

Supporting Information

A New Host Material Achieving Above 75cd/A Current Efficiency of Top-Emitting Deep-Red Phosphorescent Organic Light-Emitting Diodes

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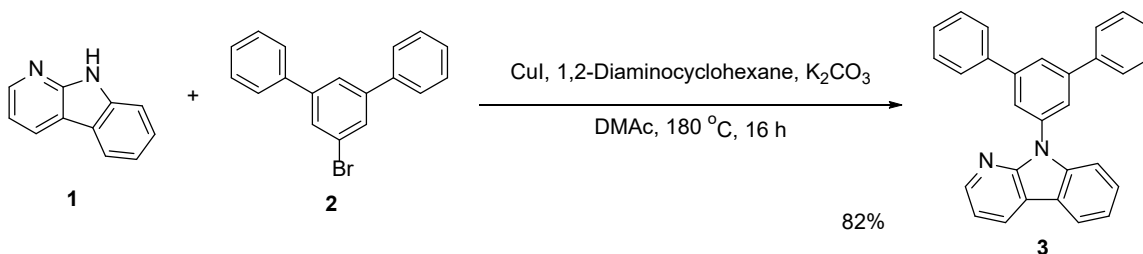
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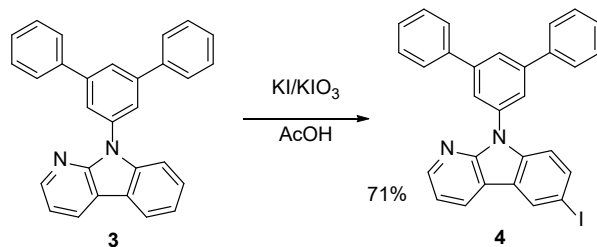
Materials and instruments

All reagents and materials with high purity of HPLC > 99.9% (sublimed) were supplied by GuanMat Optoelectronic Material Inc. ^1H NMR and ^{13}C NMR spectra were measured on a Bruker Advance III-500 spectrometer. Mass spectra were measured on a Shimadzu GCMS-QP2010 SE gas chromatograph mass spectrometer. UV-vis absorption spectra were recorded on a Shimadzu UVmini-1240 recording spectrophotometer. Photoluminescence (PL) was recorded on a Shimadzu RF-5301pc spectrophotometer. The glass transition temperatures of compounds were determined by DSC under nitrogen atmosphere using a Shimadzu DSC-60 differential scanning calorimeter. The decomposition temperature corresponding to 5% weight loss was conducted on a Shimadzu TGA-50 thermogravimetric analyzer. Cyclic voltammetry (CV) was carried out using a CorrTest CS electrochemical workstation [0.1 M Bu_4NPF_6 in dichloromethane as electrolyte, a platinum gauze as counter electrode, a Ag wire as quasi-reference, and referenced against the Fc/Fc^+ redox couple (E° 0.42 V)]. The X-ray diffraction data of the single crystal was collected using Rigaku Oxford XtaLAB Synergy (1.2KW) diffractometer.



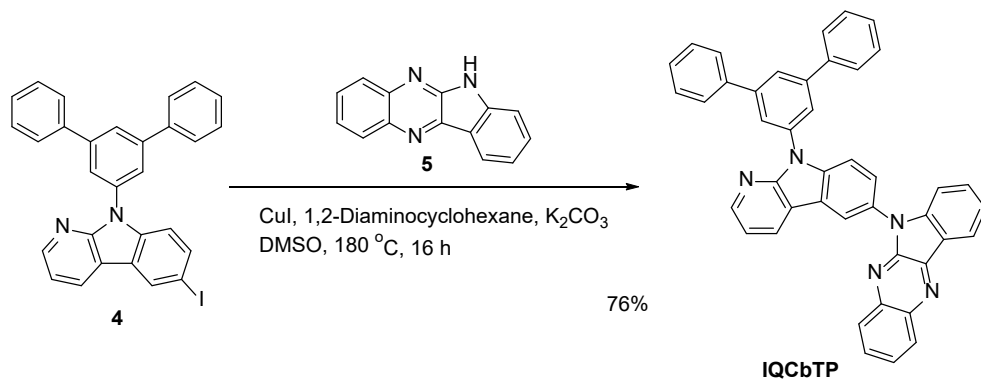
Synthesis of 9-([1,1':3',1''-terphenyl]-5'-yl)-9H-pyrido[2,3-b]indole (3). A 1 L flask was charged with 9H-pyrido[2,3-b]indole (23 g, 136.7 mmol), 5'-bromo-1,1':3',1''-terphenyl (46.5 g, 150.4 mmol), CuI (5.2 g, 27.4 mmol), 1,2-diaminocyclohexane (3.1 g, 27.4 mmol), K_2CO_3 (56.6 g, 410.1 mmol), and 670 mL N,N-dimethylacetamide. The resulting mixture was stirred for 16 h at 180 °C under N_2 . Then the reaction mixture was cooled to room temperature and poured into 2 L water. The precipitated solid was collected by filtration. Then the solid was purified by column chromatography using petroleum ether (PE)- CH_2Cl_2 (10:1) as an eluent to afford the product in 82% yield as white solid.

^1H NMR (500 MHz, Chloroform-d) δ 8.50 (dd, $J = 4.8, 1.6$ Hz, 1H), 8.41 (dd, $J = 7.7, 1.6$ Hz, 1H), 8.15 (d, $J = 7.7$ Hz, 1H), 7.91 (t, $J = 1.7$ Hz, 1H), 7.85 (d, $J = 1.6$ Hz, 2H), 7.74 – 7.68 (m, 4H), 7.59 (d, $J = 8.2$ Hz, 1H), 7.52 – 7.44 (m, 5H), 7.41 – 7.32 (m, 3H), 7.26 (dd, $J = 7.7, 4.8$ Hz, 1H). ^{13}C NMR (126 MHz, CDCl_3) δ 152.02, 146.62, 143.35, 140.48, 140.18, 137.14, 128.93, 128.43, 127.84, 127.45, 127.10, 125.52, 125.11, 121.06, 120.93, 120.88, 116.44, 116.21, 110.56. MS m/z $[\text{M}]^+$ calcd for $\text{C}_{29}\text{H}_{20}\text{N}_2$: 396.16, found: 396.10.



Synthesis of 9-([1,1':3',1''-terphenyl]-5'-yl)-6-iodo-9H-pyrido[2,3-b]indole (4). A 500 mL flask was charged with compound **3** (30 g, 75.7 mmol), KI (6.3 g, 37.8 mmol), KIO₃ (8.1 g, 37.8 mmol), and 250 mL AcOH. The resulting mixture was allowed to react for 16 h at 90 °C under N₂. Then the reaction mixture was cooled to room temperature, 500 mL CH₂Cl₂ was added to the reaction mixture, and the resulting mixture was washed with water. Then CH₂Cl₂ was removed by evaporation under reduced pressure. The resulting residue was purified by column chromatography using PE-CH₂Cl₂ (10:1) as an eluent to afford the product in 71% yield as white solid.

¹H NMR (500 MHz, Chloroform-d) δ 8.53 (dd, J = 4.8, 1.6 Hz, 1H), 8.47 (d, J = 1.7 Hz, 1H), 8.37 (dd, J = 7.7, 1.5 Hz, 1H), 7.92 (t, J = 1.7 Hz, 1H), 7.81 (d, J = 1.7 Hz, 2H), 7.75 (dd, J = 8.6, 1.7 Hz, 1H), 7.70 (d, J = 6.9 Hz, 4H), 7.48 (t, J = 7.6 Hz, 4H), 7.44 – 7.35 (m, 3H), 7.29 (dd, J = 7.8, 4.8 Hz, 1H). ¹³C NMR (126 MHz, CDCl₃) δ 151.75, 147.36, 143.46, 140.28, 139.36, 136.73, 135.38, 129.87, 128.95, 128.76, 127.92, 127.41, 125.77, 124.94, 123.27, 116.67, 115.14, 112.61, 87.79. MS *m/z* [M]⁺ calcd for C₂₉H₁₉IN₂: 522.06, found: 522.00.



Synthesis of 6-(9-([1,1':3',1''-terphenyl]-5'-yl)-9H-pyrido[2,3-b]indol-6-yl)-6H-indolo[2,3-b]quinoxaline (IQCbTP). A 500 mL flask was charged with compound **4** (28.2 g, 54.0 mmol), 6H-indolo[2,3-b]quinoxaline (7.9 g, 36.0 mmol), CuI (3.4 g, 17.9 mmol), 1,2-diaminocyclohexane (4.1 g, 36.0 mmol), K₂CO₃ (9.9 g, 72.0 mmol), and 300 mL DMSO. The resulting mixture was stirred for 16 h at 180 °C under N₂. Then the reaction mixture was cooled to room temperature and poured into 2 L water. The precipitated solid was collected by filtration.

Then the solid was purified by column chromatography using CH₂Cl₂ as an eluent to afford the crude product. Then the crude product was further purified by recrystallization with CH₂Cl₂ and PE to afford pure product in 76% yield as yellow solid. The compound was further purified with double times sublimation to achieve HPLC purity of >99.95% for single crystal preparation and for device fabrication.

¹H NMR (500 MHz, Chloroform-d) δ 8.60 – 8.55 (m, 2H), 8.46 (d, J = 2.0 Hz, 1H), 8.43 (dd, J = 7.7, 1.6 Hz, 1H), 8.38 – 8.31 (m, 1H), 8.12 – 8.05 (m, 1H), 7.97 (t, J = 1.7 Hz, 1H), 7.93 (d, J = 1.6 Hz, 2H), 7.85 (d, J = 8.6 Hz, 1H), 7.80 – 7.68 (m, 7H), 7.68 – 7.62 (m, 1H), 7.55 – 7.47 (m, 5H), 7.45 (d, J = 7.5 Hz, 1H), 7.44 – 7.38 (m, 2H), 7.30 (dd, J = 7.7, 4.8 Hz, 1H). ¹³C NMR (126 MHz, CDCl₃) δ 152.54, 147.45, 146.47, 145.61, 143.57, 140.70, 140.37, 140.20, 139.80, 139.63, 136.89, 131.17, 129.31, 129.01, 128.89, 128.38, 128.23, 127.96, 127.48, 126.59, 126.51, 125.86, 125.10, 122.76, 121.95, 121.83, 120.48, 119.68, 116.66, 116.14, 111.86, 110.56. MS *m/z* [M]⁺ calcd for C₄₃H₂₇N₅: 613.23, found: 613.20.

Table S1 Crystal data and structure refinement for IQCbTP

Identification code	GN-HS741
Empirical formula	C ₄₃ H ₂₉ N ₅ O
Formula weight	631.71
Temperature/K	293(2)
Crystal system	monoclinic
Space group	P2 ₁ /c
<i>a</i> /Å	15.6292(2)
<i>b</i> /Å	16.8330(2)
<i>c</i> /Å	13.8165(2)
α/°	90
β/°	108.900(2)
γ/°	90
Volume/Å ³	3438.96(9)
<i>Z</i>	4
ρ _{calc} /cm ³	1.220
μ/mm ⁻¹	0.588
F(000)	1320.0
Crystal size/mm ³	0.1 × 0.06 × 0.05
Radiation	CuKα (λ = 1.54184)
2θ range for data collection/°	5.978 to 149.886
Index ranges	-19 ≤ <i>h</i> ≤ 19, -20 ≤ <i>k</i> ≤ 20, -14 ≤ <i>l</i> ≤ 17
Reflections collected	24582
Independent reflections	6846 [R _{int} = 0.0281, R _{sigma} = 0.0285]
Data/restraints/parameters	6846/0/445

Goodness-of-fit on F^2	1.063
Final R indexes [$I > 2\sigma(I)$]	$R_1 = 0.0507$, $wR_2 = 0.1463$
Final R indexes [all data]	$R_1 = 0.0611$, $wR_2 = 0.1568$
Largest diff. peak/hole / $e \text{ \AA}^{-3}$	0.47/-0.35

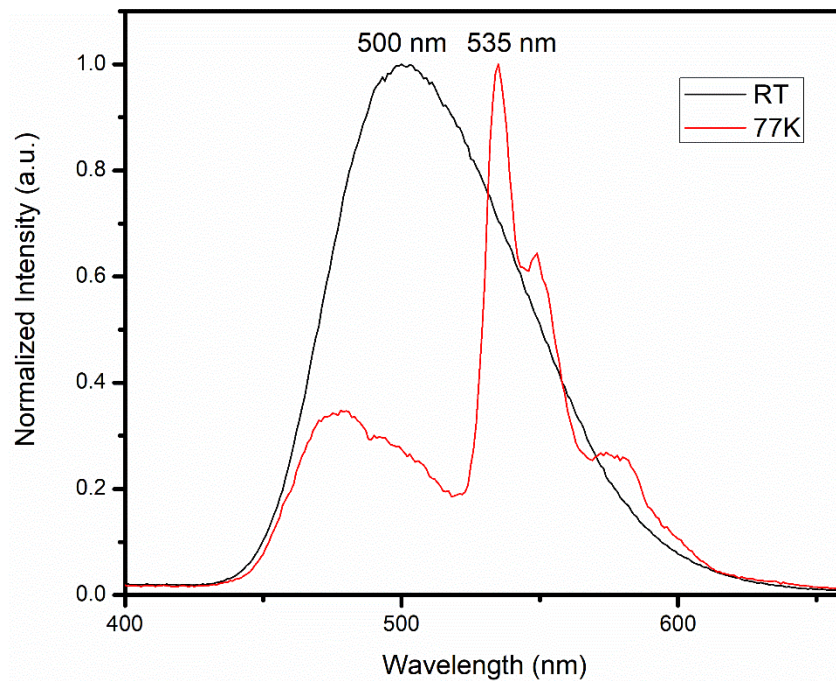


Fig. S1 77K PL of IQCbTP

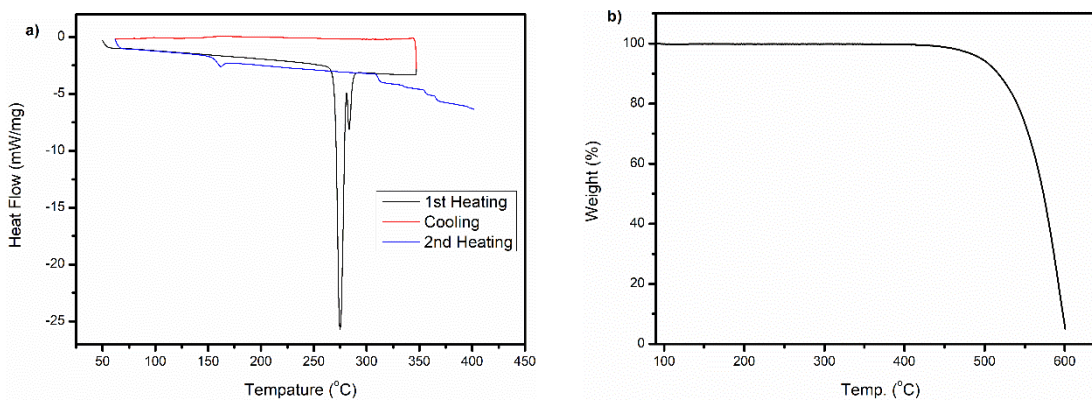


Fig. S2 a) DSC of IQCbTP. b) TGA of IQCbTP.

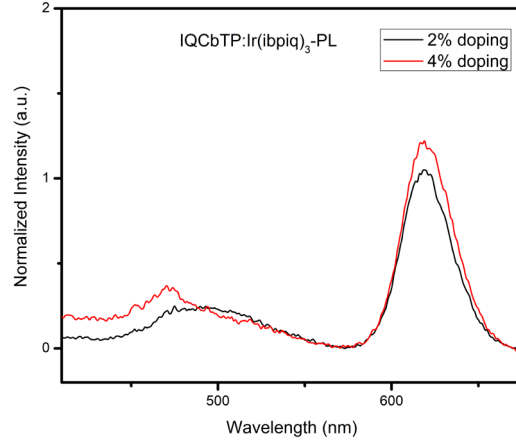


Fig. S3 The PL spectra of doped thin films (30 nm) of Ir(ibpiq)₃ (2 wt% and 4 wt%) doped in IQCbTP excited at 350 nm at room temperature in air.

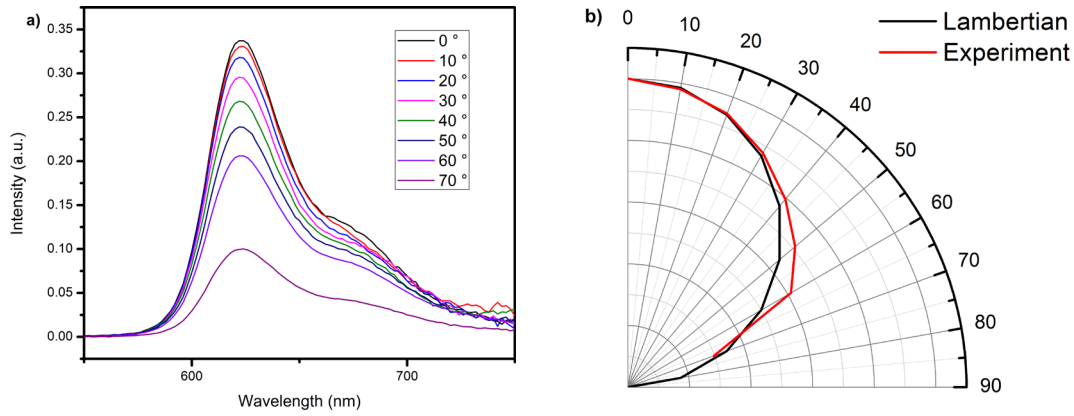


Fig. S4 a) Emission spectra at varying angles of bottom-emitting device; b) Angular distribution of emission intensity for bottom-emitting device.

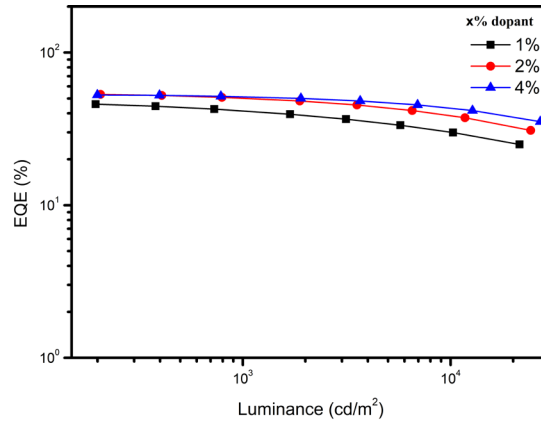


Fig. S5 EQEs of top-emission PhOLEDs calculated by assuming Lambertian emission which may be overestimated because of the microcavity effect

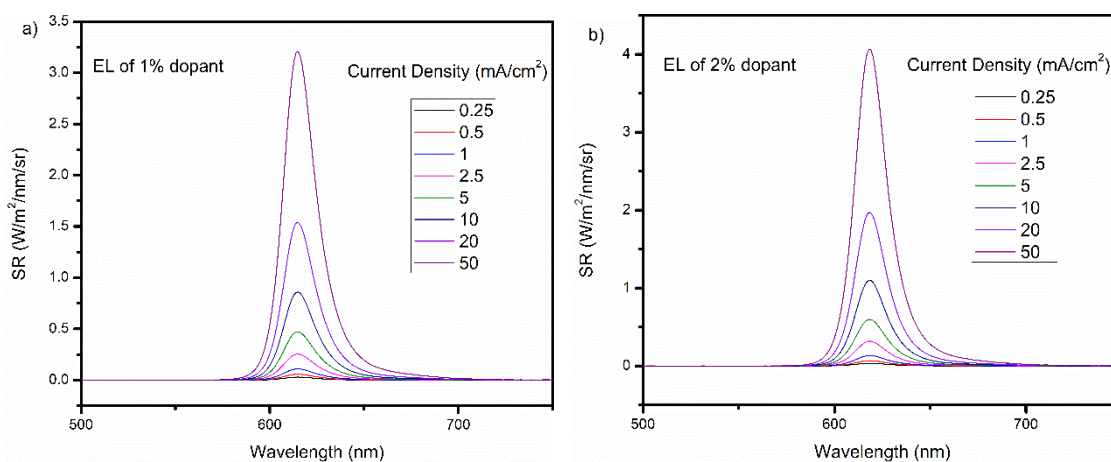


Fig. S6 EL spectra of devices with 1% dopant (a) and 2% dopant (b) in different current densities.

Table S1 Electroluminescence Characteristics of the Top-emitting Devices^a

Device	Dopant (x%)	EQE ^a (%)
A	1%	45.4, 41.5, 30.5
B	2%	53.4, 49.3, 38.8
C	4%	52.5, 51.3, 43.4

^a In the order of 200, 1000, and 10000 cd m⁻² calculated by assuming Lambertian emission which may be overestimated because of the microcavity effect.

Device fabrication and measurement of EL characteristics

PhOLEDs were fabricated on glass substrates coated with a patterned transparent ITO conductive layer (bottom-emission) or reflective ITO/Ag/ITO layer (top-emission). The substrates were cleaned in a detergent solution in deionized water at 60 °C for 5 min and then sonicated in deionized water at room temperature for 10 min. Subsequently, they were pre-dried using a jet spin washer, and then dried for 5 min in an oven at 100 °C, before being finally treated with UV/ozone plasma. The pressure during the vacuum evaporation was 5.0×10^{-5} Pa, and the film thickness was controlled using a calibrated quartz crystal microbalance during deposition. The device areas were 3.16*3.16 mm².

The current–voltage–luminance I-V-L characteristics were measured using a Keithley 2400 Source Meter in conjunction with a PR-670 Spectrascan. The devices and the PR-670 Spectrascan were fixed in a black box, and the PR-670 Spectrascan was located in forward direction (with 5

degree variation) to devices' emitting surface. The electroluminescence (EL) spectra in forward direction were also recorded by using PR-670 Spectrascan. The current efficiency in forward direction was obtained by direct measurement of luminance recorded by PR-670 Spectrascan and current–voltage recorded by Keithley 2400 Source Meter. The EQE was calculated as the total number of emitted photons divided by the total number of injected electrons from EL spectrum in forward direction by assuming a Lambertian-type emission pattern. It is worth noting that the calculation of EQE treated by this manner was just a historic and yet rough method and may not be accurate. More accurate calculation of EQE can be realized by Gather' method using angle-resolved spectroscopy.¹ OLEDs were fabricated three times to check reproducibility. All characterizations were carried out under ambient conditions at room temperature.

References

- 1 E. Archer, S. Hillebrandt, C. Keum, C. Murawski, J. Murawski, F. Tenopala-Carmona and M. C. Gather, *Advanced Optical Materials*, 2021, **9**, 2000838.