

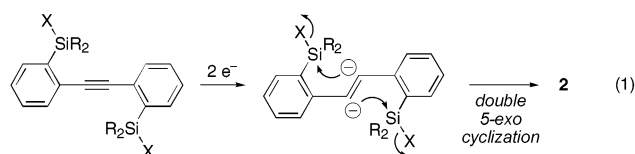
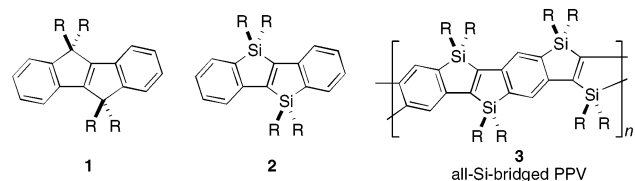
Bis-Silicon-Bridged Stilbene Homologues Synthesized by New Intramolecular Reductive Double Cyclization

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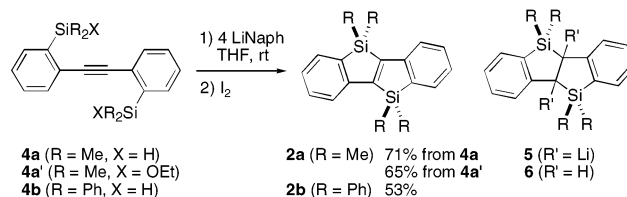
Ladder-type π -conjugated molecules^{1,2} are promising materials for organic-based devices, including light-emitting diodes,^{3,4} field effect transistors,^{5,6} and optically pumped solid-state lasers.⁷ In these molecules, flattening the π -conjugated framework by annelation eliminates the conformational disorder and effectively enhances the π -conjugation, which leads to a set of desirable properties such as high fluorescence efficiency⁸ and high carrier mobility.⁹ For instance, while *trans*-stilbene only shows a weak fluorescence ($\Phi_F \approx 0.05$) at ambient temperature, the fluorescence quantum yield of its bis-methylene-bridged derivative **1** ($R = H$) approaches unity.¹⁰ As a new ladder-type π -conjugated system, we are now interested in its silicon analogue, bis-silicon-bridged stilbene **2**. The silicon-bridges would not only stiffen the skeleton but also contribute to the electronic structure through orbital interaction, as seen in the chemistry of silole,¹¹ a substructure of **2**. In addition, this skeleton may be attractive as a model of the all-silicon-bridged poly(*p*-phenylenevinylene) **3**. While the first example of **2** ($R = Me$) was recently synthesized by Barton and co-workers on the basis of the elegant thermal isomerization of the 5,6-disiladibenzo-*[c,g]*cyclooctyne derivative,¹² we have been interested in developing a more facile and general synthetic route. We now disclose the



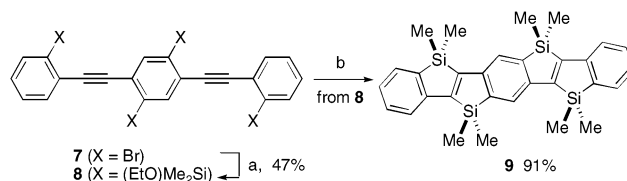
efficient synthesis of the silicon-bridged systems based on a new intramolecular reductive cyclization. The structure–property relationship of a homologous series of the synthesized compounds will also be reported.

Our new cyclization, outlined in eq 1, employs bis(*o*-silyl)-diphenylacetylene derivatives as the starting materials. We anticipated that the two-electron reduction of the acetylene moiety produces a dianion intermediate, which undergoes a double cyclization in a 5-exo mode to produce the target skeleton. Indeed, the treatment of bis(*o*-hydrodimethylsilyl)-diphenylacetylene **4a** with 4 molar amounts of lithium naphthalenide (LiNaph), followed

Scheme 1



Scheme 2^a



^a Reagents and conditions: (a) (1) *t*-BuLi (8 mol. amt.), THF, $-78^\circ C$, (2) $(Et_2N)Me_2SiCl$ (9 mol. amt.), $-78^\circ C$ to room temperature, (3) EtOH (excess), NH_4Cl (0.5 mol. amt.); (b) (1) LiNaph (8 mol. amt.), THF, room temperature, (2) I_2 (8 mol. amt.), room temperature.

by quenching with iodine, successfully produced the cyclized product **2a** in 71% yield, as shown in Scheme 1. Notably, the reaction quickly proceeded and was completed within 5 min at room temperature. As a starting material, the ethoxysilyl analogue **4a'** was also effective and produced **2a** in 65% yield. In addition, a diphenylsilyl derivative **4b** similarly gave **2b**.

In the present cyclization, the use of excess reductant as well as the iodine workup are crucial. Because the produced stilbene has a slightly lower reduction potential than that of the starting diphenylacetylene,¹³ the over-reduction of the produced stilbene skeleton competitively proceeds with the consumption of some amount of the reductant. Therefore, the use of excess reductant is essential for the complete conversion of the starting material. In addition, the iodine workup effectively regenerates the target stilbene from the “over-reduced” intermediate **5**. In fact, while the hydrolytic workup of the reaction mixture of **4a** with LiNaph (4 molar amounts) resulted in the formation of **6** in 65% yield as the major product, along with **2a** in 15% yield, the iodine workup improved the yield of **2a** up to 71% yield, as mentioned above, and suppressed the formation of **6** to 9% yield.

This methodology is applicable to the synthesis of a more extended homologue **9**, as shown in Scheme 2. Thus, as a starting material, compound **8** was prepared in 47% yield from the tetrabromide **7** via tetralithiation with *t*-BuLi followed by treatment with $(Et_2N)Me_2SiCl$ and subsequent ethanolysis. Upon treatment of **8** with excess LiNaph (8 molar amounts) at room temperature, the intramolecular reductive double cyclization proceeded at two acetylene moieties, and the iodine workup afforded the tetrakis-silicon-bridged derivative **9** in 91% yield as a bright yellow solid.

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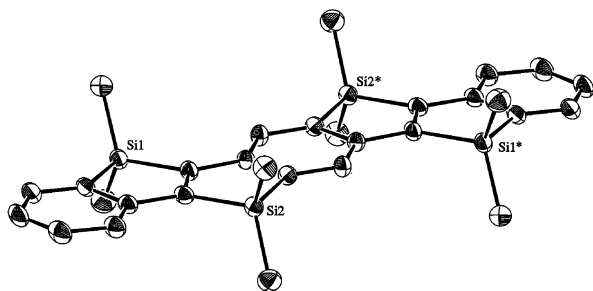


Figure 1. ORTEP drawing of **9** (50% probability for thermal ellipsoids).

Table 1. Photophysical Properties of Bridged Stilbene Derivatives

compd	UV-vis absorption ^a		fluorescence ^a		
	$\lambda_{\text{max}}/\text{nm}$	$\log \epsilon$	$\lambda_{\text{max}}/\text{nm}^b$	Φ_{F}^c	τ_s/ns^d
2a	360	4.08	426	0.58	5.5
2b	371	3.92	439	0.61	n.d.
9	424	4.43	473	0.50 ^e	3.5
	447	4.36			
1a (R = Me)	322	4.45	367	0.92 ^f	1.6

^a In THF. ^b Emission maxima upon excitation at the absorption maximum wavelengths. ^c Determined with 9,10-diphenylanthracene as a standard, unless otherwise stated. The Φ_{F} is the average value of repeated measurements within $\pm 5\%$ error. ^d Fluorescence lifetimes within ± 0.5 ns error. ^e Determined with perylene as a standard. ^f Determined with anthracene as a standard.

To the best of our knowledge, this is the first example of the tetrakis-bridged bis(styryl)benzene. The X-ray crystallographic analysis of **9** proved its highly coplanar structure due to the tetrakis-silicon bridges; the dihedral angle between the central and the outer benzene rings is 3.9° (Figure 1). This fact suggests that the π -conjugation is effectively extended over the entire molecule.

The photophysical data of the silicon-bridged stilbene homologues are summarized in Table 1, together with the data of **1a** (R = Me),¹⁴ for comparison. There are a couple of notable points: (1) The silicon-bridge significantly shifts the absorption and emission maxima to a longer wavelength. As compared with the carbon analogue **1a**, the absorption and emission maxima of **2a** are longer by about 40 and 60 nm, respectively. These significant red shifts are attributable to the electronic contribution of the silicon bridges. Thus, the orbital interaction between the σ^* orbital of the Me_2Si moiety and the π^* orbital of the stilbene framework effectively decreases the LUMO level.^{11a} Preliminary calculations at the HF/6-31G(d) level showed that the LUMO of **2a** is about 0.55 eV lower than that of **1a**, while the decrease in the HOMO level from **1a** to **2a** is only 0.19 eV. As a consequence, the silicon analogue **2a** has a smaller HOMO–LUMO energy gap and its emission color reaches the blue region, despite its rather short π -conjugation length. (2) The fluorescence quantum yield of the silicon analogues tends to be slightly lower than that of the carbon analogue **1a** (R = Me). Fluorescence lifetime measurements showed that this is mainly due to the slower radiative decay process from the excited state in **2a**. Thus, the radiative rate constant of **2a** ($k_{\text{r}} = 1.1 \times 10^8 \text{ s}^{-1}$), calculated on the basis of Φ_{F} and τ_{s} , is about one-fifth of that of **1a** ($k_{\text{r}} = 5.8 \times 10^8 \text{ s}^{-1}$), while the nonradiative rate constants are only slightly different from each other ($k_{\text{nr}} = 7.6 \times 10^7 \text{ s}^{-1}$ for **2a** vs $5.0 \times 10^7 \text{ s}^{-1}$ for **1a**). (3) The extension of the

π -conjugation from **2a** to **9** causes substantial red shifts in the absorption and emission maxima by 64 and 47 nm, respectively, without a significant decrease in Φ_{F} . Consequently, **9** exhibits an intense greenish blue emission, indicative of their potential use as a new emitting material.

In summary, we have developed a new intramolecular reductive double cyclization as an efficient synthetic method for the silicon-bridged stilbene homologues. This methodology will open a new chemistry of bridged stilbene-based π -conjugated systems, which have great potentials as new materials for the organic-based electronic and optoelectronic devices. Further studies on the electronic properties of the present compounds as well as the synthesis of more extended ladder-type π -conjugated systems such as **3** are currently in progress in our laboratory.

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Supporting Information Available: Experimental procedures and spectral data for **2**, **4**, and **7–9**, and crystallographic data of **9** (PDF and CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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