J. Am. Chem. Soc. **1996,** *118,* 11974−11975

Silole Derivatives as Efficient Electron Transporting Materials

Kohei Tamao,*[†] Manabu Uchida,[‡] Takenori Izumizawa,[‡]
Kenji Furukawa,*[‡] and Shigehiro Yamaguchi[†]

Institute for Chemical Research
Kyoto University, Uji, Kyoto 611, Japan
Yokohama Research Center
Chisso Corporation, Kanazawa-ku
Yokohama 236, Japan

Received August 13, 1996

Organic electroluminescent (EL) devices, generally composed of thin multilayers of hole transporting, emissive, and electron transporting (ET) materials sandwiched between two electrodes,[1,2] are enjoying a great deal of interest because of their possible application as large-area flat panel displays. One of the major current subjects in this field is the development of efficient ET materials.[3] In principle, the efficiency of EL depends on the quantities of injected carriers, holes, and electrons as well as the quantum yield of the emissive material. A balanced injection of holes and electrons is required to realize an efficient EL. However, the efficiency of the electron injection for the devices reported so far seems to be inferior to that of the hole injection, due to the large differences between the Fermi levels of cathode metals and the LUMO levels of the ET materials. High electron affinity may thus be the first requisite for the design of ET materials.[4] Although the low-lying LUMO levels would be readily achieved by the introduction of electron-withdrawing groups into π-conjugated systems, these traditional structural modifications might often result in the undesired formation of charge transfer complexes or exciplexes with HT or emissive materials. Consequently, the representative ET materials widely used so far are rather restricted to only a few types of compounds, such as C=N double bond-containing heterocyles,[5] metal−quinolinol complexes,[6] and cyano-substituted poly(*p*-phenylenevinylene)s.[7] Conceptually, new efficient ET materials are still being developed.

We now introduce *a silicon-containing cyclic π-electron system, silole (silacyclopentadiene),*[8,9] as a novel core component for efficient ET materials. The high electron accepting ability of the silole ring has long been experimentally known.[10] It has recently been theoretically demonstrated that the low-lying LUMO energy level of the silole ring is ascribed to the $\sigma^*-\pi^*$ conjugation between the σ^* orbital of the exocyclic σ bonds on silicon and the π^* orbital of the butadiene moiety in the ring.[11,12] This feature is conspicuous by comparison, as shown in Figure 1, of the calculated HOMO and LUMO energy levels of the silole ring with those of some nitrogen-containing cyclic compounds,[13] most of which have been used as core components of conventional ET materials.[5,14] The silole ring has the lowest LUMO energy level among them. It was thus anticipated that new efficient ET materials would be realized by using the silole ring as a core component.

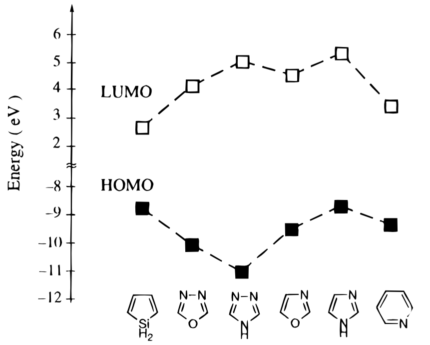
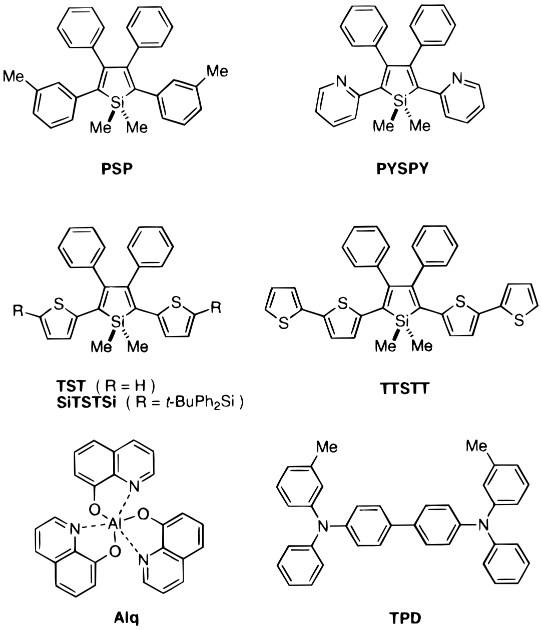


Figure 1. Comparison of HOMO and LUMO energy levels based on *ab initio* calculations at RHF/6−31G* level of theory.

Chart 1



[†] Kyoto University.

[‡] Chisso Corporation.

(1) Tang, C. W.; VanSlyke, S. A. *Appl. Phys. Lett.* **1987**, *51*, 913. Tang, C. W.; VanSlyke, S. A.; Chen, C. H. *J. Appl. Phys.* **1989**, *65*, 3610.

(2) Adachi, C.; Tsutsui, T.; Saito, S. *Appl. Phys. Lett.* **1990**, *57*, 531.

(3) (a) Strukelj, M.; Papadimitrakopoulos, F.; Miller, T. M.; Rothberg, L. J. *Science* **1995**, *267*, 1969. (b) Strukelj, M.; Miller, T. M.; Papadimitrakopoulos, F.; Son, S. *J. Am. Chem. Soc.* **1995**, *117*, 11976.

(4) It has recently been pointed out, however, that there seems to be no direct correlations between the reduction potentials of the ET materials and the performance of the devices. See ref 3.

(5) Representative efficient ET materials reported so far and their pertinent references: 1,3,4-Oxadiazole: (a) Adachi, C.; Tsutsui, T.; Saito, S. *Appl. Phys. Lett.* **1989**, *55*, 1489. (b) Adachi, C.; Tsutsui, T.; Saito, S. *Appl. Phys. Lett.* **1990**, *56*, 799. (c) Hamada, Y.; Adachi, C.; Tsutsui, T.; Saito, S. *Jpn. J. Appl. Phys.* **1992**, *31*, 1812. (d) Pei, Q.; Yang, Y. *Adv. Mater.* **1995**, *7*, 559. (e) Li, X.-C.; Cacialli, F.; Giles, M.; Grüner, J.; Friend, R. H.; Holmes, A. B.; Moratti, S. C.; Yong, T. M. *Adv. Mater.* **1995**, *7*, 898. (f) Li, X.-C.; Holmes, A. B.; Kraft, A.; Moratti, S. C.; Spencer, B. C. W.; Cacialli, F.; Grüner, J.; Friend, R. H. *J. Chem. Soc., Chem. Commun.* **1995**, 2211. (g) Berggren, M.; Granström, M.; Inganäs, O.; Andersson, M. *Adv. Mater.* **1995**, *7*, 900. (h) Kido, J.; Harada, G.; Nagai, K. *Chem. Lett.* **1996**, 161. See also refs 2 and 3. 1,2,4-Triazole: (i) Kido, J. Ohtani, C.; Hongawa, K.; Okuyama, K.; Nagai, K. *Jpn. J. Appl. Phys.* **1993**, *32*, L917. (j) Kido, J.; Kimura, M.; Nagai, K. *Science* **1995**, *267*, 1332.

(6) Tris(8-quinolinolato)aluminum(III) Alq and its derivatives: Hamada, Y. Sano, T.; Fujita, M.; Fujii, T.; Nishio, Y.; Shibata, K. *Chem. Lett.* **1993**, 905. See also ref 1.

(7) Cyano-substituted poly(*p*-phenylenevinylene): a) Greenham, N. C. Moratti, S. C.; Bradley, D. D. C.; Friend, R. H.; Holmes, A. B. *Nature* **1993**, *365*, 628. b) Moratti, S. C.; Cervini, R.; Holmes, A. B.; Baigent, D. R.; Friend, R. H.; Greenham, H. C.; Grüner, J.; Hamer, P. J. *Synth. Metal* **1995**, *71*, 2117.

(8) Dubac, J.; Laporterie, A.; Manuel, G. *Chem. Rev.* **1990**, *90*, 215.

(9) Silole-containing π-conjugated compounds: (a) Tamao, K.; Yamaguchi, S.; Shiozaki, M.; Nakagawa, Y.; Ito, Y. *J. Am. Chem. Soc.* **1992**, *114*, 5867. (b) Tamao, K.; Yamaguchi, S.; Ito, Y.; Matsuzaki, Y.; Yamabe, T.; Fukushima, M.; Mori, S. *Macromolecules* **1995**, *28*, 8668. (c) Tamao, K.; Ohno. S.; Yamaguchi, S. *J. Chem. Soc., Chem. Commun.* **1996**, 1873.

(10) (a) Janzen, E. G.; Pickett, J. B.; Atwell, W. H. *J. Organomet. Chem.* **1967**, *10*, 6. (b) O'Brien, D. H.; Breeden, D. L. *J. Am. Chem. Soc.* **1981**, *103*, 3237.

(11) Khabashesku, V. N.; Balaji, V.; Boganov, S. E.; Nefedov, O. M.; Michl, J. *J. Am. Chem. Soc.* **1994**, *116*, 320.

(12) (a) Tamao, K.; Yamaguchi, S. *Pure Appl. Chem.* **1996**, *68*, 139. (b) Yamaguchi, S.; Tamao, K. *Bull. Chem. Soc. Jpn.* **1996**, *69*, 2327.

(13) *Ab initio* calculations were carried out by using the Gaussian 92 program at the RHF/6-31G* level of theory, in which geometries of those compounds were fully optimized.

(14) Strukelj, M.; Jordan, R. H.; Dodabalapur, A. *J. Am. Chem. Soc.* **1996**, *118*, 1213.

S0002-7863(96)02829-6 CCC: $12.00

Table 1. Performance of Organic EL Devices Containing Silole Derivatives as ET Materials[a]

ET material	*I* (mA cm^{-2}) at 5 V[b]	L (cd m^{-2}) at 5 V[c]	LE (lm W^{-1})[d]	emission λ_{max} (nm)
Alq	10	240	1.5	520[e]
PYSPY/Alq[f]	28	820	1.9	520[e]
TTSTT	100	6.4	0.005	585, 602(sh)[g]
SiTSTSi	3.4	10	0.16	551[g]
PSP	0.1	<0.1	0.17	488[g]

[a] Configuration of the devices is ITO/TPD(500 Å)/ET-material(500 Å)/Mg:Ag unless otherwise stated. Thickness of all devices were arranged to be same for a meaningful comparison between different devices having different numbers of layers. [b] Current density when 5 V was applied. [c] Luminance when 5 V was applied. [d] Luminous efficiency at 100 cd m^{-2}. [e] Electroluminescence from the Alq layer. [f] ITO/TPD(500 Å)/Alq(150 Å)/PYSPY(350 Å)/Mg:Ag. [g] These electroluminescent peaks coincide with the photoluminescent peaks of the thin deposited films of each compound: TTSTT, 585(sh), 604 nm; SiTSTSi, 543 nm; PSP, 486 nm.

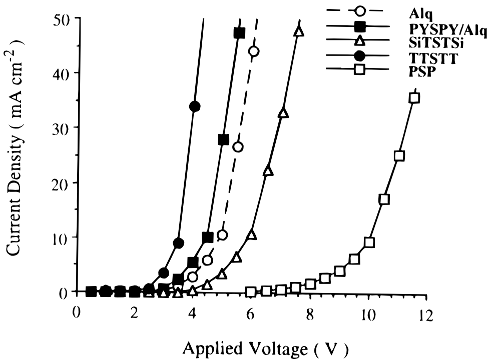


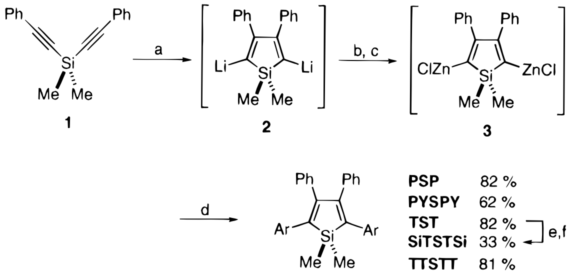
Figure 2. Current-voltage (*I-V*) characteristics of the EL devices as a function of the ET materials.

To evaluate the performance of silole derivatives as ET materials, we have examined four low-molecular weight 2,5-di(aryl)silole derivatives ARSAR, i.e., 2,5-bis(3-methylphenyl)- (PSP), 2,5-bis(2-pyridyl)- (PYSPY), 2,5-bis(5-*tert*-butyldiphenylsilyl-2-thienyl)- (SiTSTSi),[15] and 2,5-bis(bithienyl)silole (TTSTT),[9a,b] the structures being shown in Chart 1. Several devices were fabricated by using these silole derivatives as ET materials, together with indium tin oxide (ITO), *N,N′*-diphenyl-*N,N′*-bis(3-methylphenyl)-1,1′-biphenyl-4,4′-diamine (TPD), and Mg:Ag (10:1) alloy which are employed as the anode, HT material, and cathode, respectively. All layers were made by vacuum deposition.

Indeed, these devices emitted lights at rather low applied voltages. Thus, we compared the performance of the silole derivatives with that of tris(8-hydroxyquinoline)aluminum (Alq), one of the most efficient ET materials reported so far.[1,14] The data are summarized in Table 1 and the current-voltage (*I-V*) characteristics are shown in Figure 2. Remarkably, PYSPY, composed of silole and π-electron-deficient pyridine rings, shows quite high performance; the device PYSPY/Alq (entry 2), consisting of PYSPY as the ET material and Alq as the emissive material, exhibits nearly 3 times higher *I-V* efficiency (28 mA cm^{-2} at 5 V) than those obtained with the device using only Alq (entry 1). Furthermore, the luminance of our device reaches 820 cd m^{-2} at 5 V of applied voltage, while only 240 cd m^{-2} of luminance is obtained without PYSPY. The luminous efficiency of the present device (1.9 lm W^{-1} at 100 cd m^{-2}) is about 1.3 times higher than those obtained with the Alq device.

While this PYSPY could not be used as an emissive ET material due to the undesired formation of exciplexes (or CT complexes) with TPD, three other silole derivatives can be used as emissive ET materials in the ITO/TPD/ARSAR/Mg:Ag devices. The device with TTSTT exhibits one order higher *I-V* efficiency (100 mA cm^{-2} at 5 V) than that with Alq and emits a reddish-orange light, although the luminous efficiency is low. Similar devices containing SiTSTSi and PSP, which exhibit moderate current efficiencies and luminous efficiencies, emit a yellowish-green light and a greenish-blue light, respectively. It should be noted here that about a 100 nm bathochromic shift of the emission wavelength is attained by merely changing the 2,5-aryl groups of the silole from 2-methylphenyl to bithienyl. These results suggest an easy access to various colors of light, blue to red colors required for application to the full-color displays, by modification of only the 2,5-aryl groups on the silole ring. Advantageously, these structural modifications could be readily achieved by the newly developed *one-pot* synthesis of 2,5-di(aryl)silole as described below.

Scheme 1[a]



[a] Reagents and conditions: (a) LiNp (×4), THF, room temperature. (b) *t*-BuPh$_2$SiCl (×2), 0 °C, or Ph$_3$SiCl (×2), −78 °C. (c) ZnCl$_2$•TMEDA (×2), room temperature. (d) ArBr (×2.2), PdCl$_2$(PPh$_3$)$_2$ (×0.05), THF, reflux, 12 h. (e) LiTMP (×2.3), THF, 0 °C. (f) *t*-BuPh$_2$SiCl (×2.3), CuCN (×0.05), THF, room temperature.

Thus, as shown in Scheme 1, the intramolecular reductive cyclization of readily available diethynylsilane **1** using an excess amount of lithium naphthalenide (LiNp) quantitatively afforded 2,5-dilithiosilole **2**,[16] which was successively treated with the bulky *tert*-butyldiphenylchlorosilane (or triphenylchlorosilane) for quenching the remaining LiNp and with ZnCl$_2$•TMEDA. The resulting 2,5-dizinc species **3** was coupled with aryl bromides in the presence of a palladium complex catalyst[17] to afford the corresponding silole derivatives in high yields. Obviously, the present procedure is applicable to the synthesis of a variety of 2,5-di(aryl)silole derivatives by applying the appropriate aryl halides during the final coupling step.

These findings demonstrate for the first time that the silole ring is a promising candidate as a core component for efficient ET materials. Finally, it is emphasized that the silole derivatives may be regarded as only one cyclic diene containing an electropositive atom which is readily available in quantity, can be handled without special care, and has a low-lying LUMO for high electron affinities.

Acknowledgment. We thank the Ministry of Education, Science, Sports, and Culture, Japan, for the Grant-in-Aid (No. 07555280).

Supporting Information Available: Experimental details for silole derivatives and optimized geometries, total SCF energies, and HOMO and LUMO energy levels for heterocycles (6 pages). See any current masthead page for ordering and Internet access instructions.

JA962829C

---

(15) The silyl groups are introduced to improve the quality of the TST thin film. For the preparation of SiTSTSi, see the supporting information.

(16) Tamao, K.; Yamaguchi, S.; Shiro, M. *J. Am. Chem. Soc.* **1994**, *116*, 11715.

(17) Negishi, E.; Luo, F. T.; Frisbee, R.; Matsushita, H. *Heterocycles* **1982**, *18*, 117. Minato, A.; Suzuki, K.; Tamao, K. Kumada, M. *J. Chem. Soc., Chem. Commun.* **1984**, 511.