Photoluminescence, Electroluminescence, and Complex Formation of Novel *N*-7-Azaindolyl- and 2,2′-Dipyridylamino-Functionalized Siloles

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New silole compounds based on the 7-azaindolyl and 2,2′-dipyridylamino groups, 1,1-dimethyl-2,5-bis(4-*N*-7-azaindolylphenyl)-3,4-diphenylsilole (**1**), 1,1-dimethyl-2,5-bis(4′-*N*-7-azaindoylbiphenylyl)-3,4-diphenylsilole (**2**), 1,1-dimethyl-2,5-bis(*p*-2,2′-dipyridylaminophenyl)-3,4-diphenylsilole (**3**), and 1,1-dimethyl-2,5-bis(*p*-2,2′-dipyridylaminobiphenylyl)-3,4-diphenylsilole (**4**), have been synthesized and structurally characterized. These new silole compounds are capable of binding to metal ions as demonstrated by the zinc(II) complex **5** obtained from the reaction of **3** with $Zn(O_2CCF_3)_2(H_2O)_3$, where **3** functions as a bridging-chelating ligand to zinc(II) ions. The structure of siloles **1** and **3**, and complex **5** were determined by single-crystal X-ray diffraction analyses. Compound **5** displays an extended 1D polymer structure in the solid state with alternating molecules of **3** and a dinuclear unit of $Zn_2(O_2CCF_3)_4(H_2O)$. Compounds **1**−**4** are bright green emitters in solution and in the solid state with emission λ_{max} at 506, 511, 519, and 516 nm, respectively. In contrast, the emission maximum of complex **5** is blue-shifted ($\lambda_{max} = 488$ nm), which is attributed to the disruption of the conjugation of the functionalized phenyl rings with the central silole ring by zinc(II) coordination, as revealed by X-ray diffraction analysis. Electroluminescent devices using compounds **1** and **3** as the emitting layer and the electron-transporting layer have been fabricated successfully.

Organic light-emitting diodes (OLEDs) have attracted a great deal of attention recently due to their promising applications in electroluminescent displays.[1,2] OLEDs are generally composed of thin multilayers of hole-transporting (HT), emissive, and electron-transporting (ET) materials sandwiched between two electrodes.[1a,b,2b] The efficiency of OLEDs primarily depends on the quantities of the injected carriers, holes, and electrons and the quantum yield of the emissive material. The development of efficient one- or two-layer OLEDs is still a challenge, due to the limited availability of molecules that can function as an emitter and as well as either a hole- or an electron-transport material.[3−6] We have recently demonstrated that ligands containing 7-azaindoyl and 2,2′-dipyridylamino groups can produce bright blue fluorescence when bound to B(III) or Al(III) centers. Some of the boron and aluminum compounds have been used successfully as emitters in OLEDs.[7] Organosilicon compounds have become the focus of our recent research effort after several recent reports indicated that organosilicon compounds, especially siloles, show excellent properties as emitters or as electron-transporting materials in OLEDs.[8] Previous reports suggested that siloles can serve as an efficient electron-

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transporting materials in OLEDs,[8c,9c] because they possess low-lying LUMO energy levels associated with the $\sigma^*-\pi^*$ conjugation, arising from the interaction between the σ^* orbital of two exocyclic Si−C σ-bonds and the π^* orbital of the butadiene moiety.[9] In this paper, we present a new class of silole compounds for EL applications based on 7-azaindolylaryl and 2,2′-dipyridylaminoaryl groups. The 7-azaindolyl and 2,2′-dipyridylamino functional groups have open coordinate sites from the nitrogen atoms, making binding to metal centers possible, to generate luminescent metal complexes that may be useful in various applications.[7d,10] Herein we report our investigation on novel silole molecules that are 2,5-functionalized by 7-azaindolylphenyl, 7-azaindolylbiphenylyl, 2,2′-dipyridylaminophenyl, and 2,2′-dipyridylaminobiphenylyl and on their use in electroluminescent devices and as building blocks in the assembly of luminescent supramolecular structures.

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. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance 300 (300 MHz for ^{1}H and 75.3 MHz for ^{13}C) spectrometer. ^{29}Si NMR spectra were also recorded on a Bruker Advance 500 (99.4 MHz for ^{29}Si) spectrometer using tetramethylsilane as the external reference. 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. Emission lifetimes were measured on a Photon Technology International Phosphorescent lifetime spectrometer, a Timemaster C-631F equipped with a Xenon flash lamp, and digital emission photon multiplier tube using a band path of 2 nm for both excitation and emission. Redox potentials were measured by using a THF solution on a CV-50W BAS voltammetric analyzer by using a Ag/AgCl electrode as the reference electrode and platinum electrode as the working electrode. Mass spectra were recorded on a VG Quattro mass spectrometer using the electron ionization mode. Elemental analyses were performed by Canadian Microanalytical Service Ltd., Delta, British Columbia, Canada. 1-Bromo-4-(*N*-7-azaindolyl)benzene, 1-bromo-4′-(*N*-7-azaindolyl)biphenyl, *p*-(2,2′-dipyridylamino)bromobenzene, and *p*-(2,2′-dipyridylamino)bromobiphenyl were synthesized using a modified literature method.[12] Bis(phenylethynyl)dimethylsilane was prepared by the reaction of dimethyldichlorosilane and phenylacetylide lithium, which was prepared from the reaction of phenylacetylene with *n*-BuLi. ^{1}H NMR in $CDCl_3$ (δ, ppm, 25 °C): 7.56−7.53 (m, 4H), 7.35−7.33 (m, 6H), 0.52 (s, 6H). ^{13}C NMR in $CDCl_3$ (δ, ppm, 25 °C): 132.83, 129.54, 128.90, 123.39, 106.62, 91.33, 1.19. ^{29}Si NMR in $CDCl_3$ (δ, ppm, 25 °C): −39.3.

Synthesis of 1,1-Dimethyl-2,5-bis(4-*N*-7-azaindolylphenyl)-3,4-diphenylsilole (1). 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 naphthaleneide. A solution of bis(phenylethynyl)dimethylsilane (0.13 g, 0.5 mmol) in 2 mL of THF was added to the solution of lithium naphthaleneide dropwise over 2 min at room temperature. After stirring for 15 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*-7-azaindolyl)benzene (0.3 g, 1.1 mmol) and $PdCl_2(PPh_3)_2$ (0.02 g, 0.025 mmol) in 5 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 = 0.2) to provide **1** in 40% yield as a light yellow crystals. Mp: 276−278 °C. ^{1}H NMR ($CDCl_3$, δ, ppm): 8.40 (dd, J = 4.5 Hz, J = 1.2 Hz, 2H), 7.97 (dd, J = 8.4 Hz, J = 1.2 Hz, 2H), 7.60 (d, J = 8.4 Hz, 4H), 7.49 (d, J = 4.0 Hz, 2H), 7.16−7.10 (m, overlap, 6H), 7.07−7.05 (m, 6H), 6.91−6.89 (m, 4H), 6.60 (d, J = 3.6 Hz, 2H), 0.85 (s, 6H). ^{13}C NMR ($CDCl_3$, δ, ppm): 155.0, 144.1, 141.5, 139.5, 138.3, 136.8, 130.7, 130.5, 129.7, 128.4, 127.0, 123.7, 122.4, 117.3, 102.2, −2.91. ^{29}Si NMR ($CDCl_3$, δ, ppm): 8.2. MS data (EI): M^+ = 646.3 (molecular weight = 646.87). Anal. Calcd for $C_{44}H_{34}N_4Si$: C, 81.70; H, 5.30; N, 8.66. Found: C, 81.85; H, 5.27; N, 8.66.

Synthesis of 1,1-Dimethyl-2,5-bis(4′-*N*-7-azaindolylbiphenylyl)-3,4-diphenylsilole (2). In the same manner as described for **1**, the reaction of 2,5-dilithio-3,4-diphenylsilole (1.15 mmol) with 1-bromo-4′-(*N*-7-azaindolyl)biphenyl (0.88 g, 2.52 mmol) provided **2** as a bright yellow solid in 58% yield. Mp: 261−264 °C. ^{1}H NMR ($CDCl_3$, δ, ppm): 8.42 (dd, J = 4.5, 1.2 Hz, 2H), 8.01 (dd, J = 7.8, 1.5 Hz, 2H), 7.83 (d, J = 8.7 Hz, 4H), 7.72 (d, J = 8.7 Hz, 4H), 7.57 (d, J = 3.9 Hz, 2H), 7.44 (d, J = 8.4 Hz, 4H), 7.17 (dd, J = 9.0, 4.8 Hz, 2H), 7.09−7.05 (m, 10H), 6.92−6.89 (m, 4H), 6.67 (d, J = 3.6 Hz, 2H), 0.61 (s, 6H). ^{13}C NMR ($CDCl_3$, δ, ppm): 155.01, 148.25, 144.29, 141.84, 139.67, 139.62, 139.43, 138.15, 138.03, 135.39, 130.66, 130.12, 129.77, 128.76, 128.63, 128.34, 127.18, 124.70, 122.33, 117.40, 102.41, −2.77. ^{29}Si NMR ($CDCl_3$, δ, ppm): 8.1. MS data (EI): M^+ = 798.2 (molecular weight = 799.07). Anal. Calcd for $C_{56}H_{42}N_4Si$: C, 84.18; H, 5.30; N, 7.01. Found: C, 83.26; H, 5.24; N, 0.6.91.

Synthesis of 1,1-Dimethyl-2,5-bis(*p*-2,2′-dipyridylaminophenyl)-3,4-diphenylsilole (3). In the same manner as described for **1**, the reaction of 2,5-dilithio-3,4-diphenylsilole (0.5 mmol) with *p*-(2,2′-dipyridylamino)bromobenzene (0.36 g, 1.1 mmol) provided **3** as a bright yellow crystals in 38% yield. Mp: 273−274 °C. ^{1}H NMR ($CDCl_3$, δ, ppm): 8.33 (dd, J = 4.5, 1.8 Hz, 4H), 7.55 (dd, J = 6.9, 2.1 Hz, 4H), 7.05−7.02 (m, overlap, 8H), 6.95−6.92 (m, overlap, 14H), 6.88−6.84 (m, 4H), 0.56 (s, 6H). ^{13}C NMR ($CDCl_3$, δ, ppm): 158.77, 154.87, 149.16, 143.05, 141.02, 139.92, 138.17, 132.85, 130.83, 130.54, 128.18, 126.91, 126.75, 118.80, 117.83, −2.47. ^{29}Si NMR ($CDCl_3$, δ, ppm): 7.8. MS data (EI): M^+ = 752.2 (molecular weight = 753.00). Anal. Calcd for $C_{50}H_{40}N_6Si$: C, 79.76; H, 5.35; N, 11.16. Found: C, 79.23; H, 5.59; N, 10.65.

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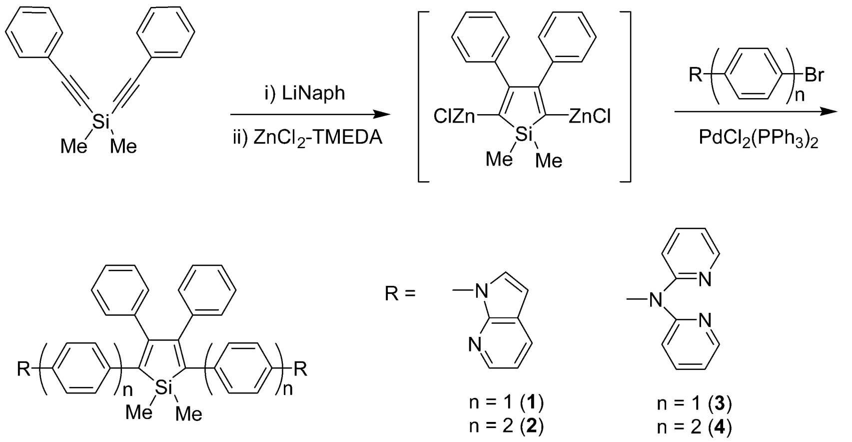
Scheme 1



Synthesis of 1,1-Dimethyl-2,5-bis(*p*-2,2′-dipyridylaminobiphenylyl)-3,4-diphenylsilole (4). In the same manner as described for **1**, the reaction of 2,5-dilithio-3,4-diphenylsilole (0.5 mmol) with *p*-(2,2′-dipyridylamino)bromobiphenyl (0.44 g, 1.1 mmol) provided **4** as a bright yellow solid in 34% yield. Mp: 278−281 °C. ^{1}H NMR (CDCl$_3$, δ, ppm): 8.36 (dd, $J = 4.5$, 1.8 Hz, 4H), 7.61−7.56 (m, overlap, 12H), 7.39 (d, $J = 8.4$ Hz, 4H), 7.23 (d, $J = 8.4$ Hz, 4H), 7.07−7.00 (m, overlap, 10H), 6.96 (dd, $J = 7.2$, 5.0 Hz, 4H), 6.89−6.86 (m, 4H), 0.58 (s, 6H). ^{13}C NMR (CDCl$_3$, δ, ppm): 158.81, 154.89, 149.27, 144.68, 141.86, 139.67, 139.40, 138.54, 138.11, 130.65, 130.02, 128.60, 128.21, 127.86, 127.04, 126.95, 118.87, 117.78, −2.82. ^{29}Si NMR (CDCl$_3$, δ, ppm): 8.0. MS data (EI): M$^+$ = 904.2 (molecular weight = 905.20). Anal. Calcd for $C_{62}H_{48}N_6Si$: C, 82.27; H, 5.34; N, 9.28. Found: C, 82.03; H, 5.32; N, 9.11.

Synthesis of [Zn$_2$(O$_2$CCF$_3$)$_4$(H$_2$O)(3)] (5). To a solution of Zn(CF$_3$COO)$_2$·3H$_2$O (0.087 g, 0.3 mmol) in THF (10 mL) was added **3** (0.11 g, 0.15 mmol). The mixture was stirred overnight. After filtration using filter agent, the yellow solution was concentrated under reduced pressure. The solution was layered with toluene and hexane, yielding colorless crystals in 52% yield. Mp: 158−161 °C. ^{1}H NMR (CD$_2$Cl$_2$, δ, ppm): 8.66 (d, $J = 3.9$ Hz, 4H), 7.82 (dd, $J = 8.1$, 1.8 Hz, 4H), 7.31−7.24 (m, overlap, 14H), 7.14−7.08 (m, overlap, 4H), 6.97−6.92 (m, 4H), 6.79 (d, $J = 8.7$ Hz, 4H), 0.65 (s, 6H). ^{13}C NMR (CD$_2$Cl$_2$, δ, ppm): 156.76, 147.72, 142.09, 139.42, 138.72, 132.32, 130.54, 130.30, 128.16, 127.47, 119.87, 118.02, −3.95. Anal. Calcd for $C_{58}H_{42}F_{12}N_6O_9SiZn_2$: C, 52.15; H, 3.02; N, 6.29. Found: C, 52.09; H, 3.08; N, 6.20.

X-ray Crystallography Analysis. Single crystals of **1** and **3** were obtained from ethyl acetate/hexanes. A single crystal of compound **5** was obtained from solvent diffusion of THF/toluene/hexanes. All data were collected on a Siemens P4 X-ray diffractometer with a smart CCD 1000 detector, operated at 50 kV and 40 mA at ambient temperature for **1** and **3** and at 77 K for **5**. The data for **1**, **3**, and **5** 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 package (version 5.10).[13] Neutral atom scattering factors were taken from Cromer and Waber.[14] Empirical absorption correction was applied to all crystals. All structures were solved by direct methods. Toluene and THF molecules were found in the crystal lattices of compound **5**. All non-hydrogen atoms were refined anisotropically. The positions of hydrogen atoms were calculated, and their contributions in structural factor calculations were included. The crystal data are summarized in Table 1. Selected bond lengths and angles for **1**, **3**, and **5** are given in Table 2.

Quantum Yield Measurement. Quantum yields of compounds **1**−**5** were determined relative to 9,10-diphenylanthracene in CH$_2$Cl$_2$ at 298 K ($\Phi = 0.95$).[15] The absorbance of all the samples and the standard at the excitation wavelength were approximately 0.098−0.109. The quantum yields were calculated using previously known procedures.[16]

Fabrication of Electroluminescent Devices. The EL device using compounds **1** and **3** as the emitting layer and the electron-transport layer was fabricated on an indium−tin oxide (ITO) substrate. Organic layers and the metal cathode layer were deposited on the substrate by conventional vapor vacuum deposition. *N*,*N*′-Di-1-naphthyl-*N*,*N*′-diphenylbenzidine (NPB) and 4,4′-dicarbazolyl-1,1′-biphenyl (CPB) were employed as the hole-transport layer and hole-blocking layer, respectively.

Results and Discussion

Syntheses and Properties of Silole Compounds. Four new silole derivatives, **1**−**4**, have been synthesized for the present study. They were synthesized by a one-pot process using bis(phenylethynyl)silane as the starting material and a modified literature procedure.[9b−9d] Intramolecular reductive cyclization of bis(phenylethynyl)silane, followed by a palladium-catalyzed cross-coupling reaction with the corresponding aryl bromides (Scheme 1) prepared by methods[12] we recently developed produced compounds **1**−**4** in good yields. **1**−**4** were characterized by ^{1}H, ^{13}C, and ^{29}Si NMR, mass spectroscopy, and elemental analyses. The new silole compounds are fairly stable upon exposure to air and moisture in solution and in the solid state. In the ^{13}C NMR spectrum of **1**−**4**, two peaks at about 158 and 154 ppm could be assigned to the carbon atoms on the five-membered silole ring. The ^{29}Si NMR signal (~8 ppm) of compounds **1**−**4** is shifted downfield considerably, compared to that of the starting material bis(phenylethynyl)dimethylsilane (−39 ppm). All four silole compounds display a high thermal stability with a melting point above 260 °C. DSC and TGA measurements indicate that these compounds do not undergo thermal decomposition to at least 300 °C. Single crystals of compounds **1** and **3** were obtained and their structures were determined by single-crystal X-ray diffraction analyses. The crystal data are given in Table 1. Selected geometrical parameters for these compounds are given in Table 2.

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

	1	**3**	**5**
formula	$C_{44}H_{34}N_4Si$	$C_{50}H_{40}N_6Si$	$C_{58}H_{42}F_{12}N_6O_9SiZn_2$·toluene·THF
fw	646.84	752.99	1518.05
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a, Å	11.681(3)	9.804(3)	12.702(3)
b, Å	13.303(3)	10.381(3)	14.933(4)
c, Å	13.344(3)	20.723(6)	20.219(4)
α, deg	61.103(4)	81.055(5)	102.594(5)
β, deg	68.788(4)	87.709(6)	105.874(5)
γ, deg	74.871(5)	75.893(6)	103.861(5)
V, Å^3	1682.9(7)	2020.5(10)	3412.2(13)
Z	2	2	2
D_{calc}, g cm^{-3}	1.276	1.241	1.477
μ, cm^{-1}	0.109	0.102	0.816
$2\theta_{max}$, deg	57.02	56.66	56.54
no. of reflns measd	12187	14725	20569
no. of reflns used	7751	9317	13775
(R_{int})	(0.0537)	(0.0602)	(0.0669)
no. of param	442	594	958
final R [$I > 2\sigma(I)$]			
R1[a]	0.0604	0.0644	0.0662
wR2[b]	0.0715	0.0964	0.1083
R (all data)			
R1[a]	0.2172	0.2767	0.2176
wR2[b]	0.0914	0.1289	0.1369
GOF on F^2	0.716	0.700	0.750

[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 $P = [\max(F_o^2,0) + 2F_c^2]/3$.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 1, 3, and 5

	Compound **1**		
Si(1)−C(1)	1.843(3)	Si(1)−C(3)	1.865(3)
Si(1)−C(2)	1.856(3)	Si(1)−C(4)	1.867(3)
C(1)−Si(1)−C(2)	109.54(14)	C(1)−Si(1)−C(4)	115.67(13)
C(1)−Si(1)−C(3)	117.52(14)	C(2)−Si(1)−C(4)	112.63(13)
C(2)−Si(1)−C(3)	107.64(13)	C(3)−Si(1)−C(4)	92.85(14)
	Compound **3**		
Si(1)−C(1)	1.850(3)	Si(1)−C(3)	1.862(3)
Si(1)−C(2)	1.849(3)	Si(1)−C(4)	1.854(4)
C(2)−Si(1)−C(1)	107.37(17)	C(2)−Si(1)−C(3)	109.92(16)
C(2)−Si(1)−C(4)	115.22(17)	C(1)−Si(1)−C(3)	118.74(15)
C(1)−Si(1)−C(4)	113.66(17)	C(4)−Si(1)−C(3)	91.62(19)
	Compound **5**		
Si(1)−C(12)	1.851(7)	Si(1)−C(9)	1.875(6)
Si(1)−C(53)	1.845(7)	Si(1)−C(47)	1.881(7)
Zn(1)−O(3)	2.081(4)	Zn(2)−N(3)	2.072(5)
Zn(1)−O(6)	2.093(4)	Zn(2)−N(1)	2.083(5)
Zn(1)−N(6)	2.102(5)	Zn(2)−O(5)	2.082(4)
Zn(1)−N(4)	2.104(5)	Zn(2)−O(4)	2.100(5)
Zn(1)−O(9)	2.226(4)	Zn(2)−O(1)	2.146(4)
Zn(1)−O(7)	2.118(5)	Zn(2)−O(9)	2.243(4)
C(53)−Si(1)−C(12)	113.3(3)	C(53)−Si(1)−C(47)	110.9(3)
C(53)−Si(1)−C(9)	110.3(3)	C(12)−Si(1)−C(47)	113.5(3)
C(12)−Si(1)−C(9)	91.0(3)	C(9)−Si(1)−C(47)	116.6(3)
O(3)−Zn(1)−O(6)	93.56(17)	N(3)−Zn(2)−N(1)	86.7(2)
O(3)−Zn(1)−N(6)	90.85(18)	N(3)−Zn(2)−O(5)	92.28(19)
O(6)−Zn(1)−N(6)	88.26(19)	N(1)−Zn(2)−O(5)	92.49(18)
O(3)−Zn(1)−N(4)	93.59(17)	N(3)−Zn(2)−O(4)	170.55(17)
O(6)−Zn(1)−N(4)	170.04(16)	N(1)−Zn(2)−O(4)	88.6(2)
N(6)−Zn(1)−N(4)	84.7(2)	O(5)−Zn(2)−O(4)	96.07(17)
O(3)−Zn(1)−O(7)	173.64(17)	N(3)−Zn(2)−O(1)	88.55(18)
O(6)−Zn(1)−O(7)	83.67(18)	N(1)−Zn(2)−O(1)	92.18(18)
N(6)−Zn(1)−O(7)	94.78(19)	O(5)−Zn(2)−O(1)	175.29(17)
N(4)−Zn(1)−O(7)	89.88(18)	O(4)−Zn(2)−O(1)	83.48(17)
O(3)−Zn(1)−O(9)	84.87(15)	N(3)−Zn(2)−O(9)	99.96(18)
O(6)−Zn(1)−O(9)	89.94(15)	N(1)−Zn(2)−O(9)	173.2(2)
N(6)−Zn(1)−O(9)	175.24(18)	O(5)−Zn(2)−O(9)	85.59(15)
N(4)−Zn(1)−O(9)	97.60(16)	O(4)−Zn(2)−O(9)	85.11(16)
O(7)−Zn(1)−O(9)	89.40(17)	O(1)−Zn(2)−O(9)	89.71(15)

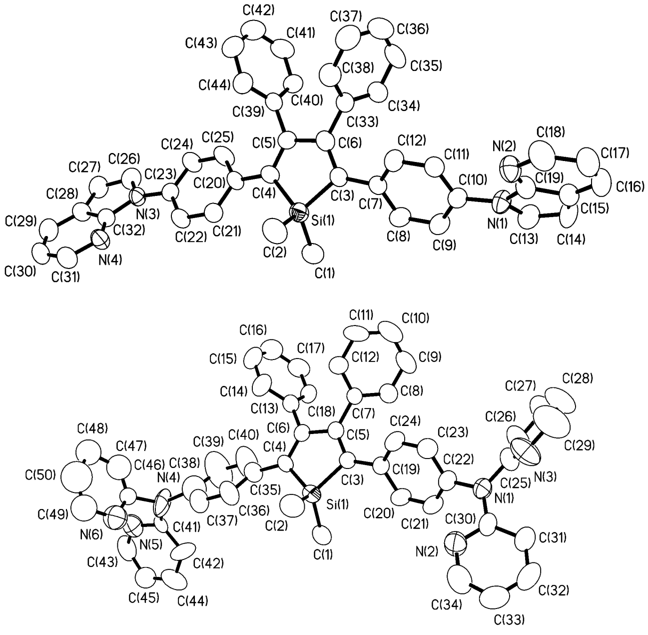

Figure 1. Diagrams showing the structure of **1** (top) and **3** (bottom) with labeling schemes. Hydrogen atoms are omitted for clarity.

As shown in Figure 1, the central silole ring in **1** and **3** is planar. The phenyl groups at the 3,4-positions in **1** and **3** are not coplanar with the central five-membered ring (their dihedral angles with the silole ring range from 57° to 74°). In contrast, the 7-azaindolyl- or 2,2′-dipyridylamino-functionalized phenyl groups at the 2,5-positions have considerable conjugation with the central ring, as indicated by their much smaller dihedral angles with the central ring (23°−47°). As shown in Table 2, the Si−methyl bond lengths [Si(1)−C(1) and Si(1)−C(2)] are somewhat shorter than those of the Si(1)−C(3) and Si(1)−C(4) bonds on the five-membered ring, consistent with related structures reported previously.[8c,17] No significant intermolecular interactions in the solid state were observed for **1** and **3**.

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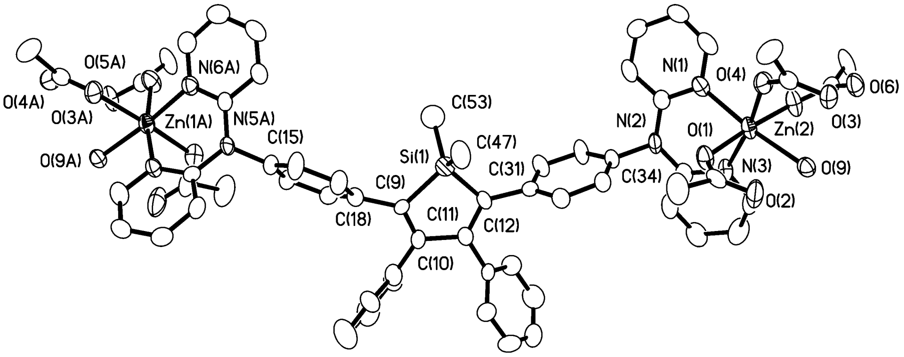
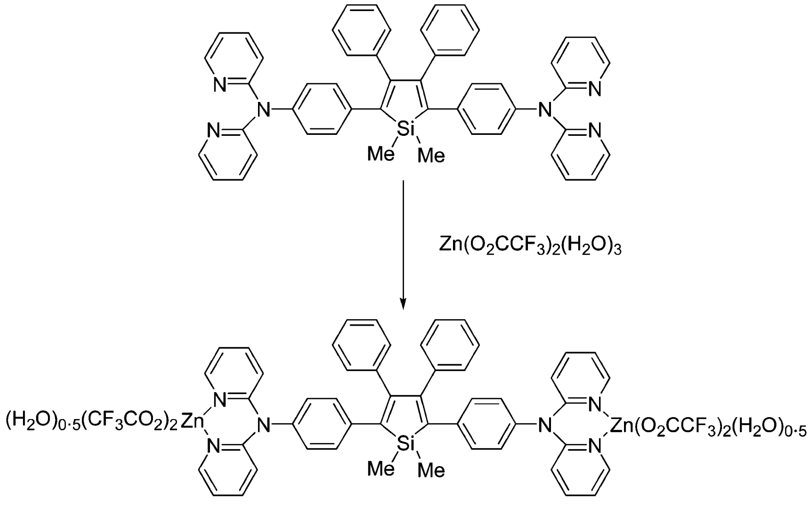


Figure 2. A diagram showing the structure of **5** with labeling schemes. Fluorine atoms and hydrogen atoms are omitted for clarity.

Scheme 2



(5)

Complex Formation. We have demonstrated recently that the 7-azaindolyl and the 2,2′-dipyridylamino groups are very useful for binding to metal ions to form supramolecular structures. Some of the suprmaolecular structures have been shown to display unique chemical and physical properties and are useful as fluorescent sensors for specific guest molecules or as emitters for OLEDs.[10,18−20] The silole compounds **1**−**4** contain either two 7-azaindolyl groups or two 2,2′-dipyridylamino groups. Therefore, we anticipated that these molecules should be capable of binding to metal ions, as we demonstrated previously for molecules that contain the same functional groups. To demonstrate this, we studied the reaction of compound **3** with Zn(II) ions. The reaction of $Zn(O_2CCF_3)_2(H_2O)_3$ with **3** in a 2:1 ratio resulted in the formation of a novel coordination compound, [($Zn_2(O_2CCF_3)_4(H_2O)$(**3**)] (**5**), in good yield, as shown in Scheme 2. Complex **5** was characterized by ^1H and ^{13}C NMR, elemental, and single-crystal X-ray diffraction analyses.

As shown in Figure 2, the two 2,2′-dipyridylamino sites in silole **3** were chelated by two Zn(II) ions, respectively, with normal Zn−N bond lengths.[10,18−19] Each Zn(II) ion is coordinated by six donor atoms—two nitrogen atoms from the pyridyl rings, three oxygen atoms from three trifluoroacetate ligands, and one oxygen atom from a H_2O ligand. The geometry of each Zn(II) ion is approximately octahedral. The most significant difference between the structure of **3** and that of **5** is the degree of conjugation between the central five-membered silole ring and the phenyl rings at the 2,5-positions. In **3**, there is a partial conjugation between these groups, as noted above. In contrast, in **5**, the degree of conjugation between the central ring and the phenyl rings at the 2,5-positions is much diminished, as evident by the much larger dihedral angles between the central five-membered ring and the two phenyl groups at the 2,5-positions (the dihedral angle between the central ring and the C(18) phenyl ring is 58.4° and between the central ring and the C(31) phenyl ring is 90.0°), as compared to those in **3**. The diminished conjugation in **5** is further evidenced by the slightly longer bond lengths of C(9)−C(18) [1.493(7) Å] and C(12)−C(31) [1.505(7) Å] in **5** compared to the corresponding ones in **3** [C(3)−C(19), 1.481(4) Å, and C(4)−C(35), 1.476(5) Å]. This subtle structural difference leads to a considerable difference in the electronic properties of **3** and **5**, as described in next section.

The most interesting feature of **5** is the formation of a one-dimensional polymer structure in the solid state, as shown in Figure 3. Two of the trifluoroacetate ligands function as bridging ligands to link Zn(1) and Zn(2) ions

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Figure 3. A diagram showing the extended structure of **5**. The fluorine atoms are omitted for clarity.

Table 3. Photoluminescent Data for Selected 1−5[a]

	λ_{max}, nm				
compd	UV/vis[b]	excitation	emission	quantum yield[c] (Φ_{em})	conditions
1	266, 376	395	499	0.01	CH_2Cl_2, 298 K
		396	477, 502		CH_2Cl_2, 77 K
		452	506		solid, 298 K
		448	474, 503		solid, 77 K
2	286, 378	396	505	0.11	CH_2Cl_2, 298 K
		396	479, 507		CH_2Cl_2, 77 K
		467	511		solid, 298 K
		466	497, 529		solid, 77 K
3	276, 388	418	511	0.04	CH_2Cl_2, 298 K
		396	493, 518		CH_2Cl_2, 77 K
		466	519		solid, 298 K
		448	484, 512		solid, 77 K
4	310, 368	395	508	0.11	CH_2Cl_2, 298 K
		396	482, 507		CH_2Cl_2, 77 K
		466	516		solid, 298 K
		465	505, 535		solid, 77 K
5	310, 368	391	492	0.08	CH_2Cl_2, 298 K
		406	488		solid, 298 K

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

together. In addition, a H_2O ligand also acts as a bridging ligand for the two Zn(II) ions. As a result, compound **5** can be described as a 1D chain compound with the silole unit **3** being linked together via the dinuclear $Zn_2(O_2CCF_3)_4(H_2O)$ unit. Although our attempts to obtain crystals suitable for an X-ray diffraction study from the reaction of **4** with $Zn(O_2CCF_3)_2(H_2O)_3$ were not successful, we believe that it is very likely that the product from this reaction has an extended 1D structure similar to that of **5**. In fact, we have observed recently that the formation of polymeric structures where ligands that contain 2,2′-dipyridylamino groups linked together by a $[Zn(O_2CCF_3)_2]_n(H_2O)_x$ ($n = 2, 4$; $x = 0-2$) unit are quite common occurrence.[21] The structure of **5** demonstrates that functionalized silole molecules such as **3** are useful as building blocks for the assembly of luminescent supramolecular structures via coordination bonds.

Electronic Properties of 1−5. The UV−vis spectra of all the compounds exhibit two intense absorption bands with λ_{max} at 260−310 nm and ∼360−390 nm, respectively, the former is attributed to the $\pi-\pi^*$ transition of the aryl groups and the latter is due to the $\pi-\pi^*$ transition of the silole ring, based on the assignment of previously reported silole compounds.[8c,22] The absorption band at $\lambda_{max} = \sim 360-390$ nm extends into the visible region and tails off at about 500 nm, which can account for the yellow-green color of **1**−**4**. Upon irradiation by UV light, compounds **1**−**4** yield greenish-blue to green emission in solution and in the solid state at ambient temperature. Table 3 summarizes the absorption and photoluminescent data of **1**−**5**. To understand the nature of luminescence displayed by **1**−**4**, we carried out molecular orbital calculations for compound **1** on the restricted Hartree−Fock (RHF) level using a standard split-valence polarized (B3LYP/6-311G**) basis set, employing the Gaussian 98 suit of programs.[23] The geometric parameters from X-ray diffraction analysis were used for the calculation. Figure 4 shows the HOMO and LUMO levels of **1**. The HOMO level is a π orbital with contributions mainly from the silole ring and the 2,5-phenyl groups, while the LUMO level is nearly a pure π^* orbital with dominating contributions from the silole ring and the 2,5-phenyl groups. The MO calculation results confirmed that the green-blue emission of compounds **1**−**4** is indeed from a $\pi-\pi^*$ transition. The emission maximum of **1**−**4** is considerably red-shifted compared to that of 2,3,4,5-tetraphenylsilole (467 nm) and 3,4-diphenyl-2,5-bis(4-biphenylyl)silole (497 nm),[8c] which can be attributed to the conjugation of the 7-azaindolyl and 2,2′-dipyridylamino unit with the aryl ring and the silole ring.

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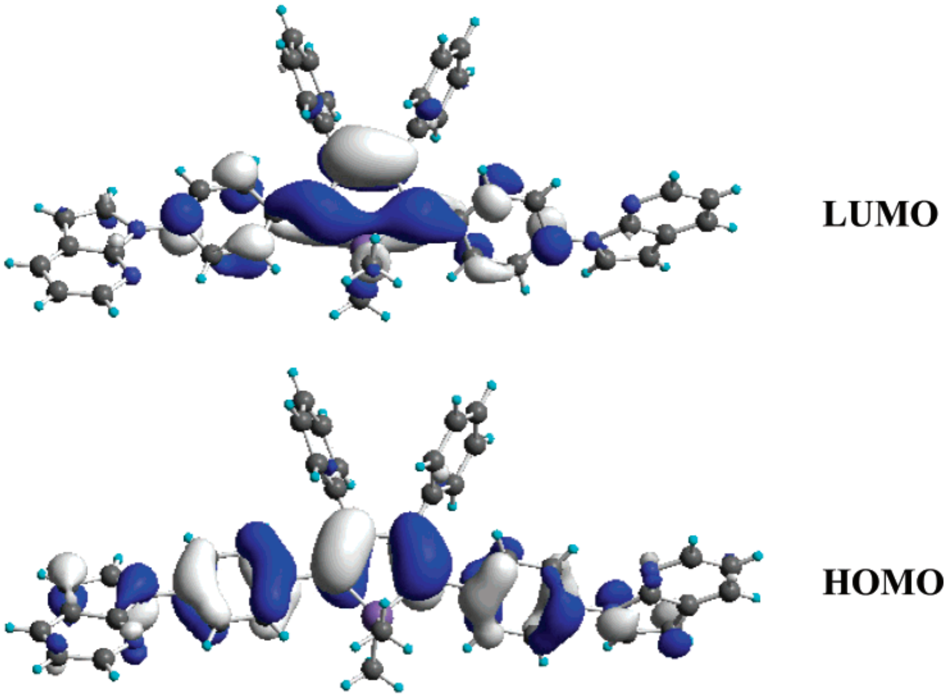

Figure 4. A diagram showing the HOMO and LUMO levels of compound **1**.

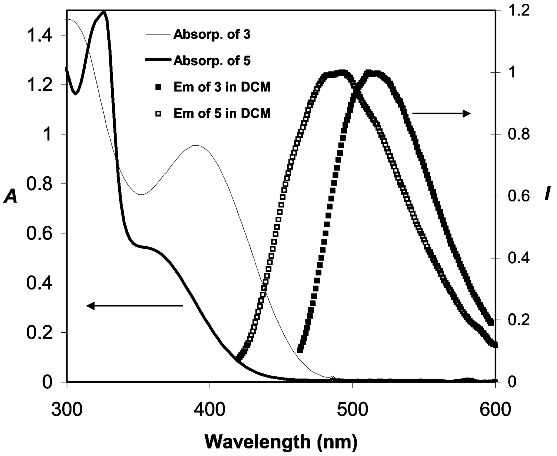

Figure 5. UV/vis and emission spectra of compounds **3** and **5** in CH_2Cl_2 (DCM).

The coordination of molecule **3** to the colorless Zn(II) ion has evidently caused a dramatic change in the electronic properties of the silole ligand. For example, **3** has a yellow-green color in solution and the solid state, attributable to its broad absorption band that covers the 400−500 nm region. In contrast, its complex **5** is almost colorless in solution and in the solid state. As shown in Figure 5, the absorption band of **3** at $\lambda_{max} = 388$ nm is blue-shifted to $\lambda_{max} = 368$ nm in compound **5** and the latter only absorbs weakly in the 400−450 nm region, consistent with the near colorless appearance of **5**. The emission spectra of complex **5** are quite different from those of compound **3**. Similarly, the emission band of **5** is also much blue-shifted, comparing to that of **3** (e.g., in CH_2Cl_2 **5** emits at $\lambda_{max} = 492$ nm while **3** emits at $\lambda_{max} = 511$ nm). The absorption and emission color difference between **3** and **5** can be explained by the fact that the degree of conjugation between the 2,5-phenyl rings and the central silole ring in **5** is much less than that in **3**, as demonstrated by their crystal structures. The reduced conjugation in **5** effectively increases the HOMO and LUMO energy gap, hence blue-shifting both absorption and emission energy.

Photoluminescent efficiencies of **1**−**4** in solution were determined to be 0.01−0.11, which are much higher than some of their closely related cousins reported previously.[8c,24] Compound **5** has a somewhat higher quantum efficiency than that of the free ligand **3**. Some groups[25] have reported that siloles have a higher PL efficiency in aggregates or in the solid state than in solution. We could not determine the PL efficiencies in the solid state due to the limitation of our spectrometer.

Electroluminescence (EL). Compounds **1** and **3** were chosen for evaluation of the uses of this group of new silole compounds in EL devices. The LUMO and HOMO levels for **1** and **3** were determined by electrochemical analysis (CV mode) and UV/vis spectra. **1** and **3** have the same LUMO energy (−2.8 eV). The HOMO energy level is −5.5 and −5.4 eV for **1** and **3**, respectively. These values are comparable to those of Alq_3, indicating their potential as electron-transport materials in OLEDs. EL devices, based on **1** and **3** as the electron-transporting layers and/or the emitting layers, were fabricated. The device structures are shown in Figure 6. The EL cell dimension was 0.13 cm^2 (±0.01 cm^2). *N*,*N*′-di-1-naphthyl-*N*,*N*′-diphenylbenzidine (NPB) was used as the hole-transport layer. The first device fabricated was A [ITO/NPB (60 nm)/silole **1** (40 nm)/borane (40 nm)/LiF (1 nm)/Al]. The borane compound in device A was a novel blue-luminescent three-coordinate organboron compound developed recently by our group and functions as an electron-transport mate-

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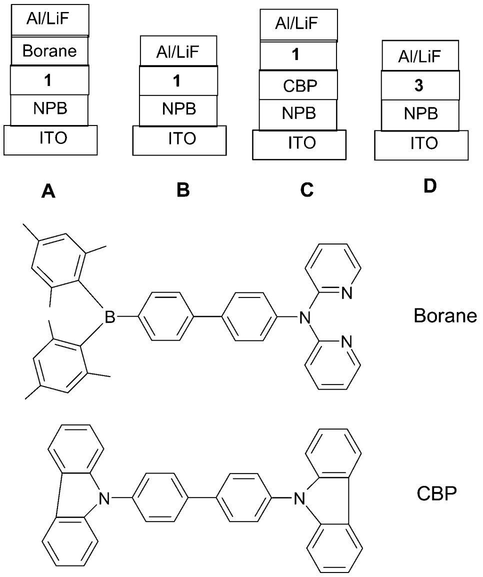

Figure 6. Diagrams showing the structures of devices A–D.

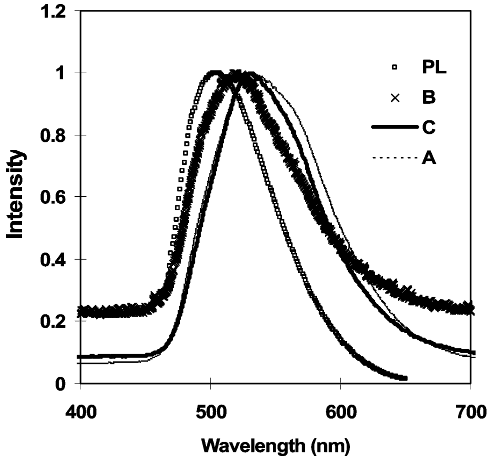

Figure 7. PL spectrum of **1** and EL spectra of devices A–C.

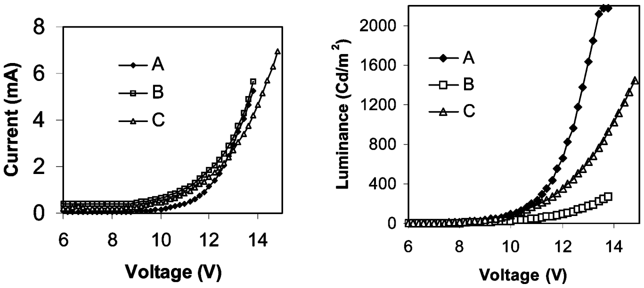

Figure 8. I–V (left) and L–V characteristics of devices A–C.

rial.[26] As shown by I–V and L–V curves in Figure 8, the turn-on voltage of device A was ~9 V. At ~13 V, the device had a brightness of ~2100 Cd/m^2, indicating that it is a bright and efficient device. The external quantum efficiency for device A was determined to be 2.8% (±0.3%). At all biased voltage in the range of 9–14 V, we observed the emission peak of a light green color. However, the EL spectrum (λ_{max} = 533 nm) was substantially red-shifted, compared to the PL spectrum (λ_{max} = 506 nm) of **1**, as shown in Figure 7, indicating the presence of exciplex emission. To rule out the possibility of exciplex between the borane and the silole layers, device B was constructed with the structure of ITO/NPB (60 nm)/silole **1** (80 nm)/Al. As shown in Figure 7, the EL spectrum (λ_{max} = 524 nm) of device B matched better with the PL spectrum than that of device A. However, the presence of exciplex emission was still evident. Considering the possibility of exciplex emission between the silole layer and the NPB layer, a hole-blocking layer, 4,4′-dicarbazolyl-1,1′-biphenyl (CBP),[7b,27] was inserted between NPB and silole in device C [ITO/NPB (60 nm)/CBP (20 nm)/silole **1** (80 nm)/LiF (1 nm)/Al]. The EL spectrum of C was essentially identical to that of A, an indication that exciplex emission was still present. The common feature of devices A–C is that the EL spectra were much more broad than the PL spectrum of siliole **1**. We have examined the PL spectra of **1** in film form and in powder form. There is no difference between the PL spectra recorded. We believe that the EL spectral shift of **1** is due to, at least partially, exciplex emission. However, the nature of this exciplex emission is yet to be fully understood. Despite the appearance of exciplex emission, devices A–C are stable and fairly bright. Similar bright EL devices based on exciplex emission involving siloles have been reported recently.[25c] The behavior of compound **3** in EL devices resembles that of **1**. A double-layer device D with the structure ITO/NPB (60 nm)/silole **3** (80 nm)/Al is illustrated here as a representative example. As shown in Figure 9, the turn-on voltage of device D is ~9 V. At ~12 V, the device D had a brightness of ~800 Cd/m^2, indicating again that the silole-based device is bright and efficient. The external quantum efficiency for device D was determined to be 0.4% (±0.04%). The PL spectrum (λ_{max} = 519 nm) of **3** almost matched the EL spectrum (λ_{max} = 534 nm) of device D with the EL spectrum being ~15 nm red-shifted. Because no previous known electron-transport layers were included in devices B–D, they demonstrate that the new silole compounds can indeed function as effective electron-transport materials in EL device. With further optimization, the device performance could be improved substantially. Extended investigation and further optimization on the EL devices based on the new siloles **1**–**4** are being carried out in our laboratory.

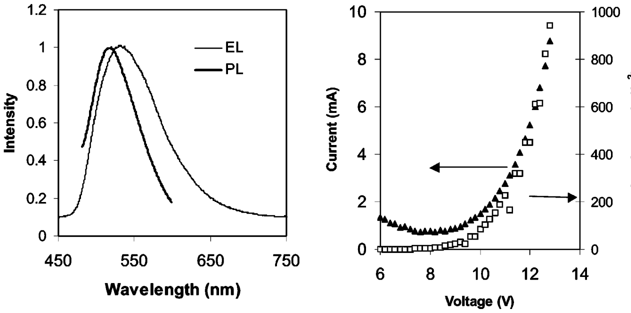

Figure 9. PL spectrum of **3**, EL spectrum of device D (left), and I–V and L–V characteristics of device D.

In summary, four novel 7-azaindolyl- or 2,2-dipyridylamino-functionalized silole compounds have been developed that show bright green-blue luminescence in the

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solid state and in solution. These compounds are useful building blocks for the construction of luminescent extended supramolecular structures using metal−ligand bonds as demonstrated by the formation and isolation of compound **5**. The coordination of a metal ion such as Zn(II) has a significant impact on the electronic properties of the silole compounds, and as a consequence, it may be possible to tune the emission color of the functionalized silole compounds by using metal ions. Two of the new silole compounds, **1** and **3**, have been demonstrated to produce a bright green emission and to function as electron-transporting materials in OLEDs. Exciplex emission appears to be involved in the EL devices of **1** and **3**, but the nature of the exciplex is yet to be understood. The new silole compounds are promising new materials for electroluminescent applications.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada for financial support.

Supporting Information Available: Listings of X-ray experimental details, atomic coordinates, thermal parameters, bond distances and angles, and a diagram for the complete drawing of the disordered molecule **3** (in PDF format) and crystallographic information files (in CIF format). This material is available free of charge via the Internet at http://pubs.acs.org.

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