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Coplanar Oligo(*p*-phenylenedisilenylene)s Based on the Octaethyl-Substituted *s*-Hydrindacenyl Groups

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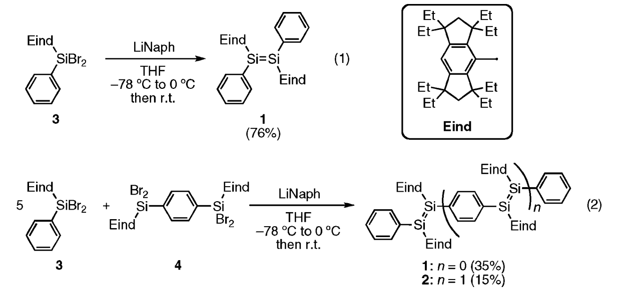
Since the stable silene (Si═C),[1] disilene (Si═Si),[2] and diphosphene (P═P)[3] were reported in 1981 by introducing a concept of steric protection with bulky substituents, a variety of unsaturated compounds of heavy main group elements have successfully been isolated by many leading scientists by using their own, newly developed bulky ligands.[4] The incorporation of multiple bonds of heavy main group elements into a π-conjugated framework would provide access to new potential materials for organic electronics. In this regard, several examples of oligomers and polymers comprising heavy multiple bonds, such as P═C,[5] P═P,[6] Si═Si,[7−9] Ge═C,[10]and Ge═Ge[11] bonds in the main chain, have recently been reported. However, this chemistry always suffers from a dilemma. While the steric protection by bulky ligands is essential to stabilize the highly reactive heavy multiple bonds, it causes the π-conjugated framework to twist, which reduces the extension of the π-conjugation. A key for the further evolution of this chemistry is undoubtedly to attain a well-defined ligand which can maintain the highly planar π-conjugated framework, in addition to providing sufficient steric protection of the reactive heavier multiple bonds.

We now present a new ligand, the 1,1,3,3,5,5,7,7-octaethyl-*s*-hydrindacen-4-yl (Eind) group.[12] By exploiting this ligand, we have succeeded in synthesizing the disilene analogues of the oligo(*p*-phenylenevinylene)s (Si-OPVs), disilastilbene **1** and tetrasiladistyrylbenzene **2** with highly coplanar π-conjugated frameworks. Their photophysical properties as well as X-ray single crystal analyses provide clear evidence for the effective extension of the π-conjugation. During the course of our investigation, Scheschkewitz et al. reported a 2,4,6-triisopropylphenyl-substituted tetrasiladistyrylbenzene derivative by a different route.[9]



The Eind-substituted Si-OPVs **1** and **2** were synthesized by the reductive coupling of the corresponding dibromosilanes **3** and **4** with lithium naphthalenide (LiNaph) in THF. Thus, the homocoupling reaction of the dibromosilane **3** afforded the disilastilbene **1** with an exclusively *E* configuration as orange crystals in 76% yield (eq 1), of which the structure was confirmed by X-ray crystallography (Figure S1). Similarly, the tetrasiladistyrylbenzene **2** was synthesized by the reductive coupling of the dibromosilane **3** and bis(dibromosilane) **4** in a 5:1 ratio (eq 2). After separation by silica gel column chromatography in a glovebox using degassed hexane and toluene as the eluent, the tetrasiladistyrylbenzene **2** was successfully isolated as purple-red crystals in 15% yield (based on **4**), together with the disilastilbene **1** in 35% yield (based on **3**) and unidentified purple higher oligomers. These disilenes are air-stable in the solid state (no decomposition in **1** was observed for at least 1 month), whereas they decomposed within 2 days in a dilute solution at room temperature in air. Their high stability demonstrated the effectiveness of the steric protection by the bulky Eind groups.

Figure 1 shows the crystal structure of **2**. Notably, the tetrasiladistyrylbenzene skeleton is entirely coplanar with the dihedral angle between the central and terminal benzene rings of 9.0°. It is also noteworthy that the Si═Si bonds adopt an almost planar geometry with the twist angles of 0.3 and 3.8° as well as the *trans*-bent angles of 0.7 and 2.7°.[13] The disilastilbene **1** also has an entirely planar geometry (Figure S1). The space-filling model (Figure 1c) shows that the *s*-hydrindacene planes of the Eind groups are orthogonal to the tetrasiladistyrylbenzene framework, and the peripheral ethyl groups effectively protect the Si═Si moieties without severe steric repulsion between themselves.

The high coplanarity, observed in **1** and **2**, is of interest, considering the fact that a disilene moiety usually has a bent and/or twisted geometry depending on the substituents.[14] In our case, within the disilene unit, the ethyl side chains on the *rigid* *s*-hydrindacene skeletons interlock with one another above and below the Si═Si moiety to enforce the planar geometry. The resulting cavity surrounded by the ethyl groups fixes the framework phenyl groups in a coplanar structure with the Si═Si plane, which is ideal for extension of the π-conjugation.

The photophysical data for **1** and **2** are summarized in Table 1, together with those of the recently reported **5**,[6] *trans*-stilbene **6**,[15] and *trans,trans*-1,4-distyrylbenzene **7**[16] for comparison. Their spectra show several features to be noted as follows: (1) The absorption maximum of **1** corresponding to the $\pi-\pi^*$ transition appears at 461 nm (ϵ 2.4 × 10^4), which is the longest value among those of the already known tetraaryldisilenes ($\lambda_{\max}$ 400−440 nm). (2) The tetrasiladistyrylbenzene **2** has an absorption maximum at 543 nm with a larger molar extinction coefficient (ϵ 3.0 × 10^4) compared to the disilastilbene **1**. (3) The $\lambda_{\max}$ of **2** is about 190 nm longer than that of the carbon analogue **7**, demonstrating that the incorporation of the Si═Si bonds into the π-conjugated system narrows the band gap. However, in terms of the degree of the extension of the π-conjugation, the shift of the absorption maximum

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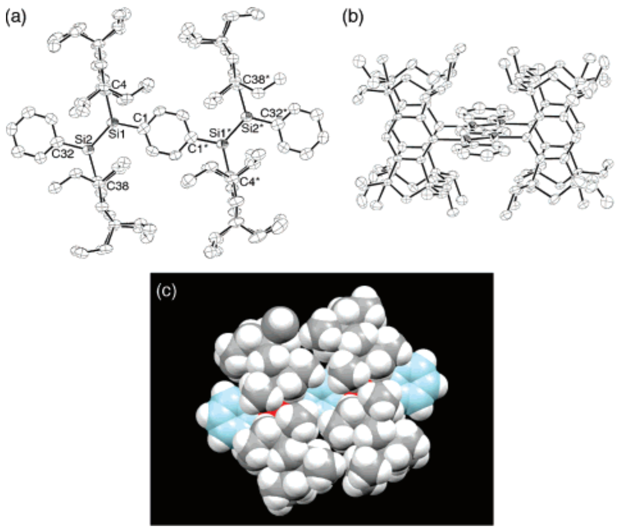

Figure 1. Crystal structures of **2**. ORTEP drawing (50% probability for thermal ellipsoids): (a) top view, (b) front view. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (°): Si1−Si2, 2.156(2); Si1−C1, 1.860(6); Si1−C4, 1.911(5); Si2−C32, 1.876(6); Si2−C38, 1.902(5); C1−Si1−C4, 114.5(3); C1−Si1−Si2, 120.4(2); C4−Si1−Si2, 125.12(19); C32−Si2−Si1, 117.51(19); C32−Si2−C38, 119.6(3); C38−Si2−Si1, 122.79(19); (c) space filling model: red, silicon; gray, carbon; white, hydrogen. Carbon atoms in the disilastyrylbenzene framework are colored light-blue for clarity.

Table 1. Photophysical Data of Disilenes **1** and **2** and Related Compounds[a]

	UV−vis absorption		fluorescence
cmpd	λ_{max}/nm (ν_{max}/cm^{-1})	ϵ/cm^{-1} M^{-1}	λ_{max}/nm (ν_{max}/cm^{-1})
1	461 (21700)	2.4×10^4	n.d.[b]
2	543 (18400)	3.0×10^4	612[c] (16300)
5[d]	508 (19700)	2.7×10^4	−
6[e]	295 (33900)	−	335 (29900)
7[f]	350 (28600)	−	385[g] (26000)

[a] Measured in *n*-hexane at room temperature. [b] Not detected. [c] Fluorescence quantum yield $\Phi_F = 0.10$, fluorescence lifetime $\tau_s = 1.8$ ns. [d] Scheschkewitz's 1,4-bis(disilenyl)benzene: $(Tip)_2Si{=}Si(Tip){-}C_6H_4{-}Si(Tip){=}Si(Tip)_2$ (**5**): Tip = 2,4,6-tri(isopropyl)phenyl (ref 9). [e] *trans*-Stilbene: PhCH=CHPh (**6**) (ref 15). [f] *trans*,*trans*-1,4-Distyrylbenzene: $PhCH{=}CH{-}C_6H_4{-}CH{=}CHPh$ (**7**) (ref 16). [g] In methylcyclohexane/3-methylpentane.

from **1** to **2** is 3300 cm^{-1} (0.41 eV), which is lower than that of the carbon counterparts (from **6** to **7**, 5300 cm^{-1}, 0.66 eV). The MO calculations for **2** indicate that the HOMO mainly localizes on the Si=Si bonds with little contribution from the phenylene moieties, while the LUMO delocalizes over the main chain.[17] This type of electronic structure may be responsible for the difference between the Si=Si containing OPVs and their carbon counterparts. (4) The absorption maximum of **2** is also red-shifted by 35 nm relative to that of Scheschkewitz's compound **5**, which has a slightly twisted π-conjugated framework. This difference reflects the effect of the extension of the π-conjugation over the highly planar tetrasiladistyrylbenzene skeleton in **2**. (5) While the disilastilbene **1** does not show any fluorescence, the extended **2** exhibits an orange fluorescence both in solution and in the solid state even at room temperature. The emission maximum was observed at 612 nm with the fluorescence quantum yield (Φ_F) and the fluorescence lifetime (τ_s) of 0.10 and 1.8 ns, respectively, in a hexane solution. To the best of our knowledge, this is the first example of a disilene derivative which exhibits a fluorescence at room temperature.[18] (6) The excitation spectrum of **2**[17] is almost identical to the absorption spectrum, indicating that the major conformer of **2** in solution is responsible for the fluorescence. The radiative rate constant (k_r) and nonradiative rate constant (k_{nr}) of **2** were 5.6×10^7 and 5.0×10^8 s^{-1}, respectively, according to the calculation with the experimental Φ_F and τ_s values. The experimental k_r value is comparable to the theoretical value of 8.5×10^7 calculated from the area of the lowest-energy absorption band.[19] These observations also support the assumption that the fluorescence is due to the predominant conformer in solution.

In summary, we have synthesized planar Si-OPVs **1** and **2** by introduction of a newly developed Eind ligand, which not only efficiently protects the reactive Si=Si bridge but also controls the Si-OPV framework to coplanar structure. Further investigation in synthesizing higher homologues of Si-OPVs and various π-extended systems is currently in progress.

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Supporting Information Available: Experimental details, spectral data, crystallographic data of **1** and **2** (PDF and CIF), and MO calculation results on **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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