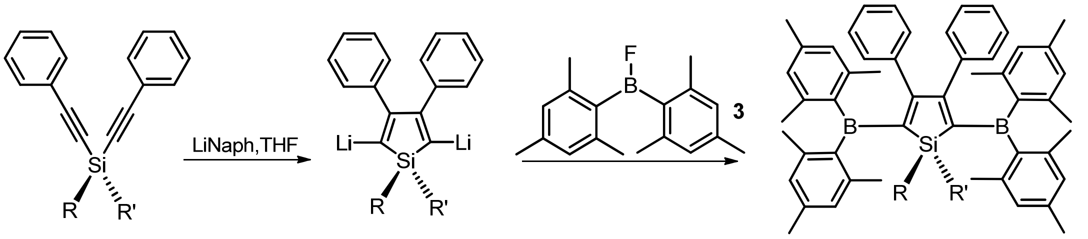
Electronic Supplementary Information (ESI)

1. General

Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl under dry nitrogen immediately prior to use. Compounds **1a-c** were prepared according to the known procedures.[1] All other chemicals and reagents were purchased from commercial sources and used as received without further purification. NMR spectra were obtained on a Bruker AV 500 spectrometer. High resolution mass spectra (HRMS) were recorded on a GCT premier CAB048 mass spectrometer operating in MALDI-TOF mode. Single crystal X-ray diffraction intensity data were collected on a Bruker–Nonices Smart Apex CCD diffractometer with graphite monochromated MoKα radiation. Processing of the intensity data was carried out using the SAINT and SADABS routines, and the structure and refinement were conducted using the SHELTL suite of X-ray programs (version 6.10). The ground-state geometries were optimized using the density functional with B3LYP hybrid functional at the basis set level of 6-31G(d). All the calculations were performed using Gaussian 09 package. UV-vis absorption spectra were measured on a SHIMADZU UV-2600 spectrophotometer. Fluorescence spectra were recorded on a Horiba Fluoromax-4 fluorescence spectrophotometer. Fluorescence quantum yields were measured using a Hamamatsu absolute PL quantum yield spectrometer C11347 Quantaurus_QY. The cyclic voltammetry measurement was conducted on a CHI610E A14297 in dichloromethane with 0.1 M tetrabutylammonium hexafluorophosphate as the supporting electrolyte at a scan rate of 100 mV s^{-1}, using platinum as the working electrode, saturated calomel electrode (SCE) as the reference electrode, and platinum wire counter electrode. The SCE reference electrode was calibrated using the ferrocene/ferrocenium (Fc/Fc^{+}) redox couple as an external standard.

2. Synthesis and Characterization



1a, R = CH_3, R' = CH_3
1b, R = CH_3, R' = Ph
1c, R = Ph, R' = Ph

2a, R = CH_3, R' = CH_3
2b, R = CH_3, R' = Ph
2c, R = Ph, R' = Ph

$(Mes)_2$DMS, R = CH_3, R' = CH_3
$(Mes)_2$MPS, R = CH_3, R' = Ph
$(Mes)_2$DPS, R = Ph, R' = Ph

Scheme S1. Schematic illustration of the synthesis of 2,5-bis(dimesitylboryl)-substituted siloles.

2,5-Bis(dimesitylboryl)-1,1-dimethyl-3,4-diphenylsilole ((Mes)$_2$DMS): A solution of lithium 1-naphthalenide (LiNaph) was prepared by stirring a mixture of naphthalene (1.3 g, 10 mmol) and lithium granular (0.07 g, 10 mmol) in dry THF (10 mL) for 4 h at room temperature under nitrogen atmosphere. **1a** (0.65 g, 2.5 mmol) dissolved in dry THF (10 mL) was then added dropwise into the solution of LiNaph, and the resultant mixture was stirred for 30 min at room temperature. **3** (1.34 g, 5 mmol) was directly added into the mixture and stirred over night.Then, the reaction was terminated by addition of 2 M hydrochloric acid. The mixture was poured into water and extracted twice with dichloromethane. The combined organic layers were washed successively with aqueous sodium chloride solution and water, and then dried over magnesium sulfate. After filtration, the solvent was evaporated under reduced pressure and the residue was purified by silica-gel column chromatography using hexane as eluent. Pale yellow solid of $(Mes)_2$DMS was obtained in 69% yield. ^{1}H NMR (500 MHz, CD_2Cl_2), δ (TMS, ppm): 6.80–6.74 (m, 2H), 6.74–6.57 (m, 16H), 2.21 (br, 36H), –0.13 (br, 6H). ^{13}C NMR (125 MHz, CD_2Cl_2), δ (TMS, ppm): 141.4, 137.9, 128.0, 127.9, 126.0, 125.6, 20.7, –2.3. HRMS ($C_{54}H_{60}B_2Si$): *m*/*z* 784.4623 (M + Na^+, calcd 781.4548).

2,5-Bis(dimesitylboryl)-1-methyl-1,3,4-triphenylsilole ((Mes)$_2$MPS): The procedure was analogous to that described for (Mes)$_2$DMS. Pale yellow solid, yield 54%. ^{1}H NMR (500 MHz, CD_2Cl_2), δ (TMS, ppm): 7.25 (m, 1H), 7.11 (m, 4H), 6.82–6.63 (m, 10H), 6.50 (br, 8H), 2.26–1.75 (m, 36H), 0.11 (s, 3H). ^{13}C NMR (125 MHz, CD_2Cl_2), δ (TMS, ppm): 167.3, 141.3, 137.6, 135.0, 128.7, 128.2, 127.7, 126.7, 126.1, 125.9, 20.6, –5.1. HRMS ($C_{59}H_{62}B_2Si$): *m*/*z* 820.4787 (M^+, calcd 820.4807).

2,5-Bis(dimesitylboryl)-1,1,3,4-tetraphenylsilole ((Mes)$_2$DPS): The procedure was analogous to that described for (Mes)$_2$DMS. Pale yellow solid, yield 15%. ^{1}H NMR (500 MHz, $CDCl_3$), δ (TMS, ppm): 7.35-7.30 (m, 6H), 7.16–7.12 (m, 4H), 7.68-7.65 (m, 2H), 6.69–6.68 (m, 8H), 6.40 (s, 8H), 2.20 (s, 12H), 1.88 (s, 24H). ^{13}C NMR (125 MHz, CD_2Cl_2), δ (TMS, ppm): 169.2, 143.8, 141.5, 139.4, 137.7, 136.8, 131.6, 129.2, 128.2, 127.7, 127.0, 126.0, 125.7, 23.5, 20.6. HRMS ($C_{64}H_{64}B_2Si$): *m*/*z* 882.4947 (M^+, calcd 882.4963).

X-Ray Crystallography

Crystal data for (Mes_2B)DMS (CCDC 1485582): $C_{54}H_{60}B_2Si$, *MW* = 758.73, monoclinic, C 1 2/c 1, $a = 20.8899(13)$, $b = 20.4880(10)$, $c = 23.843(2)$ Å, $\beta = 106.869(8)°$, $V = 9765.7(11)$ Å^3, $Z = 8$, $D\mathrm{c} = 1.032$ g cm^{-3}, $\mu = 0.080$ mm^{-1} (MoKα, $\lambda = 0.71073$), $F(000) = 3264$, $T = 293(2)$ K, $2\theta_{\max} = 25.35$ (99.7%)$^{\circ}$, 20381 measured reflections, 8940 independent reflections ($R_{\mathrm{int}} = 0.0547$), GOF on $F^2 = 0.989$, $R_1 = 0.1378$, w$R_2 = 0.2273$ (all data), Δe 0.268 and –0.219 eÅ^{-3}.

Additional Data

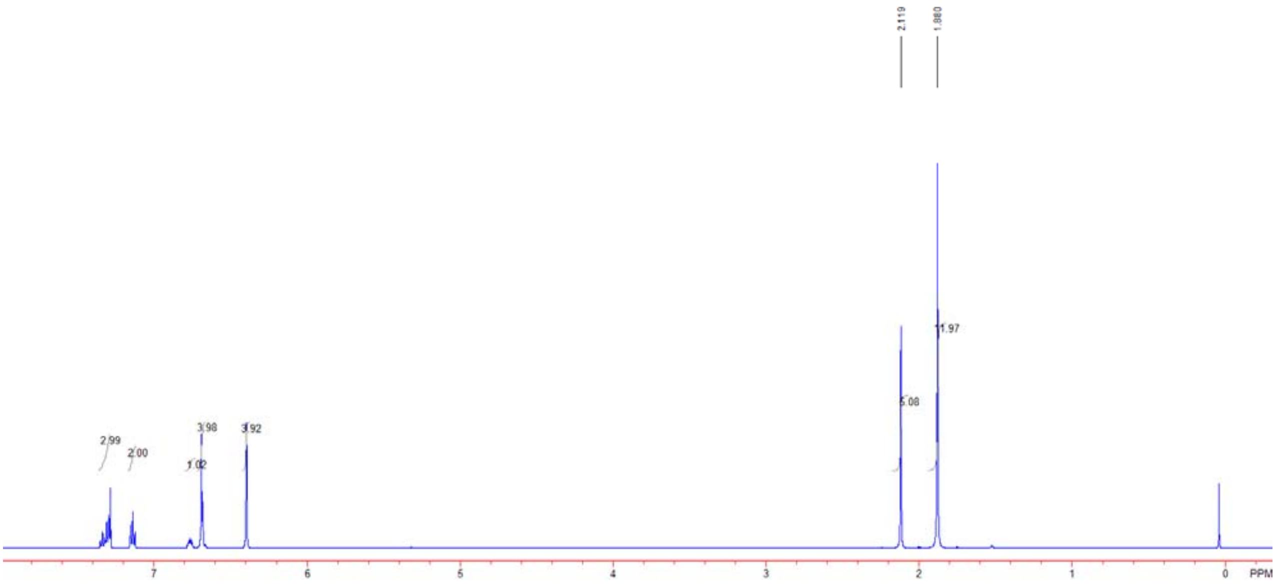


Fig. S1 ^{1}H NMR spectrum of $(Mes)_2$DPS in $CDCl_3$ at room temperature.

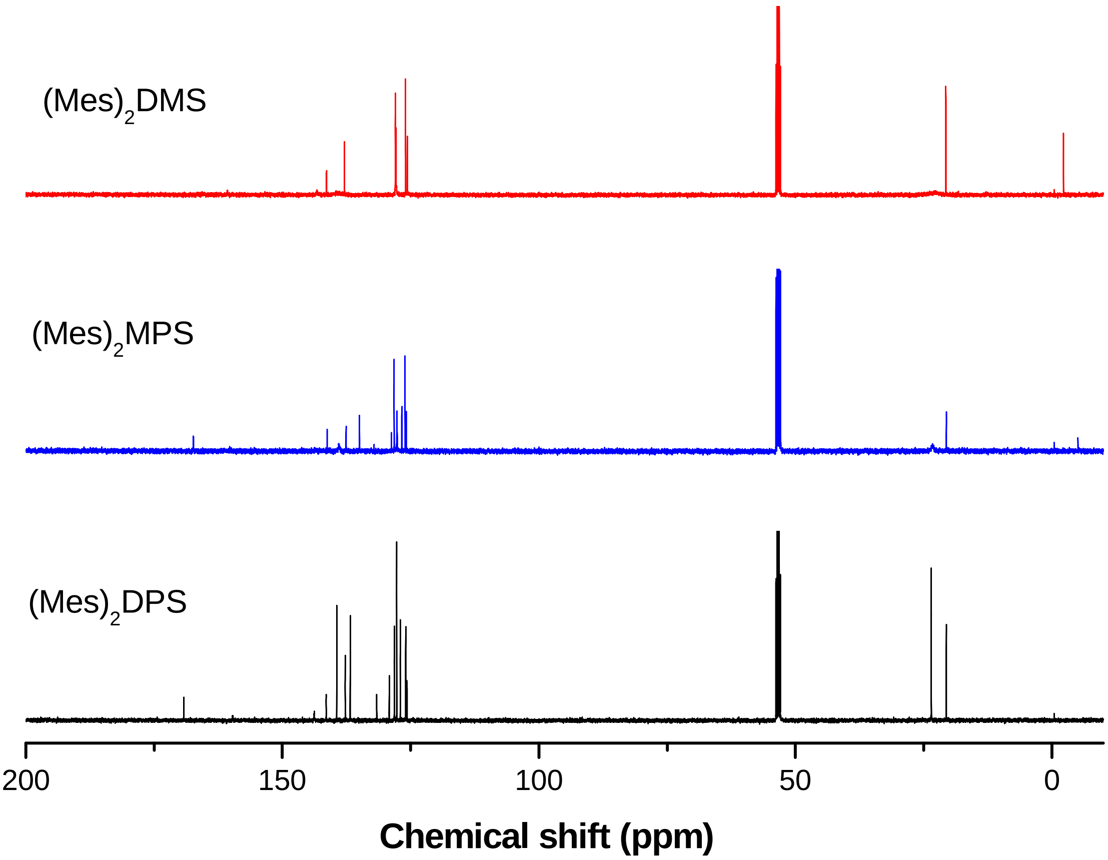


Fig. S2 ^{13}C NMR spectra of $(Mes)_2$DMS, $(Mes)_2$MPS and $(Mes)_2$DPS in CD_2Cl_2 at room temperature.

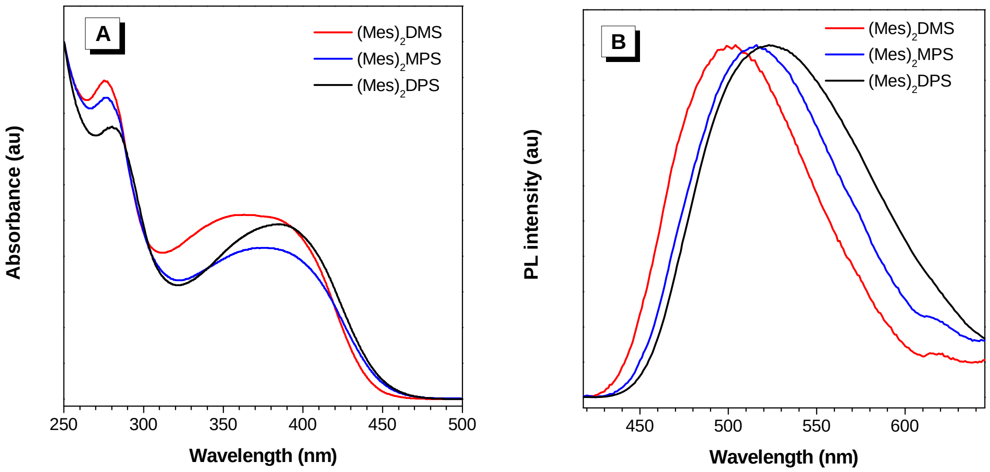


Fig. S3 (A) Absorption in THF solutions. (B) PL spectra of $(Mes)_2DMS$, $(Mes)_2MPS$ and $(Mes)_2DPS$ in films.

Reference

1. (a) Z. Zhao, Z. Wang, P. Lu, C. Y. K. Chan, D. Liu, J. W. Y. Lam, H. H. Y. Sung, I. D. Williams, Y. Ma and B. Z. Tang, *Angew. Chem. Int. Ed.*, 2009, **48**, 7608; (b) S. Yamaguchi, T. Endo, M. Uchida, T. Izumizawa, K. Furukawa and K. Tamao, *Chem. Eur. J.*, 2000, **6**, 1683.