Diphenylamino-Substituted 2,5-Diarylsiloles for Single-Layer Organic Electroluminescent Devices

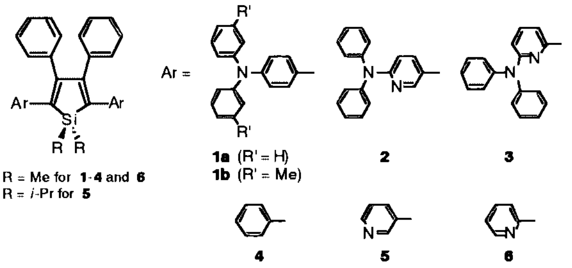
Shigehiro Yamaguchi,* Tomonori Endo, Manabu Uchida,[†] Takenori Izumizawa,[†] Kenji Furukawa,[†] and Kohei Tamao*
Institute for Chemical Research, Kyoto University, Uji, Kyoto 611-0011
[†]*Yokohama Research Center, Chisso Corporation, Kanazawa-ku, Yokohama 236-8605*

(Received November 10, 2000; CL-001026)

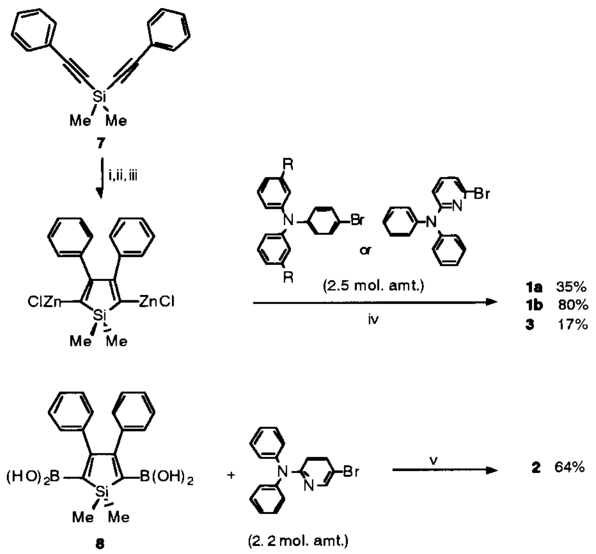
A series of diphenylamino-substituted 2,5-diarylsiloles has been prepared and their photophysical and electrochemical properties have been determined. The single layer EL devices with the ITO/silole/Mg:Ag configuration emitted a greenish-yellow light with a high luminous efficiency.

Organic electroluminescent (EL) devices have attracted considerable attention because of their wide applicability as display materials.[1] The principal mechanism of the EL is the emission from the singlet exciton which is produced by the recombination of holes and electrons injected from the anode and cathode, respectively, into the organic layer. The efficiency of the EL primarily depends on the quantities of the injected carriers. While the multi-layer cell structure consisting of the hole transporting layer and the emissive electron transporting layer is frequently employed to achieve a balanced injection of holes and electrons,[2,3] the development of new materials for a single-layer EL device is still a challenge in view of the construction of molecules having both of hole and electron transporting abilities.[4–7]

We now report new materials based on 2,5-diarylsiloles for the single-layer EL devices. We have recently demonstrated that silole works as a useful core for electron-transporting materials.[8] In particular, 2,5-di(2-pyridyl)silole has a significantly high performance which exceeds that of tris(quinolinolato)aluminum (Alq), one of the best electron-transporting materials.[9] The introduction of electron-donating diphenylamino groups to the 2,5-diarylsilole skeleton would increase the HOMO levels to add the hole-transporting ability to the electron-transporting 2,5-diarylsiloles. We have now designed three types of 2,5-diarylsiloles, *p*-(diphenylamino)phenyl-siloles **1**, [6-(diphenylamino)-3-pyridyl]-silole **2**, and [6-(diphenylamino)-2-pyridyl]-silole **3**. Their synthesis, properties, and applications to the single-layer EL devices are described herein together with a comparison to their parent derivatives **4**–**6**[10] without the diphenylamino substituents.



Scheme 1.



i, LiNaph (4 mol. amt.), THF, rt.; ii, Ph_3SiCl (2 mol. amt.), −78 °C.; iii, $ZnCl_2$(tmen) (2 mol. amt.), 0 °C ~ rt.; iv, $PdCl_2(PPh_3)_2$ (0.05 mol. amt.), THF, reflux, 12 h; v, $Pd_2(dba)_3\cdot CHCl_3$ (0.025 mol. amt.), Na_2CO_3 (2 mol. amt.), THF/H_2O = 4/1, reflux, 72 h. Mol. amt. = molar amount.

Compounds **1**–**3** have been prepared by the methods we recently developed,[10,11] as shown in Scheme 1. Thus, compounds **1** and **3** were prepared in one pot from bis(phenylethynyl)silane **7** by the intramolecular reductive cyclization[12] and subsequent Pd(0)-catalyzed cross-coupling reaction.[10] Although the 3-pyridyl silole derivative **2** was not obtained by this method, it was alternatively prepared by the Pd(0)-catalyzed cross-coupling[13] of silole-2,5-diboronic acid **8** with 6-(diphenylamino)-3-pyridyl bromide.[11] The structures of **1**-**3** have been unequivocally characterized by ^1H and ^{13}C NMR spectroscopy and elemental analysis. The siloles thus obtained have relatively high glass-transition temperatures: T_g: **1a**, 98 °C; **1b**, 81 °C; **2**, 113 °C; **3**, 68 °C.

The photophysical and electrochemical data for **1**-**3** are summarized in Table 1 together with those for silole derivatives **4**-**6** for comparison. In the UV–visible absorption spectra, com-

Table 1. Photophysical and electrochemical data for siloles **1**-**6**

Compound	UV-vis[a]		PL[a]	CV[b]
	λ_{max} / nm	(log ε)	λ_{max} / nm	E_{pa} / V
1a	423	(4.36)	528 (545)[c]	+0.32
1b	424	(4.35)	529 (545)[c]	+0.31
2	421	(4.39)	522 (544)[c]	+0.49
3	416	(3.91)	496 (517)[c]	+0.83
4[d]	359	(3.97)	467	+0.94[e]
5[d]	354	(3.96)	466	+1.14[e]
6[d]	370	(4.17)	468	+0.92[e]

[a]In chloroform, unless otherwise stated. [b]Measured under the following condition: Sample, 1 mM; nBu_4NClO_4 (0.1 M) in PhCN, unless otherwise stated. Vs. Fc/Fc^{+}. All redox processes were irreversible. [c]Emission maximum wavelengths of the vacuum vapor-deposited thin film are in the parentheses. [d]In ref. 10. [e]CH_3CN was used as a solvent.

pounds **1**–**3** have their λ_{max} around 420 nm, irrespective of the aryl groups at the 2,5-positions on the silole ring. In contrast, there are some differences in the photoluminescence. Compounds **1** and **2** have their emission bands at about 30 nm longer wavelengths than that of **3** both in solution and in the thin film. Compared with **4**–**6**, the absorption and luminescence maxima of the diphenylamino-substituted **1-3** are longer by about 40–60 nm and about 30–60 nm, respectively. These results suggest that the diphenylamino groups substantially perturb the electronic structures of the parent 2,5-diarylsilole skeletons.

Although the redox potentials of the materials do not directly correlate to their hole or electron transporting abilities, these data may be useful when considering the capabilities of the career injections from the electrodes. The cyclic voltammetry measurements have been performed for compounds **1**–**3** (Table 1). All compounds **1**–**3** showed irreversible oxidation peaks with low oxidation peak potentials (E_{pa}) around 0.3–0.8 V vs Fc/Fc$^+$, while no reduction peaks were observed. Notably, the incorporation of the diphenylamino groups caused significant negative shifts in the E_{pa}, by about 0.6 V as observed by changing from **4** to **1** and from **5** to **2**. In contrast, the E_{pa} shift from **6** to **3** is only about 0.1 V. These results ensure that the diphenylamino moieties at the "para" position of the 2,5-diaryl groups in compounds **1** and **2** significantly increase the HOMO level, whereas in the case of **3**, the diphenylamino moieties are present at the "meta" position and may affect the electronic structure mainly through an inductive effect.

The siloles **1**–**3** have been applied to the single-layer EL devices. The devices with the ITO/silole (100 nm)/Mg:Ag (10:1) configuration have been fabricated by the vacuum vapor-deposition. All siloles **1**–**3** except **1a** have sufficiently good film-forming properties for evaluating their performance. When the forward bias is applied, all the devices emit a greenish-yellow light. Their EL spectra are shown in Figure 1.

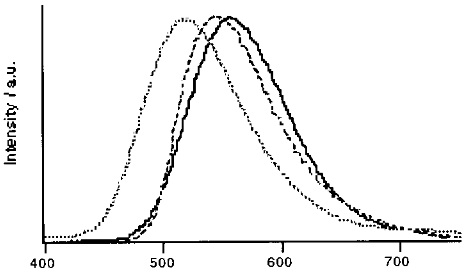


Figure 1. EL spectra of the devices with ITO/silole/Mg:Ag: **1b**, solid line; **2**, broken line; **3**, dotted line.

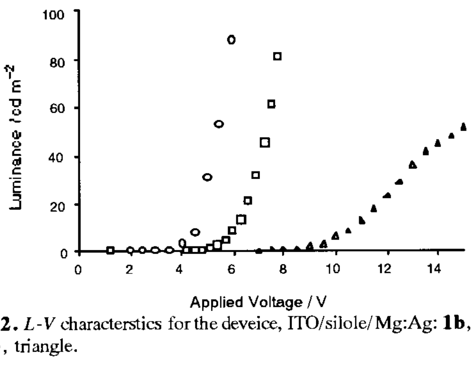


Figure 2. L-V characterstics for the deveice, ITO/silole/Mg:Ag: **1b**, circle; **2**, square; **3**, triangle.

The luminance–voltage (L–V) characteristics of the devices are shown in Figure 2 and their performances are summarized in Table 2. Some notable points are as follows: (1) The maximum luminance reached 10^3 cd m^{-2} for **1b** and **2**, although that for the device with **3** is only moderate. (2) The devices using **1b** have the lowest driving voltage with a significantly low onset voltage of about 3 V. However, as for the luminous efficiency, the device with **2** has about a five times higher value than that of **1b**. (3) The maximum current density and the luminous efficiency of the device with **3** are significantly lower than those for the device with **2**. These results suggest that the 2,5-di(3-pyridyl)silole derivative **2** has a higher hole-blocking property than the diphenylsilole derivative **1b** and thus the more balanced injection and transportation of holes and electrons are realized in the device with **2** in comparison with the case of **1b**. The large difference in the performance between **2** and **3** may be attributed to the difference in their electronic structures, suggesting the importance of the HOMO-LUMO control by introduction of appropriate substituents at the 2,5-positions.

Table 2. Performance of the single layer EL devices[a]

Silole	EL λ_{max} / nm	Max. current density / mA cm^{-2}	Max. luminance / cd m^{-2}	Luminous efficiency[b] / lm W^{-1}
1b	558	960[c]	1130[c]	0.058
2	546	340[d]	1220[d]	0.26
3	520	180[d]	180[d]	0.0063

[a] ITO/silole (100 nm)/Mg:Ag(10:1). [b] To obtain 50 cd m^{-2} of light. [c] At 11 V. [d] At 15 V.

References

1 a) A. Kraft, A. C. Grimsdale, and A. B. Holmes, *Angew. Chem. Int. Ed.*, **37**, 402 (1998). b) R. H. Friend, R. W. Gymer, A. B. Holmes, J. H. Burroughes, R. N. Marks, C. Taliani, D. D. C. Bradley, D. A. Dos Santos, J. L. Brédas, M. Lögdlund, and W. R. Salaneck, *Nature*, **397**, 121 (1999).
2 C. W. Tang and S. A. VanSlyke, *Appl. Phys. Lett.*, **51**, 913 (1987).
3 C. Adachi, T. Tsutsui, and S. Saito, *Appl. Phys. Lett.*, **57**, 531 (1990).
4 a) T. Yamamoto, T. Inoue, and T. Kanbara, *Jpn. J. Appl. Phys.*, **33**, 250 (1994). b) A. W. Grice, A. Tajbakhsh, P. L. Burn, and D. D. C. Bradley, *Adv. Mater.*, **9**, 1174 (1997). c) B. Schulz, Y. Kaminorz, and L. Brehmer, *Synth. Met.*, **84**, 449 (1997). d) W. Huang, H. Meng, W.-L. Yu, J. Gao, and A. J. Heeger, *Adv. Mater.*, **10**, 593 (1998). e) Z. Peng, Z. Bao, and M. E. Galvin, *Adv. Mater.*, **10**, 680 (1998).
5 a) N. C. Greenham, S. C. Moratti, D. D. C. Bradley, R. H. Friend, and A. B. Holmes, *Nature*, **365**, 628 (1993). b) M. Hanack, J. L. Segura, and H. Spreitzer, *Adv. Mater.*, **8**, 663 (1996). c) D.-J. Kim, S.-H. Kim, T. Zyung, J.-J. Kim, I. Cho, and S. K. Choi, *Macromolecules*, **29**, 3657 (1996).
6 a) J. Kido, G. Harada, and K. Nagai, *Chem. Lett.*, **1996**, 161. b) M. Zheng, F. Bai, Y. Li, G. Yu, and D. Zhu, *J. Polym. Sci.: Part A-1.*, **37**, 2587 (1999).
7 The dye-dispersed single-layer EL devices have also been extensively studied. For example, see: a) J. Littman and P. Martic, *J. Appl. Phys.*, **72**, 1957 (1992). b) S. Naka, K. Shinno, H. Okada, H. Onnagawa, and K. Miyashita, *Jpn. J. Appl. Phys.*, **33**, 1772 (1994).
8 S. Yamaguchi and K. Tamao, *J. Chem. Soc., Dalton Trans.*, **1998**, 3693.
9 K. Tamao, M. Uchida, T. Izumizawa, K. Furukawa, and S. Yamaguchi, *J. Am. Chem .Soc.*, **118**, 11974 (1996).
10 S. Yamaguchi, T. Endo, M. Uchida, T. Izumizawa, K. Furukawa, and K. Tamao, *Chem. Eur. J.*, **6**, 1684 (2000).
11 S. Yamaguchi, T. Goto, and K. Tamao, *Angew. Chem. Int. Ed.*, **39**, 1695 (2000).
12 K. Tamao, S. Yamaguchi, and M. Shiro, *J. Am. Chem. Soc.*, **116**, 11715 (1994).
13 N. Miyaura and A. Suzuki, *Chem. Rev.*, **95**, 2457 (1995).