Supporting Information

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Silole Polymer and Cyclic Hexamer Catenating Through the Ring Silicons

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Experimental Section

General. Melting point (mp) determination was performed by using a Yanaco MP-S3 instrument and are uncorrected. ^{1}H, ^{13}C, and ^{29}Si NMR spectra were measured with a JEOL EX-270 (270 MHz for ^{1}H, 67.8 MHz for ^{13}C, and 53.5 MHz for ^{29}Si) spectrometer in appropriate solvents. Solid state CP/MAS ^{29}Si NMR spectra were recorded on a JEOL JNM-GX400 (79.43 MHz) spectrometer (GSX solid NMR system). Chemical shifts are reported in δ ppm with reference relative to residual protio-solvent peak for ^{1}H and ^{13}C, and to TMS for solution ^{29}Si, and to polydimethylsilane (–34.00 ppm) for solid state ^{29}Si, respectively. Mass spectra were collected on a JEOL JMS-700 mass spectrometer. UV absorption spectra were recorded on a Shimadzu UV-3100PC spectrometer. Fluorescence spectra were recorded on Perkin Elmer LS 50B. The quantum yields are determined with reference to quinine sulfate (Φ_{310} = 0.55 in 0.1 M H_2SO_4).[1]

Materials. Tetrahydrofuran was freshly distilled before use from sodium/benzophenone. Other solvents were dried over appropriate desiccants and distilled before use. A granular lithium was purchased from Metallgesellschaft A G. A dispersion lithium (~ 30 wt% in mineral oil) was purchased from Aldrich. All reactions were carried out under argon unless otherwise stated.

Bis(diethylamino)bis[(4-ethylphenyl)ethynyl]silane. To a THF (60 mL) solution of (4-ethylphenyl)acetylene (5.32 g, 40.9 mmol) was added a hexane solution of *n*-BuLi (26.5 mL, 43.0 mmol) at 0 °C. After stirring at the same temperature for 30 min, $(Et_2N)_2SiCl_2$ (4.97 g, 20.5 mmol) and CuCN (91.7 mg, 1.02 mmol) were added to the mixture at 0 °C. The mixture was warmed to room temperature and stirred for 3 h. After concentration under reduced pressure, hexane

was added to the mixture. The insoluble materials were filtered off. The filtrate was concentrated. The residue was subjected to bulb-to-bulb distillation (210-230 °C/0.45 mmHg) to give the titled compound (6.70 g, 15.6 mmol) in 76% yield as viscous oil: ^{1}H NMR (C_6D_6) δ 1.09 (t, J = 7.0 Hz, 12H), 1.21 (t, J = 7.7 Hz, 6H), 2.63 (q, J = 7.7 Hz, 4H), 3.06 (q, J = 7.0 Hz, 8H), 7.12 (d, J = 7.8 Hz, 4H), 7.41 (d, J = 7.8 Hz, 4H). ^{13}C NMR (C_6D_6) δ 15.48, 15.59, 28.97, 39.56, 91.09, 105.05, 120.87, 128.04, 132.40, 145.11. ^{29}Si NMR (C_6D_6) δ –55.00. HRMS(EI) Calcd for $C_{28}H_{38}N_2Si$; 430.2835. Found; 430.2782.

1,1-Bis(diethylamino)-3,4-bis(4-ethylphenyl)-2,5-dimethylsilole. Lithium naphthalenide was prepared by stirring a mixture of granular lithium (0.22 g, 32.0 mmol) and naphthalene (4.10 g, 32.0 mmol) in THF (60 mL) at room temperature for 3 h under argon. A THF (10 mL) solution of bis(diethylamino)bis[(4-ethylphenyl)ethynyl]silane (3.46 g, 8.00 mmol) was added dropwise to the solution of lithium naphthalenide at –78 °C. The mixture was stirred at the same temperature for 1 h to give a suspension of 2,5-dilithio-1,1-diaminosilole intermediate. Dimethylsulfate (3.30 mL, 35.0 mmol) was added to the mixture at –78 °C and stirred for 10 min, The mixture was allowed to warmed to room teperature and condensed under reduced pressure. After sublimation at 70 °C/1mmHg to remove naphthalene, the residue was subjected to bulb-to-bulb distillation (175-180 °C/0.35mmHg) to afford the titled compound (2.58 g, 5.5 mmol) in 70% yield as viscous oil: ^{1}H NMR (C_6D_6) δ 1.02 (t, J = 7.6 Hz, 6H), 1.16 (t, J = 6.9 Hz, 12H), 2.06 (s, 6H), 2.35 (q, J = 7.6 Hz, 4H), 3.13 (q, J = 6.9 Hz, 8H), 6.95 (d, J = 8.1 Hz, 4H), 7.05 (d, J = 8.1 Hz, 4H). ^{13}C NMR (C_6D_6) δ 15.50, 15.57, 15.75, 28.76, 39.47, 127.211, 129.60, 131.32, 137.20, 141.71, 154.04. ^{29}Si NMR (C_6D_6) δ –8.07. HRMS(EI) Calcd for $C_{30}H_{44}N_2Si$; 460.3254. Found; 460.3291.

1,1-Dichloro-3,4-bis(4-ethylphenyl)-2,5-dimethylsiloe (1). Dry HCl gas, generated from NH_4Cl (2.94 g, 55 mmol) and conc. H_2SO_4 (2.93 g, 55.0 mmol), was bubbled through an ether (80 mL) solution of 1,1-bis(diethylamino)-3,4-bis(4-ethylphenyl)-2,5-dimethylsilole (2.53 g, 5.50 mmol) at –78 °C over 1 h. The resulting mixture was concentrated, followed by addition of dry hexane. After filtration of the insoluble ammonium salts under nitrogen, the filtrate was condensed under reduced pressure. The residue was recrystallized from hexane to give **1** (1.62 g, 4.18 mmol) in 76% as colorless crystals: mp 109-111 °C. ^{1}H NMR ($CDCl_3$) δ 1.15 (t, J = 7.7

Hz, 6H), 1.86 (s, 6H), 2.54 (q, J = 7.7 Hz, 4H), 6.72 (d, J = 7.8 Hz, 4H), 6.95 (d, J = 7.8 Hz, 4H). ^{13}C NMR ($CDCl_3$) δ 12.71, 15.31, 28.48, 126.72, 126.85, 128.97, 133.64, 142.93, 155.02. ^{29}Si NMR ($CDCl_3$) δ 9.64. Anal. Calcd for $C_{22}H_{24}Cl_2Si$; C, 68.44; H, 6.30. Found; C, 68.20; H, 6.24.

Wurtz-type Polycondensation of 1,1-Dichlorosilole 1 with Li. A mixture of **1** (360 mg, 0.93 mmol) and lithium (12.9 mg, 1.86 mmol) in THF (4.5 mL) was stirred at –20 °C for 20 h. The reaction was completed as evidenced by complete disappearance of the lithium. A THF solution of EtMgBr (1.33 M, 140 μL, 0.19 mmol) was added and stirred at –20 °C for 1 h. After addition of an aqueous solution of NH_4Cl (0.5 mL), the mixture was stirred at room temperature for 20 min. The resulting white suspension was poured into MeOH. The precipitates were collected by filtration and washed successively with water and MeOH. The white powder was dissoved in THF and reprecipitated into *i*-PrOH twice to give poly(1,1-silole) **2** (180 mg) in 61% yield as a white powder. The soluble part to *i*-PrOH was condensed and the residue was recystallized from EtOAc to give **3** (18.0 mg, 9.48 μmol) in 6% yield as colorless crystals.

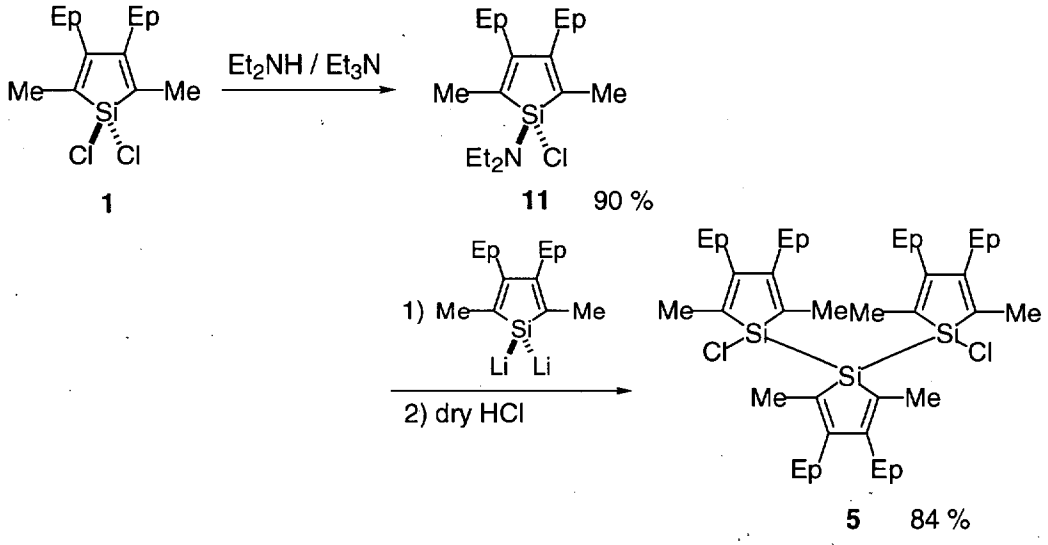
2: ^{1}H NMR spectrum of **2** in $CDCl_3$ at room temperature only show uncharacterizable broad signals, probably due to heavy hindered rotation of the polysilane main chain, but in $C_6D_5NO_2$ at elevated temperature show characterizable signals: ($C_6D_5NO_2$, at 413K) δ 0.95-1.29 (br m, 6H, ethyl CH_3), 2.41-2.79 (br m, 10H, ethyl CH_2 and 2,5-CH_3), 6.75-7.23 (br m, 8H, 3,4-C_6H_4). ^{13}C NMR (C_4D_8O, at 293K) δ 15.83, 19.03 (br), 29.27, 127.42 (br), 130.90 (br),136.72 (br), 137.37 (br),142.10 (br), 156.25 (br). ^{29}Si NMR (solid state) δ –28.0. ^{29}Si NMR spectrum in solution could not be measured due to the low solubility. IR (KBr) 2963, 1903, 1494, 830 cm^{-1}. Anal. Calcd for $(C_{22}H_{24}Si)_n$: C,83.48; H, 7.64. Found: C, 82.24; H, 7.20. The molecular weight of the polymer part after reprecipitation into MeOH is M_w = 7,600 and M_n = 6,000 ($n \approx 19$) according to the GPC approximation using polystyrene standards, which is almost same as that after reprecipitation into *i*-PrOH twice (M_w = 7,200, M_n = 6,300 ($n \approx 20$), M_w/M_n = 1.14).

3: No melting point was observed below 400 °C by DSC analysis. ^{1}H NMR ($CDCl_3$) δ 1.14 (t, J = 7.6 Hz, 36H), 2.12 (s,36H), 2.53 (q, J = 7.6 Hz, 24H), 6.69 (d, J = 7.8 Hz, 24H), 6.91 (d, J = 7.8 Hz, 24H). ^{13}C NMR ($CDCl_3$) δ 15.35, 17.74, 28.47, 126.72, 129.31, 129.42, 133.85,

136.95, 141.47, 155.51. ^{29}Si NMR ($CDCl_3$) –33.24. HRMS(FAB) Calcd for $C_{132}H_{144}Si_6$: 1897.9946. Found: 1897.9928. Anal. Cacld for $C_{132}H_{144}Si_6$: C, 83.48; H, 7.64. Found: C, 83.19; H, 7.65.

1,1"-Dichloro-1,1':1',1"-tersilole (**5**) was prepared according to Scheme S-1.

Scheme S-1



1-Chloro-1-diethylamino-3,4-bis(4-ethylphenyl)-2,5-dimethylsilole (11). To a CH_2Cl_2 (35 mL) solution of **1** (1.94 g, 5.00 mmol) were added Et_3N (0.73 mL, 5.25 mmol) and Et_2NH (0.54 mL, 5.25 mmol) at –78 °C. The mixture was gradually warmed to room temperature over 4 h and condensed under reduced pressure. Hexane was added to the mixture to form precipitates of the ammonium salt. After filtration and concentration, the residue was subjected to bulb-to-bulb distillation (204-210 °C/0.60 mmHg) to afford **11** (1.91 g, 4.50 mmol) in 90% as colorless oil: ^{1}H NMR (C_6D_6) δ 0.99 (t, J = 7.6 Hz, 6H), 1.09 (t, J = 6.9 Hz, 6H), 2.04 (s, 6H), 2.32 (q, J = 7.6 Hz, 4H), 3.06 (q, J = 6.9 Hz, 4H), 6.88 (d, J = 8.1 Hz, 4H), 6.93 (d, J = 8.1 Hz, 4H). ^{13}C NMR (C_6D_6) δ 14.26, 15.37, 16.02, 28.70, 40.42, 127.26, 128.88, 129.51, 135.66, 142.39, 154.81. ^{29}Si NMR (C_6D_6) δ –2.13. Anal. Calcd for $C_{26}H_{34}NClSi$; C, 73.63; H, 8.08; N, 3.30. Found; C, 73.56; H, 8.13; N, 3.34.

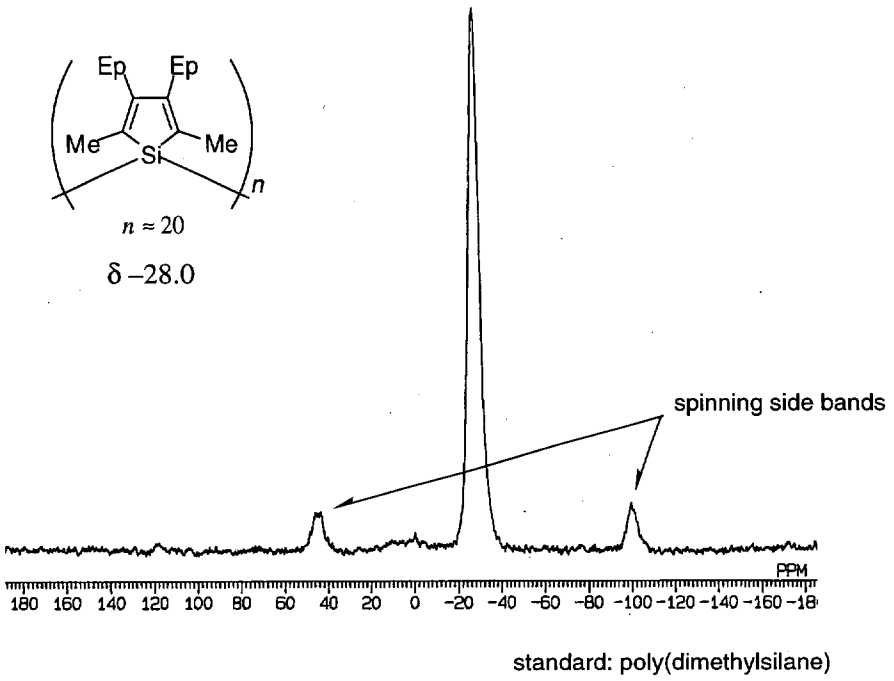
1,1"-Dichloro-3,3',3",4,4',4"-hexaxis(4-ethylphenyl)-2,2',2",5,5',5"-hexamethyl-1,1':1',1"-tersilole (5). 1,1-dilithio-3,4-bis(4-ethylphenyl)-2,5-dimethylsilole was prepared by stirring a mixture of lithium (61.4 mg, 8.84 mmol) and **1** (686 mg, 1.77 mmol) in 9 mL of THF at room temperature for 12 h. The resulting deep red solution was slowly added *via* dropping funnel to a THF (15 mL) solution of **11** (1.5 g, 3.54 mmol) at –78 °C. After stirring at the same temperature for 3 h, the mixture was condensed under reduced pressure. The residue was dissolved into 20 mL of Et_2O. To the Et_2O solution was bubbled a dry HCl gas, which generated from NH_4Cl (3.21 g, 60.0 mmol) and conc. H_2SO_4 (3.20 mL, 60.0 mmol), over 1 h at –78 °C. The mixture was concentrated, follwed by addition of dry hexane. Insoluble materials to hexane were filtered off. The filtrate was condensed under reduced pressure to give spectroscopically pure **6** (1.51 g, 1.48 mmol) in 84% yield as a white solid: ^{1}H NMR ($CDCl_3$) δ 1.06-1.23 (m, 18H), 1.97 (s, 12H), 1.99(s, 6H), 2.43-2.65 (m, 12H), 6.59-6.78 (m, 12H), 6.83-7.02 (m, 12H). ^{13}C NMR ($CDCl_3$) δ 14.41, 15.33, 15.37, 16.12, 28.48, 126.81, 129.15, 129.22, 131.21, 131.34, 134.95, 136.21, 141.89, 142.32, 154.91, 157.88. ^{29}Si NMR ($CDCl_3$) δ –39.17, 7.06. HRMS(FAB) Calcd for $C_{66}H_{72}Cl_2Si_3$: 1018.4318. Found: 1018.4272.

Coupling Reactions of 5 with Silole Dianion 4. 1,1-Dilithio-3,4-bis(4-ethylphenyl)-2,5-dimethylsilole (**4**) was prepared by stirring a mixture of lithium (19.1 mg, 2.75 mmol) and **1** (213 mg, 0.55 mmol) in 4 mL of THF at room temperature for 8 h. The resulting deep red solution was transfered to dropping funnel and slowly added to a THF (5 mL) solution of **5** (510 mg, 0.50 mmol) at –78 °C. After stirring at the same temperature for 2 h, the mixture was allowed to warm to room temperature over 10 h. Et_3N (0.14 mL, 1.00 mmol) and *i*-PrOH (0.08 mL, 1.00 mmol) were added to quench any reactive terminal at room temperature. The resulting mixture was reprecipitated into MeOH without removing THF. The precipitates were washed successively with water and MeOH to give a off-white powder. The powder was dissoved in THF and reprecipitated into *i*-PrOH twice. A white powder **2'** (302 mg) was afforded in 48% yield based on dichlorosilole. The molecular weight of 2' was determined by GPC approximation using polystyrene standards to be M_n = 2400 (n ≈ 8), M_w = 3000, M_w/M_n = 1.25. The oligomeric 2' has essentially same spectroscopic data as those of **2**: ^{1}H NMR ($C_6D_5NO_2$, at 413K) δ 0.97-1.26 (br m, 6H, ethyl CH_3), 2.34-2.75

(br m, 10H, ethyl CH_2 and 2,5-CH_3), 6.77-7.26 (br m, 8H, 3,4-C_6H_4). ^{13}C NMR ($CDCl_3$) δ 15.35, 18.15 (br.), 28.47, 126.45 (br.), 129.65 (br.), 135.78 (br.),136.47 (br.), 141.13 (br.), 155.62 (br.). ^{29}Si NMR ($CDCl_3$) δ –29.57. ^{29}Si NMR (solid state) δ –28.54. Anal. Calcd for $(C_{22}H_{24}Si)_n$: C, 83.48; H, 7.64. Found: C, 81.32; H, 7.29.

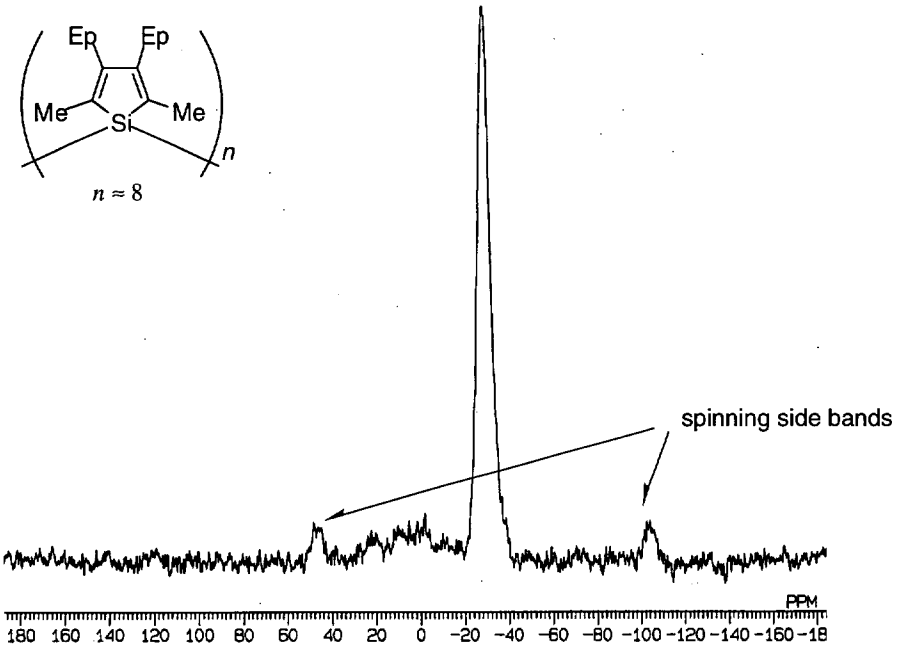
The Reaction of Poly(1,1-silole) (2) with Li. The Preparation of 2,5-Dimethyl-3,4-bis(*p*-ethylphenyl)-1,1-bis(trimethylsilyl)silole (10). A mixture of **3** (70.0 mg, 0.22 mmol/per unit, M_W = 6,800, M_n = 5,400 ($n \approx 17$), M_W/M_n = 1.26) and dispersion lithium (30 wt% in mineral oil, 51.0 mg, 2.20 mmol) in 2.5 mL of THF was stirred at 10 °C for 1 h to give a deep red solution. Trimethylsilyl chloride (200 μL, 1.58 mmol) was added to the mixture at –78 °C. The resulting mixture was stirred at –78 °C for 10 min and warmed to 0 °C. A dry hexane (6 mL) was added and stirred at 0 °C for 5 min. The precipitates were filtered and washed with hexane. The filtrate was concentrated to afford a viscous oil. The oil was further purified by GPC using 1,2-dichloroethane as an eluent to give 1,1-bis(trimethylsilyl)silole **5** (90.8 mg, 0.20 mmol) in 89% yield as a white solid: mp 33-35 °C. ^1H NMR ($CDCl_3$) δ 0.21 (s, 18H), 1.14 (t, J = 7.7 Hz, 6H), 1.89 (s, 6H), 2.52 (q, J = 7.7 Hz, 4H), 6.71 (d, J = 7.8 Hz, 4H), 6.91 (d, J = 7.8 Hz, 4H). ^{13}C NMR ($CDCl_3$) δ –0.59, 15.42, 16.53, 28.47, 126.54, 129.54, 135.42, 137.34, 141.13, 154.91. ^{29}Si NMR ($CDCl_3$) δ –30.68, –14.13. HRMS (EI) Calcd for $C_{28}H_{42}Si_3$; 462.2592. Found; 462.2596. Anal. Calcd for $C_{28}H_{42}Si_3$; C, 72.65; H, 9.15. Found; C, 72.30; H, 9.11.

Solid State ^{29}Si NMR of 2 (M_n = 6,300; $n \approx 20$)



standard: poly(dimethylsilane)

Solid State ^{29}Si NMR of 2' (M_n = 6,300; $n \approx 8$)



X-ray Crystal Structural Analysis of 3. Single crystal of **3** suitable for X-ray crystal analysis was obtained by recrystallization from diethyl malonate. Intensity data were collected at –50 ± 1 °C on a Rigaku RAXIS-IV imaging plate area detector with graphite monochromated Mo-Kα radiation to a maximum 2θ value of 55.4°. A total of 30 oscillation images each being exposed for 60.0 minutes and oscillated with 5.0° was collected. The data were corrected for Lorentz and polarization effects and secondary extinction. The crystal structure was solved by direct methods in *SAPI91*,[2] and a full-matrix least squares refinement was carried out for all non hydrogen atoms. Hydrogen atoms were included at calculated positions but not refined. All the calculations were performed using the teXsan crystallographic package from the Molecular Stracture Corp. The crystal data and analytical conditions are listed in Table S-1. The final atomic coordinates, anisotropic displacement parameters, bond lengths, and bond angles are summarized in Tables S-2 ~ S-5. The ORTEP drawing with atom labels is shown in Figure S-1.

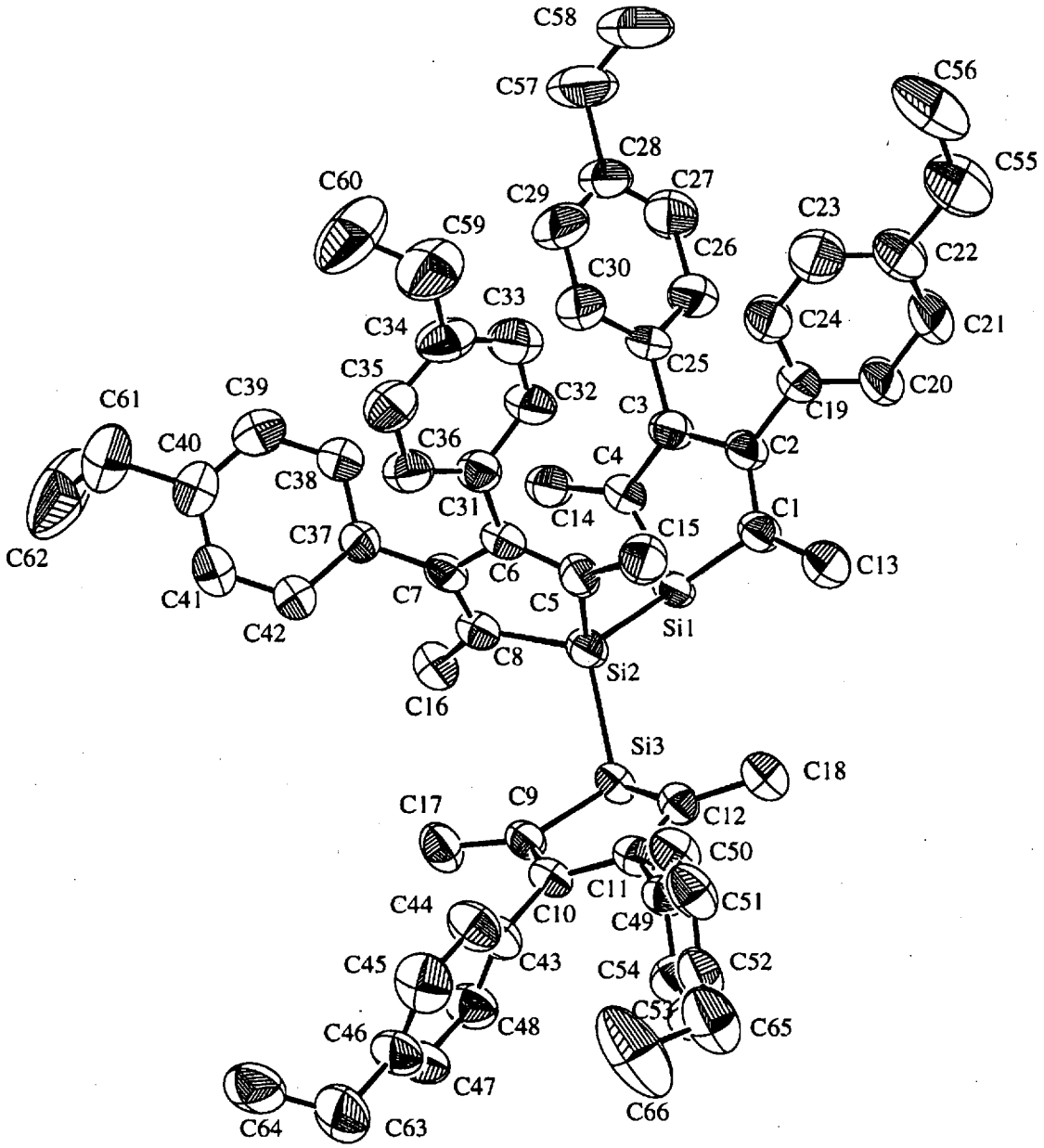


Figure S-1. X-ray crystal structure of **3** with atom-labels.

Table S-1. Experimental Details for X-ray Crystal Structural Analysis of **3**

A. Crystal Data

formula	$C_{132}H_{144}Si_6$
mol wt	1899.10
crystal color, habit	colorless, prismatic
cryst dimens, mm	0.40 x 0.10 x 0.10
cryst syst	triclinic
lattice type	Primitive
indexing images	5 osillations@60 min
detector position	105.00 mm
detector swing angle	0.00°
pixel size	0.100 mm
cell const	
a, Å	16.809(5)
b, Å	17.708(6)
c, Å	10.432(2)
α, deg	106.55(2)
β, deg	93.27(1)
γ, deg	105.22(1)
V, Å^3	2842.8701
space group	P-1 (no.2)
Z	1
D_{calcd}, g cm^{-3}	1.109
F_{000}	1020.00
μ(Mo Kα), cm^{-1}	1.22

B. Intensity Measurements

diffractometer	RAXIS-IV
temp, °C	–50
radiation	Mo Kα (λ = 0.71070 Å) graphite monochromated
detector aperture	300 mm x 300 mm
data images	30 exposures@60 min
osillation range	5.0°
detector position	105.00 mm
detector swing angle	0.00°
pixel size	0.100 mm
$2\theta_{max}$, deg	55.4
no. of collected rflns	9475
corrections	Lorents-polarization Secondary Extinction

C. Structure Solution and Refinement

structure solution	Direct Methods (SAPI91)

refinement	Full-matrix least squares
function minimized	$\sum\omega(\|Fo\|-\|Fc\|)^2$
least squares weights	$\omega = 1/\sigma^2(Fo) = [\sigma_c^2(Fo) + (p^2/4)Fo^2]$
p-factor	0.1080
anomalous dispersion	All non-hydrogen atoms
no. of unique rflns	4592 ($I > 3\sigma(I)$)
no. of variables	623
rfln/parameter ratio	7.37
R^a	0.059
$R_w{}^b$	0.082
goodness of fit	1.23
max shift/error in final cycle	0.00
maximum peak in final diff. map	0.23 e^-/Å^3
minimun peak in final diff. map	–0.24 e^-/Å^3

Table S-2. Atomic Coordinates and B_{iso}/B_{eq} of **3**

atom	x	y	z	B(eq)
Si(1)	1.09385(8)	0.12684(8)	0.5466(1)	3.67(3)
Si(2)	0.95170(8)	0.11311(8)	0.5448(1)	3.74(3)
Si(3)	0.86803(8)	–0.00943(9)	0.5653(1)	3.62(3)
C(1)	1.1513(3)	0.1794(3)	0.7207(5)	4.1(1)
C(2)	1.2002(3)	0.2540(3)	0.7202(4)	4.0(1)
C(3)	1.1939(3)	0.2728(3)	0.5891(5)	4.1(1)
C(4)	1.1428(3)	0.2141(3)	0.4840(5)	4.0(1)
C(5)	0.9415(3)	0.2069(3)	0.6691(4)	4.0(1)
C(6)	0.9187(3)	0.2527(3)	0.5973(4)	3.8(1)
C(7)	0.9008(3)	0.2144(3)	0.4464(5)	3.9(1)
C(8)	0.9148(3)	0.1407(3)	0.3970(4)	3.8(1)
C(9)	0.7574(3)	–0.0361(3)	0.4950(4)	3.7(1)
C(10)	0.7119(3)	–0.0569(3)	0.5890(4)	3.7(1)
C(11)	0.7594(3)	–0.0433(3)	0.7233(4)	3.9(1)
C(12)	0.8425(3)	–0.0146(3)	0.7357(4)	3.8(1)
C(13)	1.1423(3)	0.1517(3)	0.8440(5)	4.9(1)
C(14)	1.1306(3)	0.2209(3)	0.3443(5)	4.9(1)
C(15)	0.9548(4)	0.2284(3)	0.8191(5)	5.3(1)
C(16)	0.9088(3)	0.0939(3)	0.2498(5)	4.7(1)
C(17)	0.7228(3)	–0.0382(4)	0.3579(5)	5.0(1)
C(18)	0.8998(3)	0.0013(3)	0.8628(5)	4.9(1)
C(19)	1.2558(3)	0.3172(3)	0.8401(5)	4.8(1)
C(20)	1.3169(4)	0.2982(4)	0.9062(6)	7.4(2)
C(21)	1.3699(6)	0.3581(5)	1.0171(9)	10.8(3)
C(22)	1.3629(6)	0.4345(5)	1.0619(8)	10.1(2)
C(23)	1.3015(5)	0.4532(4)	0.9947(7)	8.6(2)
C(24)	1.2492(4)	0.3952(4)	0.8865(5)	6.0(2)
C(25)	1.2424(3)	0.3551(3)	0.5795(5)	4.3(1)
C(26)	1.3267(4)	0.3768(4)	0.5823(7)	6.3(2)
C(27)	1.3703(4)	0.4534(5)	0.5735(8)	8.0(2)
C(28)	1.3302(5)	0.5092(4)	0.5630(7)	7.1(2)
C(29)	1.2455(5)	0.4872(4)	0.5591(7)	7.0(2)

C(30)	1.2018(4)	0.4112(4)	0.5648(6)	5.7(2)
C(31)	0.9140(3)	0.3371(3)	0.6640(5)	4.2(1)
C(32)	0.9809(3)	0.3928(3)	0.7538(5)	5.0(1)
C(33)	0.9804(4)	0.4698(4)	0.8241(6)	5.9(2)
C(34)	0.9127(5)	0.4966(4)	0.8077(6)	6.1(2)
C(35)	0.8436(4)	0.4413(4)	0.7144(6)	5.8(2)
C(36)	0.8452(3)	0.3627(3)	0.6444(5)	4.9(1)
C(37)	0.8711(3)	0.2568(3)	0.3575(5)	4.0(1)
C(38)	0.9125(3)	0.3357(3)	0.3608(5)	5.1(1)
C(39)	0.8827(4)	0.3737(4)	0.2772(7)	6.5(2)
C(40)	0.8106(5)	0.3328(5)	0.1886(7)	7.2(2)
C(41)	0.7684(4)	0.2549(4)	0.1858(7)	6.8(2)
C(42)	0.7983(3)	0.2167(3)	0.2687(5)	5.2(1)
C(43)	0.6202(3)	–0.0926(3)	0.5616(5)	4.2(1)
C(44)	0.5674(3)	–0.0551(4)	0.6349(6)	5.4(1)
C(45)	0.4819(4)	–0.0895(5)	0.6034(7)	6.6(2)
C(46)	0.4478(3)	–0.1626(4)	0.4969(7)	5.8(2)
C(47)	0.5008(4)	–0.1971(4)	0.4270(6)	5.9(2)
C(48)	0.5849(3)	–0.1636(4)	0.4581(6)	5.1(1)
C(49)	0.7106(3)	–0.0652(3)	0.8295(5)	4.2(1)
C(50)	0.7034(3)	–0.0058(4)	0.9442(5)	5.1(1)
C(51)	0.6499(3)	–0.0272(4)	1.0321(5)	5.8(2)
C(52)	0.6035(3)	–0.1066(5)	1.0117(6)	6.1(2)
C(53)	0.6140(4)	–0.1648(4)	0.9025(7)	6.0(2)
C(54)	0.6667(4)	–0.1449(4)	0.8133(6)	5.5(2)
C(55)	1.4238(10)	0.4972(7)	1.185(1)	18.5(5)
C(56)	1.4517(7)	0.5738(8)	1.187(1)	14.5(4)
C(57)	1.3768(7)	0.5950(5)	0.5597(9)	11.4(3)
C(58)	1.4259(7)	0.6494(6)	0.677(1)	13.2(3)
C(59)	0.9119(6)	0.5825(5)	0.8895(7)	9.2(2)
C(60)	0.8835(7)	0.6290(6)	0.8209(8)	11.4(3)
C(61)	0.7770(6)	0.3758(6)	0.0993(10)	10.3(3)
C(62)	0.7625(9)	0.3336(7)	–0.0377(9)	14.1(4)
C(63)	0.3552(4)	–0.1989(5)	0.4647(8)	8.2(2)
C(64)	0.3151(4)	–0.1585(5)	0.3862(8)	7.8(2)
C(65)	0.5387(4)	–0.1290(5)	1.1007(7)	8.3(2)
C(66)	0.4557(5)	–0.1361(8)	1.0432(8)	12.7(3)
H(13a)	1.1673	0.1086	0.8369	5.8579
H(13b)	1.1690	0.1966	0.9223	5.8579
H(13c)	1.0848	0.1322	0.8508	5.8579
H(14a)	1.1593	0.2751	0.3453	5.8274
H(14b)	1.0729	0.2096	0.3154	5.8274
H(14c)	1.1521	0.1824	0.2838	5.8274
H(15a)	1.0127	0.2440	0.8505	6.3799
H(15b)	0.9332	0.2730	0.8578	6.3799
H(15c)	0.9270	0.1820	0.8448	6.3799
H(16a)	0.9193	0.1315	0.1992	5.6893
H(16b)	0.8545	0.0566	0.2185	5.6893
H(16c)	0.9487	0.0641	0.2388	5.6893
H(17a)	0.7435	0.0147	0.3472	6.0169
H(17b)	0.6638	–0.0530	0.3492	6.0169
H(17c)	0.7394	–0.0776	0.2905	6.0169
H(18a)	0.9246	0.0589	0.9025	5.9010
H(18b)	0.8689	–0.0201	0.9246	5.9010
H(18c)	0.9421	–0.0249	0.8416	5.9010
H(20)	1.3231	0.2444	0.8766	8.8334
H(21)	1.4122	0.3443	1.0621	13.0087
H(23)	1.2956	0.5072	1.0242	10.3319

H(24)	1.2070	0.4095	0.8422	7.2158
H(26)	1.3562	0.3391	0.5904	7.6158
H(27)	1.4290	0.4667	0.5749	9.6070
H(29)	1.2163	0.5254	0.5522	8.3944
H(30)	1.1428	0.3971	0.5585	6.8153
H(32)	1.0295	0.3767	0.7672	6.0426
H(33)	1.0281	0.5058	0.8859	7.1143
H(35)	0.7956	0.4581	0.6994	6.9242
H(36)	0.7981	0.3260	0.5822	5.8991
H(38)	0.9627	0.3647	0.4216	6.1793
H(39)	0.9123	0.4283	0.2814	7.7456
H(41)	0.7178	0.2264	0.1260	8.1908
H(42)	0.7682	0.1623	0.2643	6.2600
H(44)	0.5899	–0.0054	0.7073	6.4595
H(45)	0.4462	–0.0633	0.6545	7.9240
H(47)	0.4789	–0.2464	0.3536	7.0690
H(48)	0.6200	–0.1905	0.4064	6.1439
H(50)	0.7355	0.0499	0.9626	6.1584
H(51)	0.6451	0.0147	1.1092	6.9476
H(53)	0.5842	–0.2209	0.8873	7.2037
H(54)	0.6728	–0.1876	0.7386	6.5814
H(55a)	1.4709	0.4778	1.1934	22.1828
H(55b)	1.3962	0.4976	1.2625	22.1828
H(56a)	1.4917	0.5777	1.1260	17.4146
H(56b)	1.4771	0.6077	1.2753	17.4146
H(56c)	1.4068	0.5915	1.1591	17.4146
H(57a)	1.4119	0.5883	0.4916	13.7015
H(57b)	1.3365	0.6193	0.5358	13.7015
H(58a)	1.4444	0.7027	0.6676	15.8479
H(58b)	1.4728	0.6315	0.6953	15.8479
H(58c)	1.3944	0.6514	0.7504	15.8479
H(59a)	0.9674	0.6125	0.9309	11.0116
H(59b)	0.8775	0.5766	0.9573	11.0116
H(60a)	0.8888	0.6820	0.8817	13.6918
H(60b)	0.8267	0.6024	0.7837	13.6918
H(60c)	0.9156	0.6344	0.7502	13.6918
H(61a)	0.8163	0.4279	0.1133	12.4148
H(61b)	0.7259	0.3835	0.1266	12.4148
H(62a)	0.7434	0.3652	–0.0858	16.9429
H(62b)	0.7214	0.2822	–0.0544	16.9429
H(62c)	0.8126	0.3245	–0.0668	16.9429
H(63a)	0.3431	–0.2554	0.4142	9.7955
H(63b)	0.3327	–0.1940	0.5472	9.7955
H(64a)	0.3438	–0.1538	0.3116	9.3550
H(64b)	0.2588	–0.1903	0.3541	9.3550
H(64c)	0.3168	–0.1051	0.4420	9.3550
H(65a)	0.5392	–0.1803	1.1122	9.9136
H(65b)	0.5527	–0.0875	1.1862	9.9136
H(66a)	0.4540	–0.0846	1.0341	15.1888
H(66b)	0.4414	–0.1768	0.9569	15.1888
H(66c)	0.4171	–0.1515	1.1009	15.1888

$B_{eq} = 8/3 \times \pi^2 (U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aa^*bb^*\cos\gamma + 2U_{13}aa^*cc^*\cos\beta + 2U_{23}bb^*cc^*\cos\alpha)$

Table S-3. Anisotropic Displacement Parameters of **3**

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Si(1)	0.0401(7)	0.0418(8)	0.0470(7)	0.0011(6)	–0.0016(5)	0.0090(6)
Si(2)	0.0428(8)	0.0422(8)	0.0498(7)	0.0089(6)	–0.0004(6)	0.0074(6)
Si(3)	0.0352(7)	0.0495(9)	0.0455(7)	0.0064(6)	0.0005(5)	0.0100(6)
C(1)	0.050(3)	0.048(3)	0.050(3)	0.011(2)	–0.001(2)	0.007(2)
C(2)	0.049(3)	0.042(3)	0.052(3)	0.009(2)	–0.003(2)	0.005(2)
C(3)	0.045(3)	0.042(3)	0.060(3)	0.007(2)	0.002(2)	0.012(2)
C(4)	0.049(3)	0.043(3)	0.050(3)	0.004(2)	–0.005(2)	0.009(2)
C(5)	0.046(3)	0.051(3)	0.049(3)	0.015(2)	–0.002(2)	0.009(2)
C(6)	0.039(3)	0.044(3)	0.052(3)	0.006(2)	0.004(2)	0.005(2)
C(7)	0.031(2)	0.048(3)	0.060(3)	0.001(2)	0.003(2)	0.016(2)
C(8)	0.040(3)	0.044(3)	0.052(3)	0.006(2)	0.003(2)	0.008(2)
C(9)	0.038(3)	0.045(3)	0.049(3)	0.007(2)	–0.001(2)	0.009(2)
C(10)	0.036(2)	0.047(3)	0.048(3)	0.006(2)	0.004(2)	0.008(2)
C(11)	0.044(3)	0.043(3)	0.052(3)	0.010(2)	0.005(2)	0.007(2)
C(12)	0.046(3)	0.048(3)	0.045(2)	0.012(2)	0.001(2)	0.009(2)
C(13)	0.061(3)	0.061(4)	0.056(3)	0.014(3)	0.003(2)	0.011(3)
C(14)	0.068(3)	0.052(3)	0.054(3)	0.001(3)	0.000(2)	0.017(2)
C(15)	0.084(4)	0.059(4)	0.054(3)	0.025(3)	0.001(3)	0.008(3)
C(16)	0.054(3)	0.066(4)	0.055(3)	0.017(3)	0.001(2)	0.012(3)
C(17)	0.044(3)	0.078(4)	0.063(3)	0.009(3)	–0.003(2)	0.023(3)
C(18)	0.054(3)	0.068(4)	0.054(3)	0.011(3)	0.001(2)	0.011(3)
C(19)	0.066(4)	0.050(3)	0.055(3)	0.004(3)	–0.012(2)	0.013(3)
C(20)	0.110(5)	0.054(4)	0.089(4)	0.017(4)	–0.051(4)	0.000(3)
C(21)	0.156(8)	0.074(6)	0.137(7)	0.011(5)	–0.101(6)	0.008(5)
C(22)	0.170(8)	0.067(5)	0.094(5)	0.003(5)	–0.076(5)	–0.005(4)
C(23)	0.154(7)	0.061(5)	0.087(5)	0.025(5)	–0.034(5)	0.000(4)
C(24)	0.096(5)	0.057(4)	0.062(3)	0.021(3)	–0.016(3)	0.004(3)
C(25)	0.052(3)	0.036(3)	0.062(3)	–0.002(2)	–0.006(2)	0.010(2)
C(26)	0.059(4)	0.060(4)	0.115(5)	0.004(3)	–0.008(3)	0.032(4)
C(27)	0.066(4)	0.099(6)	0.132(6)	–0.018(4)	–0.013(4)	0.068(5)
C(28)	0.108(6)	0.052(4)	0.086(4)	–0.015(4)	–0.021(4)	0.027(3)
C(29)	0.117(6)	0.046(4)	0.097(5)	0.022(4)	0.000(4)	0.019(3)
C(30)	0.083(4)	0.055(4)	0.074(4)	0.018(3)	0.000(3)	0.016(3)
C(31)	0.047(3)	0.049(3)	0.060(3)	0.012(2)	0.006(2)	0.015(2)
C(32)	0.062(3)	0.047(4)	0.066(3)	0.005(3)	0.001(3)	0.004(3)
C(33)	0.078(4)	0.061(4)	0.074(4)	0.007(3)	0.007(3)	0.015(3)
C(34)	0.110(5)	0.044(4)	0.067(4)	0.018(4)	0.018(4)	0.007(3)
C(35)	0.086(5)	0.062(4)	0.079(4)	0.036(4)	0.020(3)	0.019(3)
C(36)	0.058(3)	0.050(4)	0.077(4)	0.014(3)	0.011(3)	0.017(3)
C(37)	0.041(3)	0.053(3)	0.060(3)	0.010(2)	0.002(2)	0.022(2)
C(38)	0.059(3)	0.059(4)	0.072(4)	0.007(3)	–0.003(3)	0.024(3)
C(39)	0.084(4)	0.066(4)	0.094(4)	0.005(3)	0.004(4)	0.040(4)
C(40)	0.095(5)	0.080(5)	0.105(5)	0.024(4)	–0.013(4)	0.046(4)
C(41)	0.076(4)	0.076(5)	0.096(5)	0.015(4)	–0.030(3)	0.025(4)
C(42)	0.059(3)	0.060(4)	0.075(4)	0.007(3)	–0.010(3)	0.027(3)
C(43)	0.040(3)	0.060(4)	0.053(3)	0.009(3)	0.007(2)	0.012(3)
C(44)	0.046(3)	0.077(4)	0.072(3)	0.014(3)	0.010(3)	0.011(3)
C(45)	0.052(4)	0.109(6)	0.101(5)	0.031(4)	0.031(3)	0.037(4)
C(46)	0.042(3)	0.079(5)	0.090(4)	–0.006(3)	0.002(3)	0.036(4)
C(47)	0.054(4)	0.063(4)	0.089(4)	–0.002(3)	0.003(3)	0.015(3)
C(48)	0.045(3)	0.060(4)	0.082(4)	0.011(3)	0.009(3)	0.015(3)
C(49)	0.040(3)	0.057(4)	0.058(3)	0.005(2)	0.004(2)	0.020(3)
C(50)	0.054(3)	0.074(4)	0.055(3)	0.005(3)	0.006(2)	0.015(3)
C(51)	0.054(3)	0.105(5)	0.049(3)	0.009(3)	0.006(2)	0.019(3)

C(52)	0.051(3)	0.115(6)	0.061(3)	0.002(4)	–0.001(3)	0.043(4)
C(53)	0.064(4)	0.073(4)	0.089(4)	–0.001(3)	0.005(3)	0.042(4)
C(54)	0.069(4)	0.069(4)	0.073(4)	0.017(3)	0.016(3)	0.028(3)
C(55)	0.33(2)	0.078(7)	0.18(1)	–0.010(9)	–0.18(1)	–0.020(7)
C(56)	0.164(10)	0.132(10)	0.166(9)	–0.021(8)	–0.079(8)	–0.011(8)
C(57)	0.186(9)	0.075(6)	0.129(7)	–0.043(6)	–0.032(6)	0.049(5)
C(58)	0.20(1)	0.075(6)	0.175(9)	–0.046(6)	–0.044(8)	0.046(6)
C(59)	0.185(9)	0.073(5)	0.082(5)	0.049(5)	0.012(5)	0.002(4)
C(60)	0.26(1)	0.104(7)	0.106(6)	0.106(8)	0.049(7)	0.042(5)
C(61)	0.155(8)	0.116(7)	0.135(7)	0.047(6)	–0.026(6)	0.061(6)
C(62)	0.34(2)	0.162(10)	0.084(6)	0.13(1)	0.026(7)	0.066(6)
C(63)	0.044(4)	0.129(7)	0.139(6)	0.001(4)	0.001(4)	0.067(5)
C(64)	0.048(4)	0.084(5)	0.153(7)	0.006(3)	0.006(4)	0.034(5)
C(65)	0.062(4)	0.165(8)	0.080(4)	–0.001(4)	0.013(3)	0.059(5)
C(66)	0.052(4)	0.29(1)	0.104(5)	0.016(6)	0.024(4)	0.043(7)

The general temperature factor expression:
$\exp(-2\pi^2(a^{*2}U_{11}h^2 + b^{*2}U_{22}k^2 + c^{*2}U_{33}l^2 + 2a^*b^*U_{12}hk + 2a^*c^*U_{13}hl + 2b^*c^*U_{23}kl))$

Table S-4. Bond Lengths (Å) of **3**

atom	atom	distance	atom	atom	distance
Si(1)	Si(2)	2.336(2)	C(10)	C(43)	1.480(6)
Si(1)	Si(3)	2.345(2)	C(11)	C(12)	1.339(6)
Si(1)	C(1)	1.861(5)	C(11)	C(49)	1.494(6)
Si(1)	C(4)	1.861(5)	C(12)	C(18)	1.505(6)
Si(2)	Si(3)	2.330(2)	C(19)	C(20)	1.370(7)
Si(2)	C(5)	1.849(5)	C(19)	C(24)	1.364(8)
Si(2)	C(8)	1.866(5)	C(20)	C(21)	1.394(8)
Si(3)	C(9)	1.846(4)	C(21)	C(22)	1.34(1)
Si(3)	C(12)	1.874(5)	C(22)	C(23)	1.38(1)
C(1)	C(2)	1.363(7)	C(22)	C(55)	1.54(1)
C(1)	C(13)	1.504(7)	C(23)	C(24)	1.362(8)
C(2)	C(3)	1.501(6)	C(25)	C(26)	1.362(8)
C(2)	C(19)	1.487(6)	C(25)	C(30)	1.382(8)
C(3)	C(4)	1.339(6)	C(26)	C(27)	1.393(9)
C(3)	C(25)	1.507(7)	C(27)	C(28)	1.36(1)
C(4)	C(14)	1.504(6)	C(28)	C(29)	1.37(1)
C(5)	C(6)	1.357(6)	C(28)	C(57)	1.527(9)
C(5)	C(15)	1.491(6)	C(29)	C(30)	1.372(9)
C(6)	C(7)	1.503(6)	C(31)	C(32)	1.374(7)
C(6)	C(31)	1.482(7)	C(31)	C(36)	1.374(7)
C(7)	C(8)	1.347(7)	C(32)	C(33)	1.353(8)
C(7)	C(37)	1.488(6)	C(33)	C(34)	1.363(9)
C(8)	C(16)	1.506(7)	C(34)	C(35)	1.409(8)
C(9)	C(10)	1.351(6)	C(34)	C(59)	1.521(9)
C(9)	C(17)	1.499(6)	C(35)	C(36)	1.383(8)
C(10)	C(11)	1.496(6)	C(37)	C(38)	1.377(7)
C(37)	C(42)	1.379(6)	C(38)	C(39)	1.389(7)
C(39)	C(40)	1.371(8)	C(40)	C(41)	1.367(9)
C(40)	C(61)	1.529(9)	C(41)	C(42)	1.385(7)
C(43)	C(44)	1.383(7)	C(43)	C(48)	1.364(7)
C(44)	C(45)	1.384(8)	C(45)	C(46)	1.399(9)
C(46)	C(47)	1.343(8)	C(46)	C(63)	1.497(8)
C(47)	C(48)	1.362(7)	C(49)	C(50)	1.386(7)

C(49)	C(54)	1.368(7)	C(50)	C(51)	1.380(7)
C(51)	C(52)	1.367(9)	C(52)	C(53)	1.357(9)
C(52)	C(65)	1.519(8)	C(53)	C(54)	1.376(8)
C(55)	C(56)	1.31(1)	C(57)	C(58)	1.38(1)
C(59)	C(60)	1.39(1)	C(61)	C(62)	1.38(1)
C(63)	C(64)	1.471(9)	C(65)	C(66)	1.45(1)

Distances are in angstroms. Estimated standard deviations in the least significant figure are given in parentheses.

Table S-5. Bond Angles (deg) of **3**

atom	atom	atom	angle	atom	atom	atom	angle
C(1)	Si(1)	C(4)	89.3(4)	C(2)	C(3)	C(4)	113.7(6)
C(1)	Si(1)	C(5)	117.4(3)	C(2)	C(3)	C(12)	119.7(7)
C(1)	Si(1)	C(8)	110.8(3)	C(4)	C(3)	C(12)	126.6(8)
C(4)	Si(1)	C(5)	111.2(3)	I(2)	C(4)	Si(1)	125.3(4)
C(4)	Si(1)	C(8)	113.4(3)	I(2)	C(4)	C(3)	124.2(5)
C(5)	Si(1)	C(8)	112.8(3)	Si(1)	C(4)	C(3)	110.4(6)
I(1)	C(1)	Si(1)	123.9(4)	Si(1)	C(5)	C(6)	111.2(5)
I(1)	C(1)	C(2)	125.0(5)	Si(1)	C(5)	C(7)	111.0(5)
Si(1)	C(1)	C(2)	111.0(5)	C(6)	C(5)	C(7)	111.4(6)
C(1)	C(2)	C(3)	115.4(6)	Si(1)	C(8)	C(9)	111.9(4)
C(1)	C(2)	C(11)	127.6(8)	Si(1)	C(8)	C(10)	110.9(4)
C(3)	C(2)	C(11)	117.0(7)	C(9)	C(8)	C(10)	110.6(6)

Angles are in degrees. Estimated standard deviations in the least significant figure are given in parentheses.

Reference

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