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Luminescence Tuning of Organoboron Quinolates through Substituent Variation at the 5-Position of the Quinolato Moiety

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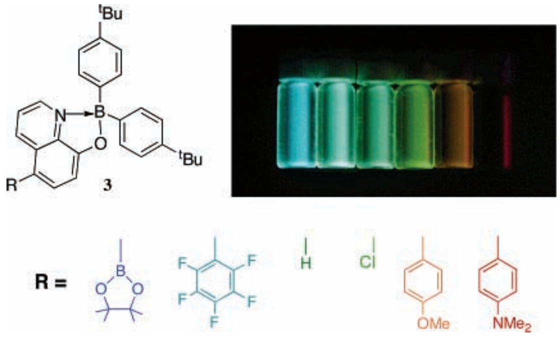
ABSTRACT



A series of organoboron quinolates with emission colors ranging from blue to red have been prepared. In comparison to the respective AlQ_3 derivatives a distinct blue-shift of the emission is observed. Theoretical calculations serve to provide insight into the nature of the frontier orbitals and the effect of the substituents in the 5-position of the quinolate ligands on the relative HOMO and LUMO energy levels. An efficient new blue emitting material with a pinacolborane substituent has been identified.

Since the discovery by Tang and VanSlyke[1] in 1987 of the application of tris-8-hydroxyquinoline aluminum (AlQ_3) to light emitting devices, intense research in both academia and industry has been focused on organic light emitting diodes (OLEDs), which are thought to have the potential to replace traditional liquid crystal displays (LCDs).[2] Inorganic and organometallic complexes play important roles as active materials in OLEDs. For instance, main group metal chelate complexes[3,4] and organoborane-functionalized conjugated aromatics[5] have been used as electron conducting and/or fluorescent emitters, while transition metal complexes such as cyclometalated platinum and iridium species[6] are known for their superior performance as phosphorescent emitters.

Modification of the chelating quinolate ligand in AlQ_3 with electron-donating or electron-withdrawing groups has been

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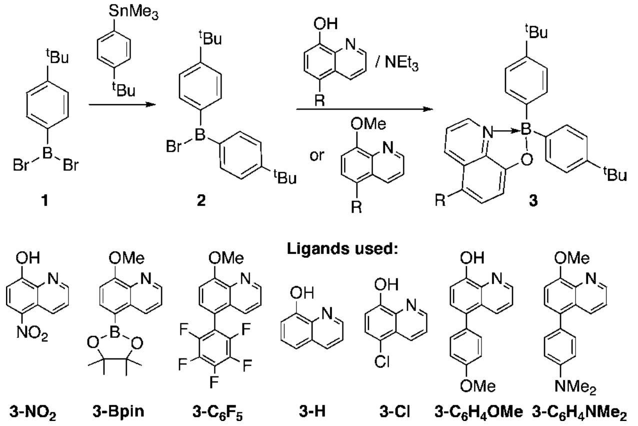
established by Anzenbacher[7] and others[8] as a straightforward method for the tuning of the optical properties of AlQ_3 and has more recently been exploited by Weck[9] for the color tuning of related AlQ_3-modified polymers. Following the initial reports by Wang, organoboron quinolates and related chelate complexes of boron have also attracted much interest,[10−15] especially since they provide efficient luminescence and in some cases better stability over their aluminum counterparts. Even bifunctional quinolate ligands have now been prepared for the assembly of new multinuclear boron quinolate materials.[15] However, until recently very few studies have been performed on the systematic tuning of the luminescence of organoboron quinolates.[16] The effect of placing methyl groups at different positions of the quinolato moiety in diphenylboron quinolate (Ph_2BQ) has been studied experimentally and by means of theoretical calculations.[11,12] Wang et al. showed in a very recent paper that attachment of benzothienyl or naphthyl groups in the 5-position of the quinolate ligand leads to a red-shift in the emission as a result of extended delocalization of the quinolate π-system into the benzothienyl substituent.[10c] Moreover, substitution with extended π systems in the 5- and 7-positions of the quinolate ligand in Ph_2BQ has been demonstrated by Slugovc to lead to a significant bathochromic shift of the emission wavelength.[13] We report here on the systematic color tuning of organoboron quinolates through modification of the 5-substituent with electron-withdrawing and electron-donating groups and compare the results with those for the respective AlQ_3 derivatives.

Scheme 1. Synthesis of Organoboron Quinolates **3**



We chose to prepare organoboron quinolate derivatives **3** (Scheme 1) in which ^{t}Bu groups are attached to the para-position of the phenyl group for simplified NMR spectroscopic analysis and better comparability with related polymeric derivatives prepared in our laboratory.[14] The electronic structure of the compounds is systematically varied through placement of different substituents in the 5-position of the quinolate moiety (Q). The common precursor **2** was readily prepared with high selectivity through reaction of **1** with 1-trimethylstannyl-4-*tert*-butylbenzene (Scheme 1). When the reaction was conducted at low temperature and stopped after 4 h, no evidence of side reactions or further conversion to the triarylborane was observed. Subsequent treatment with a series of different 8-hydroxyquinoline derivatives with varying substitution pattern as shown in Scheme 1 led to the new organoboron quinolates **3**. For the last reaction step either the free 8-hydroxy functionalized ligand can be treated with **2** in the presence of triethylamine as a base or, in a versatile new method, the methoxy-protected ligand may be directly reacted with **2** under cleavage of the O−Me bond with formation of bromomethane. Complexes **3** were obtained as crystalline solids in moderate to high yields.

FAB-MS analysis of compounds **3** showed in all cases the molecular ion peak and a fragment due to loss of a *tert*-butylphenyl group as the most intense peak. The structures were further confirmed by NMR spectroscopy. Thus, in the ^{11}B NMR all compounds showed a relatively narrow signal at ca. 12 to 13 ppm ($w_{1/2}$ ca. 400 to 650 Hz) that is strongly upfield shifted relative to the broad signal of **2** at 65 ppm ($w_{1/2}$ = 1800 Hz). The ^{1}H NMR spectra showed the expected peak patterns and integration confirmed the ratio of *tert*-butylphenyl to quinolate groups of 2:1.

DSC analyses reveal that depending on the substituent X complexes **3** melt between 230 and 330 °C and upon cooling form glasses with a glass transition in the range of 78 to 130 °C. In most cases, recrystallization occurs between 137 and 226 °C followed by a melt at the same temperature as in the first heating cycle.

The photophysical data of the new series of organoboron quinolates are summarized in Table 1. The parent compound

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Table 1. Experimental and Computed (Gaussian03)[20] Photophysical Data of Compounds **3** in Comparison to the AlQ_3 Analogues[7b,c]

	experimental data of compounds **3**				TD-DFT calculations		data of AlQ_3 analogues[d]	
compd	λ_{max}[a] (nm)	ϵ (L $mol^{-1}cm^{-1}$)	λ_{em}[a,b] (nm)	Φ (%)	λ_{exc} (nm)	oscillator strength f	λ_{max} (nm)	λ_{em} (nm)
3-NO$_2$	401	14500	456	0.1	394[c]	0.18[c]	380[e]	510[e]
3-Bpin	389	4530	485	39	412	0.10	n.a.	n.a.
3-C$_6$F$_5$	396	4900	498	30	431	0.10	388	516
3-H	395	3740	506	17	428	0.06	388	526
3-Cl	410	4030	528	8	445	0.07	402	541
3-C$_6$H$_4$OMe	419	4660	562	2	465	0.10	410	564
3-C$_6$H$_4$NMe$_2$	438	4940	625	0.1	504	0.09	422	612

[a] Concentrations were ca. 2×10^{-5} M in THF. [b] Excited at the absorption maximum. [c] Transition from HOMO-3/HOMO-2 to LUMO/LUMO+1. [d] Data in CH_2Cl_2 unless otherwise noted. [e] Polymeric analogue of AlQ_3 in $CHCl_3$; see ref 9b.

3-H shows an absorption maximum at 395 nm and green emission at 506 nm, which correlates very well with the previously reported data for Ph_2BQ ($\lambda_{max} = 395$ nm; $\lambda_{em} = 504$ nm)[10b] despite the presence of electron-donating *tert*-butyl groups in the 4-position of the phenyl rings. This observation is in agreement with reports by Wang et al. that the nature of the aryl group on boron has only a minor impact on the photophysical characteristics.[10b] However, the quantum yield for **3-H** of 17% is considerably lower than that reported for Ph_2BQ (30% in CH_2Cl_2[10b] and 23% in $CHCl_3$[9d] at room temperature). At this point the reasons for this deviation are not obvious.

Substitution at the 5-position with electron-withdrawing and electron-donating groups respectively strongly influences the absorption and emission spectra. The emission bands span a range from the blue (456 nm; X = NO_2) to the red (625 nm; X = $C_6H_4NMe_2$) that covers almost the entire visible spectrum. According to previous observations for AlQ_3 derivatives[7b,c] and calculations on boron quinolates,[12] the highest occupied π orbital (HOMO) is mainly located on the phenolate side and the lowest unoccupied π^* orbital (LUMO) is mainly located on the pyridyl moiety. By substituting the 5-position on the phenolate ring with electron-withdrawing groups the HOMO energy is thus expected to be lowered, leading to an increase in the HOMO-LUMO energy gap and thus a blue-shift in the absorption and emission spectra.[7b,c] On the other hand, electron-donating groups and groups capable of extended π conjugation at the 5-position of the phenolate ring should lead to higher HOMO levels and smaller HOMO-LUMO gaps, thus resulting in a red-shift.

The experimental observations for the organoboron quinolates **3** seem to confirm the expected trend in that the emission of the derivatives with NO_2, Bpin, and C_6F_5 groups in the 5-position is blue-shifted relative to the parent compound **3-H**, while the electron-donating groups $C_6H_4NMe_2$ and C_6H_4OMe lead to a strongly red-shifted emission. A comparison of the organoboron compounds with related AlQ_3 derivatives reported in the literature[7b,c] shows that with the exception of **3-C$_6$H$_4$NMe$_2$** the emission from the boron quinolate chromophores is blue-shifted by up to 20 nm (Table 1).[17] Such a blue-shift has been first reported by Wang[10b] for Ph_2BQ, but the observation that this trend holds for various 5-substituents of the quinolate moieties is very interesting, in that blue emitting materials, which continue to be in strong demand for device applications, should then be more easily accessible with boron quinolates. Indeed, the pentafluorophenyl-substituted derivative **3-C$_6$F$_5$** emits at 498 nm (AlQ_3 derivative: 516 nm[7b,c]) and attachment of a pinacolborane moiety in **3-Bpin** provides for blue emission at 485 nm. A further blue-shift to 456 nm can be achieved by attachment of a nitro group on the quinolate in **3-NO$_2$**. However, **3-NO$_2$** shows an unusually small Stoke's shift of 55 nm in THF and displays a very low quantum efficiency of 0.1%, which could be due to the charge-transfer character of the lowest energy absorption bands (see vide infra).[18,19] For all other organoboron quinolates significantly higher quantum efficiencies are observed with electron withdrawing (larger energy gap) than with donating substituents (Table 1). Most notably, the new pinacolborane-substituted organoboron quinolate **3-Bpin** shows a high quantum efficiency of 39%.

To further examine the precise electronic structure of compounds **3** and the nature of the orbitals involved in the electronic transitions, we optimized their geometries using DFT calculations (Gaussian03, B3LYP, 6-31G(d)) and computed the lowest energy excitations using TD-DFT calculations (Table 1, Figures 1 and 2).[20] The calculations reproduce the experimentally observed trends although the absolute excitation data deviate significantly. According to the calculations the lowest energy excitation corresponds to

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(17) A reviewer suggested that the blue-shift could be due to compounds R_2BQ only containing one quinolato group, while the emission from AlQ_3 may involve mixing between the three quinolato ligand states. As proposed in the literature based on comparison of the structural data and photophyscial properties of AlQ_3 with those of species $AlQ_2(OR)$, the relative bond strength of the M−O (M = B, Al) bonds may also play an important role; see: La Deda, M.; Aiello, I.; Grisolia, A.; Ghedini, M.; Lelj, F. *Dalton Trans.* **2006**, 330−339 and references therein.

(18) Charge transfer character has also been proposed for benzothienyl (Bt) substituted derivatives Bt_2BQ; see ref 10c.

(19) The emission spectra showed additional longer wavelength bands in DMF and DMSO (see the Supporting Information).

(20) DFT calculations were performed with the Gaussian03 program (Revision C.02, Frisch, M. J. et al. Gaussian Inc.: Wallingford CT, 2004; full listing of authors is in the the Supporting Information). Geometries and electronic properties were computed by means of the hybrid density functional B3LYP with the basis set of 6-31G(d). The input files and orbital representations were generated with Gaussview. Excitation data were calculated by using TD-DFT (B3LYP) methods.

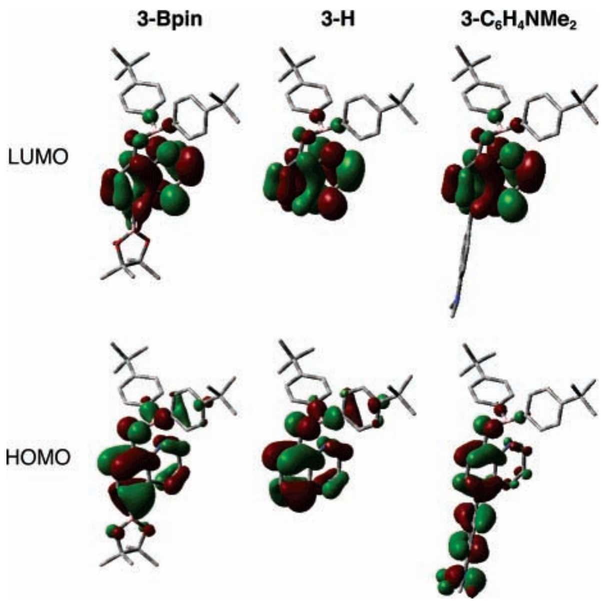

Figure 1. Computed orbitals for selected compounds **3** (contour value = 0.03).

a $\pi - \pi^*$ (HOMO to LUMO) transition for all complexes except for **3-NO_2**.

The frontier orbitals are (apart from **3-NO_2)** primarily situated on the quinolato moiety and do not show a significant contribution from the boron atom. The HOMO levels show significant contributions of the pendent substituents at the 5-position, an effect that is especially pronounced for **3-C_6H_4OMe** and **3-$C_6H_4NMe_2$** (Figure 1). The latter is consistent with recent reports on complexes with 5- and 7-substituents with extended delocalization.[10c,13] Extended conjugation leads to elevation of the HOMO levels and thus a bathochromic shift of the excitation wavelength (Figure 2). In contrast, the bathochromic shift experimentally observed for **3-Cl** can be attributed to lowering of the LUMO level rather than elevation of the HOMO. Different factors also impact the position of the frontier orbitals of the complexes, which feature electron-withdrawing substituents in the 5-position. While for **3-C_6F_5** the HOMO-LUMO gap remains essentially identical with that of **3-H** due to lowering of both the HOMO and LUMO levels, for **3-Bpin** a slight increase in the HOMO-LUMO gap is due to more pronounced elevation of the LUMO than the HOMO. The latter is possibly a result of overlap between the organic π-system and the tricoordinate boron center of the Bpin moiety in the LUMO (Figure 1), a phenomenon that is commonly observed for triarylborane species (note that the Bpin moiety is a σ-donor/π-acceptor).[21] Excitation of **3-NO_2** to S_1 is very weak ($f = 0.005$) and corresponds to charge transfer from orbitals that are centered on the B-bound phenyl rings (HOMO, HOMO-1) to the quinolato-centered LUMO orbital. The relatively strong transition to the singlet excited S_5 state ($f = 0.181$) occurs from orbitals with contributions of the B-bound Ph rings and the phenolate moiety (HOMO-3, HOMO-2) to primarily Q-NO_2 centered orbitals (LUMO, LUMO+1).[22]

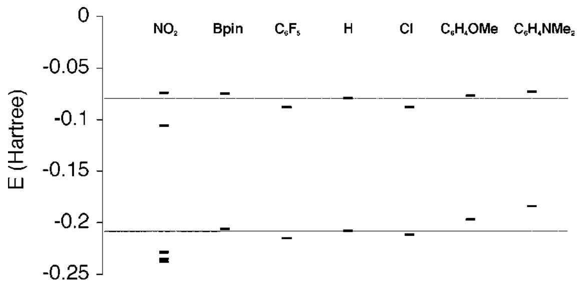

Figure 2. Calculated HOMO and LUMO energies of complexes **3** (for **3-NO_2** additional orbital levels involved in the lowest energy excitations are provided).

In conclusion, we demonstrate that direct reaction of Me-protected hydroxyquinoline derivatives with bromoboranes, Ar_2BBr, can be applied advantageously to the synthesis of a series of new organoboron quinolate derivatives. Their emission color has been tuned systematically to range from blue to red. Particularly interesting is that attachment of a pinacolborane moiety in **3-Bpin** leads to a new efficient blue emitter with high quantum efficiency of 39%. DFT calculations provide insight into the effects of 5-substituents on the HOMO and LUMO levels. Most notably, extended conjugation in the HOMO of **3-C_6H_4OMe** and **3-$C_6H_4NMe_2$** leads to lowering of the energy gap, while overlap of the empty p orbital of boron with the organic π system in **3-Bpin** is likely responsible for the observed higher energy gap.

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Supporting Information Available: Synthetic procedures and data for compounds **3** and details of the DFT calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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[22] Nitro-substituted AlQ_3 is weakly emissive: see refs 8b and 9b.