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Luminescent bi-metallic fluoroborate derivatives of bulky salen ligands†

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A family of hemisalen fluoroborate complexes has been prepared and characterized. These new fluorophores exhibit an intense blue emission upon irradiation with UV light. Interestingly, the introduction of bulky aromatic substituents enhanced the quantum yield considerably, up to 44%. Upon studying various solvents, it appeared that the effect of the phenyl substituents is more of electron donating nature than of restricting the intramolecular motion of the dyes.

Introduction

In the last few years the investigation into fluorescence materials of organic fluorine–boron complexes has received much attention, as these compounds find potential applications in medicinal chemistry, as anticancer agents applied to boron neutron capture therapy,[1] organic synthesis,[2,3] supramolecular chemistry,[4] macrocyclic chemistry,[5] organometallics,[6] dendrimers,[7] sensing and signalling,[8–10] biological probes,[11] solar cells,[12] organic light-emitting diodes,[13] among others.

Salen [*N*,*N*′-ethylenebis(salicylideneimine)] is one of the most studied ligands, due to its versatility and capacity to complex transition metal ions. Salen-type ligands may act as a N_2–O_2 complexing pocket, or as two N–O complexing pockets, depending on the metal ion, and on the length of the diamine linker.

In this way, boron salen complexes[14] are excellent candidates to fluorescence chemosensors.[15] The boron atom forms relatively strong covalent bonds with oxygen and coordinate-covalent bonds with nitrogen atoms and, thus, this element is an excellent candidate for the study of such species.[15] Boron as other compounds of group 13, aluminium, gallium, and indium, forms bimetallic complexes with salen ligands acting as two independent N–O complexing pockets.[16–19]

Here, we wish to report a series of hemisalen based fluoroborate complexes, so-called boranils,[20] decorated with bulky substituents (Fig. 1), whose luminescence properties make them promising building blocks for luminescent devices or probes.

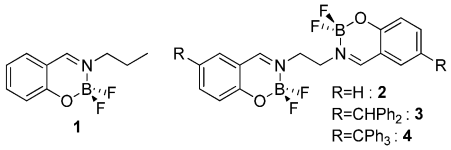
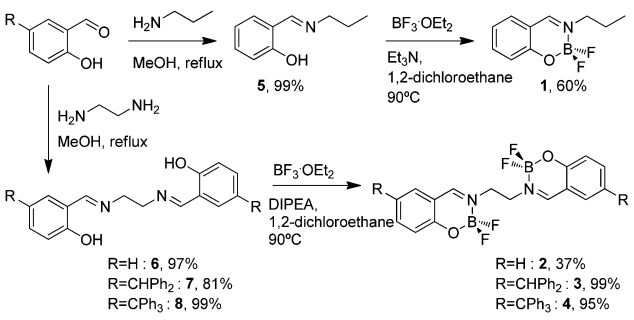


Fig. 1 Structures of the fluoroboron complexes **1–4**.

Results and discussion

The fluoroborate derivatives **1–4** were obtained in two steps according to Scheme 1. Imine **5** was synthesized in quantitative yield by the condensation of propylamine with salicylaldehyde. Imine derivatives **6–8** were synthesized by the condensation of ethylenediamine with the corresponding salicylaldehyde derivative, also in excellent yields.

Boron complexation was achieved using BF_3–OEt_2 and dry triethylamine or diisopropylethylamine (DIPEA) in 1,2-dichloroethane at 80 °C, to afford complexes **1–4** in excellent yields.[21] The structure of the complexes was confirmed by NMR, MS, and elemental analysis. In the ^{1}H NMR spectra of dyes **1–4**, the main indication of complexation is the disappearance of the



Scheme 1 Synthesis of the fluorophores **1–4**.

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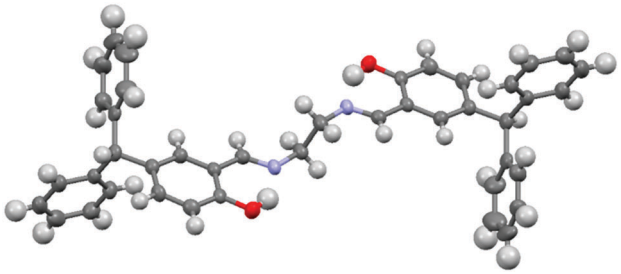

Fig. 2 Single-crystal X-ray diffraction structure of ligand **7**. Thermal ellipsoids are shown at the 50% probability level, hydrogen atoms are shown with an arbitrary radius (0.30 Å). C, grey; O, red; N, blue; H, white.

OH signal, and a broadening of the signal of the singlet attributed to the imine proton. In the ^{19}F NMR spectra, a quadruplet due to the coupling with the adjacent ^{11}B also confirmed the complexation.

Single crystals suitable for X-ray diffraction were obtained for fluoroborate complexes **1** and **2**, and for salen **7**. In the crystal structure of salen **7**, intramolecular hydrogen bonds of salicylaldimine moieties rigidify the hemisalen core (Fig. 2). These hydrogen bonds are also observed in solution, as confirmed by the chemical shift of the hydroxyl group (13.11 ppm, see ESI†). The central ethylene group adopts an eclipsed conformation, an inversion centre being located in the middle of the C–C bond.

The crystal structure of fluoroborates **1** and **2** confirmed the structure and the complexation of boron in the hemisalen pocket (Fig. 3 and 4). In both cases, the imine is co-planar with the phenyl ring. The six membered ring containing the boron is slightly distorted from planarity, the dihedral angle between the O–B–N plane and the C–C–C plane being *ca.* 11.5° and 13.5° for **1** and **2**, respectively. The boron has a slightly distorted tetrahedral geometry, with angles ranging from *ca.* 106° to

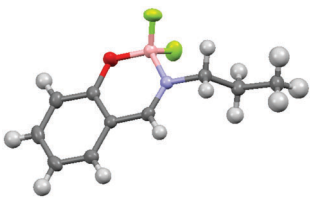

Fig. 3 Single-crystal X-ray diffraction structure of fluoroborate **1**. Thermal ellipsoids are shown at the 50% probability level, hydrogen atoms are shown with an arbitrary radius (0.30 Å). C, grey; O, red; N, blue; H, white; B, pink; F, yellow.

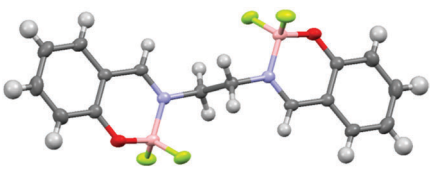

Fig. 4 Single-crystal X-ray diffraction structure of di-fluoroborate **2**. Thermal ellipsoids are shown at the 50% probability level, hydrogen atoms are shown with an arbitrary radius (0.30 Å). C, grey; O, red; N, blue; H, white; B, pink; F, yellow.

Table 1 Absorption and emission properties of boranils **1–4** in different solvents

Boranyl	λ_{abs} (nm)	ε (M^{-1} cm^{-1})	λ_{em} (nm)	Stroke shift (nm)	φ_f[a]	Solvent
1	348	8900	434	86	0.08	Toluene
1	349	5300	430	81	0.10	CH_2Cl_2
1	342	5600	434	92	0.12	MeCN
1	342	6100	429	87	0.11	Methanol
1	342	6300	432	90	0.12	Glycol[b]
2	349	2250	442	93	0.24	Toluene
2	354	32 700	442	88	0.17	CH_2Cl_2
2	350	15 200	445	95	0.26	MeCN
2	346	550	444	98	0.35	Methanol
2	341	950	449	108	0.09	Glycol[b]
3	366	10 500	457	91	0.32	Toluene
3	365	9500	464	99	0.34	CH_2Cl_2
3	361	8850	465	104	0.36	MeCN
3	359	1950	465	106	0.28	Methanol
3	349	2000	468	119	0.10	Glycol[b]
4	367	19 200	467	100	0.44	Toluene
4	365	12 100	473	108	0.35	CH_2Cl_2
4	360	11 750	476	116	0.38	MeCN
4	356	10 100	473	117	0.34	Methanol
4	360	6700	435	75	0.10	Glycol[b]

[a] Determined by comparison with fluorescein (φ_f = 0.90 in water with NaOH 0.1 mol L^{-1}). [b] Ethylene glycol.

ca. 112°, which is similar to previously reported structures.[20] The B–O and B–N distances are, respectively, shorter (1.44(7) Å and 1.43(7) Å for **1** and **2**) and longer (1.57(7) Å and 1.56(7) Å for **1** and **2**) than the ones reported,[20] presumably reflecting the absence of substituents on the phenyl rings.

The absorption, excitation and emission spectra of boranyls **1–4** were recorded in various solvents (Table 1 and Fig. 5 in dichloromethane, see ESI† for the other spectra). All compounds present two absorption bands centred at *ca.* 280 and 350 nm, the first one attributed to π–π* transition and the second one to the intraligand band. The absorption is slightly red shifted from boranyl **1** to **4**, probably due to the electron donating properties of the substituents, but the effect is very small. The molar extinction coefficient does not vary in a clear way between the different dyes, nor between the different solvents.

Fluorophores **1–4** emit in the blue region of the visible spectrum, with quantum yields ranging from 8% to 44%, larger than those previously reported for bimetallic salen boron complexes,[22] making them promising dyes for optoelectronic applications.

Compound **2** may be considered a dimer of dye **1**, two boron complexes being linked by a flexible carbon chain. The two boron complexes in **2** are not conjugated and, therefore, the differences between **1** and **2** may only be ascribed to the fact that **2** has twice the number of boron centres, the distance between these centres, or their relative orientation. The Stokes shifts increased when the dyes are decorated with phenyl substituents, but not significantly. This moderate Stokes shift, together with the fact that oxygen does not quench the emission, is consistent with a fluorescent emissive process. The shapes of the absorption and emission bands are similar

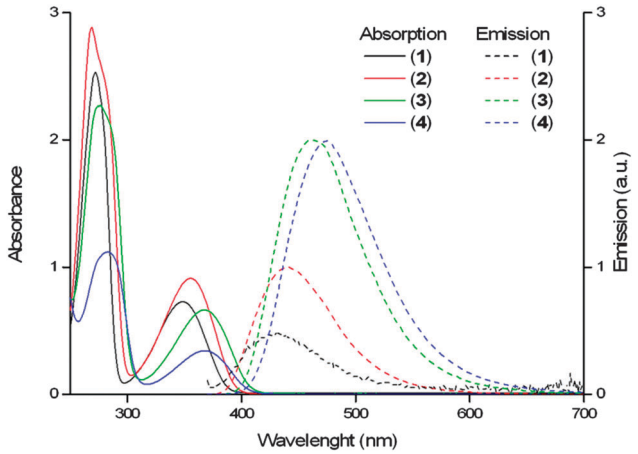

Fig. 5 Absorption (at *ca.* 10^{-5} mol L^{-1}) and emission (at *ca.* 10^{-5} mol L^{-1}, excitation at 360 nm) spectra in dichloromethane.

and seem to be symmetric, supposing the absence of a strong intramolecular charge transfer. This is consistent with the absence of influence of the polarity of the solvent on the emission wavelength and on the quantum yield for all dyes **1–4** (Table 1 and ESI†).

Adding bulky groups at the periphery of the dye induced small bathochromic shifts in the absorption and emission wavelengths, and increased the quantum yield in non-viscous solvents. These bulky groups probably do not restrict the intramolecular rotations of the dyes, because their quantum yields drop when the viscosity of the solvent increased, for example from methanol to ethylene glycol (Table 1).[23,24] This lower quantum yield could also be attributed to aggregation of the dyes **2–4** in ethylene glycol, as the absorption bands dramatically enlarged (see ESI†) to almost vanish, thus favouring self-quenching of the emission. This explanation is consistent with the non-luminescent character of dyes **1–4** in the solid state.

Conclusions

A family of new Schiff base boron complexes has been synthesized and characterized. Compared to the parent compound **1** containing a single boron centre, the dimers **2–4** exhibited larger quantum yields. Decorating the periphery of the dye with bulky phenyl substituents slightly improved the quantum yields up to 44%, probably not by restricting the internal rotations but rather through their small electron donating properties. The introduction of these new fluorophores into emitting devices, such as organic light-emitting diodes, will be the next step and is currently under consideration in our laboratory.

Experimental

Procedure for the synthesis of Shiff-base ligands 5–8

Ligands 5[25] and 6[26] were prepared according to the literature. Salicylaldehyde derivatives (2 mmol) and ethylenediamine (67 μL, 1 mmol) were dissolved in ethanol (10 mL) and the resulting solution was refluxed for one hour. After standing at room temperature for 12 h, the yellow solid was collected by filtration, washed with light petroleum (10 mL) and dried in air.

Ligand 7 = 2,2′-[(1*E*,1′*E*)-(ethane-1,2-diylbis(azanylylidene)-bis(methanylylidene))]bis(4-benzhydrylphenol). 485 mg, yield 81%. mp 225–227 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 13.11 (s, 2H, O*H*), 8.25 (s, 2H, C*H*N), 7.31–7.18 (m, 14H, aromatic C*H*), 7.11–7.05 (m, 8H, aromatic C*H*), 6.93 (d, $^4J_{H-H}$ 2.1 Hz, 2H, aromatic C*H*), 6.87 (d, $^3J_{H-H}$ 8.4 Hz, 2H, aromatic C*H*), 5.48 (s, 2H, C*H*), 3.86 (s, 4H, CH_2). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ 166.5 (*C*=N), 159.5 (*C*–OH), 143.8 (*C*–H), 134.1 (*C*–H), 133.5 (2X *C*quat), 129.3 (4X *C*–H), 128.3 (4X *C*–H), 126.3 (2X *C*–H), 118.2 (*C*quat), 116.9 (*C*quat), 59.8 (*C*–H), 55.8 (*C*–H_2). ESI(+)-MS: 601.3 $[M + H]^+$, 623.3 $[M + Na]^+$. Anal. calcd for $C_{42}H_{36}N_2O_2$: C 83.97, H 6.04, N 4.66. Found: C 84.13, H 5.97, N 4.61%.

Ligand 8 = 2,2′-[(1*E*,1′*E*)-(ethane-1,2-diylbis(azanylylidene)-bis(methanylylidene))]bis(4-tritylphenol). 90 mg, yield quant. mp 282–284 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 13.18 (s, 2H, O*H*), 8.21 (s, 2H, C*H*N), 7.27–7.09 (m, 34H, aromatic C*H*), 6.84 (d, $^3J_{H-H}$ 8.4 Hz, 2H, aromatic C*H*), 3.84 (s, 4H, CH_2). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ 166.7 (*CH*=N), 159.2 (*C*–OH), 146.6 (3X *C*quat), 137.1 (*C*–H), 135.8 (*C*–H), 133.2 (*C*–H), 131.0 (6X *C*–H), 127.5 (6X *C*–H), 126.0 (3X *C*–H), 117.4 (*C*quat), 116.1 (*C*quat), 64.1 (*C*quat), 59.7 (*C*–H_2). ESI(+)-MS: 753.3 $[M + H]^+$. Anal. calcd for $C_{54}H_{44}N_2O_2{\cdot}H_2O$: C 84.13, H 6.01, N 3.63. Found: C 84.39, H 5.73, N 3.60%.

Procedure for the synthesis of boron complexes 1–4

The ligand (1 equiv.) was dissolved in dry 1,2-dichloroethane (*ca.* 2 mL). *N*,*N*-Diisopropylethylamine (5 equiv. per hemisalen) was added, and the resulting mixture was stirred for 10 min at 80 °C after which boron trifluoride diethyl etherate (9 equiv. per hemisalen) was added dropwise. The final mixture was stirred for 30 min at 80 °C under a nitrogen atmosphere and then cooled to room temperature. CH_2Cl_2 (4 mL) was added and the crude mixture was washed with water (3 × 2 mL). The organic layer was separated, dried over Na_2SO_4 and evaporated to dryness. The residue was purified by flash chromatography [petroleum ether : EtOAc (8 : 2)].

Complex 1 = 2,2-difluoro-3-propyl-2*H*-benzo[*e*][1,3,2]oxazaborinin-3-ium-2-uide. 126 mg, yield 60%. mp 109–111 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 8.22 (d, $^3J_{H-B}$ 3.6 Hz, 1H, C*H*N), 7.59 (dd, $^3J_{H-H}$ 7.2, $^3J_{H-H}$ 8.5 Hz, 1H, aromatic C*H*), 7.40 (d, $^3J_{H-H}$ 7.5 Hz, 1H, aromatic C*H*), 7.10 (dd, $^3J_{H-H}$ 8.5 Hz, 1H, aromatic C*H*), 6.98 (dd, $^3J_{H-H}$ 7.2, $^3J_{H-H}$ 7.5 Hz, 1H, aromatic C*H*), 3.75 (t, $^3J_{H-H}$ 6.8 Hz, 2H, N–CH_2), 2.00–1.88 (m, 2H, N–CH_2–CH_2), 1.02 (t, $^3J_{H-H}$ 7.4 Hz, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): 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 (*C*quat), 36.0 (CH_2), 23.2 (CH_2), 11.1 (CH_3). ^{19}F NMR (282 MHz, $CDCl_3$) δ −161.48 (q, J = 15.5 Hz). ESI(+)-MS: 192.1 $[M - F]^+$, 234.1 $[M + Na]^+$.

Complex 2 = 3,3′-(ethane-1,2-diyl)bis(2,2-difluoro-2*H*-benzo[*e*]-[1,3,2]oxazaborinin-3-ium-2-uide). 10 mg, yield 37%. mp 263–265 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ 8.38 (s, 2H, C*H*N), 7.60 (t, $^3J_{H-H}$ 7.6 Hz, 2H, aromatic C*H*), 7.34 (d, $^3J_{H-H}$ = 7.6 Hz,

1H, aromatic C*H*), 7.09 (d, $^{3}J_{H-H}$ 7.6 Hz, 2H, aromatic C*H*), 6.94 (t, $^{3}J_{H-H}$ 7.6 Hz, 2H, aromatic C*H*), 4.37 (s, 4H, CH_2). ^{13}C NMR (75 MHz, DMSO, 25 °C): δ 168.5 (*C*=N), 157.8 (*C*–OH), 151.3 (*C*quat), 138.4 (*C*–H), 132.6 (*C*–H), 120.1 (*C*–H), 118.1 (*C*–H), 52.2 (*C*–H_2). ^{19}F NMR (282 MHz, DMSO) δ −158.15 (q, J = 14.1 Hz). ESI(+)-MS: 387.1 $[M + Na]^+$.

Complex 3 = 3,3′-(ethane-1,2-diyl)bis(2,2-difluoro-6-benzhydryl-2*H*-benzo[*e*][1,3,2]oxazaborinin-3-ium-2-uide). 42 mg, yield quant. mp 185–187 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 8.25 (s, 2H, C*H*N), 7.40 (dd, $^{3}J_{H-H}$ 8.7, $^{4}J_{H-H}$ 2.1 Hz, 2H, aromatic C*H*), 7.34–7.16 (m, 12H, aromatic C*H*), 7.12–6.90 (m, 12H, aromatic C*H*), 5.45 (s, 2H, C*H*), 4.29 (s, 4H, CH_2). ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.5 (*C*=N), 158.0 (*C*–OH), 142.3 (2X *C*–H), 140.5 (*C*–H), 136.4 (*C*–H), 132.0 (*C*–H), 129.2 (4X *C*–H), 128.6 (4X *C*–H), 126.80 (2X *C*–H), 119.3 (*C*quat), 114.9 (*C*quat), 55.6 (*C*–H), 54.1 (*C*–H_2). ^{19}F NMR (282 MHz,) δ −158.56 (bs). ESI(+)-MS: 677.3 $[M - F]^+$, 719.2 $[M + Na]^+$.

Complex 4 = 3,3′-(ethane-1,2-diyl)bis(2,2-difluoro-6-trityl-2*H*-benzo[*e*][1,3,2]oxazaborinin-3-ium-2-uide). 21 mg, yield 95%. mp > 300 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 8.23 (s, 2H, C*H*N), 7.40 (dd, $^{3}J_{H-H}$ 8.9, $^{4}J_{H-H}$ 2.2 Hz, 2H, aromatic C*H*), 7.33–7.15 (m, 20H, aromatic C*H*), 7.16–7.06 (m, 12H, aromatic C*H*), 6.97 (d, $^{3}J_{H-H}$ 8.9 Hz, 2H, aromatic C*H*), 4.29 (s, 4H, CH_2). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ 167.5 (*C*=N), 157.9 (*C*–OH), 145.8 (3X *C*quat), 143.5 (*C*–H), 139.4 (*C*–H), 132.3 (*C*–H), 130.8 (6X *C*–H), 127.8 (6X *C*–H), 126.4 (3X *C*–H), 118.4 (*C*quat), 114.0 (*C*quat), 64.0 (*C*quat), 54.1 (*C*–H_2). ^{19}F NMR (282 MHz, $CDCl_3$) δ −158.10 (bs). ESI(+)-MS: 829.3 $[M - F]^+$, 871.3 $[M + Na]^+$.

Acknowledgements

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