

supplementary Information for:

Binuclear Cyclometalated Ir(III) Complexes With Bis-Bidentate Butterfly Shaped Ligands: Synthesis, Characterizations, and Application to Efficient Yellow-Orange Light-Emitting Electrochemical Cells

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1. Materials and Methods

All reagents and solvents were purchased from commercial sources and used without further purification. NMR spectra were recorded on a Bruker 400 MHz spectrometer with D₆-DMSO as solvent. Elemental analysis was undertaken using an Elementar Vario EL CHN elemental analyzer. TOF-Mass was performed on LC-MS/MS Quattro Micro API micromass Waters 2695. FT-IR spectroscopy was performed on solid samples using a Perkin-Elmer 597 spectrometer. The electrochemical study of iridium complexes, IrL1, IrL2, (2×10⁻³ M) was conducted on a SAMA500 potentiostat electrochemical analyzer with a standard three-electrode system, a platinum disk working electrode, a platinum wire counter electrode, and Ag/AgCl as the reference electrode, and 0.1 M NBu₄PF₆ in dry CH₃CN was used as the supporting electrolyte. In CV the following parameters and equations were used: scan rate, 80 mV s⁻¹; formal potential $E^{\circ} = (E_{pa} + E_{pc})/2$ where E_{pa} and E_{pc} are anodic and cathodic peak potentials, respectively; ΔE_p is the peak-to-peak separation. The oxidation (E_{ox}) was used to calculate the HOMO/LUMO energy levels and electrochemical energy gap energy ($E_{gap\ Elc}$) using the equations $E_{HOMO} = - (4.8 + E_{ox})$ eV, $E_{g\ Elc} = [E_{1/2\ ox} - E_{1/2\ red}]$ V and $E_{LUMO} = - (4.8 + E_{red})$ eV which is the half-wave oxidation potential of ferrocene was found to be 0.43 V [1]. The optical energy gap ($E_{g\ Opt}$) was calculated from the intersection of absorption and emission spectra in acetonitrile solution. UV-visible absorption measurements were recorded with an Analytik Jena spectrophotometer in acetonitrile solutions at 298 K. Photoluminescence (PL) emission spectra were recorded in degassed solutions at 298 K using Cury Eclipse Elo fluorometer spectrophotometer. The PL spectra and PLQYs in neat films were measured with an absolute PLQY measurement system (Hamamatsu C11347) equipped with an integrating sphere. Solution photoluminescent quantum yields were calculated by a relative method utilizing [Ru(bpy)₃]²⁺ in CH₃CN solution at room temperature as a standard ($\Phi_{std} = 0.095$) [2] using the following equation:

$$\Phi_{unk} = \Phi_{std} \cdot \left(\frac{I_{unk}/A_{unk}}{A_{std}/I_{std}} \right) \cdot \left(\frac{\eta_{unk}}{\eta_{std}} \right)^2$$

In equation, Φ_{unk} is PL quantum yield of binuclear iridium complexes (IrL1 and IrL2), I_{unk} and I_{std} are the integrated areas of the PL spectra of the iridium complexes and standard respectively, A_{unk} and A_{std} are the absorbances of the iridium complexes and the standard at the excitation wavelength ($\lambda_{exc} = 350$ nm), and η_{unk} and η_{std} are the indexes of refraction of the respective solvents (taken to be equal to the neat solvents in both cases). Thin films of complexes (thickness of about 200 nm) to calculate the PLQY of film emission were obtained by spin-coating an acetonitrile solution of iridium complexes: IL ([BMIM⁺(PF₆)⁻]) with a ratio of 4:1 on a glass substrate at 1000 rpm for 20 s. After evaporation of the solvent, the neat films were dried overnight under a vacuum at room temperature.

LEC fabrication and characterization: Indium tin oxide (ITO) coated glass with a sheet resistance of 15 Ω /square and size of 1.5 × 2.0 cm was used as the transparent anode. The substrates were cleaned with isopropanol, acetone, and deionized water for 15 min in an ultrasonication bath and then dried at 100 °C for 2h. Thin films (ca. 30 nm) of poly(3,4 ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) were spin-coated onto ITO/glass substrates at 2000 rpm for 100 s and then annealed at 180 °C for 30 min in a nitrogen filled ambient. The active layer (150 nm) (IrL1 or IrL2:IL, 4:1, IL: 1-butyl-3-methylimidazolium hexafluorophosphate [BMIM⁺(PF₆)⁻]) for each LEC device was spin-coated from a 5% (w/v) acetonitrile solution at 2500 rpm for 60 s under ambient conditions. After spin coating, the devices were transferred to an inert atmosphere glove box (<0.1 ppm O₂ and H₂O) and heated at 60 °C for 12 h. Then, the Ag electrode (70 nm) was deposited by thermal evaporation and encapsulated into the glove box. The emissive area of the devices was 0.25 cm². The current density, luminescence versus the voltage and emission characteristics of LEC devices were measured using USB2000 fiber optic spectrometer, a

SAMA500 electroanalyser system, and a True Color Sensor MAZeT (MTCSiCT Sensor) with a Botest OLT OLED Lifetime-Test System.

2. Synthesis and characterization

2.1. Synthesis of precursor materials and bis-bidentate ligands:

1,10-phenanthroline-5,6-dione (phendione) and dimmer precursor complex of $[\text{Ir}(\text{ppy})_2\text{Cl}]_2$ were synthesized according to the literature reports [3, 4]. The bis(4-(2-(p-tolyl)-1H-imidazo[4,5-f][1,10]phenanthroline-1-yl)phenyl)methane (L1) and bis(4-(2-(pyridine-3-yl)-1H-imidazo[4,5-f][1,10]phenanthroline-1-yl)phenyl)methane (L2) ligands were synthesized, characterized, and approved according to our previous works [5, 6]. The mononuclear complex (Ir3) corresponding to IrL2 was synthesized according to the literature [7].

2.2. General procedure for synthesis of binuclear complexes, IrL1 and IrL2, $[(\text{Ir}(\text{ppy})_2)_2(\text{L1, 2})](\text{ClO}_4)_2$:

A mixture of 0.019 mmol of $[\text{Ir}(\text{ppy})_2\text{Cl}]_2$, 0.019 mmol of bis-bidentate ligands (L1 and L2) and 5 ml ethylene glycol was degassed by N_2 for 30 min and heated under N_2 atmosphere at 150°C for 18.0 h to give a clear yellow-orange solution. The mixture was cooled to room temperature and then, a saturated aqueous solution of NaClO_4 was added drop by drop to it until gave a pale orange-yellow precipitate and then washed several times with distilled water to remove traces of salts. The product was purified by column chromatography on silica with acetonitrile as an eluent. After the mainly yellow-orange band was collected, the solvent was removed by rotary evaporation and the solid were obtained and dried under vacuum.

CAUTION: Perchlorate salts of metal complexes with organic ligands are potentially explosive, and only small amounts of the material should be prepared and handled with great care!

$[(\text{Ir}(\text{ppy})_2)_2(\text{L1})](\text{ClO}_4)_2 \cdot 2(\text{H}_2\text{O})$ (IrL1). Yield: 62%. IR (KBr): $\tilde{\nu} = 3035$ (C-H aromatic), 2924 (C-H aliphatic), 1606 (C=C), 1092 (Cl-O) cm^{-1} . ^1H NMR (400 MHz, D6-DMSO): 9.32 (d, 2H), 8.22-8.36 (m, 6H), 8.17 (m, 2H), 8.05 (d, 2H), 7.86-8.03 (m, 8H), 7.73-7.86 (m, 4H), 7.68 (d, 2H), 7.57-7.67 (m, 4H), 7.41-7.55 (m, 10H), 6.85-7.22 (m, 16H), 6.17-6.42 (dd, 4H), 4.41 (s, 2H, CH_2 spacer), 2.10 (s, 6H, Hydrogens of methyl groups on C2 imidazole moiety). ^{13}C NMR (101 MHz, DMSO) δ 167.36, 165.67, 154.37, 151.01, 150.54, 149.78, 149.55, 148.66, 144.99, 144.65, 144.43, 140.25, 139.24, 136.58, 135.39, 132.92, 131.65, 130.77, 129.98, 129.54, 129.46, 128.22, 127.35, 126.71, 126.48, 125.58, 124.41, 124.24, 122.88, 122.47, 120.49, 21.18 (Carbon of methyl groups). Anal. calcd. For $\text{C}_{97}\text{H}_{72}\text{Cl}_2\text{Ir}_2\text{N}_{12}\text{O}_{10}$ (%): C, 57.65; H, 3.59; N, 8.32. Found (%): C, 57.69; H, 3.61; N, 8.33. MS (m/z): 895 ($[\text{IrL1}-2\text{ClO}_4]^{+2}$).

$[(\text{Ir}(\text{ppy})_2)_2(\text{L2})](\text{ClO}_4)_2 \cdot 3(\text{H}_2\text{O})$ (IrL2). Yield: 61%. IR (KBr): $\tilde{\nu} = 3040$ (C-H aromatic), 2920 (C-H aliphatic), 1639 (C=N), 1604 (C=C), 1093 (Cl-O) cm^{-1} . ^1H NMR (400 MHz, D6-DMSO): 9.35 (d, 2H), 8.80 (s, 2H), 8.55 (d, 2H), 8.23-8.35 (m, 6H), 8.16-8.22 (m, 2H), 8.09 (d, 2H), 7.86-8.02 (m, 10H), 7.84 (d, 4H), 7.73 (m, 2H), 7.65 (t, 4H), 7.45-7.59 (m, 6H), 7.42 (m, 2H), 6.89-7.13 (m, 12H), 6.29 (dd, 4H), 4.40 (s, 2H, CH_2 spacer). ^{13}C NMR (101 MHz, DMSO) δ 166.83, 151.42, 150.52, 150.42, 149.98, 149.37, 149.05, 148.51, 144.74, 144.28, 144.05, 143.94, 138.76, 136.57, 136.20, 134.34, 132.46, 131.16, 130.28, 129.67, 128.98, 128.01, 127.92, 126.51, 125.97, 125.41, 125.09, 123.88, 123.75, 123.46, 122.39, 121.93, 119.99, 114.20, 113.10, 110.82, 107.95. Anal. calcd. For $\text{C}_{93}\text{H}_{68}\text{Cl}_2\text{Ir}_2\text{N}_{14}\text{O}_{11}$ (%): C, 55.49; H, 3.41; N, 9.74. Found (%): C, 55.53; H, 3.43; N, 9.76. MS (m/z): 882 ($[\text{IrL1}-2\text{ClO}_4]^{+2}$).

3. FT-IR Spectra

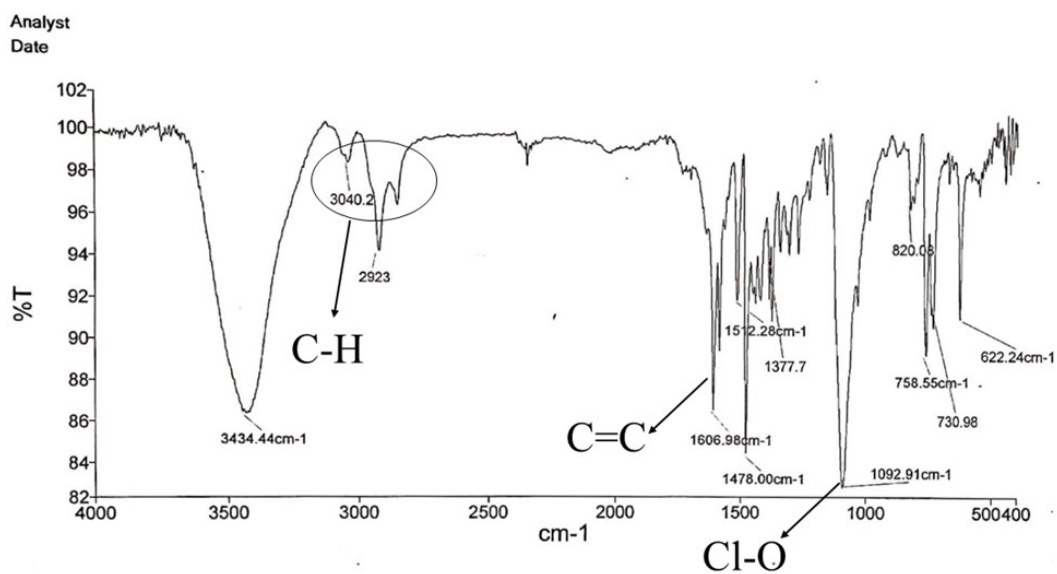


Figure S1. FT-IR spectrum of IrL1 complex in KBr

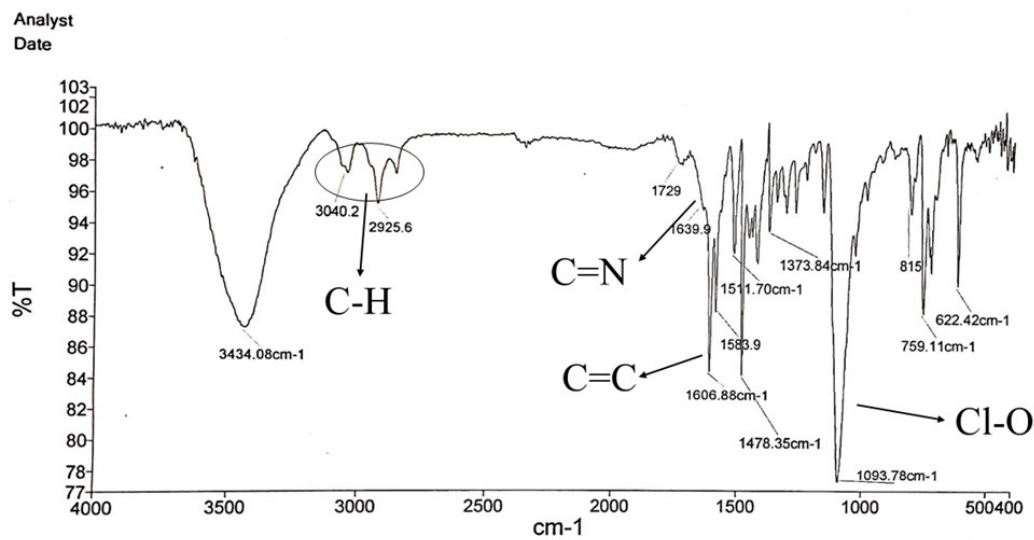


Figure S2. FT-IR spectrum of IrL2 complex in KBr

4. NMR spectra

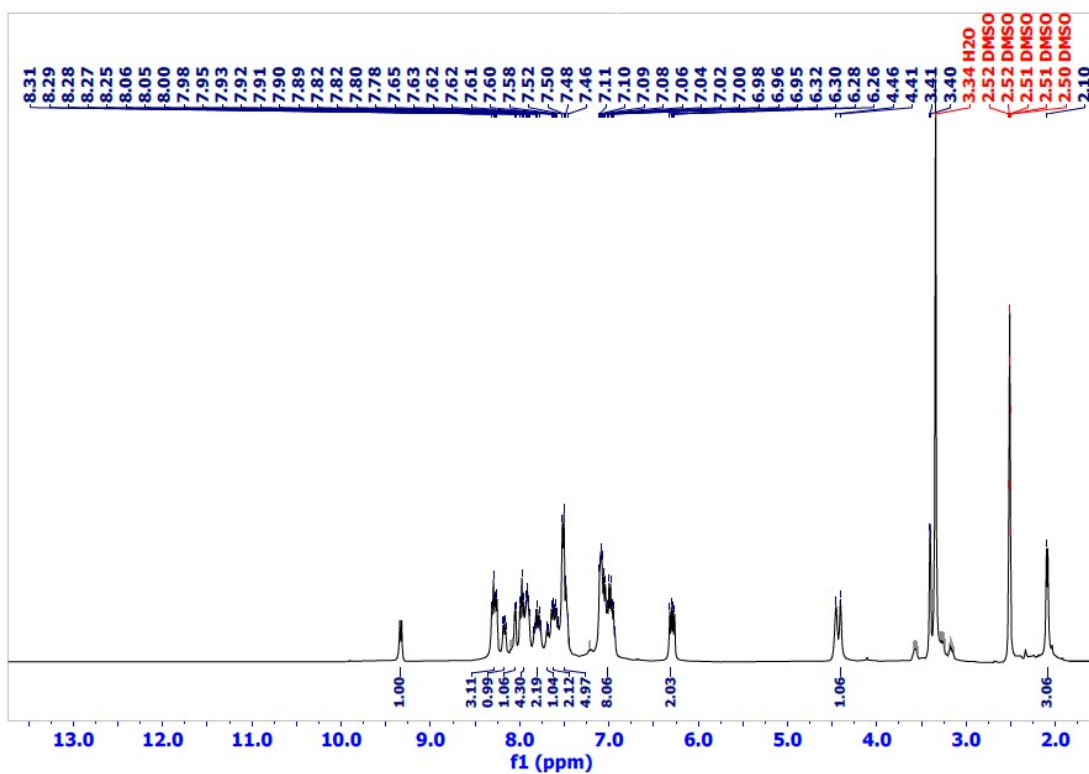


Figure S3. ¹H NMR of IrL1 in D₆-DMSO

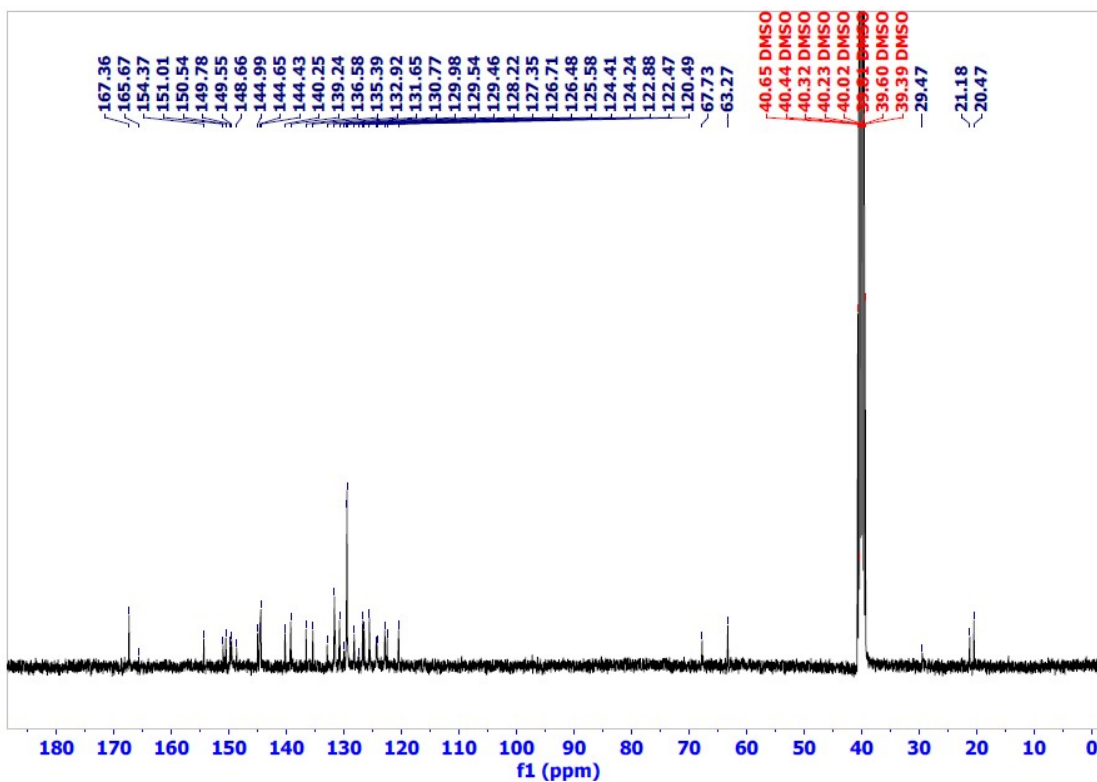


Figure S4. ¹³C NMR of IrL1 in D₆-DMSO.

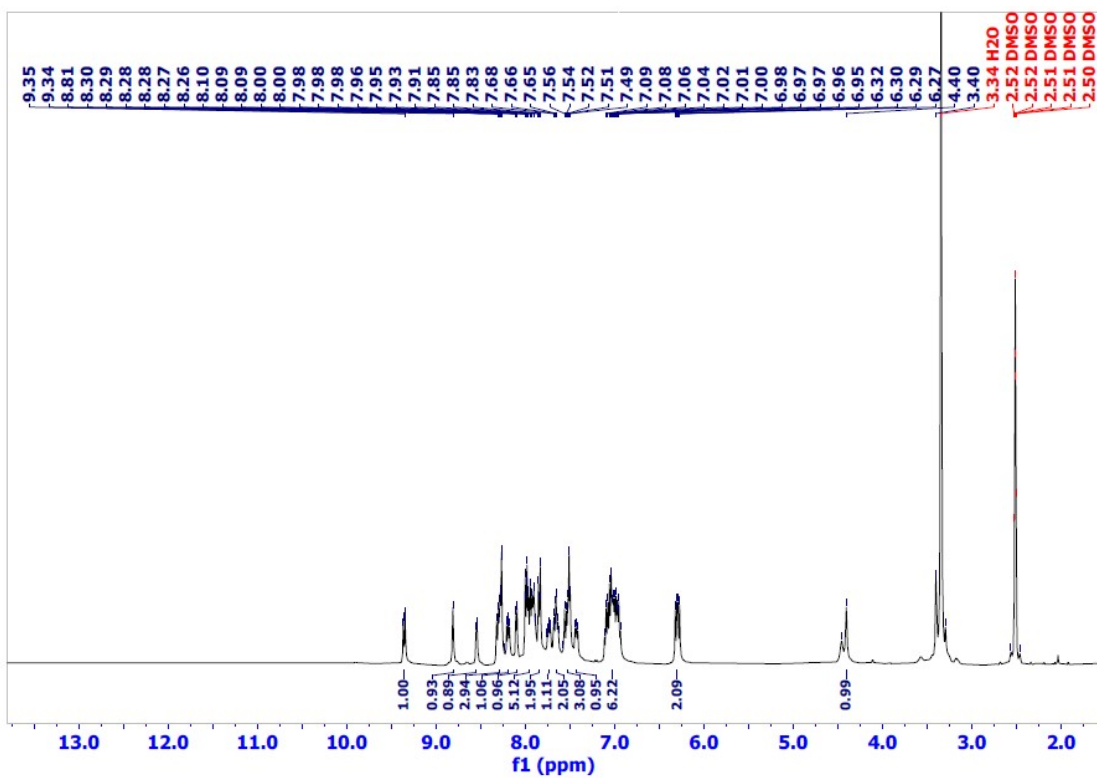


Figure S5. ¹H NMR of IrL2 in D₆-DMSO

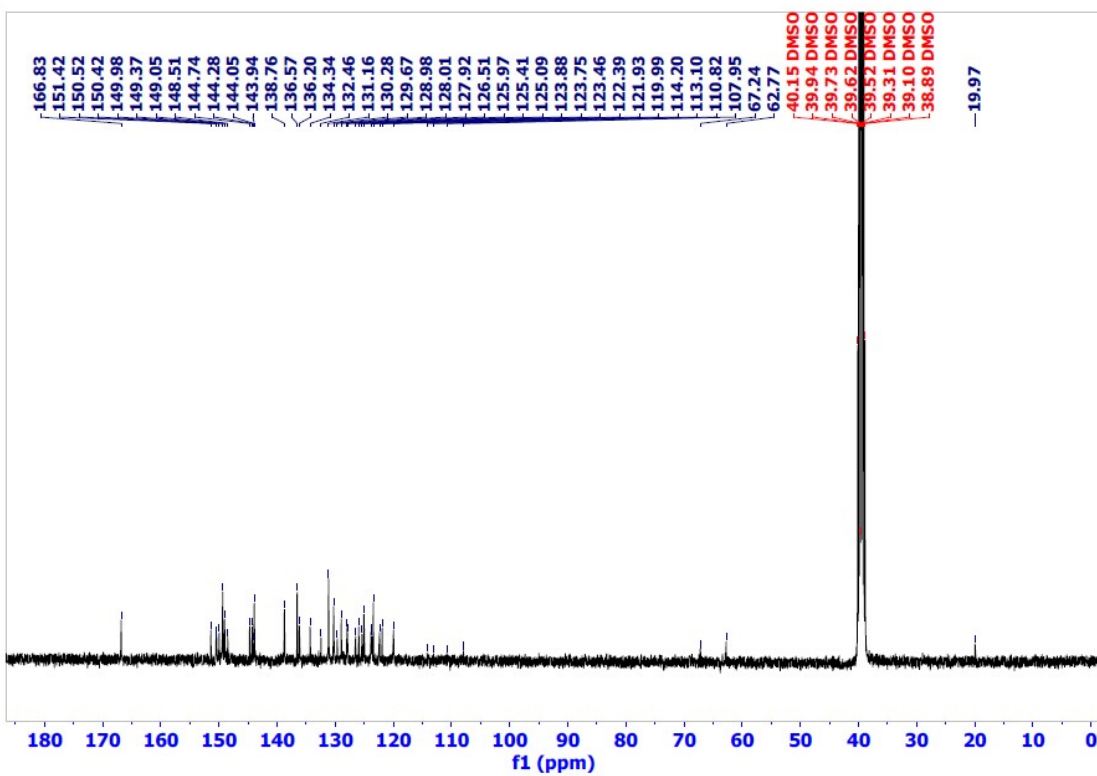


Figure S6. ¹³C NMR of IrL2 in D₆-DMSO

5. Mass Spectra

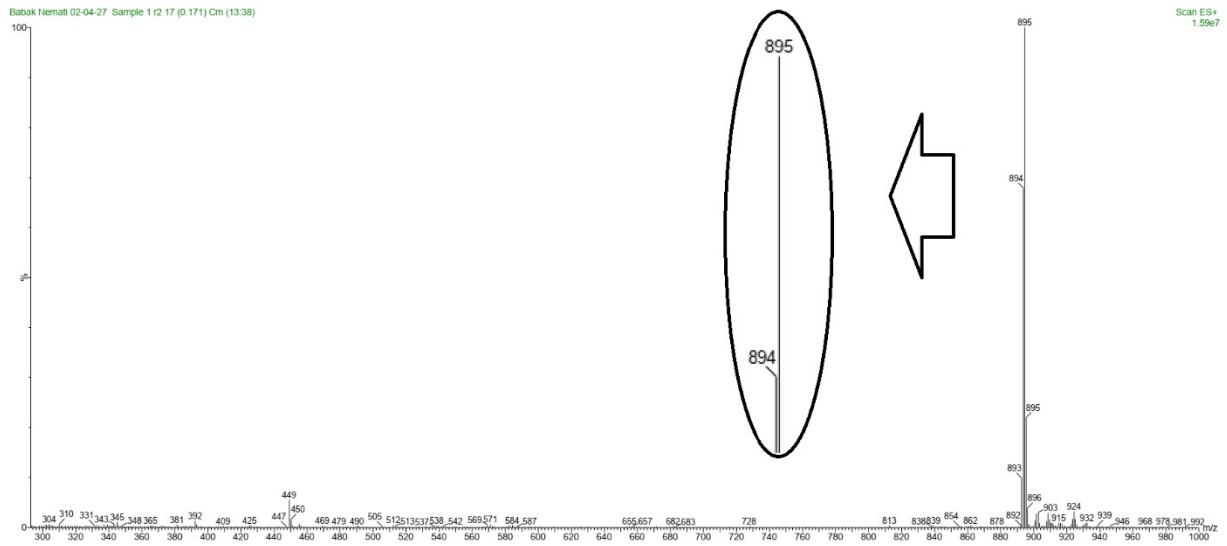


Figure S7. Mass spectrum of Irl1 complex

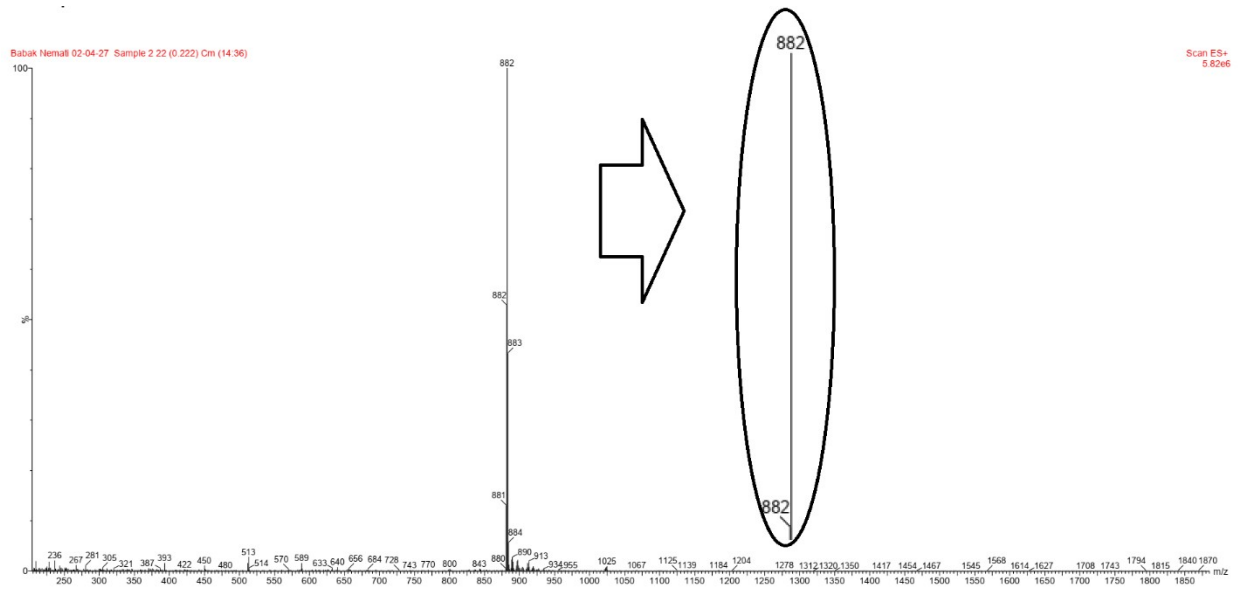
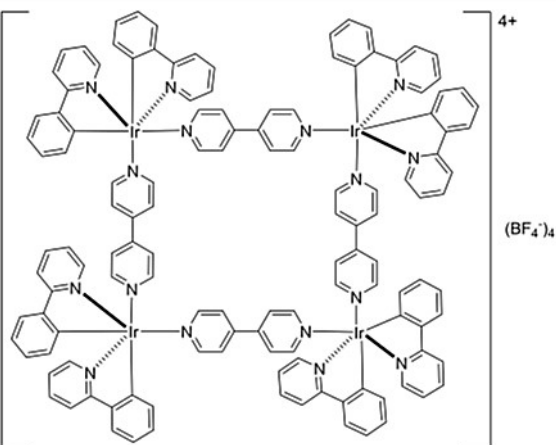
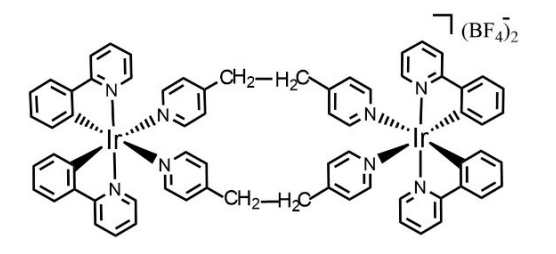
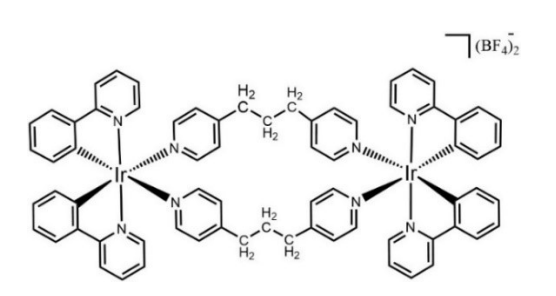
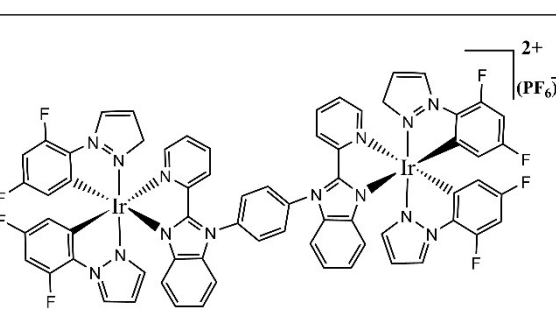
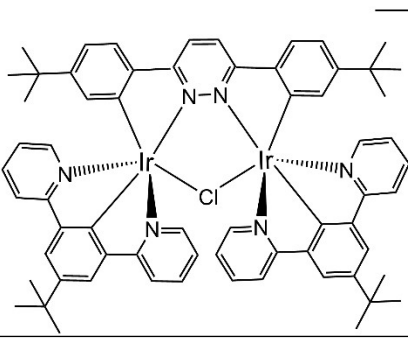
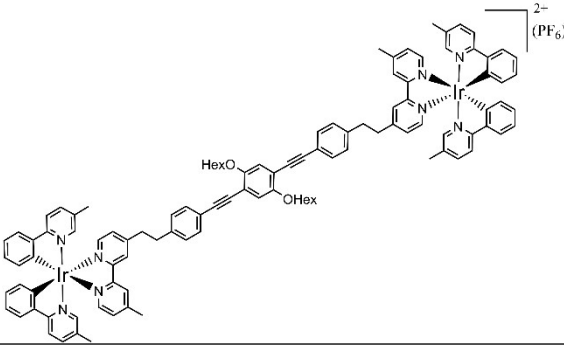
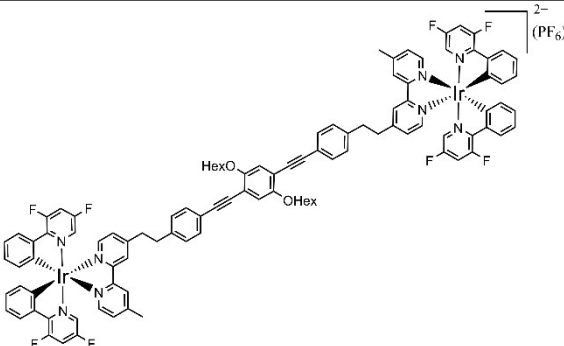
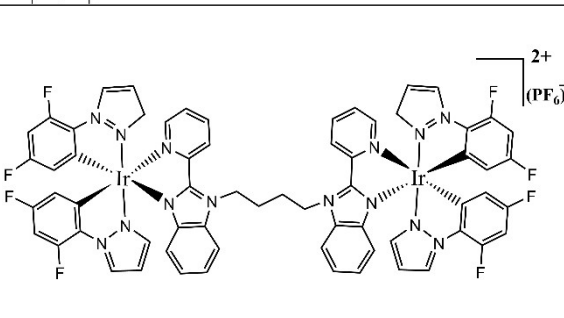
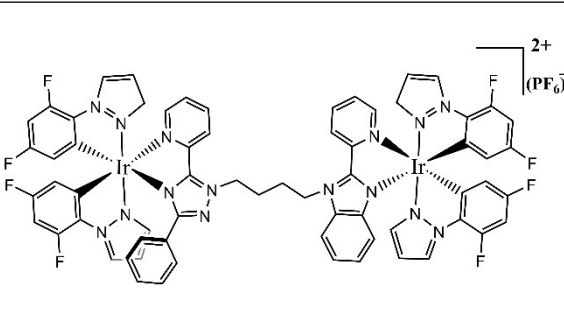


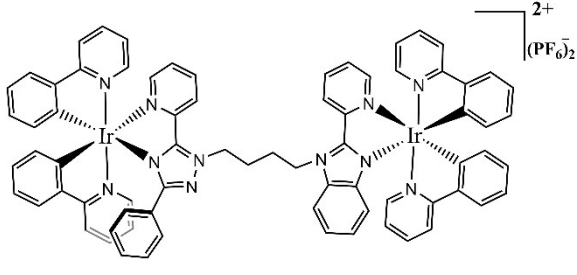
Figure S8. Mass spectrum of Irl2 complex

6. Tables

Table S1. EL properties of light-emitting electrochemical cell based on binuclear Iridium (III) complexes

Binuclear Ir(III) emitter structure	PLQY (%)	Cell configuration	$\lambda_{\text{max}}^{\text{EL}}$ (nm)	L_{max} (cd.m ⁻²)	Efficacy (cd.A ⁻¹)	Ref.
	18	ITO/ PEDOT:PSS/ Ir-ITMC/ Ag	684	41.3 (about 6 V)	-	8
	29	ITO/ PEDOT:PSS/ Ir-ITMC/ Ag	692	1.8 (about 4 V)	-	8
	74	ITO/ PEDOT:PSS/ Ir-ITMC/ Ag	560	123.3 (about 6 V)	-	8
	72.1	ITO/PEDOT:PSS/Ir-ITm:BMIM/FP6 (molar ratio 1 : 0.144)	550	5996 (10 V)	18.7	9

	33	ITO/PEDOT:PSS/Ir-ITMC/Al	588	124	1.2	10
	0.9	ITO/PEDOT:PSS/Ir-Tm:TBuAPF6 (molar ratio 1 : 1)/Al	596	10 >	-	11
	0.7	ITO/PEDOT:PSS/Ir-Tm:TBuAPF6 (molar ratio 1 : 1)/Al	540	10 >	-	11
	57	ITO/PEDOT:PSS/Ir(III) complexes:BMIM/Al	518	6475 (about 12.5 V)	31.2	12
	50	ITO/PEDOT:PSS/Ir(III) complexes:BMIM/Al	517	3368 (about 12.5 V)	40	12

	31	ITO/PEDOT:PSS/Ir(III) complexes:BMIM	580	2558 (About 12.5 V)	38.4	12
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7. References

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