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# Synthesis of Luminescent 2-(2′-Hydroxyphenyl)benzoxazole (HBO) Borate Complexes

Julien Massue,[†] Denis Frath,[†] Gilles Ulrich,*[,†] Pascal Retailleau,[‡] and Raymond Ziessel*[,†]

*Laboratoire de Chimie Organique et Spectroscopies Avancées (LCOSA), UMR 7515 CNRS, Ecole de Chimie, Polymères, Matériaux de Strasbourg (ECPM), 25 rue Becquerel, 67087 Strasbourg, Cedex 02, France, and Laboratoire de Crystallochimie, ICSN - CNRS, Bât. 27- 1 avenue de la Terrasse, 91198 Gif-sur-Yvette, Cedex, France*

*gulrich@unistra.fr; ziessel@unistra.fr*

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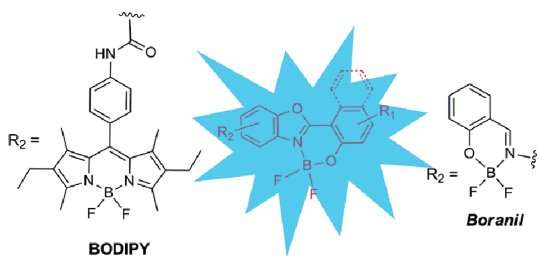
## ABSTRACT




**Complexation of boron trifluoride by a series of electron donor/acceptor substituted 2-(2′-hydroxy phenyl)benzoxazole (HBO) derivatives yields luminescent B(III) complexes with an emission wavelength ranging from 385 to 425 nm in dichloromethane or toluene. Appropriate chemical functionalization of these new dyes allows connection to different photoactive subunits (*Boranil,* BODIPY), endowing an efficient cascade energy transfer.**

Fluorophores incorporating a four-coordinate boron bound to a $\pi$-conjugated chelate have been extensively studied for various applications ranging from biological sensing and imaging to the search for new electroluminescent devices.[1] Among them, boron dipyrromethene (BODIPY) dyes have emerged as very promising due to their outstanding chemical and photophysical properties.[2] In addition to these extensively studied derivatives, new chelating groups for the B(III) fragment have recently emerged in the literature; prominent examples include N^O bidentate $\pi$-conjugated fragments coordinated to various boron-containing entities such as $BF_2$, $B(Ar)_2$, $B(ArF_5)_2$, and $B(OAr)_2$.[3]

2-(2′-Hydroxyphenyl)benzoxazole (HBO) derivatives, known for over 40 years,[4] are an interesting class of fluorophores due to their intrinsic Excited-State Intramolecular Proton Transfer (ESIPT) property which leads to a major structural reorganization of the molecules upon photoexcitation and large Stokes shifts. This interesting feature has found applications for pH sensing, chemical detection of divalent metal cations,[5] and anion sensing, including that of pyrophosphate[6] and fluoride.[7] HBO-based

[†] LCOSA, ECPM, CNRS.
[‡] Laboratoire de Crystallochimie, ICSN - CNRS.

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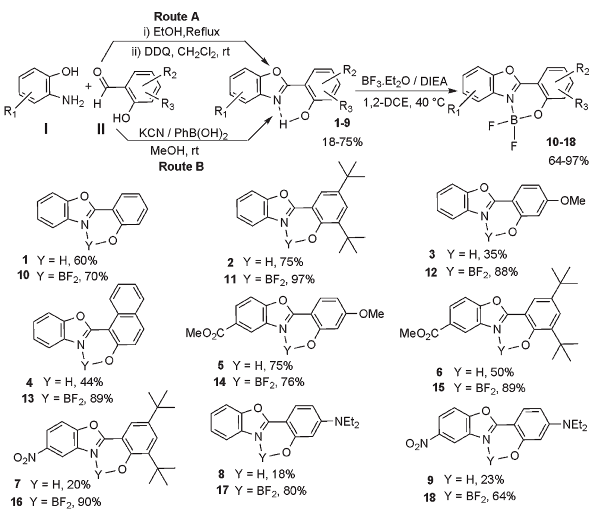
dyes are also excellent N^O chelates for various metallic centers such as Re(I),[8] Ru(II),[9] Ir(III),[10] Be(II),[11] Sc(III),[12] and Ln(III),[13] chosen with the objective of obtaining new optically tunable luminescent materials. Since, to the best of our knowledge, there is only one literature report of the coordination of a $BF_2$ fragment to 2-(2′-hydroxyphenyl)-benzoxazole,[14] the influence of molecular engineering on the photoluminescent properties of such tetrahedral boron complexes still needs to be explored.

Here, we report on the two-step preparation of a series of neutral tetrahedral B(III) complexes bearing various electron-donating/-withdrawing substituents that enable modulation of the photophysical properties. We show also that these new dyes can be connected to other photoactive subunits such as BODIPY or *Boranil* cores to afford sophisticated molecular cassettes. Preparation of the substituted 2-(2′-hydroxyphenyl)benzoxazole (HBO) **1**−**9** derivatives and their corresponding B(III) complexes **10**−**18** is summarized in Scheme 1. Depending on the nature of the substituents present on the core of the starting substituted 2-aminophenol **I** and 2-hydroxybenzaldehyde **II**, two different routes were chosen. Route A involved heating **I** and **II** together in ethanol at reflux to give the cyclic carbinolamines, which precipitated from the reaction mixture. After collection, these compounds were oxidized with a slight excess of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ). The milder one-pot Route B, used when oxidation-sensitive substituents were present, such as diethylamino groups, required potassium cyanide to promote benzoxazole cyclization in the presence of phenylboronic acid.[15]

**Scheme 1.** Synthesis of Substituted 2-(2′-Hydroxyphenyl)-benzoxazole (HBO) **1**−**9** Derivatives and Their Corresponding B(III) Complexes **10**−**18**

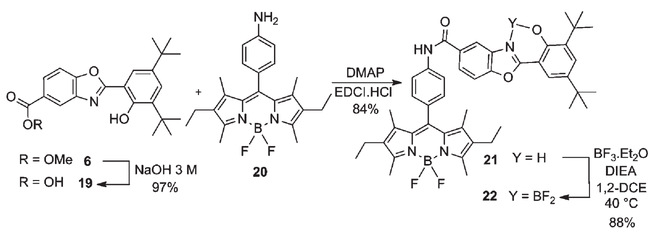



HBO dyes **1**−**9** display a distinctive downfield $^1H$ NMR signal (11 to 13 ppm) for the H-bonded phenolic proton (see Supporting Information (SI) for full characterization).

Boron complexation was achieved using $BF_3 \cdot Et_2O$ in the presence of *N*,*N*-diisopropylethylamine (DIEA) in anhydrous 1,2-dichloroethane to yield B(III) complexes **10**−**18** as off-white powders after purification by filtration through a basic $Al_2O_3$ column. The complexation reaction can be readily monitored by the loss of the downfield proton signal as well as the appearance of a triplet in the $^{11}B$ NMR spectrum (see SI) due to coupling with two equivalent fluorine nuclei ($J_{B-F}$ ~10 Hz). Note that the coupling constant is significantly lower than those reported for similar fluorescent B(III) dyes (in the range of $J_{B-F}$ = 33 Hz for BODIPY[16] and 16 Hz for *Boranil*[17] dyes).

Building upon this straightforward manner to obtain a series of luminescent HBO-based complexes, we decided to investigate their connection to other photoactive subunits.

**Scheme 2.** Synthesis of Dye **22**




Carboxylic acid functionalized derivative **19** was readily obtained from HBO **6** by a simple saponification step using a 3 M NaOH solution. Peptidic coupling of BODIPY **20**[18] bearing an aminophenyl group on position 8 with **19** proceeded under standard conditions (DMAP, EDCI). Complexation of the resulting dye **21** with $BF_3 \cdot Et_2O$ afforded, in 88% yield, the highly soluble dye **22** incorporating the two photoactive units of interest (Scheme 2).

*Boranil* dyes are also very promising fluorescent N^O chelates for a $BF_2$ fragment.[17] Functionalization of the HBO ring with a *boranil* core requires 3 steps (Scheme 3).

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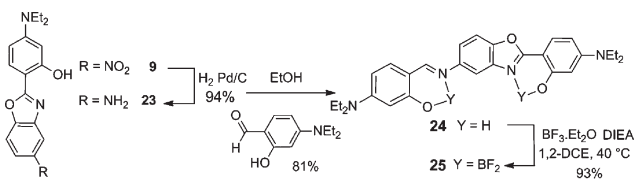
Selectively reduction of the nitro group of HBO **9** under standard conditions afforded compound **23**, which was further condensed with 2-hydroxy-4-diethylamino benzaldehyde in refluxing ethanol with a trace amount of *p*-TsOH to afford the desired imine **24**. Both N^O chelating sites react with excess $BF_3 \cdot Et_2O$ under basic conditions to yield soluble, stable dyad **25** in 93% yield.

**Scheme 3.** Synthesis of the Dyad **25**




The X-ray molecular structures of **12** and **13** are depicted in Figures 1 and 2, respectively, with selected geometric values.

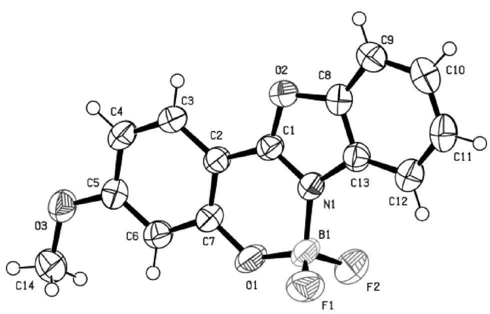



**Figure 1.** ORTEP view for **12** showing the atom-labeling scheme. Thermal ellipsoids are plotted at the 50% level. B1−N1, B1−O1, N1−C1, and N1−C13 bond lengths are 1.576(3), 1.444(3), 1.317(2) and 1.408(2) Å, and the N−B−O, N−B−F, and O−B−F angles are 108.01(17)°, 108.17(18)°/109.23(18)°, and 110.25(19)°/111.13(19)°.

In both, all the atoms are coplanar (with an overall rmsd of 0.0429 and 0.0202 Å respectively) except for the fluorines, which contribute to the fairly regular tetrahedral geometry of the boron center (with angles ranging from 107.9(2)° and 110.3 (2)° and from 108.9(2)° and 110.5(2)° in **12** and **13**, respectively). Unlike the 9 structures of difluorobenzooxazaborinin derivatives found to date in the CSD,[19] planarity appears to be imposed in the present instance by the fact that the N1−C1 bond is part of a five-membered ring. The crystal packing of both molecules is described in detail in the SI.

Photophysical data in toluene and dichloromethane for all the new fluorophores are gathered in Table 1.

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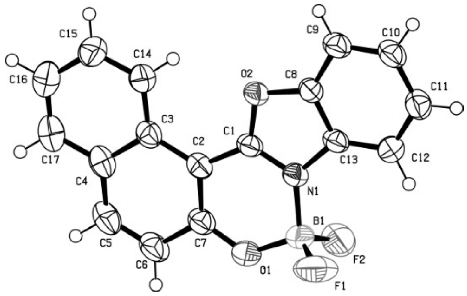


**Figure 2.** ORTEP view for **13** showing the atom-labeling scheme. Thermal ellipsoids are plotted at the 50% level. B1−N1, B1−O1, and N1−C13 bond lengths are 1.560(3), 1.441(3), and 1.405(2) Å, and the N−B−O, N−B−F, and O−B−F angles are 107.57(17)°, 108.84(17)°/109.5(2)°, and 109.9(2)°/110.41(19)°.

The absorption spectra of complexes **10**−**16** exhibit a major absorption band between 336 and 375 nm with extinction coefficients in the range 13 000−30 000 $M^{-1}$ $cm^{-1}$, whereas complexes **17**−**18** bearing a diethylamino group on the phenolic side have a red-shifted absorption maximum (385−401 nm) along with higher extinction coefficients (60 000 to 80 000 $M^{-1} \cdot cm^{-1}$). Irradiation in the lower energy absorption band gives rise to an intense emission band in the 385−439 nm range. These dyes exhibit quantum yields in the range 17−73% with good chemical and photochemical stability in apolar media.

In strong contrast, for **16** and **18** the fluorescence is heavily quenched, likely by a photoinduced electron transfer (PET) process with the neighboring nitro group.[20] Note that dissolving these complexes in polar solvents such as alcohols or DMSO leads to decomplexation of boron, as shown by the recovery of the typical ESIPT emission of the HBO ligand.[21]

The broad shape of the emission band for complexes **10**−**15**, the nonmirror symmetry with the absorption bands, and a significant Stokes shift (3300 to 4900 $cm^{-1}$) are suggestive of an intraligand charge transfer (ICT) emissive state (Figure 3a).[22] Furthermore, the nanosecond lifetime regime is in keeping with such a polarized excited state. In the case of dye **17**, bearing a diethylamino moiety, a structured, narrow, blue-shifted emission band along with a reduced Stokes shift (600 to 900 $cm^{-1}$) is observed, consistent with a weakly polarized excited state with pronounced singlet state character (Figure 3b). In this case, pronounced internal cyanine character from the diethylamino group to the imine moiety coordinated to the boron is suggested.[23] Interestingly, in the case of the naphthyl dye

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**Table 1.** Selected Optical Data Measured in Solution

| dye | $\lambda_{abs}$ (nm) | $\varepsilon$ ($M^{-1}.cm^{-1}$) | $\lambda_{em}$ (nm) | $\Delta$ ($cm^{-1}$) | $\Phi_f$ [a] | $\tau$ (ns) | solvent |
|---|---|---|---|---|---|---|---|
| **10** | 349 | 15600 | 401 | 3700 | 0.26 | 1.26 | Toluene |
| | 344 | 16100 | 395 | 3800 | 0.22 | 0.93 | $CH_2Cl_2$ |
| **11** | 362 | 13000 | 417 | 3600 | 0.36 | 2.03 | Toluene |
| | 359 | 13700 | 422 | 4300 | 0.31 | 2.19 | $CH_2Cl_2$ |
| **12** | 342 | 29700 | 385 | 3300 | 0.48 | 1.40 | Toluene |
| | 339 | 33200 | 380 | 3200 | 0.39 | 1.39 | $CH_2Cl_2$ |
| **13** | 375 | 20700 | 422 | 3000 | 0.17 | 2.19 | Toluene |
| | 373 | 19700 | 425 | 3300 | 0.28 | 1.63 | $CH_2Cl_2$ |
| **14** | 342 | 29200 | 387 | 3400 | 0.36 | 1.45 | Toluene |
| | 341 | 29700 | 384 | 3300 | 0.37 | 1.36 | $CH_2Cl_2$ |
| **15** | 365 | 11300 | 425 | 3900 | 0.73 | 2.85 | Toluene |
| | 364 | 13100 | 432 | 4300 | 0.58 | 3.36 | $CH_2Cl_2$ |
| **16** | 371 | 12700 | 439 | 4200 | 0.02 | 0.11 | Toluene |
| **17** | 385 | 79300 | 395 | 660 | 0.43 | 1.47 | Toluene |
| | 387 | 67200 | 401 | 900 | 0.42 | 2.92 | $CH_2Cl_2$ |
| **18** | 399 | 59600 | [b] | - | - | - | Toluene |
| **21** | 347 | 17100 | 538 | 1000 | 0.63 | 6.14 | $CH_2Cl_2$ |
| | 526 | 50400 | 538 | 4200 | 0.64 | | |
| **22** | 366 | 18200 | 537 | 8700 | 0.93 | 6.76 | $CH_2Cl_2$ |
| | 526 | 53700 | 537 | 390 | 0.95 | | |
| **25** | 414 | 106200 | 473 | 3000 | 0.62 | 1.45 | $CH_2Cl_2$ |

[a] Quantum yields determined in solution, using quinine sulfate as reference $\phi = 0.55$ in $H_2SO_4$ 1 N, $\lambda_{ex} = 366$ nm for dyes emitting below 480 nm and Rhodamine 6G $\phi = 0.88$ in ethanol, $\lambda_{ex} = 488$ nm for dyes emitting between 480 and 570 nm. [b] non fluorescent.

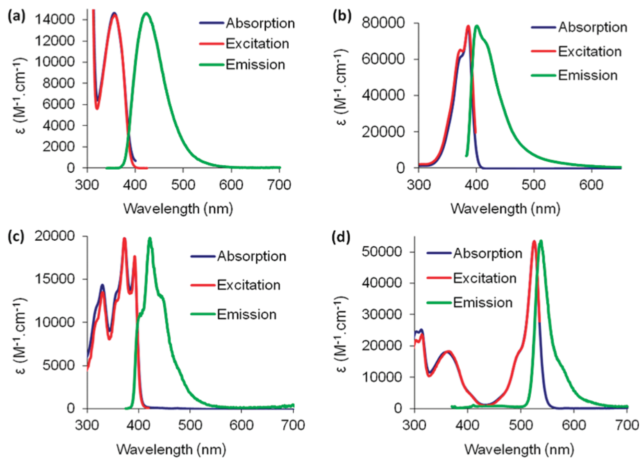


**Figure 3.** Absorption, emission, and excitation of dyes (a) **11**, (b) **17**, (c) **13**, and (d) **22** in $CH_2Cl_2$ at rt.

**13**, the molecular core is more rigid and vibronic structure is observed in the absorption and emission spectra, a situation in favor of a singlet excited state decay. The short lifetime and weak Stokes shift are in keeping with this (Figure 3c).

In the case of the dyad **22**, the absorption spectrum is a linear combination of those of the BODIPY core and the HBO borate subunit, a situation favored by the orthogonality of the two fragments.[24] By excitation of mixed dye **22** at 366 nm, insignificant residual emission of the HBO fragment was observed at 420 nm (Figure 3d) but strong emission of the BODIPY subunit at 537 nm ($\phi_{em} = 0.93$ in $CH_2Cl_2$) was observed, indicating a 98% efficiency in energy transfer from the HBO borate to the BODIPY moiety. The perfect match between absorption and excitation over the entire wavelength range confirms the efficiency and the participation of the HBO borate residue in the energy transfer process. This favorable situation is a consequence of the spectral overlap between the emission of the HBO and the absorption of the second excited state of the BODIPY fragment.[25]

Another interesting situation is generated in the case of the mixed dyad **25** which exhibits a high extinction coefficient (> 100 000 $M^{-1}\cdot cm^{-1}$) and strong emission at 473 nm with a quantum yield of 62% (Table 1).

In summary, we have synthesized a series of novel fluorescent boron complexes by chelation of HBO platforms featuring interesting spectroscopic properties in nonpolar solvents. Current work is focused on investigating their electrochemical properties in solution and optical properties in the solid state with the goal to embed them into optoelectronic devices.

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**Supporting Information Available.** Synthetic procedures, NMR spectra, crystallographic and spectroscopic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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