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Silole-containing σ- and π-conjugated compounds

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Received 15th June 1998, Accepted 28th July 1998

Synthesis, properties, and application of new σ- and π-electron systems consisting of the silole rings are described. A series of 2,5- and 1,1-difunctionalized siloles have been prepared based on the intramolecular reductive cyclization of diethynylsilanes. Starting from these functionalized siloles, oligo(2,5-silole)s and oligo(1,1-silole)s have been synthesized as model compounds for poly(2,5-silole)s and poly(1,1-silole)s, respectively, which are still veiled target molecules in this field. Some silole-containing π-conjugated cooligomers and copolymers with thiophene, pyrrole, and acetylene π-electron systems have also been prepared. They all have unique photophysical properties such as long-wavelength absorption in the UV/VIS absorption spectra. Some silole-based π-conjugated compounds have also been found to work as new useful materials for organic electroluminescent devices.

Silole (silacyclopentadiene) is a silicon-containing five-membered cyclic diene, that is a silicon analog of cyclopentadiene. Since the first synthesis of a silole, 1,1,2,3,4,5-hexaphenylsilole, by Braye and Hübel[1] in 1959, there have been extensive studies on the synthesis, reactivities, properties and coordination abilities of such compounds to transition metals, and the aromaticity of their anionic or cationic species.[2] The last two subjects are interesting in view of the comparison with cyclopentadiene and thus continue to flourish up to date.[3,4] Recently, a new aspect has been added to this silole chemistry, that is the application of the silole ring as a new building unit in material science, especially for π-conjugated polymers.[5,6] In 1989, Barton and his co-workers[7] reported the synthesis of "poly(2,5-silole)", a silole 2,5-linked homopolymer, by molybdenum or tungsten-complex catalysed or thermal polymerization of diethynylsilane. Although the structure of the polymer has later been corrected to contain a methylenesilacyclobutene skeleton instead of a silole ring,[8] their attempt prompted further intensive studies from a viewpoint of theoretical calculations. So far, a number of theoretical studies on silole-containing π-conjugated polymers have been carried out,[9–12] which have predicted some unique properties such as low band-gaps, non-linear optical properties, and thermochromism. However, there had been no report on the synthesis of silole-based conjugated compounds except for 2,5-diphenyl-substituted siloles until we started this research, apparently due to the lack of efficient synthetic methods, especially for functionalized siloles. Therefore, we have commenced the development of new silole syntheses. In this account we describe our recent results on the silole-containing σ- and π-conjugated compounds, focusing on the electronic structure, developments of new synthetic methodologies, and application to organic electroluminescent (EL) devices.

1 Unique electronic structure of silole ring

A notable feature of the silole ring is its high electron-accepting properties, that is its low-lying LUMO level. Atwell and his co-workers[13a] and O'Brien and Breeden[13b] have reported experimentally that 2,5-diphenylsilole derivatives are easily reduced by alkali metals to form the corresponding di- or tetra-anion. According to our theoretical calculations,[14] silole has a quite different electronic structure from that of cyclopentadiene.[15] *Ab initio* calculations at the HF/6-31G* level of theory show that, while the HOMO of the parent silole is about 0.4 eV lower than that of the parent cyclopentadiene, the LUMO level of the silole is more than 1.2 eV lower in comparison with that of cyclopentadiene (Fig. 1). The difference in their LUMO levels is due to the unique orbital interaction in the silole ring, as shown in Fig. 2. When the molecular orbital of silole is constructed by orbital interaction of MOs of a silylene moiety and a butadiene moiety, the low-lying LUMO of silole arises from mixture of the σ* orbital of the silylene moiety with the π* orbital of the butadiene moiety, *i.e.*, σ*–π* conjugation. It should be noted that the σ* orbital on the silicon and the lobes of π* orbital on the adjacent carbons are in phase. This orbital interaction occurs effectively due to the fixed perpendicular arrangement

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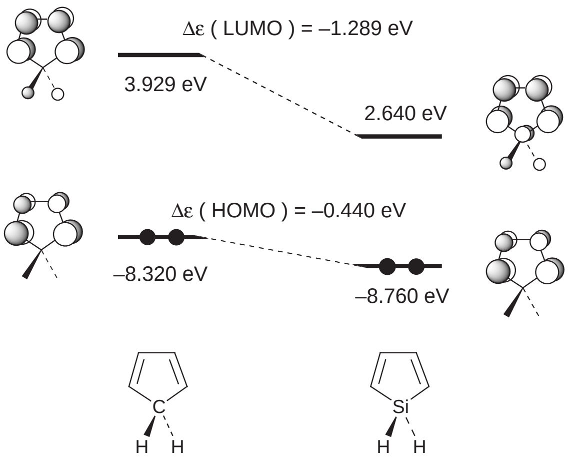


Fig. 1 Relative energy levels of the HOMO and LUMO for silole and cyclopentadiene, based on the HF/6-31G* calculations.

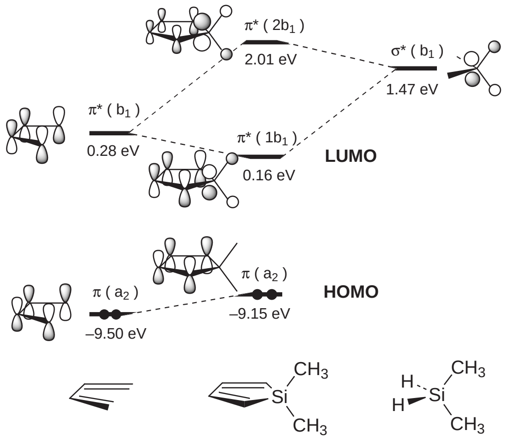
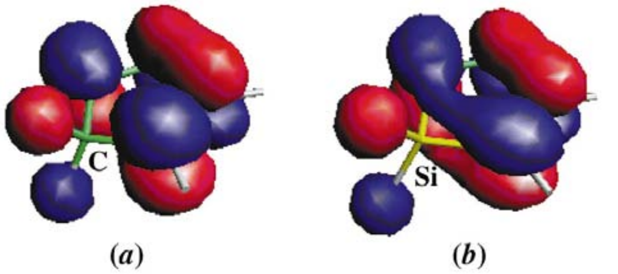


Fig. 2 Orbital correlation diagram for 1,1-dimethylsilole, based on the PM3 calculations.



(*a*) (*b*)

Fig. 3 The LUMO of cyclopentadiene (*a*) and silole (*b*).

of the plane of the silylene moiety, *i.e.* the plane involving two exocyclic σ bonds of silole, to the plane of the butadiene moiety and to the energetically comparable σ* and π* orbitals. In the case of cyclopentadiene the σ*–π* conjugation in the LUMO is almost negligible because of the much higher energy level of the corresponding exocyclic σ* orbital. The shape of the LUMO of silole is visualized in Fig. 3, together with that of cyclopentadiene for comparison.

The high electron-accepting properties of silole is further conspicuous by comparison with those of other heterocycles.[16b,17] Fig. 4 shows the comparison of the calculated HOMO and LUMO levels of silole with those of pyrrole, furan, thiophene, and pyridine, all of which are common monomer units of the conventional π-conjugated polymers. Silole has the lowest LUMO energy level among them as well as a relatively high HOMO level. We thus anticipated that the introduction of silole as a building unit would enable us to construct new σ- and π-conjugated systems having unique electronic structures.

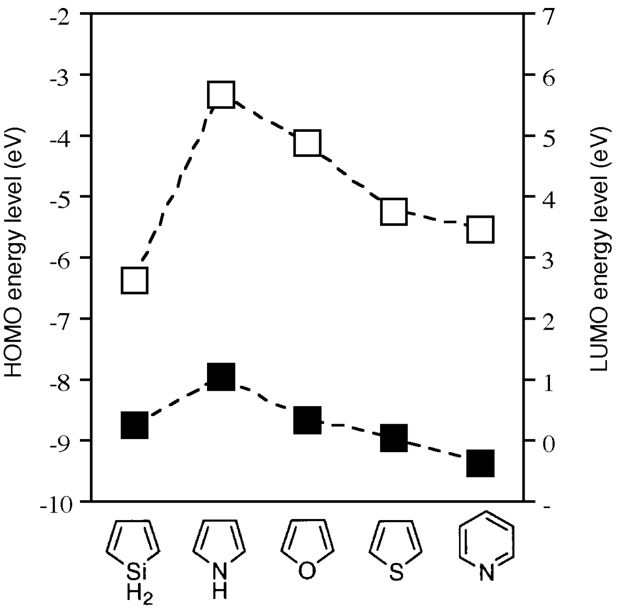
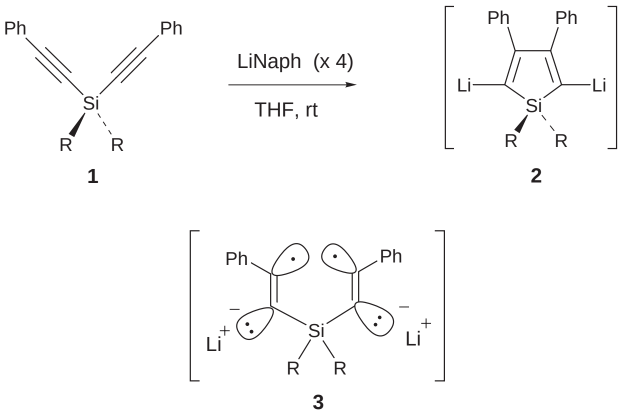


Fig. 4 Relative HOMO and LUMO levels for silole and other heterocycles, based on HF/6-31G* calculations.

2 New silole synthesis

The most straightforward synthetic route to silole-based π-conjugated compounds may be the transition metal-catalysed coupling reaction of 2,5-difunctionalized siloles. However, it was quite difficult to introduce the functionalities requisite for the coupling reaction, such as Br, I, SnR_3, and $B(OH)_2$, onto the 2,5 positions by the conventional synthetic methodologies. Only one example was the synthesis of 3-boryl-2,5-distannylsiloles, reported by Wrackmeyer and co-workers,[18] which involved the reaction of bis(stannylalkynyl)silanes with trialkylboranes. However, this method seemed to have little generality. Under the circumstances, we have developed a new versatile methodology for the synthesis of 2,5-difunctionalized siloles based on the intramolecular reductive cyclization of diethynylsilanes.[19]

The addition of di(phenylethynyl)silane **1** to an excess amount (4 mol amounts)† of lithium dihydronaphthylide (LiNaph) affords 2,5-dilithiosilole **2**, as shown in Scheme 1. The key point to attain high yield is the dropwise addition of the diethynylsilane into an "electron pool" consisting of an excess amount of reductant, and thereby both acetylene moieties are



Scheme 1 (R = alkyl or phenyl.)

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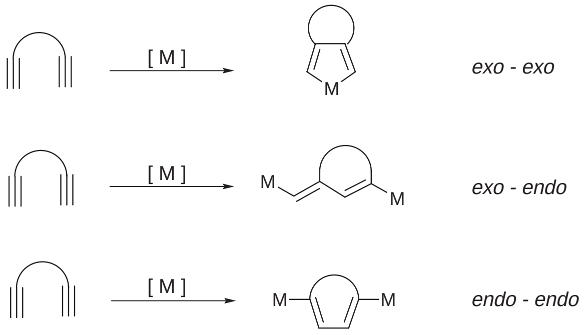
† The term "molar amount" represents the molar ratio between reactants, regardless of the stoichiometry of the given reaction, whilst the widely used "mol equivalent" should correctly be used to represent the molar ratio based on the stoichiometry.

reduced simultaneously to form a bis(anion radical) intermediate **3** that undergoes radical coupling to form the 3,4-carbon–carbon bond, leaving anions at the 2,5 positions. The phenyl group at the terminal position of acetylene is essential to obtain the dilithiosiloles. In the case of other substituents such as alkyl and silyl groups only a complex mixture is formed, probably due to cleavage of the Si–C_{sp} bond prior to the formation of the dilithiosilole.

It is noted that this reaction is conceptually new from a synthetic point of view. Metal promoted intramolecular reductive cyclization of diynes is formally classified into three types with respect to the orientations of acetylene moieties to the newly formed ring, as shown in Scheme 2.[20] Whereas the *exo-exo* mode of reductive cyclization is well known to proceed with various transition-metal two-electron reductants such as Ti^{II}, Zr^{II}, Co^{I}, Rh^{I}, Ni^{0}, Pd^{0},[21] the *exo-endo* mode[8,22] is rare and the *endo-endo* mode is unknown, to the best of our knowledge.[23] The present reductive cyclization using the one-electron lithium reductant, is the first example of the last mode of reaction. This present *endo-endo* cyclization may also be regarded as an anion analog of the Bergman cyclization, a neutral thermal cyclization of enediynes in the *endo-endo* mode,[24] and as an intramolecular version of intermolecular coupling of diphenylacetylene with lithium to afford dilithiobutadiene.[25]



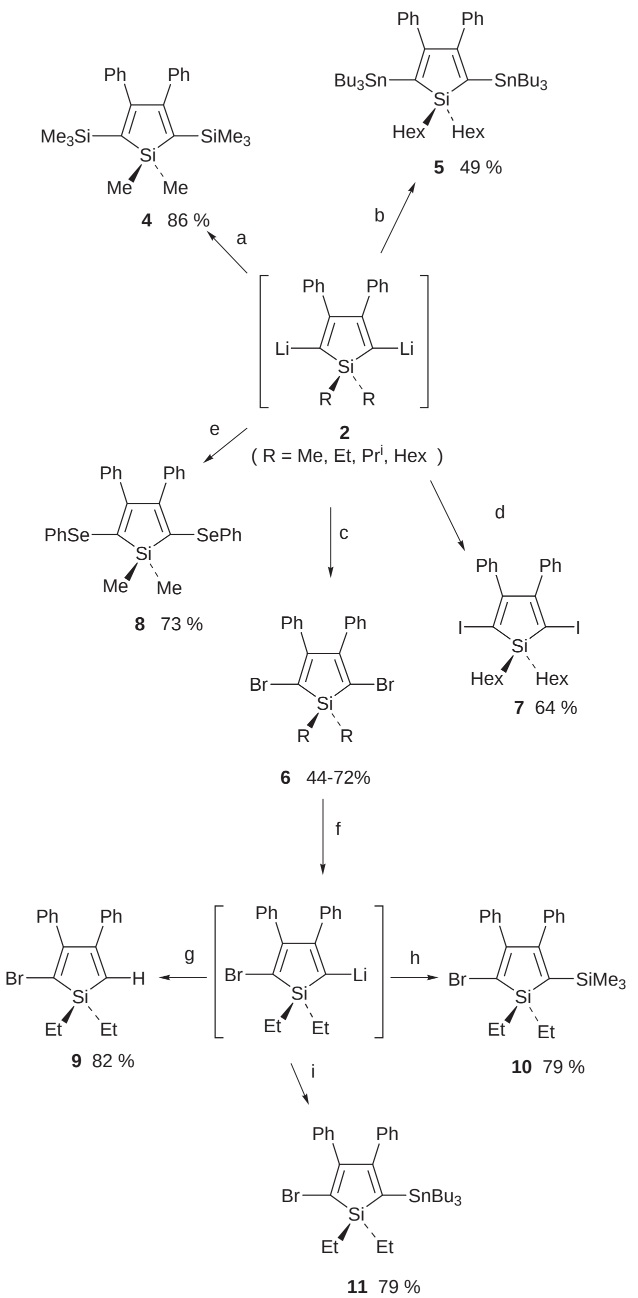
Scheme 2

By trapping with various electrophiles, 2,5-dilithiosiloles are transformed into the corresponding 2,5-difunctionalized siloles **4**–**8** having a series of functional groups such as $SiMe_3$, $SnBu_3$, Br, I and SePh, as shown in Scheme 3.[19] Furthermore, some unsymmetrical functionalized siloles **9**–**11** can also be prepared by selective monolithiation of dibromosilole **6** with *n*-BuLi followed by the treatment with the appropriate electrophiles.

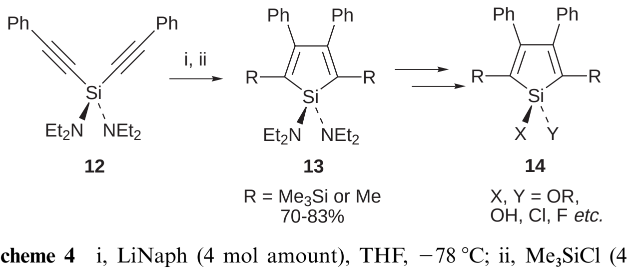
The present cyclization is applicable to the preparation of 1,1-difunctionalized siloles, as shown in Scheme 4.[26] Thus, the reaction of the diaminodiethynylsilane **12** with LiNaph cleanly proceeds at low temperature to give the 1,1-diaminosilole **13**. The conventional functional group transformation reactions from **13** afford a series of 1,1-difunctionalized siloles **14** having OR, OH, Cl, and F functionalities on the ring silicon atom. 1-Monofunctionalized siloles are also prepared by similar procedures starting from monoaminodiethynylsilanes.

A series of 2,5-diarylsiloles **15** can also be synthesized in *one pot* from the diethynylsilanes by the combination of the present cyclization with the Pd^0-catalysed cross-coupling reaction, as shown in Scheme 5.[27] Thus, the intramolecular reductive cyclization of diethynylsilanes followed by quenching with the remaining lithium dihydronaphthylide with bulky chlorosilane and transmetalation with $ZnCl_2$·tmen affords 2,5-dizinc siloles, which are subsequently treated with the appropriate aryl bromides in the presence of palladium catalyst to give the corresponding silole derivatives **15** in high yields.

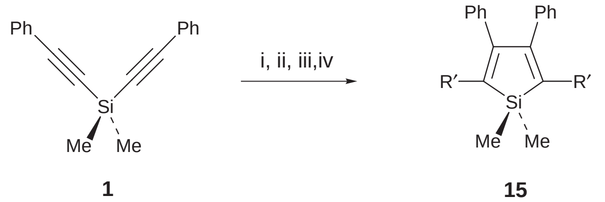
Despite the versatility, the present method has a crucial limitation, that is restriction of the 3,4 substituents only to the phenyl groups as mentioned above. In order to compensate for this, we have developed quite recently two alternative routes to silole derivatives, as shown in Schemes 6 and 7. One is the synthesis of 3,4-unsubstituted siloles **17** from the corresponding tellurophenes **16** *via* the well documented tellurium–lithium exchange reaction.[28,29] A variety of 2,5-diarylsiloles including unsymmetrical ones can be prepared by this method.[30] The



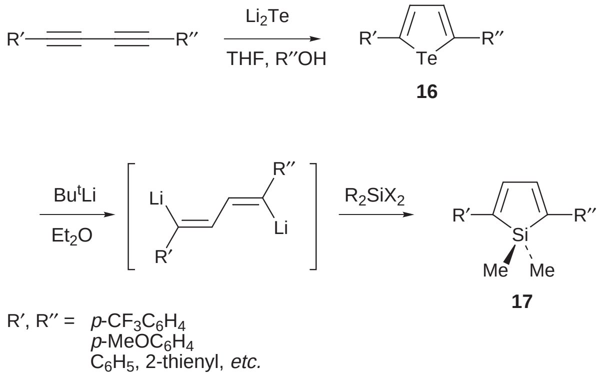
Scheme 3 Hex = hexyl = C_6H_{13}. a, Me_3SiCl (4 mol amount), rt; b, Bu_3SnCl (4 mol amount), rt; c, (1) Ph_3SiCl (2 mol amount), −78 °C, (2) Br_2 (2 mol amount), −78 °C to rt; d, ICH_2CH_2I (4 mol amount), −78 °C to rt; e, PhSeCl (4 mol amount), rt; f, Bu^nLi (1.1 mol amount), diethyl ether, −78 to 0 °C; g, water, 0 °C; h, Me_3SiCl, 0 °C to rt; i, Bu_3SnCl, 0 °C to rt.



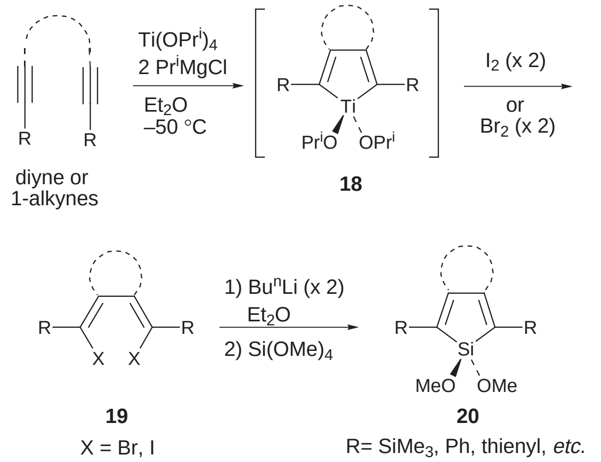
Scheme 4 i, LiNaph (4 mol amount), THF, −78 °C; ii, Me_3SiCl (4 mol amount), or $(MeO)_2SO_2$ (4 mol amount).



Scheme 5 i, LiNaph (4 mol amount), THF, rt; ii, Ph_3SiCl (2 mol amount), −78 to 0 °C; iii, $ZnCl_2$·tmen (2 mol amount), rt; iv, aryl bromide R′Br (2 mol amount), $[PdCl_2(PPh_3)_2]$ (0.05 mol amount), THF, reflux.



Scheme 6



Scheme 7

other route involves the preparation of 1,4-diiodobutadienes **19** by halogenolysis of the corresponding titanacyclopentadienes **18**.[31,32] The transformation from the diiodobutadiene to siloles *via* halogen–lithium exchange is a known procedure.[33,34] A variety of 3,4-dialkyl and 3,4-unsubstituted siloles can be obtained by this method. These two new methods will serve complementarily with the above intramolecular reductive cyclization to give new tailor-made siloles.

3 Oligo(2,5-silole)s as model compounds of poly(2,5-silole)s

Poly(2,5-silole)s may be the most interesting target molecules in this chemistry. Poly(2,5-silole) is recognized as a silicon-substituted polyacetylene, in which the labile *trans*-cisoid-transoid polyacetylene backbone is fixed by the silicon bridging. In addition to this, the ring silicon would significantly perturb the π-electronic structure of the polyacetylene backbone through the σ*–π* conjugation (Fig. 5). Poly(2,5-silole), thereby, would have unique properties different from those of the conventional polyacetylenes.

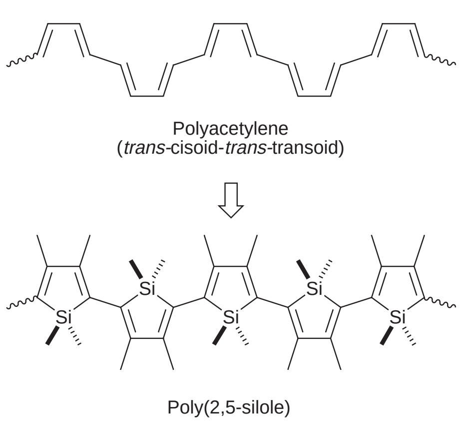


Fig. 5

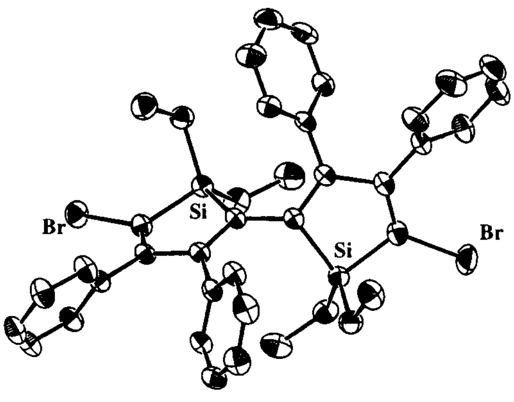
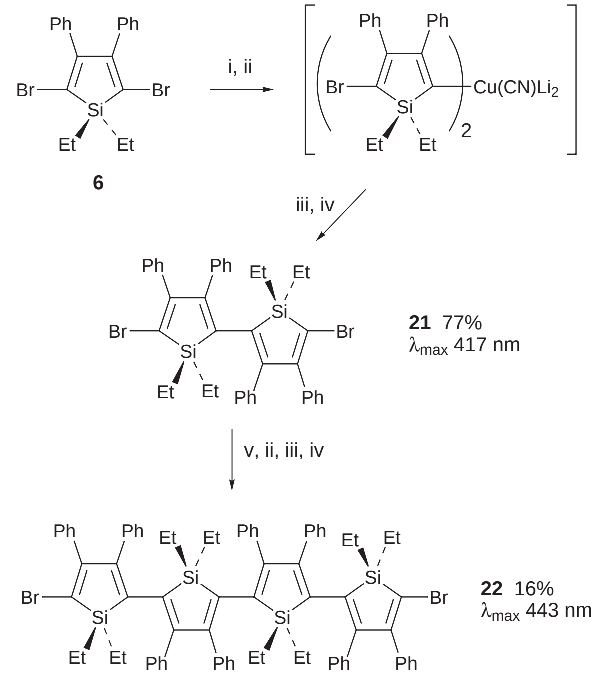


Fig. 6 Crystal structure of bisilole **21**.



Scheme 8 i, Bu^nLi (1.05 mol amount), Et_2O; ii, CuCN (0.5 mol amount), THF; iii, tmen (1.5 mol amount); iv, *p*-dinitrobenzene (5 mol amount); v, Bu^tLi (2.1 mol amount), Et_2O.

Poly(2,5-silole)s are still veiled in spite of our several attempts using 2,5-difunctionalized siloles. In the course of our studies, however, we have succeeded in the preparation of oligo(2,5-silole)s, up to the tetramer, as models of poly(2,5-silole)s, as shown in Scheme 8.[19] Thus, the dibromobisilole **21** has been prepared from the 2,5-dibromosilole **6** by selective monolithiation with *n*-BuLi followed by oxidative homocoupling through the so-called “higher-order cuprate”.[35] The

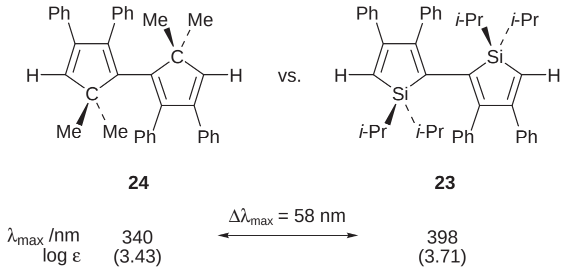


Fig. 7 Comparison of UV/VIS absorption maxima between the bisilole **23** and bicyclopentadiene **24**.

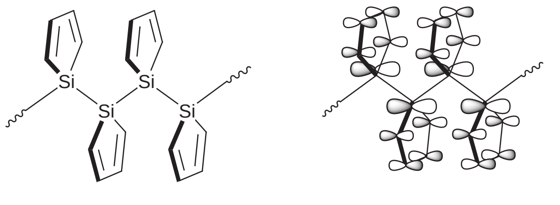


Fig. 8 Poly(1,1-silole) and schematic representation of σ^*–π^* conjugation in the LUMO.

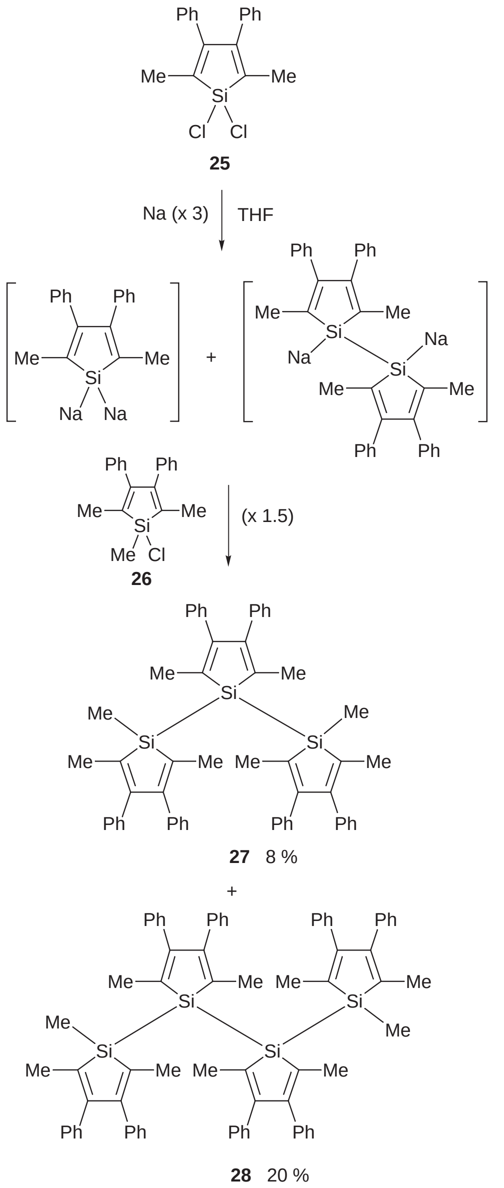
quatersilole **22**, a silole tetramer, has also been obtained by repetition of a similar procedure from dibromobisilole **21**. Crystal structure analysis of **21** revealed a highly twisted arrangement of two silole rings with a 64° torsion angle, suggesting its poor π conjugation (Fig. 6). Nevertheless, bisilole is yellow and has a characteristic band at 423 nm in the UV/VIS absorption spectrum, whilst quatersilole **22** is orange and has its absorption maximum at 443 nm.

The λ_{max} value of this bisilole is significantly long among π-conjugated compounds consisting of two cyclic diene rings. We were interested in whether this long-wavelength absorption can be ascribed to the ring silicon or not. Therefore, we have prepared the bisilole **23** and its carbon analogue, bicyclopentadiene **24**, and compared their UV/VIS absorption spectra (Fig. 7).[36] Bicyclopentadiene **24** is colourless and has its absorption maximum at 340 nm. The difference in λ_{max} between **23** and **24** on changing the central atoms from Si to C is 58 nm. Our recent theoretical study has manifested that the long-wavelength absorption of bisilole is ascribed to the low-lying LUMO energy level, due to the σ^*–π^* conjugation in the silole ring and to the distortion of the bisilole skeleton.[14]

4 Oligo(1,1-silole)s as model compounds of poly(1,1-silole)s

Silicon-catenated silole polymers, poly(1,1-silole)s, are other interesting target molecules in this field. Poly(1,1-silole)s are regarded as a new class of polysilanes with σ^*–π^* conjugation, as shown in Fig. 8. Thus, σ^*–π^* conjugation would be expected between the σ^* orbital delocalized over the polysilane main chain and the π^*-orbital localized on the *cis*-butadiene moiety in every silole ring. Indeed, high electron accepting properties of poly(1,1-silole)s due to the σ^*–π^* conjugation have been suggested by a recent theoretical study.[37] We have prepared oligo(1,1-silole)s as model compounds of poly(1,1-silole)s.

Using the 1,1-dichlorosilole **25** and 1-monochlorosilole **26**, the silole trimer, tersilole **27**, and silole tetramer, quatersilole **28**, have been synthesized, as shown in Scheme 9.[38] Thus, the reduction of **25** with alkali metal gave a silole dianion[4] and bisilole dianion,[4c,j,k] which were trapped with **26** to afford tersilole **27** and quatersilole **28**, respectively. Both oligomers have characteristic absorptions around 280–290 nm in the UV absorption spectra, which are not observed for the silole monomer and 1,1 dimer. Recently, silole homooligomers similar to ours[39] and silole-containing polysilanes[40,41] have been prepared.



Scheme 9

5 Combination of siloles with other π-electron systems

We next describe the π-electron systems consisting of silole rings and other π-conjugated rings. We are particularly interested in the combination of the electron accepting silole ring with π-electron excessive heterocycles such as thiophene and pyrrole. Introduction of the electron accepting silole rings into an electron rich polythiophene or polypyrrole π-conjugated chain would produce new π-electron systems having unique electronic structures.

So far, we have prepared a series of silole–thiophene cooligomers and copolymers.[16] Representative examples are listed in Table 1 together with their UV/VIS absorption spectral data. As anticipated, silole–thiophene π-electron systems show unique photophysical properties. For example, the thiophene–silole–thiophene compound, **29** has its absorption maximum at 416 nm, which is more than 60 nm longer than that of the thiophene trimer, terthiophene (λ_{max} 353 nm).[42] X-Ray structural analysis of **29** revealed high coplanarity of the three rings (torsion angles, 7.0 and 10.2°), as shown in Fig. 9(*a*). Furthermore, the silole–thiophene 1 : 2 copolymer **32** is ink-blue in solution and has an intense broad absorption band around 600 nm, which is more than 150 nm red shifted compared with thiophene homopolymers [*e.g.* poly(3-hexylthiophene), λ_{max} 442 nm

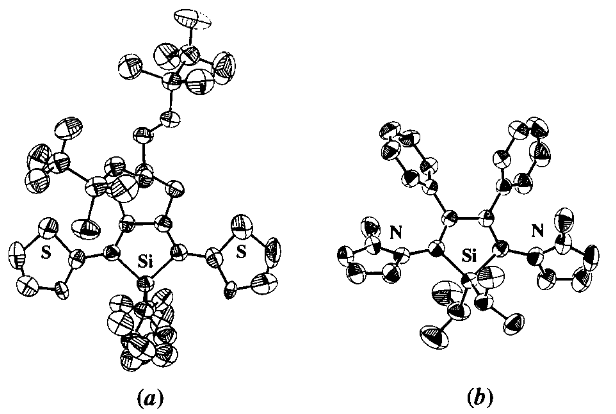
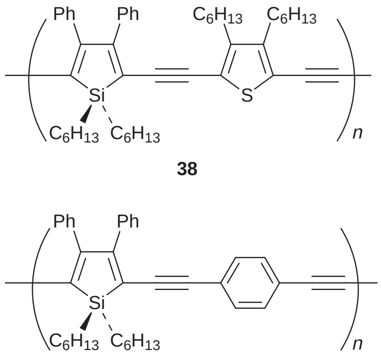


Fig. 9 Crystal structures of the 2,5-dithienylsilole **29** (*a*) and 2,5-dipyrrolylsilole compounds **35** (R = Pr^i) (*b*).



λmax 576, 605 (sh) nm

λmax 505, 527 nm

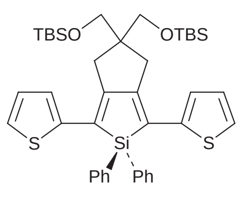
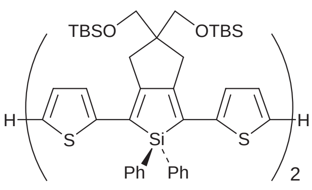
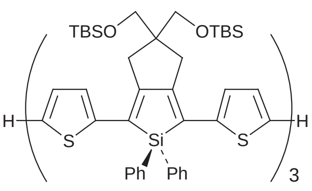
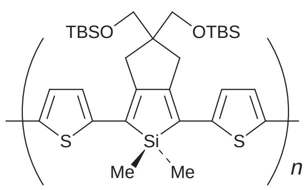
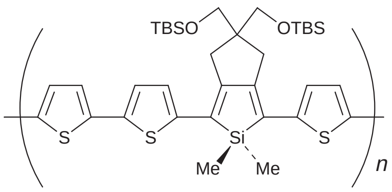
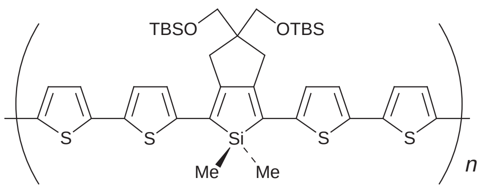
Fig. 10

in solution].[43] In a series of silole–thiophene copolymers **32**–**34** having various silole : thiophene ratios, the absorption maxima tend to shift to longer wavelengths as the contents of silole increase. *Ab initio* calculation on 2,5-dithienylsilole has revealed that both the HOMO and LUMO are delocalized over the three rings.[16b] This result suggests that the long-wavelength absorption observed for silole–thiophene π-electron systems might be ascribed to the decrease in bandgaps by the introduction of the silole rings having a relatively high-lying HOMO as well as the considerably low-lying LUMO.

Cooligomers of silole with the more π-electron excessive pyrrole have also been prepared, their absorption maxima being listed in Table 2.[17] In contrast to the coplanar conformation of three rings in 2,5-dithienylsilole, the 2,5-dipyrrolylsilole **35** has a highly twisted conformation of the three rings (torsion angles 51.7 and 55.7°) due to steric repulsion, as shown in Fig. 9(*b*), suggesting poorer π conjugation over the pyrrole–silole–pyrrole main chain. Nevertheless, the absorption maxima of **35** is almost same as that of **29** and about 130 nm longer than that of the pyrrole trimer *N*,*N*′,*N*″-trimethyl-2,2′;5′,2″-terpyrrole (λ_{max} 271 nm),[44] showing a quite unique π-electronic structure created by the combination of silole and pyrrole. Calculation on 2,5-dipyrrolylsilole revealed a high-lying HOMO delocalized over the three rings and a low-lying LUMO mostly localized on the silole ring. The extended π-conjugated systems **36** and **37**, the dimer and trimer of **35**, however, show only moderate red-shifts of absorption maxima, probably due to the highly twisted conformation of the main chain. Silole–pyrrole copolymers free from steric hindrance are thus future target molecules to be challenged.

Although acetylene-containing π-conjugated polymers generally have relatively large bandgaps,[45] polymers consisting of silole and acetylene π-electron systems have been found to have rather narrow bandgaps.[46,47] We have prepared two such types of polymers, silole–diethynylthiophene and silole–diethynylbenzene copolymers, **38** and **39**, as shown in Fig. 10. Both polymers have absorption bands at long wavelengths in the UV/VIS absorption spectra. The absorption maximum of **38** is the longest one among poly(aryleneethynylene) type polymers reported so far. The bandgaps of **38** and **39** estimated from their absorption edges are 1.77 and 2.07 eV, respectively.

Table 1 The UV/VIS absorption spectral data for silole–thiophene cooligomers and copolymers[a]

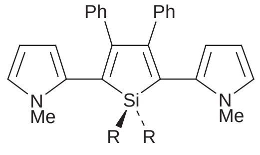
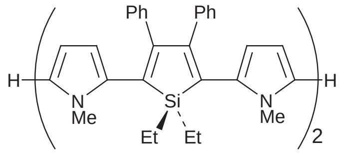
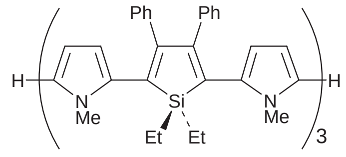
Compound[b]	λ_{max}/nm (log ε)
 **29**	416 (4.27)
 **30**	505 (4.86)
 **31**	549 (4.96)
 **32** ($n \approx 24$)	576 (4.49)[c] 618 (4.44)[c]
 **33** ($n \approx 27$)	546 (4.51)[c]
 **34** ($n \approx 41$)	549 (4.70)[c]

[a] In chloroform. [b] TBS = *tert*-Butyldimethylsilyl. [c] Per monomer unit.

6 Application to organic electroluminescent devices

As one application of silole-based π-conjugated compounds we have recently shown their possibilities as new materials for organic electroluminescent (EL) devices. Since the break-

Table 2 The UV/VIS absorption spectral data for silole–pyrrole cooligomers *

Compound	λ_{max}/nm (log ε)
 **35** (R = Et)	406 (3.93)
 **36**	436 (4.24)
 **37**	447 (4.53)

* In chloroform.

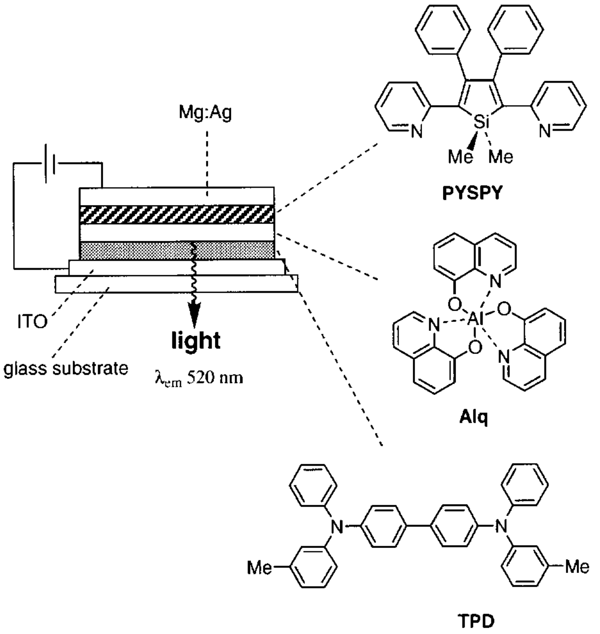


Fig. 11 Organic EL device using PYSPY, Alq, and TPD as electron-transporting, emissive, and hole-transporting materials, respectively.

through achieved by Tang and VanSlyke in 1987,[48] who introduced a thin multilayer configuration for organic EL devices, this field has been rapidly growing because of the possible application as next-generation displays. One of the current problems in this field is a lack of efficient electron transporting (ET) materials.[49] High electron affinity may be the first requisite for the design of new ET materials. We anticipated that the high electron accepting silole ring would work as a core component of new efficient ET materials. We have evaluated this possibility using 2,5-diarylsiloles **15** as silole derivatives.[27]

Among several 2,5-diarylsiloles examined, 2,5-di(2-pyridyl)-silole PYSPY has been found to show a quite high performance as an ET material in our device having ITO/TPD/Alq/PYSPY/Mg : Ag configuration, where triphenylamine dimer (TPD) and tris(quinolin-8-olato)aluminum (Alq) are employed as hole-transporting and emissive materials, respectively, and indium tin oxide (ITO) and Mg : Ag (10 : 1) alloy are used as anode and cathode, respectively, as shown in Fig. 11. The device emits a greenish yellow light from the Alq layer. The threshold applied voltage is about 3 V and the maximum luminance reached 12 000 cd m^{-2} at 10 V. The luminous efficiency at 100 cd m^{-2} is 1.9 lm W^{-1}. The performance of PYSPY as an ET material exceeds that of Alq, which is one of the best ET materials reported so far.

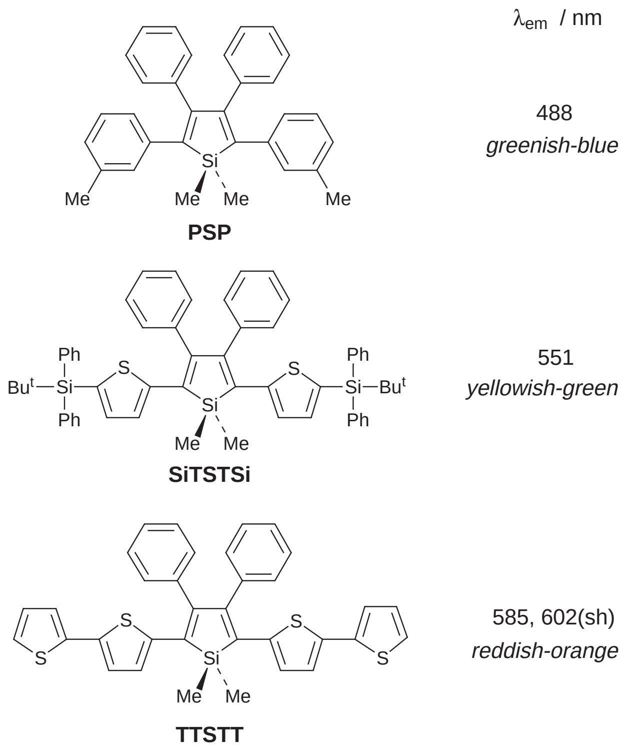


Fig. 12 Emission wavelengths of organic EL devices using 2,5-diarylsiloles as emissive electron-transporting materials. Cell configuration: ITO/TPD(500 Å)/2,5-diarylsilole(500 Å)/Mg : Ag.

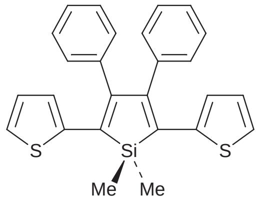
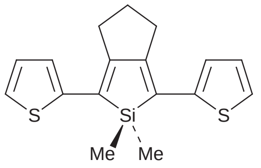
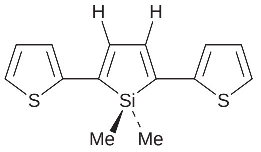
2,5-Diarylsiloles can also be applied as efficient emissive materials and the wavelengths of their luminescence are widely tunable by changing the 2,5-aryl groups, as shown in Fig. 12. Thus, in the devices having ITO/TPD/2,5-diarylsilole/Mg : Ag configuration, three types of silole derivatives PSP, SiTSTSi, and TTSTT work as emissive ET materials, emitting greenish blue, yellowish green, and reddish orange 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 from 2-methylphenyl to bithienyl. These results suggest an easy access to various colors of light, blue to red required for application to full-color displays, by modification of only the 2,5-aryl groups on the silole ring. Advantageously, these structural modifications could readily be achieved by our one-pot synthesis shown in Scheme 5.[27]

7 Structure–photophysical properties relationships

In view of the application of the silole π-electron systems, control of the photophysical properties and electronic structures by structural modification is relevant to further molecular design. To obtain a deeper insight into the structure–properties relationships, we have studied the effects of the nature of the 2,5-aryl groups, 3,4 and 1,1 substituents on the properties of 2,5-diarylsiloles.

A series of 2,5-diarylsiloles **40** having various *p*-monosubstituted phenyl groups have been prepared by the method described above.[50] Their absorption and emission maximum

Table 3 Effects of 3,4 substituents on the optical properties of 2,5-dithienylsiloles

	UV/VIS[a]	Fluorescence[a]
	λ_{max}/nm (log ε)	λ_{max}/nm ($\Phi_f \times 10^2$)[b]
 **41**	418 (4.28)	515 (0.14)
 **42**	409 (4.38)	492 (5.44)
 **43**	415 (4.22)	505 (3.90)

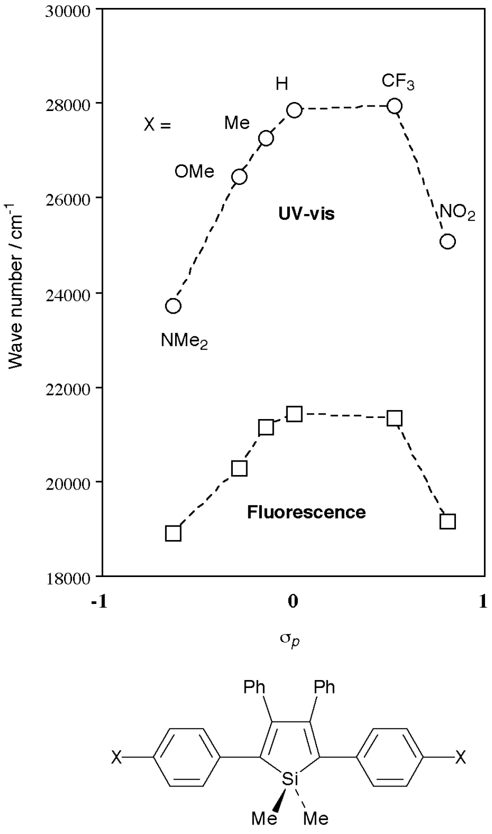
[a] In chloroform. [b] Quantum yields relative to quinine sulfate (0.55).

wavenumbers in the UV/VIS absorption and fluorescence spectra are plotted as a function of the Hammett σ_p values of the *p* substituents, as shown in Fig. 13. Bell shaped lines are obtained both for absorption and emission maxima. The conjugative substituents such as NMe_2 and NO_2 induce significant red shifts. Worthy of note is that the absorption maxima and emission wavelengths of the 2,5-diarylsiloles can be tuned in the range of 360–420 and 470–530 nm, respectively.

In Table 3 a series of 2,5-dithienylsiloles having various 3,4 substituents are listed with their maximum wavelengths in the UV/VIS absorption and fluorescence spectra.[30] Comparing the 3,4-diphenylsilole **41** or bicyclic 3,4-dialkylsilole **42** with the 3,4-unsubstituted silole **43**, the phenyl and alkyl substitutions induce red and blue shifts, respectively, both in the absorption and fluorescence spectra. It is also noted that the phenyl groups on the 3,4 positions reduce the quantum yield significantly.

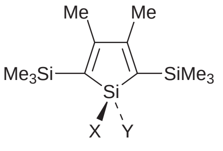
In comparison with the effects of the 2,5-aryl groups and 3,4 substituents, the effects of the 1,1 substituents on the optical properties are relatively small, as shown in Fig. 14.[51] In a series of 2,5-disilylsiloles **44** having various groups on the ring silicon atom the absorption maxima become longer as the 1,1-substituents become more electronegative, although the changes are moderate.

Considering the peculiar contribution of the central silicon atom to the π-electronic structure of silole derivatives through σ*–π* conjugation, other Group 14 metalloles are also interesting. To elucidate the effects of the central Group 14 elements, we have prepared a series of 2,5-dithienyl-substituted Group 14 metalloles from cyclopentadiene **45** to stannole **47**, and their photophysical data are compared in Table 4.[52] While significant differences exist between the cyclopentadiene and silole derivatives, the metalloles from silole to stannole show comparable absorption maxima and emission wavelengths. Theoretical calculations have revealed that the Group 14 metalloles from silole to stannole have essentially the same electronic structures and the central Group 14 elements, Si, Ge, and Sn, affect the LUMO energy levels to almost the same extent through σ*–π* conjugation.



40

Fig. 13 Plots of UV/VIS absorption and fluorescence maximum wavenumbers of 2,5-diarylsiloles **40** as a function of Hammett σ_p constants of the *p* substituents.



44

	λ_{max} / nm (log ε) in $CHCl_3$
X = Y = H	305 (3.63)
X = Y = *i*-Pr	308 (3.73)
X = Y = Ph	314 (3.73)
X = Y = OMe	315 (3.69)
X = F, Y = OH	316 (3.66)
X = Y = F	318 (3.56)

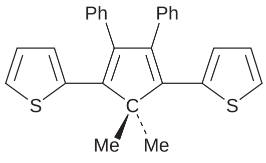
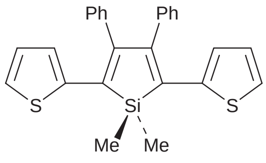
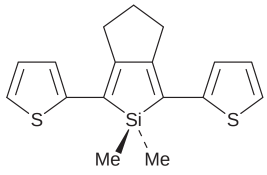
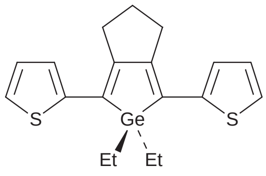
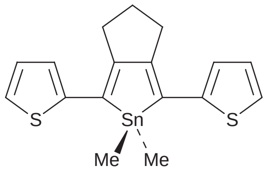
Fig. 14

8 Conclusion

In 1994 we developed a new synthetic method for the synthesis of 2,5-difunctionalized siloles based on the intramolecular reductive cyclization of diethynylsilanes. On the basis of this, we have succeeded in the preparation of several types of silole-containing π- and σ-electron systems, including oligo(2,5-silole)s and oligo(1,1-silole)s as models of poly(2,5-silole)s and poly(1,1-silole)s, respectively. All the new π-conjugated systems prepared show unique photophysical properties due to the unique electronic structure, especially the low-lying LUMO, of the silole ring. The σ*–π* conjugation in the ring is the origin of the high electron affinity of the silole ring. Based on this feature, a family of silole-based π-conjugated systems, 2,5-diarylsiloles, are new efficient materials for organic electroluminescent devices.

High electron affinity may be realized in heterocyclopentadienes having electropositive atoms as the central elements, such as boron and aluminium, besides silicon.[53] In view of the application as new electronic materials, however, only siloles

Table 4 The UV/VIS absorption and fluorescence spectral data for 2,5-dithienyl metalloles[a]

Compound	UV/VIS	Fluorescence[a]
	λ_{max}/nm (log ε)	λ_{max}/nm ($\Phi_f \times 10^2$)[b]
 **45**	368 (4.10)	461 (0.996)
 **41**	418 (4.28)	515 (0.141)
 **42**	409 (4.38)	492 (5.44)
 **46**	405 (4.37) 428 (4.24)	479 (8.72)
 **47**	406 (4.36) 430 (4.24)	479 (0.495)

[a] In chloroform. [b] Quantum yields relative to quinine sulfate (0.55).

will be utilized due to the stability problem. Substituted siloles can be handled without any special care in the air. Further developments of new silole π-conjugated systems practically applicable are now in progress in our laboratory.

9 Acknowledgements

The studies on the application to organic EL devices were carried out with Chisso Corporation. We greatly acknowledge financial support from Grant-in-Aids from the Ministry of Education, Science, Sports and Culture, Japan, Nagese Science and Technology Foundation, Ciba-Geigy Foundation (Japan) for the Promotion of Science, and the Japan High Polymer Center.

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Paper 8/04491K