

Synthesis, structures, and photophysical properties of silicon and carbon-bridged ladder oligo(*p*-phenylenevinylene)s and related π -electron systems

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Abstract

A series of partially or fully fused ladder oligo(*p*-phenylenevinylene)s (LOPVs) and related π -electron systems has been synthesized. Thus, the intramolecular reductive cyclization of *o*-silyl-substituted bis(phenylethynyl)benzenes with lithium naphthalenide produces partially silicon-bridged bis(styryl)benzenes consisting of silaindene or disilaindene skeletons. By combining this cyclization with the Friedel–Crafts type electrophilic cyclization, a homologous series of the fully fused LOPVs and related compounds, bearing silicon and carbon bridges, has been synthesized in fairly good yields. The longest example of the LOPVs is the 13-ring-fused system that has a nearly flat π -conjugated framework with a length of 2.9 nm, as proven by X-ray crystallography. All the produced ladder π -electron systems show intense fluorescence in the visible region with high quantum yields as well as relatively small Stokes shifts. As the silicon contents increase or the disilaindene skeleton is incorporated, the emission maxima shift to the longer wavelengths and the fluorescent quantum yields slightly decrease. These trends can be rationalized as due to the σ^* effect of silicon, wherein the silicon bridges contribute to the electronic structure through σ^* – π^* orbital interaction that cause the red-shifts in the emission maxima and suppress the radiative decay process from the singlet excited state.

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Keywords: Oligo(*p*-phenylenevinylene)s; Ladder π -conjugated systems; Silicon; Intramolecular reductive cyclization; Fluorescence

1. Introduction

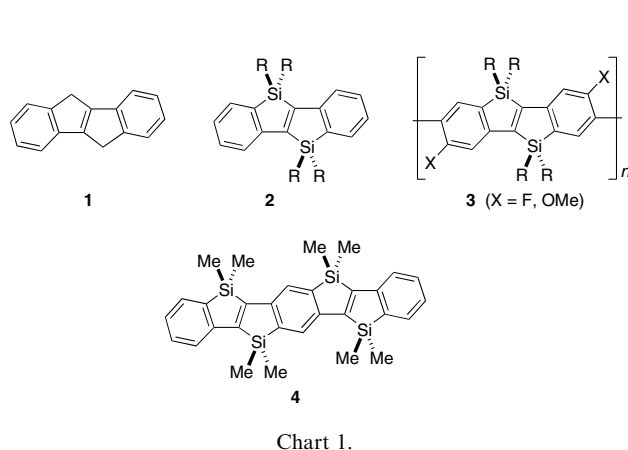
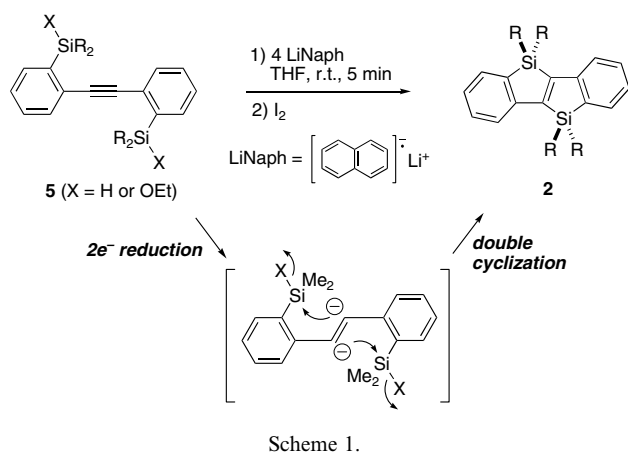
Ladder π -conjugated molecules are promising materials for organic electronics and optoelectronics, including electroluminescence (EL) devices, thin film transistors, and optically pumped lasers [1]. The virtue of this class of molecules is their rigid coplanar structures that promise enhanced π -conjugation, leading to a set of desirable properties, such as an intense luminescence and high carrier mobility. In the last decade, the persistent interest in this field has led to the synthesis of various fasci-

nating ladder 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 a limited attention has been paid to the phenylenevinylene-based ladder molecules, probably due to their difficult synthesis [6]. For example, whereas the simplest methylene-bridged stilbene **1** is well known to show an intense fluorescence with the quantum yield of nearly unity [7], its synthesis has not been improved from its original report [8] and no related work has been reported on the synthesis of its higher oligomers or polymers.

In contrast to the carbon-bridged system, significant progress has recently been made in the chemistry of its

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silicon analog, i.e., bis-silicon-bridged stilbene **2** [9]. In 1997, Barton and his coworkers [10] reported the first synthesis of the bis-silicon-bridged stilbene **2** by the elegant rearrangement of 5,6-disiladibenzo[*c,g*]cyclooctynes. They installed this skeleton as a blue-emitting pendant group on polymeric systems. We also independently reported the efficient synthesis of the silicon-bridged stilbene derivatives based on a newly developed intramolecular reductive cyclization, as shown in Scheme 1 [11]. On the basis of this methodology, we prepared various difunctionalized stilbene derivatives, and, with these derivatives in hand, we succeeded in the synthesis of a series of fluorescent π -conjugated polymers **3** [12]. However, as for the fully fused ladder oligo(*p*-phenylenevinylene)s (LOPVs), tetrakis-silicon-bridged bis(styryl)benzene **4** (Chart 1) prepared by our cyclization method was still the longest example [11]. Therefore, the exploration of more efficient and general routes to longer ladder systems has been a compelling subject in our research. By extending the chemistry of the reductive cyclization, we have now succeeded in developing the first general synthetic route to 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



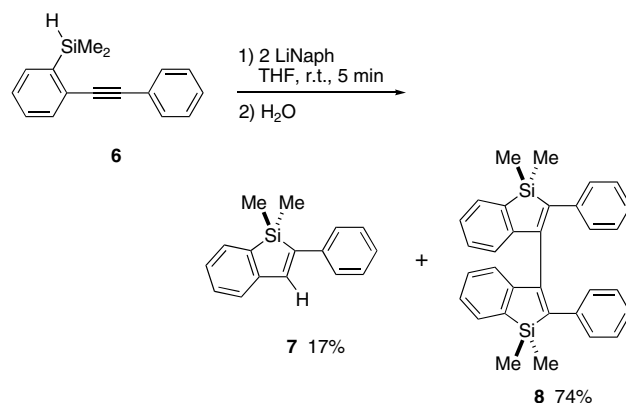
to a 13-ring-fused system. In this paper, we describe the comprehensive study of silicon and carbon-bridged LOPVs including not only the synthesis but also their structures and properties. A part of these results has already been published as communications [13,14]. The elucidation of the silicon effects on the photophysical properties is of particular interest, which will be discussed in detail in this paper.

2. Results and discussion

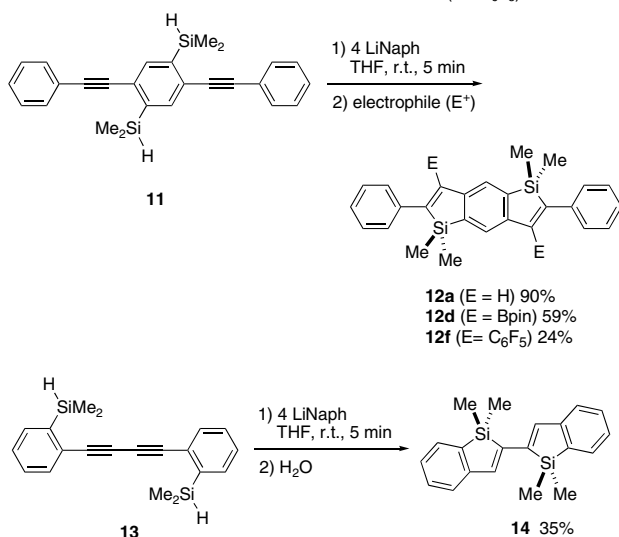
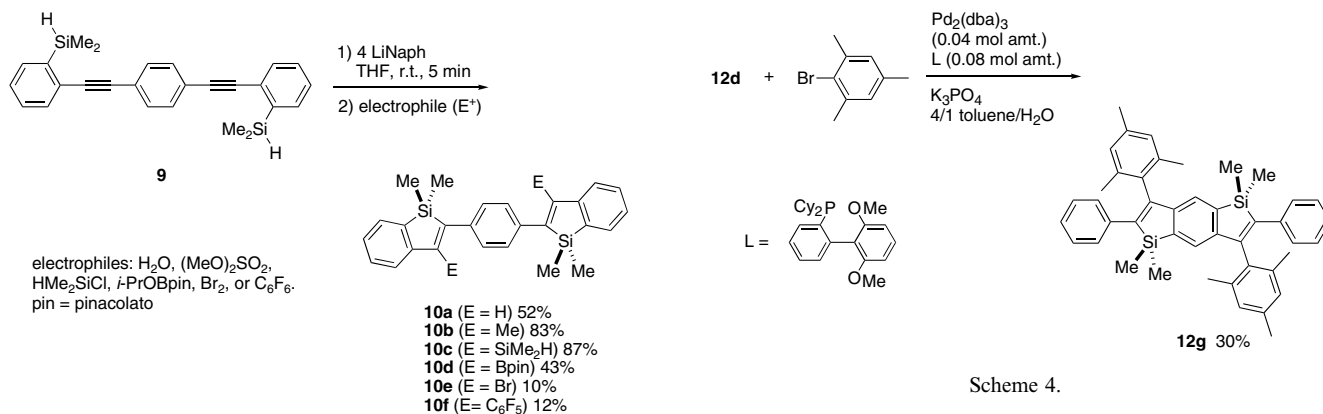
2.1. Intramolecular reductive cyclization of mono(*o*-silyl)diphenylacetylene

Our previous intramolecular reductive cyclization shown in Scheme 1 employs the bis(*o*-silyl)-substituted diphenylacetylene **5** as the starting material. The reaction of **5** with lithium naphthalenide (LiNaph) formally undergoes a two-electron reduction at the acetylene moiety to produce a dianionic intermediate, followed by the subsequent double cyclization to give the bis-silicon-bridged stilbene (disila-indeno[2,1-*a*]indene) [11]. We now extended this reaction to the synthesis of the sila-indene skeleton by replacing the starting material with mono(*o*-silyl)-substituted diphenylacetylene **6**. Thus, when compound **6** having hydrogen as the leaving group on the silicon atom was treated with a 2 mol amount of LiNaph followed by quenching with water, the desired phenylsila-indene **7** was obtained in 17% yield, together with its dimeric product **8** in 74% yield, as shown in Scheme 2 [15]. This result demonstrates that the present cyclization indeed proceeds even using the mono(*o*-silyl)-substituted derivatives, while the formation of the latter dimeric product suggests that the two-electron reduction proceeds in a stepwise fashion.

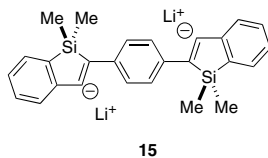
Notably, the present reductive cyclization more efficiently proceeds when π -extended diacetylenic starting materials are employed instead of the monoacetylenic compound, as shown in Scheme 3. Thus, the reaction



Scheme 2.



of bis(phenylethynyl)benzene **9**, having two silyl groups at the terminal phenyl rings, with a 4 mol amount of LiNaph followed by quenching with water afforded bis(silaindenyl)benzene **10a** in 52% yield. The use of an analogous compound **11**, having two silyl groups not at the terminal, but at the central benzene moiety, led to a totally new disila-*s*-indacene derivative **12a** in 90% yield. In addition, the present cyclization also proceeded in the case of bis(*o*-silylphenyl)diacetylene **13**, which produced bi(silaindene) **14** in 35% yield.



2.2. Functionalization of silaindene skeleton

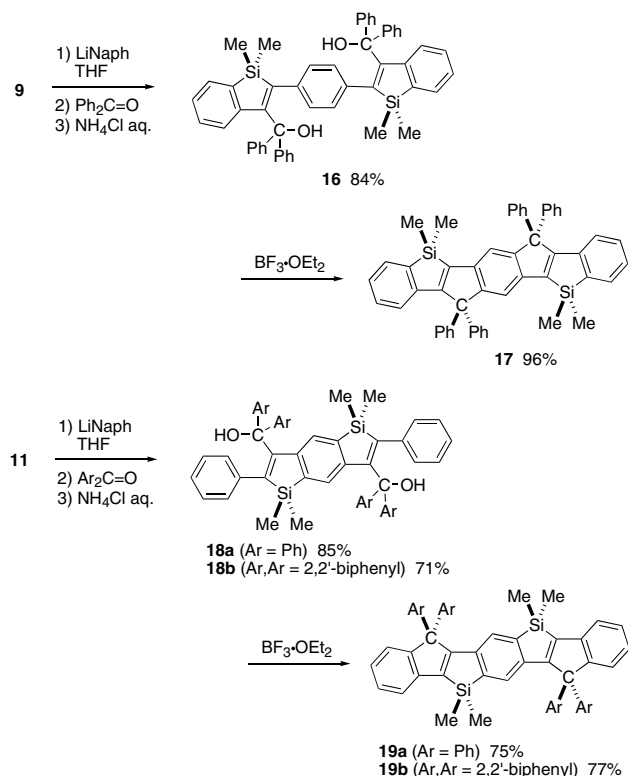
Compared with the traditional synthesis of silaindenes [16,17], the present cyclization has a great advan-

tage in terms of functionalization. The present reductive cyclization produces anionic intermediates that can be easily transformed into various functionalized derivatives by treatment with appropriate electrophiles. Thus, the reaction of **9** with a 4 mol amount of LiNaph yielded a dianionic intermediate **15**, which was subsequently trapped with various electrophiles to give a series of substituted bis(silaindenyl)benzenes **10b–10f** having Me, SiMe_2H , Bpin, Br and C_6F_5 groups, as shown in Scheme 3, although the yields of **10e** and **10f** were rather low due to undesirable side-reactions such as protonation. Similarly, 3,7-Bpin- and 3,7- C_6F_5 -substituted disilaindenes **12d** and **12f** were also synthesized. Among these functional groups, the Bpin and Br functionalities may be useful for further transformation through the well-established cross-coupling methodologies. For instance, the Pd complex-catalyzed coupling reaction of **12d** with mesityl bromide under the Buchwald's condition [18] produced 3,7-dimesityl derivative **12g** in 30% yield, as shown in Scheme 4. This compound has a strong fluorescence not only in dilute solution but also in the solid state, the details of which will be reported elsewhere.

2.3. Silicon and carbon-bridged bis(styryl)benzenes

In the synthesis of the functionalized silaindenes, noteworthy is the treatment of the anionic cyclized intermediates with ketones as the electrophile, which produces the corresponding alcohols. By combining this transformation with the traditional Friedel–Crafts type electrophilic cyclization, a very powerful method for the construction of the ladder π -conjugated frameworks [2], we next conducted the synthesis of the silicon and carbon-mixed bridged ladder phenylenevinylene derivatives.

We first examined the reaction of **9** using benzophenone as the electrophile, as shown in Scheme 5. Thus, the treatment of **9** with a 4 mol amount of LiNaph



Scheme 5.

followed by trapping with excess benzophenone gave a diol **16** in 84% yield. The next electrophilic cyclization of **16** was carried out using $\text{BF}_3 \cdot \text{OEt}_2$ as a Lewis acid. Upon the addition of $\text{BF}_3 \cdot \text{OEt}_2$ to a CH_2Cl_2 solution of **16**, the cyclization immediately took place as indicated by the appearance of an intense fluorescence, and the desired *Si,C,C,Si*-bridged bis(styryl)benzene **17** was obtained in 96% yield as a bright yellow solid. No other isomer was detected, suggesting that the electrophilic cyclization proceeded in a regio-specific manner. We also employed compound **11**, having two silyl groups at the central benzene ring, as the starting material. The successive two-step procedures afforded the *C,Si,Si,C*-bridged **19a** in a 64% overall yield via the diol **18a**.

One notable advantage of the present procedure is that the substituents on the carbon bridges can be easily modified by changing the ketones, whereas the available ketones are limited to diarylketones at this stage [19]. For example, the use of fluorenone instead of benzophenone resulted in producing the fluorene-bound bis(styryl)benzene **19b** in a 55% overall yield (based on **11**). This compound has an interesting molecular structure, as shown in Fig. 1, in which the completely coplanar bis(styryl)benzene skeleton and fluorene planes are orthogonally arranged to each other through spiro connections. The crystal data of this compound have been reported in the previous communication [14].

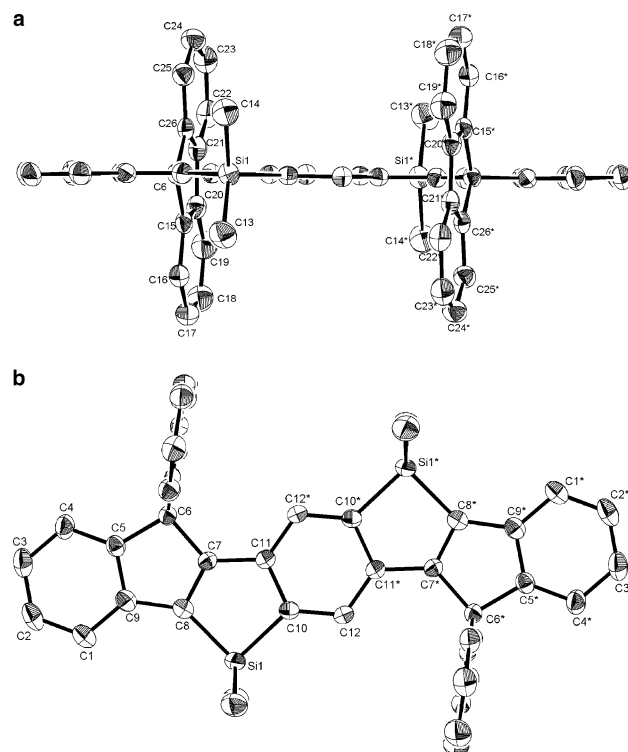


Fig. 1. ORTEP drawings of compound **19b**: (a) side view and (b) top view. Selected bond lengths (Å) and angles (°): Si1–C8, 1.870(2); Si1–C10, 1.879(2); C7–C8, 1.356(3); C7–C11, 1.468(3); C10–C11, 1.424(3); C5–C6, 1.527(3); C6–C7, 1.532(3); C5–C9, 1.406(3); C8–C9, 1.462(3); C8–Si1–C10, 91.29(9); Si1–C8–C7, 108.40(15); C8–C7–C11, 118.64(18); C7–C11–C10, 113.17(17); Si1–C10–C11, 108.49(14); C5–C6–C7, 100.74(16); C6–C7–C8, 111.78(17); C7–C8–C9, 108.95(18); C8–C9–C5, 108.81(18); C6–C5–C9, 109.71(17).

2.4. General synthetic route to the extended LOPVs and related π -electron systems

According to the results shown in Scheme 5, (*o*-silylphenyl)acetylene **20** and 2,5-bis(silyl)-1,4-diethynylbenzene **21** can be considered as the synthetic equivalents of the 3-ring-fused terminating unit **A** and 5-ring-fused spacer unit **B**, respectively, as shown in Chart 2. On the basis of this idea, we carried out the synthesis of the more extended ladder molecules **22–24** shown in Chart 3. For example, the 13-ring-fused LOPV **24**, consisting of the two terminating units **A** and the spacer unit **B** those of which were connected with two benzene linkages, was synthesized starting from **20** (R = hexyl) and **21** (R = hexyl), as shown in Scheme 6. Thus, the iterative Sonogashira coupling reactions of compound **21** with *p*-iodobromobenzene, then with **20** produced an oligo(phenyleneethynylene) derivative **25**. The reductive cyclization of **25** proceeded at the four acetylene moieties to produce the corresponding tetraol **26** in 44% yield, and the subsequent electrophilic cyclization gave the fully annelated **24** as a bright orange solid in 52%

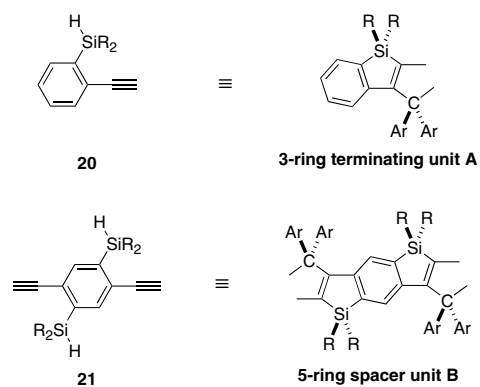


Chart 2.

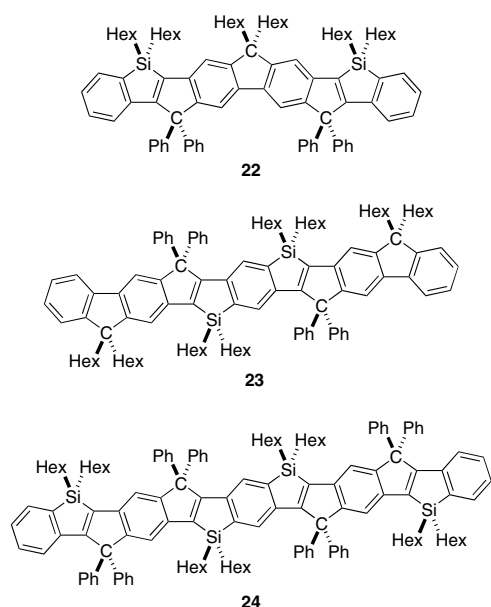
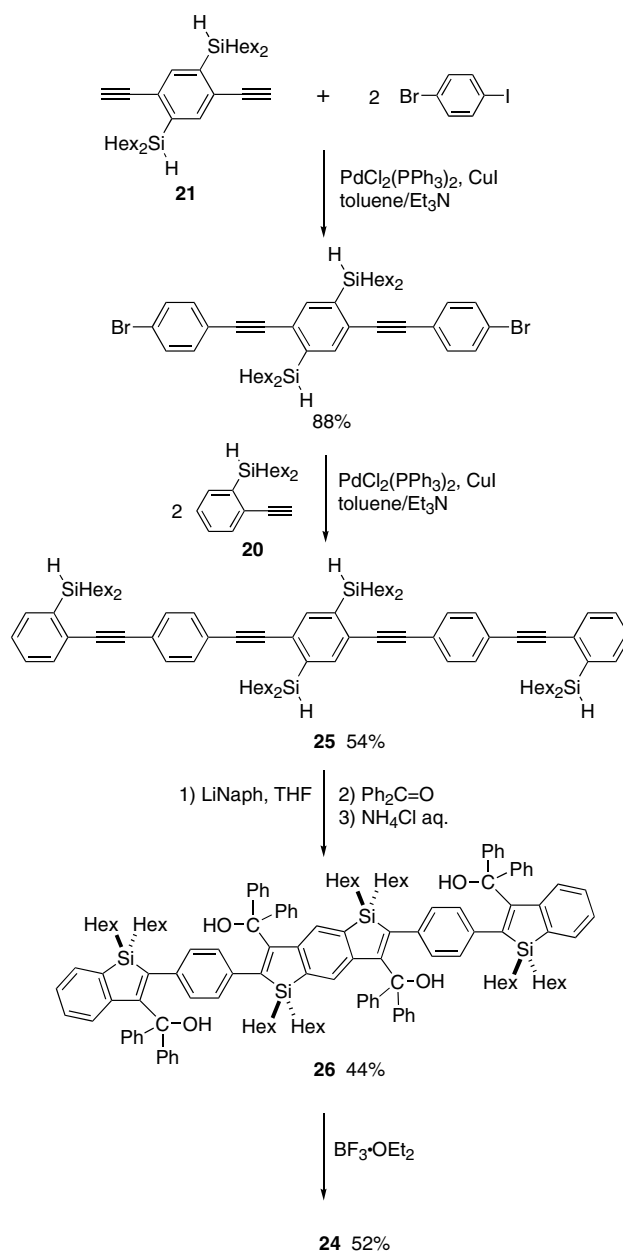


Chart 3.

yield. Similarly, the 9-ring-fused compound **22** and the 11-ring-fused system **23** were prepared from a fluorene-centered or -terminated diacetylenic compounds, **27** and **28**, respectively, by the combined procedure of the reductive cyclization with the Friedel–Crafts type cyclization, as shown in Scheme 7. The produced ladder compounds have a substantial thermal stability. For instance, the thermogravimetric analysis of **24** in a N_2 atmosphere showed that the initial 5% weight loss (T_d) occurred at 455 °C.

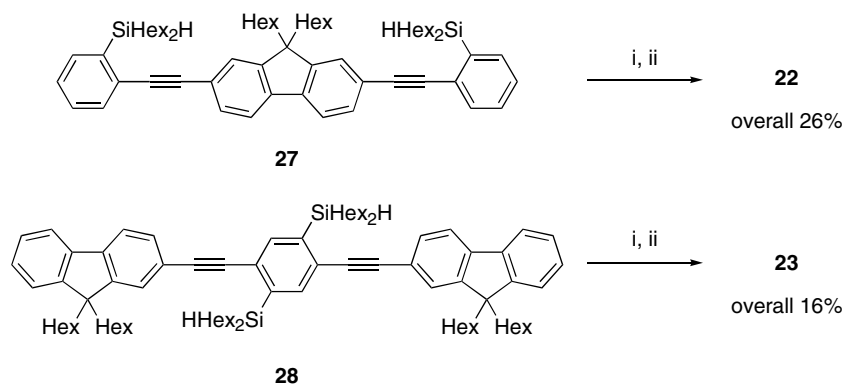
2.5. Crystal structures of the extended ladder π -conjugated systems

The structures of the 9-ring-fused system **22** and 11-ring-fused system **23** have been determined by the X-ray crystallography in this study. Their crystal data are listed in Table 1, and their ORTEP drawings are



Scheme 6.

shown in Fig. 2, together with that of the 13-ring-fused system **24**. The crystal data of **24** have been already reported in the previous communication [14]. All these compounds have nearly flat π -conjugated frameworks. The approximate lengths of the π -conjugated frameworks for **22**, **23**, and **24** are 2.1, 2.5, and 2.9 nm, respectively. The other common structural features of this series of compounds are that the flat rigid π -conjugated frameworks are covered by the substituents on the silicon and carbon bridges. Apparently, this structural characteristic helps to prevent the formation of insoluble aggregates and let them be soluble to some extent in the common organic solvents, despite their long rigid



Reagents and conditions: i, 1) LiNaph, THF; 2) Ph₂C=O; 3) NH₄Cl aq., ii, BF₃ OEt₂.

Scheme 7.

Table 1
Crystallographic data for compounds **22** and **23**

Compound	22	23
Formula	C ₉₁ H ₁₁₀ Si ₂	C ₁₁₀ H ₁₃₈ Si ₂
Mol weight (g mol ⁻¹)	1259.97	1516.38
Cryst dimens (mm)	0.20 × 0.20 × 0.10	0.20 × 0.20 × 0.20
Cryst syst	Triclinic	Monoclinic
Space group	P $\bar{1}$ (No. 2)	C2/c (No. 15)
<i>a</i> (Å)	15.8269(17)	29.430(5)
<i>b</i> (Å)	16.6540(19)	15.336(3)
<i>c</i> (Å)	17.274(2)	22.300(4)
α (°)	76.920(8)	
β (°)	68.134(7)	112.5683(8)
γ (°)	65.069(7)	
<i>V</i> (Å ³)	3818.8(8)	9294(3)
<i>Z</i>	2	4
<i>D</i> _{calcd} (g cm ⁻³)	1.096	1.084
<i>F</i> (0 0 0)	1368	3304
μ (Mo K α) (cm ⁻¹)	0.091	0.085
Temp (K)	173(2)	173(2)
No. of measd reflns	25841	37072
No. of ind reflns	13208 (<i>I</i> > 2 σ (<i>I</i>))	10605 (<i>I</i> > 2 σ (<i>I</i>))
Goodness-of-fit	1.100	1.107
Final <i>R</i> indices		
<i>R</i> ₁	0.0633	0.0670
<i>wR</i> ₂ [<i>I</i> > 2 σ (<i>I</i>)]	0.1640	0.1413

π -conjugated frameworks. For instance, compound **24** has a good solubility in THF of 0.3 g/mL.

2.6. Photophysical properties: Silicon effects on the fluorescence

The full photophysical data, including UV–vis absorption spectra, fluorescence spectra, fluorescence lifetime, and excited-state dynamics, for the synthesized ladder molecules are listed in Table 2, together with those of **4** and the parent non-substituted 1,4-bis(styryl)benzene **29** for comparisons (Scheme 8). All the ladder molecules show an intense fluorescence in the visible region. The high quantum yields (0.40–0.86) as well as the relatively small Stokes shifts (12–26 nm) are their notable common features.

A series of partially or fully bridged bis(styryl)benzenes, including *Si,n,n,Si*-bridged **10a**, *n,Si,Si,n*-bridged **12a**, *Si,C,C,Si*-bridged **17**, *C,Si,Si,C*-bridged **19a**, and *Si,Si,Si,Si*-bridged **4**, are now available, where *Si*, *C*, and *n* denote SiMe₂, CPh₂, and non-bridged moiety, respectively. For a comparison, the fluorescence spectra for the fully bridged derivatives **17**, **19a**, and **4** are shown in Fig. 3. A comparison of this series of compounds shows the effects of the silicon moieties on their photophysical properties. The notable points are summarized as follows. (1) Both the absorption and emission maxima tend to shift to longer wavelengths as the number of the silicon bridges increases. These red shifts can be ascribed to the contribution of the silicon moieties to the electronic structure through $\sigma^*-\pi^*$ conjugation in the silole substructure, which decrease the LUMO energy level [11,20]. (2) The positions of the silicon moieties also have a substantial influence on the absorption and emission maximum wavelengths. In particular, the central disilaindene skeleton more predominantly affects the photophysical properties of the bis(styryl)benzene chromophore than does the terminal silaindene skeleton. For instance, while the red-shift in the emission maxima from **17** to **4** is 30 nm, that from **19a** to **4** is only 9 nm and their emission maxima are no longer significantly different from each other. (3) This trend is also observed in the fluorescence quantum yield. The incorporation of the disilaindene skeleton tends to decrease the quantum yield, while the terminal silaindene skeleton retains the high quantum yield comparable to the parent 1,4-bis(styryl)benzene **27** ($\lambda_{\text{max,em}}$ 405 nm, Φ_{F} 0.77) [21].

On the basis of the Φ_{F} and the excited-state lifetime τ_{s} , determined by the time-resolved fluorescence spectroscopy, we calculated the radiative (k_{r}) and non-radiative (k_{nr}) decay rate constants from the singlet excited states, based on Eqs. (1) and (2). Fig. 4 shows the histogram of the rate constants, which reveals a distinct

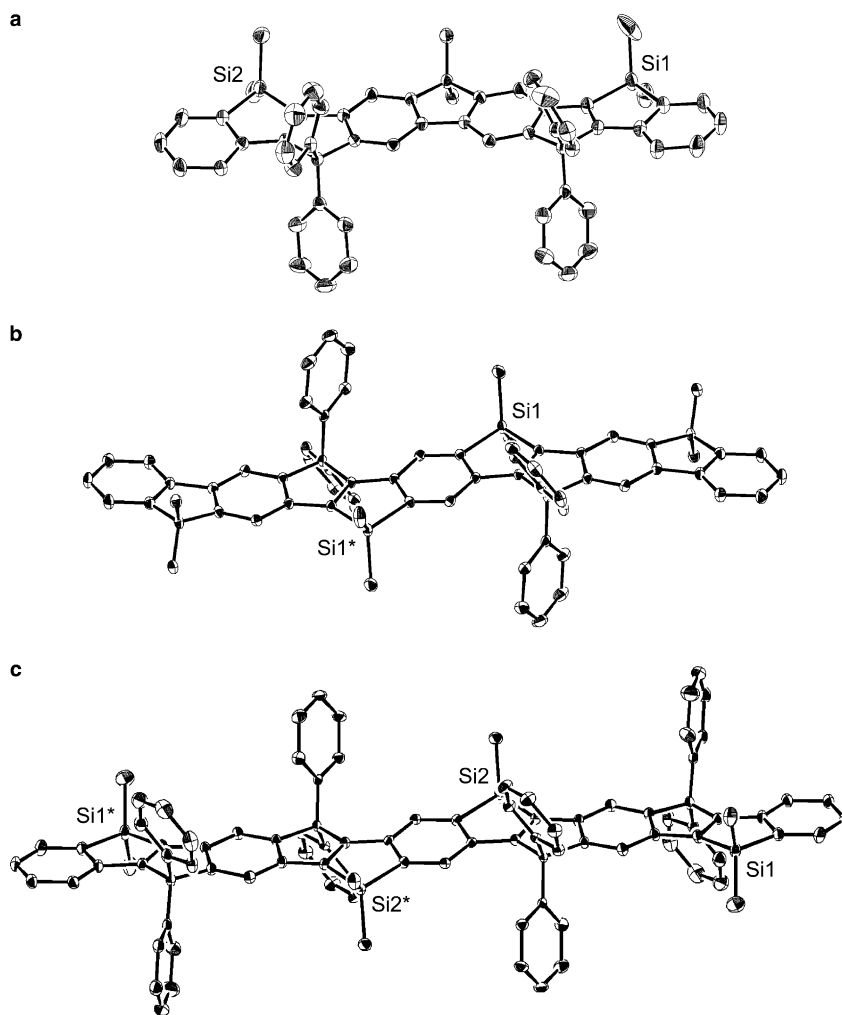


Fig. 2. ORTEP drawings of compounds (a) **22**, (b) **23**, and (c) **24** (50% probability for thermal ellipsoids). Hexyl groups on the silicon atoms and on the saturated carbon atoms in the fluorene substructures are omitted for clarity. A part of hexyl groups and phenyl groups is disordered. For the details, see Section 4.

trend. Thus, the incorporation of the disilaindacene skeleton as well as the increase in the silicon content significantly decrease the k_r , whereas the k_{nr} value only slightly increases. These results mean that the lowering of Φ_F by introducing the disilaindacene skeleton or by increasing the silicon content is based not on the accelerated non-radiative decay pathways including the internal conversion and intersystem crossing, but on the suppression of the radiative decay process.

$$k_r = \Phi_F / \tau_s, \quad (1)$$

$$k_{nr} = (1 - \Phi_F) / \tau_s, \quad (2)$$

In general, the radiative rate constant k_r has linear relationships with the square of the wavenumber of the absorption maximum ν^2 and the oscillator strength f , as shown in Eq. (3). Since the differences in ν are not very significant among the series of the bis(styryl)benzene derivatives, the decrease in the oscillator strength f may be responsible for the suppressed radiative decay process. In fact, preliminary calculations of model com-

pounds **17'** and **19'** at the TDDFT/B3LYP/6-31G(d)//B3LYP/6-31G(d) level of theory demonstrate that the decrease in the oscillator strength for the longest π - π^* transition amounts to 22% from **17'** ($f=0.91$) to **19a'** ($f=0.70$), whereas the difference in ν^2 between **17** and **19a** is only 6%. This is rationalized as due to the more significant contribution of the silicon moieties through the σ^* - π^* conjugation in the disilaindacene skeleton than in the silaindene skeleton, which results in the decreased oscillator strength of the pertinent π - π^* transition. Fig. 5 shows the calculated LUMOs for **17'** and **19'** that confirms the more significant contribution of the lobes at the silicon atoms in **19'** than in **17'**. This is the origin of the decrease in Φ_F by introducing the disilaindacene skeleton or by increasing the silicon contents.

$$k_r \approx \nu^2 f, \quad (3)$$

where ν is the wavenumber of the absorption maximum and f is the oscillator strength.

Table 2
Photophysical data for LOPVs and related π -conjugated compounds

Compound		UV–vis absorption ^a		Fluorescence ^a		Stokes shift $\Delta\lambda$	Lifetime τ_s (ns)	Radiative rate constant k_r (s ⁻¹)	Non-radiative rate constant k_{nr} (s ⁻¹)
		λ_{max} (nm) ^b	$\log \epsilon$	λ_{max} (nm) ^b	Φ_F ^c				
<i>Bis(styryl)benzenes</i>									
10a	Si,n,n,Si	397 (sh)	4.59	413	0.86	16	1.9	4.5×10^8	7.4×10^7
12a	n,Si,Si,n	420 (sh)	4.51	445	0.73	25	2.6	2.8×10^8	1.0×10^8
17	Si,C,C,Si	425	4.49	443	0.73	18	2.7	2.7×10^8	1.0×10^8
19a	C,Si,Si,C	438	4.41	464	0.56	26	3.4	1.6×10^8	1.3×10^8
4^d	Si,Si,Si,Si	447	4.36	473	0.50	26	3.8	1.3×10^8	1.3×10^8
29^e	n,n,n,n	350 ^e		405 ^e	0.77 ^e				
<i>LOPVs and related compounds</i>									
22	9-ring	433	4.80	445	0.84	12	2.5	3.4×10^8	6.4×10^7
23	11-ring	476	4.72	499	0.40	23	2.4	1.7×10^8	2.5×10^8
24	13-ring	502	4.88	523	0.59 ^f	21	2.1	2.8×10^8	2.0×10^8

^a In THF.

^b All compounds show vibronic absorption and emission bands. 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 $\pm 5\%$ errors.

^d [11].

^e The data from [21].

^f Determined with fluorescein as a standard.

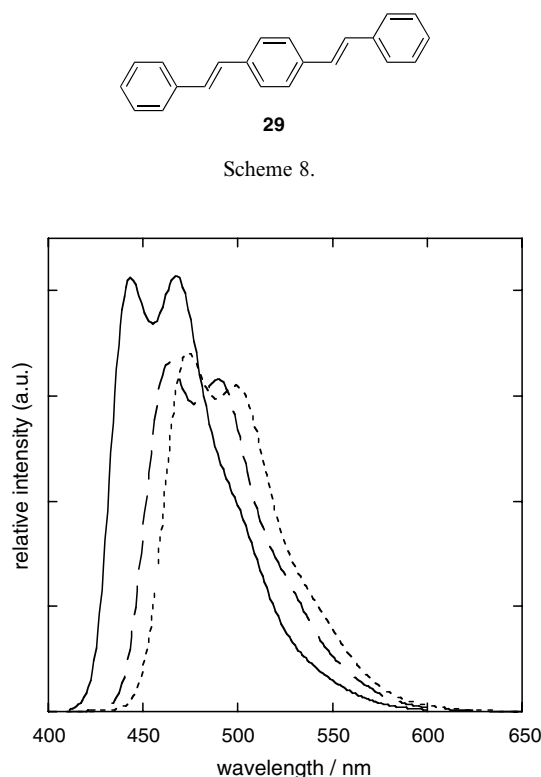


Fig. 3. Fluorescence spectra of fully bridged bis(styryl)benzenes in THF: **17**, solid line; **19a**, broken line; **4**, dotted line.

Despite these silicon effects, however, it is also noteworthy that the incorporation of the silicon moieties does not necessarily decrease the Φ_F . Thus, the siliindene skeleton does not reduce the Φ_F . This fact will be important for the further design of highly emissive mate-

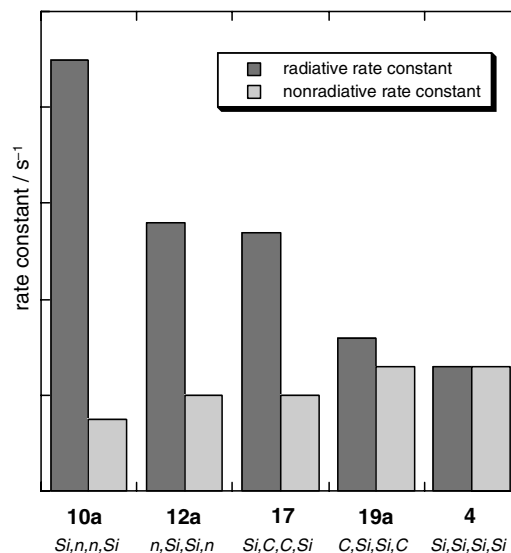


Fig. 4. Radiative (k_r) and non-radiative (k_{nr}) decay rate constants from the singlet excited states for the bridged bis(styryl)benzene derivatives.

rials based on the silicon-bridged LOPV and related materials. Beneficially, the present silaindene-containing derivatives **10a** and **17** exhibit an intense emission in the blue region and may be promising as new blue emitting materials. Their applications to the organic EL devices are currently under investigation.

In the series of long ladder systems, the extension of the π -conjugation from **22** to **23** to **24** effectively redshifts the emission maxima by about 80 nm, as shown in Fig. 6. As a consequence, the emission colors varies from blue **22** to green **23** to yellow **24**. With regard to

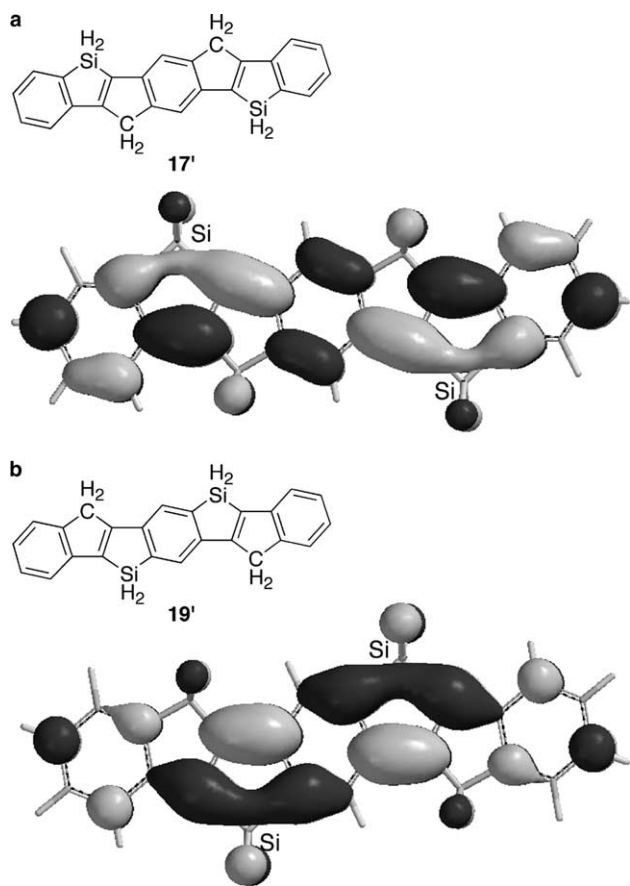


Fig. 5. Kohn-Sham LUMOs for model compounds: (a) **17'** and (b) **19'** calculated at the B3LYP/6-31G(d) level of theory.

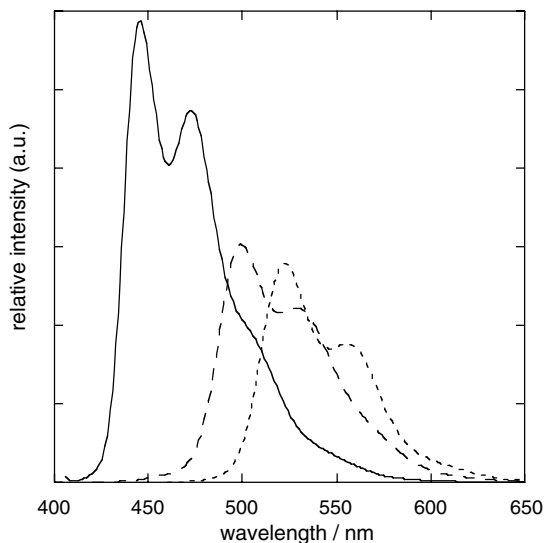


Fig. 6. Fluorescence spectra of LOPV and related π -electron systems in THF: **22**, solid line; **23**, broken line; **24**, dotted line.

the Φ_F , compounds **23** and **24** bearing the disilaindacene skeleton are again proved to have slightly low values, while the silaindene-capped fluorene **22** has a rather high quantum yield Φ_F of 0.84.

3. Conclusion

Oligo(*p*-phenylenevinylene)s are an important class of compounds not only as models of their polymeric analogs, but also as the fundamental chromophores or fluorophores for the creation of new functional π -conjugated materials. We have described the first general synthesis of the ladder type oligo(*p*-phenylenevinylene) LOPVs and related π -electron systems that have partially or fully annelated π -conjugated frameworks with silicon and carbon bridges. On the basis of the newly developed intramolecular reductive cyclizations, we have achieved their facile synthesis. Notably, our synthesis is essentially a simple reduction of the precursory acetylenic compounds with lithium naphthalene. However, the appropriate designs of the acetylenic starting materials enabled us to synthesize various types of molecules, including not only the silaindene and disilaindacene-based partially bridged π -electron systems, but also the fully silicon and carbon-bridged LOPVs and related compounds. The synthesized longest LOPV is the 13-ring-fused system **24** that has a completely flat π -conjugated framework with the length of 2.9 nm. Unambiguously, the present methodology will serve as a powerful protocol for the further synthesis of new related ladder π -conjugated materials.

The other important finding in this study is the rationalization of the silicon effect on the photophysical properties of the produced ladder molecules. The detailed inspection of the photophysical data for the series of the bis(styryl)benzenes revealed the effect of the silicon moieties. A major contribution of the silicon bridges is the participation to the LUMO through the $\sigma^*-\pi^*$ conjugation, which lowers the LUMO level resulting in the red-shift of the absorption and emission maxima, decreases the oscillator strength of the $\pi-\pi^*$ transition, and thus suppresses the radiative decay pathway from the singlet excited state. As a consequence, the fluorescence quantum yield Φ_F slightly decreases. This kind of effect may be rather general phenomena for π -conjugated systems containing heavy main group elements, and may deserve to recognize as a new concept, " σ^* effect" of main group elements. In the present ladder systems, however, it is also noteworthy that the incorporation of the silicon moiety into the π -conjugated framework does not necessarily decrease the Φ_F . Thus, the silaindene skeleton does not affect the efficiency of the fluorescence due to less significant σ^* effect in this skeleton. This fact will provide us a new design principle for the highly emissive silicon-bridged ladder π -conjugated molecules. Further studies on the design and synthesis of more promising ladder materials for the applications in organic electronics and optoelectronics are now in progress in our laboratory.

4. Experimental

Melting point (m.p.) determination was performed with a Yanaco MP-S3 instrument. ^1H and ^{13}C NMR spectra were measured with a JEOL A-400 or JEOL GSX-270 spectrometer. UV–vis absorption spectra and fluorescence spectra were measured with a Shimadzu UV-3150 spectrometer and a F-4500 Hitachi spectrometer, respectively, in degassed spectral grade THF. Time-resolved fluorescence spectra were measured using a Hamamatsu C4780 system equipped with a PLP-10 picosecond light pulser (LED wavelengths: 375 or 405 nm). Thin layer chromatography (TLC) was performed on plates coated with 0.25 mm thick silica gel 60F-254 (Merck). Column chromatography was performed using PSQ 100B (Fuji Silysia). Recycling preparative gel permeation chromatography (GPC) was performed using polystyrene gel columns (JAIGEL 1H and 2H, Japan Analytical Industry) with chloroform as an eluent. Medium pressure liquid chromatography (MPLC) was carried out using a silica gel packed column (Yamazen, Ultra Pack, SI-40B). [*o*-(Dihexylsilyl)phenyl]acetylene **20** was prepared by the lithiation of (*o*-bromophenyl)trimethylsilylacetylene with *n*-BuLi in ether, followed by treatment with dihexylchlorosilane and then desilylation in the presence of K_2CO_3 in a THF/EtOH mixed solvent. 2,5-Dibromo-1,4-bis(trimethylsilylethynyl)benzene was prepared according to the procedure described in the literature [22].

4.1. A typical procedure for the intramolecular reductive cyclization followed by the functionalization. Synthesis of compound **12d**

A mixture of granular lithium (76 mg, 10.9 mmol) and naphthalene (1.40 g, 10.9 mmol) in THF (8 mL) was stirred at room temperature under argon for 4 h. To the produced solution of lithium naphthalenide was added a solution of compound **11** (1.00 g, 2.53 mmol) in THF (3 mL) at room temperature. After stirred for 5 min, the resulting dark green solution was cooled to 0 °C and 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2.00 g, 10.8 mmol) was added. The mixture was then stirred for additional 0.5 h at the same temperature. Water was added and the mixture was extracted with CH_2Cl_2 for several times. The combined organic layer was washed with brine, dried over MgSO_4 , filtered, and concentrated under reduced pressure. A small amount of hexane was added to the resulting mixture and an insoluble material was collected by filtration, which was further washed with an additional amount of hexane to give pure **12d** (0.97 g, 1.49 mmol) in 59% yield as a pale yellow solid: m.p. >300 °C. ^1H NMR (270 MHz, CDCl_3): δ 0.36 (s, 12H), 1.29 (s, 24H), 7.18–7.36 (m, 10H), 7.61 (s, 2H). ^{13}C NMR (67.8 MHz, CDCl_3): δ -3.81, 24.87, 83.93, 126.33,

127.25, 127.85, 128.09, 140.35, 142.09, 149.74, 157.85. HRMS (FAB): 646.3291 (M^+). Anal. Calc. for $\text{C}_{38}\text{H}_{48}\text{B}_2\text{O}_4\text{Si}_2$: 646.3277.

4.2. Cross-coupling reaction. Synthesis of compound **12g**

A mixture of **12d** (100 mg, 0.155 mmol), mesityl bromide (62.0 mg, 0.311 mmol), $\text{Pd}_2(\text{dba})_3$ (5.7 mg, 6.2 μmol), 2-(dicyclohexylphosphino)-2',6'-dimethoxy-1,1'-biphenyl (5.1 mg, 12.4 μmol), and K_3PO_4 (98.7 mg, 0.464 mmol) in a 4/1 toluene/ H_2O mixed solvent (2.5 mL) was stirred at 100 °C for 51 h. After addition of 1 N HCl aqueous solution, the reaction mixture was extracted with CH_2Cl_2 . The organic layer was washed with brine, dried over MgSO_4 , filtered, and concentrated under reduced pressure. The obtained mixture was passed through a short silica gel column using CHCl_3 as an eluent. Further purification by means of a preparative GPC with CHCl_3 as an eluent gave **12g** (29 mg, 0.046 mmol) in 30% yield as a pale yellow solid: m.p. >300 °C. ^1H NMR (270 MHz, CDCl_3): δ 0.41 (s, 12H), 2.03 (s, 12H), 2.36 (s, 6H), 6.92 (s, 4H), 6.94 (s, 2H), 6.95–6.97 (m, 4H), 7.03–7.07 (m, 2H), 7.09–7.11 (m, 4H). ^{13}C NMR (100.4 MHz, CDCl_3): δ -2.94, 20.06, 21.23, 125.81, 126.14, 127.64, 128.02, 128.30, 134.97, 135.85, 136.25, 140.07, 140.09, 141.51, 148.63, 152.12. HRMS (FAB): 630.3129 (M^+). Anal. Calc. for $\text{C}_{44}\text{H}_{46}\text{Si}_2$: 630.3138.

4.3. Synthesis of 2,5-bis(dihexylsilyl)-1,4-diethynylbenzene (**21**)

To a solution of 2,5-dibromo-1,4-bis(trimethylsilylethynyl)benzene (4.00 g, 9.34 mmol) in Et_2O (140 mL) was added a hexane solution of *n*-BuLi (1.60 M, 12 mL, 19.2 mmol) dropwise at -78 °C. After stirred for 1 h, dihexylchlorosilane (4.61 g, 19.6 mmol) was added via syringe at the same temperature and the mixture was allowed to warm to room temperature over 6 h with stirring. The mixture was filtered and concentrated, and then passed through a silica gel short column (hexane, $R_f = 0.88$) to give 5.84 g (8.75 mmol) of 2,5-bis(dihexylsilyl)-1,4-bis(trimethylsilylethynyl)benzene in 94% yield as pale yellow oil, which was directly used for next desilylation reaction without further purification: ^1H NMR (400 MHz, CDCl_3): δ 0.26 (s, 18H), 0.83–0.98 (m, 20H), 1.24–1.32 (m, 32H), 4.28 (quin, $J = 3.6$ Hz, 2H), 7.59 (s, 2H).

A solution of 2,5-bis(dihexylsilyl)-1,4-bis(trimethylsilylethynyl)benzene (5.83 g, 8.73 mmol) and K_2CO_3 (241 mg, 1.74 mmol) in a 1/1 THF/EtOH mixed solvent (80 mL) was stirred for 10 h at room temperature. After concentrated under reduced pressure, hexane was added to the mixture. The insoluble material was removed by filtration and the filtrate was concentrated under

reduced pressure and subjected to column chromatography on a silica gel (hexane, $R_f = 0.83$) to give 4.45 g (8.51 mmol) of compound **21** in 97% yield as pale yellow oil: $^1\text{H NMR}$ (270 MHz, CDCl_3): δ 0.85 (t, $J = 6.9$ Hz, 12H), 0.91–0.96 (m, 8H), 1.23–1.34 (m, 32H), 3.30 (s, 2H), 4.32 (quin, $J = 3.6$ Hz, 2H), 7.63 (s, 2H). $^{13}\text{C NMR}$ (67.8 MHz, CDCl_3): δ 11.51, 14.19, 22.65, 24.72, 31.53, 32.85, 81.38, 84.31, 126.94, 139.50, 140.12.

4.4. Synthesis of tetraacetylenic starting material **25**

A mixture of compound **21** (2.00 g, 3.82 mmol), *p*-iodobromobenzene (2.22 g, 7.69 mmol), $\text{PdCl}_2(\text{PPh}_3)_2$ (54.8 mg, 0.077 mmol), and CuI (29.3 mmol, 0.154 mmol) in a 3/1 toluene/ Et_3N mixed solvent (80 mL) was stirred for 5.5 h at room temperature. After filtration of the reaction mixture, the filtrate was concentrated under reduced pressure. The mixture was subjected to column chromatography on a silica gel (hexane, $R_f = 0.83$) to give 2.81 g (3.37 mmol) of pure 2,5-bis(dihexylsilyl)-1,4-bis[(*p*-bromophenyl)ethynyl]benzene in 88% yield as a white solid: m.p. 61–63 °C. $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 0.83 (t, $J = 6.8$ Hz, 12H), 0.94–1.03 (m, 8H), 1.19–1.40 (m, 32H), 4.41 (quin, $J = 3.6$ Hz, 2H), 7.39 (d, $J = 8.4$ Hz, 4H), 7.50 (d, $J = 8.4$ Hz, 4H), 7.69 (s, 2H). $^{13}\text{C NMR}$ (67.8 MHz, CDCl_3): δ 11.71, 14.20, 22.64, 24.79, 31.54, 32.90, 91.77, 92.43, 122.13, 122.64, 127.45, 131.62, 132.61, 138.79, 139.86. Anal. Calc. for $\text{C}_{46}\text{H}_{64}\text{Br}_2\text{Si}_2$: C, 66.33; H, 7.74. Found: C, 65.98; H, 7.63%.

The mixture of 2,5-bis(dihexylsilyl)-1,4-bis[(*p*-bromophenyl)ethynyl]benzene (1.00 g, 1.20 mmol), *o*-(dihexylsilyl)phenylacetylene (0.80 g, 2.66 mmol), $\text{PdCl}_2(\text{PPh}_3)_2$ (16.8 mg, 23.9 μmol), and CuI (9.1 mg, 47.8 μmol) in 40 mL of a 3/1 toluene/ Et_3N mixed solvent was stirred at 85 °C for 16 h. After filtration of the mixture, the filtrate was concentrated under reduced pressure. The resulting mixture was subjected to column chromatography on a silica gel (hexane, $R_f = 0.56$) to give 0.82 g (0.64 mmol) of the tetraacetylenic compound **25** in 54% yield as a pale yellow sticky oil: $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 0.82–0.86 (m, 24H), 0.96–1.06 (m, 16 H), 1.22–1.43 (m, 64H), 4.44 (quin, $J = 3.6$ Hz, 4H), 7.32 (dt, $J = 1.2$ and 7.2 Hz, 2H), 7.37 (dt, $J = 1.2$ and 7.2 Hz, 2H), 7.52 (s, 8H), 7.54–7.57 (m, 4H), 7.72 (s, 2H). $^{13}\text{C NMR}$ (100.4 MHz, CDCl_3): δ 11.61, 11.76, 14.09, 22.54, 24.71, 24.75, 31.47, 31.50, 32.83, 32.85, 91.46, 92.58, 92.60, 93.31, 123.06, 123.47, 127.60, 127.66, 128.58, 129.08, 131.32, 131.33, 132.08, 135.70, 138.98, 139.15, 139.98. Anal. Calc. for $\text{C}_{86}\text{H}_{126}\text{Si}_4$: C, 81.19; H, 9.98. Found: C, 81.48; H, 10.31%.

4.5. Synthesis of tetraol compound **26**

A mixture of granular lithium (19.9 mg, 2.87 mmol) and naphthalene (0.362 g, 2.87 mmol) in THF (4 mL)

was stirred at room temperature under argon for 4 h. To the produced solution of lithium naphthalenide was added a solution of compound **25** (0.368 g, 0.29 mmol) in THF (4 mL) at room temperature. After stirred for 5 min, a THF (3 mL) solution of benzophenone (0.523 g, 2.87 mmol) was added to the reaction mixture at room temperature. The reaction mixture was stirred for 20 min and then quenched with a saturated aqueous solution of NH_4Cl . The mixture was extracted with ether. The organic layer was washed with brine, dried over MgSO_4 , filtered, and concentrated under reduced pressure. The resulting mixture was purified by silica gel column chromatography (10/1 hexane/ EtOAc , $R_f = 0.25$) to give 0.255 g (0.127 mmol) of **26** in 44% yield as a white solid: m.p. 164–166 °C. $^1\text{H NMR}$ (400 MHz, C_6D_6): δ 81–0.94 (m, 36H), 1.14–1.36 (m, 68H), 2.97 (s, 2H), 3.13 (s, 2H), 6.76–6.81 (m, 8H), 6.88 (dt, $J = 1.2$ and 7.6 Hz, 2H), 6.94 (dt, $J = 1.2$ and 7.0 Hz, 2H), 7.00–7.15 (m, 24H), 7.30 (s, 2H), 7.31 (d, $J = 8.0$ Hz, 2H), 7.46 (dd, $J = 1.2$ and 7.0 Hz, 2H), 7.55 (dd, $J = 1.2$ and 8.0 Hz, 8H), 7.62 (dd, $J = 1.2$ and 8.0 Hz, 8H). $^{13}\text{C NMR}$ (100.4 MHz, C_6D_6): δ 12.35, 14.91, 15.01, 23.56, 23.60, 24.66, 32.36, 32.47, 34.02, 34.05, 84.22, 84.22, 126.60, 127.21, 127.44, 128.22, 128.27, 128.50, 128.74, 129.13, 129.19, 129.50, 130.10, 132.08, 132.64, 137.96, 139.08, 139.47, 139.88, 146.78, 147.00, 147.34, 147.86, 148.85, 151.76, 156.36, 157.25. HRMS (FAB): 1999.1893 (M^+). Anal. Calc. for $\text{C}_{138}\text{H}_{166}\text{O}_4\text{Si}_4$: 1999.1863.

4.6. A typical procedure for the Friedel–Crafts type cyclization to synthesize the LOPVs and related π -systems. Synthesis of 13-ring-fused LOPV **24**

To a solution of tetraol **26** (0.137 g, 0.068 mmol) in CH_2Cl_2 (35 mL) was added $\text{BF}_3 \cdot \text{OEt}_2$ (34 μL , 0.272 mmol) at room temperature. After stirred for 15 min, the reaction mixture was quenched with 95% ethanol. The organic layer was washed with brine, dried over MgSO_4 , filtered, and concentrated under reduced pressure. The resulting mixture was subjected to column chromatography on a silica gel (10/1 hexane/ EtOAc , $R_f = 0.56$), followed by the further purification by means of MPLC (10/1 hexane/ EtOAc) to give 0.068 g (0.035 mmol) of **24** in 52% yield as an orange red solid: m.p. 255–258 °C. $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 0.73–0.80 (m, 32H), 0.90–0.94 (m, 8H), 1.06–1.18 (m, 56H), 1.26–1.34 (m, 8H), 7.01–7.06 (m, 6H), 7.14–7.22 (m, 28H), 7.30–7.33 (m, 18H), 7.44–7.46 (m, 2H). $^{13}\text{C NMR}$ (100.4 MHz, CDCl_3): δ 11.63, 11.83, 14.04, 22.45, 22.47, 24.05, 24.16, 31.28, 31.35, 32.80, 32.94, 66.76, 118.16, 118.46, 123.23, 125.65, 126.46, 127.56, 127.88, 127.99, 129.07, 129.11, 132.39, 141.35, 141.98, 142.44, 142.64, 142.73, 142.96, 144.44, 145.16, 145.24, 156.96, 157.22, 170.62, 171.09. Anal. Calc. for

C₁₃₈H₁₅₈Si₄: C, 85.92; H, 8.26. Found: C, 85.41; H, 8.29%.

4.7. X-ray crystallography

Single crystals of **22** and **23** suitable for X-ray crystal analysis were obtained by recrystallization from hexane and a 10/1 hexane/EtOAc mixed solvent, respectively. Intensity data were collected at 173 K on a Rigaku single crystal CCD X-ray diffractometer (Saturn 70 with MicroMax-007) with Mo K α radiation ($\lambda = 0.71070 \text{ \AA}$) and graphite monochromator. The crystal data for these compounds are summarized in Table 1. Their structures were solved by direct methods (SHELXS-97) and refined by the full-matrix least-squares on F^2 (SHELXL-97) [23]. All non-hydrogen atoms were refined anisotropically and all hydrogen atoms were placed using AFIX instructions.

In the structure of **22**, two phenyl groups on the carbon atom C9 and two hexyl groups on the silicon atoms Si1 and Si2 were disordered and solved using appropriate disorder models. Thus, for one phenyl group consisting of C32–C37, two sets of carbons, i.e., C33A, C34A, C36A, and C37A and C33B, C34B, C36B, and C37B, were placed and their occupancies were refined to be 0.80 and 0.20, respectively. Similarly, as for the other phenyl group consisting of C38–C43, two sets of carbons, i.e., C39A, C40A, C42A, and C43A and C39B, C40B, C42B, and C43B, were placed and their occupancies were refined to be 0.80 and 0.20, respectively. On the other hand, as for the hexyl group consisting of C44–C49, two sets of carbons, C44A–C49A, and C44B–C49B were placed and their occupancies were refined to be 0.52 and 0.48, respectively. As for the other hexyl group consisting of C80–C85, the terminal three carbons of C83–C85 were divided into two sets of carbons, i.e., C83A–C85A and C83B–C85B and their occupancies are refined to be 0.80 and 0.20, respectively.

In the structural analysis of compound **23**, one hexyl group on the Si1 atom consisting of C50–C65 was disordered and solved using appropriate disorder models. Thus, two sets of carbons, i.e., C52A, C53A and C52B, C53B, were placed and their occupancies were refined to be 0.58 and 0.42, respectively.

5. Supplementary material

Crystallographic data for the compounds **22** and **23** have been deposited with the Cambridge Crystallographic Data Center as supplementary publication nos. CCDC 265396 and 265397, respectively. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

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