Synthesis and Photochemical Properties of Stilbenophanes Tethered by Silyl Chains. Control of ($2\pi + 2\pi$) Photocycloaddition, Cis−Trans Photoisomerization, and Photocyclization

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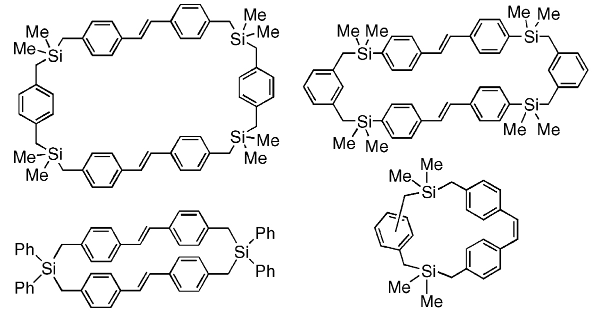
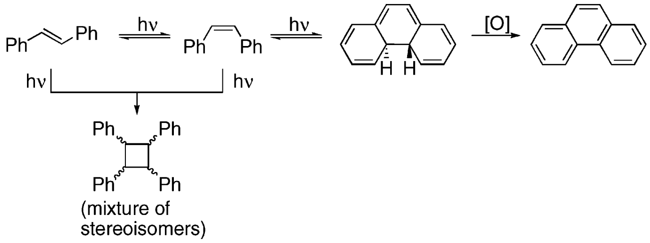


Novel macrocyclic and medium-size stilbenophanes tethered by silyl chains were synthesized, and their photochemical and photophysical properties were examined. Direct photoirradiation of macrocyclic stilbenophanes gave intramolecular photocycloadducts stereoselectively, and the efficiency increased with decreasing distance between the two stilbene units. The triplet-sensitized photoreaction of stilbenophanes caused cis−trans photoisomerization. Photoreactions of cis-fixed stilbenophanes under an oxygen atmosphere selectively gave phenanthrenophanes. Fluorescence quantum yields increased with the introduction of silyl substituents, and hence those of silyl-tethered stilbenophanes were larger than that of unsubstituted *trans*-stilbene. Intramolecular excimer emission was observed when the distances between two stilbene units in the stilbenophanes were sufficiently small.

Introduction

Photochemical properties and reactivities of stilbene and its derivatives have been extensively investigated in the last few decades.[1] Three types of photochemical reactions of stilbenes are known: (1) cis−trans photoisomerization,[2] (2) photodimerization or cross-photocycloaddition with alkenes and arenes,[3] and (3) photochemical conversion to phenanthrene derivatives via oxidative dehydrogenation of dihydrophenanthrenes[4] (Scheme 1). Among these, the cis−trans photoisomerization of stilbene is the most frequent process ($\Phi_{t-c} = 0.55$, $\Phi_{c-t} = 0.35$).[5] Photocyclization of *cis*-stilbene to give dihydrophenanthrene is a reversible process, and the quantum yield is not as high ($\Phi \approx 0.1$).[6] However, it is a synthetically useful pathway; photoreaction of stilbene derivatives at concentrations of 10^{-2} M or less minimizes the competing photodimerization in the presence of oxidants such as oxygen or iodine and gives phenanthrene derivatives in high yields. Although intermolecular photodimerization of stilbene and its derivatives is a promising

SCHEME 1. Photochemistry of Stilbenes



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process for synthesizing cyclobutane compounds, it is not an efficient process in contrast to cross-photocycloaddition, even at high concentration ($\sim 10^{-1}$ M). Moreover, because photodimerization competes with cis−trans photoisomerization, dimerized products contain a variety of regio- and stereoisomers. To overcome these problems, extensive efforts have been made. For example, photodimerization is accelerated in hydrophilic solvents such as water[7] and methanol.[8] Microcavities, for example in zeolites[9] and cyclodextrins,[10] rotaxane interaction,[11] stilbene polymers,[12] and photoirradiation to stilbene crystals,[13] have also been employed for the acceleration of the photodimerization.[14] These results can be interpreted as indicating that diminishing the distance between two stilbene double bonds is necessary for accelerating the photodimerization of stilbenes. This background prompted us to design a selective and highly efficient set of three types of photoreactions by use of stilbenophanes.

The synthesis, as well as the photochemical and photophysical properties of stilbenophanes, is less known.[15,16] The only example of a photochemical study of stilbenophanes is that of [2.2]stilbenophane reported by Wennerström et al.,[15a,b] wherein attention was focused in particular on the cis−trans photoisomerization of [2.2]-stilbenophane, but the intramolecular photodimerization of the stilbenophane was not investigated. We chose silyl chains for the connection of stilbenes, because silyl tethers can be easily removed after the event. Moreover, because of a relatively slow intersystem crossing of organosilicon compounds,[17] selective generation of excited singlet and triplet states is expected. We report herein the syntheses and photochemical properties of novel macrocyclic and medium-size stilbenophanes tethered by silyl chains. By forcing stilbenes to be a part of cyclic compounds by virtue of silyl tethers, we achieved selective occurrence of three types of photochemical reactions of stilbenes. In particular, dramatic acceleration of photodimerization can be developed depending on the distance between two stilbene units.

Results and Discussion

Synthesis of Stilbenophanes and Related Compounds. Stilbenophanes **1**−**3** were designed and synthesized as candidates having appropriate distances between two stilbene units (Scheme 2). Stilbenophanes **4a**−**c** were obtained as cis-fixed stilbenophanes. For reference compounds, 4,4′-bis(trimethylsilylmethyl)stilbene *trans*-**5** and 4,4′-bis(trimethylsilyl)stilbene *trans*-**6** were also prepared.

Syntheses of stilbenophanes **1**−**4** and related compounds **5** and **6** are shown in Schemes 3−5 and Scheme S1 (see Supporting Information). Grignard reaction of xylylene dichlorides **7a**−**c** with chlorodimethylsilane gave hydrosilanes **8a**−**c**, which were converted to chlorosilanes **9a**−**c** by treatment with $PdCl_2/CCl_4$ (Scheme 3). Chlorosilanes **9a**−**c** were then allowed to react with Mg and *p*-vinylbenzyl chloride to give bis[(*p*-vinylphenyl)methyl] derivatives **10a**−**c** in high yields. Para-substituted macrocyclic and medium-size stilbenophanes, *trans*,*trans*-**1** and **4c**, were prepared by ozonolysis of **10c** in the presence of Zn/AcOH followed by the McMurry coupling reaction[18] of **11c** by $TiCl_4$/Zn. Ortho- and meta-substituted medium-size stilbenophanes **4a**,**b** were synthesized via the McMurry coupling reaction of **11a**,**b**.

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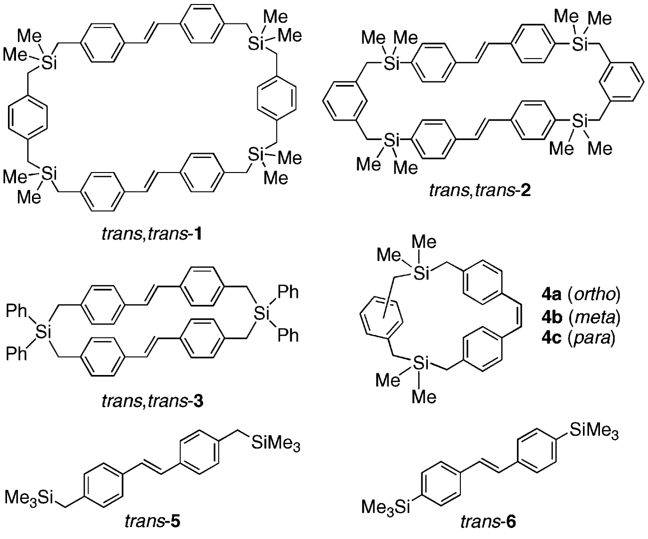
SCHEME 2. Stilbenophanes and Related Compounds



trans,*trans*-**2** was synthesized as follows. 4,4′-Dibromostilbene **12**, which was prepared by McMurry coupling of *p*-bromobenzaldehyde, was lithiated by *t*-BuLi to give 4,4′-dilithiostilbene (Scheme 4). This was then allowed to react with 1,3-bis(chlorodimethylsilylmethyl)benzene **9b** to afford stilbenophane *trans*,*trans*-**2** in 2.6% yield.

Synthesis of the smallest stilbenophane **3**, having two stilbene units, is shown in Scheme 5. A Grignard coupling reaction between dichlorodiphenylsilane and *p*-(chloromethyl)styrene produced **13**.[19] Ozonolysis of **13** followed by McMurry coupling of **14** gave *cis*,*cis*-**3** in 1.1% yield, but the desired trans,trans isomer was not obtained (vide infra).

See the Supporting Information about the synthesis of *trans*-**5** and *trans*-**6** (Scheme S1).

Structures of Stilbenophanes. The structures of the stilbenophanes *trans*,*trans*-**1**, *trans*,*trans*-**2**, *cis*,*cis*-**3**, and **4a**–**c** were determined on the basis of their spectral and analytical data, and confirmed by X-ray crystallographic analysis of *trans*,*trans*-**1** and *cis*,*cis*-**3** (Figures S1 and S2). X-ray crystallographic analysis of *trans*,*trans*-**1** showed a partial loss of planarity of the stilbene units (Figure S1). The distance between two stilbene double bonds is about 7 Å, and the two stilbene units align like stairs. X-ray crystallographic analysis of *cis*,*cis*-**3** clearly showed its cis,cis structure (Figure S2). Geometry optimization of *trans*,*trans*-**3** via an HF/3-21G* calculation showed a bent structure of the *trans*-stilbene units having 29.2 kJ/mol higher enthalpy than that of *cis*,*cis*-**3**. Indeed, the only isolable isomer was the cis,cis one in the McMurry coupling reaction of **14**.

UV Absorption of Stilbenophanes. A UV absorption spectrum of the stilbenophane *trans*,*trans*-**1** was measured in CH_2Cl_2, and was compared with those of *trans*-**5** and *trans*-stilbene at the same concentration (2×10^{-5} M) (Figure S3). Absorption maxima for both *trans*,*trans*-**1** and *trans*-**5** appeared at 328 nm, and shoulder peaks were detected for both at 345 nm. These wavelengths were shifted to a wavelength ca. 20 nm longer than those of unsubstituted *trans*-stilbene. The absorbance of *trans*,*trans*-**1** (ϵ(328 nm) = 5.86×10^4 M^{-1} cm^{-1}) was 1.5 times larger than that of *trans*-**5** (ϵ(328 nm) = 3.97×10^4 M^{-1} cm^{-1}), and the integrated absorption of *trans*,*trans*-**1** (>258 nm) was 1.64 times larger than that of *trans*-**5**, although *trans*,*trans*-**1** contains two stilbene units per molecule. These results may be due to the rigidity of the stilbene units in *trans*,*trans*-**1**.[20] A UV absorption spectrum of stilbenophane *trans*,*trans*-**2** was compared with those of *trans*-**6** and *trans*-stilbene under the same conditions. Absorption maxima of *trans*,*trans*-**2** appeared at 310 ($\epsilon = 7.25 \times 10^4$ M^{-1} cm^{-1}), 322 ($\epsilon = 6.85 \times 10^4$ M^{-1} cm^{-1}), and 339 nm ($\epsilon = 3.65 \times 10^4$ M^{-1} cm^{-1}). These wavelengths were close to those of *trans*-**6** (λ_{max} = 308 ($\epsilon = 3.65 \times 10^4$ M^{-1} cm^{-1}), 321 ($\epsilon = 4.06 \times 10^4$ M^{-1} cm^{-1}), and 335 nm ($\epsilon = 2.44 \times 10^4$ M^{-1} cm^{-1})), but the integrated absorption of *trans*,*trans*-**2** was 1.93 times larger than that of *trans*-**6**. These results suggest that the stilbenophane *trans*,*trans*-**2** has a more flexible structure than *trans*,*trans*-**1**. A UV absorption spectrum of the smallest stilbenophane *cis*,*cis*-**3** showed a broad absorption band whose maximum appeared at 288 nm ($\epsilon = 2.33 \times 10^4$ M^{-1} cm^{-1}). This spectrum resembles that of [2.2]-(4,4′)-*cis*,*cis*-stilbenophane, whose maximun appeared at 270 nm.[15b]

Direct Photoreaction of Stilbenophanes. Photoirradiation (>280 nm) of a benzene-d_6 solution containing stilbenophane *trans*,*trans*-**1** (0.02 M) by a high-pressure mercury lamp through a Pyrex filter for 1 h gave photocycloadducts **17** and **18** in a 10:1 ratio in an overall yield of greater than 90% (Scheme 6). The stereochemistry of the products was determined by ^{1}H NMR spectra of the reaction mixture. During the progress of the photoreaction of *trans*,*trans*-**1** in benzene-d_6, two sharp singlet peaks appeared at 4.5 and 4.1 ppm in a 10:1 integral ratio, which is ascribable to the hydrogens attached to the cyclobutane rings of the cis,trans,cis isomer **17** and the all-trans isomer **18**, respectively. A similar photoreaction of *trans*,*trans*-**2**, whose stilbene units are located more closely together, proceeded faster than the reaction of *trans*,*trans*-**1** to produce the cis,trans,cis isomer **19** and the all-trans isomer **20** in a 3:1 ratio. These photoreactions also proceeded efficiently in CH_2Cl_2, with similar isomeric ratios. A decrease in absorbance during the photoreaction of *trans*,*trans*-**1** in CH_2Cl_2 clearly indicates the decay of the internal stilbene units (Figure S4).

Because the efficiency of intermolecular photodimerization of stilbenes is dependent on concentration, cis–trans photoisomerization occurs preferentially in dilute conditions. In fact, photoreactions of *trans*-**5** and *trans*-**6** under the same conditions (0.02 M) did not give detectable amounts of photodimerized products. Only cis–trans photoisomerization took place, giving photostationary state mixtures in a *trans*-**5**:*cis*-**5** ratio of 40:60 and a *trans*-**6**:*cis*-**6** ratio of 16:84 (Scheme S2). In the photoreactions of stilbenophanes *trans*,*trans*-**1** and *trans*,*trans*-

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(18) (a) Mukaiyama, T.; Sato, T.; Hanna, J. *Chem. Lett.* **1973**, 1041–1044. (b) McMurry, J. E.; Fleming, M. P. *J. Org. Chem.* **1976**, *41*, 896–897. (c) McMurry, J. E.; Fleming, M. P.; Kees, K. L.; Kreoski, L. R. *J. Org. Chem.* **1978**, *43*, 3255–3266. (d) Detsi, A.; Koufaki, M.; Calogeropoulou, T. *J. Org. Chem.* **2002**, *67*, 4608–4611.

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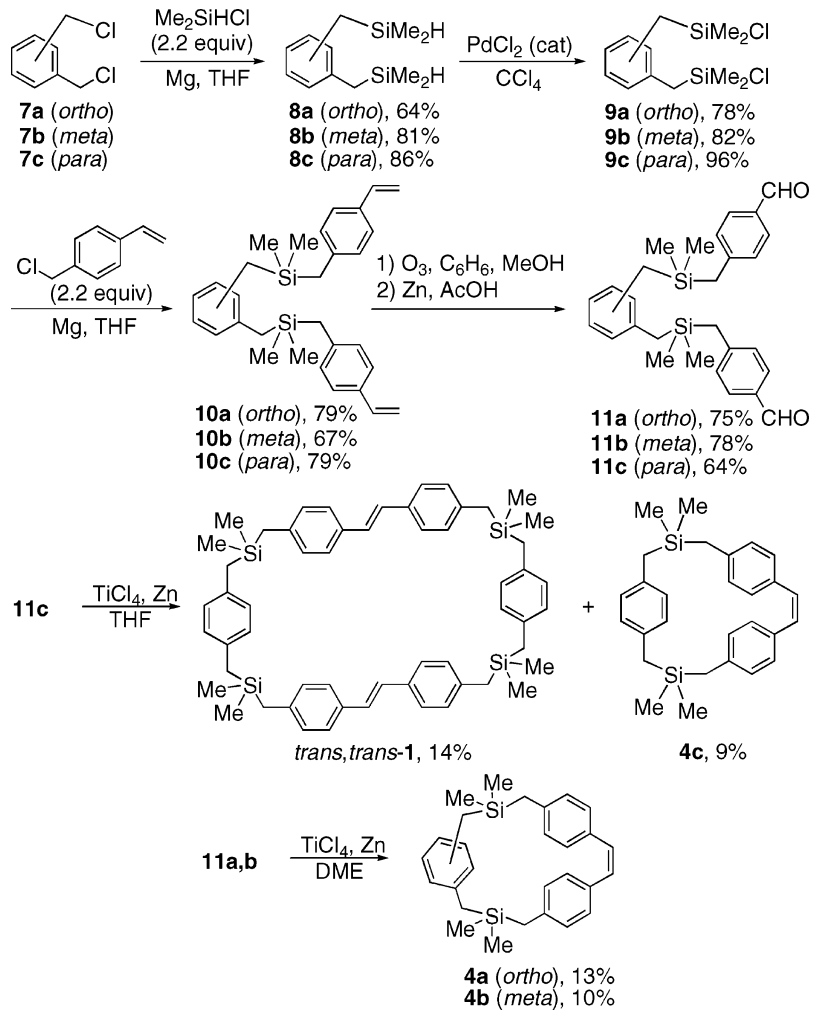
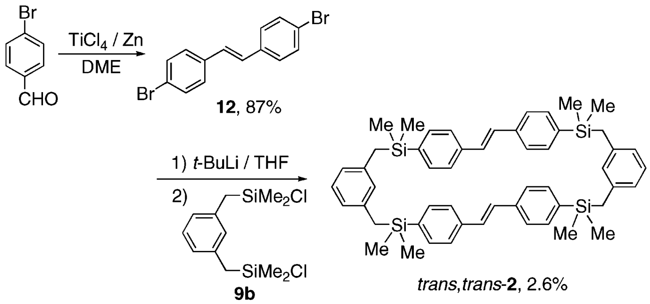
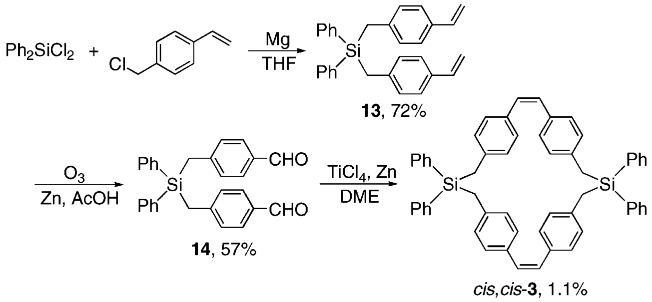
SCHEME 3. Synthesis of Stilbenophanes *trans,trans*-1 and 4a−c



SCHEME 4. Synthesis of Stilbenophane *trans,trans*-2



SCHEME 5. Synthesis of Stilbenophane *cis,cis*-3



2, the stereochemistry of the photoproducts clearly demonstrated that the intramolecular photocycloaddition took place faster than photoisomerization to cis isomers.

Rotation of the double bonds of *trans,trans*-**1** and *trans,trans*-**2** in the ground state, as shown in Scheme 7, might be a fast process, and it should occur in solution at room temperature, even though it involves the loss of resonance stabilization over two benzene rings and the double bonds.[21] In fact, this equilibrium exists at 165 K even with [2.2](4,4′)-*trans,trans*-stilbenophane.[15a] The product ratios of **17**:**18** and **19**:**20** reflect the equilibrium.

Direct photoreaction of *cis,cis*-**3** in benzene-d_6 produced the cis,trans,cis type photocycloadduct **21** quantitatively (Scheme 8). The stereochemistry was determined by ^{1}H NMR spectra, in which a signal due to the hydrogens on the cyclobutane ring of **21** appeared at 4.2 ppm. The stereochemistry of **21** clearly suggests the intermediacy of the *trans,trans*-**3**. Changes in the UV absorption spectra during the photoirradiation of a solution of

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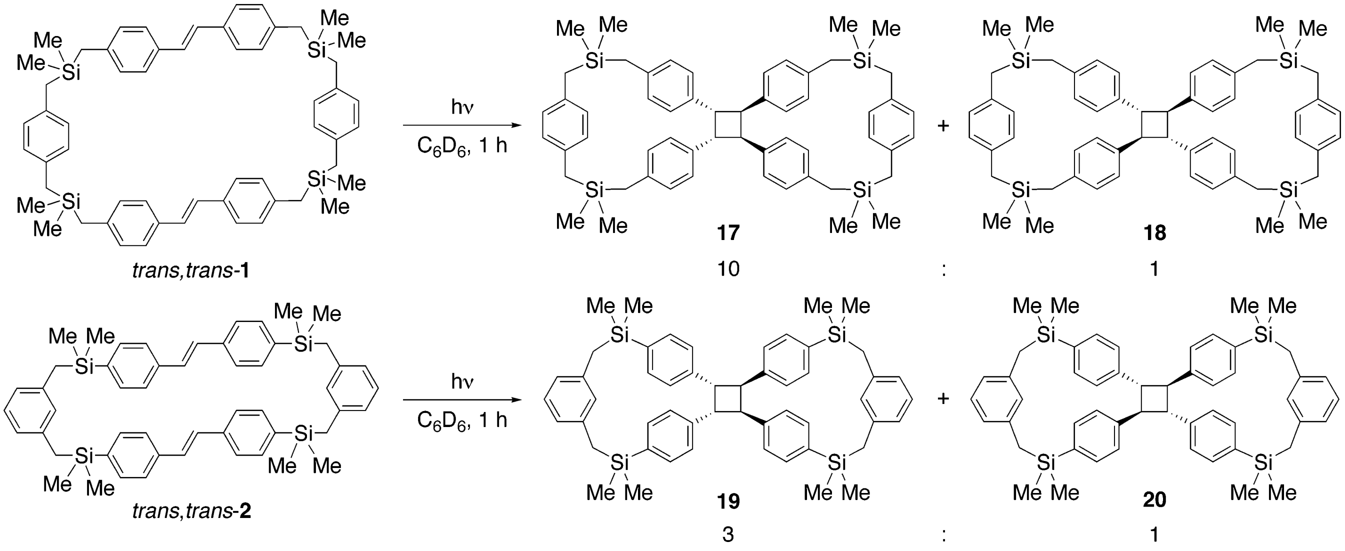
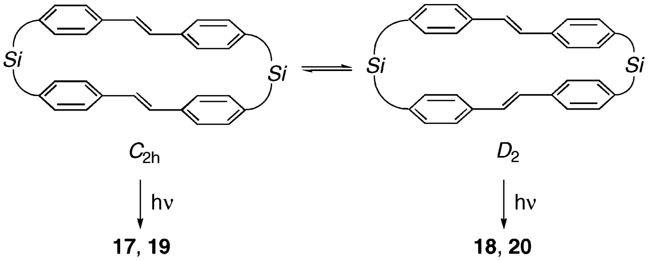
[21] The crankshaft motion has a precedent in the dynamic disorder of the stilbene crystal. See: (a) Ogawa, K.; Sano, T.; Yoshimura, S.; Takeuchi, Y.; Toriumi, K. *J. Am. Chem. Soc.* **1992**, *114*, 1041−1051. (b) Galli, S.; Mercandelli, P.; Sironi, A. *J. Am. Chem. Soc.* **1999**, *121*, 3767−3772. (c) Saito, K.; Okada, M.; Akutsu, H.; Sorai, M. *Chem. Phys. Lett.* **2000**, *318*, 75−78. (d) Khuong, T.-A. V.; Zepeda, G.; Sanrame, C. N.; Dang, H.; Bartberger, M. D.; Houk, K. N.; Garcia-Garibay, M. A. *J. Am. Chem. Soc.* **2004**, *126*, 14778−14786.

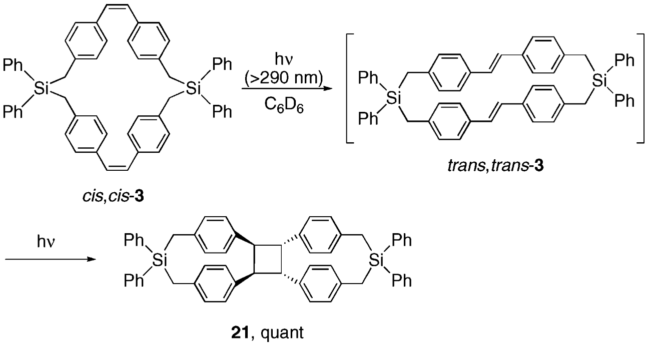
SCHEME 6. Direct Photoreaction of *trans,trans*-1 and *trans,trans*-2



SCHEME 7. Rotation of Double Bonds in Stilbenophanes



SCHEME 8. Direct Photoreaction of *cis,cis*-3



cis,cis-**3** in CH_2Cl_2 are shown in Figure S5. In the photoreaction of *cis,cis*-**3**, the absorption maxima of *cis,cis*-**3** first shifted from 288 nm to the longer wavelength (295 nm), and then decayed. This phenomenon corresponds to the photoisomerization from *cis,cis*-**3** to *trans,trans*-**3** followed by intramolecular photocycloaddition. Rotation of the double bonds of *trans,trans*-**3** shown in Scheme 7 should occur, but the D_2 conformation of *trans,trans*-**3** cannot produce an all-trans isomer, because intramolecular photodimerization of bis[(*p*-vinylphenyl)methyl]silanes produced only cis-fused cyclic compounds for steric reasons.[19,22]

Triplet-Sensitized Photoreaction of Stilbenophanes. To understand the photochemical properties of triplet stilbenophanes, triplet sensitization was carried out. Photoirradiation of benzene solutions containing *trans,trans*-**1** by using benzophenone (E_T = 288 kJ mol^{-1}) and benzil (E_T = 226 kJ mol^{-1}) caused only cis−trans photoisomerization, giving photostationary state mixtures of *trans,trans*-**1**, *cis,trans*-**1**, and *cis,cis*-**1** in approximately 1:1:1 and 2:3:6 ratios, respectively, after irradiation for 1 h, without any formation of intramolecular photocycloadducts (Scheme 9). A similar benzil-sensitized photoreaction of *trans,trans*-**2** gave a photostationary *trans,trans*-**2**/*cis,trans*-**2**/*cis,cis*-**2** mixture in a ratio of 4:28:68. Benzil-sensitized photoisomerization of *trans*-**5** and *trans*-**6** gave photostationary mixtures of *trans*-**5** and *cis*-**5** (20:80) and *trans*-**6** and *cis*-**6** (12:88), respectively (Scheme S3). From these results, triplet energies (E_T) of *trans,trans*-**1** and -**2** and *trans*-**5** and -**6** were estimated to be lower than that of unsubstituted *trans*-stilbene, and the E_T values for *trans,trans*-**2** and *trans*-**6** might be larger than those of *trans,trans*-**1** and *trans*-**5**, respectively.[1a,2b,23]

The benzophenone-sensitized photoreaction of *cis,cis*-**3** with irradiation at wavelengths greater than 360 nm gave only photocycloadduct **21** (Scheme 10). The stereochemistry of the product was the same as that obtained upon direct photoreaction. When the time dependence of the benzophenone-sensitized photoreaction of *cis,cis*-**3** was monitored by ^{1}H NMR in C_6D_6 in order to detect any intermediates, two singlet peaks (2.51 and 2.74 ppm) appeared initially, along with the decay of a singlet peak at 2.42 ppm, which is ascribable to the benzylic hydrogens on *cis,cis*-**3**; a singlet peak at 2.75 ppm then grew, and finally, all of the peaks were converted to two doublet peaks (2.81 and 2.95 ppm, J = 15.0 Hz). The two singlet peaks (2.51 and 2.74 ppm) and the singlet peak (2.75 ppm) can be assigned to *cis,trans*-**3** and *trans,trans*-**3**, respectively. These results clearly suggest that *trans,trans*-**3**, generated by the triplet isomerization of *cis,cis*-**3**, can react intramolecularly to produce photo-

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(22) (a) Mizuno, K.; Nakanishi, K.; Otsuji, Y.; Hayamizu, T.; Maeda, H.; Adachi, T.; Ishida, A.; Takamuku, S. *J. Photosci.* **2003**, *10*, 121−126. (b) Maeda, H.; Yagi, H.; Mizuno, K. *Chem. Lett.* **2004**, *33*, 388−389.

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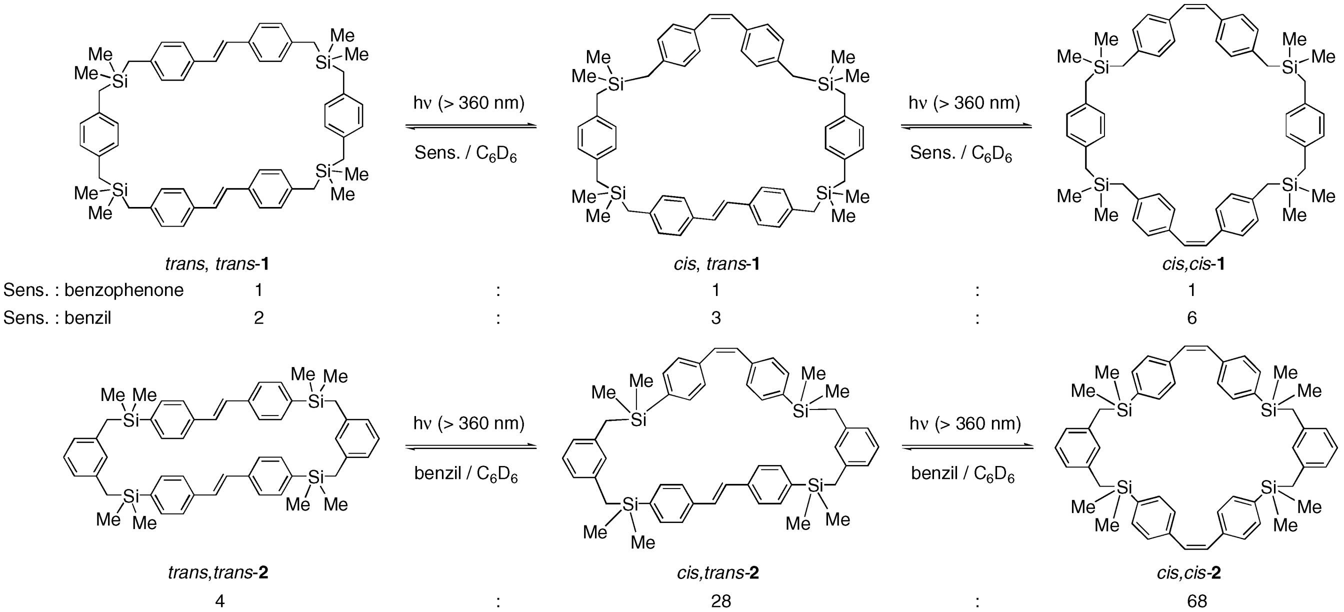
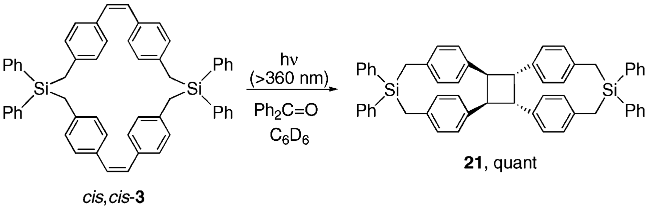
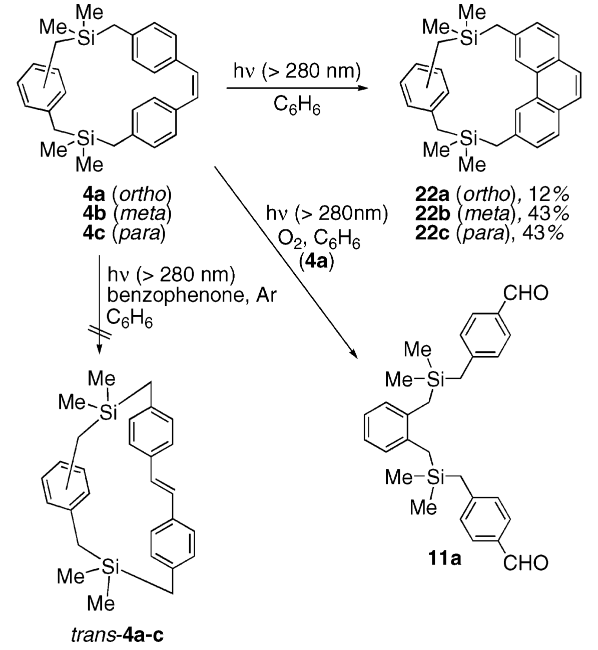
SCHEME 9. Triplet-Sensitized Photoreaction of *trans,trans*-1 and *trans,trans*-2



SCHEME 10. Triplet-Sensitized Photoreaction of *cis,cis*-3



SCHEME 11. Photoreaction of 4a–c



cycloadduct **21** from its excited triplet state. In the direct photoreaction of *cis*,*cis*-**3** shown in Scheme 8, no intermediates were observed in the time-dependent ^{1}H NMR studies, because of the rapid intramolecular photodimerization.

Photocyclization to Phenanthrenophanes. The photoreaction of the cis-fixed stilbenophanes **4a**–**c** in the presence of oxygen readily afforded phenanthrenophanes **22a**–**c** (Scheme 11). In the reaction of the ortho-derivative **4a**, dialdehyde **11a** was obtained as an oxidation product in small amounts together with the formation of **22a**,[24] probably due to the steric factor of **22a**. Benzophenone-sensitized photoreactions of **4a**–**c** were also carried out, but trans isomers of **4a**–**c** were not formed at all. UV absorption and fluorescence spectra of phenanthrenophanes **22a**–**c** and a reference compound, 3,6-bis(trimethylsilylmethyl)phenanthrene **23**, were measured in cyclohexane (Figures S6 and S7). The absorption and fluorescence spectra of **22a**–**c** were quite similar to those of **23**, which are typical spectra corresponding to those of phenanthrene derivatives.

Fluorescence of Stilbenophanes. The fluorescence spectra of *trans*,*trans*-**1** and *trans*-**5** were measured so that the same absorbance was obtained at the specified excitation wavelength (291.5 nm, Abs = 0.263); these showed that *trans*,*trans*-**1** has a greater fluorescence intensity than *trans*-**5** and unsubstituted *trans*-stilbene (Figure S8). The fluorescence quantum yields (Φ_f) of *trans*,*trans*-**1** and *trans*-**5** were determined to be 0.20 and 0.17, respectively, based on the Φ_f of *trans*-stilbene (Φ_f = 0.030 in CH_2Cl_2).[25] It is known that silyl substituents often increase the fluorescence quantum yields of aromatic hydrocarbons.[26] The result that the cyclized compound *trans*,*trans*-**1** has a higher fluorescence quantum yield than *trans*-**5** may be explained by a decrease of

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[24] It is known that photooxygenation of *trans*- and *cis*-stilbene in the presence of 9,10-dicyanoanthracene or tetraphenylporphyrin produces benzaldehyde. See: (a) Spada, L. T.; Foote, C. S. *J. Am. Chem. Soc.* **1980**, *102*, 391–393. (b) Manring, L. E.; Kramer, M. K.; Foote, C. S. *Tetrahedron Lett.* **1984**, *25*, 2523–2526. (c) Kwon, B.-M.; Foote, C. S.; Khan, S. I. *J. Org. Chem.* **1989**, *54*, 3378–3382.

[25] The reported result for Φ_f of *trans*-stilbene in hexane is 0.04: (a) Charlton, J. L.; Saltiel, J. *J. Phys. Chem.* **1977**, *81*, 1940–1944. (b) Saltiel, J.; Waller, A. S.; Sears, D. F., Jr.; Garrett, C. Z. *J. Phys. Chem.* **1993**, *97*, 2516–2522. Φ_f = 0.030 ± 0.001 in CH_2Cl_2 was determined by the integral ratio of fluorescence in CH_2Cl_2 and hexane.

TABLE 1. Fluorescence Lifetimes, Fluorescence Quantum Yields, and Rate Constants for Fluorescence Radiation of Stilbenophanes and Related Compounds

compound	τ_s[a]	Φ_f[b]	k_f[c] (s^{-1})
trans,trans-**1**	863 ps (88%), 262 ps (12%)	0.20	2.32×10^8
trans,trans-**2**	496 ps (76%), 195 ps (24%)	0.11	2.22×10^8
cis,cis-**3**	8.4 ns (94.7%), 166 ps (4.7%), 19.2 ps (0.6%)	*d*	*d*
trans-**5**	590 ps (96%), 141 ps (4%)	0.17	2.88×10^8
trans-**6**	322 ps (95%), 103 ps (5%)	0.08	2.48×10^8

[a] Fluorescence lifetimes in aerated cyclohexane at 295 K, OD = ca. 0.1, λ_{ex} = 266 nm (Ti− sapphire laser). [b] Fluorescence quantum yield in CH_2Cl_2 at 301 K, degassed by freeze−pump−thaw cycles, λ_{ex} = 291.5 nm. [c] Rate constant for fluorescence radiation, calculated by $k_f = \Phi_f/\tau_s$. [d] Not determined.

the nonradiative decay rate due to the loss of flexibility of stilbene units in *trans*,*trans*-**1**. Similar results were obtained in the fluorescence measurements of *trans*,*trans*-**2** and *trans*-**6**. The fluorescence quantum yields of *trans*,*trans*-**2** and *trans*-**6** were determined to be 0.11 and 0.08, respectively.

A fluorescence spectrum of *cis*,*cis*-**3** in CH_2Cl_2 at 2×10^{-5} M showed a broad band whose maximum intensity appeared at 441 nm (Figure S9). Stilbene itself is not such an emissive molecule. Fluorescence quantum yields of *trans*-stilbene and *cis*-stilbene are reported to be 0.04[25] and <0.001,[27] respectively, at room temperature.[28] The stilbene excimer has hardly been observed in general, with the exception of the following: γ-radiation at 77 K,[29] [2.2]stilbenophane,[15b] stilbene-linked oligonucleotides,[30] and aqueous γ-cyclodextrin solution.[31] To confirm whether the observed fluorescence spectrum is based on an intramolecular stilbene excimer or not, fluorescence lifetimes (τ_s) were measured (Table 1). The observation of a multiexponential decay suggests the existence of different emitting conformers. From the long lifetime of the major component (8.4 ns), the relatively long wavelength of the fluorescence maximum, and its lack of structure, we concluded that the emission can be assigned to the intramolecular stilbene excimer of *cis*,*cis*-**3**. The two *cis*-stilbene units are located in remote positions in the X-ray crystallographic analysis (Figure S2), but it may be possible that the *cis*-stilbene moieties in *cis*,*cis*-**3** come close enough to form an excimer by bond rotation of the silyl tethers.

Fluorescence quantum yields (Φ_f) of these compounds were determined in CH_2Cl_2 degassed by several freeze−pump−thaw cycles in order to exclude the dissolved dioxygen. Fluorescence quantum yields (Φ_f) can be described by the equation $\Phi_f = k_f\tau_s$, where k_f and τ_s represent the rate constant for fluorescence radiation and the fluorescence lifetime, respectively. The Φ_f values and calculated k_f values are also listed in Table 1. Fluorescence quantum yields and fluorescence lifetimes of silyl-substituted *trans*-stilbenes are both larger than those of unsubstituted *trans*-stilbene.[32] The fluorescence quantum yields and fluorescence lifetimes of macrocyclic stilbenophanes further increased compared with those of acyclic stilbenes.

To observe phosphorescence radiation, we measured emission spectra at low temperature (Figures S10−S13).[33] However, there was negligible phosphorescence from *trans*,*trans*-**1**, *trans*,*trans*-**2**, *trans*-**5**, and *trans*-**6** in MP at 77 K. To confirm the formation of triplet stilbene, transient absorption spectra of CH_2Cl_2 solutions containing *trans*,*trans*-**1** and *trans*-**5** upon 308 nm laser photolysis were measured (Figures S14 and S15). A transient absorption maximum appeared at 540 nm for both compounds, with lifetimes of 370 μs (*trans*,*trans*-**1**) and 240 μs (*trans*-**5**). The lifetimes of the transient absorption maxima were not influenced by dissolved oxygen. The absorption bands that appeared at 540 nm can be assigned to the radical cations of *trans*,*trans*-**1** and *trans*-**5**,[34] and therefore, we were unable to observe any triplet states in the transient absorption measurements. These data suggest that intersystem crossing from the excited singlet state to the excited triplet state is an unfavorable process, and that participation of the excited triplet state can be ruled out in experiments involving direct photoirradiation.

Conclusions

In conclusion, the intramolecular photodimerization of stilbenes was accelerated by tethering two stilbene units intramolecularly. The efficiency of the intramolecular photodimerization depends on the distance between the two stilbene double bonds. Triplet-sensitized photoreactions of stilbenophanes cause cis−trans photoisomerization, and the cis−trans ratio in the photostationary state depends on the triplet energies of the photosensitizer. Photoirradiation of cis-fixed stilbenophanes in the presence of oxygen gives the corresponding phenanthrenophanes. Fluorescence quantum yields of stilbenes increase with the introduction of silyl groups. Intramolecular photodimerization via the excited triplet state and emission of an intramolecular stilbene excimer were observed when the silyl tethers were effectively short.

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(27) (a) Saltiel, J.; Waller, A.; Sun, Y.-P.; Sears, D. F., Jr. *J. Am. Chem. Soc.* **1990**, *112*, 4580−4581. (b) Saltiel, J.; Waller, A. S.; Sears, D. F., Jr. *J. Photochem. Photobiol., A* **1992**, *65*, 29−40. (c) Saltiel, J.; Waller, A. S.; Sears, D. F., Jr. *J. Am. Chem. Soc.* **1993**, *115*, 2453−2465.

(28) Structurally rigid analogues of stilbenes are strongly fluorescent even at room temperature: (a) Saltiel, J.; Zafiriou, O. C.; Megarity, E. D.; Lamola, A. A. *J. Am. Chem. Soc.* **1968**, *90*, 4759−4760. (b) DeBoer, C. D.; Schlessinger, R. H. *J. Am. Chem. Soc.* **1968**, *90*, 803−804.

(29) Brocklehurst, B.; Bull, D. C.; Evans, M.; Scott, P. M.; Stanney, G. *J. Am. Chem. Soc.* **1975**, *97*, 2977−2978.

(30) Lewis, F. D.; Wu, T.; Burch, E. L.; Bassani, D. M.; Yang, J.-S.; Schneider, S.; Jäger, W.; Letsinger, R. L. *J. Am. Chem. Soc.* **1995**, *117*, 8785−8792.

(31) Agbaria, R. A.; Roberts, E.; Warner, I. M. *J. Phys. Chem.* **1995**, *99*, 10056−10060.

(32) For unsubstituted *trans*-stilbene, Φ_f = 0.0400, τ_s = 63.6 ps, and $k_f = 6.30 \times 10^8$ s^{-1} in hexane at 303.1 K. See ref 25b.

(33) Phosphorescence of stilbenes has rarely been observed, except in cases involving the presence of heavy atoms: (a) Görner, H. *J. Phys. Chem.* **1989**, *93*, 1826−1832. (b) Ramamurthy, V.; Caspar, J. V.; Corbin, D. R. *Tetrahedron Lett.* **1990**, *31*, 1097−1100. (c) Ramamurthy, V.; Caspar, J. V.; Eaton, D. F.; Kuo, E. W.; Corbin, D. R. *J. Am. Chem. Soc.* **1992**, *114*, 3882−3892.

(34) Hara, M.; Tojo, S.; Majima, T. *J. Photochem. Photobiol., A* **2004**, *162*, 121−128.

The synthesis of silicon-containing macrocyclic compounds has recently attracted much attention from the synthetic and structural viewpoints as well as that of molecular recognition.[35] By virtue of silyl tethers, we can achieve control of stilbene photochemistry.

Experimental Section

Stilbenophanes *trans,trans*-1 and 4c. To TiCl$_4$ (3.68 g, 19.4 mmol) in THF (50 mL) was added Zn powder (2.42 g, 37.0 mmol) at 0 °C. The mixture was refluxed for 1 h. After cooling the mixture to room temperature, we added **11c** (800 mg, 1.8 mmol) in THF (50 mL) dropwise, and the mixture was then stirred for 24 h under reflux. After cooling the mixture to room temperature, we added ethanol (10 mL), and stirring was continued. The reaction mixture was filtered through silica gel, and then evaporated. The residue was purified by column chromatography on silica gel followed by recycling preparative HPLC. Addition of acetone to a fraction gave a pure precipitate of *trans,trans*-**1** (99 mg, 13.8%). Compound **4c** was obtained from another fraction (65 mg, 9.0%). Data for *trans,trans*-**1**: colorless solid; mp 240−241 °C; ^{1}H NMR (300 MHz, CDCl$_3$) δ −0.02 (s, 24 H), 2.05 (s, 8 H), 2.11 (s, 8 H), 6.78 (d, J = 7.9 Hz, 8 H), 6.86 (s, 8 H), 6.92 (s, 4 H), 7.25 (d, J = 8.1 Hz, 8 H); ^{13}C NMR (75 MHz, CDCl$_3$) δ −3.1, 24.3, 25.0, 126.1, 127.0, 128.0, 128.4, 133.3, 135.1, 139.3; IR (KBr) 3018, 2954, 2887, 1509, 1244, 968, 853 cm^{-1}; TOF-MS, m/z = 858 (M$^+$); HRMS (EI) calcd for $C_{56}H_{68}Si_4$ 852.4398, found 852.4402. Data for **4c**: ^{1}H NMR (300 MHz, CDCl$_3$) δ 0.01 (s, 12 H), 2.05 (s, 4 H), 2.18 (s, 4 H), 6.03 (s, 2 H), 6.60 (d, J = 8.1 Hz, 4 H), 6.65 (s, 4 H), 6.80 (d, J = 8.2 Hz, 4 H); MS (EI), m/z = 145, 163, 219, 426 (M$^+$).

Stilbenophane 4a. To TiCl$_4$ (1.64 g, 8.65 mmol) in DME (50 mL) was added Zn powder (1.13 g, 17.3 mmol) at 0 °C. The mixture was refluxed for 1 h. After cooling the mixture to room temperature, we added **11a** (1.32 g, 2.88 mmol) in DME (50 mL) dropwise, and then stirred for 24 h under reflux. After cooling the mixture to room temperature, we added ethanol (20 mL), and stirring was continued. The reaction mixture was filtered through silica gel, and then evaporated. Purification by column chromatography on silica gel and recycling preparative HPLC gave **4a** (164 mg, 13.3%). Data for **4a**: colorless solid; mp 167−170 °C; ^{1}H NMR (300 MHz, CDCl$_3$) δ −0.16 (s, 12 H), 1.98 (s, 4 H), 2.10 (s, 4 H), 6.77 (d, J = 8.2 Hz, 4 H), 6.81 (s, 2 H), 6.83 (d, J = 8.1 Hz, 4 H); ^{13}C NMR (75 MHz, CDCl$_3$) δ −3.8, 21.6, 26.5, 123.8, 127.0, 129.4, 129.8, 132.1, 134.4, 135.6, 138.2; IR (KBr) 3015, 2953, 2885, 1603, 1503, 1414, 1246, 1209, 1148, 826 cm^{-1}; MS (EI), m/z = 73, 145, 264, 426 (M$^+$).

Stilbenophane 4b. To TiCl$_4$ (1.52 g, 8.0 mmol) in DME (20 mL) was added Zn powder (1.05 g, 16.0 mmol) at 0 °C. The mixture was refluxed for 1 h. After cooling the mixture to room temperature, we added **11b** (917 mg, 2.0 mmol) in DME (30 mL) dropwise, then the mixture was stirred for 24 h under reflux. After cooling the mixture to room temperature, we added ethanol (10 mL), and stirring was continued. The reaction mixture was filtered through silica gel, and then evaporated. Purification by column chromatography on silica gel (eluent, benzene:hexane = 1:2) and recycling preparative HPLC gave **4b** (81 mg, 9.7%). Data for **4b**: colorless solid; mp 114−117 °C; ^{1}H NMR (300 MHz, CDCl$_3$) δ 0.17 (s, 12 H), 1.81 (s, 4 H), 2.01 (s, 4 H), 6.38 (s, 1 H), 6.73 (s, 2 H), 6.75 (dd, J = 7.5, 1.7 Hz, 2 H), 6.85 (d, J = 8.2 Hz, 4 H), 6.97 (d, J = 8.2 Hz, 4 H), 7.08 (t, J = 7.6 Hz, 1 H); ^{13}C NMR (75 MHz, CDCl$_3$) δ −2.0, 23.4, 24.8, 123.8, 127.5, 128.1, 129.1, 130.7, 130.8, 134.0, 138.4, 139.1; IR (KBr) 3043, 2956, 2881, 1602, 1502, 1415, 1247, 843 cm^{-1}; MS (EI), m/z = 73, 145, 319, 426 (M$^+$).

Stilbenophane *trans,trans*-2. To **12** (776 mg, 2.0 mmol) in THF (300 mL) was added *t*-BuLi (1.54 M in pentane, 5.5 mL, 8.0 mmol) at −77 °C, and the mixture was stirred for 30 min. To the solution was added **9b** (1.17 g, 4 mmol) in THF (30 mmol) at −77 °C, and the mixture was stirred for an additional 30 min. Then the solution was gradually warmed to room temperature, and stirring was continued for 16 h. Ether (100 mL) and saturated NaHCO$_3$ aqueous solution were added. The organic layer was separated, dried over Na$_2$SO$_4$, and evaporated. The residue was purified by column chromatography on silica gel and recycling preparative HPLC. Addition of acetone to a fraction gave a precipitate of *trans,trans*-**2** (21 mg, 2.6%). Data for *trans,trans*-**2**: colorless solid; mp 242−244 °C; ^{1}H NMR (300 MHz, CDCl$_3$) δ 0.23 (s, 24 H), 2.11 (s, 8 H), 6.19 (s, 2 H), 6.62 (dd, J = 7.5, 1.7 Hz, 4 H), 6.95 (t, J = 7.5 Hz, 2 H), 7.09 (s, 4 H), 7.34 (d, J = 8.1 Hz, 8 H), 7.42 (d, J = 8.2 Hz, 8 H); ^{13}C NMR (75 MHz, CDCl$_3$) δ −3.2, 26.2, 124.1, 125.6, 127.7, 128.4, 129.0, 134.2, 137.7, 137.9, 139.0; IR (KBr) 2954, 1597, 1247, 1111, 838 cm^{-1}; TOF-MS, m/z = 796 (M$^+$); HRMS (EI) calcd for $C_{52}H_{60}Si_4$ 796.3772, found, 796.3785.

Stilbenophane *cis,cis*-3. To TiCl$_4$ (5.69 g, 30 mmol) in DME (50 mL) was added Zn powder (3.92 g, 60 mmol) at 0 °C. The mixture was refluxed for 1 h. After cooling the mixture to room temperature, we added bis(4-formylphenylmethyl)dimethylsilane (**14**, 1.26 g, 3 mmol) in DME (50 mL) dropwise, and then stirred the mixture for 20 h under reflux. After cooling to room temperature, we added ethanol (10 mL), and stirring was continued. The reaction mixture was filtered through silica gel, and then evaporated. Purification by column chromatography on silica gel and recycling preparative HPLC gave stilbenophane *cis,cis*-**3** (13 mg, 1.1%). Data for *cis,cis*-**3**: colorless solid; mp 280−282 °C; ^{1}H NMR (300 MHz, CDCl$_3$) δ 2.56 (s, 8 H), 6.51 (s, 4 H), 6.67 (d, J = 8.2 Hz, 8 H), 6.90 (d, J = 8.1 Hz, 8 H), 7.23−7.41 (m, 20 H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 22.8, 127.5, 128.6, 128.6, 129.5, 129.9, 133.7, 133.8, 135.5, 136.9; IR (KBr) 3014, 2923, 1509, 837 cm^{-1}; TOF-MS, m/z = 778 (M$^+$); HRMS (EI) calcd for $C_{56}H_{48}Si_2$ 776.3295, found 776.3299.

4,4′-*trans*-Bis(trimethylsilylmethyl)stilbene (*trans*-5). To TiCl$_4$ (5.69 g, 30.0 mmol) in DME (50 mL) was added Zn powder (3.92 g, 60.0 mmol) at 0 °C. The mixture was refluxed for 1 h. After cooling the mixture to room temperature, we added 4-(trimethylsilylmethyl)benzaldehyde (**16**, 3.90 g, 20 mmol) in DME (50 mL) dropwise, and then stirred for 20 h under reflux. After cooling the mixture to room temperature, we added ethanol (10 mL), and stirring was continued. The reaction mixture was filtered through silica gel, and then evaporated. Purification by column chromatography on silica gel and recycling preparative HPLC gave 4,4′-*trans*-bis(trimethylsilylmethyl)stilbene (*trans*-**5**, 382 mg, 10.7%). Data for *trans*-**5**: colorless solid; mp 137−141 °C; ^{1}H NMR (300 MHz, CDCl$_3$) δ 0.00 (s, 18 H), 2.09 (s, 4 H), 6.97 (d, J = 8.4 Hz, 8 H), 7.00 (s, 2 H), 7.35 (d, J = 8.2 Hz, 4 H); ^{13}C NMR (75 MHz, CDCl$_3$) δ −1.8, 27.1, 126.1, 127.0, 128.2, 133.3, 139.8; IR (KBr) 2954, 1510, 1246, 851 cm^{-1}; MS (EI), m/z = 73, 279, 352 (M$^+$); HRMS (EI) calcd for $C_{22}H_{28}Si_2$ 352.2042, found 352.2046.

4,4′-*trans*-Bis(trimethylsilyl)stilbene (*trans*-6). To **12** (1.14 g, 3.4 mmol) in THF (300 mL) was added *t*-BuLi (1.54 M in pentane, 9.1 mL, 14.0 mmol) at −77 °C, and the mixture was stirred for 30 min. To the solution was added Me$_3$SiCl (1.52 g, 14 mmol) in THF (30 mmol) at −77 °C, and stirring was continued for an additional 30 min. The solution was then gradually warmed to room temperature, and stirring was continued for 16 h. Ether (100 mL) and saturated NaHCO$_3$ aqueous solution were added. The organic layer was separated, dried over Na$_2$SO$_4$, and evaporated. Recrystallization from ethanol gave 4,4′-*trans*-bis(trimethylsilyl)stilbene (*trans*-**6**, 858 mg, 78%). Data for *trans*-**6**: colorless solid; mp 155−156 °C;

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[35] For silicon-containing macrocyclic compounds: (a) König, B.; Rödel, M.; Bubenitschek, P.; Jones, P. G. *Angew. Chem., Int. Ed.* **1995**, *34*, 661−662. (b) Liu, F.-Q.; Harder, G.; Tilley, T. D. *J. Am. Chem. Soc.* **1998**, *120*, 3271−3272. (c) Yoshida, M.; Goto, M.; Nakanishi, F. *Organometallics* **1999**, *18*, 1465−1470. (d) Kwon, E.; Sakamoto, K.; Kabuto, C.; Kira, M. *Chem. Lett.* **2000**, 1416−1417. (e) Mézailles, N.; Maigrot, N.; Hamon, S.; Ricard, L.; Mathey, F.; Le Floch, P. *J. Org. Chem.* **2001**, *66*, 1054−1056. (f) Unno, M.; Negishi, K.; Matsumoto, H. *Chem. Lett.* **2001**, 340−341. (g) Kyushin, S.; Kitahara, T.; Tanaka, R.; Takeda, M.; Matsumoto, T.; Matsumoto, H. *Chem. Commun.* **2001**, 2714−2715. (h) Zhang, H.; Lam, K. T.; Chen, Y. L.; Mo, T.; Kwok, C. C.; Wong, W. Y.; Wong, M. S.; Lee, A. W. M. *Tetrahedron Lett.* **2002**, *43*, 2079−2082. (i) Negishi, K.; Unno, M.; Matsumoto, H. *Chem. Lett.* **2004**, *33*, 430−431.

^{1}H NMR (300 MHz, $CDCl_3$) δ 0.28 (s, 18 H), 7.13 (s, 2 H), 7.48−7.54 (m, 8 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ −1.0, 125.7, 128.8, 133.6, 137.6, 139.9; IR (KBr) 2955, 1597, 1250, 1113, 970, 841 cm^{-1}; MS (EI), *m/z* = 73, 147, 309, 324 (M^+); HRMS (EI) calcd for $C_{20}H_{28}Si_2$ 324.1730, found 324.1714.

Direct Photoreaction of *trans,trans*-1. A C_6D_6 (1 mL) solution of *trans*,*trans*-**1** (1 mg) was degassed by bubbling of argon before photoirradiation. Photoirradiation of the solution was carried out with a 300-W high-pressure mercury lamp through a Pyrex filter for 1 h at room temperature. Two singlet peaks appeared at 4.52 and 4.10 ppm, with an integral ratio of 10:1; these were assigned to hydrogens on cyclobutane rings of **17** and **18**. See Supporting Information.

Direct Photoreaction of *trans,trans*-2. A C_6D_6 (1 mL) solution of *trans*,*trans*-**2** (1 mg) was irradiated as described above. Two singlet peaks appeared at 4.46 and 4.13 ppm, with an integral ratio of 3:1; these were assigned to hydrogens on cyclobutane rings of **19** and **20**. See Supporting Information.

Direct Photoreaction of *cis,cis*-3. A C_6D_6 (1 mL) solution of *cis*,*cis*-**3** (1 mg) was irradiated as described above. Product **21** was obtained quantitatively. Data for **21**: ^{1}H NMR (300 MHz, C_6D_6) δ 2.81 (d, J = 15.0 Hz, 4 H), 2.95 (d, J = 15.0 Hz, 4 H), 4.21 (s, 4 H), 6.33 (dd, J = 7.9, 1.8 Hz, 2 H), 6.54 (dd, J = 7.9, 1.8 Hz, 2 H), 6.70 (dd, J = 7.9, 2.0 Hz, 2 H), 6.77 (dd, J = 8.1, 1.9 Hz, 2 H), 7.12−7.32 (m, 24 H), 7.67 (dd, J = 7.6, 1.7 Hz, 2 H), 7.75 (dd, J = 7.6, 1.7 Hz, 2 H).

Triplet-Sensitized Photoreaction of *trans,trans*-1. A C_6D_6 (1 mL) solution of *trans*,*trans*-**1** (1 mg) and benzophenone (1 mg) was irradiated through a cutoff filter (>360 nm). A singlet peak at −0.10 ppm was assigned to *trans*,*trans*-**1**. Singlet peaks appearing at −0.14 and −0.02 ppm were assigned to *cis*,*trans*-**1**. A singlet peak at −0.10 ppm was assigned to *cis*,*cis*-**1**.

Triplet-Sensitized Photoreaction of *trans,trans*-2. A C_6D_6 (1 mL) solution of *trans*,*trans*-**2** (1 mg) and benzil (1 mg) was irradiated through a cutoff filter (>360 nm). A singlet peak at 0.23 ppm was assigned to *trans*,*trans*-**2**. Singlet peaks appearing at −0.01 and 0.26 ppm were assigned to *cis*,*trans*-**2**. A singlet peak at 0.14 ppm was assigned to *cis*,*cis*-**2**.

Phenanthrenophane 22a. Photoirradiation of **4a** (26 mg) in benzene (3.1 mL) in a catalytic amount of I_2 was carried out with a 300-W high-pressure mercury lamp through a Pyrex filter for 40 h at room temperature. Purification by chromatography on silica gel and recycling preparative HPLC gave **22a** (4 mg, 15.4%). Data for **22a**: colorless solid; mp 144−145 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.12 (s, 12 H), 2.18 (s, 4 H), 2.52 (s, 4 H), 7.22−7.27 (m, 4 H), 7.50−7.53 (m, 2 H), 7.55 (s, 2 H), 7.68 (d, J = 8.1 Hz, 2 H), 7.87 (d, J = 1.3 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ −1.7, 19.7, 24.0, 121.6, 125.0, 125.5, 127.9, 128.0, 129.0, 129.6, 130.4, 138.0, 139.1; IR (KBr) 3014, 2919, 2887, 1602, 1512, 1249, 1149, 846 cm^{-1}; MS (EI), *m/z* = 73, 145, 247, 262, 424 (M^+); UV (cyclohexane) λ_{max} (log ϵ) = 358 (2.89), 341 (2.82), 310 (4.08), 297 nm (4.05).

Phenanthrenophane 22b. A benzene (4.9 mL) solution of **4b** (42 mg) was bubbled by O_2 for 10 min. Photoirradiation of the solution was carried out with a 300-W high-pressure mercury lamp through a Pyrex filter for 7 h at room temperature. Purification by chromatography on silica gel and recycling preparative HPLC gave **22b** (18 mg, 43.5%). Data for **22b**: colorless solid; mp 194−198 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.21 (s, 12 H), 1.95 (s, 4 H), 2.44 (s, 4 H), 6.67 (s, 1 H), 7.12 (dd, J = 7.7, 1.4 Hz, 2 H), 7.21 (dd, J = 8.1, 1.6 Hz, 2 H), 7.30 (t, J = 7.6 Hz, 1 H), 7.54 (s, 2 H), 7.57 (s, 2 H), 7.67 (d, J = 8.1 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ −1.3, 24.0, 25.1, 122.0, 124.6, 125.0, 127.4, 127.8, 128.5, 129.0, 129.6, 132.4, 137.8, 140.2; IR (KBr) 3009, 2948, 2885, 1603, 1512, 1242, 848 cm^{-1}; MS (EI), *m/z* = 73, 145, 219, 246, 424 (M^+); UV (cyclohexane) λ_{max} (log ϵ) = 358 (3.00), 341 (2.92), 310 (4.18), 297 nm (4.14).

Phenanthrenophane 22c. A benzene (5.6 mL) solution of **4c** (47 mg) was bubbled with O_2 for 10 min. Photoirradiation of the solution was carried out with a 300-W high-pressure mercury lamp through a Pyrex filter for 7 h at room temperature. Purification by chromatography on silica gel and recycling preparative HPLC gave **22c** (20 mg, 42.6%). Data for **22c**: colorless solid; mp 204−205 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.04 (s, 12 H), 2.16 (s, 4 H), 2.52 (s, 4 H), 7.06 (s, 4 H), 7.17 (dd, J = 8.0, 1.6 Hz, 2 H), 7.29 (s, 2 H), 7.48 (s, 2 H), 7.61 (d, J = 8.1 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ −1.6, 24.7, 26.6, 121.8, 124.9, 127.6, 127.8, 128.8, 129.7, 135.5, 138.2; IR (KBr) 3015, 2949, 2884, 1604, 1511, 1250, 848 cm^{-1}; MS (EI), *m/z* = 73, 145, 219, 409, 424 (M^+); UV (cyclohexane) λ_{max} (log ϵ) = 359 (2.96), 342 (2.90), 310 (4.16), 297 nm (4.10).

3,6-Bis(trimethylsilylmethyl)phenanthrene (23). A benzene (10 mL) solution of *trans*-**5** (70 mg, 1.20 mmol) was bubbled with O_2 for 10 min. Photoirradiation of the solution was carried out with a 300-W high-pressure mercury lamp through a Pyrex filter for 40 h at room temperature. Purification by chromatography on silica gel and recycling preparative HPLC gave **23** (12 mg, 17.2%). Data for **23**: colorless solid; mp 88−92 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.04 (s, 18 H), 2.35 (s, 4 H), 7.23 (dd, J = 8.0, 1.4 Hz, 2 H), 7.57 (s, 2 H), 7.71 (d, J = 8.1 Hz, 2 H), 8.22 (s, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ −1.8, 27.8, 120.7, 125.1, 127.4, 128.1, 129.1, 129.9, 138.6; IR (KBr) 2955, 1511, 1243, 847 cm^{-1}; MS (EI), *m/z* (%) = 73, 247, 277, 350 (M^+); UV (cyclohexane) λ_{max} (log ϵ) = 358 (2.99), 341 (3.03), 308 (4.26), 296 nm (4.19).

Fluorescence Quantum Yields. Fluorescence quantum yields (Φ_f) of stilbene derivatives were determined by comparison with the data (Φ_f(*trans*-stilbene) = 0.030 ± 0.001 in CH_2Cl_2). The Φ_f value in CH_2Cl_2 was determined by the integral ratio of fluorescence in CH_2Cl_2 and hexane. The reported result for Φ_f(*trans*-stilbene) was 0.04 in hexane.[25] The absorption of sample solutions was adjusted to be ca. 0.1 at the excitation wavelength. The samples were carefully degassed by freeze−pump−thaw cycles before measurement in order to exclude the influence of dioxygen.

Fluorescence Lifetimes. The third harmonic (266 nm, fwhm 250 fs) from a mode-locked Ti−sapphire laser (800 nm, fwhm 70 fs, at 82 MHz) pumped by a CW green laser (532 nm, 4.5 W) was used for the excitation source. The repetition rate was adjusted to 4 MHz by use of a pulse-picker. The monitoring system consisted of a microchannel-plate photomultiplier (MCP) tube cooled at −20 °C and a single-photon counting module. The fluorescence photon signal detected by the MCP detector and the photon signal of the second harmonic (400 nm) of the Ti−sapphire laser were used for the start and stop pulses of the time-to-amplitude converter. The instrumental response function had a half-width of 20 ps. The fluorescence time profiles were analyzed by iterative reconvolution with the response function.

Transient Absorption. The fourth harmonic (266 nm) of an Nd^{3+}−YAG laser (pulse width 8 ns) was used as the excitation light source. The transient absorption spectra were obtained with a system capable of capturing a transient absorption spectrum with a one-shot laser pulse.

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Supporting Information Available: Schemes S1−S3 and Figures S1−S15; synthetic procedures for **8**−**16**; ^{1}H NMR, ^{13}C NMR, and TOF-MS spectra for new compounds; X-ray reports and CIFs of *trans*,*trans*-**1** and *cis*,*cis*-**3**; and details of fluorescence lifetime measurements. This material is available free of charge via the Internet at http://pubs.acs.org.

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