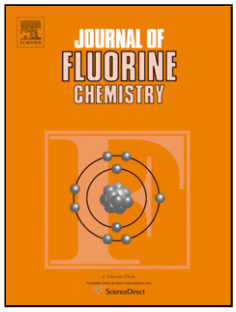

Title: Synthesis, structure and photoluminescent properties of BF_2 and BPh_2 complexes with N,O-benzazine ligands

Author: Emiliya V. Nosova Tatyana N. Moshkina Galina N. Lipunova Inna V. Baklanova Pavel A. Slepukhin Valery N. Charushin

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- BF_2 and BPh_2 complexes of 8-OH-2-Me-quinolines and 2-(2-HOC_6H_4)-quinazolinones were prepared
- Structure of complexes was confirmed by MS, ^{1}H, ^{19}F, ^{11}B NMR and X-ray
- 2-Methyl-8-hydroxyquinolines BPh_2 complexes surpass their BF_2 analogs in quantum yield
- BF_2 complex of 2-(2-OH-3,5-di(t-Bu)phenyl)-3H-quinazolin-4-one exhibits the best fluorescence

Synthesis, structure and photoluminescent properties of BF_2 and BPh_2 complexes with N,O-benzazine ligands

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Abstract

Novel N,O-bidentate BF_2 and BPh_2 complexes have been prepared in good to excellent yields through coordination of 8-hydroxy-2-methylquinolines and 2-(2-hydroxyphenyl)-3H-quinazolin-4-ones with boron trifluoride etherate or triphenylborane under mild conditions. All complexes have been characterized by ^{1}H, ^{11}B and ^{19}F NMR, mass-spectrometry and X-ray crystallography data. Some complexes have been found to exhibit a significant fluorescence in acetonitrile solutions. Electronic and site effects of substituents in both heterocyclic and phenol fragments proved to have a profound impact on quantum yields.

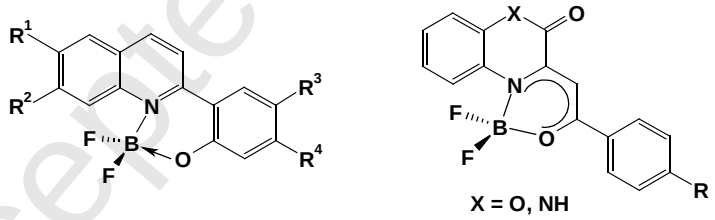
Keywords: 8-hydroxy-2-methylquinoline, 8-hydroxy-6,7-difluoro-2-methylquinoline, 8-hydroxy-2-styrylquinoline, 2-(2-hydroxyphenyl)-3H-quinazolin-4-one, N,O-bidentate ligands, BF_2 complexes, BPh_2 complexes, structural analysis, photophysical properties, fluorescence

1. Introduction

Organoboron complexes represent one of the most important types of fluorescent dyes. Not only complexes with N,N-ligands, such as boradipyrromethene (BODIPY) [1], 2-(quinolin-2-yl)-1H-phenantro[9,10-*d*]imidazole [2], but also complexes with N,O-ligands have been studied intensively for the last decade (Scheme 1). In particular, BF_2 complexes, bearing (2-

quinolin-2-yl)phenol ligands, have been shown to exhibit a strong fluorescence in both organic solvents (λ_{em} 441-492 nm in $CHCl_3$ at room temperature), and in solid state (λ_{em} 454-502 nm) [3]. Also BF_2 complexes with 3-(2-oxo-2-arylethylidene)-3,4-dihydro-1*H*-quinoxalin-2-ones and 3-(2-oxo-2-arylethylidene)-3,4-dihydro-benzo[1,4]oxazin-2-ones demonstrate a bright and intensive yellowish green fluorescence in THF solutions with maximum at 481-521 nm (φ = 0.59-0.87) [4, 5].

Difluoroboron complexes of 8-hydroxyquinoline derivatives have been mentioned in the only publication [6], dealing with photoisomerization of 3,4-*bis*-[2-(8-hydroxyquinolin-2-yl)vinyl-5-methylthiophen-4-yl]-2,5-dihydrothiophene taking place on treatmeant with boron trifluoride etherate. Diphenylboron complexes of 8-hydroxyquinolines have been studied in more detail, as analogues of 8-hydroxyquinoline aluminates with an enhanced stability comparing to aluminium-based emitters [7] and a strong π-electron accepting character of the empty p_z orbital at the boron centre [8, 9].



Scheme 1. BF_2 complexes based on N,O-ligands, described in the literature

Two main approaches to turn the emission wavelength of diphenylboron complexes are worth to be mentioned: a) incorporation of substituents into heterocyclic ligands, thus effecting the HUMO-LUMO energy levels and, therefore, on λ_{em} [10]; b) variation of substituents at the boron atom, in particular, replacement of the phenyl moiety with naphthyl, thienyl or benzo-thienyl fragments [11, 12]. 4-Fluorophenyl and C_6F_5 groups increase the Lewis acidity of the boron center, effecting the HOMO-LUMO levels, while pentafluorophenyl groups also seem to

contribute into stability of complexes [13]. Interaction of 8-hydroxyquinoline with *tris*(2-vinylphenyl)borane has also been described [14].

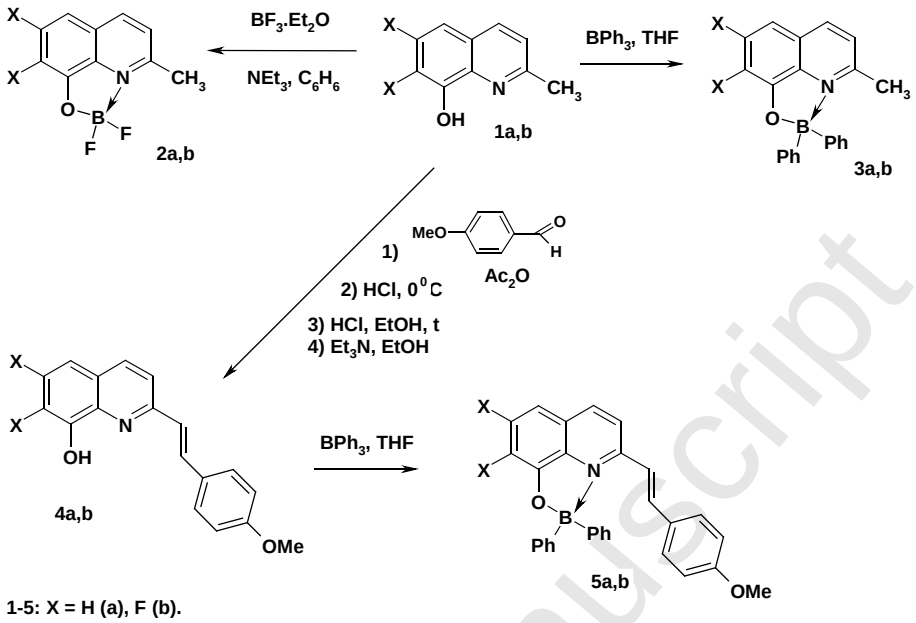
Diphenylboron complex of 8-hydroxyquinoline has been modified through incorporation of 1-naphthyl and 2-benzothienyl fragments into position 5 of the ligand [15], while the complex of 2-methyl-8-hydroxyquinoline with BPh_2 has not so far been described. Also the data on electroluminescent properties of di(mesithyl)boron complexes of 8-hydroxyquinoline and 2-methyl-8-hydroxyquinoline are available in the literature [16].

In this paper we wish to report the synthesis of novel BF_2 and BPh_2 complexes with N,O-benzazine ligands, namely the complexes with five-membered boron chelating ring, based on 2-methyl-8-hydroxyquinoline and 2-methyl-6,7-difluoro-8-hydroxyquinoline, as well as the complexes with six-membered boron chelating ring, based on 2-(2-hydroxyphenyl) substituted 3H-quinazolin-4-ones.

2. Results and discussion

Treatment of 8-hydroxy-2-methylquinoline **1a** and its 6,7-difluoroderivative **1b** with an excess of boron trifluoride etherate in the presence of triethylamine proved to result in the formation of novel BF_2 complexes **2a,b** as yellow crystalls in good to excellent yields (Scheme 2).

Unfortunately, we have failed to isolate individual difluoroboron complexes derived from the reaction of 2-styryl derivatives **4a,b** [17, 18] with $BF_3 \cdot Et_2O$ under a variety of conditions. Nevertheless, diphenylboron complexes of 2-methyl-8-hydroxyquinolines **(3a,b)** and 2-styryl-8-hydroxyquinolines **(5a,b)** have been obtained successfully on heating of the reaction solutions of ligands **1a,b** and **4a,b** with triphenylborane in tetrahydrofuran (Scheme 2).



Scheme 2. Synthesis of BF_2 and BPh_2 complexes

with 2-methyl- and 2-styryl-8-hydroxyquinolines and their 6,7-difluoro derivatives

The evidence for the structures of **2a,b, 3a,b,** and **5a,b** is provided by their spectral data, including the ^{1}H, ^{11}B, and ^{19}F NMR-spectroscopy, as well as mass-spectrometry and the elemental analysis. In the ^{19}F NMR spectra of compounds **2a,b** the resonance signals of BF_2 groups at 143-156 ppm have been observed, while the ^{1}H NMR spectra of these compounds show no OH signals. In spite of the fact, that compound **1b** exists in the zwitter-ion form in solution [18], an increase in the positive charge at the nitrogen atom of the complex **2b** results in downfield shifts for H(3), H(4) and H(5) protons in the ^{1}H NMR of the complex **2b**, relative to the corresponding signals for the ligand **1b**. In the ^{19}F NMR spectra of 6,7-difluoroderivative **2b** (δ -143.7 ppm) the signal of BF_2 group is shifted downfield considerably in comparison with the correspondent signal of the complex **2a** (δ -155.7 ppm). Also it is worth mentioning, that in the ^{11}B NMR spectrum of compound **2a** the signal at 1.01 ppm has been observed.

In the mass spectra of complexes **2a,b** the peaks of molecular ions (*m/z* 207 and 243 respectively) with 100% relative intensivity are observed.

The ^{1}H NMR spectra of complexes **3** and **5** contain no signals of OH groups, however the characteristic resonances of two phenyl residues are available. In the ^{11}B NMR spectra of these compounds the expected multiples in the region of 11.9-13.5 ppm are observed. The relative intensivities of molecular ion peaks in the mass spectra of complexes **3a,b, 5a,b** are in the range of 3-6%, it should be noted that 100% peaks correspond to the ions $[M\text{-}Ph]^{+}$.

Due to a similarity in the structures of complexes **3a,b, 5a,b**, compounds **3a** and **5a** have been selected as representatives of this family for X-ray single crystal diffraction studies, and the data of these structural elucidations are presented in Figures 1 and 2.

The boron center in both compounds has a typical tetrahedral geometry. Five-membered heterocycle is approximately planar, and it is in the plane of the tricyclic system. The boron atom shows the maximal deviation from the least-squared plane of the tricyclic system (0.062 Å for compound **3a** and 0.108 Å for compound **5a**). In case of compound **3a** carbon atoms of Ph-substituents demonstrate a strong thermal disordering. It has been taking into account by introducing into the structural model of two disordering components the with occupancy coefficients 0.5/0.5. Due to a short distance between the disordered components the thermal ellipsoids of the disordered atoms were constrained by using commands EADP in the refinement program XL of the SHELXTL program package.

Bond lengths B-X and angles Y-B-X of compounds are in good agreement with the data of earlier published papers. Each boron center in both complexes is bound with two carbon atoms of two phenyl groups. The bond angles O-B-N in complexes **3a** and **5a** are similar (98.56° and 98.2(2)°) (Table 1) and close to the published data (97.6-99.6°) [15].

The bonds lengths N(1)-B(1) in compounds **3a** (1.662 Å) and **5a** (1.657 Å) are very close to the published data N-B (1.618-1.646 Å); the bonds lengths O(1)-B(1) (1.514 Å and 1.524 Å) and bonds lengths C-B (1.599-1.614 Å) are in good agreement with O-B (1.503-1.535 Å) and C-B distances (1.578-1.606 Å), respectively [15]. The bonds lengths C-O in the heterocyclic ring (1.340 and 1.341 Å for **3a** and **5a** accordingly) are in good agreement with those typical for

phenols (1.36 Å [19]). Consequently, the unoccupied p-orbital of the boron atom does not have a significant effect on electron configuration of the quinoline system.

In crystals of **3a** and **5a** no shortened (less then sum of V-d-W radii) intermolecular contacts have been observed.

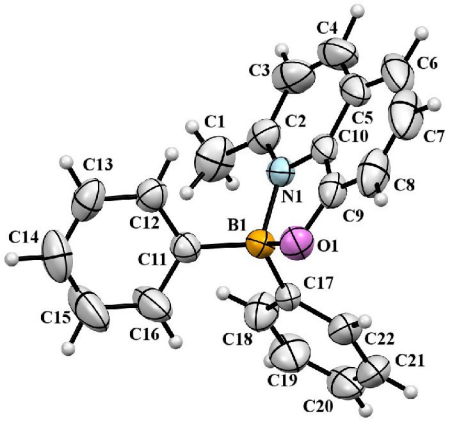


Fig. 1. ORTEP structure of compound **3a** in accordance with the XRD data

(the disordered atoms are omitted for clarity)

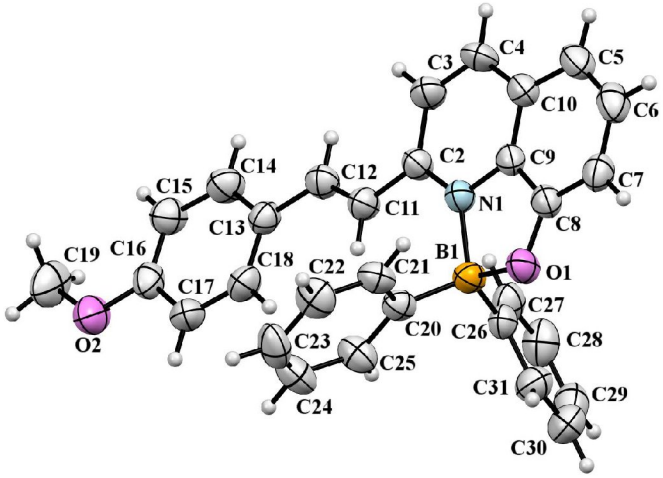


Fig. 2. ORTEP structure of compound **5a** according to the XRD data

2-(2-Hydroxyphenyl) substituted 3H-quinazolin-4-ones have been chosen as the second type of N,O-bidentate ligands, due to their structural similarity with (2-quinolin-2-yl)phenolic ligands. Although the synthesis of quinazolinone **7b** from 2-aminobenzamide and 3,5-di(*tert*-

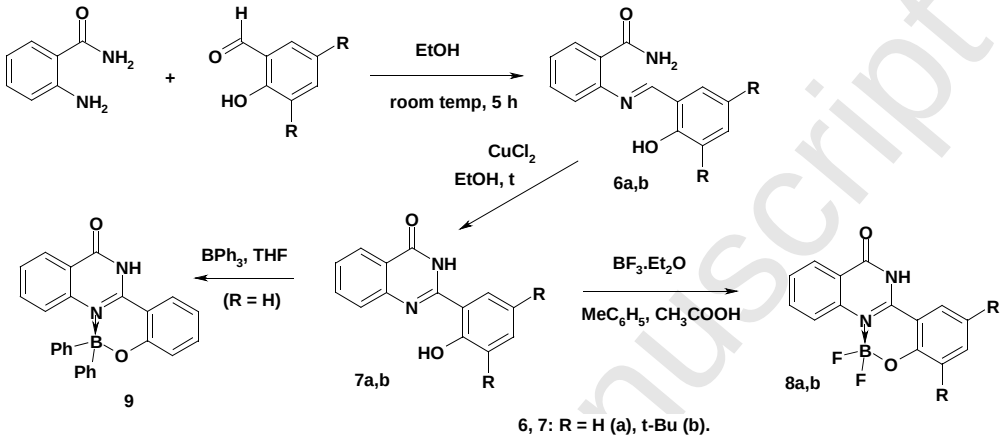
butyl)salicylic aldehyde has been described [20, 21], use of such oxidants as *bis*(acetyl-acetonato)oxovanadium and copper oxide, reported by the authors for transformation **6b→7b**, require too severe reaction conditions (heating at 120 ^{0}C for 15-24 h). We have suggested to exploit copper chloride, as oxidant for the synthesis of **7b**, thus enabling cyclization of azomethine **6b** to be carried out at 80 ^{0}C for 1.5 h. In order to obtain complexes **8a,b** a short-term heating of 2-(2-hydrohyphenyl)-3H-quinazolin-4-one **7a** and its derivative **7b** with boron trifluoride etherate in a mixture of toluene and acetic acid has been performed (Scheme 3).

The ^{19}F NMR spectra of complexes **8a,b** exhibit the resonance signals of BF_2 groups in the region of 136-151 ppm. Additionally, disappearance of the downfield hydroxy proton signals in the ^{1}H NMR spectra of these complexes provides an additional argument for the chelation of BF_2 group with these ligands. Also, broaden singlets of the NH groups in the ^{1}H NMR spectra of complexes are shifted upfield considerably relarive to the corresponding signals of the ligands. In the ^{11}B NMR spectra of complexes **8a,b** multiplet signals at 1.10 ppm are observed. The molecular ion peaks in the mass spectra of complexes **8a,b** (*m/z* 286 and 398) are less intensive (13% and 41% respectively), than those of 8-hydroxyquinoline derivatives **2a,b**.

The only complex with diphenylboron**,** which we have managed to obtain from the ligand **7a** is compound **9** which is formed on reflux of **7a** with triphenylborane in tetrahydrofuran (Scheme 3). Due to steric factors the formation of six-membered chelate rings from ligands **7** appears to be more a more difficult process, than that leading to five-membered chelates, thus taking place with 8-hydroxyquinoline derivatives **1** and **4**.

The UV-Vis absorption and fluorescence data for the complexes **2,3,5,8,** and **9** are listed in Table 2. The absorption spectra of difluoroboron complexes **2** are similar to the spectra of the corresponding ligands **1**. Transformation of ligands **1** into their diphenylboron complexes **3** is followed by a considerable bathochromic shift. The diphenylboron complexes **3** are characterized by the long-wave shift in absorption spectra in comparison with difluoroboron complexes **2**. 6,7-Difluoro compound **2b** shows a red shift of the absorption peak relative to **2a**

(Table 2). Difluoroderivatives **3b** and **5b** demonstrate a blue shift of the absorption peak in comparison with chelates **3a** and **5a**, bearing no fluorine atoms in the benzene ring. For instance, absorption and emission spectra of diphenylboron complex **3a** are presented at Fig. 3.



Scheme 3. Synthesis of BF_2 and BPh_2 complexes with 2-(2-hydrohyphenyl)-3H-quinazolin-4-ones

Unlike ligands **1** and **4**, which practically don't have luminescent properties, complexes **2, 3** and **5** show fluorescence with maxima at 390-546 nm, and their intensity depends on the nature of substituents in both the quinolone fragment and at boron atom (Table 2). The presence of fluorine atoms in the benzene ring of the difluoroboron complex **2b** leads to a substantial red shift of the emission band (λ_{max}^{fl} 392 nm for **2a** and 479 nm for **2b**), and enhances the quantum yield. In case of diphenylboron complexes with the same ligands. 6,7-difluoroderivative **3b** shows a considerable short-wave shift of the emission maximum relative to non-fluorinated analogue **3a**, while λ_{em} for **3b** practically coincides with λ_{em} for **2b**. Diphenylboron complexes **3** with 2-methyl-8-hydroxyquinoline ligands **1** show a considerable increase in quantum yields in comparison with difluoroboron complexes **2** (efficiency of luminescence for complex **3a** is 36 times higher than that for **2a**, and luminescence efficiency for **3b** is 12 times higher than that for **2b**). 2-Styryl derivatives **5a,b** demonstrate a long-wave shift of the emission maximum and a

decrease in quantum yield compared with 2-methyl analogues **3a,b.** Such effect can be explained by a better conjugation chain and an opportunity for *trans-cis*-photo-isomerization [22].

In the series of difluoroboron complexes of quinazolinones **8** incorporation of the *tert*-butyl group into the phenol fragment leads to a long-wave shift of the emission band and provides a considerable increase in quantum yield (φ = 9.3% for complex **8a,** and φ = 36.5% for complex **8b**). Absorption and emission spectra of the difluoroboron complex **8b** are presented in Fig. 4. It has been noted [3], that in the series of BF_2 complexes of (2-quinolin-2-yl)phenols higher quantum yields are characteristic for those compounds, which bear electron-donating groups in the phenol ring. Therefore, it has been assumed that these groups in the phenol fragment are more influential on quantum yields than those in the benzene ring. Comparison of BF_2 and BPh_2 complexes of the ligand **7a** (compounds **8a** and **9**) shows that replacement of fluorine atoms with phenyl groups results in the loss of luminescence properties for the complex **9** (Table 2). A similar conclusion is given in the communication [23], in which fluorescence efficiency of the BF_2 complex of 2,4-di-*t*-butyl-6-[(2,2,6,6-tetramethylpiperidin-4-ylimino)-methyl]phenol has been established to be much higher, than that of BPh_2 complex with the same ligand.

Other properties are observed for complexes **2** and **3** containing a five-membered boron chelate ring. In this case the fluorescence intensity of diphenylboron complexes **3** is much higher than that registered for BF_2 complexes **2**.

Thus, a size of the boron chelate ring, as well as electronic, steric and site effects of substituents in ligands have impact on photoluminescent properties of boron complexes.

Being compared with small values of Stokes shifts, widely observed for typical BODIPYs [24], large shift values (88-161 nm) for the obtained complexes appear to be quite impressive and promising for their further applications.

Table 1

Selected bond lengths and bond angles of complexes **3a** and **5a**

Bond length (Å)		Bond angle (°)	
Complex **3a**			
O(1)-B(1)	1.514(2)	O(1)-B(1)-N(1)	98.56(11)
N(1)-B(1)	1.662(2)	O(1)-B(1)-C(11)	109.25(12)
C(11)-B(1)	1.606(2)	O(1)-B(1)-C(17)	111.60(17)
C(17)-B(1)	1.613(6)	C(11)-B(1)-N(1)	111.13(12)
		C(11)-B(1)-C(17)	116.32(17)
		C(17)-B(1)-N(1)	108.6(2)
Complex **5a**			
O(1)-B(1)	1.524(4)	O(1)-B(1)-N(1)	98.2(2)
N(1)-B(1)	1.657(4)	O(1)-B(1)-C(26)	108.9(3)
C(20)-B(1)	1.614(5)	O(1)-B(1)-C(20)	109.3(3)
C(26)-B(1)	1.599(5)	C(26)-B(1)-C(20)	118.3(3)
		C(26)-B(1)-N(1)	110.3(3)
		C(20)-B(1)-N(1)	110.0(3)

Table 2.

Photophysical properties of ligands and complexes[a]

Compound	λ_{abs} (nm)		λ_{em} (nm)	φ, %[b]	Stokes shift (nm)
	ligand	complex			
2a	302	303	392	0.5	89
2b	293, 320	318	479	2.5	161
3a	302	379	502	18.2	123
3b	320	359	480	29	121
5a	355, 308	371, 339	546	8.5	175
5b	355, 303	365, 333,	514	3	149
8a	330	333	421	9.3	88
8b	342	355	454	36.5	99
9	330	331	430	< 1	

[a] Both absorption and emission spectra were measured in MeCN solution.

[b] The quantum yield was obtained by using quinine bisulfate as the reference compound.

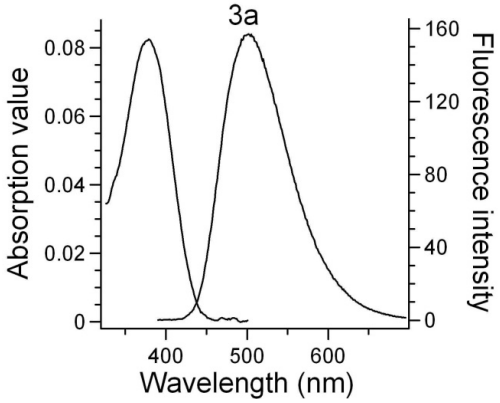


Fig. 3. Absorption and emission spectra of diphenylboron complex **3a** in acetonitrile

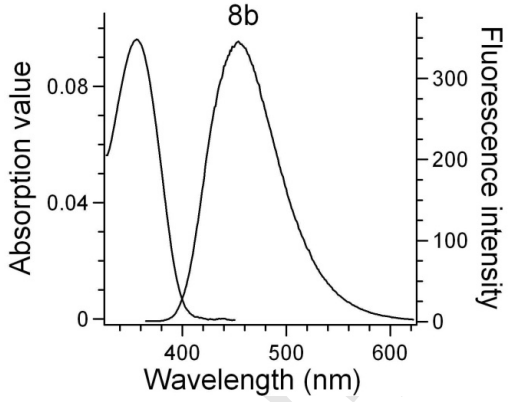


Fig. 4. Absorption and emission spectra of difluoroboron complex **8b** in acetonitrile

3. Conclusion

In this communication we have described the synthesis, structural analysis, spectral and photophysical properties for a number of novel BF_2 and BPh_2 complexes bearing 8-hydroxy-quinoline and 2-(2-hydroxyphenyl)-3H-quinazolin-4-one ligands. All these complexes have been obtained in good to excellent yield under rather mild conditions, by using simple work-up procedures. Electronic effects of substituents have been shown to play an important role for quantum yields of the corresponding complexes. High values of quantum yields and large Stokes shifts make these compounds to be considered as potential fluorescent dyes.

4. Experimental Section

4.1. General.

All reagents used were analytically pure, and some chemicals were further purified by recrystallization. Melting points were determined by a Stuart SMP3 instrument. The ^{1}H NMR (400.13 MHz), ^{19}F NMR (376.45 MHz) and ^{11}B NMR (128.4 MHz) spectra were obtained on a Bruker Avance II DMX400 spectrometer using $CDCl_3$ or DMSO-d_6 as the solvent. The ^{1}H NMR experiments were carried out using trimethylsilane as the internal standard, the ^{11}B NMR spectra

were recorded using BF_3OEt_2 (0 ppm) as the external standard, and the ^{19}F NMR spectra were recorded with $CFCl_3$ (C_6F_6 was used as secondary reference, δ_F –162.9 ppm).

Mass spectra were recorded on a SHIMADZU GCMS-QP2010 Ultra instrument with electron ionization (EI) of the sample. The absorption spectra in the range 220–800 nm were recorded on a UV–2600 spectrophotometer (λ = 310 nm) produced by Shimadzu. The fluorescence spectra were registered using a Varian Cary Eclipse spectrofluorometer (Xenon lamp), and solutions in acetonitrile were used for spectra recording.

XRD experiments of the compounds **3a** and **5a** were accomplished on an Xcalibur E diffractometer with a standard procedure (graphite-monochromated MoKα-irradiation, 295(2) K, ω-scanning with step 1°). Using Olex2 [25], the structure was solved with the Superflip [26] structure solution program using Charge Flipping and refined with the ShelXL [27] refinement package using Least Squares minimization.

The results of X-ray diffraction analysis for compounds **3a** and **5a** were deposited with the Cambridge Crystallographic Data Centre (CCDC 1055594 for compound **3a** and CCDC 1055600 for compound **5a**). These data are free and can be available at www.ccdc.cam.ac.uk.

4.2. Starting 8-hydroxyquinolines

2-Methyl-8-hydroxyquinoline **1a**, mp. 71-73 °C (lit. 72-73 °C [28]). ^1H NMR ($CDCl_3$): δ 2.76 (3H, s, CH_3), 7.15 (1H, d, H-3, J = 8.4), 7.39 (2H, m, benzo), 7.41 (1H, m, benzo), 8.06 (1H, d, H-4, J = 8.4), 8.4 (1H, br. s, OH).

2-Methyl-6,7-difluoro-8-hydroxyquinoline **1b** was obtained from 2-amino-5,6-difluorophenol using our earlier developed method [18], mp. 102-104 °C. ^1H NMR ($CDCl_3$): δ 2.74 (3H, s, CH_3), 5.32 (1H, br. s, HN^+), 7.04 (1H, dd, H-5, ^3J = 10.6, ^4J = 7.4), 7.33 (1H, d, H-3, J = 8.4), 7.99 (1H, d, H-4, J = 8.4). $^{19}F\{^1H\}$ NMR spectra ($CDCl_3$): δ -158.84 (d, F-7, J = 19.8), -134.60 (d, F-6, J = 19.8).

*4.3. Synthesis of 2-methyl-8-hydroxyquinolinatoboron difluoride (**2a**).*

To a solution of 2-methyl-8-hydroxyquinoline **1a** (0.318 g, 2 mmol) in benzene (6 mL) triethylamine (0.52 mL, 3.7 mmol) and boron trifluoride etherate (0.64 mL, 5.2 mmol) were added. Reaction mixture was stirred at 50 ^{0}C during 2 h, then solvent was evaporated and residue was washed with hexane. Yield of the complex **2a** is 0.34 g (82%), mp. 66-68 ^{0}C. ^{1}H NMR ($CDCl_3$): δ 2.74 (3H, s, CH_3), 7.15 (1H, m), 7.30 (2H, m), 7.40 (1H, m), 8.04 (1H, d, H-4, J = 8.4). ^{19}F NMR ($CDCl_3$): δ −155.72 m. ^{11}B NMR ($CDCl_3$): δ 1.01 m. MS (m/z, I_{rel} %): 207 $[M]^+$ (100), 206 (29), 188 (15), 187 (87), 186 (25), 159 (40), 140 (22), 131 (46), 130 (34), 115 (10), 114 (15), 103 (25), 102 (12), 101 (14), 89 (18), 86 (46), 77 (25), 76 (10), 63 (24), 58 (16), 50 (20), 49 (11), 48 (28), 38 (17). Anal. Calc. for $C_{10}H_8BF_2NO$, C 58.03; H 3.90; N 6.77. Found: C 57.97; H 3.86; N 6.81.

*4.4. 2-Methyl-6,7-difluoro-8-hydroxyquinolinatoboron difluoride (**2b**)*

Synthesis was acomplished by the similar method. Yield 74%, mp. > 300 ^{0}C. ^{1}H NMR ($CDCl_3$): δ 2.74 (3H, s, CH_3), 7.16 (1H, dd, H-5, ^3J = 10.8, ^4J = 7.8), 7.60 (1H, d, H-3, J = 8.4), 8.42 (1H, d, H-4, J = 8.4). ^{19}F NMR ($CDCl_3$): δ −126.46 (1F, m), -143.74 (2F, m), -153.29 (1F, m). MS (m/z, I_{rel} %): 243 $[M]^+$ (100), 242 (30), 224 (19), 223 (80), 222 (24), 150 (12), 121 (13), 120 (12), 119 (13), 109 (11), 104 (13), 101 (12), 99 (12), 85 (14), 80 (12), 74 (15), 73 (10), 50 (15), 49 (13), 48 (91), 47 (12), 38 (12). Anal. Calc. for $C_{10}H_6BF_4NO$, C 49.43; H 2.49; N 5.76. Found: C 49.38; H 2.45; N 5.80.

*4.5. Synthesis of 2-methyl-8-hydroxyquinoline BPh_2 complex (**3a**).*

To a solution of quinoline **1a** (79 mg, 0.5 mmol) in tetrahydrofuran (38 mL) 0.25M solution of triphenylborane in THF (2 mL, 0.5 mmol) was added dropwise, reaction mixture was refluxed for 12 h, solvent was evaporated and residue was washed with hexane. Yield of the complex **3a** is 0.147 g (91%), mp. 171-173 ^{0}C. ^{1}H NMR ($CDCl_3$): δ 2.56 (3H, s, CH_3), 7.12 (1H,

m, H-5), 7.23 (1H, m, H-7), 7.24-7.33 (6H, m, Ph), 7.39 (1H, d, H-3, *J* = 8.3), 7.44 (4H, m, Ph), 7.60 (1H, m, H-6), 8.32 (1H, d, H-4, *J* = 8.3). ^{11}B NMR ($CDCl_3$): δ 12.20 m. MS (m/z, I_{rel} %): 323 $[M]^+$ (6), 247 (17), 246 $[M\text{-}Ph]^+$ (100), 245 (29), 115 (25). Anal. Calc. for $C_{22}H_{18}BNO$, C 81.76; H 5.61; N 4.33. Found: C 81.68; H 5.72; N 4.29.

*4.6. 2-Methyl-6,7-difluoro-8-hydroxyquinoline BPh_2 complex (**3b**).*

Synthesis was acomplished by similar method. Yield 92%, mp. 206-208 ^{0}C. ^{1}H NMR ($CDCl_3$): δ 3.56 (3H, s, CH_3), 7.01 (1H, m, H-5), 7.29 (6H, m, Ph), 7.40 (4H, m, Ph), 7.42 (1H, d, H-3, *J* = 8.4), 8.28 (1H, d, H-4, *J* = 8.4). ^{19}F NMR {^{1}H} ($CDCl_3$): δ -157.88 (1F, d, F-7, *J* = 18.5), -128.46 (1F, d, F-6, *J* = 18.5). ^{11}B NMR ($CDCl_3$): δ 13.34 m. MS (*m/z*, $I_{rel,}$ %): 359 $[M]^+$ (4), 283 (19), 282 $[M\text{-}Ph]^+$ (100), 281 (28), 107 (13). Anal. Calc. for $C_{22}H_{16}BF_2NO$, C 73.57; H 4.49; N 3.90. Found: C 73.50; H 4.56; N 3.85.

*4.7. (E)-2-[2-(4-methoxyphenyl)vinyl]-8-hydroxyquinoline BPh_2 complex (**5a**).*

Synthesis was acomplished by similar method. Yield 86%, mp. 308-310 ^{0}C. ^{1}H NMR ($CDCl_3$): 3.81 (3H, s, MeO), 6.83 (2H, d, H-3', H-5', *J* = 8.5), 7.08 (1H, m, H-5), 7.21 (1H, m, H-7), 7.28 (2H, d, H-2', H-6', *J* = 8.5), 7.31 (6H, m, Ph), 7.35 (1H, d, CH=, *J* = 16.0), 7.44 (4H, m, Ph), 7.46 (1H, d, CH=, *J* = 16.0), 7.53 (1H, m, H-6), 7.89 (1H, d, H-3, *J* = 8.7), 8.26 (1H, d, H-4, *J* = 8.7). ^{11}B NMR ($CDCl_3$): δ 11.91 m. MS (m/z, I_{rel} %): 441 $[M]^+$ (3), 365 (27), 364 $[M\text{-}Ph]^+$ (100), 363 (25), 244 (12), 243 (14). Anal. Calc. for $C_{30}H_{24}BNO_2$, C 81.65; H 5.48; N 3.17. Found: C 81.58; H 5.56; N 3.12.

*4.7. (E)-2-[2-(4-methoxyphenyl)vinyl]-6,7-difluoro-8-hydroxyquinoline BPh_2 complex (**5b**).*

Synthesis was acomplished by the similar method. Yield 86%, mp. 311-313 ^{0}C. ^{1}H NMR ($CDCl_3$): δ 3.85 (3H, s, MeO), 6.87 (2H, d, H-3', H-5', *J* = 8.5), 6.96 (1H, m, H-5), 7.21 (2H, d,

H-2', H-6', *J* = 8.5), 7.27 (1H, d, CH=, *J* = 16.0), 7.28 (6H, m, Ph), 7.30 (4H, m, Ph), 7.48 (1H, d, CH=, *J* = 16.0), 7.93 (1H, d, H-3, *J* = 8.7), 8.24 (1H, d, H-4, *J* = 8.7). ^{19}F NMR {^{1}H} ($CDCl_3$): δ -158.36 (F-7, d, *J* = 18.5), -128.84 (F-6, d, *J* = 18.5). MS (m/z, I_{rel} %): 477 $[M]^+$ (3), 401 (26), 400 $[M\text{-}Ph]^+$ (100), 399 (25), 322 (13), 280 (11), 279 (15). Anal. Calc. for $C_{30}H_{22}BF_2NO_2$, C 75.49; H 4.65; N 2.93. Found, %: C 75.43; H 4.73; N 2.89.

4.8. Starting quinazolinones

2-(2-Hydroxyphenyl)-3H-quinazolin-4-one **7a**. Compound was obtained using method described [29], mp. 272-274 ^{0}C. ^{1}H NMR (DMSO-d_6): δ 6.94 (2H, m), 7.41 (1H, m), 7.51 (1H, m), 7.71 (1H, m), 7.83 (1H, m), 8.17 (1H, m), 8.24 (1H, m), 12.5 (1H, br.s, OH), 13.9 (1H, br. s, NH).

2-(2-Hydroxy-3,5-di(t-butyl)phenyl)-3H-quinazolin-4-one **7b.** To a solution of 2-aminobenzaide (0.7 g, 5.1 mmol) in ethanol (12.5 mL) 3,5-di(t-butyl)salicilic aldehyde (1.193 g, 5.1 mmol) was added, reaction mixture was stirred during 5 h, and solvent was evaporated. Residue was washed with hexane, azomethine **6b** was dissolved in ethanol (8 mL), $CuCl_2$ (0.36 g) was added and reaction mixture was refluxed for 1.5 h. After cooling the formed quinazolinone **7b** was filtered and recrystallized from DMSO. Yield 1.41 g (79%), mp. 288-290 ^{0}C. ^{1}H NMR (DMSO-d_6): δ 1.33 (9H, s, $(CH_3)_3$), 1.44 (9H, s, $(CH_3)_3$), 7.36 (1H, d, H-4', *J* = 2.1), 7.48 (1H, m, benzo), 7.69 (1H, m, benzo), 7.80 (1H, m, benzo), 7.97 (1H, d, H-2', *J* = 2.1), 7.69 (1H, m, H-8), 12.6 (1H, br. s, OH), 14.8 (1H, br. s, NH). Anal. Calc. for $C_{22}H_{26}N_2O_2$, C 75.40; H 7.48; N 7.99. Found: C 75.38; H 7.45; N 8.03.

*4.9. Synthesis of 2-(2-hydroxy-3,5-di(t-butyl)phenyl)-3H-quinazolin-4-onatoboron difluoride (**8b**).*

To a suspension of quinazolinone **7b** (0.138 g, 0.34 mmol) in toluene (0.51 mL) glacial acidic acid (0.51 mL) was added, mixture was warmed up to 60 ^{0}C, then boron trifluoride

etherate (0.22 mL) was added, and mixture was refluxed for 5 min. After cooling Et_2O (10 mL) was added, solvents were evaporated partially (until 1/3 of initial volume), and light-yellow solid was filtered and washed with hexane. Yield of complex **8b** is 0.118 g (87%), mp. 268-270 ^{0}C. ^{1}H NMR ($CDCl_3$): δ 1.43 (9H, s, $(CH_3)_3$), 1.54 (9H, s, $(CH_3)_3$), 7.65 (1H, m, benzo), 7.72 (1H, d, H-4', *J* = 2.0), 7.76 (1H, d, H-2', *J* = 2.0), 7.97 (1H, m, benzo), 8.38 (1H, m, benzo), 8.59 (1H, m, benzo), 11.4 (1H, br, s, NH). ^{19}F NMR ($CDCl_3$): δ -136.01 m. ^{11}B NMR ($CDCl_3$): δ 1.10 m. MS (*m/z*, I_{rel} %): 398 $[M]^+$ (41), 397 (11), 384 (18), 383 (79), 382 (19), 364 (23), 363 (100), 362 (26), 347 (14), 335 (12), 307 (17), 160 (20), 57 (35), 41 (18). Anal. Calc. for $C_{22}H_{25}BF_2N_2O_2$, C 66.35; H 6.33; N 7.03. Found: C 66.40; H 6.39; N 6.97.

*4.10. 2-(2-Hydroxyphenyl)-3H-quinazolin-4-onatoboron difluoride (**8a**).*

Synthesis was accomplished by similar method. After reaction completion the mixture was cooled, the colourless solid was filtered and washed with methanol (6 mL) and Et_2O (4 mL). Yield 76%, mp. > 300 ^{0}C. ^{1}H NMR ($CDCl_3$): δ 7.17 (1H, m), 7.29 (1H, m), 7.34 (1H, m), 7.68 (2H, m), 7.96 (1H, m), 8.39 (1H, m), 8.59 (1H, m), 11.1 (1H, br. s, NH). ^{19}F NMR ($CDCl_3$): δ −150.74 m. MS (m/z, I_{rel} %): 286 $[M]^+$ (13), 266 (30), 265 (16), 238 (17), 237 (11), 148 (10), 139 (21), 130 (12), 119 (38), 113 (19), 102 (78), 92 (56), 91 (34), 90 (100), 99 (16), 87 (12), 77 (13), 76 (39), 75 (37), 74 (17), 65 (20), 64 (67), 63 (85), 62 (26), 52 (12), 51 (17), 50 (23), 49 (34), 48 (26), 38 (60), 37 (23). Anal. Calc. for $C_{14}H_9BF_2N_2O$, C 58.79; H 3.17; N 9.79. Found: C 58.84; H 3.21; N 9.73.

*4.11. 2-(2-Hydroxyphenyl)-3H-quinazolin-4-one BPh_2 complex (**9**).*

To a solution of quinazolinone **7a** (200 mg, 0.84 mmol) in tetrahydrofurane (46 mL) 0.25M solution of triphenylborane in THF (3.4 mL, 0.84 mmol) was added dropwise, reaction mixture was refluxed during 12 h, solvent was evaporated and residue was washed with hexane. Yield of complex **9** is 0.28 g (84%), mp. > 300 ^{0}C. ^{1}H NMR ($CDCl_3$): δ 7.04 (1H, m), 7.15 (1H,

m), 7.43-7.48 (2H, m), 7.52-7.56 (4H, m), 7.62 (2H, m), 7.76-7.80 (3H, m), 7.84 (1H, m), 8.28 (3H, m), 8.35 (1H, m), 10.3 (1H, br. s, NH). ^{11}B NMR ($CDCl_3$): δ 29.96 m. Anal. Calc. for $C_{26}H_{19}BN_2O_2$, C 77.63; H 4.76; N 6.96. Found: C 77.70; H 4.82; N 6.93.

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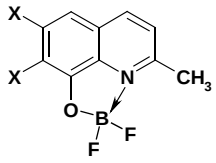
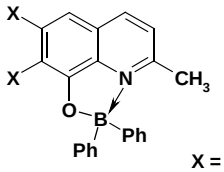
Novel N,O-bidentate BF_2 and BPh_2 complexes have been prepared in good to excellent yields through coordination of 8-hydroxy-2-methylquinolines and 2-(2-hydroxyphenyl)-3H-quinazolin-4-ones with boron trifluoride etherate or triphenylborane under mild conditions. All complexes have been characterized by ^{1}H, ^{11}B and ^{19}F NMR, mass-spectrometry and X-ray crystallography data. Some complexes have been found to exhibit a significant fluorescence in acetonitrile solutions. Electronic and site effects of substituents in both heterocyclic and phenol fragments proved to have a profound impact on quantum yields.





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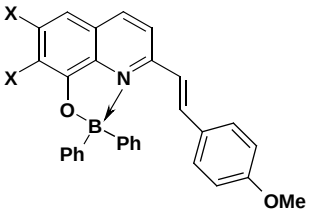

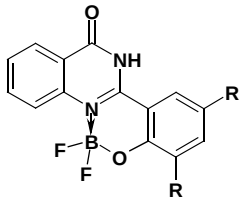

R = H, t-Bu