

Supporting Information for;

**Synthesis of Pyrimidine-cored Host Materials Bearing Phenylcarbazole for
Efficient Yellow Phosphorescent Devices: Effect of Linkage Position**

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<Experimental Section>

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 JEOL JNM-LA400 FT NMR spectrometer using CDCl₃, as the solvent, except where noted. Mass spectra were obtained on LC/mass spectrometer (Agilent Technology 6120). 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 and 2-methoxyethanol at a concentration of *ca.* 1.0 × 10⁻⁴ M for UV/vis and PL measurements, respectively. 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. 1,3-*Bis*(*N*-carbazolyl)benzene (mCP) was used as a standard material of the HOMO level. Glass transition temperature was measured by using a differential scanning calorimeter (TA, DSC Q2000) at a heating rate of 10 °C min⁻¹ under nitrogen atmosphere.

Synthesis

9-(4-Bromophenyl)-9*H*-carbazole (1). 9*H*-Carbazole (10 g, 59.85 mmol), 1,4-dibromobenzene (14 g, 60.00 mmol), K₂CO₃ (24 g, 179.55 mmol), CuI (5.71 g, 29.93 mmol) and 18-crown-6 (0.8 g, 2.99 mmol) were dissolved in DMF (180 ml) under nitrogen atmosphere. The reaction mixture was stirred for 24hrs at 130 °C. The mixture extracted to dichloromethane (DCM) and then the solution washed with distilled water three times and brine. The organic mixture dried over anhydrous MgSO₄ and filtrated. The crude product was collected by filtration and was purified by column chromatography (SiO₂) eluting with a *n*-hexane to give a white solid (9 g, 47 %): m.p. 134-135 °C; ¹H NMR (400MHz, δ) 8.19-8.16 (d,

2H), 7.77-7.74 (d, 2H), 7.50-7.41(m, 6H), 7.40-7.32 (m, 2H); ^{13}C NMR (100MHz, δ) 140.70, 136.89, 133.23, 128.83, 126.22, 123.59, 121.00, 121.53, 120.34, 109.67; MS(ESI): $m/z = 320.2$ $[\text{M}-\text{H}]^+$ (calcd. $m/z = 320.02$).

9-(3-Bromophenyl)-9H-carbazole (2). 9H-Carbazole (10 g, 59.85 mmol), 3-bromiodobenzene, (20.24 g, 71.82 mmol), CuI (5.71 g, 29.93 mmol) and 18-crown-6 (0.8 g, 2.99 mmol) were dissolved in DMF (180 ml) under nitrogen atmosphere. The reaction was following like as procedure of (1). The final product was obtained as white solid (8 g, 36 %): m.p. 66-67 °C; ^1H -NMR (400MHz, δ) 8.18-8.15 (d, 2H), 7.77 (s, 1H), 7.63-7.61 (d, 1H), 7.56-7.48 (m, 2H), 7.45-7.43 (m, 4H), 7.34-7.31 (m, 2H); ^{13}C NMR (100MHz, δ) 140.54, 139.11, 131.16, 130.51, 130.12, 126.18, 125.72, 123.56, 123.26, 120.46, 120.40, 109.66.; GC/MS (FI): $m/z = 321.11$ $[\text{M}]^+$ (calcd. $m/z = 321.02$).

9-(4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-9H-carbazole (3). 9-(4-Bromophenyl)-9H-carbazole (9 g, 27.93 mmol). *bis*(pinacolato)diboron (8.5 g, 33.47 mmol), KOAc (8.25 g, 84.06 mmol) and [1,1'-*bis*(diphenylphosphino)ferrocene]dichloropalladium(II) ($\text{Pd}(\text{dppf})\text{Cl}_2$) (1.03 g, 1.41 mmol) were dissolved in 1,4-dioxane (150 ml) under nitrogen atmosphere. The mixture was reflux for 12 hrs and extracted to DCM. The organic mixture washed distilled water and brine three times. The organic layer was dried over anhydrous MgSO_4 and filtrated. The crude product was collected by filtration and was purified by column chromatography (SiO_2) eluting with a mixture of DCM : *n*-hexane (1:1; v/v) to give a white solid (7.0 g, 68 %): m.p. 168-169 °C; ^1H NMR (400 MHz, δ) 8.19-8.17 (d, 2H), 8.11-8.10 (d, 2H), 7.65-7.63 (d, 2H), 7.50-7.42 (m, 4H), 7.48-7.31 (m, 2H), 1.44 (s, 12H); ^{13}C NMR (100 MHz, δ) 140.73, 140.51, 136.51, 126.21, 126.09, 123.65, 120.43, 120.19, 109.97, 84.21, 83.90, 25.05.; GC/MS (FI): $m/z = 369.37$ $[\text{M}]^+$ (calcd. $m/z = 369.19$)

9-(3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-9H-carbazole (4). 9-(3-Iodophenyl)-9H-carbazole (8 g, 21.68 mmol), *bis*(pinacolato)diboron (6.61 g, 26.01 mmol), KOAc (8.51 g, 86.72 mmol) and $\text{Pd}(\text{dppf})\text{Cl}_2$ (0.79 g, 1.41 mmol) were dissolved in 1,4-dioxane (150 ml) under nitrogen atmosphere. The reaction was following like as procedure of (3). The final product was obtained as white solid (5 g, 62 %): m.p. 83-84 °C; ^1H -NMR (400MHz, δ) 8.17-8.14 (d, 2H), 8.00 (s, 1H), 7.93-7.90 (d, 1H), 7.64-7.62 (d, 2H), 7.41-7.28 (m, 6H), 1.37 (s, 12H); ^{13}C NMR (100MHz, δ) 141.23, 137.40, 133.98, 133.67, 130.26, 129.43, 125.99, 123.44, 120.37, 119.90, 109.98, 84.25, 83.64, 25.18, 25.04.; GC/MS (FI): $m/z = 369.36$ $[\text{M}]^+$ (calcd. $m/z = 369.19$)

9,9'-(Pyrimidine-2,5-diylbis(4,1-phenylene))bis(9H-carbazole) (pPDPC). 5-Bromo-2-iodopyrimidine (2.16 g, 7.58 mmol), 9-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-9H-carbazole (7 g, 18.96 mmol), 2M K₂CO₃ (50 ml) and *tetrakis*(triphenylphosphine)palladium(0) (Pd(PPh₃)₄) (0.44 g, 0.38 mmol) were dissolved in toluene (100 ml) under nitrogen atmosphere. The reaction mixture was reflux for 36hrs. The mixture extracted to DCM. The solution washed with distilled water three times and brine. The organic mixture dried over anhydrous MgSO₄ and filtration. The crude product was collected by filtration and was purified by column chromatography (SiO₂) eluting with a mixture of ethyl acetate : *n*-hexane (1:4; v/v) to give a white solid (1.6 g, 37 %): m.p. 294-295 °C; ¹H-NMR (400MHz, δ) 9.20 (s, 2H), 8.80-8.78 (d, 2H), 8.20-8.19 (d, 2H), 8.18-8.17 (d, 2H), 7.94-7.92 (d, 2H), 7.80-7.79 (m, 4H), 7.57-7.47 (m, 8H), 7.36-7.40 (m, 4H); ¹³C NMR (100MHz, δ) 163.17, 155.47, 140.79, 140.75, 140.34, 138.71, 136.20, 133.52, 131.21, 129.96, 128.43, 128.08, 127.09, 126.29, 126.24, 123.83, 123.81, 120.62, 120.53, 120.50, 120.41, 110.08, 109.86.; MALDI-TOF: *m/z* = 562.22 [M]⁺ (calcd. *m/z* = 562.22).

9,9'-(Pyrimidine-2,5-diylbis(3,1-phenylene))bis(9H-carbazole) (mPDPC). 5-Bromo-2-iodopyrimidine (1.5 g, 5.42 mmol), 9-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-9H-carbazole (5 g, 13.54 mmol), 2M K₂CO₃ (40 ml) and Pd(PPh₃)₄ (0.3 g, 0.27 mmol) were dissolved in toluene (80 ml) under nitrogen atmosphere. The reaction was following like as procedure of (pPDPC). The final product was white solid (1.2 g, 39 %): m.p. 249-250 °C; ¹H-NMR (400MHz, δ) 9.09 (s, 2H), 8.79 (s, 1H), 8.63-8.62 (d, 1H), 8.20-8.18 (d, 4H), 7.87 (s, 1H), 7.79-7.69 (m, 5H), 7.51-7.41 (m, 8H), 7.35-7.31 (m, 4H).; ¹³C NMR (100MHz, δ) 163.16, 155.44, 141.00, 140.77, 139.34, 139.10, 138.40, 136.48, 131.30, 131.16, 129.51, 127.45, 127.24, 127.14, 126.27, 126.13, 125.73, 125.31, 123.70, 123.58, 120.61, 120.45, 120.12, 109.98, 109.71.; MALDI-TOF: *m/z* = 563.19 [M+H]⁺ (calcd. *m/z* = 562.22).

Fabrication of PHOLED device and measurements

The device structure of yellow PHOLEDs were indium tin oxide (ITO, 150 nm)/poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS, 60 nm)/4,4'-cyclohexylidenebis[*N,N*-bis(4-methylphenyl)benzenamine] (TAPC, 20 nm)/*N,N'*-dicarbazolyl-3,5-benzene (mCP, 10 nm)/host material: PO-01 (25 nm, 5 wt.-%)/4-(triphenylsilyl) phenyldiphenylphosphine oxide (TSPO1, 5 nm)/ 2,2',2''-(1,3,5-benzinetriyl)-

tris(1-phenyl-1-*H*-benzimidazole) (TPBi, 30 nm)/LiF (1 nm)/Al (200 nm). The device performances of the yellow PHOLEDs were characterized with Keithley 2400 source measurement unit and Minolta CS-1000 spectroradiometer.

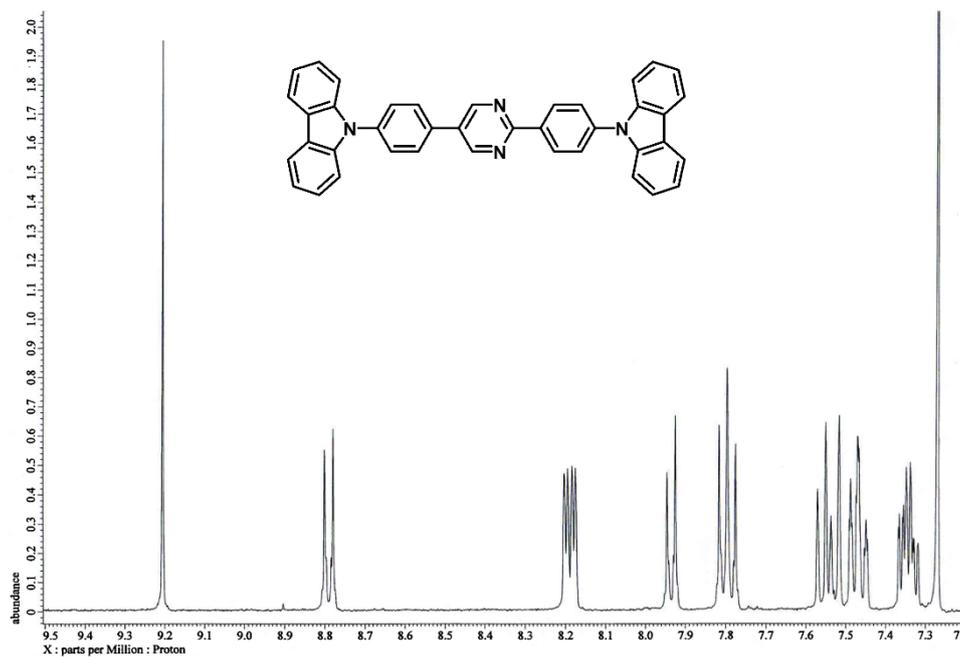


Fig. S1 ¹H NMR spectrum of pPDPC host material.

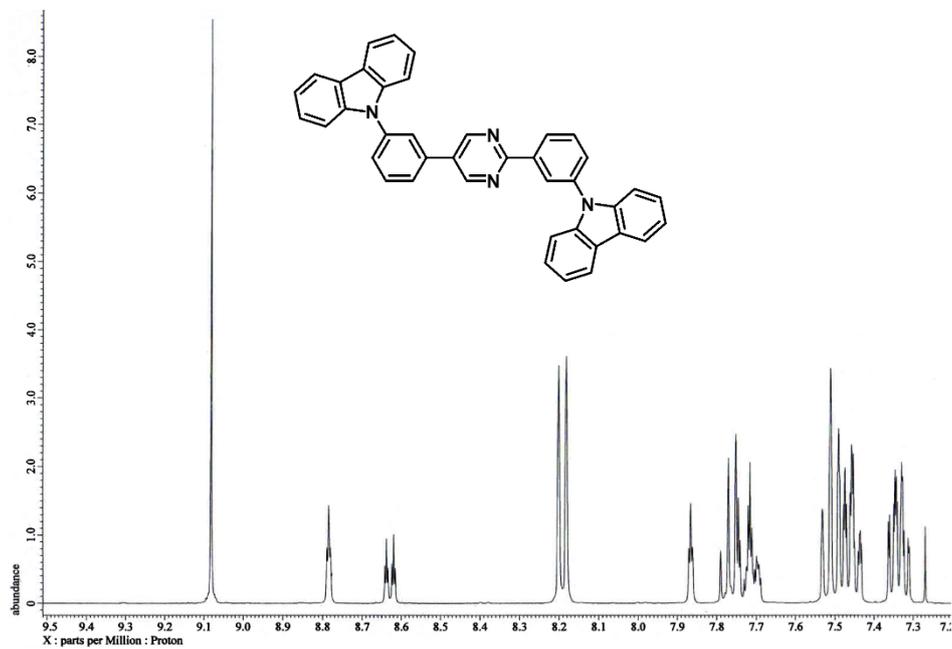


Fig. S2 ¹H NMR spectrum of mPDPC host material.

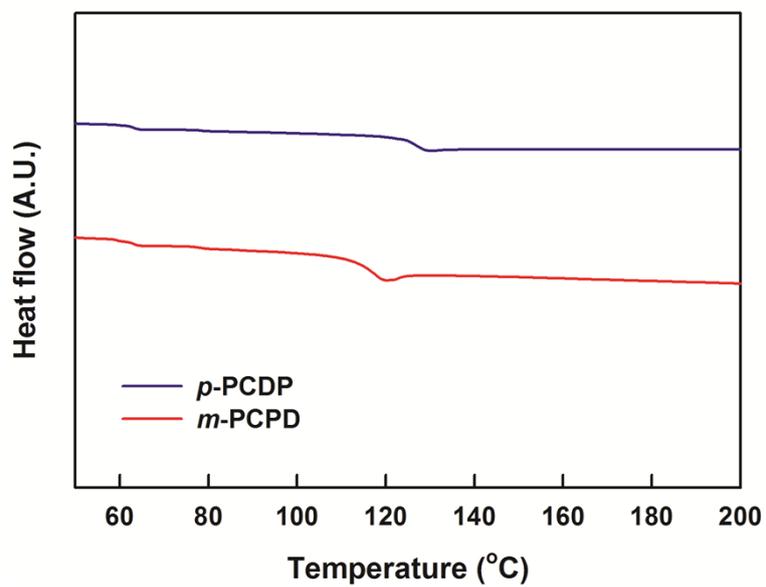


Fig. S3 DSC thermograms for pPDPC and mPDPC host materials.

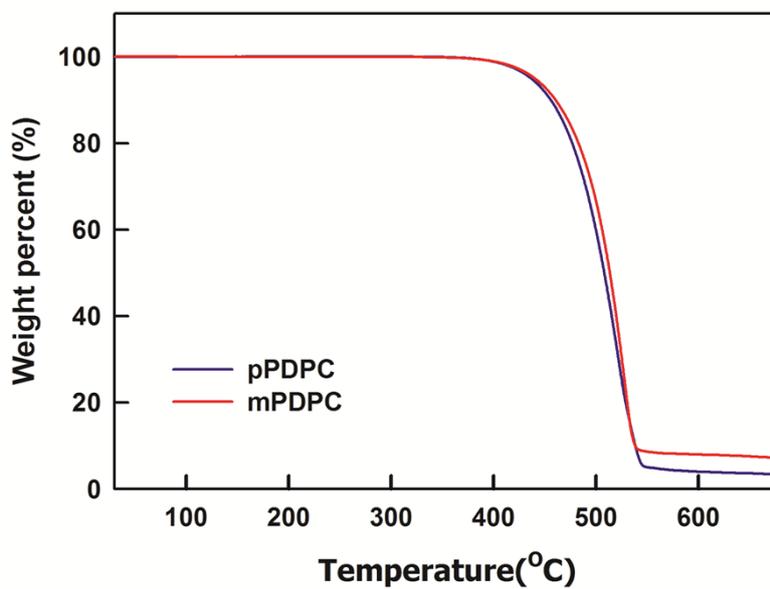


Fig. S4 TG thermograms for pPDPC and mPDPC host materials.

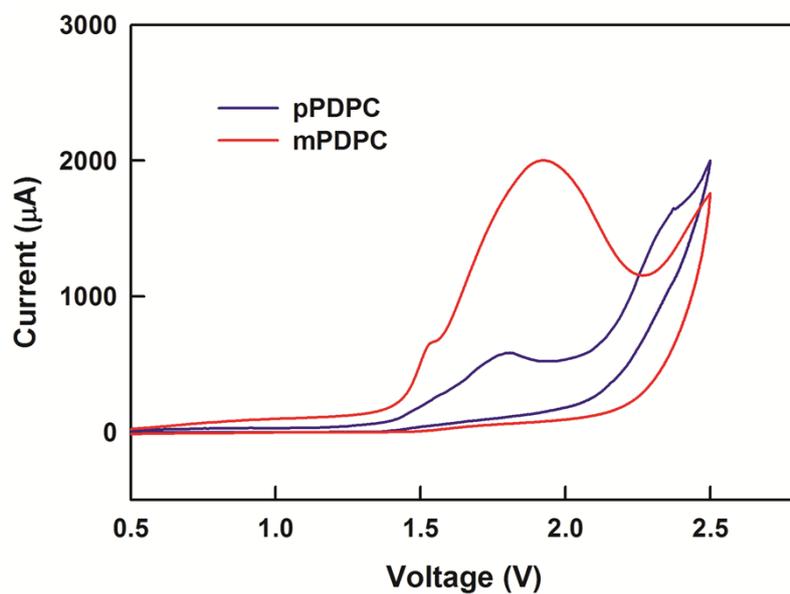


Fig. S5 Cyclic voltammograms for pPDPC and mPDPC host materials.

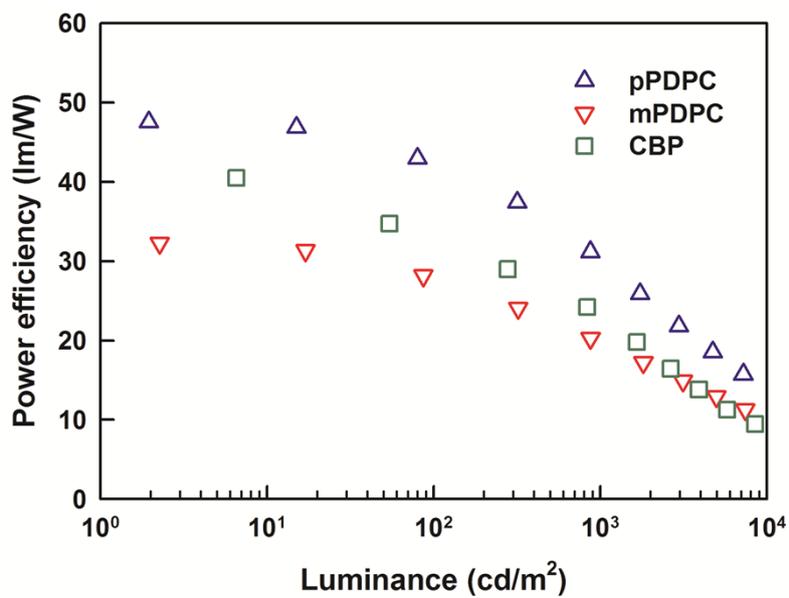


Fig. S6 Power efficiency-luminance curves of yellow PHOLEDs based on pPDPC, mPDPC and CBP.

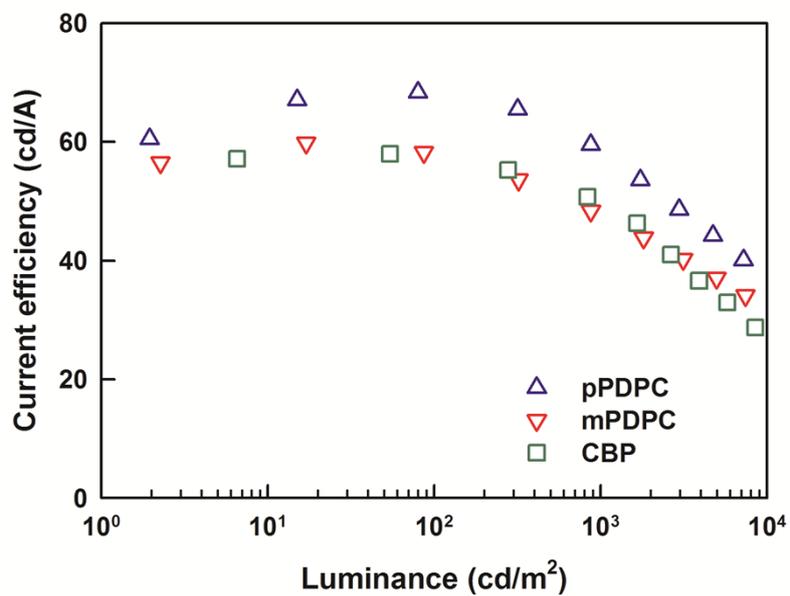


Fig. S7 Current efficiency-luminance curves of yellow PHOLEDs based on pPDPC, mPDPC and CBP.