Amorphous 2,3-Substituted Thiophenes: Potential Electroluminescent Materials

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Amorphous 2,3-disubstituted thiophenes and 2,3,5-trisubstituted thiophenes which contain two and four peripheral triarylamine moieties, respectively, have been synthesized and characterized. The compounds are weakly to moderately fluorescent with a lifetime of ~1 ns. Double-layer devices were fabricated using 2,3-bis{5′-[4′′-(diphenylamino)phenyl]-2′-thienyl}thiophene (**10**) or 2,3-bis{4-[4′((1-naphthyl)(phenyl)amino)-*p*-biphenyl]thiophene (**12**) as hole-transport as well as emitting materials. Both green light-emitting device ITO/**10**/TPBI (or Alq_3)/Mg:Ag (TPBI = (1,3,5-tris(*N*-phenylbenzimidazol-2-yl)benzene); Alq_3 = tris-(8-hydroxyquinolinato)aluminum) and blue light-emitting device ITO/**12**/TPBI/Mg:Ag exhibit promising physical performance.

Introduction

Organic electroluminescence (OEL) materials have attracted considerable attention because of their potential application in full-color flat-panel displays and organic laser diodes.[1] Amorphous molecular materials with high glass transition temperature (T_g) are highly desirable for multilayer devices in order to suppress formation of grain boundaries during operation as well as strain-driven failure[2] in a thermally stressed OLED. Compounds with an asymmetric and/or nonplanar structure generally have less tendency to pack into crystal lattice and hence favor amorphous morphology. Accordingly, Shirota and co-workers have synthesized several novel families of organic π-electron star-shaped molecules which readily form amorphous glasses above room temperature because of an increase in the number of conformers together with nonplanar molecular structures.[3] Thompson's group also systematically examined a series of triarylamines and concluded that asymmetric amine moieties were indeed beneficial to glass formation.[4]

We have been interested in the development of high-T_g amorphous materials for electroluminescent devices. Our approach is to use highly branched blocks for prevention of molecular stacking. The presence of multiple numbers of the same functional groups in a molecule may also enhance the property that the functional group imparts. For instance, hexasubstituted benzene-based star-shaped compounds containing six peripheral diarylthienylamines are capable of carrying six holes.[5] The other advantage of a highly branched building block is the incorporation of multifunctions in the molecules, and therefore, double- or single-layer devices or white light-emitting devices may be possible. In this aspect, we found that 3,6,9-trisubstituted carbazole derivatives had very high T_g values, and some double-layer green light-emitting devices of high efficiencies have been fabricated.[6] We therefore extended our studies to 2,3,5-substituted thiophene-based molecules. Polythiophene has been used in polymer LEDs.[7] Enhanced solubility and color-tuning in these polymers can be achieved through substitution at the 3- or 4-position of the thiophene moiety.[7a] Incorporation of thiophene in small molecule LEDs was also reported.[8] To our knowledge, there is yet no report on small molecule LEDs using a 2,3,5-substituted thiophene as the building block.[9] In addition to glass-forming tendency and easy incorporation of different substituents,

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the thiophene moiety may provide effective conjugation and therefore more facile color-tuning compared with its benzenoid congener.[10] In this report, we describe the syntheses and physical properties of a series of 2,3,5-substituted thiophenes. Electroluminescent devices fabricated from two 2,3-substituted thiophene derivatives are also presented.

Experimental Section

Only selected compounds and spectroscopic data will be described. Others including general procedure and physical characterization are deposited as Supporting Information.

N^5,N^5,$N^{5''}$,$N^{5''}$-Tetraphenyl-[2,2′;3′,2″]terthiophene-5,5″-diamine (1). To a flask containing a mixture of (*N*,*N*-diphenylamino)-2-(tri-*n*-butylstannyl)thiophene[11] (5.40 g, 10.0 mmol), 2,3-dibromothiophene (1.15 g, 4.76 mmol), and $PdCl_2(PPh_3)_2$[12] (70 mg, 0.10 mmol) was added DMF (5 mL). The solution mixture was heated at 80 °C for 16 h, then cooled, and added MeOH. The solid formed was collected by filtration. Further purification through column chromatograph using CH_2Cl_2/hexane (1:4) as eluent gave **1** as yellow powder (1.2 g, 45%). ^1H NMR ($CDCl_3$): $\delta = 7.28-7.19$ (m, 10 H, SC*H*, SCC*H*, and *meta-H* of C_6H_5), 7.14−7.09 (m, 8 H, *ortho-H* of C_6H_5), 7.06−6.97 (m, 4 H, *para-H* of C_6H_5), 6.92 (d, 1 H, $J = 3.6$ Hz, SCC*H*), 6.90 (d, 1 H, $J = 3.6$ Hz, SCC*H*), 6.57 (d, 1 H, $J = 3.6$ Hz, SCC*H*), 6.55 (d, 1 H, $J = 3.6$ Hz, SCC*H*). FABMS: *m/e* 581 ((M − 1)$^+$). Anal. Calcd for $C_{36}H_{26}N_2S_3$: C, 74.19; H, 4.50; N, 4.81. Found: C, 74.36; H, 4.53; N, 4.29.

N^5,N^5,$N^{5''}$,$N^{5''}$-Tetraphenyl-5′-tributylstannyl-[2,2;3′,2″]-terthiophene-5,5″-diamine (2). A solution of BuLi (11.5 mL, 18.0 mmol, 1.6 M in hexane) was added to a solution of **1** in 40 mL of THF prechilled to −78 °C and stirred for 1 h. After addition of tributyltin chloride (4.87 mL, 15.0 mmol) the solution was slowly warmed to room temperature and stirred for 24 h. The mixture was extracted with diethyl ether/brine and the organic layer dried over $MgSO_4$ and filtered. Evaporation of the solvent gave **2** as a green oil in 94% (8.8 g) yield. ^1H NMR ($CDCl_3$): $\delta = 7.21-7.10$ (m, 8 H, *meta-H* of C_6H_5 and *ortho-H* of C_6H_5), 7.07 (s, 1 H, SC*H*), 7.01−6.69 (m, 4 H, *para-H* of C_6H_5), 6.88 (d, 1 H, $J = 4.0$ Hz, SCC*H*), 6.86 (d, 1 H, $J = 4.0$ Hz, SCC*H*), 6.56 (d, 1 H, $J = 4.0$ Hz, SCC*H*), 6.53 (d, 1 H, $J = 4.0$ Hz, SCC*H*), 1.63−1.51 (m, 6 H, CH_2), 1.41−1.23 (m, 6 H, CH_2), 1.09 (t, 6 H, $J = 7.6$ Hz, SnCH_2), 0.88 (t, 9 H, $J = 7.2$ Hz, CH_3). The compound was found to be of 90% purity based on the ^1H NMR spectra and used without further purification.

The compound 1,4-bis{4′,5′-bis(5″-diphenylamino-2″-thienyl)-2′-thienyl}benzene (**3**) was synthesized by the same procedure as illustrated for **1**, except that **2** (1.87 g, 2.14 mmol) and 1,4-dibromobenzene (236 mg, 1.00 mmol) were used instead of (*N*,*N*-diphenylamino)-2-(tri-*n*-butylstannyl)thiophene and 2,3-dibromothiophene**.** Yield: 47% (580 mg). Orange powder. ^1H NMR ($CDCl_3$): $\delta = 7.55$ (s, 4 H, C_6H_4), 7.30 (s, 2 H, SCC*H*), 7.26−7.19 (m, 16 H, *meta-H* of C_6H_5), 7.15−7.13 (m, 16 H, *ortho-H* of C_6H_5), 7.02 (t, 4 H, $J = 6.9$ Hz, *para-H* of C_6H_5), 7.00 (t, 4 H, $J = 6.9$ Hz, *para-H* of C_6H_5), 6.94 (d, 2 H, $J = 3.6$ Hz, SCC*H*), 6.90 (d, 2 H, $J = 3.6$ Hz, SCC*H*), 6.57 (d, 2 H, $J = 3.6$ Hz, SCC*H*), 6.53 (d, 2 H, $J = 3.6$ Hz, SCC*H*). FABMS: *m/e* 1239 ((M + 1)$^+$). Anal. Calcd for $C_{78}H_{54}N_4S_6$: C, 75.57; H, 4.39; N, 4.32. Found: C, 75.26; H, 4.64; N, 4.14.

2,7-Bis[2′(4″-{4‴,5‴-{5⁗-[(1-naphthyl)(phenyl)amino]-2⁗-thienyl}-2‴-thienyl}phenyl)vinyl]-9,9-dihexyl-9*H*-fluorene (9). A solution of BuLi (25.4 mL, 40.6 mmol, 1.6 M in hexane) was added to a solution of 2,7-dibromo-9,9-dihexyl-9*H*-fluorene[13] (8.0 g, 16.2 mmol) in 40 mL of THF prechilled to −78 °C. The solution was stirred for 2 h at the same temperature and then warmed to −30 °C. After addition of 3.77 mL (48.8 mmol) of DMF, the solution was stirred for an additional 2 h. The solution was then brought to room temperature slowly and stirred overnight. The mixture was extracted with diethyl ether/water and the organic layer dried over $MgSO_4$ and filtered. After removal of the solvent the residue was purified by column chromatography. Compound 9,9-dihexyl-9*H*-fluorene-2,7-dicarbaldehyde (**9a**) was obtained as a yellow oil in 68% yield (1.98 g).

To a flask containing a mixture of **9a** (1.98 g, 5.47 mmol) and 4-bromophenyltriphenylphosphonium bromide (5.04 g, 10.1 mmol) was added potassium *tert*-butoxide (1.42 g, 12.7 mmol) and 40 mL of THF. The solution was refluxed at 65 °C for 24 h and cooled to room temperature. The mixture was extracted with diethyl ether/water and the organic layer dried over $MgSO_4$ and filtered. After removal of the solvent the residue was dissolved in 30 mL of toluene, and 5 mg of I_2 was added. The solution was refluxed for 20 min and cooled to room temperature. The solution was pumped dry, and the residue was extracted with CH_2Cl_2/H_2O. The organic layer was dried over $MgSO_4$ and filtered. After removal of the solvent the residue was purified by column chromatography using CH_2Cl_2/hexane (1:9) as eluent. The compound 2,7-bis[2-(4-bromophenyl)vinyl]-9,9-dihexyl-9*H*-fluorene (**9b**) was isolated as a pale yellow solid in 39% yield (1.39 g).

Compound **9** was synthesized by the same procedure as illustrated for **3** except that **9b** (2.85 g, 2.95 mmol) was used instead of 1,4-dibromobenzene. Yield: 28% (532 mg); orange yellow powder.

LEDs Fabrication and Measurement. Electron-transporting materials 1,3,5-tris(*N*-phenylbenzimidazol-2-yl)benzene (TPBI) and tris(8-hydroxyquinolinato)aluminum (Alq_3) were synthesized according to literature procedures[14,15] and were sublimed twice prior to use. Prepatterned ITO substrates with an effective individual device area of 3.14 mm^2 were cleaned as described in a previous report.[16] Double-layer EL devices using **10** and **12** as the hole-transport layer and TPBI or Alq_3 as the electron-transport layer were fabricated. All devices were prepared by vacuum deposition of 400 Å of the hole-transporting layer, followed by 400 Å of TPBI or Alq. An alloy of magnesium and silver (ca. 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 ambient environment. Light intensity was measured with a Newport 1835 optical meter.

Results and Discussion

The new compounds synthesized in this study are listed in Figure 1. Scheme 1 illustrates key steps in the syntheses of these new compounds. Appropriate triarylamines were converted to their stannyl derivatives, which were then subjected to Stille's cross-coupling reaction[17] with 2,3-dibromothiophene to form the desired compounds (**1**, **5**, **10**, and **12**) in which two triarylamines were incorporated to the 2- and 3-positions of the central thiophene ring. Star-shaped compounds with four peripheral triarylamines (**3**, **4**, **7**−**11**) were also synthesized by further stannylation of the central thiophene in the above compounds at the 5-position and subsequent Stille's cross-coupling reaction with conjugated dibromoaryls. An interesting feature of these

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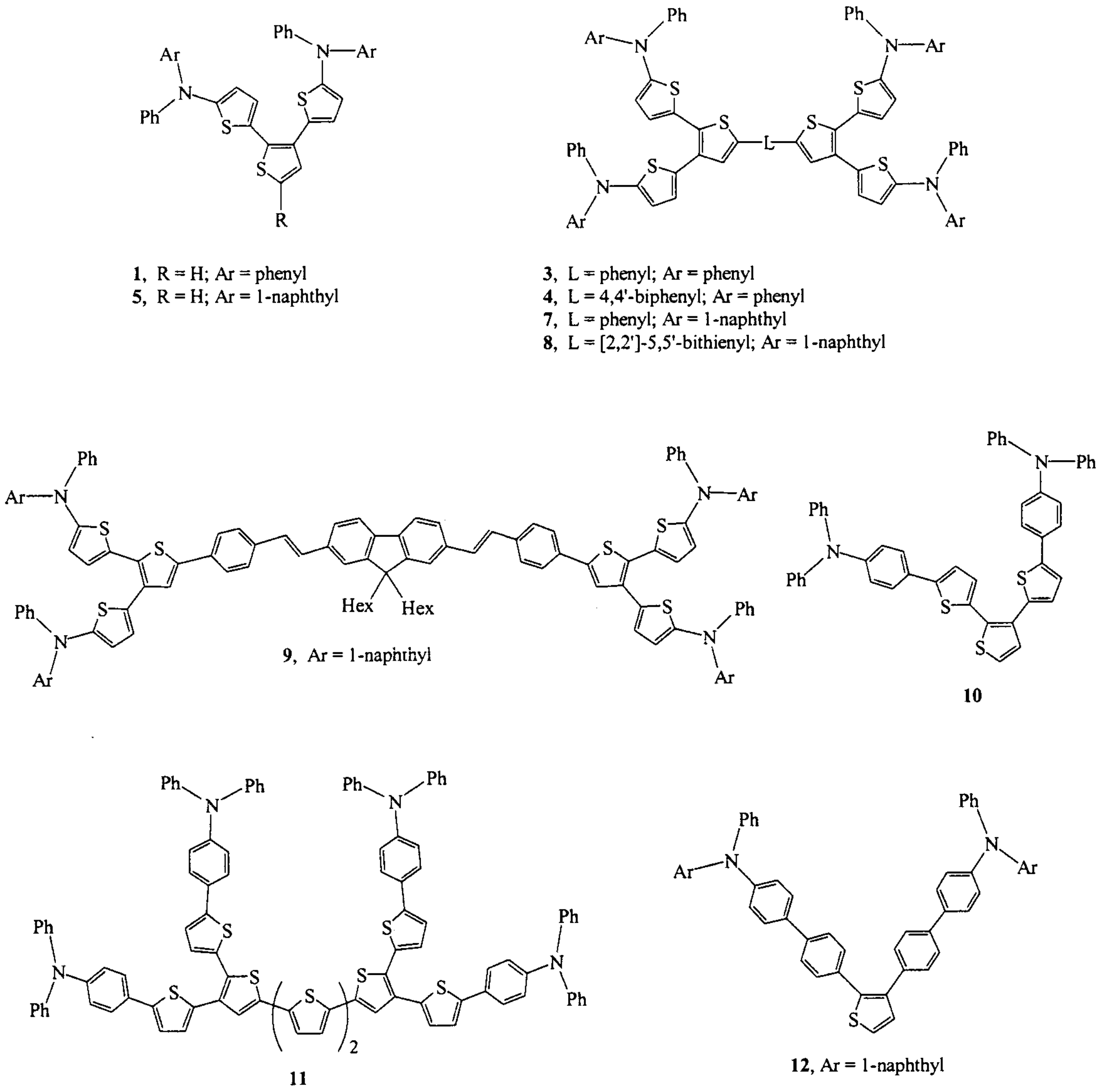

1, R = H; Ar = phenyl
5, R = H; Ar = 1-naphthyl

3, L = phenyl; Ar = phenyl
4, L = 4,4'-biphenyl; Ar = phenyl
7, L = phenyl; Ar = 1-naphthyl
8, L = [2,2']-5,5'-bithienyl; Ar = 1-naphthyl

9, Ar = 1-naphthyl

10

11

12, Ar = 1-naphthyl

Figure 1. Structures of the compounds.

compounds is that the substituents at the 2- and 3-positions of the central thiophene ring, including thienyl, phenyl, and naphthyl moieties, are magnetically nonequivalent in the ^{1}H NMR spectra.

The thermal properties of the new compounds were determined by DSC and TGA measurements (Table 1). Except for **1**, all the compounds exhibited a glass transition in the first heating cycle, and no crystallization exotherms and melting endotherms were noticed. Amorphous glass of **1** can be obtained by rapid cooling of the melt. The glass transition temperatures (T_g = 68−136 °C) and thermal decomposition temperatures (T_d = 376−567 °C) of these compounds are comparable to those of two commonly used hole-transport materials in organic light-emitting devices: α-NPD (T_g = 100 °C; T_d = 479 °C) and TPD (T_g = 60 °C; T_d = 382 °C).[6] Comparisons of T_g values between **1** (68 °C) and **5** (70 °C), **3** (114 °C) and **7** (118 °C), and **10** (83 °C) and **12** (110 °C) suggest that the 1,4-phenyl moiety is more efficient than the 2,5-thienyl moiety in raising the glass transition temperature. As expected, elongation of the conjugation chain in the homologues resulted in increasing of T_g.

A prominent feature in the cyclic voltammetry (CV) of these compounds is that the oxidation potential of the nitrogen atom in the branch at the 2-position is nonresolvable from that at the 3-position, and only a quasi-reversible two-electron redox process (**1**, **5**, **10**, and **12**) or four-electron redox process (**3**, **4**, **7**−**9**, and **11**) is observed. Figure 2 (CV and OSWV, Osteryoung square-wave voltammetry) illustrates such a two-electron redox process of the nitrogen atoms for **10** by adding ferrocene of equal concentration as the internal standard. The wave at 1.12 V vs $Ag^+/AgNO_3$ may be attributed to the oxidation of the terthiophene unit. The distance of the two nitrogen atoms and the noncoplanarity of the molecules induced by 2,3-disubstituted thiophene likely hamper the effective electronic communication of the two amines.[11,18] Compound **11** also exhibits three oxidation waves (213, 481, and 680 mV vs ferrocene) due to the central oligothiophene unit. Consistent with our

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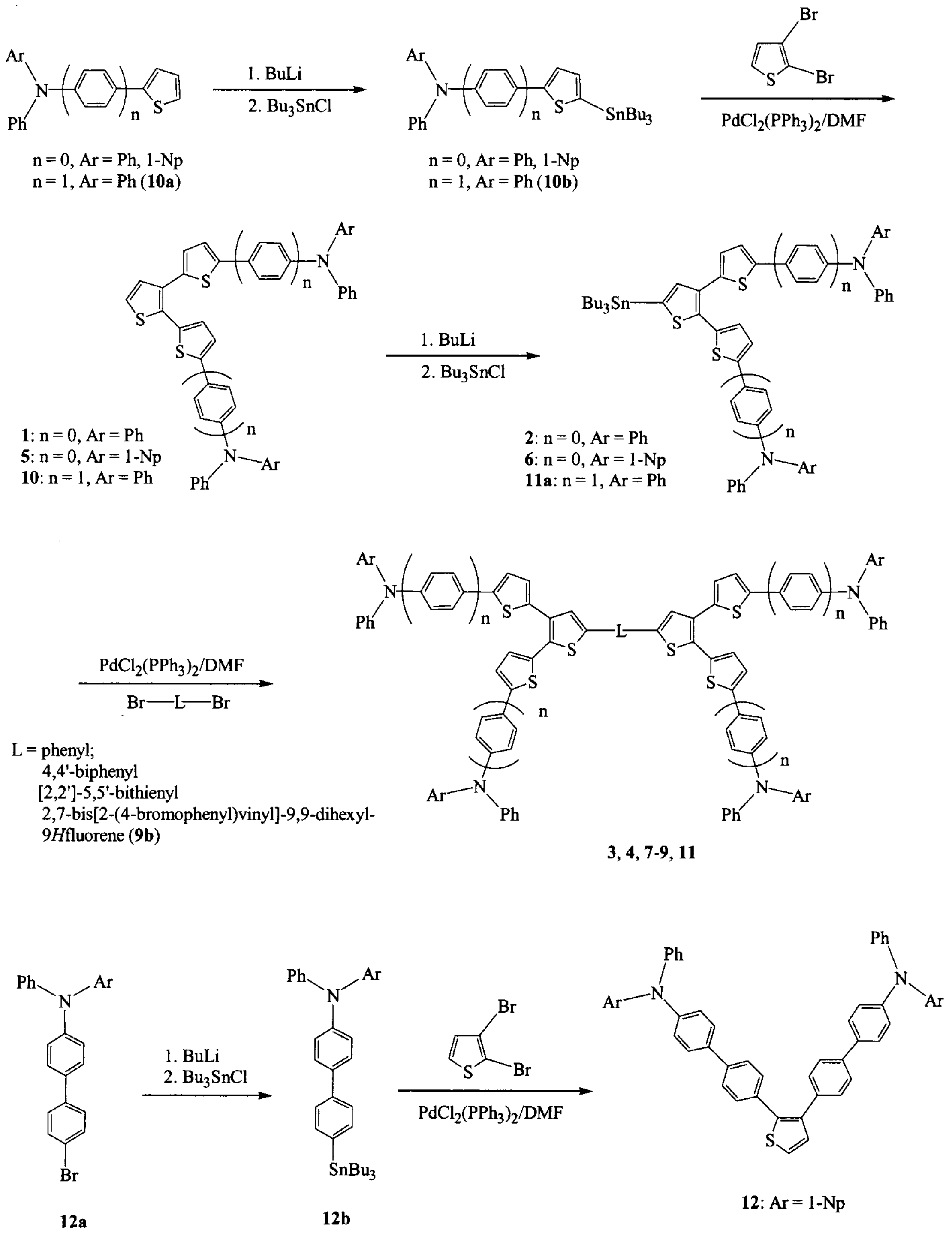
(18) The difference of the oxidation potentials corresponding to removal of the electron from the two nitrogen atoms decreases substantially from 5,5′-bis(diphenylamino)-2,2′-bithiophene (0.15 eV) to 2,5-bis(diphenylamino)thiophene (0.32 eV). Wu, I.-Y.; Lin, J. T., unpublished research.

Scheme 1



previous reports,[7,11] the oxidation potential of a diphenylthienylamine is lower than that of a triphenylamine analogue by >0.2 eV due to the electron-rich nature of the thienyl ring.[19]

The electronic absorption spectra (Table 1) of the new compounds cover a broad range. The spectra for selective compounds are shown in Figure 3. Three types of electronic transitions were observed in these compounds: (a) λ_{max} at <300 nm due to n → π^* transition; (b) λ_{max} at ~350 nm due to the π → π^* transition of π-conjugation chain extending from the 2-substituent through central thiophene to the 3-substituent, and (c) λ_{max} at >400 nm attributable to the π → π^* transition of π-conjugation chain extending from the 2-substituent through central thiophene to the 5-substituent. The third type of transition is elusive in the compounds without a 5-substituent **1**, **5**, **10**, and **12**. Only a single broad peak appears in the emission spectra for all the compounds (Figure 3). Furthermore, the same emission spectra are observed irrespective of the applied excitation wavelengths, indicating that the downhill relaxation to the lowest excited state is very efficient.[20] The rather short lifetime of the emissive state in these

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Table 1. Physical Data for 3a−3c, TPD, and NPD

compd	$T_g/T_c/T_m$,^{a} °C	T_d,^{b} °C	λ_{max},^{c} nm	$\lambda_{em}(\Phi)$,^{c} nm	E_{ox} (ΔE_p),^{d} mV	HOMO/LUMO,^{e} eV
1	68/118/171	376	297, 375	510 (0.01)	167 (138)	4.97/2.21
3	114/na/na	483	295, 368, 435	568 (0.011)	179 (72)	4.98/2.60
4	127/na/na	462	296, 357, 425	555 (0.043)	162 (54)	4.96/2.48
5	70/na/na	406	290, 350	505 (0.03)	150 (90)	4.95/2.19
7	118/na/na	486	276, 358, 434	562 (0.034)	184 (74)	4.98/2.59
8	106/na/na	491	256, 332, 456	602 (0.12)	167 (73)	4.96/2.66
9	106/na/na	482	294, 378, 415	595 (0.13)	160 (52)	4.96/2.55
10	83/na/na	467	304, 363	504 (0.071)	397 (64), 783 (64)	5.20/2.62
11	136/na/na	567	304, 394, 461	558 (0.049)	213 (159), 325 (192), 481 (205), 680 (78)	5.12/2.86
12	110/na/na	474	268, 347	442 (0.50)	485 (118)	5.28/2.33
TPD	60/na/175	382		311, 353	314 (68)	
NPD	100/na/265	479		271, 342	342 (66)	

^{a} Obtained from DSC measurements; na = not detected. ^{b} Obtained from TGA measurements. ^{c} Measured in CH_2Cl_2 solution. ^{d} Measured in CH_2Cl_2. All E_{ox} data are reported relative to ferrocene which has an E_{ox} at 320 mV relative to Ag/Ag^+, and the anodic peak−cathodic peak separation (ΔE_p) is 75 mV. The concentration of the complexes used in this experiment was 5×10^{-4} M, and the scan rate was 80 mV s^{-1}.

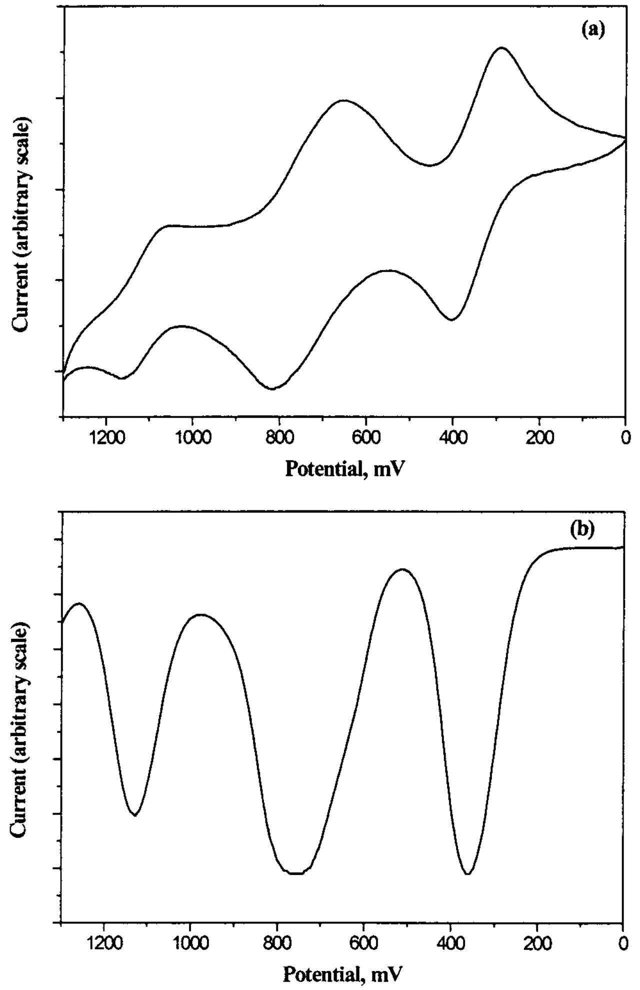

Figure 2. (a) Cyclic voltammogram of **10** in deoxygenated CH_2Cl_2/CH_3CN (1:1) containing 0.1 M TBAP at 25 °C. All potentials are in volts vs $Ag/AgNO_3$ (0.01 M in MeCN; the scan rate is 80 mV s^{-1}). (b) Osteryoung square-wave voltammogram of **10** in the same conditions as (a). Ferrocene (E_{ox} at 320 mV) of equal concentration was added as an internal standard in both (a) and (b).

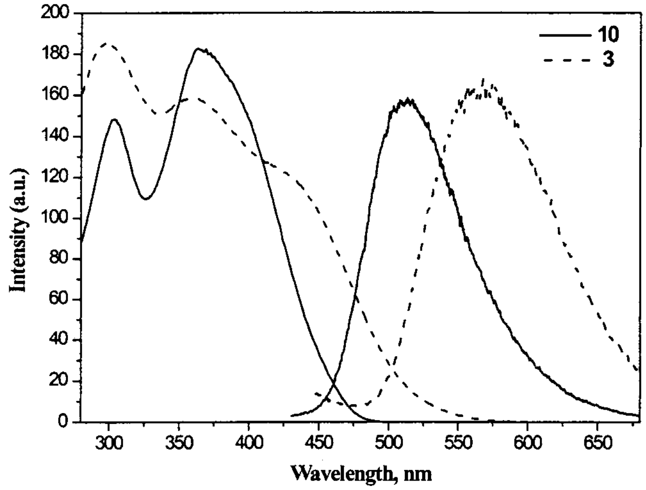

Figure 3. Absorption and emission spectra of compounds **3** and **10** in CH_2Cl_2.

compounds (**7**, τ = 670 ps; **9**, τ = 603 ps; **10**, τ = 629 ps) suggests that the origin of the emission is fluorescence instead of phosphorescence. The somewhat large Stokes shift of λ_{em} most likely stems from the excited-state-induced coplanarity of the 2- and 3-substituents. The 5;2,2′;3′,2″;5″-terthiophene moiety seems to be detrimental to the quantum efficiencies of the compounds, probably due to the heavy atom effect of the sulfur atom in the thiophene[21] or the reductive quenching of the electron-rich amine. Incorporation of a conjugated fluorene segment slightly increases the quantum efficiencies of the compounds. It is interesting to note that a dramatic enhancement of the quantum efficiency can be achieved when the 5;2,2′;3′,2″;5″-terthiophene is replaced by 2,3-diphenyl-thiophene (**12**).

Electroluminescent Properties. Among the compounds in this study, **10** and **12** were selected for the device fabrication because of their better volatilities and higher solution quantum efficiencies. The HOMO and LUMO energy levels (Table 1) of the compounds were calculated from cyclic voltammetry (referred to ferrocene's HOMO, 4.8 eV)[22] and the absorption spectra.[23] Because of the high HOMO levels and the presence of triarylamine moiety in **10** and **12**, double-layer EL devices using compounds **10** or **12** as hole-transport as well as emitting layer and 1,3,5-tris(*N*-phenylbenzimidazol-2-yl)benzene (TPBI) (type I device) or tris(8-

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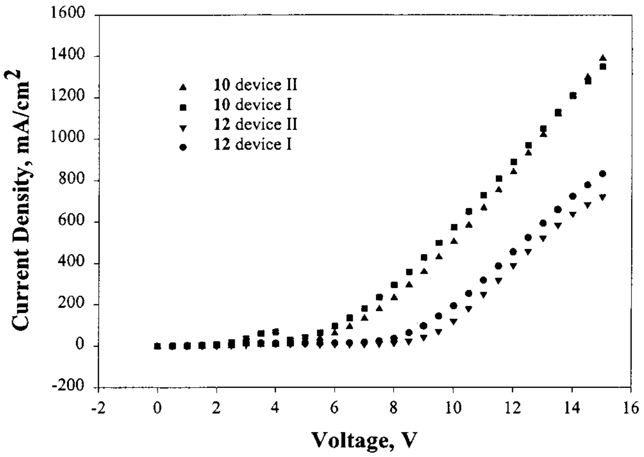

Figure 4. Current density vs applied electric field characteristic of the device ITO/**10** (or **12**)/TPBI/Mg:Ag and ITO/**10** (or **12**)/Alq$_3$/Mg:Ag.

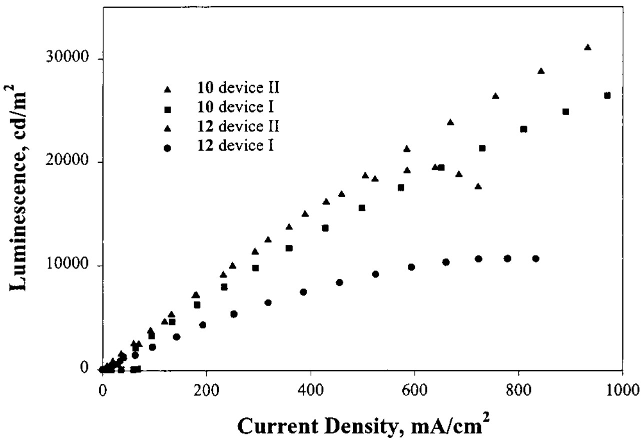

Figure 5. Luminance vs current density characteristic of the device ITO/**10** (or **12**)/TPBI/Mg:Ag and ITO/**10** (or **12**)/Alq$_3$/Mg:Ag.

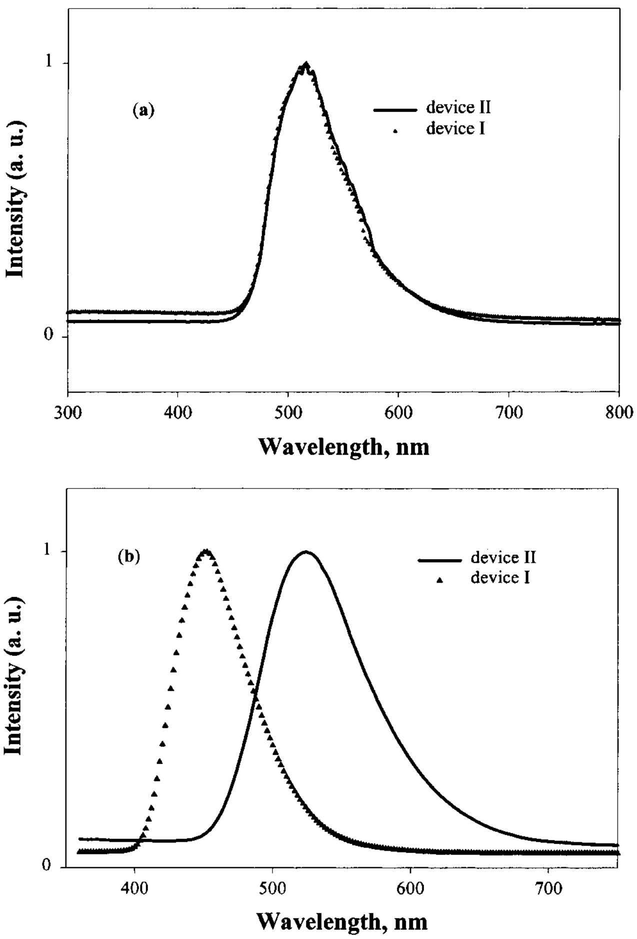

Figure 6. EL spectra of the devices I and II for **10** (a) and **12** (b).

Table 2. Performance Characteristics of the Devices

	10[a] TPBI/Alq$_3$	**12**[b] TPBI/Alq$_3$
turn-on voltage, V	2.5/3.0	2.2/1.8
max brightness, Cd/m^2	31605 at 15 V/ 37110 at 15 V	10650 at 14 V/ 19439 at 14.5 V
max external quantum efficiency, %	1.31 at 6.5 V/ 1.46 at 5.5 V	2.3 at 8.0 V/ 1.4 at 11 V
max power efficiency, lm/W	1.87 at 5.5 V/ 2.57 at 4.5 V	0.95 at 8 V/ 1.21 at 10 V
λ_{em}	516/516	450/524
CIE, *x*, *y*	0.26, 0.52/0.27, 0.53	0.17, 0.13/0.31, 0.52
voltage,[c] V	6.1/6.6	9.0/9.8
brightness,[c] Cd/m^2	3448/4053	2243/3749
external quantum efficiency,[c]%	1.30/1.43	2.14/1.32
power efficiency,[c] lm/W	1.78/1.94	0.78/1.19

[a] ITO/**10** (400 Å)/TPBI (400 Å)/Mg:Ag. [b] ITO/**12** (400 Å)/Alq$_3$ (400 Å)/Mg:Ag. [c] Taken at a current density of 100 mA/cm^2.

hydroxyquinolinato)aluminum (Alq$_3$) (type II device) as electron-transport layer were fabricated. The *I*−*V*−*L* characteristics are shown in Figures 4 and 5. The EL spectra of the two devices fabricated from **10** were superimposable and identical to the PL spectrum of **10** (Figure 6a), which implies the charge recombination occurs in the **10** layer irrespective of ETL used. On the other hand, blue light and green light were emitted from the type I and type II devices of **12** (Figure 6b), respectively. While the green light characteristic of Alq$_3$ was observed in the type II device, the excitons in the type I device were confined in the layer of **12**. Such outcomes may be rationalized from the relative energy levels of different layer materials. The energy level alignments for different devices are shown in Figure 7. Both TPBI and Alq$_3$ are effective hole blockers in the devices fabricated from **10** due to the large energy gap between the HOMO of TPBI or Alq$_3$ and **10** (1.00 eV for TPBI and 0.80 eV for Alq$_3$). The smaller gap between LUMO level of **10** and that of TPBI (0.08 eV) or Alq$_3$ (0.68 eV) allows the injection of electrons and the formation of excitons inside the **10** layer. In comparison, while the energy gap between the HOMO of TPBI and **12** (0.92 eV) is large enough for TPBI to block the holes, injection of holes from **12** into Alq$_3$ is possible due to a smaller HOMO energy gap (0.72 eV). Moreover, injection of electrons from Alq$_3$ into the **12** layer is hampered because of the large LUMO energy gap between Alq$_3$ and **12**. Therefore, recombination/excitons are confined inside the Alq$_3$ layer in the device II of **12**.

The type II device of **10** is green emitting with the following physical performance characteristics (Table 2): maximum luminescence (37110 cd/m^2), external quantum efficiency (1.36% at 300 cd/cm^2 current density), and luminous efficiency (1.94 lm/W at 300 cd/cm^2 current density). The high external quantum efficiency may be due to a higher fluorescence efficiency in the solid film than in the solution. In contrast, a device of similar structure fabricated from the isomer of **10**, 5,5″-

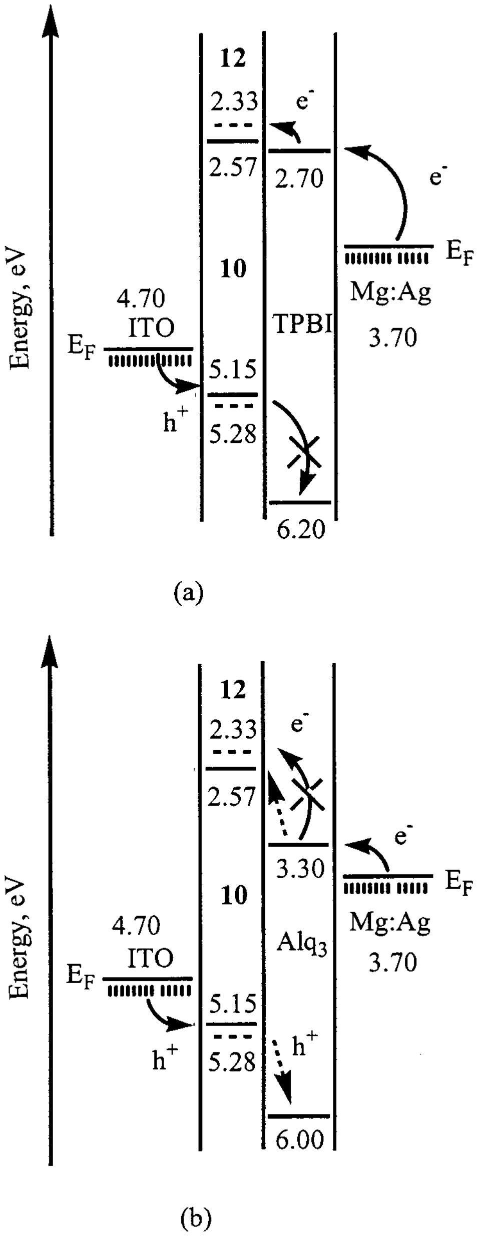

Figure 7. Relative energy alignment in ITO/**10** (or **12**)/TPBI/Mg:Ag (a) and ITO/**10** (or **12**)/Alq$_3$/Mg:Ag (b). The energy levels of **10** and **12** are represented by solid lines and dotted lines, respectively.

bis{4-[bis(4-methylphenyl)amino]phenyl}-[2,2′;5′,2″]terthiophene (**13**), was reported to be yellow emitting with the following physical performance characteristics at 300 cd/cm^2 current density: maximum luminescence, 13 000 cd/m^2; external quantum efficiency, 0.90%; luminous efficiency, 1.1 l m/W.[24] The type I device of **12** (maximum luminescence, 10 650 cd/m^2; external quantum efficiency, 2.3%) is blue-emitting and appears to be promising among known blue-emitting devices.[25]

In summary, we have synthesized amorphous 2,3-substituted thiophenes which exhibit hole-transporting and tunable light-emitting properties. The efficiency of π-conjugation of the central 2,3-substituted thiophenes is inferior to that of 2,5-substituted thiophene congeners.[24] However, the former has a greater tendency to form amorphous glass because of the lack of coplanarity.[26] These materials can be fabricated into electroluminescence devices with promising performances. 2,3,5-Substituted thiophene derivatives are also prepared. In addition to a higher glass transition temperature, these compounds have longer emission wavelength due to better π-conjugation. Further extension toward 2,3,5-substituted thiophenes with more versatile functions will be explored in future studies.

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Supporting Information Available: Data for compounds **4**–**8** and **11** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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