

Synthesis and characterization of arylamino end-capped silafluorenes for blue to deep-blue organic light-emitting diodes (OLEDs) †

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Synthesis

20 **Compound 2** To a 500 ml round flask was added 2,5-dibromonitrobenzene (50.0g, 178mmol), copper powder (27.0g, 424mmol) and DMF (200ml). The resulting mixture was heated to 125°C and stirred for 3h. The reaction mixture was cooled to room temperature and filtered. The filtrate was evaporated and the residue was recrystallized in methanol to give compound 2 (28.1g, 78%). ¹H NMR (400 MHz, CDCl₃) δ: 8.38 (d, *J* = 1.8 Hz, 2H), 7.83 (dd, *J* = 8.2, 1.9 Hz, 2H), 7.17 (t, *J* = 9.3 Hz, 2H). MS (MALDI-TOF): *m/z*: 399.7.

25 **Compound 3** To a three-necked round flask was added compound 2 (20g, 49.8mmol), 32% aq. hydrochloride (161.2ml) and ethanol (250ml) in sequence and then tin powder (22.88, 192.7 mmol) was added in 10 mins. The reaction mixture was heated to reflux and stirred for 2h. The reaction mixture was poured into ice-water (520 ml) slowly and neutralized with 20%NaOH (195ml). The mixture was extracted with ether and the organic phase was washed with brine, dried with anhydrous sodium sulfate and evaporated. The residue was purified by column chromatography to give compound 3 as light yellow solid (14.8g, 88%). ¹H NMR (400 MHz, CDCl₃) δ 6.93 (d, *J* = 1.2 Hz, 6H), 3.77 (s, 4H). MS (MALDI-TOF): *m/z*: 339.9.

30 **Compound 4** Compound 3 (20 g, 58.5 mmol) was added over 1 h into a stirring mixture of 40 % w/w nitrosylsulfuric acid in sulfuric acid (24 ml) and concentrated sulfuric acid (98%, 24 ml) at 0 °C. The resulting mixture was stirred for a further 3 hours to give a deep orange viscous solution. This mixture was then added dropwise over 1 h into an aqueous solution of potassium iodide (290 g in 300 ml H₂O) at -10 °C and the reaction was stirred overnight at room temperature. The reaction was quenched with NaOH solution until pH = 7. The product was then extracted into diethyl ether and the organic layer washed with brine, dried with anhydrous MgSO₄ and evaporated. The residue was purified by column chromatography (petroleum ether) to yield compound 4 as an off-white solid (6.7 g, 20.3%). ¹H NMR (400 MHz, CDCl₃) δ: 8.09 (d, *J* = 1.9 Hz, 2H), 7.56 (dd, *J* = 8.2, 1.9 Hz, 2H), 7.03 (d, *J* = 8.2 Hz, 2H). MS (MALDI-TOF): *m/z*: 561.7.

35 **Compound 5** To a solution of compound 4 (1.5g, 2.66mmol) in dry diethyl ether (30 ml) was added *t*-BuLi (6.65ml, 10.64mmol, 1.6mol/L in toluene) dropwise over 45 min at -78 °C under N₂. The resultant mixture was stirred 1 h at -78 °C and then (CH₃)₂SiCl₂ (0.64ml, 5.32mmol) was added. The reaction was then allowed to warm to room temperature and stirred overnight. The reaction was quenched with water, extracted with diethyl ether, washed with brine, dried over dry sodium sulfate, and evaporated. The residue was columned to give a white solid (0.68g, 69.5%). ¹H NMR (400 MHz, CDCl₃) δ: 7.71 (s, 2H), 7.63 (d, *J* = 8.3, 1.5 Hz, 2H), 7.54 (dd, *J* = 8.3, 1.9 Hz, 2H), 0.43 (s, 6H). MS (MALDI-TOF): *m/z*: 367.8.

40 **Compound 6** To a solution of compound 4 (1.5g, 2.66mmol) in dry diethyl ether (30 ml) was added *t*-BuLi (6.65ml, 10.64mmol, 1.6mol/L in toluene) dropwise over 45 min at -78 °C under N₂. The resultant mixture stirred 1 h at -78 °C and then Ph₂SiCl₂ (1.13ml, 5.32mmol) was added. The reaction was then allowed to warm to room temperature and stirred overnight. The reaction was quenched with water, extracted with diethyl ether, washed with brine, dried over dry sodium sulfate, and evaporated. The residue was columned to give a white solid (1.05g, 76.0%). ¹H NMR (400 MHz, CDCl₃) δ: 7.83 (s, 2H), 7.70 (d, *J* = 8.3 Hz, 2H), 7.66–7.54 (m, 6H), 7.45 (d, *J* = 6.2Hz, 2H), 7.38 (t, *J* = 7.4Hz, 4H). MS (MALDI-TOF): *m/z*: 492.0.

45 **TDMS** To a 100 ml Shreck flask was added compound 5 (200mg, 0.54mmol), compound 7 (468mg, 1.62mmol), Pd(OAc)₂ (6mg, 0.027mmol), P(*o*-tolyl)₃ (16mg, 0.054mmol), toluene (16ml), methanol (8ml), and 2 M K₂CO₃ solution (0.8ml). The reaction mixture was degassed with argon 3 times, heated to 75 °C, and stirred overnight under Ar. The reaction was cooled to room temperature, extracted with dichloromethane, washed with brine, dried over dry sodium sulfate, and evaporated. The residue was purified by column chromatography

with petroleum ether/dichloromethane = 10:1 to give a light green solid which was recrystallized with dichloromethane and methanol to yield **TDMS** (260mg, 69%) as gray solid. ¹H NMR (400 MHz, CDCl₃) δ: 7.90 – 7.82 (m, 4H), 7.65 (d, *J* = 8.0 Hz, 2H), 7.54 (d, *J* = 8.6 Hz, 4H), 7.29 (d, *J* = 8.1 Hz, 7H), 7.15 (t, *J* = 6.4 Hz, 11H), 7.04 (t, *J* = 7.3 Hz, 4H), 0.48 (s, 6H). ¹³C NMR (100 MHz, CDCl₃) δ: 147.72, 147.14, 146.33, 139.71, 139.47, 135.21, 131.01, 129.31, 128.71, 127.70, 124.40, 124.07, 122.93, 121.21. MS (MALDI-TOF): *m/z*: 696.2.

5 Anal. calcd. for C₅₀H₄₀N₂Si: C, 86.17; H, 5.78; N, 4.02; Si, 4.03. Found: C, 86.06; H, 5.85; N, 4.13; Si, 4.11.

CDMS Using the method for **TDMS**, **CDMS** was prepared as light yellow solid (128mg, 34.3%), with compound **5** (200mg, 0.54mmol), compound **8** (465mg, 1.62mmol), Pd(OAc)₂ (6mg, 0.027mmol), P(*o*-tolyl)₃ (16mg, 0.054mmol), toluene (16ml), methanol (8ml), and 2 M K₂CO₃ solution (0.8ml). ¹H NMR (400 MHz, CDCl₃) δ: 8.18 (d, *J* = 7.8 Hz, 4H), 8.02 (d, *J* = 8.4 Hz, 4H), 7.92 (d, *J* = 8.3 Hz, 4H), 7.82 (d, *J* = 6.8 Hz, 2H), 7.68 (d, *J* = 8.3 Hz, 4H), 7.51 (d, *J* = 8.2 Hz, 4H), 7.45 (t, *J* = 7.6 Hz, 4H), 7.32 (t, *J* = 7.4 Hz, 4H), 0.57 (s, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 146.92, 140.91, 140.29, 140.12, 139.31, 136.87, 131.5, 129.26, 128.42, 127.39, 125.98, 123.46, 121.52, 120.35, 120.00, 109.85. MS (MALDI-TOF): *m/z*: 692.3. Anal. calcd. for C₆₀H₄₄N₂Si: C, 87.77; H, 5.40; N, 3.41; Si, 3.42. Found: C, 87.52; H, 5.54; N, 3.44; Si, 3.40.

TDPS Using the method for **TDMS**, **TDPS** was prepared as light green solid (230mg, 68%), with compound **6** (200mg, 0.41mmol), compound **7** (352mg, 1.22mmol), Pd(OAc)₂ (4.6mg, 0.021mmol), P(*o*-tolyl)₃ (12mg, 0.039mmol), toluene (18ml), methanol (9ml), and 2 M K₂CO₃ solution (1 ml). ¹H NMR (400 MHz, CDCl₃) δ: 8.00 – 7.91 (m, 4H), 7.71 (d, *J* = 6.4 Hz, 6H), 7.53 (d, *J* = 8.5 Hz, 4H), 7.41 (d, *J* = 7.0 Hz, 2H), 7.36 (t, *J* = 7.1 Hz, 4H), 7.27 (dd, *J* = 8.7, 6.7 Hz, 6H), 7.14 (d, *J* = 8.1 Hz, 12H), 7.03 (t, *J* = 7.2 Hz, 4H). ¹³C NMR (100 MHz, CDCl₃) δ: 147.54, 147.21, 139.78, 136.67, 135.54, 134.85, 132.54, 132.08, 129.99, 129.50, 128.76, 128.1, 127.71, 124.42, 123.83, 122.76, 121.41. MS (MALDI-TOF): *m/z*: 820.3. Anal. calcd. for Chemical Formula: C₅₀H₃₆N₂Si: C, 86.67; H, 5.24; N, 4.04; Si, 4.05. Found: C, 86.45; H, 5.43; N, 4.15; Si, 4.17.

CDPS Using the method for **TDMS**, **CDPS** was prepared as light yellow solid (152 mg, 46%), with compound **6** (200mg, 0.41mmol), compound **8** (350mg, 1.22mmol), Pd(OAc)₂ (4.6mg, 0.021mmol), P(*o*-tolyl)₃ (12mg, 0.039mmol), toluene (18ml), methanol (9ml), and 2 M K₂CO₃ solution (1 ml). ¹H NMR (400 MHz, CDCl₃) δ: 8.17 (d, *J* = 7.8 Hz, 4H), 8.13 (s, 2H), 8.09 (d, *J* = 8.1 Hz, 2H), 7.88 (dd, *J* = 10.8, 9.2 Hz, 6H), 7.78 (d, *J* = 7.9 Hz, 4H), 7.66 (d, *J* = 8.4 Hz, 4H), 7.45 (dt, *J* = 14.8, 8.1 Hz, 14H), 7.31 (t, *J* = 7.3 Hz, 4H). ¹³C NMR (100 MHz, CDCl₃) δ: 147.88, 140.90, 140.04, 139.74, 137.25, 136.95, 135.68, 132.64, 132.31, 130.41, 129.83, 128.46, 128.34, 127.37, 126.00, 123.47, 121.92, 120.37, 120.02, 109.86. MS (MALDI-TOF): *m/z*: 816.4. Anal. calcd. for C₆₀H₄₀N₂Si: C, 88.20; H, 4.93; N, 3.43; Si, 3.44. Found: C, 87.96; H, 4.99; N, 3.38; Si, 3.41.

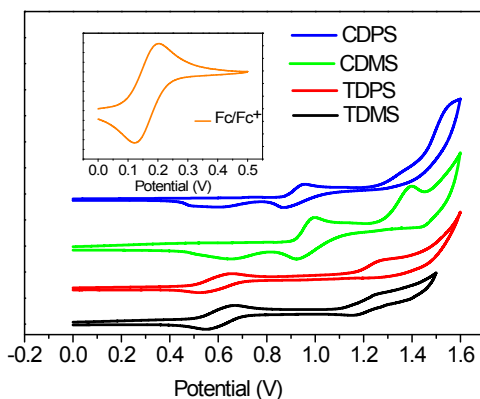


Fig. S1 Cyclic voltammograms of oxidation waves of **TDMS**, **TPMS**, **CDMS**, and **CPMS**. The inset shows the oxidation curve of ferrocene.

30 Table S1 Summary of EL device performance of silafluorene derivatives based on device B

X	Ratio (PVK:X)	V _{on} ^a (V)	V ₂₀ ^b (V)	η _{1,20} ^c (cd/A)	η _{1,max} ^d (cd/A)	η _{p,20} ^e (lm/W)	η _{p,max} ^f (lm/W)	L ₂₀ ^g (cd/m ²)	L _{max} ^h (cd/m ²)	EQE ⁱ (%)
TDMS	100:5	9.6	12.0	0.48	0.51	0.10	0.12	106	355	0.68
	100:10	8.4	12.0	0.37	0.37	0.10	0.10	82	399	0.49
	100:20	9.2	12.8	0.17	0.18	0.04	0.04	40	321	0.24
TDPS	100:5	9.0	13.2	0.62	0.62	0.15	0.16	125	302	0.63
	100:10	7.2	12.0	0.93	0.96	0.24	0.30	193	1455	0.97
	100:20	6.0	10.0	1.08	1.15	0.34	0.41	220	1323	1.16
DPFL-NPB	100:5	11.0	18.8	1.49	1.54	0.25	0.25	299	1577	1.00
	100:10	9.8	18.4	1.48	1.48	0.25	0.26	325	1021	0.97
	100:20	7.9	16.4	1.69	1.69	0.32	0.36	375	1977	1.10

^aTurn on voltage when a brightness of 1 cd/m² observed. ^bVoltage taken at a current density of 20 mA/cm². ^cCurrent efficiency at a current density of 20 mA/cm². ^dMaximum current efficiency ^ePower efficiency at a current density of 20 mA/cm². ^fMaximum power efficiency. ^gLuminance at a current density of 20 mA/cm². ^hMaximum Luminance ⁱExternal quantum efficiency at a current density of 20 mA/cm².

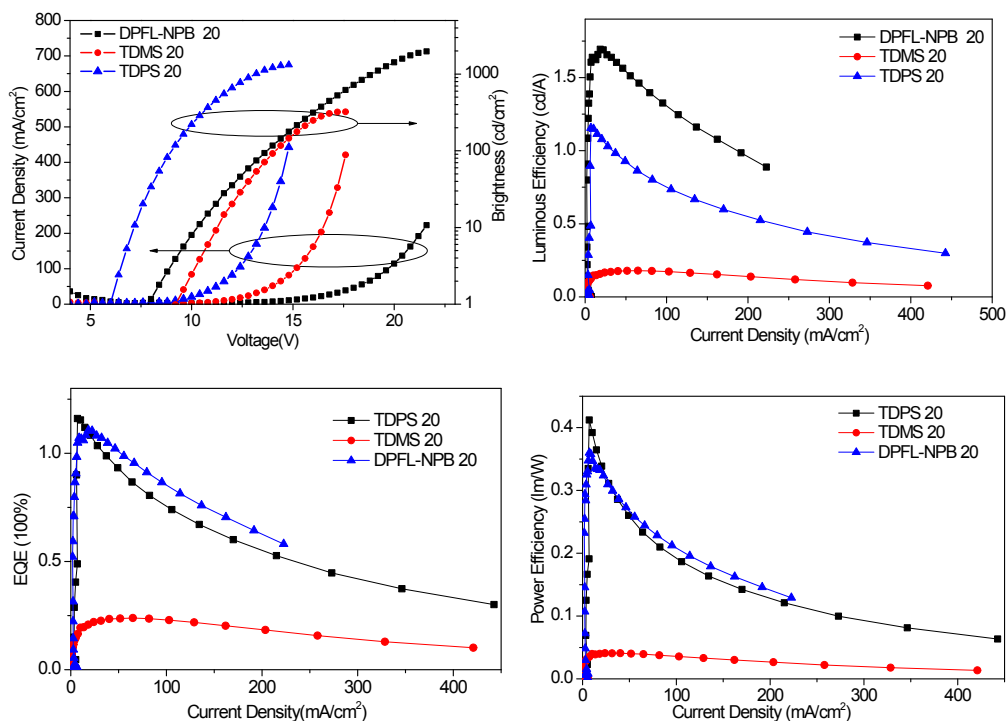


Fig. S2 Current-voltage-brightness, luminance-current density, external quantum efficiency-current density, and power efficiency-current density curves of device B with **TDMS**, **TDPS**, and **DPFL-NPB**.

5 Table S2 Summary of EL device performance of silafluorene derivatives based on device D

Device	V_{on}^a (V)	V_{20}^b (V)	$\eta_{l,20}^c$ (cd/A)	$\eta_{l,max}^d$ (cd/A)	$\eta_{p,20}^e$ (lm/W)	$\eta_{p,max}^f$ (lm/W)	L_{20}^g (cd/m ²)	L_{max}^h (cd/m ²)	EQE (%)	λ_{EL} (fwhm) ⁱ (nm)
TDMS	5.6	10.8	2.35	2.53	0.68	0.69	485	3494	2.18	449(81)
TDPS	4.4	9.6	2.78	2.81	0.91	0.91	572	5501	2.48	440(70)
DPFL-NPB	5.6	10.4	1.07	1.13	0.34	0.34	255	3502	0.66	472(100)

^aTurn on voltage when a brightness of 1 cd/m² observed. ^bVoltage taken at a current density of 20 mA/cm². ^cCurrent efficiency at a current density of 20 mA/cm². ^dMaximum current efficiency ^ePower efficiency at a current density of 20 mA/cm². ^fMaximum power efficiency. ^gLuminance at a current density of 20 mA/cm². ^hMaximum Luminance ⁱExternal quantum efficiency at a current density of 20 mA/cm².

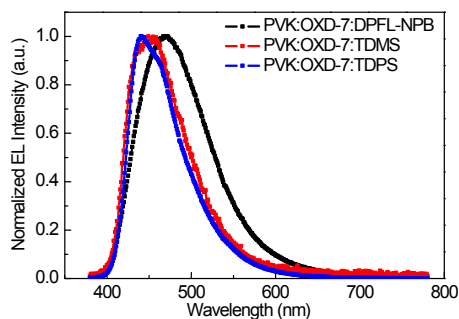


Fig. S3 EL spectra of device D with **TDMS**, **TDPS**, or **DPFL-NPB** as dopants.

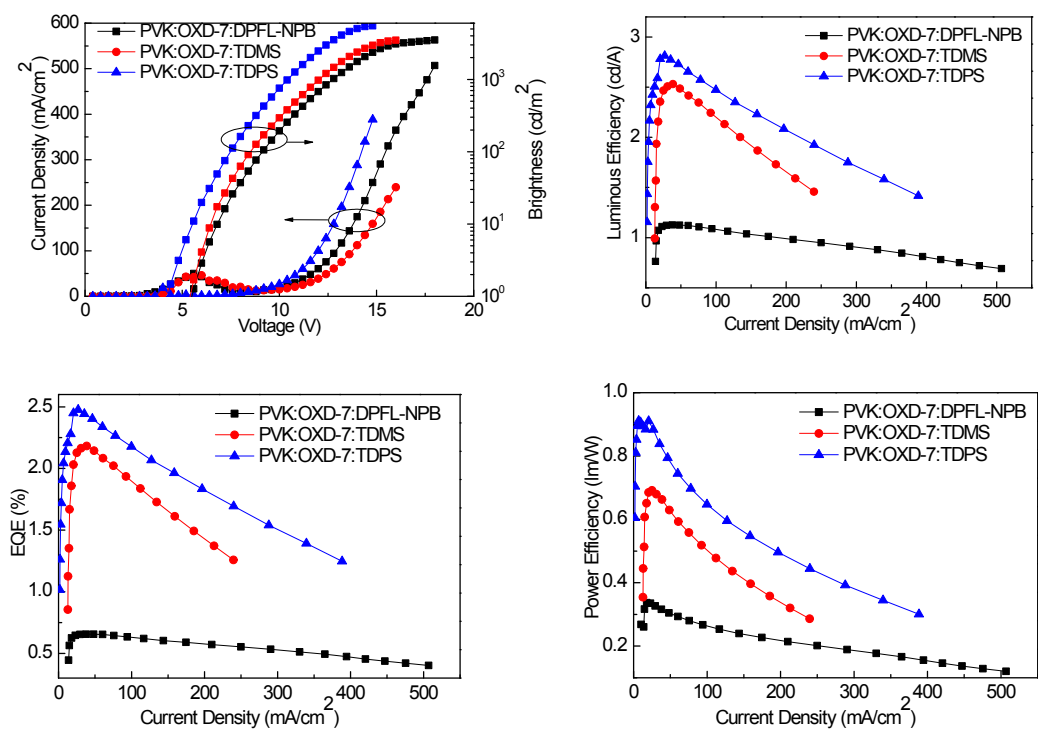


Fig. S4 Current-voltage-brightness, luminance-current density, external quantum efficiency-current density, and power efficiency-current density curves of device D with TDMS, TDPS, and DPFL-NPB.