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Organoboron Compounds with an 8-Hydroxyquinolato Chelate and Its Derivatives: Substituent Effects on Structures and Luminescence

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Four new luminescent organoboron complexes have been synthesized and fully characterized. These compounds are four-coordinate boron chelated by either 8-hydroxyquinolato (q) or functionalized 8-hydroxylquinolato ligands, including BPh$_2$(5-(1-naphthyl)-q) (**1**), BPh$_2$(5-(2-benzothienyl)-q) (**2**), B(2-benzothienyl)$_2$q (**3**), and B(2-benzothienyl)$_2$-(2-Me-q) (**4**). All four compounds have a tetrahedral geometry as established by X-ray diffraction analyses. In solution, compounds **1**–**4** have an emission maximum at 534, 565, 501, and 496 nm, respectively, at room temperature. They emit similar colors in the solid states without red shifts of the emission band due to the lack of significant intermolecular interactions in the crystal lattices. The substituent group at C5 or C2 position of the 8-hydroxyquinolato ligand has been observed to have a significant impact on the emission energy and the emission quantum efficiency of the boron complexes. Molecular orbital calculations (Gaussian 98) showed that the electronic transition of **1** and **2** is a π–π^* transition centered on the functionalized 8-hydroxyquinolato group and the electronic transition of **3** and **4** is an interligand charge transfer from the 2-benzothienyl ligand to the hydroxyquinolato ring. A double-layer electroluminescent device using **3** as the emitter has been fabricated, which produced a broad emission band with a significant contribution of exciplex emission.

Introduction

Luminescent organoboron compounds have recently received considerable attention due to their potential applications in organic light emitting devices (OLEDs).[1,2] In the study on blue luminescent materials based on 7-azaindolyl ligands, we revealed that boron compounds in general are more stable than the corresponding aluminum compounds due to the increased covalency of boron−ligand bonds, compared to aluminum−ligand bonds.[3] Three-coordinate boron complexes protected by bulky substituents have also been reported recently to be useful emitters for OLEDs.[1a−d,4] Alq$_3$ (q = 8-hydroxyquinolato) and its derivatives have been investigated extensively for their uses in OLEDs.[5a−h] Gal-

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lium(III) analogues of 8-hydroxyquinoline derivatives have also been investigated.[5i−k] In contrast, the investigation on boron compounds that contain the ligand 8-hydroxyquinoline or its derivatives has been rather limited. A few years ago we reported our investigation on BR_2q (R = ethyl, phenyl, and 2-naphthyl) and their electroluminescent properties,[6] which demonstrated that boron compounds are promising emitters for OLEDs. In order to understand the electronic effects of substituents and the ligands on the luminescent properties of the BR_2q or BR_2q' family, we have extended our investigation to boron compounds with the general formula of BAr_2q or BAr_2q' where Ar = phenyl or 2-benzothienyl, q′ = 2-methyl-q, 5-(1-naphthyl)-q, or 5-(2-benzothienyl)-q. The synthetic aspects and luminescent properties of the new boron compounds are reported herein. A preliminary study on the electroluminescent properties of B(2-benzothienyl)$_2$q is also described herein.

Experimental Section

Solvents for reactions were freshly distilled over appropriate drying agents prior to use. Reactions that required oxygen-free conditions were carried out under inert atmosphere of nitrogen in oven-dried glassware using standard Schlenk techniques. ^1H and ^{13}C NMR spectra were recorded on Bruker Avance 300 (300 MHz for ^1H, 75.3 MHz for ^{13}C) or Bruker Avance 400 (400 MHz for ^1H, 100.6 MHz for ^{13}C) spectrometers at room temperature. ^{11}B NMR spectra were also recorded on a Bruker Advance 400 (128.4 MHz for ^{11}B) spectrometer using BF_3 (Et_2O) as the external reference. Elemental analyses were performed by Canadian Microanalytical Service, Delta, British Columbia. UV−Vis spectra were obtained on a Hewlett-Packard 8562A diode array spectrophotometer. Excitation and emission spectra were recorded on a Photon Technologies International QuantaMaster model C-60 spectrometer at room temperature. Redox potentials were measured in CH_2Cl_2 solution using 0.1 M NBu_4PF_6 as the electrolyte on a CV-50W BAS voltammetric analyzer by using a Ag/AgCl electrode as the reference electrode and a platinum electrode as the working electrode at room temperature. TLC was carried out on SiO_2 (silica gel F254, Whatman). Flash chromatography was carried out on silica (silica gel 60, 70−230 mesh). Melting points were determined with a Fisher-Johns melting point apparatus without correction. 8-Hydroxyquinoline, 8-hydroxyquinaldine, BPh_3, BBr_3, 1-bromonaphthalene, and 1-benzothiophene were purchased from Aldrich Chemical Co. 5-Bromo-8-methoxyquinoline was synthesized according to literature methods,[7] and (1-naphthyl)boronic acid and (2-benzothienyl)boronic acids were prepared according to the general procedures for the preparation of aryl boronic acids.[8] BPh_2q and BPh_2(2-Me-q) were prepared using previously reported procedures.[6a]

Synthesis of BPh_2(5-(1-naphthyl)-q) (1). The synthesis of **1** involves three steps as described below.

5-(1-Naphthyl)-8-methoxyquinoline (L1a). An oven-dried resealable Schlenk flask with magnetic stirring bar was cooled to room temperature under a nitrogen purge. A condenser was connected for reflux. The flask was charged with 5-bromo-8-methoxyquinoline (0.476 g, 2 mmol), (1-naphthyl)boronic acid (0.413 g, 2.4 mmol), $NaHCO_3$ (0.400 g, 4.8 mmol), and $Pd(PPh_3)_4$ (69 mg, 0.06 mmol, 3% mmol), and then it was evacuated and backfilled three times with nitrogen again. A separate flask containing a mixture of toluene (45 mL), water (10 mL), and ethanol (10 mL) was degassed for 1 h before being transferred to the above flask via cannula. The resulting mixture was refluxed with vigorous stirring for 18 h. The reaction mixture was cooled to room temperature and separated. The aqueous phase was extracted with dichloromethane (3 × 40 mL) combined with the organic phase, dried over $MgSO_4$, and decanted for evaporation of the solvents under reduced pressure. The residue was purified by a column chromatography using ethyl acetate/hexane (4/1) as the eluent to afford **L1a** in 92% yield. ^1H NMR ($CDCl_3$, δ, ppm): 8.97 (1H, dd, $J = 1.5$ Hz, 4.0 Hz), 7.98 (1H, d, $J = 8.2$ Hz), 7.96 (1H, d, $J = 8.2$ Hz), 7.72 (1H, dd, $J = 1.5$ Hz, 8.5 Hz), 7.60 (1H, dd, $J = 7.0$, 8.2 Hz), 7.48−7.54 (3H, m), 7.38 (1H, d, $J = 8.3$ Hz), 7.33 (1H, dd, $J = 1.1$ Hz, 6.5 Hz), 7.29 (1H, dd, $J = 4.3$ Hz, 8.6 Hz), 7.20 (1H, d, $J = 7.9$ Hz), 4.21 (3H, s)

5-(1-Naphthyl)-8-hydroxyquinoline (L1b). A solution of BBr_3 (1.0 M in heptane, 3.7 mL, 3.7 mmol) was added to a solution of 5-(naphth-1-yl)-8-methoxyquinoline (**L1a**) (0.500 g, 1.75 mmol) in 25 mL of dichloromethane at 0 °C under nitrogen. The reaction mixture was warmed to room temperature and underwent further reflux with stirring for 12 h. H_2O (20 mL) was then added, and the resulting mixture was stirred for 30 min. The organic phase was separated. The aqueous layer was neutralized with saturated $NaHCO_3$ to pH 7−8 and was extracted with CH_2Cl_2 (3 × 40 mL). The combined organic phases were washed with brine. The combined dichloromethane solution was dried over $MgSO_4$ and decanted. After the solvent was removed under reduced pressure, the residue was purified by column chromatography using THF/hexane (1/1) as the eluent, giving a green solid of 5-(1-naphthyl)-8-hydroxyquinoline, **L1b**, in 45% yield. ^1H NMR ($CDCl_3$, δ, ppm): 8.82 (1H, d, $J = 3.3$ Hz), 7.98 (1H, d, $J = 8.1$ Hz), 7.96 (1H, d, $J = 8.0$ Hz), 7.79 (1H, d, $J = 8.5$ Hz), 7.60 (1H, t, $J = 8.1$ Hz), 7.54−7.47 (3H, m), 7.41 (1H, d, $J = 8.4$ Hz), 7.37 (1H, d, $J = 7.8$ Hz), 7.33 (1H, t, $J = 7.9$ Hz), 7.31 (1H, d, $J = 8.5$ Hz), 6.99 (1H, s).

Synthesis of Compound 1. Triphenylborane (80 mg, 0.33 mmol) dissolved in THF (10 mL) was added to a solution of 5-(naphth-1-yl)-8-hydroxyquinoline (**L1b**) (90 mg, 0.33 mmol) stirring in THF (15 mL). The reaction mixture became yellow with green luminescence after being stirred for a few minutes. After stirring for 12 h under reflux with TLC monitoring the completion of the reaction, the mixed solution was concentrated by vacuum. The residue was dissolved in CH_2Cl_2 and transferred to a small vial, on which hexane was slowly laid. The solution was allowed to stand at room temperature for 2 days for slow evaporation and diffusion, which gave greenish crystals of **1** in 72% yield with mp 255−256 °C. ^1H NMR ($CDCl_3$, δ, ppm): 8.64 (1H, d, $J = 5.05$ Hz,), 8.02−7.98 (3H, m), 7.74 (1H, d, $J = 7.83$ Hz,), 7.64−7.62 (3H, m), 7.56−7.49 (6H, m), 7.42−7.29 (8H, m). ^{13}C NMR ($CDCl_3$, δ, ppm): 158.44, 139.37, 138.19, 137.56, 135.44, 134.30, 133.82, 132.74, 132.04, 132.03, 128.51, 128.48, 128.04, 127.66, 127.65, 127.06, 126.44, 126.13, 125.90, 125.53, 124.19, 122.71, 109.48. ^{11}B NMR

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($CDCl_3$, δ, ppm): 11.86 ppm. Anal. Calcd (%) for $C_{31}H_{22}NBO$: C, 85.53; H, 5.09; N, 3.22; Found: C, 85.13; H, 5.03; N, 3.13.

Synthesis of BPh_2(5-(2-benzothienyl)-q) (2). As described for the formation of **1**, the synthesis of **2** also involves three steps as described below.

5-(1-Benzothien-2-yl)-8-methoxyquinoline (L2a). As in the manner described for **L1a**, to a mixture of 5-bromo-8-methoxyquinoline (0.476 g, 2 mmol), (2-benzothienyl)boronic acid (0.400 g, 2.25 mmol), $NaHCO_3$ (0.400 g, 4.8 mmol), and $Pd(PPh_3)_4$ (60 mg, 5.1 mmol, 2.5%) were added a degassed solution of toluene (40 mL), water (10 mL), and ethanol (10 mL) via cannula. The resulting mixture was refluxed with vigorous stirring for 18 h. The crude product was purified by a column chromatography using ethyl acetate/hexane (4/1) as the eluent to afford **L2a** in 52% yield. ^1H NMR ($CDCl_3$, δ, ppm): 8.98 (1H, dd, $J = 1.6$ Hz, 4.1 Hz), 8.60 (1H, dd, $J = 1.7$ Hz, 8.6 Hz), 7.90 (1H, d, $J = 8.2$ Hz), 7.85 (1H, d, $J = 7.3$ Hz), 7.67 (1H, d, $J = 8.0$ Hz), 7.45−7.37 (2H, m), 7.45 (1H, dd, $J = 1.2$ Hz, 7.2 Hz), 7.38 (1H, s), 7.12 (1H, d, $J = 8.1$ Hz), 4.16 (3H, s).

5-(Benzothien-2-yl)-8-hydroxyquinoline (L2b). To a solution of 5-(benzothien-2-yl)-8-methoxyquinoline (**L2a**) (0.294 g, 1 mmol) in 20 mL of dichloromethane was added a solution of BBr_3 (1.0 M in heptane, 2 mL, 2 mmol) at 0 °C with stirring under nitrogen. The reaction mixture was warmed to room temperature and underwent further reflux overnight. Following the same method of workup as described for **L1b** afforded **L2b** in 50% yield. ^1H NMR (DMSO, δ, ppm): 9.11 (1H, d, $J = 4.2$ Hz), 8.06 (1H, d, $J = 7.7$ Hz), 7.98 (1H, d, $J = 7.0$ Hz), 7.95 (1H, d, $J = 7.6$ Hz), 7.88 (1H, d, $J = 8.0$ Hz), 7.67 (1H, s), 7.49−7.43 (3H, m), 7.38 (1H, s), 4.80 (1H, br).

Synthesis of 2. A THF solution (10 mL) of triphenylborane (58 mg, 0.22 mmol) was transferred to a flask containing 5-(2-benzothienyl)-8-hydroxyquinoline (**L2b**) (61 mg, 0.22 mmol) dissolved in 20 mL of THF. The solution became luminescent yellow after being stirred for a few minutes. The solution was under reflux with stirring for overnight. Orange-yellow single crystals of **2** were obtained via slow evaporation and diffusion of solvents in 56% yield in the same manner as for **1**. Mp 210−211 °C. ^1H NMR ($CDCl_3$, δ, ppm): 8.92 (1H, d, $J = 7.8$ Hz), 8.66 (1H, d, $J = 4.5$ Hz), 7.92−7.86 (3H, m), 7.72 (1H, dd, $J = 5.01$ Hz, 8.51 Hz), 7.51−7.48 (4H, m), 7.45−7.39 (4H, m) 7.34−7.27 (6H, m). ^{13}C NMR ($CDCl_3$, δ, ppm): 159.56, 140.67, 140.37, 140.10, 138.22, 138.17, 135.10, 134.99, 132.42, 128.34, 128.07, 127.53, 127.42, 125.17, 124.94, 123.99, 123.69, 123.42, 122.58, 118.89, 110.15. ^{11}B NMR ($CDCl_3$, δ, ppm): 12.10 ppm. Anal. Calcd (%) for $C_{29}H_{20}NOBS$: C, 78.92; H, 4.57; N, 3.17. Found: C, 78.40; H, 4.52; N, 3.48.

Synthesis of B(2-benzothienyl)$_2$q (3). To the solution of benzothiophene (0.730 g, 5.4 mmol) in 20 mL of THF was added 3.9 mL (1.6 M, 6.2 mmol) of n-BuLi slowly. After being stirred for 1 h, the solution changed from light green to a clear brown color. BBr_3 (1.0 M in heptane, 1.8 mL, 1.8 mmol) was then added, and the color of the mixture turned to colorless. The solution was stirred for 1.5 h, and 0.260 g (2.0 mmol) of 8-hydroxyquinoline dissolved in 10 mL of THF in a separate flask was added via a double needle to the above solution. The reaction mixture became light yellow immediately with green luminescence. After being stirred for 3 h, the solution was evaporated to dryness under vacuum, and 5 mL of CH_2Cl_2 was added. The product was transferred to a small vial for crystallization after filtration by laying the hexane on the top of the CH_2Cl_2 layer. After standing for a few days, light green crystals of compound **3** were obtained in 51% yield with mp 204−205 °C. ^1H NMR ($CDCl_3$, δ, ppm): 8.73 (1H, dd, $J = 1.01$ Hz, 5.05 Hz,), 8.48 (1H, dd, $J = 1.01$ Hz, 8.34 Hz), 7.84−7.72 (5H, m), 7.68 (1H, dd, $J = 8.08$ Hz, 5.05 Hz), 7.54 (s. 2H), 7.36−7.24 (6H, m). ^{13}C NMR ($CDCl_3$, δ, ppm): 157.95, 142.35, 141.36, 140.19, 139.60, 136.94, 133.11, 128.40, 127.20, 123.72, 123.49, 123.25, 122.97, 122.27, 118.24, 113.27, 110.46. ^{11}B NMR ($CDCl_3$, δ, ppm): 8.97 ppm. Anal. Calcd for $C_{25}H_{16}NOBS_2$: C, 71.26; H, 3.83; N, 3.32. O, 3.8; B: 2.57; S, 15.22. Found: C, 70.86; H, 3.93; N, 3.21.

Synthesis of B(2-benzothienyl)$_2$(2-methyl-q) (4). To the solution of benzothiophene (0.730 g, 5.4 mmol) in 20 mL of THF was added 3.9 mL (1.6 M, 6.2 mmol) of n-BuLi slowly at 0 °C. After being stirred for 1 h, the solution changed from light green to a clear brown color. BBr_3 (1.0 M in heptane, 1.8 mL, 1.8 mmol,) was then added, and the color of the mixture turned colorless. The solution was stirred for 1.5 h, and then 0.290 g (1.8 mmol) of 2-methyl-8-hydroxyquinoline dissolved in 10 mL THF in a separate flask was added via double needle to the above solution. The reaction mixture became light yellow immediately with green luminescence. After being stirred for 3 h, the solution was evaporated to dryness under vacuum, and 5 mL of CH_2Cl_2 was added. The product was transferred to a small vial for crystallization after filtration by laying the hexane on the top of the CH_2Cl_2 layer. After standing for a few days, light green crystals of compound **4** were obtained in 53% yield with mp 208−209 °C. ^1H NMR ($CDCl_3$, δ, ppm): 8.38 (1H, d, $J = 8.34$ Hz,), 8.84−7.78 (4H, m), 7.67 (1H, t, $J = 8.08$ Hz), 7.61 (2H, s), 7.42 (1H, d, $J = 8.59$ Hz), 7.44−7.23 (6H, m), 2.78 (3H, s). ^{13}C NMR ($CDCl_3$, δ, ppm): 158.05, 154.85, 143.12, 142.09, 140.53, 137.66, 132.36, 129.32, 127.26, 126.13, 125.00, 124.31, 124.19, 123.96, 122.86, 113.88, 111.07, 21.91. ^{11}B NMR ($CDCl_3$, δ, ppm): 8.75 ppm. Anal. Calcd (%) for $C_{26}H_{18}NOBS_2$: C, 71.73; H, 4.17; N, 3.22. Found: C, 71.29; H, 4.13; N, 3.25.

X-ray Crystallography Analyses. Single-crystals of **1**−**4** obtained from CH_2Cl_2/hexane solution were mounted on glass fibers in a brass pin, and the data were collected on a Siemens P4 single-crystal X-ray diffractometer with a SMART CCD-1000 detector and graphite-monochromated Mo Kα radiation operating at 50 kV and 30 mA at 25 °C. No significant decay was observed during the data collection. Data were processed on a Pentium PC using Siemens SHELXTL software package (version 5.10).[9] Neutral atom scattering factors were taken from Cromer and Waber.[10] Empirical absorption correction was applied to all crystals. The structures were solved by direct methods. All non-hydrogen atoms were refined anisotropically. The positions of hydrogen atoms were calculated, and their contributions in structural factor calculations were included. The crystal data are summarized in Table 1. Selected bond lengths and angles are given in Table 2.

Quantum Yield Measurement. Quantum yields of compounds **1**−**4** were determined relative to 9,10-diphenylanthracene in CH_2Cl_2 at 298 K ($\Phi_r = 0.95$).[11] The absorbance of all the samples and the standard at the excitation wavelength were approximately 0.098−0.109. The quantum yields were calculated using previously known procedures.[12]

Fabrication of Electroluminescent Devices. The EL device of **3** was fabricated on an indium−tin oxide (ITO) substrate. Organic layers were deposited on the substrate by conventional vapor

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Table 1. Crystallographic Data of **1**−**4**

	1	**2**	**3**	**4**
formula	$C_{31}H_{22}BNO$	$C_{29}H_{20}BNOS$	$C_{25}H_{16}BNOS_2$	$C_{26}H_{18}BNOS_2$
fw	435.324	441.352	421.344	435.37
space group	$P2_1/c$	$P\bar{1}$	$P2_1/n$	$P2_1/c$
a/Å	16.850(5)	7.9708(16)	12.242(4)	18.36(3)
b/Å	7.776(2)	10.50(2)	17.188(6)	17.41(2)
c/Å	18.372(6)	14.353(3)	19.354(7)	13.799(19)
α, deg	90	74.011(4)	90	90
β, deg	107.837	87.716(4)	91.748(6)	100.97(2)
γ, deg	90(5)	89.802(4)	90	90
V/Å^3	2291.6(12)	1158.2(4)	4071(2)	4329(10)
Z	4	2	8	8
D_c/(g cm^{-3})	1.262	1.266	1.375	1.336
μ/mm^{-1}	0.075	0.162	0.279	0.265
$2\theta_{max}$/deg	56.72	56.44	56.64	56.68
reflns measured	14684	8263	2847	30173
reflns used (R_{int})	5222 (0.1483)	5189 (0.0154)	9567 (0.0345)	10130 (0.0319)
no. variables	308	311	541	579
final R [$I > 2\sigma(I)$]	R1^a = 0.0711 wR2^b = 0.1244	R1^a = 0.0418 wR2^b = 0.0885	R1^a = 0.059 wR2^b = 0.1511	R1^a = 0.0490 wR2^b = 0.1216
R (all data)	R1 = 0.3101 wR2 = 0.1630	R1 = 0.0893 wR2 = 0.1012	R1 = 0.1256 wR2 = 0.1737	R1 = 0.1013, wR2 = 0.1409
GOF on F^2	0.707	0.855	0.898	0.905

[a] $R1 = \sum|F_o| - |F_c|/\sum|F_o|$. [b] $wR2 = [\sum w[(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$. $w = 1/[\sigma^2(F_o^2) + (0.075P)^2]$, where $P = [\max(F_o^2, 0) + 2F_c^2]/3$.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for **1**−**4**

		1	
B(1)−O(1)	1.535(5)	O(1)−B(1)−C(1)	111.9(4)
B(1)−N(1)	1.646(5)	O(1)−B(1)−C(7)	109.3(4)
B(1)−C(1)	1.578(6)	C(1)−B(1)−C(7)	119.0(4)
B(1)−C(7)	1.606(6)	O(1)−B(1)−N(1)	97.6(3)
		C(1)−B(1)−N(1)	108.2(4)
		C(1)−B(1)−N(1)	108.5(4)
		2	
B(1)−O(1)	1.5323(19)	O(1)−B(1)−C(1)	109.73(13)
B(1)−N(1)	1.6383(19)	O(1)−B(1)−C(7)	111.07(12)
B(1)−C(1)	1.594(2)	C(1)−B(1)−C(7)	116.29(13)
B(1)−C(7)	1.596 (2)	O(1)−B(1)−N(1)	97.73(11)
		C(1)−B(1)−N(1)	109.54(11)
		C(7)−B(1)−N(1)	110.90(12)
		3	
B(1)−O(1)	1.503(4)	O(1)−B(1)−C(1)	111.3(2)
B(1)−N(1)	1.618(4)	O(1)−B(1)−C(9)	110.7(2)
B(1)−C(1)	1.603(5)	C(1)−B(1)−C(9)	114.1(2)
B(1)−C(9)	1.593(6)	O(1)−B(1)−N(1)	99.6(2)
		C(1)−B(1)−N(1)	107.8(2)
		C(9)−B(1)−N(1)	112.5(2)
		4	
B(1)−O(1)	1.528(3)	O(1)−B(1)−C(19)	109.00(19)
B(1)−N(1)	1.630(4)	O(1)−B(1)−C(11)	110.51(18)
B(1)−C(11)	1.603(4)	C(19)−B(1)−C(11)	114.2(2)
B(1)−C(19)	1.593 (4)	O(1)−B(1)−N(1)	98.48(15)
		C(19)−B(1)−N(1)	114.61(18)
		C(11)−B(1)−N(1)	108.95(4)

vacuum deposition. *N*,*N*′-Bis(1-naphthyl)-*N*,*N*′-diphenylbenzidine (NPB) was employed as the hole transport layer. The cathode composed of LiF and Al was deposited on the substrate by conventional thermal vacuum deposition. The active device area is 1.0 × 5.0 mm^2. The current/voltage characteristics were measured using a Keithley 238 Source Measure Unit. The EL spectra and the luminance for the devices were measured by using a Photo Research-650 Spectra Colorimeter.

Results and Discussion

Syntheses. Two new ligands, 5-(1-naphthyl)-8-hydroxyquinoline (**L1b**) and 5-(2-benzothienyl)-8-hydroxyquinoline (**L2b**), have been obtained by procedures shown in Scheme 1. The parent molecules **L1a** and **L2a** were obtained by using Pd catalyzed Suzuki coupling[13] between the appropriate boronic acid and 5-bromo-8-methoxyquinoline. Demethylation[14] of **L1a** and **L2a** in the presence of BBr_3 led to the isolation of **L1b** and **L2b** in 45% and 50% yields, respectively. The boron chelate compounds **1** and **2** were isolated in 52% and 50% yields, from the reaction of BPh_3 with the ligands **L1b** and **L2b**, respectively, in THF under reflux. For the synthesis of **3** and **4**, the precursor compound B(2-benzothienyl)$_3$ was first prepared in situ without a full characterization by the reaction of n-BuLi with benzothiophene to yield (2-benzothienyl)lithium, followed by the addition of $^1/_3$ equiv of BBr_3.[15] The reaction of 8-hydroxyquinoline or 8-hydroxyquinaldine with the B(2-benzothienyl)$_3$ solution resulted in the formation of compounds **3** and **4**, respectively (isolated yield 51%, 52%, respectively). Schemes 1 and 2 summarize all the synthetic steps involved for the syntheses of the boron compounds. The four boron compounds were characterized by ^{1}H, ^{13}C, and ^{11}B NMR, elemental analyses, and single-crystal X-ray diffractions. ^{11}B NMR chemical shifts of the four compounds are in the same range as those observed for diphenyl(2-aminoethoxy)boranes derivatives' spectra,[16] consistent with a tetrahedral geometry.

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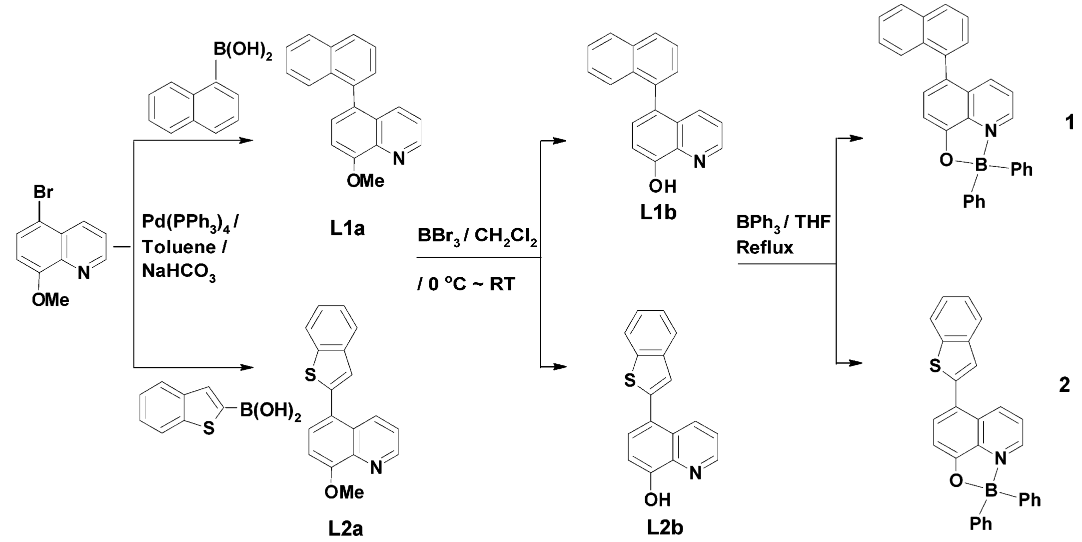
(13) (a) Miyaura, N. *Adv. Met.-Org. Chem.* **1998**, *6*, 187 and references therein. (b) Suzuki, A. *J. Organomet. Chem.* **1999**, *576*, 147 and references therein.

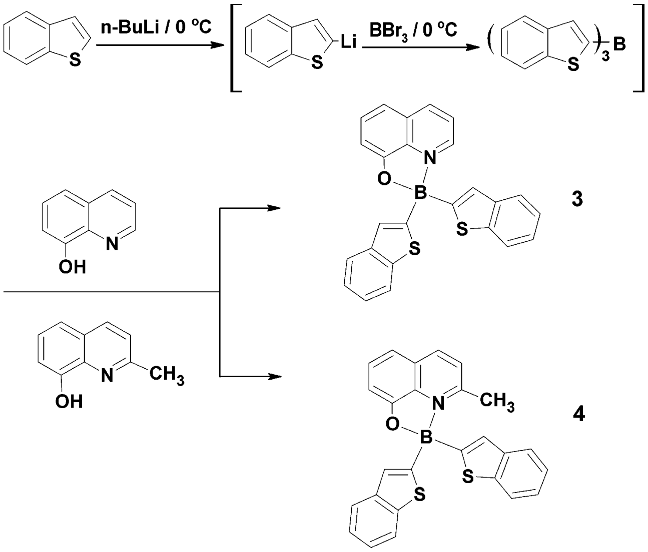
(14) (a) Wolfe, J. P.; Singer, R. A.; Yang, B. H.; Buchwald, S. L. *J. Am. Chem. Soc.* **1999**, *121*, 9550. (b) Silva, N. O.; Abreu, A. S.; Ferreira, P. M. T.; Monteiro, L. S.; Queiroz, M.-J. R. P.; *Eur. J. Org. Chem.* **2002**, 2524. (c) Gust, R.; Keilitz, R.; Schmidt, K.; von Rauch, M. *J. Med. Chem.* **2002**, *45*, 3356. (d) Queiroz, M.-J. R. P.; Dubest, R.; Aubard, J.; Faure, R.; Guglielmetti, R. *Dyes Pigm.* **2000**, *47*, 219. (e) Lopez-Alvarado, P.; Avendano, C.; Menendez, J. C. *J. Chem. Soc., Perkin Trans. 1* **1997**, 229. (f) Batt, D. G.; Maynard, G. D.; Petraitis, J. J.; Shaw, J. E.; Galbraith, W.; Harris, R. R. *J. Med. Chem.* **1990**, *33*, 360. (g) Amin, S.; Huie, K.; Hussain, N.; Balanikas, G.; Carmella, S. G.; Hecht, S. S. *J. Org. Chem.* **1986**, *51*, 1206.

(15) (a) Wrackmeyer, B.; Milius, W.; Molla, E. *Z. Naturforsch., B: Chem. Sci.* **1996**, *51*, 1811. (b) Brown, H. C.; Racherla, U. S. *J. Org. Chem.* **1986**, *51*, 427. (c) Brown, H. C.; Racherla, U. S. *Tetrahedron Lett.* **1985**, *26*, 4311.

Scheme 1



Scheme 2



All the four compounds are air-stable both in the solid state and in solution. They are also thermally stable with the melting points above 200 °C.

Crystal Structures of 1−4. The crystal structures of the four boron compounds have been determined by single-crystal X-ray diffraction analyses. The boron center in all four compounds displays a typical tetrahedral geometry, as shown in Figures 1−4. The hydroxyquinoline groups in all four molecules are chelated to the boron in the same manner to form a five-membered chelate ring. The bond angle N−B−O of the four complexes is similar, ranging from 97.6(3)° to 99.6(2)°. Each boron center in the four compounds is further bound by two carbon atoms of the two phenyl groups (for **1** and **2**) or the two benzothienyl groups (for **3** and **4**). The B−N, B−O, and B−C bond lengths are similar to those reported previously.[6,17,18] The five-membered chelate ring in each compound is coplanar with the corresponding quinoline ring. No significant $\pi-\pi$ stacking was observed in the crystal lattices of the four compounds. The dihedral angle between the naphthyl ring and quinoline ring in **1** is 87.7°; they are almost perpendicular to each other due to the steric hindrance of *ortho* hydrogen atoms. The benzothienyl ring in **2** displays a rotational disorder with 50% occupancy for each disordered sit and a dihedral angle of 46.1° (48.1°) with the quinoline ring. The much smaller dihedral angle in **2** is clearly caused by the much reduced steric interactions between the benzothienyl group and the quinoline ring, compared to the interactions between the 1-naphthyl group and the quinoline ring in **1**. As a conse-

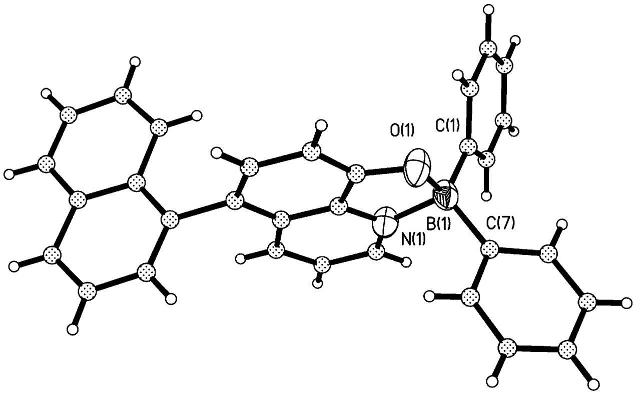


Figure 1. Molecular structure of **1** with labeling scheme and 50% thermal ellipsoids. All hydrogen atoms are omitted for clarity.

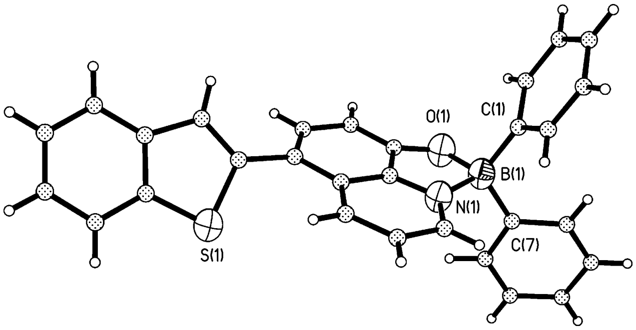


Figure 2. Molecular structure of **2** with labeling scheme and 50% thermal ellipsoids. All hydrogen atoms are omitted for clarity.

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(16) Höpfl, H.; Farfán, N.; Castillo, D.; Santillan, R.; Contreras, R.; Martínez-Martínez, F. J.; Galván, M.; Alvarez, R.; Fernández, L.; Halut, S.; Daran, J.-C. *J. Organomet. Chem.* **1997**, *544*, 175.

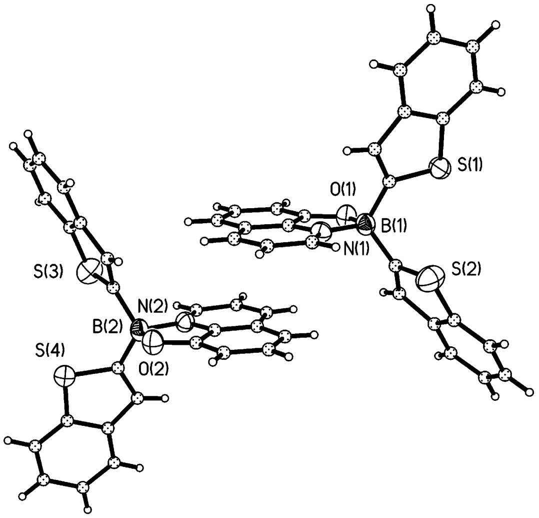

Figure 3. Molecular structure of **3** with labeling scheme and 50% thermal ellipsoids. All hydrogen atoms are omitted for clarity.

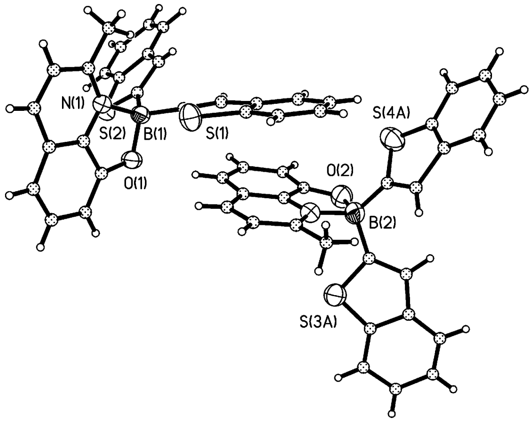

Figure 4. Molecular structure of **4** with labeling scheme and 50% thermal ellipsoids. All hydrogen atoms are omitted for clarity.

quence, the benzothienyl and the quinoline ring form partial conjugation as reflected by the slightly shortened bond length between C17−C22 (1.476 Å) in **2** compared with that between C16−C22 (1.536 Å) in **1**. There is no significant intermolecular $\pi-\pi$ stacking interaction in the crystal lattice of **1**. In **2**, there are intermolecular $\pi-\pi$ interactions involving a few atoms of the benzo portions of the benzothienyl ring with the shortest atomic separation distance being 3.73 Å. Compounds **3** and **4** have similar structures. In the asymmetric unit of **3** and **4** are two independent molecules, which form a π-stacked pair. As shown in Figures 3 and 4, the $\pi-\pi$ stacking in **3** is between two quinoline groups from the two independent molecules (the shortest atomic separation distance is 3.44 Å), while in contrast, the $\pi-\pi$ stacking in **4** is between a quinoline group from one molecule and a benzothienyl group from another molecule (the shortest atomic separation distance is 3.50 Å). These $\pi-\pi$ stacking interactions are limited between two molecules, and no extended $\pi-\pi$ stacking is observed for **3** and **4**. It is likely that the methyl group on the quinoline ligand in **4** prevents the $\pi-\pi$ stacking from occurring between two quinoline groups. Both thienyl rings in **4** are disordered in a similar manner as the 2-benzothienyl substituent in **2**. Only one set of the disordered benzothienyl ligands is shown in Figure 4. In addition to the $\pi-\pi$ stacking difference, the 2-methyl group in **4** has a subtle impact on the structure. For example, the O−B−N angle in **4** is about 1° smaller than that in **3**. The B−N and B−O bond lengths in **4** are also somewhat longer than those in **3**. Previously, Al(2-Me-q)$_3$ was reported[5d] to be unstable due to the 2-methyl group, compared to that of Alq$_3$. However, we did not observe any difference in terms of thermal and chemical stability between **3** and **4**.

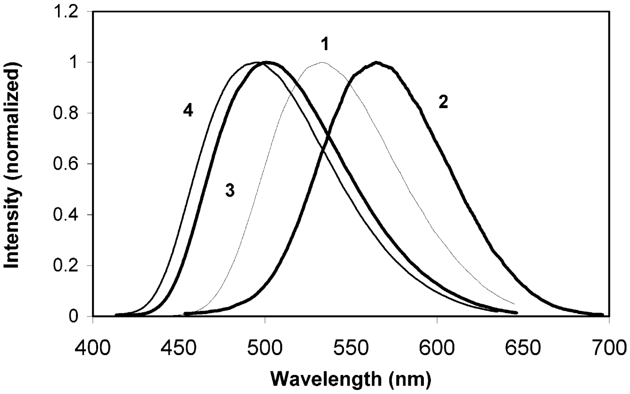

Figure 5. Emission spectra of **1**−**4** in CH_2Cl_2 at 298 K.

Table 3. Spectroscopic Data[a] for BPh_2q, BPh_2(2-Me-q), **1**−**4**

compd	UV−vis (λ_{max}, nm)	excitation (λ_{max}, nm)	emission (λ_{max}, nm)	quantum yield[b] (%)	conditions
BPh_2q	242, 264, 396	395	504	30	CH_2Cl_2, 298 K
BPh_2-(2-Me-q)	246, 266, 396	395	497	34	CH_2Cl_2, 298 K
1	298, 406	409	534	11	CH_2Cl_2, 298 K
		397	504		CH_2Cl_2, 77 K
		413	523		film, 298 K
2	232, 266, 304, 422	418	565	1.0	CH_2Cl_2, 298 K
		448	533		CH_2Cl_2, 77 K
		428	560		film, 298 K
3	238, 264, 388	394	501	18	CH_2Cl_2, 298 K
		396	483		CH_2Cl_2, 77 K
		394	496		film, 298 K
4	294, 304, 320 336, 354, 380	392	496	37	CH_2Cl_2, 298 K
		395	478		CH_2Cl_2, 77 K
		393	490		film, 298 K

[a] Concentration: $[M] = 5 \times 10^{-6}$. [b] Relative to 9,10-diphenylanthracene in CH_2Cl_2 at room temperature.

Luminescent and Electronic Properties. Upon irradiation by UV light, in solution and in the solid state at ambient temperature compounds **3** and **4** yield a bright bluish-green emission, while compounds **1** and **2** exhibit green and orange-yellow luminescence, respectively. The emission spectra in CH_2Cl_2 at ambient temperature for all four compounds are shown in Figure 5. Table 3 summarizes the luminescent data of compounds **1**−**4**. For comparison, the

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(17) (a) Niedenzu, K.; Deng, H.; Knoeppel, D.; Krause, J.; Shore, S. G. *Inorg. Chem.* **1992**, *31*, 3162. (b) Hsu, L. Y.; Mariategui, J. F.; Niedenzu, K.; Shore, S. G. *Inorg. Chem.* **1987**, *26*, 143. (c) Kiegel, W.; Lubkowitz, G.; Rettig, S. J.; Trotter, J. *Can. J. Chem.* **1991**, *69*, 1217.

(18) (a) Heller, G. *Top. Curr. Chem.* **1986**, *131*, 39. (b) Dal Negro, A.; Ungaretti, L.; Perotti, A. *J. Chem. Soc., Dalton Trans.* **1972**, *15*, 1639. (c) Binder, H.; Matheis, W.; Deiseroth, H.-J.; Han, F.-S. *Z. Naturforsch.* **1984**, *39b*, 1717. (d) Clegg, W.; Noltemeyer, N.; Shelderick, G. M.; Maringgele, W.; Meller, A. *Z. Naturforsch.* **1980**, *35b*, 1499.

Table 4. HOMO and LUMO Energy Levels for Compounds **1**−**4**

	experimentally measured			molecular orbital calculations[a]		
compd	HOMO (eV)	LUMO (eV)	$\Delta E_{optical}$ (eV)	HOMO	LUMO	Δ(HOMO − LUMO)
1	−5.69	−3.10	2.59	−0.216673	−0.088219	0.1285/3.50 eV
2	−5.53	−3.10	2.43	−0.214950	−0.093304	0.1216/3.31 eV
3	−5.71	−2.98	2.73	−0.201876	−0.097097	0.1048/2.85 eV
4	−5.70	−2.94	2.76	−0.189335	−0.086039	0.1033/2.81 eV

[a] Unit: hartree.

previously reported data for BPh_2q are also included. BPh_2(2-Me-q) was prepared, and its spectroscopic data are also included in Table 3. In solution, compounds **1**−**4** have emission maxima at 534, 565, 501, and 496 nm, respectively. The emission spectra of **3** and **4** are very similar to those of BR_2q (R = ethyl, phenyl, and 1-naphthyl) which have emission maxima at 495−504 nm reported earlier from our group,[6a] indicating that changing the R group has little impact on the emission maximum. There is, however, a small difference between the emission maxima of **3** and **4**, with the latter having a somewhat shorter emission wavelength. The same difference is also evident between BPh_2q and BPh_2(2-Me-q) as shown in Table 3. Previously, it has been demonstrated for Alq'_3 compounds that the HOMO level is dominated by the phenoxy ring while the LUMO level is dominated by the pyridyl ring of the 8-hydroxyquinoline ligand.[5d] Therefore, an electron donating substituent on the pyridyl ring will push the LUMO level up, hence increasing the HOMO−LUMO energy gap, which has been confirmed by a number of 2-methyl, 3-methyl, and 4-methyl substituted 8-hydroxyquinline complexes[5] $Al(Me\text{-}q)_3$. We therefore believe that the small blue shift of emission energy from **3** to **4** can also be attributed to the electron donating 2-methyl group in **4**. The major difference between **3** and **4** is the emission quantum efficiency: **4** is more than two times more efficient than **3**. A similar methyl substitution effect on quantum efficiency has been observed in $Al(3\text{-}Me\text{-}q)_3$ and $Al(4\text{-}Me\text{-}q)_3$ compounds.[5b] Consistently, the BPh_2(2-Me-q) also displays a higher quantum efficiency than that of BPh_2q, albeit a much smaller difference than that between **3** and **4**. We can therefore conclude that the 2-methyl group in the 8-hydroxyquinoline ligand can enhance the emission efficiency of the complex, compared to the nonsubstituted ligand.

On the basis of previous theoretical and experimental work on 8-hydroxyquinoline derivative complexes of aluminum,[5] it is anticipated that, by attaching an aryl group at the C5 position of the quinoline ring, the emission maximum should shift toward a longer wavelength. Indeed, as shown by the data in Table 4, the emission maximum of **1** and **2** was shifted by ∼35 and 66 nm, respectively, compared to that[6a] of BPh_2q (504 nm). The red shift of **2** is more pronounced than that of **1**, which can be attributed to the relatively higher degree of conjugation between the benzothienyl ring and the quinoline ring in **2**, compared to that between naphthyl and the quinoline in **1**, as confirmed by the crystal structural data. The large emission red shift of **2** can also be attributed at least partially to electronic effects since the 2-benzothienyl moiety in **2** is a more electron rich group, and hence donate electron density to the quinoline ring more effectively than the 1-naphthyl moiety in **1**. The emission efficiency of both **1** and **2** is lower than those of **3** and **4**. One notable difference between **1**−**2** and **3**−**4**, in addition to the emission energy, is the low emission efficiency displayed by **1** and **2**. A similar drastic decrease of emission efficiency by an electron donating group at the C5 position, compared to Alq_3, has been observed previously in the $Al(5\text{-}Me\text{-}q)_3$ compound.[5b] The trend we observed for the BPh_2q' compounds is consistent with the trend observed for the C5 substituted Alq'_3 compounds. The unusually small quantum yield of **2** may be further attributed to the direct attachment of the thienyl group on the 8-hydroxyquinoline chromophore, which effectively quenches the emission by perhaps the "heavy atom" effect of the sulfur atom.[19]

The emission band for compounds **1**−**4** is somewhat blue-shifted in CH_2Cl_2 at 77 K, which can be attributed to the increased environmental rigidity[19] at 77 K. The emission band of the four compounds in the solid state is almost identical to that in solution, an indication that there is little intermolecular interaction present in the solid state, as confirmed by the crystal structures. The investigation of the effects of various solvents on emission was also carried out, which showed that the emission wavelengths are independent of the polarity of solvents (e.g., toluene, THF, CH_2Cl_2, and CH_3CN).

The LUMO levels for the four compounds were determined from the electrochemical reduction potential of the complexes in CH_2Cl_2 solutions. Oxidation potentials for these complexes could not be obtained. The energy gap between HOMO and LUMO was estimated by using the UV−vis absorption edge. The HOMO energy level was calculated by using the corresponding LUMO and energy gap values. As shown in Table 4, compound **2** has the highest HOMO energy level (−5.53 eV versus −5.69 to 5.71 eV of **1**, **3**, and **4**) and the smallest band gap (2.43 eV) among the four compounds. This trend is consistent with the corresponding wavelength data shown in Table 3. Several BPh_2L compounds where L is a O, O′-chelate ligand (diolate) have been reported recently.[20] The HOMO and LUMO energy levels of these compounds are comparable to those of **1**−**4**.

Molecular Orbital Calculations. To further understand the nature of luminescence, we carried out molecular orbital calculations for the four compounds on the restricted Hartree−Fock (RHF) level using a standard split-valence

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(20) Lim, H. J.; Kim, S. M.; Lee, S.-J.; Jung, S.; Kim, Y. K.; Ha, Y. *Opt. Mater.* **2003**, *21*, 211.

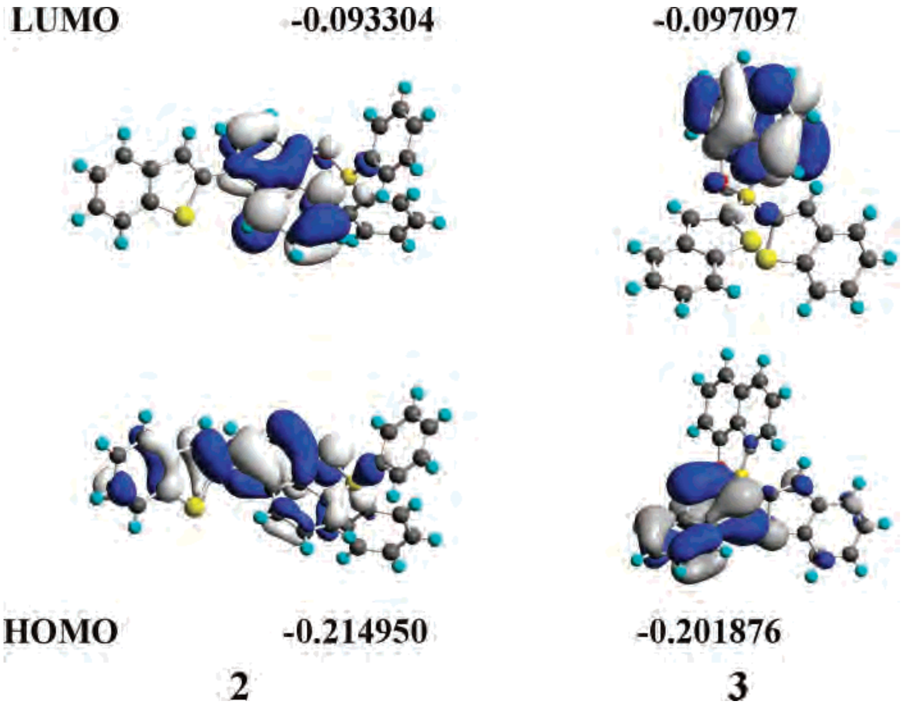

Figure 6. HOMO and LUMO levels of **2** and **3**.

polarized (3LYP/6-311G**) basis set, employing the Gaussian 98 suit of programs.[21] The orbital diagrams were generated by using the Molekel program.[22] The geometric parameters from X-ray diffraction analysis were used for the calculation. The calculated HOMO and LUMO energy levels and the difference for the four complexes are provided in Table 4. One unexpected result is that the calculated HOMO−LUMO gaps of compounds **1** and **2** are greater than those of **3** and **4**, which is obviously contradictory with the experimentally observed optical energy gap. Clearly the HOMO−LUMO gaps obtained from Gaussian 98 calculations should not be taken too seriously. Nevertheless, the MO calculated gap for **1** is bigger than that of **2**, which is consistent with the observed trend. Compounds **3** and **4** possess almost the same band gaps based on MO results, which is also consistent with experimental data. The surfaces of HOMO and LUMO for **2** and **3** along with the energy for each level are shown in Figure 6, as representative examples. All contour values are ±0.03 au. As can be seen from the diagrams, the HOMO level of compound **2** is a π orbital with contributions from both the benzothienyl substituent and the quinoline ring. In contrast, the HOMO level of **3** consists of two almost degenerate π orbitals with almost 100% contributions from the benzothienyl ligand bonded to the boron atom; one of the π orbitals is shown in Figure 6. The π^* orbital of the LUMO level for both compounds **2** and **3** involves contributions from the hydroxyquinoline ring. On the basis of the orbital diagrams in Figure 6, the electronic transition of **2** can be attributed to a π to π^* transition centered on the 5-benzothienyl-8-hydroxyquinoline ligand. In contrast, the electronic transition of **3** can be attributed to an interligand charge transfer from the benzothienyl ligand to the hydroxyquinoline ligand. Although the experimental data indicated that there is little difference between BPh_2q and B(2-benzothienyl)$_2$q (**3**) in term of emission energy, the molecular orbital calculation results showed that the electronic transition in **3** has a very different origin from that of BPh_2q: the former involves interligand charge transfer, and the latter involves a hydroxyquinoline centered $\pi \rightarrow \pi^*$ transition. The similar emission energy of **3** and BPh_2q seems to be coincidental.

Electroluminescence. Electroluminescent properties for **1** and **2** were not examined due to their poor photoluminescent efficiency and the fact that a number of BPh_2q' compounds have been demonstrated previously for use in EL devices, which indicated that compounds such as **1** and **2** should be able to act as an emitter in EL, if they were sufficiently bright. Because 8-hydroxyquinoline boron compounds that contain two 2-benzothienyl ligands are a class of previously unknown molecules, we decided to carry out a preliminary evaluation for the EL properties of compound **3**. On the basis of our previous work demonstrating that BPh_2q can function as both an emitter and an electron transport layer, a simple double-layer device with the structure of ITO/NPB(40 nm)/**3** (40 nm)/LiF (1 nm)/Al, where NPB = *N*,*N*′-bis(1-naphthyl)-*N*,*N*′-diphenylbenzidine,

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[21] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.6; Gaussian, Inc.: Pittsburgh, PA, 1998.

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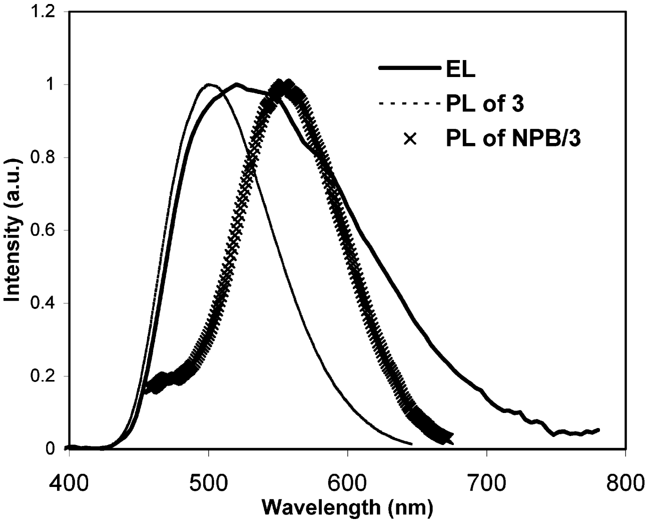

Figure 7. The EL spectrum of the device and the PL spectra of a film of **3** and a film of a 1:1 mixture of **3** and NPB.

is fabricated. The EL device produced a broad bluish-green emission band as shown in Figure 7, which is much broader than and partially matches the PL spectrum of **3**. The low energy emission zone of EL may be caused by the presence of exciplex emission between the NPB layer and **3**. Indeed, as shown in Figure 7, the PL spectrum of the film of a 1:1 mixture of **3** and NPB approximately matches the lower energy portion of the EL spectrum. Therefore, we concluded that the observed EL spectrum consists of emission from the compound **3** layer and the exciplex emission between NPB and **3**. Similar exciplex emission has been observed previously in the double-layer BPh_2q EL device.[6a] The tendency of the hydroxyquinoline boron chelates to form an exciplex with the NPB layer is in sharp contrast to that of Alq_3 and derivatives, which are known not to form exciplexes with NPB. This difference may be attributed to the structural difference between the boron and the aluminum compounds: the former has a relatively open tetrahedral geometry while the latter has a less open octahedral geometry. The turn-on voltage of the EL device is ~10 V, and the maximum brightness is ~1050 Cd/m^2 as shown in Figure 8. To compare with the performance of Alq_3, compound **3** is much less superior, in addition to its tendency to form an exciplex with the hole transport layer. As a result, no further investigation on electroluminescent properties of our boron compounds were conducted.

Conclusions

By varying the substituent group on the 8-hydroxyquinolato ligand, four new boron compounds with emission color ranging from blue-green to yellow-orange have been achieved.

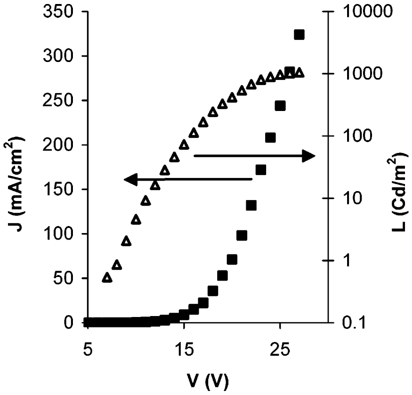

Figure 8. The $J-V$ and $L-V$ characteristics of the EL device.

The general effect of substitution at the C5 position and the C2 position of the 8-hydroxyquinolato ligand on luminescent properties observed for the boron compounds is consistent with the trend observed for related Alq'_3 compounds. Most notable is the drastic decrease of emission quantum efficiency caused by the electron donating substituent at the C5 position as demonstrated by compounds **1** and **2**, and the relatively high emission quantum efficiency displayed by **4** that has a methyl group at the C2 position of the hydroxyquinolato ligand. Unlike the $Al(2\text{-}Me\text{-}q)_3$ compound, the 2-Me-q ligand does not appear to cause notable instability for the boron compound, which probably can be explained by the presence of only one 2-Me-q chelate ligand in the boron compound that does not have as many interligand steric interactions as the three 2-Me-q ligands do in the aluminum compound. The replacement of the phenyl ligand in BPh_2q by the 2-benzothienyl ligand does not change the emission energy significantly. However, the composition of the HOMO level appears to have changed from the 8-hydroxyquinoline dominated π orbital in BPh_2q to an almost pure benzothienyl π orbital in **3** and **4**. The boron compounds such as BPh_2q in general display an emission band that is at a shorter wavelength than that of Alq_3. Compounds **1** and **2** are not suitable for use as emitters in OLEDs due to their low PL efficiency. Preliminary investigation on **3** indicates that this type of compound has the tendency to form an exciplex with the NPB hole transport layer and their performance in EL is not as satisfactory as that of the Alq_3.

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