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Air-Stable, Room-Temperature Emissive Disilenes with π-Extended Aromatic Groups

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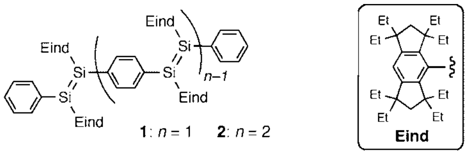
Abstract: π-Conjugated disilenes with 2-naphthyl or 2-fluorenyl groups on the silicon atoms have been synthesized as air-stable emissive red solids using the bulky 1,1,3,3,5,5,7,7-octaethyl-*s*-hydrindacen-4-yl (Eind) groups. The strong $\pi-\pi^*$ absorptions and distinct emission at room temperature, both in solution and in the solid state, have been observed due to the substantial contribution of the $3p_\pi^*$(Si−Si)−$2p_\pi^*$(carbon π-electron system) conjugation.

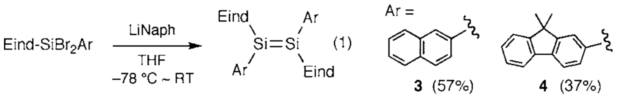
In 1981, West et al. introduced a concept of kinetic protection of the otherwise highly reactive Si=Si double bond by bulky mesityl groups, as well as Brook's and Yoshifuji's discoveries of the Si=C and P=P double bond compounds, respectively.[1] Since then, a variety of Si=Si double bond molecules have been synthesized employing the appropriately designed bulky groups[2,3] or bulky stable carbenes.[4]

During the course of our study on the π-conjugated organic architectures containing the heavy main group elements,[5] i.e., elemento-organic hybrid materials, we have recently started to investigate new π-conjugated disilenes and phosphasilenes, comprising the Si=Si and Si=P chromophores.[6] Thus, in 2007, Scheschkewitz's group[7] and we[8] independently reported the synthesis of model systems of disilene analogs of oligo(*p*-phenylenevinylene)s (Si-OPVs). In our case, for the synthesis of diphenyldisilene **1** and 1,4-bis(disilenyl)benzene **2**, we developed the rigid, fused-ring bulky 1,1,3,3,5,5,7,7-octaethyl-*s*-hydrindacen-4-yl (Eind) group as a new protecting group; the Eind groups encapsulate the reactive Si=Si moieties and produce the highly coplanar π-conjugated frameworks by their perpendicular orientation to and the interlocking ethyl side chains above and below the π-frameworks. Accordingly, the 1,4-bis(disilenyl)benzene **2** exhibits an orange fluorescence even at room temperature due to the efficient π-conjugation over the skeleton. It is emphasized that such a coplanar π-framework involving the Si=Si chromophore has so far been achieved only by our Eind group.

Following the successful achievement of **2** containing two disilene moieties on the central benzene ring, we have focused on the photophysical properties of the π-conjugated disilenes by installation of two π-extended aromatic groups to the central monodisilene unit.[9] We now report the isolation and characterization of Eind-substituted air-stable disilenes with 2-naphthyl or 2-fluorenyl groups, which do contain the highly coplanar π-frameworks and exhibit extensive emissions at room temperature both in solution and in the solid state.



1: $n = 1$ **2**: $n = 2$



(1)

3 (57%) **4** (37%)

The di(2-naphthyl)disilene **3** and di(2-fluorenyl)disilene **4** were straightforwardly synthesized by the reduction of the corresponding dibromosilanes with lithium naphthalenide in THF (eq 1). After removal of any insoluble materials and naphthalene, the disilenes **3** and **4** with an *E* configuration were isolated as red crystals in moderate yields, respectively. The disilenes **3** and **4** are quite air-stable; thus in the solid state, they can survive for more than a half year with no detectable change as confirmed by the ^{1}H NMR spectra. In a dilute hexane solution (*ca*. 10^{-5} mol/L), they decompose upon exposure to air, but slowly with a half-lifetime of *ca*. 2−4 h, much longer than that of $\mathrm{Tip_2Si{=}SiTip_2}$ (17 min),[10] as estimated by the UV−vis spectroscopy, indicative of the excellent protection ability of the Eind group.

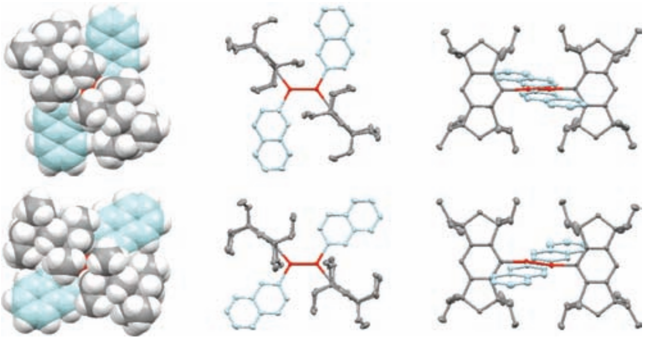


Figure 1. Molecualr structures of **3a** (top) and **3c** (bottom): space filling models (left), top views (center), and side views (right).

The X-ray crystallography of **3** showed that the Si atoms and the naphthyl groups are disordered over the two positions in the crystal, corresponding to a mixture of two rotational isomers, *s-cis*, *s-cis* (**3a**) and *s-trans*, *s-trans* (**3c**), with the occupancy factors of *ca*. 0.4/0.6.[11] Each molecule has an inversion center at the center of the Si=Si bond. Another *s-cis*, *s-trans* isomer (**3b**) has not been found in the crystal. Figure 1 shows the molecular structures of **3a** and **3c**, together with the space filling models, which demonstrate that the proximate ethyl groups of the Eind groups effectively protect the Si=Si fragment. Each isomer has an essentially coplanar

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di(2-naphthyl)disilene framework; the Si−Si−C−C torsion angles are 2.25(14)° for **3a** and 9.57(11)° for **3c**, respectively. The Si═Si bond distances of 2.1623(18) Å for **3a** and 2.1667(12) Å for **3c** are in the range of those for typical disilenes.[2] Similar rotational isomers have also been found in the crystal of **4**.[11]

Table 1. Photophysical Data of Disilenes **1**−**4**

compound[a]		λ_{max}(abs)/nm	ϵ/cm^{-1} M^{-1}	λ_{max}(em)/nm (Φ_F)	Stokes shift/cm^{-1}
1	hexane	461	2.4×10^4	n.d.[b]	
2	hexane	543	3.0×10^4	612 (0.10)	2080
3	THF	504	2.5×10^4	586 (0.01)	2780
	solid			619 (0.23)	
4	THF	510	3.0×10^4	575 (0.01)	2200
	solid			600 (0.20)	

[a] Solution or solid. [b] Not detected.

Some photophysical and electrochemical features are found as follows: (1) The UV−vis spectrum of **3** in THF shows an absorption maximum at 504 nm ($\epsilon = 2.5 \times 10^4$), which is 43 nm red-shifted from that of **1** ($\lambda_{max} = 461$ nm),[8] indicating the π-conjugation extension over the di(2-naphthyl)disilene skeleton (Table 1). The absorption peak of **4** appears at 510 nm with a higher molar extinction ($\epsilon = 3.0 \times 10^4$). (2) The disilenes **3** and **4** exhibit a weak but distinct fluorescence at room temperature in THF, thus in contrast to the fact that the diphenyldisilene **1** does not show any fluorescence in solution. The emission maxima are found at 586 nm for **3** and 575 nm for **4**. The Stokes shifts are calculated to be 2780 cm^{-1} for **3** and 2220 cm^{-1} for **4**, which are comparable to that of **2** (2080 cm^{-1})[8] but much lower than those observed for tetramesityldisilene and tetraneopentyldisilene, 4000 and 7300 cm^{-1}, respectively,[12] indicative of the structural rigidity of our compounds. (3) The disilenes exhibit strong emissions in the solid state, as shown in Figure 2. The quantum yields (Φ_F) are 0.23 for **3** and 0.20 for **4**, respectively, 20 times stronger than those in solution. The weaker fluorescence in solution may be ascribed to the free rotation of each aromatic group around the Si−C bond as observed by the ^{1}H NMR spectra.[11] (4) While the irreversible oxidation waves were observed at +0.07 V for **3** and +0.02 V for **4** by cyclic voltammetry,[13] comparable to that of **1** (+0.06 V), the quasi-reversible reduction waves are observed at −2.50 V for **3** and −2.59 V for **4**, whose values are lower than that of **1** (−2.66 V).

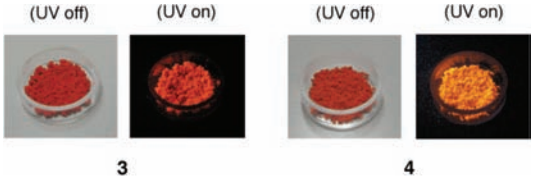

Figure 2. Photographs of **3** and **4** in air.

DFT calculations were performed for **3a**−**c** at the B3LYP/6-31G(d,p) level using the Gaussian 03 suite of programs.[14] The optimized structures of **3a** and **3c** reproduced the X-ray molecular structures. The missing isomer **3b** is also found to be a local minimum with a coplanar di(2-naphthyl)disilene skeleton.[11] These isomers have nearly the same energies; the relative energies are 0.00 (**3c**), 0.72 (**3b**), and 1.70 (**3a**) kcal mol^{-1}. Whereas the HOMOs are essentially represented by the 3p$_\pi$(Si−Si) orbital, the LUMOs involve the appreciable contribution of the 3p$_\pi$*(Si−Si)−2p$_\pi$*(naphthyl) conjugation. Thus, while the HOMO levels of **3a**−**c** (−4.249, −4.286, and −4.304 eV) are comparable to that of **1** (−4.253 eV), the LUMO levels of **3a**−**c** (−1.554, −1.488, and −1.478 eV) are lower than that of **1** (−1.330 eV), which are in good agreement with the electrochemical experimental results already mentioned.

The outstanding stability[15] of **3** and **4** would provide opportunities for future electronic and optoelectronic applications. Further investigations are now in progress.

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Supporting Information Available: Experimental details, CIF for **3** and **4**, DFT calculations, and full listing for ref 14. This material is available free of charge via Internet at http://pubs.acs.org.

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(15) These disilenes have a high thermal stability with the decomposition points of >280 °C under an argon atmosphere in a sealed tube. The temperatures at 5% weight loss (T_{d5}) are 356 °C for **3** and 308 °C for **4**, respectively.

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