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Review

New type of polysilanes: poly(1,1-silole)s

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Abstract

Poly(1,1-silole)s were synthesized for the first time in 1999, by us and by West and his coworkers, as a new type of polysilane which is expected to have a low-lying LUMO due to the σ*–π*conjugation characteristic of the silole ring. Summarized herein are the development of new synthetic methodologies and the structural aspects, photophysical properties and a unique reactivity of the resulting oligo- and poly(1,1-silole)s. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Polysilane; Silole; Polysilole; Wurtz-type coupling reaction; σ*–π* conjugation; UV spectrum; Fluoresence spectum

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1. Introduction

Polysilanes are one-dimensional polymers consisting of the silicon–silicon single bond, one of the representative interelement linkage [1]. Owing to the mobile electrons of the Si–Si linkage with high orbital energies, polysilanes have unique properties such as absorption and fluorescence in the UV region [1a] and high hole-transporting ability [2]. These distinguished properties are rationalized due to the σ-conjugation of the main chain [1a,3] and raise themselves as promising candidates for new optoelectronic materials including organic electroluminescence materials [4] and photoconducting materials [5], in addition to the materials for photoresists [6]. Current researches in this field are directed toward the elucidation of the σ-conjugation [7,8], the developments of efficient and effective synthetic methods of high polymers [9], functionalization for the further applications [10], and the creation of the new type of polysilanes [11,12]. Especially in the last subject, the control and tuning of the electronic structures of polysilanes is a fundamental goal. In general, the electronic structures of polysilanes are significantly perturbed by specific orbital interactions between polysilane main chains and the substituents [1a]. In this context, poly(1,1-silole)s, silole (silacyclopentadiene) [13] polymers catenated through the ring silicon atoms, are attractive target molecules [14]. In the silole skeleton, the orthogonally fixed arrangement of the two exocyclic single bonds on the silicon atom to the butadiene plane effectively causes the σ*–π* conjugation between the σ* orbital of the silicon moiety and the π* orbital of the butadiene moiety, leading to its low-lying LUMO, as shown in Fig. 1 [15,16]. The catenation of the silole ring at the silicon atoms in the all-*anti* fashion with respect to the polysilane chain is expected to realize the orbital interaction between the σ* orbital delocalized over the polysilane main chain and the π* orbital localized on every silole ring. Actually, a recent semiempirical calculation on the poly(1,1-silole)s has predicted their low-lying LUMO levels due to the σ*–π* conjugation [17]. In experimental, the syntheses of the poly(1,1-siloles) and related oligomers and polymers have been addressed by us and several other research groups (Chart 1): Sakurai and coworkers have reported the synthesis of silole-incorporated polysilane (**3**) [18]. Tanaka and coworkers have reported the dehydrogenative polymerization to poly(dibenzosilole) (**4**) [19]. West and coworkers have succeeded in the synthesis of poly(1,1-silole) (**5**) and their application to the organic EL devices [20]. The model studies on the oligo(1,1-silole)s (**6**) up to pentamer have also been reported by Kira and coworkers [21]. We have independently studied the oligo(1,1-silole)s (**1**) and poly(1,1-silole)s (**2**), starting from the development of the new synthetic method of the monomer, 1,1-difunctionalized siloles.

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This account is focused on our recent results of this chemistry.

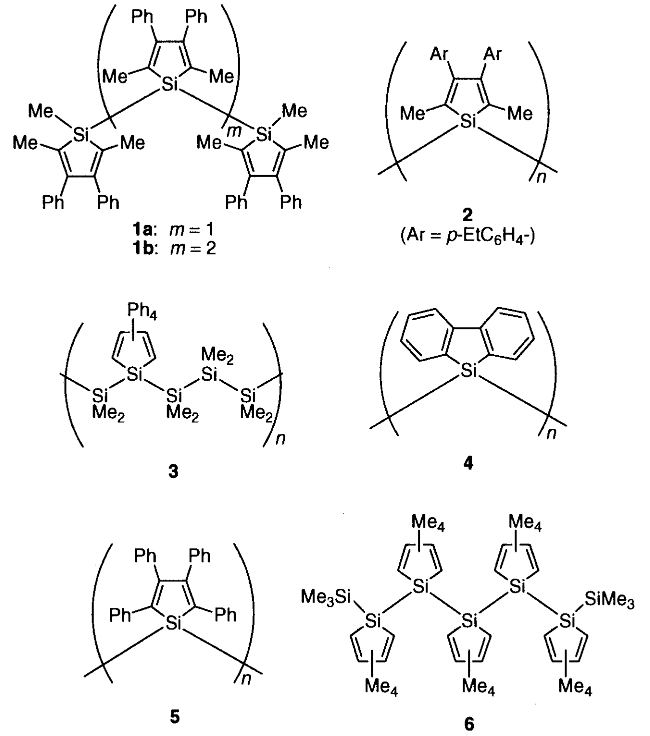


Chart 1. A list of oligo- and poly(1,1-silole)s and related compounds so far prepared.

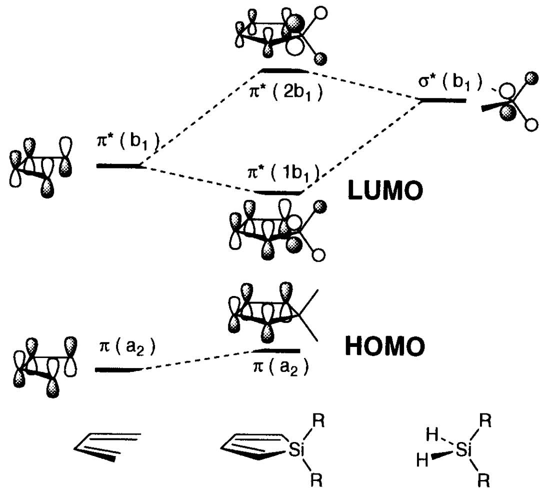
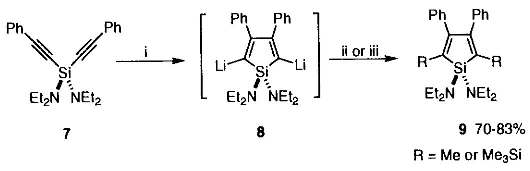


Fig. 1. Schematic drawing of orbital correlation diagram of silole (Ref. [15a]).



Scheme 1. Reagents and conditions: (i) LiNaph (4 mol amounts), THF, −78°C, 1 h; (ii) Me_3SiCl (4 mol amounts), −78°C–r.t., 8 h; (iii) $(MeO)_2SO_2$ (4 mol amounts), −78°C–r.t., 10 h.

2. Results and discussion

2.1. Monomer synthesis

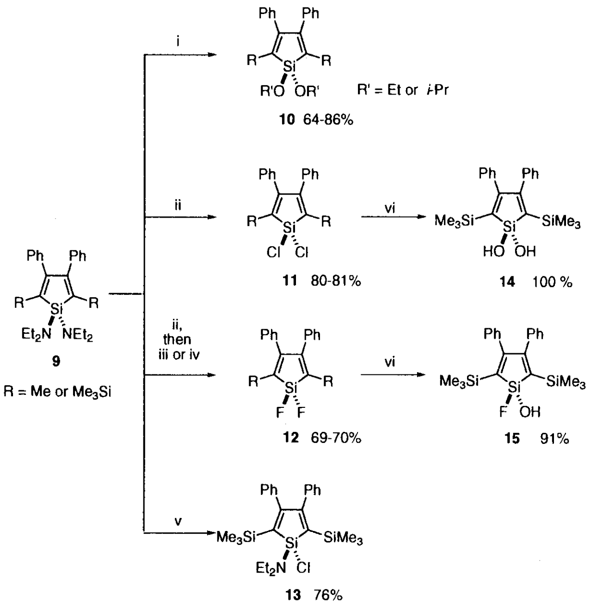
For the synthesis of poly(1,1-silole)s, 1,1-difunctionalized siloles such as 1,1-dichlorosilole are crucial precursors. However, traditional synthetic routes to them have been limited to only three types of reactions, i.e. the coupling reaction of 1,4-di(lithio)butadiene derivatives with SiX_4 [22], the flash vacuum pyrolysis of 1-allylsilacyclopent-3-ene [23], and the transmetalation from zirconacyclopentadienes [24], followed by functional group transformation [25]. We commenced with the development of new general, facile synthetic method of the 1,1-difunctionalized siloles. We have recently reported the new silole cyclization reaction, that is the intramolecular reductive cyclization of bis(phenylethynyl)silanes [26]. Based on this reaction, we have succeeded in the synthesis of 1,1-diaminosiloles which are key precursors for a series of 1,1-difunctionalized siloles [27].

The synthesis of 1,1-diaminosiloles is shown in Scheme 1. The reduction of bis(diethylamino)bis(phenylethynyl)silane (**7**) with an excess amount of lithium naphthalenide (LiNaph, 4 mol amount) at low temperature cleanly formed 2,5-dilithio-1,1-diaminosilole (**8**), which was further trapped with trimethylsilyl chloride and dimethyl sulfate to give the corresponding 1,1-diaminosiloles (**9**) in good yields.

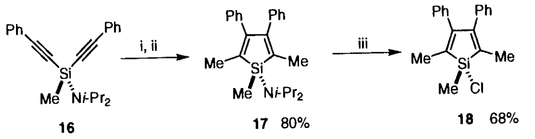
A series of 1,1-difunctionalized siloles having alkoxy, Cl, F, and OH functionalities were prepared by transformation from 1,1-diaminosiloles as shown in Scheme 2. Alcoholysis of diaminosiloles in the presence of $AlCl_3$ yielded 1,1-di(alkoxy)siloles (**10**). 1,1-Dichlorosiloles (**11**) were prepared in good yields by treatment with dry HCl gas. 1,1-Difluorosiloles (**12**) were also obtained from diaminosiloles via dichlorosiloles without isolation by subsequent treatment with $Py(HF)_x$ or ZnF_2. An unsymmetrically substituted 1,1-difunctionalized silole (**13**) is also accessible by the selective monoamination of dichlorosiloles **11** using Et_2NH–Et_3N. Hydrolysis reactions of dichlorosilole and difluorosilole afford different type of products, di(hydroxy)silole (**14**) and (fluoro)(hydroxy)silole (**15**), respectively [28].

The present methodology is also applicable to the synthesis of 1-monofunctionalized siloles. Thus, as a representative example, 1-chloro-1-methyl-2,5-dimethylsilole (**18**) was prepared from the corresponding (amino)(methyl)bis(phenylethynyl)silane (**16**) via 1-amino-1-methyl-2,5-dimethylsilole (**17**) as shown in Scheme 3.

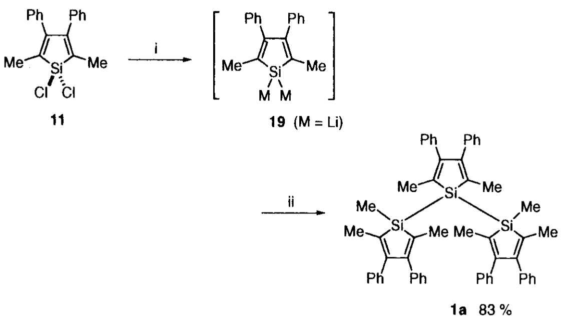
The stability of these 1,1-difunctionalized siloles is highly dependent on the bulkiness of the 2,5-substituents. Especially, the 1-halogenated siloles with 2,5-methyl groups are unstable in the air and should be stored under an inert atmosphere. These demonstrate



Scheme 2. Reagents and conditions: (i) R′OH, $AlCl_3$ (0.25 mol amount), r.t., 20 h; (ii) dry HCl gas, Et_2O, −78°C; (iii) $Py(HF)_x$ (6 mol amounts), −78°C, 0.5 h; (iv) ZnF_2 (3 mol amounts), r.t., 2 h; (v) Et_2NH (1.2 mol amounts), Et_3N (1.2 mol amounts), r.t., 20 h; (vi) $THF–H_2O$, r.t., 1 h.



Scheme 3. Reagents and conditions: (i) LiNaph (4 mol amounts), THF, −78°C, 2 h; (ii) $(MeO)_2SO_2$ (4 mol amounts), −78–0°C, 0.5 h; (iii) dry HCl gas, Et_2O, −78°C.



Scheme 4. Reagents and conditions: (i) Li (5 mol amounts), THF, 10°C, 10 h; (ii) **18** (2 mol amount), −78°C, 2 h.

the importance of the appropriate choice of 2,5-substituents for preparation and handling of the siloles having functionalities on silicon. Notably, the present methodology has a decisive merit in this respect that a variety of substituents can be introduced onto the 2,5-positions of the silole rings, although the 3,4-phenyl groups are inevitable for the present procedure [26].

2.2. Oligo(1,1-silole)s

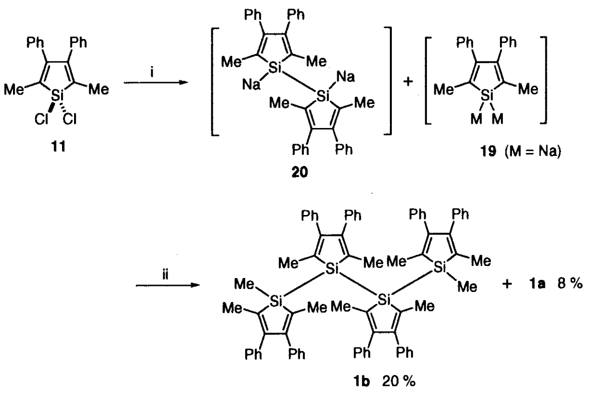
2.2.1. Synthesis

Oligo(1,1-silole)s are of interest as the models of poly(1,1-silole)s to elucidate their fundamental properties. When we started this chemistry, only a few silole dimers have been reported in the literature [29]. We have conducted the synthesis of a series of oligo(1,1-silole)s using the 1-monohalo or 1,1-dihalosilole as the crucial precursors [30].

The syntheses of tersilole (**1a**) and quatersilole (**1b**) are shown in Schemes 4 and 5, respectively. As has been well documented [29c–f, 31], silole dianion (**19**) can be cleanly prepared by the reaction of 1,1-dichlorosilole (**11**) with excess Li metal in THF. The coupling reaction of the dianion **19** with 1-chloro-1-methylsilole (**18**) gave tersilole (**1a**) in 83% yield. Quatersilole (**1b**) has been obtained by a similar coupling reaction. Our procedure was based on the recent results reported independently by Boudjouk and his coworkers [29d] and Tilley and his coworkers [29e,f] on the formation of bisilole dianions. Thus, **11** was reduced with 3 mol amounts of Na metal, resulting in the formation of a mixture of the bisilole dianion (**20**) and the silole dianion (**19**). The mixture was treated with 1-chloro-1-methylsilole (**18**) to afford quatersilole (**1b**) in 20% yield together with tersilole (**1a**) in 8% yield.

2.2.2. Structures of oligo(1,1-silole)s

Fig. 2 provides the ORTEP views of the crystal structures of tersilole (**1a**) and quatersilole (**1b**). In the structure of tersilole (**1a**), three silole rings are arranged as gauche-*anti* conformations along with the Si1–Si2–Si3 trisilane skeleton. The dihedral angles <C1–Si1–Si2–Si3 and <Si1–Si2–Si3–C2 are −64.8(4) and 172.0(4)°, respectively. In the structure of quatersilole (**20**), there is a centrosymmetric point at the center of the Si2–Si3 bond. Four silole rings have gauche-*anti*-gauche conformations along with the Si1–Si2–Si3–Si4 skeleton, having <C1–Si1–Si2–Si3, −56.7(2) and <Si1–Si2–Si3–Si4, 180°. Thus, the partial geometry of tetrasilane skeleton,



Scheme 5. Reagents and conditions: (i) Na (3 mol amounts), THF, r.t., 38 h; (ii) **18** (1.5 mol. amounts), −78°C, 3 h.

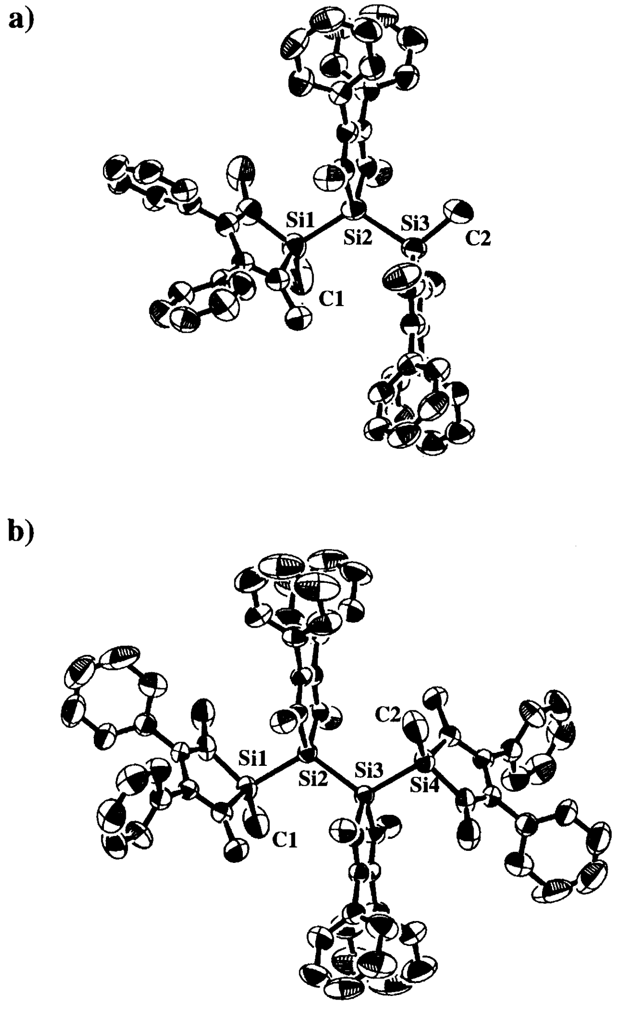
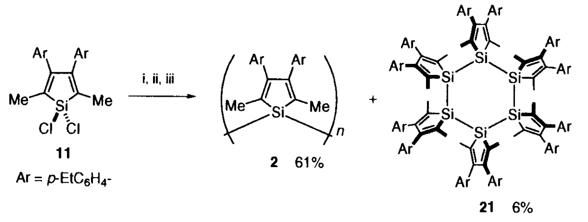


Fig. 2. ORTEP drawings (50% thermal ellipsoids) of (a) tersilole (**1a**) and (b) quatersilole (**1b**).



Scheme 6. Reagents and conditions: (i) Li (2 mol amounts), THF, −20°C, 10 h; (ii) EtMgBr (0.2 mol amount), THF, −20°C, 1 h; (iii) R from MeOH, then *i*-PrOH.

from Si1 to Si3, is quite similar to that of tersilole. These structures are contrasting to all-*anti* structures of 2,3,4,5-tetramethylsilole analogs and all-gauche structures of 2,3,4,5-tetraphenylsilole analogs, reported by Kira et al. [21] and West et al. [20], respectively. Thus, it is apparent that these conformational differences are arising from the steric congestion due to the substituents at the 2,5-positions of silole rings.

2.3. Poly(1,1-silole)s

2.3.1. Synthesis

The most straightforward route to the poly(1,1-silole)s is the Wurtz-type polycondensation of 1,1-dihalosiloles. We have actually succeeded in the synthesis of poly(1,1-silole) by a careful operation of the Wurtz-type coupling of 1,1-dichlorosilole, as shown in Scheme 6 [32]. Thus, the 1,1-dichlorosilole (**11**) was allowed to react with just 2 mol amounts of granular Li in THF at −20°C for 20 h, followed by treatment with EtMgBr to quench any reactive terminal groups. The GPC analysis of the reaction products after reprecipitation from MeOH revealed that the reaction afforded poly(1,1-silole) (**2**), but together with cyclic hexamer (**21**), as shown in Fig. 3. The oligomer was completely removed by repeated reprecipitations from *i*-PrOH to give pure poly(1,1-silole) (**2**) in 61% yield. Recrystallization of the soluble part afforded the cyclic hexamer (**21**) in 6% yield. The molecular weight of **2** estimated by GPC using polystyrene standards is $M_w = 7200$ and $M_n = 6{,}300$ ($n \approx 20$) with a very narrow polydispersity ($M_w/M_n = 1.14$). The polymer **2** is slightly soluble in THF and $CHCl_3$ and stable enough to be handled in air without special care.

The keys to achieving the synthesis of the poly(1,1-silole) are the choice of starting materials and reaction condition. We employed the dichlorosilole (**11**) which has small methyl groups at the 2,5-positions and *p*-ethyl groups on the 3,4-phenyl groups in order to reduce the steric congestion and increase the solubility of the resulting polymers. Also, the use of Li metal in THF is crucial. The polycondensation of **11** under the standard conditions for the Wurtz-type polysilane synthesis using Na in refluxing toluene only gave a mixture of oligomeric materials, which might contain the Si–O–Si linkages in light of the broad band around 1000–1100 cm^{-1} in the IR spectrum.

As an alternative route to the poly(1,1-silole)s, we have also examined the coupling reaction of the silole dianion (**19**) with chlorine-terminated tersilole (**22**) which was prepared by the reaction of **19** with **13**

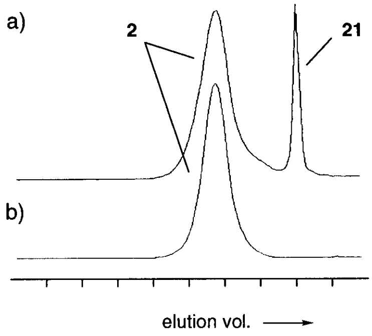
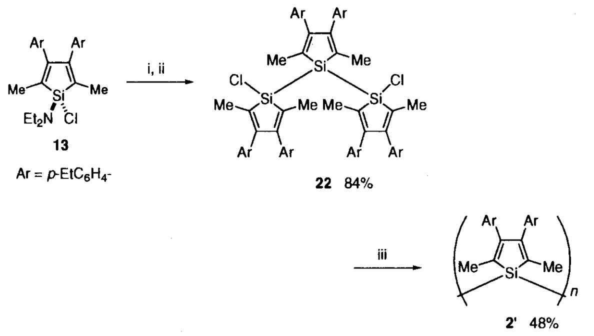


Fig. 3. GPC traces after reprecipitation from (a) MeOH, then (b) *i*-PrOH.



Scheme 7. Reagents and conditions: (i) **19** (0.5 mol amount, prepared from **11** with Li), THF, − 78°C, 3 h; (ii) dry HCl gas, Et_2O, − 78°C; (iii) **19** (1.1 mol amount, prepared from **11** with Li), THF, − 78°C, 2 h; (iv) *i*-PrOH (2 mol amounts), Et_3N (2 mol amounts), r.t.

followed by deaminochlorination, as shown in Scheme 7. The polymer **2′** having essentially the same spectroscopic data as that of **2** was obtained in 48% yield, although the molecular weight was relatively low; $M_w = 3000$ and $M_n = 2{,}400$ ($n \approx 8$) with $M_w/M_n = 1.25$. In this reaction, the cyclic hexamer was no longer obtained.

2.3.2. Photophysical properties

The oligo(1,1-silole)s and poly(1,1-silole) showed interesting photophysical properties. The data are summarized in Table 1, together with the data for monosilole (**23**) [33], bisilole (**24**) [30] and permethylated [34] and perphenylated oligosilanes [35] for comparison. As a representative example, the UV absorption and fluorescence spectra of polymer **2** are shown in Fig. 4.

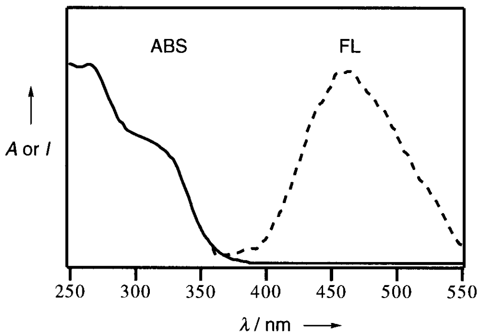
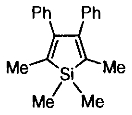


Fig. 4. UV–Vis absorption (solid line) and fluorescence spectra (dashed line) of polymer **2** in $CHCl_3$.



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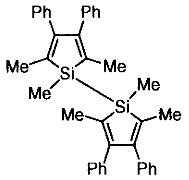

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The monosilole **23** has two absorption bands around 250 and 310 nm [33], assignable to the π–π* transitions of the phenyl and silole moieties, respectively. In comparison with the monosilole (**23**), the oligosiloles **24**, **1a** and **1b** show distinct spectra, where the absorption of the silole moieties is hidden by broad bands. Remarkably, tersilole (**1a**) and quatersilole (**1b**) have unique

Table 1
UV absorption and fluorescence spectral data for oligo(1,1-silole)s, poly(1,1-silole) and related oligosilanes

Compound		UV absorption [a]		Fluorescence [a]	
		λ_{max} (nm)	log ε	λ_{max} (nm) [b]	$\phi_f \times 10^3$ [c]
Monosilole	**23**	307	3.22	393	0.372
Bisilole	**24**	255	4.42	415	1.94
Tersilole	**1a**	279	4.60	439	1.27
Quarersilole	**1b**	288	4.59	441	1.39
Cyclo-sexisilole	**21**	285	5.07	467	0.353
Polysilole	**2**	320(sh)	4.02 [d]	460	0.314
$Ph(Ph_2Si)_3Ph$ [e]		255	4.51		
$Ph(Ph_2Si)_4Ph$ [f]		288	4.36		
$Me(Me_2Si)_3Me$ [g]		216	3.96		
$Me(Me_2Si)_4Me$[g]		235	4.17		

[a] In chloroform.

[b] Excited at the absorption maximum wavelength.

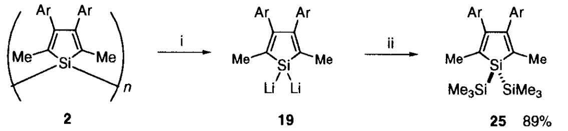
[c] Quantum yield determined with reference to quinine sulfate ($\phi_{310} = 0.55$ in 0.1 M H_2SO_4).

[d] Per silole ring unit.

[e] See Ref. [35a].

[f] See Ref. [35b].

[g] See Ref. [34].



Scheme 8. Reagents and conditions: (i) Li (excess), THF, 10°C, 1 h; (ii) Me_3SiCl, 10°C.

absorptions at around 280 and 290 nm, respectively. These absorption maxima are 50–60 nm longer than those of the permethyl oligosilanes, and in comparison with the perphenyl counterparts, **1a** has a 20 nm longer λ_{max} and **1b** has a comparable λ_{max}.

Polymer **2** has broad absorption bands with a shoulder at 320 nm, which is about 30–40 nm red-shifted relative to those of the trimer **1a** and tetramer **1b**, while an absorption maximum of the cyclic hexamer **21** is comparable to those of the oligomers. In the fluorescence spectra, the poly(1,1-silole) (**2**) has a broad emission band around 460 nm, although the quantum yield is rather low. The emission maximum wavelengths tend to shift to a longer region going from the monosilole to polymer, probably due to the mixing of the orbitals between the silole moieties and polysilane moiety.

2.3.3. *Unique chemical reactivity*

The most notable chemical properties of poly(1,1-silole) (**2**) may be the complete degradation of the polysilane skeleton with Li metal. Thus, as shown in Scheme 8, polymer **2** ($M_n = 5{,}400$) was allowed to react with an excess amount of Li in THF at 10°C to form the silole dianion **19** within 1 h as the sole product, which was trapped with Me_3SiCl to give 1,1-bis(trimethylsilyl)silole (**25**) in 89% isolated yield. This unique exhaustive degradation up to the silole dianion is totally different from the reactivity of the conventional polysilanes, which result only in the formation of the oligomeric mixtures at most, and may be consistent with the expected low-lying LUMO level of the poly(1,1-silole)s.

3. Conclusions and perspectives

The long-sought poly(1,1-silole)s are now in our hand. This new type of polysilane has been expected to have the low-lying LUMO levels due to the σ^*–π^* conjugation characteristic of the silole ring, in contrast to the traditional polysilanes, such as phenyl-substituted polysilanes which have the high-lying HOMO levels due to the σ–π conjugation between the Si–Si σ orbital and the aromatic π orbitals. The experimental results have shown that the UV absorption spectra of oligo- and poly(1,1-silole)s are not remarkably different from those of the traditional counterparts. However, the chemical reactivity of the Si–Si bond in the poly(1,1-silole) has been found to be quite unique; thus all Si–Si bonds are readily cleaved by Li reduction to form the 1,1-dilithiosilole.

Other theoretically predicted photophysical properties such as nonlinear optical properties may be explored by further experiments. A variety of new chemistries are also anticipated in this new field of polysilanes, into which we have just entered.

Acknowledgements

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