

Quinoxalines Incorporating Triarylaminies: Potential Electroluminescent Materials with Tunable Emission Characteristics

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Dipolar compounds featuring quinoxaline acceptors and various triarylamine donors were prepared in good yields and successfully employed in the fabrication of organic light-emitting diodes (OLEDs). It is also demonstrated that the emission color of these compounds can be easily tuned from bluish green to orange by suitably modifying the diarylamine and quinoxaline units independently. Increasing the donor and acceptor strengths bathochromically shifts the absorption and emission bands. These molecules possess moderate glass transition temperatures (114–152 °C) and exhibit high decomposition temperatures (441–554 °C). The two-layer OLEDs fabricated using these materials as hole-transporting and emitting layers and 1,3,5-tris(*N*-phenylbenzimidazol-2-yl)benzene or tris(8-hydroxyquinalinato)aluminum as the electron-transport layer display promising characteristics, i.e., emission color, luminance, and efficiency. Incorporation of the hole-blocking quinoxaline segments in the hole-transporting triarylamine molecules leads to the confinement of the recombination zone in it, and thus emission is realized mainly from these materials for both types of devices. The factors leading to the funneling of light through the hole-transporting layer in these layers are critically analyzed.

Introduction

The design and synthesis of materials suitable for the fabrication of organic light-emitting diodes (OLEDs) gained much impetus in the recent years because of applications envisaged for this technology in the display industry (full-color flat-panel displays).^{1,2} OLEDs normally contain three layers, with hole-transporting and emitting and electron-transporting properties, sandwiched between suitable anodes and cathodes. When voltage is applied, the holes migrate through the hole-transporting material and loosely bond with the electrons at the interface with the electron-transporting layer (ETL) to form the excitons that are responsible for the emission of light. The location of the recombination zone depends on many factors such as the energy alignment of the layers and mobility of the holes and electrons. Because the carrier mobility of the holes in the hole-transporting layer (HTL) is usually greater than that of the electrons in the ETL, some percentage of the holes can leak up to the cathode if the ETL

exhibits a matching highest occupied molecular orbital (HOMO) level. This could decrease the efficiency of the device dramatically. So, it is realized that the use of dipolar compounds incorporating both hole- and electron-transporting segments could benefit the device. First, the mobility of holes in the dipolar molecular film will be slightly lower than that in a single HTL and could facilitate the exciton formation inside the layer.³ Second, because of sufficiently low-lying lowest unoccupied molecular orbital (LUMO), it can capture electrons released from the cathode and may lead to improved performance. Finally, these dipolar compounds can act as a HTL, hole-blocking layer, and emitter layer in OLEDs.⁴

Many donor–acceptor molecules were synthesized for possible application in electroluminescent (EL) devices. Very prominent among them are oxadiazole–amine^{5,6} and pyridine/quinoline–amine dyads.⁷ Quinoxaline-

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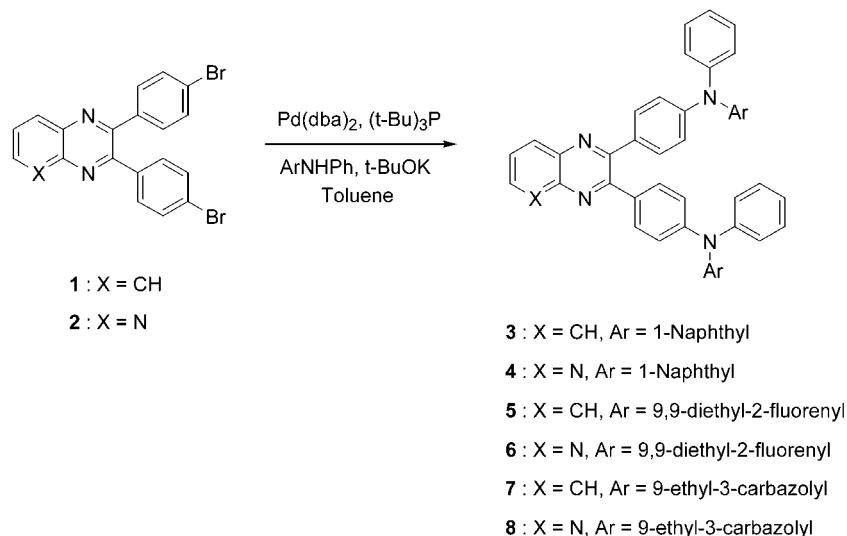
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Scheme 1



based materials were used as ETLs or hole-blocking layers in OLEDs.^{8,9} However, no systematic study was available for quinoxaline derivatives containing triarylamine units. In continuation of our interests^{10–13} in materials suitable for OLEDs, we have designed and synthesized dipolar compounds incorporating both quinoxaline and triarylamine segments. The color tuning in these molecules is realized by altering either the quinoxaline or triarylamine moieties. Additionally, they effectively act as hole-transporting materials while retaining their emission properties. Herein, we report the synthesis and use of quinoxaline-tethered triarylaminines as potential hole-transporting and emitting materials in EL devices.

Results and Discussion

Synthesis. Scheme 1 illustrates the synthesis of the dipolar compounds incorporating quinoxaline and triarylamine segments. The diarylamine unit was varied from 1-naphthylphenylamine to 9-ethyl-3-carbazolylphenylamine with an aim at tuning the HOMO of the resulting molecules. Similarly, the electron-deficient pyridopyrazine segment was used to study its effect on adjusting the LUMO energy. Compounds **3–8** were

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obtained in excellent yields from the corresponding dibromides (**1** and **2**) by using the C–N coupling strategy involving the Pd(dba)₂/(t-Bu)₃P catalyst system developed by Hartwig and coauthors.¹⁴ These compounds adopt a yellow to orange color and are soluble in a wide variety of solvents including most of the chlorosolvents.

Thermal Properties. All of the compounds form stable glasses easily and the glass transition temperature ranges from 114 to 152 °C. The pronounced stability of the glassy state in these molecules is attributed to the nonplanar molecular configurations arising from the steric hindrance of the bulky secondary amines and polar structural elements. For the same secondary amine, the pyridopyrazine derivatives (**4**, **6**, and **8**) possess higher *T*_g when compared to the quinoxaline derivatives (**3**, **5**, and **7**). This points to the fact that the more polar nature of pyridopyrazine¹⁵ is beneficial to *T*_g. Among the compounds, **8** displays the highest *T*_g probably because of the presence of both strong electron-donating carbazole and electron-withdrawing pyridyl units. Rising *T*_g because of the presence of carbazole units in amorphous molecules is well documented in the literature.^{10,16} The thermal stability of these materials also seems to be encouraging. The thermal decomposition of these materials does not occur below 440 °C in air, and the carbazole derivative **7** possesses the highest degradation temperature in the series. Also, all of the compounds are volatile enough to be vacuum deposited as thin layers.

Photophysical Characteristics. The electronic spectra of the molecules reveal two bands arising from the π – π^* and charge-transfer (CT) transitions. The lower energy transition, which exhibits positive solvatochromism, is assigned as mainly of CT character. This band shifts to longer wavelength on increasing the acceptor and donor properties of the corresponding

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Table 1. Spectral and Thermal Properties of the Dipolar Compounds

compd	λ_{abs} , nm ($\epsilon_{\text{max}} \times 10^{-3} \text{ M}^{-1} \text{ cm}^{-1}$)		λ_{em} , nm (Φ_f , %)			T_g (T_m), °C	T_d , °C
	CH ₂ Cl ₂	toluene	CH ₂ Cl ₂	toluene	film		
3	399 (21.36), 305 (21.37)	396 (19.86), 305 (25.30)	530 (17)	467 (14)	501	114 (260)	520
4	429 (23.24), 312 (38.44)	425 (16.38), 312 (24.83)	580 (6)	501 (20)	565	127 (262)	446
5	410 (22.78), 333 (51.94)	405 (23.96), 334 (49.87)	586 (6)	495 (39)	534	116 (226)	441
6	439 (22.68), 331 (60.79)	431 (24.14), 329 (58.22)	636 (<1)	534 (31)	589	122	527
7	411 (22.53), 305 (66.92), 276 (53.18)	405 (16.81), 306 (47.15)	523 (30)	566	142	554	
8	445 (24.05), 305 (71.09), 277 (59.33)	438 (20.29), 306 (55.09)	567 (15)	631	152		

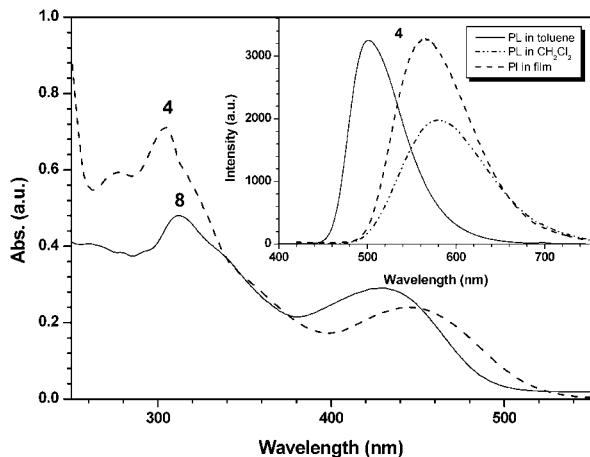


Figure 1. Absorption spectra of compounds **4** and **8** in CH₂Cl₂. The inset shows emission spectra of compound **4** in various media.

Table 2. Electrochemical Data and the Derived Orbital Energies

compd	E_{ox} , mV	E_{red} , mV	band			E_{ox} , mV	E_{red} , mV
			HOMO, eV	LUMO, eV	gap, eV		
3	+615 (65)	-2171 (82)	5.292	2.629	2.786		
4	+580 (71), +687 (78)	-1916 (70)	5.380	2.884	2.496		
5	+447 (88)	-2158 (77)	5.247	2.642	2.612		
6	+463 (79)	-1908 (77)	5.263	2.892	2.457		
7	+256 (91), +814 (56)	-2187 (86)	5.056	2.613	2.471		
8	+291 (75), +828 (67)	-1945 (80)	5.091	2.855	2.341		

segments and red shifts as the polarity of the solvent increases (Table 1). Thus, among the series, compound **8** displays the most red-shifted CT band (Figure 1). This trend is also manifested in the emission characteristics. This leads to a color tuning from bluish green to orange. The presence of a somewhat stronger dipole in the molecules **7** and **8** is reflected in the emission properties. These molecules do not emit in dichloromethane. This suggests that the polarized ground state on excitation undergoes further reorganization to attain a more polar state, which on interaction with a polar solvent relaxes to the ground state nonradiatively. However, in the solvent-casted filmy state, all of the compounds emit with appreciable intensity and the emission maximum is located between that observed for toluene and dichloromethane solutions (Figure 1, inset). This may be attributed to a medium effect.

Electrochemistry. At least two quasi-reversible redox waves were observed for all of the molecules. The anodic oxidation wave originates from the triarylamine segment and corresponds to two electrons. This shifts cathodically on increasing the donor strength (**7** > **5** > **3**) (Table 2). Similarly, the cathodic wave attributable to the reduction of the azine (pyridopyrazine or quinoxaline) segment progresses anodically on increasing

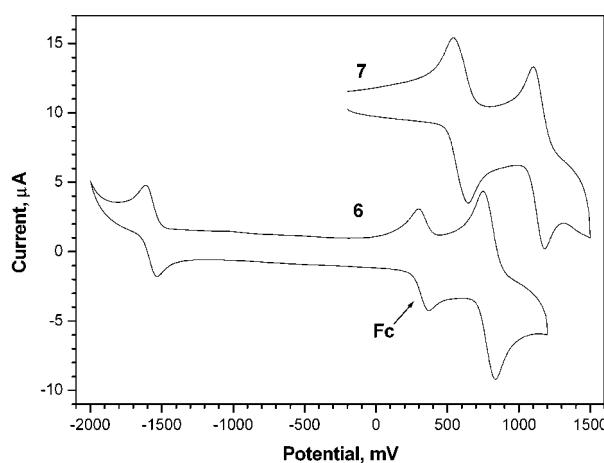


Figure 2. Cyclic voltammograms of compounds **6** and **7**. In the case of **7**, no ferrocene was added for the sake of clarity.

the acceptor strength (**4** > **3**, **6** > **5**, and **8** > **7**). A countereffect due to the electron-withdrawing azine and electron-donating triarylamine is also noticed on the oxidation and reduction potentials, respectively. The carbazole-containing compounds **7** and **8** display an additional oxidation wave at slightly high positive potentials that stems from the carbazole oxidation (Figure 2).

The energy of the HOMO of these materials was calculated with reference to ferrocene (4.8 eV) and ranges from 5.06 to 5.38 eV. Similarly, the optical edge was utilized to derive the band gap and the LUMO energies. As expected, the pyridopyrazine derivatives possess lower LUMO energies and smaller band gaps when compared to the simple quinoxaline derivatives. They (2.61–2.89 eV) are slightly higher than that observed for quinoxaline monomers^{9d} and quinoxaline–heterocycle hybrid polymers,^{9e} and this suggests that the presence of electron-donating triarylamines in the quinoxalines is responsible for the rise in the LUMO level. However, the LUMOs generally appear to lie lower than that observed for oxadiazole–amine dyads.⁵ Molecules that can stabilize the formation of both cation and anion radicals are suggested to be beneficial for OLED devices.¹⁷

OLEDs and Their Performances. Examination of the energy level alignments (Figure 3) of these compounds and 1,3,5-tris(*N*-phenylbenzimidazol-2-yl)benzene (TPBI) or tris(8-hydroxyquinolinato)aluminum (Alq₃) suggests that double-layer EL devices using **3–8** as the hole-transporting/emitting layer and Alq₃ (device A) or TPBI (device B) as the ETL are possible. It is expected that the HOMO energy barrier (0.82–1.11 eV for the TPBI devices and 0.62–0.91 eV for the Alq₃

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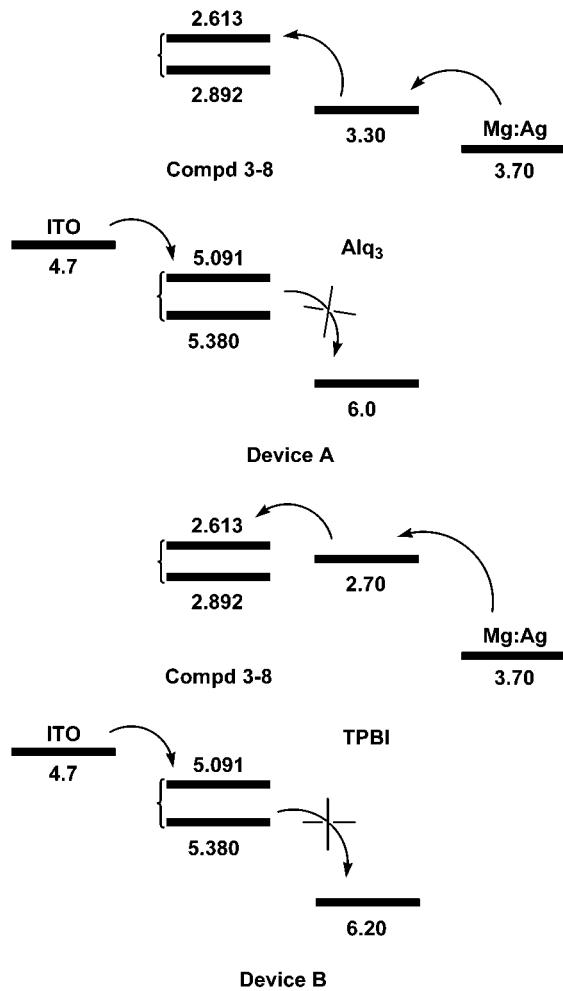


Figure 3. Energy alignments of the compounds with Alq_3 and TPBI.

devices) from the HTL to ETL heterojunction is sufficient to deter holes from injecting into the ETL layer in these devices. On the contrary, the low LUMO energy gap (0.09 to -0.19 eV for the TPBI devices and 0.41–0.69 eV for the Alq_3 devices) from ETL to HTL will allow facile injection of electrons from ETL to HTL. The LUMO of the pyridopyrazine derivatives lie lower than that of TPBI, and this must benefit electron transport from the latter.

Double-layer EL devices were fabricated using compounds **3–8** as a HTL as well as an emitting layer and TPBI or Alq_3 as the ETL. The current–voltage–luminance (I – V – L) characteristics are shown in Figures 4–6. The incorporation of electron-deficient quinoxaline within the hole-transporting materials not only deters the hole injection into ETL but also facilitates injection of the electrons from ETL to HTL. Thus, the emission in both devices originates from our compounds to give bluish green and orange lights (Figure 7). A slight blue shift in the EL spectra was noticed for compounds **4** and **6** when compared to the photoluminescence (PL) spectra of the vapor-deposited pure films. This may be due to interfacial interactions, cavity effects, or charging of the organic medium under electrical excitation.

Because the HOMOs of the molecules lie very close to the work function of indium–titanium oxide (ITO), the hole injection should be facile and the low drive voltages (defined as the voltage required to achieve a

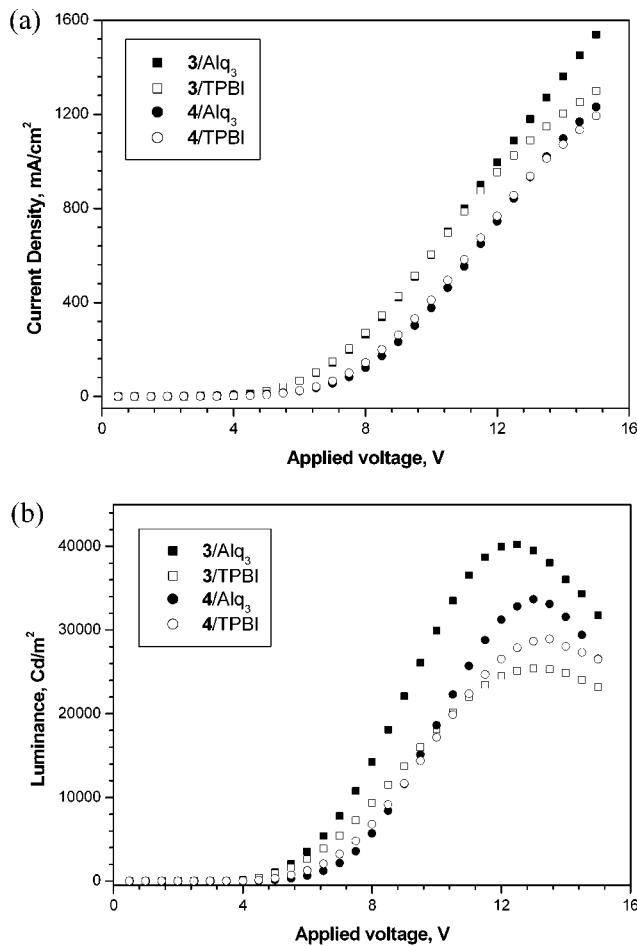


Figure 4. I – V – L characteristics for the devices involving compounds **3** and **4**.

brightness of 1 cd/m^2) for the devices seem to attest this. These nonoptimized devices exhibit promising performances (Table 3 and Figures 4–6). In particular, the device ITO/7/ Alq_3 /Mg:Ag displays exceptionally high brightness ($\sim 68\,000 \text{ cd/m}^2$ at 15 V) and external quantum efficiency (2.64%) with yellow green emission. Yellow green emission was previously reported for certain zinc complexes,¹⁸ 8-hydroxyquinolatoboron compounds,¹⁹ and numerous perylene-doped devices,²⁰ with an inferior performance to that realized for **7**. Similarly, the greenish-yellow-emitting devices derived from **4** and **6** also appear to be promising and rival that reported recently by Lee and co-workers.²¹ It is also interesting to note that the yellow emission was observed earlier for 5,5''-bis{4-[bis(4-methylphenyl)amino]phenyl}-[2,2';5'2'']terthiophene, a hole-transporting material by Shirota et al.²² with less promising parameters. Appropriate hole impeding by the insertion of a copper phthalocyanine (CuPc) layer between ITO and HTL or

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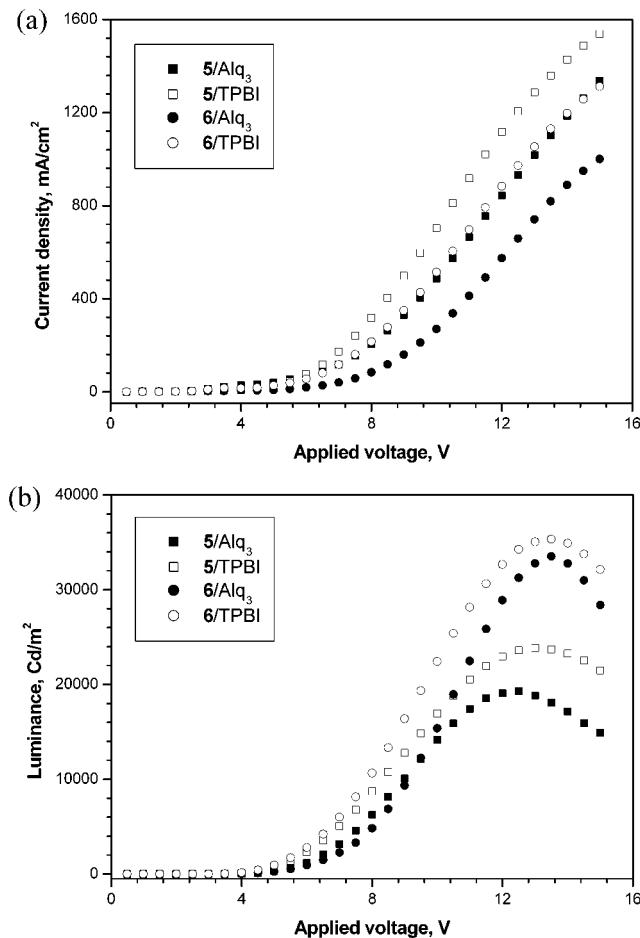


Figure 5. $I-V-L$ plots for the devices with compounds **5** and **6**.

the introduction of dopants in the HTL layer has been demonstrated to be an efficient strategy for stabilizing and improving the performance of the NPD/Alq₃ OLED devices.²³ Incorporating a quinoxaline moiety is evidently a useful approach for the hole-impeding effect. Further modification of quinoxaline derivatives toward a better device performance and stability will be conducted in the future.

Conclusions. We have synthesized a series of quinoxaline-containing triarylamines as potential hole-transporting and emitting materials for EL devices. The emission colors of these materials were tuned from bluish green to orange by changing the nature of the amine and quinoxaline units. We have fabricated many devices that emit bluish green, yellow green, or orange colors. A yellow-green-emitting device incorporating compound **7** displays exceptional physical characteristics. As is believed, embedding the quinoxaline fragment in the triarylamine compartment leads to the efficient confinement of the excitons in the HTL layer. When this strategy is extended, it is possible to obtain three-in-one molecules possessing hole-transporting and emitting and electron-transporting characteristics. Work is in progress toward improving the electron carrier capability of quinoxaline segments by the incorporation of electron-withdrawing groups such as cyano- or perfluoroarene.

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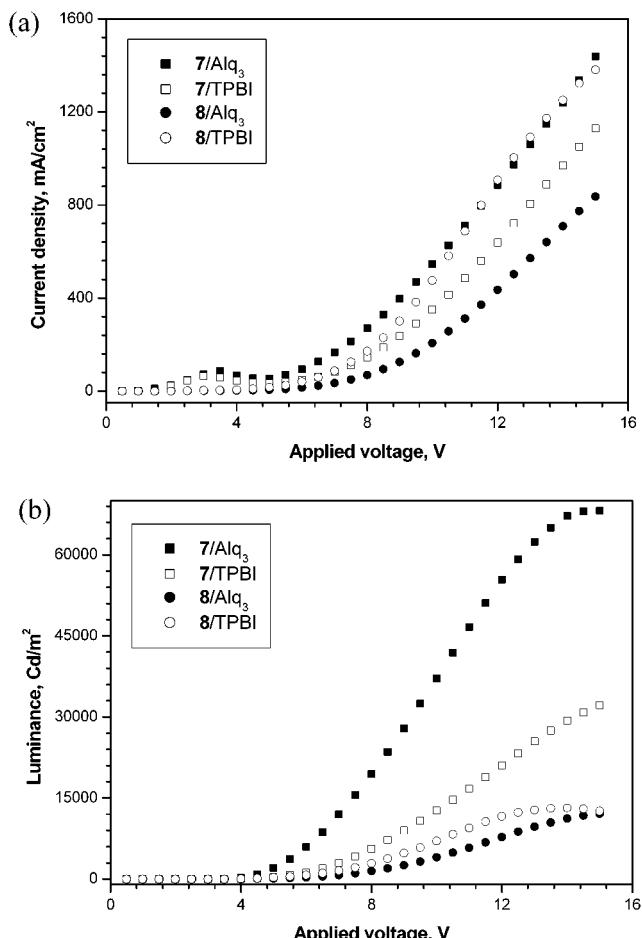


Figure 6. $I-V-L$ curves for the devices featuring compounds **7** and **8**.

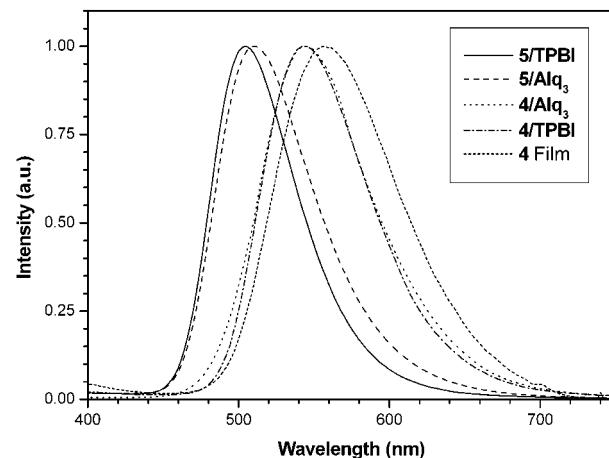


Figure 7. EL spectra of the **4/Alq₃**, **4/TPBI**, **5/TPBI**, and **5/Alq₃** devices. The PL spectrum of the vapor-deposited film of **4** is also included for comparison.

Experimental Section

General Information. Unless otherwise specified, all of the reactions were performed under a nitrogen atmosphere using standard Schlenk techniques. Toluene was distilled from sodium and benzophenone under a nitrogen atmosphere. Dichloromethane for spectroscopic and electrochemical measurements was distilled from calcium hydride under a nitrogen atmosphere. ¹H and ¹³C NMR spectra were recorded on a Bruker 300-MHz spectrometer operating at 300.135 and 75.469 MHz, respectively. Emission spectra were recorded on a Perkin-Elmer spectrofluorometer, and the quantum efficien-

Table 3. EL Data for the Compounds

compd	TPBI/Alq ₃						λ _{em} , nm (vapor-deposited film)	CIE (x, y) for (TPBI; Alq ₃)		
	turn-on voltage, V	voltage, ^a V	brightness, ^a cd/m ²	quantum efficiency, ^a %	power efficiency, ^a lm/W	λ _{em} , nm	max brightness, cd/m ² (voltage, V)	max quantum efficiency, ^a %		
3	3.5/3.0	6.5/6.5	3829/5399	1.63/1.79	1.86/2.61	492/506	25376 (13)/ 40232 (12.5)	1.8/1.8	500	0.16, 0.41; 0.22, 0.52
4	3.0/3.5	7.5/7.7	4820/4474	1.33/1.24	2.02/1.81	544/544	28943 (13.5)/ 33679 (13)	1.4/1.4	556	0.38, 0.58; 0.38, 0.57
5	3.5/3.0	6.3/7.0	3023/2494	1.24/0.99	1.52/1.16	504/510	23856 (13)/ 19291 (12)	1.3/1.2	507	0.24, 0.49; 0.27, 0.50
6	3.0/3.0	6.8/8.2	5185/5823	1.58/1.80	2.41/2.22	564/564	35336 (13)/ 33527 (13.5)	1.6/1.8	572	0.45, 0.53; 0.45, 0.52
7	3.0/2.5	7.3/6.1	3758/6509	1.47/2.34	1.61/3.34	550/552	32192 (15)/ 68147 (15)	1.5/2.6	551	0.38, 0.49; 0.39, 0.51
8	3.0/3.0	7.2/8.6	1777/2073	0.97/1.11	0.78/0.76	610/612	13141 (14)/ 12080 (15)	1.2/1.0	611	0.58, 0.41; 0.55, 0.43

^a Data are taken at a current density of 100 mA/cm².

cies were obtained by a standard method using coumarin I ($\Phi_f = 0.99$ in ethyl acetate) as the reference. All chromatographic separations were carried out on silica gel (60 M, 230–400 mesh). Cyclic voltammetry experiments were performed with a BAS-100 electrochemical analyzer. All measurements were carried out at room temperature with a conventional three-electrode configuration consisting of a platinum working electrode, an auxiliary platinum electrode, and a nonaqueous Ag/AgNO₃ reference electrode. The solvent in all experiments was CH₂Cl₂, and the supporting electrolyte was 0.1 M tetrabutylammonium hexafluorophosphate. The $E_{1/2}$ values were determined as $(E_p^a + E_p^c)/2$, where E_p^a and E_p^c are the anodic and cathodic peak potentials, respectively. All potentials reported are referenced to a Fc⁺/Fc internal standard (+0.350 V relative to the Ag/AgNO₃ electrode) and are not corrected for the junction potential. Differential scanning calorimetry measurements were carried out using a Perkin-Elmer-7 series thermal analyzer at a heating rate of 10 °C/min. Thermogravimetric analysis measurements were performed on a Perkin-Elmer TGA7 thermal analyzer. Mass spectra (fast atom bombardment) were recorded on a VG70–250S mass spectrometer. Elementary analyses were performed on a Perkin-Elmer 2400 CHN analyzer.

General Procedure for the Synthesis of the Donor-Acceptor Compounds (3–8). The dibromoquinoxaline derivative (**1** or **2**, 1.0 mmol) and the corresponding secondary amine (2.1 mmol), Pd(dba)₂ (0.04 mmol), P(t-Bu)₃ (0.04–0.06 mmol), sodium *tert*-butoxide (0.288 g, 3 mmol), and toluene (20 mL) were mixed together and heated at 80 °C for 4–6 h. The reaction was quenched with water (30 mL) and the organic layer taken into 100 mL of diethyl ether, washed with a brine solution, and dried over MgSO₄. Evaporation of the solvent under vacuum resulted in a yellow to orange color solid that was adsorbed in silica gel and purified by column chromatography using a dichloromethane–hexane mixture as the eluant. Yield and the spectroscopic data are listed below for the individual compounds.

2,3-Bis[4-(*N*-phenylnaphthylamino)phenyl]quinoxaline (3). Yellow solid. Yield: 84%. ¹H NMR (CDCl₃): δ 6.85–6.90 (m, 4 H, *o,m*-Ph), 6.97–7.02 (m, 2 H, *p*-Ph), 7.08–7.11 (m, 4 H, *o,m*-Ph), 7.15–7.24 (m, 6 H, *o,m*-Ph), 7.29–7.39 (m, 8 H, Ph, naph), 7.45 (t, $J = 7.5$ Hz, 2 H, naph), 7.65–7.71 (m, 2 H, quinoxaline), 7.76–7.86 (m, 6 H, naph), 8.07–8.12 (m, 2 H, quinoxaline). FABMS: *m/z* 716.9 (M⁺). Anal. Calcd for C₅₂H₃₆N₄: C, 87.12; H, 5.06; N, 7.82. Found: C, 86.87; H, 5.25; N, 7.62.

2,3-Bis[4-(*N*-phenylnaphthylamino)phenyl]pyrido[2,3-*b*]pyrazine (4). Dark yellow solid. Yield: 74%. ¹H NMR (CDCl₃): δ 6.85 (d, $J = 8.8$ Hz, 2 H, Ph), 6.89 (d, $J = 8.8$ Hz, 2 H, Ph), 7.02–7.04 (m, 2 H), 7.10–7.17 (m, 5 H, Ph), 7.20–7.26 (m, 5 H, Ph), 7.31–7.40 (m, 6 H, Ph), 7.43–7.49 (m, 4 H, naph), 7.60 (dd, $J = 8.2$ Hz, 1 H, pyridyl), 7.77–7.87 (m, 6 H, naph), 8.39 (dd, $J = 8.2$ and 1.6 Hz, 1 H, pyridyl), 9.04 (dd, $J = 8.2$ and 1.6 Hz, 1 H, pyridyl). FABMS: *m/z* 717.7 (M⁺). Anal.

Calcd for C₅₁H₃₅N₅: C, 85.33; H, 4.91; N, 9.76. Found: C, 84.99; H, 4.95; N, 9.57.

2,3-Bis[4-(*N*-phenyl-9,9-diethyl-2-fluorenylamino)phenyl]quinoxaline (5). Yellow solid. Yield: 89%. ¹H NMR (acetone-*d*₆): δ 0.28 (t, $J = 7.3$ Hz, 12 H, CH₃), 1.86–1.99 (m, 8 H, CH₂), 7.06–7.11 (m, 8 H), 7.15–7.18 (dd, $J = 7.6$ and 1.2 Hz, 4 H), 7.23 (d, $J = 1.2$ Hz, 2 H), 7.30–7.36 (m, 10 H), 7.55 (d, $J = 8.7$ Hz, 4 H), 7.71–7.82 (m, 6 H), 8.06–8.10 (m, 2 H, quinoxaline). FABMS: *m/z* 905.2 (M⁺). Anal. Calcd for C₆₆H₅₆N₄: C, 87.57; H, 6.24; N, 6.19. Found: C, 87.42; H, 6.37; N, 5.96.

2,3-Bis[4-(*N*-phenyl-9,9-diethyl-2-fluorenylamino)phenyl]pyrido[2,3-*b*]pyrazine (6). Orange solid. Yield: 82%. ¹H NMR (CDCl₃): δ 0.30–0.35 (m, 12 H, CH₃), 1.81–1.96 (m, 8 H, CH₂), 7.03–7.16 (m, 15 H), 7.23–7.29 (m, 9 H), 7.52 (d, $J = 8.7$ Hz, 2 H), 7.58–7.63 (m, 7 H), 8.43 (dd, $J = 8.2$ and 1.6 Hz, 1 H, pyridyl), 9.08 (dd, $J = 8.2$ and 1.6 Hz, 1 H, pyridyl). FABMS: *m/z* 906.5 (M⁺). Anal. Calcd for C₆₅H₅₅N₅: C, 86.15; H, 6.12; N, 7.73. Found: C, 85.77; H, 6.32; N, 7.62.

2,3-Bis[4-(*N*-phenyl-9-ethyl-3-carbazolylamino)phenyl]quinoxaline (7). Orange solid. Yield: 83%. ¹H NMR (acetone-*d*₆): δ 1.41 (t, $J = 7.3$ Hz, 6 H, CH₃), 4.46 (q, $J = 7.3$ Hz, 4 H, CH₂), 6.97–7.02 (m, 6 H), 7.09–7.16 (m, 6 H), 7.23–7.32 (m, 6 H), 7.41–7.50 (m, 6 H), 7.54–7.58 (m, 4 H), 7.74–7.78 (m, 2 H, quinoxaline), 7.98–8.06 (m, 6 H). FABMS: *m/z* 850.2 (M⁺). Anal. Calcd for C₆₀H₄₆N₆: C, 84.68; H, 5.45; N, 9.87. Found: C, 84.57; H, 5.46; N, 9.78.

2,3-Bis[4-(*N*-phenyl-9-ethyl-3-carbazolylamino)phenyl]pyrido[2,3-*b*]pyrazine (8). Reddish orange solid. Yield: 69%. ¹H NMR (CDCl₃): δ 1.44 (t, $J = 7.3$ Hz, 6 H, CH₃), 4.34 (q, $J = 7.3$ Hz, 4 H, CH₂), 6.99–7.05 (m, 4 H), 7.15–7.49 (m, 20 H), 7.58–7.62 (m, 3 H), 7.91–7.95 (m, 4 H), 8.40 (dd, $J = 8.2$ and 1.6 Hz, 1 H, pyridyl), 9.04 (dd, $J = 8.2$ and 1.6 Hz, 1 H, pyridyl). FABMS: *m/z* 852.2 (M⁺). Anal. Calcd for C₅₉H₄₅N₇: C, 83.17; H, 5.32; N, 11.51. Found: C, 83.02; H, 5.28; N, 11.40.

LED Fabrication and Measurement. Electron-transporting materials TPBI and Alq₃ were synthesized according to literature procedures^{24,25} and were sublimed twice prior to use. Prepatterned ITO substrates with an effective individual device area of 3.14 mm² were cleaned as described in a previous report.¹² Double-layer EL devices using carbazole derivatives as the HTL and TPBI or Alq₃ as the ETL were fabricated. All devices were prepared by vacuum deposition of 400 Å of the HTL, followed by 400 Å of TPBI or Alq₃. An alloy of magnesium and silver (~10:1, 500 Å) was deposited as the cathode, which was capped with 1000 Å of silver. The *I*–*V* curve was measured on a Keithley 2400 source meter in

(24) (a) Shi, J.; Tang, C. W.; Chen, C. H. U.S. Patent, 5,645,948, 1997. (b) Sonsale, A. Y.; Gopinathan, S.; Gopinathan, C. *Indian J. Chem.* **1976**, 14, 408.

(25) Chen, C. H.; Shi, J.; Tang, C. W. *Coord. Chem. Rev.* **1998**, 171, 161.

an ambient environment. The light intensity was measured with a Newport 1835 optical meter.

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Supporting Information Available: EL spectra of the devices A and B for compounds **3** and **6–8**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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