Toward New Materials for Organic Electroluminescent Devices: Synthesis, Structures, and Properties of a Series of 2,5-Diaryl-3,4-diphenylsiloles

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Abstract: A series of 2,5-diaryl-3,4-diphenylsiloles, with various mono-substituted phenyl groups, extended π-conjugated groups, and heteroaryl groups as aryl groups at the 2,5-positions, has been prepared by a one-pot synthesis from bis(phenylethynyl)silanes based on the intramolecular reductive cyclization followed by the palladium-catalyzed cross-coupling with aryl halides. Crystal structures and chemical reactivities toward the alkaline desilylation reactions have been studied on the 2,5-bis(*p*-monosubstituted phenyl)silole derivatives to elucidate the effects of the *p*-substituents. The UV-visible absorption and fluorescence spectra, and cyclic voltammetry of the 2,5-diarylsiloles have been systematically evaluated. Their photophysical properties as well as their electronic structures significantly depend on the nature of the 2,5-aryl groups.

Keywords: cross-coupling · cyclizations · organic electroluminescent device · silicon · siloles

Introduction

Organic electroluminescent (EL) devices, which are generally composed of thin multilayers of hole-transporting (HT), emissive, and electron-transporting (ET) materials sandwiched between two electrodes,[1, 2] have attracted much attention because of their possible application as new display materials.[3] One of the current subjects to emerge in this field is the development of efficient ET materials;[4] there is an intrinsic difficulty in the development of electron-accepting π-electron systems suitable for the ET materials. Thus, 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 used so far are rather restricted to only a few types of compounds, such as C=N double-bond-containing heteroaryls,[5] metal-quinolinol complexes,[6] cyano-substituted poly(*p*-phenylenevinylene)s,[7] and boron-substituted oligothiophenes.[8] Conceptually, new efficient ET materials are still being developed.

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Recently, we have reported the application of 2,5-diarylsiloles as new excellent ET materials.[9] Silole (silacyclopentadiene)[10] is a high electron-accepting ring due to the σ* – π* conjugation in the ring[11–13] and thus had been envisioned to work as the core component of ET materials. Indeed, one of the 2,5-diarylsiloles examined, 2,5-di(2-pyridyl)silole **1p**, showed very high performance, which exceeded that of tris(8-quinolinolato)aluminum (Alq), one of the best ET materials to date. We have also shown the potential use of fluorescent 2,5-diarylsiloles, such as **1g**, **1m**, and **1n**, as new emissive materials.[9]

We now report the full details of the chemistry of the 2,5-diarylsiloles **1**, which include their one-pot synthesis,[9, 14, 15] crystal structures, UV-visible absorption and fluorescence spectra, and electrochemical behavior. The structures of the 2,5-diarylsiloles studied herein are shown above. For the application of the 2,5-diarylsiloles as ET and emissive materials, our current interests are focused on the control and modification of the electronic structures of the 2,5-diarylsiloles as well as their photophysical properties, because the control of the HOMO and LUMO levels would be the first requisite for the design of efficient organic EL materials.[4]

Results

One-pot synthesis of 2,5-diarylsiloles from bis(phenylethynyl)silanes: We previously reported a new silole cyclization method.[16] As shown in Scheme 1, the intramolecular reductive cyclization of the readily available bis(phenylethynyl)si-

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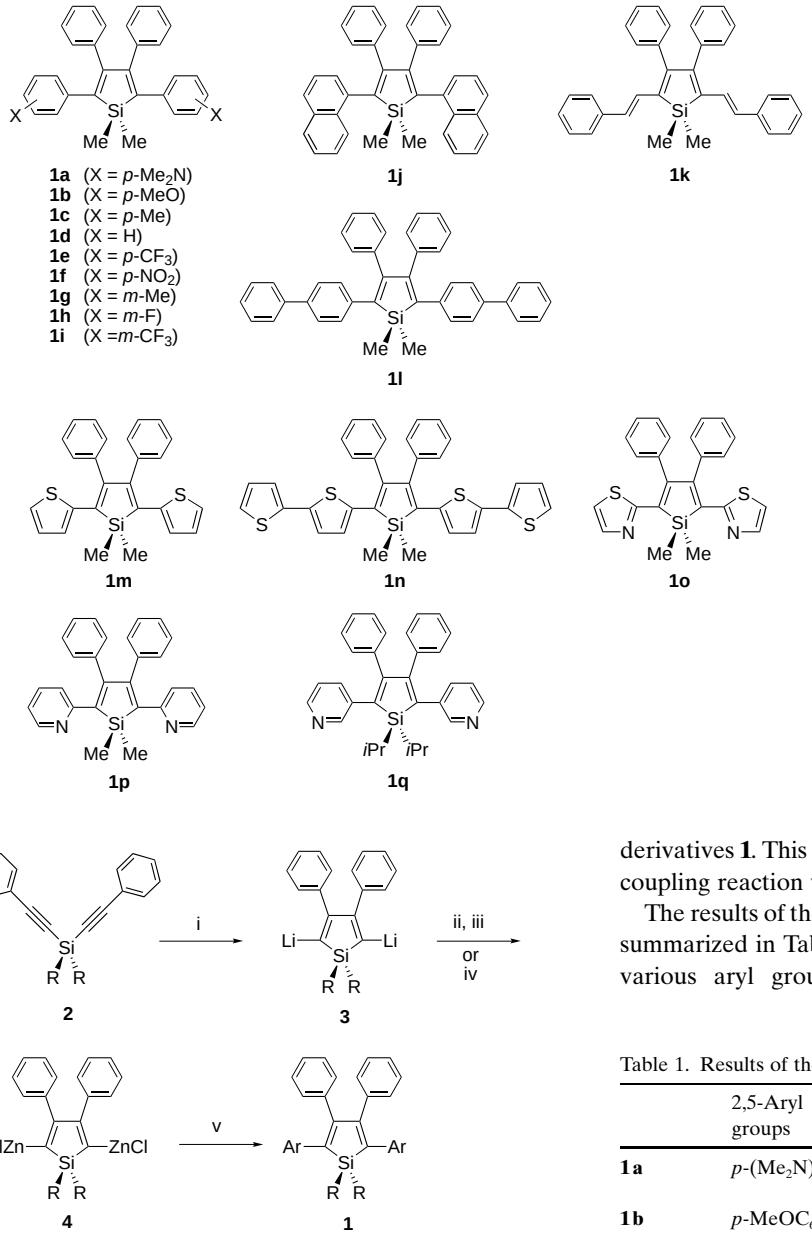


Scheme 1. One-pot synthesis of 2,5-diarylsiloles **1**. Reagents and conditions: i) LiNaph (4 equiv), THF, RT; ii) Ph_3SiCl or $tBuPh_2SiCl$ (2 equiv), −78 °C; iii) $[ZnCl_2(tmen)]$ (2 equiv), 0 °C – RT; iv) $[ZnCl_2(tmen)]$ (4 equiv), 0 °C, RT; v) aryl halide (2.0 – 2.1 equiv), $[PdCl_2(PPh_3)_2]$ (0.05 equiv), THF, reflux, 12 – 20 h.

Abstract in Japanese:

2,5 位の置換基としてモノ置換フェニル基，拡張π共役置換基，およびヘテロアリール基をもつ一連の 2,5-ジアリール-3,4-ジフェニルシロールを，ビス(フェニルエチニル)シランの分子内還元的環化反応およびそれに続く Pd 触媒クロスカップリング反応により，one-pot で合成することに成功した．2,5-ビス(*p*-モノ置換フェニル)シロールについて，結晶構造およびアルカリ脱シリル化反応に対する反応性の検討をおこない，*p*-置換基の及ぼす影響を明らかにした．また，一連の 2,5-ジアリールシロールの紫外可視吸収スペクトル，蛍光スペクトル，およびサイクリックボルタンメトリーを系統的に評価した．それらの光物性および電子構造は，2,5 位のアリール基の性質に大きく依存することが明らかとなった．

lanes **2** using an excess amount (4 equivalents) of lithium naphthalenide (LiNaph) quantitatively affords 2,5-dilithiosiloles **3**. We applied this procedure to the preparation of the 2,5-diarylsiloles (Scheme 1).

Our procedure is as follows. After the reductive cyclization of **2** with LiNaph, the reaction mixture was treated with two equivalents of bulky chlorosilanes, such as triphenylchlorosilane or *tert*-butyldiphenylchlorosilane, to quench the remaining LiNaph, mainly converting the chlorosilanes to the corresponding disilanes. Subsequently, two equivalents of $[ZnCl_2(tmen)]$ (tmen = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine) was added to the mixture to form 2,5-dizinc silole **4**, which was allowed to react with aryl bromides or iodides in the presence of $[PdCl_2(PPh_3)_2]$ to afford the corresponding silole derivatives **1**. This procedure from the cyclization to the cross-coupling reaction was carried out in one pot.

The results of the synthesis of a series of 2,5-diarylsiloles are summarized in Table 1. This method allowed us to introduce various aryl groups, which included a series of mono-

Table 1. Results of the one-pot synthesis of 2,5-diarylsiloles.[a]

	2,5-Aryl groups	quenching reagent[b]	yield [%][c]
1a	*p*-$(Me_2N)C_6H_4$	A	53
		C	97
1b	*p*-$MeOC_6H_4$	A	68
1c	*p*-MeC_6H_4	A	75
1d[d]	C_6H_5	A	70
1e	*p*-$CF_3C_6H_4$	A	67
1f[e]	*p*-$(NO_2)C_6H_4$	A	36
		C	87
1g	*m*-MeC_6H_4	B	82
1h	*m*-FC_6H_4	A	81
1i	*m*-$CF_3C_6H_4$	B	67
1j	1-naphthyl	A	42
1k	2-styryl	A	82
1l	biphenyl	A	74
1m	2-thienyl	A	82
		C	92
1n	bithienyl	A	81
1o	2-thiazolyl	A	54
1p	2-pyridyl	B	62
1q[f]	3-pyridyl	A	58

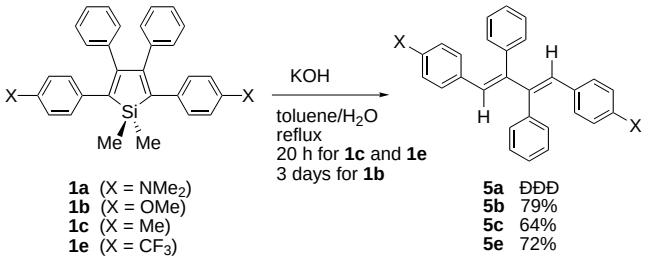
[a] Substituents at the 1,1-positions are methyl groups and the corresponding aryl bromides were used as an aryl halide for the coupling reaction, unless otherwise stated. [b] A: Ph_3SiCl (2 equiv); B: $tBuPh_2SiCl$ (2 equiv); C: $[ZnCl_2(tmen)]$ (4 equiv). [c] Isolated yields. [d] H.Gilman, S. G. Cottis, W. H. Atwell, *J. Am. Chem. Soc.* **1964**, 86, 1596. See ref. [10a]. [e] *p*-$(NO_2)C_6H_4I$ was used. [f] 1,1-Diisopropyl.

0947-6539/00/0609-1684 $ 17.50+.50/0 *Chem. Eur. J.* **2000**, *6*, No. 9

substituted phenyl groups (**1a**–**1i**), extended π-conjugated groups (**1j**–**1l**), and heteroaryl groups such as thiophenes, thiazole, and pyridine (**1m**–**1q**). This is the first general synthetic route to the 2,5-diarylsilole derivatives, although 3,4-diphenyl groups are present as inevitable substituents.[16a] All the 2,5-diarylsiloles prepared herein are air stable and can be handled without special care.

It should be mentioned that the choice of the quenching agent for the remaining LiNaph prior to the coupling reaction was a key factor for the improvement of the isolated yields of the product. Our initial choice was the bulky chlorosilanes as described above, but this sometimes caused a contamination of the product with various amounts of disiloxane formed from the chlorosilanes during the work-up steps and, therefore, required tedious repeated coloumn chromatography. In order to prevent this disturbance, we modified the procedure by using an excess amount of [$ZnCl_2$(tmen)] instead of the chlorosilanes, thus leading to the direct formation of **4**. The use of four equivalents of [$ZnCl_2$(tmen)] based on **2** was found to afford the best result. For example, in the reaction with *p*-(NO_2)C_6H_4I, this modified pocedure produced the desired silole **1f** as the sole product, and simple silica gel column chromatography gave **1f** in 87% isolated yield. Satisfactory improvements in the yields were also attained in the reactions with aryl halides containing the electron-donating Me_2N group or heteroaryl halides such as bromothiophene (Table 1).[17]

Alkaline desilylation of 2,5-bis(*p*-mono-substituted phenyl)-siloles—structure–reactivity relationship: 2,5-Diphenylsiloles have been known to be desilylated under basic conditions to produce the corresponding butadiene derivatives.[18] We examined this reaction for a series of 2,5-bis(*p*-monosubstituted phenyl)siloles, as shown in Scheme 2, in order



Scheme 2. Alkaline-desilylation of 2,5-diphenylsiloles.

to investigate the structure–reactivity relationship. Thus, a solution of **1** in toluene was heated under reflux with KOH in the presence of water. While in the cases of the *p*-Me and *p*-CF_3 derivatives, **1c** and **1e**, the reactions were completed after refluxing for 20 h to give the corresponding tetraphenylbutadienes **5c** and **5e**, respectively, the reaction of the electron-donating methoxy-substituted silole **1b** required a longer reaction period. Moreover, in the case of the *p*-Me_2N derivative **1a**, no reaction took place under the same conditions. Thus, the reactivity of the silicon–carbon bonds of the silole rings significantly depends on the nature of the 2,5-diaryl groups. The electron-donating groups tend to retard the desilylation in terms of the destabilization of the carbanionic spiecies generated during the reaction.

Crystal structures of 2,5-bis(*p*-mono-substituted phenyl)siloles: To elucidate the effects of the nature of the 2,5-diaryl groups on the structures of the 2,5-diarylsiloles, the X-ray crystal structural analyses of a series of 2,5-bis(*p*-monosubstituted phenyl)siloles, **1b**, **1c**, **1e**, and **1f**, were carried out. All the siloles have propeller-like arrangements of the four benzene rings. As a representative example, the *ORTEP* drawing of **1b** is shown in Figure 1. The selected geometrical

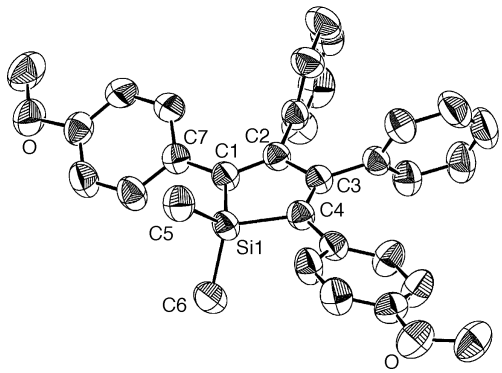


Figure 1. ORTEP drawing of **1b** (50% probability for thermal ellipsoids) with atom-labeling scheme for Table 2.

parameters for these compounds are summarized in Table 2. In all cases, the geometries of the silole rings are in the normal range and the Si1–C1 ($Si–Csp^2$) bond lengths are longer than those for the Si1–C5 ($Si–Csp^3$) bonds, as pointed out in our previous report.[14] As for the dihedral angles between the mean planes of the central silole ring and the 2,5-benzene rings, compounds **1c**, **1e**, and **1f** have comparable values (37–69°), but those for compound **1b** are rather small (~27°); this suggests that the electron-donating group induces the π conjugation more efficiently over the three benzene-silole-benzene rings.

Among the products of the alkaline desilylation reaction of **1**, the crystal structure of **5b** was also determined in order to compare it with that of the silole derivative **1b**. As shown in Figure 2, compound **5b** has a completely coplanar transoid

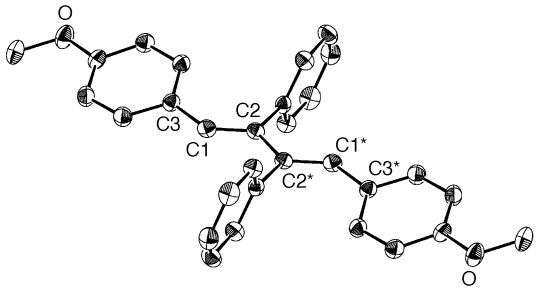


Figure 2. ORTEP drawing of **5b** (50% probability for thermal ellipsoids). Selected bond lengths [Å], bond angles [deg], and torsion angles [deg]: C1–C2 1.351(1), C1–C3 1.468(1), C2–C2* 1.480(2), C1-C2-C2* 120.8(1), C2-C1-C3 131.13(10), C1-C2-C2*-C1* 180.0, C3-C1-C2-C2* 179.9(1).

Table 2. Geometrical parameters for the crystal structures of 2,5-bis(*p*-mono-substituted phenyl)siloles.[a]

p-substituent	**1b** OMe	**1c** Me	**1e** CF_3	**1f** NO_2
bond length [Å]				
Si1−C1	1.879(1)	1.877(1)	1.865(2)	1.878(2)
Si1−C5	1.861(2)	1.852(2)	1.852(4)	1.852(3)
C1−C2	1.355(2)	1.362(2)	1.356(3)	1.361(3)
C2−C3	1.517(3)	1.512(2)	1.498(3)	1.510(2)
C1−C7	1.480(2)	1.479(2)	1.473(3)	1.475(2)
bond angle [°]				
C1-Si1-C4	92.61(9)	92.07(6)	92.03(9)	91.79(8)
C5-Si1-C6	108.2(1)	110.00(9)	111.7(2)	109.2(1)
Si1-C1-C2	107.40(10)	107.75(9)	108.1(2)	108.2(1)
C1-C2-C3	116.27(8)	116.0(1)	115.8(2)	115.9(2)
Si1-C1-C7	125.1(1)	125.48(10)	125.1(2)	124.3(1)
dihedral angle [°]				
silole with 2,5-Ph	27.55,27.55	43.19,69.63	41.32,41.34	37.32,47.03
silole with 3,4-Ph	71.02,71.02	58.21,55.28	60.02,60.13	51.94,62.11

[a] For atom-labelling scheme, see the Figure 1.

butadiene skeleton. The butadiene **5b** has a higher coplanarity between the butadiene moiety and 1,4-phenyl rings than that of the silole derivative **1b**. The dihedral angles in **5b** between the butadiene plane and 1,4-phenyl rings and between the butadiene plane and 2,3-phenyl rings are about 16° and 80°, respectively.

UV-visible absorption and fluorescence spectra of 2,5-diarylsiloles: The UV-visible absorption spectra and fluorescence spectra of the 2,5-diarysiloles **1** have been measured in chloroform. Their data are summarized in Table 3, which also contains the data for **5** and 2,5-bis(*N*-methylpyrrolyl)silole **6**, which we previously reported,[19] for comparison.

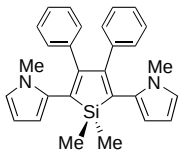


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Table 3. UV-visible absorption and fluorescence spectral data for 2,5-diarylsiloles and related compounds.[a]

	2,5-aryl groups	absorption		fluorescence	
		λ_{max} [nm]	($\log\varepsilon$)	λ_{max} [nm]	Φ_f[b]
1a	*p*-$(Me_2N)C_6H_4$	423	(4.33)	529	2.51×10^{-3}[c]
1b	*p*-$MeOC_6H_4$	379	(4.11)	493	2.40×10^{-3}
1c	*p*-MeC_6H_4	367	(4.11)	475	1.96×10^{-3}
1d	C_6H_5	359	(3.97)	467	1.43×10^{-3}
1e	*p*-$CF_3C_6H_4$	358	(4.02)	469	8.78×10^{-4}
1f	*p*-$(NO_2)C_6H_4$	399	(4.35)	522	2.66×10^{-3}
1g	*m*-MeC_6H_4	364	(3.78)	471(484)[d]	2.78×10^{-3}
1h	*m*-FC_6H_4	358	(4.00)	466	4.38×10^{-4}
1i	*m*-$CF_3C_6H_4$	358	(3.99)	468	1.09×10^{-3}
1j	1-naphthyl	340	(3.96)	435	4.71×10^{-4}
1k	2-styryl	435	(4.04)	527	4.70×10^{-2}[c]
1l	biphenyl	381	(4.32)	497	5.13×10^{-3}
1m	2-thienyl	418	(4.28)	515(525)[d]	1.41×10^{-3}
1n	bithienyl	476	(4.38)	556(604)[d]	3.90×10^{-3}[c]
1o	2-thiazolyl	413	(4.33)	504	1.02×10^{-3}
1p	2-pyridyl	370	(4.17)	468(487)[d]	7.57×10^{-4}
1q	3-pyridyl	354	(3.96)	466(470)[d]	2.56×10^{-3}
5b	*p*-$MeOC_6H_4$	348	(4.46)		
5c	*p*-MeC_6H_4	339	(4.38)		
5e	*p*-$CF_3C_6H_4$	337	(4.34)		
6[e]	*N*-Me-2-pyrrolyl	406	(3.93)		

[a] In $CHCl_3$. [b] Determined with reference to quinine sulfate, unless otherwise stated. [c] Determined with reference to fluorescein. [d] Emission maximum wavelengths of the vacuum vapor-deposited thin film (50 nm thickness) are in the parentheses. [e] Ref. [19]

In the UV-visible absorption spectra, the absorption maxima, ascribed to the $\pi-\pi^*$ transition of the 2,5-diarylsilole π-conjugated moieties, significantly depend on the nature of the 2,5-diaryl groups and vary from the UV region to the visible region. Interestingly, the λ_{max} of the 2,5-diphenylsilole derivatives **1b**, **1c**, and **1e** are about 20–30 nm longer than those of the *trans*-1,4-diphenyl-1,3-butadiene counter compounds **5b**, **5c**, and **5e**, despite the difference in the geometry of the butadiene skeletons (i.e., cisoid or transoid) and the lower coplanarity of the 1,4-diphenylbutadiene skeleton of **1b** than that of **5b** in their crystal structures, which have been already discussed. These comparisons clearly show the significant effect of the incorporation of the silicon moieties and the formation of the five-membered ring.

In the fluorescence spectra, all the siloles **1** have their emission bands in the visible region. The emission maxima also significantly depend on the 2,5-diaryl groups and vary from the bluish-green region to the reddish-orange region. The quantum yields of the present 2,5-diaryl-3,4-diphenylsiloles, determined in solution by using quinine sulfate or fluorescein as standards, are only moderate, due to the effects of the 3,4-diphenyl groups.

From the viewpoint of the application to organic EL devices, the photoluminescence spectra of the vacuum vapor-deposited thin films (50 nm thickness) were preliminarily measured for some representative compounds; the data are also included in Table 3. All the 2,5-diarylsiloles have essentially the same emission wavelengths as those in solution, except 2,5-bis(bithienyl)silole **1n**, which shows about a 50 nm red shift in comparison with that in the solution, presumably due to the formation of an excimer. Figure 3 presents the emission spectra of **1g**, **1m**, and **1n**, which correspond to greenish-blue, yellowish-green, and reddish-orange, respectively.

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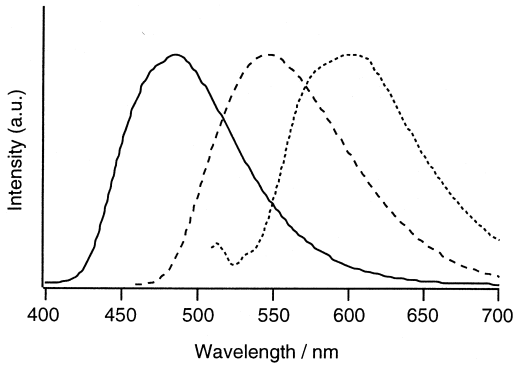

Figure 3. Photoluminescence spectra of the vacuum vapor-deposited films of some representative 2,5-diarysiloles: solid line, **1g**; dashed line, **1m**; dotted line, **1n**.

Electrochemical behavior of 2,5-diarylsiloles: The cyclic voltammetry of the 2,5-diarylsiloles **1** has been determined in order to obtain deeper insights into the electronic structures. Since most of the redox processes observed for **1** were irrevesible, their anodic peak potentials, E_{pa}, and cathodic peak potential, E_{pc}, are summarized in Table 4 in place of the oxidation potentials and reduction potentials, respectively. The data for the pyrrolyl derivative **6** is also included for comparison.[19] The redox potentials also strongly depend on the 2,5-diaryl groups. The discussion on these values will be made in the following section.

Table 4. Electrochemical data for 2,5-diarylsiloles.[a]

	aryl groups	E_{pa1} [V][b]	E_{pa2} [V][b]	E_{pc1} [V][b]	E_{pc2} [V][b]
1a	*p*-$(Me_2N)C_6H_4$	+0.11[c,d]	–	−2.43	–
1b	*p*-$MeOC_6H_4$	+0.66	+0.92	−2.30	–
1c	*p*-MeC_6H_4	+0.94	+1.08	−2.36	–
1d	C_6H_5	+1.02	+1.17	−2.27	–
1e	*p*-$CF_3C_6H_4$	+1.18	–	−1.93	−2.25
1f	*p*-$(NO_2)C_6H_4$	+1.28	–	−1.44[c,e]	−2.32
1g	*m*-MeC_6H_4	+1.12	–	−2.30	–
1h	*m*-FC_6H_4	+1.24	–	−2.15	−2.56
1i	*m*-$CF_3C_6H_4$	+1.30	–	−2.09	−2.52
1j	1-naphthyl	+1.10	+1.20	−2.36	−2.61
1k	2-styryl	+0.64	–	−2.02[c,f]	−2.25
1l	biphenyl	+0.99	–	−2.16	–
1m	2-thienyl	+0.64	–	−2.21	−2.57
1n	bithienyl	+0.55[c,g]	–	−2.04	−2.19
1o	2-thiazolyl	+0.97	–	−1.89	−2.14
1p	2-pyridyl	+1.00	–	−2.10	−2.51
1q	3-pyridyl	+1.22	–	−2.27	−2.59
6	*N*-Me-pyrrolyl	+0.40	+0.79	−2.50	–

[a] Determined by cyclic voltammetry under the following conditions: Sample, 1 mM; nBu_4NClO_4 (0.1M) in CH_3CN. All redox processes were irreversible unless otherwise stated. [b] Versus Ag/Ag^+. [c] Revesible redox process. [d] $E_{1/2} = +0.07$ V. [e] $E_{1/2} = +1.37$ V. [f] $E_{1/2} = -1.98$ V. [g] $E_{1/2} = +0.47$ V.

Discussion

The one-pot synthesis of a series of 2,5-diarylsiloles based on the intramolecular reductive cyclization of diethynylsilanes now allows us to study the structure–reactivity and structure–property relationship for the 2,5-diarylsiloles. It was found that the electron-donating substituents on the 2,5-diphenyl groups induce the effective π conjugation, and the nature of the 2,5-diaryl groups significantly affects the reactivity of the silicon–carbon bond of the silole ring for the alkali-desilylation reaction, as already mentioned. In this section, the discussion focuses on the structure–property relationship of the 2,5-diarylsiloles. On the basis of the data summarized in Tables 3 and 4, their photophysical and electrochemical properties were separately evaluated in the following three series of compounds; 1) the 2,5-bis(mono-substituted phenyl)siloles, 2) the 2,5-diarylsiloles that conatin extended π-conjugated groups, and 3) the 2,5-bis(hetero-aryl)siloles.

2,5-Bis(mono-substituted phenyl)siloles: substituent effects on the properties: In a series of 2,5-diphenylsilole derivatives **1a–1i**, the substituents on the phenyl groups at the 2,5-positions significantly affect their photophysical properties. Thus, as summarized in Table 3, the λ_{max} values of the absorption and emission spectra vary by about 60 nm in the range of 358–422 nm and 467–529 nm, respectively. In particular, the conjugative substituents, such as NMe_2 and NO_2, induce considerably low-energy absorptions and emissions. Their redox potentials also significantly depend on the substituents on the phenyl groups (Table 4). As the substituents become more electron donating, the E_{pa1} values become lower. On the other hand, as the substituents become more electron withdrawing, the E_{pc1} values become lower. It is noteworthy that the differences between the NMe_2 derivative **1a** and the NO_2 derivative **1f** exceed more than 1 V both in E_{pa1} and E_{pc1}. These results suggest that the HOMO and LUMO levels of the 2,5-diarylsiloles can be readily controlled over a wide range by modification of the 2,5-diaryl groups.

The E_{pa1} and E_{pc1} values of **1a–1i** are plotted versus the σ^+ and σ^- values[20] of the substituents, respectively, to give a good linear relationship in each case as shown in Figures 4 and 5 and Equations (1) and (2), respectively.

$$E_{pa1} = 1.02 + 0.476\,\sigma^+ \quad (r = 0.975) \tag{1}$$

$$E_{pc1} = -2.28 + 0.603\,\sigma^- \quad (r = 0.982) \tag{2}$$

Figure 6 shows the plots of the absorption maximum wavenumbers ν_{abs} and the emission maximum wavenumbers ν_{em} versus the values of ΔE ($= E_{pa1} - E_{pc1}$). A reasonably good linear relationship is obtained between ν_{em} and ΔE, as shown in Equation (3), whereas the linearity for ν_{abs} is slightly low, as shown in Equation (4); this is probably due to the effect of the noncoplanarity between the central silole ring and 2,5-benzene rings in the ground state.

$$\nu_{em} \times 10^{-4} = 1.19 + 0.281\,\Delta E \quad (r = 0.951) \tag{3}$$

$$\nu_{abs} \times 10^{-4} = 1.38 + 0.419\,\Delta E \quad (r = 0.928) \tag{4}$$

The ΔE in Equation (3) is replaced by Equations (1) and (2) to afford Equation (5), which represents a relationship between the emission wavenumbers and the σ^+ and σ^- values

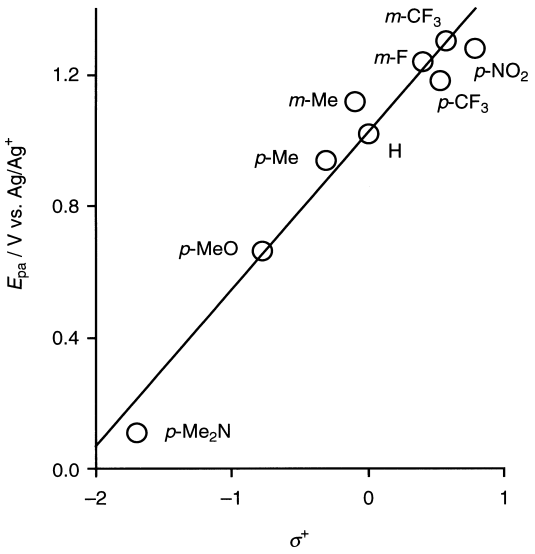

Figure 4. Plots of oxidation peak potentials as a function of the σ^+ values of the substituents on the 2,5-diphenyl groups of **1**.

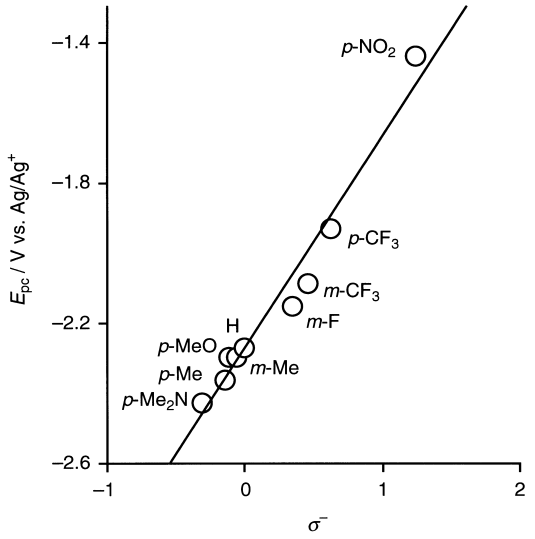

Figure 5. Plots of reduction peak potentials as a function of the σ^- values of the substituents on the 2,5-diphenyl groups of **1**.

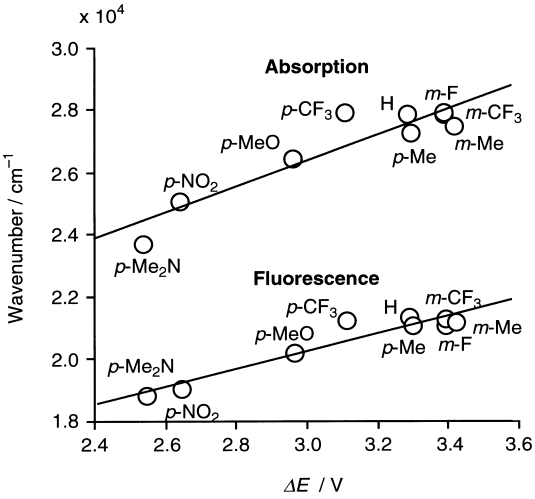

Figure 6. Plots of absorption and emission wavenumbers of **1** as a function of the ΔE ($= E_{pa1} - E_{pc1}$) values.

of the substituents. On the basis of this equation, the emission maxima of the nonsynthesized 2,5-bis(mono-substituted phenyl)siloles may be predictable with reasonable accuracy.

$$\nu_{em} \times 10^{-4} = 2.12 + 0.134\,\sigma^+ - 0.169\,\sigma^- \quad (5)$$

2,5-Diarylsiloles with extended π-conjugated groups: The effects of the π conjugation of the 2,5-diarylsiloles are discussed by comparing the data for **1j**, **1k**, and **1l** with those of the protocol diphenyl derivative **1d**. 2,5-Di(1-naphthyl)silole **1j** has its π–π* transition band at about a 20 nm shorter wavelength than the phenyl analogue **1d**. 2,5-Bis(biphenyl)-silole **1l** exhibits only a 17 nm longer wavelength absorption compared with **1d**, in spite of the introduction of two phenyl rings on each side. These results are ascribed to the ineffective extension of the π-conjugation lengths due to the perpendicular-like conformaion of the silole ring and the 2,5-diaryl groups, which is caused by the steric hindrance between them. In contrast, the styryl derivative **1k** exhibits more than 50–70 nm bathochromic shifts of the absorption and emission maxima compared with **1d**, suggesting an effective extension of the π conjugation by the styryl groups. The quantum yield of the fluorescence of **1k** is also slightly higher than those of the other 3,4-diphenyl-2,5-diarylsiloles (Table 3). According to the electrochemical data (Table 4), this extension of the π conjugation in **1k** mainly affects the HOMO level rather than the LUMO level.

2,5-Diarylsiloles with heteroaryl groups: The combination of the silole ring with other heteroaromatic rings may be another effective way to control the electronic structures of the silole π-electron systems. In this study, three kinds of heteroaryls, thiophene (**1m** and **1n**), thiazole (**1o**), and pyridine (**1p** and **1q**) rings, are incorporated at the 2,5-positions of silole.

For efficient electron-transporting (ET) materials, the low reduction potential is the first required property, which facilitates electron injection from the cathode. From this viewpoint, we introduced the pyridyl group at the 2,5-positions of the silole in the previous study,[9] since the pyridine ring is classified into π-electron deficient heteroaryls according to conventional organic chemistry.[21] As expected, it was found that 2,5-di(2-pyridyl)silole **1p** has a relatively low reduction potential (−2.10 V, vs. Ag/Ag^+), although 2,5-bis(3-pyridyl)silole **1q** (−2.27 V) only has a comparable reduction potential to the ditolylsilole **1c** (−2.36 V) and diphenylsilole **1d** (−2.27 V). The high electron affinity of **1p** should be responsible for its high performance as an ET material.

Among the 2,5-di(heteroaryl)siloles prepared herein, the thiazolyl-substituted silole **1o** has the lowest reduction potential. The first reduction peak potential (E_{pc1}) of **1o** is −1.89 V versus Ag/Ag^+ (corresponding to −1.97 V vs. Fc/Fc^+), which is even lower than that of poly(4,4′-dinonyl-2,2′-bithiazole-5,5′-diyl) (−2.16 V vs. Fc/Fc^+),[22] and comparable with that of poly(quinoxaline-2,6-diyl) ($E_{pc} = -1.83$ V vs. Ag/Ag^+), one of the most π-electron deficient systems.[23] This result suggests that the combination of the silole ring and thiazole ring may be a promising way to develop the electron-accepting π systems. A preliminary study on the application of the present 2,5-dithiazolylsilole **1o** as the ET material,

0947-6539/00/0609-1688 $ 17.50+.50/0 *Chem. Eur. J.* **2000**, *6*, No. 9

however, did not afford a satisfactory result due to the low ability to form a smooth vacuum-deposited film of **1o**; this indicates that a more precise technological modification is essential for further practical application.

Another notable point is the quite different electronic structures for the thiazolyl- (**1o**), thienyl- (**1m**), and pyrrolyl-substituted siloles (**6**), in spite of their almost equal absorption maxima (**1o**, $\lambda_{max} = 413$ nm; **1m**, $\lambda_{max} = 418$ nm; **6**, $\lambda_{max} = 406$ nm). Their first oxidation peak potentials and reduction peak potentials are compared in Figure 7. Whereas the ΔE

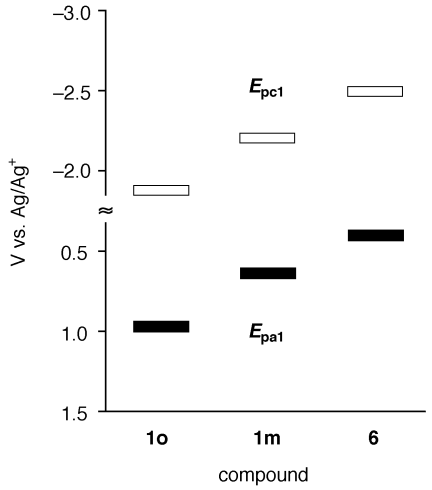

Figure 7. The first oxidation peak potentials (E_{pa1}) and the first reduction peak potentials (E_{pc1}) for 2,5-diarylsiloles.

($= E_{pa1} - E_{pc1}$) for these three compounds are almost same (2.85–2.91 V), there are big differences both in E_{pa1} and E_{pc1} among these compounds that reach 0.6 V between **1o** and **6**. Thus, **1o** is characteristic of the low-lying LUMO, while **6** has the high-lying HOMO. These results demonstrate that the appropriate choice of the heteroaryl groups enables us to control the elctronic structures, in particular, the HOMO and LUMO levels of the silole π systems over a wide range, while maintaining their emission wavelengths.

Conclusion

The first general synthetic method of the 2,5-diaryl-3,4-diphenylsiloles has been developed, which is based on the intramolecular reductive cyclization of diethynylsilanes followed by the Pd^0-catalyzed cross-coupling reaction. A series of 2,5-diarylsiloles have been prepared by this procedure in one pot from bis(phenylethynyl)silanes. Their crystal structures, chemical reactivities, and photophysical and electrochemical properties have been systematically investigated. The properties as well as the electronic structures of the 2,5-diarylsiloles are dramatically changed by the nature of the 2,5-aryl groups. In other words, the properties of the 2,5-diarylsiloles can be tuned over a wide range by the appropriate choice of the 2,5-aryl groups. Advantageously, these structural modifications can be readily achieved by the one-pot synthesis of the 2,5-diarylsiloles described herein. The present results will be informative for the further design of new organic EL materials that contain the silole as a key building unit.

Experimental Section

General considerations: Melting point determination was performed by using a differential scanning calorimeter Seiko DSC6200 or a Yanaco MP-S3 instrument. ^{1}H and ^{13}C NMR spectra were measured with a JEOL EX-270 (270 MHz for ^{1}H, and 67.8 MHz for ^{13}C) spectrometer in $CDCl_3$. Chemical shifts are reported in δ ppm with reference relative to residual protio solvent, that is, $CHCl_3$ peak for ^{1}H and the $CDCl_3$ for ^{13}C. Tetrahydrofuran was freshly distilled before use from sodium/benzophenone. Bis(phenylethynyl)silanes **2** (R = Me or *i*Pr) were prepared by the reaction of dimethyl- or diisopropyldichlorosilane and phenylethynyllithium, which was prepared from phenylacetylene and *n*BuLi in THF. Dichloro(*N*,*N*,*N*′,*N*′-tetramethylethylenediamine)zinc, [$ZnCl_2$(tmen)], was purchased from Aldrich and used without further purification.

A typical procedure for the one-pot synthesis of 2,5-diarylsiloles by using chlorosilanes as a quenching reagent

2,5-Bis(*m*-fluorophenyl)-1,1-dimethyl-3,4-diphenylsilole (1h): A mixture of lithium granular (83 mg, 12 mmol) and naphthalene (1.54 g, 12.1 mmol) in THF (12 mL) was stirred at room temperature under argon for 5 h to form a deep green solution of lithium naphthalenide (LiNaph). A solution of bis(phenylethynyl)dimethylsilane **2** (786 mg, 3.0 mmol) in THF (5 mL) was added to the solution of LiNaph dropwise over 2 min at room temperature. After stirring for 10 min, the mixture was cooled to –78 °C. A solution of chlorotriphenylsilane (1.77 g, 6.0 mmol) in THF (10 mL) was added to the mixture dropwise over 5 min. The mixture was stirred for 10 min at the same temperature and then for 20 min at 0 °C. [$ZnCl_2$(tmen)] (1.67 g, 6.6 mmol) was added as a solid to the mixture, followed by the dilution with THF (20 mL), to give a light green suspension. After stirring for an additional hour at room temperature, *m*-bromofluorobenzene (0.74 g, 6.6 mmol) and [$PdCl_2(PPh_3)_2$] (105 mg, 0.15 mmol) were successively added to the resulting suspension. The mixture was heated to reflux and stirred for 12 h. The mixture was filtered to remove insoluble materials including hexaphenyldisilane. An aqueous solution of HCl (0.5 N) was added to the filtrate, and the mixture was extracted with ether three times. The combined extract was washed with brine, dried over $MgSO_4$, and concentrated by rotary evaporation. Recrystallization of the crude mixture from hexane gave 495 mg (1.10 mmol) of **1h**. The mother liquid was condensed, passed through a short silica gel column, and purifed by preparative HPLC on silica gel ($R_f = 0.11$, hexane/EtOAc 30:1) to give 598 mg (1.33 mmol) of **1h**. The combined yield was 81 %. M.p. 181–182 °C; ^{1}H NMR: $\delta = 0.46$ (s, 6H), 6.52–6.60 (m, 2H), 6.66–6.82 (m, 8H), 6.96–7.14 (m, 8H); ^{13}C NMR: $\delta = -4.11$, 112.49 (d, $^2J_{CF} = 22.0$ Hz), 115.28 (d, $^2J_{CF} = 20.8$ Hz), 124.50 (d, $^4J_{CF} = 2.4$ Hz), 126.56, 127.53, 129.28 (d, $^3J_{CF} = 8.5$ Hz), 129.76, 138.04, 141.06, 142.05 (d, $^3J_{CF} = 7.3$ Hz), 154.72, 162.53 (d, $^1J_{CF} = 243.7$ Hz); UV/Vis ($CHCl_3$): λ_{max} (log ε): = 358 nm (4.00); elemental analysis calcd (%) for $C_{30}H_{24}F_2Si$: C 79.97, H 5.37; found C 80.25, H 5.35.

A typical procedure for the one-pot synthesis of 2,5-diarylsiloles without the use of chlorosilanes

1,1-Dimethyl-2,5-bis(*p*-nitrophenyl)-3,4-diphenylsilole (1f): By essentially the same procedure as described above, 2,5-dilithiosilole was prepared on a 2 mmol scale. [$ZnCl_2$(tmen)] (2.00 g, 8.0 mmol) was added as a solid to the mixture at 0 °C, followed by dilution with THF (10 mL), to give a black suspension. After stirring for an additional hour at room temperature, *p*-iodonitrobenzene (1.04 g, 4.2 mmol) and [$PdCl_2(PPh_3)_2$] (70 mg, 0.1 mmol) were successively added. The mixture was heated under refluxed and stirred for 14 h. An aqueous solution of HCl (1 N) was added and the mixture was extracted with ether. The combined extract was washed with brine, dried over $MgSO_4$, and concentrated. The resulting mixture was subjected to a column choromatography over silica gel ($R_f = 0.40$, benzene) to give 880 mg (1.75 mmol) of **1f** in 87 % yield. M.p. 208 °C; ^{1}H NMR: $\delta =$ 0.50 (s, 6H), 6.72–6.78 (m, 4H), 6.96–7.10 (m, 6H), 7.03 (d, $J = 8.9$ Hz, 4H), 7.99 (d, $J = 8.9$ Hz, 4H); ^{13}C NMR: $\delta = -4.17$, 123.54, 127.26, 127.87, 129.16, 129.63, 137.10, 141.65, 145.64, 146.99, 156.53; UV/Vis ($CHCl_3$): λ_{max} (log ε): 399 (4.35), 287 nm (4.32); elemental analysis calcd (%) for $C_{30}H_{24}N_2O_4Si$: C 71.41, H 4.79, N 5.55; found C 71.18, H 4.76, N 5.27.

1,1-Dimethyl-2,5-bis[*p*-(*N,N*-dimethylamino)phenyl]-3,4-diphenylsilole (1a): M.p. 269 °C; ^{1}H NMR: $\delta = 0.49$ (s, 6H), 2.87 (s, 12H), 6.47 (d, $J =$ 8.9 Hz, 4H), 6.85 (d, $J = 8.9$ Hz, 4H), 6.86 – 6.90 (m, 4H), 6.98 – 7.07 (m, 6H); ^{13}C NMR: $\delta = -2.71$, 40.36, 111.91, 125.69, 127.51, 127.87, 128.32, 130.06, 130.10, 138.99, 140.34, 148.19, 151.61; UV/Vis ($CHCl_3$): λ_{max} ($\log\varepsilon$): 423 (4.33), 258 nm (4.38); elemental analysis calcd (%) for $C_{34}H_{36}N_2Si$: C 81.55, H 7.25, N 5.59; found C 81.50, H 7.09, N 5.53.

2,5-Bis(*p*-methoxyphenyl)-1,1-dimethyl-3,4-diphenylsilole (1b): M.p. 175 °C; ^{1}H NMR: $\delta = 0.46$ (s, 6H), 3.73 (s, 6H), 6.65 (d, $J = 8.1$ Hz, 4H), 6.77 – 6.82 (m, 4H), 6.84 (d, $J = 8.1$ Hz, 4H), 6.96 – 7.03 (m, 6H); ^{13}C NMR: $\delta = -3.47$, 55.06, 113.38, 126.02, 127.48, 129.99, 130.23, 132.18, 139.32, 140.07, 152.96, 157.45; UV/Vis ($CHCl_3$): λ_{max} ($\log\varepsilon$): 379 nm (4.11); elemental analysis calcd (%) for $C_{32}H_{36}O_2Si$: C 81.00, H 6.37; found C 80.76, H 6.11.

1,1-Dimethyl-2,5-bis(*p*-methylphenyl)-3,4-diphenylsilole (1c): M.p. 188 °C; ^{1}H NMR: $\delta = 0.45$ (s, 6H), 2.24 (s, 6H), 6.76 – 6.83 (m, 8H), 6.91 (d, $J =$ 16 Hz, 4H), 6.96 – 7.02 (m, 6H); ^{13}C NMR: $\delta = -3.65$, 21.10, 126.02, 127.39, 128.66, 128.77, 129.96, 135.04, 136.73, 139.16, 141.04, 153.46; UV/Vis ($CHCl_3$): λ_{max} ($\log\varepsilon$): 367 (4.11), 253 nm (4.41); elemental analysis calcd (%) for $C_{30}H_{30}Si$: C 86.82, H 6.83; found: C 86.68, H 6.85.

2,5-Bis(*p*-trifluoromethylphenyl)-1,1-dimethyl-3,4-diphenylsilole (1e): M.p. 187 °C; ^{1}H NMR: $\delta = 0.47$ (s, 6H), 6.73 – 6.80 (m, 4H), 6.91 – 7.12 (m, 10H), 7.37 (d, $J = 8.4$ Hz, 4H); ^{13}C NMR: $\delta = -4.17$, 122.80, 125.05, 126.74, 127.64, 128.79, 129.78, 134.91, 137.74, 141.37, 143.52, 155.35; UV/Vis ($CHCl_3$): λ_{max} ($\log\varepsilon$): 358 (4.02), 250 nm (4.40); elemental analysis calcd (%) for $C_{32}H_{24}F_6Si$: C 69.80, H 4.39; found C 70.06, H 4.28.

1,1-Dimethyl-2,5-bis(*m*-methylphenyl)-3,4-diphenylsilole (1g): M.p. 128 °C; ^{1}H NMR: $\delta = 0.46$ (s, 6H), 2.16 (s, 6H), 6.66 – 6.76 (m, 4H), 6.76 – 6.89 (m, 6H), 6.95 – 7.04 (m, 8H); ^{13}C NMR: $\delta = -3.72$, 21.44, 125.95, 126.06, 126.27, 127.31, 127.71, 129.61, 129.94, 137.22, 138.98, 139.71, 141.64, 153.84; UV/Vis ($CHCl_3$): λ_{max} ($\log\varepsilon$): 364 (3.78), 252 nm (4.52); elemental analysis calcd (%) for $C_{32}H_{30}Si$: C 86.82, H 6.83; found: C 87.06, H 6.93.

2,5-Bis(*m*-trifluoromethylphenyl)-1,1-dimethyl-3,4-diphenylsilole (1i): M.p. 80 °C; ^{1}H NMR: $\delta = 0.49$ (s, 6H), 6.74 – 6.84 (m, 4H), 6.96 – 7.34 (m, 14H); ^{13}C NMR: $\delta = -4.06$, 122.35 (q, $^3J_{CF} = 3.7$ Hz), 124.03 (q, $^1J_{CF} =$ 271.7 Hz), 125.42 (q, $^3J_{CF} = 3.7$ Hz), 126.74, 127.67, 128.41, 129.72, 130.31 (q, $^2J_{CF} = 31.7$ Hz), 131.88, 137.74, 140.38, 140.84, 155.36; UV/Vis ($CHCl_3$): λ_{max} ($\log\varepsilon$): 358 (3.99), 251 nm (4.37); elemental analysis calcd (%) for $C_{32}H_{24}F_6Si$: C 69.80, H 4.39; found C 69.97, H 4.35.

1,1-Dimethyl-2,5-di(1-naphthyl)-3,4-diphenylsilole (1j): M.p. 214 – 215 °C; ^{1}H NMR: $\delta = 0.28$ (s, 6H), 6.70 – 6.90 (m, 10H), 7.00 – 7.12 (m, 2H), 7.31 (t, $J = 7.6$ Hz, 2H), 7.38 – 7.50 (m, 4H), 7.62 (d, $J = 7.6$ Hz, 2H), 7.76 – 7.84 (m, 2H), 8.00 – 8.12 (m, 2H); ^{13}C NMR: $\delta = -3.66$, 125.21, 125.48, 125.52, 125.71, 126.06, 126.54, 126.85, 128.16, 129.27, 131.97, 133.53, 138.42, 139.01, 143.65, 155.00; UV/Vis ($CHCl_3$): λ_{max} ($\log\varepsilon$): 340 nm (3.96); elemental analysis calcd (%) for $C_{38}H_{30}Si$: C 88.73, H 5.87; found C 88.97, H 5.87.

1,1-Dimethyl-3,4-diphenyl-2,5-bis(2-phenylethenyl)silole (1k): M.p. 183 – 184 °C; ^{1}H NMR: $\delta = -0.66$ (s, 6H), 6.69 (d, $J = 15.9$ Hz, 2H), 6.88 – 6.98 (m, 4H), 7.04 (d, $J = 15.9$ Hz, 2H), 7.10 – 7.36 (m, 16H); ^{13}C NMR: $\delta =$ – 1.81, 126.29, 126.61, 127.21, 127.39, 128.55, 128.82, 129.88, 131.70, 138.08, 138.17, 139.50, 156.26; UV/Vis ($CHCl_3$): λ_{max} ($\log\varepsilon$): 435 (4.04), 278 nm (4.30); elemental analysis calcd (%) for $C_{34}H_{30}Si$: C 87.50, H 6.48; found C 87.11, H 6.54.

2,5-Di(4-biphenyl)-1,1-dimethyl-3,4-diphenylsilole (1l): M.p. 256 – 258 °C; ^{1}H NMR: $\delta = 0.55$ (s, 6H), 6.82 – 6.90 (m, 4H), 6.96 – 7.08 (m, 10H), 7.20 – 7.42 (m, 10H), 7.52 – 7.58 (m, 4H); ^{13}C NMR: $\delta = -3.50$, 126.27, 126.54, 126.74, 127.01, 127.55, 128.66, 129.34, 129.96, 138.02, 138.78, 138.96, 140.74, 141.13, 154.20; UV/Vis ($CHCl_3$): λ_{max} ($\log\varepsilon$): 381 (4.32), 273 nm (4.69); elemental analysis calcd (%) for $C_{42}H_{34}Si$: C 89.00, H 6.05; found C 88.83, H 6.13.

1,1-Dimethyl-3,4-diphenyl-2,5-di(2-thienyl)silole (1m): M.p. 173 °C; ^{1}H NMR: $\delta = 0.69$ (s, 6H), 6.85 – 6.90 (m, 4H), 6.96 – 7.04 (m, 6H), 7.14 – 7.20 (m, 6H); ^{13}C NMR: $\delta = -1.90$, 125.64, 126.18, 126.86, 127.13, 128.45, 129.56, 135.17, 139.05, 142.82, 152.60; UV/Vis ($CHCl_3$): λ_{max} ($\log\varepsilon$): 418 (4.28), 266 nm (4.14); elemental analysis calcd (%) for $C_{26}H_{22}SiS_2$: C 73.19, H 5.20; found C 73.14, H 5.08.

1,1-Dimethyl-3,4-diphenyl-2,5-bis[5-(2-thienyl)-2-thienyl]silole (1n): M.p. 207 – 208 °C; ^{1}H NMR: $\delta = 0.71$ (s, 6H), 6.76 (d, $J = 3.8$ Hz, 2H), 6.90 – 6.92 (m, 4H), 6.94 (d, $J = 3.8$ Hz, 2H), 6.98 – 7.04 (m, 4H), 7.11 (dd, $J = 2.4$, 6.2 Hz, 2H), 7.14 – 7.25 (m, 6H); ^{13}C NMR: $\delta = -1.74$, 123.09, 123.36, 124.13, 127.37, 127.69, 127.87, 128.55, 129.45, 131.68, 136.46, 137.02, 137.65, 138.72, 142.17, 152.83; UV/Vis ($CHCl_3$): λ_{max} ($\log\varepsilon$): 476 nm (4.38); elemental analysis calcd (%) for $C_{34}H_{26}SiS_4$: C 69.11, H 4.43; found C 69.51, H 4.45.

1,1-Dimethyl-3,4-diphenyl-2,5-di(2-thiazolyl)silole (1o): M.p. 218 °C; ^{1}H NMR: $\delta = 0.74$ (s, 6H), 7.02 (d, $J = 3.0$ Hz, 2H), 6.98 – 7.08 (m, 4H), 7.16 – 7.32 (m, 6H), 7.41 (d $J = 3.0$ Hz, 2H); ^{13}C NMR: $\delta = -3.23$, 119.25, 127.78, 128.84, 128.99, 136.57, 137.92, 142.35, 156.46, 166.52; UV/Vis ($CHCl_3$): λ_{max} ($\log\varepsilon$): 413 nm (4.33); elemental analysis calcd (%) for $C_{24}H_{20}N_2SiS_2$: C 67.25, H 4.70, N 6.54; found C 67.37, H 4.73, N 6.42.

1,1-Dimethyl-3,4-diphenyl-2,5-di(2-pyridyl)silole (1p): M.p. 175 °C; ^{1}H NMR: $\delta = 0.58$ (s, 6H), 6.50 (d, $J = 7.8$ Hz, 2H), 6.85 – 6.98 (m, 6H), 7.05 – 7.15 (m, 6H), 7.20 (dt, $J = 1.9$, 7.8 Hz, 2H), 8,52 (dd, $J = 1.9$, 4.9, 2H); ^{13}C NMR: $\delta = -3.16$, 120.22, 122.64, 126.56, 127.92, 129.22, 135.00, 139.44, 144.53, 149.16, 155.09, 158.65; UV/Vis ($CHCl_3$): λ_{max} ($\log\varepsilon$): 370 nm (4.17); elemental analysis calcd (%) for $C_{28}H_{24}N_2Si$: C 80.73, H 5.81, N 6.72; found C 80.82, H 5.74, N 6.57.

1,1-Diisopropyl-3,4-diphenyl-2,5-di(3-pyridyl)silole (1q): M.p. 133 – 134 °C; ^{1}H NMR: $\delta = 1.04$ (d, $J = 7.6$ Hz, 12H), 1.63 (septet, $J = 7.6$ Hz, 2H), 6.68 – 6.80 (m, 4H), 6.92 – 7.08 (m, 8H), 7.08 – 7.15 (m, 2H), 8.22 (d, $J = 1.4$ Hz, 2H), 8.27 (dd, $J = 1.4$, 4.6 Hz, 2H); ^{13}C NMR: $\delta = 10.91$, 17.31, 122.88, 126.72, 127.62, 129.94, 135.76, 136.21, 136.91, 137.57, 146.59, 149.72, 158.24; UV/Vis ($CHCl_3$): λ_{max} ($\log\varepsilon$): 354 nm (3.96); elemental analysis calcd (%) for $C_{32}H_{32}N_2Si$: C 81.31, H 6.82, N 5.93; found C 81.07, H 6.86, N 5.81.

A typical procedure for the alkaline desilylation of 2,5-diarylsiloles

2,3-Diphenyl-1,4-bis(*p*-methylphenyl)-1,3-butadiene (5c). A mixture of silole **1c** (98 mg, 0.22 mmol) and potassium hydroxide (600 mg, 11 mmol) in toluene/water 2:1 mixed solvent (1.5 mL) was heated to reflux for 20 h. After dilution with an aqueous solution of HCl (0.1N), the mixture was extracted with ether several times. The combined extract was washed with brine, dried over $MgSO_4$, and concentrated. Recrystallization from a hexane/EtOAc mixed solvent afforded 54 mg (0.14 mmol) of **5c** in 64% yield. M.p. 207 °C; ^{1}H NMR: $\delta = 2.18$ (s, 6H), 6.22 (s, 2H), 6.60 (d, $J =$ 8.1 Hz, 4H), 6.82 (d, $J = 8.1$ Hz, 4H), 7.27 – 7.45 (m, 10H); ^{13}C NMR: $\delta =$ 21.08, 127.19, 128.52, 128.77, 129.40, 130.35, 131.20, 134.39, 136.35, 140.02, 144.80; UV/Vis ($CHCl_3$): λ_{max} ($\log\varepsilon$): 339 nm (4.38); elemental analysis calcd (%) for $C_{30}H_{26}$: C 93.22, H 6.78; found C 93.39, H 6.73.

2,3-Diphenyl-1,4-bis(*p*-methoxyphenyl)-1,3-butadiene (5b): M.p. 193 °C; ^{1}H NMR: $\delta = 3.68$ (s, 6H), 6.17 (s, 2H), 6.55 (d, $J = 8.9$ Hz, 4H), 6.63 (d, $J =$ 8.9 Hz, 4H), 7.27 – 7.45 (m, 10H); ^{13}C NMR: $\delta = 55.10$, 113.27, 127.15, 127.51, 127.73, 128.84, 130.28, 130.39, 130.64, 143.81, 158.13; UV/Vis ($CHCl_3$): λ_{max} ($\log\varepsilon$): 348 nm (4.46); elemental analysis calcd (%) for $C_{30}H_{26}O_2$: C 86.09, H 6.26; found C 85.80, H 6.26.

2,3-Diphenyl-1,4-bis(*p*-trifluoromethylphenyl)-1,3-butadiene (5e): M.p. 165 °C; ^{1}H NMR: $\delta = 6.33$ (s, 2H), 6.81 (d, $J = 8.4$ Hz, 4H), 7.21 – 7.40 (m, 8H), 7.41 – 7.55 (m, 6H); ^{13}C NMR: $\delta = 124.64$, 124.69, 124.74, 124.91, 127.91, 128.59, 129.09, 130.10, 131.21, 138.69, 140.49, 147.26; UV/Vis ($CHCl_3$): λ_{max} ($\log\varepsilon$): 337 nm (4.34); elemental analysis calcd (%) for $C_{30}H_{20}F_6$: C 72.87, H 4.08; found: C 72.60, H 3.98.

X-ray crystal structure analyses of 1b, 1c, 1e, 1f, and 5b: Single crystals of **1b**, **1c**, and **1e** suitable for X-ray crystal analysis were obtained by recrystallization from hexane, and single crystals of **1f** and **5b** were obtained from benzene. Intensity data were collected on a Rigaku RAXIS-IV imaging-plate area detector with graphite monochromated $Mo_{K\alpha}$ radiation to a maximum 2θ value of 55°. The data were corrected for Lorentz and polarization effects, and secondary extinction. The crystal structures were solved by direct methods in *SIR92*,[24] and a full-matrix least-squares refinement was carried out for all non-hydrogen atoms. Hydrogen atoms were included but not refined. All the calculations were performed using the teXsan crystallographic package from the Molecular Structure Corp. The crystal data and analytical conditions are listed in Table 5. In the structure of **1e**, the fluorine atoms of trifluoromethyl groups were anisotropically refined by using disorder models. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-134093 – CCDC-134097. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit @ccdc.cam.ac.uk).

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Table 5. Crystal and intensity collection data for 3,4-diphenyl-2,5-diarylsiloles (**1b**, **1c**, **1e**, and **1f**) and 2,3-diphenyl-1,4-diaryl-1,3-butadiene (**5b**).

	1b	**1c**	**1e**	**1f**	**5b**
formula	$C_{32}H_{30}O_2Si$	$C_{32}H_{30}O_2Si$	$C_{32}H_{24}F_6Si$	$C_{39}H_{33}N_2O_4Si$[a]	$C_{30}H_{26}O_2$
M_w	474.67	442.67	550.62	621.79	418.53
crystal size[mm]	$0.50\times0.50\times0.30$	$0.50\times0.20\times0.20$	$0.40\times0.40\times0.30$	$0.50\times0.20\times0.20$	$0.30\times0.10\times0.05$
crystal system	monoclinic	orthorhombic	monoclinic	monoclinic	monoclinic
space group	*C*2/*c* (no. 15)	*Pbca* (no. 61)	$P2_1/c$ (no. 14)	$P2_1/c$ (no. 14)	$P2_1/c$ (no. 14)
a [Å]	18.0428(9)	17.8334(2)	13.025(1)	14.3409(4)	5.5788(2)
b [Å]	10.1859(7)	25.3220(2)	21.292(2)	15.4006(5)	10.7763(5)
c [Å]	16.7131(7)	11.2210(1)	10.2752(7)	14.9974(2)	18.6011(9)
β [°]	119.786(3)		89.899(6)	98.364(2)	93.345(3)
V, [Å^3]	2665.8(2)	5067.15(7)	2849.5(3)	3277.1(1)	1116.37(7)
Z	4	8	4	4	2
ρ_{calcd} [g cm^{-3}]	1.183	1.160	1.283	1.260	1.245
T [°C]	20	−100	20	−100	−100
$\mu(Mo_{K\alpha})$ [cm^{-1}]	1.14	1.10	1.40	1.16	0.76
$2\theta_{max}$ [°]	55.2	55.1	55.3	55.2	55.2
collected rflns	3008	5433	5126	6079	2381
unique rflns [$I>3\sigma(I)$]	2380	4302	3397	4531	2077
rfln/parameter ratio	14.88	14.39	8.31	10.89	14.23
R[b]	0.045	0.039	0.047	0.044	0.047
R_w[c]	0.073	0.062	0.068	0.068	0.076
goodness of fit	1.47	1.43	1.41	1.18	1.19

[a] 1.5 benzene meolecules were included in the unit cell. [b] $R=\Sigma||F_o|-|F_c||/\Sigma|F_o|$. [c] $R_w=[\Sigma w(|F_o|-|F_c|)^2/\Sigma wF_o^2]^{1/2}$.

Cyclic voltammetry measurements: These were performed under the following condition: sample, 1 mM; solvent system, nBu$_4$NClO$_4$ (0.1M) in acetonitrile; Ag/Ag$^+$ reference electrode and glassy carbon working electrode; scan rate, 100 mV s^{-1}. The observed potential was corrected with reference to ferrocene ($E_{1/2}$ +0.083 V), which added as an internal standard after each measurement.

Acknowledgement

This work was partly supported by Grant-in-Aids (Nos. 07555280 and 09239103) from the Ministry of Education, Science, Sports and Culture, Japan, and by the Japan Chemical Innovation Institute.

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Received: October 18, 1999 [F2098]

  0947-6539/00/0609-1692 $ 17.50+.50/0