Blue Luminescent Organosilicon Compounds Based on 2,2′-Dipyridylaminophenyl and 2,2′-Dipyridylaminobiphenyl

Wen-Li Jia, Qin-De Liu, Datong Song, and Suning Wang*

Department of Chemistry, Queen's University, Kingston, Ontario, K7L 3N6, Canada

Received August 22, 2002

Five new luminescent organosilicon compounds, bis[*p*-(2,2′-dipyridylamino)phenyl]dimethylsilane (**1**), bis[*p*-(2,2′-dipyridylamino)-4,4′-biphenyl]dimethylsilane (**2**), *p*-(2,2′-dipyridylamino)phenyldimethylhydroxysilane (**3**), *p*-(2,2′-dipyridylamino)-4,4′-biphenyldimethylhydroxysilane (**4**), and 1,1,3,3-tetramethyl-1,3-bis[*p*-(2,2′-dipyridylamino)phenyl]disiloxane (**5**), are synthesized. The structures of compounds **1** and **3**−**5** are determined by single-crystal X-ray diffraction. All five compounds have fluorescent emissions at 379−383 nm at room temperature. At 77 K, compounds **1**−**5** have phosphorescent emission bands with λ_{max} ranging from 407 to 518 nm. Increasing the degree of conjugation of the ligand has no significant effect on the fluorescent emission energy of the complexes, but causes a substantial red shift of the phosphorescent emission energy. Both fluorescent and phosphorescent emission of these compounds originates from $\pi^* \rightarrow \pi$ transitions centered on the *p*-(2,2′-dipyridylamino)phenyl and *p*-(2,2′-dipyridylamino)-4,4′-biphenyl ligands.

Introduction

Research involving luminescent organic/organometallic complexes has become an attractive field recently due to their potential applications in sensor technologies and photochemical and electroluminescent devices.[1−3] Blue luminescent materials are one of the key color components required for full-color EL displays, and stable blue emitters are still scarce. We have demonstrated recently that ligands containing 7-azaindolyl and 2,2′-dipyridylamino groups can produce bright blue fluorescence when bound to B(III) or Al(III) centers. Some of our boron and aluminum compounds have been used successfully as emitters in OLEDs.[3a−d] Organosilicon compounds have become our recent focus mostly because several recent reports demonstrated that organosilicon compounds with aromatic chromophores have excellent charge transport properties and produce highly efficient EL devices when used as emitters or electron transport materials.[4] The exceptionally high electron mobility displayed by organosilicon emitters in EL devices is attributable to the availability of low lying empty orbitals (e.g., 3d, σ^*, etc.) and the interaction of the Si center with the ligands.[4] Due to the relatively high lability and reactivity of Si−ligand bonds, compared to the carbon analogues, organosilicon compounds can be synthesized and modified readily under mild conditions.[4,5] Furthermore, because silicon is a much heavier element than carbon, it is expected to enhance phosphorescence of the chromophore more effectively than carbon.[6] These features along with their high stability make organosilicon compounds a very attractive class of molecules. A number of luminescent organosilicon compounds have been reported recently, in-

---

(1) (a) Tang, C. W.; Van Slyke, S. A. *Appl. Phys. Lett.* **1987**, *51*, 913. (b) Tang, C. W.; Van Slyke, S. A.; Chen, C. H. J. *Appl. Phys.* **1989**, *65*, 3610. (c) Hu, N.-X.; Esteghamatian, M.; Xie, S.; Popovic, Z.; Ong, B.; Hor, A. M.; Wang, S. *Adv. Mater.* **1999**, *11*, 1460. (d) Bulovic, V.; Gu, G.; Burrows, P. E.; Forrest, S. R.; Thompson, M. E. *Nature* **1996**, *380*, 29. (e) Balzani, V.; Juris, A.; Venturi, M.; Campagna, S.; Serroni, S. *Chem. Rev.* **1996**, *96*, 759. (f) Shen, Z.; Burrows, P. E.; Bulovic, V.; Forrest, S. R.; Thompson, M. E. *Science* **1997**, *276*, 2009. (g) Paplovski, D. B. *Sens. Actuators, B* **1995**, *29*, 213. (h) Ma. Y.; Che, C.-M.; Chao, H.-Y.; Zhou, X.; Chan, W.-H.; Shen, J. *Adv. Mater.* **1999**, *11*, 852. (i) Poterini, G.; Serpone, N.; Bergkamp, M. A.; Netzel, T. L. *J. Am. Chem. Soc.* **1983**, *105*, 4639. (j) Baldo, M. A.; Thompson, M. E.; Forrest, S. R. *Nature* **2000**, *403*, 750. (k) Papkovski, D. B.; Ponomarev, G. V.; Kurochkin, I. N.; Korpela, T. *Anal. Lett.* **1995**, *28*, 2027.

(2) (a) Baldo, M. A.; O'Brien, D. F.; You, Y.; Shoustikov, A.; Sibley, S.; Thompson, M. E.; Forrest, S. R. *Nature* **1998**, *395*, 151. (b) Adachi, A.; Baldo, M. A.; Forrest, S. R.; Lamansky, S.; Thompson, M. E.; Kwong, R. C. *Appl. Phys. Lett.* **2001**, *78*, 1622. (c) O'Brien, D. F.; Baldo, M. A.; Lamansky, S.; Burrows, P. E.; Thompson, M. E.; Forrest, S. R. *Appl. Phys. Lett.* **1999**, *75*, 4. (d) Lamansky, S.; Djurovich, P.; Murphy, D.; Abdel-Razzag, F.; Lee, H.-E.; Aadachi, C.; Burrows, P. E.; Forrest, S. R.; Thompson, M. E. *J. Am. Chem. Soc.* **2001**, *123*, 4304. (e) Lamansky, S.; Djurovich, P.; Murphy, D.; Abdel-Razzag, F.; Kwong, R. C.; Tsyba, I.; Bortz, M.; Mui, B.; Bau, R.; Thompson, M. E. *Inorg. Chem.* **2001**, *40*, 1704. (f) Sprouse, S.; King, K. A.; Spellane, P. J.; Watts, R. J. *J. Am. Chem. Soc.* **1984**, *106*, 6647. (g) Lu, W.; Mi, B. X.; Chan, M. C. W.; Hui, Z.; Zhu, N.; Lee, S. T.; Che, C. M. *Chem. Commun.* **2002**, 206.

(3) (a) Wu, Q.; Esteghamatian M.; Hu, N.-X.; Popovic, Z.; Enright, G.; Tao, Y.; D'Iorio M.; Wang, S. *Chem. Mater.* **2000**, *12*, 79. (b) Liu, S.-F.; Wu, Q.; Schmider, H. L.; Aziz, H.; Hu, N.-X.; Popovic, Z.; Wang, S. *J. Am. Chem. Soc.* **2000**, *122*, 3671. (c) Wu, Q.; Esteghamatian M.; Hu, N.-X.; Popovic, Z.; Enright, G.; Breeze, S. R.; Wang S. *Angew. Chem., Int. Ed.* **1999**, *38*, 985. (d) Pang, J.; Tao, Y.; Freiberg, S.; Yang, X.-P.; D'Iorio, M.; Wang, S. *J. Mater. Chem.* **2002**, *12*, 206. (e) Seward C.; Pang, J.; Wang, S. *Eur. J. Inorg. Chem.* **2002**, 1390. (f) Pang, J.; Marcotte, E. J.-P.; Seward, C.; Brown, R. S.; Wang, S. *Angew. Chem., Int. Ed.* **2001**, *40*, 4042.

(4) (a) Uchida, M.; Izumizawa, T.; Nakano, T.; Yamaguchi, S.; Tamao, K.; Furukawa, K. *Chem. Mater.* **2001**, *13*, 2680. (b) Chan, L. H.; Lee, R. H.; Hsieh, C. F.; Yeh, H. C.; Chen, C. T., *J. Am. Chem. Soc.* **2002**, *124*, 6469. (c) Murata, H.; Malliara, G. G.; Uchida, M.; Shen, Y.; Kafafi, Z. H. *Chem. Phys. Lett.* **2001**, *339*, 161. (d) Yamaguchi, S.; Endo, T.; Uchida, M.; Izumizawa, T.; Furukawa, K.; Tamao, K. *Chem. Eur. J.* **2000**, *6*, 1683. (e) Chen, H. Y.; Lam, W. Y.; Luo, J. D.; Ho, Y. L.; Tang, B. Z.; Zhu, D. B.; Wong, M.; Kwok, H. S. *Appl. Phys. Lett.* **2002**, *81*, 574.

(5) Brook, M. A. *Silicon in Organic, Organometallic and Polymer Chemistry*; John Wiley & Sons: New York, 2000.

(6) Lakowicz, J. R. *Principles of Fluorescence Spectroscopy*, 2nd ed.; Kluwer Academic/Plenum Publishers: New York, 1999.

10.1021/om020693n CCC: $25.00
Publication on Web 12/12/2002

cluding luminescent organosilicon polymers,[7] anthracene-bound organosilicon compounds that have blue/UV fluorescent emission.[8] Some starlike organosilicon compounds have also been synthesized and demonstrated to have blue fluorescent emissions.[9] Previously, we reported that 2,2′-dipyridylaminophenyl and 2,2′-dipyridylaminobiphenyl groups are good chromophores for producing blue luminescent materials.[3d−f] Their open coordination sites from pyridine nitrogen atoms also make them possible to chelate to metal centers to generate various luminescent metal complexes.[3d−f] In this work, we report the syntheses, structures, and fluorescent and phosphorescent properties of a series organosilicon compounds based on 2,2′-dipyridylaminophenyl and 2,2′-dipyridylaminobiphenyl.

Experimental Section

All starting materials were purchased from Aldrich Chemical Co. and used without further purification. Solvents were freshly distilled over appropriate drying reagents. All experiments were carried out under a dry nitrogen atmosphere using standard Schlenk techniques unless otherwise stated. ^{1}H and ^{13}C spectra were recorded on a Bruker Advance 300 spectrometer. ^{29}Si spectra were recorded on a Bruker Advance 500 spectrometer operating at 99.4 MHz using TMS as the reference. Mass spectra were recorded on a Sciex API3 spectrometer by CI techniques. Excitation and emission spectra were obtained with a Photon Technologies International QuantaMaster Model C-60 spectrometer. Emission lifetime was measured on a Photon Technologies International Phosphorescent lifetime spectrometer. UV−visible spectra were recorded on a Hewlett-Packard 8562A diode array spectrophotometer. Elemental analyses were performed by Canadian Microanalytical Service Ltd., Delta, British Columbia, Canada. *p*-(2,2′-Dipyridylamino)bromobenzene and *p*-(2,2′-dipyridylamino)bromobiphenyl were synthesized using a modified literature method.[10]

Preparation of Bis[*p*-(2,2′-dipyridylamino)phenyl]dimethylsilane (1). Me_2SiCl_2 (0.21 mL, 1.72 mmol) was slowly added to Li[*p*-$C_6H_4NPy_2$], which was prepared from *p*-(2,2′-dipyridylamino)bromobenzene (1.18 g, 3.61 mmol) and *n*-LiBu (3.79 mmol) at −78 °C. After being stirred for 1 h, the solution was allowed to warm to ambient temperature and stirred overnight, then refluxed for 4 h. The solvent was removed by vacuum. The residue was subjected to column chromatography (THF/hexanes, 2:1) to afford pure **1** in 65% yield as colorless crystals. Mp: 202−204 °C. ^{1}H NMR in CD_2Cl_2 (δ, ppm, 25 °C): 8.30 (ddd, J = 4.8, 1.8, 0.9, 4H), 7.63−7.56 (m, 8H), 7.16 (dt, J = 8.4, 1.8, 4H), 7.05 (dt, J = 8.4, 0.9, 4H), 6.98 (ddd, J = 7.2, 4.8, 0.9, 4H), 0.43 (s, 6H). ^{13}C NMR in CD_2Cl_2 (δ, ppm, 25 °C): 158.76, 149.02, 146.81, 138.06, 135.87, 135.37, 126.85, 118.95, 117.86, −2.07. ^{29}Si NMR in CD_2Cl_2 (δ, ppm, 25 °C): −8.50. Anal. Calcd for $C_{34}H_{30}N_6Si$: C, 74.18; H, 5.45; N, 15.27. Found: C, 73.91; H, 5.46; N, 15.24.

Preparation of Bis[*p*-(2,2′-dipyridylamino)biphenyl]dimethylsilane (2). In the same manner as described for **1**, the reaction of *n*-BuLi (1.6 M, 1.62 mL, 2.56 mmol)-pretreated *p*-(2,2′-dipyridylamino)bromobiphenyl (1 g, 2.5 mmol) with Me_2SiCl_2 (0.14 mL, 1.18 mmol) provided **2** as a colorless solid in 56% yield. Mp: 118−120 °C. ^{1}H NMR in CD_2Cl_2 (δ, ppm, 25 °C): 8.31 (ddd, J = 4.8, 2.0, 0.9, 4H), 7.68−7.60 (m, 16H), 7.24 (d, J = 8.4, 4H), 7.09 (d, J = 8.4, 4H), 6.99 (ddd, J = 7.2, 5.1, 0.9, 4H), 0.66 (s, 6H). ^{13}C NMR in CD_2Cl_2 (δ, ppm, 25 °C): 158.74, 149.04, 145.38, 141.77, 138.39, 138.08, 137.70, 135.35, 128.69, 128.06, 126.95, 118.92, 117.71, −2.08. ^{29}Si NMR in CD_2Cl_2 (δ, ppm, 25 °C): −8.07. MS (CI), *m/e* 704 (47%, $(M + 1)^+$), *m/e* 625 (100%, $(M - Py)^+$). Anal. Calcd for $C_{46}H_{38}N_6Si$/THF: C, 77.49: H, 5.98; N, 10.84. Found: C, 77.07; H, 5.91; N, 10.42.

Preparation of *p*-(2,2′-Dipyridylamino)phenyldimethylhydroxysilane (3). To a THF (20 mL) solution of *p*-(2,2′-dipyridylamino)bromobenzene (1 g, 3.07 mmol) was added a hexane solution of *n*-BuLi (1.6 M, 2.2 mL, 3.52 mmol) at −78 °C. After being stirred for 1 h at this temperature, the mixture was added to Me_2SiCl_2 (0.6 mL, 4.95 mmol) via cannula and stirred for another 1 h at −78 °C. Then it was warmed to ambient temperature and stirred overnight. The solvent and the excess Me_2SiCl_2 were removed in vacuo. The residue was dissolved in CH_2Cl_2 (15 mL), and $NH_3.H_2O$ (3 mL) was added. The mixture was stirred for 3 h. The organic layer was concentrated to give a yellow residue, which was purified by a chromatography column using THF/hexanes (1:1) as the eluant to provide **3** as a colorless crystalline solid in 79% yield. Mp: 130−132 °C. ^{1}H NMR in CD_2Cl_2 (δ, ppm, 25 °C): 8.30 (ddd, J = 4.8, 1.8, 0.9, 2H), 7.64−7.58 (m, 4H), 7.17 (dt, J = 8.4, 1.8, 2H), 7.04 (dt, J = 8.4, 0.9, 2H), 6.98 (ddd, J = 7.2, 4.8, 0.9, 2H), 0.43 (s, 6H). ^{13}C NMR in CD_2Cl_2 (δ, ppm, 25 °C): 158.73, 149.02, 147.11, 138.08, 136.55, 134.96, 126.85, 118.98, 117.82, 0.45. ^{29}Si NMR in CD_2Cl_2 (δ, ppm, 25 °C): 6.25. Anal. Calcd for $C_{18}H_{19}N_3OSi$: C, 67.26: H, 5.96; N, 13.07. Found: C, 67.07; H, 6.12; N, 12.95.

Preparation of *p*-(2,2′-Dipyridylamino)-4,4′-biphenyldimethylhydroxysilane (4). In the same manner as described for **3**, the reaction of *n*-BuLi (1.6 M, 1.5 mL, 4.12 mmol)-pretreated *p*-(2,2′-dipyridylamino)bromobenzene (0.88 g, 2.19 mmol) with Me_2SiCl_2 (0.5 mL, 4.95 mmol) provided **4** as colorless crystals in 56% yield. Mp: 162−164 °C. ^{1}H NMR in CD_2Cl_2 (δ, ppm, 25 °C): 8.31 (ddd, J = 4.8, 2.0, 0.9, 2H), 7.73−7.60 (m, 8H), 7.25 (d, J = 8.7, 2H), 7.10 (dt, J = 8.4, 0.9, 2H), 7.00 (ddd, J = 7.2, 4.8, 0.9, 2H), 0.45 (s, 6H). ^{13}C NMR in CD_2Cl_2 (δ, ppm, 25 °C): 158.73, 149.03, 145.40, 142.08, 138.79, 138.35, 138.10, 134.30, 128.69, 128.05, 126.90, 118.94, 117.72, 0.45. ^{29}Si NMR in CD_2Cl_2 (δ, ppm, 25 °C): 7.23. Anal. Calcd for $C_{24}H_{23}N_3OSi$: C, 72.54; H, 5.79; N, 10.58. Found: C, 72.08; H, 5.82; N, 10.39.

Preparation of 1,1,3,3-Tetramethyl-1,3-bis[*p*-(2,2′-dipyridylamino)phenyl]disiloxane (5). To a CH_2Cl_2 (6 mL) solution of *p*-(2,2′-dipyridylamino)phenyldimethylhydroxysilane (45 mg, 0.14 mmol) was added hydrochloride acid (0.5 mL). After being stirred overnight, aqueous ammonia was added to the mixture until the pH of the aqueous layer was about 7. The solution was then extracted with CH_2Cl_2, and the extract was dried over $MgSO_4$. After filtration, the filtrate was concentrated to about 1 mL. Slow diffusion of hexane into a CH_2Cl_2 solution gave rise to colorless crystals of **5** after a few days in 68% yield. Mp: 145−147 °C. ^{1}H NMR in CD_2Cl_2 (δ, ppm, 25 °C): 8.36 (ddd, J = 5.1, 1.8, 0.75, 4H), 7.67−7.61 (m, 8H), 7.19 (d, J = 8.4, 4H), 7.04 (ddd, J = 7.5, 5.1, 0.9, 4H), 6.95 (d, J = 8.4, 4H), 0.44 (s, 12H). ^{13}C NMR in CD_2Cl_2 (δ, ppm, 25 °C): 155.59, 147.23, 144.65, 138.83, 138.30, 135.17, 126.98, 118.78, 116.9, 1.00. ^{29}Si NMR in CD_2Cl_2 (δ, ppm, 25 °C): −0.99. Anal. Calcd for $C_{36}H_{36}N_6OSi_2$: C, 69.19: H, 5.81; N, 13.45. Found: C, 69.71; H, 5.80; N, 13.34.

---

(7) (a) Gradwell, S. E.; Kepler, C. L. *Macromolecules* **2002**, *35*, 2871. (b) Matsumi, N.; Umeyama, T.; Chujo, Y. *Macromolecules* **2001**, *34*, 3510. (c) Ohshita, J.; Hashimoto, M.; Iida, T.; Tang, H.; Kunai, A. *Organometallics* **2001**, *20*, 4296. (d) Sakamaki, K.; Ohshita, J.; Kunai, A.; Nakao, H.; Adachi, A.; Okita, K. *Appl. Organomet. Chem.* **2001**, *15*, 939. (e) Kwak, G.; Masuda, T. *J. Polym. Sci: Part A: Poly. Chem.* **2002**, *40*, 535.

(8) (a) Yamaguchi, S.; Akiyama, S.; Tamao, K. *J. Am. Chem. Soc.* **2000**, *122*, 6793. (b) Yamaguchi, S.; Akiyama, S.; Tamao, K. *Organometallics* **1998**, *17*, 4347.

(9) (a) Ishikawa, M.; Teramura, H.; Lee, K. K.; Schneider, W.; Naka, A.; Kobayashi, H.; Yamaguchi, Y.; Kikugawa, M.; Ohshita, J.; Kunai, A.; Tang, H.; Harima, Y.; Yamabe, T.; Takeuchi, T. *Organometallics* **2001**, *20*, 5331. (b) Tang, H.; Zhu, L.; Harima, Y.; Yamashita, K.; Lee, K. K.; Naka, A.; Ishikawa, M. *J. Chem. Soc., Perkin, Trans.* **2000**, 1976. (c) Sonoda, T.; Rahmat, H.; Ozaki, M.; Yoshino, K. *Appl. Phys. Lett.* **1999**, *75*, 2193. (d) Ishikawa, M.; Lee, K. K.; Schneider, W.; Naka, A.; Yamabe, T.; Harima, Y.; Takeuchi, T. *Organometallics* **2000**, *19*, 2406.

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

Table 1. Data Collection and Processing Parameters 1, 3−5

	1	3	4	5
formula	$C_{34}H_{30}N_6Si$	$C_{18}H_{19}N_3OSi$	$C_{24}H_{23}N_3OSi$	$C_{36}H_{36}N_6OSi_2$
fw	550.73	321.45	397.54	624.89
space group	$P2_1/c$	$C2/c$	$P\bar{1}$	$P2_1/n$
a/Å	9.4669(15)	24.426(6)	10.953(2)	17.694(4)
b/Å	10.5822(16)	10.168(3)	13.403(3)	8.967(2)
c/Å	29.086(5)	14.629(3)	16.501(3)	21.017(5)
α/deg	90	90	71.378(4)	90
β/deg	91.313(3)	110.132(5)	76.530(4)	90.969(4)
γ/deg	90	90	72.198(4)	90
V/Å	32913.1(8)	3411.2(14)	2160.9(7)	3334.3(13)
Z	4	8	4	4
D_c/g cm^{-3}	1.256	1.252	1.222	1.245
μ/cm^{-1}	1.15	1.45	1.28	1.45
$2\theta_{max}$/deg	56.54	56.60	56.68	56.54
no. of reflns measd	20514	11975	15757	23326
no. of reflns used (R_{int})	6906 (0.0253)	4055 (0.0315)	9920 (0.0253)	7907 (0.0584)
no. of params	490	284	641	406
final R [$I > 2\sigma(I)$]				
R1[a]	0.0382	0.0389	0.0686	0.0492
wR2[b]	0.0874	0.0731	0.1697	0.0904
R (all data)				
R1[a]	0.0751	0.0993	0.1852	0.1708
wR2[b]	0.0996	0.0858	0.2060	0.1145
goodness of fit on F^2	0.934	0.868	0.812	0.793

[a] $R1 = \sum[|F_o| - |F_c|]/\sum|F_o|$. [b] $wR2 = \{\sum[w(F_o^2 - F_c^2)]/\sum(wF_o^2)\}^{1/2}$.

X-ray Crystallographic Analysis. Single crystals of **1** and **3** were obtained from a solution of CH_2Cl_2/hexanes. A suitable single crystal of **4** was obtained from CH_2Cl_2/toluene, and those for **5** were obtained from THF/hexanes. Data were collected on a Siemens P4 single-crystal X-ray diffractometer with a CCD-1000 detector and graphite-monochromated Mo Kα radiation, operating at 50 kV and 30 mA at 25 °C. The data collection ranges over the 2θ ranges are 3.56−56.6° for **1**, 2.64−56.7° for **2**, 4.10−56.5° for **3**, and 3.04−56.5° for **4**. No significant decay was observed for all samples. Data were processed on a PC using the Bruker SHELXTL software package[11] (version 5.10) and are corrected for Lorentz and polarization effects. Compounds **1** and **3**−**5** crystallize in four different space groups, which belong to the monoclinic space group $P2_1/c$ for **1**, $C2/c$ for **3**, $P2_1/n$ for **5**, and triclinic space group $P\bar{1}$ for **4**, respectively. All structures were solved by direct methods. All non-hydrogen atoms except two methyl carbon atoms (C25 and C26) in compound **4** were refined anisotropically. All hydrogen atoms in **1** and **3**, all aromatic hydrogen atoms, and the hydrogen atoms that are bound to the oxygen atoms in **4** were located directly from different Fourier maps. Other hydrogen atoms were calculated, and their contributions were included. Two of the methyl groups (C(25) and C(26)) show some degree of disordering, resulting in relatively large thermal parameters. The crystallographic data for compounds **1**, **3**, **4**, and **5** are given in Table 1. Selected bond lengths and angles for **1**, **3**, **4**, and **5** are listed in Table 2.

Quantum Yield Measurements. Fluorescent quantum yields of the complexes were determined relative to 9,10-diphenylanthracene in THF at 298 K ($\theta_r = 0.95$).[12] The absorbances of all the samples and the standard at the excitation wavelength were approximately 0.092−0.109. The quantum yields were calculated using previously reported procedures.[13] The excitation wavelength for all the samples is 338 nm. Because all the compounds have phosphorescent emission only at low temperature (77 K), phosphorescent quantum yields at ambient temperature were not determined.

Results and Discussions

Syntheses and Characterization of Compounds 1−5. Addition of $Si(CH_3)_2Cl_2$ to Li[*p*-ArNPy$_2$] (Ar = phenyl, 4,4′-biphenyl, respectively) in ~1:2 ratio, which are prepared from the reaction of *n*-BuLi and *p*-(2,2′-dipyridylamino)bromobenzene or *p*-(2,2′-dipyridylamino)bromo-4,4′-biphenyl at −78 °C, provides Si(p-Ph-NPy$_2$)$_2$(CH$_3$)$_2$ (**1**) and Si(p-biPh-NPy$_2$)$_2$(CH$_3$)$_2$ (**2**), respectively, in moderate yields. The reactions of $Si(CH_3)_2Cl_2$ with Li[*p*-Ar-NPy$_2$] in 1:1 ratio, followed by the treatment of aqueous NH_4OH, result in the formation of Si(p-Ph-NPy$_2$)(CH$_3$)$_2$(OH) (**3**) and Si(p-biPh-NPy$_2$)(CH$_3$)$_2$(OH) (**4**), in good yields, if the Li[*p*-Ar-NPy$_2$] compound is added to the solution of $Si(CH_3)_2Cl_2$. If the addition order is reversed, i.e., add the silicon compound to the solution of the ligand, compounds **1** and **2** are obtained as the major product, instead. The correct order of addition of the starting material to maintain the ratio of Si versus the ligand at ≥1:1 through the entire reaction is critical for the successful synthesis of **3** and **4**. Compounds Si(*p*-A-NPy$_2$)(CH$_3$)$_2$Cl are assumed to be the intermediates that lead to the subsequent formation of compounds **3** and **4**. Due to their poor stability, we did not attempt to isolate and characterize these intermediates. In the presence of acid, compound **3** can be condensed readily to form the oxo-linked dinuclear compound **5**, [Si(p-Ph-NPy$_2$)(CH$_3$)$_2$]$_2$O. The reactivity displayed by the silicon compounds in the synthesis of **1**−**5** is consistent with the well-established chemistry of organosilicon compounds containing Si−Cl and Si−OH bonds.[14] The synthetic procedures for **1**−**5** are summarized in Scheme 1. These new silicon compounds are fully characterized by ^1H, ^{13}C, and ^{29}Si NMR and elemental analyses. The ^{29}Si chemical shifts for compounds **1**−**5** (relative to TMS) are −8.50, −8.07, 6.25, 7.23, and −0.99, respectively, which are in the

---

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

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

[13] Demas, N. J.; Crosby, G. A. *J. Am. Chem. Soc.* **1970**, *92*, 7262.

[14] Armitage, D. A. In *Comprehensive Organometallic Chemistry*, Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: Oxford, 1995; Vol. 2, Chapter 1, p 2.

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

	Compound **1**		
Si(1)−C(1)	1.862(2)	C(1)−Si(1) −C(2)	110.62(13)
Si(1)−C(2)	1.858(2)	C(1)−Si(1)−C(3)	108.16(9)
Si(1)−C(3)	1.8781(15)	C(1)−Si(1)−C(19)	108.55(9)
Si(1)−C(19)	1.8807(14)	C(2)−Si(1)−C(3)	110.82(9)
		C(2)−Si(1)−C(19)	109.31(9)
		C(3)−Si(1)−C(19)	109.34(6)
	Compound **3**		
Si(1)−O(1)	1.6347(14)	O(1)−Si(1)−C(1)	105.77(12)
Si(1)−C(1)	1.850(2)	O(1)−Si(1)−C(2)	110.82(12)
Si(1)−C(2)	1.856(2)	O(1)−Si(1)−C(3)	110.50(8)
Si(1)−C(3)	1.8706(17)	C(1)−Si(1)−C(2)	110.13(14)
		C(1)−Si(1)−C(3)	110.29(10)
		C(2)−Si(1)−C(3)	109.29(10)
	Compound **4**		
Si(1)−O(1)	1.631(3)	O(1)−Si(1)−C(1)	109.4(2)
Si(1)−C(1)	1.820(5)	O(1)−Si(1)−C(2)	107.3(2)
Si(1)−C(2)	1.853(6)	O(1)−Si(1)−C(3)	110.95(17)
Si(1)−C(3)	1.884(4)	C(1)−Si(1)−C(2)	109.4(3)
Si(2)−O(2)	1.575(3)	C(1)−Si(1)−C(3)	110.0(2)
Si(2)−C(25)	1.911(7)	C(2)−Si(1)−C(3)	109.8(2)
Si(2)−C(26)	1.810(9)	O(2)−Si(2)−C(25)	106.8(3)
Si(2)−C(27)	1.865(4)	O(2)−Si(2)−C(26)	110.5(3)
		O(2)−Si(2)−C(27)	113.89(17)
		C(25)−Si(2)−C(26)	105.0(4)
		C(25)−Si(2)−C(27)	106.8(3)
		C(26)−Si(2)−C(27)	113.1(3)
	Compound **5**		
Si(1)−O(1)	1.6298(18)	O(1)−Si(1)−C(1)	110.80(13)
Si(1)−C(1)	1.849(3)	O(1)−Si(1)−C(2)	109.11(13)
Si(1)−C(2)	1.841(3)	O(1)−Si(1)−C(3)	107.44(11)
Si(1)−C(3)	1.864(3)	C(1)−Si(1)−C(2)	110.07(18)
Si(2)−O(1)	1.6295(18)	C(1)−Si(1)−C(3)	109.91(13)
Si(2)−C(19)	1.839(3)	C(2)−Si(1)−C(3)	109.47(14)
Si(2)−C(20)	1.845(3)	O(1)−Si(2)−C(19)	107.31(12)
Si(2)−C(21)	1.864(3)	O(1)−Si(2)−C(20)	109.93(13)
		O(1)−Si(2)−C(21)	108.52(10)
		C(19)−Si(2)−C(20)	109.94(15)
		C(19)−Si(2)−C(21)	110.66(13)
		C(20)−Si(2)−C(21)	110.41(13)
		Si(1)−O(1)−Si(2)	148.33(12)

typical range of ^{29}Si chemical shifts previously observed for silicon compounds[5] with ligand environments resembling those of **1**−**5**. Attempts to grow single crystals of compound **2** were unsuccessful. Single-crystal X-ray diffraction analyses are carried out for **1** and **3**−**5**.

Crystal Structures. The structure of compound **1** is shown in Figure 1. The Si atom adopts a typical tetrahedral geometry surrounded by carbon atoms only. The Si−C bond lengths vary considerably but are within the normal range of Si−C bond lengths.[14−16] The Si−C (phenyl) bonds are about 0.02 Å longer than those of Si−C (methyl) bonds, which could be attributed to the relatively large size of the phenyl group. The amino nitrogen atoms on the two PhNPy$_2$ ligands are essentially coplanar with the three bound carbon atoms and have a trigonal planar geometry. Compound **2** is believed to have a structure similar to that of **1**.

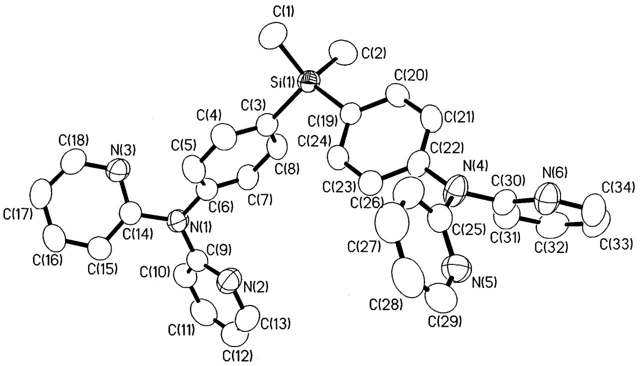
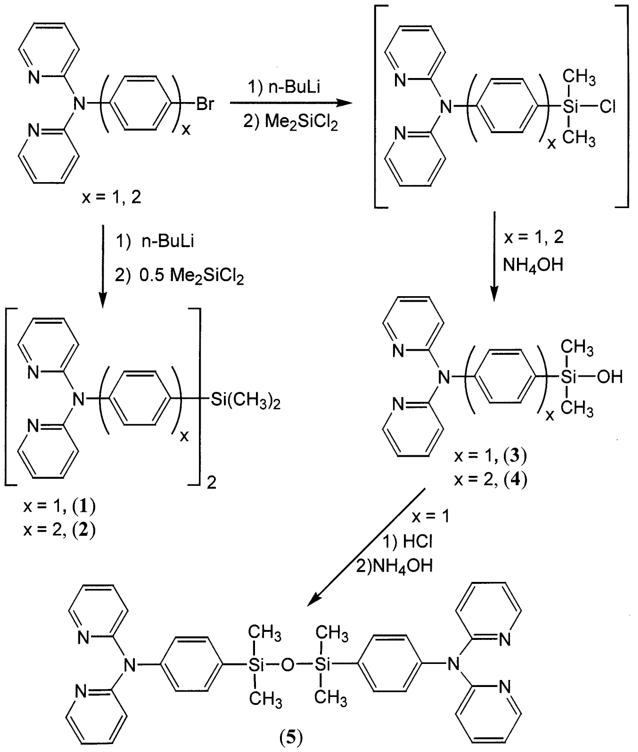


Figure 1. Molecular structure of **1** with 50% thermal ellipsoids and labeling schemes.

Scheme 1



The structures of compounds **3** and **4** are shown in Figures 2a and 3a, respectively. In the asymmetric unit of **4**, there are two independent molecules that display essentially the same structure. Therefore, only one of the independent molecules of **4** is shown in Figure 3a. The silicon atoms in both **3** and **4** are surrounded by two methyl groups, one hydroxy ligand, and the Ar−NPy2 ligand in a tetrahedral geometry. The Si(1)−O(1) bond length is over 0.2 Å shorter than all Si−C bonds, attributable to the fact that the Si−O bond energy is much higher than that of a Si−C bond.[17] The Si−O and Si−C bond lengths observed in **3** and **4** are typical.[14−16] Again, as observed in compound 1, the Si−C (phenyl) bond lengths are slightly longer than those of Si−C (methyl), due to the steric effect of the relatively big phenyl group. The biphenyl group in **4** is not coplanar, but has a dihedral angle between the two phenyl rings of 30.0° and 33.5°, respectively, for the two independent molecules. Although the molecular structures of **3** and **4** resemble each other, the extended structure of these two compounds in the crystal lattice is quite different.

---

(15) (a) Churchill, M. R.; Lake, C. H.; Chao, S. H. L.; Beachley, O. T. *J. Chem. Soc., Chem. Commun.* **1993**, 1577. (b) Millevolte, A. J.; Powell, D. R.; Johnson, S. G.; West, R. *Organometallics* **1992**, *11*, 1091. (c) Beckmann, J.; Jurkschat, K.; Müller, D.; Rabe, S.; Schürmann, M. *Organometallics* **1999**, *18*, 2326. (d) Beckmann, J.; Jurkschat, K.; Rabe, S.; Schürmann, M.; Dakternieks, D.; Duthie, A. *Organometallics* **2000**, *19*, 3272.

(16) (a) Rüdinger, C.; Bissinger, P.; Beruda, H.; Schmidbaur, H. *Organometallics* **1992**, *11*, 2867. (c) McCarthy, W. Z.; Corey, J. Y.; Corey, E. R. *Organometallics* **1984**, *3*, 255.

(17) Housecroft, C. E.; Sharpe, A. G. *Inorganic Chemistry*, 1st ed.; Harlow: Prentice Hall, 2001.

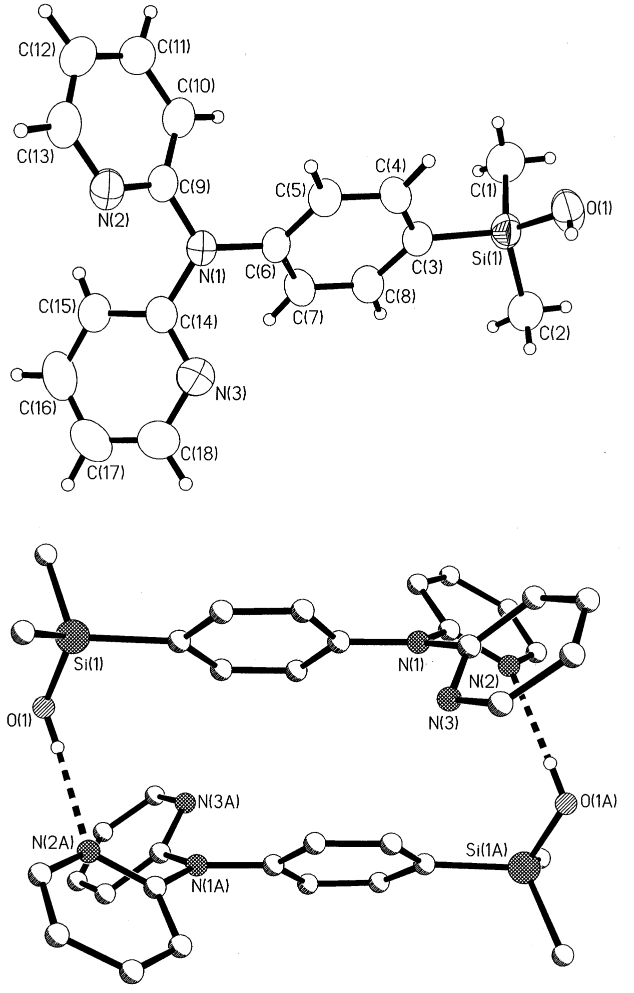


Figure 2. (a) Molecular structure of **3** with 50% thermal ellipsoids and labeling schemes. (b) Hydrogen-bonded dimer structure of **3**. All the hydrogen atoms except hydroxyl hydrogen atoms are omitted for clarity.

For compound **3**, two molecules couple through two hydrogen bonds between the OH group of one molecule and a nitrogen atom (N(2)) of a pyridyl group from the neighboring molecule, forming an antiparallel head to tail dimer structure (Figure 2b), as evident by the distance between the two electronegative elements O(1)···(N(2A), 2.875(4) Å. In contrast, compound **4** displays two types of hydrogen bonds. The first type is similar to that observed in **3**, i.e., a hydrogen bond between the hydroxy group and a nitrogen atom of a pyridyl ring from the neighboring molecule, as indicated by the distance of O(2)···N(3B), 2.759(8) Å (Figure 3b). The second type is a hydrogen bond between two oxygen atoms of the hydroxy groups from the two independent molecules (O(1)···O(2) = 2.785(7) Å). Consequently, compound **4** has a one-dimensional hydrogen-bonded polymer structure in the solid state.

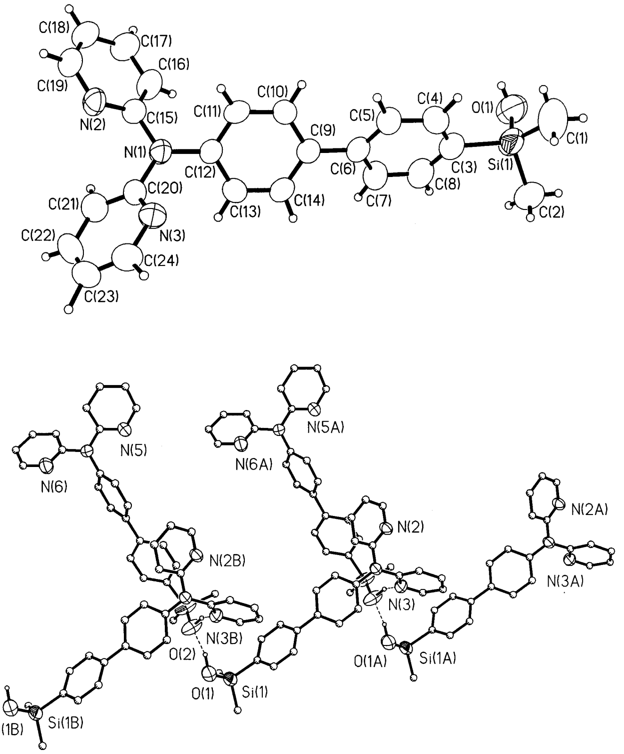


Figure 3. (a) Molecular structure of **4** with 50% thermal ellipsoids and labeling schemes. (b) Hydrogen-bonded extended 1D structure of **4**. For clarity, all hydrogen atoms except those of OH groups are omitted.

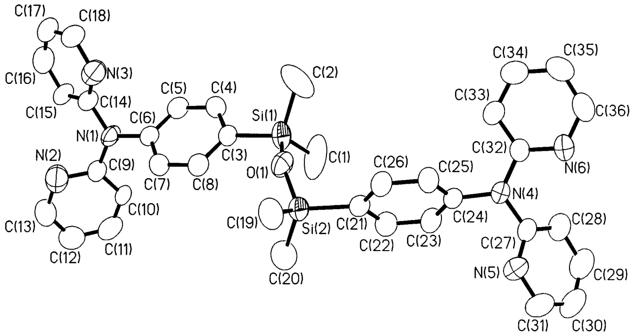


Figure 4. Molecular structure of **5** with 50% thermal ellipsoids and labeling schemes. For clarity, all hydrogen atoms are omitted.

The hydroxy group of **3** and **4** allows condensation of these molecules with other Si−OH groups via the elimination of H_2O. In fact, we have been able to attach compounds **3** and **4** to surfaces that have a Si-OH functionality. The details will be published elsewhere in due course. Compound **5** demonstrates the consequence of the condensation reaction between two molecules of **3**. The structure of compound **5** is shown in Figures 4. As observed in compounds **1**, **3**, and **4**, the silicon atom in **5** also has a tetrahedral geometry. The coordination environment around the silicon atom resembles that of **3**. The average Si−C (methyl) bond length is 1.844(3) Å and the average Si−C (phenyl) bond length is 1.864(3) Å for compound **5**, consistent with the trend observed in **1**, **3**, and **4**. The oxygen atom in **5** bridges two silicon atoms in a bent fashion, as shown by the bond angle of Si(1)−O(1)−Si(2), 148.33(12)°, which is comparable with previously known Si−O−Si angles in silicon compounds containing aromatic substituents (134.4−180.0°).[15c,d]

Luminescent Properties. Upon irradiation UV light at ambient temperature, compounds **1**−**5** emit a violet color both in solution and in the solid state. At ambient temperature, the emission maximum of compounds **1**, **3**, and **5** in THF solution is at 379 nm, and the emission maximum of compounds **2** and **4** in THF solution is at 382−383 nm as shown in Figure 5, which

Table 3. Fluorescence and Phosphorescence Data for Compounds 1–5

compd	UV–vis, nm[a]	excitation λ_{max}, nm	emission λ_{max}, nm	decay lifetime (τ, μs)[b]	quantum yields (Φ)[c]	conditions
1	238, 274, 300	338	379		0.084	THF, 298 K
		325	380			solid, 298 K
		311	384			THF, 77 K
			407	7.9(1)		
			423	7.5(2)		
2	240, 254, 306	338	383		0.21	THF, 298 K
		354	401			solid, 298 K
		299	395			THF, 77 K
			487	5.1(1)		
			519	4.6(1)		
3	238, 272, 300	338	379		0.046	THF, 298 K
		321	394			solid, 298 K
		311	384			THF, 77 K
			408	8.0(3)		
			426	8.3(2)		
4	240, 256, 308	338	382		0.17	THF, 298 K
		322	398			solid, 298 K
		301	391			THF, 77 K
			487	7.4(2)		
			518	6.10(9)		
5	238, 272, 300	338	379		0.072	THF, 298 K
		328	381			solid, 298 K
		311	407	7.8(3)		THF, 77 K
			430	6.46(9)		

[a] All data were collected for THF solution ([M] = 2.5 × 10^{-5}) at ambient temperature. [b] A reliable lifetime could not be obtained for the fluorescent emission due to the limitation of the instrument, which cannot measure lifetimes in the nanosecond regime. [c] Relative to 9,10-diphenylanthracene in THF at ambient temperature.

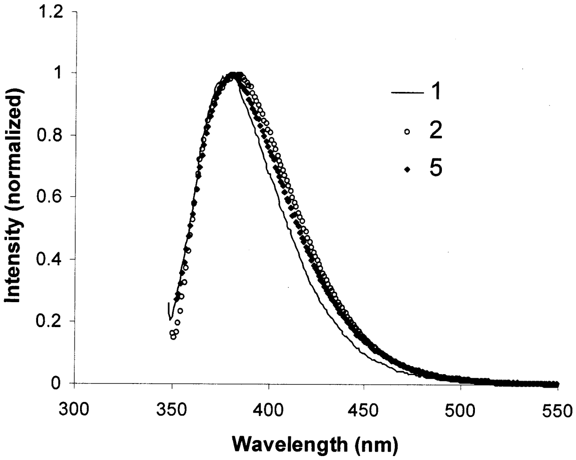


Figure 5. Emission spectra of compounds **1**, **2**, and **5** in THF at 298 K. The spectrum of **3** is similar to those of **1** and **5**. The spectrum of **4** is similar to that of **2**. For clarity, the spectra of **3** and **4** are not shown.

are attributed to fluorescence of the 2,2′-dipyridylamino unit.[3d–f,10] The emission lifetimes of fluorescence are not provided, due to the limitation of our spectrometer. Although compounds **1**–**5** have almost identical emission spectra in THF solution at 298 K, they could be classified into two groups by the results of emission quantum yield measurements. The quantum yields of **1**–**5** are 0.084, 0.21, 0.046, 0.17, and 0.072, respectively, as shown in Table 3. Compounds **1**, **3**, and **5** have a much lower quantum yield, compared to those of **2** and **4**, which have quantum yields 2–3 times higher than those of compounds **1**, **3**, and **5**. The difference between the group of **1**, **3**, and **5** and the group of **2** and **4** is that the former have a phenyl unit between the 2,2′-dipyridylamino chromophore and the silicon atom, while the latter have a biphenyl unit. The increased conjugation in **2** and **4** appears to enhance the quantum yield of the compounds.

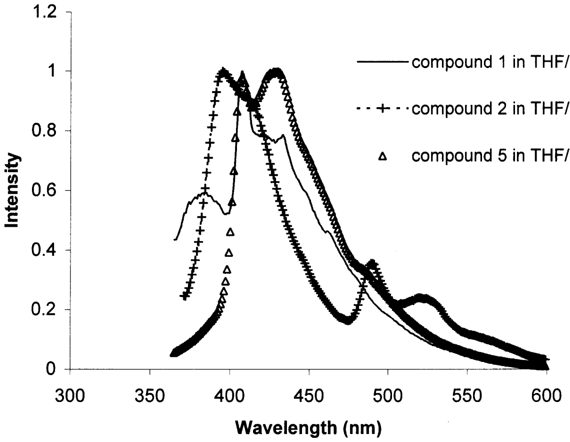


Figure 6. Full emission spectra of compounds **1**, **2**, and **5** in THF at 77 K. The spectra of **3** and **4** are not shown for clarity (they are similar to those of **1** and **2**, respectively).

In the solid state, the emission maximum of **2**–**4** is found at 401, 394, and 398 nm, respectively, ~15–18 nm red-shifted from those in THF solution. This red shift may be caused by intermolecular interactions in the solid state. The existence of intermolecular hydrogen bonds in compounds **3** and **4** as shown by the crystal structures may be a factor contributing to the red shift. There is essentially no shift of the solid state emission for compounds **1** and **5**, compared to those in solution.

At 77 K, the THF solutions of **1**–**5** all display new emission bands in addition to the fluorescent bands observed at ambient temperature. These new emission bands are all at longer wavelengths than those of fluorescent bands, as shown by Figure 6 and Table 3. Using a time-resolved phosphorescence spectrometer, we were able to remove the fluorescent emission bands from the spectra. The resulting low-energy emission bands, as shown in Figure 7, are at 403 and 423 nm for **1**, 484 and 519 nm for **2**, 408 and 426 nm for **3**, 487 and 518 nm for **4**, and 407 and 430 nm for **5**. The decay

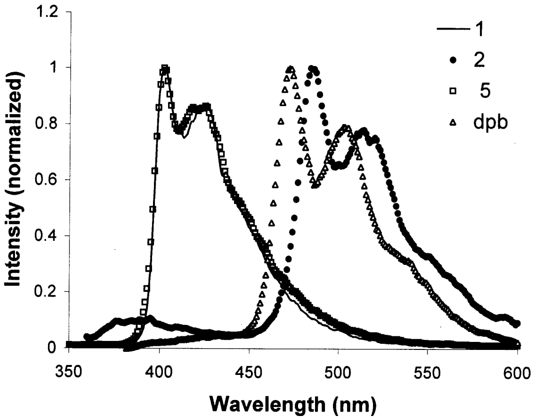


Figure 7. Phosphorescent emission spectra of **1**, **2**, **5**, and the free ligand dpb in THF at 77 K obtained using a time-resolved phosphorescence spectrometer. For clarity, the spectra of **3** and **4** are not shown (they are similar to **1** and **2**, respectively.)

lifetimes of these emission bands were determined to range from 4.6(1) to 8.3(2) μs, which are close to the triplet lifetime of organosilicon compounds reported previously.[18] We therefore attribute these low-energy emission bands to phosphorescence. These phosphorescent bands overlap considerably with the corresponding fluorescent bands, which may explain their relatively short emission lifetime. As shown in Table 3, under the same condition, the emission spectra and UV absorption bands of compounds **1**, **3**, and **5** resemble each other. The same is also true for compounds **2** and **4**. The major difference between these two groups is that the phosphorescent emission bands of **1**, **3**, and **5** are at a much higher energy than those of **2** and **4**, which clearly indicates the involvement of the phenyl and biphenyl groups in the phosphorescent emissions.

To further determine the origin of the fluorescent and phosphorescent emission, we prepared the free ligand 4-di(2-pyridyl)aminobiphenyl (dpb) and investigated its luminescent properties. Dpb has a fluorescent band at $\lambda_{max} = 370$ nm, which resembles those of **2** and **4** but is about 12 nm blue-shifted. As shown in Figure 7, the phosphorescent emission band of dpb also resembles those of **2** and **4**, confirming that both fluorescent and phosphorescent emissions of the complexes are indeed originated from the ligand. The binding of the silicon atom to the ligand causes the red shift of both fluorescent and phosphorescent emission. The major difference between the complexes and the free ligand is that the free ligand dpb has a much longer emission lifetime (473 nm, 20(1) μs; 506 nm, 15(1) μs) than those of **2** and **4**. The relatively short phosphorescent emission lifetimes of the complexes are consistent with the enhancement of the phosphorescent emission by the silicon atom in the complexes.[6]

In summary, five new organosilicon compounds based on 2,2′-dipyridylaminophenyl and 2,2′-dipyridylaminobiphenyl have been synthesized. These compounds display both fluorescent and phosphorescent emissions. The fluorescent and phosphorescent emission bands from these compounds cover the region of violet to blue green. The relatively short decay lifetime of the phosphorescent emission and the chemical stability make these compounds potential candidates for applications in OLEDs. Further investigation on the uses of the new silicon compounds in OLEDs and surface modifications is in progress.

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

Supporting Information Available: X-ray diffraction data for **1** and **3**−**5**, including tables of atomic coordinates, thermal parameters, bond lengths and angles, and hydrogen parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

OM020693N

---

[18] Kwon, J. H.; Lee, T. S.; Shim, S. C. *J. Org. Chem.* **1994**, *59*, 1108.