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Syntheses, Structures, and Electroluminescence of New Blue/Green Luminescent Chelate Compounds: Zn(2-py-in)$_2$(THF), BPh$_2$(2-py-in), Be(2-py-in)$_2$, and BPh$_2$(2-py-aza) [2-py-in = 2-(2-pyridyl)indole; 2-py-aza = 2-(2-pyridyl)-7-azaindole]

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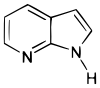
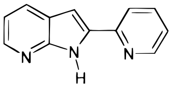
Abstract: Four novel blue/green luminescent compounds, Zn(2-py-in)$_2$(THF) (**1**), BPh$_2$(2-py-in) (**2**), Be(2-py-in)$_2$ (**3**), and BPh$_2$(2-py-aza) (**4**), where 2-py-in = 2-(2-pyridyl)indole and 2-py-aza = 2-(2-pyridyl)-7-azaindole, have been synthesized and fully characterized. The 2-py-in ligand and 2-py-aza ligand in the new compounds are chelated to the central atom. Compounds **2**−**4** are air stable and readily sublimable, with a melting point above 250 °C. In the solid state, compounds **1**−**4** have an emission maximum at λ 488, 516, 490, and 476 nm, respectively. The structures of compounds **2** and **4** are similar. The blue shift of emission energy displayed by compound **4**, in comparison to that of **2**, is attributed to the presence of an extra nitrogen atom in the 2-py-aza ligand as confirmed by ab initio calculations on compounds **2** and **4**. Electroluminescent devices of compounds **3** and **4** were fabricated by using *N*,*N*′-di-1-naphthyl-*N*,*N*′-diphenylbenzidine (NPB) as the hole transporting layer, Alq$_3$ (q = 8-hydroxyquinolato) as the electron transporting layer, and compound **3** or **4** as the light emitting layer. At 20 mA/cm^2 the EL device of **3** has an external efficiency of 1.06 cd/A while the EL device of **4** has an external efficiency of 2.34 cd/A, demonstrating that compounds **3** and **4** are efficient and promising emitters in electroluminescent devices.

Introduction

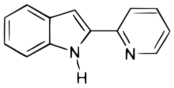
Luminescent organic/organometallic compounds have attracted much attention recently because of their potential applications in electroluminescent displays.[1−3] Luminescent chelate complexes have been shown to be particularly useful in electroluminescent (EL) displays because of their relatively high stability and volatility.[3] The most well-known example of such chelate compounds is Alq$_3$, q = deprotonated 8-hydroxyquinoline, a green emitter and an electron transporter in organic EL devices.[1,4] We have been interested in blue luminescent chelate compounds because they are one of the key color components required for full-color EL displays and are still rare. We reported recently that boron and aluminum complexes containing 7-azaindole ligands produce a bright blue luminescence.[5] Blue electroluminescent devices using B$_2$R$_2$(7-azaindole)$_2$(O) (R = Ph, ethyl) have been fabricated successfully.[5a] Due to the geometry of the 7-azaindole ligand, it can only bind to the central atom as either a terminal ligand or a bridging ligand.[5] We anticipated that if we can modify the 7-azaindole ligand so that it can chelate to a central atom, we could improve the stability and the performance of the EL devices where 7-azaindole based compounds are used as the emitter. The new ligands we chose to investigate are 2-(2-pyridyl)-7-azaindole and 2-(2-pyridyl)indole. The 2-(2-pyridyl)indole ligand was chosen because it has a structure similar to that of 2-(2-pyridyl)-7-azaindole but can only function as a chelating ligand, thus providing us an opportunity to do a comparative study on the effect of bonding modes and electronic factors on luminescence



7-azaindole



2-(2-pyridyl)-7-azaindole



2-(2-pyridyl)indole

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of the complex. Three novel complexes with 2-(2-pyridyl)indole and one new boron compound with 2-(2-pyridyl)-7-azaindole have been synthesized and characterized structurally. The details of syntheses, structures, and luminescent and electroluminescent properties of these new compounds are reported herein.

Experimental Section

All starting materials were purchased from Aldrich Chemical Co. and used without further purification, unless otherwise stated. Tetrahydrofuran, hexane, and toluene solvents were distilled from sodium and benzophenone under a nitrogen atmosphere. Dichloromethane was distilled from P_2O_5 under a nitrogen atmosphere. ^1H NMR spectra were recorded on Bruker Avance 300 MHz spectrometers. Excitation and emission spectra were recorded on Fluoromax-2, Instruments S.A., Inc. Elemental analyses were performed by Guelph Chemical Laboratories Ltd, Guelph, Ontario and Canadian Microanalytical Service, Ltd, Delta, British Columbia. 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 on a Fisher-Johns melting point apparatus. The syntheses of 2-(2-pyridyl)-7-azaindole and 2-(2-pyridyl)indole were based on a modified literature method[6] for related compounds.

Synthesis of 1-Benzenesulfonyl-7-azaindole. To a vigorously stirred mixture of 7-azaindole (5.91 g, 50 mmol), 50% aqueous NaOH (50 mL), water (75 mL) and tetrabutylammonium bromide (1.61 g, 5 mmol) was added dropwise $PhSO_2Cl$ (9.71 g, 55 mmol) in benzene (50 mL) over an hour at ambient temperature. After the mixture had been stirred at ambient temperature for 2 h, the aqueous phase was removed. The organic phase was washed twice with 1 M aqueous $NaHCO_3$ (30 mL), water (30 mL), and saturated brine (30 mL), and then dried over Na_2SO_4. The solvent was evaporated in a vacuum. The residue was washed with anhydrous ether to give white powder (11.2 g, yield 87%). Recrystallization from ethyl acetate and hexane produces a colorless crystalline product. Mp 127−128 °C. ^1H NMR in $CDCl_3$: δ 8.44 (1H, d, $J = 4.8$ Hz), 8.21 (2H, d, $J = 7.4$ Hz), 7.86 (1H, d, $J = 7.8$ Hz), 7.75 (1H, d, $J = 4.0$ Hz), 7.42−7.64 (3H, m), 7.19 (1H, dd, $J = 7.8$, 4.8 Hz), 6.61 (1H, d, $J = 4.0$ Hz).

Synthesis of 1-Benzenesulfonylindole. The same procedure used for 1-Benzenesulfonyl-7-azaindole was employed. From indole (5.85 g, 50 mmol) and $PhSO_2Cl$ (9.71 g, 55 mmol) 1-benzenesulfonylindole was obtained (9.8 g, yield 76%). Mp 76−78 °C. ^1H NMR in $CDCl_3$ (δ, ppm, 25 °C): 8.03 (1H, d, $J = 8.2$ Hz), 7.88−7.94 (2H, m), 7.59 (1H, d, $J = 3.7$ Hz), 7.41−7.58 (3H, m), 7.20−7.38 (3H, m), 6.68 (1H, d, $J = 3.7$ Hz).

Synthesis of 1-(Benzenesulfonyl)-2-(2-pyridyl)-7-azaindole. To a solution of 1-benzenesulfonyl-7-azaindole (3.89 g, 15.1 mmol) in 25 mL of anhydrous THF at 0 °C was slowly added a solution of LDA (1.5 M in cyclohexane, 11.2 mL, 16.6 mmol). The resulting mixture was stirred for 30 min at this temperature, then a solution of anhydrous $ZnCl_2$ (0.5 M in THF, 33.2 mL) was added. The mixture was stirred at room temperature for another 30 min. In a separated flask a solution of 2-bromopyridine (1.84 g, 11.6 mmol) in 10 mL of anhydrous THF was added to a solution containing a catalyst prepared by reaction of a $Pd(PPh_3)_2Cl_2$ (0.326 g, 0.464 mmol) in 5 mL of anhydrous THF with diisobutylaluminum hydride (1.0 M in hexane, 0.94 mL, 0.928 mmol), and the mixture was stirred at ambient temperature for 10 min. The resulting mixture was transferred via cannula to the solution of 1-(benzenesulfonyl)-2-(7-azaindolyl) zinc chloride prepared above. The mixture was refluxed for 6 h under N_2, cooled to room temperature, and poured into saturated aqueous Na_2CO_3. The aqueous phase was extracted with diethyl ether, and the organic extracts were concentrated to give a brown residue that was purified by a chromatographic column using hexane/ethyl acetate (6:1) as the eluant to obtain 1-(benzenesulfonyl)-2-(2-pyridyl)-7-azaindole (3.6 g, yield 92%). ^1H NMR in $CDCl_3$ (δ, ppm, 25 °C): 8.75 (1H, ddd, $J = 4.8$, 1.6, 0.9 Hz), 8.50 (1H, dd, $J = 4.8$, 1.6 Hz), 8.19 (2H, m), 7.81−7.88 (2H, m), 7.72 (1H, d, $J = 7.8$ Hz), 7.36−7.60 (4H, m), 7.22 (1H, dd, $J = 7.8$, 4.8 Hz), 6.77 (1H, s).

Synthesis of 1-(Benzenesulfonyl)-2-(2-pyridyl)indole. The same procedure used for 1-(benzenesulfonyl)-2-(2-pyridyl)-7-azaindole was employed. From 1-benzenesulfonylindole (3.88 g, 15.1 mmol) and 2-bromopyridine (1.84 g, 11.6 mmol) was obtained 1-(benzenesulfonyl)-2-(2-pyridyl)indole (3.78 g, 97%). ^1H NMR in $CDCl_3$ (δ, ppm, 25 °C): 8.71 (1H, ddd, $J = 4.9$, 1.6, 0.9 Hz), 8.22 (1H, dd, $J = 8.3$, 0.6 Hz), 7.82 (1H, td, $J = 7.5$, 1.7 Hz), 7.74 (1H, d, $J = 7.8$ Hz), 7.67 (2H, m), 7.25−7.53 (7H, m), 6.90 (1H, s).

Synthesis of 2-(2-Pyridyl)-7-azaindole. A solution of 1-(benzenesulfonyl)-2-(2-pyridyl)-7-azaindole (2.0 g, 5.97 mmol), ethanol (340 mL), and 10% aqueous NaOH (34 mL) was heated at reflux overnight. The resulting mixture was concentrated, and the residue was dissolved in CH_2Cl_2. The organic solution was washed with water and aqueous Na_2CO_3, dried, and concentrated. After being run through a chromatographic column using eluant $CHCl_3/CH_3OH$, (20:1), the residue afforded pure 2-(2-pyridyl)-7-azaindole (0.90 g, 77%). Mp 215−216 °C. ^1H NMR in $CDCl_3$ (δ, ppm, 25 °C): 10.90 (1H, br s), 8.69 (1H, ddd, $J = 4.8$, 1.6, 1.0 Hz), 8.46 (1H, dd, $J = 4.8$, 1.6 Hz), 7.98 (1H, dd, $J = 7.8$, 1.3 Hz), 7.85 (1H, m), 7.76 (1H, td, $J = 7.8$, 1.7 Hz), 7.24 (1H, ddd, $J = 7.8$, 4.8, 1.2 Hz), 7.12 (1H, dd, $J = 7.8$, 4.8 Hz), 6.99 (1H, d, $J = 1.8$ Hz). Anal. Calcd for $C_{12}H_9N_3$: C, 73.83; H, 4.65; N, 21.52. Found: C, 73.26; H, 4.48; N, 21.58.

Synthesis of 2-(2-Pyridyl)indole. This compound was obtained by the same procedure as above. From 1-(benzenesulfonyl)-2-(2-pyridyl)indole (2.15 g, 6.44 mmol) was obtained 2-(2-pyridyl)indole (1.0 g, 80%). Mp 154−155 °C. ^1H NMR in $CDCl_3$ (δ, ppm, 25 °C): 9.70 (1H, br), 8.60 (1H, dd, $J = 4.9$, 1.0 Hz), 7.83 (1H, dd, $J = 8.0$, 1.0 Hz), 7.44 (1H, td, $J = 7.6$, 1.7 Hz), 7.69 (1H, d, $J = 7.9$ Hz), 7.42 (1H, dd, $J = 8.0$, 0.9 Hz), 7.10−7.31 (3H, m), 7.04 (1H, d, $J = 1.2$ Hz).

$Zn(2\text{-py-in})_2(THF)$ (1). Butyllithium (1.6 M in hexane, 0.75 mL, 1.2 mmol) was added slowly to 15 mL of THF solution containing 2-(2-pyridyl)indole (0.233 g, 1.2 mmol) at −78 °C under N_2. After the mixture was stirred for half of an hour, zinc chloride (0.50 M in THF, 1.2 mL, 0.6 mmol) was added. The mixture was warmed to room temperature, stirred for 3 h, concentrated, and recrystallized from CH_2Cl_2. Yellow crystals of **1** (0.220 g, yield 82%) were obtained. Mp 271−272 °C. ^1H NMR in $CDCl_3$ (δ, ppm, 25 °C): 7.98−8.06 (4H, m), 7.80−7.91 (2H, m), 7.71−7.74 (2H, m), 7.25 (2H, s), 7.00−7.12 (8H, m), 3.75 (m, 4H), 1.75 (m, 4H). Anal. Calcd for $C_{26}H_{18}N_4Zn$: C, 69.11; H, 4.02; N, 12.40. Found: C, 68.32; H, 4.05; N, 12.05.

$B(2\text{-py-in})Ph_2$ (2). 2-(2-Pyridyl)indole (0.194 g, 1.0 mmol) was dissolved in 10 mL of toluene. After the mixture was stirred for 10 min, BPh_3 (1.0 mmol, 0.240 g) was added to the solution under N_2, and the mixture was heated for 4 h at 80 °C. After the solution was cooled to room temperature, the mixture was evaporated to dryness in a vacuum and moved to a drybox. The mixture was dissolved in THF. Yellow crystals of compound **2** were obtained in 65% yield. Mp 255 °C. ^1H NMR ($CDCl_3$, δ, ppm, 25 °C): 8.39 (1H, d, $^3J = 5.7$ Hz), 7.99−7.88 (2H, m), 7.69 (1H, d, $^3J = 7.8$ Hz), 7.28−7.18 (12H, m), 7.10 (1H, s), 7.08−6.69 (2H, m). Anal. Calcd for $C_{25}H_{19}N_2B$: C, 83.82; H, 5.35; N, 7.82. Found: C, 84.20; H, 5.06; N, 7.87.

$Be(2\text{-py-in})_2$ (3). Butyllithium (1.6 M in hexane, 0.75 mL, 1.2 mmol) was added slowly to 15 mL of THF solution containing 2-(2-pyridyl)indole (0.233 g, 1.2 mmol) at −78 °C under N_2. After the mixture was stirred for half an hour, berylium chloride (0.048 g, 0.6 mmol) was added. The mixture was warmed to room temperature, stirred for 3 h, concentrated, and recrystallized from CH_2Cl_2. Light yellow crystals of **3** (0.160 g, yield 67%) were obtained. Mp >300 °C. ^1H NMR in $CDCl_3$ (δ, ppm, 25 °C): 7.88−8.00 (4H, m), 7.70 (2H, dt, $J = 5.4$, 1.2 Hz), 7.65−7.70 (2H, m), 7.16 (2H, s), 6.90−7.04 (8H, m). Anal. Calcd for $C_{26}H_{18}N_4Be$: C, 78.98; H, 4.56; N, 14.17. Found: C, 77.82; H, 4.49; N, 13.95. This compound was analyzed three times using crystals of compound **3** at two analytical companies.

$BPh_2(2\text{-py-aza})$ (4). Triphenyl boron (0.291 g, 1.2 mmol) was added to 20 mL of THF solution containing 2-(2-pyridyl)-7-azaindole (0.234 g, 1.2 mmol) under N_2. The mixture was stirred at reflux for 4 h. After the mixture was cooled to room temperature, it was concentrated by vacuum and transferred to an inert atmosphere drybox. The residue was recrystallized from CH_2Cl_2/hexane, yielding colorless crystals of compound **4** (0.307 mg, yield 71%). Mp 291−292 °C. ^1H NMR in

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Table 1. Crystallographic Data

	1	**2**	**3**	**4**
formula	$C_{30}H_{26}N_4OZn$	$C_{25}H_{19}N_2B$	$C_{26}H_{18}N_4Be$	$C_{24}H_{18}N_3B$
fw	523.91	358.23	395.45	359.22
space group	$P4_12_12$	$P2_1/n$	$Pnna$	$P2_12_12_1$
a/Å	13.872(2)	9.191(5)	23.417(5)	8.916(6)
b/Å	13.872(2)	15.607(14)	13.460(3)	11.965(12)
c/Å	15.043(2)	13.510(7)	13.346(3)	17.726(9)
α/deg	90	90	90	90
β/deg	90	102.347(15)	90	90
γ/deg	90	90	90	90
V/Å^3	2894.6(8)	1893(2)	4206.6(16)	1891(2)
Z	4	4	8	4
D_c, g cm^{-3}	1.202	1.257	1.249	1.262
μ, cm^{-1}	8.75	0.73	0.75	0.75
$2\theta_{\max}$, ^{o}	50	45.6	45	50
reflns measd	2637	2649	2759	3726
reflns used (R_{int})	2544 (0.032)	2472 (0.10)	2759 (0.00)	3338(0.025)
no. of variables	191	253	281	253
final R [$I > 2\,\sigma(I)$]	$R_1^a = 0.0556$, $wR_2^b = 0.1425$	$R_1^a = 0.0864$, $wR_2^b = 0.1306$	$R_1^a = 0.0650$, $wR_2^b = 0.1440$	$R_1^a = 0.0603$, $wR_2^b = 0.1173$
R (all data)	$R_1 = 0.0669$, $wR_2 = 0.1550$	$R_1 = 0.2354$, $wR_2 = 0.1781$	$R_1 = 0.1489$, $wR_2 = 0.1808$	$R_1 = 0.1211$, $wR_2 = 0.1449$
goodness-of-fit on F^2	1.037	1.069	1.069	1.018

[a] $R_1 = \sum|F_o| - |F_c|/\sum|F_o|$. [b] $wR_2 = [\sum w[(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$. $w = 1/[\sigma^2(F_o^2) + (0.075P)^2]$, where $P = [\max(F_o^2, 0) + 2F_c^2]/3$.

$CDCl_3$ (δ, ppm, 25 °C): 8.51 (1H, m), 8.47 (1H, dd, $J = 4.5$, 1.6 Hz), 7.98−8.13 (3H, m), 7.20−7.42 (11H, m), 7.10 (1H, s), 7.03, dd, $J = 8.0$, 4.5 Hz). Anal. Calcd for $C_{24}H_{18}N_3B$: C, 80.24; H, 5.05; N, 11.70. Found: C, 78.84; H, 5.10; N, 11.45. Again this sample was also analyzed three times at two different analytical companies using crystals. The carbon content is however consistently low in all analyses. Incomplete combustion of carbon in samples **3** and **4** could be the cause of the low carbon.

X-ray Crystallographic Analysis. All crystals were obtained either from CH_2Cl_2/hexane solutions or from THF/hexane solutions. All crystals were mounted on glass fibers except compound **1**, which was sealed in a glass capillary under nitrogen. All data were collected on a Siemens P4 single-crystal diffractometer with graphite-monochromated Mo Kα radiation, operating at 50 kV and 35 mA at 23 °C. The data for **1** and **4** were collected over 2θ 3−50° while the data for **2** and **3** were collected over 2θ 3−45°. Three standard reflections were measured every 197 reflections. No significant decay was observed for all samples. Data were processed on a Pentium PC using Siemens SHELXTL software package[7] (version 5.0) and corrected for Lorentz and polarization effects. Neutral atom scattering factors were taken from Cromer and Waber.[8] The crystals of **3** and **4** belong to the orthorhombic space groups *Pnna* and $P2_12_12_1$, respectively, uniquely determined by systematic absences. The crystals of **1** belong to the tetragonal space group $P4_12_12$ while the crystals of **2** belong to the monoclinic space group $P2_1/n$, uniquely determined by systematic absences. All structures were solved by direct methods. The coordinated THF molecule in compound **1** is disordered. Partial modeling on this THF ligand was achieved. All non-hydrogen atoms were refined anisotropically, except the disordered atoms. The positions for all hydrogen atoms except those attached to the disordered THF molecule were calculated and their contributions in structural factor calculation were included. The crystallographic data for compounds **1**−**4** are given in Table 1.

Fabrication of Electroluminescent Devices. The EL devices using **3** and **4** as the emitting layer were fabricated on an indium−tin oxide (ITO) substrate, which was cleaned by an ultraviolet ozone cleaner immediately before use. Organic layers and a metal cathode composed of magnesium silver alloy ($Mg_{0.9}Ag_{0.1}$) were deposited on the substrate by conventional vapor vacuum deposition. Prior to the deposition, all the materials were purified via a train sublimation method.[9] *N*,*N*′-Di-1-naphthyl-*N*,*N*′-diphenylbenzidine (NPB) was employed as the hole transport layer in all devices. The device structures and the thickness of each layer are listed in Table 3. To obtain the photoluminescence (PL) spectra, a thin film (100 nm) deposited on a quartz substrate was measured with a fluorescence spectrophotometer. The current−voltage characteristics were measured using a Keithley 238 current/voltage unit. The light intensity of the EL device was measured by a Minolta Chroma Meter CS100. The EL spectrum was obtained by an in-house setup made up of a series of electronic components including a monochromator (Instruments SA Inc), a photomultiplier tube, and a photon counter.

Results and Discussion

Ligands. Our previous work has established that the deprotonated 7-azaindole ligand is an efficient blue emitter when bound to two central atoms in a bridging mode.[5] Although the bridging mode of the 7-azaindole ligand contributes significantly to the overall stability of the complex, it often results in the formation of dinuclear and polynuclear complexes that are difficult to sublime due to the high molecular weight. We therefore decided to modify the 7-azaindole ligand so that it can bind to a central atom by a chelate mode. We attached a 2-pyridyl group at the 2 position of indole and 7-azaindole using the procedure outlined in Scheme 1, resulting in the formation of new ligands 2-(2-pyridyl)indole (2-py-in) and 2-(2-pyridyl)-7-azaindole (2-py-aza). In the synthesis of 2-(2-pyridyl)indole, the required 2-indolylzinc chloride was easily obtained by metalation of 1-(benzenesulfonyl)indole with LDA followed by the treatment of the resulting 2-lithioindole with anhydrous $ZnCl_2$. Cross-coupling reactions of 2-indolylzinc chloride with 2-bromopyridine in the presence of 2 mol % of a catalyst prepared from $PdCl_2(PPh_3)_2$ and DIBAH (DIBAH = diisobutylaluminum hydride) in refluxing THF afforded the 2-(2-pyridyl)indole. The 2-(2-pyridyl)-7-azaindole was synthesized by the same strategy. Unlike the 2-py-aza ligand which has two potential bonding modes, bridging and chelate, the 2-py-in ligand has only the chelate bonding mode, making the reaction simpler. Despite the fact that both compounds have similar structures, the melting point of 2-py-aza is about 50 °C higher than that of 2-py-in, the possible cause of which is likely the difference of hydrogen bonds of these two molecules in the solid

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[7] SHELXTL crystal structure analysis package, Bruker Axs, Analytical X-ray System, Madison, Wisconsin, 1995; Version 5.

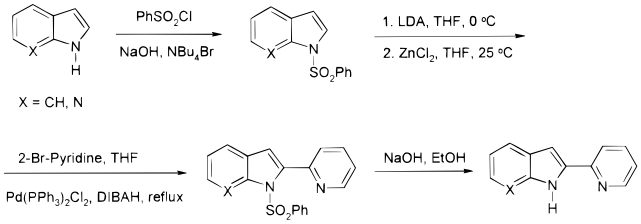
[8] Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, AL, 1974; Vol. 4, Table 2.2A.

[9] Wagner, H. J.; Loutfy, R. O.; Hsiao, C. K. *J. Mater. Sci.* **1982**, *17*, 2781.

Table 2. Selected Bond Lengths (Å) and Angles (deg)

		Compound **1**	
Zn(1)−N(2)	1.968(3)	N(2)−Zn(1)−N(2A)	138.8(2)
Zn(1)−N(1)	2.189(4)	N(2)−Zn(1)−N(1)	79.75(14)
Zn(1)−O(1)	2.204(6)	N(2A)−Zn(1)−N(1)	106.96(13)
N(1)−C(5)	1.330(6)	N(1)−Zn(1)−N(1A)	161.4(2)
N(1)−C(1)	1.347(6)	N(2)−Zn(1)−O(1)	110.60(11)
N(2)−C(6)	1.376(5)	N(1)−Zn(1)−O(1)	80.69(11)
N(2)−C(13)	1.376(5)		
		Compound **2**	
N(1)−C(1)	1.329(8)	N(2)−B(1)−C(20)	115.1(6)
N(1)−C(5)	1.358(8)	N(2)−B(1)−C(14)	111.2(6)
N(1)−B(1)	1.633(9)	C(20)−B(1)−C(14)	115.4(7)
B(1)−N(2)	1.561(9)	N(2)−B(1)−N(1)	93.5(6)
B(1)−C(20)	1.587(10)	C(20)−B(1)−N(1)	109.1(6)
B(1)−C(14)	1.602(10)	C(14)−B(1)−N(1)	110.3(6)
N(2)−C(6)	1.369(7)		
N(2)−C(13)	1.370(8)		
		Compound **3**	
N(4)−C(26)	1.364(6)	N(4A)−Be(2)−N(4)	129.3(6)
N(4)−C(19)	1.373(5)	N(4A)−Be(2)−N(3)	111.75(19)
N(4)−Be(2)	1.665(5)	N(4)−Be(2)−N(3)	93.7(2)
N(3)−C(14)	1.336(6)	N(4A)−Be(2)−N(3A)	93.7(2)
N(3)−C(18)	1.359(6)	N(3)−Be(2)−N(3A)	119.0(6)
N(3)−Be(2)	1.747(6)	N(2A)−Be(1)−N(2)	126.1(6)
N(2)−C(13)	1.373(5)	N(2)−Be(1)−N(1A)	111.56(17)
N(2)−C(6)	1.387(5)	N(2)−Be(1)−N(1)	93.29(19)
N(2)−Be(1)	1.668(5)	N(1A)−Be(1)−N(1)	124.1(6)
N(1)−C(5)	1.343(6)		
N(1)−C(1)	1.347(6)		
N(1)−Be(1)	1.753(6)		
		Compound **4**	
N(1)−C(13)	1.343(5)	N(2)−B(1)−C(7)	113.4(3)
N(1)−C(17)	1.354(5)	N(2)−B(1)−C(1)	109.6(3)
N(1)−B(1)	1.637(5)	C(7)−B(1)−C(1)	118.9(3)
N(3)−C(23)	1.337(5)	N(2)−B(1)−N(1)	94.8(3)
N(3)−C(24)	1.344(5)	C(7)−B(1)−N(1)	108.7(3)
N(2)−C(24)	1.353(5)	C(1)−B(1)−N(1)	108.6(3)
N(2)−C(18)	1.392(5)		
N(2)−B(1)	1.550(5)		
C(7)−B(1)	1.604(5)		
C(1)−B(1)	1.616(5)		

Scheme 1. The Synthesis of Ligands



state. In the solid state, 2-py-aza has a week emission at $\lambda_{max} = 420$ nm while 2-py-in does not show any visible emission at all.

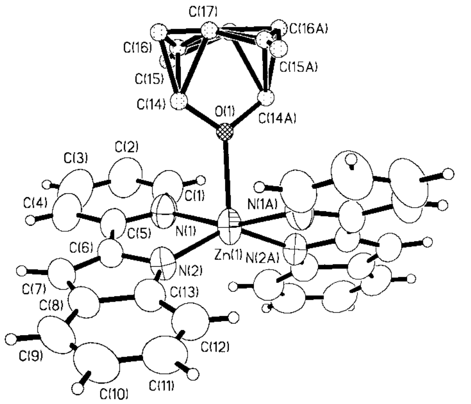


Figure 1. A diagram showing the molecular structure of compound **1** with 50% thermal ellipsoids and labeling schemes.

Complexes. The complexes of 2-(2-py)indole and 2-(2-py)-7-azaindole were synthesized by two approaches: (a) substitution of halide ligands by 2-py-in or 2-py-aza anions produced by the reactions of butyllithium with the neutral ligand or (b) the direct reaction of BPh_3 with the neutral 2-py-in or 2-py-aza ligands. A zinc(II) complex with the new ligand, 2-py-indole, was synthesized first. However, the complex is not stable in the air, which led us to investigate the synthesis of more stable beryllium and boron compounds. The three systems investigated involve using $ZnCl_2$, $BeCl_2$, and BPh_3 as the starting materials, respectively. The reactions of Li[2-py-aza] with $ZnCl_2$ or $BeCl_2$ produced a dark colored solution and no clean products could be isolated while the reaction of Li[2-py-in] with $ZnCl_2$ or $BeCl_2$ in a 2:1 ratio yielded a bright yellow solution, from which Zn(2-py-in)$_2$(THF) (**1**) or Be(2-py-in)$_2$ (**3**) was isolated. The reason for this drastic reaction difference of 2-py-in and 2-py-aza toward halide compounds has not been well understood. It is however likely that the 2-py-aza ligand forms several products with the halides (NMR data indeed suggested this) because of its versatile bonding modes while the only chelate bonding mode available to 2-py-in made it possible to produce a clean product. The reactions of BPh_3 with 2-py-in and 2-py-aza produced a bright yellow compound, BPh_2(2-py-in) (**2**), and a pale yellow compound, BPh_2(2-py-aza) (**4**), respectively. Compound **1** is air-sensitive while compounds **2**−**4** are stable in the air. The stability difference between compound **1** and **2**−**4** is attributed to the fact that the Zn−N(indole) bonds are highly polarized or ionic in comparison to the corresponding B−N and Be−N bonds which are mostly covalent, hence more stable. A similar trend has been observed in aluminum complexes versus boron complexes when 7-azaindole ligands are involved.[5]

Another important and common feature among compounds **1**−**4** is the substantial increase of melting points in comparison to those of the free ligand. For example, the free ligand 2-(2-pyridyl)indole has a melting point of 155 °C but the complexes **1**−**3** have melting points above 250 °C, especially compound **3**, which has a melting point greater than 300 °C, a highly desired property for the practical application in electroluminescent devices. Compounds **2**−**4** can be sublimed readily under vacuum. No attempts were made to sublime compound **1** due to its poor stability. Compounds **1**−**4** have been fully characterized by NMR, elemental, and single-crystal X-ray diffraction analyses. Selected bond lengths and angles for all compounds are listed in Table 2.

Structure of Compound 1. The structure of compound **1** is shown in Figure 1. The molecule of **1** has a C_2 symmetry while

Table 3. EL Device Data

device	hole transport (thickness, nm)	emitting layer (thickness, nm)	electron transport (thickness, nm)	C.I.E. (*x*, *y*)	eff. at 20 mA/cm^2, cd/A
A	NPB (60)	**3** (75)		0.306, 0.500	1.06
B	NPB (60)	**4** (20)	Alq_3 (40)	0.279, 0.463	0.57
C	NPB (60)/Bicarb (20)	**4** (20)	Alq_3 (40)	0.200, 0.325	2.34

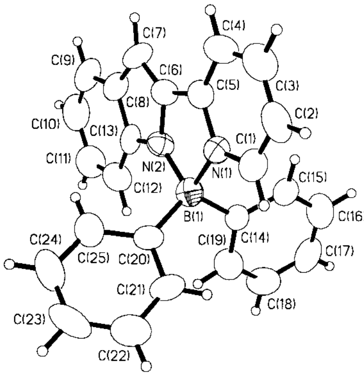


Figure 2. A diagram showing the molecular structure of compound **2** with 50% thermal ellipsoids and labeling schemes.

the crystal is chiral because of the chiral space group $P4_12_12$. The structure of **1** can be best described as a distorted trigonal bipyramid with O(1), N(2), and N(2) on the basal plane (the sum of bond angles on the basal plane is 358°.). Two 2-(2-py)-indole ligands are chelated to the Zn(II) center. The shortest bond is between Zn(1) and the negatively charged indole atom N(2), 1.968(3) Å, while the longest bond is between Zn(1) and the disordered THF oxygen atom O(1), 2.204(6) Å. Five-coordinate Zn(II) complexes are quite common and many examples have been reported previously.[10] The structure of **1** resembles that[10c] of $[Zn(8\text{-aminoquinoline})_2(H_2O)]^{2+}$. Compound **1** loses the coordinate THF molecule readily when subjected to vacuum. The poor stability of **1** in air is believed to be caused by the reaction of the negatively charged 2-(2-py)indole ligand with moisture, resulting in the rupture of Zn−N(indole) bonds.

Structure of Compound 2. The structure of compound **2** is shown in Figure 2. The boron atom in **2** has a typical tetrahedral geometry. The 2-(2-py)indole ligand is chelated to the boron center in a similar fashion as in compound **1**. The B(1)−N(2) (indole) bond (1.561(9) Å) is shorter than the B(1)−N(1) (pyridyl) bond (1.633(9) Å) but similar to those of previously reported 7-azaindole boron complexes.[5] The bond angles around the boron atom range from 93.5(6)° to 115.4(7)°. The B−C bond lengths in **2** are also in the normal range.

Structure of Compound 3. There are two independent molecules of **3** in the asymmetric unit of the crystal lattice, each of which has a 2-fold rotation symmetry. The bond lengths and angles of the two independent molecules are similar. Therefore, only the structure of one of the molecules, Be(1), is shown in Figure 3. The Be(II) center has a distorted tetrahedral geometry, as indicated by the bond angles around the Be(II) center, ranging from 93.7(2)° to 129.3(6)°. Similar tetrahedral structures of beryllium compounds have been observed previously.[3a,11] The Be−N bond lengths (1.665(5)−1.753(6) Å) are substantially longer than the corresponding ones in compound **2**. Both steric and electronic factors are believed to be responsible for this discrepancy. A few four-coordinate electroluminescent Be(II) complexes have been reported previously.[3a−c] Compound **3** is however the first example of electroluminescent Be(II) compounds where the Be(II) center is chelated by nitrogen donor atoms only. Efforts to make the analogue of **3** using 2-(2-py)-7-azaindole were unsuccessful.

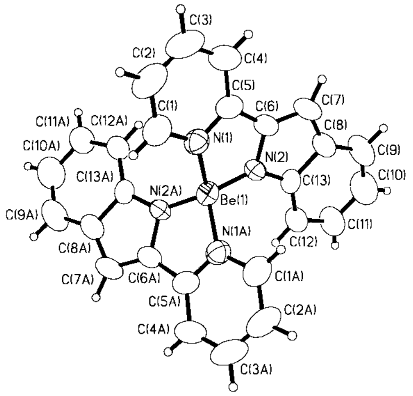


Figure 3. A diagram showing the molecular structure of compound **3** with 50% thermal ellipsoids and labeling schemes.

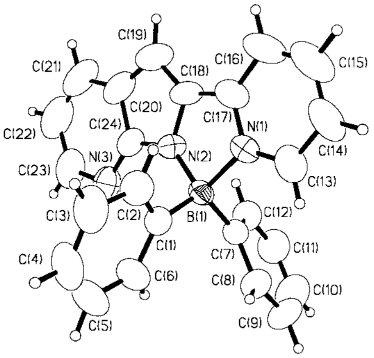


Figure 4. A diagram showing the molecular structure of compound **4** with 50% thermal ellipsoids and labeling schemes.

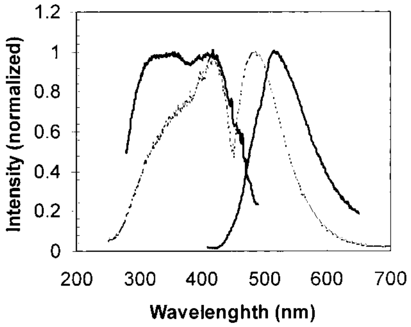


Figure 5. PL (excitation and emission) spectra of compounds **1** (dashed line) and **2** (solid line).

Structure of Compound 4. The structure of compound **4** is similar to that of compound **2** as shown in Figure 4. The B−N and B−C bond lengths and angles are also similar to those of **2**. Despite the fact that the 2-(2-pyridyl)-7-azaindole ligand has three nitrogen binding sites, only two of the nitrogen atoms N(1) and N(2) are bound to the boron center in a similar fashion as in compound **2**. The bond lengths and angles around the boron center in compound **4** are similar to those of **2**. Although the molecular structure of compound **4** resembles that of **2**, these two compounds crystallize in two different space groups: compound **2** being in the centric, monoclinic space group $P2_1/n$, while compound **4** is in the chiral, orthorhombic space group $P2_12_12_1$. This difference is caused undoubtedly by the replacement of a CH (C(12)) in 2-(2-pyridyl)indole by a nitrogen atom (N(3)) in 2-(2-pyridyl)-7-azaindole. It is however surprising that a subtle difference in the ligands could cause such a dramatic difference in the packing of molecules **2** and **4** in the crystal lattice. Even more surprising is the fact that the melting

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(10) (a) Prince, R. H. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon Press: New York, 1987; Vol. 5, Chapter 56.1. (b) Auf der Heyde, T. P. E. *Acta Crystallogr.* **1984**, *B40*, 582. (c) Kerr, M. C.; Preston, H. S.; Ammon, H. L.; Huheey, J. E.; Stewart, J. M. *J. Coord. Chem.* **1981**, *11*, 111. (d) Smith, H. W. *Acta Crystallogr.* **1975**, *B31*, 2701.

(11) Tamoto, N.; Adachi, C.; Nagai, K. *Chem. Mater.* **1997**, *9*, 1077.

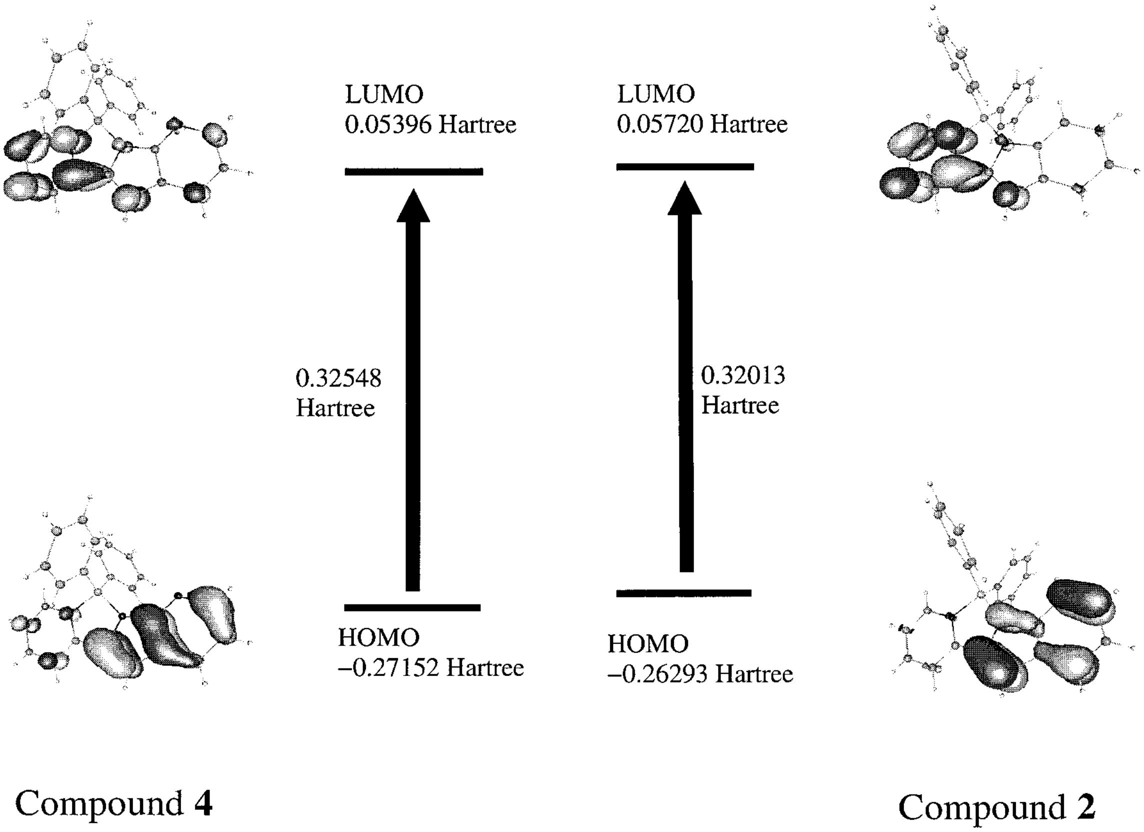

Figure 6. Ab inito calculation results on HOMO and LUMO levels of **2** and **4**.

point of compound **4** is about 40 °C higher than that of **2**. Although the crystal lattice difference must contribute somewhat to the melting point difference between **2** and **4**, electronic factors must also contribute to some extent because the nitrogen atom, more electronegative than the carbon atom, can cause some difference in crystal lattice energy, thus resulting in melting point difference. Compound **4** is much more stable toward air than dinuclear compounds $B_2R_2(O)(7\text{-aza})_2$ where the 7-azaindole ligand acts as a bridging ligand.[5a,b] The enhanced stability of **4** can be attributed to the chelate bonding mode of the 2-py-7-azaindole ligand. Similarly, the chelate effect is believed to contribute to the overall stability of compounds **2** and **3**.

Photoluminescent and Electroluminescent Properties of Compounds 1−4. Compounds **1**−**4** produce a bright blue/green color in solution and the solid state upon irradiation by UV light. The emission maximum of compounds **1**−**4** is at 488, 516, 490, and 476 nm, respectively. The PL spectra of powder samples of **1**−**4** match those of films. The fact that compounds **1**−**4** have a similar emission band in solution, solid, or films indicates that the luminescence observed in these compounds is a molecular property, attributable to a $\pi^*-\pi$ transition of the 2-(2-py)indole ligand or the 2-(2-py)-7-azaindole ligand. The luminescence of compounds **1**−**4** is in sharp contrast to those of the free ligands which have either no emission at all in the visible region (2-(2-py)indole) or a weak emission at 420 nm (2-(2-py)-7-azaindole). The dramatic red shift of emission energy of 2-(2-py)-7-azaindole complex **4** in comparison to that of free 2-(2-py)-7-azaindole can be attributed to the removal of the proton from 2-(2-py)-7-azaindole, which is consistent with the results of our earlier studies on luminescent di(2-pyridyl)amine and 7-azaindole complexes that revealed that the deprotonation of the ligand decreases the $\pi^*-\pi$ gap, thus resulting in a red shift in emission energy.[5] The role of the central ion in compounds **1**−**4** is therefore simply to stabilize the negatively charged ligand via the formation of coordination bonds.[5]

Compounds **2** and **4** have a similar structure but the emission energy of **4** has a ~40 nm blue shift relative to that of **2**. The replacement of a CH in the indole ligand by a N atom in the 7-azaindole ligand apparently increases the $\pi^*-\pi$ energy gap, which is not surprising since the nitrogen atom is more electronegative than the carbon atom, thus capable of lowering the HOMO level and increasing the HOMO and LUMO gap. To rationalize the blue-shift displayed by compound **4** relative to that of **2**, we performed ab initio calculations on the Restricted-Hartree−Fock (RHF) level using a standard split-valence polarized (6-31G*) basis set, employing the Gaussian98 suite of programs.[12] The geometric parameters employed in the calculations were from crystal structure data. In Figure 6, we plotted the energies of the Highest Occupied Molecular Orbitals (HOMO's) and Lowest Unoccupied Molecular Orbitals (LUMO's) for compounds **2** and **4**, together with surfaces on which those orbitals attain values of ±0.05 atomic units. As one may see, the HOMO's of both compounds are π orbitals localized on the fused ring systems, i.e., the indole portion of **2**, and the 7-azaindole part of **4**, respectively. Therefore, the energy of the HOMO stands to be lowered by the replacement of a C−H

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[12] 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. D.; Fox, J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, Revision A.6; Gaussian, Inc.: Pittsburgh, PA, 1998.

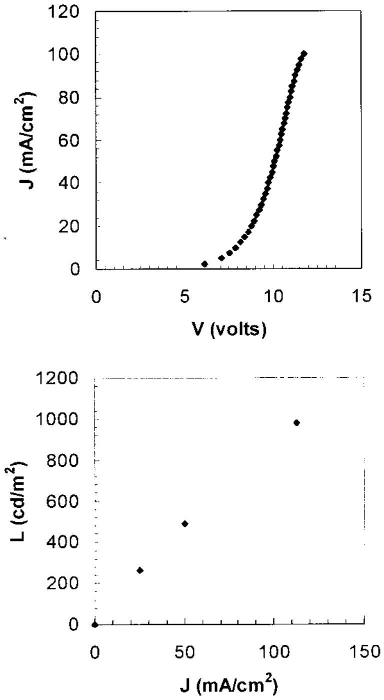

Figure 7. Top: J−V curve of device **A**. Bottom: L−J curve of device **A**.

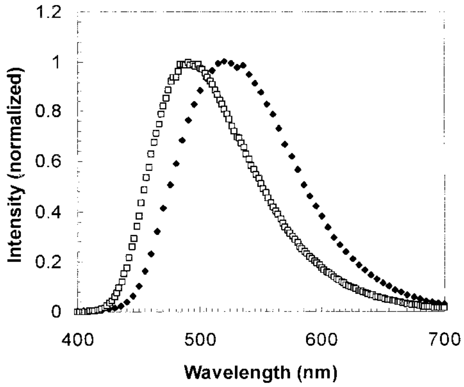

Figure 8. PL (empty square) and EL (solid diamond) spectra of compound **3** and device **A**.

group in **2** by a more electronegative N in **4**. The fact that this lowering is still rather small might be assigned to the nodal surfaces near the nitrogen atoms in the HOMO of **4**, while the HOMO in **2** has appreciable values near the nitrogen. On the other hand, the lowering effect from the nitrogen is considerably smaller for the LUMO's that are virtually identical for the two compounds, and largely localized on the pyridine portion of the ligand, i.e., away from the indole or 7-azaindole group. The overall effect is a widening of the gap by a relatively small amount from **2** to **4**. This is consistent with the observation of a shift in the fluorescence from green in **2** to blue in **4**. Although the energy value of the HOMO−LUMO gap from Hatree−Fock calculations does not match the experimentally measured emission energy because only the ground state was taken into consideration in the calculation, the trend predicted by the calculation is qualitatively correct.

Among compounds **1**−**3** which contain the same chromophore, i.e., 2-(2-py)indole, **3** has the highest thermal stability (highest melting point) and chemical stability, thus most promising for practical applications. The electroluminescent properties of **3** were therefore investigated. As the only 2-(2-py)-7-azaindole complex, compound **4** has a fairly high melting point (291 °C) and chemical stability. The electroluminescent properties of **4** were therefore also investigated. The electroluminescent device (**A**) for compound **3** was fabricated by using NPB (*N*,*N*′-di-1-naphthyl-*N*,*N*′-diphenylbenzidine) as the hole transport layer, **3** as the light emitting layer, and the electron transport layer. The takeoff voltage of device **A** is ~7 V as shown in Figure 7. The external device efficiency is 1.06 cd/A. The EL maximum of device **A** is at 515 nm, approximately matching that of PL (Figure 8), confirming that the light in device **A** is from compound **3**. When Alq_3 was used as the electron transport layer, a similar electroluminescence as that of device **A** was obtained.

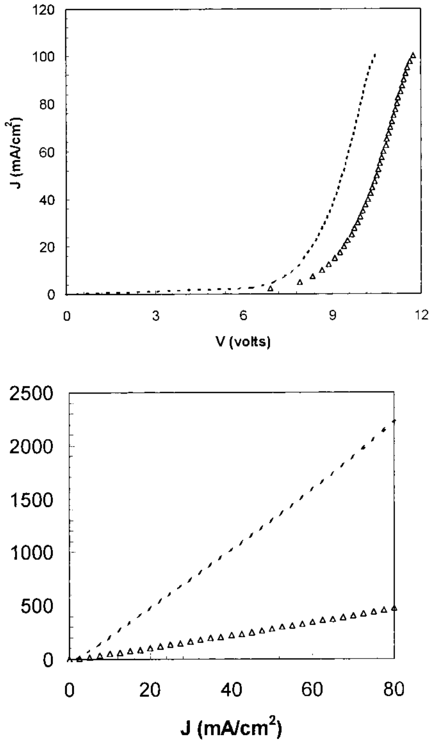

Figure 9. Top: J−V curves (empty triangle, device **B**; dashed line, device **C**). Bottom: L−J curve (empty triangle, device **B**; dashed line, device **C**).

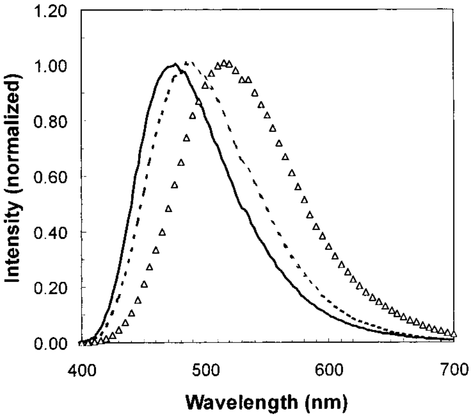

Figure 10. PL (solid line) and EL (empty triangle, device **B**; dashed line, device **C**).

For compound **4** two EL devices (**B** and **C**) were fabricated by using NPB as the hole transport layer, **4** as the light emitting layer, and Alq_3 as the electron transport layer. The takeoff voltage for both devices is at ~8 and 9 V, respectively (Figure 9). The EL maximum for device **B** is at 515 nm, a substantial shift from that of PL (476 nm) of **4** as shown in Figure 10. The possible cause for this red shift is the formation of an exciplex between the NPB layer and the emitting layer. Similar phenomena have been observed previously in EL devices using boron complexes as the light emitting layer and NPB as the hole transport layer.[3e] To eliminate the exciplex, a bicarbazole layer is added between the NPB layer and the compound **4** layer in device **C**. The EL spectrum of device **C** indeed matches well the PL of compound **4** with the emission maximum at 490 nm. Furthermore, as shown in Figure 9, device **C** is much more efficient than that of device **B** (at 20 mA/cm^2 the external efficiency for device **B** is 0.57 cd/A while device **C** has an efficiency of 2.34 cd/A.). The relatively low efficiency of device **B** is consistent with the formation of an exciplex, which is known to reduce the efficiency of the EL device.[11]

In summary, four new blue/green luminescent compounds have been synthesized by using modified indole and 7-azaindole ligands. Two of these compounds have been demonstrated to produce a bright blue/green light in electroluminescent devices. The new boron and beryllium compounds are promising materials in electroluminescent applications. Efforts to further improve electroluminescent performances of the new compounds are underway.

Acknowledgment. We thank the Natural Science and Engineering Research Council of Canada and Xerox Research Foundation for financial support.

Supporting Information Available: Tables of atomic coordinates and isotropic thermal parameters, bond lengths and angles, anisotropic thermal parameters, and hydrogen parameters for **1**−**4** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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