Supplementary Information for

Luminescent Bi-Metallic Fluoroborates derivatives of bulky Salen ligands

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Synthesis and characterization

2,2-Difluoro-3-propyl-2H-benzo[e][1,3,2]oxaborin-3-ium-2-uide 1

Schiff base ligand 5 (1 equiv., 1 mmol, 163 mg) was dissolved in dry 1,2-dichloroethane (2.5 mL) under nitrogen atmosphere. Dry Et₃N (10 equiv., 10 mmol, 1.22 mL) and BF₃·OEt₂ (10 equiv., 10 mmol, 1.40 mL) were successively added, and the resulting solution was stirred at 90°C for one hour. At room temperature, water (5 mL) was added and the organic phase was extracted with dichloromethane (3 X 5 mL). The organic phases were combined, dried over sodium sulfate and concentrated under reduced pressure. Silica gel flash column chromatography of the residue (eluent: dichloromethane) gave the product as a white solid (126 mg, 60%). mp 109-111 °C. ¹H NMR (300 MHz, CDCl₃, 25 ºC): δ = 8.22 (d, 3 Jₜ-H 3.6 Hz, 1H, CHN), 7.59 (dd, 3 Jₜ-H 7.2, 3 Jₜ-H 8.5 Hz, 1H, aromatic CH), 7.40 (d, 3 Jₜ-H 7.5 Hz, 1H, aromatic CH), 7.10 (dd, 3 Jₜ-H 8.5 Hz, 1H, aromatic CH), 6.98 (dd, 3 Jₜ-H 7.2, 3 Jₜ-H 7.5 Hz, 1H, aromatic CH), 3.75 (t, 3 Jₜ-H 6.8 Hz, 2H, N-CH₂), 2.00-1.88 (m, 2H, N-CH₂-CH₂), 1.02 (t, 3 Jₜ-H 7.4 Hz, 3H, CH₃). ¹³C NMR (75 MHz, CDCl₃, 25ºC): δ = 164.0 (C-O), 159.0 (C=N), 138.0 (C-H), 131.3 (C-H), 120.0 (C-H), 119.2 (C-H), 115.2 (Cquat), 36.0 (CH₂), 23.2 (CH₃), 11.1 (CH₃). ¹⁹F NMR (282 MHz, CDCl₃) δ -161.48 (q, J = 15.5 Hz). ESI(+)-MS: 192.1 [M-F]⁺, 234.1 [M+Na]⁺.
3,3’-(Ethane-1,2-diyl)bis(2,2-difluoro-2H-benzo[e][1,3,2]oxazaborinin-3-ium-2-uide) 2

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\begin{align*}
\text{F} & \quad \text{B} \\
\text{N} & \quad \text{O} \\
\text{N} & \quad \text{B} \quad \text{F}
\end{align*}
\]

2,2’-((1E,1’E)-[Ethane-1,2-diylbis(azanylylidene)]bis(methanylylidene)]bisphenol 6 (20 mg, 0.074 mmol) was dissolved in dry 1,2-dichloroethane (1.2 mL). N,N-Diisopropylethylamine (0.74 mmol; 129 μL) was added, and the resulting mixture stayed under magnetic stirring for 10 min at 80ºC after which boron trifluoride diethyl etherate (1.34 mmol; 165 μL) was added dropwise. The final mixture was stirred for 30 min. at 80ºC under nitrogen atmosphere and then cooled until room temperature. CH\textsubscript{2}Cl\textsubscript{2} (4 mL) was added and the crude mixture was washed with water (3 x 2 mL). The organic layer was separated, dried over Na\textsubscript{2}SO\textsubscript{4} and evaporated to dryness. The residue was purified by flash chromatography [petroleum ether:EtOAc (7:3)] to afford the compound as a white solid (10 mg, 37%). mp 263-265 ºC. \textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}, 25 ºC) \(\delta = 8.38 \text{ (s, 2H, CHN)}\), 7.60 (t, \(3J_{\text{HH}} = 7.6 \text{ Hz , 2H, aromatic CH}\)), 7.34 (d, \(3J_{\text{HH}} = 7.6 \text{ Hz, 1H, aromatic CH}\)), 7.09 (d, \(3J_{\text{HH}} = 7.6 \text{ Hz, 2H, aromatic CH}\)), 6.94 (t, \(3J_{\text{HH}} = 7.6 \text{ Hz, 2H, aromatic CH}\)), 4.37 (s, 4H, CH\textsubscript{2}). \textsuperscript{13}C NMR (75 MHz, DMSO, 25ºC): \(\delta = 168.5 \text{ (C=\text{N})}, 157.8 \text{ (C-O)}, 151.3 \text{ (Cquat), 138.4 (C-H), 132.6 (C-H), 120.1 (C-H), 118.1 (C-H), 52.2 (C-H)}\). \textsuperscript{19}F NMR (282 MHz, DMSO) \(\delta = -158.15 \text{ (q, J = 14.1 Hz)}.\) ESI(+) -MS: 387.1 [M+Na]\textsuperscript{+}.

3,3’-(Ethane-1,2-diyl)bis(6-benzhydryl-2,2-difluoro-2H-benzo[e][1,3,2]oxazaborinin-3-ium-2-uide) 3

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\begin{align*}
\text{F} & \quad \text{B} \\
\text{N} & \quad \text{O} \\
\text{N} & \quad \text{B} \quad \text{F}
\end{align*}
\]

2,2’-((1E,1’E)-[Ethane-1,2-diylbis(azanylylidene)]bis(methanylylidene)]bis(4-benzylphenol) 7 (20 mg: 0.03 mmol) was dissolved in dry 1,2 dichloroethane (1.2 mL). N,N-Diisopropylethylamine (0.3 mmol; 52 μL) was added, and the resulting mixture stayed under magnetic stirring for 10 min at 80 ºC after which boron trifluoride diethyl etherate (0.54 mmol; 67 μL) was added dropwise. The final mixture was stirred for 30 min. at 80 ºC under nitrogen atmosphere and then cooled until room temperature. CH\textsubscript{2}Cl\textsubscript{2} (4 mL) was added and
the crude mixture was washed with water (3 x 2 mL). The organic layer was separated, dried over Na$_2$SO$_4$ and evaporated to dryness. The residue was purified by flash chromatography [petroleum ether:EtOAc (8:2)] to afford the product as a green pale solid (42 mg, quant.). mp 185-187 °C. $^1$H NMR (300 MHz, CDCl$_3$, 25 °C): $\delta = 8.25$ (s, 2H, CHN), 7.40 (dd, $^3$J$_{H-H}$ 8.7, $^4$J$_{H-H}$ 2.1 Hz, 2H, aromatic CH), 7.34-7.16 (m, 12H, aromatic CH), 7.12-6.90 (m, 12H, aromatic CH), 5.45 (s, 2H, CH), 4.29 (s, 4H, CH$_2$). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 167.5 (C=N), 158.0 (C-OH), 142.3 (2 X C-H), 140.5 (C-H), 136.4 (C-H), 132.0 (C-H), 129.2 (4 X C-H), 128.6 (4 X C-H), 126.8 (2 X C-H), 119.3 (Cquat), 114.9 (Cquat), 55.6 (C-H), 54.1 (C-H$_2$). $^{19}$F NMR (282 MHz) $\delta$ -158.56 (bs). ESI(+)-MS: 677.3 [M-F]$^+$, 719.2 [M+Na]$^+$.

3,3’-(Ethane-1,2-diyl)bis(2,2-difluoro-6-trityl-2H-benzo[e][1,3,2]oxazaborinin-3-ium-2-uide) 4

2,2’-((1E,1’E)-(Ethane-1,2-diylbis(azanylylidene))bis(methanylylidene))bis(4-tritylphenol) 8

(20 mg, 0.026 mmol) was dissolved in dry 1,2 dichloroethane (1.2 mL). N,N-diisopropylethylamine (0.26 mmol, 45 μL) was added, and the resulting mixture stayed under magnetic stirring for 10 min at 80 °C after which boron trifluoride diethyl etherate (0.48 mmol, 59 μL) was added dropwise. The final mixture was stirred for 30 min at 80 °C under nitrogen atmosphere and then cooled until room temperature. CH$_2$Cl$_2$ (4 mL) was added and the crude mixture was washed with water (3 x 2 mL). The organic layer was separated, dried over Na$_2$SO$_4$ and evaporated to dryness. The residue was purified by flash chromatography [petroleum ether:EtOAc (8:2)] to afford the product as a white solid (21 mg, 95%). mp > 300 °C. $^1$H NMR (300 MHz, CDCl$_3$, 25 °C): $\delta = 8.23$ (s, 2H, CHN), 7.40 (dd, $^3$J$_{H-H}$ 8.9, $^4$J$_{H-H}$ 2.2 Hz, 2H, aromatic CH), 7.33-7.15 (m, 20H, aromatic CH), 7.16-7.06 (m, 12H, aromatic CH), 6.97 (d, $^3$J$_{H-H}$ 8.9 Hz, 2H, aromatic CH), 4.29 (s, 4H, CH$_2$). $^{13}$C NMR (75 MHz, CDCl$_3$, 25°C): $\delta$ 167.5 (C=N), 157.9 (C-OH), 145.8 (3 X Cquat), 143.5 (C-H), 139.4 (C-H), 132.3 (C-H), 130.8 (6 X C-H), 127.8 (6 X C-H), 126.4 (3 X C-H), 118.4 (Cquat), 114.0 (Cquat), 64.0 (Cquat), 54.13 (C-H$_2$). $^{19}$F NMR (282 MHz, CDCl$_3$) $\delta$ -158.10 (bs). ESI(+)-MS: 829.3 [M-F]$^+$, 871.3 [M+Na]$^+$. 3
(E)-2-[(Propylimino)methyl]phenol 5

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Salicylaldehyde (1 equiv., 2 mmol, 244 mg) and propylamine (1 equiv., 2 mmol, 118 mg) were dissolved in methanol (10 mL) and the resulting solution was refluxed for one hour, after which the solvent was removed under reduced pressure to yield the product 5 as a yellow oil (360 mg, quant.). It was used in the following step without purification.

2,2'-(1E,1'E)-[Ethane-1,2-diylbis(azanylylidene)]bis(methanylylidene)diphenol 6

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\begin{align*}
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\end{align*}
\]


Salicylaldehyde (2 equiv., 2 mmol, 244 mg) and ethylenediamine (1 equiv., 1 mmol, 60 mg) were dissolved in ethanol (10 mL) and the resulting solution was refluxed for one hour. After three days at room temperature, the yellow crystals that formed were collected by filtration, washed with petroleum ether (10 mL) and dried in air. The product was obtained as pale yellow crystals (260 mg, 97%). mp 105-107 °C. \(^1\)H NMR (300.13 MHz, CDCl\(_3\), 25 °C): \(\delta = 13.23 \text{ (s, 2H, OH)}\), 8.36 (s, 2H, CHN), 7.32-7.21 (m, 4H, aromatic CH), 6.94 (d, \(^3\)J\(_{H-H}\) 7.5 Hz, 2H, aromatic CH), 6.85 (ddd, \(^3\)J\(_{H-H}\) 0.9, \(^3\)J\(_{H-H}\) 7.5, \(^3\)J\(_{H-H}\) 7.5 Hz, 2H, aromatic CH), 3.95 (s, 4H, CH\(_2\)).

2,2'-(1E,1'E)-[Ethane-1,2-diylbis(azanylylidene)]bis(methanylylidene)bis(4-benzhydrylphenol 7

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\begin{align*}
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5-Benzhydryl-2-hydroxybenzaldehyde (2 equiv., 2 mmol, 576 mg) and ethylenediamine (1 equiv., 1 mmol, 60 mg) were dissolved in ethanol (10 mL) and the resulting solution was refluxed for two hour. After 12 h at room temperature, the yellow crystals that formed were collected by filtration, washed with ethanol (10 mL) and dried in air. The product was obtained as pale yellow crystals (485
mg, 81%). mp 225-227 °C. $^1$H NMR (300 MHz, CDCl$_3$, 25 °C): $\delta = 13.11$ (s, 2H, OH), 8.25 (s, 2H, CHN), 7.31-7.18 (m, 14H, aromatic CH), 7.11-7.05 (m, 8H, aromatic CH), 6.93 (d, $^4$J$_{HH}$ 2.1 Hz, 2H, aromatic CH), 6.87 (d, $^3$J$_{HH}$ 8.4 Hz, 2H, aromatic CH), 5.48 (s, 2H, CH), 3.86 (s, 4H, CH$_2$).

$^{13}$C NMR (75 MHz, CDCl$_3$, 25°C): $\delta = 166.5$ (C=N), 159.5 (C-OH), 143.8 (C-H), 134.1 (C-H), 133.5 (2 X Cquat), 129.3 (4 X C-H), 128.3 (4 X C-H), 126.3 (2 X C-H), 118.2 (Cquat), 116.9 (Cquat), 59.8 (C-H), 55.8 (C-H).

ESI (+)-MS: 601.3 [M+H]$^+$, 623.3 [M+Na]$^+$. Anal. Calcd for C$_{42}$H$_{36}$N$_2$O$_2$: C 83.97, H 6.04, N 4.66. Found: C 84.13, H 5.97, N 4.61%.

2,2'-(1E,1'E)-[Ethane-1,2-diylbis(azanylylidene)]bis(methanylylidene)]bis(4-tritylphenol 8

5-Trityl-2-hydroxybenzaldehyde (2 equiv., 0.25 mmol, 91 mg) and ethylenediamine (1 equiv., 0.12 mmol, 7.2 mg) were dissolved in ethanol (10 mL) and the resulting solution was refluxed for one hour. At room temperature, the yellow solid that formed was collected by filtration, washed with ethanol (10 mL) and dried in air. The product was obtained as a pale yellow solid (90 mg, quant.).

mp 282-284 °C. $^1$H NMR (300 MHz, CDCl$_3$, 25 °C): $\delta = 13.18$ (s, 2H, OH), 8.21 (s, 2H, CHN), 7.27-7.09 (m, 34H, aromatic CH), 6.84 (d, $^3$J$_{HH}$ 8.4 Hz, 2H, aromatic CH), 3.84 (s, 4H, CH$_2$).

$^{13}$C NMR (75 MHz, CDCl$_3$, 25°C): $\delta = 166.7$ (CH=N), 159.2 (C-OH), 146.6 (3 X Cquat), 137.1 (C-H), 135.8 (C-H), 133.2 (C-H), 131.0 (6 X C-H), 127.5 (6 X C-H), 126.0 (3 X C-H), 117.4 (Cquat), 116.1 (Cquat), 64.1 (Cquat), 59.7 (C-H)$_2$.

ESI (+)-MS: 753.3 [M+H]$^+$. Anal. Calcd for C$_{54}$H$_{44}$N$_2$O$_2$ H$_2$O: C 84.13, H 6.01, N 3.63. Found: C 84.39, H 5.73, N 3.60%. 

5
NMR spectra

2,2-Difluoro-3-propyl-2H-benzo[e][1,3,2]oxazaborinin-3-ium-2-ulide 1

$^1$H NMR spectrum

$^{13}$C NMR spectrum
$^{19}$F NMR spectrum

3,3’-(Ethane-1,2-diy)bis(2,2-difluoro-2H-benzo[e][1,3,2]oxazaborinin-3-iium-2-uide) 2

$^1$H NMR spectrum
$^{13}$C NMR spectrum

$^{19}$F NMR spectrum
3,3’-(Ethane-1,2-diyl)bis(6-benzydryl-2,2-difluoro-2H-benzo[e][1,3,2]oxazaborinin-3-ium-2-uide) 3

$^1$H NMR spectrum

$^{13}$C NMR spectrum
$^{19}$F NMR spectrum

3,3’-((Ethane-1,2-diyl)bis(2,2-difluoro-6-trityl-2H-benzo[e][1,3,2]oxazaborin-3-ium-2-uide) 4

$^1$H NMR spectrum

$^{13}$C NMR spectrum
2,2’-((1E,1’E)-[Ethane-1,2-diylbis(azanylylidene)]bis(methanylylidene)]bis(4-benzhydrylphenol)

1H NMR spectrum

13C NMR spectrum
2,2’-[(1E,1’E)-[Ethane-1,2-diylbis(azanylylidene)]bis(methanylylidene)]bis(4-tritylphenol 8

$^1$H NMR spectrum

$^{13}$C NMR spectrum
## Absorption, excitation and emission results

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<th>Emission max (nm)</th>
<th>Stroke shift (nm)</th>
<th>Quantum yield (^{(a)})</th>
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(a) Determined by comparison with fluorescein (\(\phi_f = 0.90\) in water with NaOH 0.1 mol.L\(^{-1}\))
Absorption, excitation and emission spectra of boron fluorophores:

Fluorophore 1 at 2.19 $10^5$ M:
Fluorophore 2 at $1.53 \times 10^{-5}$ M:
Fluorophore 3 at $3.99 \times 10^{-5}$ M:
Fluorophore 4 at $3.27 \times 10^{-5}$ M: