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Ladder Distyrylbenzenes with Silicon and Chalcogen Bridges: Synthesis, Structures, and Properties

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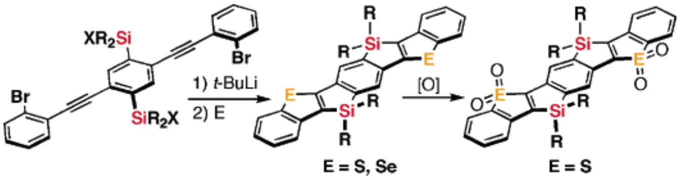
ABSTRACT



A cascade-type anionic double cyclization of (*o*-silylphenyl)(*o*-halophenyl)acetylenes via lithiation followed by treatment with elemental chalcogen produces silicon and chalcogen-bridged stilbenes. Based on this reaction, a series of silicon and sulfur- or silicon and selenium-bridged ladder distyrylbenzenes have been synthesized. Their chemical modification by oxidation, crystal structures, and photophysical properties are described.

Ladder π-conjugated systems with fused polycyclic skeletons are an important class of materials for organic electronics.[1] Their flat and rigid π-conjugated frameworks promise the effective extension of the π-conjugation without any conformational disorder, thus leading to a set of desirable properties such as an intense luminescence and high carrier mobility. Although ladder oligo- or poly(*p*-phenylene)s with methylene[2] or heteroatom bridges[3] are a representative example, whose significant potentials for applications have been proven by recent extensive research, their vinylogous homologues, ladder oligo- or poly(*p*-phenylenevinylene)s (LOPVs or LPPVs), have attracted only limited attention to date.[4−7] As a new entry into this class of compounds, we are now interested in a silylene and chalcogen (S or Se)-bridged LPPV skeleton (Figure 1). The introduction of the silylene bridges would make it possible to perturb the

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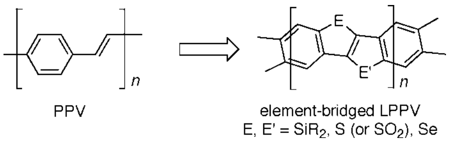
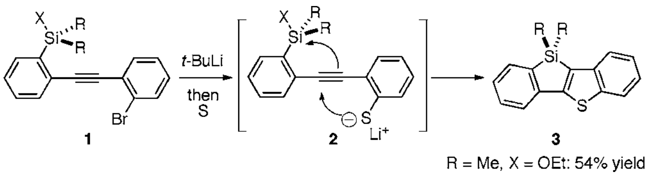


Figure 1. Structural modification of poly(*p*-phenylenevinylene)s to the silicon and chalcogen-bridged ladder derivatives.

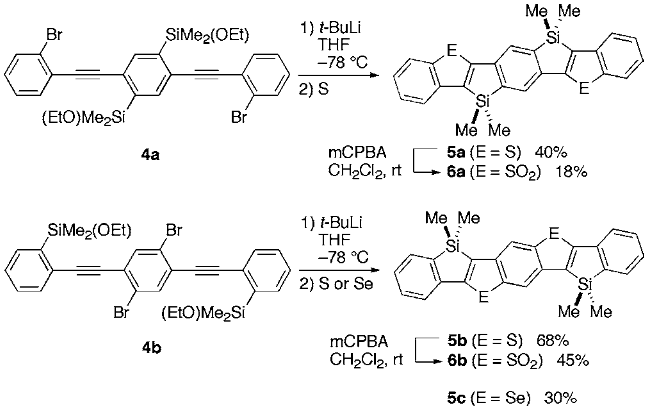
electronic structure through the $\sigma^*-\pi^*$ conjugation in the silole substructure.[8] In addition, the incorporation of the thiophene or selenophene substructure would enhance the chemical stability by increasing the aromatic character of the π-conjugated frameworks. The possible electronic tuning by the chemical oxidation from the thiophene substructure to the thiophene-*S,S*-dioxide would also be of notable merit.[9] As a model of this ladder system, we now disclose a synthetic route to the silicon and chalcogen-bridged distyrylbenzenes. Their chemical modification by oxidation, crystal structures, and photophysical properties were also investigated.

Our strategy to construct the Si,S-bridged ladder phenylenevinylene skeletons is based on a new cascade-type anionic cyclization from the (*o*-silylphenyl)(*o*-bromophenyl)acetylene precursors **1**, as shown in Scheme 1. Thus, the lithium−halogen exchange reaction of **1** with *t*-BuLi followed by treatment with elemental sulfur produces a thiolate anion **2**, which further undergoes the 5-*endo-dig* mode cyclization, followed by a subsequent nucleophilic substitution at the silicon center to give the double-cyclized Si,S-bridged stilbene **3**. In fact, compound **1** (R = Me, X = OEt) was successfully converted into **3** in a 54% yield. It is worth noting that the 5-*endo-dig* mode cyclization of (*o*-ethynylbenzene)thiolate is a general methodology for the construction of the benzothiophene skeleton.[10] In our reaction, the incorporation of the silyl group at the appropriate position allows us to synthesize the doubly cyclized product.

Scheme 1



Scheme 2



On the basis of this cascade cyclization, a series of ladder distyrylbenzenes **5** were successfully synthesized from the diacetylenic starting materials, as shown in Scheme 2. Thus, **5a** having the silylene and sulfur bridges at the inner and outer positions, respectively, was obtained from **4a** in a 40% yield, while the reaction of **4b** afforded **5b**, which possesses the silylene and sulfur bridges at the inverse positions compared to **5a**. Noticeably, this reaction also successfully proceeds with selenium instead of sulfur, yielding selenophene-derivative **5c** in a 30% yield. The oxidation of the produced ladder molecules **5a** and **5b** with 5 molar amounts of *m*CPBA afforded the corresponding thiophene-*S,S*-dioxide derivatives **6a** and **6b** in 18% and 45% yields, respectively. All of the ladder compounds are soluble in common solvents such as THF and $CHCl_3$. The thermogravimetric analysis revealed that not only the ladder compounds **5** but also the thiophene-*S,S*-dioxide derivatives **6** have high thermal stability with their decomposition temperatures T_{d5} for a 5% weight loss beyond 300 °C (**5a**, 307 °C; **5b**, 308 °C; **5c**, 318 °C; **6a**, 360 °C; **6b**, 355 °C), indicative of possible fabrication of vapor-deposited films using these compounds.

An X-ray crystallographic analysis confirmed that all of the ladder compounds **5** and **6** have highly coplanar π-conjugated frameworks (see Supporting Information). Among them, it is worth noting that **5a** having the silylene bridges at the inner positions forms a slipped face-to-face packing structure, as shown in Figure 2. In general, the incorporation of the tetra-coordinate silicon bridges is a disadvantage for forming a densely packed structure, since the substituents on the silicon atoms prevent the formation of close π-stacking. In **5a**, however, the substituents on the silicon atoms play a role as a guide to regulate the intermolecular interaction in the slipped face-to-face fashion. This might be beneficial to achieving a high carrier mobility. In this structure, the interfacial distance of the adjacent molecules is about 3.6 Å.

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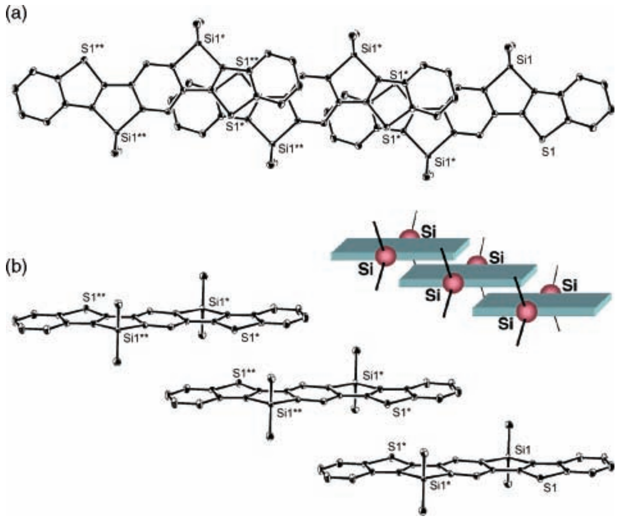


Figure 2. Crystal structure of Si,S-bridged distyrylbenzene **5a**: (a) top view and (b) side view (50% thermal probability for ellipsoids).

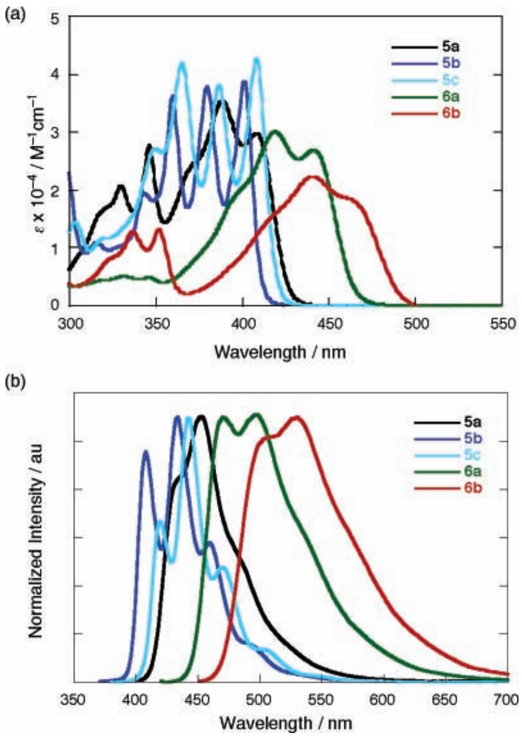


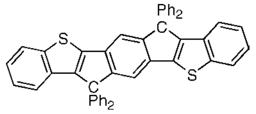
Figure 3. UV−vis absorption and fluorescence spectra of the ladder distyrylbenzenes **5** and **6** in THF.

The UV−vis absorption and fluorescence spectra of the ladder distyrylbenzenes are shown in Figure 3, and their data are summarized in Table 1, together with those of the C,S-bridged congener **7**[11] for comparison. These data are discussed from the viewpoints of (1) effect of the positions of the silylene and sulfur briges, (2) effect of the bridging elements, and (3) effect of the chemical oxidation.

Table 1. Photophysical and Electrochemical Data for a Series of Si,S- or Si,Se-Bridged Distyrylbenzenes and Related Compounds

	absorption[a]		fluorescence[a]		redox potential[b]	
cmpd	$\lambda_{\max}$/nm[c]	log ϵ	$\lambda_{\max}$/nm[c]	Φ_F[d]	$E_{ox,1/2}$	$E_{red,1/2}$
5a	409	4.47	432(sh)[f]	0.56	0.71	*e*
5b	401	4.59	408	0.43	0.63, 1.00	*e*
5c	408	4.63	420	0.02	0.62	*e*
6a	442	4.43	470	0.91	*e*	−1.71, −2.00
6b	468(sh)[f]	4.35	507	0.50	*e*	−1.49, −1.90
7	394	4.73	408	0.75	0.70	*e*

[a] In THF. [b] Determined by cyclic voltammetry: 1 mM concentration of sample, with *n*-Bu_4NPF_6 (0.1 M) in CH_2Cl_2 or THF for oxidation or reduction, respectively. Potentials are given against ferrocene/ferrocenium couple (Fc/Fc$^+$). [c] Only the longest absorption and shortest emission maximum wavelengths are given. [d] Absolute fluorescence quantum yield, determined by a calibrated integrating sphere system. [e] Not observed. [f] The highest emission band for **5a** and highest absorption band for **6b** are located at 453 and 441 nm, respectively.



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For the absorption spectra in THF, the Si,S-bridged distyrylbenzenes **5a** and **5b** have their longest absorption maxima at 409 and 401 nm, respectively, while the fluorescence spectra of these compounds show an intense blue emission with the shortest maxima at 432 and 408 nm, respectively. The fluorescence quantum yields of **5a** and **5b** are 0.56 and 0.43, respectively. The significantly small Stokes shift of **5b** ($\Delta\nu_{\max}$ 427 cm^{-1}) is worthy of note, while that of **5a** is 1302 cm^{-1}. These comparisons demonstrate that the positions of the silylene and sulfur briges affect the electronic structure more significantly in the excited state.

A comparison of **5b** and **5c** shows the effect of the chalcogen elements. The selenophene derivative **5c** also shows a blue fluorescence at 420 nm, which is slightly longer than that of **5b**. As for the fluorescence quantum yield, **5c** has a significantly low value (Φ_F 0.02) compared to that of **5b**, probably due to the heavy element effect of the selenium. On the other hand, the comparison between **5a** and **7** indicates the effect of the silylene bridges. Comparing with **7**, **5a** shows a 24 nm red shift in the emission maxima, proving the effect of the silylene bridge. The orbital interaction between the silylene moiety and the π-conjugated framework may be responsible for this difference (vide infra).

The thiophene-*S*,*S*-dioxide derivatives **6a** and **6b** exhibit a greenish-yellow fluorescence. Their emission maxima red shift by about 40 and 100 nm compared to **5a** and **5b**, respectively. In addition, the oxidized derivatives **6a** and **6b** tend to have fluorescence quantum yields higher than those of **5a** and **5b**. The oxidation of the thiophene ring to the thiophene-*S*,*S*-dioxide loses the aromatic character of the

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thiophene ring, and the resulting π system should be regarded as the ladder distyrylbenzenes with the silylene bridges and the strongly electron-withdrawing SO_2 bridges. This difference is responsible for the red-shifted and enhanced fluorescence.

To obtain a deeper insight into the effect of the bridging elements, we carried out density functional theory (DFT) calculations (B3LYP/6-31G(d)) for **5**−**7**. Figure 4a shows the relative Kohn−Sham HOMO and LUMO energy levels. A comparison between **5a** and **7** demonstrates that the orbital interaction between the silylene bridges and π-conjugated framework mainly affects the LUMO level through the $\sigma^*-\pi^*$ conjugation (Figure 4b). This type of orbital interaction occurs more effectively in **5a** having the disilaindacene substructure compared to the case of **5b**.[12] Among the compounds, the *S*,*S*-dioxidized derivatives **6a** and **6b** have rather low-lying LUMOs, to which the SO_2 moiety significantly contributes, as shown in Figure 4b. In addition to the inductive effect of the SO_2 moiety, the effective $\sigma^*-\pi^*$ orbital interaction between the SO_2 moiety and π-conjugated skeleton must also play an important role for decreasing the LUMO levels.

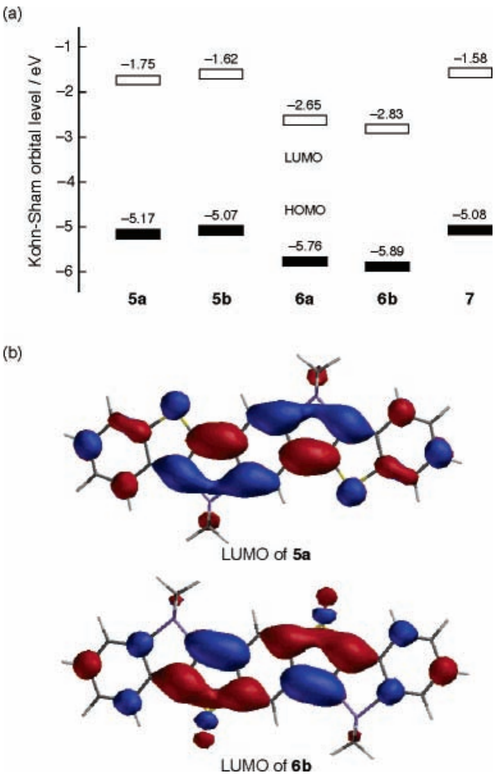

Figure 4. DFT calculations of **5**−**7** (B3LYP/6-31G(d)): (a) plot of the Kohn−Sham HOMO and LUMO energy levels and (b) pictographical presentation of the LUMOs of **5a** and **6b**.

We also evaluated the electrochemical properties by cyclic voltammentry. Figure 5 shows the cyclic voltammograms for **5** and **6**, and their data are listed in Table 1. Whereas **5** shows only reversible one-step or two-step oxidation waves, in sharp contrast the *S*,*S*-dioxidized derivatives **6** exhibit only reversible two-step reduction waves. These results confirm the significant electronic perturbation from the p-type to n-type by the oxidation of the sulfur atoms. In addition, the reversible redox processes observed for **6** are worth noting. The nonaromatic character of the thiophene-*S*,*S*-dioxide ring does not diminish the electrochemical stability.

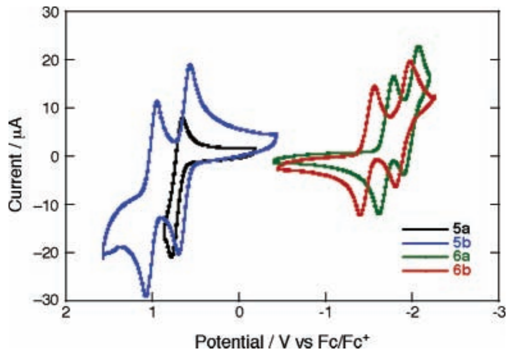

Figure 5. Cyclic voltammograms of **5** and **6**. Measurement conditions: sample 1 mM in CH_2Cl_2 for **5** and THF for **6** with *n*-Bu_4NPF_6 (0.1 M); scan rate 0.10 V s^{-1}.

In summary, a cascade-type anionic double cyclization allows us to synthesize a series of silicon and chalcogen (S or Se)-bridged distyrylbenzenes. The sulfur derivatives are further transformed into the *S*,*S*-dioxidized derivatives by chemical oxidation. All of the produced ladder compounds have coplanar π-conjugated frameworks, in which the substituents on the silicon atoms play an important role in regulating the packing structure. In addition, not only their intense fluorescences but also their reversible redox behavior indicate their potential use in organic electronic devices. Further study along this line is now in progress.

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Supporting Information Available: Experimental procedures, spectral data for all new compounds, and crystallographic data in CIF format and ORTEP drawings of **5** and **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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