Thermolysis of bis(pentacoordinate) silicon compound bearing two 1-fluorodisilanyl units at 4- and 8-positions on 1,5-bis(dimethylamino)naphthalene ring: construction of disilapyrene skeleton and cyclophane-shaped siloxane dimer

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Abstract

The thermolysis of a bis(pentacoordinate) silicon compound having two pentacoordinate silicon units at the 4- and 8-positions on the 1,5-bis(dimethylamino)naphthalene ring in the presence of diphenylacetylene affords a 1,6-dihydro-1,6-disilapyrene derivative. This reaction might proceed through a two-site silylene trapping with two acetylene molecules accompanied by an amino group migration from the naphthyl carbon atom to the silicon atom. The dimethylamino group on each silicon atom can easily be converted into a variety of functional groups. One of the disilapyrene derivatives, bis(silanol), dimerizes by a dehydrocondensation reaction using dicyclohexylcarbodiimide to form a cyclophane-shaped molecule in 76% yield. The cyclic dimer showing a greenish yellow luminescence exhibits the UV-absorption and emission spectra characteristic of a transannular interaction between two proximal chromophores in cyclophane-shaped molecules.
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1. Introduction

The reaction of pentacoordinate fluorodisilane **1** with diphenylacetylene affords the 1-silaphenalene product **2** under thermal conditions as described in a previous paper (Scheme 1) [1]. This reaction proceeds through an α-elimination of fluorosilane from the pentacoordinate disilane to generate a nitrogen-coordinated silylene which is trapped with the acetylene molecule. The mechanistic study of this reaction has clearly demonstrated that the base-coordinated silylene shows an enhanced nucleophilic character toward electrophiles

and that the sila-ylide character is definitely reflected upon the reaction product. During this reaction, the diphenylacetylene molecule is incorporated between the silicon atom and the naphthyl carbon atom to form a silicon-containing six-membered ring. Such a ring forming reaction providing a fused ring system is very attractive for synthetic organic chemistry.

In this paper, we describe a synthetic application of this key reaction to construct a novel polycyclic disilapyrene derivative, that is, the thermal degradation of the bis(pentacoordinate) silicon compound **3** having two pentacoordinate fluorodisilane units at the 4- and 8-positions on the 1,5-diaminonaphthalene ring in the presence of diphenylacetylene. The synthesis and photophysical properties of a cyclophane-shaped cyclic siloxane dimer are also described.

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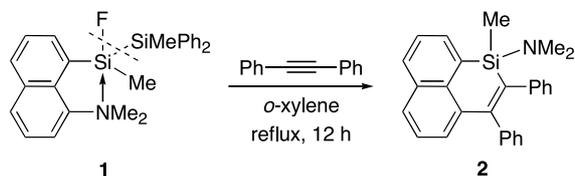
Scheme 1.

2. Results and discussion

2.1. Preparation and structure

The bis(pentacoordinate) silicon compound **3** was prepared in one-pot starting from 1,5-bis(dimethylamino)naphthalene **4** as shown in Scheme 2. Thus the bis-metallated intermediate **5** [2] was trapped with two molar amounts of 1,1-difluorodisilane to afford **3** as a mixture of two isomers (ca. 1:1) in the total yield of 38%. The X-ray crystallographic analysis of one isomer, *meso*-**3**, revealed the bis(pentacoordinate) structure as shown in Fig. 1, and the structural parameters were compared with the reported values for the pentacoordinate fluorodisilane **1** [1b] as summarized in Table 1. The interatomic distances between the nitrogen atom and the pentacoordinate silicon atom are 2.770(1) and 2.728(1) Å which are somewhat shorter than that of **1**.

The bond lengths and angles around the pentacoordinate silicon center(s) as well as their %TBP characters [3] are comparable to that of the thermally labile *mono*(pentacoordinate) counterpart **1**, indicating that the bis(pentacoordinate) silicon compound **3** has a suitable structure for the α-elimination of fluorosilane under thermal conditions, thus generating the silylene species. The ^{29}Si-NMR chemical shift of the pentacoordinate silicon atoms of **3** is −3.8 ppm in benzene-d_6 which is also comparable to that of **1** (−3.6 ppm).

2.2. Thermal degradation

A solution of the bis(pentacoordinate) silicon compound **3** and 2 mol amounts of diphenylacetylene in *o*-xylene was heated at 145 °C for 12 h to afford the 1,6-
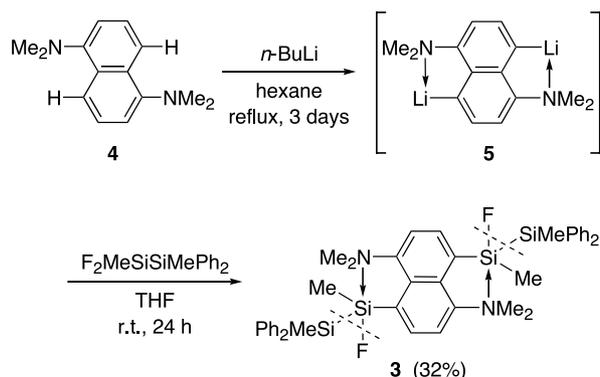
Scheme 2.

dihydro-1,6-disilapyrene derivative **6** as a mixture of *cis* and *trans* stereoisomers (ca. 1:1) in the total yield of 71% (Scheme 3) [4]. It is postulated that this reaction proceeds in a pathway similar to that previously presented for the reaction of *mono*(pentacoordinate) counterpart **1** with diphenylacetylene affording the silaphenalene **2** [1b]. Thus, the generation of silylene species (or sila-ylide) by the α-elimination of fluorosilane from the pentacoordinate silicon center and the trapping with diphenylacetylene occur at two sites during the reaction course, resulting in the fused ring formation.

The disilapyrene compound has not yet been reported, while some 1,6-disubstituted pyrene derivatives are known [5]. The structure of this disilapyrene skeleton was confirmed by the X-ray crystallographic analysis of a methyl-substituted derivative, 1,1,6,6-tetramethyl-1,6-disilapyrene **8**, which was prepared from **6** in two steps, as shown in Scheme 4. Thus, the treatment of a solution of **6** in benzene with 47% HF almost quantitatively afforded the bis-fluorinated compound **7** and the subsequent methyl substitution reaction using an excess amount of methyllithium gave **8** in 66% yield. The single crystal of **8** suitable for X-ray crystallographic analysis was obtained by recrystallization from a mixed solvent of benzene/ethanol and the ORTEP drawing revealed a silicon containing polycyclic structure with C_i symmetry as shown in Fig. 2. The silicon containing six-membered rings are slightly distorted with a deviation of Si1 from the mean plane defined by C1–C2–C3–C4–C5 of 0.2223 Å.

2.3. Synthesis of cyclophane-shaped dimer

Since the disilapyrene mentioned above have an unusual π-electron system and a functional group on each silicon atom, we examined a possibility of utilizing such compounds as a building-block for functional polymers. One of the derivatives, 1,6-dihydroxy-1,6-disilapyrene **9**, prepared from **6** with 5% HCl in 90% yield, was used in a dehydro-condensation reaction using dicyclohexylcarbodiimide (DCC) as a dehydrating agent (Scheme 5) [6,7]. Thus, the dehydration reaction of **9** at 160 °C for 12 h resulted in the formation of a mixture of oligomerized products. Separation of the mixture preformed by gel permeation chromatography (GPC) afforded a cyclic dimer **10** as the main fraction in 76% yield, along with a small amount of linear oligomers.

The cyclic dimer **10** was obtained as a yellow powder, which emits a yellow-green luminescence in solution. The molecular structure of such a dimeric product was confirmed by NMR, IR, and MS spectroscopies, and X-ray crystallographic analysis of a butyl-substituted analogue **10′** which was obtained in a similar sequence using bis(4-butylphenyl)acetylene in place of diphenyla-
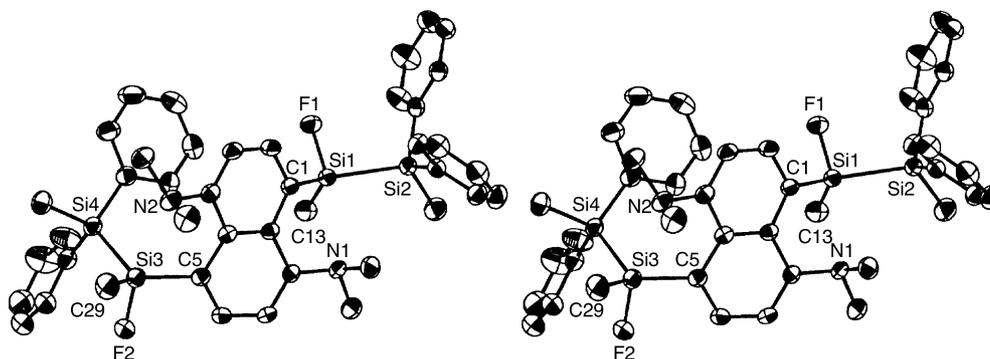
Fig. 1. X-ray structure of *meso*-**3** in stereo view at 60% probability level. All hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Si1–Si2 2.3649(5), Si1–C13 1.882(2), Si1–C1 1.885(2), Si1–F1 1.6415(9), N1···Si1 2.770(1), Si3–Si4 2.3878(6), Si3–C29 1.873(2), Si3–C5 1.888(2), Si3–F2 1.646(1), N2···Si3 2.728(1), N1···Si1–F1 168.67(5), N2···Si3–F2 168.50(5).

Table 1
Selected interatomic distances (Å), angles (°) and dihedral angles (°), and %TBP *meso*-**3** and **1**

	meso-**3**		**1**
Interatomic distances			
N1···Si1 (N2···Si3)	2.770(1)	2.728(1)	2.852(2)
F1–Si1 (F2–Si3)	1.6415(9)	1.646(1)	1.637(2)
Si1–Si2 (Si3–Si4)	2.3649(5)	2.3878(6)	2.3711(9)
Angles			
N1···Si1–F1 (N2···Si3–F2)	168.67(5)	168.50(5)	166.10(9)
F1–Si1–Si2 (F2–Si3–Si4)	98.21(4)	101.38(4)	95.59(7)
Dihedral angles			
C1–C2–C3/C6–C7–C8	12.38	5.09	12.80
(C5–C6–C7/C2–C3–C4)			
Si1–C1–C8/N1–C8–C1	22.92	23.11	29.94
(Si3–C5–C4/N2–C4–C5)			
Pentacoordination characters			
%TBP$_a$	52	51	57
%TBP$_e$	76	74	80

Ref. [1b].
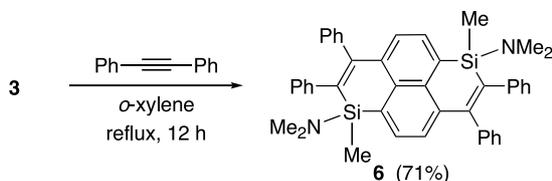
Scheme 4.

Scheme 3.

cetylene as the trapping agent. The ORTEP drawing of **10′** shown in Fig. 3 reveals a cyclophane-shaped structure, in which two disilapyrene rings are accumulated and connected by two siloxane bridges. Fig. 4 shows the space-filling model of the core structure of **10′**. The inter-atomic distance between C13 and C14*, that is nearly the gap between the two disilapyrene units,
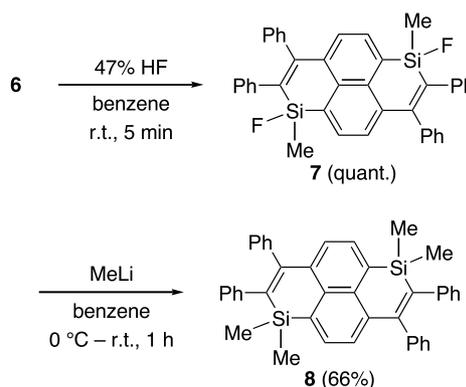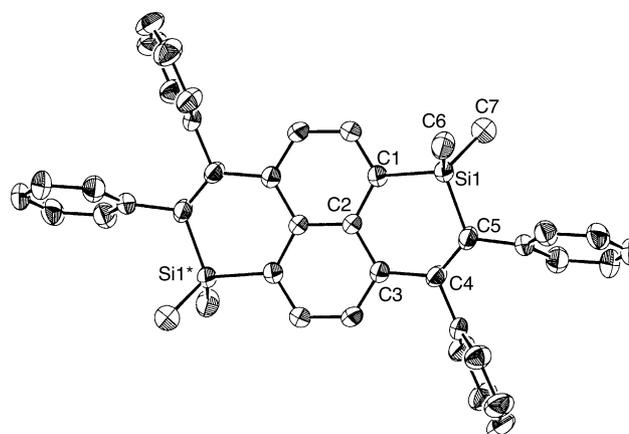
Fig. 2. X-ray structure of **8** at 60% probability level. All hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Si1–C6 1.827(3), Si1–C7 1.822(3), Si1–C5 1.852(2), C4–C5 1.352(3), Si1–C1 1.856(2).

is 3.768(3) Å, which is somewhat longer than the sum of the van der Waals radii of two carbon atoms (3.40 Å) [8].

Scheme 5.
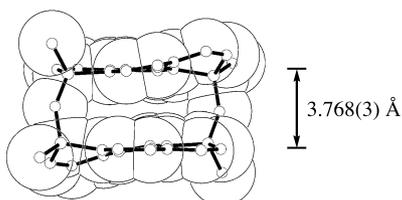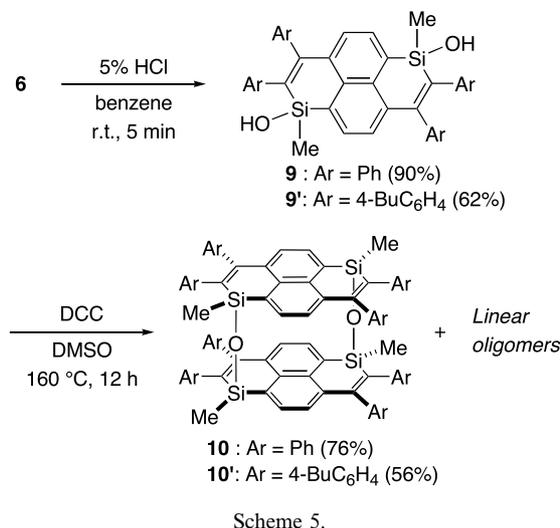
Fig. 4. Space-filling model of the core of **10′**.

2.4. Photophysical properties

Fig. 5 shows the UV–vis absorption and emission spectra of **10** together with those of the reference monomer **8** in benzene, and the photophysical data are summarized in Table 2. The transformation into the cyclized structure apparently gives rise to a remarkable change in spectra as follows. (1) The longest wavelength absorption band of the cyclophane **10** appears at 412 nm, which is ca. 20 nm red-shifted compared with that of the monomer **8**. (2) The emission spectra show a red-shifted band at 488 nm and a 10-fold increase in the fluorescence intensity for **10** in comparison with **8** [quantum yield, Φ: 0.00810 (**8**) and 0.0825 (**10**)]. A transannular π-electron interaction and an excimer formation between two proximal chromophores, char-acteristic of layered cyclophane molecules, could explain these results even though the distance of 3.77 Å is longer than the estimated value for such interactions (∼ 3.3 Å) [9].

3. Conclusion

The unique reaction mode of a nitrogen-coordinated silylene toward diphenylacetylene has been applied to construct the novel polycyclic 1,6-dihydro-1,6-disilapyr-ene skeleton. The cyclophane-shaped dimer with two siloxane bridges, selectively prepared in the dehydro-condensation reaction using DCC, shows a red-shifted UV–vis absorption spectrum and an emission spectrum of increased intensity, characteristic of the molecules in which two aromatic planes are facing each other. Although the origin of the somewhat long-distance transannular interaction remains to be clarified, these observations may provide a new model of hetero-cyclophanes containing a silicon-substituted fused ring system.

4. Experimental

4.1. General

All reactions were performed under nitrogen, unless stated otherwise. The solvents were purified and dried by standard techniques. The ^{1}H (300 MHz) NMR spectra were recorded by Varian Mercury 300 spectro-meter. The ^{13}C (67.9 MHz), ^{19}F (254 MHz), ^{29}Si (53.7 MHz) NMR spectra were recorded by JEOL JNM-EX 270 spectrometer. The ^{1}H and ^{13}C chemical shifts are referenced to internal benzene-d_6 (^{1}H, δ 7.200 and ^{13}C, δ 128.00 ppm) or THF-d_8 (^{13}C, δ 25.20 ppm). The ^{19}F and ^{29}Si chemical shifts are referenced to external CFCl$_3$ (0 ppm) and Me$_4$Si (0 ppm), respectively. Column chromatography was performed using Kieselgel (70–230 mesh) (Merck). Recycling preparative GPC was performed by using JAIGEL 1H, 2H (Japan Analytical Industry, Co., Ltd). IR spectra were recorded by IR-810
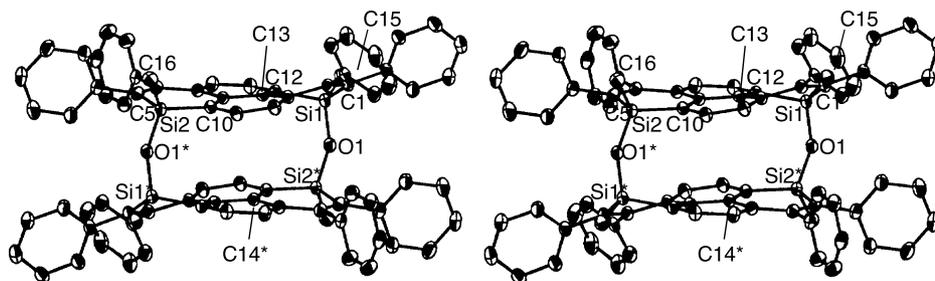
Fig. 3. X-ray structure of **10′** in stereo view at 50% probability level. All hydrogen atoms, butyl group on each phenyl ring, and solvent molecules are omitted for clarity. Selected bond lengths (Å) and angles (°): Si1–C1 1.860(3), Si1–C12 1.839(2), Si1–C15 1.875(3), Si1–O1 1.636(2), Si2–C5 1.859(2), Si2–C10 1.846(2), Si2–C16 1.842(3), Si2–O1* 1.662(2), Si1–O1–Si2* 147.0(1).
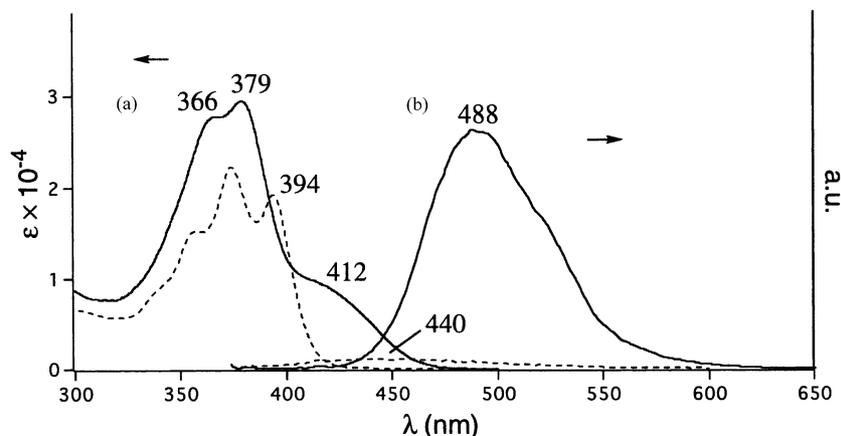
Fig. 5. (a) UV absorption and (b) emission spectra of **8** (···) and **10** (—) in benzene.

Table 2
Photophysical data of **8** and **10** in benzene

Compound	UV–vis		FL	
	λ_{abs} (nm)	ε	λ_{abs} (nm) [a]	Φ_f [b]
8	358	15 200	440	0.00810
	374	22 200		
	394	19 200		
10	366	27 700	488	0.0825
	379	29 500		
	412	9880		

[a] Excited at 366 nm.
[b] Determined with reference to anthracene.

Infrared spectrophotometer as KBr plate. UV–vis absorption spectra were recorded by Shimadzu UV-3100PC spectrometer. Fluorescence spectra were recorded by a Perkin Elmer LS50B. Melting points were determined with Yanaco MP-S3 instrument and are uncorrected. Mass spectra and elemental analyses were performed at the Mass Spectrum and Microanalysis Division of Institute for Chemical Research, Kyoto University.

4.2. Bis(pentacoordinate) silicon compound (3)

To a solution of 1,5-bis(dimethylamino)naphthalene **4** (8.57 g, 40.0 mmol) in hexane (40 ml) was added *n*-BuLi (1.63 mol l^{-1} hexane sol., 73.6 ml, 120 mmol) at room temperature. After refluxing for 3 days, the resulting 4,8-dilithio-1,5-bis(dimethylamino)naphthalene **5** formed as a cream-color precipitate was washed with hexane several times under nitrogen. To a suspension of **5** in THF (120 ml) was added 1,1-difluoro-1,2-dimethyl-2,2-diphenyldisilane [1b] (32.1 g, 115 mmol) at 0 °C. The reaction mixture was allowed to warm up to room temperature and stirred at that temperature for **5** h. After removal of lithium salt by filtration, the filtrate

was evaporated and the crude product was recrystallized from hexane to afford **3** (11.0 g, 15.0 mmol; 38%) as colorless solids (a mixture of *meso* and *rac* isomers (ca. 1:1)). One of the isomers, *meso*-**3**, was separated by the repeated recrystallization from hexane. *meso*-**3** M.p.: 143 °C (dec.) (from benzene). ^{1}H-NMR (C$_6$D$_6$) δ 0.71 (S, 6H), 0.77 (d, $J = 9.2$ Hz, 6H), 2.06 (s, 6H), 2.14 (s, 6H), 6.79 (d, $J = 7.6$ Hz, 2H), 7.14–7.20 (m, 12H), 7.55–7.62 (m, 8H), 8.35 (d, $J = 6.8$ Hz, 2H); ^{13}C-NMR (C$_6$D$_6$) δ −2.16, 2.71 (d, $J = 18$ Hz), 47.11, 47.62, 115.71, 128.07, 128.12, 129.07, 130.28, 130.46, 135.50, 135.56, 135.67, 136.77, 137.72, 137.79, 154.00; ^{29}Si-NMR (C$_6$D$_6$) δ −21.42 (d, $J = 38$ Hz), −3.54 (d, $J = 296$ Hz); ^{19}F-NMR (C$_6$D$_6$) δ −144.86. Anal. Calc. for C$_{42}$H$_{48}$N$_2$SI$_4$F$_2$: C, 68.99; H, 6.62; N, 3.83. Found: C, 69.01; H, 6.64; N, 3.88. *rac*-**3**; ^{1}H-NMR (C$_6$D$_6$) δ 0.62 (S, 6H), 0.79 (d, $J = 9.0$ Hz, 6H), 2.05 (s, 6H), 2.11 (s, 6H), 6.79 (d, $J = 7.5$ Hz, 2H), 7.14–7.18 (m, 12H), 7.59–7.63 (m, 8H), 8.38 (d, $J = 6.9$ Hz, 2H); ^{13}C-NMR (C$_6$D$_6$) δ −2.61, 2.78 (d, $J = 18$ Hz), 45.23, 49.71, 115.82, 128.15, 129.04, 129.94, 130.13, 135.50, 135.57, 135.81, 136.69, 136.84, 137.76, 137.87, 154.16; ^{29}Si-NMR (C$_6$D$_6$) δ −21.85 (d, $J = 37$ Hz), −2.96 (d, $J = 298$ Hz); ^{19}F-NMR (C$_6$D$_6$) δ −146.12.

4.3. 1,6-Dimethyl-1,6-bis(dimethylamino)-2,3,7,8-tetraphenyl-1,6-dihydro-1,6-dihydro-1,6-disilapyrene (6)

A solution of **3** (3.66 g, 5.0 mmol) and diphenylacetylene (1.78 g, 10.0 mmol) in *o*-xylene (2.5 ml) was heated under reflux for 12 h. The standing of this reaction mixture at room temperature afforded **6** (2.34 g, 3.57 mmol; 71%) as yellow solids (a mixture of *cis* and *trans* isomers (ca. 1:1)). The following data are for the mixture; ^{1}H-NMR (C$_6$D$_6$) δ 0.45–0.46 (s, 6H), 2.46–2.48 (s, 12H) 6.89–7.02 (m, 4H), 7.06–7.18 (m, 16H), 7.59 (d, $J = 7.5$ Hz, 2H), 7.68 (d, $J = 7.2$ Hz, 2H); ^{13}C-NMR (C$_6$D$_6$) δ −2.44, −2.19, 38.35, 38.39, 125.23, 126.42, 127.82, 127.91, 128.56, 130.80, 130.95, 131.07,

131.13, 134.25, 134.29, 134.51, 134.58, 134.95, 137.63, 142.65, 143.74, 143.92, 143.96, 153.95; ^{29}Si-NMR (C_6D_6) δ -21.22, -21.12. Anal. Calc. for $C_{44}H_{42}N_2Si_2$: C, 80.68; H, 6.46; N, 4.28. Found: C, 80.58; H, 6.38; N, 4.31.

4.4. 1,6-Difluoro-1,6-dimethyl-2,3,7,8-tetraphenyl-1,6-dihydro-1,6-disilapyrene (7)

To a solution of **6** (328 mg, 0.50 mmol) in benzene (2.5 ml) was added a 47% aqueous solution of HF (2.5 ml) at room temperature and stirred for 5 min. The organic layer separated, washed with water several times and dried over Na_2SO_4. After evaporation of solvent, the crude product was suspended in hexane to afford **7** (304 mg, 0.50 mmol; $\sim$100%) as yellow solids (a mixture of *cis* and *trans* isomers (ca. 1:1)). The following data are for the mixture; ^{1}H-NMR (C_6D_6) δ 0.47–0.49 (d, $J = 6.3$–6.6 Hz, 6H), 6.89–6.94 (t, $J = 7.5$ Hz, 2H), 7.00–7.17 (m, 18H), 7.49–7.52 (d, $J = 7.5$ Hz, 2H), 7.60–7.64 (dd, $J = 7.5$, 1.2 Hz, 2H); ^{13}C-NMR (C_6D_6) δ -3.18, -3.09, -2.85, -2.74, 126.04, 126.94, 127.34, 127.84, 128.54, 128.74, 130.61, 130.75, 130.86, 130.91, 131.15, 131.18, 131.88, 133.97, 134.04, 135.15, 138.35, 140.70, 140.90, 141.42, 141.48, 156.21; ^{29}Si-NMR (C_6D_6) δ -9.32, -9.17, -3.93, -3.81; ^{19}F-NMR (C_6D_6) δ -149.73, -149.30. Anal. Calc. for $C_{40}H_{30}Si_2F_2$; C, 79.43; H, 5.00. Found: C, 79.14; H, 5.13.

4.5. 1,1,6,6-Tetramethyl-2,3,7,8-tetraphenyl-1,6-dihydro-1,6-disilapyrene (8)

To a solution of **7** (60 mg, 0.10 mmol) in benzene (5.0 ml) was added a 1.14 mol l^{-1} Et$_2$O solution of MeLi (0.88 ml, 1.0 mmol) at 0 °C. The mixture was allowed to warm up to room temperature and stirred for 1 h. The reaction mixture was treated with a saturated aqueous solution of NH$_4$Cl, extracted with benzene, and dried over Na$_2$SO$_4$. After evaporation of solvent, the crude product was suspended in hexane to afford **8** (38 mg, 0.064 mmol; 64%) as pale yellow solids. M.p.: $>$ 300 °C (from benzene). The following data are for the mixture; ^{1}H-NMR (C_6D_6) δ 0.39 (s, 12H), 6.86–7.15 (m, 20H), 7.48 (d, $J = 3.5$ Hz, 4H). ^{13}C-NMR (C_6D_6) δ -0.15, 125.35, 126.44, 128.48, 128.53, 128.63, 128.86, 130.63, 130.88, 133.88, 135.41, 137.91, 142.65, 143.27, 143.37, 153.14; ^{29}Si-NMR (C_6D_6) δ -21.64. Anal. Calc. for $C_{42}H_{36}Si_2$: C, 84.51; H, 6.08. Found: C, 84.47; H, 6.14.

4.6. 1,6-Dihydroxy-1,6-dimethly-2,3,7,8-tetraphenyl-1,6-dihydro-1,6-disilapyrene (9′)

To a solution of **6** (197 mg, 0.30 mmol) in benzene (12 ml) was added 5% HCl (6.0 ml) at room temperature and the mixture was stirred for 5 min. The reaction

mixture was treated with a saturated aqueous solution of NaHCO$_3$, extracted with benzene, and dried over Na$_2$SO$_4$. After filtration and evaporation of solvent, the crude product was suspended in hexane to afford **9** (163 mg, 0.27 mmol; 90%) as yellow solids (a mixture of *cis* and *trans* isomers (ca. 1:1)). The following data are for the mixture; ^{1}H-NMR (C_6D_6) δ 0.43–0.43 (s, 6H), 1.41–1.42 (s, 2H), 6.90–7.16 (m, 20H), 7.58–7.62 (d, $J = 7.5$ Hz, 2H), 7.71–7.74 (d, $J = 7.5$ Hz, 2H); ^{13}C-NMR (C_4D_8O) δ -0.96, -0.85, 125.28, 126.65, 127.85, 128.14, 129.10, 130.63, 130.66, 131.06, 131.44, 133.99, 137.98, 142.81, 143.20; ^{29}Si-NMR (C_4D_8O) δ -19.09. Anal. Calc. for $C_{40}H_{32}O_2Si_2$: C, 79.96; H, 5.37. Found: C, 80.03; H, 5.31.

4.7. Dehydro-condensation of 9′ with DCC

A solution of **9** (60 mg, 0.10 mmol) and DCC (103 mg, 0.50 mmol) in DMSO (2.0 ml) was warmed up to 160 °C and stirred for 12 h. The reaction mixture was treated with water, extracted with chloroform, and dried over Na$_2$SO$_4$. The crude product was subjected to GPC with CHCl$_3$ as eluent to afford **10** (44 mg, 0.038 mmol; 76%) as light yellow solids. M.p.: 281 °C (dec.) (from benzene). ^{1}H-NMR (C_6D_6) δ 0.55 (s, 12H), 6.94–7.25 (m, 44H), 7.80 (d, $J = 7.5$ Hz, 4H): ^{13}C-NMR (C_6D_6) δ -0.84, 125.55, 126.42, 127.77, 128.13, 128.72, 130.50, 130.55, 131.24, 132.82, 133.36, 133.99, 137.43, 142.15, 143.14, 153.54; ^{29}Si-NMR (C_6D_6) δ -23.42. Anal. Calc. for $C_{80}H_{60}O_2Si_4$; C, 82.43; H, 5.19. Found; C, 82.22; H, 5.09.

4.8. 2,3,7,8-Tetrakis(4-butylphenyl)-1,6-dihydroxy-1,6-dimethyl-1,6-dihydro-1,6-disilapyrene (9′)

A solution of **3** (366 mg, 0.50 mmol) and bis(4-butylphenyl)acetylene (290 mg, 1.0 mmol) in *o*-xylene (2.5 ml) was heated under reflux for 12 h. The reaction mixture was treated with 5% HCl (2.5 ml), extracted with Et$_2$O, and dried over Na$_2$SO$_4$. After usual work-up, the crude product was suspended in hexane to afford **9′** (252 mg, 0.31 mmol; 62%) as yellow solids (a mixture of *cis* and *trans* isomers (ca. 2:1); stereochemistries were not assigned). The following data are for the mixture; ^{1}H-NMR (C_6D_6) δ 0.48–0.50 (s, 6H), 0.87 (t, $J = 7.5$ Hz, 6H), 0.93 (t, $J = 7.2$ Hz, 6H), 1.17–1.34 (m, 8H), 1.42–1.59 (m, 8H), 2.42 (t, $J = 7.8$ Hz, 4H), 2.48 (t, $J = 6.9$ Hz, 4H), 7.00–7.09 (m, 12H), 7.71–7.78 (m, 4H); ^{13}C-NMR (C_6D_6) δ -0.84, -0.75, 14.33, 14.36, 22.69, 22.77, 33.84, 33.98, 35.69, 35.75, 127.78, 128.17, 128.89, 130.91, 131.00, 131.11, 134.19, 134.42, 134.44, 134.52, 138.33, 139.70, 139.90, 140.00, 140.95, 143.42, 154.03; ^{29}Si-NMR (C_6D_6) δ -17.46 (*major isomer*), -17.41 (*minor isomer*). Anal. Calc. for $C_{56}H_{64}O_2Si_2$: C, 81.50; H, 7.82. Found: C, 81.43; H, 7.91.

Table 3
Experimental details for X-ray structural analysis of *meso*-**3**, **8** and **10'**

	meso-**3**	**8**	**10'** $(C_6H_6)_3$
Molecular formula	$C_{42}H_{48}N_2Si_4F_2$	$C_{42}H_{36}Si_2$	$C_{130}H_{136}Si_4O_2$
Formula weight	731.19	596.92	1842.85
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$(#2)	$P2_1/n$(#14)	$P2_1/n$(#14)
a (Å)	12.5966(5)	9.7620(6)	13.0172(3)
b (Å)	14.9337(4)	10.8526(6)	17.1908(6)
c (Å)	11.5433(4)	15.2383(8)	23.8745(6)
α (°)	106.838(2)		
β (°)	101.594(2)	96.212(3)	90.791(2)
γ (°)	71.360(2)		
V (Å^3)	1955.2100	1604.9(1)	5342.0(2)
Z	2	2	2
Crystal description	Colorless, prismatic	Colorless, prismatic	Yellow, prismatic
Crystal size (mm)	$0.30 \times 0.30 \times 0.20$	$0.30 \times 0.25 \times 0.15$	$0.40 \times 0.15 \times 0.15$
Temperature (°C)	−100	−100	−100
Radiation	Mo−K$_\alpha$ ($\lambda = 0.71070$ Å) graphite monochromated		
μ (Mo−K$_\alpha$) (cm^{-1})	1.94	1.40	1.08
$2\theta_{max}$ (°)	55.1	55.1	55.8
No. of collected reflections	7834	3454	10 049
No. of observations ($I > 3\sigma(I)$)	6467	2731	7395
No. of variables	643	200	632
Reflection/parameter ratio	10.06	13.65	11.70
R	0.038	0.060	0.056
R_w	0.058	0.083	0.083
Goodness-of-fit	1.35	1.12	1.09

4.9. Dehydro-condensation of **9'** with DCC

Essentially the same procedures as described above, using **9'** (83 mg, 0.10 mmol) and DCC (103 mg, 0.50 mmol) in DMSO (2.0 ml), followed by the purification by GPC with CHCl$_3$ as eluent afforded **10'** (45 mg, 0.028 mmol; 56%) as light yellow solids. M.p.: 277 °C (dec.) (from benzene). ^{1}H-NMR (C$_6$D$_6$) δ 0.65 (s, 12H), 0.89 (t, $J = 7.2$ Hz, 12H), 0.98 (t, $J = 7.2$ Hz, 12H), 1.19–1.43 (m, 16H), 1.45–1.70 (m, 16H), 2.42–2.59 (m, 16H), 7.03–7.16 (m, 24H), 7.28–7.37 (m, 12H), 7.52 (d, $J = 7.8$ Hz, 2H), 7.93 (d, $J = 7.5$ Hz, 2H); ^{13}C-NMR (C$_6$D$_6$) δ −0.58, 14.34, 14.39, 22.77, 22.87, 33.89, 34.22, 35.72, 35.92, 128.77, 129.99, 130.72, 131.29, 132.92, 133.50, 134.07, 137.79, 139.57, 139.90, 140.23, 140.47, 142.99, 153.67; ^{29}Si-NMR (C$_6$D$_6$) δ −23.29. Anal. Calc. for C$_{112}$H$_{124}$O$_2$Si$_4$: C, 83.32; H, 7.74. Found: C, 83.06; H, 7.81.

4.10. X-ray structural analysis of *meso*-**3**, **8** and **10'**

Single crystals of *meso*-**3**, **8** and **10'** suitable for X-ray crystallography were obtained by recrystallization from benzene (*meso*-**3** and **8**) or from benzene/EtOH (10:1) (**10'**). The unit cell of **10'** contains three molecules of benzene as crystalline solvent. Intensity data were collected on a Rigaku RAXIS-IV imaging plate area detector with graphite monochromated Mo−K$_\alpha$ radia-

tion. The data were corrected for Lorentz and polarization effects and secondary extinction. The crystal structures were resolved by direct methods in SIR92 and a full-matrix least-squares refinement was carried out for all non-hydrogen atoms. Hydrogen atoms were included but not refined. All the calculations were performed using the TEXSAN crystallographic package from Molecular Structure Corp. The crystal data and analytical conditions are listed in Table 3.

5. Supplementary material

Crystallographic data for the structure analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 207079-207081 for compounds *meso*-**3**, **8**, and **10'**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EX, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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