Structural Optimization of 2,5-Diarylsiloles as Excellent Electron-Transporting Materials for Organic Electroluminescent Devices

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We have already reported that 2,5-di(2-pyridyl)silole (PySPy) has high performance as an electron-transporting material (ETM) for organic electroluminescent devices (OELDs). For the purpose of developing more practicable ETMs, we have now prepared three new 2,5-diarylsilole derivatives, PPySPyP, PyPySPyPy, and PyPSPPy, having 6-phenyl-2-pyridyl, 6-(2-pyridyl)-2-pyridyl, and 3-(2-pyridyl)phenyl as the aryl groups, respectively, and have studied their structure−properties relationships. These derivatives have higher glass transition temperatures when compared to PySPy. Among these compounds and tris(8-hydroxyquinolino)aluminum (Alq), the bipyridylsilole derivative, PyPySPyPy, showed the highest electron-transporting abilities. The efficiency of a device consisting of ITO/triphenyldiamine derivative/Alq/PyPySPyPy/MgAg reached 2.2 lm/W at 3.4 V. Furthermore, the half-life time of a device consisting of ITO/triphenylamine dimer derivative/Alq/PyPySPyPy/LiF/Al was nearly 3 times longer than that of the control device without PyPySPyPy under a constant current.

Introduction

Since the first report of a thin multilayer organic electroluminescent device (OELD) using low molecular weight molecules by Tang and VanSlyke,[1] considerable effort has been devoted to the development of both emitting and charge-transporting materials. The tri-arylamine derivatives, such as TPD (see Chart 1), represent a class of good hole-transporting materials (HTMs), and the current research is in the stage of improving their film durability by increasing their glass transition temperatures (T_g).[2] In contrast, the exploration of new candidates is still required for the development of efficient electron-transporting materials (ETMs). So far, a variety of ETMs have been reported, which include various metal−chelate complexes[3] and π-electron compounds based on oxadiazole,[4] triazole,[5] phenanthroline,[6] and so on.[7] In general, however, the performance of OEL devices is still limited by the low electron

Chart 1. Structures of 2,5-Diarylsilole Derivatives, Alq and TPD
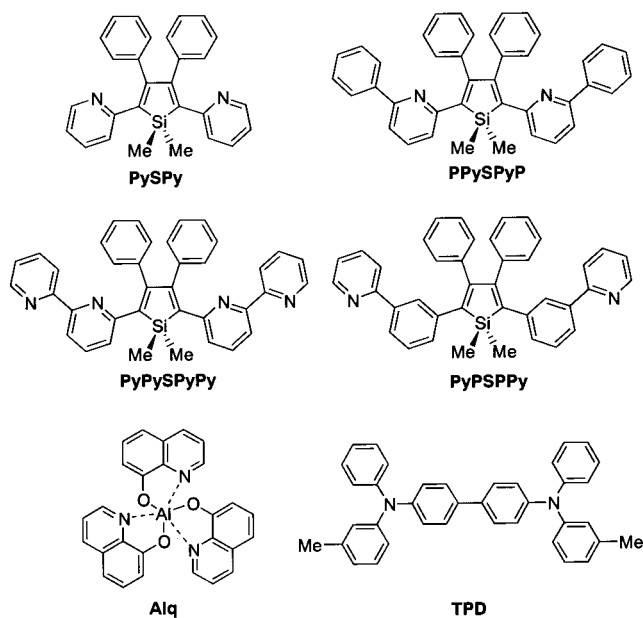
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(7) For example: (a) Bettenhausen, J.; Greczmiel, M.; Jandke, M.; Strohriegl, P. *Synth. Met.* **1997**, *91*, 223. (b) Noda, T.; Shirota, Y. *J. Am. Chem. Soc.* **1998**, *120*, 9714. (c) Noda, T.; Ogawa, H.; Shirota, Y. *Adv. Mater.* **1999**, *11*, 283. (d) Sakamoto, Y.; Suzuki, T.; Miura, A.; Fujikawa, H.; Tokito, S.; Taga, Y. *J. Am. Chem. Soc.* **2000**, *122*, 1832. (e) Strukelj, M.; Papadimitrakopoulos, F.; Miller, T. M.; Rothberg, L. J. *Science* **1995**, *267*, 1969.

injection and the low transporting abilities of the existing ETMs. In comparison with Alq (see Chart 1), one of the best emitting ETMs, some ETMs so far developed indeed exhibit better luminous efficiencies, but the applied voltages for attaining the identical current density are not often reduced. This result should be rationalized as being due not to the higher electron injection and transporting ability of the employed ETM but to the higher blocking effect of the ETM toward the charge and/or exciton. From this viewpoint, we have recently found a new and promising ETM, 2,5-di(2-pyridyl)silole PySPy (see Chart 1), which has both a higher electron injection and transporting ability as well as higher blocking effect relative to Alq.[8] However, unfortunately, PySPy had a serious problem for practical application, i.e., low film stability due to its ready crystallization. We now report the "second stage" research on the pyridyl–silole derivatives, that is, the structural optimization for improvement of the film durability as well as the intrinsic electron-injection and -transporting abilities.

Experimental Section

6-Bromo-2,2′-bipyridyl. A hexane solution of *n*-BuLi (54.9 mL/1.6 M, 88 mmol) was added to a diethyl ether solution of 2-bromopyridine (12.64 g, 80 mmol) dropwise over 40 min at −78 °C. The mixture was stirred for 15 min at the same temperature and then $ZnCl_2$(tmen) (22.22 g, 88 mmol) was added as a solid. The mixture was stirred for 1 h at room temperature. To the resulting suspension, a THF (96 mL) solution of 2,6-dibromopyridine (28.43 g, 120 mmol) and PdCl$_2$-(PPh$_3$)$_2$ (1.40 g, 2.0 mmol) were successively added. The mixture was refluxed with stirring for 16 h. After filtration of the mixture with washing by a toluene (100 mL), ether and THF were removed by rotary evaporation from the filtrate. A HCl aqueous solution (50 mL, 1.5 M) was added to the solution and the product was extracted to the aqueous solution. This procedure was repeated 10 times. After neutralization, the product was extracted with toluene. The extract was washed with water, dried over MgSO$_4$, and concentrated. Silica gel column chromatography (heptane/EtOAc = 3/1, R_f = 0.36) followed by recrystallization from heptane gave 7.08 g (30.4 mmol) of pure 6-bromo-2,2′-bipyridyl in 38% yield as a white solid: ^{1}H NMR (CDCl$_3$) δ 7.31−7.35 (m, 1H), 7.49 (dd, J = 8 and 1.2 Hz, 1H), 7.67 (t, J = 8 Hz,1H), 7.80−7.85 (m, 1H), 8.36−8.42 (m, 2H), 8.66−8.68 (m, 1H).

1-Bromo-3-(2-pyridyl)benzene. This compound was prepared in 49% yield essentially in the same procedure as described for 6-bromo-2,2′-bipyridyl using *m*-dibromobenzene instead of 2,6-dibromopyridine: ^{1}H NMR (CDCl$_3$) δ 7.25−7.27 (m, 1H), 7.34 (t, J = 8 Hz, 1H), 7.52−7.55 (m, 1H), 7.70 (bd, J = 7.6 Hz, 1H), 7.75−7.77 (m, 1H), 7.90−7.92 (m, 1H), 8.17−8.18 (m, 1H), 8.69−8.70 (m, 1H).

2-Bromo-6-phenylpyridine. This compound was prepared in 46% yield essentially in the same procedure as described for 6-bromo-2,2′-bipyridyl using bromobenzene instead of 2-bromopyridine: ^{1}H NMR (CDCl$_3$) δ 7.40−7.49 (m, 4H), 7.60 (t, J = 8 Hz, 1H), 7.69 (dd, J = 8 and 0.8 Hz,1H), 7.98−8.00 (m, 2H).

A typical procedure for the synthesis of the 2,5-diarylsiloles is given for PyPySPyPy (see also ref 9).

PyPySPyPy. To a THF solution of lithium naphthalenide (60 mmol, prepared from lithium and naphthalene in 47 mL of THF) was added a THF (12 mL) solution of bis(phenylethynyl)dimethylsilane (3.91 g, 15 mmol) at room temperature. The

mixture was stirred for 10 min. A THF (15 mL) solution of triphenylchlorosilane (9.85 g, 30 mmol) was then added to the mixture at 0 °C. After the mixture was stirred for 10 min, $ZnCl_2$(tmen) (15.1 g, 60 mmol) was added as a solid. The mixture was then diluted with 40 mL of THF and stirred for 1 h at room temperature. To the resulting suspension, a THF (12 mL) solution of 6-bromo-2,2′-bipyridyl (7.05 g, 30 mmol) and PdCl$_2$(PPh$_3$)$_2$ (526 mg, 0.75 mmol) was successively added. The mixture was refluxed with stirring for 12 h. After filtration of the mixture, a 0.5 N HCl aqueous solution was added to the filtrate, followed by extraction with toluene. The extract was washed with water, dried over MgSO$_4$, and concentrated. Silica gel column chromatography (*n*-heptane/EtOAc = 3/1, R_f = 0.3) followed by recrystallization from a *n*-heptane/EtOAc mixed solvent gave 4.83 g (8.46 mmol) of pure PyPySPyPy in 57% yield as a light yellow solid. For the application to the OEL device, the product was further purified by distillation under high vacuum (240 °C, 1 × 10^{-3} Pa): ^{1}H NMR (CDCl$_3$) δ 0.79 (s, 6H), 6.58 (dd, J = 7.6 and 0.8 Hz, 2H), 6.97−7.16 (m, 10H), 7.28−7.32 (m, 2H), 7.39 (t, J = 8.0 Hz, 2H), 7.82−7.87 (m, 2H), 8.10 (dd, J = 7.6 and 0.8 Hz, 2H), 8.41−8.44 (m, 2H), 8.66−8.68 (m, 2H); ^{13}C NMR (CDCl$_3$) δ −2.27, 118.23, 121.35, 123.31, 123.76, 127.09, 128.51, 129.51, 136.67, 137.14, 139.98, 144.46, 149.40, 155.62, 156.30, 157.10, 157.88. Anal. Calcd for C$_{38}$H$_{30}$N$_4$Si: C, 79.97; H, 5.30; N, 9.82. Found: C, 79.80; H, 5.26; N, 9.59.

PyPSPPy. This compound was prepared in 22% yield essentially in the same procedure as described for PyPySPyPy using 1-Bromo-3-(2-pyridyl)benzene instead of 6-bromo-2,2′-bipyridyl: ^{1}H NMR (CDCl$_3$) δ 0.59 (s, 6H), 6.88−7.06 (m, 12H), 7.16−7.30 (m, 6H), 7.47 (t, J = 2.0 Hz, 2H), 7.65 (m, 2H), 7.76−7.78 (m, 2H), 8.63−8.65 (m, 2H); ^{13}C NMR (CDCl$_3$) δ −3.49, 120.82, 122.16, 124.75, 126.60, 127.89, 127.91, 128.85, 129.84, 130.40, 136.84, 139.26, 139.36, 140.31, 142.04, 149.87, 154.66, 158.01. Anal. Calcd for C$_{40}$H$_{32}$N$_2$Si: C, 84.47; H, 5.67; N, 4.93. Found: C, 84.45; H, 5.67; N, 4.97.

PPySPyP. This compound was prepared in 22% yield essentially in the same procedure as described for PyPySPyPy using 2-bromo-6-phenylpyridine instead of 6-bromo-2,2′-bipyridyl: 43% yield; ^{1}H NMR (CDCl$_3$) δ 0.77 (s, 6H), 6.49 (d, J = 7.6 Hz, 2H), 6.97−7.18 (m, 10H), 7.28−7.33 (m, 2H), 7.38−7.50 (m, 8H), 8.02−8.05 (m, 4H); ^{13}C NMR (CDCl$_3$) δ −2.48, 117.16, 121.39, 126.77, 126.98, 128.23, 128.73, 128.76, 129.36, 136.18, 139.90, 139.95, 144.72, 155.84, 156.42, 158.19. Anal. Calcd for C$_{40}$H$_{32}$N$_2$Si: C, 84.47; H, 5.67; N, 4.93. Found: C, 84.42; H, 5.56; N, 4.69.

Fabrication of OEL Devices. Organic layers were thermally evaporated onto an ITO-coated glass substrate with monitoring of film thickness by an oscillating quartz thickness monitor. The emitting area was defined by using a shadow mask to be 0.5 × 0.5 cm². The power supply was controlled using a personal computer and GP-IB. The light−current curve was measured with an ADVANTEST R6450 digital multimeter. The luminance was measured with a TOPCOM BM-7 luminance meter. The EL spectra were measured with a HITACHI U-4010 fluorescence spectrophotometer.

Results and Discussion

The compounds studied herein include 2,5-di(2-pyridyl)silole (PySPy) and three 2,5-bis(biaryl)siloles bearing 6-phenyl-2-pyridyl (PPy), 6-(2-pyridyl)-2-pyridyl (PyPy), and 3-(2-pyridyl)phenyl (PyP) groups (Chart 1). The molecular design for the new siloles PPySPyP and PyPySPyPy relies on the introduction of additional outer aryl groups at the 6-position of the 2-pyridyl group in the 2,5-di(2-pyridyl)silole skeleton to improve the thin film stability, keeping their emission wavelengths comparable to that of PySPy. In general, to decrease the band gap of the material is not desirable because the charge carrier, both hole- and electron-transporting materials, with narrow band gaps often reduce the

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**Table 1. Thermal and Photophysical Properties of
2,5-Diarylsiloles**

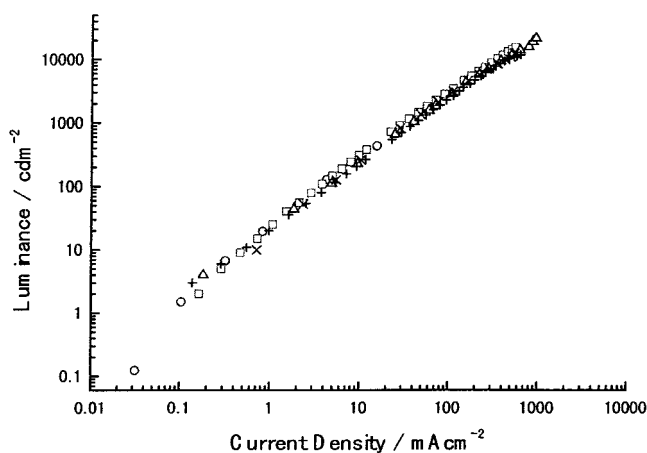| compd	mp (°C)	T_g (°C)	UV−vis absorption, λ_{max} (nm)		PL, λ_{max} (nm)	
			solution[a]	film[b]	solution[a]	film[b]
PySPy	175	c	378	380	480	487
PPySPyP	200	81	388	393	487	496
PyPySPyPy	240	77	386	390	489	495
PyPSPPy	218	81	364	371	488	487

[a] In THF solution. [b] The vacuum-deposited thin film with 100 nm of thickness. [c] Cannot be determined.

performance of the devices due to energy transfer and/ or charge carrier transfer from an emitting layer, especially in the case of a bluer emitting material. Compound PyPSPPy was designed to clarify the effects of the aryl groups directly connected to the silole ring in comparison with its pyridyl analogues PPySPyP and PyPySPyPy. These compounds can be readily prepared from bis(phenylethynyl)dimethylsilane in a one-pot procedure (see Experimental Section).[8,9] They were purified by column chromatography or recrystallization, followed by distillation or sublimation under high vacuum.

The fundamental thermal and photophysical properties of the siloles are summarized in Table 1. The melting points of the biaryl-substituted derivatives were over 200 °C, which are about 25−65 °C higher than that of PySPy. Although the T_g of PySPy could not be measured because of its ready crystallization, the biaryl-substituted siloles have a relatively high T_g around 80 °C, independent of the substituents. While the amorphous film of PySPy formed by vapor deposition resulted in crystallization upon standing for a while, the films of biaryl-substituted derivatives did not show any crystallization at ambient temperature. From the results, the biaryl-substituted derivatives are thus expected to have a lower crystallinity compared with PySPy, which has a lower melting point and hence has a lower T_g.

In the UV−visible absorption spectra, all siloles have their absorption maxima around 360−390 nm both in solution and in the solid state. The 2,5-diphenylsilole derivative, PyPSPPy, has about a 10−20 nm shorter λ_{max} than those of the other three 2,5-dipyridylsilole derivatives. In the photoluminescence (PL) spectra, all four siloles emit bluer lights with their maximum wavelengths around 480−495 nm. The PL spectra of their thin films essentially coincide with those in solution. The introduction of the outer aryl groups to PySPy causes only about 10-nm red shifts in the absorption and emission maxima, suggesting comparable HOMO−LUMO energy gaps to one another.

To evaluate the performance of the present siloles as ETMs, devices consisting of three layers, TPD(50 nm)/ Alq(15 nm)/silole(35 nm), were fabricated in which the TPD and Alq work as hole-transporting and emitting materials, respectively. As a control experiment, the standard two-layer device[10] having the TPD(50 nm)/Alq-(50 nm) structure was also fabricated, where Alq works as both the electron-transporting and emitting materials. In both types of devices, the organic layers were

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Figure 1. Luminance−current density ($L−J$) characteristics of the OEL devices with ITO/TPD/Alq/Silole/Mg:Ag and ITO/TPD/Alq/Mg:Ag structures. ETM: PyPySPyPy (△), PPySPyP (□), PyPSPPy (○), PySPy (×), and Alq only (+).
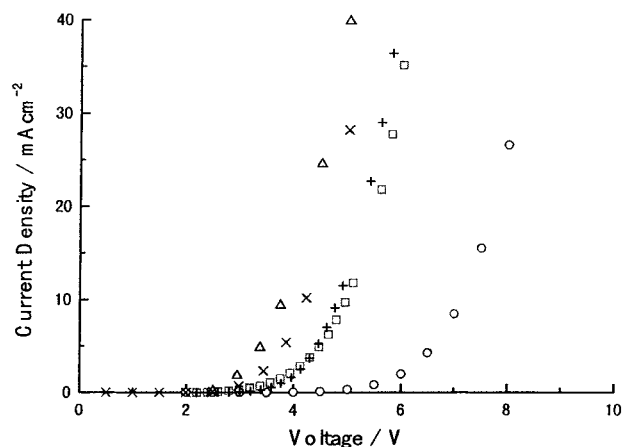
Figure 2. Current density−applied voltage ($J−V$) characteristics of the OEL devices with ITO/TPD/Alq/Silole/Mg:Ag and ITO/TPD/Alq/Mg:Ag structures. ETM: PyPySPyPy (△), PPySPyP (□), PyPSPPy (○), PySPy (×), and Alq only (+).

sandwiched between ITO as the anode and a Mg:Ag alloy (mole ratio = 10/1) as the cathode.

All the devices emit green lights from Alq while no emission from any exciplex or CT complex was observed, indicating that the silole derivatives only served as the ETM. As shown in Figure 1, all devices using the siloles as the ETM showed essentially comparable luminance−current density ($L−J$) properties to one another with about a 2.2−2.7 cd A[−1] $L−J$ efficiency, which is slightly higher than the efficiency of the control device without a silole (2.2 cd A[−1]). These results demonstrate the slightly higher hole and/or exciton blocking effect of the silole derivatives compared with that of Alq.
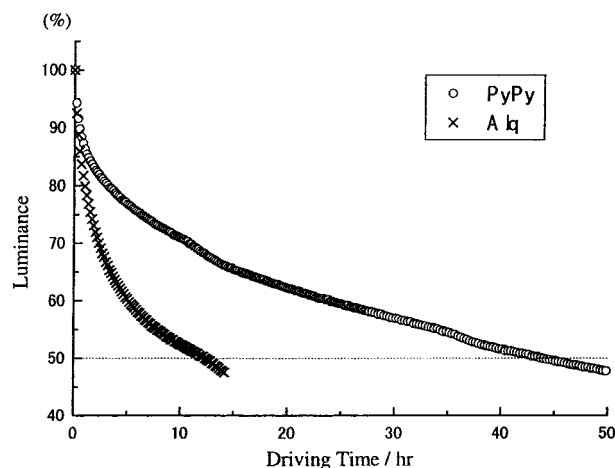
Figure 2 shows the current density−applied voltage ($J−V$) properties. It should be noted that the performance of each device is significantly dependent on the ETM employed, in contrast to the slight dependence of the $L−J$ properties on the ETMs. Some notable points are summarized as follows. (1) The devices using the three 2,5-di(2-pyridyl)silole derivatives have lower or comparable driving voltages and higher luminous efficiencies relative to the control device with only Alq, indicating the higher or comparable electron-injection and -transporting abilities of these siloles compared to those of Alq. In contrast, (2) the performance of the 2,5-

diphenylsilole derivative, PyPSPPy, is inferior to those of the 2,5-dipyridylsiloles and Alq. This clearly demonstrates that the 2-pyridyl-based groups at the 2,5-positions of the silole skeleton play a key role in the higher performance. (3) A comparison among the three 2,5-dipyridylsilole derivatives demonstrates the important role of the outer aryl groups. Thus, while the outer phenyl derivative, PPySPyP, has a performance comparable to the parent 2,5-dipyridylsilole, PySPy, the outer pyridyl derivative, PyPySPyPy, exhibits a much higher performance. The light from the device with PyPySPyPy can be recognized by the naked eye, even below a 2.5-V applied voltage, and its luminous efficiency reached 2.2 lm/W at 3.4 V. Such a higher performance by PyPySPyPy should be attributed to the electron-accepting properties of the outer pyridyl groups.

The performance level of PyPySPyPy as an ETM is further demonstrated by testing the longevity of the device. The device for this measurement employed aluminum as the cathode together with a very thin film (0.5 nm) of LiF between the silole layer and the aluminum cathode.[11] The performance of the device fabricated without any sealing technique was monitored at a 50 mA cm^{-2} current density. Figure 3 shows the luminance-driving time plot for the device with PyPySPyPy, together with the data for the device having Alq as the emitting ETM for comparison. The initial luminances of the devices with PyPySPyPy and without PyPySPyPy started at 1620 and 1330 cd m^{-2}, respectively. The half-life time of the luminance for the device with PyPySPyPy (43 h) was nearly 3 times longer than that for the device without it. It is likely that the

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Figure 3. Plots of luminance vs driving time for the OEL devices having ITO/TPD(50 nm)/Alq(15 nm)/PyPySPyPy(35 nm)/LiF(0.5 nm)/Al(100 nm) (○) and ITO/TPD(50 nm)/Alq(50 nm)/LiF(0.5 nm)/Al(100 nm) (×) structures.

insertion of the silole layer into the device improves the charging and thus the longevity.

Conclusion

Three new 2,5-bis(biaryl)silole derivatives have been prepared and the substituent effects have been studied from the viewpoint of the application to ETMs for OELDs. They have higher T_g's and thus improve the morphological stability in their evaporated films when compared with the those of 2,5-dipyridylsilole. The bipyridylsilole derivative, PyPySPyPy, shows very high performance and durability as the ETM for OELDs, which satisfy the criteria for practical use.