Supplementary Materials

Unexpected ortho C-H bond activation in coordinated 7,8-benzoquinoline: Synthesis and characterisation of a heteroleptic Ir(III) 7,8-benzoquinoline complex

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Contents:

1. Experimental:

1.1 Materials:

The $IrCl_3.3H_2O$, pyridine-2-aldoxime, 7,8-benzoquinoline, 2-(2,4-difuorophenyl)pyridine were purchased from Sigma-Aldrich and used without further purification. All the solvents were dried by reported methods[1] and distilled prior to use. The dichloro bridged dimers $[Ir(benzq)_2(\mu\text{-}Cl)_2Ir(benzq)_2]$ and $[Ir(F_2ppy)_2(\mu\text{-}Cl)_2Ir(F_2ppy)_2]$ were prepared from $IrCl_3.3H_2O$ by 7,8-benzoquinoline (benzq) and 2(2,4-difluorophenyl)pyridine (F_2ppy) by using the method described by Nonoyama.[2]

1.2 Physical measurement

The infrared spectrum was recorded in ATR mode on a Thermo Scientific Nicolet iS5 FT-IR spectrophotometer. An Agilent Carry 100 UV-Vis spectrophotometer was used to collect the electronic spectra. Cyclic voltammetry measurements were performed with the help of a CH Instruments model CHI760E with acetonitrile solutions of the complexes containing $[(n\text{-}C_4H_9)_4N]ClO_4$ (TBAP) as supporting electrolyte. The three electrode measurements were carried out at 298K under a dinitrogen atmosphere with a platinum disk working electrode, a platinum wire auxiliary electrode and a saturated calomel reference electrode (SCE). Elemental analyses were carried out on a Thermo Finnigan Flash EA1112 series elemental analyser. ^1H NMR data were recorded on a Bruker 400 MHz spectrometer using DMSO-d_6 as solvent. A Thermo Fisher liquid chromatograph mass spectrometer was used for determination of mass of all the complexes.

1.3 Crystal structure determination

X-ray quality single crystal of $[Ir(benzq\text{-}\kappa N, \kappa C^{10})(benzq\text{-}\kappa C^2)(Hpyrald)(Cl)]$ (3) was obtained from slow evaporation of dichoromethane-hexane mixture in room temperature. Data was collected on a Bruker SMART APEX CCD single crystal diffractometer, equipped with a graphite monochromator and a MoKα fine-focus sealed tube (λ = 0.71073 Å) was used to determine the unit cell parameters and to collect the data at 298K. SMART software was used for data acquisition and SAINT-plus software was used for data extraction[3]. The absorption corrections were performed with the help of the SADABS program.[4] The structures were solved by direct method and refined on F^2 by full matrix least-squares procedures. All the non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were included at idealized positions using a riding model. The SHELX-97 programs [5] accessible in the WinGX software suite [6] were used for structure solution and refinement. The ORTEP-3 package[6] was used for molecular graphics. Crystallographic data was deposited with Cambridge Crystallographic Data Centre with CCDC No. 2050870 for $[Ir(benzq\text{-}\kappa N, \kappa C^{10})(benzq\text{-}\kappa C^2)(Hpyrald)(Cl)]$ **(3)** Selected crystal and refinement data are listed in **Table S1**.

1.4 Computational Methods

The metal complex [Ir(benzq-κN, κC^{10})(benzq-κC^{2})(Hpyrald)(Cl)](2) was optimized using the Gaussian 09 Rev D.01 programme[7] in gas phase at the B3LYP-D3 level of theory.[8] The basis set used for iridium was LanL2DZ [9], whereas carbons, hydrogens and nitrogens were treated with 6-31g** basis set [10,11]. Stationary states were authenticated through Hessian indices examination. The time dependent density functional theory (TD-DFT) calculation were performed on the gas phase optimized geometry for all complexes using SMD continuum solvation model developed by Truhlar and Cramer [12].

1.5 Synthesis of [Ir(benzq)$_2$(pyrald)](2) and [Ir(benzq-κN, κC^{10})(benzq-κC^{2})(Hpyrald)(Cl)] (3)

In a100ml round bottom flask pyridine-2-aldoxime (52 mg, 0.42mmol) and triethylamine (0.06 ml, 0.42 mmol) were taken in 25 ml ethanol. The mixture was thoroughly mixed by stirring and added with [(benzq)$_2$Ir(μ-Cl)$_2$Ir(benzq)$_2$] (benzq=7,8 benzoquinoline) (200 mg, 0.17mmol). The whole mixture was refluxed under N_2 atmosphere for 18 hours at 80°C. The reddish yellow solution thus obtained was dried under vacuum and the solid was purified on a neutral aluminium oxide column. Eluting with dichloromethane resulted a reddish yellow band as [Ir(benzq-κN, κC^{10})(benzq-κC^{2})(Hpyrald)(Cl)] (**3**). Further eluting with dichloromethane and acetone (2:1) produced an yellow coloured fraction as [Ir(benzq)$_2$(pyrald)](**2**). The yields of the complexes were found to be 50 mg (21%) for (2) and 103mg (45%) for (3) respectively. The preparation of complexes (2) and (3) also could be achieved in 2-methoxy ethanol in reflux condition.

Selected IR bands for complex Ir(benzq)$_2$(pyrald)] (2) (ATR, cm^{-1}), (Fig. S2): 1737(m), 1601(s), 1564(m), 1470(s), 1445(m), 1403(m), 1327(s), 1146(s), 1104(w), 831(s), 751(s), 718(s), 676(s), 526(m), 425(m).

Elemental analysis: Anal. Calcd. for $C_{32}H_{22}ClN_4OIr$ (**2**): C, 57.39; H, 3.16; N, 8.37. Found: C, 58.24; H, 3.38; N, 8.50

ESI-MS for complex (2) (Fig. S3) : Theoretical mass for $C_{32}H_{21}N_4OIr$, **[Ir(benzq)$_2$(pyrald)]** (**2**), 670.13; Found for $C_{32}H_{21}N_4OIr$, **[Ir(benzq)$_2$(pyrald)]** (**2**), 670.86.

^{1}H NMR for complex Ir(benzq)$_2$(pyrald)] (2) (400 MHz, DMSO-d$_6$), (**Fig. S4**): δ 8.81 (dd, *J* = 5.4, 1.0 Hz, 1H), 8.54 (ddd, *J* = 8.0, 2.8, 1.0 Hz, 2H), 8.32 (s, 1H), 8.01 (dd, *J* = 5.4, 1.0 Hz, 1H), 7.96 – 7.74 (m, 5H), 7.69 (ddd, *J* = 10.9, 8.5, 3.4 Hz, 2H), 7.50 (d, *J* = 8.1 Hz, 1H), 7.45 (d, *J* = 7.7 Hz, 1H), 7.41 – 7.30 (m, 2H), 7.10 (t, *J* = 7.5 Hz, 1H), 6.98 (t, *J* = 7.5 Hz, 1H), 6.89 (t, *J* = 6.5 Hz, 1H), 6.22 (d, *J* = 6.9 Hz, 1H), 6.05 (d, *J* = 7.0 Hz, 1H).

Selected IR bands for complex (3) (ATR, cm^{-1}) (**Fig. S5**): 1603(s), 1497(s), 1470(s), 1422(w), 1327(s), 127(w), 1125(s), 1084(w), 835(s), 752(s), 720(s), 676(s), 611(s), 562(s), 478(s), 434(s).

Elemental analysis: Anal. Calcd. for $C_{32}H_{22}ClN_4OIr$ (**3**): C, 54.42; H, 3.14; N, 7.93. Found: C, 54.96; H, 3.20; N, 8.06

ESI-MS for complex (3) (Fig. S6) : Theoretical mass for $C_{32}H_{22}N_4OClIr$, [Ir^{III}(benzq-κN, κC^{10})(benzq-κC^2)(Hpyrald)(Cl)] (**3**), 706.11; Found for $C_{32}H_{22}N_4OClIr$, [Ir^{III}(benzq-κN, κC^{10})(benzq-κC^2)(Hpyrald)(Cl)] **(3)**, 706.83.

^{1}H NMR for complex (3) (400 MHz, DMSO-d_6), (Fig. S7): δ 9.66 (d, J = 8.5 Hz, 1H), 8.99 (s, 1H), 8.64 (d, J = 5.3 Hz, 1H), 8.53 (s, 1H), 8.26 (d, J = 8.0 Hz, 1H), 8.14 (d, J = 8.1 Hz, 1H), 8.03 (t, J = 8.1 Hz, 2H), 7.90 (dd, J = 14.0, 8.3 Hz, 4H), 7.73 (dt, J = 16.9, 8.7 Hz, 5H), 7.50 – 7.36 (m, 1H), 7.31 (d, J = 5.5 Hz, 1H), 7.02 (d, J = 8.6 Hz, 1H), 6.94 (t, J = 6.1 Hz, 1H).

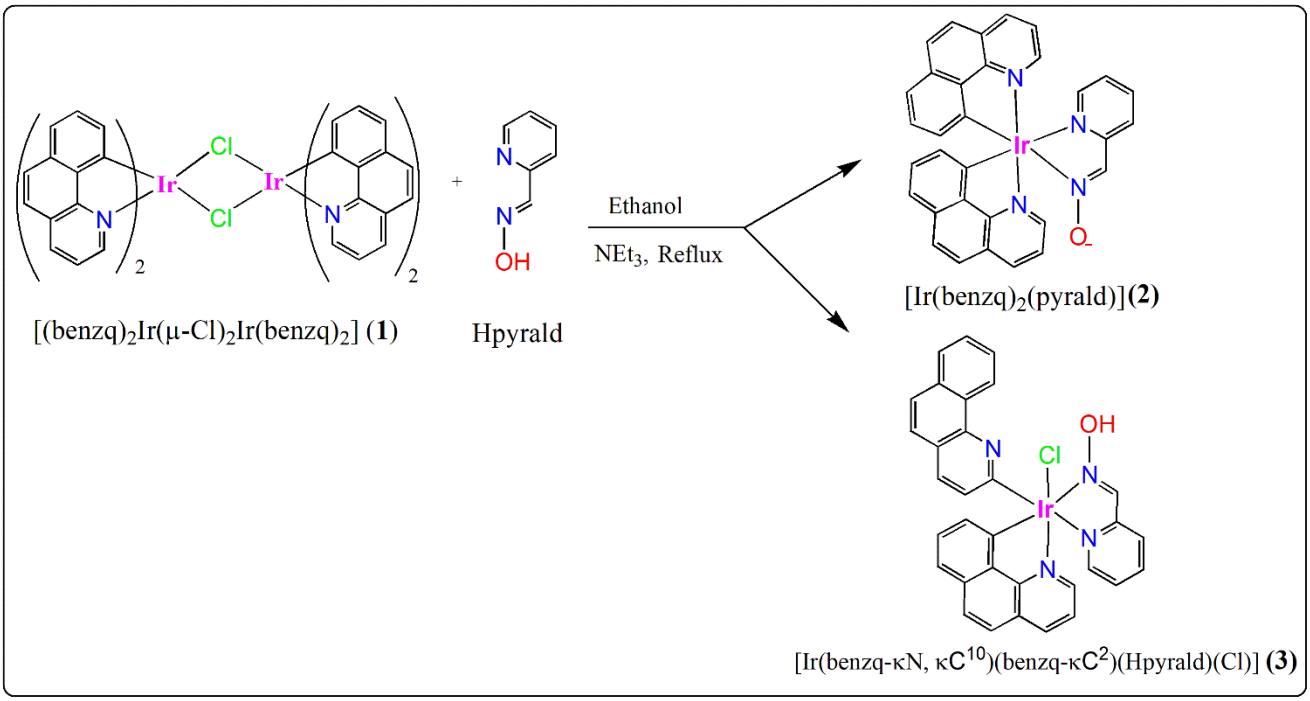

Fig. S1: Synthetic scheme of complex (**2**) and (**3**)

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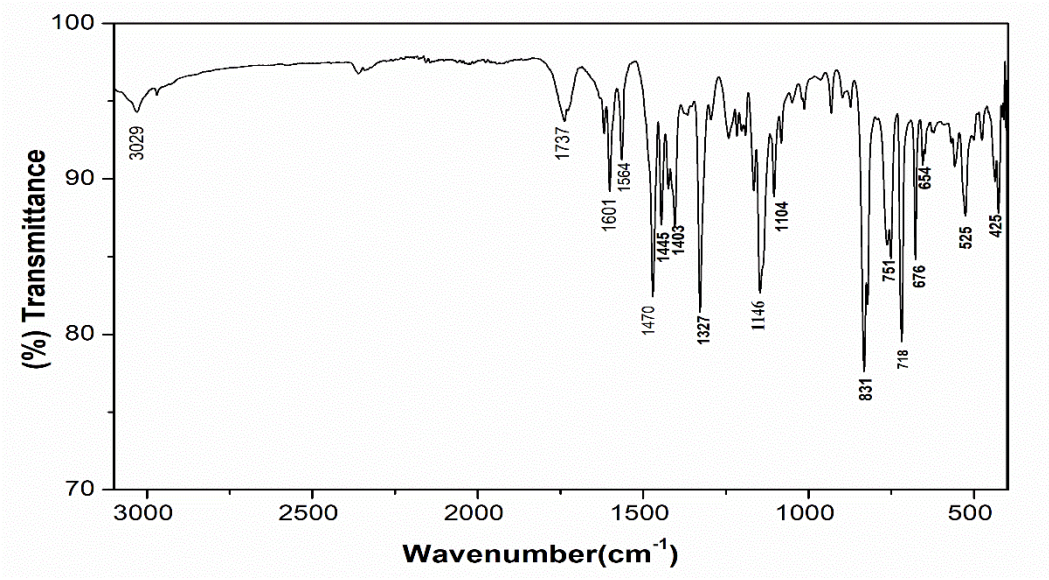


Fig. S2: IR spectrum of [Ir(benzq)$_2$(pyrald)] **(2)** in ATR mode

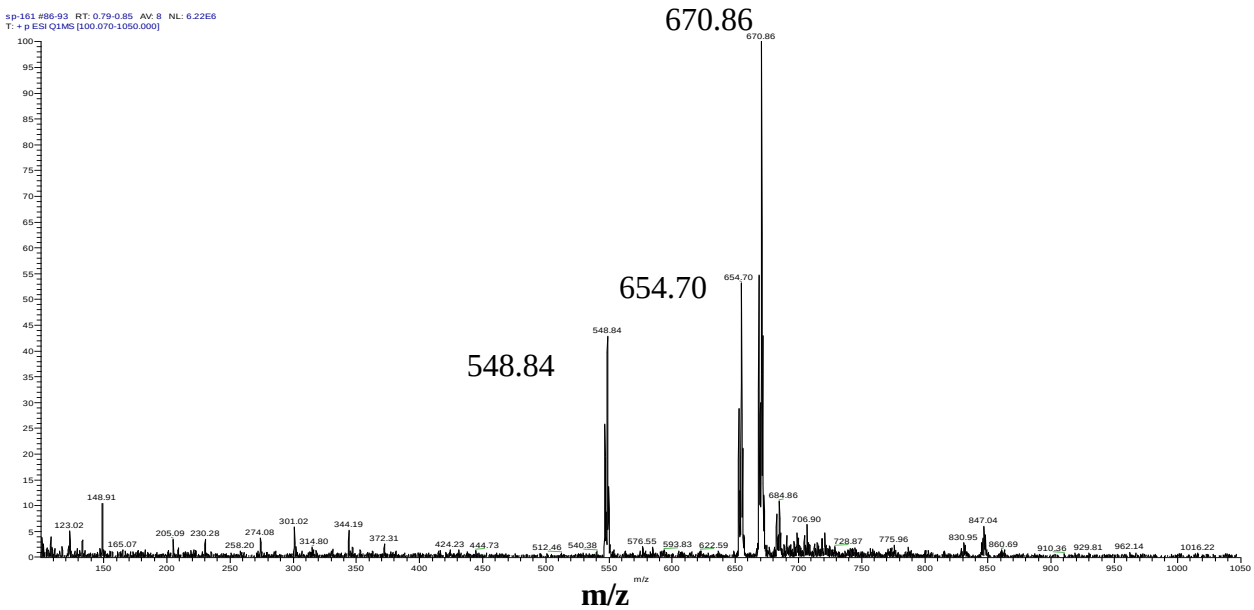


Fig. S3: ESI Mass spectrum of [Ir(benzq)$_2$(pyrald)] **(2)**

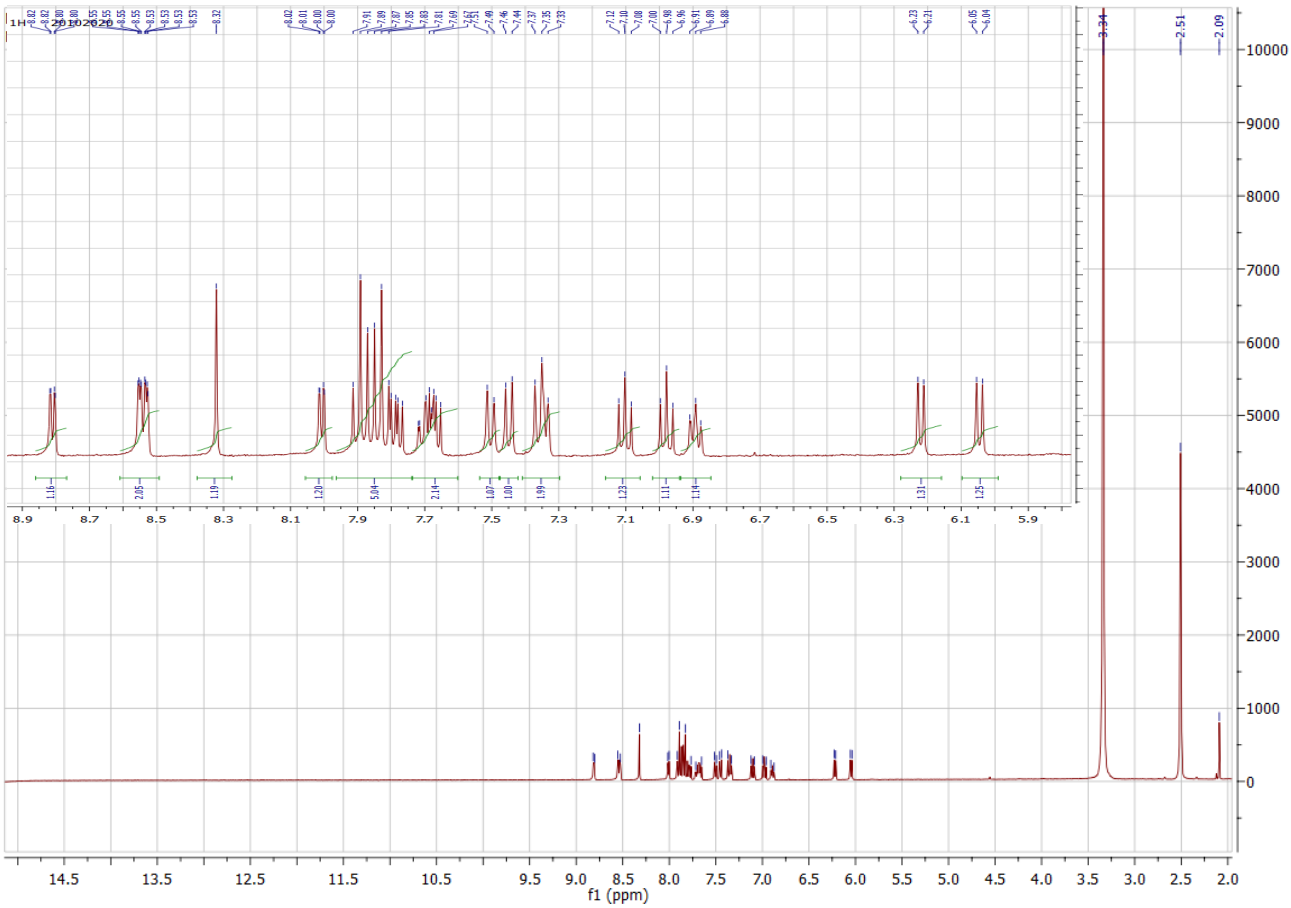


Fig. S4: ^{1}H NMR spectrum of [Ir(benzq)$_2$(pyrald)] **(2)**in DMSO-d$_6$ along with the enlarged part of 5.9 to 8.9 ppm

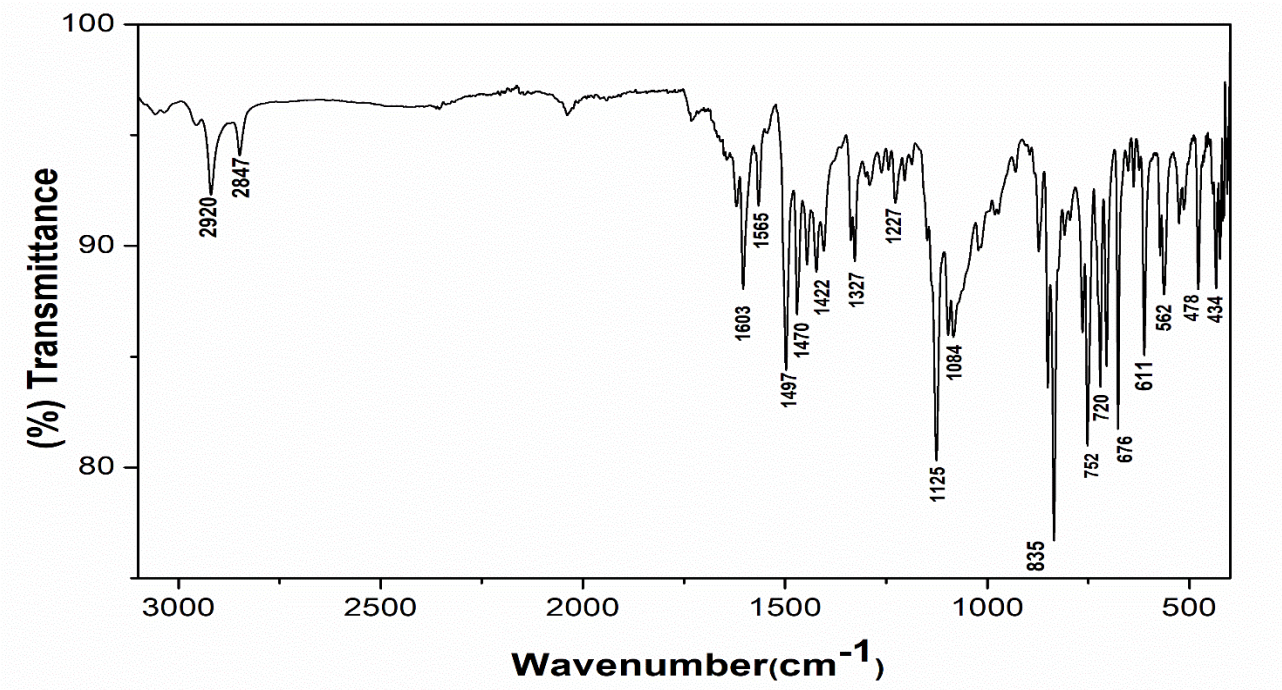


Fig. S5: IR spectrum of [Ir(benzq-κN, κC^{10})(benzq-κC^{2})(Hpyrald)(Cl)] **(3)** in ATR mode

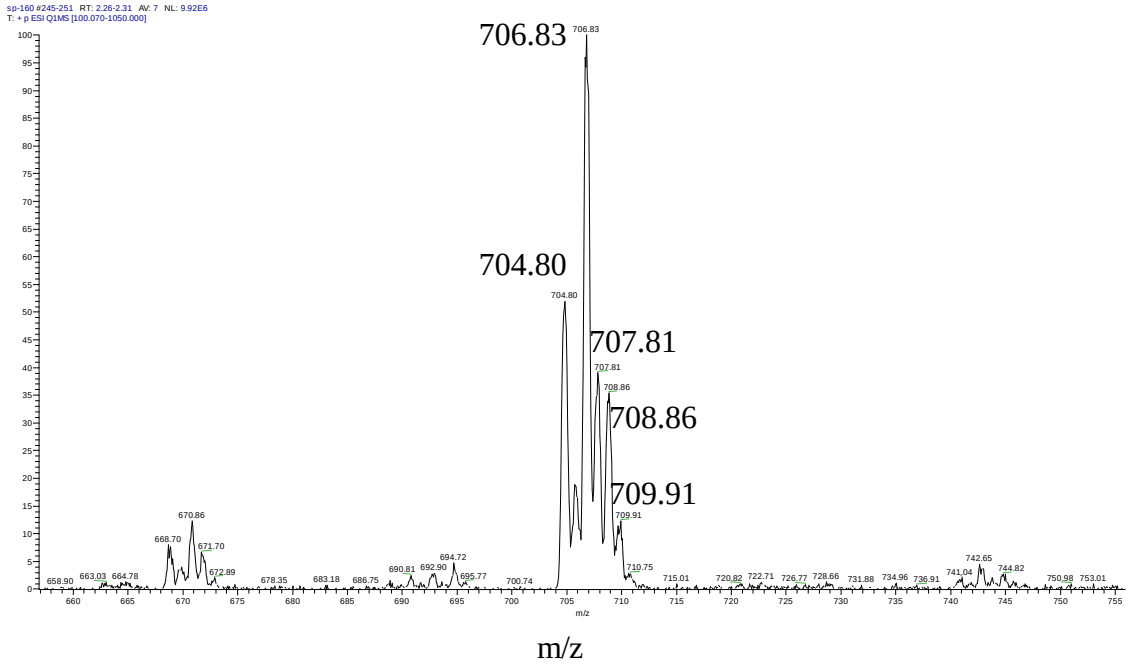


Fig. S6: ESI Mass spectrum of [Ir(benzq-κN, κC^{10})(benzq-κC^{2})(Hpyrald)(Cl)] **(3)**

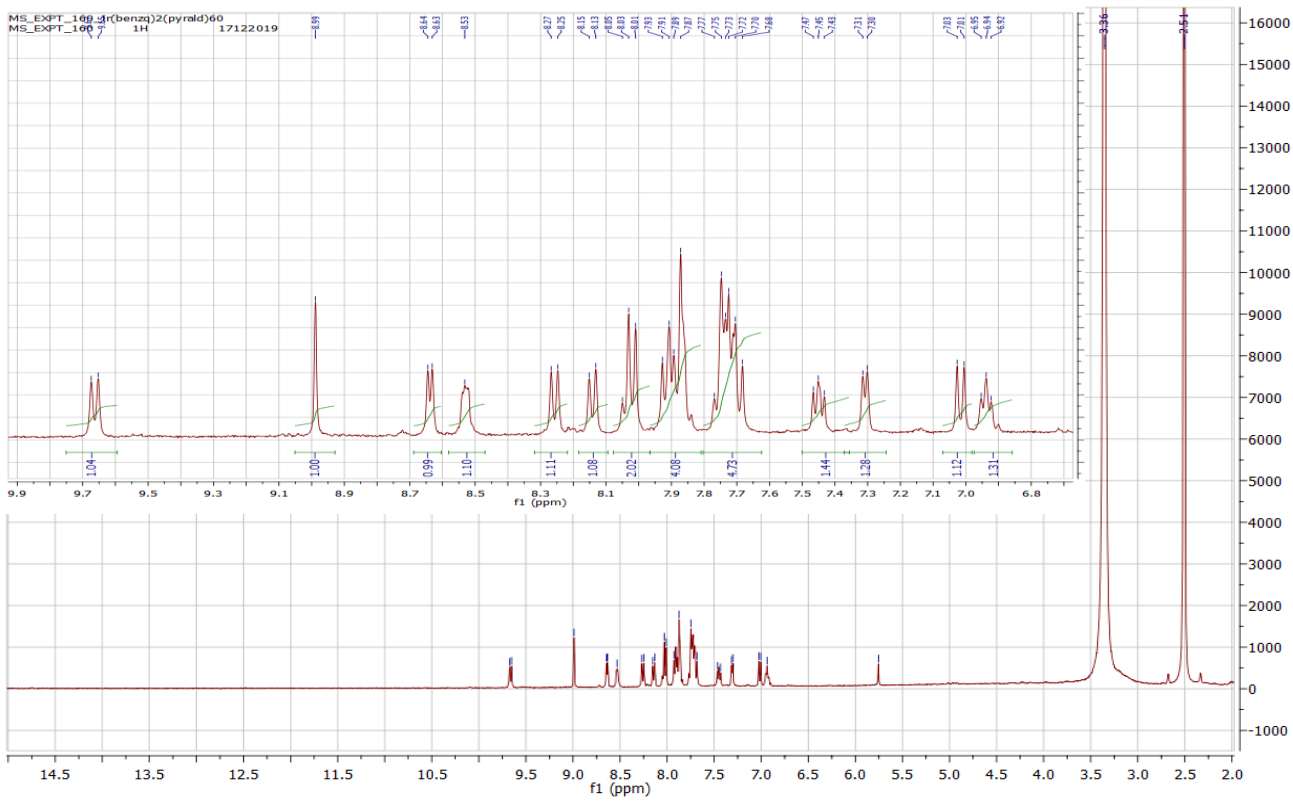


Fig. S7: : ^{1}H NMR spectrum of [Ir(benzq-κN, κC^{10})(benzq-κC^{2})(Hpyrald)(Cl)] **(3)** in DMSO-d$_6$ along with the enlarged part of 6.6 to 9.9 ppm

Table S1: Crystallographic data for complex [Ir(benzq- κN, κC^{10})(benzq-κC^{2})(Hpyrald)(Cl)] (**3**)

	[Ir(benzq- κN, κC^{10})(benzq-κC^{2})(Hpyrald)(Cl)] (3)
Empirical formula	C_{32} H_{22} Cl Ir N4 O
Formula wt	706.21
Crystal system	Monoclinic
Space group	$P2_1/n$
a (Å)	9.2148(14)
b (Å)	28.241(5)
c (Å)	10.6998(14)
α (°)	90.0
β (°)	109.745(4)
γ (°)	90.0
V(A^3)	2620.8(7)
Z	4
ρ(Mg m^{-3})	1.790
μ(mm^{-1})	5.231
Reflection collected	78829
Reflection unique	5389
Parameters	352
R1 (obs)	0.0336
wR2	0.0551
GOF	1.026
Largest peak	1.00
Deepest Hole	-0.7780

Table S2: Selected bond distances and angles of [Ir(benzq- κN, κC^{10})(benzq-κC^{2})(Hpyrald)(Cl)] (**3**)

Bond length (Å)			
Ir(1)-Cl(1)	2.3683(12)	Ir(1)-N(4)	2.118(4)
Ir(1)-N(1)	2.043(3)	Ir(1)-C(14)	2.023(5)
Ir(1)-N(3)	2.124(4)	Ir(1)-C(11)	2.031(5)
Bond angles (°)			
C(14)-Ir(1)-C(11)	90.72(19)	C(11)-Ir(1)-N(4)	171.72(16)
C(14)-Ir(1)-N(4)	96.09(18)	N(1)-Ir(1)-N(4)	93.69(14)
C(14)-Ir(1)-N(3)	173.36(19)	N(1)-Ir(1)-Cl(1)	173.44(10)
C(11)-Ir(1)-N(3)	95.63(18)	N(4)-Ir(1)-N(3)	77.42(16)

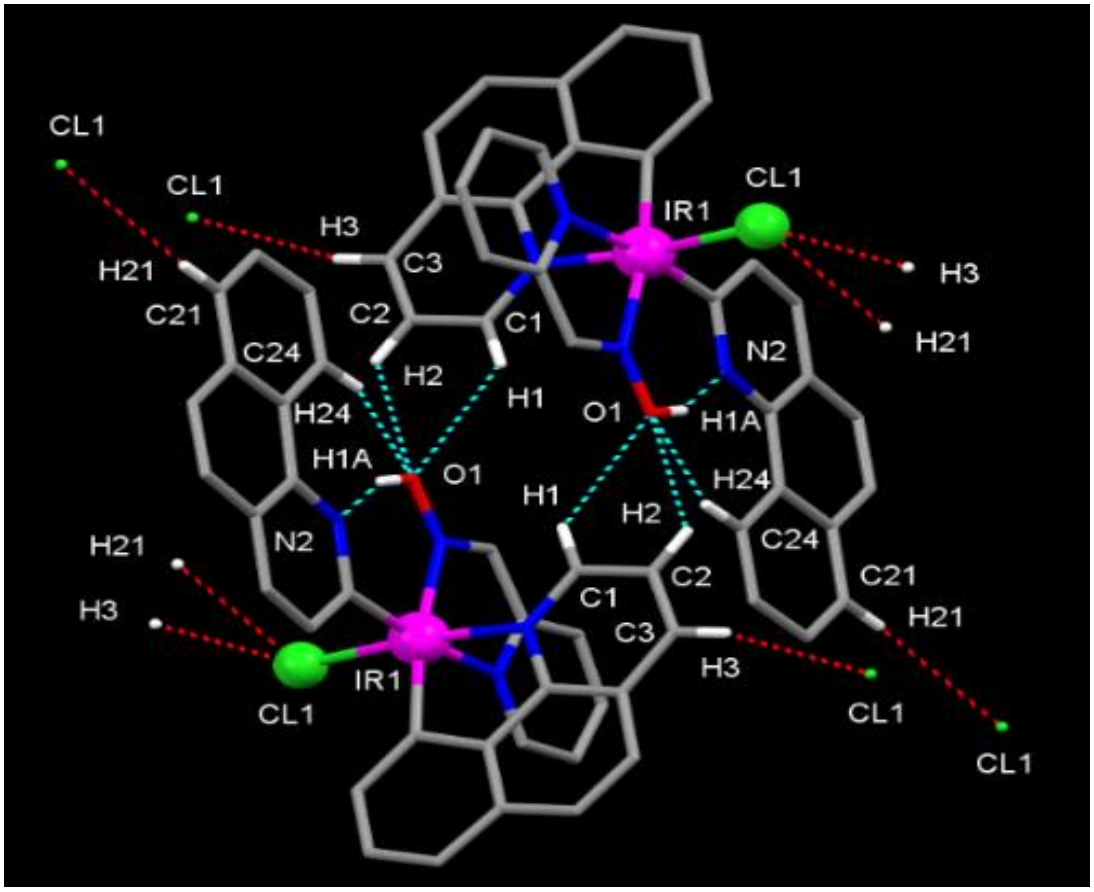
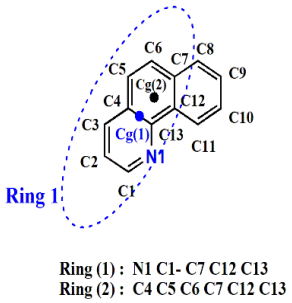


Fig. S8: The hydrogen bonded dimer of [Ir(benzq- κN, κC^{10})(benzq-κC^{2})(Hpyrald)(Cl)] (**3**) with different types of hydrogen bonds.

Table: S3: List of hydrogen bonds and C-H-π interactions in [Ir(benzq-κN, κC[10])(benzq-κC[2])(Hpyrald)(Cl)] (**3**)

D-H….A	D-H (Å)	H…..A (Å)	D…..A (Å)	D-H….A (°)
O1-H1A…N2	0.82	1.84	2.609(5)	157
C24-H24…O1	0.93	2.32	3.221(7)	160
C1-H1…..O1[i]	0.93	2.56	3.204(6)	127
C2-H2….O2[i]	0.93	2.675	3.259	121.45
C3-H3….*Cl*1[ii]	0.93	2.77	3.677(5)	165
C21-H21…*Cl*1 [iii]	0.93	2.78	3.647(8)	155
C29-H29…Cg1[iv]	0.93	2.59	3.507(3)	168
C29-H29…Cg2[iv]	0.93	2.65	3.493(8)	151



Symmetry codes: (i) 1-x, -y, -z (ii) x, y, 1+z (iii) 2-x, -y, 1-z (iv) -1+x, y, z
Cg1 = N1/C1-C7, C12, C13 Cg2= C4-C7, C12, C13

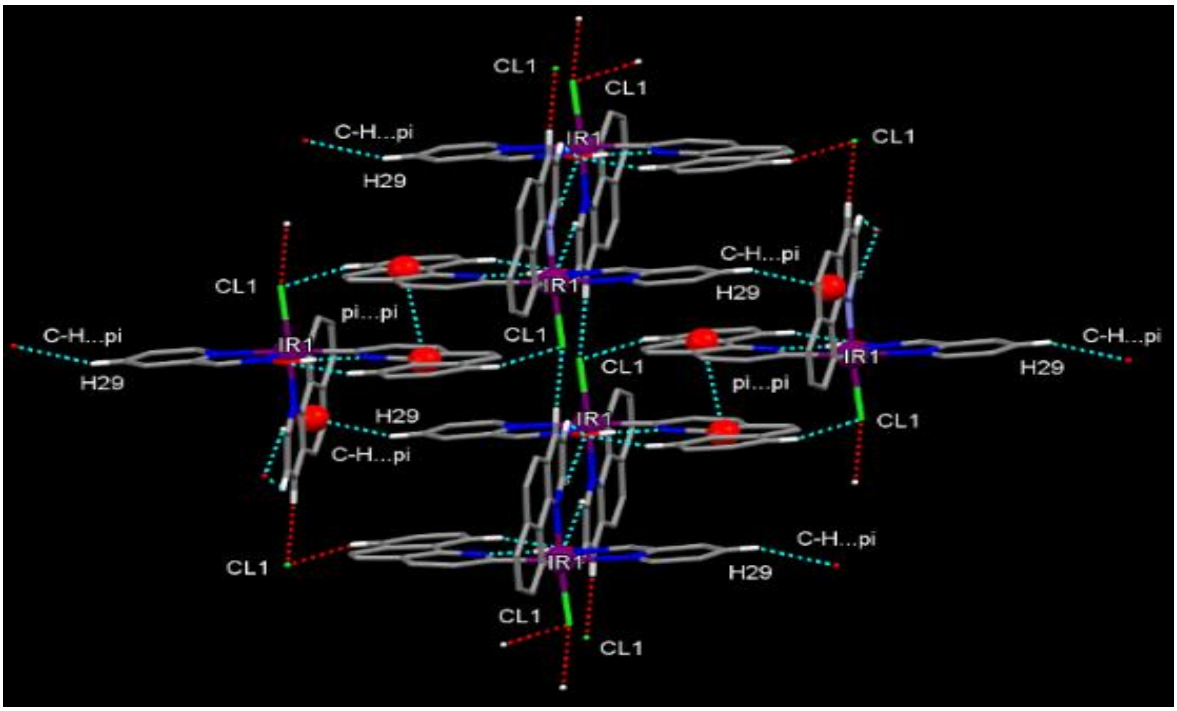
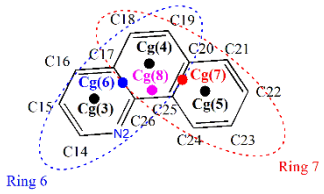


Fig. S9: The π…π and C-H…π interactions in [Ir(benzq-κN, κC[10])(benzq-κC[2])(Hpyrald)(Cl)] (**3**) (red spheres depict centroids)

Table: S4: List of Intermolecular stacking parameters

Centroids	$d_{\pi-\pi}$ (Å)	Cg-Cg distance	Slippage distance (Å)	α/ °	β/°	γ/°
Cg7-Cg8^{v}	3.4895(11)	3.547(2)	0.635	1.88(14)	10.3	10.3
Cg8-Cg5^{v}	3.4857(12)	3.541(3)	0.639	2.7(2)	10.4	9.9
Cg8-Cg7^{v}	3.4893(11)	3.546(2)	0.633	1.88(14)	10.3	10.3
Cg7-Cg7^{v}	3.5279(12)	3.624(3)	0.829	0.00(17)	13.2	13.2
Cg6-Cg5^{v}	3.4768(12)	3.512(3)	0.462	3.3(2)	7.6	8.7
Cg4-Cg5^{v}	3.527(1)	3.622(3)	0.868	1.8(3)	13.9	12.4



Ring (3) : N2 C14 C15 C16 C17 C26
Ring (4) : C17 C18 C19 C20 C25 C26
Ring(5) : C20-C25
Ring(6) : N2 C14-C20, C25 C26
Ring (7) : C17 C18 C18 C20 C21-C26
Ring (8) : whole ring

Symmetry code: (v) 2-x, -y, 1-z ; I and J are two aromatic rings: Cg = Centroid

$d_{\pi-\pi}$ = Average perpendicular distances of Cg(J) on ring I and Cg(I) on ring J

Slippage distance = Distance between Cg(I) and perpendicular projection of Cg(J) on Ring I

α = Dihedral angle between the planes (I and J) of interacting rings

β = Angle Cg(I)-Cg(J) vector and normal to plane I

γ = Angle Cg(I)-Cg(J) vector and normal to plane J

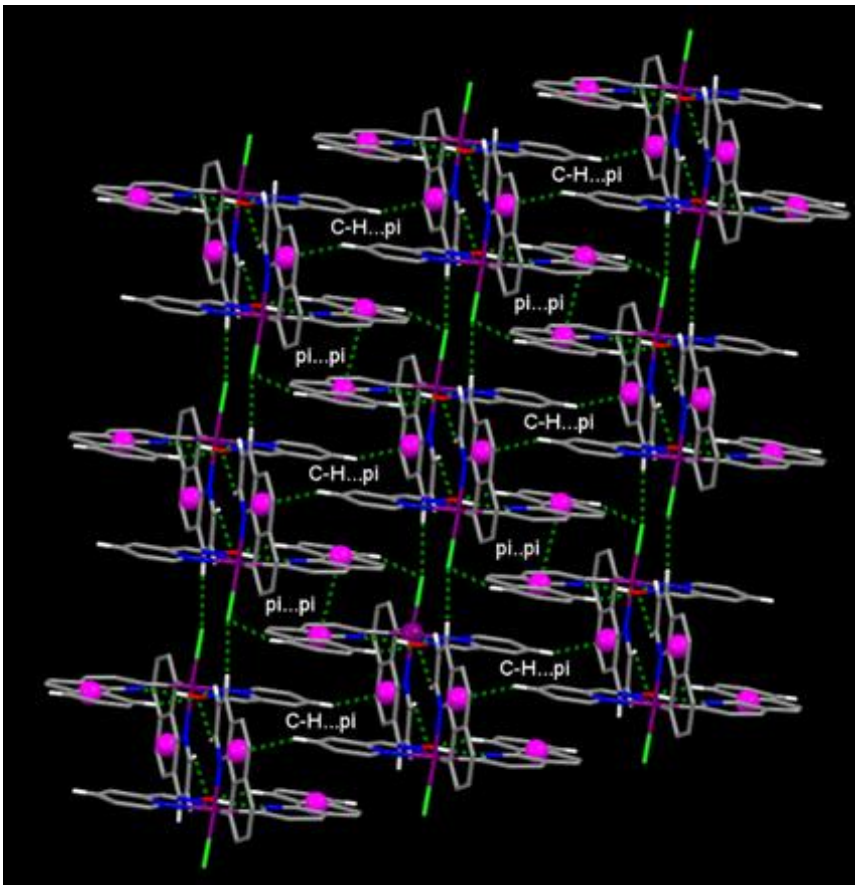


Fig. S10: The packing diagram of [Ir(benzq-κN, κC[10])(benzq-κC[2])(Hpyrald)(Cl)] (**3**)is viewed perpendicular to (010) plane (pink spheres depicts centroids, ---- lines represent hydrogen bonding and C-H…pi interactions)

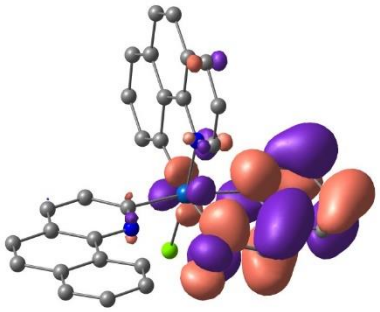
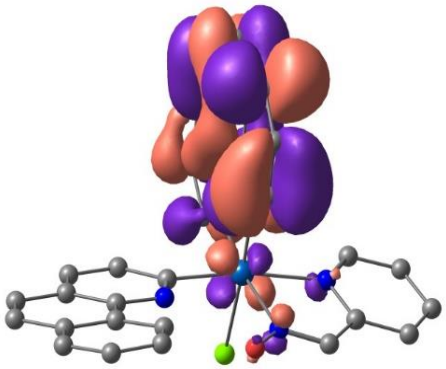
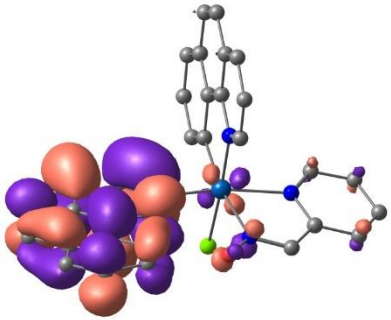
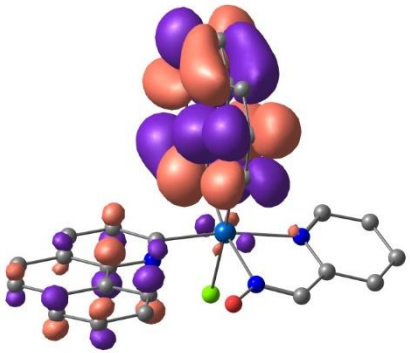
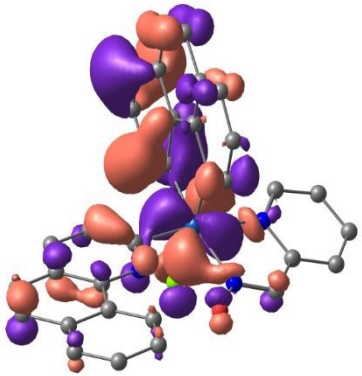
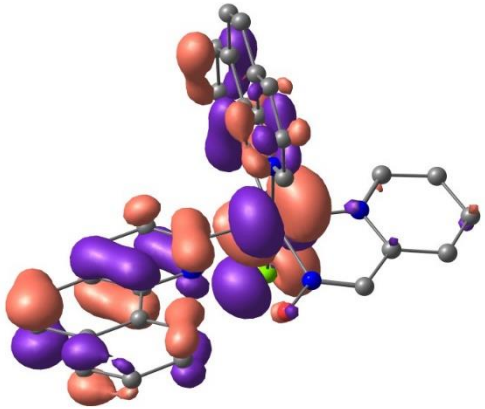
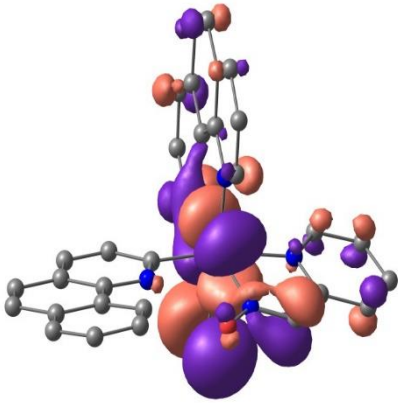
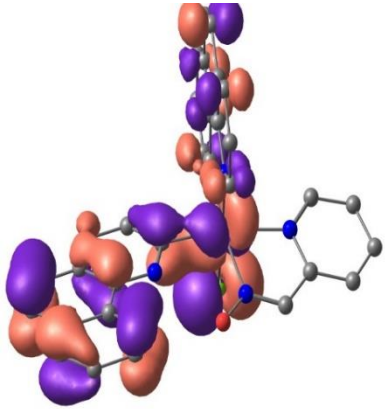
			
LUMO	LUMO+1	LUMO+2	LUMO+3
-1.8928 eV	-1.6226 eV	-1.1861 eV	-1.0074 eV
			
HOMO)	HOMO-1	HOMO-2	HOMO-3
-5.3571 eV	-5.4788 eV	-5.6788 eV	-5.9286 eV

Fig. S11. The Kohn–Sham orbital contours (isosurface contour value = 0.03) for key orbitals of the [Ir(benzq- κN, κC^{10})(benzq-κC^{2})(Hpyrald)(Cl)] (**3**) computed at the TD-DFT/SMD$_{(Dichloromethane)}$/B3LYP-D3/def2-TZVP (Ir), 6-31G** (C, H, N, O, Cl) level of theory. Hydrogens are omitted for clarity

Table S5: Selected TDDFT data of [Ir(benzq- κN, κC^{10})(benzq-κC^2)(Hpyrald)(Cl)] (**3**)

Complex	Nature of transition	Energy(eV)	Oscillator factor	Computed λ_{max}(nm)	Observed λ_{max}(nm)
Complex (**2**)	HOMO→LUMO	2.7403	0.0066	452.44	**Not observed**
	HOMO-1→LUMO	2.7938	0.0134	443.78	425
	HOMO-2→LUMO	3.0443	0.0994	407.27	425
	HOMO-1→LUMO+1	3.1956	0.0325	387.98	384
	HOMO-3→LUMO+1	3.4869	0.0103	355.57	355

Table S6: Electronic, Emission and Electrochemical data of complex (**2**) and (**3**)

Complex	Electronic spectral data λ (nm) (ε x 10^3 ($M^{-1}cm^{-1}$))[a]	Phosphorescence data[a]	Electrochemical data[b] [E(V) vs SCE]
[Ir(benzq-κN, κC^{10})(pyrald)] (2)	500(1.52)[c], 428(7.68)[c], 382(13.79)[c], 282(49.26), 258(63.15)	539, 591	0.94[d], 1.35[d] , -1.32[e]
[Ir(benzq- κN, κC^{10})(benzq-κC^2)(Hpyrald)(Cl)] (3)	500(0.94)[c], 425(6.35)[c], 384(12.09)[c], 355(16.35)[c], 282(52.32)	594, 641	1.27[d],1.59[d], -1.41[e] [1.06V, -1.14 (Hpyrald)][f]

[a] =dichloromethane solution
[b] = in acetonitrile solution
[c] = shoulder
[d] = E_a values
[e] =E_c values
[f] = E_a and E_c values of pyridine-2-aldoxime

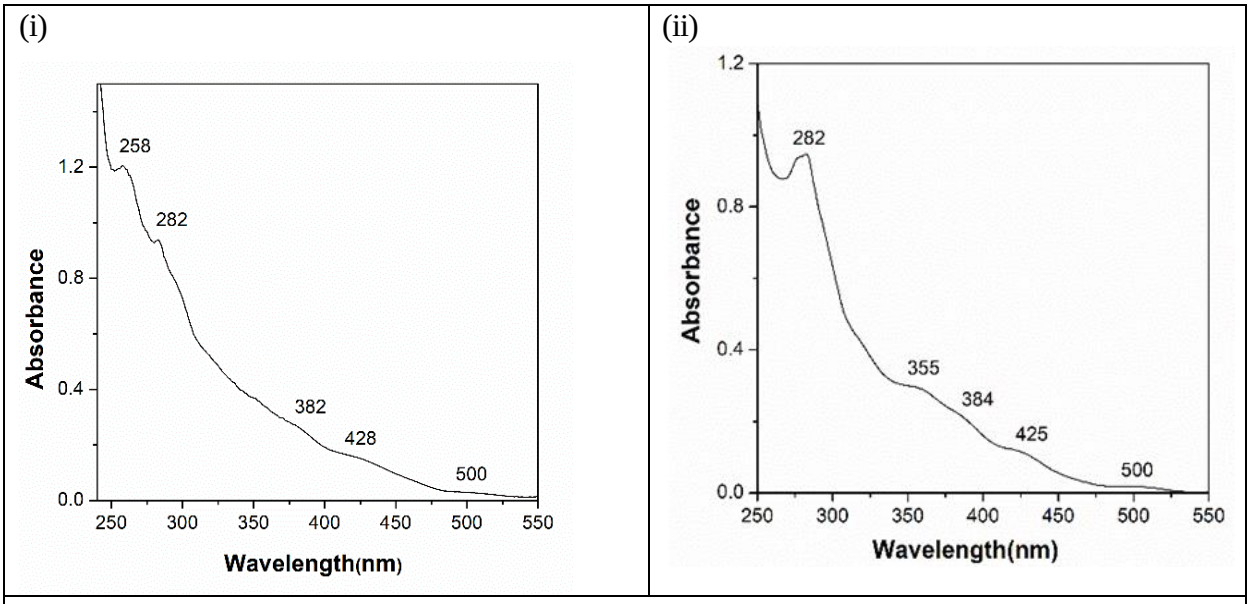


Fig. S12: UV-Vis spectrum of (i) complex (**2**) and (ii) complex (**3**) in dichloromethane medium

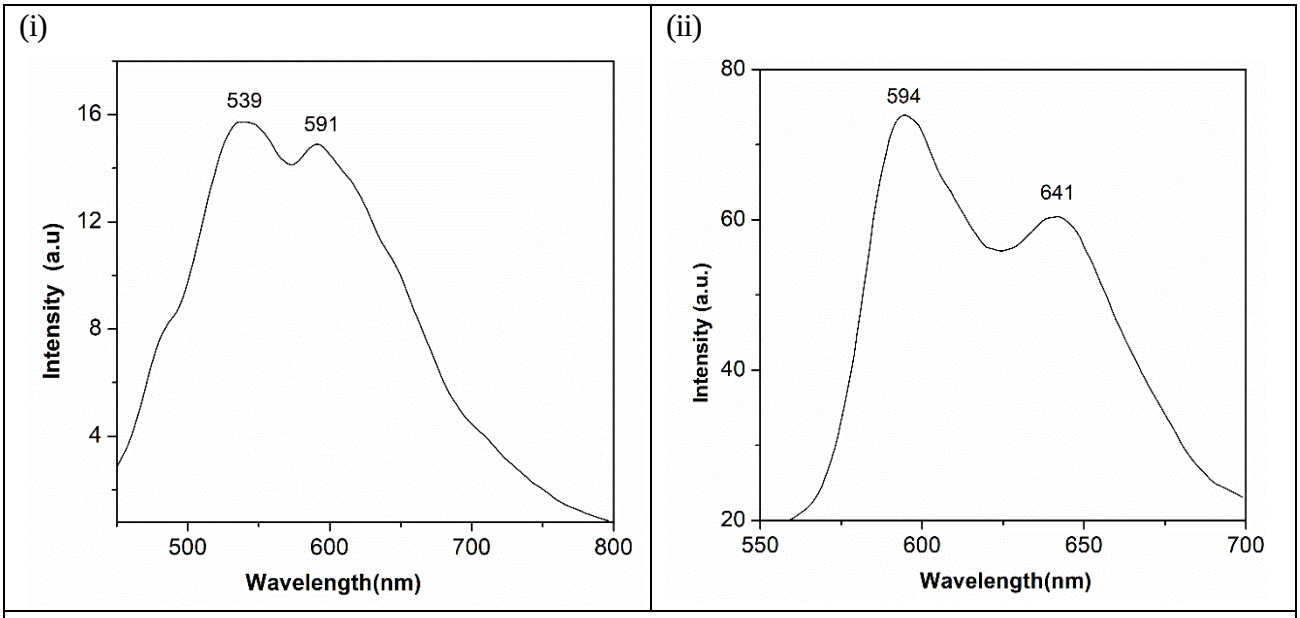
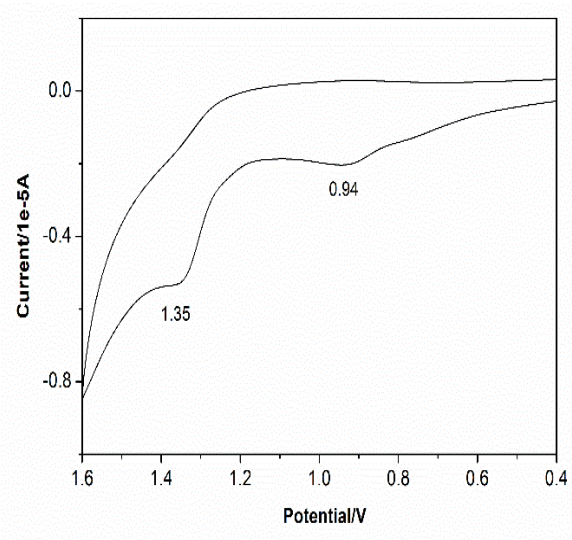


Fig. S13: Emission spectrum of (i) complex (**2**) and (ii) complex (**3**) in dichloromethane medium

(i)



(ii)

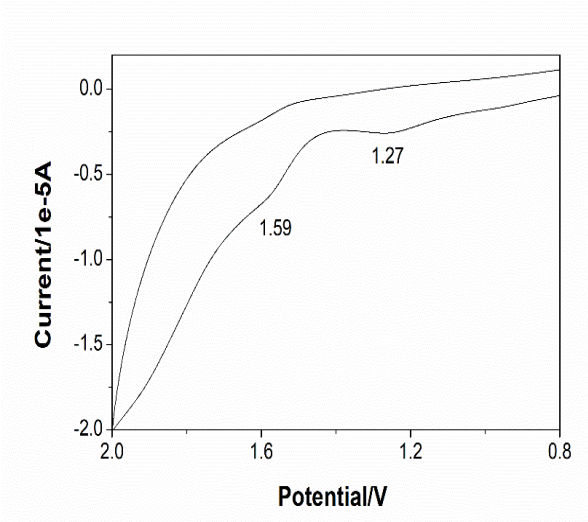


Fig. S14: Cyclic voltammogram of (i) complex (**2**) and (ii) complex (**3**) in acetonitrile solution