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# 2-(2′-Hydroxyphenyl)benzimidazole and 9,10-Phenanthroimidazole Chelates and Borate Complexes: Solution- and Solid-State Emitters

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## ABSTRACT

**The synthesis, structural, and optical properties of a series of luminescent N-alkylated 2-(2′-hydroxyphenyl)benzimidazole (HBI) or N-arylated 9,10-phenanthroimidazole (HPI) borate complexes are described. The optical properties of these complexes as well as their corresponding ligands were evaluated in solution and the solid state. Efficient emission in the blue-green region was obtained with quantum yields up to 91% in $CH_2Cl_2$ and 27% in the solid state. These emissions originate from excited state intramolecular proton transfer (ESIPT) for the ligands and from a singlet excited state for the borate complexes.**

The emergence of new and specific technological demands of efficient fluorophores for various applications ranging from biological labeling to organic electronics is pushing numerous researchers to investigate new fluorescent systems. These new functional fluorescent dyes should possess overstandard chemical and photochemical stability, high absorption coefficient and quantum yields, as well as a tunability of both absorption and emission bands, which allow them to fit the application requirements. Reaching most of the desired features, the boron dipyrromethene (BODIPY) family is nowadays one of the leading fluorescent systems. Its peculiar properties arise from the rigidification of a cyanine backbone by boron(III) complexation.[1] But they suffer from some drawbacks, such as very small Stokes' shifts and weak solid-state emission. The BODIPY need to be decorated with peripheral bulky substituents in order to avoid significant aggregation-caused quenching (ACQ), despite high-quantum yields in the solution phase.[2] The borate chelation strategy has been recently extended with success to tetrahedral complexes incorporating N^N[3] or N^O[4] chelates. These compounds

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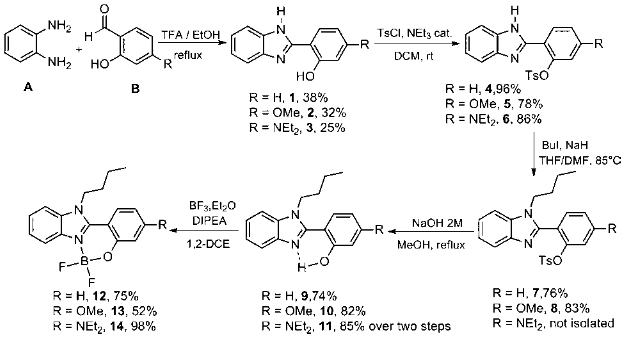
have shown pronounced Stokes'shifts (difference between the lowest energy band in the absorption spectrum and the highest energy band in the emission spectrum) due to the dissymmetrical character of the ground state vs the excited state.[5] Moreover, several examples of boron difluoride ($BF_2$) complexes have been reported to intrinsically exhibit intense luminescence as powders, crystals, and embedded in films.[6] Obtaining solid-state luminescent emitters is propelled by applications ranging from organic light-emitting diodes (OLEDs)[7] and luminescent displays[8] to solid-state lasers[9] and fluorescent sensors.[10] Aprahamian and co-workers showed that the solid-state fluorescent quantum yield of $BF_2$−hydrazone complexes depends on several parameters: (1) the planarity of the molecule, (2) the dipole moment, and (3) the number of $\pi-\pi$ interactions between neighboring dyes.[11] The key factor to design efficient solid-state molecular emitters is the elimination of parameters inducing concentration quenching in aggregated states. We recently reported the synthesis of tetrahedral boron complexes based on 2-(2′-hydroxyphenyl)benzoxazole (HBO) core. These luminescent complexes show interesting optical properties both in solution and the solid-state.[12]

Here, we report on the preparation of a series of N-alkylated 2-(2′-hydroxyphenyl)benzimidazole (HBI) or 2-(2′-hydroxyphenyl)-9,10-phenanthroimidazole (HPI) and their corresponding $BF_2$ complexes. To the best of our knowledge, there is only one report describing related HBI borate complexes with no photophysical investigations.[13] We show that these chelates and their $BF_2$ complexes display attractive luminescent properties both in solution and in the solid state. We also demonstrate that these dyes can be connected to a BODIPY subunit leading to sophisticated molecular dyads.

**Scheme 1.** Synthesis of HBI Dyes **9-11** and Their Borate Complexes **12−14**



Preparation of the substituted HBI **9−11** and their corresponding boron complexes **12−14** is shown in Scheme 1. To construct the benzimidazole core, *o*-phenylenediamine **A** was condensed with 4-substituted salicylaldehydes **B** in refluxing ethanol overnight with acidic catalysis to provide benzimidazoles **1−3** in 25−38% yield. Protection of the phenol with tosyl chloride in the catalytic presence of a base was easily achieved in dichloromethane at rt to give benzimidazoles **4−6** in 78−96% yield. Subsequent alkylation using butyl iodide in THF/DMF in the presence of sodium hydride followed by tosyl deprotection in basic conditions afforded N^O chelates **9−11** which displayed a distinctive downfield $^1$H NMR signal for the H-bonded phenolic proton (see the Supporting Information for full characterization). Note that these compounds are fluorescent in the solid-state due to an intrinsic excited-state intramolecular proton transfer (ESIPT) process.[14] Boron complexation was achieved using an excess of $BF_3 \cdot Et_2O$ in 1,2-DCE in the presence of a base. Purification by filtration on basic $Al_2O_3$ afforded HBI borate complexes **12−14** in 52−98% yield.

HPI **15** and **16** were obtained in a one-step reaction[15] of 9,10-phenanthrenedione **C**, benzaldehyde **D**, and 4-methyl- or 4-iodoaniline with ammonium acetate in acetic acid at reflux in 34 and 19% yield, respectively. HPI **15** (R = I) was then coupled with 4-*tert*-butylphenylacetylene or ethynyl-BODIPY under Sonogashira cross-coupling reaction conditions ($PdCl_2(PPh_3)_2$ 10%, CuI 5% in toluene/$NEt_3$) to yield HPI **18** and **19** in 73 and 56% yield, respectively. Subsequent boron complexation using $BF_3 \cdot Et_2O$ under basic conditions of **15** (R = Me), **18** ($R = -PhC{\equiv}CPh^tBu$) and **19** ($R = -PhC{\equiv}CPh$BODIPY) afforded HPI borate complexes **17**, **20**, and **21** in 72, 75, and 40% yield, respectively (Scheme 2).

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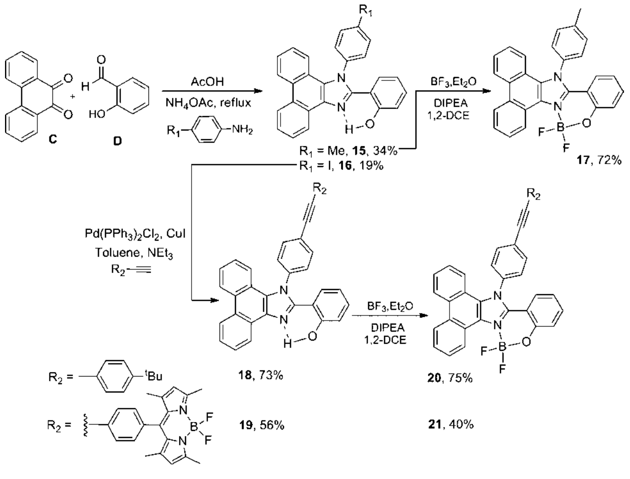
**Scheme 2.** Synthesis of HPI dyes **15**, **18**, and **19** and Their Borate Complexes **17**, **20**, and **21**



The X-ray molecular structures of HPI dye **15** and HBI borate complex **14** are depicted in Figures 1 and 2, respectively, with selected geometric values.

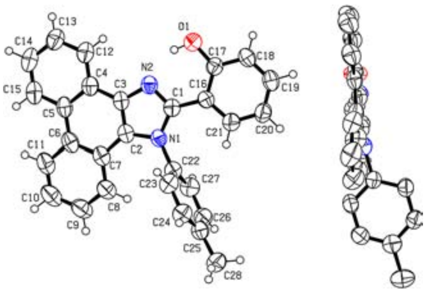


**Figure 1.** (Left) ORTEP view for **15** showing the atom-labeling scheme. Thermal ellipsoids are plotted at the 50% level. (Right) perpendicular view to highlight the slightly concave distortion of the pentacyclic platform enforced by the tolyl substitution at N1. C22−N1−C2 and C3−N2−C1 angles are 124.23(17) and 105.63(17)°.

In **15**, the phenol group is coplanar with the HPI cycle via an intramolecular H-bond interaction between the O1H1 hydroxyl group and one of the nitrogen N2 atoms of the imidazole fragment, with the tolyl group being almost perpendicular (dihedral angle of 88.0°). This contributes to the overall relative planarity of the 24-atom platform. In **14**, the apparent distortion of the HBI core, characterized by the meaningful dihedral angle value of 18.0° between the phenolate and the benzimidazole cycles, is likely due to the butyl and trans diethylamino group substitution. The boron center displays a fairly regular tetrahedral geometry. The B1−O1 and B1−N1 bonds (1.453 and 1.552 Å) are similar to the borate complexes of benzazole.[12] In the crystal structure, the molecular arrangement is similar to corrugated layers parallel to the (−3 0 2) plane (see the Supporting Information for a full description of the molecular packing).

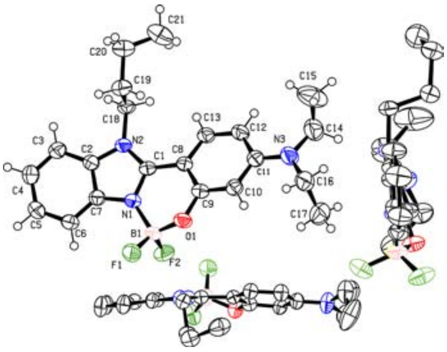


**Figure 2.** (Left) ORTEP view for **14** showing the atom-labeling scheme. Thermal ellipsoids are plotted at the 50% level. (Right) perpendicular view to highlight the distortion at the B atom. H-atoms are omitted for clarity. B1−N1, B1−O1, C1−N1/C1−N2, and N1−C7 bond lengths are 1.552(4), 1.453(3), 1.352(3)/1.348(3), and 1.395(3) Å, and the N1−B1−O1, O1−B1−F1/2, and N1−B1−F1/2 angles are 107.5(2), 108.8(2)/111.6(2), and 109.4(2)/109.3(2)°.

Photophysical data in solution and in the solid-state (dispersed in KBr pellets) for all compounds are gathered in Table 1 (in $CH_2Cl_2$) and Table S1, Supporting Information (in toluene).

All compounds absorbed in the UV-A region with relatively high absorption coefficients, as expected for $\pi-\pi^*$ transitions of polyaromatics. In the dyad cases (**19**, **21**), an additional absorption band due to the BODIPY moiety is observed at ca. 500 nm. More structured vibronic bands are observed for the HPI family, as expected for extended and rigid conjugated structures. A hyperchromic effect appears when electrodonating groups (e.g., diethylamino) are inserted on the phenol side of HBI dyes.

Two main photophysical phenomena are observed for the emission. For the HBO ligands, an ESIPT process, characteristic of hydroxybenzazole family is responsible for the large Stokes' shifts $\Delta_{SS}$ (Figure 3a,b).[14,16] Indeed, the tautomerization in the excited state leads to the excited keto form (K*) responsible of the lower energy emission. The emission derived from the excited enol form (E*) is weakly observed as a small shoulder in 360−400 nm region and is enhanced in solvents with stronger dipolar moments (Figure 3a and Figure S3, Supporting Information).[16] The emissions of the K* state have a nanosecond scale lifetime, and the quantum yields are relatively good in the case of **11** (21% and 12% in toluene and $CH_2Cl_2$ respectively), due to the strong donor group on the phenol side and in the case of the HPI systems **15** (25 and 15% in toluene and $CH_2Cl_2$ respectively) (Figure 3). For the latter, the extended delocalization and the steric restriction of rotational deactivation reduce the nonradiative deactivation.[17]

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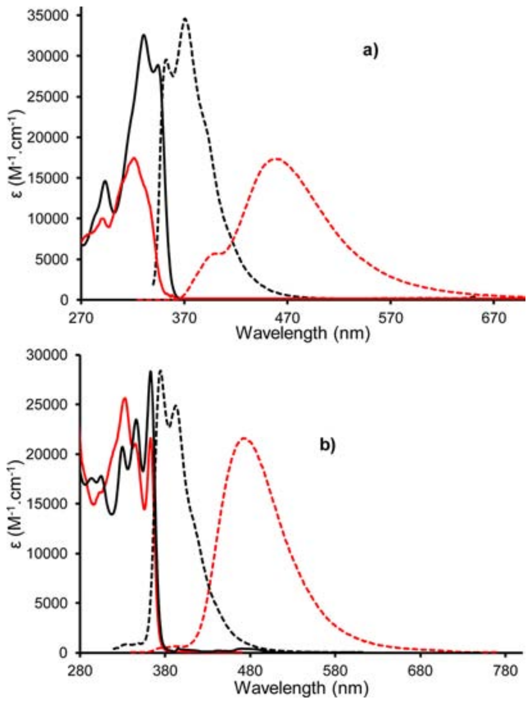

**Figure 3.** (a) Absorption (plain) and emission (dotted) spectra of **10** (red) and **13** (black). (b) Absorption (plain) and emission (dotted) spectra of **15** (red) and **17** (black) in $CH_2Cl_2$ at rt.

The borate complexes show efficient emissions (up to $\Phi$ = 91%) with relatively fine and structured emission bands (Figure 3), a lifetime of ca. 1.5 ns, and a Stokes' shift between 350 and 2000 $cm^{-1}$ (with exception for **12**). The emissions are mirror image of the absorptions (Figure 3), and no modification was observed in deaerated solvents. These compounds seem to emit preferentially from a singlet excited state rather than a low-lying excited state with a internal charge transfer (ICT) character as previously observed with HBO-borate complexes.[12] As expected, in light of their emissive properties, the HBI and HPI borate act both as efficient light-harvesting antennas in dyads **19** and **21** (see Figures S23–S26, Supporting Information). The excitonic energy transfer (EET) is almost quantitative leading to the unique emisson of the BODIPY subunit when exciting at 360 nm. The efficient overlap of the antenna emission with the BODIPY absorption, as well as the short distance between both chromophores explain the strength of the energy transfer. Interestingly, most of the compounds exhibit a non-negligible solid-state emission, with $\Phi_F$ up to 26–28% for **12** and the HPI and HPI borate derivatives (see Figures S27–S36, Supporting Information). For HPI **15**, the crystal packing shows almost no $\pi$–$\pi$ intermolecular orbital overlap, this is probably one of the factors accounting for a good solid state quantum yield.[17]

**Table 1.** Optical Data Measured in Aerated Solution and in the Solid State

| dye | $\lambda^a$(max) (nm) | $\varepsilon$ ($M^{-1}.cm^{-1}$) | $\lambda_{em}$ (max) (nm) | $\Delta$ ($cm^{-1}$) | $\Phi_F{}^b$ | $\tau$ (ns) | matrix |
|---|---|---|---|---|---|---|---|
| **9** | 338 | 14500 | 387 | 3700 | 0.25 | 1.04 | $CH_2Cl_2$ |
| | 372 | | 415 | 2800 | 0.04 | 0.41/2.90 | solid$^c$ |
| **10** | 322 | 17400 | 458 | 9200 | 0.03 | 1.75 | $CH_2Cl_2$ |
| | 333 | | 465 | 8500 | 0.03 | 1.23/2.93 | solid |
| **11** | 346 | 39300 | 444 | 6400 | 0.12 | 1.78 | $CH_2Cl_2$ |
| | 371 | | 447 | 4600 | 0.04 | 0.2/0.98 | solid |
| **12** | 334 | 19700 | 382 | 3800 | 0.32 | 0.99 | $CH_2Cl_2$ |
| | 366 | | 389 | 1600 | 0.26 | 1.69 | solid |
| **13** | 331 | 32600 | 371 | 745 | 0.65 | 1.28 | $CH_2Cl_2$ |
| | 352 | | 394 | 3100 | 0.04 | 0.28/1.7 | solid |
| **14** | 375 | 71600 | 393 | 1200 | 0.13 | 1.94 | $CH_2Cl_2$ |
| | 394 | | 409 | 900 | 0.07 | 0.34/1.62 | solid |
| **15** | 363 | 25700 | 472 | 6400 | 0.15 | 1.51 | $CH_2Cl_2$ |
| | 379 | | 473 | 5200 | 0.12 | 0.46/1.64 | solid |
| **17** | 363 | 28400 | 393 | 662 | 0.91 | 1.63 | $CH_2Cl_2$ |
| | 383 | | 429 | 1420 | 0.17 | 0.47/1.39 | solid |
| **18** | 362 | 21300 | 489 | 7200 | 0.08 | 0.77 | $CH_2Cl_2$ |
| | 374 | | 474 | 5600 | 0.28 | 0.22/3.24 | solid |
| **19** | 362/502 | 77300 | 513 | 430 | 0.25 | 2.26 | $CH_2Cl_2$ |
| | 370 | | 473 | 5900 | | 0.38 | solid |
| **20** | 364 | 20700 | 393 | 2000 | 0.53 | 1.86 | $CH_2Cl_2$ |
| | 373 | | 473 | 2000 | 0.27 | 0.63/2.42 | solid |
| **21** | 363/502 | 74500 | 513 | 430 | 0.24 | 2.30 | $CH_2Cl_2$ |
| | 380 | | 441 | 3600 | | 0.76 | solid |

[a] $\lambda$ denotes $\lambda_{abs}$ for solution-state absorption or $\lambda_{exc}$ for solid-state excitation. [b] Quantum yields determination: in solution, using quinine sulfate as reference $\Phi$ = 0.55 in $H_2SO_4$ (1 N), excitation at 366 nm for dyes emitting below 480 nm or rhodamine 6G, $\Phi$ = 0.88 in ethanol, excitation at 488 nm for dyes emitting between 480 and 570 nm; in the solid-state at a concentration of around $10^{-4}$ M. [c] Recorded in KBr pellets.

In summary, we have prepared an original series of N-alkylated 2-(2′-hydroxyphenyl)benzimidazole (HBI) or 2-(2′-hydroxyphenyl)-9,10-phenanthroimidazole (HPI) and their corresponding $BF_2$ complexes and studied their optical properties. The ligands exhibit fluorescence which originates from an ESIPT and the borate complexes from a singlet excited state (no boron decomplexation of the dyes has been observed during the photophysical studies). They show intense fluorescence in solution and in the solid state. These series of compounds are of paramount importance for the design of efficient blue emitters, suitable for various applications: as antenna for cassette systems or as blue solid-state emitters.

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**Supporting Information Available.** Synthetic procedures, $^1H$ and $^{13}C$ NMR spectra, and crystallographic and spectroscopic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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The authors declare no competing financial interest.