

Supporting Information for:

Asymmetric Design of Bipolar Host Materials with Novel 1,2,4-Oxadiazole Unit in Blue Phosphorescent Device

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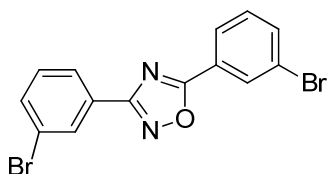
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General procedures: The starting compounds, i.e. benzoic acid, benzonitrile, 3-bromobenzonitrile, 3-bromobenzoic acid and hydroxylamine hydrochloride were purchased from Bepharma limited and used as received. The reagents and the required materials, potassium carbonate, sodium tert-butoxide, tris(dibenzylideneacetone)-dipalladium were purchased from Sigma Aldrich and were used without further purification. THF was purified by PURE SOLV (Innovative Technology) purification system. Chromatographic separations were carried out using silica gel (200-300nm).

^1H NMR and ^{13}C NMR spectra were recorded on a Varian Unity Inova 400 spectrometer. Mass spectra were recorded on a Thermo ISQ mass spectrometer using a direct exposure probe. UV-Vis absorption spectra were recorded on a Perkin Elmer Lambda 750 spectrophotometer. PL spectra and phosphorescent spectra were recorded on a Hitachi F-4600 fluorescence spectrophotometer. DSC was performed on a TA DSC 2010 unit at a heating rate of 10 °C/min under nitrogen, and the T_g was determined from the second heating scan. TGA was performed on a TA SDT 2960 instrument at a heating rate of 10 °C/min under nitrogen, and temperature at 5% weight loss was used as the T_d . CV was carried out on a CHI600 voltammetric analyzer at room temperature with a conventional three-electrode configuration, consisting of a platinum disk functioning as working electrode, a platinum wire functioning as auxiliary electrode, and an Ag wire functioning as pseudo-reference electrode, using ferrocenium-ferrocene (Fc^+/Fc) as the internal standard. Nitrogen-purged dichloromethane was used as solvent for the oxidation scan and DMF for the reduction scan with tetrabutylammoniumhexafluorophosphate (TBAPF₆) (0.1 M) as the supporting electrolyte. The cyclic voltammograms were obtained at a scan rate of 100 mV/s. Theoretical calculations were performed with the use of Gaussian 09 program based on density functional theory (DFT) approach at the B3LYP level.

Preparation of DCzmOXD-1, DCzmOXD-2 and mCzmOXD

Preparation of 3,5-bis(3-bromophenyl)-1,2,4-oxadiazole (mBrmOXD)

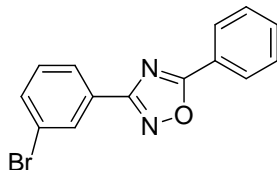


3-bromobenzonitrile (5.00 g, 27.47 mmol), hydroxylamine hydrochloride (4.20 g, 60.44 mmol) and triethylamine (6.40 g, 8.77 ml, 63.37 mmol) were dissolved by 40 ml ethanol and 2 ml water in a 100 ml flask, then the mixture was heated to 75 °C for 12 hours. After cooled to room temperature 65 ml of water was added to the solution, then the ethanol was evaporated from the solution with a rotary evaporator to get white powder precipitated out of the water. Dried the white powder 3-bromo-N'-hydroxybenzimidamide after it was filtered, then it can be used directly in the next step. 3-bromobenzoic acid (4.02 g, 20.00 mmol) and sulfurous dichloride (4.76 g, 2.92 ml, 40.00 mmol) were added in a 100 ml flask, then the mixture was stirred at room temperature for 10 minutes, 76 °C refluxed for 30 minutes, stirred at 80 °C for 3 hours. Redundant sulfurous dichloride was removed by reduced pressure distillation, then 3-bromobenzoyl chloride was achieved. Then 3-bromo-N'-hydroxybenzimidamide (4.18 g, 19.46 mmol) afforded before and 20 ml DMF were added into the flask, and heated to 120 °C stirred for 30 minutes. After cooling to room temperature, the reaction mixture was dumped into ice water and filtered, washed with water. The crude material was

purified by column chromatography with 1:3 (v/v) dichloromethane/ petroleum ether as the eluent to give a white solid (6.42 g).

84.5% yield. ^1H NMR (400MHz, CDCl_3) δ (ppm): 8.39-8.33 (m, 2H), 8.16-8.14 (d, J = 8.0 Hz, 1H), 8.12-8.10 (d, J = 8.0 Hz, 1H), 7.75-7.65 (m, 2H), 7.47-7.38 (m, 2H). ^{13}C NMR (CDCl_3) δ (ppm): 174.64, 167.99, 135.90, 134.34, 131.11, 130.74, 130.56, 130.48, 128.65, 126.68, 126.05, 125.88, 123.23, 123.01. MS (EI): m/z 380.15 [M^+]. Anal. calcd for $\text{C}_{14}\text{H}_8\text{Br}_2\text{N}_2\text{O}$ (%): C 44.25, H 2.12, N 7.37; found: C 44.26, H 2.03, N 7.20.

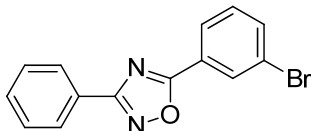
Preparation of 3-(3-bromophenyl)-5-phenyl-1,2,4-oxadiazole (mBrmOXD-1)



mBrmOXD-1 was synthesized according to the same procedure as for mBrmOXD by using 3-bromobenzonitrile (5.00 g, 27.47 mmol) and benzoic acid (2.44 g, 20.00 mmol). mBrmOXD-1 (5.23 g) was afforded as a white solid.

86.8% yield. ^1H NMR (400MHz, CDCl_3) δ (ppm): 8.35-8.22(t, 1H), 8.34-8.20(m, 2H), 8.12-8.10 (d, J = 8.0 Hz, 1H), 7.67-7.54 (m, 4H), 7.40-7.36 (t, 1H). ^{13}C NMR (CDCl_3) δ (ppm): 176.02, 167.88, 137.42, 134.17, 132.94, 130.56, 130.43, 129.17, 128.96, 128.22, 126.04, 124.12, 122.96. MS (EI): m/z 300.2 [M^+]. Anal. calcd for $\text{C}_{14}\text{H}_9\text{BrN}_2\text{O}$ (%): C 55.84, H 3.01, N 9.30; found: C 55.74, H 2.87, N 8.89.

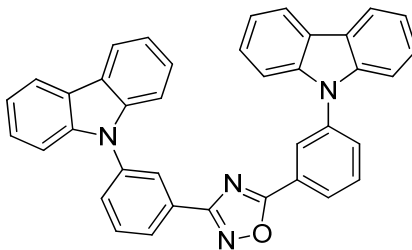
Preparation of 5-(3-bromophenyl)-3-phenyl-1,2,4-oxadiazole (mBrmOXD-2)



mBrmOXD-2 was synthesized according to the same procedure as for mBrmOXD by using benzonitrile (2.83 g, 27.47 mmol) and 3-bromobenzoic acid (4.02 g, 20.00 mmol). mBrmOXD-2 (5.27 g) was afforded as a white solid.

87.5% yield. ^1H NMR (400MHz, CDCl_3) δ (ppm): 8.39-8.38(t, 1H), 8.18-8.14 (m, 3H), 7.75-7.73 (d, J = 8.0 Hz, 1H), 7.55-7.50 (m, 3H), 7.46-7.42 (t, 1H). ^{13}C NMR (CDCl_3) δ (ppm): 174.36, 169.11, 135.70, 131.37, 131.09, 130.69, 128.92, 127.56, 126.71, 126.66, 126.13, 123.17. MS (EI): m/z 302.09 [M^+]. Anal. calcd for $\text{C}_{14}\text{H}_9\text{BrN}_2\text{O}$ (%): C 55.84, H 3.01, N 9.30; found: C 56.04, H 3.00, N 9.13.

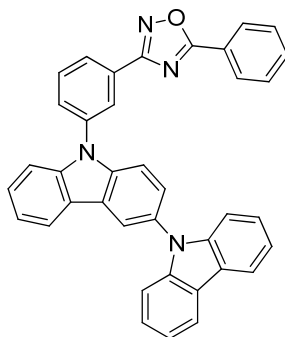
Preparation of 3,5-bis(3-(9*H*-carbazol-9-yl)phenyl)-1,2,4-oxadiazole (mCzmOXD)



mBrmOXD (3.80 g, 10.00 mmol), carbazole (5.01 g, 30.00 mmol) dissolved in anhydrous xylene (60

mL) under an argon atmosphere. Sodium*tert*-butoxide, S-PHOS and tris(dibenzylideneacetone)dipalladium(0) were added to the reaction mixture. The mixture was stirred at 110 °C for 48 h. After the reaction was finished, the organic layer was separated and washed with dichloromethane and water, then the organic layer was dried over by anhydrous Na₂SO₄, filtered and evaporated under reduced pressure. The crude material was purified by column chromatography with 1:3 (v/v) dichloromethane/petroleum ether as the eluent to give a white solid state mCzmOXD (3.85 g). 69.7% yield. ¹HNMR (400MHz, CDCl₃) δ (ppm): 8.44-8.41 (d, *J* = 14.4 Hz, 2H), 8.29-8.25 (m, 2H), 8.16-8.14 (d, *J* = 8.0 Hz, 2H), 7.83-7.73 (m, 4H), 7.46-7.39 (m, 8H), 7.32-7.27 (m, 4H). ¹³CNMR (CDCl₃) δ (ppm): 175.19, 168.56, 140.70, 140.53, 138.85, 138.50, 131.35, 130.89, 130.55, 129.87, 129.74, 129.38, 128.74, 126.91, 126.64, 126.40, 126.22, 126.10, 125.99, 123.64, 123.53, 120.46, 120.37, 120.20. MS (EI): *m/z* 552.51 [M⁺]. Anal. calcd for C₃₈H₂₄N₄O (%): C 82.59, H 4.38, N 10.14; found: C 82.58, H 4.37, N 10.23.

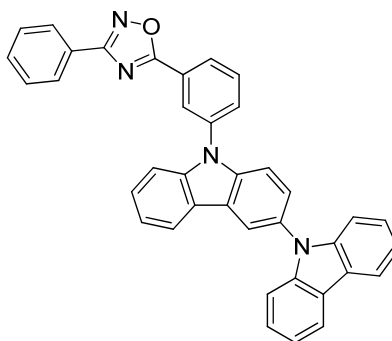
Preparation of 3-(3-(9*H*-[3,9'-bicarbazol]-9-yl)phenyl)-5-phenyl-1,2,4-oxadiazole (DCzmOXD-1)



DCzmOXD-1 was synthesized according to the same procedure as for mCzmOXD by using mBrmOXD-1 (3.01 g, 10.00 mmol) and 9*H*-3,9'-bicarbazole (4.98 g, 15.00 mmol). 9*H*-3,9'-bicarbazole was prepared as reported. DCzmOXD-1 (4.55 g) was afforded as a white solid.

82.3% yield. ¹HNMR (400MHz, CDCl₃) δ (ppm): 8.50 (s, 1H), 8.33-8.30 (m, 2H), 8.23-8.22 (d, *J* = 7.2 Hz, 2H), 8.19-8.17 (d, *J* = 8.0 Hz, 2H), 8.14-8.12 (d, *J* = 8.0 Hz, 1H), 7.82-7.80 (m, 2H), 7.63-7.49 (m, 7H), 7.42-7.41 (m, 4H), 7.34-7.28 (m, 3H). ¹³CNMR (CDCl₃) δ (ppm): 176.16, 168.35, 141.89, 141.51, 139.93, 138.22, 132.99, 130.75, 130.20, 129.81, 129.26, 129.21, 128.26, 126.88, 126.81, 126.32, 125.91, 125.72, 124.60, 124.14, 123.17, 123.14, 120.70, 120.32, 119.66, 119.60, 110.87, 110.14, 109.85. MS (EI): *m/z* 552.47 [M⁺]. Anal. calcd for C₃₈H₂₄N₄O (%): C 82.59, H 4.38, N 10.14; found: C 82.29, H 4.33, N 10.24.

Preparation of 5-(3-(9*H*-[3,9'-bicarbazol]-9-yl)phenyl)-3-phenyl-1,2,4-oxadiazole (DCzmOXD-2)



DCzmOXD-2 was synthesized according to the same procedure as for mCzmOXD by using mBrmOXD-2 (3.01 g, 10.00 mmol) and 9*H*-3,9'-bicarbazole (4.98 g, 15.00 mmol). DCzmOXD-2 (4.45 g) was afforded as a white solid.

80.5% yield. ¹H NMR (400MHz, CDCl₃) δ (ppm): 8.55(s, 1H), 8.39-8.37 (d, *J* = 7.6 Hz, 1H), 8.32-8.31(s, 1H), 8.20-8.18 (d, *J* = 8.0 Hz, 4H), 8.15-8.13 (d, *J* = 8.0 Hz, 1H), 7.94-7.86 (m, 2H), 7.65-7.51 (m, 7H), 7.41-7.29 (m, 7H). ¹³C NMR (CDCl₃) δ (ppm): 174.81, 169.24, 141.84, 141.34, 139.75, 138.57, 131.41, 131.30, 131.10, 130.44, 128.95, 127.60, 127.31, 126.77, 126.45, 125.92, 125.82, 124.74, 123.23, 123.18, 120.93, 120.79, 120.33, 119.69, 110.71, 109.95, 109.80. MS (EI): *m/z* 552.68 [M⁺]. Anal. calcd for C₃₈H₂₄N₄O (%): C 82.59, H 4.38, N 10.14, O 2.90; found: C 82.17, H 4.35, N 10.16.

Device Fabrication and Testing

Materials deposited at ca. 2 x 10⁻⁶ Torr onto ITO-coated glass substrates to fabricate the OLEDs mentioned in this paper. The ITO surface was cleaned ultrasonically – sequentially with acetone, ethanol, and deionized water, then dried in an oven, and finally exposed to UV-ozone for about 30 min. Organic layers were deposited subsequently at a rate of 2-3 Å/s, Liq was deposited at 0.2 Å/s and then capped with Al (ca. 4 Å/s) through a shadow mask without breaking the vacuum. For all the devices, the emitting areas were determined by the overlap of two electrodes as 0.09 cm². The EL spectra, CIE coordinates and *J-V-L* curves of the devices were measured with a PHOTO RESEARCH SpectraScan PR 655 photometer and a KEITHLEY 2400 SourceMeter constant current source at room temperature.

Figure S1. ¹H NMR spectrum of DCzmOXD-1.

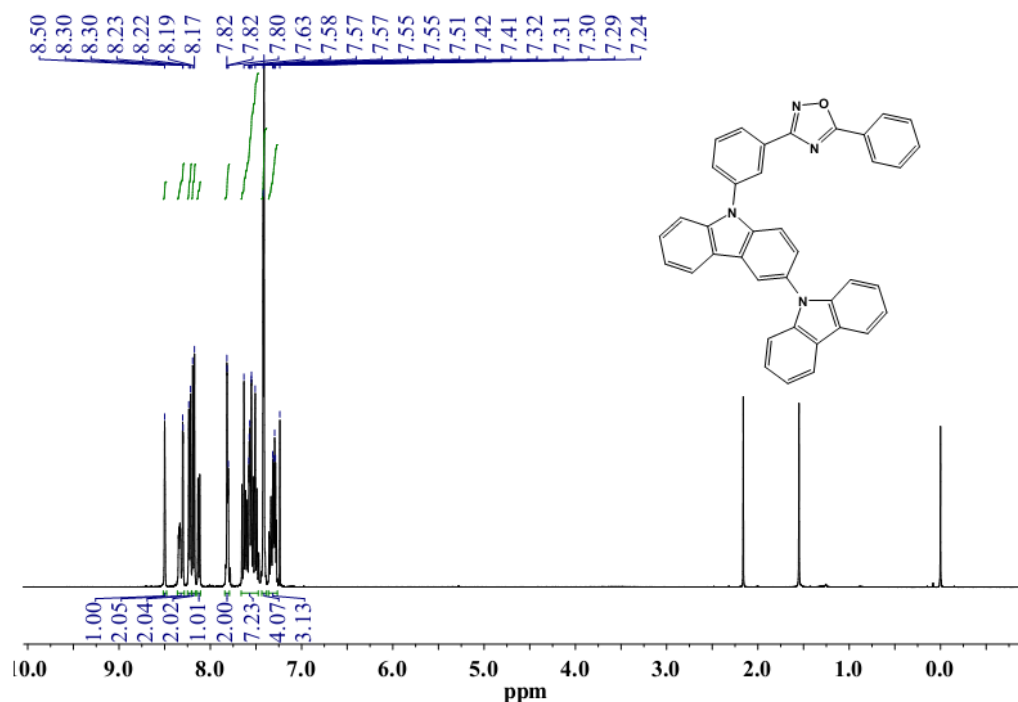


Figure S2. ^{13}C NMR spectrum of DCzmOXD-1.

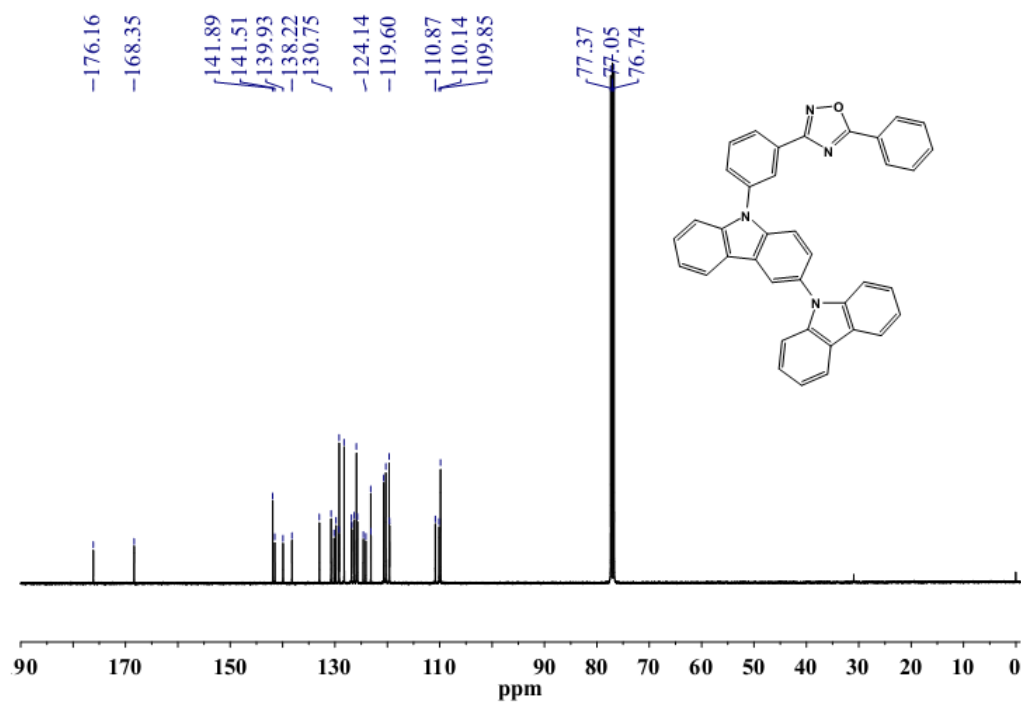


Figure S3. ^1H NMR spectrum of DCzmOXD-2.

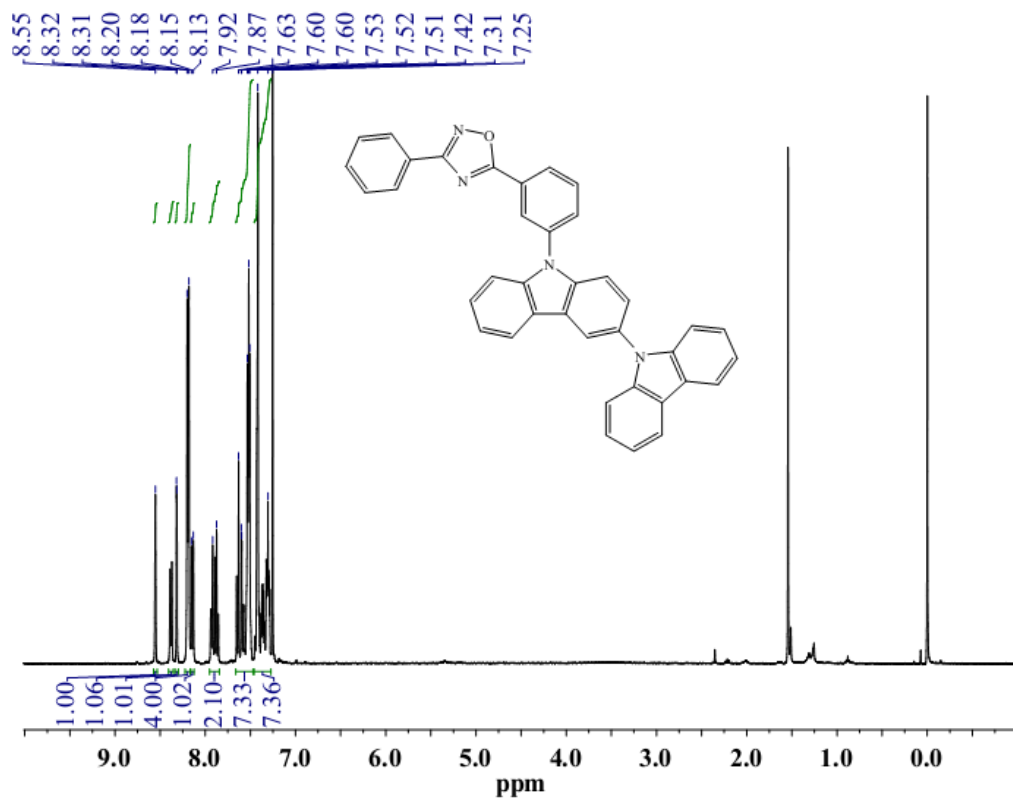


Figure S4. ^{13}C NMR spectrum of DCzmOXD-2.

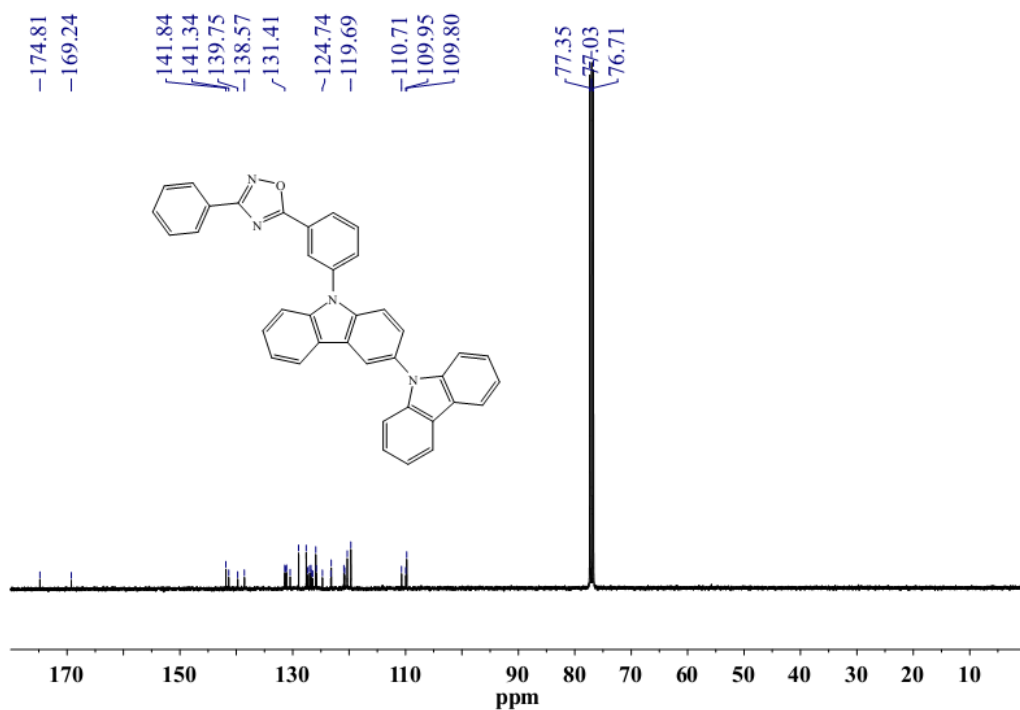


Figure S5. ^1H NMR spectrum of mCzmOXD.

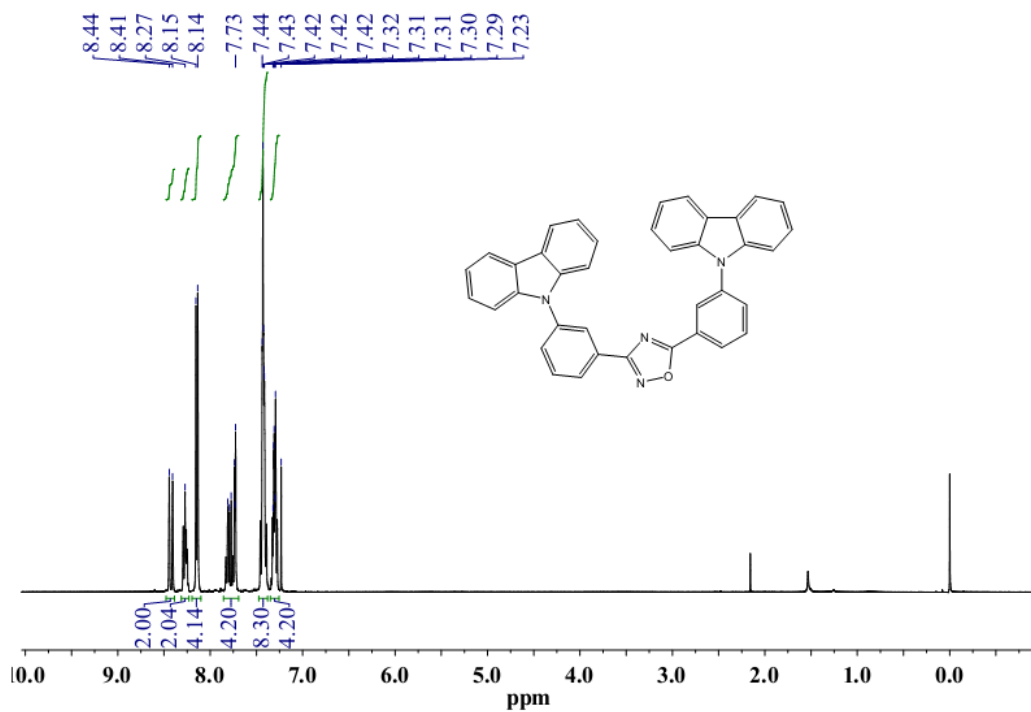


Figure S6. ^{13}C NMR spectrum of mCzmOXD.

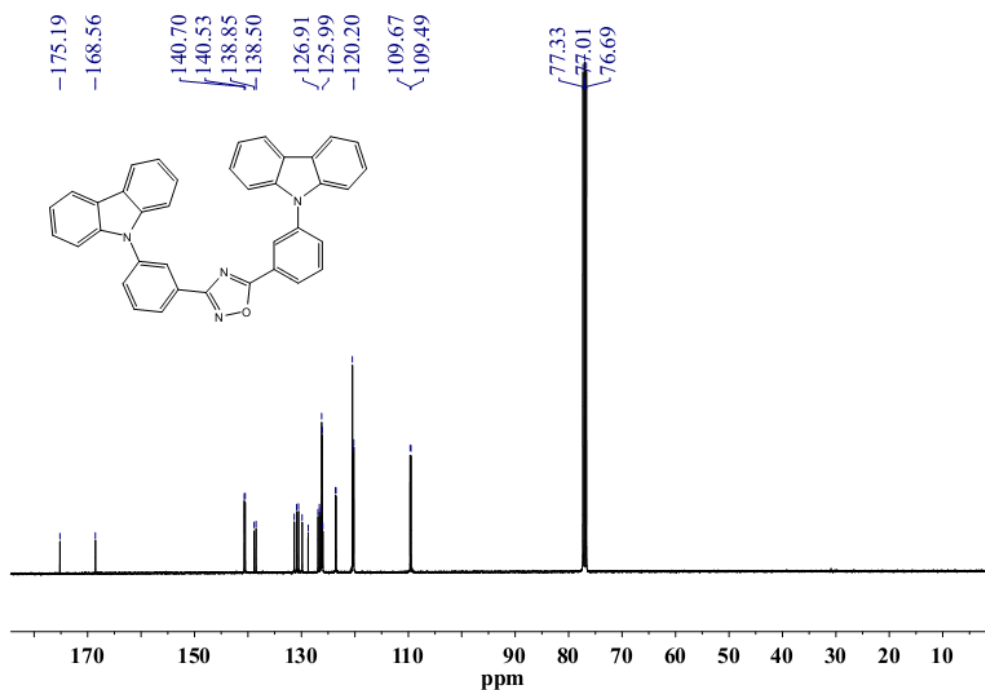
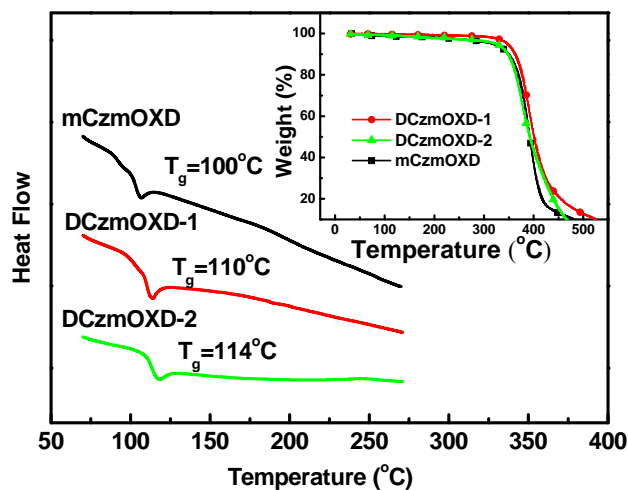


Figure S7. DSC traces recorded at a heating rate of 10 °C/min. Inset: TGA traces recorded at a heating rate of 10 °C/min.



As shown in Figure S7, glass-transition temperatures (T_g) were 110 °C, 114 °C and 100 °C, for DCzmOXD-1, DCzmOXD-2 and mCzmOXD respectively, indicating the isomers with two carbazole rings at one side present slightly higher morphological stability. TGA data of the three materials revealed that they possess excellent thermal stability. Thermal decomposition temperatures (T_d) at 5% weight loss were observed at 362 °C 347 °C 334 °C. Therefore the good thermal and morphological stability of these three materials make them potential organic materials for vacuum evaporation OLED.

Figure S8. Cyclicvoltammograms in CH_2Cl_2 for oxidation and DMF for reduction.

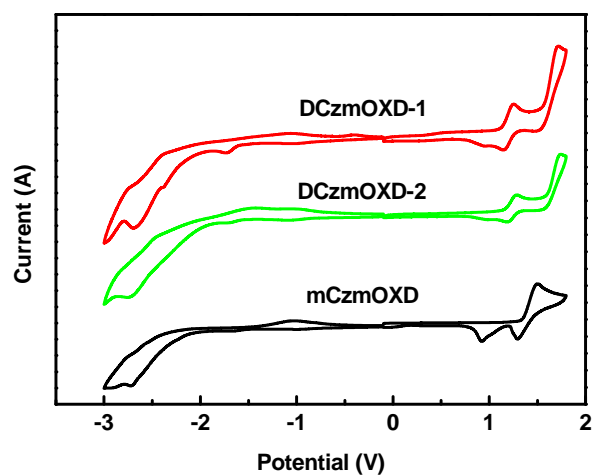
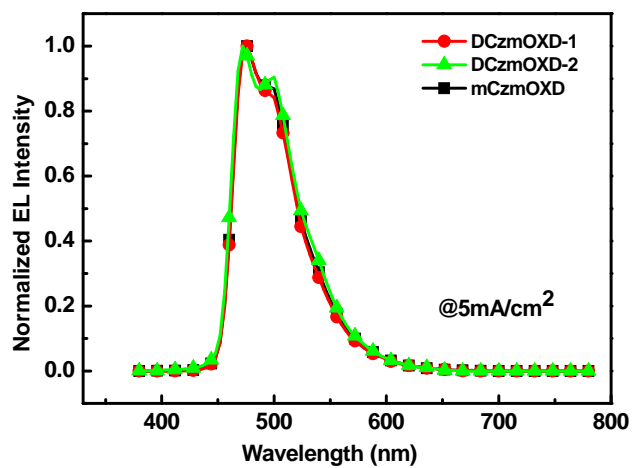
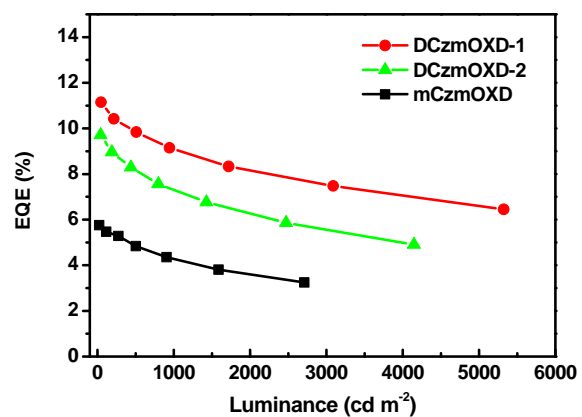


Figure S9. The EL spectra of devices at 5 mA cm^{-2} .



CIE coordinates of these three devices are all (0.15, 0.36) when measured at 5 mA/cm^2 .

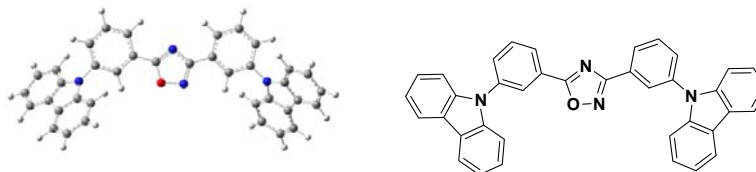
Figure S10. EQE of devices at different luminance.



Theoretical Calculations

The density functional theory (DFT) calculations were carried out using the GAUSSIAN program. at B3LYP/6-31g(d) level.

mCzmOXD

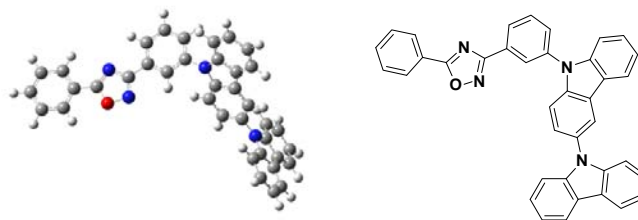


Two carbazoles in molecule mCzmOXD are not in the same plane with the diphenyl-1,2,4 oxadiazole, but they can still conjugated with the phenyls. mCzmOXD has the HOMO ($E_{\text{HOMO}} = -5.38$ eV) located on the β -phenyl carbazole moiety and the LUMO ($E_{\text{LUMO}} = -1.94$ eV) located on the diphenyl-1,2,4 oxadiazole moiety. However, the HOMO-1 ($E = -5.54$ eV) locates on the α -phenyl carbazole moiety with a small energy gap (0.06 eV) below the HOMO, and the distributions of HOMO-1 and LUMO have some overlaps, so HOMO-1 \rightarrow LUMO could be found in the $S_0 \rightarrow S_1$ absorption. The same conclusion is obtained in HOMO \rightarrow LUMO+1. Therefore the $S_0 \rightarrow S_1$ absorption at 406.0 nm (3.05 eV, $f = 0.0031$) is formed by the HOMO \rightarrow LUMO transition (67%), mixed with HOMO-1 \rightarrow LUMO (17%) and HOMO \rightarrow LUMO+1 (11%).

Table S1: Molecular orbital energies and diagrams of mCzmOXD.

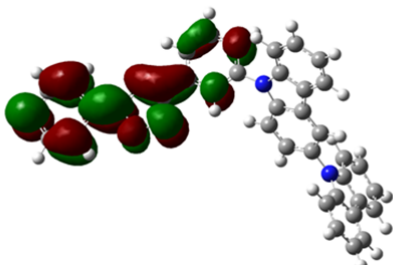
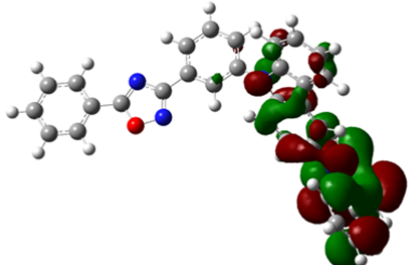
mCzmOXD	Orbital Energy	Orbital Diagram
LUMO+1	-1.27 eV	
LUMO	-1.94 eV	
HOMO	-5.38 eV	
HOMO-1	-5.54 eV	

DCzmOXD-1

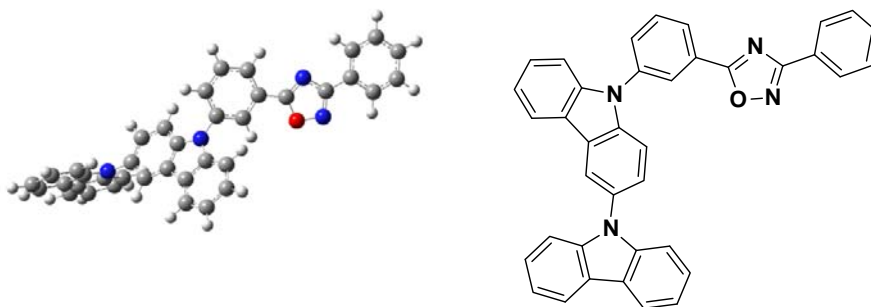


In DCzmOXD-1 the 3,9'-bicarbazole moiety possess non-coplanar alignment to the diphenyl-1,2,4 oxadiazole moiety. DCzmOXD-1 has the HOMO ($E_{\text{HOMO}} = -5.10$ eV) located on the β -3,9'-bicarbazole moiety and the LUMO ($E_{\text{LUMO}} = -1.83$ eV) located on the diphenyl-1,2,4 oxadiazole moiety. The $S_0 \rightarrow S_1$ absorption at 416.9 nm (2.97 eV, $f = 0.008$) mainly raised from the HOMO \rightarrow LUMO transition (69.8%).

Table S2: Molecular orbital energies and diagrams of DCzmOXD-1.

DCzmOXD-1	Orbital Energy	Orbital Diagram
LUMO	-1.83 eV	
HOMO	-5.10 eV	

DCzmOXD-2



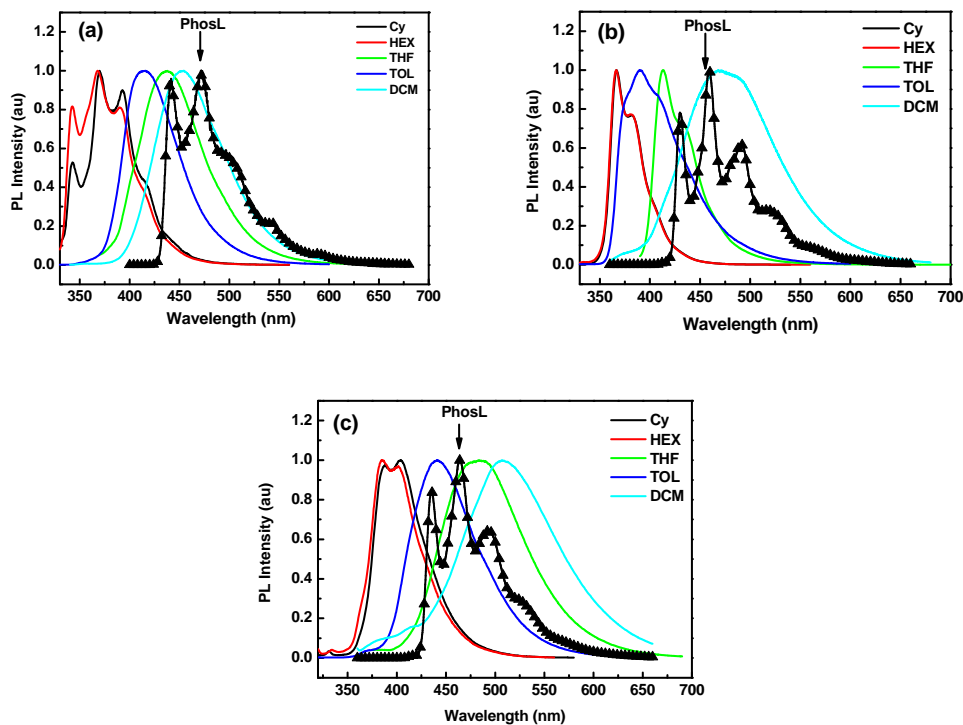
The 3,9'-bicarbazole moiety in molecule DCzmOXD-2 are also not in the same plane with the diphenyl-1,2,4 oxadiazole. DCzmOXD-2 has the HOMO ($E_{\text{HOMO}} = -5.20$ eV) located on the α -3,9'-bicarbazole moiety and the LUMO ($E_{\text{LUMO}} = -1.94$ eV) located on the diphenyl-1,2,4 oxadiazole moiety. However, the HOMO-2 ($E = -5.82$ eV) locating on the α -phenyl-3,9'-bicarbazole moiety has some overlaps with the distribution of LUMO, so HOMO-2 \rightarrow LUMO could be found in the $S_0 \rightarrow S_1$ absorption. Therefore the $S_0 \rightarrow S_1$ absorption at 425.0 nm (2.92 eV, $f = 0.0041$) is formed by the HOMO \rightarrow LUMO transition (69%), mixed with HOMO-2 \rightarrow LUMO (13%).

Table S3: Molecular orbital energies and diagrams of DCzmOXD-2.

DCzmOXD-2	Orbital Energy	Orbital Diagram
LUMO	-1.94 eV	
HOMO	-5.20 eV	
HOMO-2	-5.82 eV	

The strong charge transport property of these three molecules can also be certified by the solvation effect of these molecules.

Figure S11. Fluorescence spectra in different solvents: cyclohexane, hexane, THF, toluene and dichloromethane.



The fluorescence spectra in different solvents for (a) mCzmOXD (b) DCzmOXD-1 and (c) DCzmOXD-2 are shown above. Solvent chromic effect can be found in all the three materials, and the fluctuation range of DCzmOXD-2 (386 nm-510 nm) is bigger than mCzmOXD (369 nm-453 nm) and DCzmOXD-1 (366 nm-472 nm).

Besides what we found interesting in the calculation results is that the differences between singlet energy and triplet energy (ΔE_{ST}) for mCzmOXD DCzmOXD-1 and DCzmOXD-2 are 0.225 eV 0.032 eV and 0.091 eV. The pretty low ΔE_{ST} in DCzmOXD-1 and DCzmOXD-2 indicate that they may have a potential application in thermally-activated delay fluorescence (TADF) based OLED.