π-Electron systems containing Si=Si double bonds

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ABSTRACT
Sterically large substituents can provide kinetic stabilization to various types of low-coordinate compounds. For example, regarding the chemistry of the group 14 elements, since West et al. introduced the concept of kinetic protection of the otherwise highly reactive Si=Si double bond by bulky mesityl (2,4,6-trimethylphenyl) groups in 1981, a number of unsaturated compounds of silicon and its group homologs have been successfully isolated by steric effects using the appropriate large substituents. However, the functions and applications of the Si=Si π-bonds consisting of the 3p electrons on the formally sp²-hybridized silicon atoms have rarely been explored until 10 years ago, when Scheschkewitz and Tamao independently reported the model systems of the oligo(phenylenedisilenylene)(Si–OPVs) in 2007. This review focuses on the recent advances in the chemistry of π-electron systems containing Si=Si double bonds, mainly published in the last decade. The synthesis, characterization, and potential application of a variety of donor-free π-conjugated disilene compounds are described.

1. Introduction
In the periodic table, silicon is located just below carbon in the Group 14 elements, but carbon and silicon have different roles and functions in nature. While carbon is a central element in the organic substances that constitute the body of all living things, silicon is a key element in the stable materials mainly consisting of the inorganic substances that constitute the earth’s crust and is widely used in glass, semiconductors, concrete, ceramics, etc. Strange!ly, there is no organosilicon material containing C–Si bonds in nature except for silicon carbide in meteorites. Therefore, every organosilicon compound is an artificial substance created by human technology. While a variety of allotropes of carbon, such as diamond, graphite, fullerenes, and carbon nanotubes, are known as a stable material mainly consisting of the sp²- or sp³-hybridized carbon atoms, the stable form of silicon only possesses a diamond-type structure based on the formally sp³-hybridized silicon atoms. Can sp³-hybridized silicon atoms exist as a stable substance? In recent years, silicene, the silicon analog of graphene, has attracted much attention, from both experimentalists and theoreticians, as a new two-dimensional allotrope of silicon [1-3]. Theoretical studies predict that repeating units in pure silicon nanosheets do not exhibit a planar hexagonal geometry like graphene but a non-classical propellane motif, presumably due to the instability associated with sp³-hybridized silicon atoms [4].

In general, the Si–Si π-bond is much weaker than the C–C π-bond essentially due to the less effective overlap of the two adjacent 3p orbitals relative to that of the 2p orbitals, corresponding to the greater covalent atomic radius of silicon (1.11(2) Å) than that of carbon (sp³-C; 0.76(1), sp³-C; 0.73(2), and sp-C; 0.69(1) Å) [5]. In 1981,
West, Fink, and Michl demonstrated for the first time that disilene (R₂Si=SiR₂) (1), the silicon analog of alkene, can be created based on the concept of kinetic stabilization using sterically demanding substituents, protecting the highly reactive Si=Si double bond, as shown in Figure 1, which produced a significant change in the main group chemistry [6–11]. In fact, after the finding of this isolatable disilene 1, many kinds of unsaturated compounds of silicon have been successfully obtained by virtue of the steric effects of the bulky protecting groups [12–22]. For recent representative examples, since 2000, silaaromatics (2) [23–25], trisilaallenes (R₂Si=Si=SiR₂) (3) [26,27], and disilynes (RSi≡SiR) (4) [28–31] have been isolated using the appropriately designed bulky aryl, alkyl, and silyl substituents, respectively. Also, a tricyclic aromatic isomer of hexasilabenzen (5) [32] and a disilicon(0) fragment coordinated by the N-heterocyclic carbenes (NHCs) (6) [33] were synthesized as stable crystalline compounds. In 2011, we reported the synthesis of a cyclobutadiene (CBD) silicon analog, i.e. tetrasilacyclobutadiene (7), with a planar rhombic charge-separated structure originating from the polar Jahn–Teller distortion [34]. This is the first persila[n] annulene compound, (SiR)ₙ (n is an even number equal to or greater than 4), with a cyclic structure consisting of formally sp²-hybridized silicon atoms, which will open a new facet of silicon π-science.

Although the fundamental chemistry of the low-coordinated compounds of silicon has been steadily established year-by-year, the functions and applications of the Si–Si π-bonds consisting of the 3pπ electrons on the formally sp²-hybridized silicon atoms have rarely been explored. In main group element chemistry, recent synthetic efforts have been directed toward investigating the combination of the multiple bonds of the heavier main group elements and the carbon π-electron systems due to their unique electronic properties and potentially useful technological applications for organic

![Figure 1. Examples of stable unsaturated silicon compounds.](image-url)
electronics, which would offer a new avenue to functional organoelement materials [35–45]. However, this chemistry always faces a formidable challenge. While the sufficient steric effects of the bulky substituents are crucial in protecting the highly reactive heavier multiple bonds, it may cause twisting of the π-framework, which prevents the preferred extension of the π-conjugation over the skeleton. In order to further develop this chemistry toward advanced materials science and technology, we have designed a series of fused-ring bulky 1,1,3,3,5,5,7,7-octara-R-substituted s-hydrindacen-4-yl groups, called the ‘Rind’ groups, as shown in Figure 2, where R denotes the initial of the substituents on the benzylic positions of the hydridacene skeleton [46]. The Rind groups are actually giant aryl hydrocarbon substituents. Nevertheless, they can be easily prepared by organic synthetic methods, including the intramolecular Friedel-Crafts double cyclization [47]. In addition, various R groups (R1, R2, R3, and R4 groups) can be introduced at the four benzylic positions of the hydridacene skeleton. While the peripheral R1 and R2 groups can control their physical properties such as crystallinity and solubility, the proximal R3 and R4 groups can directly change the steric (size and shape) effects of the Rind groups. Also, the Rind groups have a rigid structure based on the fused-ring system and show a high chemical stability due to the full substitution at all the benzylic positions, whose C–H bonds are generally more reactive than other C–H bonds. The term ‘Rind’ in English describes the thick outer skin of some types of fruits such as an orange and melon, which is fully in accordance with our research idea, i.e. Rind can keep the inside fresh. Actually, the Rind groups provide us great opportunities to study a variety of low-coordinate compounds of the main group elements [34,48–62] and coordinatively unsaturated transition metal complexes [63–71].

In this review, we describe the recent progress in developing organic π-electron architectures featuring Si–Si double bonds, mainly focusing on the following four topics: (1) oligo(p-phenylenedisilanylene)s; π-conjugation between benzene rings and Si–Si units, (2) air-stable emissive disilenes with naphthyl groups; potential applicability in electroluminescence devices, (3) disilene π-system with pyrenyl groups; evidence for intramolecular charge-transfer emission, and (4) disilene–thiophene π-systems; future organosilicon chemistry for developing advanced materials.

2. Oligo(p-phenylenedisilanylene)s; π-conjugation between benzene rings and Si–Si units

Poly(p-phenylenvinylene)s (PPVs) with alternating benzene rings and C=C double bonds are some of the most attractive conducting polymers due to their excellent stability and processability and unique electronic and optical properties, which can be used for various applications in modern electrochemistry [72,73]. Oligo(p-phenylenesilylene)s (OPVs) have also received extensive attention as linear monodispersed π-conjugated oligomers with well-defined molecular structures and tunable optoelectronic properties [74–76]. Since the Si=Si units possess a narrower energy gap between the highest occupied molecular orbital and the lowest unoccupied molecular orbital (HOMO–LUMO) relative to the C=C units [12–22], the disilene analogs of OPVs, oligo(p-phenylenedisilanylene)s (Si–OPVs), would provide new opportunities for application to a range of organic electronic devices.

In 2007, model systems of the Si–OPVs (8a and 9–11) were synthesized by the groups of Scheschkewitz and Tamao employing the bulky Tip (2,4,6-trisopropylphenyl) and Eind (R1 = R2 = R3 = R4 = Et) groups [77,78]. As shown in Scheme 1, the phenyl-substituted disilene, (Tip)2Si=Si(Tip)Ph (8a), and the para-phenylenebridged tetrasiladiene 9 can be obtained as yellow and red crystals in 58% and 72% yields by the reaction of the isolatable disilenyllithium, (Tip)2SiLi(DME)2, (DME = 1,2-dimethoxyethane) (12) [79], which is a silicon analog of vinylolithium, with iodobenzene and 1,4-diiodobenzene. In contrast, compounds 10 and 11 have been prepared by the reductive co-condensation of the two kinds of dibromosilanes, (Eind)SiBr2 (13) and [(Eind)SiBr2]2(1,4-C6H4) (14), with a 5:1 molar ratio using lithium naphthalenide (LiNaph) as a homogeneous reducing agent (Scheme 2), in which 13 and 14 serve as the end-capping unit and central building unit for the Si–OPVs, respectively. The resulting monomer 10 and dimer 11 can be separated by silica gel column chromatography in a glove box using hexane and toluene as the eluents, leading to the isolation of yellow-orange crystals of 10 in 35% yield and red crystals of 11 in 15% yield. However, the higher oligomers, such as the trimer and tetramer, could not be obtained in a pure form mainly due to their poor solubility in common organic solvents.

In addition to the initial achievements, Scheschkewitz et al. prepared a series of para-functionalized-phenyln-substituted disilenes, (Tip)2Si=Si(Tip)(4–X–Ph) (X = F (8b), Cl (8c), Br (8d), I (8e), SiMe3 (8f)) [80], which are shown in Figure 3. The laterally functionalized...
disilenes 8b–e can be synthesized by a similar reaction between the disilenyllithium 12 and the para-functionalized-phenyl iodides (4–X–PhI). In addition, the para-trimethylsilylphenyldisilene 8f has been obtained as a major product by the reaction of the para-bromo-phenyldisilene 8d with 2 equiv of tert-butyllithium (tBuLi) followed by the addition of trimethylchlorosilane (Me₃SiCl). The disilenes 8a–d exhibit a good correlation of the ultraviolet–visible (UV–vis) absorptions with the electronic Hammett parameters. As shown in Figure 3, the meta-phenylene-bridged tetrasiladiene (15), which is a regioisomer of 9, has also been isolated as orange crystals in 85% yield by the reaction of 12 with 1,3-diiodobenzene [80].

As shown in Scheme 3, we have recently obtained the new Si–OPVs (16–19) having the modified Rind group, (HexO)MEind group, with a hexyloxy chain at the para position of the MEind (R¹ = R² = Me, R³ = R⁴ = Et) group.

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**Scheme 1.** Synthesis of compounds 8a and 9.

**Scheme 2.** Synthesis of compounds 10 and 11.

**Figure 3.** Disilenes 8 and 15.
The bulky (HexO)MEind groups effectively encapsulate the reactive Si=Si units and produce the highly coplanar Si–OPVs π-frameworks. The selected structural parameters of 16 and 17 are summarized in Table 1, together with those of 8a–d, 9–11, and 15 for comparison. The disilene cores of 16 and 17 display an almost planar geometry. The trans-bent angles ($\theta$) between the Si–Si vector and the C–Si–C plane are estimated to be 1.65(8)$^\circ$ for 16 and 0.62(12) and 3.38(13)$^\circ$ for 17, which are comparable to those of 10 ($\theta = 2.72(14)^\circ$) and 11 ($\theta = 0.7(3)$ and 2.7(3)$^\circ$) and much smaller than those of 8a ($\theta = 22.8$ and 22.0$^\circ$), 9 ($\theta = 16.45(10)$ and 19.31(10)$^\circ$), and 15 ($\theta = 20.3$ and 26.7$^\circ$). These X-ray data show the

Scheme 3. Synthesis of compounds 16–19.

Figure 4 shows the molecular structures of 16 (a) and 17 (b) determined by X-ray crystallography.
Table 1. X-ray structural parameters of disilenes.

| Compound   | Trans-bent angle (θ (deg)) | Si=Si bond length (Å) | References |
|------------|----------------------------|-----------------------|------------|
| 1          | 12.4                       | 2.143(2)              | 10, 11, 19 |
| C,H1       | 18                         | 2.160(1)              | 7–9, 11, 19|
| 1-THF      | 0                          | 2.146                 | 11, 19     |
| 8a         | 22.8                       | 2.175(1)              | 77         |
| 8b         | 5.5, 5.9                   | 2.147(1)              | 80         |
| 8c         | 15.8, 23.8                 | 2.173(4)              | 80         |
| 8d         | 16.2, 24.5                 | 2.170(7)              | 80         |
| 9          | 16.45(10)                  | 2.1674(8)             | 77         |
| 10         | 2.72(14)                   | 2.1593(16)            | 80         |
| 11         | 0.7(13), 2.7(3)            | 2.1562(2)             | 80         |
| 15         | 20.3, 26.7                 | 2.189(1)              | 80         |
| 16         | 1.65(8)                    | 2.1626(8)             | 81         |
| 17         | 0.62(12), 3.38(13)         | 2.1642(8)             | 81         |
| 22a        | 27.9                       | 2.1735(15)            | 87         |
| 22b        | 32.3                       | 2.1851(12)            | 88         |
| 23a        | 8.9                        | 2.2032(2)             | 89         |
| 23b        | 11.3                       | 2.1871(10)            | 89         |
| 24         | 4.93(12)                   | 2.1688(2)             | 90         |
| 25a        | 2.25(14)                   | 2.1623(18)            | 91         |
| 25b        | 9.57(11)                   | 2.1667(12)            | 91         |
| 29         | 8.22(8), 2.96(8)           | 2.1718(6)             | 97         |
| 31         | 11.4, 6.9                  | 2.1754(12)            | 100        |
| 32a        | 4.0, 4.9                   | 2.1697(6)             | 101        |
| 32b        | 7.5, 7.7                   | 2.1699(5)             | 101        |
| 32c        | 10.5, 26.2                 | 2.1826(6)             | 101        |
| 33b        | 15.5, 16.1, 26.0, 20.6,    | 2.1846(5)             | 101        |
|            | 20.0                       | 2.1295(9)             |            |
| 33c        | 11.9, 20.2                 | 2.1764(2)             | 101        |
| 34a        | 6.7, 7.2                   | 2.1453(6)             | 102        |
| 34b        | 7.5, 17                    | 2.1516(7)             | 102        |
| 34c        | 11.6, 3.2                  | 2.1525(6)             | 102        |
| 35a        | 6.7, 4.2                   | 2.1460(8)             | 102        |
| 35b        | 13.5, 9.7                  | 2.1530(8)             | 102        |
| 35c        | 5.5, 13                    | 2.1622(6)             | 102        |
| 35d        | 4.7, 3.5                   | 2.1483(9)             | 102        |
| 37         | 19.12(12), 13.5(6)         | 2.1712(11)            | 86         |
| 38         | 5.44(10)                   | 2.1584(9)             | 86         |

Si=Si double bonds. The λ_{max}(abs) values provide a good fit to Meier’s equation [83], which enables the estimation of an effective conjugation length (ECL) of nine repeat units (n_{ECL} = 9) and the absorption maximum of 635 nm for the infinite chain (λ_{∞(abs)} = 635 nm). These estimated values (n_{ECL} = 9 and λ_{∞(abs)} = 635 nm) for the Si-OPVs are lower and longer than those of the carbon counterpart, OPVs (n_{ECL} = 11 and λ_{∞(abs)} = 481 nm), respectively [84]. Thus, the inclusion of the Si=Si double bonds into the carbon π-conjugated systems may cause a significant change in the electronic and absorption properties.

While the monomer 16 does not show any emission like 10, the dimer 17, trimer 18, and tetramer 19 exhibit an intense fluorescence in THF at room temperature (Figure 5(b)). The emission maxima (λ_{max(ex)}) are observed at 613 nm for 17, 643 nm for 18, and 668 nm for 19, one of which is similar to that of 11 (612 nm). The quantum yields (Φ_F) increased from 0.11 to 0.48 with the increasing number of repeated units. In contrast, the Stokes shifts (Δν_Stokes) decreased from 2000 cm^-1 for 17 to 1420 cm^-1 for 19, which are lower than those of the flexible carbon-based OPVs (3199–3029 cm^-1) [83] and higher than those of the rigid carbon-bridged OPVs (772–583 cm^-1) [85], suggesting the moderate rigidity of the Si–OPVs frameworks supported by the perpendicularly-fixed (HexO)MEind groups.

These studies reveal the possibility of constructing the π-conjugated disilene systems alternating the carbon-based 2πn and silicon-based 3πn-electrons, where the Si=Si double bonds would be promising building blocks. We hope that the present studies would provide a further challenge for the pure and applied chemistry of disilene copolymers containing various carbon π-electron systems. Actually, we very recently succeeded in obtaining some disilene–thiophene π-systems as model compounds for the disilene–thiophene copolymers [86], which are described in the latter part of this review.

3. Air-stable emissive disilenes with naphthyl groups; potential applicability in electroluminescence devices

After the initial findings of the model compounds of the Si–OPVs, the π-electron systems containing a Si=Si chromophore attracted much attention from the viewpoint of their potentially useful properties and unique functions. For example, as shown in Figure 6, a new type of disilene bearing metallocceny1 groups has been synthesized by Sasamori, Tokitoh, and co-workers [87,88]. The 1,2-bis(metallocceny1)disilenes (22) exhibit a multistep redox process in the cyclic voltammograms, thus indicating the potential application of the disilene π-system as electrochemical materials. Tokitoh et al. have also shown that the 1,2-dialkynyldisilenes (23) can be obtained as a stable crystalline compound by taking advantage of the steric protection using the bulky

excellent structural controllability of the Rind groups, where the proximate ethyl side chains on the s-hydrida-case skeletons can interlock with one another above and below the Si=Si moieties to enforce the planar structure.

The photophysical data of the Si–OPVs (16–19) are summarized in Table 2. The absorption color gradually changes from yellow for 16 to blue for 19, as shown in Figure 5(a). The UV–vis spectra in THF exhibit absorption maxima (λ_{max(abs)) at 465 nm for 16, 546 nm for 17, 581 nm for 18, and 610 nm for 19, some of which are comparable to those of the Eind-based Si–OPVs (461 nm for 10 and 543 nm for 11 in hexane). The high molar extinction coefficients of 16–19 (ε = 2.8–7.1 × 10^4 cm^{-1} M^{-1}) are assignable to the allowed HOMO → LUMO (π → π^*) transitions, which are supported by the theoretical calculations using time-dependent density functional theory (TD-DFT) [82]. It should be noted that the λ_{max(abs)) values of 10 (461 nm) and 16 (465 nm) are more than 40 nm red-shifted from that of tetramesityldisilene 1 (420 nm) [6], indicating the π-conjugation over the 1,2-diphenyldisilene (disilastilbene) skeleton. In addition, the considerable bathochromic shifts with the increasing Si=Si units are most likely interpreted in terms of the extended π-conjugation over the entire Si–OPVs skeleton, thus providing clear evidence for the efficient π-conjugation between the benzene rings and
The disilenes \( \text{24} \) and \( \text{25} \) are extraordinarily air-stable in the solid state of more than several years with no detectable change as confirmed by the proton nuclear magnetic resonance (\( ^1\text{H NMR} \)) spectra, which indicates the excellent protection abilities of the Eind group. The disilenes \( \text{24} \) and \( \text{25} \) decompose in a dilute solution (ca. 10\(^{-5} \) mol L\(^{-1} \)) upon exposure to air with a half-lifetime of 2–4 h, which is rather longer than that previously reported for (Tip)\(_2\)Si=Si(Tip)\(_2\) (17 min) [92], as monitored by the UV–vis absorption spectroscopy.

Figure 7 shows the molecular structures of \( \text{24} \) and \( \text{25} \) confirmed by X-ray crystallography. Both molecules have an inversion center at the midpoint of the Si=Si double bond with an E-configuration. In the crystal of \( \text{24} \), the hydrogen atoms at the peri-position on the 1-naphthyl groups participate in the CH–π interaction.

### Table 2. Photophysical data for disilenes.

| Compound | \( \lambda_{\text{max}} \text{(abs) (nm)} \) | \( \lambda_{\text{max}} \text{(ex) (nm)} \) | \( \Delta
\text{ν}_{\text{Stokes}} \text{(cm}^{-1} \)) | \( \Phi_F \) | References |
|----------|--------------------------------|----------------|----------------|---------|------------|
| 1 (hexane) | 420 [1.0 × 10\(^4\)] | 505 | 4000 | <0.01 | 6, 9 |
| 8a (hexane) | 439 [1.9 × 10\(^4\)] | 77 |
| 8b (hexane) | 437 [1.7 × 10\(^4\)] | 80 |
| 8c (hexane) | 445 [1.9 × 10\(^4\)] | 80 |
| 8d (hexane) | 447 [1.6 × 10\(^4\)] | 80 |
| 9 (hexane) | 508 [2.7 × 10\(^4\)] | 77 |
| 10 (hexane) | 461 [2.4 × 10\(^4\)] | 78 |
| 11 (hexane) | 543 [3.0 × 10\(^4\)] | 80 |
| 15 (hexane) | 450 [3.9 × 10\(^4\)] | 80 |
| 16 (THF) | 465 [2.8 × 10\(^4\)] | 81 |
| 17 (THF) | 546 [4.3 × 10\(^4\)] | 613 | 2000 | 0.11 | 81 |
| 18 (THF) | 581 [5.0 × 10\(^4\)] | 643 | 1660 | 0.46 | 81 |
| 19 (THF) | 610 [7.1 × 10\(^4\)] | 668 | 1420 | 0.48 | 81 |
| 22a (hexane) | 427 [2.4 × 10\(^4\)] | 87 |
| 22b (hexane) | 430 [2.2 × 10\(^4\)] | 88 |
| 23a (hexane) | 437 [2.4 × 10\(^4\)] | 89 |
| 23b (hexane) | 469 [3.1 × 10\(^4\)] | 89 |
| 24 (THF) | 521 [9.5 × 10\(^4\)] | 614 | 2910 | <0.01 | 90 |
| 24 (solid) | 522 [3.2 × 10\(^4\)] | 625 |
| 25 (THF) | 504 [2.5 × 10\(^4\)] | 586 | 2780 | <0.01 | 91 |
| 25 (solid) | 619 | 0.23 | 91 |
| 28 (THF) | 590 [1.3 × 10\(^4\)] | 661 | 0.03 | 98 |
| 29 (THF) | 566(sh) [2.0 × 10\(^4\)] | 676 | 0.03 | 98 |
| 29 (acetonitrile) | 575 [7.2 × 10\(^4\)] | 694 | 0.03 | 98 |
| 29 (acetonitrile) | 564(sh) [3.7 × 10\(^4\)] | 712 | 0.04 | 98 |
| 31 (3-MP\(^2\)) | 525 [420] | 100 |
| 31 (1,2-DCB\(^2\)) | 535 [480] | 100 |
| 32a (hexane) | 538 [1.4 × 10\(^4\)] | 100 |
| 32b (hexane) | 583 [1.6 × 10\(^4\)] | 101 |
| 32c (hexane) | 394(sh) [5.6 × 10\(^4\)] | 101 |
| 33a (hexane) | 581 [2.55 × 10\(^4\)] | 101 |
| 33b (hexane) | 439(sh) [4.0 × 10\(^4\)] | 101 |
| 33c (hexane) | 441(sh) [7.0 × 10\(^4\)] | 101 |
| 34a (hexane) | 430 [2.1 × 10\(^4\)] | 102 |
| 34b (hexane) | 430 [1.7 × 10\(^4\)] | 102 |
| 34c (hexane) | 463 [6.8 × 10\(^4\)] | 102 |
| 34d (hexane) | 550 [3.8 × 10\(^4\)] | 102 |
| 35a (hexane) | 463 [2.1 × 10\(^4\)] | 102 |
| 35b (hexane) | 488 [4.6 × 10\(^4\)] | 570 | <0.01 | 102 |
| 35b (solid) | 613 | 0.015 | 102 |
| 35c (hexane) | 484 [1.2 × 10\(^4\)] | 574 | <0.01 | 102 |
| 35c (solid) | 587 | 0.04 | 102 |
| 35d (hexane) | 597 [7.5 × 10\(^4\)] | 102 |
| 35d (solid) | 816 | 0.05 | 102 |
| 37 (THF) | 459 [1.1 × 10\(^4\)] | 86 |
| 38 (THF) | 530 [1.3 × 10\(^4\)] | 86 |
| 38 (solid) | 691 | 0.11 | 86 |

\(^{a}\)3-methylpentane. \(^{b}\)1,2-dichlorobenzene.
with the benzene ring of the perpendicularly-oriented Eind groups, producing the highly coplanar di(1-naphthyl)disilene skeleton, favorable for the efficient π-conjugation involving the Si=Si unit. In the crystal of 25, the Si atoms and the 2-naphthyl groups are disordered over the two positions, which corresponds to a mixture of two rotational isomers, s-cis, s-cis (25a) and s-trans, s-trans (25b), with the occupancy factors of ca. 0.40/0.60. Each rotational isomer has an essentially coplanar di(2-naphthyl)disilene framework. The selected structural parameters of 24, 25a, and 25b are summarized in Table 1. The trans-bent angles (θ) are estimated to be 4.93(12)° for 24, 2.25(14)° for 25a, and 9.57(11)° for 25b. The Si=Si bond distance is 2.1688(7) Å for 24, 2.1623(18) Å for 25a, and 2.1667(12) Å for 25b, which are comparable to those of 10 (2.1593(16) Å), 11 (2.156(2) Å), 16 (2.1626(8) Å), and 17 (2.1642(8) Å) and in the standard range of those reported for disilenes [15].

As shown in Figure 8, the disilenes 24 and 25 exhibit a strong absorption and emission at room temperature both in solution and in the solid state mainly due to the highly coplanar 1,2-dinaphthyldisilene π-frameworks. The photophysical data of 24 and 25 are summarized in Table 2. In the UV–vis spectra in THF, the absorption maxima (λ_{max(\text{abs})}) appear at 521 nm for 24 and 504 nm for 25, which are red-shifted from that of 10 (461 nm), indicative of the effective π-conjugation over the dinaphthyldisilene skeletons. The emission maxima (λ_{max(ex)}) are found at 614 nm for 24 and at 586 nm for 25. The Stokes shift (Δν_{Stokes}) values are estimated to be 2910 cm\(^{-1}\) for 24 and 2780 cm\(^{-1}\) for 25, which are higher than that of 11 (2080 cm\(^{-1}\)) but much lower than those of the tetramesityldisilene [8] and tetraneopentyldisilene (7300 cm\(^{-1}\)) [93], thus indicating

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**Figure 5.** Photographs of the THF solutions of 16–19 at room temperature: (a) under room light; (b) under 360 nm UV light.

**Figure 6.** Disilenes 22 and 23.

**Scheme 4.** Synthesis of compound 24.
the structural rigidity of the dinaphthyldisilene skeletons. Each of the disilenes 24 and 25 shows a weaker emission in solution relative to that in the solid state mainly ascribed to the free-rotation of the naphthyl groups around the Si–C bonds in solution.

Figure 9 shows the frontier molecular orbitals of 24, 25a, and 25b afforded by the DFT computations at the B3LYP/6-31G** level [82]. While the HOMOs mainly consist of the π(Si–Si) orbital, the LUMOs involve the appreciable contribution of the π*(Si–Si)–π*(naphthalene) conjugation. The HOMO and LUMO energy levels of 24 (–4.209 and –1.572 eV) are somewhat higher and lower than those of 25a (–4.249 and –1.554 eV) and 25b (–4.304 and –1.478 eV). Accordingly, the HOMO–LUMO energy gap for 24 (2.637 eV) is slightly smaller than those of 25a (2.695 eV) and 25b (2.826 eV). These calculations are in good qualitative agreement with the experimental data, a slightly longer absorption maximum (λ_max(abs)) for 24 (521 nm) relative to 25 (504 nm), which are based on the fact that the larger HOMO and LUMO lobes are at the 1-position than at the 2-position of the naphthalene ring.

The resulting 1,2-dinaphthyldisilenes 24 and 25 also exhibit a high thermal stability with a decomposition point of 245–248 °C for 24 and 282–285 °C for 25 under an argon atmosphere. The exceptional air and thermal...
Actually, as shown in Figure 10, we have found that the disilene 25 can emit light in an organic light-emitting diode (OLED) [94]. To the best of our knowledge, this is the first demonstration of electroluminescence (EL) from a disilene compound in OLEDs. A typical stabilities would open up new opportunities for application in a range of organic electronic devices, since the Si=Si unit possesses a narrower HOMO–LUMO energy gap than the C=C unit [12–22].

Figure 8. Photographs of the THF solutions (left) and solid in the air (right) of 24 and 25: (a) under room light; (b) under 365 nm UV light.

Figure 9. Frontier molecular orbitals of 24, 25a, and 25b together with the energy levels.
Following the successful achievements of the \((E)\)-1,2-dinaphthyldisilenes 24 and 25, we focused on the development of further \(\pi\)-extended disilene molecules. For example, \((E)\)-1,2-di(1-pyrenyl)disilene (28) can be considered as a fascinating \(\pi\)-system with two \(\pi\)-extended pyrenyl groups consisting of four fused benzene rings. As shown in Scheme 6, we have examined the reductive treatment of the \(E\)-ind- and 1-pyrenyl-substituted dibromosilane, \((E)\)-ind-(1-pyrenyl)SiBr\(_2\) (30), with a sufficient amount of lithium naphthalenide (LiNaph) in THF. However, unexpectedly, we obtained the \(Z\) isomer, \((Z)\)-1,2-di(1-pyrenyl)disilene (29), as purple crystals in 43% yield [97]. The disilene 29 is not very stable in the air and even in the solid state, which is in sharp contrast to the fact that the red crystals of \((E)\)-1,2-dinaphthyldisilenes 24 and 25 can survive in the air for more than several years. Although the formation mechanism of 29 is not yet clear, this is the first selective formation of the \(Z\) isomer of the acyclic disilene by the reductive coupling of monosilane precursors. The attractive \(\pi\)-\(\pi\) interaction between the pyrenyl groups may play a role in determining the stereochemy during in the Si–Si bond-forming processes.

![Multi-thin-layer pattern has been used for the OLEDs, in which three organic molecular layers, i.e. poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT-PSS) [95] as the hole-injecting layer, the disilene 25 with a host molecule of poly(9,9-diocetylfluorene) (PFO) in the weight ratio of 1:1 as the light-emitting and hole transporting layer, and 2,2',2''-(1,3,5-benzinetriyl)-tris(1-phenyl-1-H-benzimidazole) (TPBi) as the hole-blocking and electron-transporting layer, are sandwiched between a transparent ITO (indium tin oxide) anode and metallic LiF/Al cathode on a glass substrate. This device emits a bright orange light from the disilene 25 at the applied voltage of 5 V.

Although the total performance is rather low and still far from a practical application (the maximum brightness of \(I_{\text{max}} = 119\text{ cd m}^{-2}\) at the driving voltage of 8.5 V, the luminance efficiency \(\eta_{\text{lum}}\) and the current efficiency \(L_J\) at a luminance of 100 cd m\(^{-2}\) of 0.013 lm W\(^{-1}\) and 0.035 cd A\(^{-1}\), the external quantum efficiency (EQE) of 0.014%, and the half-life of 76.5 min of the orange light emission at a 25 mA cm\(^{-2}\) current density with the initial light output of 14.6 cd m\(^{-2}\)), this study provides a new avenue for investigations to explore the applied chemistry of unsaturated compounds of the heavier main group elements. The air-stable, emissive 1,2-dinaphthyldisilenes 24 and 25 are now commercially available [96].

### 4. Disilene \(\pi\)-system with pyrenyl groups; evidence for intramolecular charge-transfer emission

Following the successful achievements of the \((E)\)-1,2-dinaphthyldisilenes 24 and 25, we focused on the development of further \(\pi\)-extended disilene molecules. For example, \((E)\)-1,2-di(1-pyrenyl)disilene (28) can be considered as a fascinating \(\pi\)-system with two \(\pi\)-extended pyrenyl groups consisting of four fused benzene rings. As shown in Scheme 6, we have examined the reductive treatment of the \(E\)-ind- and 1-pyrenyl-substituted dibromosilane, \((E)\)-ind-(1-pyrenyl)SiBr\(_2\) (30), with a sufficient amount of lithium naphthalenide (LiNaph) in THF. However, unexpectedly, we obtained the \(Z\) isomer, \((Z)\)-1,2-di(1-pyrenyl)disilene (29), as purple crystals in 43% yield [97]. The disilene 29 is not very stable in the air and even in the solid state, which is in sharp contrast to the fact that the red crystals of \((E)\)-1,2-dinaphthyldisilenes 24 and 25 can survive in the air for more than several years. Although the formation mechanism of 29 is not yet clear, this is the first selective formation of the \(Z\) isomer of the acyclic disilene by the reductive coupling of monosilane precursors. The attractive \(\pi\)-\(\pi\) interaction between the pyrenyl groups may play a role in determining the stereochemy during in the Si–Si bond-forming processes.

![Scheme 6. Synthesis of compound 29.](image-url)
As shown in Figure 11, the molecular structure of 29 has been unambiguously characterized by X-ray crystallography to adopt a Z-configuration. The two Eind groups and the two 1-pyrenyl groups mesh in a gear-like fashion centering around the disilene core with the Si=Si bond length of 2.1718(6) Å and the trans-bent angles ($\theta$) of 8.22(8)° and 2.96(8)° (Table 1). The two pyrene rings are twisted about the Si=Si unit with the Si–Si–C–C torsion angles of 52.66(13)° and 48.73(14)°, which intramolecularily interact with each other to have a $\pi$–$\pi$ stacking with a distance between the centers of the two pyrene rings of 3.635 Å.

The photophysical data of 29 are summarized in Table 2. In the UV–vis spectrum of 29 in THF, two broad absorption bands are observed with the absorption maxima ($\lambda_{\text{max}}\text{(abs)}$) at 519 and 575 nm, together with a strong absorption around 350 nm due to the pyrene ring itself. The $\lambda_{\text{max}}\text{(abs)}$ values are found to be not sensitive to the solvent polarity. In contrast, as shown in Figure 12, the emission maximum ($\lambda_{\text{max}}\text{(ex)}$) of 29 is dependent on the solvent polarity and red-shifted from 661 nm in hexane to 676 nm in THF and to 694 nm in acetone (dielectric constant: hexane 1.88, THF 7.58, acetone 20.56) [98]. These data indicate the intramolecular charge-transfer (ICT) emission at room temperature, which may originate from the arrangement of the two 1-pyrenyl groups twisted from the Si=Si double bond.

The photophysical properties of 29 are theoretically supported by DFT studies including excited-state calculations [97]. Figure 13 shows the three pertinent molecular orbitals of 29. Although the HOMO is represented by the $\pi$(Si–Si) orbital, the LUMO involves a substantial $\pi^*(\text{Si–Si})–\pi^*(\text{pyrene})$ conjugation. The LUMO+1 corresponds to the $\pi^*(\text{pyrene})$ orbital. The natural population analysis (NPA) charge distribution [99] exhibits a more charge-separated character for the (Z)-1,2-di(1-pyrenyl)disilene skeleton in the excited state compared to the ground state, which is consistent with the $\pi$(Si–Si) $\rightarrow$ $\pi^*(\text{pyrene})$ ICT excited state based on the electron transfer from the disilene $\pi$-donor toward the pyrene $\pi$-acceptor.

As shown in Figure 14, in regard to the ICT behavior of the disilenes, a unique ICT absorption by 9-anthryl-substituted trialkyldisilene (31) has been found by Iwamoto, Kira, and co-workers, in which the anthracene ring is orthogonal to the Si=Si unit [100]. The disilene 31 can be obtained as blue-purple crystals by the reaction
Figure 14. Disilenes 31–33.

Figure 15. Disilenes 34 and 35.
of the correspondingtrialkyldisilene with 9-bromoan-
thracene. Iwamoto et al. also very recently reported a
series of heteroaryl-substituted disilenes (32a–c and
33a–c), where heteroaryl groups serve as electron ac-
tors for Si=Si double bonds in ICT transitions [101].
These disilenes can also be prepared by the treatment of
the corresponding dialkylalysilidenes with heteroaryl
halides and dihalides. In the crystal structures of 32a,
32b, 33b, and 33c, the heteroaryl groups are almost per-
pendicular to the Si=Si double bond mainly due to the
steric repulsion between the bulky cyclic alky substru-
ents, mesityl group, and the heteroaryl groups.

Very recently, Scheschkewitz et al. also reported the
photophysical properties of some related (oligo)aromatic
species having one or two Si=Si double bonds (34a–d
and 35a–d), which have been prepared by the reaction
of the triaryldisilene 12 with aryl halides and dihalides
[102]. The tetrasiladienes 35b–d exhibit a fluorescence at
room temperature. DFT calculations suggest the partial
CT character of the excited state. It is important to note
that the 9,10-anthracene-bridged tetrasiladiene 35d is
from a near-infrared emissive disilene compound (\(\lambda_{\text{max}}\text{ex}) = 816 \text{ nm} \).

In order to obtain the initial target molecule, (E)-1,2-
di(1-pyrenyl)disilene 28, we examined the photoreaction
of 29 [103]. As shown in Figure 16, after the photolysis
(\(\lambda = 530 \text{ nm} \)) of 29 in THF at room temperature, the
solution color has changed from purple to blue. In the
UV–vis absorption spectrum, a relatively new sharp
peak appeared around at 590 nm, which is 15 nm red-
shifted from that of 29 (575 nm), with a higher molar
extinction coefficient (\(\varepsilon = 1.3 \times 10^{4} \text{ cm}^{-1} \text{ M}^{-1} \)) relative to
that of 29 (\(\varepsilon = 7.2 \times 10^{3} \text{ cm}^{-1} \text{ M}^{-1} \)), thus indicating the
formation of a more \(\pi\)-extended system. The absorption
spectral change with an isosbestic point at 540 nm sug-
ests a clean photoisomerization process from (Z)-
29 to (E)-28. Unfortunately, the blue 28 has not yet been
isolated in a pure form due to its labile nature, but the
DFT calculations indicate the highly coplanar (E)-1,2-
di(1-pyrenyl)disilene skeleton induced by the orthog-
onal arrangement of the Eind groups [90]. In order to
confirm the formation of 28, we are now investigating
on alternative synthetic route using the Eind-substituted
(E)-1,2-dibromosilane, (Eind)BrSi=SiBr(Eind), as a pre-
cursor [54].

5. Disilene–thiophene \(\pi\)-systems; future
organosilicon chemistry for developing
advanced materials

As already described, the construction of novel \(\pi\)-con-
jugated disilene systems consisting of the carbon-based
2\(\pi\) and silicon-based 3\(\pi\)-electrons would provide
exciting opportunities to explore new organosilicon
chemistry for organic–inorganic hybrid materials,
since the Si=Si units have a narrower HOMO–LUMO
gap compared to the C=C counterparts [12–22]. Very

recently, we studied a new type of \(\pi\)-conjugation between
the Si=Si double bond and aromatic heterocycles. As
shown in Figure 17, we previously examined the syn-
thesis and electronic properties of a series of oligothi-
ophenes (36a–c) with the bulky EMind (R\(^{1} = R^{2} = \text{Et},
R^{3} = R^{4} = \text{Me} \)) groups [50]. The orthogonal orientation
of the EMind groups has proven to be useful to produce
coplanar arrangement of oligothiophene backbones.
Based on these fundamental investigations, we have set
out to examine the possibility to construct disilene–thi-
ophene \(\pi\)-conjugated systems by the introduction of the
Rind groups.

As shown in Schemes 7 and 8, we have designed and
synthesized two new disilenes, 1,2-bis(thiophen-2-yl)
disilene (37) and 1,2-bis(2,2′-bithiophen-5-yl)disilene
(38), as model compounds of the disilene–thiophene
copolymers [86]. The disilenes 37 and 38 can be isolated
as orange and purple crystals, respectively, by the reduc-
tion of the corresponding thienyl- and bithienyl-substi-
tuted dibromosilanes (39 and 40).

Figure 18 shows the X-ray molecular structures of
37 and 38. Each molecule has an inversion center at the
middle of the Si=Si double bond with an E-configuration.
As shown in Figure 19, there were found several rota-
tional isomers of 37 and 38 in the crystals. For 37, the
thiophene units are disordered over the two positions
with the occupancy factors of ca. 0.90/0.10, which
is consistent with the existence of a mixture of three

![Figure 16. Photographs of the THF solutions of 29: (a) before
irradiation; (b) after irradiation at 530 nm.](image)

![Figure 17. Oligothiophenes 36.](image)
Figure 18. Molecular structures of (a) 37a and (b) 38a determined by X-ray crystallography.
rotational isomers, s-cis, s-cis (37a), s-cis, s-trans (37b), and s-trans, s-trans (37c), with the occupancy factors of ca. 0.81/0.18/0.01. For 38, while the inner thiophene rings are ordered in the crystal with an s-trans, s-trans conformation, the outer thiophene rings are disordered over the two orientations with the occupancy factors of ca. 0.76/0.24. Thus, the three rotational isomers, anti-(s-trans, s-trans)-anti (38a), syn-(s-trans, s-trans)-anti (38b), and syn-(s-trans, s-trans)-syn (38c), exist in the crystal with the ratio of ca. 0.58/0.36/0.06. It is worth mentioning that all the NMR data for 37 and 38 indicate the free-rotation around the Si–C bonds and the exocyclic C–C bonds in solution at room temperature on the NMR time scale.

The major structural parameters of 37 and 38 are summarized in Table 1. The disilene 37 has a trans-bent structure with the trans-bent angles (θ) of 19.12(12)° for 37a and 37b and 13.5(6)° for 37b and 37c. The Si atoms assume a somewhat pyramidal geometry with the sum of the bond angles around the Si atom (ΣSi) of ca. 355.5–357.5°. The disilene core of 38 exhibits a more coplanar arrangement relative to 37 with the trans-bent angle (θ) of 5.44(10)°. The Si atoms have an almost planar geometry; the sum of the bond angles around the Si atom (ΣSi) is 359.7°. The bithiophene moieties in 38 are slightly twisted with the dihedral angles between the inner and outer thiophene rings of 21.0(3)° for 38a and 38b and 28.6(10)° for 38b and 38c. The Si=Si double bond lengths of 2.1712(11) Å for 37 and 2.1584(9) Å for 38 are in the range of those for typical disilenes [16].

The photophysical data of 37 and 38 are summarized in Table 2. As shown in Figure 20, the absorption color clearly changes from the yellow of 37 to the red-purple of 38. In the UV–vis spectrum of 37 in THF, the absorption maximum (λ_{max}(abs)) appears at 459 nm, comparable to that of 10 (461 nm), which indicates the efficient π-conjugation between the Si=Si double bond and the two thiophene moieties. For 38, the absorption peak is
As shown in Figure 20, the \( \pi \)-extended disilene 38 displays a weak but distinct emission both in solution and in the solid state, while the disilene 37 does not show any emission at room temperature. The emission maximum (\( \lambda_{\text{max (ex)}} \)) of 38 appears at 688 nm in THF with the quantum yield (\( \Phi_F \)) of 0.01. The Stokes shift (\( \Delta \nu_{\text{Stokes}} \)) of 38 (4330 cm\(^{-1}\)) is more than twice as high as that of 11 (2080 cm\(^{-1}\)). These emission properties in solution may be explained by the structural flexibility of the 1,2-bis(bithienyl)disilene skeleton compared to observed at 530 nm, which is 71 nm red-shifted from that of 37 (459 nm) and similar to that of 11 (543 nm). This large bathochromic shift is most likely interpreted in terms of the extension of the \( \pi \)-conjugation with the increasing number of thiophene units. In addition, the \( \lambda_{\text{max (abs)}} \) value of 38 is 116 nm longer than that of the EMind-substituted quaterthiophene 36a (414 nm in CH\(_2\)Cl\(_2\)) [50]. Thus, the insertion of the Si=Si double bond into the quaterthiophene skeleton causes a considerable narrowing of the HOMO–LUMO gap.

Figure 21. Frontier molecular orbitals of 37a and 38a together with the energy levels.
the 1,4-bis(disilenyl)benzene skeleton. The disilene 38 exhibits a relatively strong emission at 691 nm in the solid state with the quantum yield (Φf) of 0.11, which is about 10 times stronger than that in solution. The weaker emission in solution is attributable to the free-rotation of the bithienyl groups around the Si–C bonds and the exocyclic C–C bonds as observed in the 1H NMR spectrum.

In order to further clarify the structural and electronic properties of the disilenes 37 and 38, we performed DFT calculations at the B3LYP-D3/6-31G(d,p) level [82]. The DFT studies indicated a rather flexible geometry around the disilene core in 37. Thus, the optimized structures of 37a (C1 symmetry), 37b (Cs symmetry), and 37c (C1 symmetry) exhibit an entirely coplanar 1,2-dithienyldisilene skeleton (θ = 0.0°–0.1°), which are different from the X-ray structures (θ = 19.12(12)° and 13.5(6)°) found in the crystal. These rotational isomers have almost the same energies with the relative energies of 0.00 (37a), 1.12 (37b), and 2.48 (37c) kcal mol⁻¹. The optimized structure of 38a (C1 symmetry) shows a slightly more trans-bent configuration (θ = 10.8°) relative to that found in the crystal (θ = 5.44(10)°). The dihedral angles between the inner and outer thiophene rings are estimated to be 17.8°, which are somewhat smaller than those of the experimental X-ray values (21.0(3)° and 28.6(10)°). The differences between the X-ray and DFT structures are mainly due to the flexibility of the main chains consisting of the Si=Si unit and the thiophene rings, which would be easily affected by the crystal packing forces.

The molecular orbitals of 37a and 38a are depicted in Figure 21 in which the HOMOs mainly consist of the π(Si–Si) orbital along with a small contribution of the π(thiophene) and π(bithiophene) orbitals, while the LUMOs delocalize over the entire 1,2-dithienyldisilene and 1,2-bis(bithienyl)disilene frameworks. The HOMO level of 38a (–4.211 eV) is comparable to that of 37a (–4.222 eV), while the LUMO level of 38a (–1.681 eV) is much lower than that of 37a (–1.350 eV) due to the extended π*(Si–Si)–π*(bithiophene) conjugation. The HOMO–LUMO energy gap for 38a (2.530 eV) is smaller than that for 37a (2.871 eV), which are in good agreement with the UV–vis absorption data. The TD-DFT calculations almost reproduce the absorption spectra with the absorption wavelengths at 466 nm for 37a and 558 nm for 38a, which are comparable to those observed for 37 (459 nm) and 38 (530 nm), assignable to the HOMO → LUMO (π→π*) transitions.

In this study, we have demonstrated for the first time that the Si=Si double bond can fully conjugate with aromatic heterocycles using the appropriate steric effects due to the bulky Eind groups. The experimental and theoretical studies provide clear evidence for the effective π-conjugation between the Si=Si chromophore and thiophene units, originating from the essentially coplanar (bi)thiophene–Si=Si–(bi)thiophene skeletons. Further studies to develop promising disilene–thiophene copolymers for future application in a range of organic electronic devices are now in progress.

Figure 22. Compounds 5, 7, and 41–43.
would provide new opportunities for application in a range of electronic devices, because the Si=Si units have a smaller HOMO–LUMO energy gap compared to the C=C units. Some silicon analogs of 1,3-butadiene, i.e. the tetrasila-1,3-butadienes (45–47), have been obtained employing the bulky substituents [107–109]. We hope that further progress will be made in the construction and functions of the cyclic and linear π-electron systems involving the Si=Si double bonds.

**Acknowledgments**

The calculations and experiments described in this article have been performed with many collaborators, whose names appear in the references. The authors wish to express their sincere thanks to all of them for their kind collaboration, in particular, Prof Kohei Tamao, for his continuous discussions.

**Disclosure statement**

No potential conflict of interest was reported by the authors.

**Funding**

This research is partially supported by the Precursory Research for Embryonic Science and Technology (PRESTO) from Japan Science and Technology Agency (JST); Ministry of Education, Culture, Sports, Science and Technology (MEXT) of Japan for Scientific Research on Innovative Areas, ‘Stimuli-responsive Chemical Species for the Creation of Functional Molecules’ [#2408] [grant number 24109003]; Scientific Research (B) [grant numbers 24350031, 15H03788]; MEXT-Supported Program for the Strategic Research Foundation at Private Universities 2014–2018 subsidy from MEXT and Kindai University. N.H. acknowledges the support by a Grant-in-Aid for JSPS Fellows from the Japan Society for the Promotion of Science (JSPS) [grant number JP16J01036].

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6. **Concluding remarks**

In this review, we have addressed the recent progress related to the chemistry of π-electron systems containing Si=Si double bonds. Especially, the unique steric effects of the fused-ring bulky Rind groups enabled us to isolate a series of structurally well-defined discrete π-conjugated disilene molecules, which exhibit an efficient delocalization of 2π- and 3π-electrons over the skeletons. In other words, the properly designed bulky protecting groups play pivotal roles in the structural determination and in the control of the electronic properties in the π-electron systems consisting of the carbon π-systems and Si=Si double bond(s). We hope that the present studies will provide a future challenge of pure and applied organoelement chemistry toward advanced materials science and technology.

As shown in Figure 22, after the achievement of the first persila[n]annulene compound, i.e. tetrasila-cyclobutadiene (n = 4) (7) [34], extensive efforts have been devoted to the design and synthesis of hexasilabenzenes (n = 6) (41) with a cyclic system consisting of the six formally sp²-hybridized silicon atoms. The hexasilabenzenes 41 can be regarded as the smallest fragment for silicene [1–3], the silicon analog of graphene with a two-dimensional honeycomb structure. Although some related hexasilabenzenes isomers (5, 42, and 43) were synthesized as a stable crystalline compound [32,104,105], the long-considered hexasilabenzenes 41 has not been isolated and remains elusive. In particular, novel electronic and optical properties as well as exotic silicon aromaticity arising from the six 3π-electrons in 41 have attracted much attention from both experimentalists and theoreticians [106].

Also, as shown in Figure 23, a silicon analog of the linear polyacetylene, i.e. polysilyne (44), with repeating disilene (RSi≡SiR) units, has yet to be achieved and remains as a dream compound for chemists, which

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6. **Figure 23. Compounds 44–47.**
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