

Supporting Information (SI)

**Naphthyridin-based Iridium(III) Complexes for Green to Red OLEDs
with EQEs over 30% and Low Efficiency Roll-off**

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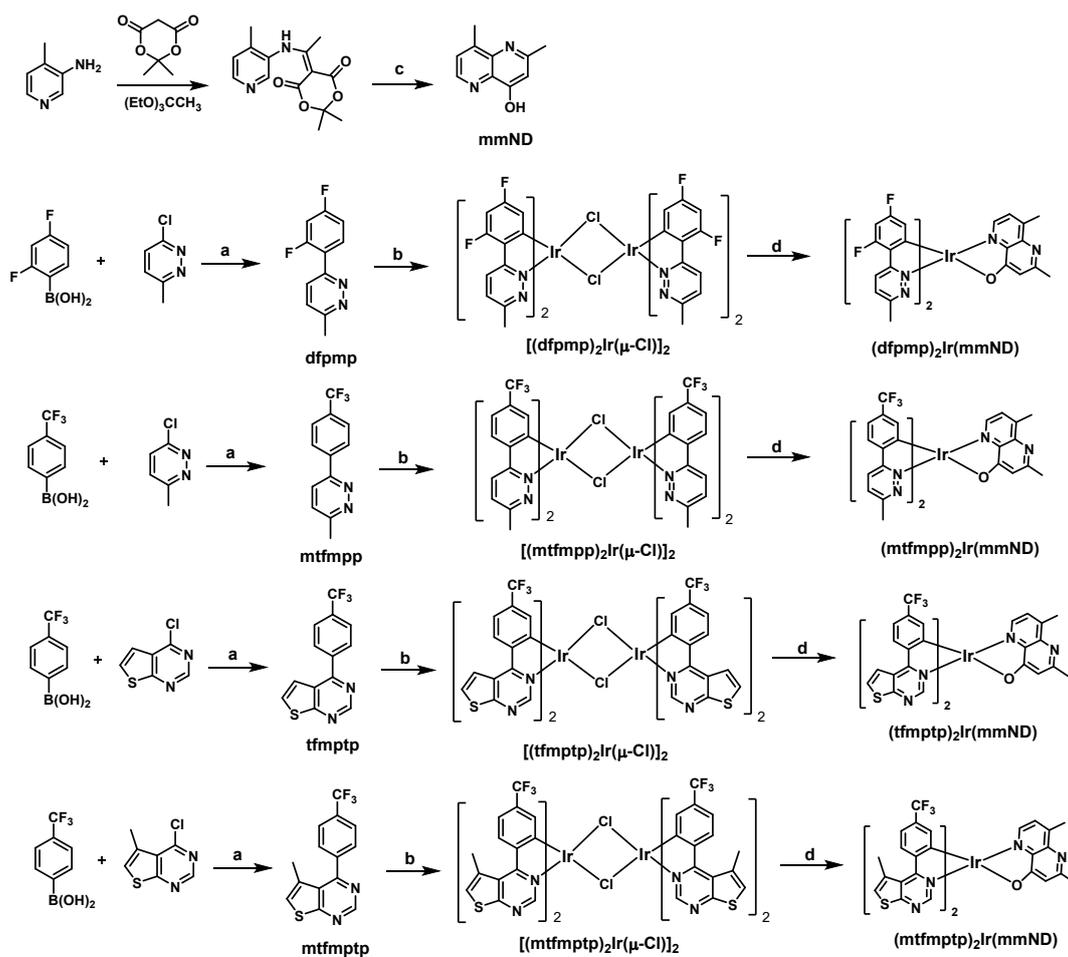
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Materials and Measurements

All reagents and chemicals were purchased from commercial sources and used without further purification. ^1H NMR spectra were recorded by Bruker Advanced II (400 MHz) spectrometers and MERCURYVX300 using CDCl_3 as solvent and tetramethylsilane (TMS) as the internal standards. High resolution mass spectra (HRMS) were measured by Thermo Scientific LTQ Orbitrap XL mass spectrometer. Elemental analyses for C, H, and N were performed on an Elementar Vario MICRO analyzer. Thermo gravimetric analyses (TGAs) were performed on a NETZSCH STA 449C instrument under nitrogen with a heating rate of $10\text{ }^\circ\text{C min}^{-1}$. The absorption and photoluminescence spectra were measured on a Shimadzu UV-2700 recording spectrophotometer and a Hitachi F-4600 photoluminescence spectrophotometer, respectively. The decay lifetimes were performed on PicoQuant Fluotime300 in degassed CH_2Cl_2 solution at room temperature. Absolute PLQYs in degassed CH_2Cl_2 solution and doped TCTA films were obtained using a Quantaaurus-QY measurement system (C9920-02, Hamamatsu Photonics).

Synthesis of Ligands and Iridium Complexes



Scheme S1 The synthetic routes of the ligands and Ir(III) complexes: (a) Pd(PPh₃)₄, Na₂CO₃, THF-H₂O, 80 °C, 12 h; (b) IrCl₃, EtOCH₂CH₂OH-H₂O, 110 °C, 12 h; (c) Ph₂O, 220 °C, 1 h; (d) mmND, EtOCH₂CH₂OH, 115 °C, 12 h.

The ancillary ligand 2,8-Dimethyl-1,5-naphthyridin-4-ol (mmND) was synthesized according to the reported procedure.¹ Yield: 74%. ESI-MS, m/z: calcd. 174.1 [M]; found 175.2 [M+H]⁺.

The main ligands 3-(2,4-difluorophenyl)-6-methylpyridazine (dfpmp), 3-methyl-6-(4-(trifluoromethyl)phenyl)pyridazine (mtfmpp), 4-(4-(trifluoromethyl)phenyl)thieno[2,3-d]pyrimidine (tfmptp), 5-methyl-4-(4-(trifluoromethyl)phenyl)thieno[2,3-d]pyrimidine (mtfmptp) were synthesized according to the reported procedure.² dfpmp. Yield: 81%. ESI-MS, m/z: calcd. 206.1 [M]; found 207.3 [M+H]⁺; mtfmpp. Yield: 83%. ESI-MS, m/z: calcd. 238.1 [M];

found 239.2 [M+H]⁺; tfmptp. Yield: 86%. ESI-MS, m/z: calcd. 280.0 [M]; found 281.3 [M+H]⁺; mtfmptp. Yield: 82%. ESI-MS, m/z: calcd. 294.0 [M]; found 295.1 [M+H]⁺.

The IrCl₃·3H₂O (0.76 g, 2.14 mmol) and 2.4 equivalent of cyclometalated ligand (5.14 mmol) were added in a 2-ethoxyethanol and water mixture. Then, the solution was heated for 16 h at 110 °C. After the addition of water, precipitated powder of [(C^N)₂Ir(μ-Cl)]₂ chloride-bridged dimer was filtered and reacted with mmND for 12 h at 110 °C. The solution was concentrated and the resulting residue was purified by silica gel column chromatography (CH₂Cl₂/petroleum ether 1:2 (v/v)) and vacuum sublimation gave power.

(dfpmp)₂Ir(mmND): Yield: 71%. ¹H NMR (400 MHz, CDCl₃) δ 8.29 (dd, *J* = 8.9, 1.6 Hz, 2H), 7.44 (d, *J* = 4.9 Hz, 1H), 7.29 (dd, *J* = 8.8, 6.8 Hz, 2H), 7.14 (d, *J* = 4.9 Hz, 1H), 6.74 (s, 1H), 6.60-6.30 (m, 2H), 5.82 (ddd, *J* = 19.6, 8.5, 2.3 Hz, 2H), 2.75 (s, 3H), 2.57 (s, 3H), 2.55 (s, *J* = 3.46 Hz, 3H), 2.24 (d, *J* = 5.0 Hz, 3H). HR-MS, m/z: calcd for C₃₂H₂₄F₄N₆OIr⁺ [M+H]⁺ 777.15715, found 777.15778.

(mtfmpp)₂Ir(mmND): Yield: 72%. ¹H NMR (400 MHz, CDCl₃) δ 7.97 (dd, *J* = 8.8, 4.1 Hz, 2H), 7.65 (dd, *J* = 17.9, 8.1 Hz, 2H), 7.40-7.28 (m, 3H), 7.23 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.16 (dd, *J* = 8.1, 1.1 Hz, 1H), 7.10 (dd, *J* = 4.9, 0.7 Hz, 1H), 6.75 (s, 1H), 6.60 (s, 1H), 6.56 (s, 1H), 2.73 (s, 3H), 2.59 (s, 3H), 2.56 (s, 3H), 2.28 (s, 3H). HR-MS, m/z: calcd for C₃₄H₂₆F₆N₆OIr⁺ [M+H]⁺ 841.16960, found 841.16974.

(tfmptp)₂Ir(mmND): Yield: 40%. ¹H NMR (400 MHz, CDCl₃) δ 9.23 (s, 1H), 8.34 (dd, *J* = 8.3, 3.6 Hz, 2H), 8.17 (dd, *J* = 9.2, 6.3 Hz, 2H), 8.10 (s, 1H), 7.84 (dd, *J* = 6.2, 3.6 Hz, 2H), 7.41-7.30 (m, 2H), 7.28 (d, *J* = 1.3 Hz, 1H), 7.20 (d, *J* = 4.9 Hz, 1H), 6.79 (s, 1H), 6.73 (s, 1H), 6.57 (s, 1H), 2.73 (s, 3H), 2.56 (s, 3H). HR-MS, m/z: calcd for C₃₆H₂₂F₆N₆OS₂Ir⁺ [M+H]⁺ 925.08245, found 925.08252.

(mtfmptp)₂Ir(mmND): Yield: 35%. ¹H NMR (400 MHz, CDCl₃) δ 9.07 (s, 1H), 8.06-7.82 (m, 3H), 7.46 (dd, *J* = 6.3, 1.0 Hz, 2H), 7.32 (d, *J* = 4.9 Hz, 1H), 7.28 (dd, *J* = 8.4, 1.4 Hz, 1H), 7.21 (dd, *J* = 9.9, 2.9 Hz, 2H), 6.86 (s, 1H), 6.72 (s, 1H), 6.55 (s,

1H), 2.74 (s, 3H), 2.71 (d, $J = 0.9$ Hz, 6H), 2.57 (s, 3H). HR-MS, m/z : calcd for $C_{38}H_{26}F_6N_6S_2OIr^+$ $[M+H]^+$ 953.11375, found 953.11322.

X-ray Crystallography

The single crystals of the three complexes were obtained from slow evaporation of methanol / CH_2Cl_2 solution at room temperature. And its X-ray-diffraction data were carried out on a Bruker APEX2 SMART CCD diffractometer using monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å) at room temperature. Cell parameters were retrieved using SMART software and refined using SAINT on all observed reflections. Data were collected using a narrow-frame method with scan widths of 0.30° in ω and an exposure time of 10 s/frame. Crystal structures were solved by direct methods using the SHELXL-2014/7' software. None-hydrogen atoms were refined anisotropically by full-matrix least-squares calculations on F^2 using SHELXL-2014/7', while the hydrogen atoms were directly introduced at calculated position and refined in the riding mode.

Cyclic Voltammetry Measurements and Theoretical Calculations

Cyclic voltammetry (CV) was measured on a CHI voltammetric analyzer at room temperature with the conventional three-electrode configuration, consisted of a platinum column working electrode, a platinum wire auxiliary electrode, and an Ag wire pseudo reference electrode. Cyclic voltammograms were recorded using tetrabutylammonium hexafluorophosphate (TBAPF6) (0.1 M) dissolved in dichloromethane (5 mL) as the supporting electrolyte, and ferrocenium-ferrocene (Fc^+/Fc) as the external standard, at the scan rate of 100 mV s^{-1} . The onset potential was determined from the intersection of two tangents of the rising and background current in cyclic voltammogram. We perform theoretical calculations employing Gaussian09 software with B3LYP function. The basis set of 6-31G(d, p) was used for C, H, N, O, and F atoms while the LanL2DZ basis set was employed for Ir atoms. The

solvent effect of CH₂Cl₂ was taken into consideration using conductor like polarizable continuum model (C-PCM).

OLEDs Fabrication and Measurement

All the devices were grown on glass substrates pre-coated with a 160 nm-180 nm thick layer of indium tin oxide (ITO) with a sheet resistance of 10 Ω per square. Before loading into the deposition system, the ITO substrates were pre-cleaned carefully and the surface was treated by oxygen plasma for 15 minutes. After UV ozone treatment, hole-injection material HATCN (6 nm) was firstly thermally deposited on, followed by the hole-transporting material HAT-CN (0.2%): TAPC (50 nm), emissive layer 1 (the phosphors doped in the host TCTA, 10 nm), emissive layer 2 (the phosphors doped in 2,6DCzPPy, 10 nm), and electron-transporting material Tm3PyP26PyB (60 nm). Finally, a cathode composed of lithium fluoride (LiF, 1 nm)/aluminum (Al, 150 nm) was sequentially deposited onto the substrate in the vacuum of 10⁻⁶ Pa. The current density-voltage-luminance (*J-V-L*) characteristics were measured using a Keithley 2400 Source meter and a Keithley 2000 Source multimeter equipped with a calibrated silicon photodiode. The EL spectra were tested using a brightness light distribution characteristics measurement system C9920-11. The EQE of the EL device was calculated based on the photo energy examined using the photodiode, the EL spectrum and the current passing through the device. All measurements were carried out at room temperature under ambient conditions.

Tables and Figures

Table S1 The crystallographic data of (dfpmp)₂Ir(mmND), (mtfmp)₂Ir(mmND) and (tfmpt)₂Ir(mmND).

	(dfpmp) ₂ Ir(mmND)	(mtfmp) ₂ Ir(mmND)	(tfmpt) ₂ Ir(mmND)
Formula	C ₃₂ H ₂₃ F ₄ IrN ₆ O	C ₃₄ H ₂₅ F ₆ IrN ₆ O	C ₃₆ H ₂₁ F ₆ IrN ₆ OS ₂
Formula weight	775.76	839.80	923.91

T (K)	293(2)	100.01(10)	100.00(10)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Triclinic	monoclinic	triclinic
Space group	P-1	P2 ₁ /c	P-1
<i>a</i> (Å)	11.0832(7)	18.4863(9)	11.5334(10)
<i>b</i> (Å)	12.5203(11)	22.5162(15)	11.9246(8)
<i>c</i> (Å)	13.3416(7)	17.5769(9)	14.2870(10)
<i>α</i> (deg)	96.709(6)	90	110.222(6)
<i>β</i> (deg)	94.289(5)	95.202(5)	110.748(7)
<i>γ</i> (deg)	114.031(8)	90	96.327(6)
<i>V</i> (Å ³)	1664.0(2)	7286.1(7)	1662.5(2)
<i>Z</i>	2	8	2
ρ_{calcd} (g/cm ³)	1.548	1.531	1.846
μ (Mo K α) (mm ⁻¹)	4.067	3.729	4.217
<i>F</i> (000)	756.0	3280.0	900.0
Range of transm factors (deg)	4.06-49.998	4.24-50	3.94-49.992
Reflns collected	12347	35046	10980
Unique(<i>R</i> _{int})	5849(0.0373)	12816(0.0705)	5845(0.0356)
<i>R</i> _I [<i>I</i> > 2 σ (<i>I</i>)]	0.0418	0.0663	0.0340
<i>wR</i> ₂ (all data)	0.0920	0.1639	0.0742
GOF on <i>F</i> ²	1.041	1.045	1.058

$$R_1^a = \sum ||F_o| - |F_c|| / \sum F_o, \quad wR_2^b = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)]^{1/2}$$

Table S2 Selected bond lengths and angles of (dfpmp)₂Ir(mmND), (mtfmp)₂Ir(mmND) and (tfmptp)₂Ir(mmND).

Bond length	(dfpmp) ₂ Ir(mmND)	(mtfmp) ₂ Ir(mmND)	(tfmptp) ₂ Ir(mmND)
Selected	Bond length (Å)	Bond length (Å)	Bond length (Å)
Ir-C(1)	1.991(6)	1.97(1)	1.996(4)
Ir-C(2)	2.008(6)	2.034(10)	2.010(5)
Ir-N(1)	2.005(5)	2.031(8)	2.033(4)
Ir-N(2)	2.020(5)	2.028(8)	2.039(4)

Ir-N(3)	2.112(5)	2.115(8)	2.144(4)
Ir-O(1)	2.145(4)	2.155(7)	2.155(3)
Selected	(°)	(°)	(°)
C(1)-Ir-N(1)	80.7(3)	80.2(3)	80.13(17)
C(2)-Ir-N(2)	80.1(2)	80.6(4)	79.81(17)
O(1)-Ir-N(3)	78.06(17)	78.5(3)	77.58(13)
N(1)-Ir-N(2)	174.8(2)	175.0(3)	176.75(13)

Table S3 The electronic cloud density distribution.

Complex	Orbital	Energy/eV	Energy/eV	Composition (%)		
		(Calculated)	(experiment)	Main ligands	Ir	Ancillary Ligands
(dfmpmp) ₂ Ir(mmND)	HOMO	-5.47	-5.65	9.03	22.76	68.21
	LUMO	-1.98	-3.24	93.50	4.39	2.11
(mtfmpmp) ₂ Ir(mmND)	HOMO	-5.44	-5.57	9.33	23.08	67.59
	LUMO	-2.08	-3.29	94.14	4.19	1.67
(tfmptp) ₂ Ir(mmND)	HOMO	-5.60	-5.68	10.32	25.42	64.25
	LUMO	-2.43	-3.55	95.33	3.35	1.32
(mtfmptp) ₂ Ir(mmND)	HOMO	-5.57	-5.66	9.57	25.78	64.65
	LUMO	-2.46	-3.57	96.30	2.50	1.20

Table S4 Device performances of the single light-emitting layer devices **S1-S4** based on the four iridium complexes at optimized dopant ratios.

Device	$V_{\text{turn-on}}^{\text{a}}$ (V)	L_{max} (cd m ⁻²)	$\eta_{\text{c,max}}$ (cd A ⁻¹)	$\eta_{\text{ext,max}}$ (%)	$\eta_{\text{p,max}}$ (lm W ⁻¹)	$\eta_{\text{c}}^{\text{b}}$ (cd A ⁻¹)	$\eta_{\text{ext}}^{\text{b}}$ (%)	Roll-off ratio ^c (%)
S1-7%	2.8	106271	76.1	22.3	74.6	71.8	20.7	7.2
S2-5%	2.9	105238	77.9	23.6	71.9	75.8	22.0	6.8
S3-4%	3.0	119818	66.4	25.7	65.1	47.9	18.4	28.4
S4-5%	3.0	88754	44.1	23.2	39.5	33.9	17.7	23.7

a) Turn on voltage at 1 cd m^{-2} ; b) Recorded at 1000 cd m^{-2} ; c) Measured at 1000 cd m^{-2} in contrast to the EQE_{max} .

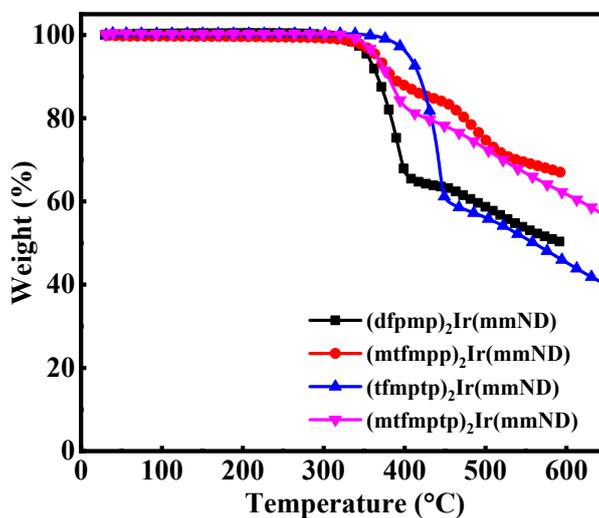


Fig. S1 The TG curves of the four complexes.

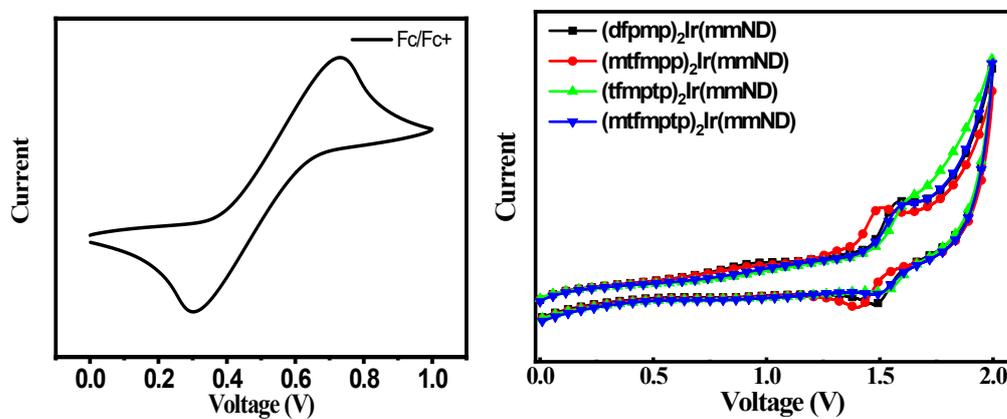


Fig. S2 Cyclic voltammograms of the four iridium(III) complexes and Fc/Fc^+ .

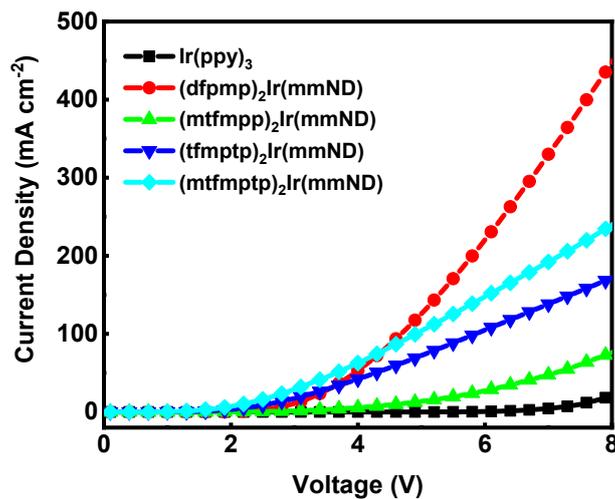


Fig. S3 The current density versus voltage curves of the electron-only devices.

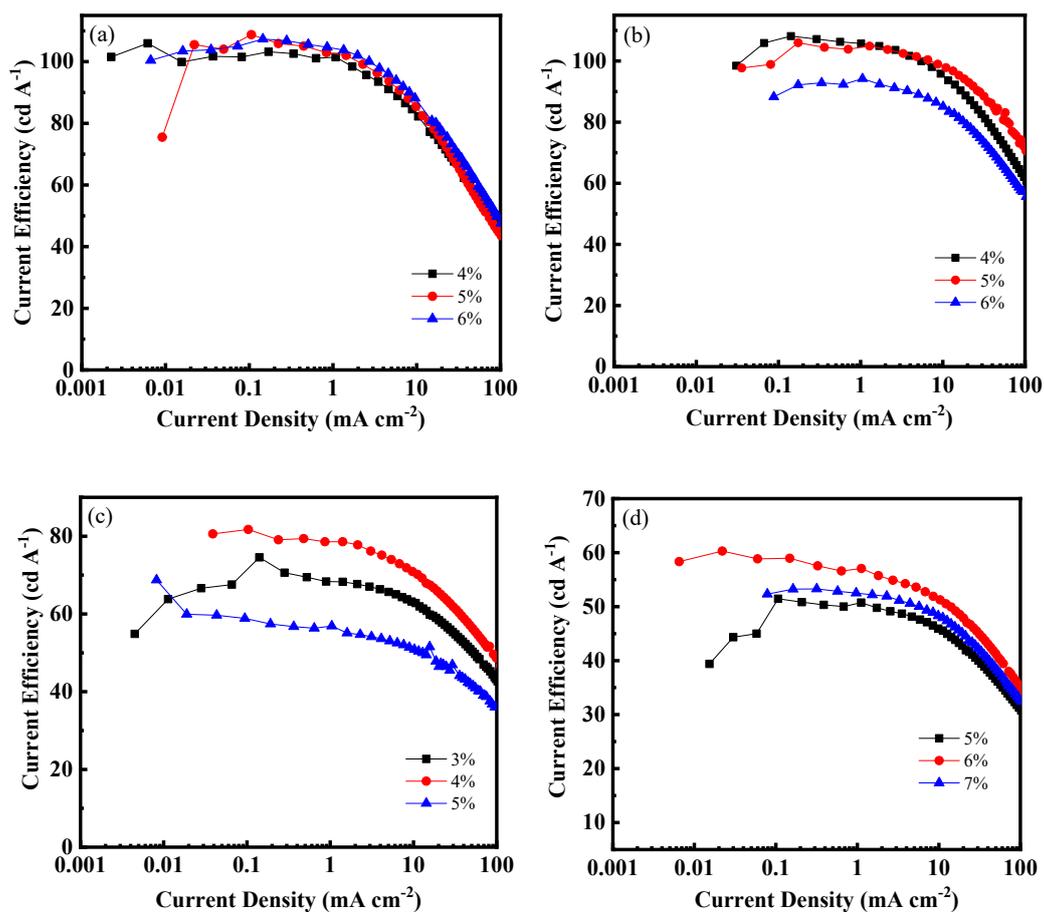


Fig. S4 The current efficiency versus current density curves with different doped concentration: a) device D1; b) device D2; c) device D3; d) device D4.

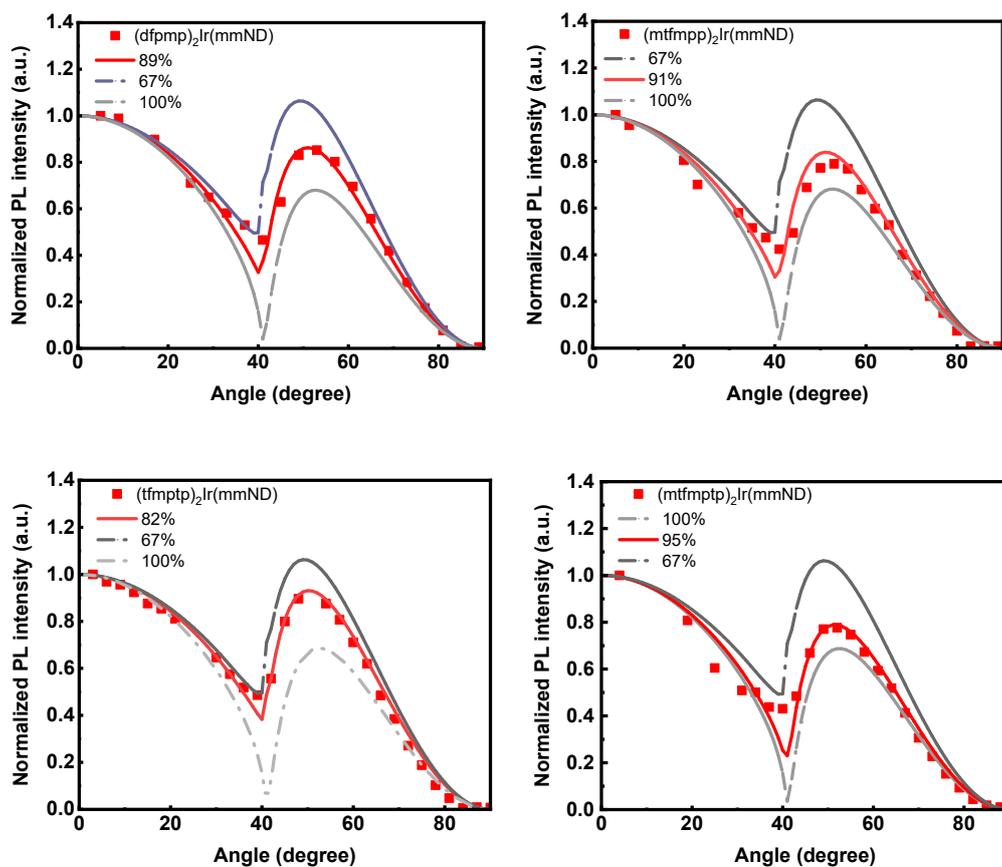


Fig. S5 The angular dependent *p*-polarized PL intensity spectra of the four complexes in 4 wt% evaporated TCTA host.

References

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- 2 X. Ning, C. Zhao, B. Jiang, S. Gong, D. Ma and C. Yang, *Dyes. Pigm.*, 2019, **164**, 206-212.