Supporting Information

Substituent Position Engineering of Diphenylquinoline-based Ir(III) Complexes for Efficient Orange and White PhOLEDs with High Color Stability/Low Efficiency Roll-Off Using Solution-Processed Emission Layer

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Experimental Section

General Information

All reagents and solvents were purchased from Aldrich Chemical Co. and Alfa Aesar and used without further purification. All reactions were carried out in an inert and dry environment under anhydrous N₂ atomosphere, which was dried by passing through a column of calcium sulfate. ¹H, ¹³C NMR spectra were recorded on a Varian Mercury plus 300 MHz spectrometer and the chemical shifts (δ) were recorded as ppm units in CDCl₃ using tetramethylsilane (TMS) as an internal standard. The UV-visible and PL spectra were recorded with JASCO V-570 and Hitachi F-4500 spectrophotometers at room temperature. The Cyclic voltammetry (CV) studies were carried out with CHI 600C potentiostat (CH Instruments) at a scan rate of 100 mVs⁻¹ in 0.1 M solution of tetra-n-butylammonium tetrafluoroborate as a supporting electrolyte in anhydrous methylene dichloride (CH₂Cl₂). A three-electrode cell with platinum electrode as the working electrode, Ag/AgCl as the reference electrode, and a platinum wire as the counter electrode was used. Thermal analyses were carried out on Mettler Toledo TGA/SDTA 851e under N₂ atmosphere at a heating rate of 10°C min⁻¹. The density functional theory (DFT) calculations were conducted by employing the Becke's three parameterized Lee-Yang-Parr exchange functional (B3LYP) using a suite of Gaussian 09 programs. High resolution mass (HR-ESI Mass) spectra data were obtained from the Korea Basic Science Institute (Daejeon Center, Korea).





Scheme S1. Synthetic route of Ir(III) complexes

Synthesis of 4-phenyl-2-(2-(trifluoromethyl)phenyl)quinoline [*o*-L]. A mixture of 2'-(trifluoromethyl)acetophenone (4.50 g, 23.92 mmol), 2-aminobenzophenone (4.72 g, 15.86 mmol), diphenylphosphate (DPP) (7.18 g, 28.70 mmol), and *m*-cresol (25 mL) was flushed with N₂ while stirring at room temperature for 30 min and then refluxed for 12 h at 140°C. The reaction mixture was distilled to remove *m*-cresol, residue was diluted with CH₂Cl₂ and washed with 10% sodium hydroxide solution followed by sodium chloride solution and the resultant organic layer was dried over anhydrous MgSO₄ and evaporated the solvent. The residue was then purified by column chromatography on silica gel [hexane:ethyl acetate (EtOAc), 9:1 v/v] to furnish *o*-L as a white powder (5.25 g, 62.83%).

The 4-phenyl-2-(3-(trifluoromethyl)phenyl)quinoline [m-L] and 4-phenyl-2-(4-(trifluoromethyl)phenyl)quinoline [p-L] were synthesized with their corresponding starting materials by the similar procedure.

o-L. ¹H NMR (300 MHz, CDCl₃, 25°C, TMS): δ= 8.26-8.23 (d, 1H), 8.00 (d, 1H), 7.83-7.75 (m, 2H), 7.67-7.65 (m, 2H), 7.56-7.55 (m, 6H), 7.53-7.52 (m, 2H); ¹³C NMR (75 MHz, CDCl₃, 25°C, TMS): δ= 157.6, 148.3, 148.1, 140.2, 137.8, 131.7, 131.5, 130.0, 129.7, 129.6, 128.6, 128.5, 128.4, 128.3, 126.8, 126.4, 125.6, 122.8, 122.1.

m-L. A white powder (5.00 g, 59.83 %). ¹H NMR (300 MHz, CDCl₃, 25°C, TMS): δ= 8.53 (s, 1H), 8.42-8.40 (d, 1H), 8.23-8.26 (d, 1H), 7.95-7.92 (d, 1H), 7.84 (s, 1H), 7.80-7.72 (m, 2H), 7.67-7.48 (m, 7H); ¹³C NMR (75 MHz, CDCl₃, 25°C, TMS): δ= 159, 148.7, 138.7, 138.1, 134, 131.3, 130.1, 125.7, 125.5, 125.4, 123.4.

p-L. A white powder (4.86 g, 58.16 %). ¹H NMR (300 MHz, CDCl₃, 25°C, TMS): δ= 8.34-8.29 (d, 2H), 8.28-8.22 (dd, 1H), 7.96-7.90 (m, 1H), 7.84-7.82 (m, 1H), 7.80-7.74 (m, 3H), 7.59-7.50 (m, 6H); ¹³C NMR (75 MHz, CDCl₃, 25°C, TMS): δ= 154.95, 149.45, 148.70, 138.05, 130.95, 130.20, 129.45, 128.55, 127.70, 126.75, 15.90, 125.65, 124.20, 130.95, 130.20, 129.60, 128.50, 127.70, 126.75, 125.50.

Synthesis of *o*-LIrpic. The ligand *o*-L (4.00 g, 11.45 mmol) and IrCl_{3.3}H₂O (1.84 g, 5.73 mmol) were added to a mixture of 2-ethoxyethanol and water (120 mL, 3:1 v/v). The reaction mixture was stirred at 140°C for 20 h under N₂ atmosphere and a red precipitate was obtained after cooling to room temperature. The precipitate was collected and washed with water (150 mL) and methanol (70 mL), subsequently dried under vacuum to afford the desired cyclometalated Ir(III) μ -chloride bridged dimer as a brown solid. The intermediate dimer was used for the following reaction without further purification. The dimer (0.50 g, 0.27 mmol) and picolinic acid (0.17 g, 1.35 mmol) were mixed with Na₂CO₃ (0.28 g, 2.70 mmol) in 2-ethoxyethanol (40 mL). The mixture was refluxed for 12 h under N₂ atmosphere. After cooling to room temperature, the crude solution was poured into water and extracted with EtOAc, dried with anhydrous MgSO₄ and evaporated the solvent under vacuum. The residue was then purified by column chromatography on silica gel (hexane:EtOAc, 6:4 v/v) to furnish *o*-LIrpic as a red solid (0.15 g, 24.48%).

The above methodology was used for synthesis of *m*-LIrpic and *p*-LIrpic with their corresponding starting materials.

o-LIrpic. ¹H NMR (300 MHz, CDCl₃, 25°C, TMS): δ= 8.85 (d, 1H), 8.19 (s, 1H), 8.09-7.99

(m, 3H), 7.90-7.81 (m, 3H), 7.75-7.70 (m, 1H), 7.62 (m, 11H), 7.47-7.36 (m, 3H), 7.30-7.26 (m, 2H), 7.14 (d, 1H), 7.03 (d, 1H), 6.65-6.90 (t, 2H), 6.48 (d, 1H); ¹³C NMR (75 MHz, CDCl₃, 25°C, TMS): δ = 171.64, 168.41, 166.52, 154.50, 151.91, 150.24, 148.69, 148.16, 145.45, 144.10, 142.86, 141.11, 139.27, 137.30 138.12, 137.00, 131.60, 130.94, 129.22, 129.07, 128.92, 128.46, 128.37, 128.18, 128.08, 127.68, 127.36, 127.26, 126.99, 126.41, 126.31, 126.20, 125.92, 125.64, 125.47, 122.20, 121.88, 121.79, 121.24, 121.24, 120.95, 120.85. HRESI-MS: *m/z* (%): 1011.19 (100) [M⁺], 1012.19 (51) [M⁺+H], 1010.19 (30) [M⁺-H].

m-LIrpic. An orange solid (0.10 g, 18.32%). ¹H NMR (300 MHz, CDCl₃, 25°C, TMS): *δ*= 8.72 (d, 1H), 8.49 (d, 1H), 8.42 (d, 1H), 7.88-7.79 (m, 2H), 7.74-7.66 (m, 4H), 7.64-7.50 (m, 11H) 7.46-7.37 (m, 4H), 7.34-7.27 (m,1H)), 7.24-7.17 (m, 1H), 6.93-6.82 (m, 2H), 6.81-6.66 (m, 2H); ¹³C NMR (75 MHz, CDCl₃, 25°C, TMS): *δ*= 171.81, 168.85, 167.23, 155.97, 154.58, 152.36, 151.85, 151.74, 148.71, 147.43, 146.63, 145.91 136.91, 136.73, 135.05, 132.21, 130.34, 129.65, 129.35, 129.22, 128.92, 127.66, 127.54, 127.39, 127.06, 126.87, 126.74, 126.39, 126.19, 126.08, 125.61, 125.40, 124.9, 124.51, 124.03, 123.60, 122.60, 122.64, 117.75, 116.88; HRESI-MS: *m/z* (%): 1011.19 (100) [M⁺], 1012.19 (51) [M⁺+H], 1010.19 (30) [M⁺-H].

p-LIrpic. An orange solid (0.12 g, 21.98%). ¹H NMR (300 MHz, CDCl₃, 25°C, TMS): *δ*= 8.76 (d, 1H), 8.10 (m, 3H), 7.95-7.84 (m, 2H), 7.88-7.80 (m, 3H), 7.72-7.55 (m, 13H), 7.46-7.39 (m, 1H), 7.38-7.35(m, 3H), 7.23 (m, 2H), 6.93-6.86 (m, 1H), 6.56 (m, 1H); ¹³C NMR (75 MHz, CDCl₃, 25°C, TMS): *δ*= 171.82, 168.75, 167.01, 152.43, 151.68, 151.57, 150.53, 149.84, 148.68, 147.79, 145.78, 137.99, 137.08, 137.00, 132.67, 132.63, 132.06, 131.03, 130.49, 130.34, 129.93, 129.71, 129.30, 129.13, 128.86, 128.83, 127.62, 127.57, 127.51, 127.09, 126.36, 126.25, 126.00, 125.79, 125.30, 121.90, 119.21, 119.27, 118.44, 118.15, 117.18; HRESI-MS: *m/z* (%): 1011.19 (100) [M⁺], 1012.19 (51) [M⁺+H], 1010.19 (30) [M⁺-H]. **Synthesis of** *o***-LIrtmd.** Ancillary ligand 2,2,6,6-tetramethylheptane-3,5-diketonate (tmd) was

reacted with *o*-L based dimer as per the procedure mentioned above to obtain *o*-LIrtmd as red solid (0.10 g, 17.27%). Similar methodology was used for the synthesis of other Ir(III) complexes *m*-LIrtmd and *p*-LIrtmd.

o-LIrtmd. ¹H NMR (300 MHz, CDCl₃, 25°C, TMS): δ= 8.45(s, 2H), 8.22-8.19 (d, 2H), 7.86-7.83 (d, 2H), 7.62-7.57 (m, 10H), 7.44-7.40 (m, 4H), 7.35-7.30 (m, 2H), 7.04-7.01 (d, 2H), 6.76-6.71 (m, 2H), 4.77(s, 1H), 0.61 (s, 18H); ¹³C NMR (75 MHz, CDCl₃, 25°C, TMS): δ= 193.99, 167.70, 155.17, 149.12, 141.26, 138.03, 130.23, 129.75, 128.84, 127.65, 127.02, 126.56, 125.48, 124.93, 121.09, 120.98, 120.58, 120.49, 88.54, 27.86; HRESI-MS: *m/z* (%): 1072.30 (100) [M⁺], 1073.30 (60) [M⁺+H], 1071.30 (36) [M⁺-H].

m-LIrtmd. A red solid (0.12 g, 20.73%). ¹H NMR (300 MHz, CDCl₃, 25°C, TMS): δ= 8.37-8.45 (d, 1H), 8.06 (s, 3H), 7.86-7.83 (d, 2H), 7.70-7.57 (m, 12H), 7.48-7.28 (m, 4H), 6.92-6.88 (m, 4H) 4.95 (s, 1H), 0.67 (s, 18H); ¹³C NMR (75 MHz, CDCl₃, 25°C, TMS): δ= 194.47, 168.39, 157.43, 150.88, 149.13, 147.71, 137.40, 136.54, 131.09, 29.56, 128.84, 127.18, 126.43, 125.78, 124.52, 123.65, 122.70, 121.61, 116.99, 89.02, 40.70, 27.71; HRESI-MS: *m/z* (%): 1072.30 (100) [M⁺], 1073.30 (60) [M⁺+H], 1071.30 (36) [M⁺-H].

p-LIrtmd. A red solid (0.14 g, 24.18%). ¹H NMR (300 MHz, CDCl₃, 25°C, TMS): δ= 8.26-8.21 (d, 2H), 8.04 (d, 2H), 7.96-7.91 (m, 3H), 7.83-7.78 (m, 3H), 7.63-7.58 (m, 9H), 7.44-7.29 (m, 5H), 7.25-7.20 (m, 1H), 6.97-6.94 (d, 1H), 4.91-4.86 (d, 1H), 0.67 (s, 18H); ¹³C NMR (75 MHz, CDCl₃, 25°C, TMS): δ= 194.25, 168.19, 151.23, 151.13, 150.68, 149.09, 137.77, 132.96, 130.68, 129.59, 129.31, 128.89, 128.79, 126.96, 126.51, 125.92, 125.78, 125.10, 117.87, 117.18, 88.93, 27.72; HRESI-MS: *m/z* (%): 1072.30 (100) [M⁺], 1073.30 (60) [M⁺+H], 1071.30 (36) [M⁺-H].

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Fig. S1 The ¹H NMR spectra of *o-/m-/p-*LIrpic





Fig. S2 The ¹H NMR spectra of *o-/m-/p*-LIrtmd.



Fig. S3 (a) TGA thermograms of Ir(III) complexes at a heating rate of 10 °C min⁻¹ under N_2 atmosphere and (b) PL spectra of Ir(III) complexes in film state spin casted using CHCl₃.

Steady-State Absorption and Emission Measurements at Room Temperature.

An UV-Vis-NIR spectrophotometer (Agilent Technologies, Cary 5000) and a fluorescence spectrophotometer (Varian, Cary Eclipse) were used to measure the absorption and emission spectra, respectively.

Phosphorescence Measurements.

In order to excite the Ir(III) complexes, a 416 nm pulse was generated by using a H_2 -Raman shifter using the third harmonic (355 nm) of a Q-switched Nd:YAG laser (Continuum, Surelite II; pulse width of 4.5 ns). The phosphorescence spectra were recorded by an ICCD detector (Andor, iStar) equipped to a monochromator (DongWoo Optron, Monora 500i). The temporal profiles were measured using a monochromator equipped with a photomultiplier (Zolix Instruments Co., CR 131) and a digital oscilloscope (Tektronix, TDS-784D). All sample solutions were argon saturated to remove oxygen.



Fig. S4 Decay profiles of Ir(III) complexes (a) in CH₂Cl₂ at room temperature (b) in 2-MeTHF at 77 K



Fig. S5 Cyclic voltammograms of Ir(III) complexes in anhydrous CH_2Cl_2 solvent with 0.1 M TBAClO₄ as supporting electrolyte at a scan rate of 100 mVs⁻¹.

Ir(III) Complex	НОМО	LUMO
<i>o</i> -LIrpic		
<i>m</i> -LIrpic		
<i>p</i> -LIrpic		
<i>o-</i> LIrtmd		



Fig. S6 Optimized geometries of Ir(III) complexes from DFT calculation.

PhOLEDs fabrication and measurements

General procedure

An indium tin oxide (ITO) glass substrate with a sheet resistance of 20 Ω per square was washed sequentially with a substrate-cleaning detergent, deionized water, acetone, and isopropyl alcohol. Finally the ITO glass substrate was treated in a UV-ozone chamber for 15 min. A layer of PEDOT:PSS (4083, 40 nm) was spin coated onto the ITO glass substrate, which was then baked in air at 150°C for 20 min. Emitting layer (EML) was processed with chlorobenzene solvent and all solutions used for the PhOLEDs fabrication were filtered with 0.20 lm PTFE (hydrophobic) syringe filter. Thickness of the films were measured using the α -Step IQ surface profiler (KLA Tencor, San Jose, CA). All the electroluminescent characteristics of the PhOLEDs were measured with a programmable Keithley model 236 power sources and spectra scan CS-1000 photometer.

Monochromatic PhOLEDs

The EML consists of 1,1-bis(4-methylphenyl)-aminophenyl-cyclohexane (TAPC) and 2,6bis(3-(carbazol-9-yl)phenyl)pyridine (DCzPPy) (4:6 w/w) doped with 10 wt% of the Ir(III) complex was then spin-coated onto the PEDOT:PSS coated substrate and then annealed at 80°C for 30 min in glove box. Finally, 1,3,5-tri(m-pyrid-3-yl-phenyl)benzene (TmPyPB), LiF, and the cathode (Al) were subsequently vacuum deposited on top of the EML with an effective area of 4 mm² at a pressure 5×10^{-6} Torr. The configuration of monochromatic PhOLEDs are ITO/PEDOT:PSS (40 nm)/TAPC:DCzPPy:emitter (10 wt%) (40 nm)/TmPyPB (50 nm)/LiF (1 nm)/Al (100 nm).

White PhOLEDs

The EML using ternary host system consists of poly(vinylcarbazole) (PVK), N,N-dicarbazolyl-3,5-benzene (mCP), and 2,2'-(1,3-phenylene)*bis*[5-(4-tert-butylphenyl)-1,3,4-oxadiazole (OXD-7), where the doping ratios of blue:orange were 17:0.01 (device **W1**)/17:0.015 (device **W2**) was then spin-coated onto the PEDOT:PSS coated substrate and then annealed at 80°C for 30 min in glove box. Finally, 1,3,5-tri(1-phenyl-1H-benzo[d]imidazol-2-yl)phenyl (TPBi), LiF, and the cathode (Al) were subsequently vacuum deposited on top of the EML with an effective area of 4 mm² at a pressure 5×10^{-6} Torr. The configuration of white PhOLEDs are ITO/PEDOT:PSS (40 nm)/PVK:mCP:OXD-7 (37.5:37.5:25) (85 wt%): blue:orange (x:y, 15 wt%) (50 nm)/ (TPBi) (30 nm)/LiF (1 nm)/Al (100 nm).



Fig. S7 (a) Phosphorescence spectra of Ir(III) complexes in 2-MeTHF matrix at 77 K (λ_{ex} : 416 nm) and (b) UV-visible absorption and PL spectra of TAPC, DCzPPy, and TAPC:DCzPPy spin casted films in CHCl₃.



Fig. S8 AFM topographic images of (a) TAPC:DCzPPy mixed host, (b-d) TAPC:DCzPPy:*o*-/*m*-/*p*-LIrpic and (e-g) TAPC:DCzPPy:*o*-/*m*-/*p*-LIrtmd films formed by the spin coating process.



Fig. S9 Comparison of EL spectra at 30 mAcm⁻² with PL of (a) *o-/m-/p*-LIrpic and (b) PL of *o-/m-/p*-LIrtmd.



Fig. S10. CIE coordinates versus Luminance of the PhOLEDs with (a) *o-/m-/p*-LIrpic and (b) *o-/m-/p*-LIrtmd.

Table S1 Summary of the state-of-the-art de	vice performances	of solution-processed	orange/orange-
red PhOLEDs using small molecule host ma	iterials.		

Year	Previous	EML	CIE	LE, PE	EQE
	Literature	Configuration	(x, y)		
2007	Ref. [2]	CBP	(0.52, 0.47)	11.19 cdA ⁻¹ , 2.69 lmW ⁻¹	3.94%
2008	Ref. [3]	CzOXD	(0.50, 0.36)	3.8 cdA ⁻¹ , 0.44 lmW ⁻¹	-
2009	Ref. [4]	m-MTDATA:	(0.60, 0.38)	7.70 cdA ⁻¹ , 3.26 lmW ⁻¹	4.45%
		TPBI	(0.60, 0.38)	6.51 cdA ⁻¹ , 2.37 lmW ⁻¹	3.80%
2010	Ref. [5]	m-MTDATA:	(0.58–0.59, 0.41)	20.0 cdA ⁻¹ , 16.8 lmW ⁻¹	10.8%
		TPBI			
2012	Ref. [6]	CBP	(0.60, 0.40)	14.49 cdA ⁻¹ , 7.38 lmW ⁻¹	8.73%
2012	Ref. [7]	dendritic host (H2)	(0.531,0.466)	49.7 cdA ⁻¹ , 43.9 lmW ⁻¹	17.6%
2013	Ref. [8]	CBP	(0.53, 0.46)	20.18 cdA ⁻¹	7.81%
2013	Ref.[9]	CBP:TPD:PBD	(0.526, 0.469)	18.5 cdA ⁻¹ , 6.9 lmW ⁻¹	7.0%
			(0.600, 0.397)	26.9 cdA ⁻¹ , 12.1 lmW ⁻¹	14.2%
2014	Ref. [10]	Non-doped	(0.57, 0.42)	12.4 cdA ⁻¹ , 6.6 lmW ⁻¹	8.8%
2015	This work	TAPC:DCzPPy	(0.528, 0.469)	43.90 cdA ⁻¹ , 22.98 lmW ⁻¹	17.14%



Fig. S11 Device structure and energy levels of the white PhOLEDs.



Fig. S12 (a) Current density-voltage-luminance (J-V-L) and (b) LE-J-PE characteristics.

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