

Supporting information

Molecular design tactics enhancing negative polaron stability of p-type host for long device lifetime by fusion of carbazole with furan

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Experimental

General information

9-Phenyl-9*H*,9'*H*-3,3'-bicarbazole was supplied from LG chem. All chemicals were purchased from chemical distributors and were not further purified. 4,6-Dibromodibenzo[*b,d*]furan and 4,4,4',4',5,5,5',5'-octamethyl-2,2'-bi(1,3,2-dioxaborolane) were purchased from SY innovation. [1,1'-Bis(diphenylphosphino)ferrocene]dichloropalladium(II) and tetrakis(triphenylphosphine)palladium (0) were supplied from GOM Technology CO.. Potassium acetate and potassium carbonate were provided from Duksan Sci. Co.. 1,4-Dioxane, anhydrous magnesium sulfate, *o*-DCB and *N,N*-dimethylformamide (DMF) were a product of Daejung Chemicals & Metals CO. LTD. Dichloromethane (MC), *n*-hexane (HEX), tetrahydrofuran (THF) and toluene were available from Samchun Pure Chemical Co.. 1-Bromo-2-nitrobenzene, triphenylphosphine, iodobenzene and sodium *tert*-butoxide were purchased from Alfa Aesar. Tri-*tert*-butylphosphine and palladium(II) acetate were supplied from P&H tech Co.. 1,10-Phenanthroline and copper(I) iodide were provided from Sigma Aldrich Co.. The solvents for the NMR analysis were deuterated dimethyl sulfoxide- d_6 (DMSO- d_6) and deuteriochloroform (CDCl $_3$ - d) were also provided from Sigma Aldrich Co.. For all wet-purified column chromatography, silica gel was used as a stationary phase. The final materials were purified by vacuum sublimation to achieve 99.9% purity before device

test. The ^1H and ^{13}C nuclear magnetic resonance (NMR) spectra were obtained using a Unity Inova (Varian, 500, 300 MHz) spectrometers. Gas chromatography high resolution mass spectrometry (GC-HRMS) was performed using a JEOL, JMS-700. The ultraviolet-visible (UV-vis) spectra were recorded with UV-vis spectrophotometer (JASCO, V-730) and the photoluminescence (PL) spectra were observed using a fluorescence spectrophotometer (PerkinElmer, LS-55). Both were performed using THF solution of the sample. The singlet and triplet energy values were measured at 77 K using a frozen THF solution in liquid nitrogen. The HOMO and LUMO were calculated and estimated using a cyclic voltammetry (Ivium Tech., Iviumstat). The T_d and T_g were measured by DSC (DSC 6100, SEIKO INST) and TGA (TG/DTA6100, SEIKO INST) at a heating rate of 10 °C/min in a nitrogen atmosphere.

Device fabrication and measurements

All layers of the device stack were deposited by thermal evaporation at high pressure vacuum of 3.0×10^{-7} torr. The fabricated devices were encapsulated with a glass lid to protect it from oxygen and moisture. Electrical characterization of the devices was carried out using Keithley 2400 source meter and optical characterization was performed using CS 2000 spectroradiometer.

Synthesis

9,9'-Diphenyl-9*H*,9'*H*-3,3'-bicarbazole (BCzPh)

9-Phenyl-9*H*,9'*H*-3,3'-bicarbazole (2.00 g, 4.90 mmol), iodobenzene (1.80 g, 8.81 mmol), powdered potassium carbonate (2.03 g, 14.7 mmol), copper(I) iodide (0.93 g, 4.90 mmol) and 1,10-phenanthroline (0.44 g, 2.45 mmol) were dissolved in DMF (15 ml). The reaction mixture was stirred and heated to reflux for 12 h under a nitrogen atmosphere at 250 °C. After the reaction was completed, the mixture was washed in distilled water three times and then

extracted by MC. The separated MC layer was dried using an anhydrous magnesium sulfate. The crude material was wet-purified by column chromatography using an eluent of MC: HEX (3: 1) mixture. As a result, a white powder was obtained as a product. Additionally, the powder was recrystallized from toluene.

Yield 43.0% (1.02 g), ^1H NMR (500 MHz, $\text{CDCl}_3\text{-d}$) δ 8.46 (d, $J = 1.5$ Hz, 2H), 8.24 (d, $J = 7.7$ Hz, 2H), 7.77 (dd, $J = 8.5, 1.8$ Hz, 2H), 7.67 – 7.60 (m, 8H), 7.53 – 7.39 (m, 8H), 7.32 (ddd, $J = 7.9, 6.0, 2.0$ Hz, 2H). ^{13}C NMR (126 MHz, $\text{CDCl}_3\text{-d}$): δ 141.56, 140.24, 138.00, 134.58, 130.13, 127.66, 127.30, 126.26, 126.05, 124.19, 123.78, 120.64, 120.20, 119.11, 110.24, 110.11, 77.48, 77.23, 76.97. GC-HRMS (FAB+) m/z 484.1941 [(M+H)+]; Calcd. For $\text{C}_{36}\text{H}_{24}\text{N}_2$, 484.1939.

4,6-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)dibenzo[*b,d*]furan

4,6-Dibromodibenzo[*b,d*]furan (40.0 g, 123 mmol) and 4,4,4',4',5,5,5',5'-octamethyl-2,2'-bi(1,3,2-dioxaborolane) (87.2 g, 344 mmol), [1,1'-bis(diphenylphosphino)ferrocene]dichloropalladium(II) (1.79 g, 2.45 mmol) and powdered potassium acetate (36.1 g, 368 mmol) were dissolved in 1,4-dioxane (300 ml). The reaction mixture was stirred and heated to reflux for 16 h under a nitrogen atmosphere at 200 °C. After the reaction was completed, the work-up processes was same as those of BCzPh. The crude material was wet-purified by column chromatography using an eluent of MC: HEX (9: 1) mixture. As a result, a brown powder was obtained as a product.

Yield 60.3% (31.1 g), ^1H NMR (300 MHz, DMSO-d_6) δ 8.27 (td, $J = 7.5, 1.3$ Hz, 2H), 7.76 – 7.70 (m, 2H), 7.42 – 7.35 (m, 2H), 1.36 (d, $J = 4.9$ Hz, 24H).

4,6-Bis(2-nitrophenyl)dibenzo[*b,d*]furan

4,6-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)dibenzo[*b,d*]furan (30.0 g, 71.4 mmol), 1-

bromo-2-nitrobenzene (43.3 g, 214 mmol), powdered potassium carbonate (29.6 g, 214 mmol) and tetrakis(triphenylphosphine)palladium (0) (2.48 g, 2.14 mmol) were dissolved in THF (150 ml) and distilled water (50 ml). The reaction mixture was stirred and heated to reflux for 12 h under a nitrogen atmosphere at 200 °C. After the reaction was completed, the work-up processes was same as those of 4,6-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)dibenzo[*b,d*]furan. The crude material was wet-purified by column chromatography using an eluent of MC: HEX (1: 1) mixture. As a result, a yellow powder was obtained as a product. Yield 65.2% (19.1 g), ¹H NMR (300 MHz, DMSO-*d*₆) δ 8.22 (ddd, *J* = 55.5, 11.2, 5.6 Hz, 2H), 8.02 – 7.26 (m, 9H), 7.23 – 6.58 (m, 2H), 3.39 (s, 1H).

5,10-Dihydrofuro[3,2-*c*:4,5-*c'*]dicarbazole

4,6-Bis(2-nitrophenyl)dibenzo[*b,d*]furan (18.0 g, 43.9 mmol), triphenylphosphine (46.0 g, 175 mmol) were dissolved in *o*-DCB (60 ml). The reaction mixture was stirred and heated to reflux for 16 h under a nitrogen atmosphere at 270 °C. After the reaction was completed, the work-up and purification processes were the same as those of 4,6-bis(2-nitrophenyl)dibenzo[*b,d*]furan. As a result, a white powder was obtained as a product. Yield 44.2% (6.71 g), ¹H NMR (300 MHz, CDCl₃-*d*) δ 8.69 (d, *J* = 7.4 Hz, 2H), 8.32 (s, 2H), 8.02 (d, *J* = 8.3 Hz, 2H), 7.60 – 7.41 (m, 8H).

5,10-Diphenyl-5,10-dihydrofuro[3,2-*c*:4,5-*c'*]dicarbazole (DBFBCzPh)

5,10-Dihydrofuro[3,2-*c*:4,5-*c'*]dicarbazole (1.50 g, 4.33 mmol), iodobenzene (1.86 g, 9.10 mmol) and sodium *tert*-butoxide (0.83 g, 8.66 mmol) were dissolved in 1,4-dioxane (25 ml). Then, palladium(II) acetate (0.03 g, 0.13 mmol) and tri-*tert*-butylphosphine (0.44 g, 2.17 mmol) were added into the mixed solution. The reaction mixture was stirred and heated to reflux for 12 h under a nitrogen atmosphere at 120 °C. After the reaction was completed, the

work-up and purification processes were the same as those of BCzPh. As a result, a white powder was obtained as a product. Additionally, the powder was recrystallized from toluene. Yield 32.0% (0.69 g), ^1H NMR (500 MHz, $\text{CDCl}_3\text{-d}$) δ 8.81 – 8.75 (m, 2H), 7.97 (d, $J = 8.4$ Hz, 2H), 7.68 – 7.63 (m, 8H), 7.55 – 7.47 (m, 8H), 7.42 (d, $J = 8.4$ Hz, 2H). ^{13}C NMR (126 MHz, $\text{CDCl}_3\text{-d}$): δ 151.24, 140.91, 140.75, 138.09, 130.16, 127.92, 127.61, 125.97, 123.08, 121.33, 120.73, 117.64, 117.43, 110.04, 109.29, 105.69, 77.47, 77.22, 76.97. GC-HRMS (FAB+) m/z 498.1725 [(M+H)+]; Calcd. For $\text{C}_{36}\text{H}_{22}\text{N}_2\text{O}$, 498.1732.

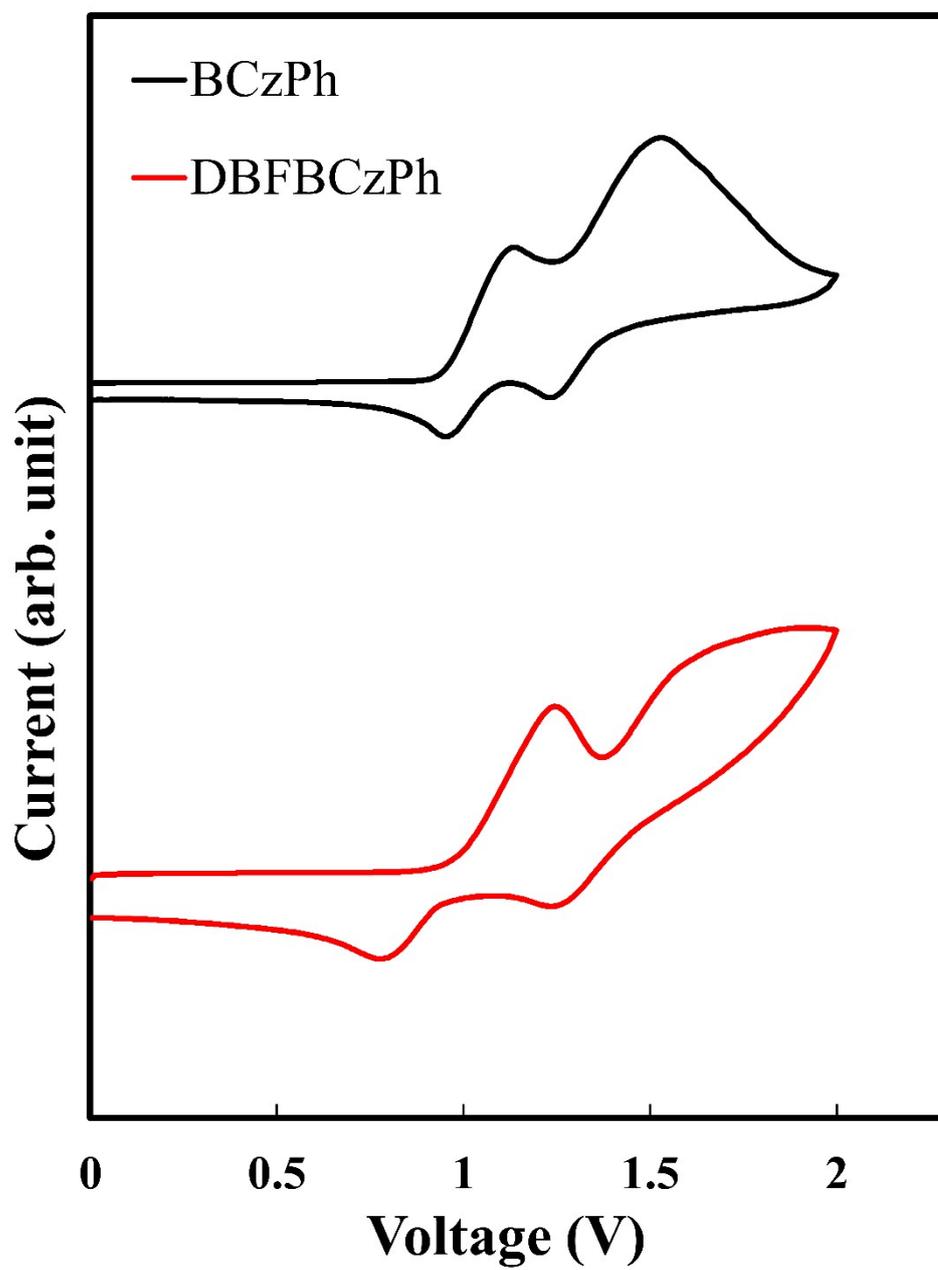


Figure S1. The cyclic voltammetry data of host materials.

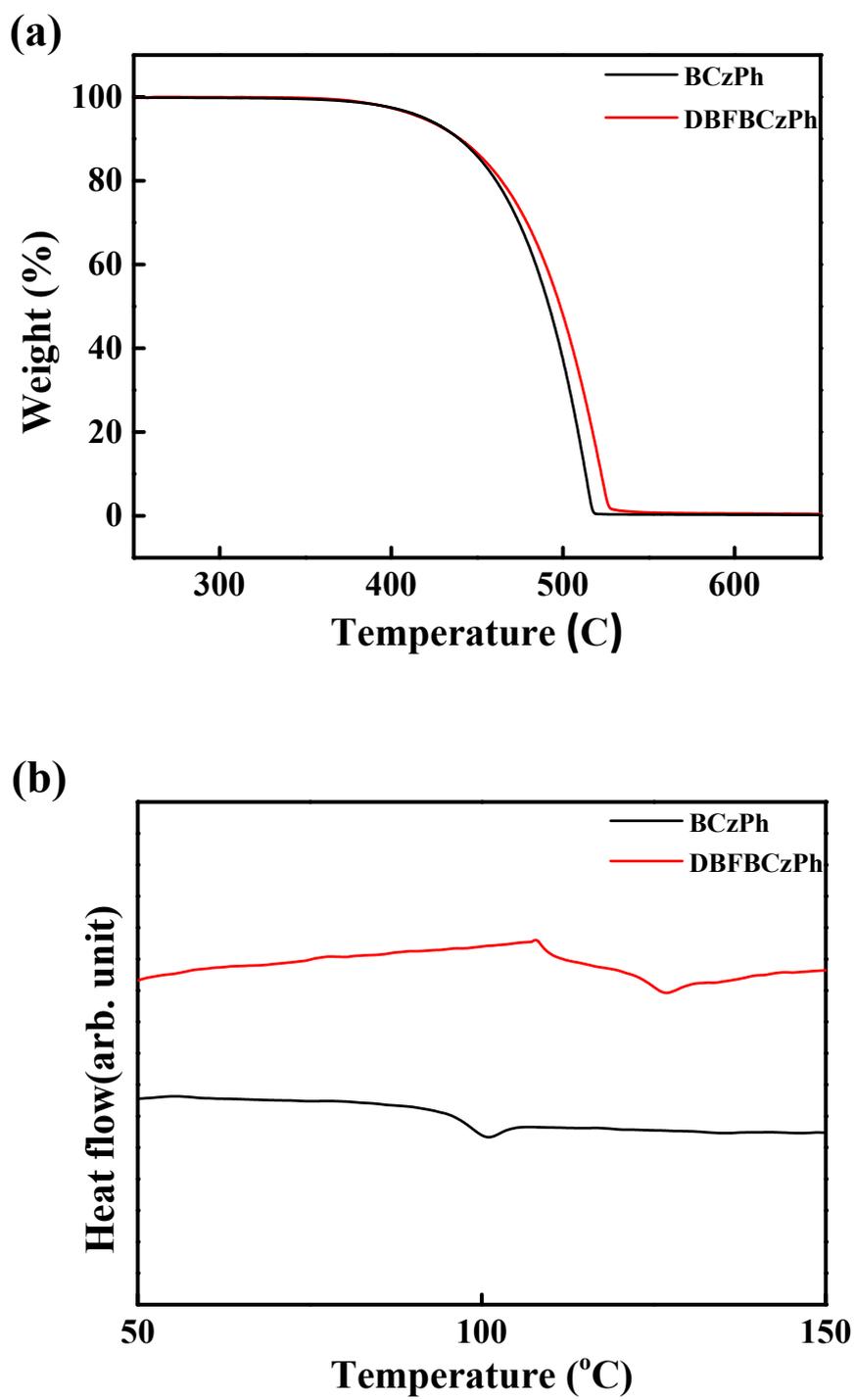


Figure S2. (a) TGA and (b) DSC data of host materials.

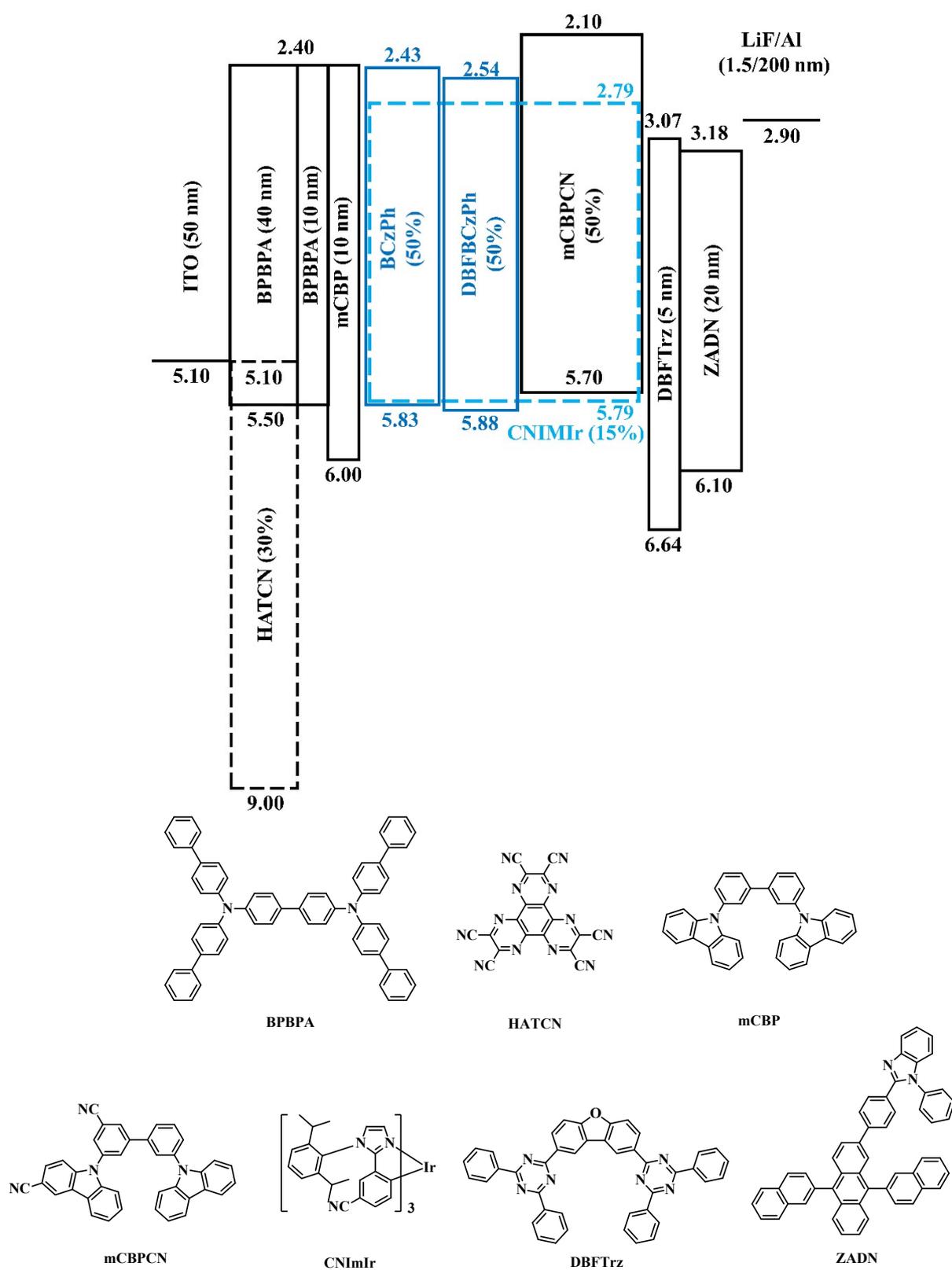
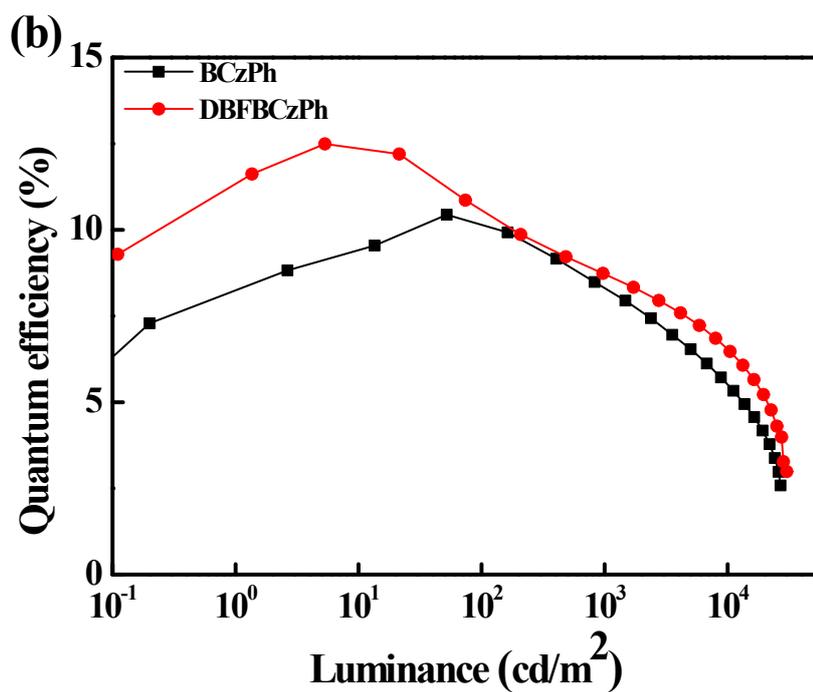
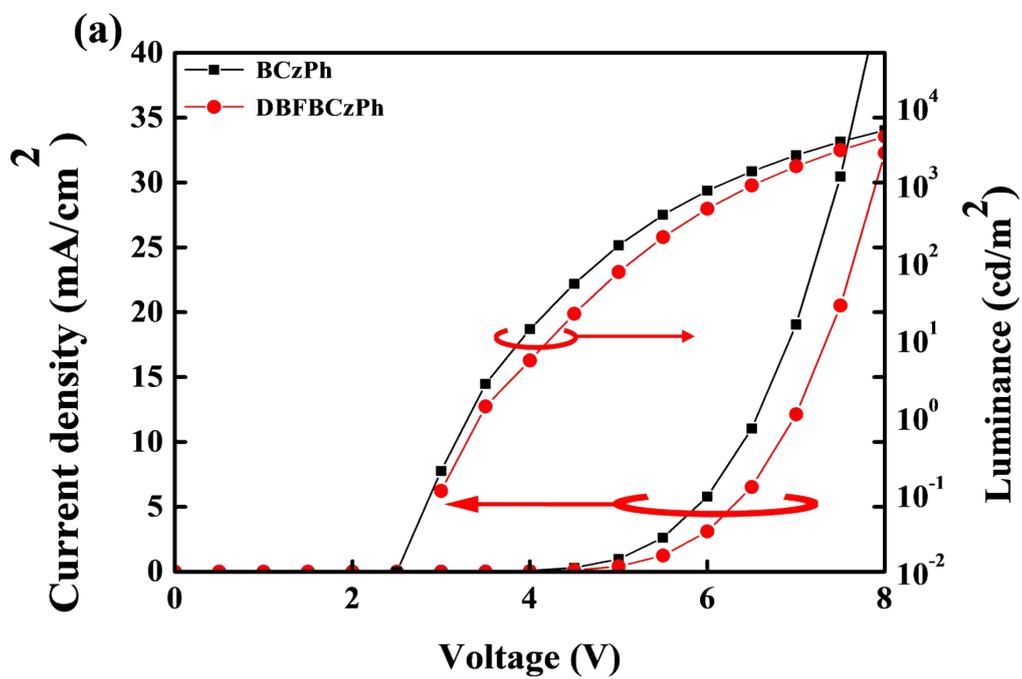


Figure S3. The energy level diagram of lifetime devices and chemical structure of the materials with BCzPh and DBFBCzPh.



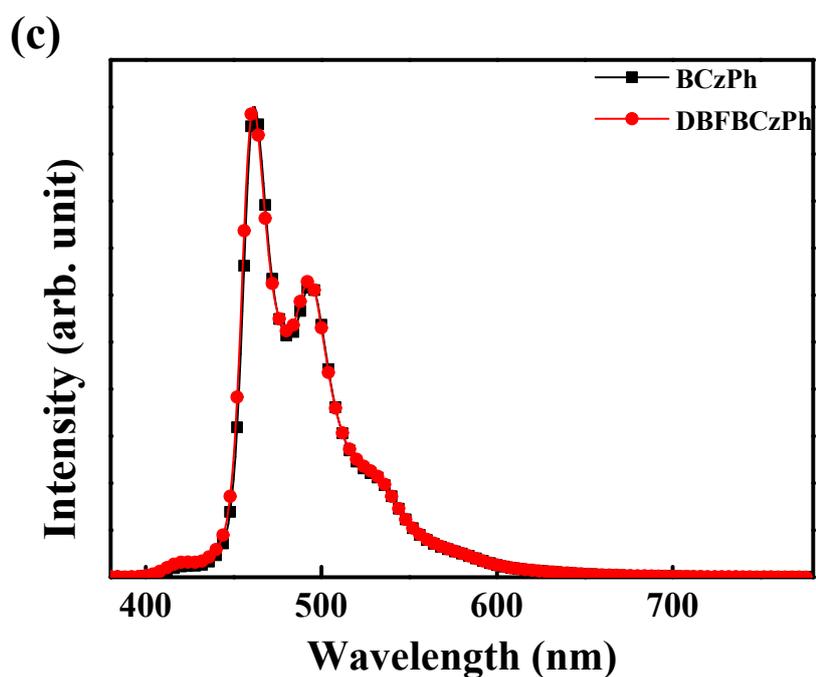


Figure S4. (a) The J - V - L data, (b) EQE- L and (c) EL spectra of the BCzPh and DBFBCzPh lifetime devices.

Table S1. Summarized lifetime device performances of the BCzPh and DBFBCzPh.

	Current efficiency		Power efficiency		External quantum		CIE	Device
	[cd/A]		[lm/W]		efficiency [%]		(x, y)	lifetime ^(a)
	1000cd/m ²	Max	1000cd/m ²	Max	1000cd/m ²	Max	1000cd/m ²	[h]
BCzPh	14.1	17.8	7.2	13.3	8.3	10.4	(0.15, 0.24)	250.4
DBFBCzPh	14.8	21.7	7.1	18.3	8.7	12.5	(0.15, 0.24)	505.9

^(a) LT50 at 200 cd/m²