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Silicon-Bridge Effects on Photophysical Properties of Silafluorenes

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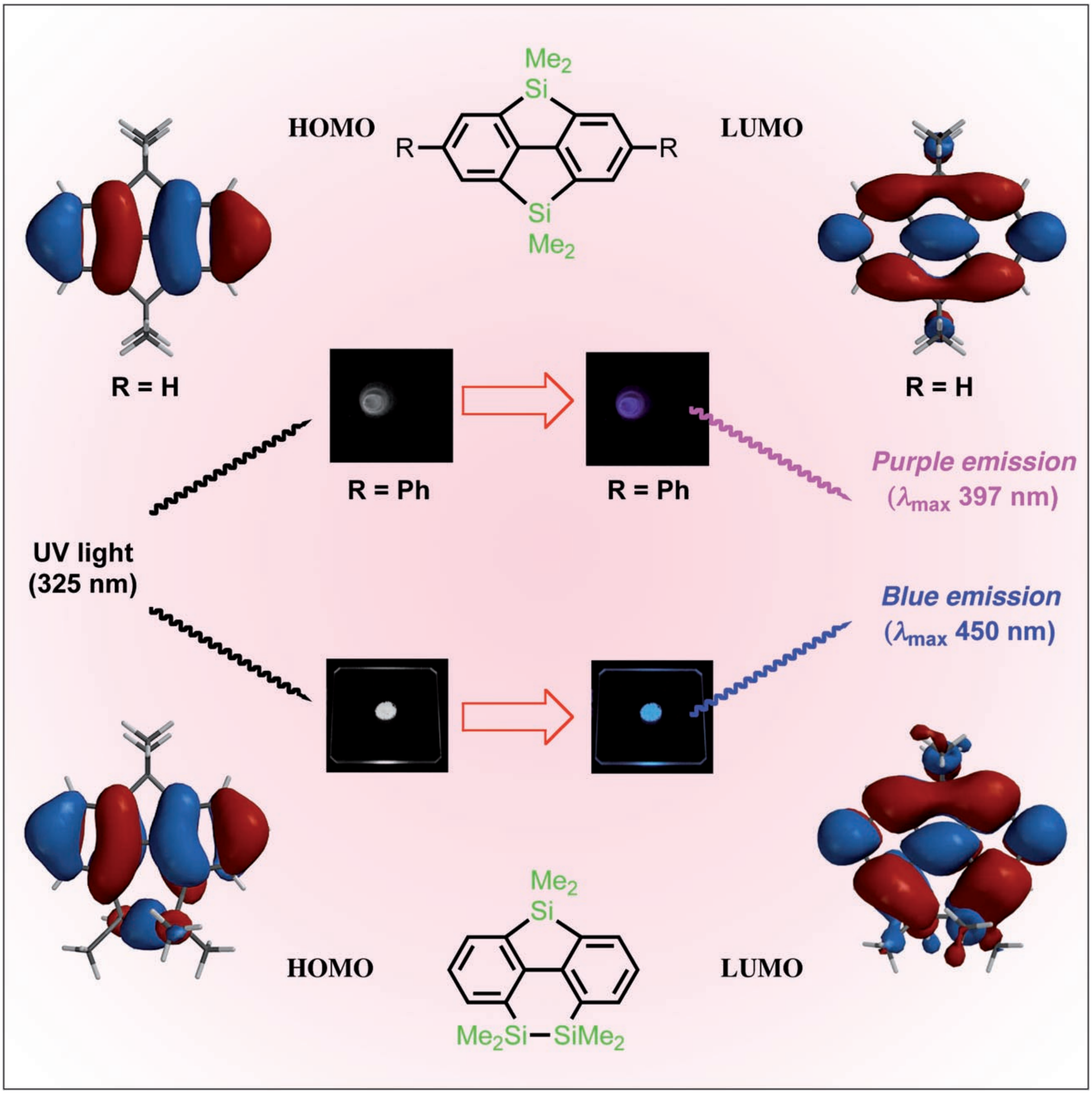
Dedicated to Professor Ryoji Noyori on the occasion of his 70th birthday

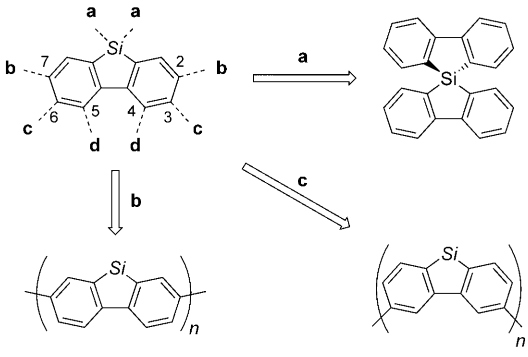


Abstract: The preparation of 4,5-dimethylsilylene- or 4,5-tetramethyldisilylene-bridged 9-silafluorenes was achieved by lithiation of 2,2′,6,6′-tetrabromobiphenyls followed by silylation with dichlorodimethylsilane or 1,2-dichloro-1,1,2,2-tetramethyldisilane, respectively. X-ray analysis of the silylene-bridged silafluorene revealed that the molecular framework was perfectly planar and four Si−C(methyl) σ bonds were completely orthogonal to the plane. Both the silicon atoms and the benzene rings were significantly deformed from the normal tetrahedral and hexagon shapes, respectively. The silicon bridge at the 4,5-positions was found to induce a red shift of the absorption and fluorescence spectra measured in cyclohexane, compared with 9-silafluorenes. It is remarkable that the disilylene-bridged silafluorene emitted blue light ($\lambda_{em} = 450$ nm) with a large Stokes shift. The emission maxima of the silicon-bridged silafluorenes in thin films were similar to those measured in cyclohexane solution. DFT calculations suggested that introduction of the silicon bridge led to increases in both the HOMO and LUMO levels compared with 9-silafluorene.

Keywords: arenes · chromophores · conjugation · luminescence · silicon

Introduction

Extensive research has been made on the preparation of π-conjugated molecules as advanced materials for electronic and photonic applications.[1] Since chemical and physical properties of such conjugated compounds are closely related to their electronic structures, it is indispensable to control the effective conjugation length of the π-electron system for attaining the desired properties.[2] The use of silylene bridges between π-conjugated modules such as phenylene, vinylene, and thienylene is one of the effective strategies for the extension of conjugated systems, because the bridge induces not only coplanarity but also a lowering of the LUMO of the parent conjugated system consisting of the modules due to σ*–π* conjugation between the π* orbitals of the parent framework and σ* orbitals of two exocyclic carbon–silicon σ bonds.[3] Representative examples include silylene-bridged butadienes (siloles),[4] 2,2′-bithiophenes,[5] and oligo(*p*-phenylenevinylene)s.[6] Recently, 9-silafluorene, which can be regarded as a silylene-bridged biphenyl, has emerged as a new module of functional organic materials such as light-emitting and conducting materials.[7] The structural modifications reported so far are classified into three categories, as illustrated in Scheme 1: spirosilabifluorene (**a**) and oligomer/(co)polymer connecting at the 2,7- (**b**) or 3,6-positions (**c**), whereas there is, to our knowledge, no example of elaboration at the 4,5-positions (**d**) except for 4,5-sulfur-bridged silafluorenes.[8] To explore the potential of a silafluorene framework as a conjugated module for functional organic materials,[9] we became interested in an additional silicon bridge at the 4,5-positions, which should impart greater rigidity, strain, and/or some torsion to the framework together with the electronic silicon effect. Reported herein are the preparation, structure, photophysical properties, and DFT calculations of 4,5-silylene- and 4,5-disilylene-bridged silafluorenes **1** and **2** (Figure 1). The additional silicon bridges are found to induce large Stokes shifts, and **1** and **2** exhibit violet and blue emission, respectively, upon irradiation with UV light.



Results and Discussion

Preparation of Silicon-Bridged Silafluorenes 1 and 2

At the outset, stepwise preparation of **1a** was examined. Bromine–lithium exchange of 2,2′,6,6′-tetrabromobiphenyl

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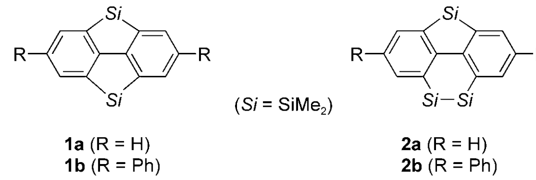
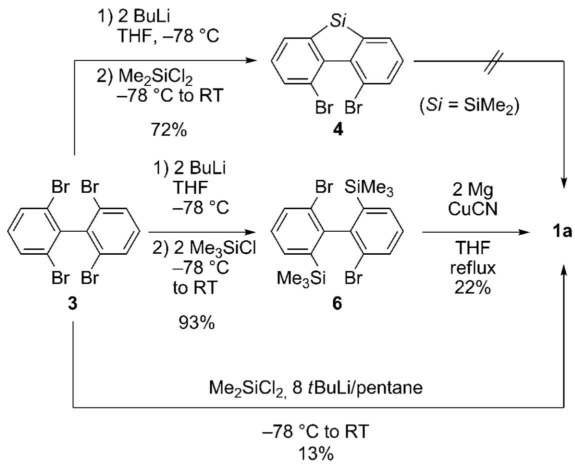


Figure 1. Silicon-bridged silafluorenes **1** and **2**.

(**3**) with two equivalents of BuLi in THF followed by silylation with Cl_2SiMe_2 gave 4,5-dibromosilafluorene **4** in 72% yield (Scheme 2).[10] Subsequent treatment of **4** with BuLi, *tert*-BuLi, or Mg under various conditions followed by the addition of Cl_2SiMe_2 resulted in the production of 9,9-dimethyl-9-silafluorene (**5a**), the reduced form of **4**, as a major product along with a trace amount of **1a**. Then, **3** was first converted into bis(trimethylsilyl)biphenyl **6** in 93% yield by dilithiation and silylation with $ClSiMe_3$. Double cyclization of the di-Grignard reagent generated from **6** with Mg metal afforded the desired **1a** in 22% yield.[11] Lithiation of **6** with *t*BuLi resulted in the production of a complex mixture. Alternatively, we found that **1a** was produced directly in 13% yield together with **5a** when a mixture of **3** and Cl_2SiMe_2 was treated with a pentane solution of *t*BuLi at −78 °C and then the mixture was allowed to warm to room temperature.

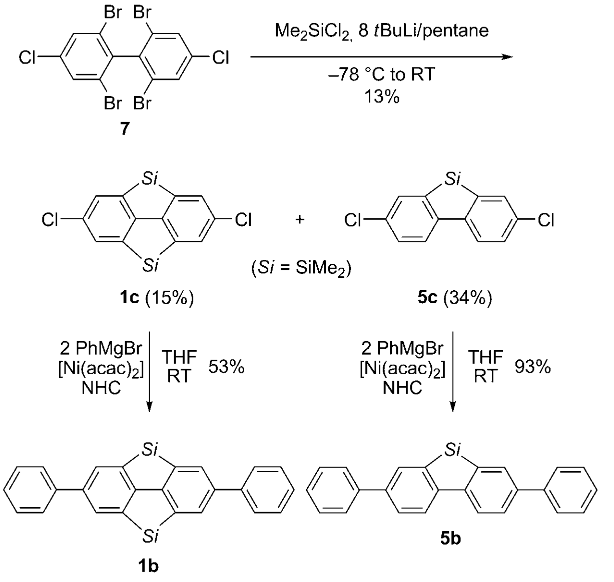


Scheme 2. Preparation of silylene-bridged silafluorene **1a**.

Abstract in Japanese:

ジメチルジクロロシランもしくは 1,2-ジクロロ 1,1,2,2-テトラメチルジシラン共存下，2,2’,6,6’-テトラブロモビフェニルをジリチオ化もしくはテトラリチオ化することにより，4,5-位がシリレンもしくはジシリレン基で架橋された 9-シラフルオレンを合成した。単結晶Ｘ線構造解析により，シリレン架橋シラフルオレンの分子骨格は完全な平面をなし，メチル基四つはその分子平面に対して垂直に配置していることがわかった。ケイ素原子とベンゼン環はゆがんだ四面体構造や六角形構造をとっていた。シラフルオレンの 4,5-位にケイ素架橋を導入すると，紫外吸収および蛍光スペクトルが長波長シフトすることがわかった。特に，ジシリレン基で架橋したシラフルオレンは青色発光し，非常に大きなストークスシフトを示すことがわかった。分子軌道計算の結果によりケイ素架橋はＨＯＭＯおよびＬＵＭＯの上昇を誘起すると考えられる。

The one-pot protocol, when applied to 4,4′-dichlorobiphenyl (**7**), produced silylene-bridged silafluorene **1c** and silafluorene **5c** in 15% and 34% yields, respectively (Scheme 3). Nickel-catalyzed cross-coupling reaction of **1c** or **5c** with phenylmagnesium bromide proceeded at room temperature to give 2,7-diphenylated silafluorene **1b** or **5b** as a colorless solid, respectively.[12] The silicon bridge remained intact under the coupling conditions.

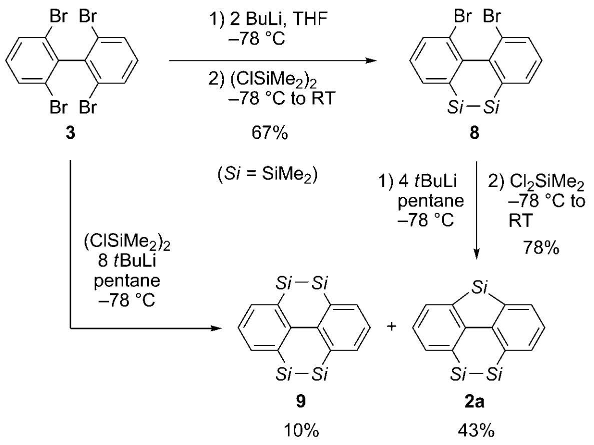


Scheme 3. Preparation of silylene-bridged silafluorene **1b** and silafluorene **5b** (NHC: 1,3-bis(2,6-di-isopropylphenyl)imidazolium chloride).

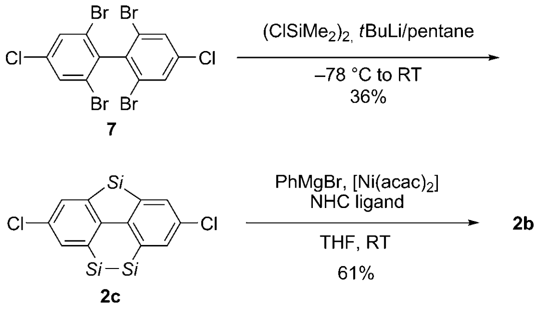
Disilylene-bridged silafluorenes **2** were prepared either by a stepwise or a one-pot procedure (Scheme 4). Thus, after **3** was converted into **8** by dilithiation with BuLi followed by silylation with $(ClSiMe_2)_2$, repeating the lithiation–silylation sequence with Cl_2SiMe_2 gave disilylene-bridged biphenyl **2a** in 78% yield. Meanwhile, when a mixture of **3** and $(ClSiMe_2)_2$ was treated with *t*BuLi in pentane, **2a** was produced as a major product in 43% yield together with bis(disilylene)-bridged biphenyl **9**.[13]

Preparation of **2b** was effected in a manner similar to the preparation of **1b** (Scheme 5). Biphenyl **7** was transformed into 2,7-dichloro-4,5-disilylene-bridged biphenyl **2c** in 36% yield by a one-pot procedure. Phenylmagnesium bromide was coupled with **2c** in the presence of a $[Ni(acac)_2]$/N-heterocyclic carbene catalyst to give **2b** as a colorless solid.

Single crystals of **1a** suitable for X-ray diffraction analysis were obtained by recrystallization from hexane.[14,15] The molecular framework consisting of the biphenyl moiety and the two dimethylsilylene bridges is perfectly planar, and four $Si-C_{Me}$ σ bonds are completely perpendicular to the planes: an ideal conformation for σ*–π* conjugation (Figure 2). The geometry of the silicon atoms is significantly deformed from a normal tetrahedral shape like that report-



Scheme 4. Preparation of disilylene-bridged silafluorene **2a**.



Scheme 5. Preparation of disilylene-bridged silafluorene **2b** (NHC: 1,3-bis(2,6-di-isopropylphenyl)imidazolium chloride).

ed for silafluorenes.[7p] For example, the C2-Si1-C8 bond angle is expanded to 113.75(8)°, while the C2-Si1-C4 angle is extremely narrowed to 92.76(6)°, which is much smaller than the standard value (109.5°) of an sp^3-hybridized silicon atom. The bond lengths between the bridge silicon and aromatic carbon atoms are 1.8820(15) and 1.8881(15) Å, slightly longer than the normal Si−C bond length (1.87 Å) or that of previously reported silafluorenes. It should be noted that the inner angles of the benzene rings are also largely deviated from the normal angle (120°). Thus, ∡C2-C1-C4a is 126.00(12)°, while ∡C1-C2-C3 and ∡ C1-C4a-C6a are 116.21(12)° and 115.48(13)°, respectively. As such large deformation has not been observed in previously reported silafluorenes,[7p] the deviation is presumably ascribed to the double bridge of the dimethylsilylene groups at the biphenyl moiety.

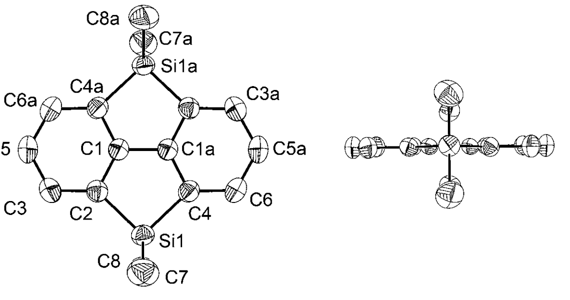


Figure 2. Molecular structure of **1a**; right: side view. For clarity, hydrogen atoms are omitted. Selected bond lengths [Å] and angles [°]: Si1-C7 1.859(2), Si1-C8 1.8591(17), Si1-C2 1.8820(15), Si1-C4 1.8881(15), C1-C2 1.3956(18), C1-C4a 1.3957(18), C1-C1a 1.462(2), C4-C1a 1.3957(18); C7-Si1-C8 110.94(10), C7-Si1-C2 112.29(8), C8-Si1-C2 113.75(8), C7-Si1-C4 112.74(8), C8-Si1-C4 113.30(8), C2-Si1-C4 92.76(6), C2-C1-C4a 126.00(12), C2-C1-C1a 117.16(14), C4a-C1-C1a 116.85(14), C1-C2-C3 116.21(12), C1-C2-Si1 106.59(9), C3-C2-Si1 137.19(11), C6-C4-C1a 115.48(13), C6-C4-Si1 137.88(11), C1a-C4-Si1 106.58(9).

Photophysical properties of **1a**, **1b**, **2a**, and **2b** are summarized in Table 1, along with those of **5a** and **5b** for comparison. UV spectra measured in cyclohexane are shown in Figure 3. For **1a**, **2a**, and **5a**, as well as **1b**, **2b**, and **5b**, respectively, the absorption spectra are similar in shape while the dimethylsilylene and tetramethyldisilylene bridges were found to induce a red shift of the spectra, indicating that the silicon atom introduced at the 4,5-positions of 9-silafluorenes could influence the electronic structures and extend the conjugation system owing to σ–π (σ*–π*) conjugation (for molecular-orbital calculations, see below).

Table 1. Photophysical properties of **1a**, **1b**, **2a**, **2b**, **5a**, and **5b** in cyclohexane.[a]

Compd	Absorption		Emission	
	λ_{max} [nm]	ε [$M^{-1}cm^{-1}$]	λ_{max} [nm][b]	Φ_F[c]
1a	207	43570	361	0.08
	285	12070		
2a	223	46670	450	0.05
	289	10680		
5a	210	39680	338	0.16
	277	12940		
1b	230	48880	397	0.26
	324	38860		
2b	233	45980	418	0.33
	327	31550		
5b	221	50660	379	0.72
	316	43400		

[a] Measured at 1×10^{-5} M in cyclohexane. [b] Irradiation was effected with UV light ($\lambda=265$ nm). [c] Calculated using terphenyl ($\Phi_F=0.87$) as a standard.

Normalized fluorescence spectra of **1a**, **1b**, **2a**, **2b**, **5a**, and **5b**, measured in cyclohexane upon excitation at 265 nm, are shown in Figure 4. Emission maxima are red shifted in the order of $\mathbf{5}<\mathbf{1}<\mathbf{2}$, which corresponds to a bathochromic shift of the absorption spectra shown in Figure 3. Noteworthy is that disilylene-bridged silafluorenes **2a** and **2b** exhibit extremely large Stokes shifts (Table 1), which suggests significant structural differences between the ground and excited states. Considering that blue emission is achieved with oligomers/polymers when fluorenes and silafluorenes are employed as the components,[7,16] it is remarkable that **2a** itself emits blue light ($\lambda_{max}=450$ nm) as a single component (Figure 5), although the fluorescent quantum yields are low.[17] Changing the solvent from cyclohexane to chloroform or acetonitrile resulted in a bathochromic shift of the

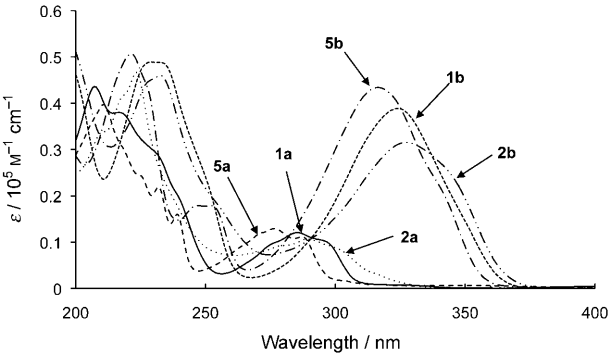


Figure 3. UV spectra of **1a**, **1b**, **2a**, **2b**, **5a**, and **5b**.

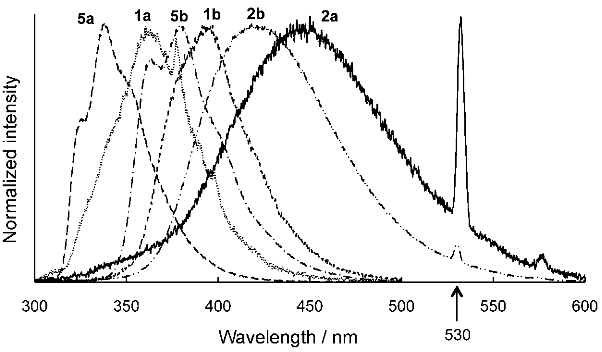


Figure 4. Normalized fluorescence spectra of **1a**, **1b**, **2a**, **2b**, **5a**, and **5b** in cyclohexane. Signals at 530 nm were harmonic overtones of the excitation light (265 nm).

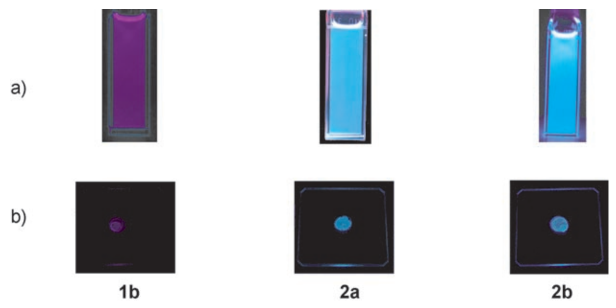


Figure 5. Photographs of **1b**, **2a**, and **2b** under UV light ($\lambda = 254$ nm): a) 1×10^{-5} M in cyclohexane; b) thin film spin coated on a quartz plate.

emission maximum of **2a** (465 nm in each case), suggesting solvent stabilization of the charge-transfer excited states.

Solid silafluorenes **1**, **2**, and **5** also emitted fluorescence upon irradiation of UV light. Fluorescence spectra of the thin films prepared by spin coating of their dichloromethane solutions on a quartz plate are shown in Figure 6, and their emission maxima and quantum yields are listed in Table 2. The emission maxima are almost identical or slightly red shifted to those measured in cyclohexane solution, suggesting that intermolecular interaction of these compounds in the solid state is weak.

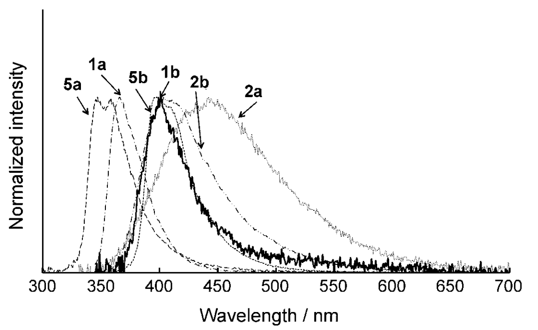


Figure 6. Normalized fluorescence spectra of **1a**, **1b**, **2a**, **2b**, **5a**, and **5b**.

Table 2. Fluorescence properties of **1a**, **1b**, **2a**, **2b**, **5a**, and **5b** in a spin-coated thin film.

Compd	λ_{ex} [nm][a]	λ_{em} [nm][b]	Φ_F[c]
1a	300	361	0.11
2a	325	450	0.12
5a	300	338	0.16
1b	325	397	0.17
2b	290	418	0.46
5b	325	379	0.65

[a] Excitation wavelength. [b] Wavelength of emission maxima. [c] Absolute quantum yield determined by a calibrated integrating sphere system.

Molecular-orbital calculations of **1a**, **1b**, **2a**, **2b**, **5a**, and **5b** were carried out by DFT methods at the B3LYP/6-31G*//B3LYP/6-31G* level. The optimized structure of **1a** is the same as observed in the X-ray analysis; the biphenyl moiety is completely flat and the inner angles wedged between the silicon-substituted aromatic carbon atoms in the benzene rings are greatly expanded (125.5°). On the other hand, as shown in Figure 6, the biphenyl moiety of **2a** is slightly twisted with a dihedral angle C3-C4-C6-C7 of 10.7°, while the inner C3-C4-C5 angle is 118.966°, which is comparable to the standard angle (120°) of a benzene ring. The Si1−Si2 bond length (2.318 Å) in **2a** is shorter than the normal value (2.35 Å). Noteworthy is that the methyl groups (C1 and C2) on Si1 and Si2 are oriented almost antiperiplanar to each other and perpendicular to the silafluorene plane (Figure 7, side view), which looks ideal for σ*–π*

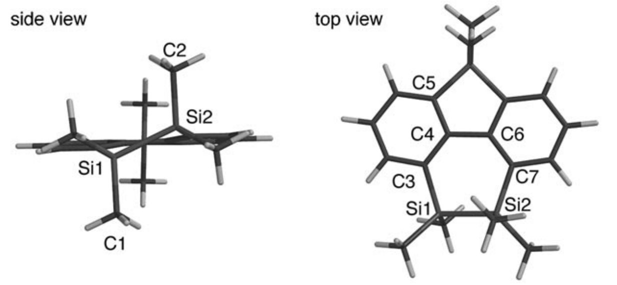


Figure 7. Optimized structure of **2a** by DFT calculations. Selected bond lengths [Å] and angles [°]: Si1-Si2 2.318, Si1-C1 1.902, Si2-C2 1.903, Si1-C3 1.900, Si2-C7 1.899, C3-C4 1.421, C4-C5 1.425, C4-C6 1.518, C6-C7 1.421; C3-Si1-Si2 101.477, C3-Si1-C1 108.960, C7-Si2-C2 108.978, Si1-Si2-C7 101.522, Si1-C3-C4125.562, C3-C4-C5 118.966, C3-C4-C6 127.333, C5-C4-C6 113.678.

conjugation. Probably owing to such arrangements of the methyl groups, the silicon atoms are largely deformed from a normal tetrahedral shape; for example, the C3-Si1-Si2 bond angle is narrowed to 101.5°. Calculated orbital energies are summarized in Table 3. Compared with **5a**, the additional silylene bridge raised both the HOMO and LUMO levels of **1a**. Unexpected elevation of the LUMO level may be ascribed to the deformation of the benzene rings. On the other hand, incorporation of the disilylene bridge into **5a** elevated the energy level of the HOMO located on the biphenyl system and the Si–Si σ bond, and expectedly lowered the LUMO level that was delocalized on the biphenyl system and the silicon atoms but not extended to the Si–Si σ bond (Figure 8). The decrease of the HOMO–LUMO gaps in the order of **5a**>**1a**>**2a**>**5b**>**1b**>**2b** is consistent with a bathochromic shift of the absorption edges shown in Figure 3. Meanwhile, time-dependent DFT (TDDFT) calculations of **2a** indicate that the first transition consists of a HOMO–LUMO transition as a major contribution. Hence, the large Stokes shift and the solvent effect on emission maximum of **2a** may be ascribed to intramolecular charge transfer from the disilylene to the silylene moieties. In addition, we carried out DFT calculations on the triplet state of **2a** as a model of the excited state of **2a**. The triplet-state energy was found to be 0.09676 hartree (471 nm), which does not contradict the fluorescence emission maximum (450 nm).

Table 3. HOMO and LUMO energies of **1a**, **1b**, **2a**, **2b**, **5a**, and **5b**.[a]

Compd	LUMO [eV]	HOMO [eV]	HOMO–LUMO gap [eV]
1a	−0.80	−5.62	4.82
2a	−0.98	−5.68	4.70
5a	−0.92	−5.78	4.86
1b	−1.19	−5.34	4.14
2b	−1.33	−5.43	4.10
5b	−1.30	−5.45	4.15

[a] Calculated at the B3LYP/6-31G*//B3LYP/6-31G* level.

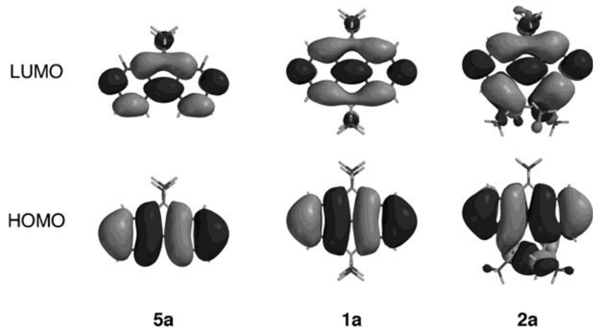


Figure 8. Molecular-orbital drawings of the HOMOs and LUMOs of **1a**, **2a**, and **5a** calculated by DFT at the B3LYP/6-31G*//B3LYP/6-31G* level.

Conclusions

In summary, we have demonstrated that a silicon bridge at the 4,5-positions of silafluorenes with a silylene or disilylene moiety is effective for extension of the conjugated system with the aid of σ*–π* conjugation and some degree of steric constraint. In particular, the disilylene-bridged silafluorenes exhibit large Stokes shifts to result in blue emission as a single component in both solution and thin film. These results imply that silicon-bridged silafluorenes can serve as a new class of conjugated modules. Furthermore, this research confirms the validity of molecular design involving a double silicon bridge[18] between conventional π-conjugated modules as a method for tuning electronic structures of the parent systems.

Experimental Section

General

Melting points were determined using a YANAKO MP-500D and not corrected. ^{1}H NMR spectra were measured on JEOL EX270 (270 MHz), JMN ECP-500 (500 MHz), Varian Mercury 200 (200 MHz), 300 (300 MHz), and 400 (400 MHz) spectrometers. The chemical shifts of ^{1}H NMR are expressed in parts per million downfield referenced to internal tetramethylsilane ($\delta = 0$ ppm), chloroform ($\delta = 7.26$ ppm), or benzene ($\delta = 7.16$ ppm). Splitting patterns are indicated as s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. ^{13}C NMR spectra were measured on JEOL EX270 (68 MHz), JMN ECP-500 (125 MHz), Varian Mercury 200 (50 MHz), 300 (75 MHz), and 400 (100 MHz) spectrometers with tetramethylsilane as an internal standard ($\delta = 0$ ppm), [D]chloroform ($\delta = 77.0$ ppm), or [D$_6$]benzene ($\delta = 128.4$ ppm). ^{29}Si NMR spectra were measured on a JEOL EX270 (54 MHz), JMN ECP-500 (99 MHz), and Varian Mercury 400 (80 MHz) spectrometers with tetramethylsilane as an internal standard ($\delta = 0$ ppm). UV spectra were recorded with a Shimadzu UV-2100PC spectrometer. Spin-coated thin films of silafluorenes on a quartz plate were prepared from dichloromethane solutions with a MIKASA SPINCOATER MS-A100. Fluorescence spectra of cyclohexane solutions were measured with a Shimadzu RF-5300PC spectrometer. Fluorescence spectra of thin films were measured with a Hamamatsu Photonics C9920–02, and absolute quantum yields were determined by a calibrated integrating sphere system. IR spectra were recorded on a Shimadzu FTIR-8400 spectrometer. GC–MS analyses were performed with a JEOL JMS-700 by electron ionization at 70 eV. FAB-MS analyses were performed with a JEOL JMS-HX110 A spectrometer with a 3-nitrobenzyl alcohol or thioglycerol matrix. Elemental analyses were carried out with a YANAKO MT2 CHN CORDER machine at the Elemental Analysis Center of Kyoto University. TLC analyses were performed with Merck Kieselgel 60 F$_{254}$ and column chromatography was carried out using Wakogel C-200 or Merck Kieselgel 60 (230–400 mesh). Preparative recycling gel permeation chromatography (GPC) was performed with a JAI LC-908 chromatograph equipped with JAIGEL-1H and -2H columns (chloroform as an eluent). Preparative recycling high-performance liquid chromatography (HPLC) was performed with a JAI LC-908 chromatograph equipped with 5SL-II columns (hexane and ethyl acetate as an eluent). All manipulations of oxygen- and moisture-sensitive materials were carried out under argon.

Synthesis

4: To a solution of 2,2′,6,6′-tetrabromobiphenyl (**3**, 0.82 g, 1.75 mmol) in THF (25 mL) was added BuLi (1.60 M in hexane, 2.4 mL, 3.8 mmol) at −78 °C over a period of 15 min. The reaction mixture was stirred for 4 h before addition of dichlorodimethylsilane (0.46 mL, 3.8 mmol) at −78 °C over a period of 10 min. The reaction mixture was allowed to warm to room temperature. To the solution was added sat. NaHCO$_3$ aq. solution

(20 mL). The aqueous layer was extracted with dichloromethane (20 mL × 2). The combined organic layer was dried over anhydrous magnesium sulfate and concentrated in vacuo. The crude product was purified by column chromatography on silica gel (hexane/diethyl ether 10:1) to give **4** (0.46 g, 72 % yield) as a colorless solid. M.p. 107.8–108.8 °C. R_f 0.58 (hexane/diethyl ether 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.39$ (s, 6H), 7.18 (dd, $J = 7.9$, 6.9 Hz, 2H), 7.55 (dd, $J = 6.9$, 1.2 Hz, 2H), 7.65 ppm (dd, $J = 7.9$, 1.2 Hz, 2H); ^{13}C NMR (68 MHz, $CDCl_3$): $\delta = -2.5$, 120.3, 128.8, 130.6, 135.9, 144.6, 147.8 ppm; ^{29}Si NMR (54 MHz, $CDCl_3$): $\delta = -19.6$ ppm; IR (KBr): $\tilde{\nu} = 3036$, 2957, 2899, 1437, 1379, 1244, 1213, 1076, 991, 851, 806, 768, 741, 714, 658, 642 cm^{-1}; EI-MS (70 eV): m/z: 370 ($[M]^+ + 4$, 39), 368 ($[M]^+ + 2$, 75), 366 ($[M]^+$, 38), 355 (52), 353 (100), 351 (51), 289 (29), 287 (28), 274 (18), 272 (19), 207 (18), 193 (14), 191 (14), 165 (25). HRMS (EI) calcd for $C_{14}H_{12}Br_2Si$: $[M]^+$, 365.9075; found: 365.9085. Elemental analysis (%) calcd for $C_{14}H_{12}Br_2Si$: C 45.68, H 3.29; found: C 45.44, H 3.35.

6: To a solution of **3** (0.152 g, 0.32 mmol) in THF (4.6 mL) was added BuLi (1.55 M in hexane, 1.10 mL, 1.70 mmol) at −78 °C over a period of 20 min. The reaction mixture was stirred for 1.5 h before addition of chlorotrimethylsilane (0.30 mL, 2.4 mmol) at −78 °C over a period of 15 min. The resulting mixture was allowed to warm to room temperature and then quenched with sat. $NaHCO_3$ aq. solution (10 mL). The aqueous layer was extracted with diethyl ether (15 mL × 2). The combined organic layer was dried over anhydrous magnesium sulfate and concentrated in vacuo. The crude product was purified by column chromatography on silica gel (hexane/diethyl ether 10:1), giving rise to **6** (0.138 g, 93 % yield) as colorless prisms. M.p. 79.4–80.4 °C. R_f 0.79 (hexane/ethyl acetate 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = -0.03$ (s, 18H), 7.25 (dd, $J = 7.9$, 7.5 Hz, 2H), 7.57 (dd, $J = 7.5$, 1.2 Hz, 2H), 7.64 ppm (dd, $J = 7.9$, 1.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 0.4$, 125.7, 128.6, 132.7, 133.6, 142.8, 147.2 ppm; ^{29}Si NMR (80 MHz, $CDCl_3$): $\delta = -2.5$ ppm; IR (KBr): $\tilde{\nu} =$ 3047, 2957, 2897, 1558, 1541, 1387, 1263, 1250, 1144, 1113, 1080, 1067, 851, 841, 777, 766, 748 cm^{-1}; EI-MS (70 eV): m/z: 458 ($[M]^+ + 4$, 4), 456 ($[M]^+ + 2$, 6), 454 ($[M]^+$, 3), 443 (31), 441 (55), 439 (25), 355 (7), 353 (12), 351 (7), 289 (100), 287 (94). HRMS (EI) calcd for $C_{18}H_{24}Br_2Si_2$: $[M]^+$, 453.9783; found: 453.9771. Elemental analysis (%) calcd for $C_{18}H_{24}Br_2Si_2$: C 47.37, H 5.30; found: C 47.34, H 5.26.

1a: A solution of **6** (61 mg, 0.13 mmol), magnesium turnings (14 mg, 0.57 mmol), and copper cyanide (2.4 mg, 0.03 mmol) in THF (1.4 mL) was vigorously stirred at 85 °C for 24 h before quenching with sat. $NaHCO_3$ aq. solution (10 mL). The aqueous layer was extracted with dichloromethane (50 mL × 1 and 20 mL × 2). The combined organic layer was dried over anhydrous magnesium sulfate and concentrated in vacuo. The crude product was subjected to column chromatography on silica gel (hexane/dichloromethane 10:3) and subsequently purified by preparative HPLC (hexane) to give **1a** (8.0 mg, 22 % yield) as colorless prisms and 9,9-dimethyl-9*H*-dibenzosilole (**5a**; 8.7 mg, 22 % yield) as a colorless oil. M.p. 195 °C. R_f 0.58 (hexane/dichloromethane 10:3). ^{1}H NMR (270 MHz, $CDCl_3$): $\delta = 0.48$ (s, 12H), 7.22 (t, $J = 7.2$ Hz, 2H), 7.58 ppm (d, $J = 7.2$ Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = -2.7$, 127.5, 133.7, 133.8, 160.0 ppm; ^{29}Si NMR (80 MHz, $CDCl_3$): $\delta = 7.3$ ppm; IR (KBr): $\tilde{\nu} = 3044$, 3030, 2966, 2899, 1364, 1246, 853, 802, 766, 652, 428 cm^{-1}; EI-MS (70 eV): m/z: 269 ($[M]^+ + 3$, 3), 268 ($[M]^+ + 2$, 14), 267 ($[M]^+ + 1$, 40), 266 ($[M]^+$, 92), 251 (100), 235 (22), 221 (34), 205 (12), 191 (10), 125 (12), 118 (37). HRMS (EI) calcd for $C_{16}H_{18}Si_2$: $[M]^+$, 266.0947; found: 266.0960. Elemental analysis (%) calcd for $C_{16}H_{18}Si_2$: C 72.11, H 6.81; found: C 71.84, H 6.76.

One-pot synthesis of **1a**: To a mixture of **3** (0.15 g, 0.31 mmol) and dichlorodimethylsilane (0.55 mL, 4.5 mmol) was added a pentane solution of *t*BuLi (1.46 M, 2.7 mL, 3.9 mmol) at −78 °C over a period of 10 min. The resulting solution was stirred at −78 °C for 5 min and then allowed to warm to room temperature before quenching with water (10 mL). The reaction mixture was diluted with dichloromethane (30 mL), and the aqueous layer was extracted with dichloromethane (15 mL × 2). The combined organic layer was dried over anhydrous magnesium sulfate and concentrated in vacuo. The crude product was purified by column chromatography on silica gel (hexane/dichloromethane 10:3) to afford a mixture of **1a** and **5a**. Preparative GPC of the mixture gave **1a** (11 mg, 13 % yield) as colorless prisms.

2,6-Dibromo-4-chloro-1-iodobenzene: To a solution of 2,6-dibromo-4-chloroaniline (100 g, 0.36 mol) in conc. HCl (190 mL) was added a solution of sodium nitrite (27 g, 0.39 mol) in water (120 mL) dropwise at 0 °C over a period of 75 min. The solution was stirred at 0 °C for 2 h, and then was poured into a solution of potassium iodide (510 g, 3.0 mol) in water (680 mL) at 0 °C. The resulting solution was stirred vigorously at room temperature overnight. Dichloromethane (750 mL) and sat. Na_2CO_3 aq. solution (200 mL) were successively added to the flask at room temperature. The aqueous layer was extracted with dichloromethane (500 mL × 2). The combined organic layer was dried over anhydrous magnesium sulfate and concentrated in vacuo. The crude product was purified by recrystallization from benzene/ethanol, giving rise to 2,6-dibromo-4-chloro-1-iodobenzene (120 g, 82 % yield) as colorless needles. M.p. 109.6–110.2 °C (benzene/ethanol 1:1). R_f 0.43 (hexane/diethyl ether 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.58$ ppm (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 107.2$, 130.8, 131.4, 135.3 ppm; IR (KBr): $\tilde{\nu} = 3090$, 3053, 2937, 2924, 2891, 1547, 1533, 1522, 1383, 1369, 1352, 1236, 1190, 1167, 1128, 1117, 1076, 1001, 860, 795, 737, 671, 540, 498 cm^{-1}; EI-MS (70 eV): m/z: 400 ($[M]^+ + 6$, 14), 398 ($[M]^+ + 4$, 71), 396 ($[M]^+ + 2$, 100), 394 ($[M]^+$, 44), 269 (28), 190 (19), 109 (17), 74 (26). HRMS (EI) calcd for $C_6H_2Br_2ClI$: $[M]^+$, 393.7256; found: 393.7249. Elemental analysis (%) calcd for $C_6H_2Br_2ClI$: C 18.19, H 0.51; found: C 18.25, H 0.65.

7: To a suspension of 2,6-dibromo-4-chloro-1-iodobenzene (51 g, 0.13 mol) and anhydrous copper(II) chloride (105 g, 0.78 mol) in diethyl ether (400 mL) was added a hexane solution of BuLi (1.60 M, 86 mL, 0.14 mol) at −78 °C over a period of 2.5 h. The resulting mixture was allowed to warm to room temperature overnight before quenching with water (200 mL) at 0 °C. The aqueous layer was extracted with dichloromethane (400 mL × 1 and 200 mL × 2). The combined organic layer was dried over anhydrous magnesium sulfate and concentrated in vacuo. The crude product was purified by column chromatography on silica gel (hexane), giving rise to **7** (11.3 g, 33 % yield) as a colorless solid. M.p. 128.5–129.5 °C. R_f 0.55 (hexane). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.68$ ppm (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 124.5$, 131.8, 135.8, 139.8 ppm; IR (KBr): $\tilde{\nu} = 3071$, 2966, 2926, 2853, 1566, 1533, 1406, 1375, 1354, 1182, 1130, 1117, 1105, 858, 783, 746, 727, 584 cm^{-1}; EI-MS (70 eV): m/z: 544 ($[M]^+ + 10$, 12), 542 ($[M]^+ + 8$, 47), 540 ($[M]^+ + 6$, 93), 538 ($[M]^+ + 4$, 100), 536 ($[M]^+ + 2$, 54), 534 ($[M]^+$, 12), 459 (22), 378 (46), 264 (15), 229 (10), 218 (26), 189 (14), 183 (12). HRMS (EI) calcd for $C_{12}H_4Br_4Cl_2$: $[M]^+$, 533.6423; found: 533.6431. Elemental analysis (%) calcd for $C_{12}H_4Br_4Cl_2$: C 26.76, H 0.75; found: C 26.92, H 0.88.

Preparation of **1c** and **5c**: To a mixture of **7** (5.1 g, 9.4 mmol) and dichlorodimethylsilane (11.0 mL, 91 mmol) was added a pentane solution of *t*BuLi (1.59 M, 60 mL, 95 mmol) at −78 °C over a period of 15 min. The resulting suspension was stirred at −78 °C for 10 min and was allowed to warm to room temperature overnight before quenching with sat. $NaHCO_3$ aq. solution (150 mL). The mixture was diluted with dichloromethane (300 mL), and the aqueous layer was extracted with dichloromethane (200 mL × 1 and 100 mL × 2). The combined organic layer was dried over anhydrous magnesium sulfate and concentrated in vacuo. The crude product was purified by column chromatography on silica gel (hexane) to afford **1c** (0.47 g, 15 % yield) and **5c** (0.90 g, 34 % yield) as colorless solids, respectively. **1c**: M.p. 203.3–204.3 °C. R_f 0.53 (hexane). ^{1}H NMR (270 MHz, $CDCl_3$): $\delta = 0.49$ (s, 12H), 7.52 (s, 4H); ^{13}C NMR (68 MHz, $CDCl_3$): $\delta = -2.8$, 133.8, 134.0, 135.6, 156.7; ^{29}Si NMR (54 MHz, $CDCl_3$): $\delta = 9.1$; IR (KBr): $\tilde{\nu} = 3042$, 2966, 2926, 2853, 1362, 1248, 1119, 1078, 854, 785, 758, 660, 453 cm^{-1}; EI-MS (70 eV): m/z: 339 ($[M]^+ + 5$, 4), 338 ($[M]^+ + 4$, 15), 337 ($[M]^+ + 3$, 18), 336 ($[M]^+ + 2$, 66), 335 ($[M]^+ + 1$, 25), 334 ($[M]^+$, 90), 319 (100), 289 (10), 152 (18). HRMS (EI) calcd for $C_{16}H_{16}Cl_2Si_2$: $[M]^+$, 334.0168; found: 334.0166. Elemental analysis (%) calcd for $C_{16}H_{16}Cl_2Si_2$: C 57.30, H 4.81; found: C 57.00, H 4.78. **5c**: M.p. 145.0–145.2 °C. R_f 0.44 (hexane). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta =$ 0.43 (s, 6H), 7.39 (dd, $J = 8.3$, 2.2 Hz, 2H), 7.56 (d, $J = 2.2$ Hz, 2H), 7.68 ppm (d, $J = 8.3$ Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = -3.5$, 122.1, 130.3, 132.6, 133.7, 141.0, 145.0 ppm; ^{29}Si NMR (80 MHz, $CDCl_3$): $\delta = 1.7$ ppm; IR (KBr): $\tilde{\nu} = 3049$, 2984, 1445, 1391, 1381, 1240, 1140, 1097, 1088, 853, 824, 785, 754, 662 cm^{-1}; EI-MS (70 eV): m/z: 283 ($[M]^+ + 5$, 2), 282 ($[M]^+ + 4$, 9), 281 ($[M]^+ + 3$, 9), 280 ($[M]^+ + 2$, 39), 279 ($[M]^+ + 1$, 12), 278 ($[M]^+$, 57), 263 (100), 199 (14), 165 (14). HRMS (EI) calcd for

$C_{14}H_{12}Cl_2Si$: $[M]^+$, 278.0085; found: 278.0080. Elemental analysis (%) calcd for $C_{14}H_{12}Cl_2Si$: C 60.22, H 4.33; found: C 59.97, H 4.35.

1b: A Schlenk tube was charged with [Ni(acac)$_2$] (11 mg, 4.4 μmol), 1,3-bis(2,6-di-isopropylphenyl)imidazolium chloride (22 mg, 0.052 mmol), **1c** (25 mg, 0.074 mmol), and THF (1.5 mL) under an argon atmosphere. To the solution was added a THF solution of phenylmagnesium bromide (1.07 M, 0.50 mL, 0.54 mmol) at room temperature. After 7 days, the reaction was quenched with methanol (3 mL). The organic solvent was removed with a rotary evaporator. The residue was diluted with dichloromethane (70 mL) and sat. NaCl aq. solution (25 mL). The aqueous layer was extracted with dichloromethane (30 mL × 2). The combined organic layer was dried over anhydrous magnesium sulfate and concentrated in vacuo. The crude product was purified by column chromatography on silica gel (hexane/ethyl acetate 10:1) to give **1b** (17 mg, 53 % yield) as colorless prisms. M.p. 215.6 °C (sublimation). R_f 0.55 (hexane/ethyl acetate 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.55$ (s, 12 H), 7.34 (tt, $J = 7.5$, 1.4 Hz, 2 H), 7.45 (dd, $J = 7.8$, 7.5 Hz, 4 H), 7.64 (dd, $J = 7.8$, 1.4 Hz, 4 H), 7.82 ppm (s, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = -2.5$, 126.9, 127.3, 128.7, 133.3, 134.3, 140.8, 142.4, 158.9 ppm; ^{29}Si NMR (80 MHz, $CDCl_3$): $\delta = 8.0$ ppm; IR (KBr): $\tilde{\nu} = 3103$, 3082, 3057, 3026, 2957, 2926, 2895, 2851, 1387, 1252, 1061, 1028, 856, 829, 779, 758, 698, 658, 521 cm^{-1}; EI-MS (70 eV): m/z: 421 ($[M]^+ + 3$, 4), 420 ($[M]^+ + 2$, 16), 419 ($[M]^+ + 1$, 43), 418 ($[M]^+$, 100), 403 (64), 209 (10), 194 (16). HRMS (EI) calcd for $C_{28}H_{26}Si_2$: $[M]^+$, 418.1573; found: 418.1569.

5b: A Schlenk tube was charged with [Ni(acac)$_2$] (14 mg, 5.3 μmol), 1,3-bis(2,6-di-isopropylphenyl)imidazolium chloride (24 mg, 0.057 mmol), **5c** (25 mg, 0.089 mmol), and THF (1.5 mL). To the solution was added a THF solution of phenylmagnesium bromide (1.07 M, 0.50 mL, 0.54 mmol) at room temperature. The resulting solution was stirred at room temperature for 9 h before quenching with methanol (3 mL). The organic solvent was removed under reduced pressure. The residue was dissolved in dichloromethane (70 mL) and sat. NaCl aq. solution (25 mL). The aqueous layer was extracted with dichloromethane (30 mL × 2). The combined organic layer was dried over anhydrous magnesium sulfate and concentrated in vacuo. The crude product was purified by column chromatography on silica gel (hexane/ethyl acetate 10:1) to give **5b** (30 mg, 93 % yield) as colorless needles. M.p. 241.8–242.7 °C. R_f 0.77 (hexane/ethyl acetate 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.50$ (s, 6 H), 7.36 (tt, $J = 7.5$, 1.3 Hz, 2 H), 7.47 (dd, $J = 7.9$, 7.5 Hz, 4 H), 7.67 (dd, $J = 7.9$, 1.3 Hz, 4 H), 7.69 (dd, $J = 7.6$, 1.9 Hz, 2 H), 7.87 (d, $J = 1.9$ Hz, 2 H), 7.92 ppm (d, $J = 7.6$ Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = -3.1$, 121.2, 127.0, 127.2, 128.8, 129.2, 131.5, 139.8, 140.1, 141.2, 146.6 ppm; ^{29}Si NMR (80 MHz, $CDCl_3$): $\delta = 0.7$ ppm; IR (KBr): $\tilde{\nu} = 3061$, 3032, 2957, 2918, 2849, 1389, 1248, 1151, 1067, 1022, 905, 851, 835, 826, 781, 760, 694 cm^{-1}; EI-MS (70 eV): m/z: 364 ($[M]^+ + 2$, 10), 363 ($[M]^+ + 1$, 36), 362 ($[M]^+$, 100), 347 (75), 174 (14). HRMS (EI) calcd for $C_{26}H_{22}Si$: $[M]^+$, 362.1491; found: 362.1507.

8: To a solution of **3** (0.20 g, 0.43 mmol) in THF (6.5 mL) was added BuLi (1.60 M in hexane, 0.62 mL, 0.99 mmol) at −78 °C over a period of 5 min. The reaction mixture was stirred at −78 °C for 1 h before the addition of 1,2-dichloro-1,1,2,2-tetramethyldisilane (0.12 mL, 0.64 mmol). The resulting mixture was allowed to warm to room temperature overnight before quenching with sat. $NaHCO_3$ aq. solution (10 mL). The aqueous layer was extracted with ethyl acetate (50 mL × 1 and 30 mL × 2). The combined organic layer was dried over anhydrous magnesium sulfate and concentrated in vacuo. The crude product was purified by column chromatography on silica gel (hexane/ethyl acetate 10:1) to give **8** (0.12 g, 67 % yield) as colorless prisms. M.p. 154.4–154.8 °C. R_f 0.48 (hexane/ethyl acetate 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = -0.22$ (s, 6 H), 0.42 (s, 6 H), 7.20 (dd, $J = 8.0$, 7.3 Hz, 2 H), 7.44 (dd, $J = 7.3$, 1.3 Hz, 2 H), 7.67 (dd, $J = 8.0$, 1.3 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = -5.7$, −5.5, 125.7, 128.7, 132.1, 133.8, 139.2, 145.4 ppm; ^{29}Si NMR (80 MHz, $CDCl_3$): $\delta = -23.1$ ppm; IR (KBr): $\tilde{\nu} = 3047$, 2957, 2895, 1558, 1541, 1383, 1242, 1070, 854, 837, 818, 795, 779, 770, 752, 735, 723, 656, 638 cm^{-1}; EI-MS (70 eV): m/z: 428 ($[M]^+ + 4$, 12), 426 ($[M]^+ + 2$, 22), 424 ($[M]^+$, 11), 413 (4), 411 (8), 409 (4), 347 (60), 345 (56), 331 (26), 329 (24), 265 (100), 237 (59). HRMS (EI) calcd for $C_{16}H_{18}Br_2Si_2$: $[M]^+$, 423.9314; found: 423.9310. Elemental analysis (%) calcd for $C_{16}H_{18}Br_2Si_2$: C 45.08, H 4.26; found: C 45.34, H 4.22.

2a: To a solution of **8** (41 mg, 0.097 mmol) in THF (1.5 mL) was added tBuLi (1.57 M in pentane, 0.25 mL, 0.39 mmol) at −78 °C. The reaction mixture was stirred at −78 °C for 40 min before the addition of dichlorodimethylsilane (20 μL, 0.17 mmol). The resulting mixture was allowed to warm to room temperature overnight before quenching with sat. $NaHCO_3$ aq. solution (10 mL). The aqueous layer was extracted with ethyl acetate (50 mL × 1 and 20 mL × 2). The combined organic layer was dried over anhydrous magnesium sulfate and concentrated in vacuo. The crude product was purified by column chromatography on silica gel (hexane/ethyl acetate 10:1) and subsequently by preparative HPLC (hexane) to give **2a** (25 mg, 78 % yield) as a colorless solid. M.p. 63.9 °C. R_f 0.28 (hexane). ^{1}H NMR (270 MHz, $CDCl_3$): $\delta = 0.36$ (s, 12 H), 0.40 (s, 6 H), 7.24 (dd, $J = 7.2$, 7.1 Hz, 2 H), 7.63 (dd, $J = 7.1$, 1.6 Hz, 2 H), 7.64 ppm (dd, $J = 7.2$, 1.6 Hz, 2 H); ^{13}C NMR (68 MHz, $CDCl_3$): $\delta = -3.2$, −2.8, 125.9, 133.4, 134.6, 136.4, 139.9, 154.8 ppm; ^{29}Si NMR (54 MHz, $CDCl_3$): $\delta = -32.9$, −2.5 ppm; IR (KBr): $\tilde{\nu} = 3038$, 3017, 2953, 2893, 1362, 1246, 1138, 856, 833, 818, 795, 762, 658, 642 cm^{-1}; EI-MS (70 eV): m/z: 327 ($[M]^+ + 3$, 2), 326 ($[M]^+ + 2$, 6), 325 ($[M]^+ + 1$, 14), 324 ($[M]^+$, 42), 309 (23), 251 (100), 236 (24), 221 (13), 73 (13). HRMS (EI) calcd for $C_{18}H_{24}Si_3$: $[M]^+$, 324.1186; found: 324.1194. Elemental analysis (%) calcd for $C_{18}H_{24}Si_3$: C 66.59, H 7.45; found: C 66.59, H 7.41.

One-pot synthesis of **2a**: To a mixture of **3** (0.81 g, 1.72 mmol) and 1,2-dichloro-1,1,2,2-tetramethyldisilane (1.70 mL, 9.1 mmol) was added a pentane solution of tBuLi (1.47 M, 10.0 mL, 14.7 mmol) at −78 °C over a period of 45 min. The mixture was stirred for 25 min at −78 °C and then at room temperature overnight before quenching with sat. $NaHCO_3$ aq. solution (30 mL). Dichloromethane (40 mL) was added, and the separated aq. phase was extracted with dichloromethane (20 mL × 2). The combined organic layers were dried over anhydrous magnesium sulfate and concentrated in vacuo. The crude products were separated by column chromatography on silica gel (hexane), giving rise to **2a** (0.24 g, 43 % yield) as a colorless solid and **9** (66 mg, 10 % yield) as colorless prisms. **9**: M.p. 147.2–148.2 °C. R_f 0.56 (hexane). ^{1}H NMR (270 MHz, $CDCl_3$): $\delta = -0.20$ (s, 12 H), 0.40 (s, 12 H), 7.17 (t, $J = 7.3$ Hz, 2 H), 7.46 ppm (d, $J = 7.3$ Hz, 4 H); ^{13}C NMR (68 MHz, $CDCl_3$): $\delta = -5.5$, −5.0, 125.6, 134.7, 136.2, 152.0 ppm; ^{29}Si NMR (54 MHz, $CDCl_3$): $\delta = -25.3$ ppm; IR (KBr): $\tilde{\nu} = 3036$, 2961, 2947, 2893, 1358, 1246, 858, 839, 795, 783, 764, 642 cm^{-1}; EI-MS (70 eV): m/z: 385 ($[M]^+ + 3$, 3), 384 ($[M]^+ + 2$, 10), 383 ($[M]^+ + 1$, 19), 382 ($[M]^+$, 43), 324 (22), 309 (43), 251 (100), 236 (16), 221 (20), 116 (83), 73 (14). HRMS (GC–MS) calcd for $C_{20}H_{30}Si_4$: $[M]^+$, 382.1425; found: 382.1432. Elemental analysis (%) calcd for $C_{20}H_{30}Si_4$: C 62.75, H 7.90; found: C 62.36, H 7.89.

2c: To a mixture of **7** (0.33 g, 0.61 mmol) and 1,2-dichloro-1,1,2,2-tetramethyldisilane (1.00 mL, 5.4 mmol) was added a pentane solution of tBuLi (1.46 M, 4.6 mL, 6.7 mmol) at −78 °C over a period of 12 min. The resulting suspension was stirred at −78 °C for 23 min and then at room temperature for 26 h before quenching with sat. $NaHCO_3$ aq. solution (20 mL). The resulting solution was diluted with dichloromethane (50 mL). The separated aqueous layer was extracted with dichloromethane (30 mL × 2). The combined organic layer was dried over anhydrous magnesium sulfate and concentrated in vacuo. The crude product was purified by column chromatography on silica gel (hexane) to give **2c** (86 mg, 36 % yield) as a colorless solid. M.p. 139.9–140.9 °C. R_f 0.59 (hexane). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.35$ (s, 12 H), 0.40 (s, 6 H), 7.52 (s, 2 H), 7.52 ppm (s, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = -3.5$, −3.3, 133.0, 133.2, 135.8, 137.3, 142.7, 151.9 ppm; ^{29}Si NMR (54 MHz, $CDCl_3$): $\delta = -31.3$, −1.5 ppm; IR (KBr): $\tilde{\nu} = 2955$, 2897, 1358, 1250, 1130, 860, 841, 779, 766, 662 cm^{-1}; EI-MS (70 eV): m/z: 397 ($[M]^+ + 5$, 4), 395 ($[M]^+ + 3$, 12),394 ($[M]^+ + 2$, 36), 392 ($[M]^+$, 46), 377 (100), 319 (23), 284 (18). HRMS (EI) calcd for $C_{18}H_{22}Cl_2Si_3$: $[M]^+$, 392.0406; found: 392.0406. Elemental analysis (%) calcd for $C_{18}H_{22}Cl_2Si_3$: C 54.94, H 5.63; found: C 55.04, H 5.60.

2b: A Schlenk tube was charged with [Ni(acac)$_2$] (23 mg, 9.0 μmol), 1,3-bis(2,6-di-isopropylphenyl)imidazolium chloride (35 mg, 0.083 mmol), **2c** (51 mg, 0.13 mmol), and THF (2.2 mL). To the solution was added a THF solution of phenylmagnesium bromide (1.07 M, 0.80 mL, 0.86 mmol) at room temperature. The reaction mixture was stirred at room temperature for 46 h before quenching with methanol (5 mL). The organic solvent was removed under reduced pressure. The residue was dissolved with dichloromethane (70 mL) and sat. NaCl aq. solution (25 mL). The aqueous layer was extracted with dichloromethane (30 mL × 2). The combined organic layer was dried over anhydrous magnesium sulfate and concentrated in vacuo. The crude product was purified by column chromatography on silica gel (hexane/ethyl acetate 20:1) to give **2b** (38 mg, 61 % yield) as colorless plates. M.p. 180.5 °C. R_f 0.59 (hexane/ethyl acetate 20:1). ^{1}H NMR (400 MHz, CDCl$_3$): $\delta = 0.42$ (s, 12 H), 0.47 (s, 6 H), 7.38 (tt, $J = 7.5$, 1.5 Hz, 2 H), 7.49 (dd, $J = 8.0$, 7.5 Hz, 4 H), 7.68 (dd, $J = 8.0$, 1.5 Hz, 4 H), 7.86 (s, 2 H), 7.86 ppm (s, 2 H); ^{13}C NMR (100 MHz, CDCl$_3$): $\delta = -3.2$, -2.9, 127.1, 127.2, 128.8, 132.3, 135.1, 135.4, 138.2, 140.9, 141.2, 153.7; ^{29}Si NMR (80 MHz, CDCl$_3$): $\delta = -32.4$, -2.2 ppm; IR (KBr): $\tilde{\nu} = 2953$, 2916, 2849, 1246, 860, 849, 779, 760, 698 cm^{-1}; EI-MS (70 eV): m/z: 479 ($[M]^+ + 3$, 6), 478 ($[M]^+ + 2$, 20), 476 ($[M]^+$, 88), 461 (18), 418 (31), 403 (100), 388 (12), 373 (12). HRMS (EI) calcd for C$_{30}$H$_{32}$Si$_3$: $[M]^+$, 476.1812; found: 476.1808.

9,9-Dimethyl-9*H*-dibenzosilole (**5a**): Compound **5a** was prepared according to the reported procedure (reference [10a]).

Calculations

Molecular structures were optimized by DFT methods at the B3LYP/6-31G(d) level using the Gaussian 98 package. Energy levels of molecular orbitals were calculated by the gauge-including atomic orbital (GIAO) method at the B3LYP/6-31G(d)//B3LYP/6-31G(d) level. Absolute energies (in hartree) of calculated compounds are as follows: −1199.613183 (**1a**), −1568.961063 (**2a**), −831.4637551 (**5a**), −1661.727562 (**1b**), −2031.076499 (**2b**), and −1293.579145 (**5b**). Results on TDDFT calculations of **2a** are as follows: excitation energies (4.1355 eV, 299.80 nm) and oscillator strengths (0.0890). Transitions (coefficients in the CI expansion) of excited state 1: 86 to 88 (0.22316), 86 to 89 (0.14298), 87 to 88 (0.57336), 87 to 89 (−0.25130).

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[14] **1a**: $C_{16}H_{18}Si_2$, crystal size $0.5\times0.5\times0.5$ mm^3, space group *Pbca* (orthorhombic), $a=7.717(3)$, $b=11.581(5)$, $c=17.359(7)$ Å, $V=1551.4(11)$ Å^3, $Z=4$, $\rho_{\text{calcd}}=1.141$ g cm^{-3}, $\mu(\text{Mo}_{K\alpha})=0.210$ mm^{-1}. Data were measured on a Bruker SMART APEX diffractometer ($\text{Mo}_{K\alpha}$ radiation, $\lambda=0.71073$ Å) at 300 K, and the structure was solved by direct methods. Of 8501 reflections collected, 1670 were unique reflections ($R_{\text{int}}=0.0267$); data/restraints/parameters 1670/0/84; final R indices $[I>2\sigma(I)]$: $R_1=0.0405$, $wR_2=0.1173$; R indices (all data): $R_1=0.0432$, $wR_2=0.1260$. CCDC-650887 contains the supplementary crystallographic data for **1a**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data request/cif.

[15] No single crystals of **2a** suitable for X-ray analysis were obtained, although we attempted the recrystallization under various conditions.

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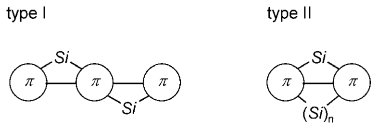
[17] Since the excitation spectra of **2a** is coincident with the absorption spectra, a possibility that the emission is originated from an impurity can be ruled out.

[18] Bis-silicon-bridged stilbene derivatives developed by Yamaguchi and co-workers (ref. [6]) are illustrated as type I, while the double-silicon-bridge motif presented herein is exemplified as type II.



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