Supporting information

Bipolar Host Based High Triplet Energy Electroplex for Over 10,000 h Lifetime in Deep Blue Phosphorescent Organic Light-Emitting Diodes

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Experimental

General information

Triphenylsilyl chloride (Acros organics), 1,3-dibromobenzene and sodium tert-butoxide (Alfa Aesar Co., Inc.), tri-tert-butylphosphine (Inco Co.), n-butyl lithium (2.5 M in hexane) and magnesium turnings (Aldrich Chem. Co.), and tris(dibenzylideneacetone)dipalladium(0) (Pd₂(dba)₃, P&H tech Co.) were used without further purification. Carbazole (Aldrich Chem. Co.) was recrystallized from toluene. Tetrahydrofuran (THF) and toluene (Samchun pure chemical Co. Ltd) were distilled over sodium and calcium hydride. Solvent for the NMR analysis was deuterated chloroform (CDCl₃). The ¹H and ¹³C nuclear magnetic resonance (NMR) spectra were recorded on Oxford 300 NMR (Oxford Instruments, 300 MHz), Avance-500 (Bruker, 500 MHz) spectrometer. Elemental analysis (EA) was recorded on

Vario EL cube (Elementa) analyzer. The ultraviolet-visible (UV-vis) spectra were obtained using UVvis spectrophotometer (JASCO, V-730), and the photoluminescence (PL) spectra were recorded on a fluorescence spectrophotometer (PerkinElmer, LS-55). UV-vis and PL measurements were carried out using a diluted THF solution. Singlet and triplet energies were measured under a liquid nitrogen condition using a frozen toluene solution. The HOMO and LUMO levels were estimated using cyclic voltammetry (Ivium Tech., Iviumstat). The mass spectra were recorded using Advion, ExpresionL CMS spectrometer in APCI mode.

Synthesis

(3-Bromophenyl)triphenylsilane

1,3-Dibromobenzene (5.00 g, 21.19 mmol) in an anhydrous THF under a nitrogen atmosphere was stirred at -77 °C, and then 2.5M n-butyl lithium in hexane (8.48 ml, 21.20 mmol) was added dropwisely. The reaction mixture was stirred for 1 h at -77 °C. Triphenylsilyl chloride (7.5 g, 25.43 mmol) solution in anhydrous THF was added slowly into the solution. The reaction mixture was allowed to warm up to room temperature gradually and stirred for 12 h. Distilled water was added slowly into the reaction mixture. The reaction mixture was extracted using methylene chloride/distilled water and the organic layer was dehydrated using MgSO₄. The organic layer was evaporated to remove solvent. The product

was purified by column chromatography with a methylene chloride and n-hexane (1:8) eluent. A white solid was obtained (3.44 g, yield 39.06%).

¹H NMR (500 MHz, CDCl₃): δ 7.66 (t, *J* = 0.9 Hz, 1H), 7.56 – 7.53 (m, 7H), 7.48 – 7.43 (m, 4H), 7.38 (dd, *J* = 11.2, 4.3 Hz, 6H), 7.27 – 7.22 (t, 1H). MS (APCI) m/z 416.05 [(M+H)⁺].

2-Chloro-4-phenyl-6-(3-(triphenylsilyl)phenyl)-1,3,5-triazine

Magnesium turnings (0.43 g, 17.69 mmol) and iodine(0.45 g, 1.77 mmol) were dissolved in an anhydrous THF. The mixture was stirred for 10 min. (3-Bromophenyl)triphenylsilane (5.14 g, 12.39 mmol) solution in anhydrous THF was added slowly into the mixture. This mixture was heated under reflux for 1 h. After cooled down to room temperature, the reaction mixture was added slowly into the solution of 2,4-dichloro-6-phenyl-1,3,5-triazine (2.00 g, 8.85 mmol) in an anhydrous THF. The reaction mixture was heated up and refluxed for 4 h. The reaction mixture was extracted using methylene chloride/distilled water and the organic layer was dehydrated using MgSO₄. The organic layer was evaporated to remove solvent. The product was purified by column chromatography with a methylene chloride and n-hexane (1:2) eluent. As a result, the 2-chloro-4-phenyl-6-(3-(triphenylsilyl)phenyl)-1,3,5-triazine was obtained as a white powder (1.39 g, yield 21.31%)

¹H NMR (300 MHz, CDCl₃): δ 8.89 (s, 1H), 8.64 (d, *J* = 7.9 Hz, 1H), 8.48 – 8.42 (m, 2H), 7.87 (d, *J* = 7.3 Hz, 1H), 7.68 – 7.57 (m, 7H), 7.56 – 7.40 (m, 12H). MS (APCI) m/z 527.14 [(M+H)+].

9-(4-Phenyl-6-(3-(triphenylsilyl)phenyl)-1,3,5-triazin-2-yl)-9H-carbazole(SiCzTrz)

Carbazole (0.22 g 1.33 mmol), 2-chloro-4-phenyl-6-(3-(triphenylsilyl)phenyl)-1,3,5-triazine (0.7 g, 1.33 mmol), sodium t-butoxide (0.20 g,2.05 mmol), and tri-tetra-butylphosphine (0.01 g, 0.05 mmol) were added into a 2-neck round bottomed flask and dissolved in toluene (13 ml). Pd₂(dba)₃ (0.12 g, 0.13 mmol) was added and the reaction mixture was heated to reflux condition and then the mixture was refluxed for 12 h in a nitrogen condition. The reaction mixture was extracted using methylene chloride/distilled water and the organic layer was dehydrated using MgSO₄. The organic layer was evaporated to remove solvent. The product was purified by column chromatography with a methylene

chloride and n-hexane (1:1) eluent. The obtained white powder was further purified through recrystallization and sublimation. A white powder was obtained as a product (0.33 g, yield 50.21%) ¹H NMR (500 MHz, CDCl₃): δ 9.06 (d, *J* = 8.2 Hz, 3H), 8.80-8.78 (m, 1H), 8.68 – 8.58 (m, 2H), 8.05 (dd, *J* = 7.5, 0.9 Hz, 2H), 7.87 (dt, *J* = 7.3, 1.2 Hz, 1H), 7.73 – 7.62 (m, 8H), 7.61 – 7.54 (m, 2H), 7.53 – 7.46 (m, 3H), 7.45 – 7.36 (m, 10H). ¹³C NMR (125 MHz, CDCl₃): δ 140.78, 139.28, 137.40, 136.69, 136.35, 135.83, 135.46, 134.08, 132.90, 130.44, 130.00, 129.32, 128.93, 128.63, 128.27, 127.22, 126.81, 123.40, 119.78, 117.95. MS (APCI) m/z 657.24 [(M+H)⁺]. Elemental anal. calcd for C 45, H 32, N 4 : C 82.28, H 4.91, N 8.53; found: C 85.27, H 4.76, N 8.45.

 Table S1. Material Characterization Data of SiCzTrz.

	Es ^a	E_{T}^{b}	HOMO ^c	LUMO ^d	T_g^{e}	$T_d{}^f$
SiCzTrz	3.23 eV	3.10 eV	- 6.06 eV	- 2.75 eV	98.5 °C	449 °C

^aCalculated from the fluorescent spectrum onset, measured in THF at room temperature. ^bCalculated from the onset of phosphorescent spectrum, measured in THF at 77 K. ^cMeasured from cyclic voltammetry scanning. ^dCalculated from HOMO-LUMO gap of the UV-Vis absorption spectrum. ^eTg: glass-transition temperatures. ^fThermal decomposition temperature at 5% weight loss.



Figure S1. Cyclic voltammetry scan data of the SiCzTrz.



Figure S2. Molecular simulation results of the SiCzTrz.



Figure S3. The single carrier device data of the SiCzTrz.



Figure S4. (a) Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) results of the SiCzTrz.



Figure S5. Chemical structure of the materials and energy level diagram of (a) device I, (b) II, (c) III and (d) reference device.



Figure S6. Voltage rise of the hole only and electron only devices of SiCzTrz and DBFTrz hosts during electrical stress.



Figure S7. The variation of device CIE y value by luminance.



Figure S8. (a) Current density-voltage-luminance, (b) external quantum efficiency-luminance, and (c) EL spectra (d) device lifetime of the SiCzTrz reference device.