Novel Blue Luminescent/Electroluminescent 7-Azaindole Derivatives: 1,3-Di(*N*-7-azaindolyl)benzene, 1-Bromo-3,5-Di(*N*-7-azaindolyl)benzene, 1,3,5-Tri(*N*-7-azaindolyl)benzene, and 4,4′-Di(*N*-7-azaindolyl)biphenyl

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Four novel blue luminescent organic compounds have been synthesized and fully characterized. These new compounds are 7-azaindole derivatives, including 1,3-di(*N*-7-azaindolyl)benzene (**1**), 1-bromo-3,5-di(*N*-7-azaindolyl)benzene (**2**), 1,3,5-tri(*N*-7-azaindolyl)-benzene (**3**), and 4,4′-di(*N*-7-azaindolyl)biphenyl (**4**). The crystal structures of **1** and **4** were determined by X-ray diffraction analyses. Electroluminescent devices using **3** or **4** as the emitter have been fabricated, which confirmed that compounds **3** and **4** can function as a blue emitter and a hole transport material in electroluminescent devices.

Introduction

Since Tang and Van Slyke reported[1] the first double-layer green organic electroluminescent (EL) device using Alq$_3$ (q = 8-hydroxyquinolinyl) in 1987, there have been intense research activities in organic EL devices.[2,3] Blue emitters for organic EL devices remain the most sought-after materials.[3] We have demonstrated recently that 7-azaindole forms a variety of blue luminescent Al(III) and B(III) compounds readily upon reactions with trialkylaluminum, trialkylboron, or triarylboron.[4] Some of the 7-azaindole boron compounds have been shown to be efficient blue emitters in EL devices.[5,6] To achieve a bright blue emission, the removal of the 7-azaindole

proton is necessary in most of our previously reported Al(III) and B(III) compounds. However, as a consequence of the presence of a negatively charged 7-aza-indolyl ligand, the compounds do not have a long-term stability in EL devices. Therefore, our recent efforts have focused on the modification of 7-azaindole to improve the stability and performance of compounds based on 7-azaindole. One of the modifications we carried out was to replace the proton on the indole nitrogen atom by an aromatic group. Several new 7-azaindole derivatives have been synthesized. When the 7-azaindolyl group is bound to benzene or biphenyl by the nitrogen atom of the indole ring, it was found that the emissions of the new 7-azaindole derivatives show a red shift from the UV region to the blue region compared to 7-azaindole. In addition, most of the new compounds have a melting point much higher than that of 7-azaindole. Some of the new 7-azaindole derivatives have been found to be promising in EL devices. Syntheses, characterizations, and luminescence properties of 1,3-di(*N*-7-azaindolyl)benzene, 1-bromo-3,5-di(*N*-7-azaindolyl)benzene, 1,3,5-tri(*N*-7-azaindolyl)benzene, and 4,4′-di(*N*-7-azaindolyl)biphenyl are described herein. Electroluminescent devices using 1,3,5-tri(*N*-7-azain-dolyl)benzene or 4,4′-di(*N*-7-azaindolyl)biphenyl as the emitter and the hole transport material are also presented.

Experimental Section

General Procedures. All reactions were carried out under a nitrogen atmosphere. All reagent-grade solvents were used without further purification. The starting materials were purchased from Aldrich Chemical Co. and used without further purification. ^{1}H and ^{13}C NMR were recorded on Bruker Avance 300 MHz and AM 400 MHz spectrometers. Elemental analyses were performed by Canadian Microanalytical Service Ltd., Delta, British Columbia, Canada. Thin-layer chromatography (TLC) was carried out on SiO$_2$ (silica gel F254, Whatman).

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Column chromatography was carried out on silica (silica gel, 70-230 mesh 60). Melting points were measured on a Fisher-Johns melting point apparatus. Excitation and emission spectra were recorded on a Photon Technologies International QuantaMaster model C-60 spectrometer. Oxidation potentials were measured on a CV-50W voltammetric analyzer by using an Al/AgCl electrode as the reference electrode and a platinum electrode as the working electrode.

Synthesis of 1,3-Di(*N*-7-azaindolyl)benzene (1). 7-Aza-indole (14 mmol, 1.654 g), 1,3-dibromobenzene (5 mmol, 1.180 g), potassium carbonate (12 mmol, 1.658 g), and cupric sulfate (0.1 mmol, 0.025 g) were mixed in a flask. The mixture was heated at 210 °C for 6 h under nitrogen. After cooling to ambient temperature, the reaction mixture was dissolved in 300 mL of CH_2Cl_2 and washed by water. The organic layer was separated, dried by sodium sulfate, and concentrated by vacuum. The residue was passed through a column on silica using a 3:1 hexanes/ethyl acetate solution as the eluent. The solution collected was evaporated by vacuum and redissolved in 5 mL of CH_2Cl_2, and then 2 mL of hexanes was added to the solution to crystallize the product. After one night of standing, colorless crystals of compound **1** were obtained in 57% yield with a mp of 110 °C. ^{1}H NMR (δ, CDCl$_3$, ppm, 298 K): 8.40 (dd, ^3J = 4.8 Hz, ^3J = 1.2 Hz, 2H, azain), 8.31 (t, ^3J = 2.1 Hz, 1H, benzene), 8.00 (dd, ^3J = 7.8 Hz, ^3J = 1.5 Hz, 2H, azain), 7.79 (dd, ^3J = 7.5 Hz, 2H, benzene), 7.70 (t, ^3J = 3.3, 1H, benzene), 7.64 (d, ^3J = 3.9 Hz, 2H, benzene), 7.17 (q, ^3J = 7.8 Hz, ^3J = 4.8, 2H, azain), 6.68 (d, ^3J = 3.6 Hz, 2H, azain). ^{13}C NMR (δ, CDCl$_3$, ppm, 298 K): 143.68 (azain), 140.68 (benzene), 130.17 (benzene), 129.22 (benzene), 127.87 (azain), 121.47 (azain), 119.20 (benzene), 116.92 (azain), 102.08 (azain). Elemental analysis for $C_{20}H_{14}N_4$, calcd: C, 77.40; H, 4.55; N, 18.05. Found: C, 77.10; H, 4.43; N, 18.01. MS: m/z = 310.3 (M$^+$).

Syntheses of 1-Bromo-3,5-di(*N*-7-azaindolyl)benzene (2) and 1,3,5-Tri(*N*-7-azaindolyl)benzene (3). 1,3,5-Tribro-mobenzene (4 mmol, 1.259 g), 7-azaindole (16 mmol, 1.890 g), potassium carbonate (16 mmol, 2.211 g), and cupric sulfate (0.1 mmol, 0.025 g) were added to a flask. The mixture was heated at 210 °C for 9 h under nitrogen. After cooling to ambient temperature, the mixture was dissolved in 300 mL of CH_2Cl_2 and washed by water. The organic layer was separated, dried by sodium sulfate, and concentrated by vacuum. The residue was passed through a column on silica using a 3:1 hexanes/ethyl acetate solution as the eluent. The first collection was a small amount of 1,3-dibromo-5-(*N*-7-azaindole)benzene. The second collection contained compound **2**. The solution was evaporated by vacuum, and 0.50 g of compound **2** was obtained in 32% yield with a mp of 214 °C. The third collection contained compound **3**. Compound **3** (0.92 g) was obtained after recrystallization from CH_2Cl_2/hexanes in 54% yield with a mp of 220 °C.

*Compound **2**.* ^{1}H NMR (δ, CDCl$_3$, ppm, 298 K): 8.38–8.35 (m, 3H, azain and benzene), 7.97–7.94 (m, 4H, azain and benzene), 7.57 (d, ^3J = 3.6 Hz, 2H, azain), 7.14 (dd, ^3J = 7.5 Hz, ^3J = 4.5 Hz, 2H, azain), 6.65 (d, ^3J = 4.2 Hz, 2H, azain). ^{13}C NMR (δ, CDCl$_3$, ppm, 298 K): 143.59 (azain), 139.98 (benzene), 129.05 (azain), 127.31 (azain), 123.50 (benzene), 116.99 (azain), 102.46 (azain). Elemental analysis for $C_{20}H_{13}N_4$-Br, calcd: C, 61.71; H, 3.37; N, 14.39. Found: C, 61.30; H, 3.05; N, 14.43. MS: m/z = 389.2 (M$^+$).

*Compound **3**.* ^{1}H NMR (δ, CDCl$_3$, ppm, 298 K): 8.36 (d, ^3J = 5.1 Hz, 3H, azain), 8.34 (s, 3H, benzene), 7.97 (dd, ^3J = 7.5 Hz, ^3J = 1.8 Hz, 3H, azain), 7.70 (d, ^3J = 4.2 Hz, 3H, azain), 7.14 (dd, ^3J = 7.5 Hz, ^3J = 4.5 Hz, 3H, azain), 6.67 (d, ^3J = 3.6 Hz, 3H, azain). ^{13}C NMR (δ, CDCl$_3$, ppm, 298 K): 143.72 (azain), 129.20 (azain), 127.77 (azain), 117.05 (benzene), 116.12 (azain), 102.36 (azain). Elemental analysis for $C_{27}H_{18}N_6$ /0.3 CH_2Cl_2, calcd: C, 72.55; H, 4.08; N, 18.59. Found: C, 72.35; H, 3.99; N, 18.41. MS: m/z = 426.3 (M$^+$).

Synthesis of 4,4′-Di(*N*-7-azaindolyl)biphenyl (4). 7-Aza-indole (12 mmol, 1.418 g), 4,4′-dibromobiphenyl (5 mmol, 1.5601 g), potassium carbonate (12 mmol, 1.6585 g), and cupric sulfate (0.2 mmol, 0.0499 g) were added to a flask. The mixture was heated at 210 °C for 12 h under nitrogen. After cooling to

Table 1. Crystallographic Data

	1	4
formula	$C_{20}H_{14}N_4$	$C_{26}H_{18}N_4$
fw	310.36	386.46
space group	$P2_12_12_1$	$P2_1/c$
a/Å	7.3545(19)	9.6984(19)
b/Å	9.7061(18)	8.1737(17)
c/Å	21.074(4)	12.176(3)
β/deg	90	101.537(5)
V/Å^3	1504.3(6)	945.7(3)
Z	4	2
D^o/g cm^{-3}	1.370	1.357
T/°C	23	23
μ/cm^{-1}	0.84	0.82
2θmax/deg	47	46.5
reflns measured	1121	4595
final R ($I > 2\sigma(I)$)	R1^a= 0.0535, wR2^b= 0.124	R1^a= 0.0458, wR2^b= 0.1208
R (all data)	R1 = 0.0865, wR2 = 0.1546	R1 = 0.0651, wR2 = 0.1317
goodness of fit on F^2	0.998	0.877

^{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 $P = [\max(F_o^2, 0) + 2F_c^2]/3$.

ambient temperature, the mixture was dissolved in 300 mL of CH_2Cl_2 and washed by water. The organic layer was separated, dried by sodium sulfate, and concentrated by vacuum. The residue was passed through a column on acti-vated carbon (top part) and silica (bottom part) using a 3:1 hexanes/ethyl acetate solution as the eluent. The solution collected was evaporated by vacuum, the residue was dissolved in a small amount of CH_2Cl_2, and then 2 mL of hexanes was added to the solution to crystallize the product. After one night of standing, colorless crystals of compound **4** were obtained in 63% yield with a mp of 219–220 °C. ^{1}H NMR (δ, CDCl$_3$, ppm, 298 K): 8.38 (d, ^3J = 7.2 Hz, 2H, azain), 7.96 (d, ^3J = 7.5 Hz, 2H, azain), 7.86–7.64 (m, 8H, phenyl), 7.53 (d, ^3J = 3.3 Hz, 2H, azain), 7.13 (dd, ^3J = 7.8 Hz, ^3J = 4.8 Hz, 2H, azain), 6.63 (d, ^3J = 3.3 Hz, 2H, azain). ^{13}C NMR (δ, CDCl$_3$, ppm, 298 K): 143.73 (azain), 129.27 (azain), 128.06 (phenyl), 127.76 (azain), 124.28 (phenyl), 116.88 (azain), 101.92 (azain). Elemental analysis for $C_{26}H_{118}N_4$, calcd: C, 80.81; H, 4.69; N, 14.50. Found: C, 80.42; H, 4.66; N, 14.50. MS: m/z = 386.3 (M$^+$).

X-ray Crystallographic Analyses. All crystals were ob-tained from solutions of CH_2Cl_2/hexanes and were mounted on glass fibers. The data of **1** were collected on a Siemens P4 single-crystal diffractometer with graphite-monochromated Mo Kα radiation, and the data of **4** were collected on Siemens Smart CCD 1000 diffractometer, operating at 50 kV and 35 mA at 23 °C. The data for compounds **1** and **4** were collected over a 2θ range of 3–47° and 3–46.5°, respectively. Three standard reflections were measured every 197 reflections. No significant decay was observed for all samples during the data collection. Data were processed on a Pentium III PC using the Siemens SHELXTL software package (version 5.1) and cor-rected for Lorentz and polarization effects. Neutral atom scattering factors were taken from Cromer and Waber.[7] The crystal of **4** belongs to the monoclinic space group $P2_1/c$, and the crystal of **1** belongs to the orthorhombic space group $P2_12_12_1$. All structures were solved by direct methods. All non-hydrogen atoms were refined anisotropically. The positions for all hydrogen atoms were either calculated or located from difference Fourier maps, and their contributions in the struc-tural factor calculation were included. The crystallographic data for compounds **1** and **4** are given in Table 1. Selected bond lengths and angles are given in Table 2.

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.

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Table 2. Selected Bond Lengths [Å] and Angles [deg] for 1 and 4

Compound **1**			
N(2)−C(7)	1.328(8)	C(7)−N(2)−C(6)	113.3(5)
N(2)−C(6)	1.347(8)	C(7)−N(1)−C(1)	108.0(5)
N(1)−C(7)	1.371(7)	C(7)−N(1)−C(16)	128.7(5)
N(1)−C(1)	1.392(9)	C(1)−N(1)−C(16)	123.0(6)
N(1)−C(16)	1.429(8)	C(14)−N(4)−C(13)	113.2(6)
N(4)−C(14)	1.333(8)	C(8)−N(3)−C(14)	106.3(6)
N(4)−C(13)	1.342(9)	C(8)−N(3)−C(20)	124.5(6)
N(3)−C(8)	1.384(9)	C(14)−N(3)−C(20)	129.0(5)
N(3)−C(14)	1.388(9)	N(2)−C(7)−N(1)	126.1(6)
N(3)−C(20)	1.410(8)	N(4)−C(14)−N(3)	124.5(6)
Compound **4**			
N(1)−C(1)	1.378(3)	C(1)−N(1)−C(7)	106.79(18)
N(1)−C(7)	1.381(2)	C(1)−N(1)−C(13)	124.74(18)
N(1)−C(13)	1.419(2)	C(7)−N(1)−C(13)	128.46(18)
C(7)−N(2)	1.331(3)	N(2)−C(7)−N(1)	125.56(18)
N(2)−C(5)	1.333(3)	C(7)−N(2)−C(5)	114.0(2)

Organic layers and a metal cathode composed of Al were deposited on the substrate by conventional vapor vacuum deposition. Prior to the deposition, all the organic materials were purified via a train sublimation method.[8] No standard hole transport materials were used in all devices. 2-(4-Biphenylyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole (PBD) was employed as the electron transport layer in all devices. On the anode, copper phthalocyanine (CuPc) was used to facilitate hole injections, and LiF was used in the cathode to facilitate electron injection. The active device area is 1.0×5.0 mm². The current/voltage characteristics were measured using a Keithley 238 current/voltage unit. The EL spectra and the luminance for the devices were measured by using a Photo Research-650 Spectra Colorimeter.

Results and Discussion

Syntheses and Structures. The syntheses of the title compounds were accomplished by using Ullmann condensation methods[9] where copper(II) and K_2CO_3 are used as catalyst and bromide scavenger, respectively, as shown in Scheme 1. 1,3-Di(*N*-7-azaindolyl)benzene,

Scheme 1
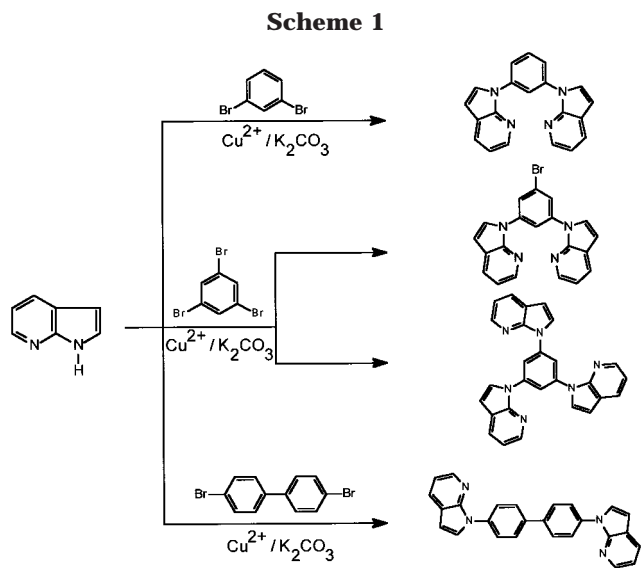
1, was obtained by the reaction of 1,3-dibromobenzene and 7-azaindole in a 1:2 ratio, and compounds **2** and **3**,

(8) Wagner, H. J.; Loutfy, R. O.; Hsiao, C. K. *J. Mater. Sci.* **1982**, *17*, 2781.

(9) (a) Goodbrand, H. B.; Hu, N. X. *J. Org. Chem.* **1999**, *64*, 670. (b) Lindley, J. *Tetrahedron* **1984**, *40*, 1433. (c) Fanta, P. E. *Synthesis* **1974**, 1.
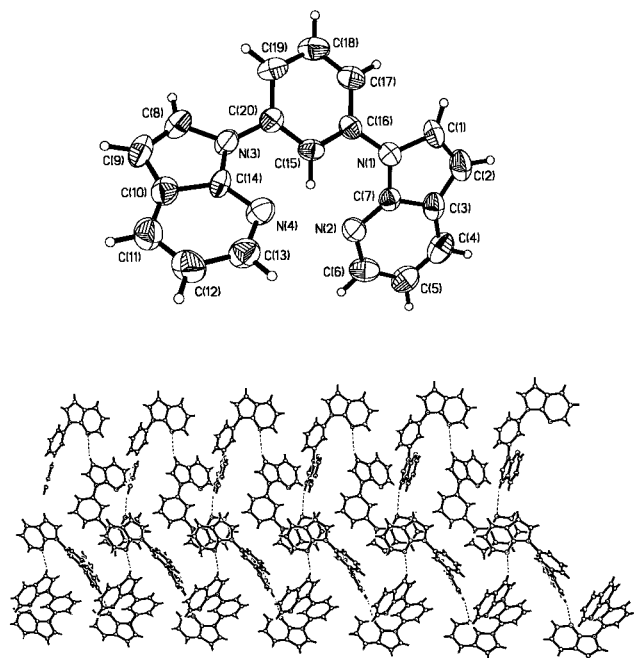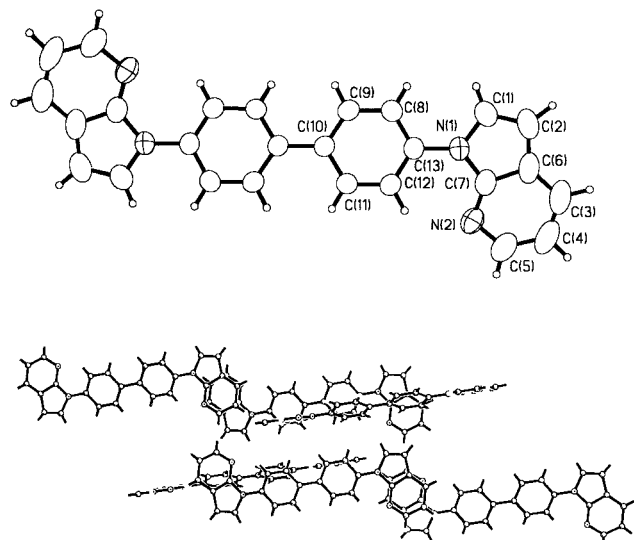
Figure 1. Top: the molecular structure of **1** with labeling schemes and 50% thermal ellipsoids. Bottom: unit cell packing diagram of **1**.

1-bromo-3,5-di(*N*-7-azaindolyl)benzene and 1,3,5-tri(*N*-7-azaindolyl)benzene, were obtained by the reaction of 7-azaindole with 1,3,5-tribromobenzene in a 3:1 ratio. The reaction temperature and thorough mixing of all reactants are the key factors that affect the yield of the product. Repeated separation by column chromatography is necessary to obtain pure compounds **2** and **3**. Compound **4**, 4,4′-di(*N*-7-azaindolyl)biphenyl, was obtained from the reaction of 7-azaindole with 4,4′-dibromobiphenyl. In compounds **1**−**3**, 7-azaindolyl groups are attached to a benzene or bromobenzene molecule, whereas in compound **4** two 7-azaindolyl groups are attached to the 4 and 4′ positions of the biphenyl. The synthesis of compound **4** is motivated by the fact that biphenyl-based diamines (e.g., NPD) are well-known in EL devices as hole transport materials.[1−3, 10]

Compounds **1**−**4** were fully characterized by NMR, mass spectroscopy, and elemental analyses. All four compounds are stable toward air and moisture in solution and the solid state. One important feature of compounds **1**−**4** is that they all have a melting point (110 °C for **1**, 214 °C for **2**, and 220 °C for **3** and **4**) higher than that of 7-azaindole (105 °C). The dramatic melting point difference from **1**−**4** is likely caused by the change of molecular weight and intermolecular interactions in the solid state. Therefore, attempts were made to examine the crystal structures of **1**−**4**. For compounds **1** and **4**, single crystals suitable for X-ray diffraction analyses were obtained. Attempts to grow single crystals of **2** and **3** were unsuccessful. The structures of compounds **1** and **4** were examined by a single-crystal X-ray diffraction analysis.

The crystal of **1** belongs to the chiral space group $P2_12_12_1$. As shown in Figure 1, the two 7-azaindolyl groups in **1** are not coplanar with the benzene ring but

(10) Hosokawa, C.; Higashi, H.; Nakamora, H.; Kusumoto, T. *Appl. Phys. Lett.* **1995**, *67*, 3853.

Figure 2. Top: the molecular structure of **4** with labeling schemes and 50% thermal ellipsoids. Bottom: unit cell packing diagram of **4**.

are on opposite sides of the benzene ring, attributable to steric interactions. The C(7)−N(1)−C(16) angle (128.7-(5)°) is bigger than that of C(1)−N(1)−C(16) (123.0(6)°). The bond angles of the other 7-azaindolyl group are similar. The N(1)−C(16) and N(3)−C(20) bond lengths are 1.429(8) and 1.410(8) Å, respectively, which are similar to those of previously reported 7-azaindolyl compounds.[4,6] The unit cell packing diagram given in Figure 1 (bottom) shows that molecules of **1** have an extended chiral chain arrangement in the solid state but no intermolecular $\pi-\pi$ stacking, which may account for the low melting point of **1**.

The crystal structure of **4** has an inversion center. As shown in Figure 2 (top), the arrangement of the 7-aza-indolyl groups in compound **4** is similar to that of **1**; that is, the 7-azaindolyl groups are not coplanar with the biphenyl rings. The biphenyl portion of **4** is planar. The dihedral angle between the 7-azaindolyl ring and the biphenyl ring is 21.7°. The N(1)−C(1), N(1)−C(7), and N(1)−C(13) bond lengths are 1.378(3), 1.381(2), and 1.419(2) Å, respectively, which are similar to those C−N bonds in compound **1**. The N(1) is coplanar with the three bound carbon atoms, and the sum of bond angles around N(1) is 360°. There is an extensive stacking between molecules of **4** in the crystal lattice as shown by Figure 2 (bottom). The shortest intermolecular separation distance of 3.433 Å is between two pyridyl rings. The relatively high molecular weight and intermolecular stacking in the solid state may account for the much higher melting point of **4** in comparison to that of **1**.

Luminescent Properties of Compounds 1−4. 7-Azaindole emits at 360 nm in solution (toluene or CH_2Cl_2) and the solid state. In contrast, compound **1**, 1,3-di(*N*-7-azaindolyl)benzene emits a purple color in the solid state (λ_{max} = 384 nm) and solution (λ_{max} = 392 nm, CH_2Cl_2 or toluene), as shown in Figure 3 (top). The conjugation of the 7-azaindolyl ring with the benzene ring is clearly responsible for the decrease of band gap and thus the red shift of the emission energy observed in **1**. Compound **2** emits a blue color at λ_{max} = 428 nm in the solid state and at λ_{max} = 416 nm in solution (CH_2Cl_2 or toluene) (Figure 3, bottom). The only difference
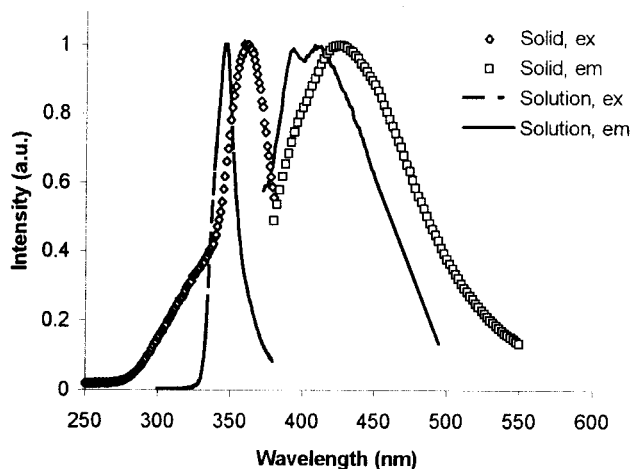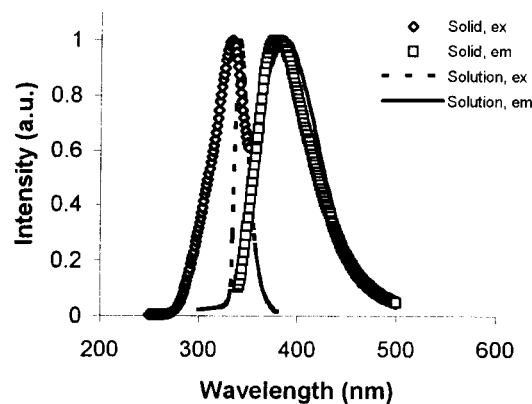
Figure 3. Top: PL of **1** in solution (CH_2Cl_2) and the solid state. Bottom: PL of **2** in solution (CH_2Cl_2) and the solid state.
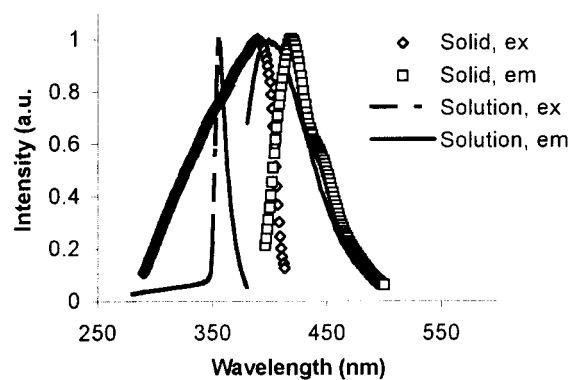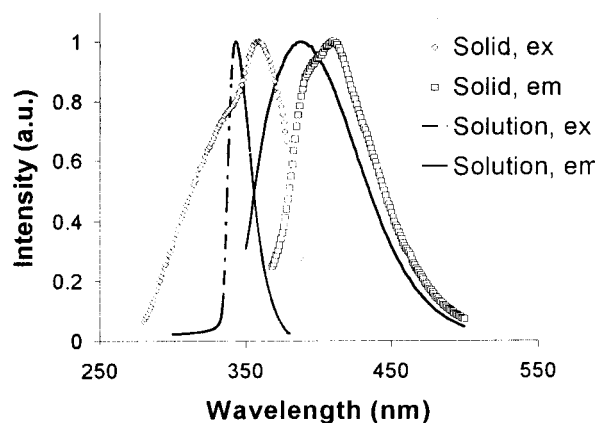
Figure 4. Top: PL of **3** in solution (CH_2Cl_2) and the solid state. Bottom: PL of **4** in solution (CH_2Cl_2) and the solid state.

Table 3. EL Device Structures

device	CuPc thickness (Å)	NPD thickness (Å)	EML (3 or 4) thickness (Å)	PBD thickness (Å)	LiF thickness (Å)	Al thickness (Å)
1	100	0	**3**, 400	200	15	1500
2	0	0	**4**, 500	200	15	1500
3	100	0	**4**, 400	200	15	940

Table 4. Electronic and Optical Properties of Compounds 3 and 4

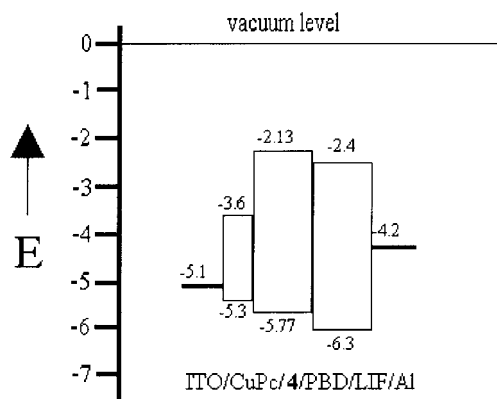|	$\lambda_{max(abs)}$ (nm)	abs edge (nm, eV)	oxidation potential (V) vs NHE	emission max (nm)	quantum yield	calcd HOMO (eV)	calcd LUMO (eV)
3	318	330, 3.76	1.45	410, solid 382, film	0.50	−5.95	−2.19
4	320	341, 3.64	1.27	426, solid 390, film	0.55	−5.77	−2.13

Figure 5. An energy level diagram for device 3. The energy levels of the LiF layer are not shown.

Figure 6. Top: PL (film) of **3** and EL of device 1. Bottom: luminance−current−voltage characteristics of device 1.

between **1** and **2** is that compound **2** contains a bromine atom, which appears to lower the band gap in **2** and shift the emission energy to the blue region. Similarly, compound **3** emits a blue color at $\lambda_{max} = 410$ nm in the solid state and a purple-blue color at $\lambda_{max} = 392$ nm in solution (CH$_2$Cl$_2$ or toluene) (Figure 4, top). The emission spectra of **2** and **3** in solution show a blue shift (about 13−18 nm) compared to their solid-state spectra, which is attributable to intermolecular interactions in the solid state. The conjugation of the 7-azaindolyl ring with the benzene group is again believed to be responsible for the red shift of emission energy observed in **2** and **3** in comparison to that of 7-azaindole.

The photoluminescent efficiencies of **1**, **2**, and **3** in solution were determined to be 0.26, 0.11, and 0.50, respectively, relative to that of 9,10-diphenylanthracene (0.90). The bromine is likely responsible for the low efficiency of compound **2**. The relatively high quantum efficiency of **3** indicates that **3** is a bright emitter. Moreover, we believe that the relatively high luminescent efficiency for **3** is due to the increasing number of 7-azaindolyl groups that contribute to the overall luminescent efficiency.

Compound **4**, 4,4′-di(*N*-7-azaindolyl)biphenyl, emits a bright blue color in the solid state at $\lambda_{max} = 426$ nm when irradiated by UV light. In the solution (CH$_2$Cl$_2$ or toluene), the emission maximum of **4** is at $\lambda_{max} = 405$ nm (Figure 4, bottom). The red shift of emission energy for **4** from the solution to the solid state is clearly caused by intermolecular $\pi-\pi$ interactions in the solid state as confirmed by the crystal structure of **4**. The photoluminescent efficiency of **4** in solution was determined to be 0.55 relative to that of 9,10-diphenylanthracene, indicating that it is a bright emitter.
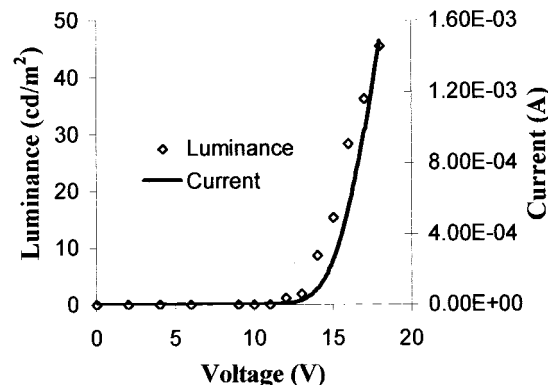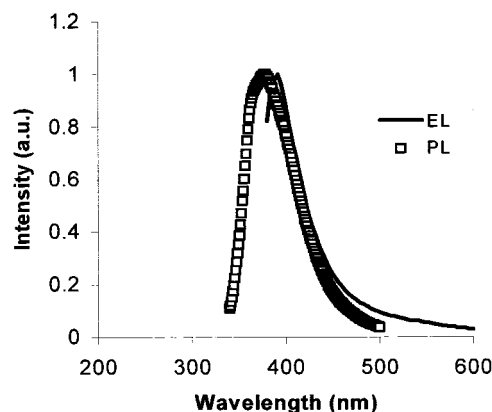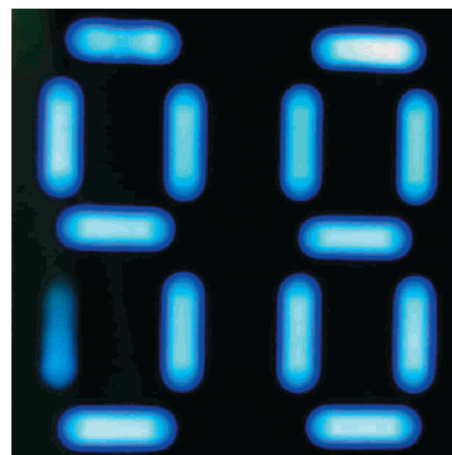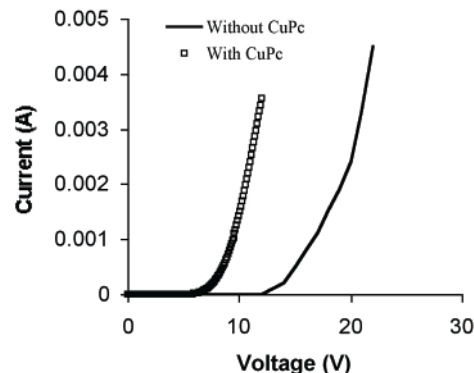
Electroluminescence of Compounds 3 and 4. As shown above, compound **1** has a low melting point and compound **2** has a low luminescent efficiency. Therefore, they are not good candidates for EL devices. In contrast, compounds **3** and **4** have a high melting point and a high luminescent efficiency, making them possible candidates for EL applications. The electroluminescent properties of compounds **3** and **4** were therefore investigated. The electroluminescent devices were fabricated by high-vacuum (<10^{-6} Torr) thermal deposition of organic materials on glass substrates precoated with indium−tin-oxide (ITO). In our initial experiments, *N,N*-di-1-naphthyl-*N,N*-diphenyl-1,1′-biphenyl-4,4′-diamine (NPD) was employed as the hole transport layer. However, we observed that devices using NPD as the hole transport material have a much lower luminance than the devices without an NPD layer. Therefore, we decided not to use NPD as the hole transport material. An oxadiazole derivative (PBD) was used as the electron
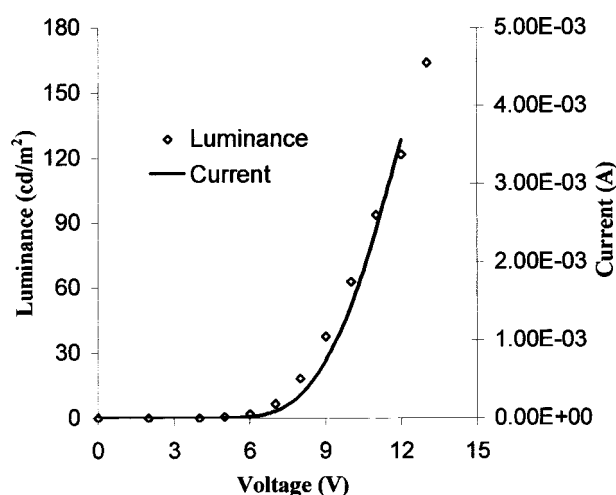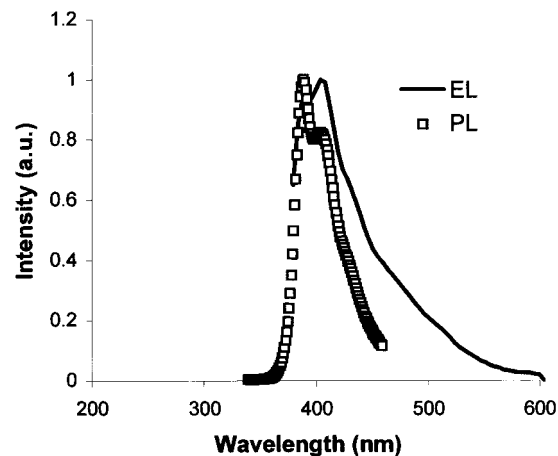
Figure 7. Top: PL (film) of **4** and EL of device 3. Bottom: luminance−current−voltage characteristics of device 3.

Figure 8. Top: luminance−current−voltage characteristics of device 2 and device 3. Bottom: a photograph showing the blue EL light from device 3.

transport material in all devices. Compounds **3** and **4** were used as the emitter layer (EML) and the hole transport layer in the devices. In some of the devices, copper phthalocyanine (CuPc) was used as the hole injecting layer. LiF was used as the electron injecting layer in all devices. The compositions of the EL devices are shown in Table 3.

The oxidation potentials were obtained by electrochemical measurements using ferrocence as the standard. The highest occupied molecular orbital (HOMO) energy levels relative to the vacuum level were calculated by using the oxidation potential (after being converted to the potential relative to the standard hydrogen electrode potential, NHE) and the ferrocence HOMO energy level of −4.8 eV (relative to the vacuum level) as the standard.[11] The HOMO energy levels thus obtained for **3** and **4** are listed in Table 4. The band gaps were obtained from the absorption spectra of compounds **3** and **4**. The lowest unoccupied molecular orbital (LUMO) energy level was calculated from the values of the band gap and HOMO energy. An energy level diagram for device 3 (ITO/CuPc/**4**/PBD/LiF/Al) is shown in Figure 5. (The energy levels of LiF are not shown because LiF has a very large band gap (12 eV) and

functions as an effective electron injector by tunneling injection.[12]) The electronic and optical properties of compounds **3** and **4** are summarized in Table 4.

One EL device for compound **3** with the structure of ITO/CuPc/**3**/PBD/LiF/Al (device 1) was fabricated. As shown in Figure 6 (top), the EL of device 1 is similar to the PL of **3** (thin film), indicating that the light is from compound **3.** At all the biased voltages in the range of 12−18 V, we observed the emission peak at 395 nm with a dark blue color. The current−voltage and luminance−voltage curves of device 1 are shown in Figure 6 (bottom). Device 1 shows a turn-on voltage of about 12.5 V for current and luminance.

Two EL devices with structures of ITO/**4**/PBD/LiF/Al (device 2) and ITO/CuPc/**4**/PBD/LiF/Al (device 3), shown in Table 4, were fabricated. At all the biased voltages in the range of 6−14 V, we observed the emission peak at 404 nm with a dark blue color for both devices. Figure 7 (top) shows that the PL (thin film) of **4** matches the EL of device 3, confirming that the observed blue light is from compound **4**. Figure 7 (bottom) also shows the current−voltage and luminance−voltage curves of device 3, which has a turn-on voltage of about 7 V for current and luminance. A photograph showing the image of device 3 is shown in Figure 8 (bottom). The significant difference between devices 2 and 3 is that there is no CuPc layer in device 2. For comparison,

(11) Pommerehne, J.; Vestweber, H.; Guss, W.; Mahrt, R. F.; Bassler, H.; Porsch, M.; Daub, J. *Adv. Mater.* **1995**, *7*, 551.

(12) Hung, L. S.; Tang, C. W.; Mason, M. G. *Appl. Phys. Lett.* **1997**, *70*, 13.

Figure 8 (top) shows the current−voltage characteristics for devices 2 and 3. The turn-on voltage for device 3 is 7 V, significantly lower than that of device 2 (13 V), which confirms that CuPc facilitates the hole injection by perhaps decreasing the band gap between ITO and compound **4**, consistent with the energy diagram in Figure 5. A similar phenomenon was reported by Jen and co-workers.[13] The facts that no standard hole transport materials such as NPD or TPD are present in devices 1−3 and that devices 1−3 are more efficient than the devices containing an NPD layer lead us to believe that compounds **3** and **4** can function not only as emitters but also as hole transport materials. Further investigation on the utility of compounds **3** and **4** as hole transport materials is being conducted in our laboratory.

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(13) Liu, Y.; Ma, H.; Jen, A. K-Y. *Chem. Mater.* **1999**, *11*, 27.

In summary, four novel blue-purple luminescent organic compounds have been synthesized and fully characterized. Two of them, 1,3,5-tri(*N*-7-azaindolyl)-benzene (**3**) and 4,4′-di(*N*-7-azaindolyl)biphenyl (**4**), have been demonstrated to be promising blue emitters and hole transport materials in organic electroluminescent devices.

Supporting Information Available: Tables containing crystal data and structure refinement, atomic coordinates and equivalent isotropic displacement parameters, bond lengths and angles, anisotropic displacement parameters, and hydrogen coordinates and isotropic displacement parameters for compounds **1** and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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