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Far-Red and Near-Infrared Boron Schiff Bases (BOSCHIBAs) Dyes Bearing Anionic Boron Clusters

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Dedicated to Prof. Herbert Höpfl.

Here, we report a short series of six new boron Schiff bases (BOSCHIBAs), four of them bearing anionic boron clusters. The boron complexes (**1**–**2**) were synthesized by the multicomponent reaction. The Boron Schiff bases were appropriately functionalized with boron cluster anions $[B_{12}H_{12}]^{2-}$ (**3**–**4**) and $[3,3'\text{-}Co(C_2B_9H_{11})_2]^-$ (**5**–**6**). Remarkably, BOSCHIBAs bearing $[B_{12}H_{12}]^{2-}$ showed fluorescence emission to the NIR and far-red regions (**3**: 747 nm, **4**: 690 nm), while **5** and **6** exhibited emission in the UV region (**5**: 525 and **6**: 475 nm). Notably, complexes **2**, **5**, and **6** showed the highest photostability, followed by the boron complexes **1** and **3**, which suggest that the nature of the boron cluster influences photostability properties. Compounds **3**–**4** represent the first example of boron Schiff bases bearing boron cluster anions $[B_{12}H_{12}]^{2-}$ exhibiting fluorescence emission in the NIR and far-red regions, make them potential candidates as fluorescence probes for bioimaging.

Introduction

In the fluorescence imaging technologies, which offer high imaging resolution, there is growing interest in the design and synthesis of near-infrared (NIR I, 700–950 nm) fluorescent materials due to relevant advantages such as low phototoxicity, deep tissue penetration, and minimum interference from autofluorescence in living systems.[1] Also, it is important, the fluorescent materials with potential application in fluorescence imaging technologies must show low cytotoxicity, good photostability in solution *in vitro* and *in vivo*.

We have been interested in green synthesis of fluorescent materials derived from main group elements searching new applications such as OLEDs,[2] dyes for bioimaging[3] and biomaterials,[4] and electro-acceptor in solar cells.[5] The Boron Schiff Bases (BOSCHIBAs) have been gained tremendous attention due to nonlinear optical,[6] fluorescent properties,[7] fabrication of OLEDs,[8] and biological applications.[9] Recently, our research group has reported that BOSCHIBAs derived from 2-hydroxynaphthalenes and anilines (Figure 1A)[10] or amino acids (Figure 1C)[11] exhibited fluorescent staining *in vitro* (B16F10 cells), less cytotoxicity, good photostability, easy and low-cost synthesis. Remarkably, both **B** and **C** derivatives showed good aqueous solubility and the potential to be functionalized for further investigations due to aryl-OH and carboxylic acid groups as we have previously reported on organotin derivatives (*vide infra*).

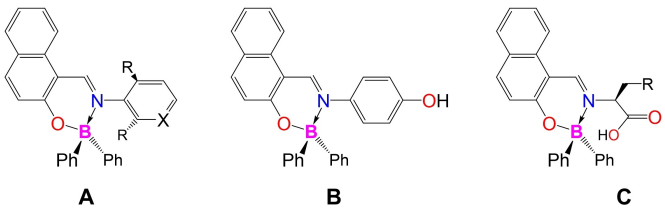

Figure 1. Boron Schiff bases previous reported **A**–**C**.

Anionic metallacarboranes, in especial the well-known cobaltabisdicarbollide, usually called COSAN, $[3,3'\text{-}Co(C_2B_9H_{11})_2]^-$, have demonstrated to have extraordinary chemical, thermal and photochemical stabilities.[12–14] COSAN is an hydrophobic species,[15,16] with low nucleophilic character, high molecular volume and low charge density.[17] The hydrophobic nature of COSAN provides to its protonated form and sodium salt exceptional amphiphilic character, making them soluble in water and organic solvents.[18] Likewise, these properties give the COSAN the unique capacity to self-assemble into micelles and monolayer vesicles in aqueous media.[19–23] Noticeably, COSAN is able to cross the lipid bilayer cell membrane and accumulate in living cells,[24,25] and has demonstrated to bind to glucose unis.[26] Besides, radiolabeling COSAN with an appropriate radioisotope (^{124}I) leads to suitable theragnostic agents for in vivo visualization by Positron Emission Tomography (PET) and boron carriers for boron neutron capture therapy (BNCT).[27–29] All these characteristic make COSAN and derivatives promising pharmacophores for biomedical

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applications,[30–32] among them for cancer therapy,[33,34] or as antimicrobial agents.[35]

On the other hand, another remarkable anionic boron clusters is the *closo*-dodecaborate dianion, $[B_{12}H_{12}]^{2-}$, and derivatives,[36] which have also demonstrate to have high chemical stability and hydrolytic capacity especially for their sodium salts,[37–39] which along with the low toxicity,[40] make them ideal candidates to design pharmacophores.[41–44] Despite the enormous advance of highly emissive carborane-based compounds over the past decades, the development of luminescent systems bearing anionic boron clusters, in especial COSAN and *closo*-dodecaborate, has been very limited,[45] and only a few examples reported by us[46–49] and others[50–52] are known. In general, all these systems were essentially designed for theragnostic applications, aiming to improve the intracellular boron release required in BNCT combined with fluorescence imaging.

In a recent work,[49] we have reported the synthesis of fluorescent organotin dyes bearing anionic boron clusters, where we demonstrated that linking $[B_{12}H_{12}]^{2-}$ (Figure 2D) and COSAN (Figure 2F) into organotin complexes overcame the solubility problems of the latter that usually aggregated in the culture media preventing the cell internalization. Coupling both boron clusters to organotin produced a different fluorescence staining effect in cells; those conjugates bearing $[B_{12}H_{12}]^{2-}$ produced nucleoli and cytoplasmic staining, while the COSAN derivatives remained staining the cytoplasm of the cell. To the best of our knowledge, only one example of a carborane-containing triblock copolymer conjugated with a Near-Infrared (NIR) fluorescence probe has been reported in the literature,[53] whereas there are no examples of NIR fluorescent probes containing anionic boron clusters, thus it deserves to be explored.

Herein, we report for the first time a set of dyes obtained by coupling BOSCHIBAs to two different anionic boron clusters, $[B_{12}H_{12}]^{2-}$ and $[3,3'\text{-Co}(1,2\text{-}C_2B_9H_{11})_2]^-$, through two different linkers. All dyes were fully characterised by standard spectroscopic techniques. The absorption and emission properties as well as the photostability of all of them were studied in solution. The influence of the different boron clusters to their respective properties were analysed. Main Text Paragraph.

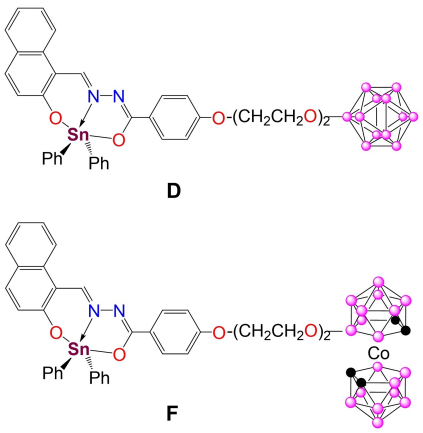


Figure 2. Organotin dyes bearing anionic boron clusters.

Results and Discussion

Synthesis and characterization

Boron Schiff bases **1** and **2** were achieved through the multicomponent condensation reaction of 2-hydroxynaphthaldehyde with the corresponding amines and the diphenylborinic acid (synthesized *in situ)*, (Scheme 1) in good yields of 85 and 90 %, respectively; compound **1** resulted in a yellow solid while compound **2** was a green solid. Boron clusters-containing dyes **3**–**4** were synthesized from the *closo*-dodecaborate derivative $[NBu_4][B_{12}H_{11}(C_4H_8O_2)]$, whereas compounds **5**–**6** were got from the zwitterion $[3,3'\text{-Co}(8\text{-}C_4H_8O_2\text{-}1,2\text{-}C_2B_9H_{10})(1',2'\text{-}C_2B_9H_{11})]$, using similar conditions to those previously described for the nucleophilic oxonium ring-opening reaction.[47,49,54,55] In a first step, deprotonation of the –OH group in the nucleophile precursors **1** and **2** was achieved with K_2CO_3 as the base CH_3CN, and then the deprotonated species acts as nucleophile to produce the opening of the oxonium ring (Scheme 1).

As usual, all reactions were monitored by ^{11}B NMR spectroscopy and compared with their parent species.[56–60] To finish, **3** and **4** were isolates as $[NBu_4]^+$ salts, whereas **5** and **6** were obtained as $[NMe_4]^+$ salts. The chemical structures of **1**–**6** were fully characterized by FT-IR, NMR (^1H, $^1H\{^{11}B\}$, $^{13}C\{^1H\}$and $^{11}B\{^1H\}$) spectroscopy, mass spectrometry for precursors **1** and **2**, MALDI-TOF high resolution mass spectrometry for **5**–**6**, and elemental analysis (Figures S1–S30). In Table 1 and Table 2 the main NMR chemical shifts for **3**–**6** are collected.

In solid state, the FT-IR spectral analysis showed the stretching vibration bands attributed to the azomethane group

Table 1. Selected ^{11}B NMR and IR data (cm^{-1}).

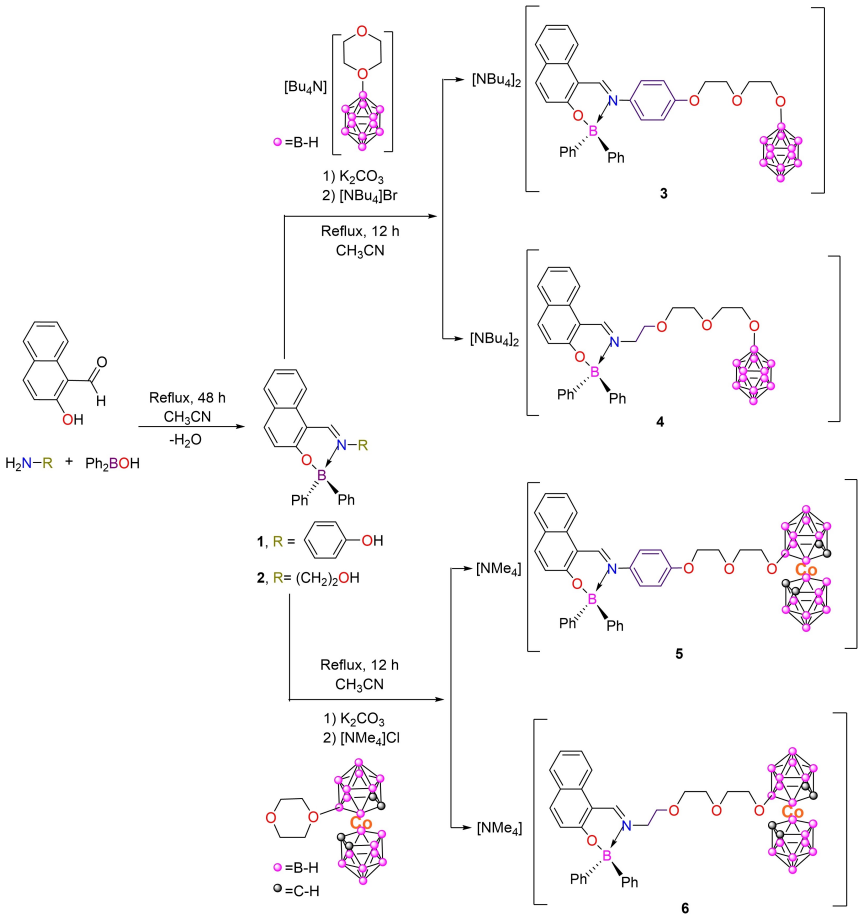
Comp	$^{11}B\{^1H\}$ B{1}-O	B{12}-H	B{8}-O	FT-IR B-H	C=N
1[a]	~	~	~	~	1627
2[b]	~	~	~	~	1627
3[a]	8.00	−21.15	~	2470	1629
4[a]	7.62	−20.79	~	2542	1617
5[a]	~	~	24.34	2525	1623
6[a]	~	~	24.42	2528	1623

[a] $(CD_3)_2CO$. [b] $CDCl_3$.

Table 2. Selected ^1H and ^{13}C NMR.

Comp	^1H H11	H18	H21	Hα	CH-Cos	^{13}C C11	Cα	N→B
1[a]	9.37	~	~	~	~	156.9		8.89
2[b]	8.89	~	~	~	~	159.4		5.77
3[a]	9.43	3.98	4.54	3.39	~	148.3	58.5	5.59
4[a]	9.47	3.90	4.55	3.39	~	160.6	58.5	5.34
5[a]	9.41	3.78	4.10	3.45	4.29	158.3	55.2	7.54
6[a]	9.35	3.84	4.15	3.47	4.29	160.2	55.2	5.42

[a] $(CD_3)_2CO$. [b] $CDCl_3$



Scheme 1. Synthesis of Boron Schiff bases **1**–**2** and the BOSCHIBAs bearing anionic boron clusters **3**–**6**.

(C=N) for precursors **1**–**2** in a range of 1625–1627 cm^{-1}. A broad band characteristic of the ν(B–H) bond that established the presence of boron clusters appears in the range 2470–2542 cm^{-1} for **3**–**4**, whereas for **5**–**6** this band was observed at around 2526 cm^{-1}. In solution, the existence of the N→B coordinate bond in precursors **1**–**2** was confirmed by $^{11}B\{^1H\}$ NMR spectra, which showed a broad resonance at 8.89 and 5.77 ppm, respectively (Table 1, and Figure S3 and Figure S8), characteristic of tetracoordinated boron compounds derived from diphenylborinate acid.[61]

In addition, the $^{11}B\{^1H\}$ NMR spectrum was the perfect tool to predict the suitable formation of expected compounds **3**–**6**, through changes in the chemical shift of resonances after the ring opening reaction, assigned to B(1)-O for **3**–**4** and B(8)-O for **5**–**6**, which confirmed the opening of the dioxane ring. The $^{11}B\{^1H\}$ NMR of **3** and **4** showed 10:1:1:1 pattern between δ −21.15 and 7.62 ppm, where the lowest downfield resonance was attributed to the B–O. Compounds **5** and **6** displayed 1:5:6:3:1:2:1 pattern in the region from δ −27.08 to 24.42 ppm, which is characteristic for COSAN derivatives after completion through the opening ring reaction. In ^{13}C NMR spectra of derivatives **3**–**4** and **5**–**6**, the C-11 resonance was shifted to 148.43 (**3**), 160.60 (**4**), 158.39 (**5**) and 160.24 (**6**) ppm, when compared to their respective precursors 156.95 (**1**) and 159.41 (**2**) ppm, attributed to the coupling of the respective boron cluster. ^1H NMR spectra confirmed the formation of Schiff bases **1**–**2**, with resonances in the range δ 8.89–9.37 ppm, characteristic of an imine proton. Furthermore, ^1H NMR spectra of compounds **3**–**6** indicated the boron clusters coupling through the suitable linkers by the appearance of new proton resonances in the range of 3.29–4.55 ppm for **3**–**4** and 3.51–4.15 ppm for **5**–**6**, attributed to the ethyl ether chain protons. It is important to note that, dyes **3**–**6** showed resonances due to the imino proton (H-11) between 9.35–9.47 ppm, which were shifted to higher frequencies with respect to their precursors **1**–**2** (9.37 and 8.89 ppm, respectively). This shift was probably due to the electronic density exerted by the boron clusters after the formation of the covalent bond O–C. In addition, all resonances corresponding to the respective cations were also observed. The mass spectra for compound **2** showed a mass loss that corresponds to the phenyl group attached to the boron atom, resulting in its molecular ion, while **1** showed a mass loss a phenyl group (Scheme S2). Proposed fragmentations of **1**–**6** are shown in Schemes S2–S4.

Photophysical properties

The photophysical properties of precursors **1**–**2** and their respective derivatives functionalized with anionic boron clusters **3**–**6** were analysed in CH_3CN. Table 3 gathers the most relevant absorption and emission data for all compounds. Absorption spectra are displayed in Figure 3. All of them exhibited a broad absorption band, in the range from 381 to 404 nm (Table 3), due to the HOMO-LUMO electronic transition in the molecules. For all dyes bearing anionic boron clusters, a slight blue shift with respect to the starting precursors **1**–**2** was observed. Another notable feature of the present system is the electronic transitions n-π* of the substituent groups: a phenol ring in **1** and a primary alcohol in **2**. The optical band gap E_g, between 2.57 and 2.78 eV, suggested a general classification of our materials as semiconductors.

For compounds **1**–**6** the excitation and absorption spectra completely matched, which indicated that the emission energies come from the same electronic transitions that give rise to the absorption. Figure 4 displays the fluorescence spectra of **1**–**6**, where it was observed that all of them exhibited maxima of emission after excitation with their respective maxima of absorption. It should be noted that their emission profiles showed a very broad range of emission maxima from 380 to 747 nm.

Table 3. Photophysical properties of the compounds **1**–**6** in CH_3CN.

Comp	λ_{max}	ε *10^4 [M^{-1}cm^{-1}]	λ_{em} [nm]*	Δλ [nm]	Φ [%][a]
1	327, 404	0.6	525	121	3.16
2	326, 396	0.7	474	78	1.61
3	327, 398	0.7	747	349	0.50
4	326, 397	0.5	690	293	0.75
5	316, 398	0.6	525	127	1.21
6	317, 381	0.7	475	94	0.76

[a] Quantum yields determined by using quinine sulphate as standard.

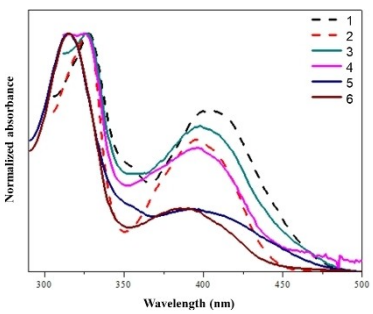


Figure 3. Absorption spectra of compounds **1**–**6** in CH_3CN.

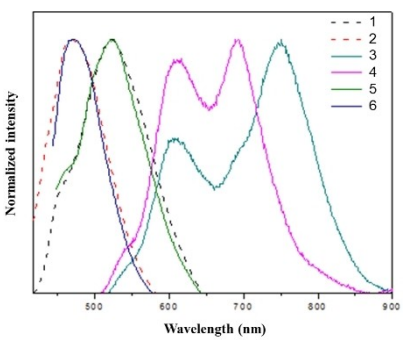


Figure 4. Emission spectra of compounds **1**–**6** in CH_3CN.

The most remarkable emission properties were observed for dyes **3** and **4** bearing the dianion *closo*-dodecaborate, which exhibited emission maxima in the NIR and far-red spectrum, at 747 nm and 690 nm respectively, being significantly red-shifted (~220 nm in both cases) with respect to their corresponding precursors **1** and **2** (Table 3). This suggested that functionalization with this anionic boron cluster strongly affected the geometry in the excited state of the fluorophore. There is no influence of the different linkers on the emission properties were detected, since the red-shift with regards to their precursors was almost the same for both dyes. Nevertheless, COSAN derivatives **5** (λ_{em} = 525 nm) and **6** (λ_{em} = 475 nm) exhibited essentially the same emission maximum than their respective precursors **1** (λ_{em} = 525 nm) and **2** (λ_{em} = 474 nm), which suggested that functionalization with these clusters does not favour the electronic transitions in these molecules.

Fluorescent quantum yield values (Φ_F) between 1.61–3.16% were obtained for Schiff bases **1**–**2**; nevertheless, when they were functionalized with the different anionic boron cluster a decrease of the quantum efficiency was produced to give 0.50%, 0.75%, 1.21% and 0.76% for **3**–**6** respectively (Table 3). This result would imply that functionalization with this kind of boron clusters causes a strongly quenching of the luminescence, most likely because the presence of boron cluster prevents the electronic transition in the molecule. The phenomenon of fluorescence quenching was previously observed in different kind of compounds bearing COSAN moieties, such as organotin dyes[49] and metallacarborane-perylenediimide conjugates.[62] In the latter, one or two COSAN units were tethered to the perylenediimide dye to produce switchable luminescent molecules, in which the emitted fluorescence could be reversible modulated upon application of a redox stimuli. There, demonstrated that to achieve redox-controlled fluorescence switching in COSAN-fluorophore systems it is required a suitable composition and structure that allow a tuneable excited-state interaction between the dye and the COSAN as to selectively quench fluorescence in one of the redox states and selective access to the redox switching of the COSAN derivative without affecting the fluorophore. The larger Stokes shift (Δλ) indicates that, the geometry of the molecules changes dramatically after excitation and non-radiative losses mainly due to internal conversion.

Photostability study

One of the main requirements for a fluorophore to be use as a fluorescent probe for bioimaging applications, is its high photostability. We have incorporated bulky groups into the molecules and evaluated the photostability of compounds **1**–**6**.

The stability of the boron complexes after exposure to UV light at 365 nm was evaluated by measuring the absorbance every 10 minutes for 1 hour in air at room temperature. According to data displayed in Figure 5 and Figure S31, almost all the compounds showed high photostability following the order: **2** > **3** ~ **5** > **6** > **1**. Only compound **4** underwent a photo-degradation lower than 15% after 40 minutes of exposure (Figure 5). Furthermore, after irradiation of **1**–**6** at 312 nm for 40 minutes at room temperature, it was detected different photostabilities; after 20 minutes of irradiation, precursor **1** was degraded around a 78% and **4** a 60%. Furthermore, compounds **2**, **5**, and **6** showed a lower degradation than 70% after 40 minutes, which indicate that at higher energy they show the highest photostability (Figure 6 and Figure S32).

These results seem indicate that the photostability can be modulated by the nature of the boron cluster and the linker between the BOSCHIBA and the cluster. Compound **4** bearing $[B_{12}H_{12}]^{2-}$ and the alkyl linker showed always the lower photostability, whereas **5** and **6** with COSAN were the most stable. In addition, compound **3** shows good photostability at long wavelength, which make it an excellent candidate as fluorescence probe.

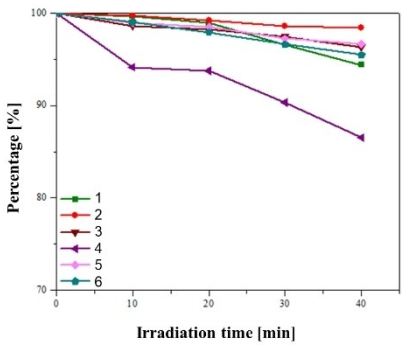


Figure 5. Photostability of **1**–**6** obtained from absorption spectra (1 mg/50 ml) in CH_3CN upon irradiation with an ultraviolet lamp at 365 nm.

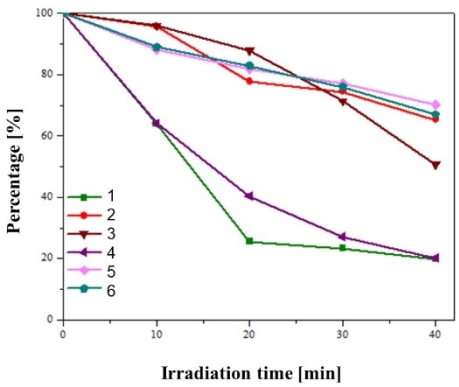


Figure 6. Photostability of **1**–**6** obtained from absorption spectra (1 mg/50 ml) in CH_3CN upon irradiation with an ultraviolet lamp at 312 nm.

Conclusion

BOSCHIBAs **1** and **2** were excellent starting materials to synthesise new emissive dyes by coupling dianionic $[B_{12}H_{12}]^{2-}$ (**3**–**4**) and monoanionic $[3,3'\text{-}Co(C_2B_9H_{11})_2]^-$ (**5**-**6**) boron clusters through suitable linkers. The obtained dyes exhibit attractive photophysical properties that can be modulated by the nature of the cluster. Remarkably, dyes **3** and **4** bearing $[B_{12}H_{12}]^{2-}$ represent the first examples of BOSCHIBA with fluorescence emission in the far-red and near-infrared (NIR) regions with maxima of emission at 747 and 690 nm, respectively. Regarding the photostability, compound **4** showed low photostability at both irradiation wavelength, 365 and 312 nm, whereas dyes **5** and **6** bearing COSAN anion revealed the highest photostability, followed by **3**. All these properties make them potential candidates as fluorescence probes for *in vitro* and *in vivo* imaging.

Experimental Section

Instrumentation: IR spectra were measured on a PerkinElmer Spectrum Shimadzu FTIR-ATR 8300 spectrophotometer for solid samples; the data was reported in wave number ν in cm^{-1}. UV spectra were obtained with a Shimadzu 2401 PC UV/VIS spectrophotometer and emission measurements were performed on a Fluorolog-3 research spectrometer. ^1H NMR (300.13 MHz and 400 MHz) and ^{13}C (75.47 MHz and 100 MHz) spectra were recorded using a Bruker ARX 300 and other equipment Brucker Advance. The ^{11}B {^1H} (96.29 MHz) spectra recorded on a Bruker ARX 300 spectrometer. All NMR spectra were performed in acetone deuterated ($CD_3)_2CO$) solvent at 22 °C and chloroform ($CDCl_3$). The ^{11}B {^1H}NMR shifts were corresponding to external $BF_3{\cdot}OEt_2$, while the ^1H (300.13 MHz) (400 MHz) and ^{13}C (75.47 MHz) (100 MHz) and NMR shifts were relative to $SiMe_4$. Chemical shifts were reported in units of parts per million (ppm) downfield from the reference, and all coupling constants (*J*) are reported in Hertz (Hz). The mass spectra for compounds **3**–**6** were recorded in the negative ion mode using a Bruker Biflex MALDI-TOF-MS (N_2 laser; λ_{ex}337 nm (0.5 ns pulses); voltage ion source 20.00 kV (Uis1) and 17.50 kV (Uis2)) while, for compounds **1**–**2** high resolution mass spectra were acquired by LC/MSD TOF on an Agilent Technologies instrument with APCI as ionization source.

Materials: All reactions were performed under nitrogen atmosphere employing standard Schlenk techniques. Solvents were reagent grade and purified before using by distillation from appropriate drying agents. All starting materials were purchased from Aldrich Chemical Company. The phenylborinic acid (Ph_2BOH) was prepared *in situ* as previously reported in the literature, the tetrabutyl ammonium salt of *closo*-dodecaborate-dioxanate ($[Bu_4N][B_{12}H_{11}(C_4H_8O_2)]$) and the zwitterion COSAN-dioxanate ([8-$(OCH_2CH_2)_2$-3,3′-Co(1,2-$C_2B_9H_{10}$)(1′,2′-$C_2B_9H_{11}$)]) were prepared following procedures described in the literature.[56]

Synthesis of compound 1–6.

Synthesis of (E)-4-(((2-((diphenylboryl)oxy)naphthalen-1-yl) methylene)amino)phenol (1). A solution of 2-hydroxynaphtaldehyde (0.5 g, 2.9 mmol), 4-aminophenol (0.317 g, 2.9 mmol) and diphenylborinate acid (1.307 g, 5.80 mmol) in acetonitrile were heated under reflux for 48 h, using a Dean-Stark apparatus for the removal of the water. The reaction mixture was slowly cooled to

room temperature. The precipitated was filtrated and washed with hexane; the product obtained was a yellow solid with yield of 85%. FTIR υ_{max} cm^{-1}: 1627 (C=N), 830 (C–$H_{Aromatic}$), 1345 (C=$C_{Aromatic}$), 703 (O–B). ^1H NMR (300.13 MHz, $(CD_3)_2CO$)) δ: 6.68 (d, 2H, ^3J=9 Hz, H-14, H-13), 7.13 (m, 7H, H-3, 4H-*m*, 2H-*p*), 7.33 (d, 2H, ^3J=15 Hz, H-13, H-17), 7.39 (t, 1H, ^3J=15 Hz, H-7), 7.46 (d, 4H, ^3J=6 Hz, 4H-*o*), 7.58 (t, 1H, ^3J=15 Hz, H-8), 7.83 (d, 1H, ^3J=6.0 Hz, H-6), 8.05 (d, 1H, ^3J=9 Hz, H-4), 8.33 (d, 1H, ^3J=9.0 Hz, H-9), 8.66 (s, 1H, C15-OH), 9.37 (s, 1H, H-11) ppm. ^{13}C NMR (75.47 MHz, $(CD_3)_2CO$)) δ: 111.81 (C-1), 114.92 (C-14, C-16), 120.34 (C-9), 121.00 (C-13, C-17), 124.04 (C-3), 125.46 (C-7), 125.89 (C-5), 126.04 (C-*m*), 126.60 (C-*p*), 128.75 (C-8), 129.15 (C-6), 132.59 (C-10), 133.32 (C-4), 133.77 (C-*o*), 138.67 (C-12), 139.27 (C-*i*), 156.95 (C-11), 158.03 (C-15), 164.01 (C-2) ppm. $^{11}B\{^1H\}$ NMR (96.29 MHz, $(CD_3)_2CO$)) δ: 8.89 ppm. APCI-MS: *m/z* (%): 428.18 (47.85) [M^+1], 380.18 (43.01) [M^+ -C_4], 350.13 (47.85) [M^+-C_2H_5], 302.13 (100) [M^+ -C_4], 364.10 (9.14) [M^+ -CH_3CH_2].

Synthesis of (*E*)-2-(((2-((diphenylboryl)oxy)naphthalen-1-yl) methylene)amino)ethanol (2). Preparation of **2** was accomplished like that of **1** from 2-hydroxynaphtaldehyde (0.5 g, 2.90 mmol), 2-aminoethanol (0.1773 g, 2.90 mmol) and phenylboronic acid (1.307 g, 5.80 mmol). The product obtained was a yellow solid with yield (90%). FTIR-ATR: υ_{max} cm^{-1}: 1627 (C=N), 830 (C–$H_{Aromatic}$), 1348 (C=$C_{Aromatic}$), 705 (O–B). ^1H NMR (400 MHz, $CDCl_3$) δ: 3.24 (t, 2H, ^3J=8 Hz, H-13), 3.62 (t, 2H, ^3J=12 Hz, H-12), 7.07 (d, 1H, ^3J=8 Hz, H-3), 7.17 (m, 6H, 4H-*m*, 2H-*p*), 7.24 (t, 1H, ^3J=12 Hz, H-7), 7.43 (m, 5H, 4H-*o*, H-8), 7.61 (d, 1H, ^3J=8.0 Hz, H-6), 7.78 (d, 1H, ^3J=8 Hz, H-4), 7.83 (d, 1H, ^3J=8.0 Hz, H-9), 3.66 (s, 1H, C13-OH), 8.89 (s, 1H, H-11) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 57.29 (C-13), 60.40 (C-12), 109.44 (C-1), 118.97 (C-9), 121.48 (C-3), 123.79 (C-7), 126.60 (C-*p*), 127.26 (C-*m*), 127.55 (C-5), 128.62 (C-8), 129.30 (C-6), 132.18 (C-10), 133.07 (C-4), 138.95 (C-*o*, C-*i*), 159.41 (C-11), 163.84 (C-2) ppm. $^{11}B\{^1H\}$ NMR (96.29 MHz, $(CD_3)_2CO$)) δ: 5.77 ppm. APCI-MS: *m/z* (%): 380.18 (20.18) [M^+1], 302.13 (100) [M^+ -C_6H_5], 192.16 (7.53) [M^+ -C_7H_9O].

Synthesis of compound 3. A mixture of (*E*)-4-(((2-((diphenylboryl) oxy)naphthalen-1-yl)methylene)amino)phenol **1** (22 mg, 0.051 mmol), $[Bu_4N][B_{12}H_{11}(C_4H_8O_2)]$ (24 mg, 0.051 mmol) and K_2CO_3 (71.19 mg, 0.515 mmol) was refluxed in acetonitrile for 12 hours, the solution was cooled at room temperature. The excess of K_2CO_3 was filtered out, the volume of acetonitrile was reduced under reduced pressure and the residue was dissolved in EtOH. Then, a saturated aqueous solution of tetrabutylammonium bromide, $(Bu_4N)Br$, was added, which was filtered out and washed several times with distilled water to obtain **3** as a brown sticky oil in 84% yield. FTIR-ATR: υ_{max} cm^{-1}: 2470 (B–H), 1629 (C=N), 1377 (C–$H_{Aromatic}$), 1220 (C–O), 882 (O–B). UV/VIS (CH_3CN): $\lambda_{abs/max}$, ε_{max}*10^3: 398, 6.96 $M^{-1}cm^{-1}$. ^1H NMR (300.13, $(CD_3)_2CO$)) δ: 0.98 (t, 24H, ^3J=15 Hz, H-δ), 1.44 (sextet, 16H, ^3J=36 Hz, H-γ), 1.79 (quintet, 16H, ^3J=30 Hz, H-β) 3.29 (t, 2H, ^3J=12 Hz, H-20) 3.39 (t, 16H, ^3J=15 Hz, H-α), 3.88 (t, 2H, ^3J=12 Hz, H-19), 3.94 (t, 2H, ^3J=9 Hz, H-18) 4.54 (t, 2H, ^3J=9 Hz, H-21), 7.15 (m, 11H, H-3, 4H-*m*, 2H-*p*, H-13, H-17, H-14, H-16), 7.35 (t, 1H, ^3J=15 Hz, H-7), 7.48 (d, 4H, ^3J=6 Hz, 4H-*o*), 7.58 (t, 1H, ^3J=15 Hz, H-8), 7.79 (d, 1H, ^3J=9 Hz, H-6), 8.0 (d, 1H, ^3J=9.0 Hz, H-4), 8.29 (d, 1H, ^3J=6 Hz, H-9), 9.43(s, 1H, H-11) ppm. ^{13}C NMR (75.47 MHz, $(CD_3)_2CO$)) δ: 13.07 (C-δ), 19.50 (C-γ), 23.68 (C-β), 57.35 (C-21), 58.58 (C-α), 64.64 (C-20), 68.08 (C-19), 69.10 (C-18), 110.18 (C-1), 114.20 (C-14, C-16), 120.13 (C-9), 121.13 (C-13, C-17), 123.63 (C-3), 125.19 (C-7), 125.95 (C-5), 126.70 (C-*m*), 127.50 (C-*p*), 128.63 (C-8), 128.92 (C-6), 132.49 (C-10), 133.11 (C-4), 133.76 (C-*o*), 138.12 (C-12), 138.28 (C-*i*), 148.43 (C-11), 150.01 (C-15), 160.48 (C-2) ppm. $^{11}B\{^1H\}$ NMR (96.29 MHz, $(CD_3)_2CO$)) δ: −15.74 (d, 10B, ^3J=123.25 Hz, B(2)-B(11)), −21.15 (s, 1B, B-12), 5.59 (s, 1B, N→B), 8.00 (s,1B, B-3) ppm. MALDI-TOF-MS *m/z* (%): 566.41 (5.58) [M^+ -C_7H_5], 321.28 (21.22) [M^+ -$C_{16}H_{12}OB$], 304.73 (100) [M^+-CH_4], 260.78 (79.88) [M^+ -C_3H_7], 199.25 (12.85) [M^+-C_3H_7O], 141.25 (87.15) [M^+-$C_2H_4O_2$]. Elem anal. Calcd for $C_{65}H_{112}N_3O_4B_{13}$: C; 68.53, H; 9.83, N; 3.68 Found: C; 66.72, H; 9.76, N; 3.32.

Synthesis of compound 4. The same procedure used for the preparation of **3** was followed, but using starting compound **2** (*E*)-2-(((2-((diphenylboryl)oxy)naphthalen-1-yl)methylene)amino) ethanol (21 mg, 0.053 mmol), $[Bu_4N][B_{12}H_{11}(C_4H_8O_2)]$ (24 mg, 0.053 mmol) and K_2CO_3 (73.09 mg, 0.528 mmol). After work up, compound **4** was isolated as a brown sticky oil in 95% yield. FTIR-ATR: υ_{max} cm^{-1}: 2542 (B–H), 1617 (C=N), 1346 (C–$H_{Aromatic}$), 1184 (C–O), 884 (O–B). UV/VIS (CH_3CN): $\lambda_{abs/max}$, ε_{max}*10^3: 397, 7.25 $M^{-1}cm^{-1}$. ^1H NMR (300.13, $(CD_3)_2CO$)) δ: 0.98 (t, 24H, ^3J=12 Hz, H-δ), 1.44 (sextet, 16H, ^3J=36 Hz, H-γ), 1.78 (quintet, 16H, ^3J=33 Hz, H-β) 3.30 (t, 2H, ^3J=12 Hz, H-13), 3.39 (t, 16H, ^3J=15 Hz, H-α), 3.64 (t, 2H, ^3J=12 Hz, H-12), 3.90 (t, 2H, ^3J=12 Hz, H-14) 3.93 (t, 4H, ^3J=9 Hz, H-15, H-16), 4.55 (t, 2H, ^3J=9 Hz, H-17), 7.17 (m, 7H, H-3, 4H-*m*, 2H-*p*), 7.34 (t, 1H, ^3J=15 Hz, H-7), 7.48 (d, 4H, ^3J=9 Hz, 4H-*o*), 7.59 (t, 1H, ^3J=18.0 Hz, H-8), 7.78 (d, 1H, ^3J=6 Hz, H-6), 7.99 (d, 1H, ^3J=9.0 Hz, H-4), 8.32 (d, 1H, ^3J=9 Hz, H-9), 9.47 (s, 1H, H-11) ppm. ^{13}C NMR (75.47 MHz, $(CD_3)_2CO$)) δ: 13.10 (C-δ), 19.51 (C-γ), 23.68 (C-β), 57.30 (C-13), 58.59 (C-α), 59.42 (C-12), 64.85 (C-17), 67.19 (C-16), 72.72 (C-14), 79.58 (C-15), 110.22 (C-1), 120.31 (C-9), 120.99 (C-3), 123.65 (C-7), 125.16 (C-*p*), 125.98 (C-*m*), 126.73 (C-5), 127.50 (C-8), 128.70 (C-6), 128.90 (C-10), 132.52 (C-4), 133.14 (C-*i*), 138.12 (C-*o*), 160.60 (C-11), 163.14 (C-2) ppm. $^{11}B\{^1H\}$ NMR (96.29 MHz, $(CD_3)_2CO$)) δ: −15.69 (d, 10B, ^3J=74.14 Hz, B(2)-B(11)), −20.79 (s, 1B, B-12), 5.34 (s, 1B, N→B), 7.62 (s,1B, B-3) ppm. MALDI-TOF-MS *m/z* (%): 518.86 (17.32) [M^+ -C_7H_5], 392.99 (24.58) [M^+ -C_6H_5OB], 267.26 (78.21) [M^+ - $C_{10}H_7N$], 141.23 (100) [M^+ -$C_6H_8O_3$]. Elem anal. Calcd for $C_{61}H_{112}N_3O_4B_{13}$: C; 67.14, H; 10.26, N; 3.85 Found: C; 64.84, H; 9.77, N; 3.38.

Synthesis of compound 5. A mixture of (*E*)-4-(((2-((diphenylboryl) oxy)naphthalen-1-yl)methylene)amino)phenol **1** (26 mg, 0.060 mmol), $[8\text{-}(OCH_2CH_2)_2\text{-}3,3'\text{-}Co(1,2\text{-}C_2B_9H_{10})(1',2'\text{-}C_2B_9H_{11})]$ (25 mg, 0.060 mmol), and K_2CO_3 (84.13 mg, 0.608 mmol) was refluxed in acetonitrile for 12 hours, the solution was cooled at room temperature. The excess of K_2CO_3 was filtered out, the volume of acetonitrile was reduced under reduced pressure and EtOH was added to the residue. Then a saturated aqueous solution of tetramethylammonium chloride, $(Me_4N)Cl$, was added followed by filtration and washing several times with distilled water, to get **5** as a yellow solid in 70% yield. FTIR-ATR: υ_{max} cm^{-1}: 2525 (B–H), 1623 (C=N), 1249 (C–$H_{Aromatic}$), 1097 (C–O), 885 (O–B). UV/VIS (CH_3CN): $\lambda_{abs/max}$, ε_{max}*10^3: 398, 8.67 $M^{-1}cm^{-1}$. ^1H MNR (300.13, $(CD_3)_2CO$)) δ: 3.57 (t, 4H, ^3J=9 Hz, H-19, H-20) 3.78 (t, 2H, ^3J=9 Hz, H-18), 4.10 (t, 2H, ^3J=12 Hz, H-21), 6.83 (d, 2H, ^3J=9 Hz, H-14, H-16), 7.13 (m, 7H, H-3, 4H-*m*, 2H-*p*, H-13), 7.27 (d, 2H, ^3J=9 Hz, H-13 H-17), 7.40 (t, 1H, ^3J=12 Hz, H-8), 7.47(d, 4H, ^3J=6 Hz, 4H-*o*), 7.59 (t, 1H, ^3J=15 Hz, H-7), 7.82 (d, 1H, ^3J=9 Hz, H-6), 8.05 (d, 1H, ^3J=9.0 Hz, H-4), 8.36 (d, 1H, ^3J=9 Hz, H-9), 3.45 (s, 12H, 12H-α), 4.29 (s, 4H, CH-COSAN), 9.41 (s, 1H, H-11) ppm. ^{13}C RMN (75.47 MHz, $(CD_3)_2CO$)) δ: 46.43 (C-24, C-25), 54.54 (C-22, C-23) 55.26 (C-α), 67.84 (C-21), 68.43 (C-20), 69.24 (C-19), 72.05 (C-18), 111.87 (C-1), 114.24 (C-14, C-16), 120.48 (C-13, C-17), 120.99 (C-3), 124.07 (C-7), 125.98 (C-5), 126.58 (C-*m*, C-*p*), 127.69 (C-9), 128.69 (C-8), 129.12 (C-6), 133.64 (C-10), 133.10 (C-4), 133.78 (C-*o*), 139.38 (C-12), 139.50 (C-*i*), 158.39 (C-11), 158.49 (C-15), 164.12 (C-2) ppm. $^{11}B\{^1H\}$ NMR (96.29 MHz, $(CD_3)_2CO$)) δ: −17.45 (d, 5B, ^3J=298.49 Hz, B–H), −6.43 (d, 6B, ^3J=71.25 Hz, B–H), −1.93 (d, 3B, ^3J=174.28 Hz, B–H), −27.06 (s, 1B, B–H), 1.86 (s, 1B, B–H), 5.36 (s, 2B, B–H, N→B), 24.34 (s,1B, B-8) ppm. MALDI-TOF-MS *m/z* (%): 836.32 (100) [M^+1], 760.21 (14.61) [M^+ -C_6H_5], 428.27 (22.22) [M^+ -$C_{23}H_{16}ONB$], 384.25 (7.01) [M^+ -OC_2H_4]. Elem anal. Calcd for $C_{41}H_{62}N_2O_4B_{19}Co$: C; 53.97, H; 6.90, N; 3.07 Found: C; 50.06, H; 6.91, N; 3.18.

4.3.6. Synthesis of compound 6. The same procedure used to prepare compound 5 was followed for compound 5 was followed

for the preparation of compound **6**, but using the starting compound **2**, (*E*)-2-(((2-((diphenylboryl)oxy)naphthalen-1-yl) methylene)amino)ethanol (23 mg, 0.060 mmol), using [8-$(OCH_2CH_2)_2$-3,3′-Co(1,2-$C_2B_9H_{10}$)(1′,2′-$C_2B_9H_{11}$)] (24 mg, 0.053 mmol) and K_2CO_3 (73.09 mg, 0.528 mmol), to obtain **6** as a yellow solid in 90% yield. FTIR-ATR: υ_{max} cm^{-1}: 2528 (B–H), 1623 (C=N), 1251 (C–$H_{Aromatic}$), 1098 (C–O), 884 (O–B). ^{1}H NMR (300.13, $(CD_3)_2CO$)) δ: 3.33 (t, 2H, ^3J = 9 Hz, H-13) 3.51 (t, 2H, ^3J = 9 Hz, H-15, H-16), 3.62 (t, 2H, ^3J = 12 Hz, H-12), 3.84 (t, 2H, ^3J = 12 Hz, H-14), 4.15 (t, 2H, ^3J = 9 Hz, H-17), 7.17 (m, 7H, H-3, 4H-*m*, 2H-*p*), 7.37 (t, 1H, ^3J = 12 Hz, H-7), 7.47 (d, 4H, ^3J = 6 Hz, 4H-*o*), 7.57 (t, 1H, ^3J = 15.0 Hz, H-8), 7.82 (d, 1H, ^3J = 6 Hz, H-6), 8.02 (d, 1H, ^3J = 9.0 Hz, H-4), 8.19 (d, 1H, ^3J = 6 Hz, H-9), 3.47 (s, 12H, 12H-α), 4.29 (s, 4H, CH-COSAN), 9.35 (s, 1H, H-11) ppm. ^{13}C NMR (75.47 MHz, $(CD_3)_2CO$)) δ: 46.43 (C-20, C-21), 54.50 (C-18, C-19) 55.22 (C-α), 57.35 (C-13), 59.29 (C-12), 61.17 (C-17), 68.39 (C-16), 71.81 (C-15), 72.56 (C-14), 110.07 (C-1), 119.62 (C-9), 121.10 (C-3), 123.70 (C-7), 126.04 (C-*p*), 126.75 (C-*m*), 127.54 (C-5), 128.56 (C-8), 129.11 (C-6), 132.43 (C-10), 133.10 (C-4), 138.30 (C- *o*, C-*i*), 160.25 (C-11), 163.32 (C-2) ppm. ^{11}B{^{1}H} NMR (96.29 MHz, $(CD_3)_2CO$)) δ: −17.45 (d, 5B, ^3J = 303.31 Hz, B–H), −6.41 (d, 6B, ^3J = 66.44 Hz, B–H), −1.94 (d, 3B, ^3J = 170.43 Hz, B–H), −27.08 (s, 1B, B–H), 1.80 (s, 1B, B–H), 5.52 (s, 2B, B–H, N→B), 24.42 (s,1B, B-8) ppm. MALDI-TOF-MS *m/z* (%): 833.44 (22.22) [M^+1], 456.34 (33.91) [M^+-$C_{23}H_{17}ONB$], 428.33 (100) [M^+-C_2H_4], 383.38 (10.52) [M^+-OC_2H_4], 340.30 (5.84) [M^+ -OC_2H_4]. Elem anal. Calcd for $C_{37}H_{62}N_2O_4B_{19}Co$: C; 51.41, H; 7.29, N; 3.24 Found: C; 52.3, H;7.30, N; 2.93.

Absorbance, emission, and luminescence quantum yields

UV-Vis absorption spectra were measured on a Shimadzu 2401 PC spectrophotometer. Optical band gap (E_g) was determined from the intercept of the X axis of the tangent of the absorption spectrum drawn at an absorbance of 0.1. The emission spectra were recorded with a Perkin-Elmer LS 50B spectrofluorometer, by exciting 10 nm below the longer wavelength absorption band. Fluorescence quantum yields in solution (Φ) were determined according to the procedure reported in the literature and using quinine sulphate in H_2SO_4 0.1 M (Φ = 0.54 at 310 nm) as the standard. Temperature was regulated at 25.0±0.5 °C using water circulating bath. The absorbance of the three solutions at the excitation wavelength lower than 0.1 were analysed for each sample and the quantum yield was averaged.

Supporting information (see footnote on the first page of this article): The details of ^{1}H, ^{11}B, ^{13}C, NMR (2D experiments), absorption, and emission spectra. TOF MS, IR are included.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: References

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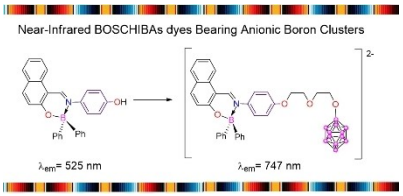
FULL PAPERS

New boron Schiff bases (BOSCHIBAs) were functionalized with boron cluster anions $[B_{12}H_{12}]^{2-}$ (**3**–**4**) and $[3,3'\text{-}Co(C_2B_9H_{11})_2]^-$ (**5**–**6**). Remarkably, BOSCHIBAs bearing $[B_{12}H_{12}]^{2-}$ showed fluorescence emission to the NIR and far-red regions (**3**: 747 nm, **4**: 690 nm). Compounds **3** and **4** represent the first example of boron Schiff bases bearing boron cluster anions $[B_{12}H_{12}]^{2-}$ exhibiting fluorescence emission in the NIR and far-red regions, make them potential candidates as fluorescence probes for bioimaging.



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