(Z)-1,2-Di(1-pyrenyl)disilene: Synthesis, Structure, and Intramolecular Charge-Transfer Emission

Megumi Kobayashi,[†] Naoki Hayakawa,[‡] Tsukasa Matsuo,*,[†,‡,§] Baolin Li,[†] Takeo Fukunaga,[∥] Daisuke Hashizume,[∥] Hiroyuki Fueno,[⊥] Kazuyoshi Tanaka,[⊥] and Kohei Tamao*,[†,#]

[†]Functional Elemento-Organic Chemistry Unit, RIKEN Advanced Science Institute, 2-1 Hirosawa, Wako, Saitama 351-0198, Japan

[‡]Department of Applied Chemistry, Faculty of Science and Engineering, Kinki University, 3-4-1 Kowakae, Higashi-Osaka 577-8502, Japan

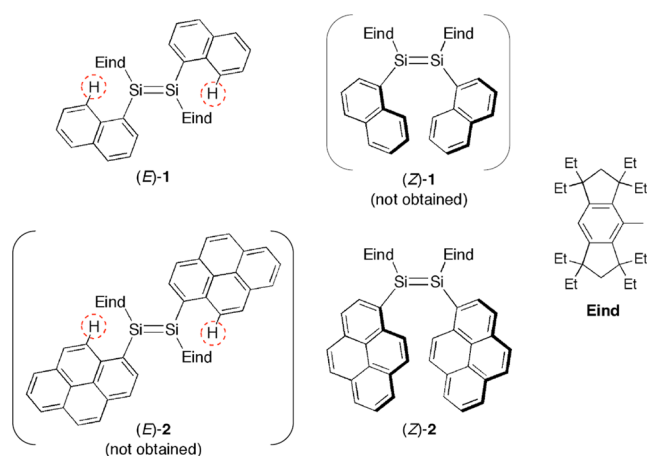[§]JST, PRESTO, 4-1-8 Honcho Kawaguchi, Saitama 332-0012, Japan

[∥]Materials Characterization Support Unit, RIKEN Center for Emergent Matter Science (CEMS), 2-1 Hirosawa, Wako, Saitama 351-0198, Japan

[⊥]Department of Molecular Engineering, Graduate School of Engineering, Kyoto University, Nishikyo-ku, Kyoto 615-8510, Japan

S *Supporting Information*

ABSTRACT: (Z)-1,2-Di(1-pyrenyl)disilene containing bulky 1,1,3,3,5,5,7,7-octaethyl-s-hydrindacen-4-yl (Eind) groups has been obtained as purple crystals by the reductive coupling reaction of the corresponding dibromosilane with lithium naphthalenide. An X-ray crystallographic analysis revealed an Eind- and pyrenyl-meshed molecular gear around the disilene core adopting the Z configuration, in which the two pyrenyl groups intramolecularly interact through the π−π stacking with a distance of 3.635 Å between the centers of the two pyrene rings. The disilene π-system exhibits a π(Si−Si) → π*(pyrene) intramolecular charge-transfer (ICT) fluorescence at room temperature, whose wavelengths depend on the solvent polarity. The photophysical properties are theoretically supported by computational studies including excited-state calculations.

Figure 1. 1,2-Di(1-naphthyl)disilene **1** and 1,2-di(1-pyrenyl)disilene **2** together with the structure of Eind group.

The intrinsic electronic communications between unsaturated bonds of the heavier main group elements[1] and carbon π-electron systems have recently been studied from the view points of their potentially useful properties and unique functions.[2] For example, a variety of disilene π-systems incorporating Si═Si double bond(s) have been developed by us[3] and other research groups,[4,5] based on the concept of kinetic stabilization featuring bulky protecting groups.[6] In our series of studies based on the fused-ring bulky 1,1,3,3,5,5,7,7-octa-R-substituted-s-hydrindacen-4-yl (Rind) groups,[7] we reported the highly coplanar π-conjugated (E)-1,2-diaryldisilene derivatives containing the phenyl, 1-naphthyl, and 2-naphthyl groups on silicon atoms as the first members of air-stable, room-temperature emissive aryldisilenes.[3] Recently, we found that even the (E)-1,2-di(1-naphthyl)disilene, (E)-**1**, has a highly coplanar diaryldisilene skeleton despite the existence of the *peri*-H atom in the 1-naphthyl groups (Figure 1); in addition, rather unexpectedly, the *peri*-H atom participates in the CH−π interaction with the aromatic ring of the perpendicularly oriented Rind groups.[3e] This unexpected result prompted us to investigate the further π-extended diaryldisilene molecules by introduction

of polycyclic aromatic groups. We now find, very unexpectedly, that in the 1-pyrenyl case, which also has the *peri*-H atom, only the Z isomer, (Z)-1,2-di(1-pyrenyl)disilene, (Z)-**2**, is exclusively obtained in which the two 1-pyrenyl groups are twisted from the Si═Si bond to cause the intramolecular π−π stacking. This report deals with the synthesis, structural aspects, and the photophysical properties of (Z)-**2**, focusing on the fluorescence originating from the intramolecular charge-transfer (ICT) excited state due to electron transfer from the disilene unit to the twisted pyrene rings.[8]

As illustrated in Scheme 1, a precursor for **2**, the Eind- and 1-pyrenyl-substituted dibromosilane, (Eind)(1-pyrenyl)SiBr₂ (**4**), was prepared by the reaction between tribromosilane (Eind)SiBr₃ (**3**) and 1-pyrenyllithium in Et₂O. The subsequent treatment of **4** with a sufficient amount of lithium naphthalenide (LiNaph) in THF resulted in the formation of a deep purple solution, from which purple crystals of **2** were obtained. The NMR measurements of the purple crystals indicate the formation

Scheme 1. Synthesis of Disilene (Z)-2
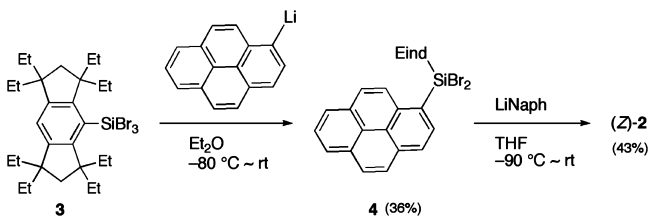
of **2** as a sole product, with no sign of geometrical isomerization in solution. For example, the ^{29}Si NMR spectrum in C_6D_6 at 293 K exhibits only one resonance at 58.7 ppm, characteristic of the disilene silicon atoms.[1] Compound **2** is, however, not thermally stable in solution and decomposes in C_6D_6 at 333 K with a gradual fading in color within about a half day.[9] This disilene **2** is not very stable in the air even in the solid state, in sharp contrast to other (E)-1,2-diaryldisilenes, like (E)-**1**, protected by the Eind groups, which show a high air-stability of more than several years.[3]

The molecular structure of **2** was determined by a single-crystal X-ray diffraction analysis to have a unique Z configuration, as shown in Figure 2. In this (Z)-**2**, the Eind and 1-pyrenyl groups fit together in a gear-like arrangement around the disilene core with the typical Si=Si bond length[1] of 2.1718(6) Å and rather small trans-bent angles of 8.22(8) and 2.96(8)°. The two pyrene rings are no longer in-plane with the Si=Si bond, but substantially twisted with the torsion angles of 52.66(13)° for Si2−Si1−C57−C70 and 48.73(14)° for Si1−Si2−C73−C86. In the crystal, the two pyrene rings closely interact through π−π stacking, but not completely parallel to each other; some pertinent inter-ring distances are as follows: the two ipso-carbon atoms C57···C73 = 3.636(2) Å, the two end carbon atoms C64···C80 = 4.036(3) Å, and the distance between the centers of the two pyrene rings = 3.635 Å.

This is the first example of the selective formation of the Z isomer of the acyclic disilene via reductive coupling of monosilane precursors.[9,10] To estimate the relative stability of the E and Z isomers of **1** and **2**, we performed DFT computations at the B3LYP/6-31G(d,p) level using the Gaussian 09 program package.[11] In **1**, the E isomer is more thermodynamically favorable than the Z isomer. Thus, (E)-**1** is 8.26 kcal mol^{-1} more stable than (Z)-**1**, being in agreement with the experimental results.[3e] The missing (E)-**2** is also 5.21 kcal mol^{-1} more stable than (Z)-**2**. We also examined the optimized structures of the isomers of **2** using the hybrid B3LYP and the long-range correction by the Coulomb-attenuating method (CAM) at the CAM-B3LYP/6-31G(d,p) level,[12] showing that (E)-**2** is 4.71 kcal mol^{-1} more stable than (Z)-**2**. In sharp contrast to these data, (Z)-**2** is found to be 5.01 kcal mol^{-1} more stable than (E)-**2** by using the semiempirical generalized gradient approximation (GGA) type density functional constructed with a long-range dispersion correction at the B97-D/6-31G(d,p) level.[13] These results demonstrate that the theoretical estimation of the relative stability of the E and Z isomers of **2** would not be helpful to figure out a plausible mechanism, either kinetic or thermodynamic control, for the selective formation of (Z)-**2**. Thus, the mechanism to produce (Z)-**2** is not currently clear, but an attractive π−π interaction between the pyrenyl groups may play a role in determining the stereochemistry somewhere in the Si−Si bond-forming processes.[14] The reaction course to the two geometrical isomers, the (E)- and (Z)-diaryldisilenes, may be determined with respect to the π-extension of the aromatic rings;
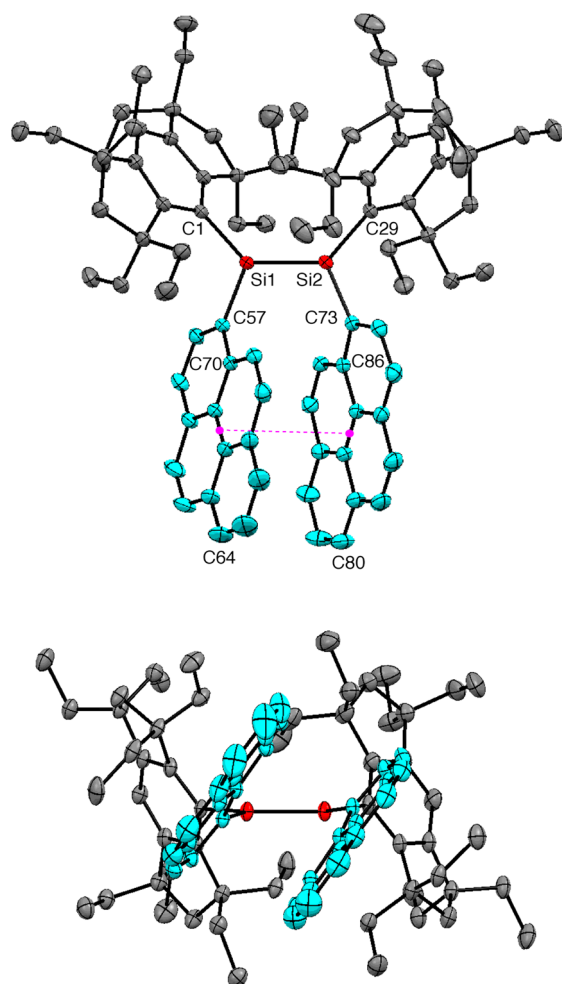
Figure 2. Molecular structures of (Z)-**2** (50% probability ellipsoids): top view (top) and front view (bottom). Hydrogen atoms and disordered ethyl groups are not shown. Selected atomic distances (Å), bond angles (deg), and torsion angles (deg): Si1−Si2 = 2.1718(6), Si1−C1 = 1.9050(14), Si1−C57 = 1.8778(14), Si2−C29 = 1.8979(14), Si2−C73 = 1.8808(15), C57···C73 = 3.636(2), C64···C80 = 4.036(3), the distance between the two pyrene ring centers (purple dotted line) = 3.635, C1−Si1−Si2 = 131.30(5), C1−Si1−C57 = 116.98(6), C57−Si1−Si2 = 111.62(6), C29−Si2−Si1 = 130.91(5), C29−Si2−C73 = 114.53(7), C73−Si2−Si1 = 113.78(5), Si2−Si1−C57−C70 = 52.66(13), Si1−Si2−C73−C86 = 48.73(14).

the bicyclic naphthalene ring to the E isomer vs the tetracyclic pyrene ring to the Z isomer.

Some photophysical data of (Z)-**2** are summarized in Table 1 together with some pertinent (E)-**1**[3e] data for comparison. Figure 3 reproduces the absorption and emission spectra of (Z)-**2** in a THF solution together with the solid state emission. Several features are as follows: (1) The UV−vis spectrum of (Z)-**2** in THF shows two broad absorption bands with the absorption maxima λ_{max}(abs) at 519 nm (sh, $\varepsilon = 6.1 \times 10^3$) and 575 nm ($\varepsilon = 7.2 \times 10^3$) together with a strong absorption around 350 nm due to the pyrene ring itself. The λ_{max}(abs) values are not significantly dependent on the solvent polarity.[15] (2) The disilene (Z)-**2** emits light with a low Φ_F in solution (0.99×10^{-5} to 2.02×10^{-4} M) and in the solid state at room temperature. In contrast to (E)-**1**, the emission maximum λ_{max}(em) of (Z)-**2** is dependent on the solvent polarity and red-shifted from 661 nm in hexane to 676 nm in THF and to 694 nm in acetone. The emission color change of (Z)-**2** in three different solvents is reproduced in

Table 1. Photophysical Data of Disilenes (E)-1 and (Z)-2

compd	state[a]	λ_{max}(abs) nm	ε cm^{-1} M^{-1}	λ_{max}(em) nm (Φ_F)[b]
(E)-1[c]	hexane	519	8.9×10^3	596 (<0.01)
	THF	521	9.5×10^3	614 (<0.01)
	acetone	529	3.9×10^3	609 (<0.01)
	solid			635 (0.05)
(Z)-2	hexane	506	2.6×10^3	661 (0.03)[e]
		566(sh)[d]	2.0×10^3	
	THF	519(sh)	6.1×10^3	676 (0.03)[e]
		575[d]	7.2×10^3	
	acetone	508	4.6×10^3	694 (0.03)[e]
		564(sh)[d]	3.7×10^3	
	solid			712 (0.04)

[a]In solution or in the solid state. Dielectric constant: hexane 1.88, THF 7.58, acetone 20.56 (ref 15). [b]During irradiation at 365 nm. Φ_F = quantum yield of emission. [c]The data is from ref 3e. [d]There is also a strong absorption around 350 nm due to the pyrene ring itself. [e]Weak emission of pyrene excimer is also observed around 450 nm due to partial decomposition of (Z)-2 during measurements of the emission spectra.
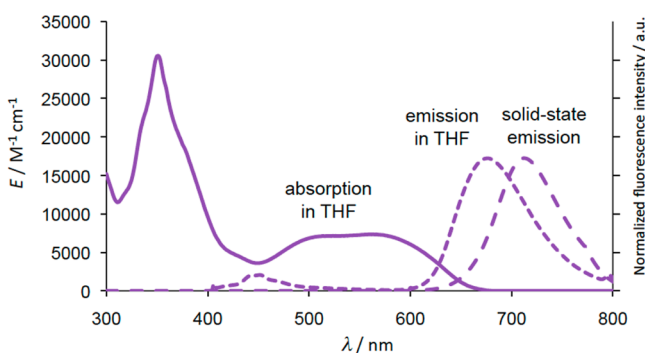

Figure 3. UV−vis absorption and emission spectra of (Z)-2 in THF solution together with the solid state emission spectrum.

Figure 4. All of these results suggest the intramolecular charge transfer (ICT) emission based on the two pyrenyl groups twisted from the Si═Si bond.

Figure 5 shows the three pertinent molecular orbitals of (Z)-2. While the HOMO mainly consists of the π(Si−Si) orbital with almost no contribution of the π(pyrene) orbital, the LUMO involves a substantial π^*(Si−Si)−π^*(pyrene) conjugation. The slightly high-lying LUMO+1 is primarily represented by the π^*(pyrene) orbital. The absorption wavelengths are determined

Figure 4. Photographs showing the effect of solvent polarity on the emission color of (Z)-2 when excited by 365 nm light: (left to right) hexane, THF, and acetone.
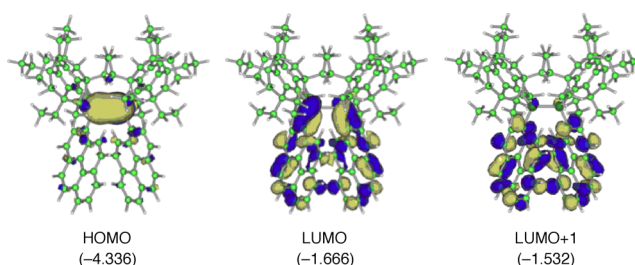

Figure 5. Selected molecular orbitals of (Z)-2 (top view) together with the energy levels (eV) in parentheses.

to be 566 and 538 nm based on the TD-DFT calculations, comparable to the observed values, each of which is mainly assignable to the HOMO → LUMO and HOMO → LUMO+1 transitions.

Since the π-extended pyrene would act as an excellent π-acceptor due to its low-lying LUMO, we have also investigated the optimized structure of (Z)-2 in the first excited singlet state by the TD-DFT method. The results are summarized as follows: (1) The two pyrenyl groups twisted from the Si═Si bond more closely interact in the excited state, similar to the intramolecular excimer formation.[16,17] Thus, the theoretical distances between the two pyrene rings in the first excited state (C57···C73 = 3.3326, C64···C80 = 4.0617, and the distance between the two pyrene ring centers = 3.8406 Å) are significantly smaller than those in the ground state (C57···C73 = 3.5190, C64···C80 = 6.1245, and the distance between the two pyrene ring centers = 4.6778 Å). (2) The emission wavelengths are 617 and 765 (weaker) nm based on the computations of the absorption wavelengths of the optimized excited-state structure as a ground state, comparable to the experimental values. (3) While the Si═Si bond distance is elongated from 2.2004 to 2.3082 Å upon excitation, the Si−C$_{ipso}$(pyrene) distances are shortened from 1.9025 to 1.8463 Å, demonstrating that (Z)-2 has the lower double-bond character of the Si═Si bond in the excited state. This is totally in accordance with the Wiberg bond index (WBI);[18] the Si−Si bond order in the excited state (1.140) is much lower than that in the ground state (1.702). (4) The natural population analysis (NPA) charge distribution[19] exhibits a more charge-separated character for the di(1-pyrenyl)disilene skeleton in the excited state compared to the ground state; the Si atoms are more positive (+1.046 vs +0.822) and the C$_{ipso}$(pyrene) atoms are more negative (−0.621 vs −0.488). These electronic configurations are consistent with the π(Si−Si) → π^*(pyrene) ICT excited state originating from the electron transfer from the disilene π-donor toward the pyrene π-acceptor.

■ ASSOCIATED CONTENT

ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b11970.

Experimental details and details of the calculations (PDF)
Crystallographic data for (Z)-2 (CIF)

■ AUTHOR INFORMATION

Corresponding Authors
*t-matsuo@apch.kindai.ac.jp
*tamao@riken.jp

Present Address
#RIKEN Global Research Cluster, 2−1 Hirosawa, Wako, Saitama 351−0198, Japan

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