High-Efficiency Blue Phosphorescent Organic Light-Emitting Diodes using a Carbazole and Carboline-Based Host Material

Sun Jae Kim,[a] Young Jae Kim,[b] Young Hoon Son,[b] Jung A Hur,[a] Tae Wan Lee,[a] Min Ju Cho,[a] Jung Keun Kim,[c] Sunghoon Joo,[c] Joong Hwan Yang,[c] Geesung Chae,[c] Kihang Choi,[a] Jang Hyuk Kwon, [b*] Dong Hoon Choi*

[a] Department of Chemistry, Research Institute for Natural Sciences, Korea University, 5 Anam-dong, Sungbuk-Gu, Seoul, 136-701 Republic of Korea. Fax: +82-2-925-4284; Tel: +82-2-3290-3140; E-mail: dhchoi8803@korea.ac.kr.
[b] Department of Information Display, Kyung Hee University, Dongdaemoon-gu, Seoul 130-701 Republic of Korea, Fax: +82-2-961-9154; Tel: +82-2-961-0948; E-mail: jhkwon@khu.ac.kr,
[c] LG Display, Co., LTD. 1007 Deogeon-ri, Wollong-myeon, Paju-si, Gyeonggi-do, 413-811 Republic of Korea

Experimental

1. Materials

All commercially available starting materials and solvents were purchased from Aldrich, TCI, Fluka, and Acros Organics, and used without further purification unless otherwise stated. Intermediate compound 1 and 2 were synthesized according to literature.[1]

Synthesis of 9-(4-(9H-pyrido[2,3-b]indol-9-yl)phenyl)-9H-3,9'-bicarbazole (pBCb2Cz) : Compound 9-(4-bromophenyl)-9*H*-pyrido[2,3-*b*]indole (**1**) (1.7 g, 5.26 mmol), 9*H*-3,9'-bicarbazole (**2**) (1.92 g, 5.78 mmol), and K_3PO_4 (5.58 g, 2.63 mmol) in toluene were added. The mixture was heated at 60℃ for 1 h, then CuI (0.2 g, 1.05 mmol) and trans-1,2-diaminocyclohexane (0.3 g, 2.63 mmol) were added. The reaction mixture was refluxed for 24 h. The resulting suspension was cooled to room temperature and filtered through celite. The collected organic solution was concentrated, and purified by flash chromatography on silica gel (hexane: dichloromethane = 1: 2) to give **pBCb2Cz** (1.8 g, 60%) as a white powder.

^{1}H-NMR (400 MHz, $CDCl_3$): δ(ppm) 8.97 (d, *J* = 2.36 Hz, 1H), 8.77 − 8.73 (m, 2H), 8.64 (dd, *J* = 1.56, 5.08 Hz, 1H), 8.42 (dd, *J* = 1.56, 7.84 Hz, 1H), 8.29 (d, *J* = 1.96 Hz, 1H), 8.24 (dd, *J* =

2.36, 8.04 Hz, 2H), 8.21 (d, J = 7.84 Hz, 2H), 7.78 (dd, J = 1.96, 8.64 Hz, 1H), 7.55 (d, J = 7.84 Hz, 1H), 7.50 – 7.46 (m, 3H), 7.44 (d, J = 3.92 Hz, 3H), 7.40 – 7.30 (m, 6H).

^{13}C NMR (75 MHz, CDCl$_3$) : δ(ppm) 151.52, 149.50, 146.88, 146.74, 141.56, 140.73, 137.74, 136.68, 131.98, 131.85, 128.88, 127.04, 126.33, 125.95, 123.70, 123.21, 122.89, 120.62, 120.56, 120.36, 117.81, 119.58, 117.72, 117.50, 115.43, 109.68, 109.44.

Anal. Calcd. for C$_{41}$H$_{26}$N4 : C, 85.69; H, 4.56; N, 9.75, found : C, 85.64; H, 4.73; N, 9.62.
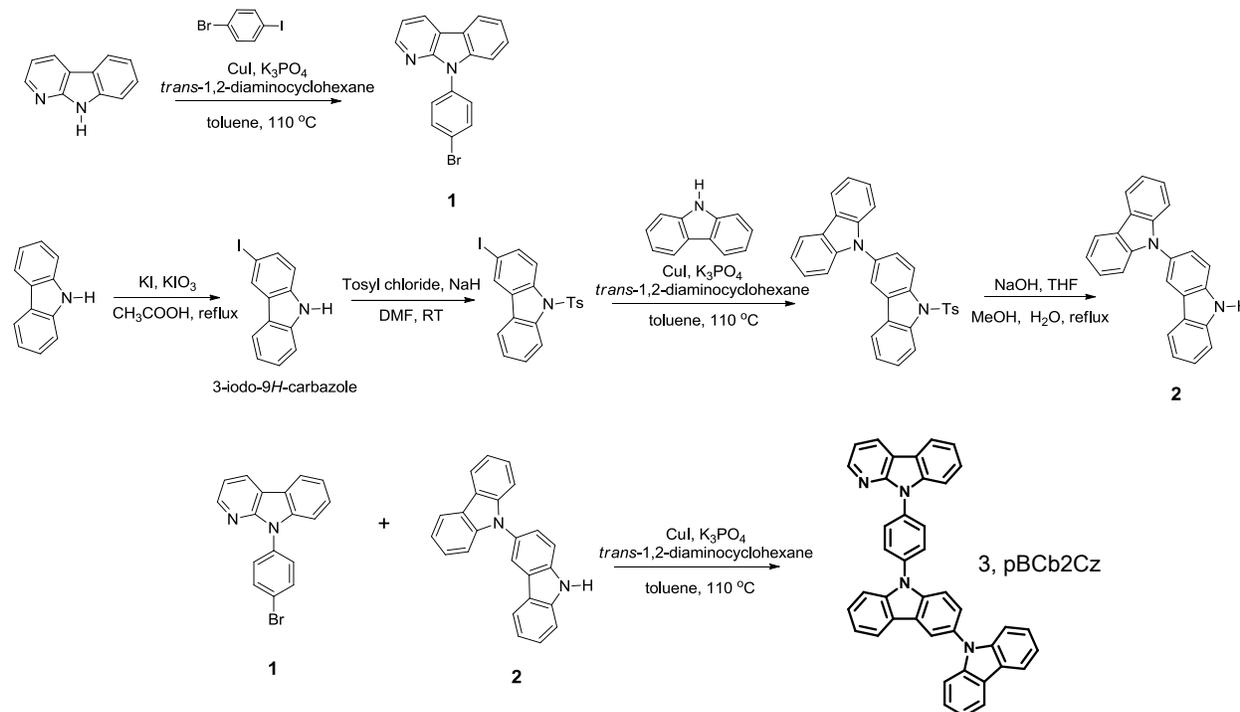
Scheme 1S. Synthetic procedure for pBCb2Cz.

2. Instrumental analysis

^{1}H and ^{13}C NMR spectra were recorded on a Varian Mercury 400 MHz spectrometer using deuterated chloroform (CDCl$_3$-d) purchased from Cambridge Isotope Laboratories, Inc. Elemental analyses were performed by the Center for Organic Reactions using an EA1112 elemental analyzer (Thermo Electron Corporation). Thermal properties were studied under a nitrogen atmosphere on a Mettler DSC 821e instrument. Thermal gravimetric analysis (TGA)

was conducted on a Mettler TGA50 thermal analysis system under a heating rate of 10 $^{\circ}$C/min. The redox property of host material thin film was examined by CV conducted using a potentiostat (EA161, eDAQ). A 0.10 M tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) solution in freshly dried acetonitrile was employed as the electrolyte. The Ag/AgCl and Pt wire (0.5 mm in diameter) electrodes were utilized as reference and counter electrodes, respectively. The scan rate was 50 mV s^{-1}. Absorption spectra of film samples were obtained using a UV-vis spectrometer (HP 8453, PDA type) in the wavelength range of 190-1100 nm. Photoluminescence (PL) spectra were recorded with a Hitachi F-7000 fluorescence spectrophotometer.

3. Device fabrication and measurement

The sublimated grade di-[4-(*N,N*-ditolyl-amino)-phenyl]cyclohexane (TAPC) and *N, N′*-dicarbazolyl-3,5-benzene (mCP) was purchased from Jilin OLED Material Tech Co., Ltd and were used as the HTL and host material, respectively. Twice sublimated 1,3,5-tri[(3-pyridyl)-phen-3-yl]benzene (TmPyPB) from Daejoo Electronic Materials was used as an ETL. Bis(3,5-difluoro-2-(2-pyridyl)phenyl-(2-carboxypyridyl)iridium(III) (FIrpic) from Luminescence Technology was used as the sky blue phosphorescent dopant material. Iridium(III) bis(3′,5′-difluoro-4′-cyanophenyl-pyridinato-N,C$^{2'}$) picolinate (FCNIrpic) from P&H Tech was used as the deep blue phosphorescent dopant material. The deep blue device structure is ITO (150nm)/ TAPC (60)/ mCP (10nm)/ pBCb2Cz or mCP: 10% FCNIrpic (30nm)/ TmPyPB (25nm)/ LiF (1.5nm)/ Al (100nm).

To fabricate blue PhOLED devices, we used a clean glass substrate coated with a 150 nm thickness of ITO layer having a sheet resistance 10 Ω/□ as an anode. The active patterns size of 2 x 2 mm^2 were formed by the photolithography and wet etching processes. The ultrasonic cleaned glass substrate in an isopropyl alcohol, acetone, and methanol was rinsed in deionized water, and finally treated in ultraviolet (UV)-ozone for 3 min. The ozone gas was generated using UV light

to excite the oxygen in the air inside the chamber. Each organic layer was deposited under a pressure of ~ 10^{-7} torr with total deposition rate of ~ 0.5 Å/s. Subsequently, 0.5 nm thickness of lithium fluoride (LiF) and 100 nm thickness of aluminum (Al) were deposited in a vacuum chamber without breaking the vacuum and used as a cathode.

Hole-only and electron-only devices were fabricated to compare with current density in host material. The device structure of the hole-only device was ITO (150nm)/ 1,1-bis[4-[*N,N*-di(*p*-tolyl)amino]-phenyl] cyclohexane (TAPC) (80nm)/ pBCb2Cz or mCP (30nm)/ TAPC (40nm)/ Al (100nm) for enhancing the hole injection and suppressing the electron injection. The structure of electron-only device was ITO (150nm)/3,3′-(5′-(3-(pyridin-3-yl)phenyl)-[1,1′:3′,1″-terphenyl]-3,3″-diyl)dipyridine (TmPyPB) (80nm)/ pBCb2Cz and mCP (30nm)/ TmPyPB (40nm)/ LiF (1.5nm)/ Al (100nm) for enhancing the electron injection and suppressing the hole injection.

Single carrier devices with mCP or pBCb2Cz for the measurement of hole and electron carrier mobility were fabricated and the carrier mobilities were determined by SCLC (space charge limited current) method. Hole only devices (HODs) were fabricated with the configuration of ITO/ MoO_3 (1 nm)/ mCP or pBCb2Cz (200 nm)/ MoO_3 (5 nm)/ Al for the evaluation of hole mobility. The thin MoO_3 layer on a metal electrode was inserted to make ohmic contact so that SCLC region can be investigated clearly in all the devices.[2] In addition, the electron only devices (EODs) of ITO (150 nm) / mCP or pBCb2Cz (200 nm)/ LiF (1.5 nm)/ Al (100 nm) were fabricated for the evaluation of electron mobility.[3]

The current density-voltage (*J-V*) and luminance-voltage (*L-V*) data of blue PhOLEDs were measured employing a Keithley SMU 238 and a Minolta CS-100A. The electroluminescence

(EL) spectra and Commission Internationale de I'Eclairage (CIE) color coordinate were obtained

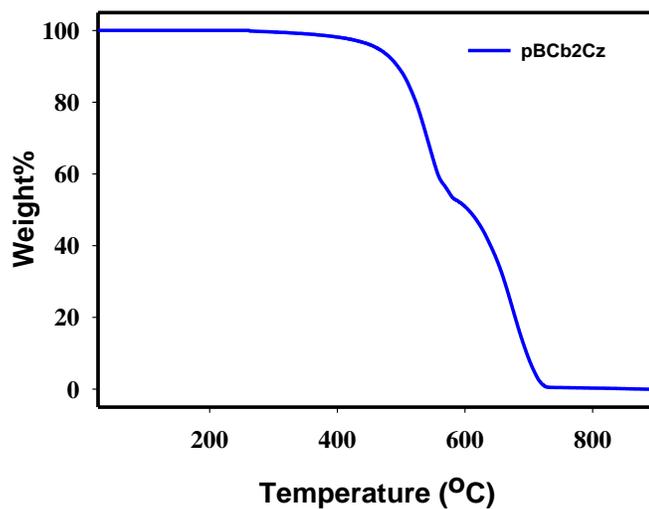using a Minolta CS-2000.

4. Thermal Analysis

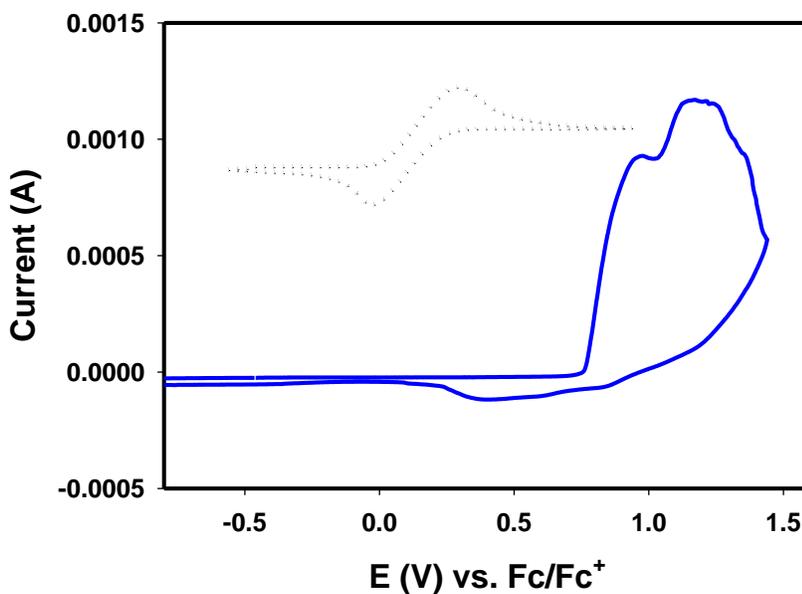**Fig. 1S.** Thermogravimetry analysis of **pBCb2Cz**

5. Cyclic Voltammetry

Fig. 2S. Cyclic Voltammogram of **pBCb2Cz**. *sample: film on Pt plate electrode

Table 1S. Measured and calculated parameters of **pBCb2Cz**

	T_g (°C)	T_d (°C)	abs [a] (nm)	PL [a] (nm)	$\lambda_{\text{cut-off}}$ [a] (nm)	E_T [b] (eV)	E_g^{opt} [c] (eV)	HOMO [d] (eV)	LUMO [d] (eV)
pBCb2Cz	146	491	295	387	362	2.93	3.43	-5.69	-2.26

[a] Measured in $CHCl_3$ with a concentration of 10^{-5} M.
[b] Measured from the first phosphorescent emission peak of the low-temperature PL spectrum at 77 K.
[c] Estimated from the onset of the absorption spectrum and $E_g^{\text{opt}} = 1240/\lambda_{\text{cut-off}}$.
[d] HOMO = -e (4.8V + (E(V vs Fc/Fc$^+$) (0.89V)), LUMO = E_g^{opt} + HOMO.
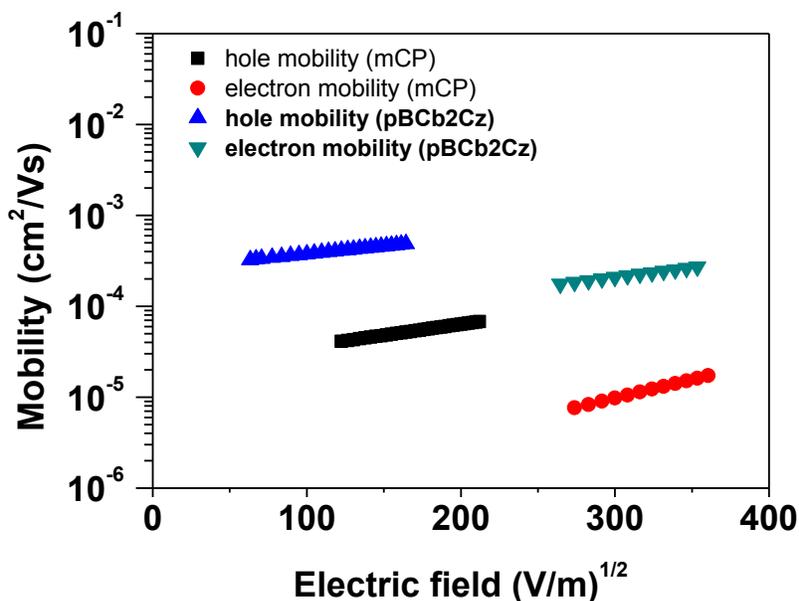

Fig. 3S The relationship of hole and electron mobility vs the electric field. The mobilities of mCP and pBCb2Cz were determined by SCLC method.

Carrier mobility depending on the electric field as a function of voltage in our devices was plotted as shown in Fig. 3S. The hole mobilities of mCP and pBCb2Cz were calculated to be 4.49×10^{-4} cm^2/Vs and 2.24×10^{-3} cm^2/Vs at 0.3 MV/cm^2, respectively.

The electron mobilities of mCP and pBCb2Cz were also determined to be 1.00×10^{-4} cm^2/Vs and 7.03×10^{-4} cm^2/Vs at 0.3 MV/cm^2, respectively. In brief, the hole and electron mobilities of

pBCb2Cz were found to be much higher than those of mCP. These data can support the bipolar

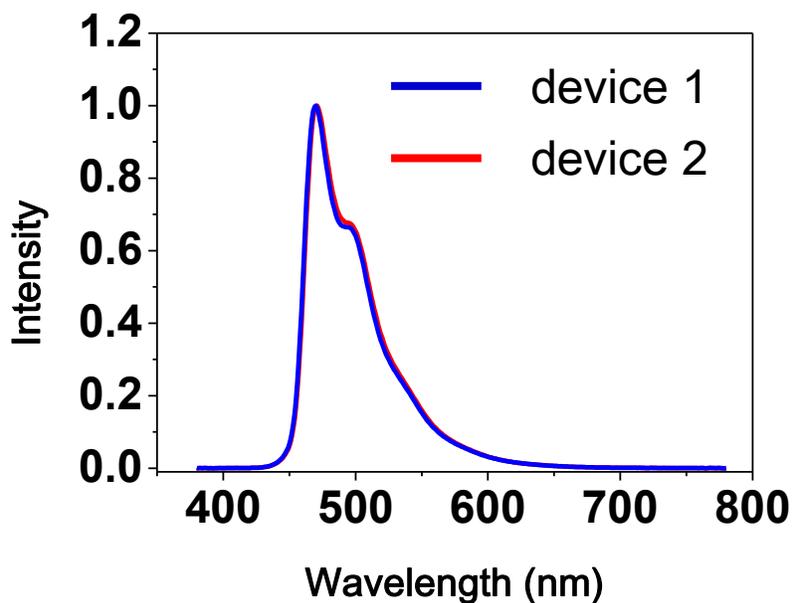characteristics of pBCb2Cz for improving the blue PHOLED device performances.

Fig. 4S Electroluminescence spectra of mCP and pBCb2Cz devices. Device configuration: [ITO

(100 nm)/ TAPC (45 nm)/FIrpic 6 wt % doped mCP (device **1**) and pBCb2Cz (device **2**) (15

nm)/TmPyPB (40 nm)/LiF (1.5 nm)/Al (100 nm)]

Table 2S. Device performances of the devices **1** and **2** at 1000 cd/m^2

	Turn on (V)	Operation Voltage (V)	Luminous efficiency (cd/A)	Power efficiency (lm/W)	EQE (%)	CIE (x, y)
Device 1	3.1	5.2	31.2 (36.4)[a]	20.2 (33.7)[a]	18.7 (22.2)[a]	(0.151,0.302)
Device 2	2.8	4.3	36.7 (38.3)[a]	28.4 (34.6)[a]	22.0 (23.0)[a]	(0.151,0.312)

[a] Maximum efficiency of the device.

6. Deep Blue PhOLEDs with FCNIrpic: device structures and performances

Device 3 : TAPC(60) / mCP(10) / mCP : 10% FCNIrpic(30) / TmPyPB(25) / LiF(1.5) / Al(100)

Device 4 : TAPC(60) / mCP(10) / pBCb2Cz : 10% FCNIrpic(30) / TmPyPB(25) / LiF(1.5) / Al(100)
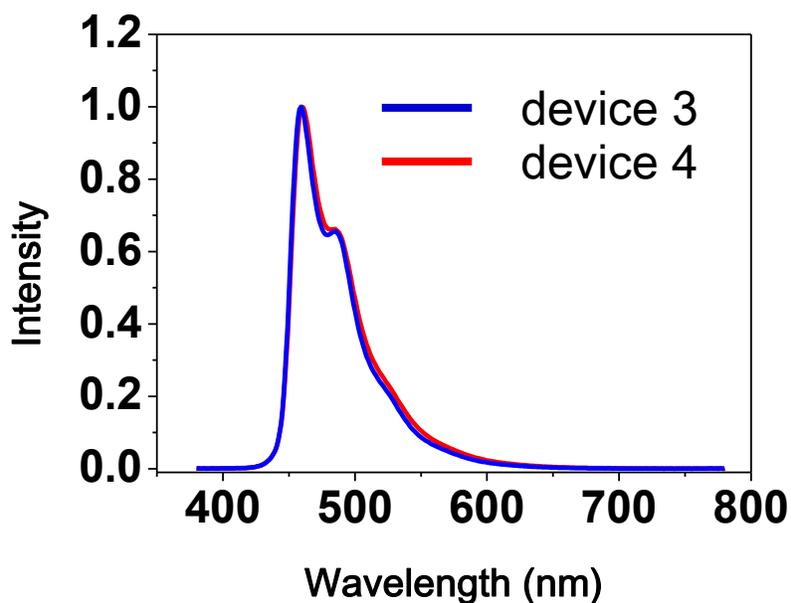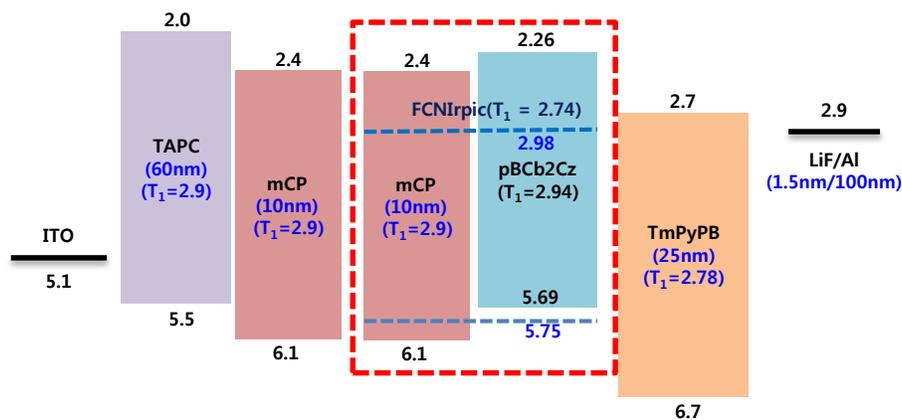
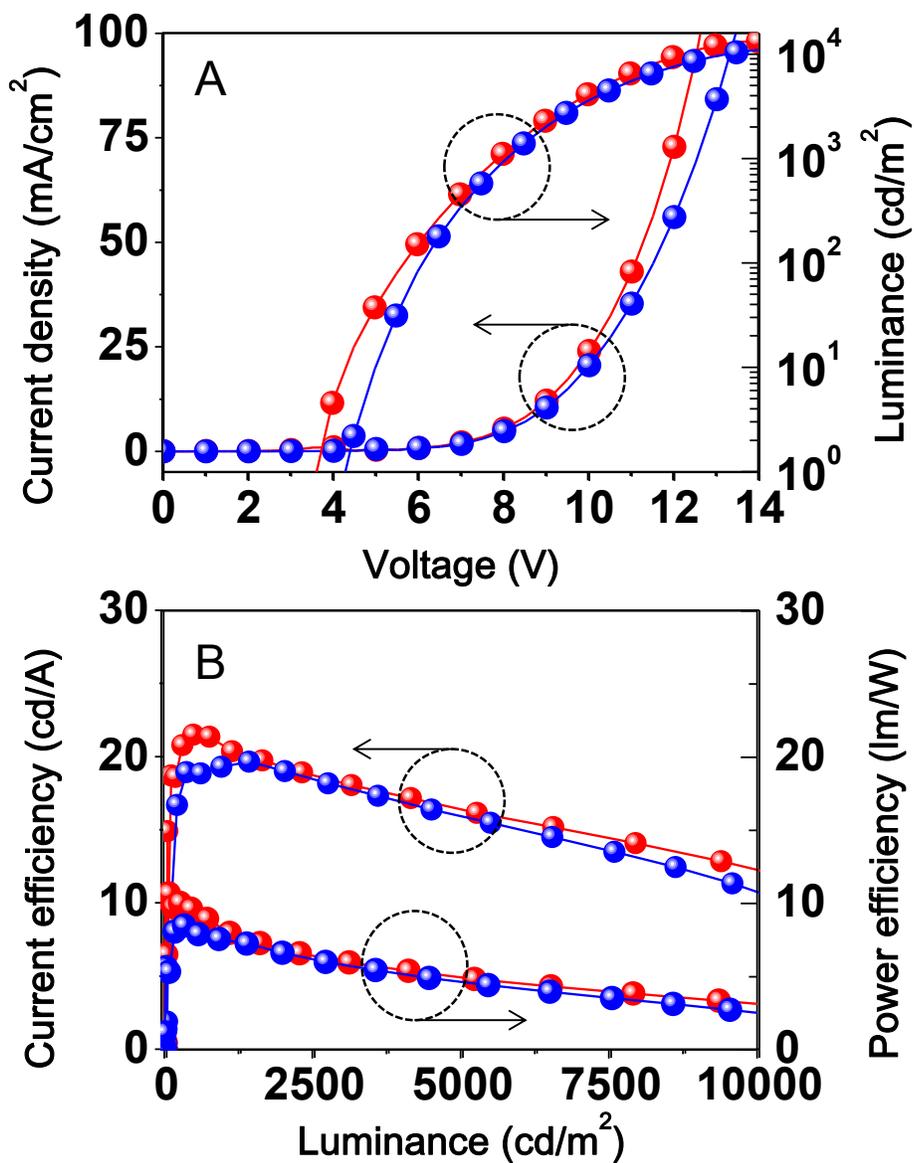**Fig. 5S.** Device configuration and EL spectra of blue PhOLEDs made of FCNIrpic dopant.

Fig. 6S A: $J-V-L$ characteristics of device 3 and 4. **B**: CE-L and $PE-L$ characteristics of blue OLEDs using pBCB2Cz (red sphere) and mCP (blue sphere). 10 wt % FCNIrpic-doped device.

Table 3S. Device performances of the devices **3** and **4** at 1000 cd/m^2

	Turn on (V)	Operation Voltage (V)	Luminous efficiency (cd/A)	Power efficiency (lm/W)	EQE (%)	CIE (x, y)
Device 3	4.2	8.1	19.3 (19.6)[a]	7.5 (8.5)[a]	15.3 (15.5)[a]	(0.144, 0.196)
Device 4	3.5	7.8	20.7 (21.5)a	8.2 (10.7)[a]	15.6 (16.2)[a]	(0.148, 0.211)

[a]: maximum efficiency of the device.

References

1. H. –Y. Oh, I. –B. Song, and S. –H. Park, Ger. Offen., 2012, DE 102011054855.

2. T. Matsushima, Y. Kinoshita and H. Murata, Appl. Phys. Lett., 2011, 91, 253504.

3. M. A. Khan, W. Xu, K.-U.-Haq, Y. Bai, X. Y. Jiang, Z. L. Zhang and W. Q. Zhu, J. Appl. Phys. 2008, 103, 014509.