Dyes and Pigments 111 (2014) 16–20

Contents lists available at ScienceDirect

Dyes and Pigments

journal homepage: www.elsevier.com/locate/dyepig

Δ^1-pyrroline based boranyls: Synthesis, crystal structures and luminescent properties

Francisco Cardona [a], João Rocha [b], Artur M.S. Silva [a, *], Samuel Guieu [a, b, **]

[a] QOPNA, Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal
[b] CICECO, Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal

ARTICLE INFO

Article history:
Received 28 March 2014
Received in revised form
17 May 2014
Accepted 19 May 2014
Available online 29 May 2014

Keywords:
Pyrroline ligand
Heterocycle
Boron complex
Fluorescence
Crystal structure
Dyes

ABSTRACT

Two new Δ^1-pyrroline ligands and their corresponding boron complexes have been synthesized and characterized. Their luminescent properties were investigated, the boron complexes emitting brightly around 410 nm. The presence of the exocyclic double bond has no influence on their electronic properties, meaning that this part of the complex could be used to fine tune their properties without disturbing their fluorescence.

1. Introduction

The development of innovative fluorescent dyes is of great significance, given their potential applications as labels in biomedical analysis [1], molecular sensors [2,3], and light emitting devices [4,5]. Boron dipyrromethene (BODIPY) [6–8] and azadipyrromethene (aza-BODIPY) [6,9–12] dyes (Fig. 1) have arisen as very promising due to their outstanding chemical and photophysical properties [8]. Their chemical versatility allowed a variety of applications covering from biolabeling [13] to solar cells [14] and nanoparticle engineering [15]. Nevertheless, the synthesis of such dyes remains tedious, involving linear stepwise syntheses with relatively low global yields [11]. Recently, the search for alternative fluorescent dyes led to a new family of fluorescent boron complexes, based on *N*- and *O*-donor ligands, so-called boranils [16–22] (Fig. 1). This kind of organoboron complexes is easily synthesized, potentially on a large scale. They can be modified using common reaction procedures, which allow a fine-tuning of their photophysical properties in order to adapt them to a given application [11,23,24].

We disclose here the straightforward synthesis of versatile boranils **1** and **2** (Fig. 2) based on a Δ^1-pyrroline core. These complexes were obtained from common precursors, and could easily be modified to be used as scaffolds for connecting an additional chromophoric moiety or reactive centre.

2. Material and methods

2.1. General

Melting points were measured in a Reichert Thermovar apparatus fitted with a microscope and are uncorrected. NMR spectra were recorded with Bruker DRX 300 spectrometers (300 for ^{1}H, 75 MHz for ^{13}C and 282 MHz for ^{19}F), in $CDCl_3$ as solvent, if not stated otherwise. Chemical shifts (δ) are reported in ppm and coupling constants (J) in Hz; internal standard was residual peak of the solvent. Unequivocal ^{13}C assignments were made with the aid of 2D *g*HSQC and *g*HMBC (delays for one-bond and long-range J C/H couplings were optimised for 145 and 7 Hz, respectively) experiments. Positive-ion ESI mass spectra were acquired using a Q-TOF 2 instrument [Nitrogen was used as nebuliser gas and argon as collision gas. The needle voltage was set at 3000 V, with the ion source at 80 °C and desolvation temperature at 150 °C. Cone voltage was 35 V]. High resolution mass spectra analysis (HRMS-ESI$^+$) were performed on a microTOF (focus) mass spectrometer. Ions were

* Corresponding author.
** Corresponding author. CICECO, Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal.
E-mail addresses: francisco.cardona@ua.pt (F. Cardona), rocha@ua.pt (J. Rocha), artur.silva@ua.pt (A.M.S. Silva), sguieu@ua.pt (S. Guieu).

http://dx.doi.org/10.1016/j.dyepig.2014.05.026
0143-7208/

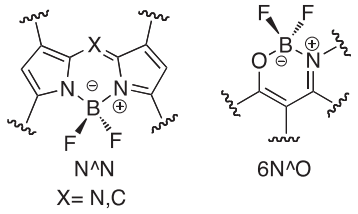


Fig. 1. BODIPY and boranil chelating complexes.

generated using an ApolloII (ESI) source. Ionization was achieved by electrospray, using a voltage of 4500 V applied to the needle, and a counter voltage between 100 and 150 V applied to the capillary. Elemental analyses were obtained with Carlo Erba 1108 and LECO 932 CHNS analysers. Preparative thin-layer chromatography was performed with Merck silica gel (60 DGF_{254}). Column chromatography was performed with Merck silica gel 60 (70–230 mesh). All other chemicals and solvents used were obtained from commercial sources and were either used as received or dried by standard procedures.

Compounds **3** [25], **4** [11], **5** [26], **6** [27], **7** [28], **8** [29], **9** [30], have already been described, and their spectroscopic data were consistent with the literature.

2.2. General procedures

2.2.1. General procedure for the synthesis of compounds *3, 6 and 7*

An aqueous solution of sodium hydroxide (30%, 25 mL) was slowly added to a methanol solution (30 mL) of the appropriate acetophenone (5.0 mmol). After the solution had been cooled to room temperature, benzaldehyde or cinnamaldehyde (6.0 mmol) was added. The mixture was stirred at room temperature for 20 h and was then poured into water (100 mL), ice (100 g), and conc. hydrochloric acid (pH adjusted to ca. 2). The obtained solid was removed by filtration, dissolved in dichloromethane (50 mL), and washed with an aqueous solution of sodium hydrogen carbonate (5%, 30 mL). The organic layer was collected and dried with anhydrous sodium sulfate, and the solution was concentrated to dryness. The residue was recrystallized from ethanol.

2.2.2. General procedure for the synthesis of compounds *4, 8 and 9*

To a solution of the appropriate substrate (1 equiv.) in nitromethane (so that final concentration is 0.3 mol.L^{-1}) at room temperature, 1,8-diazabicyclo[5.4.0]undec-7-ene (0.2 equiv.) was added dropwise. The resulting solution was stirred for 2 h at room temperature, and concentrated under vacuum. The residue was purified by flash chromatography [(petroleum ether/EtOAc 9:1)] to afford pure compounds **4**, **8** and **9**.

2.2.3. General procedure for the synthesis of compounds *5, 10 and 11*

2.2.3.1. Procedure A. To a stirred solution of nitro derivative **4**, **8** or **9** (1 equiv.) in THF/MeOH (2/1) were added acetic acid (16 equiv.) and Fe (45 equiv.) successively at room temperature, and the resulting mixture was heated at 65 °C for 10 h under nitrogen atmosphere. After cooling down to room temperature, the reaction mixture was filtrated through celite, rinsed with AcOEt. The whole mixture was washed with a saturated aqueous solution of $NaHCO_3$, brine, dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by silica flash column chromatography [petroleum ether/EtOAc (8:2)].

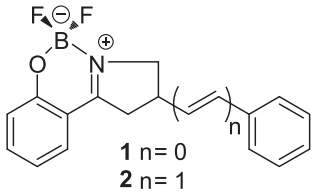


Fig. 2. Δ^1-Pyrroline based boranils **1** and **2**.

2.2.3.2. Procedure B. Compound **4**, **8** or **9** (1 equiv.), zinc powder (10 equiv.), ammonium acetate (10 equiv.) and dry methanol (so that final concentration of Michael adduct is 0.1 mol L^{-1}) were added to a flask under nitrogen. The slurry was stirred at room temperature for 12 h. Then the solid was removed by filtration and the solvent evaporated under reduced pressure affording the crude product, which was purified by silica flash column chromatography [petroleum ether/EtOAc (9:1)].

2.2.4. General procedure for the synthesis of compounds *1 and 2*

The appropriate Δ^1-pyrroline **10** or **11** (1 equiv) was dissolved in dry 1,2-dichloroethane (so that the concentration is 0.04 mol.L^{-1}). Dry triethylamine (10 equiv) was added, and the resulting solution was stirred for 10 min at 80 °C. Boron trifluoride-diethyl etherate (18 equiv) was added dropwise and the final solution was stirred for 30 min at 80 °C under 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 silica flash column chromatography [petroleum ether: EtOAc (7:3)] to afford the pure compounds.

2.3. Synthesis

2.3.1. 2-(2-Hydroxyphenyl)-4-phenyl-Δ^1-pyrroline *10*

Employing the general procedure B and using 1-(2-hydroxyphenyl)-4-nitro-3-phenylbutan-1-one **8** (59 mg, 0.21 mmol), ammonium acetate (158 mg, 2.06 mmol), and zinc powder (134 mg, 2.06 mmol) in dry methanol (1.2 mL) gave pure 2-(2-hydroxyphenyl)-4-phenyl-Δ^1-pyrroline **10** (35 mg, 0.15 mmol). Yield: 60%; pale brown solid; mp 91–93 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44-7.16 (m, 7H, H-4′, H-6′, H-2″, H-6″, H-3″, H-5″, H-4″), 7.03 (d, J = 8.2 Hz, 1H, H-3′), 6.86 (dd, J = 7.5, 7.5 Hz, 1H, H-5′), 4.53 (dd, J = 16.1, 8.2 Hz, 1H, H-5), 4.13 (dd, J = 16.1, 5.6 Hz, 1H, H-5), 3.72–3.45 (m, 2H, H-4, H-3), 3.15 (dd, J = 16.6, 5.6 Hz, 1H, H-3). ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.1, 160.9, 144.3, 132.5, 129.2, 128.8, 126.8, 126.7, 118.3, 117.2, 116.8, 67.7, 43.7, 41.2. ESI(+)–MS: m/z: 238.1 $[M+H]^+$. ESI(+)–HRMS calcd. for $C_{16}H_{16}NO$: 238.1226, found: 238.1225.

2.3.2. (E)-2-(2-Hydroxyphenyl)-4-styryl-Δ^1-pyrroline *11*

Employing the general procedure B and using (*E*)-1-(2-hydroxyphenyl)-3-(nitromethyl)-5-phenylpent-4-en-1-one **9** (36 mg, 0.11 mmol), ammonium acetate (86 mg, 1.12 mmol), and zinc powder (73 mg, 1.12 mmol) in dry methanol (1.2 mL) gave pure (*E*)-2-(2-hydroxyphenyl)-4-styryl-Δ^1-pyrroline **11** (20 mg, 0.076 mmol). Yield: 68%; pale green oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 13.71 (s, 1H, OH), 7.58–7.14 (m, 7H, H-4′, H-6′, H-2″, H-6″, H-3″, H-5″, H-4″), 7.02 (d, J = 8.2 Hz, 1H, H-3′), 6.87 (dd, J = 7.5, 7.5 Hz, 1H, H-5′), 6.49 (d, J = 15.8 Hz, 1H, H-β), 6.22 (dd, J = 15.8, 8.2 Hz, 1H, H-α), 4.34 (dd, J = 16.6, 7.6 Hz, 1H, H-5), 3.93 (dd, J = 16.6, 5.4 Hz, 1H, H-5), 3.45–3.15 (m, 2H, H-4, H-3), 3.01–2.89 (m, 1H, H-3). ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.4, 160.9, 136.9, 132.5, 131.4, 130.6, 129.3, 128.6, 127.5, 126.1, 118.3, 117.2, 116.9, 65.5, 41.6, 39.8. ESI(+)–MS: m/z: 264.1 $[M+H]^+$. Anal. Calcd for $C_{18}H_{17}NO$: C 82.10, H 6.51, N 5.32; found: C 82.25, H 6.82, N 5.38%.

2.3.3. 5,5-difluoro-2-phenyl-1,2,3,5-tetrahydrobenzo[e]pyrrolo[1,2-c][1,3,2]oxazaborinin-4-ium-5-uide ***1***

Employing the general procedure and using 2-(2-hydroxyphenyl)-4-phenyl-Δ^1-pyrroline **10** (70 mg, 0.295 mmol), triethylamine (299 mg, 0.41 mL, 2.95 mmol), and boron trifluoride-diethyl etherate (754 mg, 0.65 mL, 5.31 mmol) in dry 1,2-dichloroethane (1.5 mL) gave pure 5,5-difluoro-2-phenyl-1,2,3,5-tetrahydrobenzo[*e*]pyrrolo[1,2-*c*][1,3,2]oxazaborinin-4-ium-5-uide **1** (79 mg, 0.277 mmol). Yield: 94%; white solid; mp 123–125 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.57 (ddd, 1H, $J = J = 8.5$, 7.5, 1.2 Hz, H-4′), 7.50-7.19 (m, 6H, H-6′, H-2″, H-6″, H-3″, H-5″, H-4″), 7.12 (d, $J = 8.5$ Hz, 1H, H-3′), 6.95 (dd, $J = 7.5$, 7.5 Hz, 1H, H-5′), 4.58 (dd, $J = 15.0$, 8.2 Hz, 1H, H-5), 4.27 (dd, $J = 15.0$, 5.7 Hz, 1H, H-5), 3.96–3.78 (m, 2H, H-4, H-3), 3.41 (dd, $J = 18.1$, 5.7 Hz, 1H, H-3). ^{13}C NMR (75 MHz, $CDCl_3$) δ 175.8, 159.3, 140.8, 137.9, 129.2 (2 × C), 128.9, 127.7, 126.7 (2 × C), 119.8, 119.7, 112.9, 60.3, 42.0, 39.9. ^{19}F NMR (282 MHz, $CDCl_3$) δ −138.03 (dq, $J = 29.5$, 14.4 Hz, 1F), -138.68 (dq, $J = 29.5$, 14.4 Hz, 1F). ESI(+)-MS: *m/z*: 266.1 $[M-F]^+$. Anal. Calcd for $C_{18}H_{17}NO$: C 67.41, H 4.95, N 4.91; found: C 67.26, H 5.03, N 5.02%.

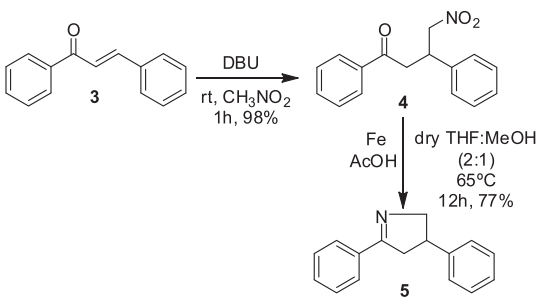
2.3.4. (E)-5,5-difluoro-2-styryl-1,2,3,5-tetrahydrobenzo[e]pyrrolo[1,2-c][1,3,2]oxazaborinin -4-ium-5-uide ***2***

Employing the general procedure and using (*E*)-2-(2-hydroxyphenyl)-4-styryl-Δ^1-pyrroline **11** (42 mg, 0.159 mmol), triethylamine (161 mg, 0.22 mL, 1.595 mmol), and boron trifluoride-diethyl etherate (408 mg, 0.35 mL, 2.87 mmol) in dry 1,2-dichloroethane (1.0 mL) gave pure (*E*)-5,5-difluoro-2-styryl-1,2,3,5-tetrahydrobenzo[*e*]pyrrolo[1,2-*c*][1,3,2]oxazaborinin-4-ium-5-uide **2** (45 mg, 0.143 mmol). Yield: 90%; pale brown solid; mp 129–131 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.59 (ddd, $J = 8.4$, 7.4, 1.2 Hz, 1H, H-4′), 7.43 (dd, $J = 7.8$, 1.2 Hz, 1H, H-6′), 7.42-7.22 (m, 5H, H-2″, H-6″, H-3″, H-5″, H-4″), 7.14 (d, $J = 8.4$ Hz, 1H, H-3′), 6.97 (dd, $J = 7.4$, 7.8 Hz, 1H, H-5′), 6.58 (d, $J = 15.7$ Hz, 1H, H-β), 6.21 (dd, $J = 15.7$, 8.1 Hz, 1H, H-α), 4.44 (dd, $J = 14.8$, 8.2 Hz, 1H, H-5), 4.08 (dd, $J = 14.8$, 6.5 Hz, 1H, H-5), 3.77-3.46 (m, 2H, H-4, H-3), 3.24 (dd, $J = 17.8$, 6.0 Hz, 1H, H-3). ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.0, 159.3, 137.9, 135.9, 132.8, 128.9, 128.7 (2 × C), 128.1, 127.7, 126.3 (2 × C), 119.9, 119.7, 113.0, 58.7, 40.3, 38.5. ^{19}F NMR (282 MHz, $CDCl_3$) δ −161.25 (dq, $J = 29.3$, 14.2 Hz), -161.82 (dq, $J = 28.3$, 14.2 Hz). ESI(+)–MS: *m/z*: 292.2 $[M-F]^+$. ESI(+)–HRMS calcd. for $C_{18}H_{16}BFNO$: 292.1307; found: 292.1303.

3. Results and discussion

3.1. Synthesis and characterization

The synthesis of boranils **1** and **2** involved the preparation of the Δ^1-pyrroline core. As this synthesis proved to be temperamental it was first optimized on a model compound (Scheme 1).



Scheme 1. Optimization of the conditions on a model compound.

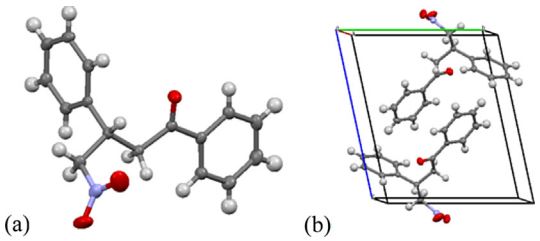


Fig. 3. Molecular structure of compound **4** (only one enantiomer is shown for clarity) (a) and unit cell content (b). Thermal ellipsoids are shown at the 50% probability level, hydrogen atoms are shown with an arbitrary radius (0.30Å). C, grey; O, red; N, blue; H, white. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

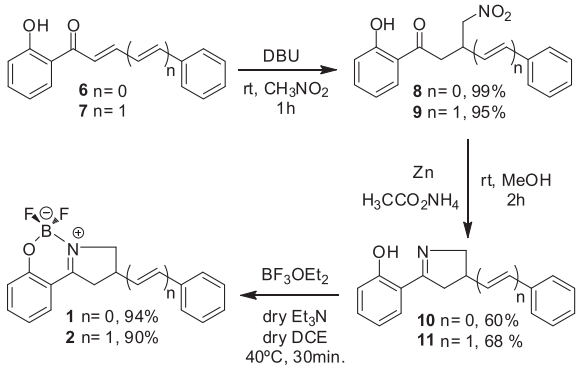
Michael addition of nitromethane to chalcone **3** was attempted using two different kinds of base sources, a secondary amine (Et_2NH) and an amidine (diazabicyclo[5.4.0]undec-7-ene). This second one gave the better yields. The structure of the racemic product **4** was confirmed by single crystal X-ray diffraction (Fig. 3).

The reduction of the nitro group could lead to side reactions, due to the presence of a ketone and to the *in situ* formation of an imine. To accomplish this reduction two experimental conditions already presented in the literature were tested [31,32]: i) zinc, ammonium acetate, palladium on carbon (10%w/w), MeOH, 12 h, rt; and ii) iron, acetic acid, THF:MeOH/(2:1), 12 h, 65 °C. The best results were obtained using iron as the reducing agent and acetic acid as the proton source. Δ^1-Pyrroline derivative **5** was obtained as a racemic mixture in 77% yield.

The boron complexes **1** and **2** were obtained following this optimized strategy (Scheme 2). Michael addition of nitromethane to 2′-hydroxychalcone **6** [30] or 2′-hydroxycinamylideneaceto phenone **7** [26] using DBU as base gave the corresponding Michael adducts **8** and **9** in nearly quantitative yield [33].

For the synthesis of Δ^1-pyrroline derivatives **10** and **11**, the reduction of the nitro group followed by nucleophilic intramolecular ring cyclization/dehydration sequence was attempted using the iron/acetic acid strategy. Unfortunately this strategy was not the best for these derivatives. The reduction with zinc and ammonium acetate in methanol gave better yields and an easier purification. The use of palladium was avoided due to the potential reduction of the double bond present in compound **11**. The corresponding Δ^1-pyrrolines **10** and **11** were obtained in 60% and 68% yields, respectively.

Boron complexation was achieved using BF_3–OEt_2 and anhydrous triethylamine in 1,2-dichloroethane at 40 °C, to give complexes **1** and **2** in 94% and 90% yield, respectively. The structure of the complexes was confirmed by NMR, MS, and elemental analysis.



Scheme 2. Synthesis of the boranil derivatives **1** and **2**.

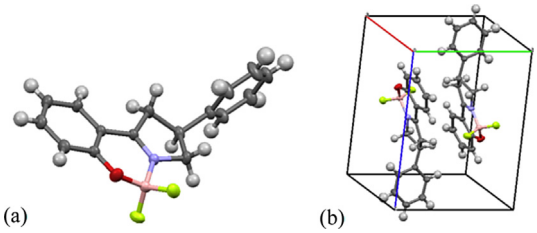


Fig. 4. Molecular structure of compound **1** (only one enantiomer is shown for clarity) (a) and unit cell content (b). Thermal ellipsoids are shown at the 50% probability level, hydrogen atoms are shown with an arbitrary radius (0.30Å). C, grey; O, red; N, blue; H, white; B, pink; F, yellow. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 1
Selected Optical data measured in dichloromethane.

Dye	λ_{abs} (nm)	ε(M^{-1} cm^{-1})[a]	λ_{em} (nm)[b]	φf (%)[c]
10	313	5300	n.a.	<0.1
11	314	7300	n.a.	<0.1
1	343	4000	410	2.6
2	341	5700	409	2.6

[a] ε (M^{-1} cm^{-1}) is determined by linear regression of 4 measurements in the range 10^{-4} M to 10^{-6} M in dichloromethane.
[b] Excitation at 340 nm.
[c] Quantum yields are determined with excitation at 340 nm, by linear regression of 4 measurements in the range of absorption 0 to 0.2, by comparison with fluorescein (quantum yield 0.90 at excitation 470 nm in a solution of NaOH 0.01 M in water).

Complex **1** gave single crystals by slow evaporation of a saturated solution in dichloromethane (Fig. 4). Analysis of the crystal structure confirmed the structure of the compound, with the planarity of the 6-membered ring containing the boron atom. The Δ^1-pyrroline core disrupts the conjugation between the emissive centre and the phenyl ring, which should prevent any bathochromic effect.

3.2. Absorption and emission properties

Photophysical data were recorded in dichloromethane for all the new fluorophores (Table 1 and Fig. 5).

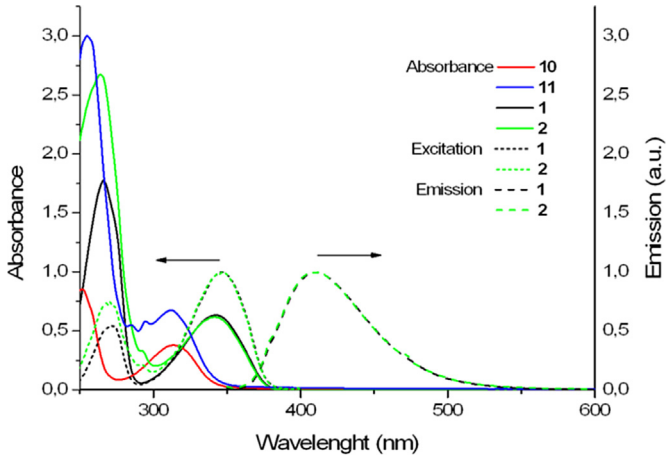


Fig. 5. Absorption (0.1 mM) spectra of dyes **10**, **11**, **1** and **2**, normalized excitation (0.001 mM, emission at 410 nm) and normalized emission (0.001 mM, excitation at 340 nm) spectra of dyes **1** and **2** in dichloromethane.

Schiff-base ligands **10** and **11** present an absorption band centred at ca. 310 nm. The absorption spectra of complexes **1** and **2** exhibit a major absorption band at ca. 340 nm. The coordination of **10** and **11** with boron seems to have a bathochromic effect on the absorption properties, without interfering much with their intensities. Even if some Schiff-base containing compounds have been reported to be luminescent, ligands **10** and **11** are non-emissive in solution. On the contrary, boron complexes **1** and **2** are photoluminescent with a maximum emission at 410 nm, with low quantum yields of 2.6%. The introduction of a fluoroborate centre probably restricts the non-emissive relaxation pathways, such as internal charge transfer and torsional vibrations, thus promoting the fluorescence. The excitation spectra of **1** and **2** match their absorption spectra, and are nearly mirror images of their emission spectra, which indicate that the emission happens through fluorescence from S_1 to S_0 energy levels. The conjugation between the boron complex and the phenyl ring or the styrene is disrupted by the Δ^1-pyrroline core, thus the introduction of the extra double bond has almost no effect on the absorption and emission properties of the fluorophores.

4. Conclusion

In conclusion, the synthesis of Δ^1-pyrrolines boranil complexes has been successfully achieved, leading to new fluorophores in a straightforward manner and with high overall yields. Efforts to extend their emission to the red part of the electromagnetic spectrum are currently underway. In order to tune their interaction with biological systems, an enantioselective version of these new fluorophores is also being developed in our laboratory.

Acknowledgement

Thanks are due to the University of Aveiro and the Portuguese Fundação para a Ciência e a Tecnologia (FCT) for funding the Organic Chemistry Research Unit (project PEst-C/QUI/UI0062/2013), the CICECO Associate Laboratory (PEst-C/CTM/LA0011/2013) and the Portuguese National NMR Network (RNRMN). SG also thanks the FCT for a postdoctoral grant (SFRH/BPD/70702/2010).

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.dyepig.2014.05.026. CCDC-990043 and CCDC-990044 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK. Fax: C44 1223 336 033. E-mail: deposit@ccdc.cam.ac.uk).

References

[1] Killoran J, Allen L, Gallagher JF, Gallagher WM, O'shea DF. Synthesis of BF_2 chelates of tetraarylazadipyrromethenes and evidence for their photodynamic therapeutic behaviour. Chem Commun; 2002:1862–3.
[2] Beer G, Niederalt C, Grimme S, Daub J. Redox switches with chiroptical signal expression based on binaphthyl Boron dipyrromethene conjugates. Angew Chem Int Ed 2000;3:3252–5.
[3] Yamaguchi S, Akiyama S, Tamao K. Colorimetric fluoride ion sensing by boron-containing π-electron systems. J Am Chem Soc 2001;123:11372–5.
[4] Wang S. Luminescence and electroluminescence of Al(III), B(III), Be(II) and Zn(II) complexes with nitrogen donors. Coord Chem Rev 2001;215:79–98.
[5] Liu Y, Guo J, Zhang H, Wang Y. Highly efficient white organic electroluminescence from a double-layer device based on a boron hydroxyphenylpyridine complex. Angew Chem Int Ed 2002;41:182–4.
[6] Loudet A, Burgess K. BODIPY dyes and their derivatives: syntheses and spectroscopic properties. Chem Rev 2007;107:4891–932.

[7] Boens N, Leen V, Dehaen W. Fluorescent indicators based on BODIPY. Chem Soc Rev 2012;41:1130–72.
[8] Ulrich G, Ziessel R, Harriman A. The chemistry of fluorescent bodipy dyes: versatility unsurpassed. Angew Chem Int Ed 2008;47:1184–201.
[9] Rogers MAT. Tetra-arylazadipyrromethines: a new class of synthetic colouring matter. Nature 1943;151. 504–504.
[10] Rogers MAT. 2,4-Diarylpyrroles. Part I. Synthesis of 2,4-diarylpyrroles and 2,2′,4,4′-tetra-arylazadipyrromethines. J Chem Soc (Resumed); 1943:590–6.
[11] Gorman A, Killoran J, O'Shea C, Kenna T, Gallagher WM, O'Shea DF. In vitro demonstration of the heavy-atom effect for photodynamic therapy. J Am Chem Soc 2004;126:10619–31.
[12] Grossi M, Palma A, McDonnell SO, Hall MJ, Rai DK, Muldoon J, et al. Unravelling the reaction mechanism of the reductive ring contraction of 1,2-pyridazines. J Org Chem 2012;77:9304–12.
[13] Wu L, Loudet A, Barhoumi R, Burghardt RC, Burgess K. Fluorescent cassettes for monitoring three-component interactions *in vitro* and in living cells. J Am Chem Soc 2009;131:9156–7.
[14] Rousseau T, Cravino A, Ripaud E, Leriche P, Rihn S, De Nicola A, et al. A tailored hybrid BODIPY–oligothiophene donor for molecular bulk heterojunction solar cells with improved performances. Chem Commun 2010;46:5082–4.
[15] Tokoro Y, Nagai A, Chujo Y. Nanoparticles via H-aggregation of amphiphilic BODIPY dyes. Tetrahedron Lett 2010;51:3451–4.
[16] Rao Y-L, Wang S. Four-coordinate organoboron compounds with a π-conjugated chelate ligand for optoelectronic applications. Inorg Chem 2011;50:12263–74.
[17] Massue J, Frath D, Ulrich G, Retailleau P, Ziessel R. Synthesis of luminescent 2-(2′-Hydroxyphenyl)benzoxazole (HBO) borate complexes. Org Lett 2011;14:230–3.
[18] Zhou Y, Kim JW, Kim MJ, Son W-J, Han SJ, Kim HN, et al. Novel bi-nuclear boron complex with pyrene ligand: red-light emitting as well as electron transporting material in organic light-emitting diodes. Org Lett 2010;12:1272–5.
[19] Zhang Z, Bi H, Zhang Y, Yao D, Gao H, Fan Y, et al. Luminescent boron-contained ladder-type π-conjugated compounds. Inorg Chem 2009;48:7230–6.
[20] Tokoro Y, Nagai A, Chujo Y. Synthesis of π-conjugated polymers containing organoboron Benzo[h]quinolate in the main chain. Macromolecules 2010;43:6229–33.
[21] Frath D, Azizi S, Ulrich G, Ziessel R. Synthesis of luminescent 2-(2′-Hydroxyphenyl)benzoxazole (HBO) borate complexes. Org Lett 2012;14:4774–7.
[22] Frath D, Azizi S, Ulrich G, Retailleau P, Ziessel R. Facile synthesis of highly fluorescent boranil complexes. Org Lett 2011;13:3414–7.
[23] Jameson LP, Dzyuba SV. Aza-BODIPY: improved synthesis and interaction with soluble Aβ1–42 oligomers. Bioorg Med Chem Lett 2013;23:1732–5.
[24] Tasior M, O'Shea DF. BF_2-Chelated tetraarylazadipyrromethenes as NIR fluorochromes. Bioconjug Chem 2010;21:1130–3.
[25] Liu D-N, Tian S-K. Stereoselective synthesis of polysubstituted alkenes through a phosphine-mediated three-component system of aldehydes, α-Halo carbonyl compounds, and terminal alkenes. Chem A Eur J 2009;15:4538–42.
[26] Liang Y, Dong D, Lu Y, Wang Y, Pan W, Chai Y, et al. One-pot synthesis of substituted Δ^1-pyrrolines through the Michael addition of nitroalkanes to chalcones and subsequent reductive cyclization in aqueous media. Synthesis; 2006:3301–4.
[27] Krohn K, Ahmed I, John M. Enantioselective synthesis of flavan-3-ols using a mitsunobu cyclization. Synthesis; 2009:779–86.
[28] Silva AMS, Pinto DCGA, Tavares HR, Cavaleiro JAS, Jimeno ML, Elguero J. Novel (E)- and (Z)-2-Styrylchromones from (E,E)-2′-Hydroxycinnamylideneaceto phenones – xanthones from daylight photooxidative cyclization of (E)-2-Styrylchromones. Eur J Org Chem; 1998:2031–8.
[29] Loudet A, Bandichhor R, Burgess K, Palma A, McDonnell SO, Hall MJ, et al. B,O-chelated azadipyrromethenes as near-IR probes. Org Lett 2008;10:4771–4.
[30] Oliva CG, Silva AMS, Resende DISP, Paz FAA, Cavaleiro JAS. Highly enantioselective 1,4-Michael additions of nucleophiles to unsaturated aryl ketones with organocatalysis by bifunctional cinchona alkaloids. Eur J Org Chem; 2010:3449–58.
[31] Kawai H, Yuan Z, Kitayama T, Tokunaga E, Shibata N. Efficient access to trifluoromethyl diarylpyrrolines and their N-Oxides through enantioselective conjugate addition of nitromethane to β,β-disubstituted enones. Angew Chem Int Ed 2013;52:5575–9.
[32] Guo S, Xie Y, Hu X, Huang H. Highly diastereo- and enantioselective tandem reaction toward functionalized pyrrolidines with multiple stereocenters. Org Lett 2011;13:5596–9.
[33] Oliva CG, Silva AMS, Paz FAA, Cavaleiro JAS. Highly enantioselective and regioselective conjugate addition of nitromethane to 1,5-Diarylpenta-2,4-dien-1-ones using bifunctional cinchona organocatalysts. Synlett; 2010:1123–7.