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# Synthesis of luminescent BPh<sub>2</sub>-coordinated 2-(2'-hydroxyphenyl)benzoxazole (HBO)<sup>†</sup>

Julien Massue,\*<sup>a</sup> Pascal Retailleau,<sup>b</sup> Gilles Ulrich\*<sup>a</sup> and Raymond Ziessel\*<sup>a</sup>

Triphenylborane (BPh<sub>3</sub>) has been successfully coordinated to five  $\pi$ -conjugated aromatic systems containing a N^O bidentate 2-(2'-hydroxyphenyl)benzoxazole (HBO) ligand. Complexes **6–8** are directly substituted on the phenolic side of the HBO core while the structure of derivatives **9–10** includes a 4-dibutylaminophenyl module linked through an ethynyl fragment, at position 4 or 5. The crystal structure of complexes **8** and **10** reveals different solid-state molecular packing depending on the substitution, a herringbone molecular packing being observed for complex **8** while the dibutylamino fragment present in complex **10** is in favour of a lamellar structure. The optical properties are highly dependent on the nature and the position of substituents. Solvatochromic charge-transfer emissions are observed for substitution at position 3 or 5 while singlet emission is favoured when position 4 is functionalized. Solid-state fluorescence reveals that complex **8** possesses red-shifted emission when dispersed in a KBr matrix.

#### Introduction

The 2-(2'-hydroxyphenyl)benzoxazole (HBO) and benzothiazole (HBT) derivatives<sup>1</sup> are a class of fluorophores known for over 40 years that exhibit a bright emission in the solid state as a consequence of an intrinsic Excited-State Intramolecular Proton Transfer (ESIPT).<sup>2</sup> This major reorganisation of the molecule upon photoexcitation leads to improved Stokes shifts and pronounced solvatochromism. These interesting features have made these dyes emerge as promising luminescent materials for pH and chemical sensing of cations<sup>3</sup> or biologically relevant anions.<sup>4</sup> ESIPT displaying compounds have also successfully been embedded in optoelectronic devices<sup>5</sup> such as light-emitting diodes or transistors or recently used as triplet-state sensitizers in dyads for photodynamic therapy (PDT) applications.<sup>6</sup>

Several studies have also pointed out the fact that HBO- or HBT-based fragments were excellent N<sup>O</sup> chelating entities towards a large variety of metals.<sup>7</sup> ESIPT is consequently absent but large Stokes shifts are usually maintained due to the nonsymmetric structure of HBO or HBT and new properties can arise from the presence of a nearby decorated metallic centre (Scheme 1).

Numerous examples report their incorporation in the coordination sphere of metallic centres with the goal to create optically tunable luminescent emitters.<sup>8</sup> Among them, bis(2-(2-hydroxyphenyl)benzothiazolate)-zinc [Zn(BTZ)<sub>2</sub>] has been widely studiedas a white electroluminescent material that exhibits majorelectron-transporting properties.<sup>9</sup>

Following a pioneer paper,<sup>10</sup> we recently reported the synthesis of several substituted HBO fragments coordinated to a boron trifluoride moiety.<sup>11</sup> These bright complexes thus obtained exhibit emission properties that could be fine-tuned by introducing relevant electronic substituents at different positions of the phenolic side.<sup>12</sup>  $\pi$ -Conjugated aromatic systems coordinated to one or several boron biphenyl fragments (BPh<sub>2</sub>) have received widespread interest for their use in electroluminescent devices.<sup>13</sup>



**Scheme 1** (a) General structure of HBO/HBT dyes displaying the ESIPT process; (b) use as  $N^O$  bidentate ligands.

<sup>&</sup>lt;sup>a</sup> Laboratoire de Chimie Moléculaire et Spectroscopies Avancées (LCOSA), ICEES-LCOSA, UMR CNRS 7515, École Européenne de Chimie, Polymères et Matériaux (ECPM), 25 rue Becquerel, 67087 Strasbourg Cedex 02, France. E-mail: massue@unistra.fr, gulrich@unistra.fr, ziessel@unistra.fr

<sup>&</sup>lt;sup>b</sup> Laboratoire de Cristallochimie. ICSN – CNRS Bât 27 – 1 avenue de la Terrasse.

<sup>91198</sup> Gif-sur-Yvette Cedex, France

<sup>&</sup>lt;sup>†</sup> CCDC 891069 (complex **8**) and CCDC 891070 (complex **10**). For crystallographic data in CIF or other electronic format see DOI: 10.1039/c3nj41052h

For example, 8-hydroxyquinolinate diphenylboron  $(BPh_2q)$  was found to be an interesting alternative to the well-known tris(8-hydroxyquinolinate)aluminum (Alq<sub>3</sub>) for organic lightemitting diodes (OLEDs) because of its stability and high emission quantum yield.<sup>14</sup> It was thus interesting to study the impact of the coordination of triphenylborane (BPh<sub>3</sub>) to substituted HBO ligands on the chemical and photochemical stability and on the photophysical properties. The comparison of the optical properties between the BPh<sub>2</sub> and the BF<sub>2</sub> complexes is likely to open the way to subtle luminescence fine-tuning within this family of dyes.

Herein, we report the synthesis, crystal structures and photoluminescence properties of five  $BPh_2$  HBO borate complexes, either directly substituted with electron donating (ED) groups (<sup>t</sup>Bu, OMe, NEt<sub>2</sub>) or through an ethynyl fragment (-C=C-PhNBu<sub>2</sub>).

#### **Results and discussion**

#### Syntheses

HBO ligands 1–3 (ref. 11) and 4–5 (ref. 12) were synthesized according to reported procedures. Targeted BPh<sub>2</sub> complexes 6–8 and 9–10 were obtained by reacting the relevant ligand with an excess of triphenylborane (6 equivalents) in toluene at 60 °C for 1 hour. Note that a base is not required as BPh<sub>3</sub> is used as a proton scavenger releasing benzene as a side-product. Purification by filtration on a basic Al<sub>2</sub>O<sub>3</sub> column, eluting with CH<sub>2</sub>Cl<sub>2</sub>, afforded the desired complexes 6–10 as beige to orange powders with yields ranging from 66 to 95% (Scheme 2).

These complexes were unambiguously characterized by <sup>1</sup>H, <sup>13</sup>C and <sup>11</sup>B NMR spectroscopy in CDCl<sub>3</sub> at room temperature. A typical example is depicted in Fig. 1 with the <sup>1</sup>H NMR of ligand 3 along with the <sup>1</sup>H and <sup>13</sup>C NMR of the corresponding BPh<sub>2</sub> complex 8. HBO ligand 3 exhibits a distinctive downfield <sup>1</sup>H signal resonating as a broad singlet at 11.5 ppm attributed

(+) + (+)

**Scheme 2** Synthesis of BPh<sub>2</sub> complexes **6–10**.



**Fig. 1** (a) <sup>1</sup>H NMR spectrum of ligand **3** in  $CDCl_3$  at room temperature (300 MHz) and (b) <sup>1</sup>H and <sup>13</sup>C NMR spectra of BPh<sub>2</sub> complex **8** in  $CDCl_3$  at room temperature (300 and 75.4 MHz respectively).

to the H-bonded phenolic proton that disappears upon complexation to BPh<sub>3</sub>. The chelation of the BPh<sub>3</sub> fragment is further evidenced by a splitting of the multiplets corresponding to the aromatic protons of the HBO core and the appearance of additional multiplets for the BPh<sub>2</sub> subunit. <sup>13</sup>C spectra are in accordance with expected signals for tertiary and quaternary aromatic carbons. Finally, coordination to the boron centre leads to the appearance of a broad signal in <sup>11</sup>B spectroscopy between 5.5 and 6.1 ppm for complexes **6–10**.

#### X-ray structures

Monocrystals of complexes **8** and **10** were grown by slow diffusion of pentane in a concentrated  $CH_2Cl_2$  solution at room temperature. The X-ray molecular structures of **8** and **10** are shown in Fig. 2 and 3, respectively, with selected geometric values.<sup>15</sup>

In both structures, the boron has a similar distorted tetrahedral geometry with angles ranging from 105.7(3) to 116.1(2)° and from 104.0(2) to 116.1(3)° in **8** and **10**, respectively. The largest angle corresponds to the spreading of both phenyl groups attached to the boron atom. A distortion of the tetracyclic platform around the B–O bond is common for these types of complexes. Both these atoms deviate significantly by 0.130(4) and -0.105(3) Å from the least-squares mean plane defined by the 15 other atoms with a root mean square deviation of 0.0128 Å in **8**. Unlike the non-substituted outer phenyl twisted known structures,<sup>16</sup> the overall planarity seems to be recovered by the joint contribution of the *syn*-diethylamino substituent and the relative B-phenyl orientation (dihedral angle of 56.4°) deviating from the usual orthogonality as observed for **10** (85.3°).



**Fig. 2** (Left) Ortep view for **8** showing the atom-labelling scheme. Thermal ellipsoids are plotted at the 30% level. (Right) Perpendicular view to highlight the distortion at the B atom. B1–N1, B1–O1, B1–C14, B1–C20, C1–N1, N1–C7, and C8–O1 bond lengths are 1.616(3), 1.502(3), 1.610(3), 1.611(3), 1.322(2), 1.403(2), and 1.339(2), and the N–B–O, C–B–C, N–B–C, O–B–C, B–N–C, C1–N1–B1, C7–N1–B1 and B–O–C angles are 105.66(16), 116.71(18), 106.95(16), 108.19(17), 108.22(17), 110.53(18), 121.98(17), 130.96(16) and 126.55(16)°.



**Fig. 3** (Left) Ortep view for **10** showing the atom-labelling scheme. Thermal ellipsoids are plotted at the 30% level. (Right) Perpendicular view to highlight the distortion at the B atom. H-atoms are omitted for clarity. B1–N1, B1–O2, B1–C14, B1–C20, C1–N1, N1–C7, and O2–C8 bond lengths are 1.614(4), 1.484(4), 1.612(4), 1.605(4), 1.319(3), 1.413(3) and 1.340(3), N–B–O, C–B–C, N–B–C, O–B–C, C1–N1–B1/C7–N1–B1, and B–O–C angles are 104.0(2), 116.1(3), 108.3(2)/109.1(2), 110.8(2)/107.8(2), 119.3(2)/134.0(2) and 120.5(2)°.

With respect to **10**, elongated ethynyl-phenyl substitution in C11 deforms again the tetracyclic platform, the outer phenyl making a dihedral angle of  $10.8^{\circ}$  with the planar heterobicycle and the maximum deviation of O and B atoms from this plane exceeds 0.3 Å.

The B1–O1 and B1–N1 distances are in the same range for **8** and **10** (1.502 Å *vs.* 1.484 Å for B1–O1 and 1.616 Å *vs.* 1.614 Å for B1–N1) and are fairly similar to those in HBO borate complexes reported in the literature.<sup>11,12</sup> It is also noticeable that the B1–O1 and B1–N1 distances take intermediate values (*ca.* 1.61 Å between 1.64 and 1.50 Å, and *ca.* 1.49 Å between 1.55 and 1.42(2) Å, respectively), in comparison with some reported *boranil* complexes substituted by either BPh<sub>2</sub> or BF<sub>2</sub> fragments.<sup>17</sup>

The solid-state packing of the conjugated planar platforms is affected by the nature, the size and the position of attachment of



**Fig. 4** (a) A view part of the crystal structure of **8**, showing the C-H··· $\pi$  (dashed lines) hydrogen bonds developed around a molecule (dark) at a general position. In dark grey neighbouring molecules in front; in light grey, molecules in the back; (b) view of the molecular packing down highlighting the herringbone molecular packing.

the substituents, which can promote basically two types of packing morphology, a 'herring-bone' structure (rather favoured in the absence of side chains, Fig. 4) and a lamellar structure (usually in the presence of linear alkyl side chains, Fig. 5).<sup>18</sup> When viewed down the short molecular axis which is parallel to the crystallographic a axis, complexes 8 appear to be stacked pairwise in a herringbone-like structure, whereas complexes 10 stack along the crystallographic b axis forming infinite layers along the *a* axis parallel to (0 - 1 3) and (0 1 3) alternately every distance corresponding to c/2. The stacks are canted relative to the stack axis with an angle of *ca*. 65°. In the crystal of complex 8, despite a cofacial orientation with a distance of ca. 3.45 Å between inversion-related pairwise molecules, there is little  $\pi$ -overlap between them. The main cohesive forces are instead provided by the C-H··· $\pi$  non-conventional hydrogen bonds involving the two orthogonal phenyl groups and the benzyl moiety of the heterobicycle of a molecule at general positions x, y, z and six neighbours (Fig. 4). As seen previously, the two orthogonal phenyl groups interact with the conjugated main groups;  $\pi - \pi$  interactions are present and involve the tetracycle of one molecule at x, y, z and the part benzyl-ethynyl-phenyl moiety of the adjacent molecule at 1/2 - x, -1/2 + y, z with an average centroid-centroid distance of 3.69 Å.

#### Photophysical properties

Photophysical data of complexes 6–10 in various solvents are gathered in Table 1.

All  $BPh_2$  HBO borate complexes except 8 display unstructured absorption spectra with a major band located between



**Fig. 5** (a) Part of the crystal structure of **10** showing the  $\pi$ - $\pi$  stacking as well as the edge-to-face (cyan dotted lines) interactions; (b) view of the molecular packing down the *a* axis with guidelines for the (0 - 1 3) and (0 1 3) planes.

302 and 434 nm with extinction coefficients ranging between 9200 and 42000 M<sup>-1</sup> cm<sup>-1</sup>, depending on the electronic substitution on the hydroxyphenyl core. More intense bands are observed below 300 nm, characteristic of the  $\pi$ - $\pi$ \* transitions of the phenyl rings. In the case of dye 8, where the phenolic side of the HBO core is directly substituted with a diethylamino group, a structured, narrow absorption band is observed with a higher extinction coefficient (45 900  $M^{-1}$  cm<sup>-1</sup>) with respect to complexes 6 and 7. Note that all the absorption spectra are centered in the UV region, regardless of the substitution, and do not show pronounced solvatochromism.

Interestingly, irradiation in the lower energy absorption band for complexes 6-10 leads to an intense emission band located in the visible region with a maximum wavelength

Table 1 Optical data of complexes 6-10 measured in solution at room



Fig. 6 Absorption (---) and emission (--) spectra of complexes 6-8 in CH<sub>2</sub>Cl<sub>2</sub> at room temperature. Excitation wavelengths were 380, 376 and 389 nm for complexes 6, 7, and 8, respectively.

ranging between 427 and 556 nm and quantum yields from 7 to 82% (Table 1 and Fig. 6-8).

The absorption and emission spectra of the directly substituted BPh<sub>2</sub> HBO borate complexes 6-8 in CH<sub>2</sub>Cl<sub>2</sub> are shown in Fig. 6. Complexes 6 and 7 bearing two <sup>t</sup>Bu groups or a methoxy group at positions 5, 3 and 4, respectively, exhibit similar photophysical characteristics such as a large, unstructured absorption band ( $\lambda_{abs}$  = 390 nm for **6** and 366 nm for **7**) and a symmetrical emission band ( $\lambda_{em}$  = 472 nm for 6,  $\Phi$  = 82% and  $\lambda_{\rm em}$  = 427 nm for 7,  $\Phi$  = 44%). These features are consistent with a weak internal charge-transfer (ICT). In the case of complex 8, a structured, narrow, absorption band is observed with an increased extinction coefficient ( $\lambda_{abs}$  = 399 nm,  $\varepsilon$  = 45 900 M<sup>-1</sup> cm<sup>-1</sup>). The emission band ( $\lambda_{em}$  = 414 nm for 8,  $\Phi$  = 67%) mirrors the absorption band and features reduced Stokes shift (900 cm<sup>-1</sup>), consistent with a weakly polarized excited state. These experimental observations are indicative of a singlet state emission with a significant internal cyanine character and are reminiscent of what was previously observed on BF<sub>2</sub> HBO borate complexes.<sup>11</sup> The short lifetime (1.9 ns) is in keeping with such a statement. Comparison of complexes 6-8 with their corresponding BF<sub>2</sub> complexes<sup>11</sup> shows in each case a

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Dye	$\lambda_{abs}$ (nm)	$\stackrel{\epsilon}{(M^{-1} cm^{-1})}$	$\lambda_{\rm em}$ (nm)	$\Delta (\mathrm{cm}^{-1})$	${\Phi_{\mathrm{f}}}^a$	τ (ns)	Solvent
6	390	9200	472	4500	0.82	8.4	$CH_2Cl_2$
7	366	10 000	427	3900	0.44	4.1	$CH_2Cl_2$
8	399	45 900	414	900	0.67	1.9	$CH_2Cl_2$
9	423	35 000	488	3100	0.79	1.8	Toluene
	434	38 000	552	4900	0.63	2.5	$CH_2Cl_2$
	324	38 000	491	10500	0.08	2.1	$CH_2Cl_2 + HCl_2$



40000 CH<sub>2</sub>Cl<sub>2</sub> + HCl <sub>aas</sub> Toluene ε (M<sup>-1</sup>.cm<sup>-1</sup>) 30000 THE 20000 10000 0 300 500 700 λ (nm)

<sup>a</sup> Quantum yields determined in solution, using quinine sulfate as reference  $\Phi$  = 0.55 in H<sub>2</sub>SO<sub>4</sub> 1 N,  $\lambda_{ex}$  = 366 nm for dyes emitting below 480 nm, Rhodamine 6G  $\Phi$  = 0.88 in ethanol,  $\lambda_{ex}$  = 488 nm for dyes emitting between 480 and 570 nm.

Fig. 7 Absorption and emission spectra of complex 9 in various solvents at room temperature. Excitation wavelengths were 427, 315, 415 and 425 nm for CH<sub>2</sub>Cl<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub> + HCl, toluene and THF respectively

temperature



Fig. 8 Absorption (---) and emission spectra (--) of complex 10 in various solvents at room temperature. Excitation wavelengths were 335, 295 and 325 nm for  $CH_2CI_2$ ,  $CH_2CI_2$  + HCl and toluene.

bathochromic shift for both the absorption and emission bands and an increase of the quantum yield. This observed red-shift is only moderate in the case of complex 8 ( $\lambda_{abs}$  = 399 nm,  $\lambda_{\rm em}$  = 414 nm,  $\Phi$  = 67% compared to  $\lambda_{\rm abs}$  = 387 nm,  $\lambda_{\rm em}$  = 401 nm,  $\Phi$  = 42% for the corresponding BF<sub>2</sub> complex). This shift increases as the electron donating ability decreases. Indeed, complex 6 bearing <sup>t</sup>Bu groups is more strongly bathochromically shifted ( $\lambda_{abs}$  = 390 nm,  $\lambda_{em}$  = 472 nm,  $\Phi$  = 82% for 6 compared to  $\lambda_{abs}$  = 359 nm,  $\lambda_{em}$  = 422 nm,  $\Phi$  = 31% for the BF<sub>2</sub> analogue) than complex 7 substituted by a methoxy fragment  $(\lambda_{abs} = 366 \text{ nm}, \lambda_{em} = 427 \text{ nm}, \Phi = 44\% \text{ for 7 compared to } \lambda_{abs} =$ 339 nm,  $\lambda_{em}$  = 380 nm,  $\Phi$  = 39% for the BF<sub>2</sub> analogue). Switching the BF<sub>2</sub> fragment for a BPh<sub>2</sub> reduces the strength of the ICT which presumably decreases non-radiative deactivations and is therefore responsible for an increased quantum yield. Nevertheless, BPh<sub>2</sub> being less electron-attractor than BF<sub>2</sub>, the ICT is therefore weaker and the emission should not be bathochromically shifted as observed. One tentative explanation is that the electronic donation of the phenyl groups induces an increase of the energy level for the HOMO; whereas the energy level of the LUMO remains unaffected. As a consequence the HOMO-LUMO gap decreases and the emission is therefore bathochromically shifted. This case has already been observed on BODIPY dyes.<sup>19</sup> It also seems that the nature of the emission (ICT or singlet) has an influence on the amplitude of the bathochromic shift observed for the BPh2 HBO borate complexes compared to the BF2 ones; ICT emission seems to lead to stronger red-shifts when switching from BF2 to BPh2 than singlet emission. This is specifically the case for complexes 6 and 7.

To check if these features are also present in ethynylextended HBO borate complexes, the absorption and emission spectra of the 4-dibutylaminophenyl ethynyl-extended HBO borate complexes 9 and 10 were recorded in various solvents (Fig. 7 and 8).

Complex 9 displays a major unstructured absorption band located mostly in the UV region between 324 and 434 nm ( $\varepsilon = 35\,000-40\,000 \text{ M}^{-1} \text{ cm}^{-1}$ ). This band is very mildly solvatochromic except after protonation of the nitrogen in CH<sub>2</sub>Cl<sub>2</sub> using HCl gas where it undergoes a pronounced blue-shift with respect to the maximum absorption wavelength in CH<sub>2</sub>Cl<sub>2</sub>  $(\lambda_{abs} = 324 \text{ nm } \nu s. \lambda_{abs} = 434 \text{ nm})$ . Compared to the respective maximum absorption of the corresponding BF<sub>2</sub> complexes,<sup>12</sup> all BPh2 complexes exhibit a significant red-shift (around 1900 cm<sup>-1</sup>) in all solvents except in CH<sub>2</sub>Cl<sub>2</sub> after protonation. Irradiation of the maximum absorption band leads to an intense emission band located in the visible region between 488 and 556 nm ( $\Phi$  = 8 to 79%). In all solvents, the emission of the BPh<sub>2</sub> complexes is red-shifted with respect to their corresponding  $BF_2$  analogues (around 1500 cm<sup>-1</sup>). Protonation of the lone electron pair of the nitrogen in CH<sub>2</sub>Cl<sub>2</sub> with HCl<sub>gas</sub> leads to a significant blue-shift for both the absorption and the emission ( $\lambda_{abs}$  = 434 nm,  $\lambda_{em}$  = 552 nm for **9** in CH<sub>2</sub>Cl<sub>2</sub> vs.  $\lambda_{abs}$  = 324 nm,  $\lambda_{em}$  = 491 nm for 9 in CH<sub>2</sub>Cl<sub>2</sub> + HCl<sub>gas</sub>) and a dramatic decrease of the quantum yield ( $\Phi$  = 63% in CH<sub>2</sub>Cl<sub>2</sub> vs.  $\Phi$  = 8% in CH<sub>2</sub>Cl<sub>2</sub> + HCl<sub>gas</sub>). No precipitation of the salts is observed; however, the formation of soluble aggregates could not be excluded.

Complex **10** displays similar photophysical characteristics with a major unstructured absorption band ( $\lambda_{abs} = 302$  to 340 nm,  $\varepsilon = 35\,000-42\,000 \text{ M}^{-1} \text{ cm}^{-1}$ ), which gives rise, upon irradiation, to an emission located in the visible region ( $\lambda_{em} =$ 498 to 534 nm,  $\Phi = 7$  to 13%) (Fig. 8). This is a major improvement compared to its BF<sub>2</sub> analogue whose fluorescence was quenched in CH<sub>2</sub>Cl<sub>2</sub> due to strong non-radiative deactivations through ICT.<sup>12</sup> ICT is similarly featured in complex **10** as evidenced by the strong blue-shift and quantum yield increase observed upon protonation of the nitrogen doublet using HCl<sub>gas</sub> but is weaker than in its BF<sub>2</sub> analogue, presumably due to the less electron accepting nature of the BPh<sub>2</sub> fragment.

Monoexponential decays are observed for all compounds with lifetimes being on the nanosecond scale.<sup>20</sup>

Finally, solid-state emission and excitation were recorded for complex **8**, in order to correlate with the molecular packing observed in the X-ray structure whereas complex **10** did not exhibit any fluorescence in the solid state. As shown in Fig. 9, complex **8** displays a broad intense emission band in the solid state after irradiation at 390 nm.

Optical data for complex 8 in the solid state are red-shifted with respect to the CH<sub>2</sub>Cl<sub>2</sub> solution ( $\lambda_{exc} = 427$  nm,  $\lambda_{em} = 464$  nm *vs.*  $\lambda_{abs} = 399$  nm,  $\lambda_{em} = 414$  nm). The quantum yield,



Fig. 9 Solid-state excitation (---) and emission (--) recorded in KBr pellets of complex 8 along with solution excitation in  $CH_2Cl_2$  (grey scale, ---). Excitation wavelength was 427 nm.

calculated from a spectrometer fitted with an integrating sphere, was found to be  $\Phi = 13\%$ . Biexponential decay is observed presumably due to the presence of various packing of the molecule in the KBr matrix ( $\tau_1 = 2.4$  ns,  $\tau_2 = 5.6$  ns).

#### Conclusion

We have successfully coordinated a triphenylborane fragment to differently substituted HBO pincer ligands. The substituents are either directly linked to the hydroxyphenyl core or through an ethynyl spacer. Two complexes were characterized by X-ray diffraction on single crystals. Depending on the electronic substitution and its position on the HBO core, different photophysical behaviours were observed. The locally excited state is either a charge-transfer or a singlet emission. In all cases, the optical data recorded in solution and the solid-state showed a significant red-shift both for the absorption and emission with respect to the BF<sub>2</sub> analogues.

#### Experimental

All reactions were performed under a dry atmosphere of argon. All chemicals were received from commercial sources and used without further purification. Chromatographic purifications were conducted using 40–63  $\mu$ m silica gel or basic aluminium oxide. <sup>1</sup>H-, <sup>13</sup>C- and <sup>11</sup>B NMR spectra were acquired at 25 °C on either a Bruker AV 300 or a Bruker AV 400 spectrometer. Deuterated solvents were used as the lock and residual non-deuterated solvents as the internal references.

## General procedure for the synthesis of HBO borate complexes 6-10

To a stirred solution of the corresponding HBO in toluene  $(0.1 \text{ mL mg}^{-1})$ , BPh<sub>3</sub> (6 equivalents) was added as a powder under argon. The resulting mixture was stirred at 60 °C for 1 hour. The crude solution was then filtered through a column of basic Al<sub>2</sub>O<sub>3</sub>, eluting with CH<sub>2</sub>Cl<sub>2</sub>, and the solvents were evaporated *in vacuo*. Pure BPh<sub>2</sub> HBO borate complexes **6–10** were obtained as beige to orange powders after recrystallisation in pentane or cyclohexane.

HBO borate complex 6. Beige powder. 95%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ (ppm): 7.71 (d, 1H, CH Ar, J = 2.7 Hz), 7.66 (d, 1H, CH Ar, J = 8.4 Hz), 7.63 (d, 1H, CH Ar, J = 2.4 Hz), 7.47–7.50 (m, 4H, CH Ar), 7.38 (t, 1H, CH Ar, J = 8.4 Hz), 7.25– 7.31 (m, 7H, CH Ar), 7.06 (d, 1H, CH Ar, J = 8.4 Hz), 1.47 (s, 9H, CH<sub>3</sub>), 1.38 (s, 9H, CH<sub>3</sub>). <sup>13</sup>C NMR (75.4 MHz, CDCl<sub>3</sub>) δ (ppm): 162.5, 160.2, 149.1, 140.5, 140.0, 133.5, 133.3, 132.8, 129.1, 128.3, 127.1, 126.5, 126.4, 125.9, 125.3, 119.5, 117.3, 111.1, 106.5, 35.3, 34.4, 31.3, 29.7. <sup>11</sup>B NMR (128.38 MHz, CDCl<sub>3</sub>) δ (ppm): 6.13. Anal. calculated for C<sub>33</sub>H<sub>34</sub>BNO<sub>2</sub>: C, 81.31; H, 7.03; N, 2.87%; found C, 81.04; H, 6.72; N, 2.51%. EI-MS (*m*/*z*): 487.2 (100).

**HBO borate complex** 7. Beige powder. 94%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 7.73 (d, 1H, CH Ar, J = 8.7 Hz), 7.63 (d, 1H, CH Ar, J = 8.1 Hz), 7.50–7.53 (m, 4H, CH Ar), 7.24–7.41 (m, 8H, CH Ar), 7.01 (d, 1H, CH Ar, J = 7.8 Hz), 6.74 (d, 1H, CH Ar, J = 2.4 Hz), 6.53 (dd, 1H, CH Ar, J = 8.7 Hz), 3.90

(s, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (75.4 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 167.8, 165.6, 161.5, 149.0, 133.4, 133.1, 127.4, 127.3, 126.8, 126.4, 125.7, 117.1, 111.2, 109.0, 103.1, 101.2, 55.7. <sup>11</sup>B NMR (128.38 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 6.08. Anal. calculated for C<sub>26</sub>H<sub>20</sub>BNO<sub>3</sub>: C, 77.06; H, 4.97; N, 3.46%; found C, 76.82; H, 4.69; N, 3.27%. EI-MS (*m*/*z*): 405.0 (100).

HBO borate complex 8. Yellow crystals. 88%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ (ppm): 7.59 (d, 1H, CH Ar, J = 9 Hz), 7.54 (d, 1H, CH Ar, J = 8.1 Hz), 7.47–7.50 (m, 4H, CH Ar), 7.15–7.31 (m, 8H, CH Ar), 6.88 (d, 1H, CH Ar, J = 7.8 Hz), 6.41 (d, 1H, CH Ar, J = 2.7 Hz), 6.28 (dd, 1H, CH Ar, J = 6.6 Hz), 3.44 (q, 4H, CH<sub>2</sub>, J = 7.2 Hz), 1.24 (t, 6H, CH<sub>3</sub>, J = 7.2 Hz). <sup>13</sup>C NMR (75.4 MHz, CDCl<sub>3</sub>) δ (ppm): 164.7, 161.7, 155.1, 148.8, 133.9, 133.1, 127.4, 127.2, 127.1, 126.4, 125.8, 124.5, 116.3, 110.7, 104.8, 99.7, 96.2, 44.8, 12.7. <sup>11</sup>B NMR (128.38 MHz, CDCl<sub>3</sub>) δ (ppm): 5.54. Anal. calculated for C<sub>29</sub>H<sub>27</sub>BN<sub>2</sub>O<sub>2</sub>: C, 78.04; H, 6.10; N, 6.28%; found C, 77.74; H, 5.70; N, 5.88%. EI-MS (*m*/*z*): 446.2 (100).

HBO borate complex 9. Orange powder. 66%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ (ppm): 7.72 (d, 1H, CH Ar, J = 8.1 Hz), 7.60–7.65 (m, 2H, CH Ar), 7.43–7.47 (m, 5H, CH Ar), 7.39 (d, 2H, CH Ar, J = 9 Hz), 7.23–7.30 (m, 7H, CH Ar), 6.99 (d, 2H, CH Ar, J = 8.1 Hz), 6.59 (d, 2H, CH Ar, J = 9 Hz), 3.30 (t, 4H, CH<sub>2</sub>, J = 7.8 Hz), 1.54–1.64 (m, 4H, CH<sub>2</sub>), 1.31–1.43 (m, 4H, CH<sub>2</sub>), 0.97 (t, 6H, CH<sub>3</sub>, J = 7.5 Hz). <sup>13</sup>C NMR (75.4 MHz, CDCl<sub>3</sub>) δ (ppm): 162.8, 161.2, 149.2, 148.5, 141.4, 133.8, 133.4, 133.1, 128.8, 128.8, 127.3, 127.3, 127.2, 127.1, 126.8, 126.7, 126.3, 125.7, 122.5, 122.0, 117.5, 111.4, 111.2, 107.7, 106.7, 96.4, 87.5, 50.7, 29.4, 20.3, 14.0. <sup>11</sup>B NMR (128.38 MHz, CDCl<sub>3</sub>) δ (ppm): 5.41. Anal. calculated for C<sub>41</sub>H<sub>39</sub>BN<sub>2</sub>O<sub>2</sub>: C, 81.72; H, 6.52; N, 4.65%; found C, 81.50; H, 6.38; N, 4.41%. EI-MS (*m/z*): 602.2 (100).

HBO borate complex 10. Yellow crystals. 80%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ (ppm): 7.95 (d, 1H, CH Ar, J = 2.4 Hz), 7.62–7.68 (m, 2H, CH Ar), 7.43–7.46 (m, 5H, CH Ar), 7.35 (d, 2H, CH Ar, J = 9 Hz), 7.15–7.28 (m, 7H, CH Ar), 7.01 (d, 2H, CH Ar, J = 8.1 Hz), 6.59 (d, 2H, CH Ar, J = 9 Hz), 3.29 (t, 4H, CH<sub>2</sub>, J = 7.8 Hz), 1.54–1.64 (m, 4H, CH<sub>2</sub>), 1.27–1.43 (m, 4H, CH<sub>2</sub>), 0.97 (t, 6H, CH<sub>3</sub>, J = 7.2 Hz). <sup>13</sup>C NMR (75.4 MHz, CDCl<sub>3</sub>) δ (ppm): 161.4, 159.9, 148.2, 146.9, 139.4, 132.2, 132.0, 131.7, 128.0, 127.5, 127.2, 126.4, 125.9, 125.8, 125.5, 124.3, 116.7, 114.2, 110.5, 110.2, 107.5, 107.1, 89.2, 84.6, 49.7, 28.4, 19.3, 13.0. <sup>11</sup>B NMR (128.38 MHz, CDCl<sub>3</sub>) δ (ppm): 5.74. Anal. calculated for C<sub>41</sub>H<sub>39</sub>BN<sub>2</sub>O<sub>2</sub>: C, 81.72; H, 6.52; N, 4.65%; found C, 81.58; H, 6.37; N, 4.37%. EI-MS (*m/z*): 602.2 (100).

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- 15 Crystallographic data for complex 8: C<sub>29</sub>H<sub>27</sub>BN<sub>2</sub>O<sub>2</sub>, Mr = 446.34, colourless block, 0.39  $\times$  0.35  $\times$  0.18 mm, monoclinic, space group  $P2_1/c$  (no 14), a = 14.4020(2) Å, b =8.9147(1) Å, c = 18.3569(12) Å,  $b = 92.158(7)^{\circ}$ , V =2355.16(16) Å<sup>3</sup>, Z = 4,  $r_{calcd}$  = 1.259 g cm<sup>-3</sup>,  $2q_{max}$  = 136.48°, 12 222 measured reflections, 4253 independent,  $-17 \leq h \leq 14, -10 \leq k \leq 6, -22 \leq l \leq 19, R_{(int)} =$ 0.0474,  $\mu = 0.615 \text{ mm}^{-1}$ , multi-scan absorption correction,  $T_{\min}$  = 0.751 and  $T_{\max}$  = 0.895, 310 parameters were refined against all reflections,  $R_1 = 0.0735$ ,  $wR_2 = 0.1296$  based on all observed F values,  $R_1 = 0.0530$ ,  $wR_2 = 0.1119$  (3059 reflections with I > 2s(I),  $Dr_{\min}$  and  $r_{\max} = -0.216$  and 0.185 e<sup>-3</sup>, extinction coefficient 0.00214(18), GOF = 1.126 based on  $F^2$ . Crystallographic data for complex 10:  $C_{41}H_{39}BN_2O_2$ , Mr = 602.55, pale yellow triangular plate, 0.58  $\times$  0.26  $\times$ 0.12 mm, orthorhombic, space group *Pbca* (no 61), a =18.9987(3) Å, b = 14.3343(3) Å, c = 25.2809(17) Å, V =6884.8(5) Å<sup>3</sup>, Z = 8,  $r_{\text{calcd}}$  = 1.163 g cm<sup>-3</sup>,  $2q_{\text{max}}$  = 136.5°, 20 818 measured reflections, 6262 independent,  $-22 \le h \le$ 22,  $-8 \leq k \leq$  17,  $-22 \leq l \leq$  29,  $R_{(int)}$  = 0.0274,  $\mu$  =  $0.547 \text{ mm}^{-1}$ , multi-scan absorption correction, relative  $T_{\min}$ = 0.719 and  $T_{\text{max}}$  = 0.936, 437 parameters were refined against all reflections,  $R_1 = 0.0980$ , w $R_2 = 0.2191$  based on all observed F values,  $R_1 = 0.0612$ ,  $wR_2 = 0.1641$  (3965 reflections with I > 2s(I)), 87 soft restraints on bond lengths,  $Dr_{\min}$  and  $r_{\max} = -0.279$  and 0.401 e<sup>-3</sup>, GOF = 1.165 based on  $F^2$ . CCDC 891069 (complex 8) and CCDC 891070 (complex 10)<sup>†</sup>.
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- 19 C. Goze, G. Ulrich, L. J. Mallon, B. D. Allen, A. Harriman and R. Ziessel, *J. Am. Chem. Soc.*, 2006, **128**, 10231.
- 20 Luminescence lifetimes were measured on an Edinburgh Instruments spectrofluorimeter equipped with a R928 photomultiplier and a PicoQuant PDL 800-D pulsed diode connected to a GwInstec GFG-8015G delay generator. No filter was used for the excitation. Lifetimes were deconvoluted with FS-900 software using a light-scattering solution (LUDOX) for instrument response.