Communication

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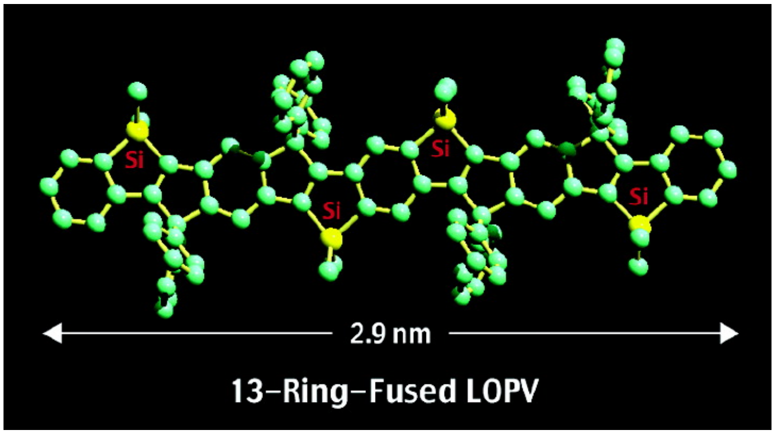

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Ladder Oligo(*p*-phenylenevinylene)s with Silicon and Carbon Bridges

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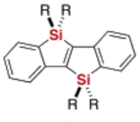
Ladder molecules with annelated π-conjugated frameworks are promising materials for broad applications in organic-based devices, including light-emitting diodes, thin film transistors, and optically pumped lasers.[1] Their rigid coplanar structures promise enhanced π-conjugation, which leads to a set of desirable properties, such as intense luminescence and high carrier mobility. The recent persistent interest in this field has led to considerable progress in the synthesis of various types of molecules, such as ladder oligo- or poly(*p*-phenylene)s with carbon[2] or heteroatom bridges,[3] polyacenes and heteroacenes,[4] and related π-conjugated systems.[5] However, only limited attention has been paid to phenylenevinylene-based ladder molecules, probably due to the lack of efficient synthetic routes.[6] As an example, Barton recently reported the synthesis of bis-silicon-bridged stilbene **1** by the elegant rearrangement of 5,6-disiladibenzo[*c*,*g*]cyclooctynes and installed this skeleton as a pendant group on polymeric systems.[7] We also independently reported the efficient route to the silicon-bridged stilbene derivatives based on a newly developed cyclization.[8] However, tetrakis-silicon-bridged bis(styryl)benzene **2** thus prepared was the longest example of the ladder oligo(phenylenevinylene)s (LOPVs) reported thus far. Therefore, the exploring of more efficient and general routes to the longer ladder systems has been a compelling subject in our research. We now report the first versatile synthetic methodology for the LOPVs and related π-electron systems annelated with silicon and carbon bridges. This methodology allows us to synthesize a homologous series of molecules up to a 13-ring-fused system.



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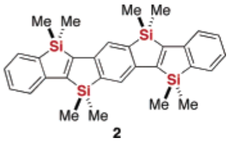

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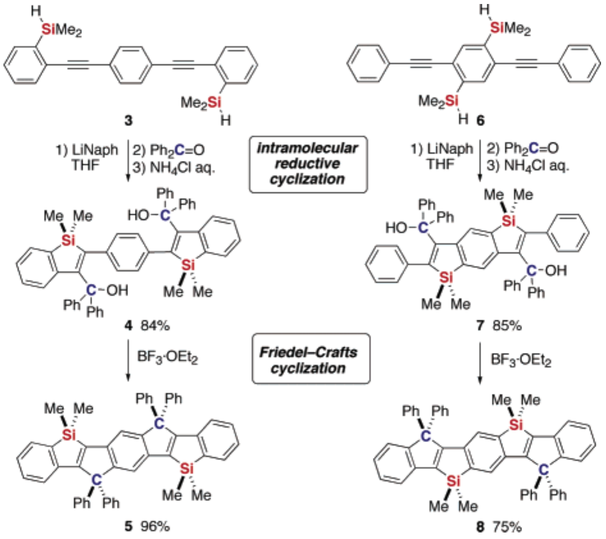
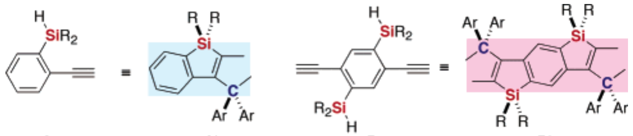
Our strategy for the construction of the Si,C-bridged LOPV skeleton is to combine two types of cyclization, that is the intramolecular reductive cyclization of mono(*o*-silylphenyl)acetylene derivatives and the Friedel−Crafts-type cyclization with a Lewis acid. We recently reported the former reaction as an efficient method for the preparation of various functionalized silaindenes,[9] while the latter electrophilic cyclization has been broadly employed to synthesize the ladder oligo- or poly(*p*-phenylene)s.[2]

We first examined the reactions of two kinds of starting materials, i.e., 1,4-bis(phenylethynyl)benzenes **3** and **6** that have two silyl groups at the terminal and central benzene rings, respectively. Thus, the treatment of **3** with 4 mol amounts of lithium naphthalenide (LiNaph) followed by trapping the produced dianionic species with excess benzophenone gave a diol **4** in 84% yield. The next electrophilic cyclization of **4** was carried out using $BF_3 \cdot OEt_2$ as a Lewis acid. Upon the addition of $BF_3 \cdot OEt_2$ to a CH_2Cl_2 solution of **4**, the cyclization immediately took place as indicated by the appearance of a strong fluorescence, and the desired Si,C,C,Si-bridged bis(styryl)benzene **5** was obtained in 96% yield as a bright yellow solid (Scheme 1). No other regioisomers were detected. Similarly, starting from **6**, the successive two-step procedures afforded the C,Si,Si,C-bridged **8** in 64% overall yield via a diol **7**. Advantageously, the substituents on the carbon bridges can be easily modified by changing the ketones. For example, the use of fluorenone instead of benzophenone resulted in producing fluorene-bound bis(styryl)benzene **9** (Chart 1) that has an interesting spiro structure (Supporting Information).

Scheme 1





A **A′** **B** **B′**

These results indicate that (*o*-silylphenyl)acetylene **A** and 2,5-bis(silyl)-1,4-diethynylbenzene **B** can serve as synthetic equivalents of the 3-ring-fused terminating unit **A′** and 5-ring-fused spacer unit **B′**, respectively, since the starting acetylenic materials of the present methodology are readily obtainable by the Sonogashira coupling of **A** or **B** with appropriate halogenated π-systems. On the basis of this idea, we carried out the synthesis of more extended ladder molecules as shown in Chart 1. Thus, the 9-ring-fused compound **10**, consisting of two terminating units **A′** and a fluorene spacer, was prepared from compound **A** and 2,7-diiodofluorene by the three-step reaction, which included the Sonogashira coupling of these compounds, the reductive cyclization, and the electrophilic cyclization. Similarly, the use of 2-iodofluorene and compound **B**

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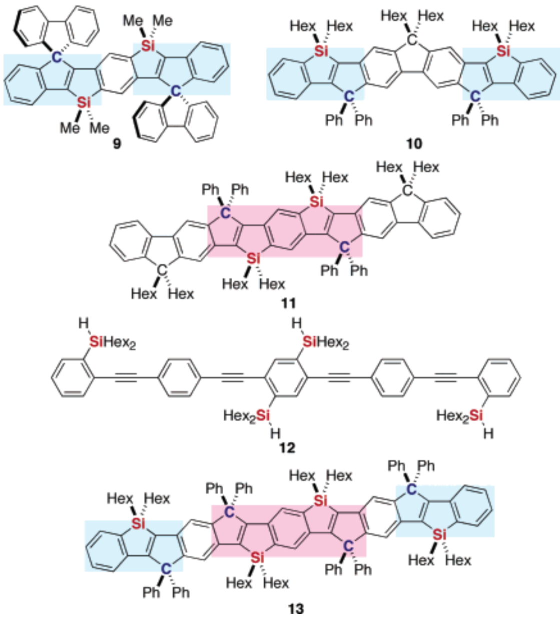
Chart 1



as the starting materials resulted in producing the 11-ring-fused system **11** in which two fluorene skeletons were connected with the 5-ring ladder unit **B′**. Finally, we have succeeded in the preparation of the 13-ring-fused LOPV **13** by connecting the two terminating units **A′** and the spacer unit **B′** with two benzene linkages. Thus, the iterative Sonogashira coupling reactions of compound **B** with *p*-iodobromobenzene and then with **A** produced an oligo(phenyleneethynylene) derivative **12**. The reductive cyclization of **12** proceeded at the four acetylene moieties to produce the corresponding tetraol in 44% yield, and the subsequent electrophilic cyclization gave the fully annelated **13** as a bright-orange solid in 52% yield. This compound has a good solubility toward common solvents such as THF (0.3 g/mL) and has a substantial thermal stability ($T\text{-}d_5$ 455 °C, under N_2). Figure 1 shows the crystal structure of **13**. Notably, this compound has a nearly flat π-conjugated framework with a length of ca. 2.9 nm.

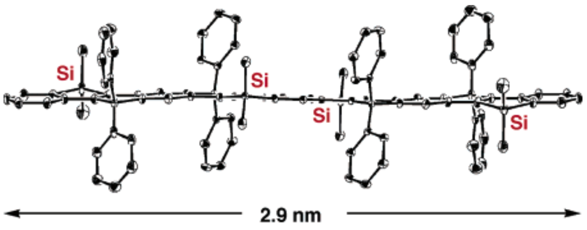


Figure 1. ORTEP drawing of **13** (50% probability for thermal ellipsoids). Hexyl groups on the silicon bridges are omitted for clarity. The hexyl groups at the terminal silicon bridges are highly disordered.

All the ladder molecules show intense fluorescence in the visible region, as their data are summarized in Table 1. The high quantum yields as well as the relatively small Stokes shifts (12−26 nm) are their notable common features. A comparison among the bis(styryl)-benzene derivatives **2**, **5**, and **8** shows that the Φ_F value increases in the order of **2** < **8** < **5**, while the emission maxima shift to shorter wavelengths over 30 nm in the same order. These results demonstrate a distinct effect of the silicon bridges on the fluorescence. The character of the disilaindacene moiety may be predominant relative to that of the terminal silaindene moiety. In the series of extended systems, the extension of the π-conjugation from **10** to **11** to **13** effectively red-shifts the emission maxima by about 80 nm with a slight decrease in Φ_F. As a consequence, the emission colors varies from blue **10** to green **11** to yellow **13**. As for the electrochemical properties, the cyclic voltammetry of the LOPV **13** has been investigated as a representative example. This compound shows two quasi-reversible redox processes both for the oxidation (E_{pa} 0.34, 0.64 V vs Fc/Fc$^+$) and reduction (E_{pc} −2.51, −2.84 V vs Fc/Fc$^+$), indicative of its potential as an ambipolar carrier transporting material. Further studies on the solid-state electronic properties, such as the carrier mobility and luminescence properties, for this series of ladder molecules are currently in progress.

Table 1. Photophysical Data for LOPVs and Related Compounds

	UV–vis absorption^a		fluorescence^a	
cmpd	λ_{max}/nm^b	log ϵ	λ_{max}/nm^b	$\phi_F{}^c$
5	425	4.49	443	0.73
8	438	4.41	464	0.56
2^d	447	4.36	473	0.50
10	433	4.80	445	0.84
11	476	4.72	499	0.40
13	502	4.88	523	0.59^e

[a] In THF. [b] All compounds show vibronic absorption and emission spectra. Only the longest absorption maxima and the shortest emission maxima are reported in this table. [c] Determined with perylene as a standard, unless otherwise stated. The (Φ_F is the average values of repeated measurements within ±5% errors. [d] Reference 8. [e] Determined with fluorescein as a standard.

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Supporting Information Available: Experimental details and spectral and analytical data for the ladder molecules, a cyclic voltammogram of **13**, ORTEP drawings and CIF files of **9** and **13**. This material is available free of charge via the Internet at http://pubs.acs.org.

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