Supplementary Materials

Experimental Procedure:

A solution of disilirane **1a** (54.6 mg, 0.1mmol) in benzonitrile and toluene (1:1) (5 ml) and another solution of C_{60} (3.6 mg, $5X10^{-3}$ mmol) in benzonitrile and toluene 1:1 ratio (5 ml) were placed individually in a two legged Pyrex tube. These solutions were mixed after degassed by freeze-pump-thaw cycles under reduced pressure by using a diffusion pump and irradiated with a 500W halogen lamp (cutoff<400 nm) for 12 hr. Separation by preparative HPLC (Japan Analytical Industry LC-08) using toluene as eluent and recrystallization afforded **2a** and **3a** in 51% and 18% yields, respectively. **2b** was also obtained by the same procedure.

2a: ^{1}H-NMR (500 MHz, CD_2Cl_2) δ 7.24(m, H), 7.15(brs, 2H), 7.14(brs, 2H), 6.55(s, 4H), 6.50(s, 4H), 2.23(s, 12H), 2.17(s, 6H), 2.16(s, 6H), 2.05(s, 12H), 1.61(s, 2H); ^{13}C-NMR (125 MHz, CD_2Cl_2) δ 201.18, 143.60, 143.46, 143.03, 138.45, 137.33, 134.73, 131.51, 129.14*, 128.65, 127.64, 125.89, 24.70, 23.37, 20.31, 20.29, 11.12, *One peak was overlapped. Detected by gradient HMQC.; ^{29}Si-NMR (100 MHz, CD_2Cl_2) δ -0.21, -8.25; FT-IR (neat) 1604 cm^{-1}; UV-Vis (λ_{max}, hexane) 219, 225, 272 nm; FAB MS, m/z 650 (M+H). For **2b**: ^{1}H-NMR (500 MHz, CD_2Cl_2) δ 7.60(dd, J=2.0, 6.5 Hz, 2H), 7.23-7.38(m, 7H), 7.00(d, J=7.5 Hz, 4H), 6.99(d, J= 7.5 Hz, 4H), 3.07(q, J= 7.3 Hz, 4H), 2.68(q, J= 7.3 Hz, 4H), 2.62(q, J= 7.3 Hz, 4H), 2.43(q, J= 7.3 Hz, 4H), 0.77(t, J= 7.3 Hz, 12H), 0.61(t, J= 7.3 Hz, 12H); ^{13}C-NMR (125 MHz, CD_2Cl_2) δ 201.71, 150.08, 149.13, 145.13, 135.45, 133.08, 129.62, 129.61, 129.03, 127.47, 127.15, 125.93, 125.72, 29.93, 28.32, 15.13, 14.31; ^{29}Si-NMR (100 MHz, CD_2Cl_2) δ -6.38, -19.47; FT-IR (neat) 1587 cm^{-1}; UV-Vis (λ_{max}, hexane) 213, 239, 253 nm; FAB MS, m/z 708 (M+H). For **3a**: ^{1}H-NMR (500 MHz, CD_2Cl_2) δ 7.69(d, J= 7.0 Hz, 4H), 6.86(s, 4H), 6.84(d, J= 7.0 Hz,

2H), 6.76(t, J= 7.0 Hz, 4H), 6.21(s, 4H), 2.96(s, 12H), 2.53(s, 12H), 2.75(s, 6H), 2.13(s, 6H), 2.12(s, 2H) ; ^{13}C-NMR (125 MHz, CD_2Cl_2) δ 178.78, 144.74, 144.26, 139.09, 138.70, 138.64, 135.28, 133.56, 130.88, 130.27, 129.88, 129.04, 127.99, 25.30, 24.72, 21.46, 21.18, 14.94. ; ^{29}Si-NMR (100 MHz, CD_2Cl_2) δ -15.98; FT-IR (neat) 1604 cm^{-1}; UV-Vis (λ_{max}, hexane) 222, 261 nm; FAB MS, m/z 753 (M+H).

Crystallographic foot-notes for the structures:

Reflection data for both structures were collected using a Rigaku AFC-7R four-circle diffractometer employing graphite monochromated Mo(K_α) radiation at 296 K. The data were corrected for Lorentz, polarization and crystal absorption. The Neutral atom scattering factors used in the refinements were taken from Cromer and Waber[a] and corrected for anomalous dispersion.[b] All hydrogens were add in calulated positions (C-H = 0.97 Å and =C-H = 1.08 Å) but not refined. Calculations were performed on an O2 workstation using the teXsan crstallographic software package from Molecular Structure Corp. A complete set of atomic coordinates, bond lenghts and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre and are available with the respective CCDC numbers below:

Crystallographic data for $Dep_2SiOSiDep_2$/PhCN (2b): $C_{47}H_{57}NOSi_2$, M_W = 708.14, monoclinic, space group $P2_1/n$ (No. 14), a = 10.618(4) Å, b = 24.758(7) Å, c = 15.958(4), b = 97.39(3)°, V = 4160(2) $Å^3$, d_{calcd} = 1.13g/cm^3, Z = 4, F (000) = 1528.00, μ = 1.20 cm^{-1}. A colorless crystal of dimensions 0.20 X 0.40 X 0.70 mm was used to collect a total of 11266 unique reflections in the range $2.8 < 2\theta > 60.0°$. The transmission factors range from 0.60 to 1.00, and the secondary extinction coefficient is equal to 2.929e-08. The final refinement using 4614 reflections ($I > 3.0\sigma(I)$) and 461 parameters

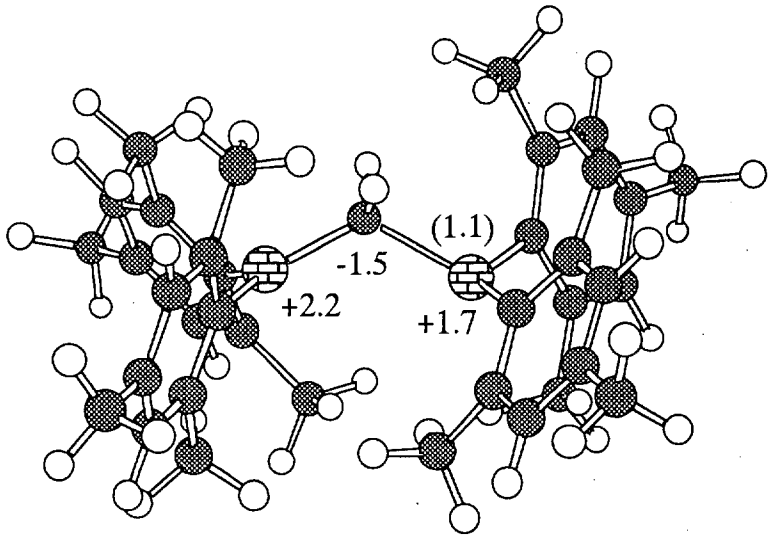
converged R = 0.063 and R_W = 0.060. The corresponding Fourier map show electron density features between 0.34 and -0.32 $e^-/Å^3$. The structure's data number is CCDC - 102853.

Crystallographic data for $Mes_2SiCH_2SiMes_2/2PhCN$ (3a): $C_{56.4}H_{61.4}N_2Si_2$, M_W = 823.49, monoclinic, space group $P2_1/n$ (No. 14), a = 12.374(3) Å, b = 25.227(3) Å, c = 15.628(3), b = 98.98(3)°, V = 4818(1) $Å^3$, d_{calcd} = 1.13g/cm^3, Z = 4, F (000) = 1767.2, μ = 1.12 cm^{-1}. A colorless crystal of dimensions 0.10 X 0.15 X 0.40 mm was used to collect a total of 8518 unique reflections in the range $2.8 < 2\theta > 55.0°$. The data required no decay corrections; the transmission factors range from 0.80 to 1.00, and the secondary extinction coefficient is equal to 2.929e-08. The crystal lattice contains a benzene molecule whose occupancy parameter refined to 0.9. The final refinement using 4614 reflections ($I > 2.0\sigma(I)$) and 504 parameters converged with R = 0.069 and R_W = 0.076. The corresponding residual electron density features are between 0.82 and -0.56 $e^-/Å^3$. The structure's data number is CCDC - 102854.

(a) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, **1974**; Vol. IV, Table 2.2B.

(b) Cromer, D. T.; Mann, B. J. *Acta Crystallogr.* **1968**, *A24*, 321.

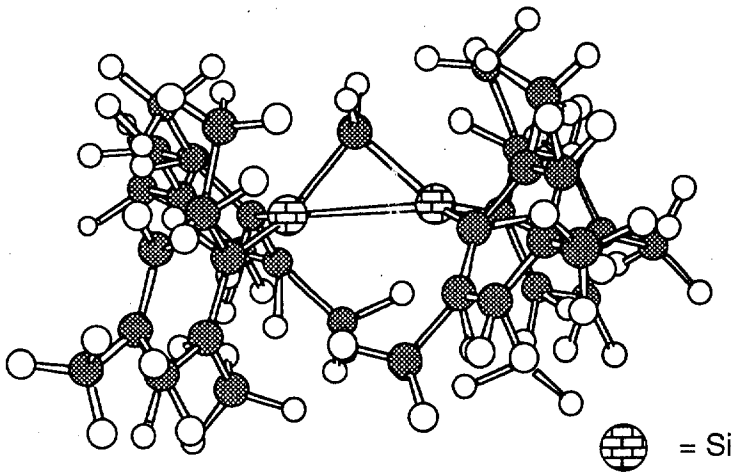
Supplementary Materials



α-spin LOMO -1.95
HOMO -9.18
β-spin LOMO -1.93
HOMO -10.80

= Si
= C
= H

Fig. 1. AM1 optimized structure of $\mathbf{1a}^{+\cdot}$. The charge and spin (in parentheses) densities and HOMO-LUMO levels (eV) at HF/3-21G//AM1 are also shown.



LUMO 2.95
HOMO -5.91

= Si
= C
= H

Fig. 2. AM1 optimized structure of **1a**.