, $\beta$= 97.314(7) °, $\gamma$= 92.112(7) °, V= 672.24(6) Å$^3$, Z=2, $r_{\text{calc}}$= 1.527 g.cm$^{-3}$, $2\theta_{\text{max}}$ = 136.36 °, F (000) = 316 e-, 8798 measured reflections, 2393 independent, -6 ≤ h ≤ 9, -10 ≤ k ≤ 10, -11 ≤ l ≤ 12, R(int)= 0.0689, $\mu$=0.998 mm$^{-1}$, multi-scan absorption correction, relative $T_{\text{min}}$= 0.706 and $T_{\text{max}}$=1.000, 273 parameters were refined against all reflections, R$_1$= 0.0604, wR$_2$= 0.1537 (using all 2389 data) based on observed $F$ values, R$_1$= 0.0481, wR$_2$= 0.1252 (1781 reflections with $I$>2$s$(I)), Extinction coefficient : 0.017(3), Dr$_{\text{min}}$ and r$_{\text{max}}$ = - 0.272 and 0.315 e.Å$^{-3}$, extinction coefficient 0.019(3), GOF= 1.173 based on $F^2$. 
CCDC 845870 (12) and CCDC 845871 (13) contain the supplementary crystallographic data. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336033; or deposit@ccdc.cam.uk).

The arrangement of the planar molecules in both crystal structures is strongly governed by π–π stacking forces. This is particularly true for crystal structure of 12, which crystallized in the triclinic P -1 space group and has a layered–type structure with the molecules lying approximately parallel to the (-1 0 1) crystallographic plane with an average interplanar d(-2 0 2) distance of 3.45Å. The extensive stacking is however non-optimal with sliding generated by weak interlayer C(aryl) – H … F interactions (2.259 Å) parallel to c and involving molecules at x, y, z and 1-x, -y, 1-z positions, and concerns concave faces of inversion-related molecules (Fig. S1 Upper). Within the layers, the molecules are aligned through weak C(aryl) – H … O (2.453 Å) along the b direction and also cohesively surrounded by van der Waals contacts (Fig. S2 lower). With respect to 12, which crystallized in the monoclinic space group P 21/c, pairs of inversion-related molecules interacting through C(aryl) – H … F form strips elongating towards the [-1 2 0 ] and [1 2 0 ] directions, alternatively at z = 0 and at z=1/2, and with a relative 45°8 angle (Fig 3 upper). The strips stack in an offset way along the a direction with interlayer distances alternating between 3.425 Å and 3.548 Å (Fig S1 Middle) and interleave in the c axial direction to form a supramolecular structure of corrugated layers (Fig S1 Lower).
Figure S1. (Upper) A view, down the a-axial direction of the cell, showing the molecular strips of inversion-related 12 dimers (dots indicate the Caryl-H … F hydrogen bonds) at z= 0 and z = ½. (Middle) Perpendicular view to the precedent one showing the stacking of the strips. (Lower), Resulting corrugated layers waving around the bc plane.
Figure S2. (Upper) A view, down the b-axial direction of the cell, showing of the interlayer weak hydrogen bonds between aryl groups and fluorine atoms from adjacent layers of 13. (Lower) view orthogonal to the precedent one along the [-2 0 1] direction emphasizing the molecular stacking.
6) References


(7) CrystalClear-SM Expert 2.0 r4 (Rigaku, 2009)

