

Supplementary Information for;

**Synthesis and Blue Phosphorescent Device Performances of a New
Bipolar Host Material Containing Pyrazino[2,3-b]indole Moiety**

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General Procedure:

Chemicals were commercially purchased and used without further purification. Thin layer chromatography (TLC) was conducted on flexible sheets precoated SiO₂ (Baker-flex; IB2-F) and visualized by UV light. Column chromatography was conducted by using silica gel (60-200 mesh; Fisher Scientific Co.). Melting point was determined on melting point apparatus (MEL-TEMP; model 1102D). ¹H and ¹³C NMR spectra were recorded on Varian Gemini 300 NMR spectrometer using CDCl₃, as the solvent, except where noted. Mass spectra were obtained on GC/mass spectrometer (Jeol Co.; AccuTOF GCv 4G). Photophysical properties were analyzed by using UV/vis spectrometer (Scinco Co.; S-3100) and photoluminescence (PL) spectrometer (Hitachi High Technologies; F-7000). The host material was dissolved in THF at a concentration of *ca.* 1.0 × 10⁻⁴ M for UV/vis and PL measurements. Triplet energy of the host material was calculated from low temperature PL spectrum measured in the liquid nitrogen (77 K) condition. Cyclic voltammetry measurement was conducted by using potentiostat (SP-50; Bio-Logic Science Instruments) in electrolyte solution, which is CH₃CN with tetrabutylammonium perchlorate at 0.1 M concentration. Ag was used as the reference electrode and Pt was the counter electrode. The host material was coated on indium-tin-oxide substrate and immersed in the electrolyte solution for measurement. Ferrocene was used as the internal standard material. Glass transition temperature was measured by using a differential scanning calorimeter (Melter-Toledo; DSC 820e) at a heating rate of 10 °C min⁻¹ under nitrogen atmosphere.

Synthesis:

Acetyl-1*H*-3-indolyle trifluoromethanesulfonate (1). Lithium diisopropylamide (2M solution in THF, 18.75 mL, 37.5 mmol) was added to a -78 °C solution of 1-acetyl-1*H*-indol-3(2*H*)-one (3.25 g, 18.55 mmol) in THF (150 mL) under nitrogen atmosphere. The mixture was stirred for 20 min at -78 °C and *N*-phenyl-*bis*(trifluoromethanesulfonimide) (20.00 g, 55.98 mmol) in THF (100 mL) was added. The mixture was stirred for 16 hrs at room temperature. The solvent was evaporated; water (150 mL), and ethyl acetate (150 mL) were added. After neutralization with 10 % HCl, the aqueous layer was extracted with ethyl acetate (3 × 150 mL); the organic layer was dried over anhydrous MgSO₄. After removing the solvent by evaporator, the residue was purified by column chromatography (SiO₂) eluting with a mixture of ethyl acetate:petroleum ether (1:9; v/v) to give a solid (4.38 g, 77%); m.p. = 68-70 °C ; ¹H NMR δ 2.65 (s, 3H), 7.34-7.43 (m, 2H), 7.46 (s, 1H), 7.48-7.59 (m, 1H), 8.44 (d, 1H); ¹³C NMR δ 23.8, 115.2, 116.8, 117.1, 118.7, 122.2, 124.6, 127.1, 133.1, 133.3, 168.2.

5*H*-Pyrazino[2,3-*b*]indole (2). Ethylenediamine (1.29 g, 29.29 mmol) and triflate **1** (3.00 g, 9.76 mmol) were dissolved in DMF (100 mL) and Pd(PPh₃)₄ (0.56 g, 0.49mmol) were added. The solution was heated and stirred at 65°C for 1 hr. Water (100 mL) was added and the solution was neutralized and extracted with ethyl acetate (3 × 100 mL). The organic layer was dried over anhydrous MgSO₄. After removing the solvent by evaporator, the residue was purified by column chromatography (SiO₂) eluting with a mixture of ethyl acetate:petroleum ether (3:7; v/v) to give a solid (1.15 g, 70%); m.p. = 243-246°C; ¹H NMR (DMSO-*d*₆) δ 7.28-

7.34 (m, 1H), 7.55-7.59 (m, 2H), 8.20 (d, 1H), 8.40 (d, 1H), 8.48 (d, 1H), 12.12 (br s, 1H); ¹³C NMR (DMSO-d₆) δ 113.7, 120.9, 122.1, 122.6, 130.6, 136.8, 138.1, 141.6, 141.8, 147.1; MS (GC-MS/EI): m/z = 169.14 [M⁺] (calcd. m/z = 169.06).

9-(3-bromophenyl)-9H-carbazole (3). Carbazole (10g, 59.85mmol), 1,3-dibromobenzene (14g, 60.00mmol), K₂CO₃ (24g, 179.55mmol), CuI (5.71g, 29.93mmol) and 18-crown-6 (0.8g, 2.99mmol) were dissolved in DMF (180ml) under nitrogen atmosphere. The reaction mixture was stirred for 24hrs at 130 °C. The mixture was extracted to CH₂Cl₂. The solution was washed with water and brine. The combined organic mixture was dried over anhydrous MgSO₄ and filtrated. The crude material was purified by column chromatography (SiO₂) eluting with *n*-hexane to give a white solid (9.0g, 47%): m.p.64-65 °C; ¹H NMR δ 8.17 (d, 2H), 7.77 (s, 1H), 7.63 (d, 1H), 7.55-7.47(m, 2H), 7.46-7.43(m, 4H), 7.35-7.31 (m, 2H); ¹³C NMR δ 140.73, 139.30, 131.27, 130.68, 130.33, 126.28, 125.90, 123.70, 123.37, 120.54, 120.50, 109.77.

5-(3-(9H-carbazol-9-yl)phenyl)-5H-pyrazino[2,3-*b*]indole (CzPhPZ; 4). 5H-Pyrazino[2,3-*b*]indole (1g, 5.91mmol), 9-(3-bromophenyl)-9H-carbazole (2.28g, 7.10mmol), K₂CO₃ (3.30g, 23.88mmol), CuI (0.60g, 3.00mmol) and 18-crown-6 (0.08g, 0.30mol) were dissolved in DMF (30ml) under nitrogen atmosphere. The reaction mixture was reflux for 24hrs. The mixture was extracted to CH₂Cl₂. The solution was washed with water three times and brine. The combined organic mixture was dried over anhydrous MgSO₄ and filtrated. The crude material was purified by column chromatography (SiO₂) eluting with a mixture of *n*-hexane:ethyl acetate (3:1; v/v) to give a yellow solid (0.8g 33%): m.p.187-188 °C; ¹H NMR δ 8.61 (d, 1H), 8.48-8.30 (m, 2H), 8.17 (d, 2H), 7.98-7.96 (m, 1H), 7.91-7.85 (m, 1H), 7.83-7.79 (m, 1H), 7.77-7.72 (m, 2H), 7.65 (d, 3H), 7.49-7.44 (m, 3H), 7.35-7.31 (m, 2H); ¹³C NMR δ 141.12, 140.70, 140.06, 139.30, 138.17, 137.01, 136.92, 131.13, 129.74, 126.30, 126.14, 125.52, 125.46, 123.80, 122.33, 122.06, 120.56, 120.51, 120.43, 110.86, 110.03; MS (GC-MS/EI): m/z = 410.30 [M⁺] (calcd. m/z = 410.15).

Fabrication of PHOLED device and measurements

The device structure of blue PHOLEDs was indium tin oxide (150 nm)/ poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (60 nm)/ *Tris*(4-carbazoyl-9-ylphenyl)amine (20 nm)/ *N,N'*-dicarbazoyl-3,5-benzene (10 nm)/New Host: *Bis*[2-(4,6-difluorophenyl)pyridinato-C²,*N'*](picolinato)iridium(III) (FIrpic) (25 nm, *x* wt.-%)/4-(triphenylsilyl) phenyldiphenylphosphine oxide (5 nm)/1,3,5-*Tris*(1-phenyl-1*H*-benzimidazol-2-yl)benzene (30 nm)/LiF (1 nm)/Al (200 nm). The electrical characteristics of the blue PHOLEDs were analyzed with Keithley 2400 source measurement unit. Light-emitting performances were characterized with CS1000 spectroradiometer.

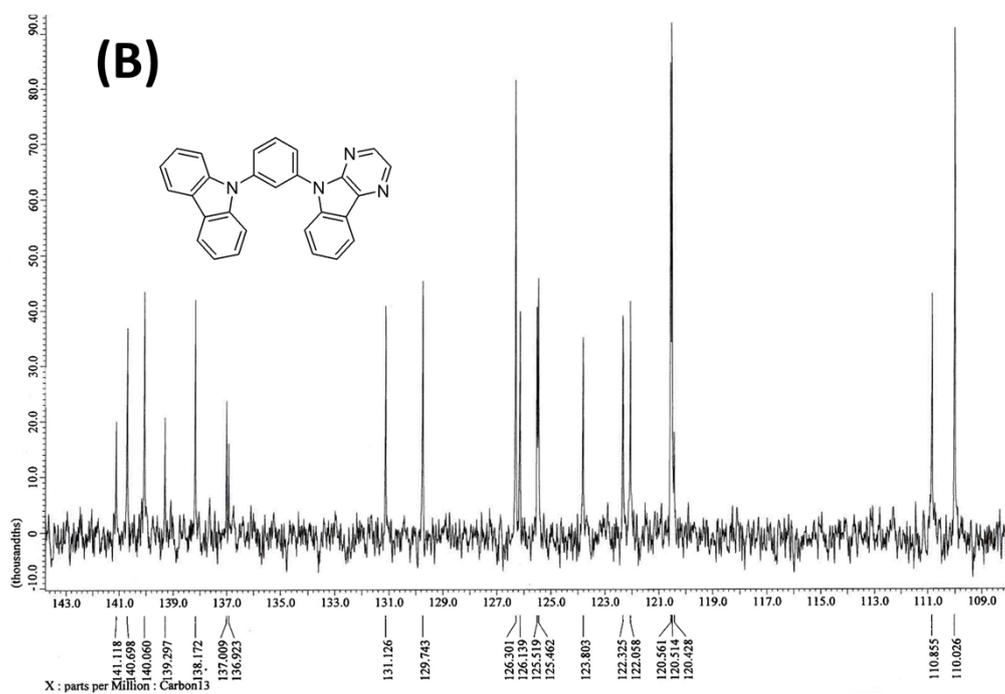
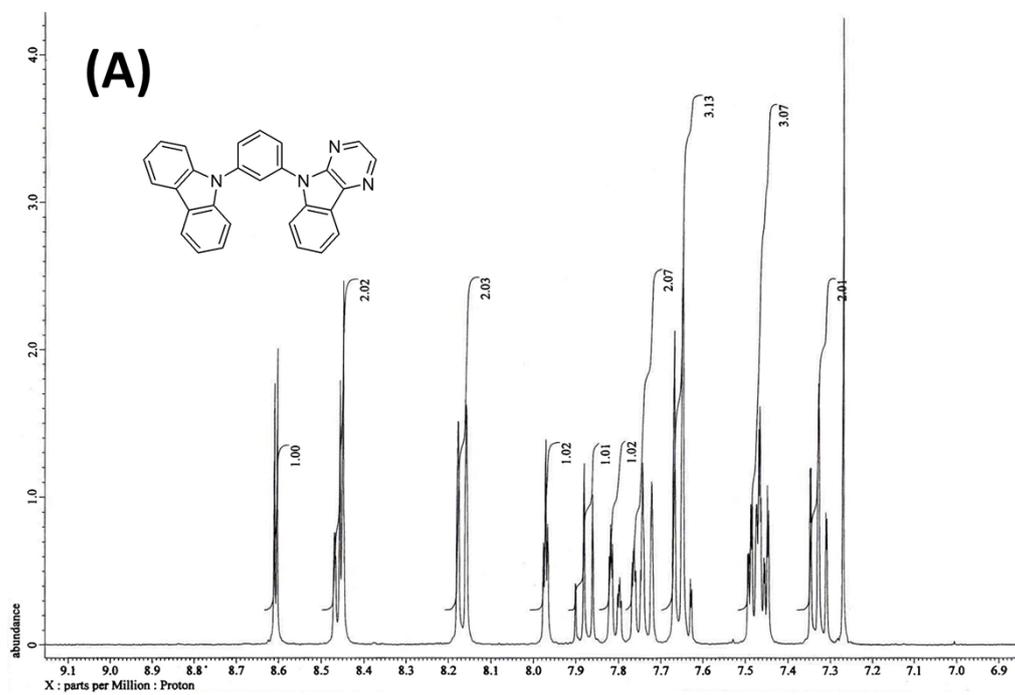


Figure S1. ^1H NMR (A) and ^{13}C NMR (B) spectra of CzPhPz.

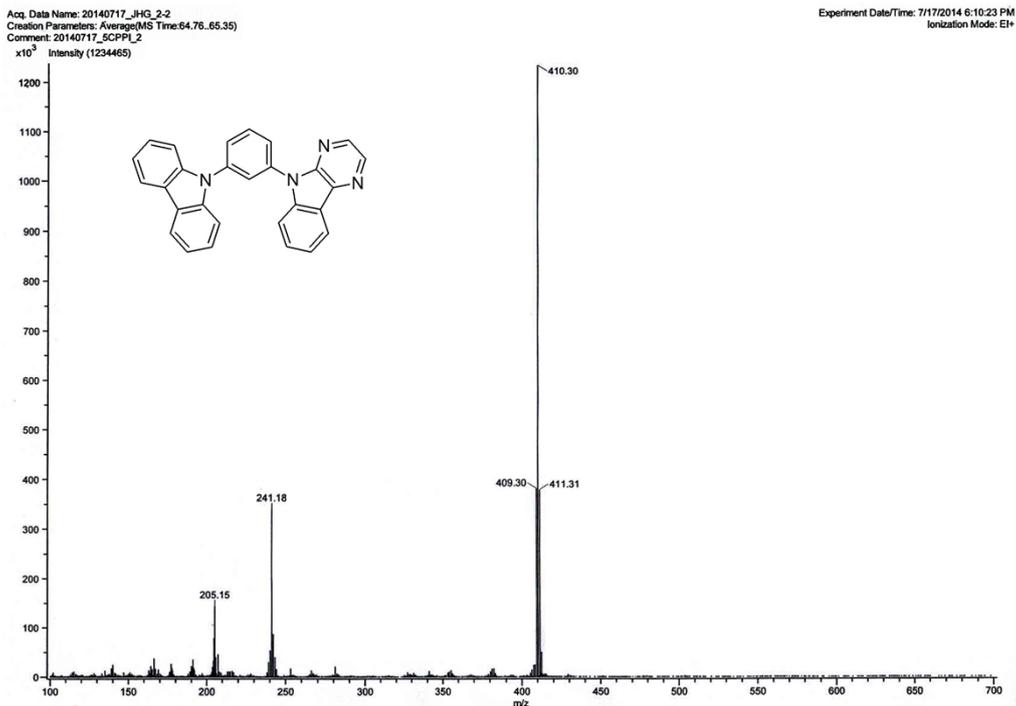


Figure S2. GC-Mass spectra of CzPhPz.

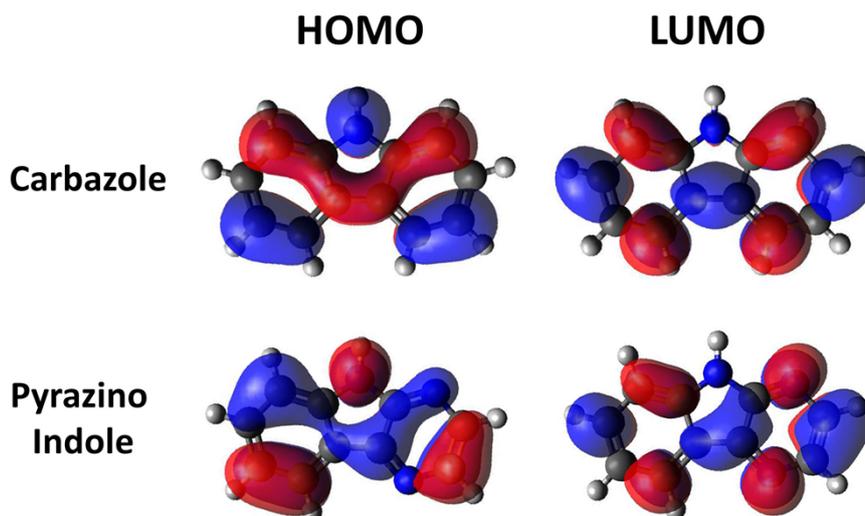


Figure S3. HOMO and LUMO distribution of 9*H*-carbazole and 5*H*-Pyrazino[2,3-*b*]indole.

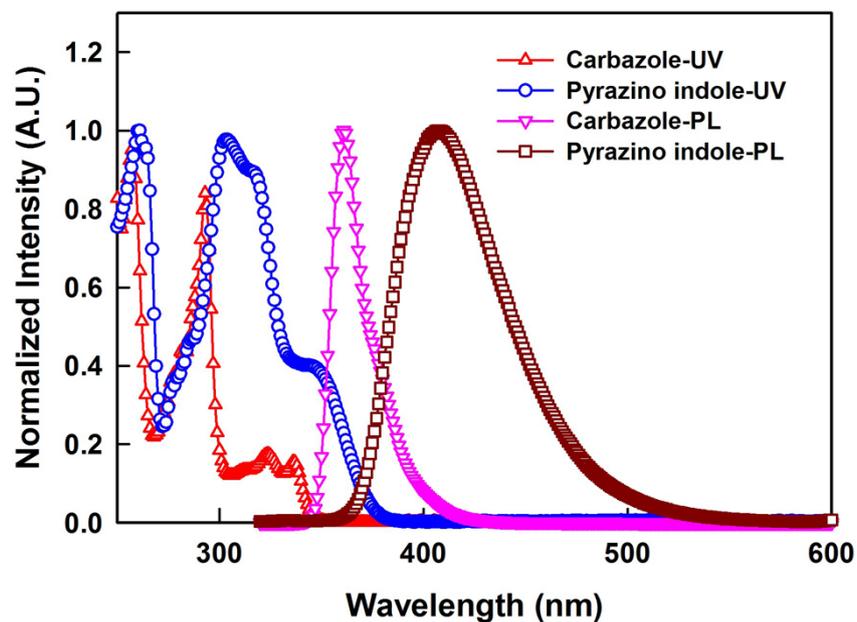


Figure S4. UV/vis and solution PL spectra of 9*H*-carbazole and 5*H*-Pyrazino[2,3-*b*]indole. (emission was excited at 330 nm).

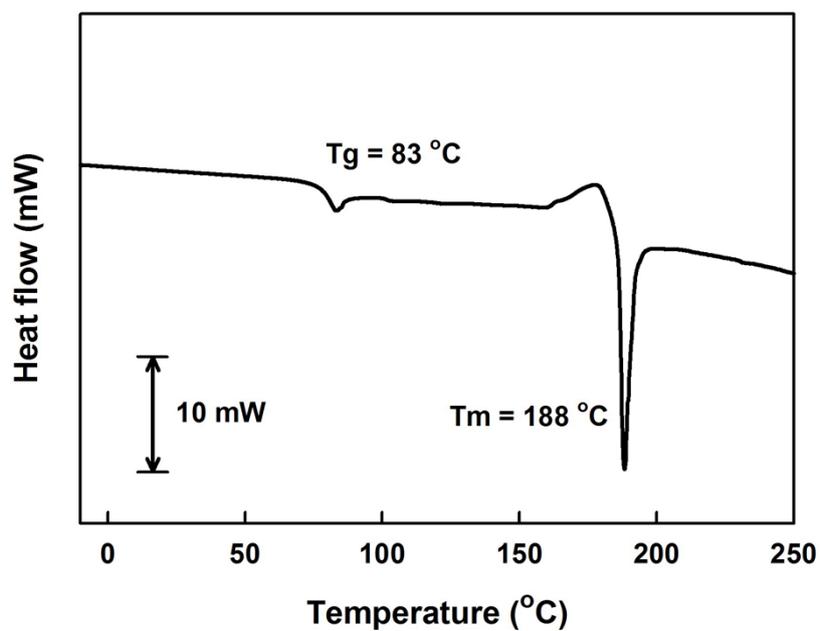


Figure S5. DSC thermograms of CzPhPz.

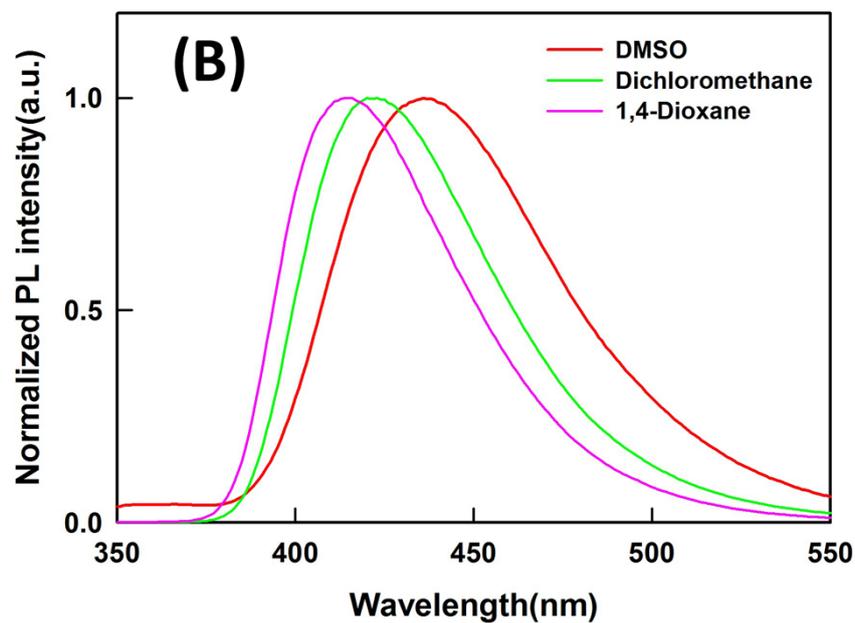
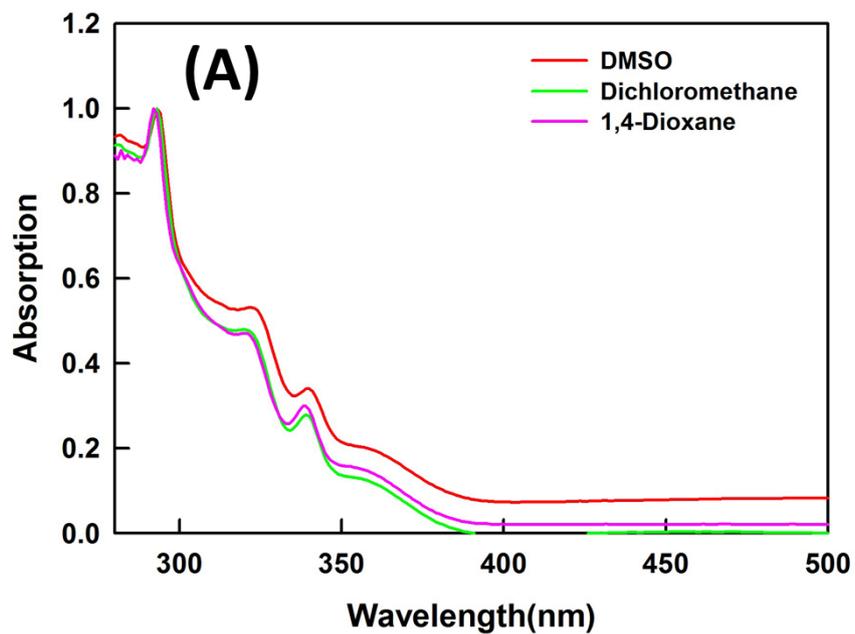


Figure S6. Room-temperature absorption and PL spectra of **CzPhPz** in various organic solvents (excited at 340 nm). (A) Absorption spectra for **CzPhPz**; (B) PL spectra for **CzPhPz**.

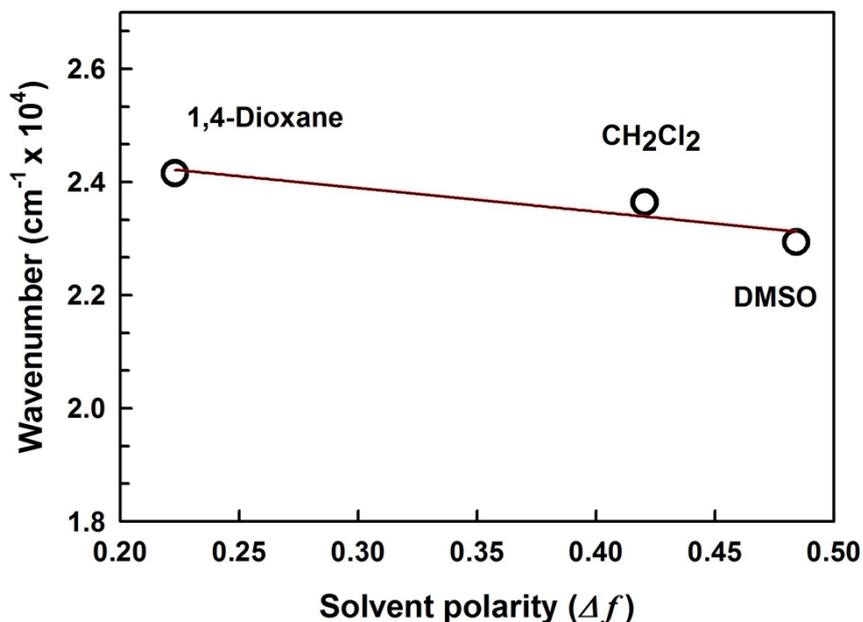


Figure S7. The plot of emission peak frequencies of **CzPhPz** solutions as a function of solvent polarities. Δf is the solvent polarity parameter function and is generally expressed as $\Delta f = (\epsilon - 1)/(2\epsilon + 1)$, where ϵ denotes the static dielectric constant of the solvent.

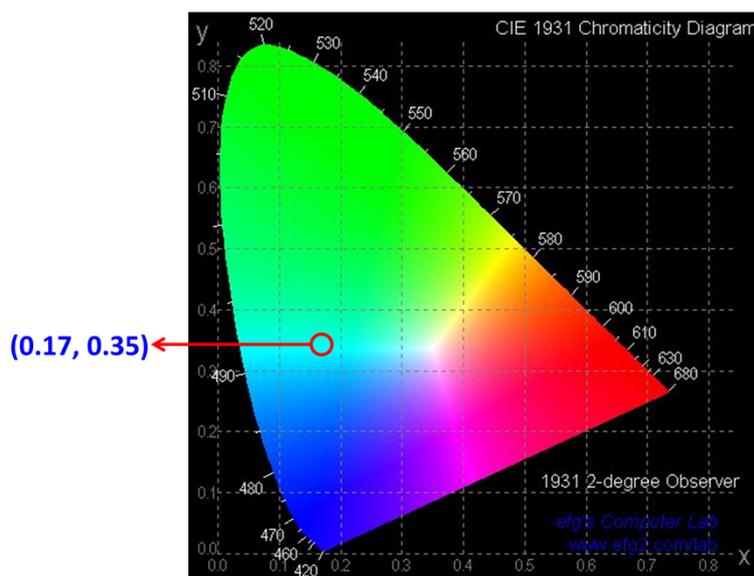


Figure S8. Schematic illustration of CIE color coordinate for **CzPhPz**-based PHOLED.

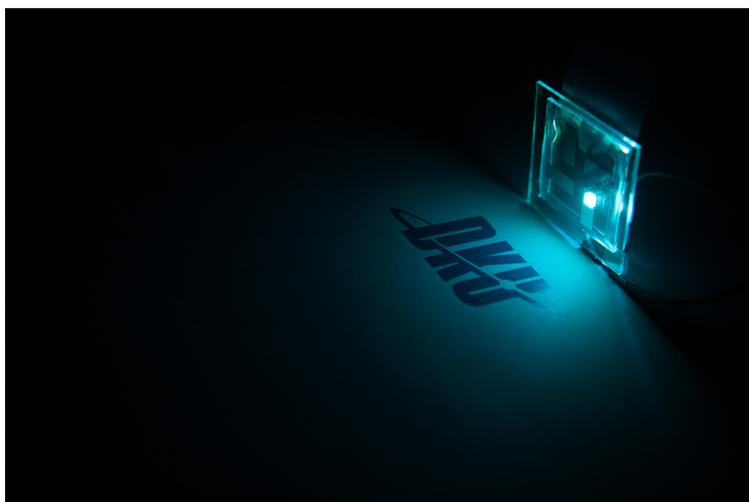


Figure S9. Photo image of the operating **CzPhPz**-based PHOLED.

Table S1. Molecular simulation results of *9H*-carbazole and *5H*-Pyrazino[2,3-*b*]indole.

Sample name	HOMO (eV)	LUMO (eV)	Bandgap (eV)	Triplet energy (eV)	PL _{max} (nm)
Carbazole	-5.44	-0.64	4.80	3.19	361
Pyrazino indole	-6.00	-1.52	4.48	2.97	408

Table S2. Light-emitting characteristics of **CzPhPz** at different FIrpc concentration.

Doping Concentration of FIrpc (wt.-%)	Color coordinate (CIE _{x,y})	EL _{max} (nm)
5	(0.17, 0.35)	473
10	(0.17, 0.36)	473
20	(0.17, 0.36)	473
30	(0.17, 0.37)	474

