2,3,4,5-Tetrafunctionalized Siloles: Syntheses, Structures, Luminescence, and Electroluminescence

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Six new diethynylsilane compounds with the general formula Si(C≡C−R)$_2$R′$_2$ (R = *p*-*N*-indolylphenyl, R′ = Me, **1**; R′ = Ph, **2**; R = *p*-*N*-7-azaindolylphenyl, R′ = Me, **3**; R′ = Ph, **4**; R = *p*-2,2′-dipyridylaminophenyl, R′ = Me, **5**; R′ = Ph, **6**) have been synthesized and fully characterized. Compounds **1**, **2**, and **4** have been found to undergo intramolecular cyclization in the presence of Li-naphthyl to form the corresponding 2,5-dilithiosiloles, which after methylation by CH$_3$I or undergoing Pd-catalyzed cross-coupling reactions with the appropriate arylbromide produced six new silole compounds: 1,1-diphenyl-2,5-dimethyl-3,4-bis(4-*N*-7-azaindoylphenyl)silole (**7**), 1,1-diphenyl-2,3,4,5-tetrakis(4-*N*-indoylphenyl)silole (**8**), 1,1-dimethyl-2,5-bis(4-*N*-7-azaindoylphenyl)-3,4-bis(4-*N*-indoylphenyl)silole (**9**), 1,1-dimethyl-2,5-bis(*p*-2,2′-dipyridylaminophenyl)-3,4-(4-*N*-indoylphenyl)silole (**10**), 1,1-dimethyl-2,5-bis(4-(*N*-1-naphthylphenylamino)phenyl)-3,4-bis(4-*N*-indoylphenyl)silole (**11**), and 1,1-dimethyl-2,5-bis(4′-(*N*-1-naphthylphenylamino)biphenyl)-3,4-bis(4-*N*-indoylphenyl)silole (**12**). Compounds **8**−**12** are a new class of silole molecules that are functionalized at the 2-, 3-, 4-, and 5-positions by indolylphenyl, 7-azaindolylphenyl, 2,2′-dipyridylaminophenyl, (*N*-1-naphthyl)(*N*-phenyl)aminophenyl, or (*N*-1-naphthyl)(*N*-phenyl)aminobiphenyl. The structures of compounds **3**, **5**, and **8** were determined by single-crystal X-ray diffraction analysis. Siloles **8**−**12** emit a green color in solution and the solid state, while in contrast silole **7** emits a blue color with the emission maximum at 445 nm. The effects of substituent groups at different positions of the silole ring on structures and luminescent properties have been examined. A single-layer EL device with compound **11** being sandwiched between the ITO anode and the LiF/Al cathode layers has been fabricated successfully.

Introduction

Silole (1-silacyclopentadiene) is a silicon-containing five-membered cyclic diene. Since the first reported synthesis of silole by Braye and Hübel[1] in 1959, there have been extensive studies on the synthesis, reactivity, properties,[2] and coordination abilities[3] of silole and its derivatives to transition metals. Recently, a new aspect has been added to the silole chemistry, that is, the application of the siloles as a new class of materials for organic light-emitting devices (OLEDs). Siloles in general possess low-lying LUMO energy levels, compared with the cyclopentadiene analogues, which are often associated with $\sigma^*-\pi^*$ conjugation arising from the interaction between the σ^* orbital of two exocyclic σ bonds on the ring silicon and the π^* orbital of the butadiene moiety.[4] As a result, siloles have been found to be able to serve as efficient electron-transport materials in OLEDs.[5] To date three types of siloles (**A**−**C**) have been reported for use in OLEDs. Siloles **A** were reported for use as emitting materials,[6] and siloles **B** and **C** were reported for use as emitters as well as electron-

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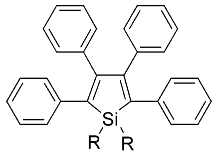

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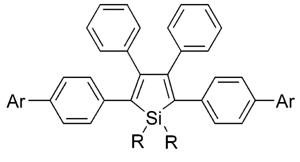

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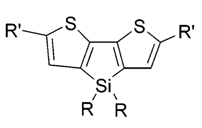

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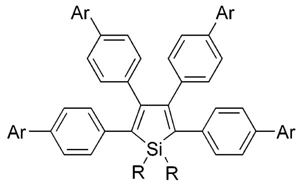

D

transporting materials.[5,7] Some members of siloles **B**, e.g., 2,5-bis(2,2′-bipyridine-6-yl)-1,1-dimethyl-3,4-diphenylsilole, have been reported to display a remarkable high mobility for electron transport that is better than that of the most widely used electron-transport material, tris(8-hydroxyquinolinolato)aluminum(III) (Alq_3), in OLEDs.[5b,8] These 2,5-difunctionalized siloles are available generally by intramolecular reductive cyclization of bis(phenylethynyl)silane.[9] We have demonstrated recently that silole compounds functionalized at the 2- and 5-positions by 7-azaindolyl and 2,2′-dipyridylamino groups can act as emitters as well as electron-transport materials in OLEDs.[10] In addition, they are capable of binding to metal ions to form extended coordination polymers.[10] Although 1,1-difunctionalizd or 2,5-difunctionalized siloles have been well documented, examples of siloles functionalized at the 2,3,4,5-positions[11] such as **D** are still rare because the synthetic methods available for 2,3,4,5-functionalized siloles are quite limited. In this work, we report the synthesis, structures, and fluorescent and electroluminescent properties of new 2,3,4,5-functionalized silole compounds based on indolyl, 7-azaindolyl, 2,2′-dipyridylamino, and (1-naphthyl)phenylamino groups.

Experimental Section

All experiments were carried out under a dry nitrogen atmosphere using standard Schlenk techniques. Solvents were freshly distilled from appropriate drying reagents prior to use. All starting materials were purchased from Aldrich and used without further purification. ^1H and ^{13}C NMR spectra were recorded on a Bruker Avance 300 (300 MHz for ^1H and 75.3 MHz for ^{13}C) spectrometer in $CDCl_3$. Chemical shifts were reported in δ ppm with reference relative to residual protio solvent. ^{29}Si NMR spectra were also recorded on a Bruker Advance 500 (99.4 MHz for ^{29}Si) spectrometer using tetramethylsilane as the external references. Melting points were determined with a Fisher-Johns melting point apparatus and were uncorrected. UV/vis spectra were obtained on a Hewlett-Packard 8562A diode array spectrophotometer. Excitation and emission spectra were obtained with a Photon Technologies International QuantaMaster Model C-60 spectrometer. Elemental analyses were performed by Canadian Microanalytical Service Ltd., Delta, British Columbia, Canada. 1-Bromo-4-(*N*-indolyl)benzene, 1-bromo-4-(*N*-7-azaindolyl)benzene, *p*-(2,2′-dipyridylamino)bromophenyl, 1-bromo-4-(*N*-1-naphthylphenylamino)benzene, 1-bromo-4′-(*N*-1-naphthylphenylamino)biphenyl, 4-(*N*-indolyl)phenylacetylene, 4-(*N*-7-azaindolyl)phenylacetylene, and *p*-(2,2′-dipyridylamino)phenylacetylene were synthesized by recently reported procedures.[12c,13]

Synthesis of Bis(4-(*N*-indolyl)phenylethynyl)dimethylsilane (1). To a Et_2O (25 mL) solution of 4-(*N*-indolyl)phenylacetylene (0.89 g, 4.10 mmol) was added n-BuLi (2.6 mL, 4.10 mmol, 1.6 M solution in hexane) at −78 °C. After stirring at the same temperature for 2 h, Me_2SiCl_2 (0.25 mL, 2.05 mmol) was added at −78 °C. The mixture was warmed to room temperature and stirred for overnight. The solvent was removed under reduced pressure. The mixture was dissolved in CH_2Cl_2 and washed with water. The organic layer was dried over $MgSO_4$ and filtered, and the solvent was removed under reduced pressure. The residue was subjected to column chromatography (ethyl acetate/hexane, 1:9) to afford pure **1** in 82% yield as a colorless solid. Mp: 101−103 °C. ^1H NMR in $CDCl_3$ (δ, ppm, 25 °C): 7.73−7.69 (m, overlap, 6H), 7.61 (d, J = 8.1, 2H), 7.51 (d, J = 8.4 Hz, 4H), 7.37 (d, J = 3.3 Hz, 2H), 7.31−7.22 (m, 4H), 6.74 (d, J = 3.3 Hz, 2H), 0.58 (s, 6H). ^{13}C NMR in $CDCl_3$ (δ, ppm, 25 °C): 140.82, 136.24, 134.21, 130.27, 128.20, 124.38, 123.36, 121.98, 121.42, 121.18, 111.16, 105.92, 105.09, 92.11, 1.17. ^{29}Si NMR in $CDCl_3$ (δ, ppm, 25 °C): −39.1. Anal. Calcd for $C_{34}H_{26}N_2Si$: C, 83.23; H, 5.34; N, 5.71. Found: C, 83.15; H, 5.29; N, 5.72.

Synthesis of Bis(4-(*N*-indolyl)phenylethynyl)diphenylsilane (2). In the same manner as described for **1**, the reaction of n-BuLi (1.44 mL, 2.30 mmol, 1.6 M solution in Hx) and 4-(*N*-indolyl)phenylacetylene (0.50 g, 2.30 mmol) with diphenyldichlorosilane (0.30 mL, 1.15 mmol) provided **2** as a colorless solid in 62% yield. Mp: 105−107 °C. ^1H NMR in $CDCl_3$ (δ, ppm, 25 °C): 7.96−7.92 (m, 2H), 7.78 (d, J = 8.7 Hz, 4H), 7.73−7.60 (m, 6H), 7.55−7.49 (m, overlap, 10H), 7.38−7.35 (m, 4H), 7.30−7.21 (m, 2H), 6.74 (d, J = 3.3 Hz, 2H). ^{13}C NMR in $CDCl_3$ (δ, ppm, 25 °C): 141.12, 136.18, 135.63, 134.45, 133.45, 131.10, 130.27, 128.89, 128.18, 124.37, 123.40, 121.99, 121.46, 120.82, 111.16, 108.71, 105.18. ^{29}Si NMR in $CDCl_3$ (δ, ppm, 25 °C): −47.9. Anal. Calcd for $C_{44}H_{30}N_2Si$: C, 85.96; H, 4.92; N, 4.56. Found: C, 85.78; H, 4.86; N, 4.48.

Synthesis of Bis(4-(*N*-7-azaindolyl)phenylethynyl)-dimethylsilane (3). In the same manner as described for **1**, the reaction of n-BuLi (0.60 mL, 0.92 mmol, 1.6 M solution in Hx) and 4-(*N*-7-azaindolyl)phenylacetylene (0.2 g, 0.92 mmol) with dimethyldichlorosilane (0.06 mL, 0.46 mmol) provided **3** as colorless crystals in 62% yield. Mp: 87−89 °C. ^1H NMR in $CDCl_3$ (δ, ppm, 25 °C): 8.41 (dd, J = 4.8 Hz, 1.2 Hz, 2H), 7.99 (dd, J = 7.8, 1.5 Hz, 2H), 7.85 (d, J = 8.7 Hz, 4H), 7.69 (d, J = 8.7 Hz, 4H), 7.55 (d, J = 3.6 Hz, 2H), 7.17 (dd, J = 9.0 Hz, 4.5 Hz, 2H), 6.67 (d, J = 3.6 Hz, 2H), 0.55 (s, 6H). ^{13}C NMR in

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$CDCl_3$ (δ, ppm, 25 °C): 148.17, 144.34, 139.52, 133.90, 129.84, 127.88, 123.66, 122.54, 120.88, 117.68, 106.16, 103.09, 91.77, 1.21. ^{29}Si NMR in $CDCl_3$ (δ, ppm, 25 °C): −39.2. Anal. Calcd for $C_{32}H_{24}N_4Si$: C, 78.02; H, 4.91; N, 11.37. Found: C, 77.94; H, 4.78; N, 11.12.

Synthesis of Bis(4-(*N*-7-azaindolyl)phenylethynyl)-diphenylsilane (4). In the same manner as described for **1**, the reaction of n-BuLi (1.92 mL, 3.07 mmol, 1.6 M solution in Hx) and 4-(*N*-7-azaindolyl)phenylacetylene (0.67 g, 3.07 mmol) with diphenyldichlorosilane (0.38 mL, 1.54 mmol) provided **4** as colorless solid in 57% yield. Mp: 88−92 °C. ^1H NMR in $CDCl_3$ (δ, ppm, 25 °C): 8.41 (dd, $J = 4.8$ Hz, 1.2 Hz, 2H), 7.99 (dd, $J = 7.8$, 1.5 Hz, 2H), 7.94−7.91 (m, 4H), 7.87 (d, $J = 8.7$ Hz, 4H), 7.77 (d, $J = 8.7$ Hz, 4H), 7.57 (d, $J = 3.6$ Hz, 2H), 7.50−7.48 (m, 6H), 7.18 (dd, $J = 9.0$ Hz, 4.8 Hz, 2H), 6.68 (d, $J = 3.6$ Hz, 2H). ^{13}C NMR in $CDCl_3$ (δ, ppm, 25 °C): 148.19, 144.38, 139.83, 135.65, 134.13, 133.69, 130.99, 129.87, 128.84, 127.82, 123.72, 122.56, 120.54, 117.75, 109.09, 103.21, 88.83. ^{29}Si NMR in $CDCl_3$ (δ, ppm, 25 °C): −47.9. Anal. Calcd for $C_{42}H_{28}N_4Si$: C, 81.79; H, 4.58; N, 9.08. Found: C, 81.70; H, 4.60; N, 8.98.

Synthesis of Bis(*p*-(2,2′-dipyridylamino)phenylethynyl)dimethylsilane (5). In the same manner as described for **1**, the reaction of n-BuLi (1.20 mL, 1.85 mmol, 1.6 M solution in Hx) and *p*-(2,2′-dipyridylamino)phenylacetylene (0.50 g, 1.85 mmol) with dimethyldichlorosilane (0.12 mL, 0.93 mmol) provided **5** as colorless crystals in 68% yield. Mp: 108−110 °C. ^1H NMR in $CDCl_3$ (δ, ppm, 25 °C): 8.38 (d, $J = 3.6$ Hz, 4H), 7.61 (dd, $J = 8.0$, 7.7 Hz, 4H), 7.52 (d, $J = 8.4$ Hz, 4H), 7.13 (d, $J = 8.4$ Hz, 4H), 7.00 (m, 8H), 0.49 (s, 6H). ^{13}C NMR in $CDCl_3$ (δ, ppm, 25 °C): 158.32, 149.26, 138.56, 134.17, 126.76, 119.41, 118.09, 106.32, 91.54, 1.20. ^{29}Si NMR in $CDCl_3$ (δ, ppm, 25 °C): −39.4. Anal. Calcd for $C_{38}H_{30}N_6Si$: C, 76.22; H, 5.05; N, 14.04. Found: C, 76.05; H, 4.89; N, 13.97.

Synthesis of Bis(*p*-(2,2′-dipyridylamino)phenylethynyl)diphenylsilane (6). In the same manner as described for **1**, the reaction of n-BuLi (0.80 mL, 1.33 mmol, 1.6 M solution in Hx) and *p*-(2,2′-dipyridylamino)phenylacetylene (0.36 g, 1.33 mmol) with diphenyldichlorosilane (0.14 mL, 0.67 mmol) provided **6** as a colorless solid in 42% yield. Mp: 109−112 °C. ^1H NMR in $CDCl_3$ (δ, ppm, 25 °C): 8.36 (d, $J = 4.8$ Hz, 4H), 7.89−7.86 (m, 4H), 7.63−7.57 (m, 8H), 7.46−7.42 (m, 6H), 7.14 (d, $J = 8.4$ Hz, 4H), 7.04−6.97 (m, 8H). ^{13}C NMR in $CDCl_3$ (δ, ppm, 25 °C): 158.36, 149.37, 146.44, 138.53, 135.58, 134.36, 133.88, 130.86, 128.76, 126.70, 119.48, 118.16, 109.31, 88.44. ^{29}Si NMR in $CDCl_3$ (δ, ppm, 25 °C): −48.1. Anal. Calcd for $C_{48}H_{34}N_6Si$: C, 79.75; H, 4.74; N, 11.62. Found: C, 79.72; H, 4.71; N, 11.49.

Synthesis of 1,1-Diphenyl-2,5-dimethyl-3,4-bis(4-*N*-7-azaindoylphenyl)silole (7). A mixture of lithium (0.02 g, 2.9 mmol) and naphthalene (0.38 g, 2.9 mmol) in 4 mL of THF was stirred at room temperature under nitrogen for 4 h to form a deep dark green solution of lithium naphthalenide. A soulution of bis(4-(*N*-7-azaindolyl)phenylethynyl)diphenylsilane (**4**) in 4 mL of THF was added to the solution of lithium naphthalenide dropwise over 2 min at room temperature. After stirring for 15 min, the mixture was cooled to 0 °C, and methyliodide (0.2 mL, 2.92 mmol) was added. The mixture was stirred for 14 h, and the mixture was extracted with CH_2Cl_2. The extract was washed with H_2O and dried over $MgSO_4$, and all volatiles were removed under reduced pressure. The residue was chromatographed with ethyl acetate/hexane (1:3) as the eluent to afford pure **7** in 38% yield as a pale yellow solid. Mp: 105−108 °C. ^1H NMR in $CDCl_3$ (δ, ppm, 25 °C): 8.38 (dd, $J = 4.5$, 1.5 Hz, 2H), 7.95 (dd, $J = 7.8$, 1.5 Hz, 2H), 7.75−7.71 (m, 4H), 7.67 (d, $J = 8.4$ Hz, 4H), 7.52−7.46 (m, 8H), 7.16−7.09 (m, 6H), 6.59 (d, $J = 3.6$ Hz, 2H), 2.03 (s, 6H). ^{13}C NMR in $CDCl_3$ (δ, ppm, 25 °C): 156.03, 148.07, 137.39, 137.11, 136.47, 136.11, 134.45, 133.23, 131.12, 130.69, 129.63, 128.98, 128.48, 123.08, 117.25, 102.20, 16.09. ^{29}Si NMR in $CDCl_3$ (δ, ppm, 25 °C): −4.7. Anal. Calcd for $C_{44}H_{34}N_4Si$: C, 81.70; H, 5.30; N, 8.66. Found: C, 81.45; H, 5.21; N, 8.61.

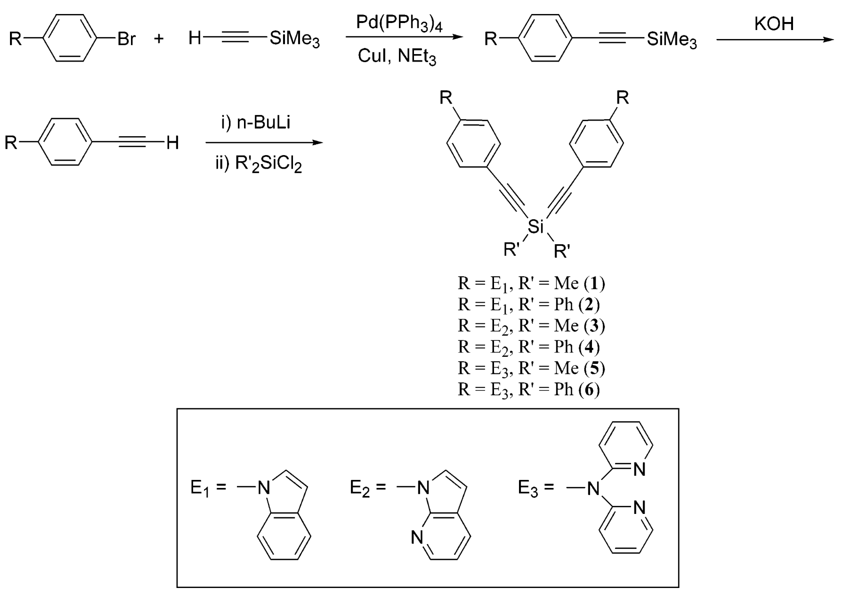
Synthesis of 1,1-Diphenyl-2,3,4,5-tetrakis(4-*N*-indoylphenyl)silole (8). A mixture of lithium (0.014 g, 2 mmol) and naphthalene (0.26 g, 2 mmol) in 2 mL of THF was stirred at room temperature under nitrogen for 3 h to form a deep dark green solution of lithium naphthalenide. A soulution of bis(4-(*N*-indolyl)phenylethynyl)diphenylsilane (**2**) (0.30 g, 0.5 mmol) in 2 mL of THF was added to the solution of lithium naphthalenide dropwise over 2 min at room temperature. After stirring for 25 min, the mixture was cooled to 0 °C. $ZnCl_2$(tmeda) (0.50 g, 2 mmol) was added as a solid to the mixture at 0 °C, followed by dilution with 5 mL of THF, to give a black suspension. After stirring for an additional hour at room temperature, a solution of 1-bromo-4-(*N*-indolyl)benzene (0.30 g, 1.1 mmol) and $PdCl_2(PPh_3)_2$ (0.02 g, 0.025 mmol) in 10 mL of THF was added. The mixture was refluxed for 14 h. After it was cooled to room temperature, 100 mL of 1 M HCl solution was added and the mixture was extracted with CH_2Cl_2. The combined extract was washed with brine and dried over $MgSO_4$, and all volatiles were removed under reduced pressure. The residue was purified by a column chromatography using ethyl acetate/hexane (1:10) as the eluent ($R_f = 0.1$) to provide **8** in 65% yield as light yellow crystals. Mp: 262−264 °C. ^1H NMR ($CDCl_3$, δ, ppm): 7.85 (dd, $J = 7.0$ Hz, $J = 1.5$ Hz, 4H), 7.69−7.65 (m, 6H), 7.57−7.44 (m, overlap, 8H), 7.36−7.25 (m, overlap, 10H), 7.22−7.11 (m, overlap, 18H), 6.68 (d, $J = 3.3$ Hz, 2H), 6.65 (d, $J = 3.3$ Hz, 2H). ^{13}C NMR ($CDCl_3$, δ, ppm): 156.27, 139.99, 138.85, 138.17, 137.56, 137.14, 136.56, 136.11, 136.02, 131.77, 131.36, 131.07, 130.82, 129.83, 129.05, 128.07, 123.98, 122.94, 121.61, 120.87, 110.98, 104.25. ^{29}Si NMR ($CDCl_3$, δ, ppm): −5.5. MS data (EI): $M^+ = 998.38$ (molecular weight = 999.31). Anal. Calcd for $C_{72}H_{50}N_4Si$: C, 86.54; H, 5.04; N, 5.61. Found: C, 86.35; H, 5.12; N, 5.57.

Synthesis of 1,1-Dimethyl-2,5-bis(4-*N*-7-azaindoylphenyl)-3,4-bis(4-*N*-indoylphenyl)silole (9). In the same manner as described for **8**, the reaction of 1,1-dimethy-2,5-dilithio-3,4-bis(4-*N*-indoylphenyl)silole (0.5 mmol) with 1-bromo-4-(*N*-7-azaindolyl)benzene (0.30 g, 1.1 mmol) provided **9** as a bright yellow solid in 32% yield. Mp: 265−268 °C. ^1H NMR ($CDCl_3$, δ, ppm): 8.43 (d, $J = 2.7$ Hz, 4H), 7.67 (d, $J = 7.8$ Hz, 4H), 7.62−7.56 (m, 4H), 7.38 (d, $J = 8.1$ Hz, 2H), 7.24−6.93 (m, overlap, 22H), 6.66 (d, $J = 3.0$ Hz, 2H), 0.62 (s, 6H). ^{13}C NMR ($CDCl_3$, δ, ppm): 154.8, 148.1, 139.01, 137.72, 137.87, 136.34, 131.91, 131.04, 129.99, 128.36, 127.05, 124.10, 123.05, 121.80, 121.02, 119.93, 119.08, 117.71, 113.47, 110.93, 104.31, 102.80, −2.64. ^{29}Si NMR ($CDCl_3$, δ, ppm): 8.6. Anal. Calcd for $C_{60}H_{44}N_6Si$: C, 82.16; H, 5.06; N, 9.58. Found: C, 81.91; H, 5.12; N, 9.61.

Synthesis of 1,1-Dimethyl-2,5-bis(*p*-2,2′-dipyridylaminophenyl)-3,4-(4-*N*-indoylphenyl)silole (10). In the same manner as described for **8**, the reaction of 1,1-dimethyl-2,5-dilithio-3,4-bis(4-*N*-indoylphenyl)silole (0.5 mmol) with *p*-(2,2′-dipyridylamino)bromobenzene (0.36 g, 1.1 mmol) provided **10** as a bright yellow solid in 42% yield. Mp: 271−273 °C. ^1H NMR ($CDCl_3$, δ, ppm): 8.37 (d, $J = 4.8$ Hz, 4H), 7.68 (d, $J = 7.5$ Hz, 2H), 7.57 (dd, $J = 9.0$, 1.8 Hz, 4H), 7.40 (d, $J = 8.1$ Hz, 2H), 7.27 (d, $J = 8.4$ Hz, 4H), 7.15−6.93 (m, overlap, 26H), 6.67 (d, $J = 3.0$ Hz, 2H), 0.63 (s, 6H). ^{13}C NMR ($CDCl_3$, δ, ppm): 158.72, 153.47, 149.24, 143.41, 142.07, 138.66, 138.30, 138.10, 136.96, 136.41, 131.94, 130.87, 130.01, 128.40, 126.84, 124.12, 123.05, 121.79, 120.99, 118.99, 117.90, 110.97, 104.27, −2.56. ^{29}Si NMR ($CDCl_3$, δ, ppm): 8.4. Anal. Calcd for $C_{66}H_{50}N_8Si$: C, 80.62; H, 5.13; N, 11.40. Found: C, 80.45; H, 5.20; N, 11.29.

Synthesis of 1,1-Dimethyl-2,5-bis{*p*-(*N*-1-naphthyl)(*N*-phenyl)aminophenyl}-3,4-bis(4-*N*-indoylphenyl)silole (11). In the same manner as described for **8**, the reaction of 1,1-dimethyl-2,5-dilithio-3,4-bis(4-*N*-indoylphenyl)silole (0.69 mmol) with 1-bromo-4-(*N*-1-naphthylphenylamino)benzene (0.57 g, 1.52 mmol) provided **11** as a bright yellow solid in 52% yield.

Scheme 1



Mp: 236−238 °C. ^{1}H NMR (CDCl$_3$, δ, ppm): 7.92 (d, $J = 8.4$ Hz, 2H), 7.88 (d, $J = 8.4$ Hz, 2H), 7.77 (d, $J = 8.1$ Hz, 2H), 7.66 (d, $J = 7.5$ Hz, 2H), 7.50−7.42 (m, 4H), 7.35 (m, 6H), 7.25−6.81 (m, overlap, 32H), 6.65 (d, $J = 3.0$ Hz, 2H), 0.54 (s, 6H). ^{13}C NMR (CDCl$_3$, δ, ppm): 158.52, 154.83, 149.22, 143.32, 134.09, 132.98, 131.22, 127.59, 126.68, 126.00, 124.62, 124.02, 121.53, 119.90, 117.74, 115.02, 110.00, 103.14, −2.52. ^{29}Si NMR (CDCl$_3$, δ, ppm): 7.6. Anal. Calcd for $C_{78}H_{58}N_4Si$: C, 86.79; H, 5.42; N, 5.19. Found: C, 86.71; H, 5.49; N, 5.24.

Synthesis of 1,1-Dimethyl-2,5-bis{4′-(*N*-1-naphthyl)(*N*-phenyl)aminobiphenyl}-3,4-bis(4-*N*-indoylphenyl)-silole (12). In the same manner as described for **8**, the reaction of 1,1-dimethyl-2,5-dilithio-3,4-bis(4-*N*-indoylphenyl)silole (0.50 mmol) with 1-bromo-4′-(*N*-1-naphthylphenylamino)biphenyl (0.55 g, 1.10 mmol) provided **12** as a bright yellow solid in 29% yield. Mp: 271−273 °C. ^{1}H NMR (CDCl$_3$, δ, ppm): 7.96 (d, $J = 8.7$ Hz, 2H), 7.91 (d, $J = 7.8$ Hz, 2H), 7.80 (d, $J = 8.1$ Hz, 2H), 7.66 (d, $J = 6.6$ Hz, 2H), 7.53−7.36 (m, overlap, 20H), 7.30−7.21 (m, 8H), 7.16−6.97 (m, overlap, 22H), 6.65 (d, $J = 3.3$ Hz, 2H), 0.59 (s, 6H). ^{13}C NMR (CDCl$_3$, δ, ppm): 158.79, 154.76, 149.25, 144.70, 139.67, 139.35, 138.51, 138.00, 130.65, 129.82, 127.94, 126.74, 124.57, 122.65, 121.40, 120.48, 113.02, 103.33, −2.87. ^{29}Si NMR (CDCl$_3$, δ, ppm): 7.7. Anal. Calcd for $C_{90}H_{66}N_4Si$: C, 87.77; H, 5.40; N, 4.55. Found: C, 87.91; H, 5.77; N, 4.70.

X-ray Crystallographic Analysis. Single crystals of **3** and **5** were obtained from a solution of CH_2Cl_2/hexane. A suitable single crystal of **8** was obtained from THF/toluene/hexane. All data were collected on a Siemens P4 X-ray diffractometer with a CCD-1000 detector, operated at 50 kV and 40 mA at ambient temperature. The data for **3**, **5**, and **8** were collected over 2θ ranges of 57.02°. No significant decay was observed during the data collection. The structural solution and refinement were performed on a PC using Siemens SHELXTL software packing (version 5.10).[14] Neutral atom scattering factors were taken from Cromer and Waber.[15] Empirical absorption correction was applied to all crystals. All structures were solved by direct methods. THF molecules were found in the crystal lattices of compound **8**. All non-hydrogen atoms were refined anisotropically. The positions of hydrogen atoms were calculated, and their contributions in structural factor calculations were included.

Quantum Yield Measurement. Quantum yields of compounds **1**−**12** were determined relative to 9,10-diphenylanthracene in CH_2Cl_2 at 298 K ($\Phi_r = 0.95$).[16] The absorptions of all the samples and the standard at the excitation wavelength were approximately 0.098−0.109. The quantum yields were calculated using previously reported procedures.[17]

CV Measurements. Cyclic voltammetry was performed using a BAS CV-50W analyzer with scan rates of 50 mV s^{-1}. The electrolytic cell was a conventional three-compartment cell, with a Pt working electrode, Pt auxiliary electrode, and Ag/AgCl reference electrode. All experiments were performed at room temperature using 0.1 M tetrabutylammonium hexaflurophosphate (TPAP) as supporting electrolyte and THF as solvent. Ferrocene ($FeCp_2^+/FeCp_2$, 0.50 V) was used as the internal standard.

Fabrication of Electroluminescent Devices. Silole **11** was applied to the single-layer EL devices. The EL device was fabricated on an indium−tin oxide (ITO) substrate. The organic layer and the metal cathode layer (LiF/Al) were deposited on the substrate by conventional vapor vacuum deposition.

Results and Discussion

Syntheses and Strucutres of Di(R-ethynyl)-dialkylsilane Compounds. The precursor compounds **1**−**6** with the general formula Si(C≡C−R)$_2$R′$_2$ were synthesized first according to Scheme 1. These compounds have a reasonable stability and have the potential for conversion to the desired 2,3,4,5-functionalized siloles. The functional groups R include *N*-indolyl, *N*-7-azaindolyl, and 2,2′-dipyridylamino, which are known to be good fluorescent chromophores; hence the resulting siloles have the potential for applications in OLEDs. Furthermore, the 7-azaindolyl and the 2,2′-dipyridylamino groups have Lewis base sites that can be used for binding to metal ions for the formation of luminescent metal-silole complexes. The functionalized acetylene molecules 4-(*N*-indolyl)phenylacetylene, 4-(*N*-7-azaindolyl)phenylacetylene, and *p*-(2,2′-dipyridylamino)-phenylacetylene were synthesized using a procedure

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[14] *SHELXTL NT Crystal Structure Analysis Package*, Version 5.10; Bruker AXS, Analytical X-ray System: Madison, WI, 1999.

[15] Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, AL, 1974; Vol. 4, Table 2.2A.

[16] Murov, S. L.; Carmichael, I.; Hug, G. L. *Handbook of Photochemistry*, 2nd ed.; Marcel Dekker: New York, 1993.

[17] Demas, N. J.; Crosby, G. A. *J. Am. Chem. Soc.* **1970**, *29*, 7262.

Table 1. Crystallographic Data for Compounds 3, 5, and 8

	3	5	8
formula	$C_{32}H_{24}N_4Si$	$C_{38}H_{30}N_6Si$	$C_{72}H_{50}N_4Si/3THF$
fw	492.64	598.77	1215.56
space group	*Cc*	$C222_1$	$P\bar{1}$
a, Å	5.428(2)	15.192(6)	13.004(11)
b, Å	22.986(10)	22.410(10)	14.475(12)
c, Å	21.607(9)	11.173(5)	18.847(16)
α, deg	90.00	90	99.195(17)
β, deg	95.415(7)	90	91.799(16)
γ, deg	90.00	90	100.804(18)
V, Å^3	2683.6(19)	3804(3)	3433(5)
Z	4	4	2
D_{calc}, g cm^{-3}	1.219	1.046	1.176
μ, cm^{-1}	0.115	0.093	0.087
$2\theta_{max}$, deg	56.58	56.70	56.72
no. of reflns measd	9258	13 429	24 250
no. of reflns used	5013	4518	15 381
(R_{int})	(0.0397)	(0.0910)	(0.0842)
no. of params	371	204	766
final *R* [$I > 2\sigma(I)$]			
R1^a	0.0714	0.0667	0.0925
wR2^b	0.2104	0.1527	0.2019
R (all data)			
R1^a	0.0864	0.2389	0.3419
wR2^b	0.2210	0.1920	0.2657
GOF on F^2	1.087	0.770	0.716

[a] $R1 = \sum|F_o| - |F_c|/\sum|F_o|$. [b] $wR2 = [\sum w[(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (0.075P)^2]$, where $P = [\mathrm{Max}(F_o^2,0) + 2F_c^2]/3$.

reported recently by our group.[13] The reaction of $SiCl_2R'_2$ (R′ = Me, Ph) with the corresponding R-phenylethynyllithium in a 1:2 ratio, which was prepared by the reaction of a corresponding R-phenylacetylene with n-BuLi at −78 °C, produced compounds **1**−**6** in good yields. Compounds **1**−**6** were fully characterized by ^1H, ^{13}C, and ^{29}Si NMR and elemental analyses. In the ^{13}C NMR spectra of **1**−**6**, the resonance at 85−105 ppm could be assigned to the C≡C carbon atoms. The ^{29}Si chemical shifts for compounds **1**−**6** (relative to TMS) are in the region of about −48 to −39 ppm, which are in the typical range of ^{29}Si NMR chemical shifts previously observed for diethynyl silicon compounds.[18] In addition to two ethynyl ligands, the Si atoms in compounds **1**, **3**, and **5** are coordinated by two methyl groups, while the Si atoms in **2**, **4**, and **6** are bound by two phenyl groups. As a consequence, **1**, **3**, and **5** display almost identical ^{29}Si chemical shifts (−39.1, −39.2, and −39.4 ppm, respectively). The ^{29}Si chemical shifts of **2**, **4**, and **6** are also nearly identical (−47.9, −47.9, −48.1 ppm, respectively), but substantially shifted upfield, compared to those of **1**, **3**, and **5**. Clearly the phenyl ligand enhances the electron density on the Si atom, compared to the methyl ligand.

Single crystals of compounds **3** and **5** were obtained, and their structures were determined by single-crystal X-ray diffraction analyses. The crystal data are given in Table 1. Selected bond distances and angles are given in Table 2. Both compounds crystallize in chiral space groups (*C*c and $C222_1$). The structures of **3** and **5** are shown in Figures 1 and 2, respectively. One of the phenyl rings (C3) in **3** is rotationally disordered over two sites with an occupancy factor for each site being 50%. Only one of the disordered rings is shown in Figure 1. Compound **5** possesses a crystallogrpahically imposed C_2 symmetry. Both compounds have a typical tetrahedral geometry and similar bond angles. The Si−C (C≡C) bonds in both compounds are somewhat longer than the Si−C (methyl) bonds. One interesting difference between **3** and **5** is that the Si−C bonds in **3** are all longer than the corresponding ones in **5**, the cause of which is not obvious. The bond distances of the ethynyl portion in both molecules are similar. The ethynyl ligand is linearly bound to the Si atom in both compounds.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 3, 5, and 8

Compound **3**			
Si(1)−C(1)	1.832(5)	Si(1)−C(16)	1.827(5)
Si(1)−C(31)	1.860(5)	Si(1)−C(32)	1.848(5)
C(1)−C(2)	1.213(7)	C(2)−C(3)	1.438(6)
C(16)−C(17)	1.214(7)	C(17)−C(18)	1.446(6)
N(1)−C(6)	1.424(5)	N(3)−C(21)	1.412(6)
C(1)−Si(1)−C(16)	108.6(2)	C(31)−Si(1)−C(32)	112.6(3)
C(16)−Si(1)−C(31)	108.0(2)	C(1)−Si(1)−C(31)	109.3(2)
C(1)−Si(1)−C(32)	108.5(2)	C(16)−Si(1)−C(32)	109.8(3)
C(2)−C(1)−Si(1)	177.4(4)	C(17)−C(16)−Si(1)	178.2(4)
Compound **5**			
Si(1)−C(1)	1.791(6)	Si(1)−C(19)	1.834(5)
C(1)−C(2)	1.221(7)	C(2)−C(3)	1.453(7)
N(3)−C(6)	1.404(6)		
C(1)−Si(1)−C(1′)	106.6(3)	C(1)−Si(1)−C(19)	108.6(2)
C(1′)−Si(1)−C(19)	110.3(2)	C(19)−Si(1)−C(19′)	112.4(4)
C(2)−C(1)−Si(1)	177.4(5)		
Compound **8**			
Si(1)−C(1)	1.865(5)	Si(1)−C(4)	1.861(5)
Si(1)−C(57)	1.858(6)	Si(1)−C(63)	1.862(6)
C(1)−C(2)	1.349(6)	C(2)−C(3)	1.513(7)
C(3)−C(4)	1.342(6)	C(1)−C(5)	1.473(7)
C(2)−C(18)	1.478(7)	C(4)−C(44)	1.487(7)
C(10)−N(1)	1.430(7)	C(21)−N(3)	1.424(7)
C(34)−N(5)	1.434(7)	C(47)−N(7)	1.425(8)
C(1)−Si(1)−C(4)	91.9(3)	C(57)−Si(1)−C(63)	109.5(3)
Si(1)−C(1)−C(2)	108.4(4)	C(1)−C(2)−C(3)	115.2(5)
Si(1)−C(1)−C(5)	125.5(4)	Si(1)−C(4)−C(44)	124.1(4)
C(57)−Si(1)−C(4)	117.7(3)	C(4)−Si(1)−C(63)	111.4(3)
C(57)−Si(1)−C(1)	110.4(3)		

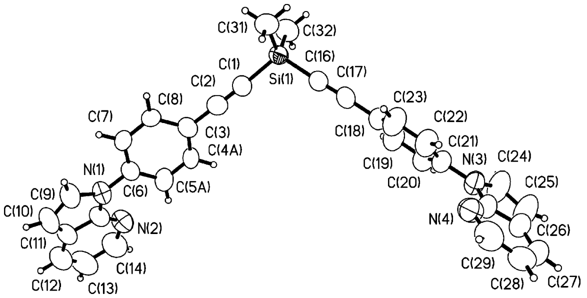

Figure 1. Diagram showing the molecular structure of **3** with labeling scheme.

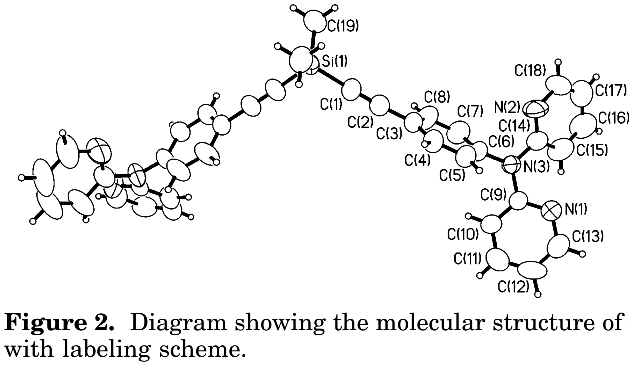

Figure 2. Diagram showing the molecular structure of **5** with labeling scheme.

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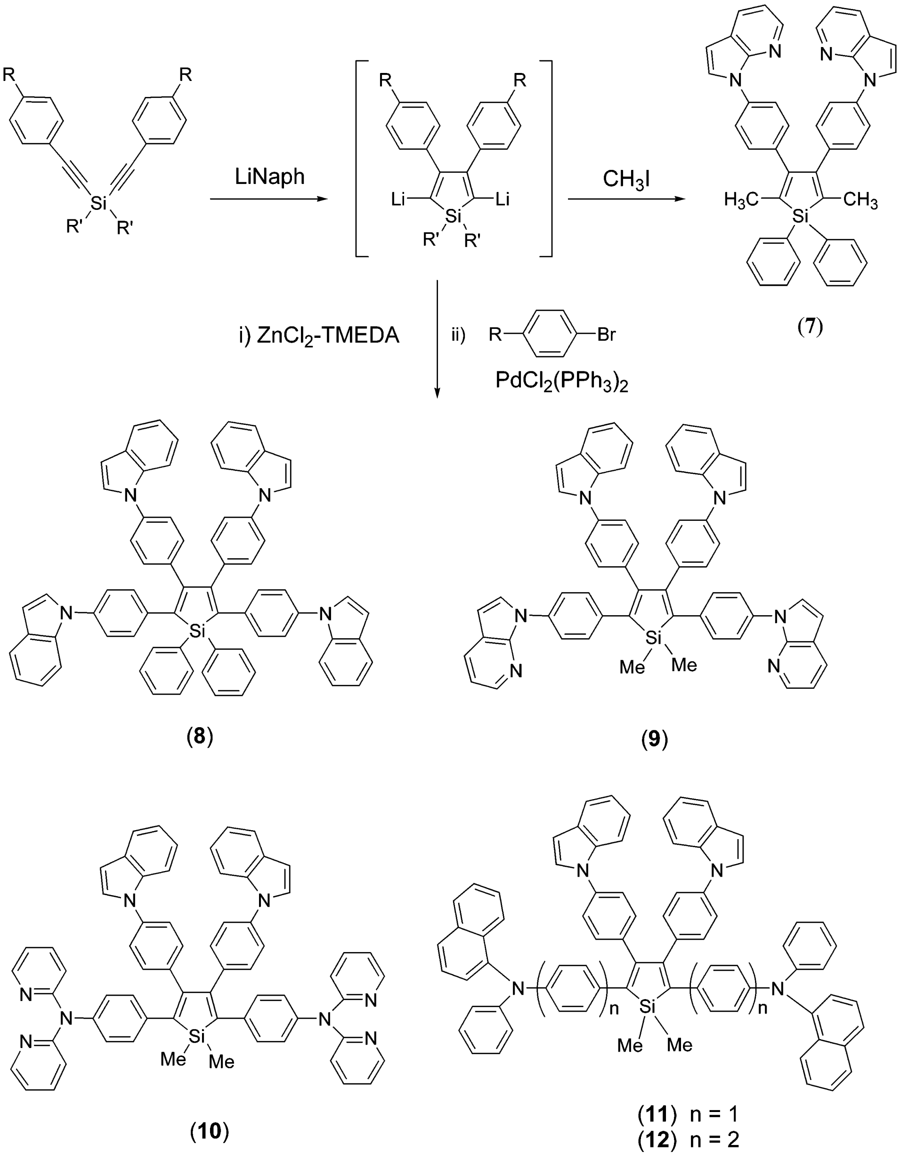
(18) (a) Yanmaguchi, S.; Jin, R.-Z.; Tamao, K. *Organometallics* **1997**, *16*, 2230. (b) Wong, W. Y.; Wong, C. K.; Lu, G. L.; Lee, A. W. M.; Cheah, K. W.; Shi, J. X. *Macromolecules* **2003**, *36*, 983.

Scheme 2



Syntheses and Structures of Silole Compounds. By using the diethynylsilane compounds Si(ethynyl-R)$_2$R′$_2$, **1**, **2**, and **4**, as the starting materials and a modified literature procedure,[9] six new 2,3,4,5-tetrafunctionalized siloles, **7**−**12**, have been synthesized for the present study (Scheme 2). Compounds **1**, **2**, and **4** were found to be an efficient reactant for the intramolecular reductive cyclization in an endo-endo mode upon treatment with lithium naphthalenide (LiNaph) to form 2,5-dilithiosiloles. The subsequent cross-coupling reactions catalyzed by Pd(PPh$_3$)$_2$Cl$_2$ with the corresponding arylbromides prepared by our methods reported recently[12c,13] produced the 2,3,4,5-tetra-aryl-functionalized silole compounds **8**−**12** in moderate yields. The 2,5-dimethyl-3,4-di-7-azaindolylphenyl-functionalized silole **7** was obtained by the methylation of the corresponding 2,5-dilithiosilole. Attempts to use bis(2,2′-dipyridylamino)phenylethynylsilanes **5** and **6** as the starting materials to synthesize the corresponding tetrafunctionalized siloles by the same procedure as for **7** and **8**−**12** were unsuccessful, perhaps due to steric hindrance by the relatively bulky 2,2-dipyridylamino groups in the intramolecular cyclization step. **7**−**12** were fully characterized by ^{1}H, ^{13}C, and ^{29}Si NMR and elemental analyses. These new siloles are fairly stable upon exposure to air and moisture in solution and in the solid state. In the ^{13}C NMR spectrum of **7**−**12**, two peaks at ∼150 ppm could be assigned to the carbon atoms on the five-membered silole ring. The ^{29}Si NMR signals (−5 to 8 ppm) of compounds **7**−**12** are compatible with the ^{29}Si chemical shifts reported previously for related silole compounds and are all shifted downfield considerably, compared to those of the starting material compounds **1**, **2**, and **4**. The 1,1-diphenyl siloles **7** and **8** display a negative but similar ^{29}Si chemical shift (−4.7 and −5.5 ppm, respectively), while the 1,1-dimethyl siloles **9**−**12** all display a positive but similar ^{29}Si chemical shift (8.6, 8.4, 7.6, and 7.7 ppm, respectively). This trend is consistent with that observed in the silane compounds **1**−**6**. The four silole compounds **8**−**12** display a high thermal stability with a melting point above 230 °C. In contrast, the 2,5-dimethyl silole **7** has the lowest molecular weight and consequently has the lowest melting point, 110 °C, among the six new silole compounds.

A single crystal of compound **8** was obtained, and its structure was determined by single-crystal X-ray dif-

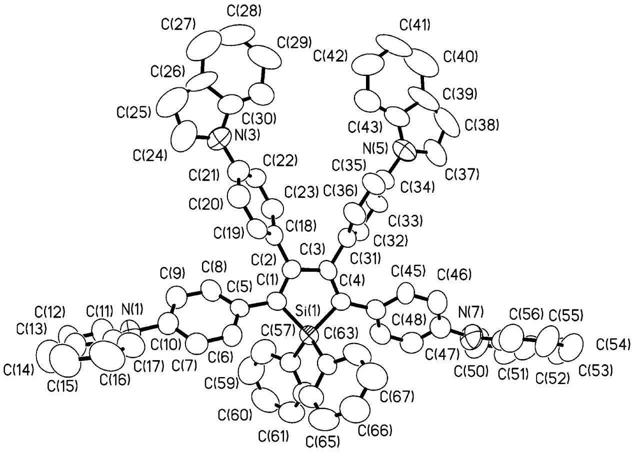


Figure 3. Diagram showing the structure of **8** with labeling scheme.

fraction analysis. The crystal data are given in Table 1. Selected geometrical parameters for this compound are given in Table 2. The structure of **8** is shown in Figure 3. The Si atom has an approximate tetrahedral geometry with four similar Si−C bond lengths that are typical for siloles.[9b,19] The central silole ring in **8** is planar. The indolyl-functionalized phenyl groups at the 3,4-positions in **8** are not coplanar with the central five-membered ring (their dihedral angles with the silole ring are 49.0° and 57.5°, respectively). The indolyl-functionalized phenyl groups at the 2,5-positions are also not coplanar with the central ring, but have significantly smaller dihedral angles with the central ring (45.5° and 46.2°, respectively), consistent with related 2,5-difunctionalized structures reported previously.[10] No significant intermolecular interactions in the solid state were observed for **8**.

Luminescent Properties. Table 3 summarizes the absorption and photoluminescent data of **1**−**12**. The UV−vis spectra of compounds **1**−**6** exhibit an intense absorption band between 242 and 368 nm, indicating that electronic transitions are mostly $\pi-\pi^*$, originating from the arylacetylide ligands as previously reported in related ethynylsilanes.[20] Upon irradiation by UV light at ambient temperature, compounds **1**−**6** emit a violet-blue color with the emission maximum ranging from 357 to 389 nm in solution and 380 to 442 nm in the solid state. The general trend is that in solution the 7-azaindolyl-functionalized molecules **3** and **4** have the shortest emission wavelength, while the indolyl-functionalized molecules **1** and **2** have the longest emission wavelength, consistent with the assignment of a $\pi-\pi^*$ transition involving the heterocyclic functional groups. The same trend of emission energy was also observed on *N*,*N*-chelate boron compounds that contain either the 7-azaindolyl or the indolyl groups.[21] The emission spectra of compounds **1**−**3** in the solid state match approximately those in solution, while the emission spectra of **4**−**6** in the solid state are substantially red-shifted compared to the solution emission spectra. The crystal structure of **5** did not reveal any significant $\pi-\pi$ intermolecular interactions. Instead, there is a significant intermolecular hydrogen-bonding interaction between the pyridyl nitrogen atom N(2) and the proton H(12A′) on C(12′) from a pyridyl group of the neighboring molecule. It is possible that such intermolecular interaction may be responsible for the red-shift of emission energy.

Table 3. Photoluminescent Data for Compounds 1−12[a]

	λ_{max}, nm			quantum yield[c] (Φ_{em})	conditions
	UV/vis[b]	excitation	emission		
1	276, 318	331	389	0.21	CH_2Cl_2, 298 K
		335	400		solid, 298 K
2	274, 322	346	395	0.53	CH_2Cl_2, 298 K
		337	384		solid, 298 K
3	282, 296	322	365	0.17	CH_2Cl_2, 298 K
		330	380		solid, 298 K
4	286, 306	324	357	0.16	CH_2Cl_2, 298 K
		385	427		solid, 298 K
5	310, 368	346	378	0.10	CH_2Cl_2, 298 K
		394	442		solid, 298 K
6	242, 332	346	373	0.35	CH_2Cl_2, 298 K
		363	408		solid, 298 K
7	272, 298	350	438	0.06	CH_2Cl_2, 298 K
		396	445		solid, 298 K
8	264, 388	395	517	0.02	CH_2Cl_2, 298 K
		395	527		solid, 298 K
9	304, 394	397	518	0.02	CH_2Cl_2, 298 K
		418	520		solid, 298 K
10	262, 394	395	516	0.02	CH_2Cl_2, 298 K
		396	521		solid, 298 K
11	298, 370, 422	466	538	0.07	CH_2Cl_2, 298 K
		466	545		solid, 298 K
12	260, 330	448	530	0.06	CH_2Cl_2, 298 K
		466	548		solid, 298 K

[a] Concentration: [M] = 5×10^{-6}. [b] In CH_2Cl_2 at 298 K. [c] Relative to 9,10-diphenylanthracene in CH_2Cl_2 at ambient temperature.

The UV−vis spectrum of **7** has two absorption bands at 272 and 298 nm, respectively. In contrast, the UV−vis spectra of siloles **8**−**12** exhibit two intense absorption bands with λ_{max} at 260−298 and ~330−394 nm, respectively. The first absorption band is attributed to the $\pi-\pi^*$ transition of the functionalized aryl groups, and the second absorption band is attributed to the $\pi-\pi^*$ transition of the silole ring, based on the assignment of previously reported silole compounds.[4c,9b,10] Compound **7** is colorless. The second absorption band of **8**−**12** extends into the visible region and tails off at about 520 nm, which can account for the yellow color of compounds **8**−**12**. Upon irradiation by UV light, compounds **8**−**12** display green-yellow emission in solution and in the solid state at ambient temperature. In contrast, compound **7** displays a blue emission color in solution and the solid state, which is unique among the six silole compounds reported herein. Compound **7** has the same composition as that of 1,1-dimethyl-2,5-bis(*N*-7-azaindolylphenyl)-3,4-diphenylsilole (**7a**) reported recently by our group.[10] However, **7a** emits at λ_{max} = ~500 nm, about 60 nm red-shifted, compared to that of **7**, which can be clearly explained by the structural difference between these two molecules. **7** has no aryl groups at the 2,5-positions, while **7a** has two *N*-7-azaindolylphenyl groups at the 2,5-positions. Because the aryl groups at the 2,5-positions have much less steric interactions, thus

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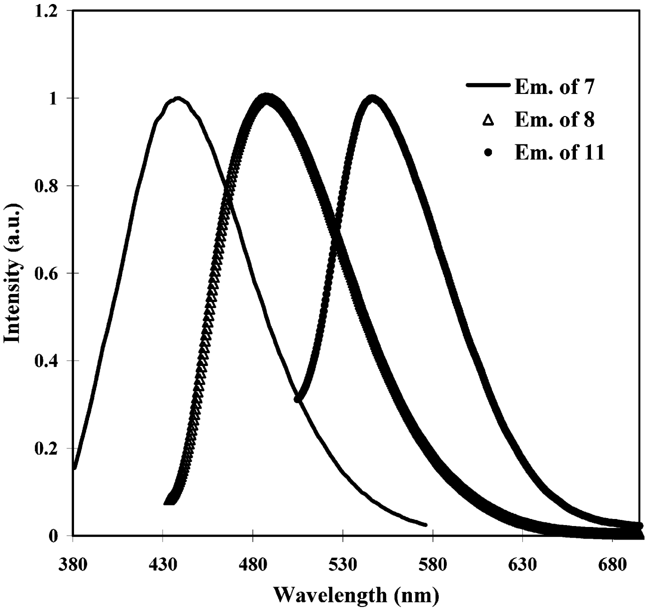

Figure 4. Emission spectra of compounds **7**, **8**, and **11** in the solid state.

can conjugate with the central five-membered silole ring much more effectively than the aryl groups at the 3,4-positions, **7a** emits at a longer wavelength than **7** does. The same argument can also be applied to the emission color difference between **7** and compounds **8**–**12** (which all contain aryl groups at the 2,5-positions). The emission spectra of **7**, **8**, and **11** are shown in Figure 4 as representative examples. The emission spectra of **7**–**12** indicate the possibility of tuning the luminescence of siloles by varying the positions of the aryl substituent groups on the silole ring. Photoluminescent efficiencies of the siloles in solution were determined to be 0.02–0.07, which are typical, compared to those of previously reported silole compounds.[6b,9b,10] It has been reported by several groups[5c,6d] that siloles have much higher PL efficiencies in film forms or in the solid state than in solution. Unfortunately we do not have the facility to measure the PL efficiency of films and solids for our new compounds.

Electroluminescence (EL). Previously we have reported the electroluminescent properties of 2,5-difunctionalized silole compounds containing either 2,2-dipyridylamino or 7-azaindolyl groups. In this study, we focused the electroluminescent property study on compound **11** because the (*N*-1-naphthyl)phenylamino group[22] in **11** and **12** is known to be able to transport holes and the silole ring is known to transport electrons in EL devices.[9,10] Molecules **11** and **12** therefore possess both hole- and electron-transport groups, in addition to being an emitter, which may enable the achievement of electroluminescence by using a simple single-layer or a double-layer device structure. The LUMO and HOMO levels for **11** were determined by electrochemical analysis (CV mode) and UV/vis spectra. The LUMO and HOMO levels for silole **11** are −2.6 and −5.0 eV, respectively. These values are comparable to the LUMO level of Alq_3, a well-known electron-transport material,[23] and the HOMO level of *N*,*N*′-di-1-naphthyl-*N*,*N*′-diphenylbenzidine (NPB), a well-known hole-transport material,[22] indicating their potential as both electron- and hole-transport materials. To test this idea, a single-layer EL device with compound **11** being sandwiched between the ITO anode and the LiF/Al cathode (ITO/**11** (80 nm)/LiF (1 nm)/Al) was fabricated. As shown by I–V and L–V curves in Figure 5, the turn-on voltage of the single-layer device was ~10 V. At 30 V, the device had a brightness of ~350 cd/m^2, indicating that the silole-based single-layer device is moderately bright and efficient. At all biased voltages in the range 10–30 V, we observed the emission peak of a light yellow color. However, the EL spectrum (λ_{max} = 560 nm) was substantially red-shifted, compared to the PL spectrum of **11**, as shown in Figure 4. We have examined the PL spectra of **11** in film form and in powder form. There is no difference between the PL spectra recorded. The origin of the EL red-shift has not been understood. With further optimization, the device performance could be

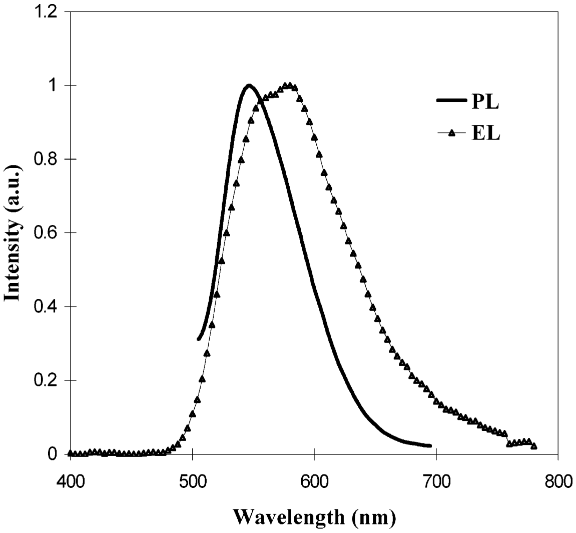

Figure 5. PL spectrum of **11** and the EL spectrum of the device.

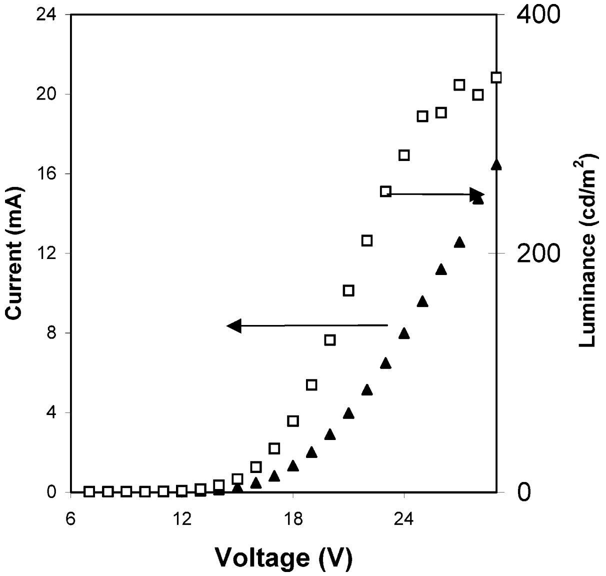

Figure 6. I–V and L–V characteristics of the EL device.

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improved substantially. Extended investigation and further optimization on the EL devices based on the new siloles **7**−**12** are being carried out in our laboratory and will be reported in due course.

In summary, we have synthesized a series of new diethynylsilane compounds based on indolyl, 7-azaindolyl, and 2,2′-dipyridylamino, some of which are efficient reactants for the intramolecular reductive cyclization for the generation of new siloles. New 2,3,4,5-tetrafunctionalized silole compounds **8**−**12** by heterocyclic groups such as indolyl, 7-azaindolyl, 2,2′-dipyridylamino, and (*N*-1-naphthyl)(*N*- phenyl)amino have been achieved. Our investigation has shown that it is possible to tune the emission color of siloles by varying the positions of the aryl substituents on the silole ring. A new silole compound, **11**, that possesses both a hole- and an electron-transport functionality has been successfully applied to a single-layer electroluminescent device, which produced a moderate yellow-green emission, an indication that the new silole compounds **11** and **12** may be able to function as either a bifunctional molecule (an emitter and a hole- or electron-transport layer) or a trifunctional molecule (an emitter, a hole-transport and an electron-transport layer) in EL devices. The full potential of the new silole compounds for applications in OLEDs needs to be further investigated.

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

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