Synthesis and Luminescence of Silicon-Bridged Bithiophene- and Triarylamine-Containing Molecules

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A new family of dithienosiloles that contain two peripheral triarylamine moieties have been synthesized for use in organic light-emitting devices (OLEDs). The compounds are strongly fluorescent. We studied EL (electroluminescent) properties of these compound in multilayer EL devices having the following structure: ITO/TPD/compound **2b**−**5b**/BCP/Alq₃/ Al:Li (ITO = indium tin oxide; TPD = 1,4-bis(phenyl-*m*-tolylamino)biphenyl; BCP = 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline; Alq₃ = tris(8-hydroxyquinolinolato)aluminum (III)). Among the devices, green light-emitting device ITO/TPD/**2b**/BCP/Alq₃/Al:Li exhibits the highest EL performance.

Introduction

Amorphous triaryldiamines of benzidine with high glass transition temperatures (T_g) are widely used as thermally stable hole-transporting layers for organic light-emitting devices.[1] Another synthetic method of forming amorphous glasses can be achieved by replacing the benzidine group by heteroarenes with a low symmetry, such as thiophene,[2] 2,2′-bithiophene,[3] isothianaphthalenes,[4] and 2,2′:5′,2″-terthiophene.[5] Such thiophene bis(triarylamines) and diarylaminophenyl compounds show interesting hole-transporting properties and color-tunable emitting materials.[6] π-Conjugated systems, silole, on the other hand, have been intensively studied as a novel core component for efficient electron-transporting materials due to the small band gap and high electron affinity.[7] Ohshita et al.[8] have reported the synthesis of silicon-bridged bithiophenes and demonstrated that they exhibit high electron-transporting

properties. Hole-transporting and electron-transporting properties are opposing functions associated with different structural features. Recently, synthetic research has been carried out incorporating the above functions in the same molecule in an effort to attain a better performance.[9] Adachi et al.[10] synthesized interesting bipolar materials that were composed of oxadiazole and triphenylamine groups as an EM (emitting material). Later many bipolar materials featuring combinations such as triarylamineoxadiazole,[11] triarylaminopyridine,[12] dialkylaminopyran,[13] and triarylaminoboryl[14] were synthesized and applied in OLED. These compounds were shown to improve electron and hole injection into the emitting layer due to a high HOMO (highest occupied molecular orbital) and low LUMO

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Scheme 1.   Synthesis of 4,4-Diphenyl-2,6-bis(4-diarylamino-*p*-aryl)dithienosiloles

amine derivatives	products	yield
2a	**2b**	72%
3a	**3b**	68%
4a	**4b**	52%
5a	**5b**	45%
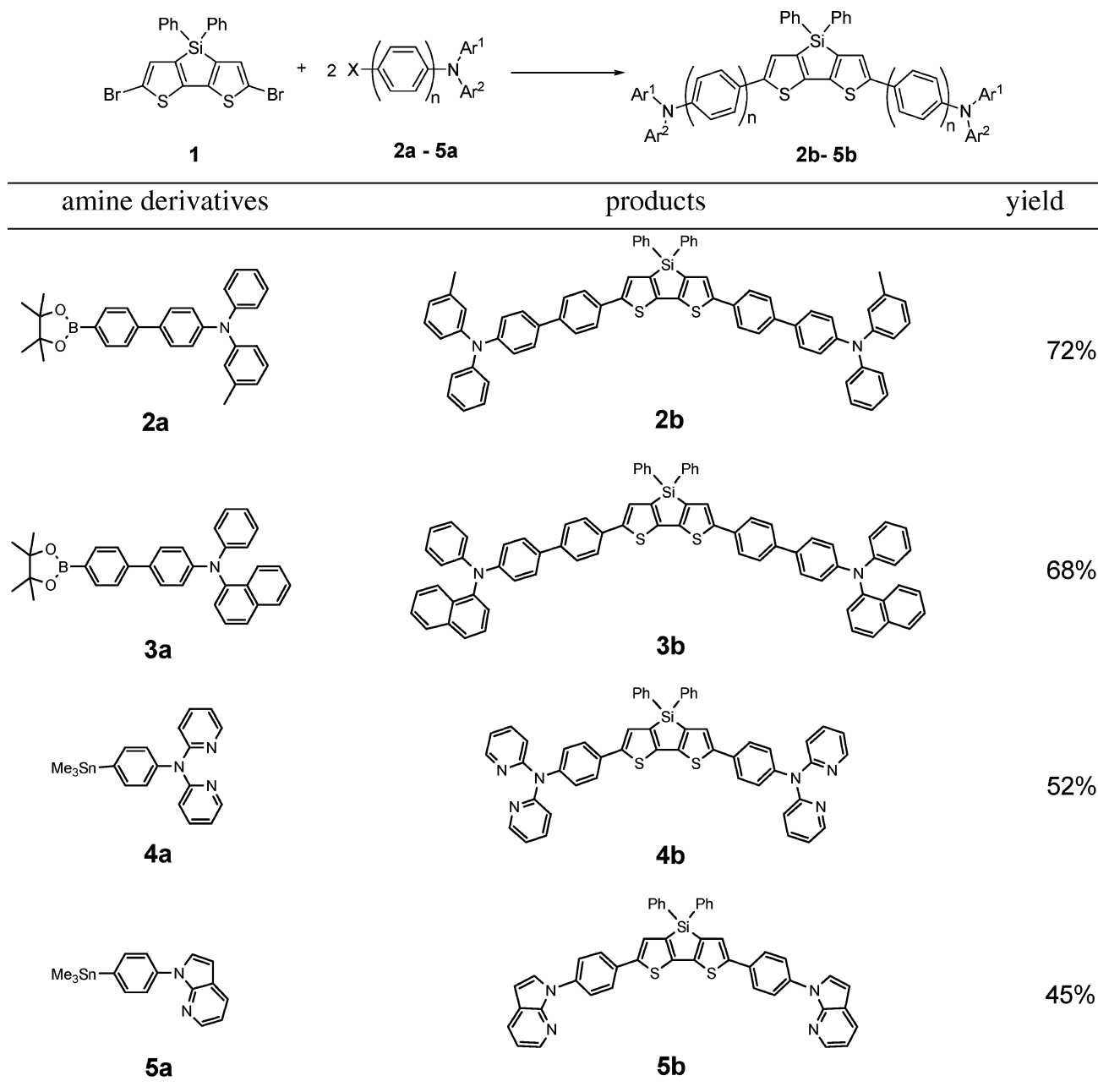
(lowest unoccupied molecular orbital). Accordingly, when we incorporated the diarylamino unit as a hole-transporting compound and silicon-bridged bithiophene as an electron-transporting unit into the molecular structure of emitters, we could expect improved bipolar character and EL characteristics.

We now describe (i) the successful incorporation of a silicon-bridged bithiophene into diarylaminophenyl units; (ii) the optical properties of novel bis(diarylaminophenyl)silole; and (iii) the electroluminescent properties of multiple-layer EL devices.

Results and Discussion

Synthesis and Thermal Properties. The scheme of synthesis and the structures of arylamine derivatives and dibromodithienosilole are given in Scheme 1. The 4,4-diphenyl-2,6-bis(4-diarylamino-4-biphenylyl)dithieno-siloles (**2b** and **3b**) were obtained by the reaction of

dibromodithienosilole (**1**)[8] with the corresponding boro-lane[15] (**2a** and **3a**) by Suzuki coupling reaction in the presence of Pd(PPh$_3$)$_4$ and K$_2$CO$_3$. 4,4-Diphenyl-2,6-bis-[4-(dipyridylamino)phenyl]dithienosilole (**4b**) and 4,4-diphenyl-2,6-bis[4-(7-azaindol-1-yl)phenyl]dithieno-silole (**5b**) were synthesized by further stannylation of 2,2′-(dipyridylamino)phenyl and 4-(7-azaindol-1-yl)phen-yl[16] and subsequent Stille cross-coupling reaction with dibromodithienosilole. All of the new compounds were fully characterized with spectroscopic techniques, including ^{1}H and ^{13}C NMR spectroscopy and high-resolution mass spectroscopy. The ^{13}C NMR spectrum of **4b** reveals the expected 17 lines in the aromatic region. The ^{29}Si NMR spectrum of **4b** reveals a single resonance at

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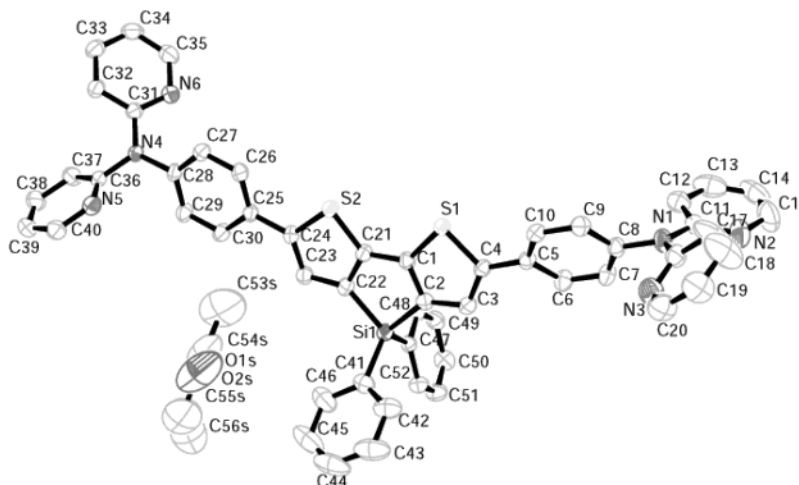(16) Kang, Y.; Wang, S. *Tetrahedron Lett.* **2002**, *43*, 3711.

Figure 1. Molecular structure of **4b** showing the atom-numbering scheme. Selected distances (Å) and angles (deg): C(22)−Si(1) 1.880(2), C(1)−C(21) 1.454(3), C(24)−C(25) 1.475(3), C(2)−Si(1)−C(22) 91.62(11), C(41)−Si(1)−C(47) 109.27(11).

Table 1. Photophysical and Electrochemical Data for the Compounds 2b−5b

compd	T_g, °C	UV[a] λ_{max}, nm	PL[a] λ_{max}, nm	PL in film λ_{max}, nm	Φ_{fl}[b], (%)	$E_{ox}(\{E_{onset}\}^{ox})$, V vs SCE	$E_g{}^c$, eV	HOMO/LUMO, eV
2b	92	387, 308	495	531	22	0.99 (0.91)	2.69	−5.31/−2.62
3b	112	385	492	528	12	1.00 (0.92)	2.64	−5.32/−2.68
4b		417, 324, 291	500	525	83	0.88 (0.83)	2.61	−5.23/−2.62
5b		405, 324, 276	490	518	62	0.96 (0.89)	2.55	−5.29/−2.74

[a] Measured in $CHCl_3$. [b] Determined by the dilution method. [c] Calculated by optical edge.

−20.4 ppm, in accord with the values for silicon-bridged bithiophenes that appear at −20 ppm. The structure of **4b** has been determined by X-ray crystallography.[17] The structure of **4b** is shown in Figure 1. Crystallographic data and processing parameters are given in ref 17. The X-ray study of **4b** indicates complete planarity in the tricyclic system, possessing a C_2 axis. The thiophene rings are almost planar, with maximum deviations from the mean plane of the thiophene ring of 0.03 Å for C24. The bond angles and distances for **4b** are comparable to those found in silicon-bridged bithiophene.[18] All of the compounds are soluble in common organic solvents such as dichloromethane, THF, and toluene.

The thermal properties of the new compounds were determined by DSC and TGA measurements (Table 1). All the compounds are thermally stable up to 280 °C in air. The compounds **2b**−**3b** readily form glass on cooling the melt sample. The glass transition temperatures (T_g = 92−112 °C) are higher than those of commonly used hole-transporting materials, 1,4-bis(1-naphthylphenylamino)biphenyl (α-NPD, T_g = 100 °C) and 1,4-bis-(phenyl-*m*-tolylamino)biphenyl (TPD, T_g = 60 °C).[1a] The incorporation of the asymmetric nature of **2b**−**3b** at the peripheral amines is intended to facilitate formation of amorphous glasses.

Photophysical Properties. The UV absorption spectra were taken in $CHCl_3$ and are shown in Figure 2, with the λ_{max} values collected in Table 1. The absorption spectra of **2b**−**5b** exhibit an intense absorption band

(17) Crystal data. Compound **4b**: $C_{56}H_{44}N_6O_2S_2Si$, M = 925.18, triclinic, space group $P\bar{1}$, a = 9.9720(10) Å, b = 14.7777(16) Å, c = 16.6067(18) Å, α = 74.422(2)°, β = 84.049(2)°, γ = 80.928(2)°, U = 2323.0(4) Å³, Z = 2, μ(Mo Kα) = 0.192 mm⁻¹, 14 374 reflections measured, 10 384 unique (R_{int} = 0.01621). The final R_w (F^2) was 0.1664 (all data).
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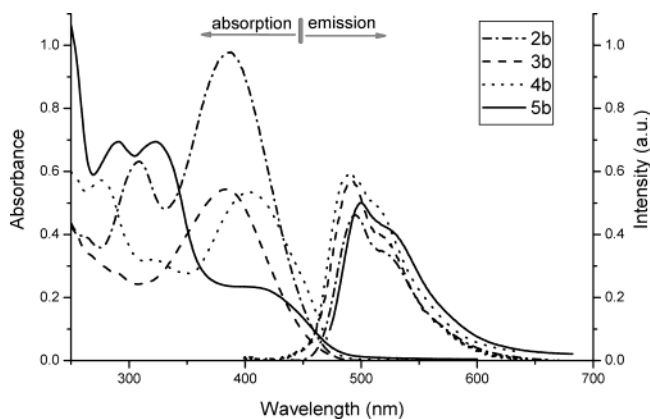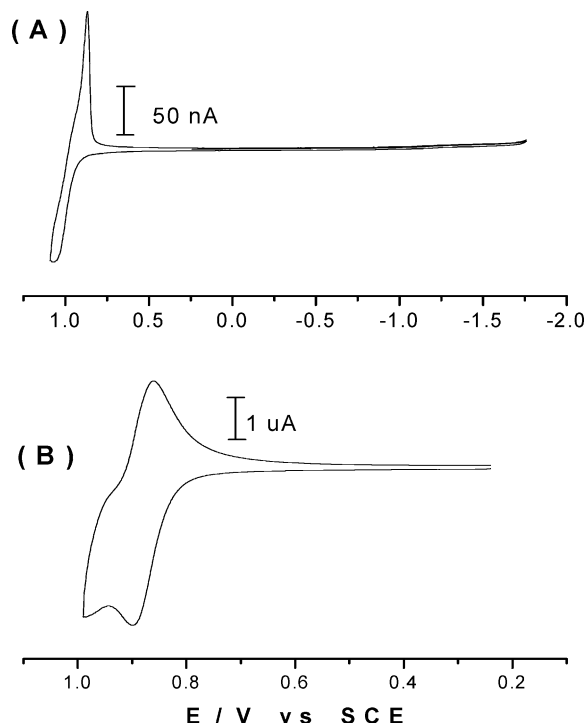

Figure 2. Absorption and emission spectra of **2b**−**5b** in $CHCl_3$.

between 385 and 417 nm, indicating that electronic transitions are mostly π→π*, originating from the π-conjugation chain extending from the conjugated substituents on the dithienosilole, and absorption bands at <325 nm are assigned as n→π* transitions. The absorption maximum is significantly red-shifted (35−70 nm) compared to that previously reported for dithienosilole,[8a] but the absorption is comparable to that of diaryldithienosiloles and 2,5-dithienylsilole derivatives,[8b] indicating that the introduction of both aryl groups on the central dithienosilole leads to a smaller band gap energy. The red shifts of **4b** and **5b** from **2b** and **3b** can be explained by the fact that the rigid dipyridylamino and azaindole groups have stronger electron-donating ability than the triarylamine groups. Compounds **2b**−**5b** exhibit intense fluorescence emission in the green wavelength region (492−500 nm). In addition, the same emission spectra are obtained irrespective of the applied excited wavelengths, indicating that downhill relaxation to the lowest excited state is

Figure 3. Cyclic voltammograms of 1 mM **2b** (A) and **4b** (B) at a platinum disk electrode (dia. = 100 μm for A and 1.6 mm for B); in THF containing 0.1 M TBAP; v = 0.5 V/s for A and 0.1 V/s for B, respectively.

efficient.[19] The somewhat large Stokes shift (~110 nm) of λ_{em} in **2b** and **3b** most likely stems from the excited state induced coplanarity of the amino substituents.

Electrochemistry. The cyclic voltammograms (CVs) of **2b**–**5b** were measured in THF containing 0.1 M tetrabutylammonium perchlorate (TBAP). Table 1 summarizes the oxidation potentials of **2b**–**5b**, 0.88–1.00 V vs SCE, obtained from CV experiments. No reduction waves of **2b**–**4b** were observed in the potential scan range from −1.76 to 1.09 V except **5b**. A typical CV of **2b** (Figure 3A) shows no redox waves arising from the reduction of **2b** but a redox wave arising from oxidation of **2b** at 0.99 V, where a platinum disk (dia. = 100 μm) electrode with a scan rate of 0.5 V/s was used. The shape of the CV wave implies adsorption/precipitation of the oxidation product of **2b** presumably because of the change of the solubility upon oxidation.[20] A similar trend was observed in the CV of **3b** (not shown). However, the reversibility of the redox wave arising from the oxidation is much improved in **4b** and **5b** (Figure 3B). The CV of **5b** reveals two irreversible reduction waves at −1.37 and −1.66 V, which is probably ascribed to the 7-azaindole moiety (not shown). Overall, the electrochemical properties of **2b**–**4b** are similar to those of diaryldithiensiloles reported by Oshita et al.[8] Thus, their assignments can be applied to these compounds.

The HOMO energy levels of **2b**–**5b** are calculated from the onset of oxidation potential according to the equation IP (ionization potential) = {$(E_{onset})^{ox}$ + 4.4} V,[21] and the LUMO energy level is obtained by the subtraction of the optical band gap from the IP (Table 1).

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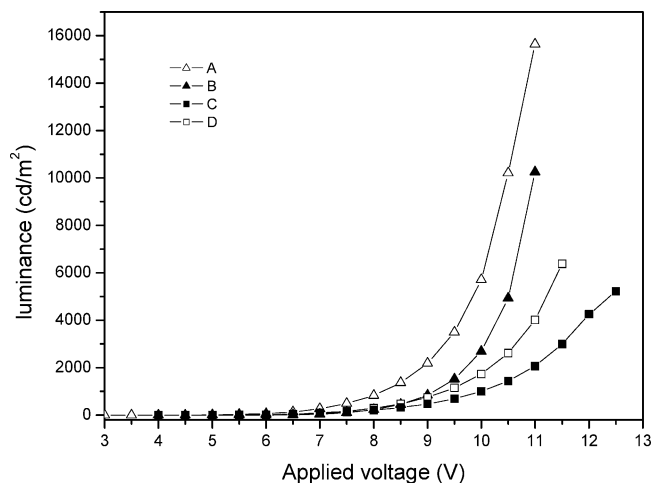(21) Agrawal, A. K.; Jenekhe, S. A. *Chem. Mater.* **1996**, *8*, 579.

Figure 4. Luminance vs applied electric field characteristics of the devices A–D.

Electroluminescent Devices. Since the compounds **2b**–**5b** possess both silole and amino groups, they might be used in OLED as hole-transporting, electron-transporting, or emitting layer. We have investigated all three possibilities in our device. Among the compounds, **2b** was selected for the device fabrication because of its better volatility and higher quantum efficiency. To check whether **2b** can permit the injection of both holes and electrons from the electrodes and transport them in a solid device, two devices were fabricated, with compound **2b** having the following structures: ITO/TPD (50 nm)/**2b** (50 nm)/Al:Li and ITO/**2b** (50 nm)/Alq$_3$ (50 nm)/Al:Li. The device ITO/TPD/**2b**/Al:Li (power efficiency, 0.092 lm/W; luminance, 64 cd/m^2, external quantum efficiency, 0.04 at 100 mA of current density) failed to produce reasonable light output. However, the device ITO/**2b**/Alq$_3$/Al:Li produced a green light and reached the maximum value of 1530 cd/m^2 at 13 V. The observation clearly suggests that the compound **2b** transports holes better than it carries electrons. To evaluate emitting properties of the compounds **2b**–**5b**, we fabricated multilayer EL devices: ITO/TPD (50 nm)/compounds **2b**–**5b** (20 nm)/BCP (10 nm)/Alq$_3$ (20 nm)/Al:Li with device A, B, C, and D corresponding to **2b**, **3b**, **4b**, and **5b**, respectively. They consist of the emitting layer of compounds **2b**–**5b** with the hole-transporting layer of TPD, the hole-blocking layer of BCP, and electron-transporting layer of Alq$_3$. The BCP, as an effective hole-blocking layer, was deposited to prevent carrier recombination in the Alq$_3$. The I-V-L characteristics are shown in Figure 4 and Figure 5. The turn-on voltage of the devices A–D is about 4 V. Obviously device A has the highest luminescence among all the devices. The EL spectra (Figure 6) of the four devices fabricated from **2b**–**5b** were superimposable to the PL spectra (Figure 2) of **2b**–**5b**, which implies that charge combination occurs in the **2b**–**5b** layer. Table 2 summarizes the maximum luminances, luminous efficiencies, and quantum efficiencies of EL for the multiple-layer devices. The device A is green emitting with the following performance characteristics: maximum luminance (15 000 cd/m^2), luminous efficiency (1.4 lm/W at 300 cd/m^2). The high external quantum efficiency may be due to higher fluorescence efficiency in the solid film than in the solution. This result indicates that the layer of **2b** as an emitting source shows comparable luminous char-
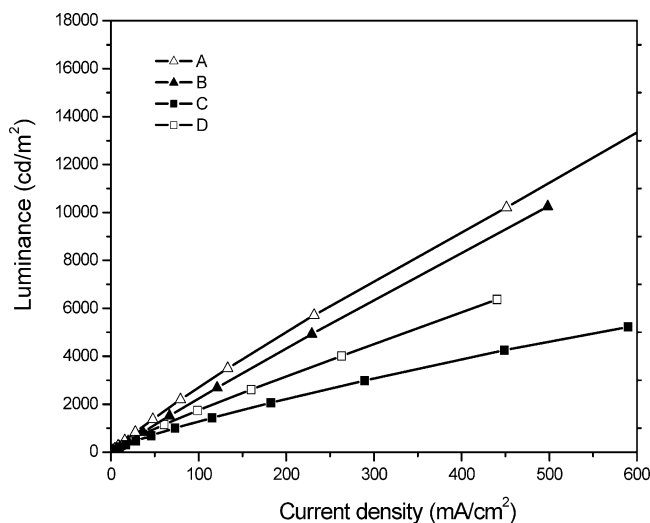
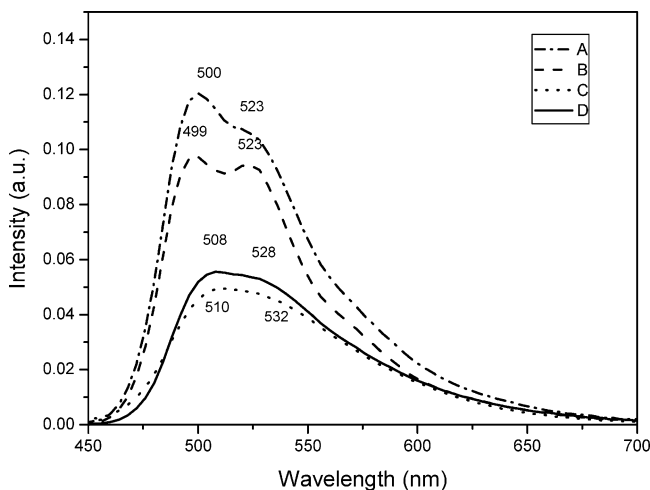**Figure 5.** Luminance vs current density characteristics of the devices A−D.

Figure 6. EL spectra of devices A−D.

Table 2. Electroluminescence Characteristics of Devices

device[a]	maximum luminance (cd/m²)	luminous efficiency at 300 cd/m² (lm/W)	quantum efficiency (%)
A	15 000 (at 11 V)	1.4	1.2
B	10 000 (at 11 V)	0.88	0.87
C	5200 (at 12.5 V)	0.69	0.63
D	6400 (at 11.5 V)	0.92	0.85

[a] Devices are fabricated as follows: ITO/TPD (50 nm)/compounds **2b−5b** (20 nm)/BCP (10 nm)/Alq₃ (20 nm)/Al:Li with device A, B, C, and D corresponding to **2b**, **3b**, **4b**, and **5b**, respectively.

acteristics relative to the layer of Alq₃, which is known as a typical green-emitting substance and that the EL originates from the electronically excited singlet state of compound **2b**.

In summary, we were able to incorporate a dithienosilole group into bis(diarylamino)aryl using the Suzuki coupling reaction or Stille cross-coupling reaction. Compounds **2b−5b** exhibit intense fluorescence emission in the green wavelength region. EL devices based on compounds **2b−5b** were fabricated. Device A with **2b** as the emitter offers bright green emission with good luminous efficiency and very high luminance, which is comparable to those of Alq₃.

Experimental Section

All experiments were performed under a nitrogen atmosphere in a Vacuum Atmospheres drybox or by standard Schlenk techniques. THF, toluene, and ether were distilled from sodium benzophenone. *n*-Hexane, CH₂Cl₂, and pentane were dried and distilled from CaH₂. ¹H, ¹³C, and ²⁹Si NMR spectra were recorded on a Varian Mercury 300 spectrometer. The absorption and photoluminescence spectra were recorded on a Perkin-Elmer Lambda 2S UV−visible spectrophotometer and a Perkin-Elmer LS fluorescence spectrometer, respectively. The fluorescence quantum yields in chloroform using 9,10-diphenylanthracene as the standard were determined by the dilution method.[22] The fluorescence decay curves were recorded on a PTI fluorescence Master 2M1 luminescence spectrophotometer using a PTIG2-3300 nitrogen laser for excitation. DSC measurements were carried out on a Perkin-Elmer DSC7 calorimeter at a heating rate of 10 °C/min under a nitrogen atmosphere. All the electrochemical measurements were carried out in THF solutions containing 1 mM complex and 0.1 M tetrabutylammonium perchlorate (TBAP) at room temperature using a BAS 100B electrochemical analyzer. Freshly distilled, degassed THF was used as the solvent. A platinum microdisk (dia. 100 *μ*m) or disk (dia. 1.6 mm) electrode and platinum wire were used as a working and counter electrode, respectively. The reference electrode used was Ag|AgNO₃ (BAS). Then, all the potential values shown were calibrated vs SCE, unless otherwise specified, by correcting Fc|Fc⁺ redox potential measured in 0.2 M LiClO₄/CH₃-CN as 0.31 V vs SCE.[23] 4,4-Diphenyl-2,6-dibromodithienosilole,[8b] 4-bromo-4′-(1-naphthylphenylamino)biphenyl, 4-bromo-4′-(phenyl-*m*-tolylamino)biphenyl,[16] dipyridin-2-yl-(4-bromophenyl)-amine, and 1-(4-bromophenyl)pyrrolo[2,3-*b*]pyridine[17] were prepared according to the literature.

2-{4-[4′-(Phenyl-*m*-tolylamino)-4-biphenylyl]}-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2a). To a stirred THF solution (25 mL) of 4-bromo-4′-(phenyl-*m*-tolylamino)biphenyl (0.50 g, 1.20 mmol) was added a solution of *n*-BuLi (1.5 mL, 1.6 M in hexane) at −78 °C, and the reaction mixture was stirred for 30 min. To this was added 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.25 mL). The reaction mixture was warmed to ambient temperature and stirred for 24 h. The solvent was removed under reduced pressure and extracted with CH₂Cl₂. The pure product **2a** was isolated by chromatographic workup (eluent: CH₂Cl₂/hexane (1:1), R_f = 0.2) in 75% yield. Mp: 91−93 °C. ¹H NMR (CDCl₃): δ 7.85 (d, 2H, *J* = 8.1 Hz), 7.58 (d, 2H, *J* = 8.1 Hz), 7.49 (d, 2H, *J* = 8.1 Hz), 7.29−6.85 (m, 11H), 2.28 (s, 3H, Ph-C*H₃*), 1.36 (s, 12H, C-C*H₃*). ¹³C{¹H} NMR (CDCl₃): δ 147.7, 143.4, 142.5, 139.6, 138.4 135.3, 134.6, 130.9, 129.8, 128.5, 128.0, 127.7, 126.1, 125.8, 125.1, 124.2, 124.0, 123.2, 83.9, 25.0, 21.1. MS: *m/z* 461 [M⁺]. Anal. Calcd for C₃₁H₃₂BNO₂: C, 80.70; H, 6.99. Found: C, 80.22; H, 6.76.

2-{4-[4′-(1-Naphthylphenylamino)-4-biphenylyl]}-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3a). Compound **3a** was prepared using the same procedure as described for **2a** in 72% yield. Mp: 95−97 °C. ¹H NMR (CDCl₃): δ 7.96 (d, 1H, *J* = 8.2 Hz), 7.90 (d, 1H, *J* = 8.0 Hz), 7.84 (d, 2H, *J* = 8.2 Hz), 7.64 (d, 1H, *J* = 8.0 Hz), 7.57−6.90 (m, 15H), 1.35 (s, 12H, C-C*H₃*). ¹³C{¹H} NMR (CDCl₃): δ 148.24, 143.49, 143.44, 135.44, 135.36, 133.88, 131.40, 130.32, 129.09, 128.58, 127.96, 127.76, 127.33, 126.77, 126.43, 125.94, 125.36, 124.38, 122.67, 122.17, 121.87, 121.40, 83.88, 25.02. MS: *m/z* 497 [M⁺]. Anal. Calcd for C₃₄H₃₂BNO₂: C, 82.09; H, 6.48. Found: C, 81.72; H, 6.26.

Dipyridin-2-yl-(4-trimethylstannylphenyl)amine (4a). To a stirred THF solution (30 mL) of dipyridin-2-yl-(4-bromophenyl)amine (0.73 g, 2.24 mmol) was added a solution of *n*-BuLi (1.69 mL, 1.6 M)/hexane at −78 °C, and the mixture

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was stirred for 1 h at that temperature. The solution was warmed to ambient temperature and stirred for 1 h. The solution was cooled to −78 °C, and Me$_3$SnCl (2.7 mL, 1 M in THF) was added. The solution was warmed to room temperature and stirred for 12 h. The pure product **4a** was isolated by chromatographic workup (eluent: EA/hexane (1:1), R_f = 0.3) in 63% yield. ^{1}H NMR (CDCl$_3$): δ 8.32 (d, 2H, J = 6.2 Hz), 7.53 (dd, 2H, J = 6.8 Hz, 6.2 Hz), 7.48 (d, 2H, J = 8.7 Hz), 7.15 (d, 2H, J = 8.7 Hz), 6.99 (d, 2H, J = 8.1 Hz), 6.91 (dd, 2H, J = 8.1 Hz, J = 6.8 Hz), 0.28 (s, 9H, Sn−CH_3). ^{13}C-{^{1}H} NMR (CDCl$_3$): δ 158.2, 148.7, 148.4, 145.1, 139.1, 137.5, 126.7, 118.2, 117.1, −9.5. MS: m/z 411 [M$^+$]. Anal. Calcd for C$_{19}$H$_{21}$N$_3$Sn: C, 55.65; H, 5.16. Found: C, 55.45; H, 5.05.

1-(4-Trimethylstannylphenyl)pyrrolo[2,3-*b*]pyridine (5a). Compound **5a** was prepared using the same procedure as described for **4a** in 54% yield. ^{1}H NMR (CDCl$_3$): δ 8.37 (dd, 1H, J = 4.8 Hz, J = 1.5 Hz), 7.97 (dd, 1H, J = 7.8 Hz, J = 1.5 Hz). 7.73 (d, 2H, J = 7.8 Hz), 7.65 (d, 2H, J = 7.8 Hz), 7.51 (d, 1H, J = 4.8 Hz), 7.12 (dd, 1H, J = 7.8 Hz, J = 4.5 Hz), 6.62 (d, 1H, J = 4.5 Hz), 0.33(s, 9H, Sn-CH_3). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 143.9, 143.4, 140.3, 138.6, 136.8, 129.1, 127.7, 123.7, 121.6, 117.3, 116.1, −9.9. MS: m/z 358 [M$^+$]. Anal. Calcd for C$_{16}$H$_{18}$N$_2$-Sn: C, 53.82; H, 5.08. Found: C, 53.61; H, 4.97.

4,4-Diphenyl-2,6-bis{4-[4′-(phenyl-*m*-tolylamino)-4-biphenylyl]}dithienosilole (2b). To a mixture of borolane **2a** (0.46 g, 1.00 mmol), silole **1** (0.21 g, 0.42 mmol), and Pd(PPh$_3$)$_4$ (0.05 g) were added degassed 2 M K$_2$CO$_3$ (2.1 mL, 4.2 mmol) and toluene (30 mL). The yellow solution was refluxed for 3 days. The solvent was removed in vacuo and extracted with CH$_2$Cl$_2$. The solution was chromatographed using CH$_2$Cl$_2$/hexane (1:1) as eluent to afford **2b** in 72% yield. Mp: 130C. ^{1}H NMR (CDCl$_3$): δ 7.66−6.86 (m, 46H), 2.28 (s, 6H, Ph-CH_3). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 147.8, 147.6, 144.4, 141.1, 140.1, 140.0, 139.3, 136.3, 135.7, 135.6, 134.9, 134.0, 132.3, 132.2, 131.9, 130.5, 129.8, 128.4, 127.7, 127.3, 127.1, 126.9, 126.2, 125.1, 124.3, 123.3, 122.7, 121.2, 21.8. ^{29}Si NMR (CDCl$_3$): δ −19.4. MS: m/z 1012 [M$^+$]. Anal. Calcd for C$_{70}$H$_{52}$N$_2$S$_2$Si: C, 82.96; H, 5.17. Found: C, 83.22; H, 5.30.

4,4-Diphenyl-2,6-bis{4-[4′-(1-naphthylphenylamino)-4-biphenylyl]}dithienosilole (3b). Compound **3b** was prepared using the same procedure as described for **2b**. ^{1}H NMR (CDCl$_3$): δ 7.96 (d, 2H, J = 8.1 Hz), 7.90 (d, 2H, J = 8.1 Hz), 7.80 (d, 2H, J = 8.3 Hz), 7.66−6.98 (m, 46H). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 148.2, 148.1, 145.4, 144.3, 144.1, 143.4, 140.1, 140.0, 136.4, 135.7, 135.6, 135.4, 134.9, 133.2, 132.2, 132.1, 131.4, 129.1, 128.5, 128.3, 127.9, 127.5, 126.8, 126.4, 124.4, 122.7, 122.2, 121.9, 120.4. ^{29}Si NMR (CDCl$_3$): δ −19.8. MS: m/z 1085

[M$^+$]. Anal. Calcd for C$_{76}$H$_{52}$N$_2$S$_2$Si: C, 84.09; H, 4.83. Found: C, 83.78; H, 4.72.

4,4-Diphenyl-2,6-bis[4-(dipyridylamino)phenyl]dithienosilole (4b). To a stirred toluene solution (20 mL) of **4a** and silole **1** (0.19 g, 0.48 mmol) was added LiCl (0.08 g, 1.92 mmol) and Pd(PPh$_3$)$_2$Cl$_2$ (0.01 g). The solution was refluxed for 3 days. The solvent was removed in vacuo and extracted with CH$_2$Cl$_2$. The solution was chromatographed using ethyl acetate as eluent to afford **4b**. ^{1}H NMR (CDCl$_3$): δ 8.34−7.16 (m, 36H). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 158.1 157.9, 149.4, 148.8, 148.4, 145.6, 144.2, 144.1, 140.9, 137.6, 135.4, 131.5, 127.3, 126.9, 118.5, 117.4, 116.9. ^{29}Si NMR (CDCl$_3$): δ −20.4. MS: m/z 836 [M$^+$]. Anal. Calcd for C$_{52}$H$_{36}$N$_6$S$_2$Si: C, 74.61; H, 4.33. Found: C, 74.39; H, 4.15.

4,4-Diphenyl-2,6-bis[4-(7-azaindol-1-yl)phenyl]dithienosilole (5b). Compound **5b** was prepared using the same procedure as described for **4b**. ^{1}H NMR (CDCl$_3$): δ 8.40 (dd, 2H, J = 4.2 Hz, J = 1.5 Hz), 7.98 (dd, 2H, J = 4.8 Hz, J = 1.5 Hz), 7.83−7.77 (m, 12H), 7.55 (d, 2H, J = 3.6 Hz), 7.49 (s, 2H), 7.47−7.39 (m. 6H), 7.15 (dd, 2H, J = 8.1 Hz, J = 4.8 Hz), 6.65 (d, 2H, J = 3.6 Hz). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 149.7, 145.5, 143.0, 141.2, 137.6, 136.2, 134.9, 132.4, 131.5, 129.5, 128.9, 128.4, 128.0, 127.3, 126.3, 126.0, 124.8, 121.8. ^{29}Si NMR (CDCl$_3$): δ −21.6. MS: m/z 730 [M$^+$]. Anal. Calcd for C$_{46}$H$_{30}$N$_4$S$_2$Si: C, 75.58; H, 4.14. Found: C, 75.31; H, 3.98.

Fabrication of OLED Devices. The ITO electrode was cleaned by sonication in a detergent solution for 4 min and washed with distilled water. Further sonication in 1,1,1-trichloroethane for 3 min was done before blowing dry under nitrogen. Organic EL devices were fabricated by sequential vacuum deposition of organic materials onto an ITO, followed by vacuum deposition of Li and Al onto the organic layer. The organic layers were deposited at a rate of 0.2 nm/s at 10^{-5} Torr. The current−voltage and luminance were measured with a Keithley 2400 Source and a Newport Optical meter.

Supporting Information Available: This material is available free of charge via the Internet at http://pubs.acs.org.

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