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# Aggregation-induced emission enhancement of chiral boranils<sup>†</sup>

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New boranils based on chiral benzylamines have been synthesized and their photophysical properties studied. These BF<sub>2</sub>-complexes exhibit a bright blue fluorescence in solution and in the solid state, and exhibit aggregation-induced emission enhancement. The chirality of the ligand, even if it is not directly located at the boron center, has consequences on the circular dichroism of the complexes.

## 1. Introduction

Four-coordinate organoboron complexes have emerged as promising materials for optoelectronics, including organic light-emitting diodes (OLEDs), organic field-effect transistors, photo-responsive materials, and sensory and imaging materials.<sup>1-3</sup> Concerning OLED applications, although numerous red and green emitters showing good electroluminescence performance have been reported,<sup>4</sup> efficient blue emitters are still missing, in particular deep blue emitters for electroluminescent devices.<sup>5-7</sup>

Complexes of boron-dipyrromethene (BODIPY) derivatives,<sup>8-11</sup> boranils<sup>12–15</sup> and boron  $\beta$ -diketonates<sup>16–22</sup> feature high fluorescence quantum yields and an excellent photostability. While many four-coordinate organoboron complexes exhibit excellent fluorescence properties in dilute solutions, few examples are available of emissive dyes in the solid state. This is mainly due to aggregationcaused quenching (ACQ), prompted by inherent strong intermolecular  $\pi$ - $\pi$  stacking interactions that consume the excitation energy. Nevertheless, certain dyes present a behaviour opposite to ACQ, *i.e.*, aggregation-induced emission (AIE)<sup>23-27</sup> or aggregationinduced emission enhancement (AIEE).<sup>28-34</sup> In this case, the dye exhibits quenched or faint emission in solution but strong fluorescence upon aggregation. Based on theoretical and experimental studies, the restriction of intramolecular rotation (RIR) has been proposed as the main cause of this phenomenon. Because these materials emit both in solution and in the aggregate state they are of much interest.<sup>35</sup> Very few examples of chiral

 (+)-3a-R
 (-)-3a-S
 3b

 Fig. 1
 Structures of compounds (+)-3a-(R), (-)-3a-(S) and 3b.

 boron complexes exhibiting AIEE have been reported and they are

boron complexes exhibiting AIEE have been reported and they are mainly based on polymeric compounds.<sup>36,37</sup>

Herein, the synthesis and a comparative study of two enantiomeric boranils and a similar achiral compound are presented (Fig. 1). The dyes exhibit bright blue fluorescence in solution and in the solid state, presenting a strong AIEE effect.

### Experimental section

#### 2.1 General

All reagents were purchased from Sigma-Aldrich and used without any further purification. The compounds were purified by column chromatography on silica gel (Merck, 35–70 mesh), by preparative TLC carried out on 20 cm  $\times$  20 cm glass plates, coated with silica gel (0.5 mm thick) or by crystallization.

<sup>1</sup>H, <sup>19</sup>F and <sup>13</sup>C NMR spectra were recorded on a Bruker 300 and 500 [300.13 MHz (<sup>1</sup>H), 282.41 MHz (<sup>19</sup>F), 75.47 MHz (<sup>13</sup>C) or 500.13 MHz (<sup>1</sup>H)]. Unequivocal <sup>13</sup>C assignments were made on the basis of 2D HSQC and HMBC experiments (<sup>1</sup>H/<sup>13</sup>C) (the delays for long-range  $J_{C/H}$  couplings were optimized for 7 Hz experiments). CDCl<sub>3</sub> was used as the solvent and tetramethylsilane (TMS) as the internal standard. Chemical shifts  $\delta$  are reported in parts per million (ppm) relative to TMS ( $\delta = 0$ ), and the values of coupling constants (J) are given in Hertz (Hz).



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<sup>†</sup> Electronic supplementary information (ESI) available: NMR spectra of new compounds, absorption and emission spectra. CCDC 1852252-1852256. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/ c8nj03228a

High-resolution mass spectra analysis (HRMS-ESI<sup>+</sup>) was performed on an LTQ OrbitrapTM XL hybrid mass spectrometer. Ultravioletvisible (UV-vis) spectra in solutions were obtained on a Shimadzu UV-2501 PC spectrophotometer (1 cm path length quartz cell) and the UV-vis absorption spectra of the solids were measured at room temperature on a JASCO V-560 instrument. The excitation and emission spectra, also in solutions, were recorded with a Jobin Yvon FluoroMax-3 spectrofluorometer and a IASCO spectrofluorometer. Fluorescence quantum yields,  $\varphi_{\rm f}$ , were determined using fluorescein in 0.1 M NaOH water solution as a fluorescence standard ( $\varphi_f = 0.90$ ). The CD spectra in solutions were obtained on a J-1500 CD spectrometer. The absolute emission quantum yields in the solid state were measured using a system (Quantaurus-QY Plus C13534, Hamamatsu) with a 150 W xenon lamp coupled to a monochromator for wavelength discrimination, an integrating sphere as the sample chamber, and a multichannel analyzer for signal detection. Melting points were determined on a BUCHI Melting point apparatus and are uncorrected. For crystal structure determination, a suitable single-crystal was mounted on a glass fibre with the help of silicon grease. Data were collected at 180(2) K on a Bruker X8 Kappa APEX II charge coupled device (CCD) area-detector diffractometer (MoKa graphite-monochromated radiation,  $\lambda = 0.71073$  Å). Single crystals suitable for X-ray diffraction were grown from CH<sub>2</sub>Cl<sub>2</sub> solutions of 2a-(R), 2a-(S), 3a-(R), 3a-(S) and 3b. Full details are given in the ESI.† Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 1852252-1852256.†

#### 2.2 Synthesis

(R,E)-2-{[1-(Phenylethyl)imino]methyl}phenol 2a-(R). (R)-(+)- $\alpha$ -Methylbenzylamine (1.5 equiv., 1.5 mL, 8.76 mmol) and salicylaldehyde (1 equiv., 0.60 mL, 5.84 mmol) were added to methanol (20 mL), and the reaction mixture was heated to reflux for 4 h. After being cooled down to room temperature, the solvent was removed under reduced pressure to afford the product 2a-(R) as a yellow solid. The compound was purified by recrystallization in ethanol (1.29 g, 5.72 mmol, 98%). Yellow solid. m.p. 75-76 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  13.55 (s, 1H, OH), 8.40 (s, 1H, CH=N), 7.22-7.36 (m, 7H, Harom), 6.96 (d, <sup>3</sup>J<sub>H-H</sub> 8.2, 1H, Harom), 6.87 (td, <sup>3</sup>J<sub>H-H</sub> 7.5, <sup>4</sup>J<sub>H-H</sub> 1.0 Hz, 1H, Harom), 4.54 (q,  ${}^{3}J_{H-H}$  6.7 Hz, 1H, CH), 1.63 (d,  ${}^{3}J_{H-H}$  6.7 Hz, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  163.6 (CH=N), 161.2 (C-OH), 144.0 (Carom) 132.4 (CHarom), 131.5 (CHarom), 128.8 (2C, CHarom), 127.4 (CHarom), 126.5 (2C, CHarom), 119.0 (Carom), 118.8 (CHarom), 117.1 (CHarom), 68.7 (CH), 25.1 (CH<sub>3</sub>). HRMS- $\text{ESI}^+ m/z$  for  $[C_{15}H_{15}NO + H]^+$  calcd 226.1232, found 226.1218.

(*S*,*E*)-2-{[[(1-Phenylethyl)imino]methyl}phenol 2a-(*S*). (*S*)-(-)- $\alpha$ -Methylbenzylamine (1 equiv., 1.0 mL, 5.84 mmol) and salicylaldehyde (1 equiv., 0.60 mL, 5.84 mmol) were added to methanol (20 mL), and the reaction mixture was heated to reflux overnight. After being cooled down to room temperature, the solvent was removed under reduced pressure to afford the product 2a-(*S*) as a yellow solid. The compound was purified by recrystallization in ethanol (1.08 g, 4.80 mmol, 82%). Yellow solid. m.p.: 75–76 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 13.56 (s, 1H, OH), 8.40 (s, 1H, CH=N), 7.22–7.36 (m, 7H, Harom), 6.96 (d,  ${}^{3}J_{H-H}$  8.2 Hz, 1H, Harom), 6.86 (td,  ${}^{3}J_{H-H}$  7.5,  ${}^{4}J_{H-H}$  1.0 Hz, 1H, Harom), 4.54 (q,  ${}^{3}J_{H-H}$  6.7 Hz, 1H, CH), 1.63 (d,  ${}^{3}J_{H-H}$  6.7 Hz, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 163.6 (CH=N), 161.2 (C–OH), 144.0 (Carom) 132.4 (CHarom), 131.5 (CHarom), 128.8 (2C, CHarom), 127.4 (CHarom), 126.5 (2C, CHarom), 119.0 (Carom), 118.7 (CHarom), 117.1 (CHarom), 68.7 (CH), 25.1 (CH<sub>3</sub>). HRMS-ESI<sup>+</sup> m/z for [C<sub>15</sub>H<sub>15</sub>NO + H]<sup>+</sup> calcd 226.1232, found 226.1224.

(*E*)-2-[(Benzylimino)methyl]phenol  $2b^{38}$ . Benzylamine (1 equiv., 0.546 mL, 5.00 mmol) and salicylaldehyde (1 equiv., 0.522 mL, 5.00 mmol) were added to methanol (10 mL), and the reaction mixture was heated to reflux for one hour. After being cooled down to room temperature, the solvent was removed under reduced pressure to afford the product 2b as a yellow oil. The compound was purified by flash column chromatography over silica gel, using dichloromethane as the eluent (1.07 g, 5.0 mmol, quantitative). Yellow oil.

(R)-2,2-Difluoro-3-(1-phenylethyl)-2H-benzo[e][1,3,2]oxazaborinin-3-ium-2-uide 3a-(R). Compound 2a-(R) (1 equiv., 0.7 mmol, 155 mg) was dissolved in 1,2-dichloroethane (5 mL), into which triethylamine (4 equiv., 2.8 mmol, 0.4 mL) and boron trifluoride etherate complex (4 equiv., 2.8 mmol, 0.4 mL) were added. The mixture was refluxed under an atmosphere of nitrogen for 24 h. After that, the mixture was poured into water (100 mL), and was extracted with dichloromethane, followed by drying over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After the removal of the solvent, the crude product was purified by column chromatography (silica gel) using dichloromethane as the eluent to afford 3a-(R) (151 mg, 0.6 mmol, 79%). White solid. m.p.: 165-166 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.01 (s, 1H, CH=N), 7.56 (ddd, <sup>3</sup>J<sub>H-H</sub> 8.6, <sup>3</sup>J<sub>H-H</sub> 7.7, <sup>4</sup>J<sub>H-H</sub> 1.6 Hz, 1H, Harom), 7.37–7.48 (m, 5H, Harom), 7.24 (dd, <sup>3</sup>J<sub>H-H</sub> 7.7, <sup>4</sup>J<sub>H-H</sub> 1.6 Hz, 1H, Harom), 7.09 (d,  ${}^{3}J_{H-H}$  8.6 Hz, 1H, Harom), 6.91 (td,  ${}^{3}J_{H-H}$  7.7,  ${}^{4}J_{H-H}$  0.8 Hz, 1H, Harom), 5.58 (q, <sup>3</sup>J<sub>H-H</sub> 6.9 Hz, 1H, CH), 1.87 (d, <sup>3</sup>J<sub>H-H</sub> 6.9 Hz, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  163.4 (CH=N), 159.0 (C-O), 138.7 (Carom) 138.4 (CHarom), 131.6 (CHarom), 129.4 (2C, CHarom), 129.0 (CHarom), 128.2 (2C, CHarom), 120.0 (CHarom), 119.6 (CHarom), 115.5 (Carom), 59.0 (CH), 20.8 (CH<sub>3</sub>). <sup>19</sup>F NMR (282 MHz, CDCl<sub>3</sub>)  $\delta$  –160.0 (d, <sup>2</sup>J<sub>F-F</sub> 15.4 Hz, 1F), -160.2 (d,  ${}^{2}J_{F-F}$  15.4 Hz, 1F). HRMS-ESI<sup>+</sup> m/z for  $[C_{15}H_{14}BF_2NO + H]^+$  calcd 274.1218, found 274.1200.

(S)-2,2-Difluoro-3-(1-phenylethyl)-2H-benzo[e][1,3,2]oxazaborinin-3-ium-2-uide 3a-(S). Compound 2a-(S) (1 equiv., 0.7 mmol, 150 mg) was dissolved in 1,2-dichloroethane (5 mL), into which triethylamine (2 equiv., 1.4 mmol, 0.2 mL) and boron trifluoride etherate complex (4 equiv., 2.8 mmol, 0.4 mL) were added. The mixture was refluxed under an atmosphere of nitrogen for 24 h. After that, the mixture was poured into water (100 mL), and was extracted with dichloromethane, followed by drying over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After removal of the solvent, the crude product was purified by column chromatography (silica gel) using dichloromethane as the eluent to afford **3a-(S)** (147 mg, 0.5 mmol, 77%). White solid. M.P.: 165–166 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.02 (s, 1H, CH=N), 7.56 (ddd, <sup>3</sup>J<sub>H-H</sub> 8.6, <sup>3</sup>J<sub>H-H</sub> 7.5, <sup>4</sup>J<sub>H-H</sub> 1.60 Hz, 1H, Harom), 7.37–7.48 (m, 5H, Harom), 7.24 (dd,  ${}^{3}J_{H-H}$  7.5,  ${}^{4}J_{H-H}$  1.6 Hz, 1H, Harom), 7.09 (d,  ${}^{3}J_{H-H}$  8.6 Hz, 1H, Harom), 6.91 (td,  ${}^{3}J_{H-H}$  7.5,  ${}^{4}J_{H-H}$  0.8 Hz, 1H, Harom), 5.47 (q,  ${}^{3}J_{H-H}$  6.9 Hz, 1H, CH), 1.87 (d,  ${}^{3}J_{H-H}$  6.9 Hz, 3H, CH<sub>3</sub>).  ${}^{13}$ C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  163.4 (CH=N), 159.0 (C–O), 138.7 (Carom), 138.4 (CHarom), 131.6 (CHarom), 129.4 (2C, CHarom), 129.0 (CHarom), 128.2 (2C, CHarom), 120.0 (CHarom), 119.6 (CHarom), 115.5 (Carom), 59.0 (CH), 20.8 (CH<sub>3</sub>).  ${}^{19}$ F NMR (282 MHz, CDCl<sub>3</sub>)  $\delta$  –160.0 (d,  ${}^{2}J_{F-F}$  15.6 Hz, 1F), –160.2 (d,  ${}^{2}J_{F-F}$ 15.6 Hz, 1F). HRMS-ESI<sup>+</sup> m/z for [C<sub>15</sub>H<sub>14</sub>BF<sub>2</sub>NO + HF + H]<sup>+</sup> calcd 294.1280, found 294.9195.

3-Benzyl-2,2-difluoro-2H-benzo[e][1,3,2]oxazaborinin-3-ium-2-uide 3b. Compound 2b (1 equiv., 3.0 mmol, 633 mg) was dissolved in dichloromethane (10 mL), and triethylamine (2 equiv., 6.0 mmol, 1.16 mL) and boron trifluoride etherate complex (2 equiv., 6.0 mmol, 0.835 mL) were added. The solution was stirred at room temperature for 1 h, and then the solvent was removed under reduced pressure. The product was purified by flask column chromatography over silica gel, eluent dichloromethane, to afford the product as off-white crystals after crystallization in DCM (350 mg, 1.40 mmol, 47%). White solid. m.p.: 128-129 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.94 (br s, 1H, CH=N), 7.57 (ddd,  ${}^{3}J_{H-H}$  8.6,  ${}^{3}J_{H-H}$  7.3,  ${}^{4}J_{H-H}$ 1.7 Hz, 1H, Harom), 7.50–7.42 (m, 3H, Harom), 7.39 (dd, <sup>3</sup>J<sub>H-H</sub> 7.7, <sup>4</sup>*J*<sub>H-H</sub> 1.7 Hz, 2H, Harom), 7.25 (dd, <sup>3</sup>*J*<sub>H-H</sub> 7.1, <sup>4</sup>*J*<sub>H-H</sub> 1.7 Hz, 1H, Harom), 7.10 (dd, <sup>3</sup>*J*<sub>H-H</sub> 8.6, <sup>4</sup>*J*<sub>H-H</sub> 1.0 Hz, 1H, Harom), 6.92 (ddd,  ${}^{3}J_{H-H}$  7.3,  ${}^{3}J_{H-H}$  7.1,  ${}^{4}J_{H-H}$  1.0 Hz, 1H, Harom), 4.95 (s, 2H, CH<sub>2</sub>). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 163.7 (CH=N), 159.1 (C-O), 138.5 (CHarom), 133.1 (Carom), 131.6 (CHarom), 130.3 (CHarom), 129.7 (CHarom), 129.4 (CHarom), 120.1 (CHarom), 119.6 (CHarom), 115.6 (Carom), 55.2 (CH<sub>2</sub>). <sup>19</sup>F NMR (282 MHz, CDCl<sub>3</sub>)  $\delta$  -161.44 (d, <sup>2</sup>J<sub>F-F</sub> 14.7 Hz, 1F), -161.55 (d, <sup>2</sup>J<sub>F-F</sub> 14.7 Hz, 1F). HRMS-ESI<sup>+</sup> m/z for  $[C_{14}H_{12}BF_2NO + H]^+$  calcd 260.1053, found 260.1045.

## 3. Results and discussion

#### 3.1 Synthesis

Boranils were obtained following a two-step strategy (Scheme 1). First, the imines **2a-(***R***)**, **2a-(***S***)** and **2b** were prepared by a condensation between salicylaldehyde and the appropriate amines in refluxing methanol. The chiral amines were optically pure, and a single enantiomer was obtained after the condensation step, as confirmed by single crystal X-ray diffraction (see ESI†). The boron complexation was performed using BF<sub>3</sub>·Et<sub>2</sub>O under basic conditions (triethylamine) in refluxing 1,2-dichloroethane. After purification, the three boranils were



Scheme 1 Synthesis of boranils (+)-3a-(R), (-)-3a-(S) and 3b

obtained in high yields. The structure of the compounds was confirmed by standard spectroscopic techniques including <sup>1</sup>H NMR, <sup>13</sup>C NMR, <sup>19</sup>F NMR, and HRMS (see ESI†). The formation of the complexes was confirmed by <sup>1</sup>H NMR, which showed the disappearance of the OH singlet, and a shift in the peak of the imine proton. The presence of two <sup>19</sup>F NMR doublets confirmed the complexation because in the chiral complexes the two fluorides are diastereotopic. The crystal structures of the asymmetric ligands and the three boranils unequivocally confirmed their structures, and the configuration of the asymmetric carbon in the case of (+)-2a-(*R*), (-)-2a-(*S*), (+)-3a-(*R*) and (-)-3a-(*S*).

#### 3.2 Photophysical properties

The absorption and emission spectra of (+)-**3a-(**R**)**, (-)-**3a-(**S**)** and **3b** are shown in Fig. 2. The three boranils possess similar molecular structures, with the only difference being in the alkyl bridge between the imine and phenyl moieties. As expected, they present almost identical absorption and emission spectra. The absorption and emission maxima of the two enantiomers are 351 nm and 430 nm, respectively. The absorption and emission maxima of **3b** are slightly red shifted (352 and 433 nm, respectively). All compounds exhibit a bright blue fluorescence under irradiation at 254 nm or 365 nm. The fluorescence quantum yields of the boranils in CH<sub>2</sub>Cl<sub>2</sub> solution are *ca.* 34%, and are similar for the chiral and achiral dyes (Table 1).

The photophysical properties of the dyes in solution are almost independent of the solvent (Table 1), as the absorption and emission maxima, molar extinction coefficients and quantum yields are very similar in toluene,  $CH_2Cl_2$ , methanol and acetonitrile. This was expected when compared to other boranils reported in the literature.<sup>15</sup>

Solid-state emission spectra are shown in Fig. 2. The emission maxima are similar to the maxima measured in solution, indicating that the dyes do not form excimers in the solid state. The quantum yields are lower, 8–13% and 11% for the enantiomers and the achiral dye, respectively (Table 1). The measurement of the



Fig. 2 Absorption (full lines) and fluorescence spectra (short dotted lines) excited at the corresponding  $\lambda_{abs\,max}$  of compounds (+)-**3a-(***R***)**, (-)-**3a-(***S***)** and **3b** in CH<sub>2</sub>Cl<sub>2</sub> and in the solid state at room temperature (at  $1 \times 10^{-5}$  mol L<sup>-1</sup>).

Table 1 Photophysical properties of (+)-3a-(R), (-)-3a-(S) and 3b

Dyes	$\lambda_{\mathrm{abs}}{}^{a}$	$\varepsilon^{b} \left( \mathrm{M}^{-1} \mathrm{~cm}^{-1} \right)$	$\lambda_{\rm em}{}^c$	$\varphi_{\mathbf{f}}^{d}$ (%)	Solvent
3a-( <i>R</i> )	354	52 000	433	31	Toluene
	351	32 500	430	32	$CH_2Cl_2$
	350	24 300	431	33	MeCN
	347	24500	430	35	MeOH
	n.a.	n.a.	420	13	Solid
3a-( <i>S</i> )	354	46 600	433	32	Toluene
	351	31 800	430	34	$CH_2Cl_2$
	350	14 900	432	36	MeCN
	347	24 900	430	37	MeOH
	n.a.	n.a.	420	8	Solid
3b	352	22 000	436	35	Toluene
	352	25 900	433	36	$CH_2Cl_2$
	350	31 800	434	37	MeCN
	346	20 800	432	40	MeOH
	n.a.	n.a.	434	11	Solid

<sup>*a*</sup> Absorption maximum  $\lambda_{abs}$  (nm). <sup>*b*</sup> Molar absorption coefficients  $(M^{-1} \text{ cm}^{-1})$ . <sup>c</sup> Fluorescence maximum  $\lambda_{em}$  (nm). <sup>d</sup> In solution: determined by comparison with fluorescein ( $\varphi_{\rm f}$  = 0.90 in water with NaOH 0.1 mol  $L^{-1}$ <sup>39</sup> at room temperature; in the solid state: measured using an integrating sphere, the excitation wavelength was 375 nm.

quantum yields in the solid state was carried out using a "pellet" obtained by compressing the crystals of the compounds, in order to get a sample which can be handle in the fluorimeter: this compressing process seems to change the crystalline arrangement of the molecules, and to induce a quenching of the emission (as seen by the naked eye, the single crystals of the compounds shine more brightly than the "pellet" when put under a UV lamp). As the compression is not controlled, it is somehow different for the three boranils and this is reflected in the quantum yield measurement.

Fig. 3a shows the circular dichroism (CD) spectra of (+)-3a-(R), (-)-3a-(S) and 3b in CH<sub>2</sub>Cl<sub>2</sub>. (+)-3a-(R) and (-)-3a-(S) show mirror image CD spectra with their maxima matching the maxima of the absorption spectra. As expected, compound 3b does not present any CD. The chirality of the two enantiomers was therefore confirmed by CD showing the optical purity of the compounds.



Fig. 3 CD spectra of compounds 3a-(S), 3a-(R) and 3b in solution  $(CH_2Cl_2, c = 10^{-5} M)$  (a) and in suspension (THF-water, 80% and 90% of water) (b).



Fig. 4 Aggregation-induced emission enhancement of (a) 3a-(R), (b) 3a-(S) and (c) 3b in THF-water mixtures. (d) Aggregation-induced emission enhancement of all compounds in THF-water mixtures.

#### 3.3 Aggregation-induced emission enhancement

To assess the AIEE characteristics of the dyes, the spectra of solutions/suspensions in THF-water mixed solvents with increased water fractions  $(f_w)$  were recorded (Fig. 4). For all compounds, when the water fraction was increased from 0 to 80 vol%, the emission intensity was almost unchanged. However, for a fraction of water above 80%, the compounds precipitated and self-aggregated, and the fluorescence showed a considerable enhancement.

The observation of an AIEE effect is in contradiction with the values of the quantum yields in the solid state, which are lower than those measured in solution (Table 1). But as explained in the previous section, the measurement of the quantum yields is carried out using a pellet, and not using single crystals. It seems that the boranils presented here are sensitive to the crystalline phase, and grinding and compressing the crystals to produce a pellet may induce a change from a crystalline phase to an amorphous one.

The CD spectra of the suspensions were also recorded (Fig. 3b). As expected, achiral compound 3b does not present any CD, but the enantiomers (+)-3a-(R) and (-)-3a-(S) present mirror image CD spectra, proving that the chirality of the dyes is preserved in the aggregate forms.

#### 3.4 Crystal structures

Single crystals suitable for X-ray diffraction were grown by slow evaporation of a saturated solution in CH<sub>2</sub>Cl<sub>2</sub>. The crystal structures of 2a-(R) and 2a-(S) are not discussed here, as they only confirmed the structure of the ligands and their chirality. The two enantiomers (+)-3a-(R) and (-)-3a-(S) crystallized in the monoclinic non-centrosymmetric space group  $P2_1$ , with Z = 2, while 3b crystallized in the orthorhombic centrosymmetric space group *Pbca* with Z = 8 (Fig. 5). The crystal structures of (+)-3a-(R) and (-)-3a-(S) confirmed the configuration of the asymmetric centres. All bond distances and angles are in a normal range.<sup>40</sup> B-N and B-O bond lengths in (+)-3a-(R) (B-O 1.420 Å, B-N 1.550 Å), (-)-3a-(S) (B-O 1.446 Å, B-N 1.571 Å) and 3b (B–O 1.450 Å, B–N 1.572 Å) are in accordance

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Fig. 5 Structure of **3a-(***R***)**, **3a-(***S***)** and **3b** revealed by single-crystal X-ray diffraction. Ellipsoids are drawn at the 50% level, hydrogen atoms are shown as spheres of an arbitrary radius of 0.30 Å; C, grey; H, white; N, blue; O, red; B pink (top). Crystal packing of **3a-(***R***)** and **3b** viewed down the *b* axis (down).

with those reported for similar compounds.<sup>14,15,41</sup> In all crystals, the boranil cycle and the phenol ring are coplanar, while the benzylic ring is not. The fluorine atoms are involved in weak intermolecular hydrogen bonds C–H···F. There are no close contacts between aromatic rings.

The crystal structures provide an insight into the AIEE properties of the dyes. In solution, the torsional vibrations of the benzyl group may provide a non-radiative relaxation channel, which lowers the emission efficiency. In the crystals, these vibrations seem to be restricted, therefore forcing the dyes to emit. In the meantime, the absence of close contacts between the aromatic rings excludes the formation of J- or H-aggregates and excimers as a potential reason for the emission enhancement observed between solution and the solid state.

## 4. Conclusions

Three new boranils have been prepared, two of which are based on enantiopure chiral amines. The chiral center is located on the carbon adjacent to the nitrogen, close to the chromophoric part of the dyes, and the sigma-pi hyperconjugation may be responsible for the distinct CD feature observed. These dyes present a moderate quantum yield in both solution and the solid state. Consideration of the crystal structures allowed the AIEE effect observed for the dyes to be rationalized, and the restriction of intramolecular rotations is proposed as the main cause of the emission enhancement observed. These boranils emit brightly in the solid state, and may find application as blue emitting materials.

## Conflicts of interest

There are no conflicts to declare.

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