

## Blue-Emitting Anthracenes with End-Capping Diarylamines

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A new series of 2-*tert*-butyl-9,10-bis(bromoaryl)anthracenes have been synthesized from 2-*tert*-butyl-9,10-anthraquinone. Palladium-catalyzed C–N bond formation between these bromo compounds and diarylamines provides stable 2-*tert*-butyl-9,10-diarylanthracenes containing two peripheral diarylamines (**anth**). They possess high thermal decomposition temperature ( $T_d > 450$  °C) and form a stable glass ( $T_g > 130$  °C). Furthermore, they are fluorescent in the blue region with moderate to good quantum efficiencies. Two types of light-emitting diodes (LED) were constructed from **anth**, (I) ITO/**anth**/TPBI/Mg:Ag and (II) ITO/**anth**/Alq<sub>3</sub>/Mg:Ag, where TPBI and Alq<sub>3</sub> are 1,3,5-tris(*N*-phenylbenzimidazol-2-yl)-benzene and tris(8-hydroxyquinolinato)aluminum, respectively. In type I devices, the **anth** function as the hole-transporting and emitting material. In type II devices, emission from Alq<sub>3</sub> is observed. Several blue-light-emitting type I devices exhibit good maximum brightness and physical performance. The relation between the energy levels of the **anth** and the performance of the light-emitting diode is discussed.

### Introduction

Electroluminescent (EL) devices based on small organic molecules or polymers attracted considerable interest<sup>1</sup> after the reports by Tang et al.<sup>2</sup> in 1987 and Friend et al.<sup>3</sup> in 1990. Substantial progress has been made so that the application of organic light-emitting devices (OLEDs) for flat panel displays is becoming very promising. Red-, green-, and blue-emitting materials are all important for full-color displays. The wide band gaps of the blue emitters will lead to larger energy gaps between their LUMO levels and the Fermi level of the cathode or between their HOMO level and the Fermi level of the anode. Such an outcome will hamper injection of the carriers into the emitters and is detrimental to the performance of the device fabricated. Some blue OLED devices were reported to exhibit good physical performance,<sup>4</sup> such as maximum luminescence, power efficiency, current efficiency, and external quantum efficiency. Nevertheless, new blue-emitting materials still receive considerable attention, not only for use as a blue light source in their own right but also as host for downhill energy transfer to green- or red-emitting materials.

Vacuum deposition of small organic molecules as thin films was first utilized by Kodak's group for multiple-

layer OLEDs.<sup>2</sup> Better efficiency of the device can be achieved through proper choice of electron- and hole-transport materials. The devices can be simplified to a double-layer structure if materials with dual functions, i.e., emitting and electron transporting or emitting and hole transporting, were used. The durability of multi-layer devices strongly depends on the thermal and morphological stability of materials in each layer. Amorphous materials possessing high glass transition temperature ( $T_g$ ) should have better opportunity for retaining the film morphology during device operation. A very simple concept for the formation of amorphous glass is nonplanar molecular structure, because easy packing of molecules and hence ready crystallization can be retarded. Nonplanar configuration can be easily achieved with the use of star-shaped molecules<sup>5</sup> or incorporation of bulky moieties<sup>6</sup> in the molecules.

In our continuous studies on organic electroluminescent materials, we decided to develop blue-emitting

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materials possessing high  $T_g$  and hole-transporting properties. Such materials are appropriate for multi-layer white light-emitting devices, since blue-emitting layers are normally deposited nearer the anode to avoid absorption of the blue light by materials of lower band gap.<sup>7</sup> A logical strategy for this purpose is the combination of a strong blue-emitting luminophore with an efficient hole-carrying moiety. The luminophore we chose was 9,10-diphenylanthracene (DPA), which has been widely used in chemiluminescence.<sup>8</sup> Light-emitting polymers containing DPA moieties were reported;<sup>9</sup> however, use of DPA as an emitter in EL devices was not pursued, because of its poor film-forming property.<sup>10</sup> In this paper we report compounds with a 9,10-diarylanthracene core and two peripheral diarylamines. Although the steric interactions of 9,10-phenyl rings with hydrogen atoms in the peri-positions of the anthracene unit (1,8 and 4,5) cause an out-of-plane twisting of about 60°,<sup>11</sup> a *tert*-butyl group is incorporated in the anthracene moiety to further suppress aggregation of planar anthracene segments. The *tert*-butyl group should also improve the solubility of the compounds in common solvents. To the best of our knowledge, only one patent described a similar approach using anthracene without a *tert*-butyl group.<sup>12</sup> Double-layer EL devices using these compounds as hole-transporting layer and emitting layer and Alq<sub>3</sub> [tris(8-quinololinolato)-aluminum]<sup>13</sup> or TPBI [1,3,5-tris(*N*-phenylbenzimidazol-2-yl)benzene]<sup>1b</sup> as electron-transporting layer were fabricated and described.

## Experimental Section

Unless otherwise specified, all the reactions were carried out under nitrogen atmosphere using standard Schlenk techniques. Solvents were dried by standard procedures. All column chromatography was performed with the use of silica gel (230–400 mesh, Macherey-Nagel GmbH & Co.) as the stationary phase. The <sup>1</sup>H NMR spectra were recorded on a Bruker AC400 spectrometer. Electronic absorption spectra were measured in dichloromethane using a Cary 50 Probe UV-visible spectrophotometer. Emission spectra were recorded by a Hitachi F-4500 fluorescence spectrometer. Emission quantum yields were measured with reference to 3,6-bis(1-

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pyrenylphenylamino)-9-phenylcarbazole<sup>14</sup> in dichloromethane with an excitation wavelength around 365 nm. 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 platinum working and auxiliary electrodes and a nonaqueous Ag/AgNO<sub>3</sub> reference electrode. The  $E_{1/2}$  values were determined as  $1/2(E_p^a + E_p^c)$ , where  $E_p^a$  and  $E_p^c$  are the anodic and cathodic peak potentials, respectively. All potentials reported are not corrected for the junction potential. The solvent in all experiments was CH<sub>2</sub>Cl<sub>2</sub> and the supporting electrolyte was 0.1 M tetrabutylammonium perchlorate. DSC measurements were carried out using a Perkin-Elmer 7 series thermal analyzer at a heating rate of 10 °C/min. TGA measurements were performed on a Perkin-Elmer TGA7 thermal analyzer. Mass spectra (FAB) were recorded on a VG70-250S mass spectrometer. Elementary analyses were performed on a Perkin-Elmer 2400 CHN analyzer. Only the syntheses of selected compounds are described. Others are deposited as Supporting Information.

Compounds 2-*tert*-butyl-9,10-bis(4-bromophenyl)anthracene (**1**), 2-*tert*-butyl-9,10-bis(6-bromopyridin-2-yl)anthracene (**2**), and 2,6-di-*tert*-butyl-9,10-bis(4-bromophenyl)anthracene (**3**) were synthesized by a similar procedure as described for **1**.

**2-*tert*-Butyl-9,10-bis(4-bromophenyl)anthracene (1).** To 1,4-dibromobenzene (2.36 g, 10 mmol) dissolved in diethyl ether (100 mL) was added 6.25 mL of *n*-butyllithium (1.6 M in hexane) slowly at -78 °C. To the suspension, 2-*tert*-butylanthraquinone (1.38 g, 5.0 mmol) in ether (20 mL) was added dropwise at -78 °C. The mixture was left to reach room temperature. Cold water (300 mL) was added and the organic phase separated. The water phase was extracted with ether (2 × 50 mL). The combined organic fractions were dried over magnesium sulfate and the volatiles removed in vacuo to deliver a foamy residue. To this residue were added potassium iodide (3.0 g, 18 mmol), sodium hypophosphite monohydrate (3.0 g, 34 mmol), and acetic acid (30 mL), and the mixture was heated under reflux for 2 h. After cooling, the white precipitate was collected, washed with plenty of water, and dried. The compound was not further purified but gave satisfactory elemental analyses. Yield = 2.52 g (93%). Mp = 251 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 1.26 (s, 9 H, CH<sub>3</sub>), 7.29–7.35 (m, 6 H, C<sub>6</sub>H<sub>4</sub>, H-6 and H-7 of anthracene), 7.44 (dd, 1 H, J = 9.2, 2.0 Hz, H-3 of anthracene), 7.54 (d, 1 H, J = 1.4 Hz, H-1 of anthracene), 7.59–7.63 (m, 3 H, H-4, H-5 and H-8 of anthracene), 7.71–7.74 (m, 4 H, C<sub>6</sub>H<sub>4</sub>). FAB MS (m/e): 544 (79-Br<sup>81</sup>Br, (M+1)<sup>+</sup>). Anal. Calcd for C<sub>30</sub>H<sub>24</sub>Br<sub>2</sub>: C, 66.20; H, 4.44. Found: C, 66.58; H, 4.52.

Compounds 2-*tert*-butyl-9,10-bis[4-(1-naphthylphenylamino)phenyl]anthracene (**4**), 2-*tert*-butyl-9,10-bis[4-(imino-stilbenyl)phenyl]anthracene (**5**), 2-*tert*-butyl-9,10-bis[4-(imino-dibenzyl)phenyl]anthracene (**6**), 2-*tert*-butyl-9,10-bis[6-(1-naphthylphenylamino)pyridin-2-yl]anthracene (**7**), and 2,6-di-*tert*-butyl-9,10-bis[4-(1-naphthylphenylamino)phenyl]anthracene (**9**) were synthesized by a similar procedure, as described below. Compound 2-*tert*-butyl-9,10-bis[4-(1-naphthylphenylamino)biphen-4-yl]anthracene (**8**) was synthesized by a different procedure and will be described separately.

A two-necked round-bottomed flask was charged with Pd<sub>2</sub>(dba)<sub>3</sub> (0.01 mol % per halogen atom), NaO<sup>-</sup>Bu (1.5 equiv per halogen atom), halides (1–2 mmol), and amines (1 equiv per halogen atom). Dry toluene was added, and the reaction was stirred under nitrogen for 10 min. Tri-*tert*-butylphosphine (0.02 mol %) in dry toluene was added through a syringe (the stock solution contained 0.823 mmol of the phosphine in 1 mL of dry toluene). The reaction mixture was heated at 80 °C until TLC indicated total consumption of amine. After cooling, the mixture was filtered through a thin pad of Celite. The filtrate was diluted with ether and the organic phase was washed with water and brine. After drying over MgSO<sub>4</sub> and removing of

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the volatiles, the residue was purified by chromatography using  $\text{CH}_2\text{Cl}_2$ /hexane (1:1) as eluant and followed by recrystallization from  $\text{CH}_2\text{Cl}_2$ /hexane. For the compound **8**, no chromatography was necessary.

**Compound 8.** A two-necked flask was charged with 1-bromo-4-iodobenzene (2.0 g, 7.07 mmol), *N*-phenyl-1-naphthylamine (1.55 g, 7.07 mmol),  $\text{NaO}^+\text{Bu}$  (815 mg, 8.48 mmol),  $\text{Pd}(\text{OAc})_2$  (16 mg, 1 mmol % of halide),  $\text{P}(\text{t-Bu})_3$  (2 mol % of halide), and dry toluene (50 mL). The mixture was heated at 90 °C for 12 h. After cooling, the mixture was extracted with ether and the organic phase was washed with water and brine and dried over anhydrous  $\text{MgSO}_4$ . After evaporation of the volatiles, the residue was purified by column chromatography using hexane as eluant. *N*-(4-bromophenyl)-*N*-(1-naphthyl)-*N*-phenylamine (**8a**) was obtained as colorless solid (2.01 g, 76%).

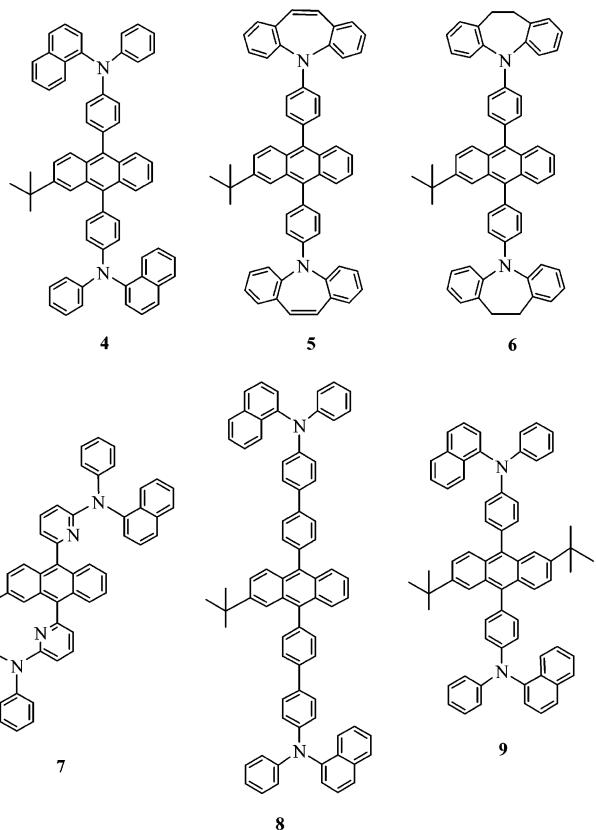
The Grignard reagent obtained from the reaction of **8a** (2.26 g, 6.0 mmol) and Mg (218 mg, 9.0 mmol) in 80 mL of THF was added dropwise to a mixture of **1** (2.10 g, 3.0 mmol) and  $\text{Ni}(\text{dppp})\text{Cl}_2$  (33 mg, 1 mol % of **1**) in 80 mL of THF over a period of 30 min. The mixture was refluxed for 24 h, cooled, and quenched with water. The solvent was removed by rotatory evaporation, and the residue was extracted with water and ether. The organic phase was dried over anhydrous  $\text{MgSO}_4$ , and then the volatiles were removed. The residue was purified by column chromatography using  $\text{CH}_2\text{Cl}_2$ /hexane (1:1) as eluant. Compound **8** was obtained as yellow solid in 53% (1.55 g) yield after recrystallization from  $\text{CH}_2\text{Cl}_2$ /hexane.

**LEDs Fabrication and Measurement.** Double-layer EL devices using compounds **5–9** as the emitting as well as hole-transporting layer and  $\text{Alq}_3$  or TPBI as electron-transporting layer were fabricated. All devices were prepared by vacuum deposition of 400 Å of hole-transporting layer, followed by 400 Å of  $\text{Alq}_3$  or TPBI. An alloy of magnesium and silver (ca. 8:1, 500 Å) served as the cathode, which was capped with 1000 Å of silver. The I–V curve was measured on a Keithley 2000 Source Meter in ambient environment. Light intensity was measured with a Newport 1835 Optical Meter.

## Results and Discussion

The new compounds synthesized in this study are illustrated in Figure 1. Scheme 1 outlines the synthetic procedures. The syntheses of the unknown halides (**1–3**) were accomplished by following the procedure developed by Smet et al.<sup>15</sup> Thus, monolithiated species<sup>16</sup> were allowed to react with 2-*tert*-butylanthraquinones at –78 °C in diethyl ether or THF. The isolation of intermediate diols was not attempted, but the crude products were treated with potassium iodide and sodium hypophosphite monohydrate in boiling acetic acid. Compounds **1–3** were obtained in high yields and were used without any purification. The catalyst developed by Koie and co-workers<sup>17</sup> and Hartwig et al.,<sup>18</sup>  $\text{Pd}_2(\text{dba})_3/\text{P}(\text{t-Bu})_3$  (where dba is dibenzylideneacetone) in the presence of  $\text{NaO}^+\text{Bu}$ , efficiently catalyzed aromatic C–N bond formation from **1–3** and an arylamine to provide the triarylamines **4–9**.

The thermal properties of the new compounds were determined by DSC and TGA measurements (Table 1). All the compounds are thermally stable up to 400 °C in air. The compounds **4–9** readily form glass on cooling



**Figure 1.** Structure of the anthracene compounds.

(10 °C/min) the melt sample. The glass transition temperatures ( $T_g$  = 131–201 °C) are higher than those of commonly used hole-transporting materials, 1,4-bis(1-naphthylphenylamino)biphenyl ( $\alpha$ -NPD,  $T_g$  = 100 °C) and 1,4-bis(phenyl-*m*-tolylamino)biphenyl (TPD,  $T_g$  = 60 °C).<sup>18</sup> The asymmetric nature of **4–9** at the peripheral amines or the central anthracene may dramatically hamper the facile packing of the molecules.<sup>19</sup> The order of  $T_g$ , iminodibenzyl > iminostilbene > naphthylphenylamine is consistent with that reported for  $\text{Ar}_1\text{Ar}_2\text{N}$ –biphenyl– $\text{NAr}_1\text{Ar}_2$ .<sup>19b</sup> It is also interesting that replacement of the biphenyl unit in  $\text{Ar}_1\text{Ar}_2\text{N}$ –biphenyl– $\text{NAr}_1\text{Ar}_2$  by a more rigid anthracene raises the  $T_g$  by >60 °C. It is conceivable that **8** has higher  $T_g$  than **4**, due to the presence of two additional phenyl groups in the former. In contrast, incorporation of an additional *tert*-butyl group in the anthracene moiety of **4** lowers the  $T_g$  (**9** vs **4**). Although the polar nature of pyridine is beneficial to raising  $T_g$ , such effect may be counteracted by the meta-substitution of the diarylamines. Consequently, compound **7** has a lower  $T_g$  than **4**.

**Optical Properties.** The absorption and luminescence spectra of the compounds were measured in  $\text{CH}_2\text{Cl}_2$ , and the pertinent data are presented in Table 1. The  $\lambda_{\text{max}}$  values are in the range 260–460 nm. Peaks at ~350–400 nm with characteristic vibronic pattern are attributed to the  $\pi \rightarrow \pi^*$  transition of anthracene.<sup>20</sup> The electronic absorption energy of these compounds including halide precursors are very similar, despite the somewhat different oxidation potential of the peripheral

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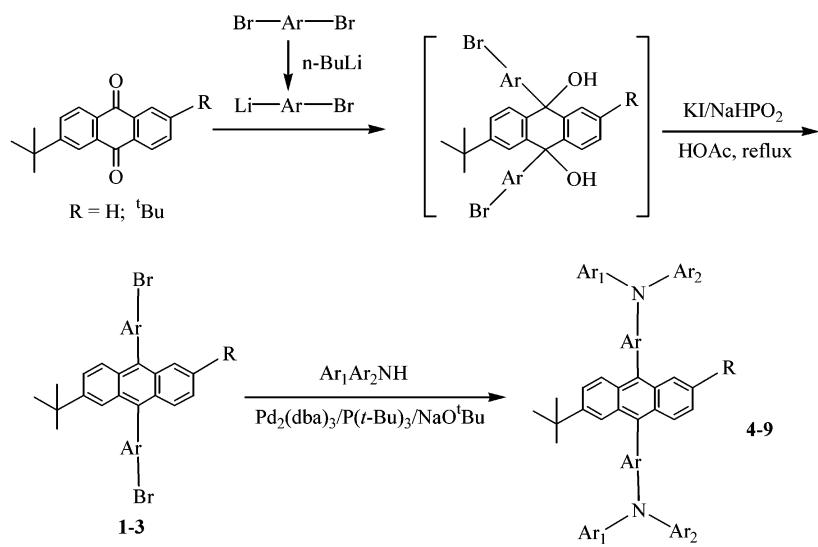
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Scheme 1



Ar = 1,4-phenyl; 4,4'-biphenyl; 2,6-disubstituted pyridyl  
R = H, t-Bu

Table 1. Physical Data for the Compounds

compd	$T_g/T_c/T_m,^a$ °C	$T_d,^b$ °C	$\lambda_{\text{max}},^c$ nm	$\lambda_{\text{em}} (\Phi_f),^d$ nm	$\lambda_{\text{em}},^e$ nm	$E_{\text{ox}} (\Delta E_p),^f$ mV	HOMO/LUMO, <sup>g</sup> eV
<b>4</b>	142/na/255	410	398, 380, 360, 303, 263	472 (0.62)	468	448 (97)	5.25/2.38
<b>5</b>	170/na/353	405	399, 380, 360, 295, 265	466 (0.47)	471	379 (108)	5.18/2.33
<b>6</b>	201/324/393	415	400, 380, 360, 295, 268	470 (0.59)	477	358 (111)	5.16/2.33
<b>7</b>	140/na/na	400	395, 375, 358, 280, 263	467 (0.47)	472	786 (i)	5.57/2.60
<b>8</b>	157/na/264	410	396, 378, 359, 325, 266	450 (0.69)	459	512 (164), 750 (103)	5.31/2.38
<b>9</b>	138/280/375	405	398, 380, 360, 303, 268	467 (0.53)	467	420 (109)	5.21/2.34
TPD	60/175	382	311, 353			314 (68)	
NPD	100/265	479	271, 342			342 (66)	
ITO							4.70 ( $E_F$ )/na
TPBI	129	na	304	376	375	1300 (i)	6.20/2.70
Alq <sub>3</sub>	177	428	385	510 (0.15)	534	na	6.09/2.95
Mg:Ag							na/3.70 ( $E_F$ )

<sup>a</sup> Obtained from DSC measurements. <sup>b</sup> Obtained from TGA measurements. <sup>c</sup> Measured in CH<sub>2</sub>Cl<sub>2</sub> solution. <sup>d</sup> Measured in CH<sub>2</sub>Cl<sub>2</sub> solution. <sup>e</sup> Film samples. <sup>f</sup> Measured in CH<sub>2</sub>Cl<sub>2</sub>. All  $E_{\text{ox}}$  data are reported relative to ferrocene, which has an  $E_{\text{ox}}$  at 226 mV relative to Ag/Ag<sup>+</sup> and the anodic peak–cathodic peak separation ( $\Delta E_p$ ) is 90 mV, i = irreversible process. The concentration of the complexes used in this experiment was  $2.5 \times 10^{-4}$  M and the scan rate was 100 mV s<sup>-1</sup>. <sup>g</sup> na: not available.

amines (vide infra). Out-of-plane twisting of the phenyl from central anthracene possibly deteriorates the extended  $\pi$ -conjugation through the molecules. All compounds exhibit a featureless emission, displaying Stoke shifts of ca. 70 and 40 nm, respectively, for nonhalide compounds and halide compounds. It is interesting that the halide compounds **1–3** are very bright blue-emitting materials with a quantum efficiency comparable to that of 9,10-diphenylanthracene ( $\Phi_f \sim 0.90$ ). For comparison, 9,10-dibromoanthracene has a much lower quantum efficiency ( $\Phi_f \sim 0.20$ ). Apparently, direct attachment of the bromine atoms to the luminous anthracene moiety in the later results in a significant heavy atom effect,<sup>21</sup> which is detrimental to fluorescence. The lower quantum efficiencies of **4–9** than those of **1–3** may be attributed to the reductive quenching of the amino moieties.

**Electrochemistry.** From cyclic voltammetry (CV) and Osteryoung square wave voltammetry (OSWV) measurements, compounds **4–6**, **8**, and **9** were found to exhibit a quasireversible two-electron redox process (Table 1) occurring at the peripheral amines. Such an

outcome may be due to the noncoplanarity of the central anthracene with 9,10-substituents, which results in negligible electronic communication between amines. Only irreversible oxidation was found for **7**, possibly due to the presence of electron-deficient pyridine ring. The oxidation potential increases in order of **6** < **5** < **9** < **4** < **8** < **7** and is consistent with the electron-withdrawing ability of the substituents at the nitrogen atom. These values are significantly higher than that of TPD or  $\alpha$ -NPD and further substantiate the lack of the electronic communication between amines in the former. 9,10-Diphenylanthracene was reported to form a radical cation upon photooxidation.<sup>22</sup> The second one-electron oxidation wave observed in **8** may be attributed to the formation of such a cation, since an extra phenyl spacer may reduce the repulsive force with the amino cation.

**Electroluminescent Properties.** Double-layer EL devices using compounds **anth** (**5–9**) as the hole-transporting as well as emitting layer and TPBI (1,3,5-tris(*N*-phenylbenzimidazol-2-yl)benzene) (type I devices) or Alq<sub>3</sub> (tris(8-quinolinolato)aluminum) (type II devices) as emitting as well as electron-transport layer were

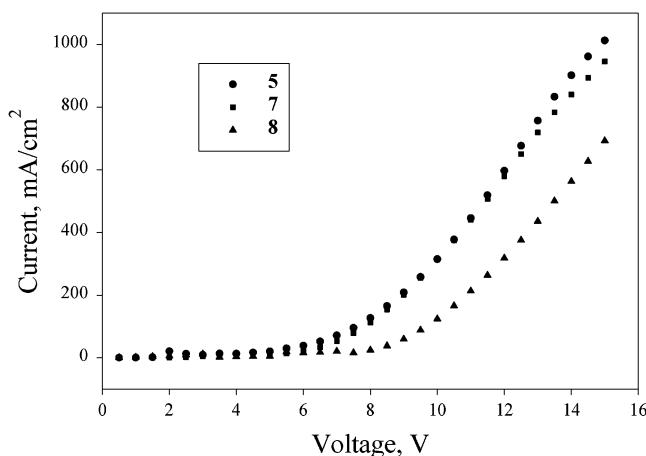
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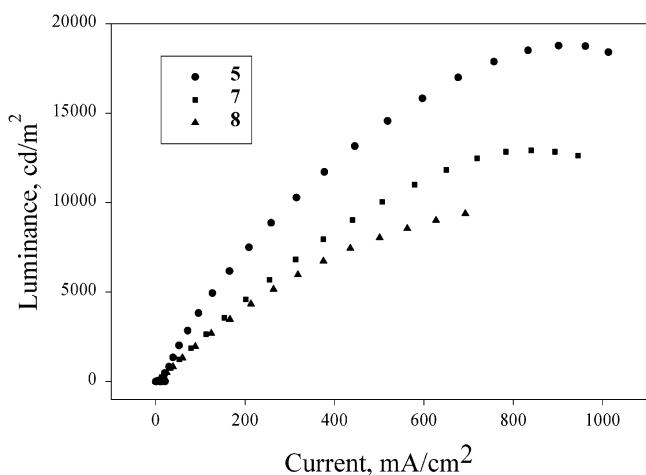
**Table 2. Electroluminescence Data for the Compounds**

compd	for TPBI/Alq <sub>3</sub>						
	turn-on voltage, V	voltage, <sup>a</sup> V	brightness, <sup>a</sup> cd/m <sup>2</sup>	quantum efficiency, <sup>a</sup> %	power efficiency, <sup>a</sup> lm/W	$\lambda_{em}$ , nm	CIE x, y
<b>5</b>	3.5/3.6	7.6/7.4	3979/3617	2.8/1.5	1.7/1.5	466/510	0.17, 0.21/0.27, 0.45
<b>6</b>	3.5/3.5	7.6/7.1	6539/3083	3.8/1.3	2.7/1.4	476/514	0.17, 0.28/0.29, 0.45
<b>7</b>	3.9/4.1	7.8/7.7	2374/2334	1.8/1.1	1.0/1.0	462/496	0.15, 0.15/0.23, 0.38
<b>8</b>	4.3/4.2	9.7/8.5	2194/3042	2.0/1.2	0.7/1.1	456/512	0.15, 0.12/0.27, 0.47
<b>9</b>	3.6/3.6	5.1/7.0	697/3505	0.4/1.3	0.4/1.6	472/522	0.17, 0.24/0.30, 0.50

<sup>a</sup> Taken at a current density of 100 mA/cm<sup>2</sup>.



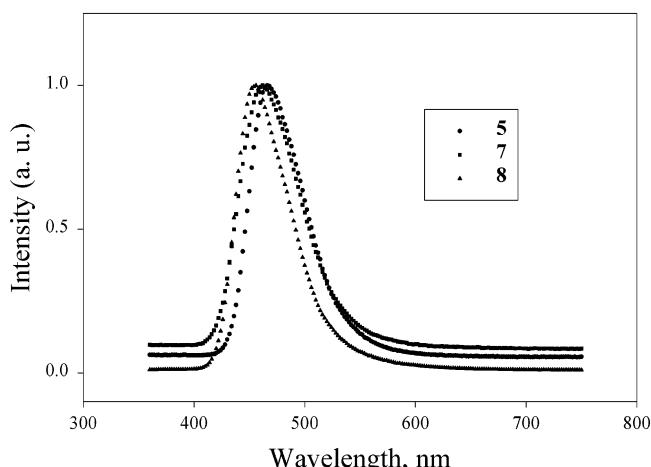
**Figure 2.** Current density vs applied electric field characteristics of the device ITO/anth/TPBI/Mg:Ag.



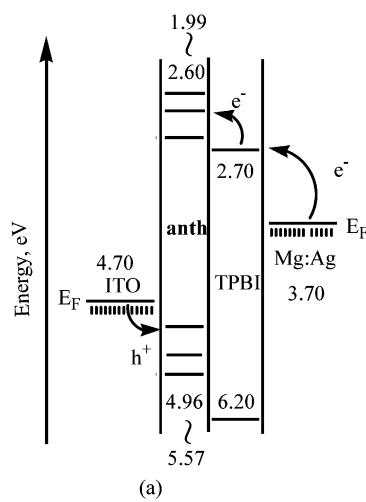
**Figure 3.** Luminance vs current density characteristics of the device ITO/anth/TPBI/Mg:Ag.

fabricated. The *I*–*V*–*L* characteristics are shown in Figures 2 and 3, and important electroluminescence data are shown in Table 2. While green-light emission from Alq<sub>3</sub> at ~510 nm was observed in the type II device, the type I device emits the blue light characteristic of the compounds in this study (Figure 4). These blue-emitting devices fabricated from **7** and **8** exhibit better color purity, and their nonoptimized performances appear to be very promising when compared with competitive blue-emitting OLEDs of different device structures reported recently (Table 3). Other salient features of the blue-emitting materials in this study include high solution fluorescence quantum yield, high glass transition temperature, and hole-transporting capability.

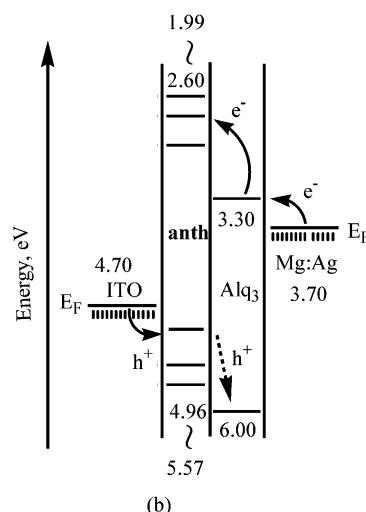
The HOMO energy levels of **anth** were calculated from cyclic voltammetry (vide supra) and by comparison



**Figure 4.** EL spectra of device I.



(a)



(b)

**Figure 5.** Relative energy alignments in ITO/anth/TPBI/Mg:Ag (a) and ITO/anth/Alq<sub>3</sub>/Mg:Ag (b).

Table 3. Electroluminescence Data for Blue-Emitting Devices<sup>a</sup>

device no.	emitting materials	$L_{\max}$ , (cd/m <sup>2</sup> )	$J$ , $V$ at $L_{\max}$ (mA/cm <sup>2</sup> , V)	$L$ , $\eta_c$ , $\eta_p$ , $\eta_{\text{ext}}$ at $x$ (mA/cm <sup>2</sup> , cd/m <sup>2</sup> , cd/A, lm/W, %)	CIE $x$ , $y$ [ $\lambda_{\text{em}}$ , nm]	ref
1	7	12 922	840, 14	2374, 2.2, 1.0, 1.8 at $x$ = 100	0.15, 0.15	this work
2	8	9 386	693, 15	2194, 2.2, 0.7, 2.0 at $x$ = 100	0.15, 0.12	this work
3	amino-substituted distyrylarylene	10 000	300, 14	277, 3.4, 1.5, 2.4 at $x$ = 8	[475]	4a
4	4,4-bis[N-(1-naphthyl)-N- phenylamino]biphenyl	10 000	500, 10	150, na, 1.1, na at $x$ = 10	0.15, 0.16	4e
5	dipyrazolopyridine derivative	11 200	460, 14	maximum $\eta_{\text{ext}}$ = 3.2%	0.18, 0.17	4f
6	pyrazoloquinoline derivatives	13 300	na, 14	maximum $\eta_{\text{ext}}$ = 3.4% [455]	0.19, 0.16	4m
7	tetraphenylsilane derivative	19 000	674, 15	3000, 3.0, 1.0, 2.3 at $x$ = 100	0.16, 0.18	4i,n
8	lithium tetra-(2-methyl-8- hydroxyquinolinato)boron	6 900	600, 15	maximum $\eta_p$ = 1.3 lm/W [470]	0.19, 0.16	4c
9	bis(2-methyl-8-quinolinolato)- aluminum(III) hydroxide	14 070	480, na	4025, 5.0, na, na at $x$ = 80	[485]	4g
10	zinc-chelate complexes	11 000	na, 18	na, 1.8, na, 1.5 at $x$ = 300	0.17, 0.16 [449]	4h
11	bis[2-(2-hydroxyphenyl)- pyridinyl]beryllium	15 000	na, 12	1500, 4.2, 1.9, na at $x$ = 30	[460]	4k
12	1-(2-hydroxyphenyl)- benzoxazolatolithium	14 600	1000, 20	maximum $\eta_c$ = 1.9 cd/A [447]	0.15, 0.11	4l

<sup>a</sup>  $L_{\max}$ , maximum luminance;  $L$ , luminance;  $J$ , current density;  $V$ , voltage;  $\eta_c$ , current efficiency;  $\eta_p$ , power efficiency;  $\eta_{\text{ext}}$ , external quantum efficiency; na, not available.

with ferrocene (4.8 eV).<sup>23</sup> These together with absorption spectra were then used to obtain the LUMO energy levels (Table 1).<sup>19b,24</sup> The different emission zone found in the devices I and II can be understood by comparing the HOMO/LUMO levels of the compounds and those of TPBI and Alq<sub>3</sub> (Figure 4). In the type I device, TPBI functions as an effective hole-blocker, due to the large barrier for holes to cross from the HOMO of **anth** to the HOMO of TPBI. Therefore, the excitons are confined in the **anth** layer. On the contrary, a larger barrier for electrons to cross from the LUMO of Alq<sub>3</sub> to the LUMO of **anth** confines the excitons in the Alq<sub>3</sub> layer. It is interesting to note that the type I device fabricated from compound **7** has good performance, despite the low HOMO and LUMO levels. We speculate that compound **7** has good electron affinity, which can rapidly transport electrons from the TPBI layer toward the anode to recombine with holes in **anth**.

In summary, we have synthesized a series of new luminophores with a *tert*-butyl-9,10-diarylanthracene as the core to connect two peripheral diarylamines. The anthracenyl core imparts high  $T_g$  and maintains blue emission from the molecules. Blue-emitting **10** (Figure 6) has also been obtained by the same strategy.<sup>25</sup> Further extension to other star-shaped congeners containing four peripheral diarylamines is ongoing. A more

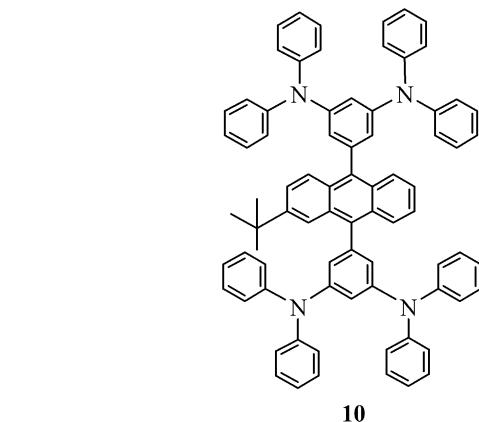


Figure 6. Structure of compound **10**.

comprehensive study, including the incorporation of electron-deficient segments for electron-transport emitting materials will also be explored.

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**Supporting Information Available:** Data are presented for compounds **2–7** and **10** (PDF file). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(25) The synthesis and characterization of the compound **10** is deposited as Supporting Information.