Supporting Information

Highly Efficient, Little Efficiency Roll-Off Orange-Red Electrophosphorescent Devices Over Wide Range of Doping Concentration Based on A Bipolar Transporting Iridium Complex

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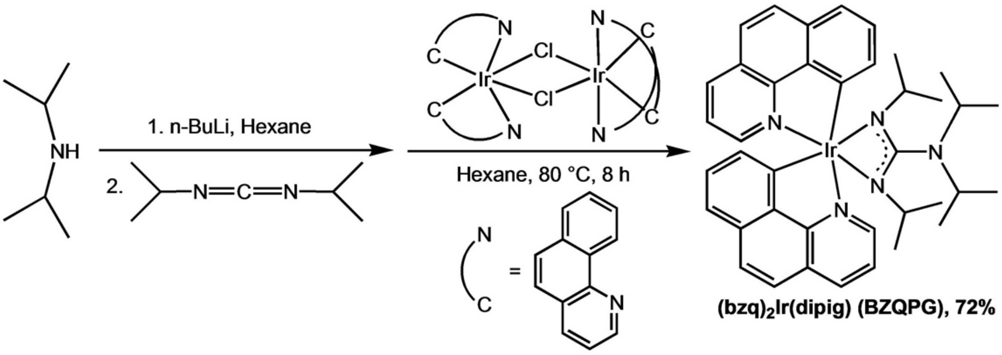
***General Information*:** Materials obtained from commercial suppliers were used without further purification. Anhydrous hexane was distilled with sodium benzophenone ketyl under nitrogen atmosphere and degassed by the freeze-pump-thaw method. All glassware, syringes, magnetic stirring bars and needles were dried in a convection oven for at least 4 h. Reactions were monitored with thin layer chromatography (TLC). Commercial TLC plates (Silica gel 60 F254, Merck Co.) were visualized under UV light at 254 and 365 nm. Silica column chromatography was done with silica gel 60 G (particle size 5~40 μm, Merck Co.). ^{1}H NMR spectra were recorded on a Bruker AVANCE 300 MHz spectrometer with tetramethylsilane as an internal standard. Mass spectra were measured on a GC/MS mass spectrometer. Elemental analyses were performed on a flash EA 1112 spectrometer. Absorption spectra were obtained using a Shimadzu UV-2550 UV-vis spectrometer. PL spectra were recorded on a Perkin-Elmer LS-55 fluorescence spectrometer with a Xe arc lamp excitation source. All solvents were degassed via three freeze-pump-thaw cycles. Emission lifetime experiments were performed by the time-correlated single-photon counting (TCSPC) system under right-angle sample geometry. A 379 nm picosecond diode laser (Edinburgh Instruments EPL375, repetition rate 20 MHz) was used to excite the samples. The PL emission was collected by a photomultiplier tube (Hamamatsu H5783p) connected to a TCSPC board (Becker&Hickel SPC-130). The time constant of the instrument response function (IRF) is ca. 220 ps. Electrochemical measurements were performed with a BAS 100W Bioanalytical electrochemical work station, using Pt working electrode, platinum wire as auxiliary electrode, and a porous glass wick Ag/Ag$^+$ as reference electrode. The voltammograms were referenced to the ferrocene/ferrocenium couple and the scan rate was 100 mV s^{-1}. We obtained only the reversible oxidation potential for (bzq)$_2$Ir(dipig) (BZQPG) in DMF, which can be utilized to calculate the HOMO level from the onset of this oxidation potential in the cyclic voltammetry

(CV) wave. No reversible reduction wave being available to estimate the LUMO level was detected within the electrochemical window of CH_2Cl_2, THF and DMF. Therefore, the LUMO level of BZQPG was determined by considering the difference between its HOMO level and the corresponding E_g, which is calculated from the absorption edge of its UV-vis spectrum. The time-of-flight (TOF) technique involves generation of carriers near one electrode with a short pulse of light and observation of the current displaced in the external circuit by the motion of the carriers through the sample. The sample for TOF measurement was prepared on the glass substrate covered with indium tin oxide (ITO) layer with the structure of [ITO/BZQPG (1 μm)/Al]. An intense short duration (5-6 ns) light pulse from a frequency-tripled (355 nm) Nd:YAG laser was incident at one side of the sample to generate photocarriers. The sample was mounted in a vacuum and the measurement was made at the electric field of 5.0×10^5 V cm^{-1} at 293 K.

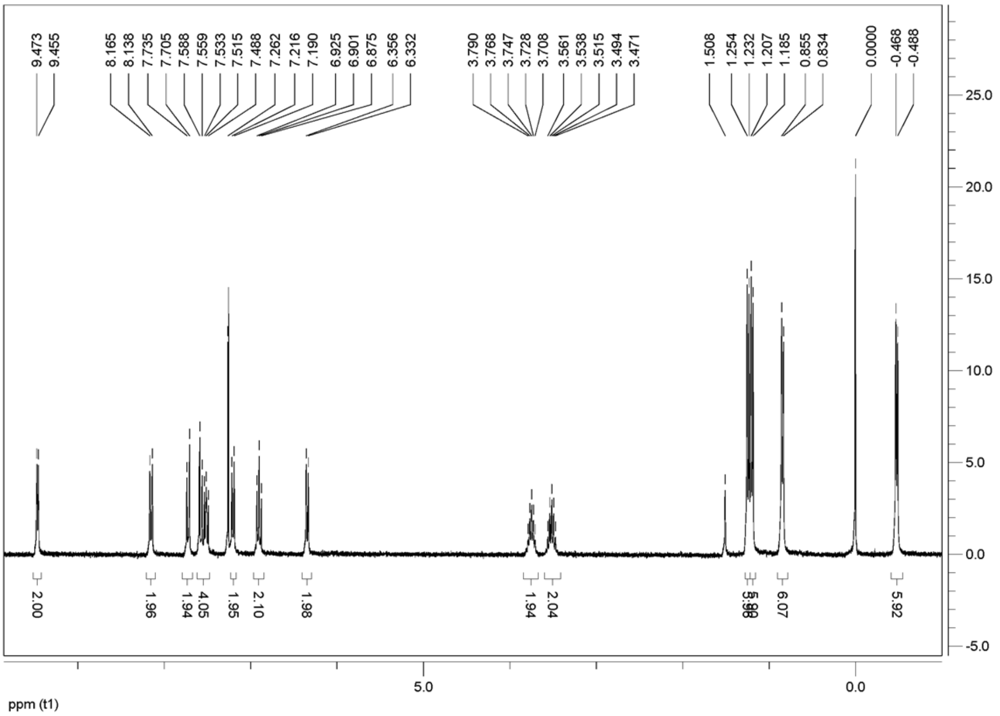
***Fabrication of the OLEDs and EL Measurements*:** The general architecture of the multilayer diodes is as follows. The ITO (indium-tin oxide) coated glass substrates (20 Ω/square) were first cleaned in ethanol, acetone, and soap ultrasonic baths. All organics were purified by gradient sublimation and thermally evaporated at a rate of 1.0 Å s^{-1} at a pressure of ca. 3.5 x 10^{-4} Pa. A LiF layer (0.5 nm) was deposited at a rate of 0.2 Å s^{-1}. The Al cathode was deposited at a rate of 10 Å s^{-1} and the active area of the diode segments was 2 x 3 mm^2. EL spectra and brightness-current density-voltage characteristics were measured by combining a Spectrascan PR-650 spectrophotometer with a computer-controlled direct-current power supply Keithley model 2400 voltage-current source under ambient conditions at room temperature.

[(bzq)$_2$Ir(μ-Cl)]$_2$ was synthesized according to a modified Nonoyama procedure,[S1] by refluxing $IrCl_3.nH_2O$ (2.5 g, 7 mmol) with 2.5 equiv of the ligand of benzoquinoline (3.1 g) in a 3:1 (v/v) mixture of 2-methoxyethanol and water for 6-7 h. The reaction mixture was cooled to room temperature and water was added to precipitate the product. The resulting mixture was filtered and the precipitate was then washed with hexane and ethyl ether several times to provide [(bzq)$_2$Ir(μ-Cl)]$_2$ in 82% yield.

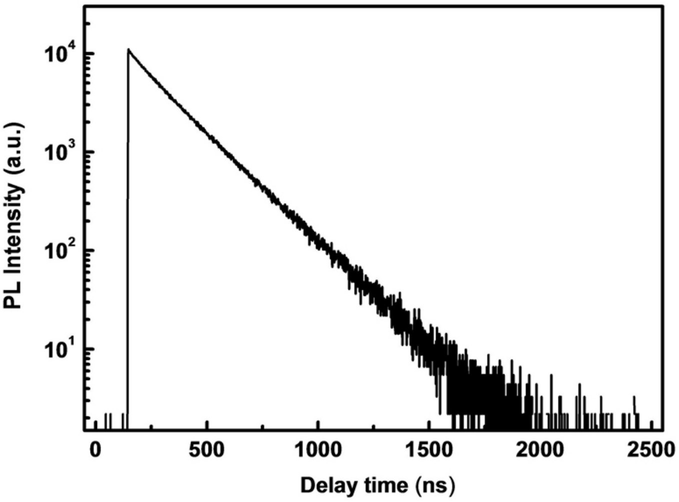
(bzq)$_2$Ir(dipig) (BZQPG): A hexane solution of n-BuLi (0.20 mL x 2.5 M) was added to diisopropylamine (50 mg, 0.5 mmol) in hexane (10 mL) under argon. The reaction mixture was stirred at room temperature for 30 min, and then added dropwise to *N,N*-diisopropylcarbodiimide (63 mg, 0.5 mmol). The colorless solution was stirred for another 30 min, and then added dropwise to [$(bzq)_2Ir(\mu\text{-}Cl)]_2$ (292 mg, 0.25 mmol) in hexane solvent (20 mL). After stirring at 80 °C for 8 h, the reaction mixture was cooled to room temperature. The solvent was evaporated under vacuum, and the product was washed with Et_2O (20 mL) three times to give a red powder $(bzq)_2Ir(dipig)$ (BZQPG) (72 %). ***$(bzq)_2Ir(dipig)$ (BZQPG)***: MS: *m/z* 774.99 (M^+). Anal. Calcd for $C_{39}H_{44}IrN_5$: C, 60.44; H, 5.72; N, 9.04. Found: C, 60.24; H, 5.78; N, 8.92. ^1H NMR (300 MHz, $CDCl_3$) δ 9.46 (d, J = 5.4 Hz, 2H), 8.15 (d, J = 8.1 Hz, 2H), 7.72 (d, J = 8.8 Hz, 2H), 7.59–7.49 (m, 4H), 7.20 (d, J = 7.8 Hz, 2H), 6.90 (t, J= 7.8 Hz, 2H), 6.34 (t, J = 7.2 Hz, 2H), 3.79–3.71 (m, 2H), 3.56–3.47 (m, 2H), 1.24 (d, J = 6.6 Hz, 6H), 1.20 (d, J = 6.6Hz, 6H), 0.84 (d, J = 6.3 Hz, 6H), -0.48 (d, J = 6 Hz, 6H).



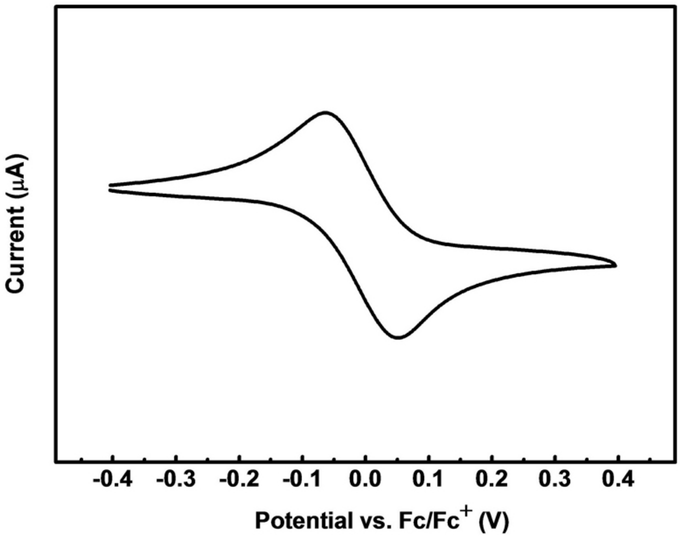
S-Scheme 1. Synthesis of iridium complex $(bzq)_2Ir(dipig)$ (BZQPG).



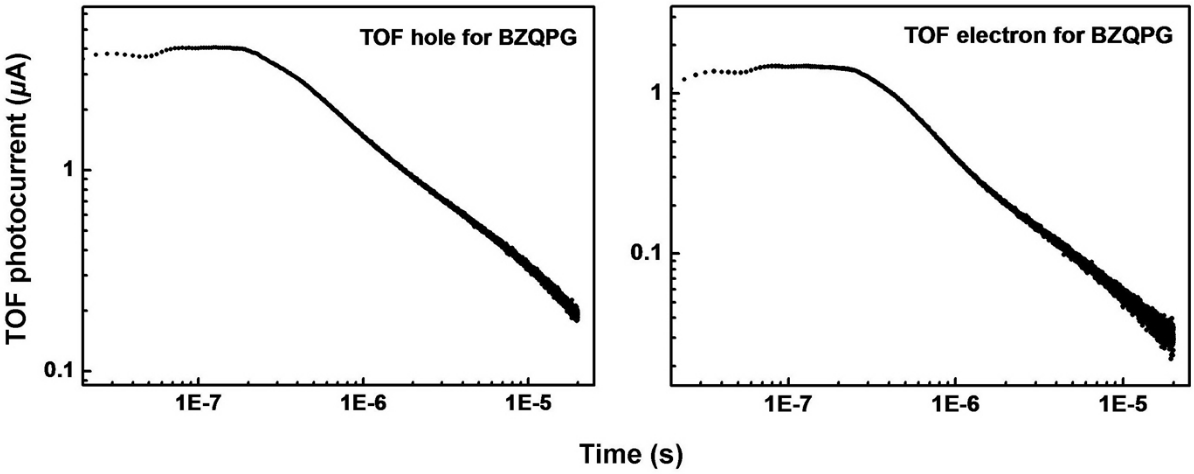
S-Fig. 1. ^1H NMR spectrum of BZQPG in $CDCl_3$.



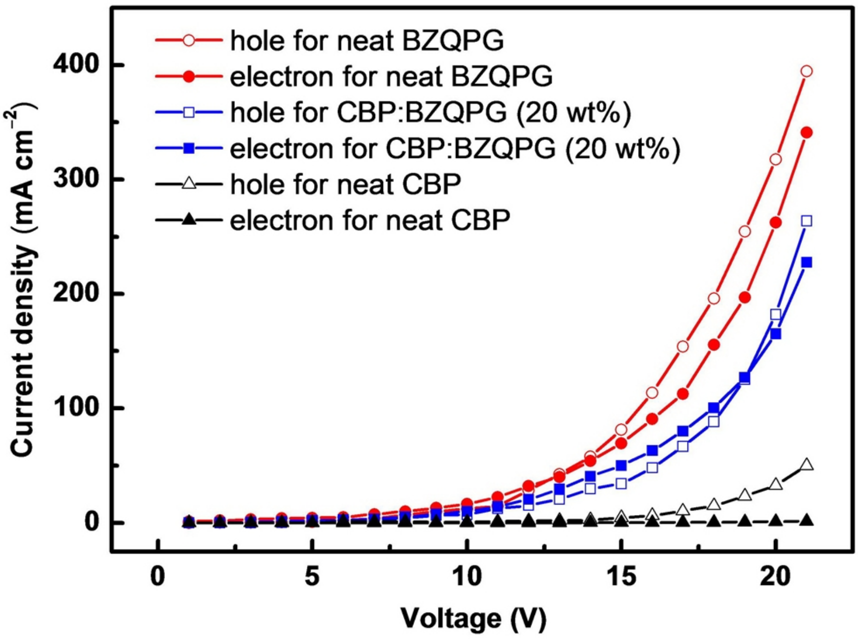
S-Fig. 2. Transient photoluminescence decay of BZQPG.



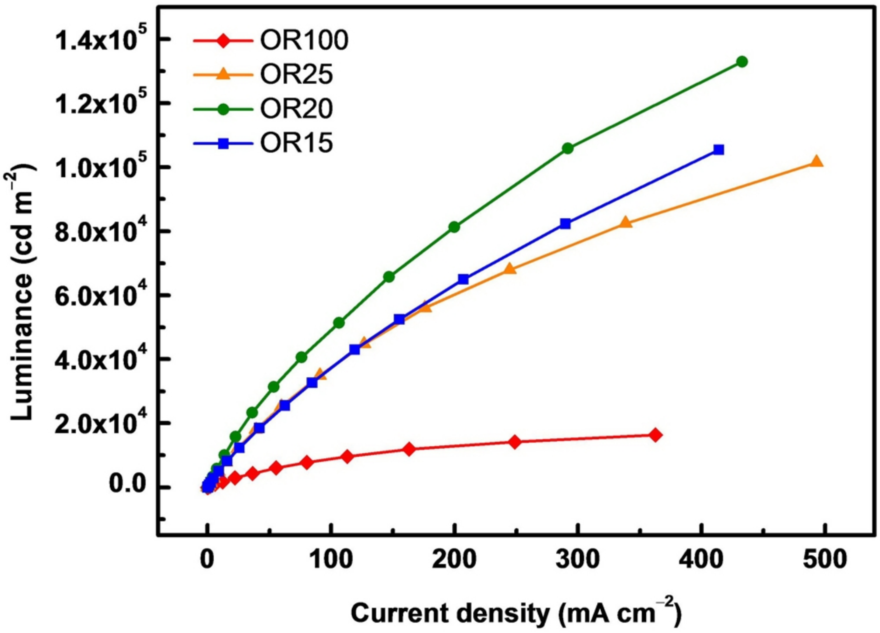
S-Fig. 3. Cyclic voltammogram of BZQPG.



S-Fig. 4. Typical time of flight transient BZQPG.



S-Fig. 5. Current density-voltage curves of the hole only and electron only devices for the neat films of BZQPG and CBP, and doped film of CBP:BZQPG (20 wt%).



S-Fig. 6. Luminance-current density (*L-J*) curves of OR15, OR20, OR25 and OR100.

SI-References:

S1 M. Nonoyama, *Bull. Chem. Soc. Jpn.* 1974, **47**, 767.