
Supporting information

Experimental

General information

1,3-diiodobenzene and sodium tert-butoxide (t-BuONa), 2-(dicyclohexylphosphino)biphenyl and (1,8-diazabicyclo[5,4,0]undec-7-ene) (DBU) (TCI Chem. Co.) were used without further purification. Copper iodide (CuI), trans-1,2-diaminocyclohexane, palladium on carbon (Pd/C), 1,1'-bis(diphenylphosphine)ferrocene (DPPF), 9*H*-carbazole, 18-crown-6, 1-bromo-2-diodobenzene, 4-aminopyridine, 1,2,3,4-tetrahydro- β -carboline, para-xylene (p-xylene) and 4,5-Bis(diphenylphosphino)-9,9-dimethylxanthene (Xantphos) (Aldrich Chem. Co.), dimethylformamide (DMF), sodium carbonate (Na₂CO₃), dimethylacetamide (DMAC) and tert-butyl alcohol (Duksan Sci. Co.), 1,4-dioxane (Samchun Sci. Co.), palladium(II) acetate (Pd(OAc)₂) and tris(dibenzylideneacetone)-dipalladium (Pd₂(dba)₃) (P&H tech Co.), potassium phosphate (K₃PO₄) (Daejung Sci. Co.) were also used as received. Toluene was distilled over sodium and calcium hydride.

The ¹H and ¹³C nuclear magnetic resonance (NMR) was recorded on a Avance 500 (500 MHz) spectrometer. Fluorescence spectrophotometer (HITACHI, F-7000) and ultraviolet-visible (UV-Vis) spectrophotometer (Shimadzu, UV-2501PC) were used to measure photoluminescence (PL) spectra and UV-Vis spectra. Low temperature PL measurement of the synthesized materials was carried out at 77 K using a dilute solution of the materials. The differential scanning calorimeter (DSC) measurements were performed using a Mettler DSC 822e under nitrogen at a heating rate of 10 °C/min to measure the melting point (T_m) and glass transition temperature (T_g). The mass spectra were recorded using a JEOL JMS-700 spectrometer in FAB mode and elemental analysis were recorded using a CE instrument Flash 2000. The HOMO energy levels were measured with a cyclic voltammetry (CV). CV measurement of organic materials was carried out in acetonitrile solution with tetrabutylammonium perchlorate at 0.1 M

concentration. Ag was used as the reference electrode and Pt was the counter electrode. Organic materials were coated on indium tin oxide substrate and were immersed in electrolyte for analysis.

Synthesis

Synthetic scheme of the CzCb1, CzCb2, and CzCb3 compounds is described in **Scheme S1**.

9-(3-iodophenyl)-9H-carbazole (1)

Diiodobenzene (5 g, 15.16 mmol), 9H-carbazole (1.27 g, 7.58 mmol), CuI (0.15 g, 0.76 mmol), K₃PO₄ (1.62 g, 7.58 mmol), and 18-crown-6 (0.2 g, 0.76 mmol) were dissolved in 1,4-dioxane under nitrogen atmosphere. The reaction mixture was stirred and refluxed for 24h. The mixture was filtered and diluted with dichloromethane and washed with distilled water. The organic layer was dried over anhydrous MgSO₄ and evaporated in vacuo to give the crude product. The extract was evaporated to dryness affording a solid, which was further purified by column chromatography by dichloromethane/n-hexane.

¹H NMR (500 MHz, CDCl₃): δ 8.12 (d, 2H, J=3.75 Hz), 7.92 (t, 1H, J=1.17 Hz), 7.78 (d, 1H, J=4 Hz), 7.54 (dd, 1H, J=4.25, 4.25 Hz), 7.37-7.42 (m, 4H), 7.27-7.32 (m, 3H) MS (FAB) m/z 369 [(M + H)⁺].

3-Bromo-N-phenylpyridin-2-amine (2)

3-Bromo-N-phenylpyridin-2-amine was synthesized according to the method described in literature¹.

9H-pyrido[2,3-b]indole (α-carboline) (3)

9H-pyrido[2,3-b]indole was prepared according to the synthetic method reported earlier².

9-(3-(9H-carbazol-9-yl)phenyl)-9H-pyrido[2,3-b]indole (CzCb1)

9-(3-Iodophenyl)-9H-carbazole (1) (1.4 g, 3.79 mmol), α-carboline (0.71 g, 4.17 mmol), CuI (0.22 g, 1.14 mmol), K₃PO₄ (1.61 g, 7.58 mmol), and trans-1,2-diaminocyclohexane (0.13 g, 1.14 mmol) were dissolved in 1,4-dioxane under nitrogen atmosphere. The reaction mixture was stirred and refluxed for

36h. The mixture was diluted with dichloromethane and washed with distilled water. The organic layer was dried over anhydrous MgSO₄ and evaporated in vacuo to give the crude product. The extract was evaporated to dryness affording a white solid, which was further purified by column chromatography using dichloromethane/hexane as an eluent.

Yield 52%, T_m 163 °C. ¹H NMR (500 MHz, CDCl₃): δ 8.52 (d, 1H, J=3.00 Hz), 8.37 (d, 1H, J=4.25 Hz), 8.12 (dd, 3H, J=9.75, 9.75 Hz), 7.95 (s, 1H), 7.78-7.84 (m, 2H), 7.63-7.69 (m, 4H), 7.48 (t, 1H, J=5.17 Hz), 7.44 (t, 2H, J=5.17 Hz), 7.22-7.35 (m, 4H) ¹³C NMR (500 MHz, CDCl₃): δ 151.8, 146.5, 140.6, 139.6, 138.9, 137.8, 130.7, 128.3, 127.1, 126.1, 125.6, 125.4, 123.6, 121.1, 120.3, 120.2, 116.5, 110.3, 110 MS (FAB) m/z 410 [(M + H)⁺]. Anal. Calcd for C₂₉H₁₉N₃: C, 85.06; H, 4.68; N, 10.26. Found: C, 85.04; H, 4.66; N, 10.22.

9H-pyrido[3,4-b]indole (β-carboline) (4)

9H-pyrido[3,4-b]indole was prepared according to literature method³.

9-(3-(9H-carbazol-9-yl)phenyl)-9H-pyrido[3,4-b]indole (CzCb2)

CzCb2 was synthesized by the same procedure as the synthesis of CzCb1 except that β-carboline was used instead of α-carboline.

Yield 50%, T_m 164 °C. ¹H NMR (500 MHz, CDCl₃): δ 8.99 (s, 1H), 8.54 (s, 1H), 8.14 (d, 3H, J=13.00 Hz), 7.97 (d, 1H, J=2.25 Hz), 7.83 (t, 1H, J=5.33 Hz), 7.78 (s, 1H), 7.71 (d, 1H, J=4.00 Hz), 7.67 (d, 1H, J=3.75 Hz), 7.50-7.57 (m, 4H), 7.43 (t, 2H, J=5.17 Hz), 7.27-7.34 (m, 3H) ¹³C NMR (500 MHz, CDCl₃): δ 141.3, 140.5, 140.3, 139.6, 138.4, 133, 131.4, 129.2, 128.8, 126.4, 126.2, 125.5, 125.1, 123.6, 121.9, 121.8, 121, 120.4, 114.5, 110.4, 109.5 MS (FAB) m/z 410 [(M + H)⁺]. Anal. Calcd for C₂₉H₁₉N₃: C, 85.06; H, 4.68; N, 10.26. Found: C, 84.92; H, 4.62; N, 9.97.

N-(2-bromophenyl)pyridin-4-amine (5)

The synthesis of N-(2-bromophenyl)pyridin-4-amine was described in previous work⁴.

5H-pyrido[4,3-b]indole (γ -carboline) (6)

5H-pyrido[4,3-b]indole was synthesized by the same method described in literature⁴.

5-(3-(9H-carbazol-9-yl)phenyl)-5H-pyrido[4,3-b]indole (CzCb3)

CzCb3 was synthesized by the same procedure as the synthesis of CzCb1 except that γ -carboline was used instead of α -carboline.

Yield 50%, T_m 225 °C. ¹H NMR (500 MHz, CDCl₃): δ 9.37 (s, 1H), 8.54 (d, 1H, $J=3.00$ Hz), 8.18 (d, 1H, $J=3.75$ Hz), 8.13 (d, 2H, $J=4.00$ Hz), 7.84 (t, 1H, $J=5.33$ Hz), 7.72-7.75 (m, 2H), 7.63 (d, 1H, $J=4.00$ Hz), 7.46-7.54 (m, 4H), 7.42 (t, 2H, $J=5.50$ Hz), 7.37 (m, 2H), 7.30 (t, 2H, $J=5.00$ Hz) ¹³C NMR (500 MHz, CDCl₃): δ 145.6, 144.7, 143.1, 140.6, 140.5, 139.6, 138.1, 131.4, 127.2, 126.6, 126.2, 125.4, 125, 123.6, 121.9, 121.7, 120.8, 120.4, 120.2, 110.1, 109.5, 104.9 MS (FAB) m/z 410 [(M + H)⁺]. Anal. Calcd for C₂₉H₁₉N₃: C, 85.06; H, 4.68; N, 10.26. Found: C, 83.90; H, 4.63; N, 10.18.

Device fabrication and measurements

The device structure of blue PHOLEDs was indium tin oxide (ITO, 50 nm)/poly(3,4-ethylenedioxythiophene);poly(styrenesulfonate) (PEDOT:PSS, 60 nm)/4,4'-cyclohexylidenebis[*N,N*-bis(4-methylphenyl)aniline] (TAPC, 20 nm)/1,3-bis(*N*-carbazolyl)benzene (mCP, 10 nm)/CzCb1 or CzCb2 or CzCb3 : iridium(III) bis((3,5-difluoro-4-cyanophenyl)pyridine) picolinate (FCNIrpic) (25 nm, 5%)/diphenylphosphine oxide-4-(triphenylsilyl)phenyl (TSPO1, 30 nm)/LiF (1 nm)/Al (200 nm). Electron only device with a device structure of ITO (50 nm)/Ca (5 nm)/CzCb1 or CzCb2 or CzCb3 (25 nm)/TSPO1 (30 nm)/LiF (1 nm)/Al (200 nm) was also prepared to compare electron density in the emitting layer.

PEDOT:PSS was spin coated on ultraviolet/O₃ treated ITO substrate and other organic materials were deposited by vacuum thermal evaporation at a vacuum pressure of 1.0×10^{-6} torr. Evaporation rate of organic materials was 0.1 nm/s except FCNIrpic. After LiF/Al deposition, devices were encapsulated with

a glass lid with CaO getter inside. The device performances of the blue PHOLEDs were measured with Keithley 2400 source measurement unit and CS1000 spectroradiometer. Voltage scan was used to measure the device performances of the blue PHOLEDs.

References

1. T. Iwaki, A. Yasuhara, T. Sakamoto, *J. Chem. Soc., Perkin Trans. 1*, 1999, 1505.
2. J. K. Laha, P. Petrou, G. D. Cuny, *J. Org. Chem.*, 2009, 74, 3152.
3. C. Portmann, C. Prestinari, T. Myers, J. Scharfe, K. Gademann, *ChemBioChem* 2009, 10, 889.
4. K. Sako, H. Aoyama, S. Sato, Y. Hashimoto, M. Baba, *Bioorg. Med. Chem.* 2008, 16, 3780.

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Table S1. Energy levels of carboline derivatives.

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	HOMO (eV)	LUMO (eV)	Bandgap (eV)	Triplet energy (eV)
CzCb1	-6.06	-2.55	3.51	2.88
CzCb2	-6.06	-2.62	3.44	2.96
CzCb3	-6.08	-2.49	3.59	2.98
mCP	-6.10	-2.40	3.70	2.90

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Scheme S1. Synthetic scheme of CzCb1, CzCb2 and CzCb3.

Figure S1. Current density-voltage curves of electron only devices of CzCb1, CzCb2 and CzCb3.

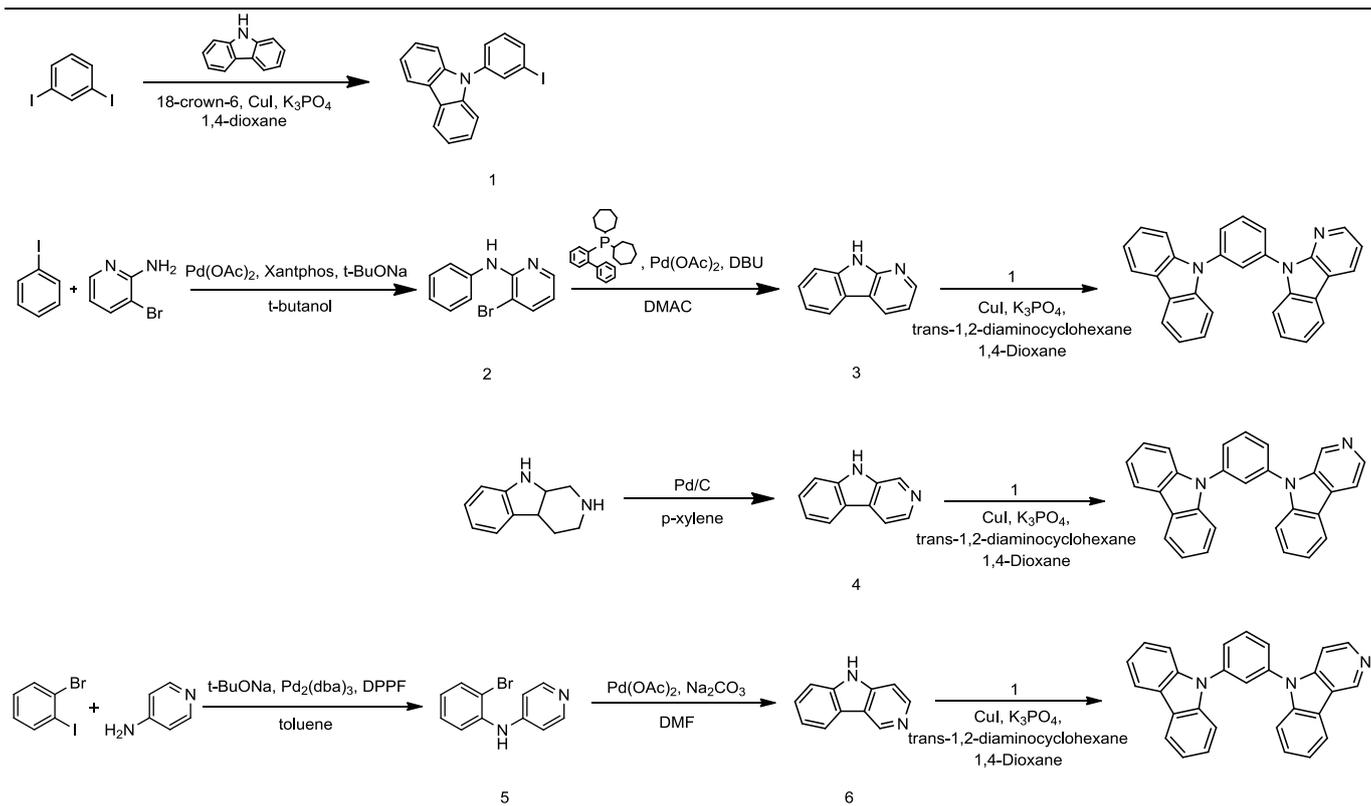
Figure S2. Electroluminescence spectra of CzCb1, CzCb2 and CzCb3.

Figure S3. Solution UV-Vis and PL and low temperature PL spectra of α , β , and γ carboline.

Figure S4. First scan DSC curves of CzCb1, CzCb2 and CzCb3.

Figure S5. Second scan DSC curves of CzCb1, CzCb2 and CzCb3.

Figure S6. Geometrical structure of CzCb1, CzCb2 and CzCb3.



Scheme S1

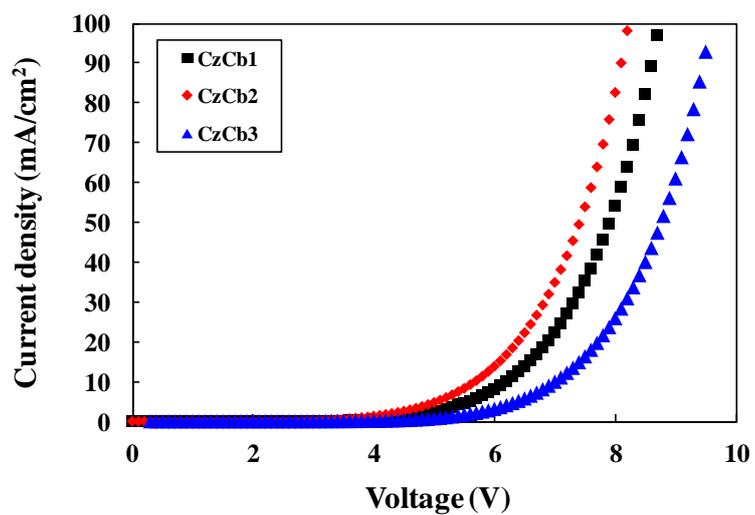


Figure S1

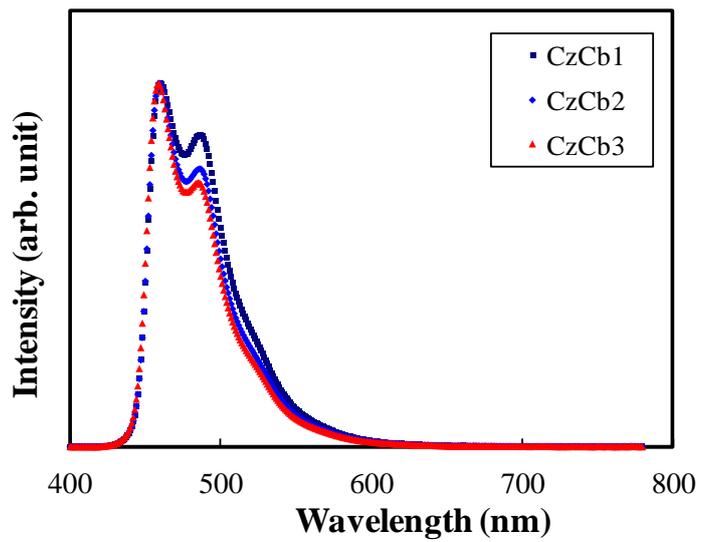


Figure S2

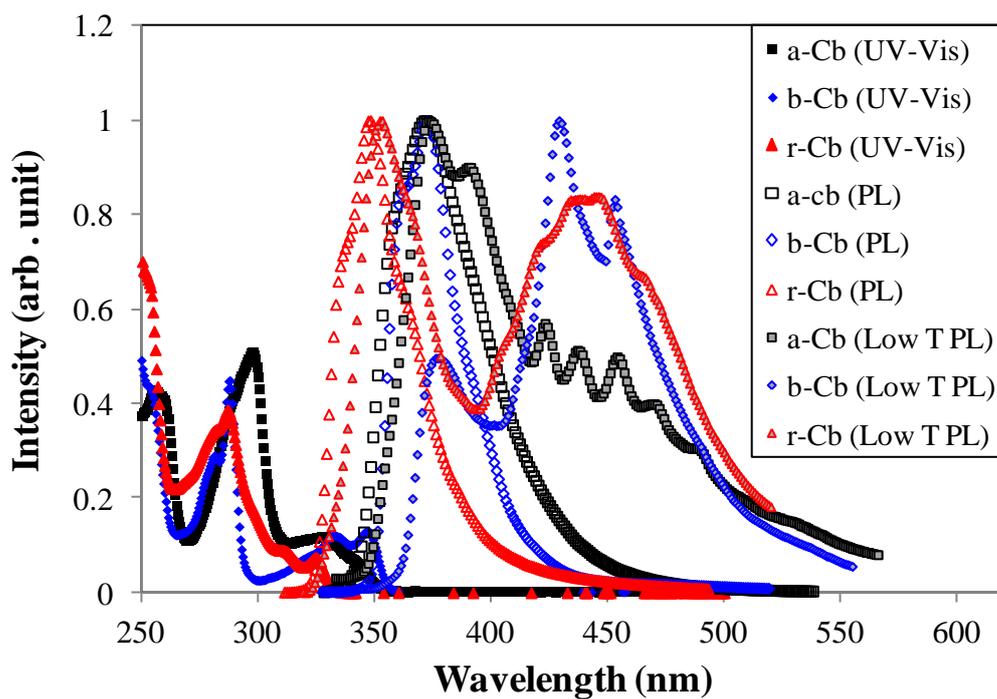


Figure S3

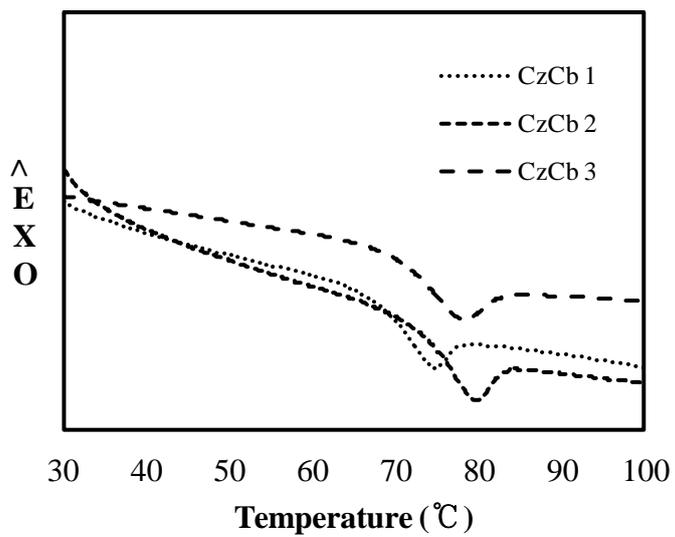


Figure S4

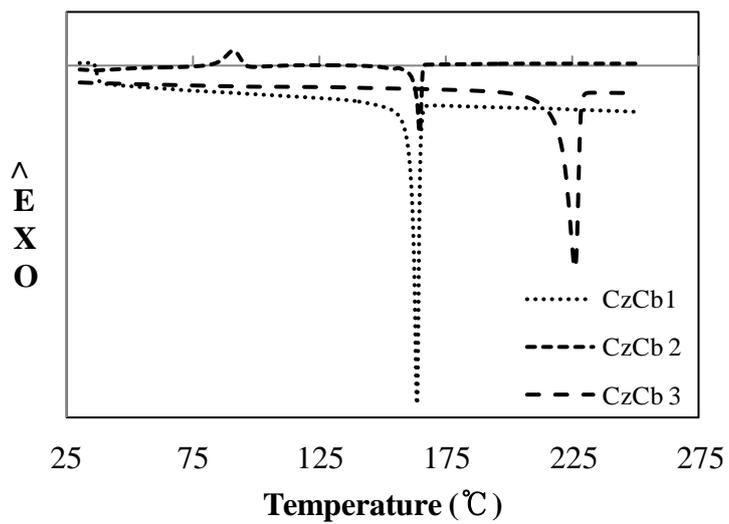


Figure S5

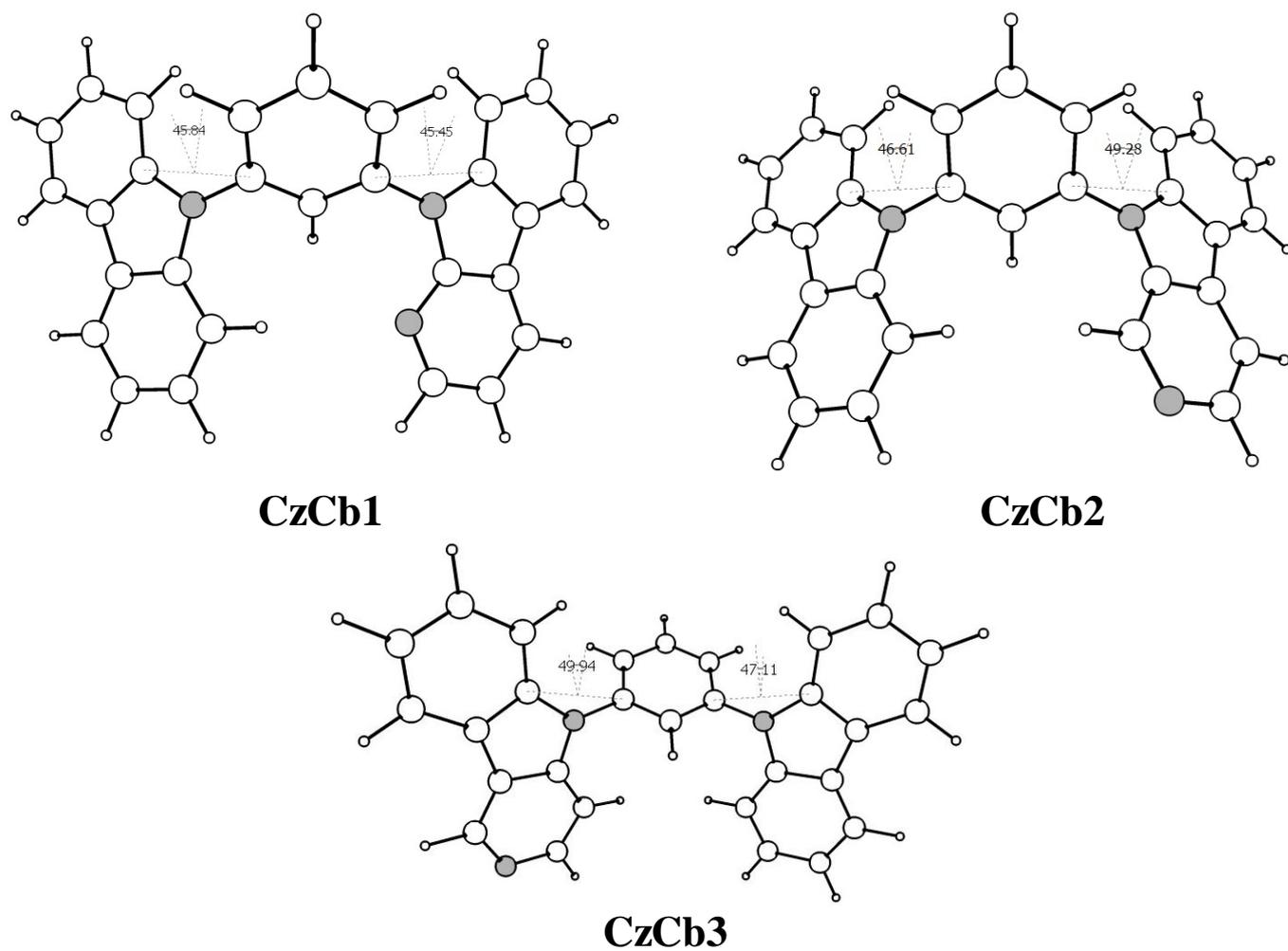


Figure S6