

Air-Stable, Room-Temperature Emissive Disilenes with π -Extended Aromatic GroupsMegumi Kobayashi,[†] Tsukasa Matsuo,^{*,†} Takeo Fukunaga,[‡] Daisuke Hashizume,[‡] Hiroyuki Fueno,[§] Kazuyoshi Tanaka,[§] and Kohei Tamao^{*,†}

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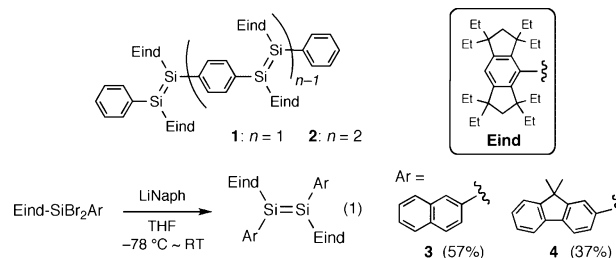
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Abstract: π -Conjugated disilenes with 2-naphthyl or 2-fluorenyl groups on the silicon atoms have been synthesized as air-stable emissive red solids using the bulky 1,1,3,3,5,5,7,7-octaethyl-*s*-hydrindacen-4-yl (Eind) groups. The strong π - π^* absorptions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

In 1981, West et al. introduced a concept of kinetic protection of the otherwise highly reactive $\text{Si}=\text{Si}$ double bond by bulky mesityl groups, as well as Brook's and Yoshifuji's discoveries of the $\text{Si}=\text{C}$ and $\text{P}=\text{P}$ double bond compounds, respectively.¹ Since then, a variety of $\text{Si}=\text{Si}$ 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 $\text{Si}=\text{Si}$ and $\text{Si}=\text{P}$ chromophores.⁶ Thus, in 2007, Scheschkevit's group⁷ and we⁸ 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 $\text{Si}=\text{Si}$ 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 $\text{Si}=\text{Si}$ 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.



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 ¹H 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 $\text{Tip}_2\text{Si}=\text{SiTip}_2$ (17 min),¹⁰ as estimated by the UV-vis spectroscopy, indicative of the excellent protection ability of the Eind group.

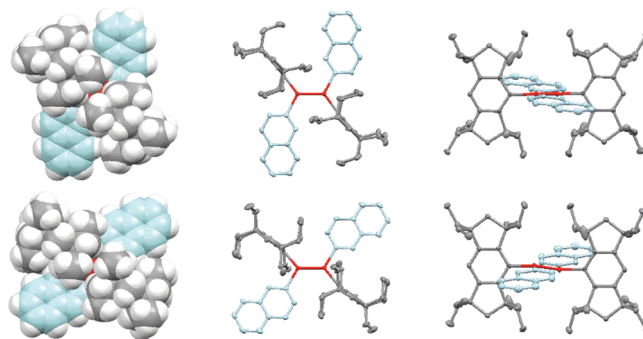


Figure 1. Molecular structures of **3a** (top) and **3c** (bottom): space filling models (left), top views (center), and side views (right).

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 $\text{Si}=\text{Si}$ 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 $\text{Si}=\text{Si}$ 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	$\lambda_{\text{max}}(\text{abs})/\text{nm}$	$\epsilon/\text{cm}^{-1} \text{ M}^{-1}$	$\lambda_{\text{max}}(\text{em})/\text{nm}$ (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** ($\lambda_{\text{max}} = 461$ 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 2200 cm^{-1} for **4**, which are comparable to that of **2** (2080 cm^{-1})⁸ but much lower than those observed for tetramesityldisilene and tetraeneopentylidene, 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 ¹H 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).

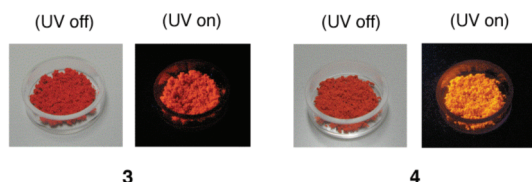


Figure 2. Photographs of **3** and **4** in air.

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_π(Si–Si) orbital, the LUMOs involve the

appreciable contribution of the 3p_π*(Si–Si)–2p_π*(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 stability¹⁵ 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>.

References

- (1) (a) West, R.; Fink, M. J.; Michl, J. *Science* **1981**, *214*, 1343. (b) Brook, A. G.; Abdesaken, F.; Gutekunst, B.; Gutekunst, G.; Kallury, R. L. *J. Chem. Soc., Chem. Commun.* **1981**, 191. (c) Yoshifuji, M.; Shima, I.; Inamoto, N. *J. Am. Chem. Soc.* **1981**, *103*, 4587.
- (2) For reviews, see: (a) Okazaki, R.; West, R. *Adv. Organomet. Chem.* **1996**, *39*, 231. (b) Power, P. P. *Chem. Rev.* **1999**, *99*, 3463. (c) Lee, Y. Y.; Sekiguchi, A. *Organometallics* **2004**, *23*, 2822. (d) Kira, M.; Iwamoto, T. *Adv. Organomet. Chem.* **2006**, *54*, 73. (e) Wang, Y.; Robinson, G. H. *Chem. Commun.* **2009**, 5201.
- (3) For recent examples, see: (a) Weidenbruch, M.; Willms, S.; Saak, W.; Henkel, G. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2503. (b) Iwamoto, T.; Tamura, M.; Kabuto, C.; Kira, M. *Science* **2000**, *290*, 504. (c) Ishida, S.; Iwamoto, T.; Kabuto, C.; Kira, M. *Nature* **2003**, *421*, 725. (d) Kinjo, R.; Ichinohe, M.; Sekiguchi, A.; Takagi, N.; Sumitomo, M.; Nagase, S. *J. Am. Chem. Soc.* **2007**, *129*, 7766. (e) Sasamori, T.; Yuasa, A.; Hosoi, Y.; Furukawa, Y.; Tokitoh, N. *Organometallics* **2008**, *27*, 3325. (f) Abersfelder, K.; White, A. J. P.; Rzepa, H. S.; Scheschkewitz, D. *Science* **2010**, *327*, 564. (g) Sato, T.; Mizuhata, Y.; Tokitoh, N. *Chem. Commun.* **2010**, *46*, 4402.
- (4) Wang, Y.; Xie, Y.; Wei, P.; King, R. B.; Schaefer, H. F., III; Schleyer, P. v. R.; Robinson, G. H. *Science* **2008**, *321*, 1069.
- (5) For reviews, see: (a) Yamaguchi, S.; Akiyama, S.; Tamao, K. *J. Organomet. Chem.* **2002**, *652*, 3. (b) Yamaguchi, S.; Tamao, K. *Chem. Lett.* **2005**, *34*, 2. (c) Matsuo, T.; Kobayashi, M.; Tamao, K. *Dalton Trans.* **2010**, 39, 9203.
- (6) Li, B.; Matsuo, T.; Hashizume, D.; Fueno, H.; Tanaka, K.; Tamao, K. *J. Am. Chem. Soc.* **2009**, *131*, 13222.
- (7) Bejan, I.; Scheschkewitz, D. *Angew. Chem., Int. Ed.* **2007**, *46*, 5783.
- (8) Fukazawa, A.; Li, Y.; Yamaguchi, S.; Tsuji, H.; Tamao, K. *J. Am. Chem. Soc.* **2007**, *129*, 14164.
- (9) The intramolecular charge-transfer transition of the 9-anthryldisilene has been reported, in which the anthryl group is orthogonal to the Si=Si bond; see: Iwamoto, T.; Kobayashi, M.; Uchiyama, K.; Sasaki, S.; Nagendran, S.; Isobe, H.; Kira, M. *J. Am. Chem. Soc.* **2009**, *131*, 3156.
- (10) Watanabe, H.; Takeuchi, K.; Fukawa, N.; Kato, M.; Goto, M.; Nagai, Y. *Chem. Lett.* **1987**, *16*, 1341.
- (11) See Supporting Information for details.
- (12) (a) West, R. *Pure Appl. Chem.* **1984**, *56*, 163. (b) Shizuka, H.; Tanaka, H.; Okazaki, K.; Kato, M.; Watanabe, H.; Nagai, Y.; Ishikawa, M. *J. Chem. Soc., Chem. Commun.* **1986**, 748.
- (13) (a) Shepherd, B. D.; West, R. *Chem. Lett.* **1988**, *17*, 183. (b) Kira, M.; Ishima, T.; Iwamoto, T.; Ichinohe, M. *J. Am. Chem. Soc.* **2001**, *123*, 1676. (c) Schäfer, A.; Weidenbruch, M.; Müller, T.; Pravinkumar, K.; Becker, J. Y. *Chem.–Eur. J.* **2009**, *15*, 8424.
- (14) Frisch, M. J. *Gaussian 03*, revision E.01; Gaussian Inc.: Wallingford, CT, 2004.
- (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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