Electronic supporting information

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Manipulating MLCT transition character with ppy-type fourcoordinate organoboron skeleton for highly efficient long-wavelength Ir-based phosphors in organic light-emitting diodes

Zhao Feng,^{*a*} Yue Yu, ^{*a*, *c*} Xiaolong Yang,^{*a*} Yuanhui Sun,^{*a*} Daokun Zhong,^{*a*} Xuming Deng,^{*a*} Guijiang Zhou, *, ^{*a*} and Zhaoxin Wu*, ^{*b*, *d*}

^aMOE Key Laboratory for Nonequilibrium Synthesis and Modulation of Condensed Matter, Department of Chemistry, School of Chemistry, State Key Laboratory for Mechanical Behavior of Materials, Xi'an Jiaotong University, Xi'an 710049, P. R. China. E-mail: zhougj@mail.xjtu.edu.cn. ^bKey Laboratory of Photonics Technology for Information, School of Electronic and Information Engineering, Xi'an Jiaotong University, Xi'an 710049, P. R. China. E-mail: zhaoxinwu@mail.xjtu.edu.cn

^cSchool of Physics and Optoelectronic Engineering, Xidian University, Xi'an 710071, P. R. China. ^dCollaborative Innovation Center of Extreme Optics, Shanxi University, Taiyuan 030006, P. R. China.

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General experimental information

All commercially available chemicals and reagents was used with no further purification. All solvents for reactions were distilled and dried via standard methods prior to use. All reactions were monitored by analytical thin layer chromatography (TLC) purchased from Merck & Co., Inc., Purification was performed with flash column chromatography and preparative TLC plates made of silica gel (300-400 mesh). ¹H and ¹³C NMR spectra were measured with a Bruker Avance 400 MHz spectrometer in CDCl₃ solution. Chemical shifts were reported in δ ppm and referenced to the solvent residual peak at δ 7.26 ppm for ¹H and 77.0 ppm for ¹³C NMR spectra, respectively. UV-vis absorption spectra were recorded on a Perkin Elmer Lambda 950 spectrophotometer. Emission spectra and lifetimes for the final asymmetric heteroleptic cyclometalated Ir(III) complexes were performed on an Edinburgh Instruments, Ltd., (FLSP 920) fluorescence spectrophotometer. Phosphorescent quantum yields (Φ_n) were measured in CH₂Cl₂ solution and referenced to *fac*-[Ir(ppy)₃] ($\Phi_p = 0.97$) at 293 K.¹ The thermal gravimetric analysis data were collected on a NETZSCH STA 409C instrument. Cyclic voltammetry (CV) was performed with a Princeton Applied Research model 273A potentiostat at a scan rate of 100 mV s⁻¹. All the CV measurements were carried out in a three-electrode compartment cell with a Ptsheet counter electrode, a glassy-carbon working electrode, and an Ag/AgCl reference electrode. The supporting electrolyte was a 0.1 M acetonitrile solution of [nBu₄N]BF₄, using ferrocene as internal standard. The data of elemental analyses were acquired on a Flash EA 1112 elemental analyzer. Fast atom bombardment (FAB) mass spectra were recorded on a Finnigan MAT SSQ710 system.

General procedure for the synthesis of OP/MP/PP

Under a nitrogen atmosphere, to a solution of 1-bromo-2-iodobenzene/1-bromo-3-iodobenzene/1bromo-4-iodobenzene (1.0 equiv) and catalyst Pd(PPh₃)₄ (0.03 equiv) in toluene was dropwise added 2-(tributylstannyl)pyridine (1.1 equiv). The reaction mixture was magnetically stirred at 110 °C for 16 h. After the reaction mixture was cooled to room temperature, the solvent was evaporated to dryness under vacuum. The residue was chromatographed by a silica gel column a proper petroleum ether/ ethyl acetate eluent system to give the target product **OBr/MBr/PBr**.

OBr. Yield: 83%. ¹H NMR (400 MHz, CDCl₃, δ): 8.63 (d, *J* = 4.8 Hz, 1H), 7.67 (td, *J* = 7.6, 1.6 Hz, 1H), 7.58 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.51 (d, *J* = 7.6 Hz, 1H), 7.45 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.31 (td, *J* = 7.6, 1.2 Hz, 1H), 7.20 (ddd, *J* = 7.6, 4.8, 1.2 Hz, 1H), 7.16 (td, *J* = 8.0, 2.0 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃, δ): 158.23, 149.31, 141.13, 135.75, 133.19, 131.33, 129.64, 127.45, 124.66, 122.34, 121.67.

MBr. Yield: 81%. ¹H NMR (400 MHz, CDCl₃, δ): 8.68 (d, *J* = 4.8 Hz, 1H), 8.16 (t, *J* = 1.6 Hz, 1H), 7.89 (dt, *J* = 8.0, 1.2 Hz, 1H), 7.74 (td, *J* = 7.6, 2.0 Hz, 1H), 7.67 (d, *J* = 7.6 Hz, 1H), 7.52 (ddd, *J* = 8.0, 2.0, 1.2 Hz, 1H), 7.32 (t, *J* = 8.0 Hz, 1H), 7.25 – 7.22 (m, 1H). ¹³C NMR (100 MHz, CDCl₃, δ): 155.72, 149.69, 141.31, 136.83, 131.77, 130.17, 129.93, 125.31, 122.97, 122.60, 120.51.

PBr. Yield: 86%. ¹H NMR (400 MHz, CDCl₃, δ): 8.68 (d, J = 4.8 Hz, 1H), 7.87 (d, J = 8.8 Hz, 2H),
7.75 (td, J = 7.6, 2.0 Hz, 1H), 7.69 (d, J = 8.0 Hz, 1H), 7.60 (d, J = 8.4 Hz, 2H), 7.25 (ddd, J = 7.2,
4.8, 1.2 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃, δ): 156.23, 149.74, 138.22, 136.86, 131.85, 128.44,
123.41, 122.40, 120.28.

General procedure for the synthesis of OBN/MBN/PBN

Under a nitrogen flow, to a stirred solution of **OBr/MBr/PBr** (1.0 equiv) and *N,N*diisopropylethylamine (1.0 equiv) in dry CH_2Cl_2 was added BBr₃ (1.0 M in hexane, 3.0 equiv). After the reaction mixture was stirred at room temperature for 24 h, saturated K₂CO₃ aqueous solution was added dropwise till the bubble vanished. Then, the mixture was poured into water and extracted with CH_2Cl_2 three times. The combined organic phase was washed with saturated salt water and dried with anhydrous Na₂SO₄. After filtration and solvent evaporation, the residue was redissolved in dry CH_2Cl_2 under a nitrogen atmosphere. Tributyl(phenyl)stannane (2.5 equiv) and AlCl₃ (0.1 equiv) was added in sequence. After it was stirred at room temperature for 16 h, the reaction mixture was passed through a short plug of silica gel. The resulting solution was evaporated to dryness under reduced pressure. The target product was obtained through silica gel column chromatography using a proper petroleum ether/ CH_2Cl_2 eluent system.

OBN. Yield: 41%. ¹H NMR (400 MHz, CDCl₃, δ): 9.21 (d, J = 8.4 Hz, 1H), 8.54 (d, J = 5.6 Hz, 1H), 8.12 (td, J = 8.0, 1.6 Hz, 1H), 7.65 (d, J = 7.2 Hz, 1H), 7.50 (d, J = 7.2 Hz, 1H), 7.45 (td, J = 6.4, 1.2 Hz, 1H), 7.23 (d, J = 7.6 Hz, 1H), 7.20 – 7.15 (m, 10H). ¹³C NMR (100 MHz, CDCl₃, δ): 156.92, 144.45, 140.49, 133.63, 133.08, 131.96, 131.67, 129.40, 127.49, 125.89, 122.50, 122.05, 118.82. MBN. Yield: 38%. ¹H NMR (400 MHz, CDCl₃, δ): 8.47 (d, J = 5.6 Hz, 1H), 8.50 (td, J = 8.0, 1.6 Hz, 1H), 8.01 (d, J = 7.6 Hz, 1H), 7.87 (d, J = 7.6 Hz, 1H), 7.58 (d, J = 8.0 Hz, 1H), 7.35 (td, J = 6.4, 1.6 Hz, 1H), 7.30 – 7.28 (m, 4H), 7.24 – 7.19 (m, 7H). ¹³C NMR (100 MHz, CDCl₃, δ): 156.97, 143.88, 140.73, 138.04, 135.23, 134.28, 127.99, 127.68, 127.21, 126.03, 122.90, 120.72, 118.19. PBN. Yield: 53%. ¹H NMR (400 MHz, CDCl₃, δ): 8.49 (d, J = 5.6 Hz, 1H), 8.03 (td, J = 7.6, 1.2 Hz, 1H), 7.98 (d, J = 8.0 Hz, 1H), 7.86 (d, J = 2.0 Hz, 1H), 7.71 (d, J = 8.4 Hz, 1H), 7.46 (dd, J = 8.4, 2.0 Hz, 1H), 7.38 (td, J = 6.4, 1.6 Hz, 1H), 7.25 – 7.16 (m, 10H). ¹³C NMR (100 MHz, CDCl₃, δ): 157.38, 144.13, 140.75, 134.54, 133.72, 132.99, 129.25, 127.51, 127.02, 125.93, 123.09, 122.26, 118.18.

General procedure for the synthesis of L-OBN/L-MBN/L-PBN

Under a nitrogen atmosphere, to a solution of OBN/MBN/PBN (1.0 equiv) and catalyst Pd(PPh₃)₄

(0.03 equiv) in toluene was dropwise added 2-(tributylstannyl)pyridine (1.1 equiv). The reaction mixture was magnetically stirred at 110 °C for 16 h. After the reaction mixture was cooled to room temperature, the solvent was evaporated to dryness under vacuum. The residue was chromatographed by a silica gel column a proper petroleum ether/ CH_2Cl_2 eluent system to give the target product L-

OBN/L-MBN/L-PBN.

L-OBN. Yield: 84%. ¹H NMR (400 MHz, CDCl₃, δ): 8.79 (d, *J* = 4.8 Hz, 1H), 8.48 (d, *J* = 5.6 Hz, 1H), 7.88 (td, *J* = 7.6, 2.0 Hz, 1H), 7.78 (dd, *J* = 7.2, 0.8 Hz, 1H), 7.69 (td, *J* = 8.0, 1.6 Hz, 1H), 7.54 (d, *J* = 7.6 Hz, 1H), 7.46 (t, *J* = 7.6, 1H), 7.43 (ddd, *J* = 7.6, 4.8, 0.8 Hz, 1H), 7.28 – 7.13 (m, 12H), 6.97 (d, *J* = 8.0 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃, δ): 159.97, 157.91, 149.58, 144.20, 139.80, 138.16, 137.07, 133.22, 133.04, 130.63, 130.34, 128.26, 127.37, 125.67, 124.39, 122.80, 121.61, 121.58.

L-MBN. Yield: 82%. ¹H NMR (400 MHz, CDCl₃, δ): 8.72 (dt, J = 4.8, 1.2 Hz, 1H), 8.62 (d, J = 0.8 Hz, 1H), 8.53 (d, J = 5.6 Hz, 1H), 8.20 (d, J = 8.0 Hz, 1H), 8.08 (td, J = 7.6, 1.2 Hz, 1H), 7.97 (dd, J = 7.6, 1.6 Hz, 1H), 7.82 (d, J = 7.6 Hz, 1H), 7.77 (dd, J = 4.4, 1.2 Hz, 2H), 7.40 (td, J = 6.4, 1.2 Hz, 1H), 7.27 – 7.13 (m, 11H). ¹³C NMR (100 MHz, CDCl₃, δ): 158.30, 157.52, 149.64, 144.14, 140.59, 137.57, 136.84, 133.10, 131.05, 129.73, 127.45, 125.76, 122.17, 122.03, 120.43, 120.34, 118.52. L-PBN. Yield: 85%. ¹H NMR (400 MHz, CDCl₃, δ): 9.10 (d, J = 1.2 Hz, 1H), 8.74 (dd, J = 8.4, 2.0 Hz, 1H), 8.70 (d, J = 4.8 Hz, 1H), 8.12 (d, J = 8.8 Hz, 1H), 7.92 (d, J = 7.6 Hz, 1H), 7.78 (td, J = 7.6, 1.6 Hz, 1H), 7.74 (d, J = 7.2 Hz, 1H), 7.67 (d, J = 8.0 Hz, 1H), 7.45 (td, J = 7.2, 1.2 Hz, 1H), 7.35 (td, J = 7.6, 1.2 Hz, 1H), 7.31 (ddd, J = 7.6, 4.8, 0.8 Hz, 1H), 7.29 (dd, J = 8.0, 1.6 Hz, 4H), 7.23 – 7.13 (m, 6H). ¹³C NMR (100 MHz, CDCl₃, δ): 158.21, 152.30, 150.25, 142.44, 138.72, 137.18, 135.62, 133.94, 133.15, 131.35, 130.83, 127.46, 126.06, 125.71, 123.55, 121.89, 120.26, 118.00.

General Procedure for the Synthesis of IrOBN/IrMBN/IrPBN

Under a nitrogen atmosphere, to a mixture of 2-ethoxyethanol and H₂O (3/1, v/v) were added L-OBN/L-MBN/L-PBN (2.1 equiv) and IrCl₃·nH₂O (1.0 equiv, 60 wt% Ir content), respectively. The reaction mixture was stirred at 110 °C for 16 h. After cooled to room temperature, the resultant mixture was poured into a saturated solution of NaCl. The precipitated colored Ir(III) μ -chloro-bridged dimer was obtained through filtration and dried under vacuum. Subsequently, thallium(I) acetylacetonate [Tl(acac)] (1.02 equiv) was correspondingly added to an dry CH₂Cl₂ solution of the colored Ir(III) μ chloro-bridged dimer. The reaction mixture was stirred at room temperature overnight. Centrifugation was conducted to remove the inorganic salt, and the solvent was removed under vacuum from the organic phase. The residue was purified with preparative thin-layer chromatography (TLC) made of silica gel using proper eluent. Caution: thallium(I) acetylacetonate (Tl(acac)) is extremely toxic and must be dealt with carefully.

IrOBN. Yield: 38%. ¹H NMR (400 MHz, CDCl₃, δ): 8.50 (d, *J* = 5.2, 2H), 8.46 (d, *J* = 5.6 Hz, 2H), 8.37 (d, *J* = 8.4 Hz, 2H), 8.10 (d, *J* = 8.0 Hz, 2H), 7.88 (td, *J* = 7.6, 1.2 Hz, 2H), 7.62 (td, *J* = 7.6, 1.2 Hz, 2H), 7.24 – 7.21 (m, 6H), 7.15 – 7.05 (m, 18H), 6.96 (d, *J* = 7.6 Hz, 2H), 6.02 (d, *J* = 7.6 Hz, 2H), 5.26 (s, 1H), 1.84 (s, 6H). ¹³C NMR (100 MHz, CDCl₃, δ): 184.91, 168.05, 158.23, 148.93, 148.34, 144.70, 142.07, 139.10, 135.77, 135.47, 133.53, 133.10, 130.06, 127.24, 127.16, 125.43, 125.33, 122.17, 121.57, 121.31, 120.61, 100.50, 28.72. ¹¹B NMR (128 MHz, CDCl₃, δ): 2.48. FAB-MS (m/z): 1080 [M]⁺; Anal. Calcd (%) for C₃₃H₂₃IrN₂O₆: C, 67.72; H, 4.38; N, 5.18; found: C, 67.68; H, 4.41; N. 5.16.

IrMBN. Yield: 33%. ¹H NMR (400 MHz, CD₂Cl₂, δ): 8.42 (d, J = 5.2, 2H), 8.29 (d, J = 6.0 Hz, 2H), 8.04 (s, 2H), 8.05 – 7.97 (m, 6H), 7.81 (td, J = 8.0, 1.6 Hz, 2H), 7.22 (td, J = 6.6, 1.2 Hz, 2H), 7.14 (td, *J* = 6.6, 1.2 Hz, 2H), 7.11 – 7.05 (m, 6H), 6.94 – 6.86 (m, 14H), 6.59 (s, 2H), 5.27 (s, 1H), 1.76 (s, 6H). ¹³C NMR (100 MHz, CD₂Cl₂, δ): 182.26, 165.39, 157.31, 148.92, 146.43, 143.99, 143.63, 140.52, 137.58, 133.73, 132.55, 129.69, 127.59, 127.35, 125.62, 125.41, 122.83, 121.84, 120.72, 118.63, 117.42, 104.69, 30.08. FAB-MS (m/z): 1080 [M]⁺; Anal. Calcd (%) for C₃₃H₂₃IrN₂O₆: C, 67.72; H, 4.38; N, 5.18; found: C, 67.74; H, 4.37; N. 5.13.

IrPBN. Yield: 42%. ¹H NMR (400 MHz, CDCl₃, δ): 8.60 (d, *J* = 4.8 Hz, 2H), 8.30 (d, *J* = 5.6 Hz, 2H), 7.97 (d, *J* = 8.0 Hz, 2H), 7.88 (s, 2H), 7.78 (qd, *J* = 8.0, 1.6 Hz, 4H), 7.50 (d, *J* = 8.4 Hz, 2H), 7.28 (dd, *J* = 8.0, 1.6 Hz, 4H), 7.20 – 7.03 (m, 20H), 6.69 (s, 2H), 5.24 (s, 1H), 1.81 (s, 6H). ¹³C NMR (100 MHz, CDCl₃, δ): 184.75, 168.55, 158.23, 148.44, 148.23, 143.70, 139.67, 137.06, 136.53, 133.50, 133.06, 127.21, 127.10, 126.36, 125.93, 125.51, 125.10, 121.72, 121.10, 119.69, 118.74, 100.52, 28.80. FAB-MS (m/z): 1080 [M]⁺; Anal. Calcd (%) for C₃₃H₂₃IrN₂O₆: C, 67.72; H, 4.38; N, 5.18; found: C, 67.65; H, 4.35; N. 5.23.

X-ray Crystallography

The single crystal of **IrOBN** suitable for X-ray diffraction studies was cultivated through slow diffusion of n-hexane into its solvent mixture of CH_2Cl_2 and chloroform. Single-crystal data were collected on a Bruker SMART CCD diffractometer (Mo K α radiation and $\lambda = 0.71073$ Å) in ϕ and ω scan modes. The molecular structures were solved using direct methods followed by difference Fourier syntheses and refinements were completed by full-matrix least-squares techniques against F^2 using SHELXL-97 program.² The positions of hydrogen atoms were calculated and refined isotropically using a riding model. All other non-hydrogen atoms were refined isotropically. Absorption corrections were applied using SADABS.³

Theoretical computation

DFT calculations were conducted with the B3LYP method for all the final cyclometalated Ir(III) complexes. The 6-31G (d, p) basis set was applied for non-metallic C, H, O, N, and B atoms, while a LanL2DZ basis set for effective core potentials were employed for Ir atoms.^{4,5} Excitation behaviors were acquired by the TD-DFT calculations on the basis of the optimized ground state (S₀) geometries. Additionally, the lowest triplet state (T₁) geometries were optimized using the UB3LYP method and analysis of the natural transition orbital (NTO) was carried out for S₀ \rightarrow T₁ excitation. All of the calculations were performed using the *Gaussian 09* program.⁶

OLED fabrication and measurements

The pre-cleaned ITO-patterned glass substrates were treated with ozone for 20 min. Afterwards, a 3 nm-thick hole injection layer of MoO₃ was deposited onto the surface of ITO glass. Then, deposition of 4,4'-bis[N-(1-naphthyl)-N-phenyl-amino]biphenyl (NPB) was performed to form *ca.* 40 nm-thick hole-transporting and electron-blocking layer. Co-evaporation of the Ir(III) complex and 4,4'-*N*,*N*-dicarbazole-biphenyl (CBP) was conducted to obtained a doped CBP region with a thickness of *ca.* 20 nm. Finally, 1,3,5-tris[N-(phenyl)-benzimidazole]-benzene (TPBi) (40 nm), LiF (1 nm) and Al cathode (100 nm) were successively evaporated at a base pressure less than 10^{-6} Torr. The EL spectra and CIE coordinates were recorded using a PR650 spectra colorimeter. The *J*–*V*–*L* curves of the devices were recorded by a Keithley 2400/2000 source meter and the luminance was measured using a PR650 SpectraScan spectrometer.

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Electronic supporting information



Fig. S1 ¹H NMR spectra of IrOBN, IrMBN, and IrPBN.





Fig. S3 ¹³C NMR spectra of IrOBN, IrMBN, and IrPBN.

compound	IrOBN				
CCDC No.	1916158				
Formula	$C_{64}H_{47}B_2Cl_8IrN_4O_6$				
Formula weight	1401.47				
Crystal system	Triclinic				
Space group	Pī				
<i>a</i> (Å)	14.570(5)				
<i>b</i> (Å)	14.688(5)				
<i>c</i> (Å)	16.570(6)				
α (deg)	86.389(4)				
β (deg)	64.107(4)				
$\gamma(\text{deg})$	74.086(4)				
$V(Å^3)$	3061.2(19)				
Ζ	2				
D_{calcd} (g cm ⁻³)	1.520				
Crystal size (mm ³)	0.420×0.132×0.085				
F (000)	1396				
μ (mm ⁻¹)	2.577				
θ range (deg)	1.597-25.009				
diffrn reflns number	29439				
reflns number total	10757				
no. of parameter	686				
<i>R</i> 1, <i>wR</i> 2 [$I > 2.0\sigma$ (I)] ^{<i>a</i>}	0.0547, 0.1447				
R1, wR2 (all data)	0.0635, 0.1535				
GOF on $F^{2 b}$	1.039				
${}^{a}R1 = \Sigma F_{0} - F_{c} / \Sigma F_{0} . \ wR2 = \{ \Sigma [w(F_{0}^{2} - F_{c}^{2})^{2}] / \Sigma [w(F_{0}^{2})^{2}] \}^{361/2}.$					
${}^{b}\operatorname{GOF} = [(\Sigma w F_{0} - F_{c})^{2} / (N_{obs} - N_{param})]^{1/2}.$					

 Table S1 Crystal and data parameters for IrOBN.

 Table S2 Selected structural parameters of IrOBN.

Bond angles (°)			Bond lengths (Å)		
C(20)-Ir(1)-C(44)	93.3(3)	C(20)-Ir(1)-N(2)	80.2(2)	C(20)-Ir(1)	1.990(6)
C(20)-Ir(1)-N(3)	94.5(2)	C(20)-Ir(1)-O(1)	89.8(2)	C(44)-Ir(1)	2.001(7)
C(20)-Ir(1)-O(2)	174.1(2)	C(44)-Ir(1)-N(2)	98.6(2)	Ir(1)-N(2)	2.037(6)
C(44)-Ir(1)-N(3)	80.3(2)	C(44)-Ir(1)-O(1)	173.4(2)	Ir(1)-N(3)	2.038(5)
C(44)-Ir(1)-O(2)	89.2(2)	N(2)-Ir(1)-N(3)	174.5(2)	Ir(1)-O(1)	2.147(5)
N(2)-Ir(1)-O(1)	87.6(2)	N(2)-Ir(1)-O(2)	94.2(2)	Ir(1)-O(2)	2.147(5)
N(3)-Ir(1)-O(1)	93.8(2)	N(3)-Ir(1)-O(2)	91.1(2)	B(1)-C(3)	1.601(13)
O(2)-Ir(1)-O(1)	88.3(2)	C(3)-B(1)-C(7)	115.1(7)	B(1)-C(7)	1.677(11)
C(3)-B(1)-C(23)	111.2(8)	C(3)-B(1)-N(1)	109.9(7)	B(1)-C(23)	1.619(11)
C(23)-B(1)-C(7)	115.6(6)	N(1)-B(1)-C(7)	107.2(7)	B(1)-N(1)	1.618(11)

N(1)-B(1)-C(23)	95.9(6)	C(41)-B(2)-C(57)	114.5(6)	B(2)-C(41)	1.623(10)
C(41)-B(2)-N(4)	95.5(5)	C(56)-B(2)-C(41)	112.5(6)	B(2)-C(56)	1.609(11)
C(56)-B(2)-C(57)	113.7(6)	C(56)-B(2)-N(4)	109.6(6)	B(2)-C(57)	1.631(12)
N(4)-B(2)-C(57)	109.5(6)			B(2)-N(4)	1.626(9)



Fig. S4 TGA traces of these ppy-type cyclometalated Ir(III) complexes.



Fig. S6 Electrostatic potential surface maps of (a) **L-OBN**, (b) **L-MBN**, and (c) **L-PBN** at the electron density of 0.001 a.u..



Fig. S5 Molecular orbital (MO) distribution patterns (isocontour value = 0.030) of the parent $Ir(ppy)_2(acac)$ (**ppy** = 2-phenylpyridine) on the basis of their optimized S₀ geometries.



Fig. S7 Photoluminescence (PL) spectra of these ppy-type cyclometalated Ir(III) complexes doped into CBP films (8 wt%) at 293 K.



Fig. S8 Photoluminescence (PL) spectra of these ppy-type cyclometalated Ir(III) complexes in CH_2Cl_2 solutions recorded at 77 K



Fig. S9 Cyclic voltammetry (CV) traces of these ppy-type cyclometalated Ir(III) complexes.



Fig. S10 Current–density–voltage–luminance (J-V-L) curves for the devices except the optimized ones.





Fig. S11 Relationship between EL efficiencies and luminance for the devices except the optimized ones.