

Supporting documents

One-Pot Synthesis of Strong Solid State Emitting Monocyclometalated Iridium(III) Complexes: Study of their Aggregation Induced Enhanced Phosphorescence

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Experimental

Materials: Iridium(III) chloride hydrate, 2-phenylpyridine, 2-chloropyridine, 2,4-difluoroboronic acid, palladium(0)tetrakis(triphenylphosphine), triphenylphosphine, 2-ethoxyethanol were purchased from Sigma Aldrich Chemical Company Ltd. The solvents were bought from Merck company.

Characterization: ¹HNMR, ¹³CNMR and ³¹PNMR spectra were recorded in 400 MHz Bruker NMR spectroscopy. Infra-red spectrum was recorded in FTIR Shimadzu (IR prestige-21). UV-Vis absorption spectra were recorded in Shimadzu Spectrophotometer with model UV-1800. The photoluminescence (PL) spectra were recorded in Spectrofluorometer (Fluoro max-4) Horiba Jobin Yvon. The excitations used for PL are 380nm, 385nm and 375nm for Flrpic, **2a** and **2b**, respectively (in solid/solution state). Elemental analyses were furnished on Elementar, VARIO III. SEM image was obtained by JEOL JSM-6390LV. Emission life-time in thin-film were obtained by exponential fit of emission decay curves recorded on Horiba Jobin Yvon model fluorocube-01-NL Spectrofluorometer.

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Syntheses and characterizations of 1, 2a and 2b: To a stirred solution of $\text{IrCl}_3 \cdot 3\text{H}_2\text{O}$ (0.5025 mmol) in 2-ethoxy ethanol (6 mL), triphenylphosphine (1.507 mmol) was added and the reaction mixture was refluxed at 130°C for **5h**. Then, 2-phenylpyridine (for **2a**) [2-(2,4-difluorophenyl)pyridine (for **2b**)] (1.252 mmol) were added to the reaction mixture and it was further refluxed for **3h**. The reaction mass was brought to room temperature. The resulted solid mass was triturated and washed with hexane followed by ethanol for several times to obtain a light green solid (57%) of **2a** (**2b**). These complexes were purified through recrystallization from a mixture of DCM and hexane (1:1). X-ray quality single crystals of **2b** were collected from the solution. The intermediate, **1** was synthesized on refluxing the mixture of $\text{IrCl}_3 \cdot 3\text{H}_2\text{O}$ and triphenylphosphine in 2-ethoxyethanol for 5h. The solid pale yellow product was separated out from the solution, filtered and washed the residue by methanol and ethylacetate for several times. For **1**, ^1H NMR (400 MHz, CDCl_3) δ 7.57 (dd, $J = 14.0, 7.5$ Hz, 1H), 7.45 – 7.37 (m, 9H), 7.24 – 7.19 (m, 5H), 7.08 (dt, $J = 17.0, 8.1$ Hz, 12H), 6.99 (t, $J = 7.5$ Hz, 12H), 6.82 – 6.75 (m, 4H), - 19.27 (dt, $J = 29.2, 8.5$ Hz, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 207.00, 206.95, 135.30, 135.20, 135.10, 135.05, 135.00, 132.67, 132.40, 132.16, 132.13, 132.06, 131.96, 129.56, 129.19, 128.57, 128.45, 127.16, 127.11, 127.06, 127.01, 126.90, 30.94; ^{31}P NMR (162 MHz, CDCl_3) δ 2.41, 7.54, 9.54. Anal. Calc for $\text{C}_{54}\text{H}_{45}\text{P}_3\text{ClIr}$ (MW = 1013.80): C, 63.92; H, 4.44. Found. C, 63.90, H, 4.47.

For **2a**, ^1H NMR (400 MHz, CDCl_3) δ 8.86 (d, $J = 5.5$ Hz, 1H), 7.35 – 7.22 (m, 14H), 7.10 (t, $J = 7.3$ Hz, 7H), 7.05 – 6.98 (m, 12H), 6.57 – 6.47 (m, 2H), 6.29 (d, $J = 7.8$ Hz, 1H), 5.97 – 5.80 (m, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 166.31, 149.61, 143.46, 135.28, 134.10, 134.05, 133.99, 132.03, 131.77, 131.51, 130.04, 128.88, 127.26, 127.21, 127.16, 122.36, 120.43, 119.21, 117.00; ^{31}P NMR (162 MHz, CDCl_3) δ 9.25. Anal. Calc for $\text{C}_{47}\text{H}_{39}\text{NP}_2\text{ClIr}$ (MW = 906.80): C, 62.20; H, 4.30, N, 1.54. Found. C, 62.18, H, 4.33, N, 1.55.

For F_2ppy , ^1H NMR (400 MHz, d^6 -DMSO) δ 8.72 (d, $J = 4.6$ Hz, 1H), 7.99 (dd, $J = 16.3, 8.3$ Hz, 1H), 7.91 (t, $J = 7.7$ Hz, 1H), 7.77 (d, $J = 7.9$ Hz, 1H), 7.44 – 7.35 (m, 2H), 7.24 (t, $J = 8.4$ Hz, 1H).

For **2b**, ^1H NMR (400 MHz, CDCl_3) δ 8.94 (d, $J = 5.5$ Hz, 1H), 7.75 (d, $J = 8.6$ Hz, 1H), 7.46 – 7.24 (m, 13H), 7.14 (t, $J = 7.3$ Hz, 6H), 7.10 – 7.04 (m, 12H), 6.66 – 6.55 (m, 1H), 5.94 (ddd, $J =$

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13.1, 9.0, 2.4 Hz, 1H), 5.69 (dd, $J = 9.5, 2.1$ Hz, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 149.90, 136.06, 134.02, 133.97, 133.92, 131.53, 131.27, 131.01, 129.26, 127.41, 127.36, 127.31, 126.55, 121.63, 121.46, 120.66; ^{31}P NMR (162 MHz, CDCl_3) δ 7.78. Anal. Calc for $\text{C}_{47}\text{H}_{37}\text{NP}_2\text{F}_2\text{ClIr}$ (MW = 942.80): C, 59.82; H, 3.92, N, 1.48. Found. C, 59.79, H, 3.91, N, 1.47.

Fabrication of thin-film of 2a and 2b on substrate for PL measurement: The 10^{-3}M solution of **2a**, **2b** and FIrpic (in toluene) were prepared. Two drops of the solution were placed on thin glass substrate ($2 \times 2\text{cm}^2$) and the solvent was allowed to evaporate slowly.

Fabrication of thin-film for SEM image: Two drops of solution of **2a** in 90% $\text{H}_2\text{O}/\text{THF}$ was poured onto the Si-wafer ($2 \times 2\text{cm}^2$). The solvent was allowed to evaporate and the film was dried in vacuum.

Preparation of solution of THF/ H_2O and THF/PEG of 2a (2b) for PL measurement: 10^{-4}M stock solution of **2a** (**2b**) was prepared in THF. Four 10ml volumetric flasks were taken and labeled them as 0%, 30%, 60% and 90%. 1mL of stock solution was added to each of the flask. Then, volume was filled to 10ml through addition of 9ml, 6ml, 3ml and 1ml water to 0%, 30%, 60% and 90% labeled flasks, respectively. The solution of **2a** (**2b**) in THF/PEG was prepared in the same way.

X-ray single crystal diffraction study:

Single crystal X-ray diffraction data were collected on Bruker AXS Kappa Apex II diffractometer equipped with Oxford Cryosystem 700Plus liquid nitrogen based cooling device. The data set was recorded at 100K using ϕ and ω scans such that the data is completed up to 70 degrees in two theta. Data reduction and standard processing were done using APEX II¹ suite available from Bruker AXS. The crystal structure was solved using direct methods (SHELXS97)² available in the Olex2³ suite and the structure was refined by full matrix least squares refinement process using SHELXL97.² Geometric calculations were carried out using PARST97⁴ and PLATON97.⁵

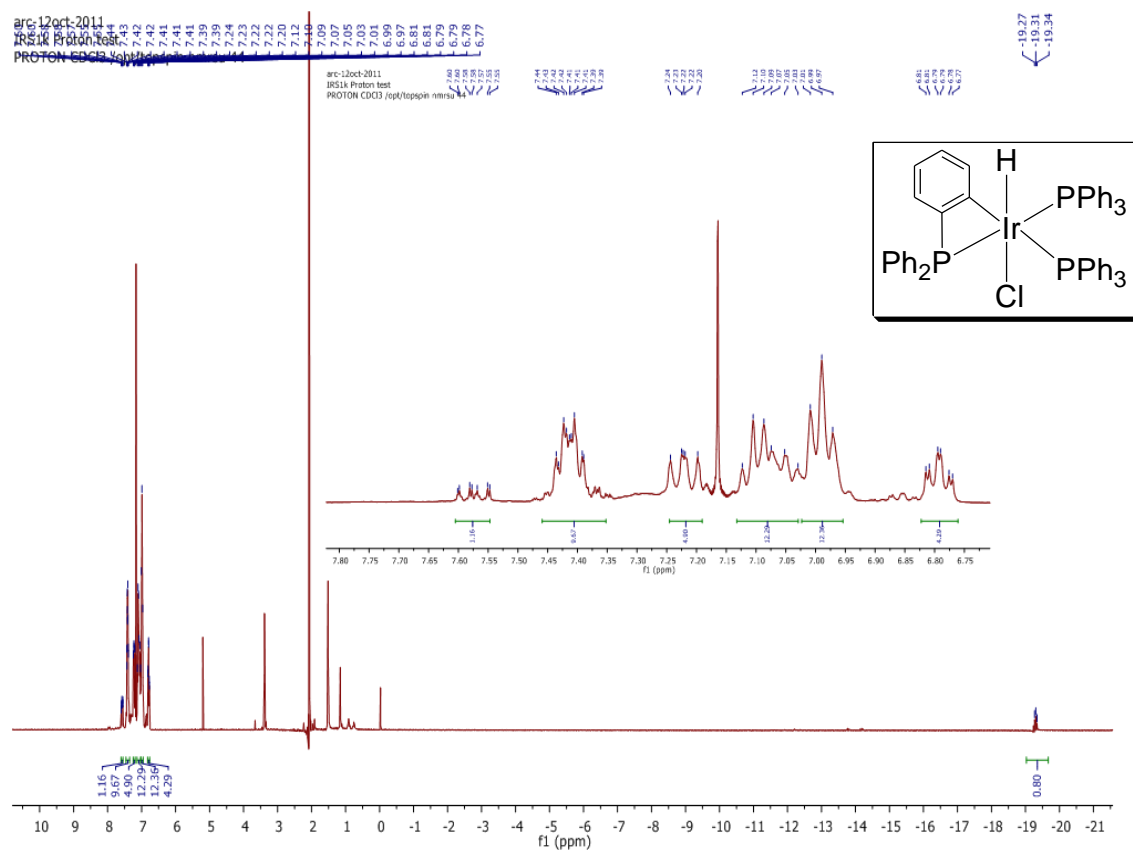


Fig. S1 ^1H NMR spectrum for the second intermediate, **1** [δ 7.57 (dd, $J = 14.0, 7.5$ Hz, 1H), 7.45 – 7.37 (m, 9H), 7.24 – 7.19 (m, 5H), 7.08 (dt, $J = 17.0, 8.1$ Hz, 12H), 6.99 (t, $J = 7.5$ Hz, 12H), 6.82 – 6.75 (m, 4H), -19.27 (dt, $J = 29.2, 8.5$ Hz, 1H)].

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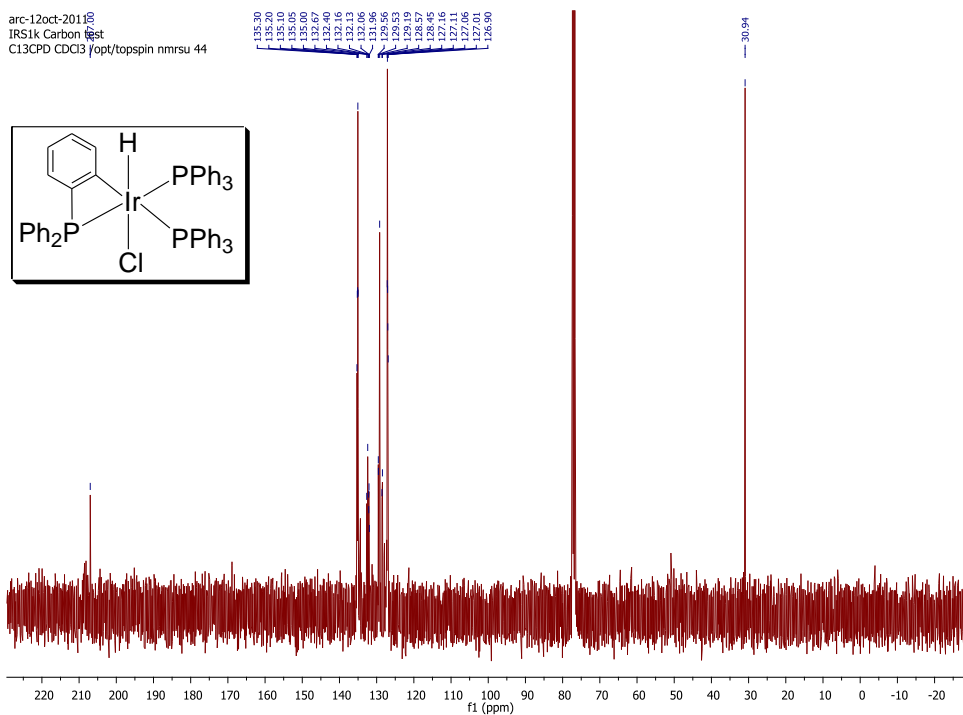


Fig. S2. ¹³CNMR spectrum for the second intermediate, **1** (δ 207.00, 206.95, 135.30, 135.20, 135.10, 135.05, 135.00, 132.67, 132.40, 132.16, 132.13, 132.06, 131.96, 129.56, 129.19, 128.57, 128.45, 127.16, 127.11, 127.06, 127.01, 126.90, 30.94).

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IRS1k P31 test
P31 CDCl3 /opt/topspin hmrsv 44

—7.54

—9.54

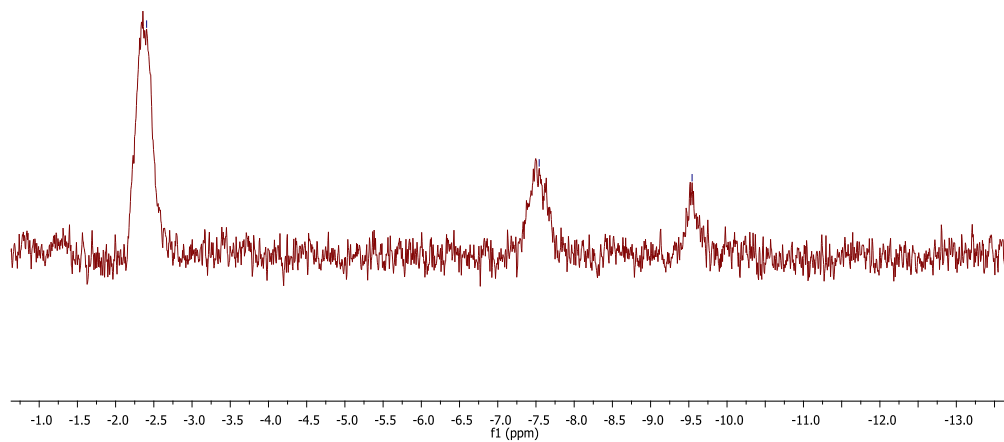
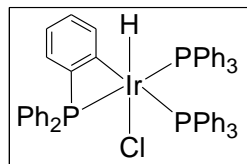


Fig. S3 ^{31}P NMR spectrum for the second intermediate, **1** (δ 2.41, 7.54, 9.54).

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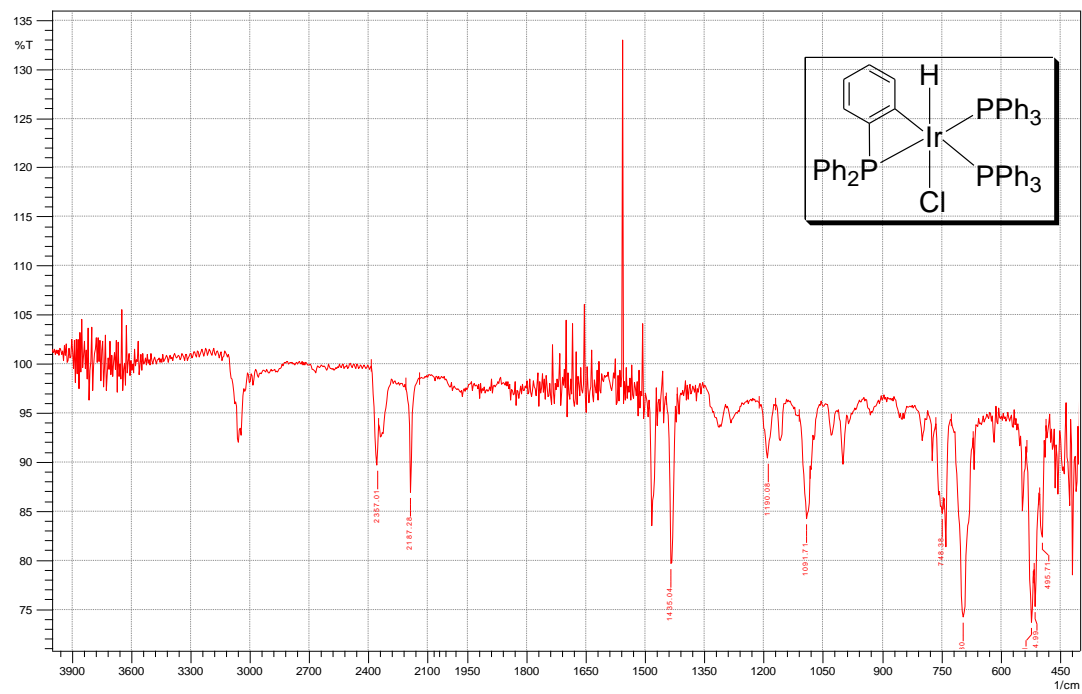


Fig. S4 FTIR spectrum for **1** (2187 cm^{-1} shows the $\nu(\text{Ir-H})\text{cm}^{-1}$).

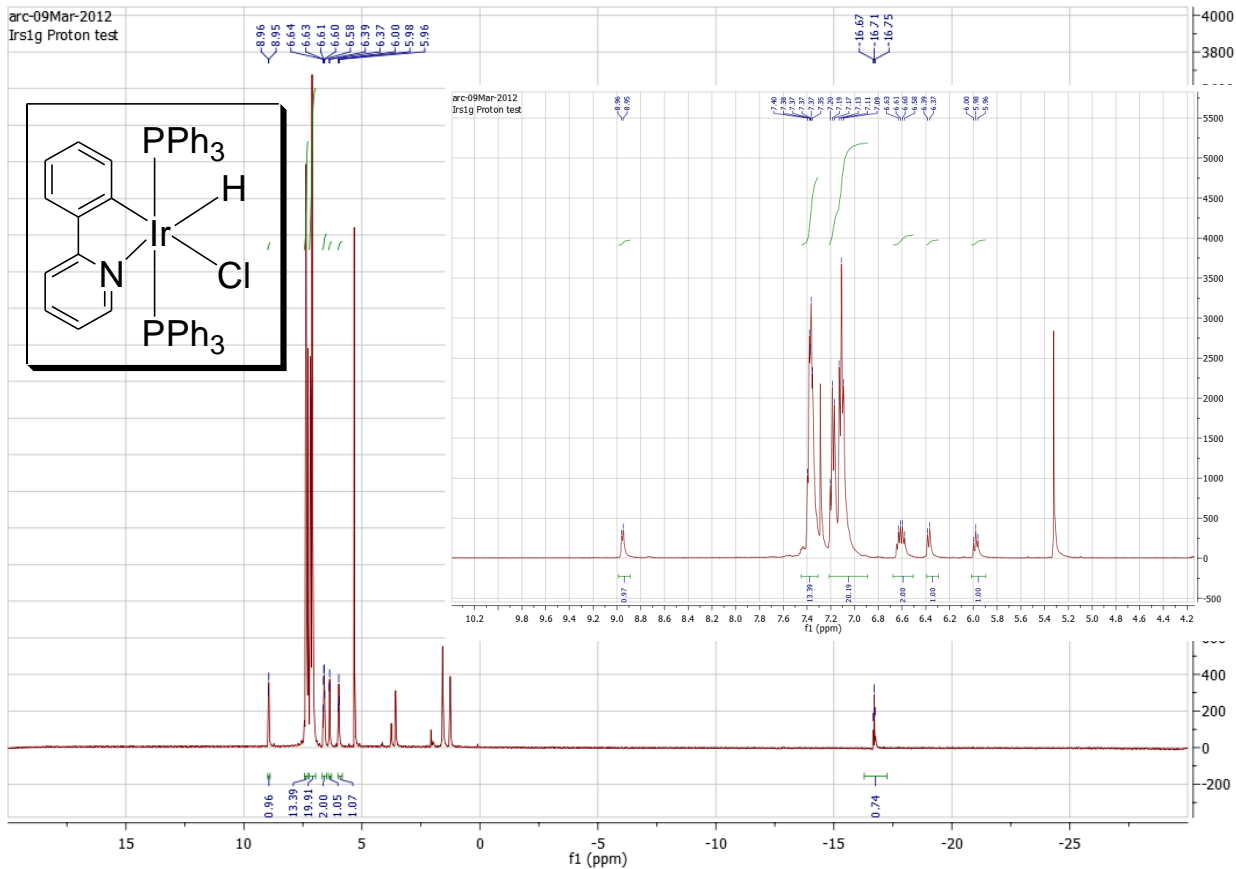


Fig. S5 ¹H NMR spectrum for the complex, **2a** [δ 8.86 (d, J = 5.5 Hz, 1H), 7.35 – 7.22 (m, 14H), 7.10 (t, J = 7.3 Hz, 7H), 7.05 – 6.98 (m, 12H), 6.57 – 6.47 (m, 2H), 6.29 (d, J = 7.8 Hz, 1H), 5.97 – 5.80 (m, 1H)].

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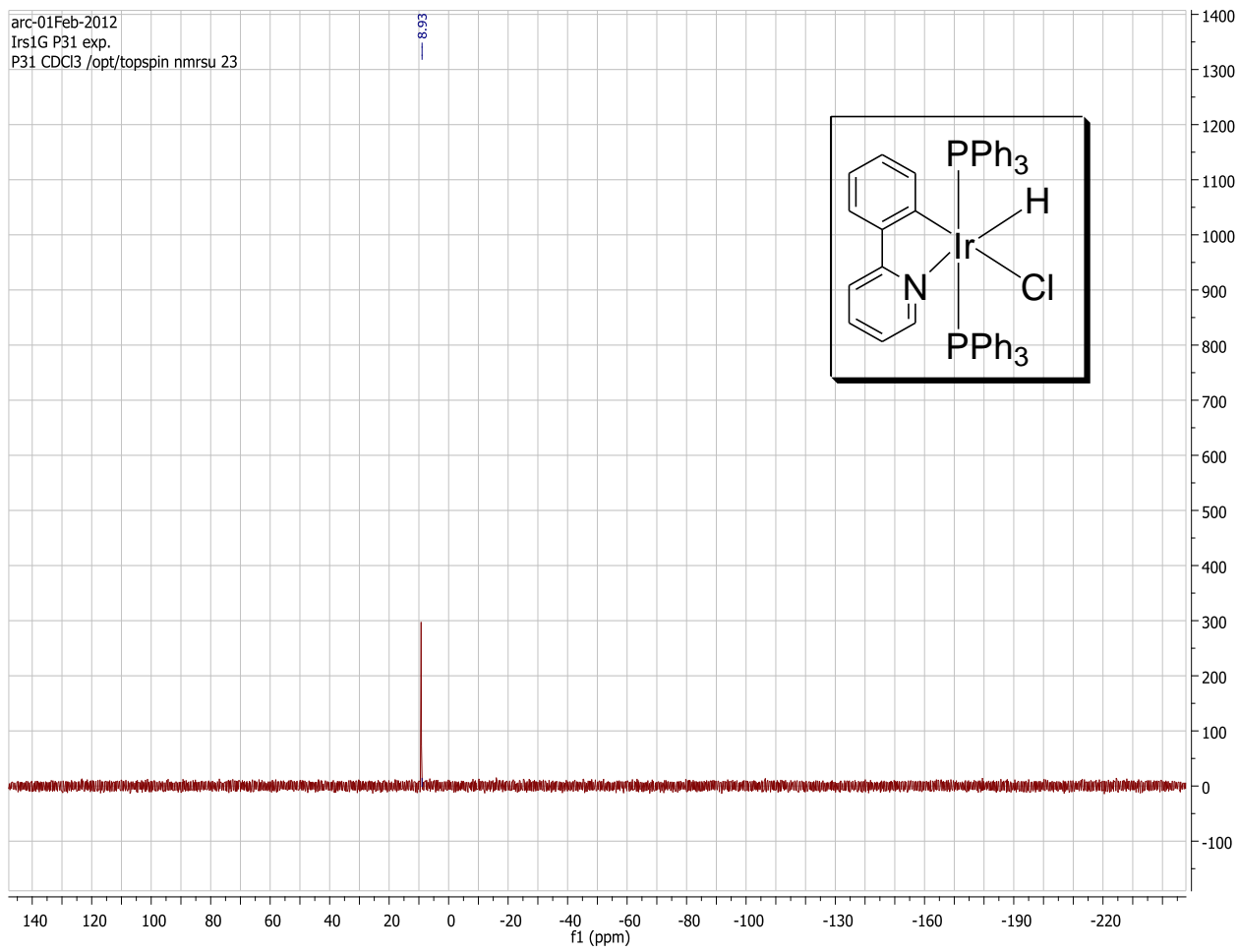
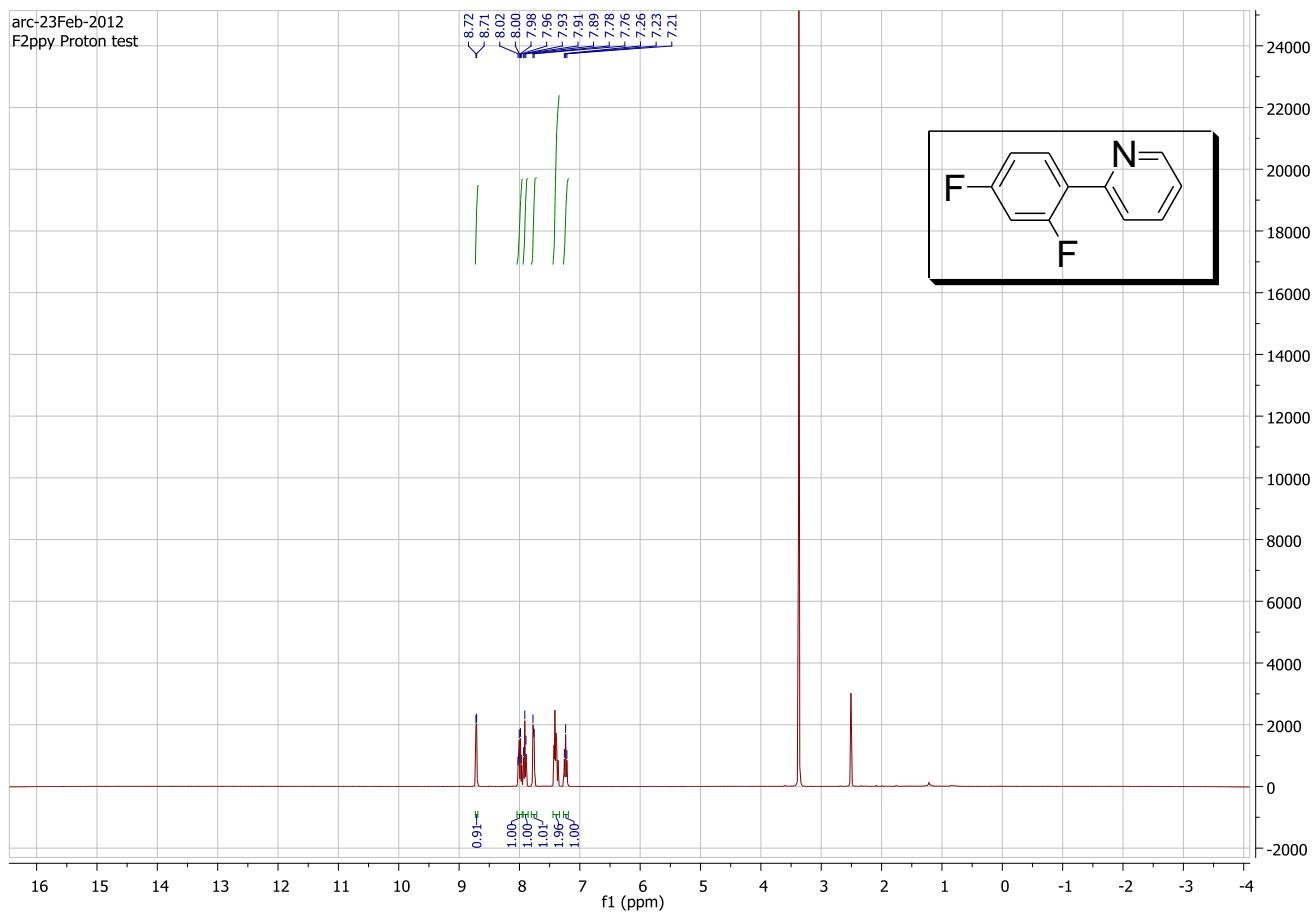
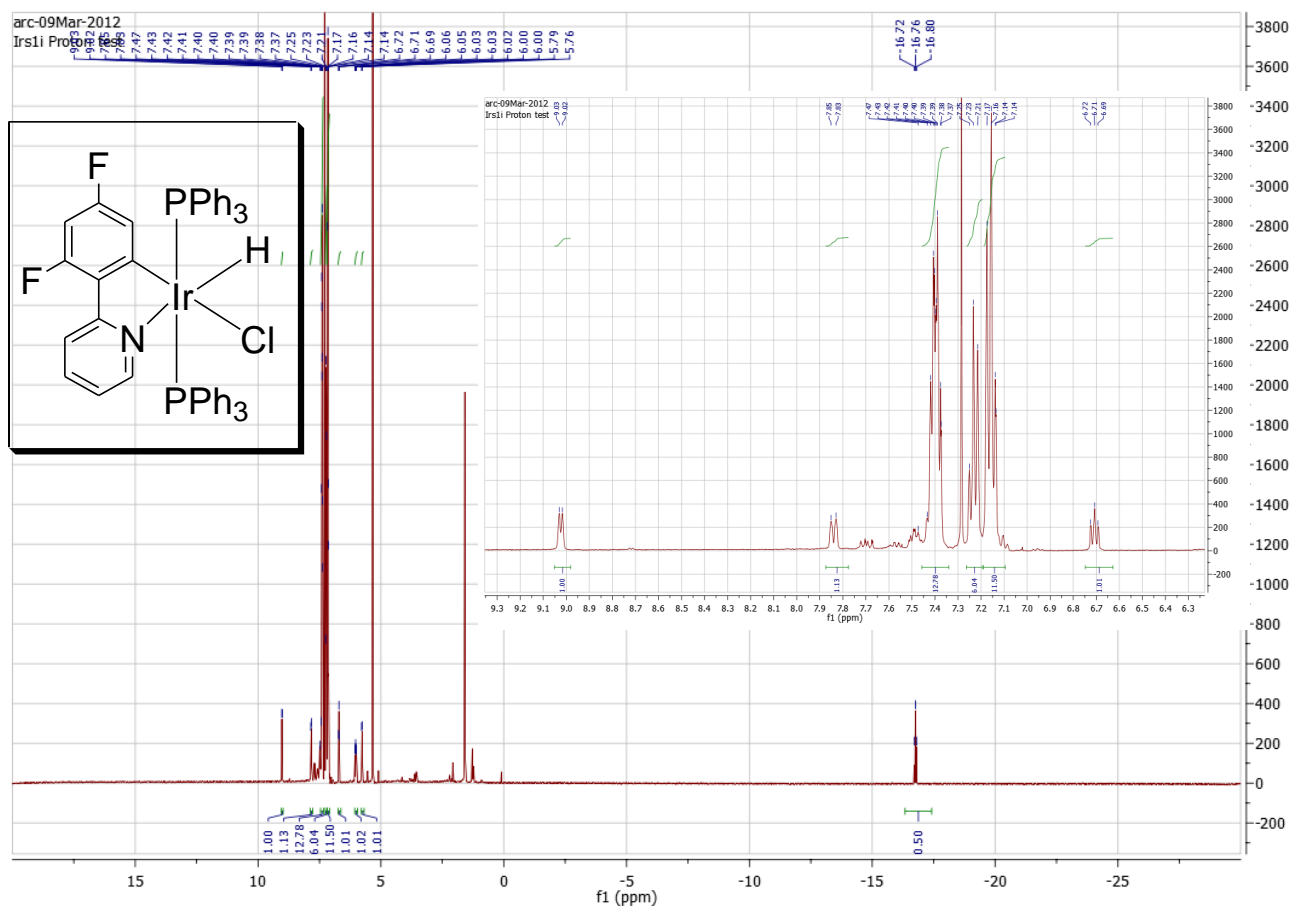


Fig. S7 ³¹P NMR spectrum for **2a** (δ 9.25).

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A



B

Fig. S8 ¹H NMR spectrum for F₂ppy (A) and the complex, **2b** (B) [(For A, δ 8.72 (d, *J* = 4.6 Hz, 1H), 7.99 (dd, *J* = 16.3, 8.3 Hz, 1H), 7.91 (t, *J* = 7.7 Hz, 1H), 7.77 (d, *J* = 7.9 Hz, 1H), 7.44 – 7.35 (m, 2H), 7.24 (t, *J* = 8.4 Hz, 1H); For B, δ 8.94 (d, *J* = 5.5 Hz, 1H), 7.75 (d, *J* = 8.6 Hz, 1H), 7.46 – 7.24 (m, 13H), 7.14 (t, *J* = 7.3 Hz, 6H), 7.10 – 7.04 (m, 12H), 6.66 – 6.55 (m, 1H), 5.94 (ddd, *J* = 13.1, 9.0, 2.4 Hz, 1H), 5.69 (dd, *J* = 9.5, 2.1 Hz, 1H)].

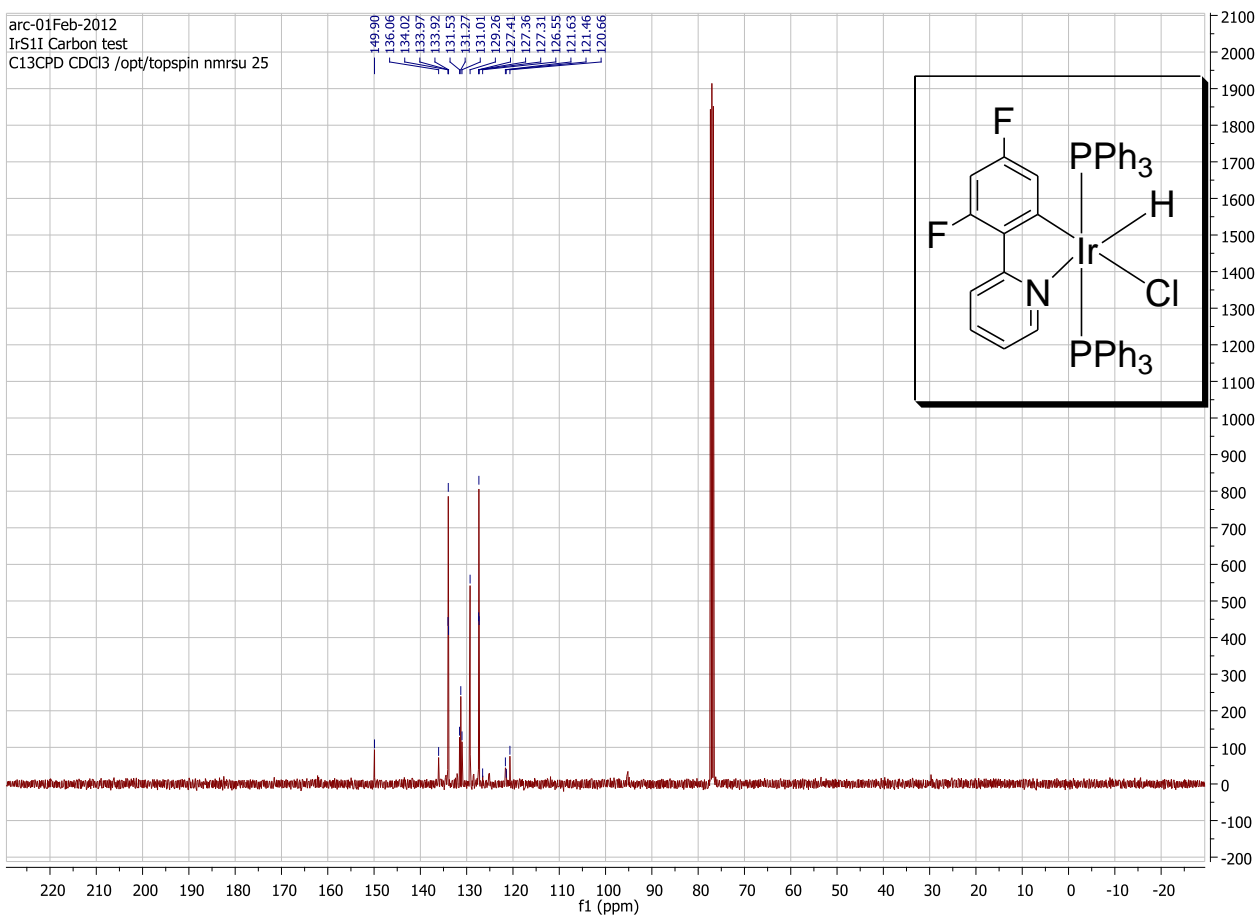


Fig. S9 ¹³CNMR spectrum for **2b** (δ 149.90, 136.06, 134.02, 133.97, 133.92, 131.53, 131.27, 131.01, 129.26, 127.41, 127.36, 127.31, 126.55, 121.63, 121.46, 120.66)

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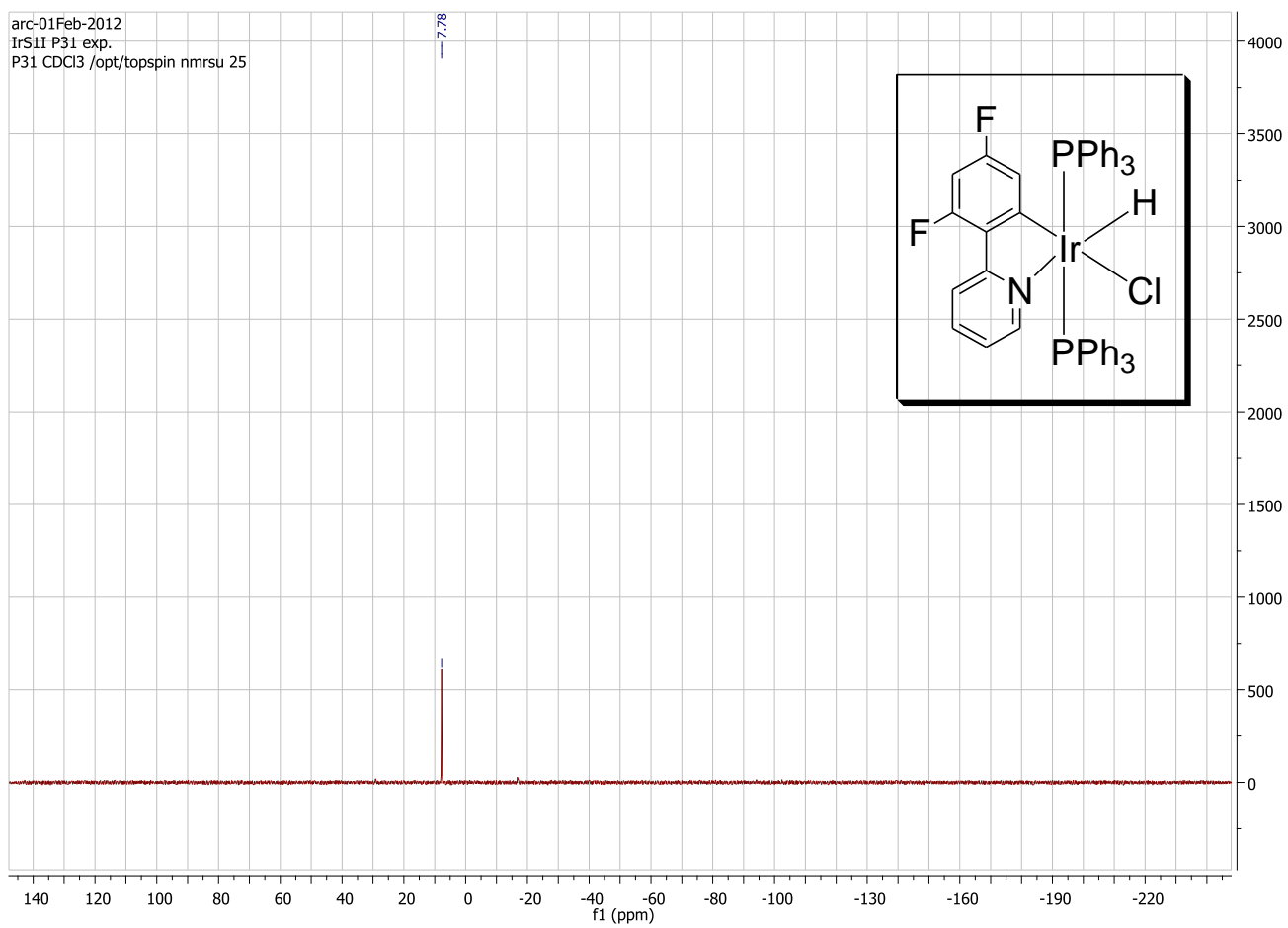


Fig. S10 ³¹P NMR spectrum for **2b** (δ , 7.78ppm).

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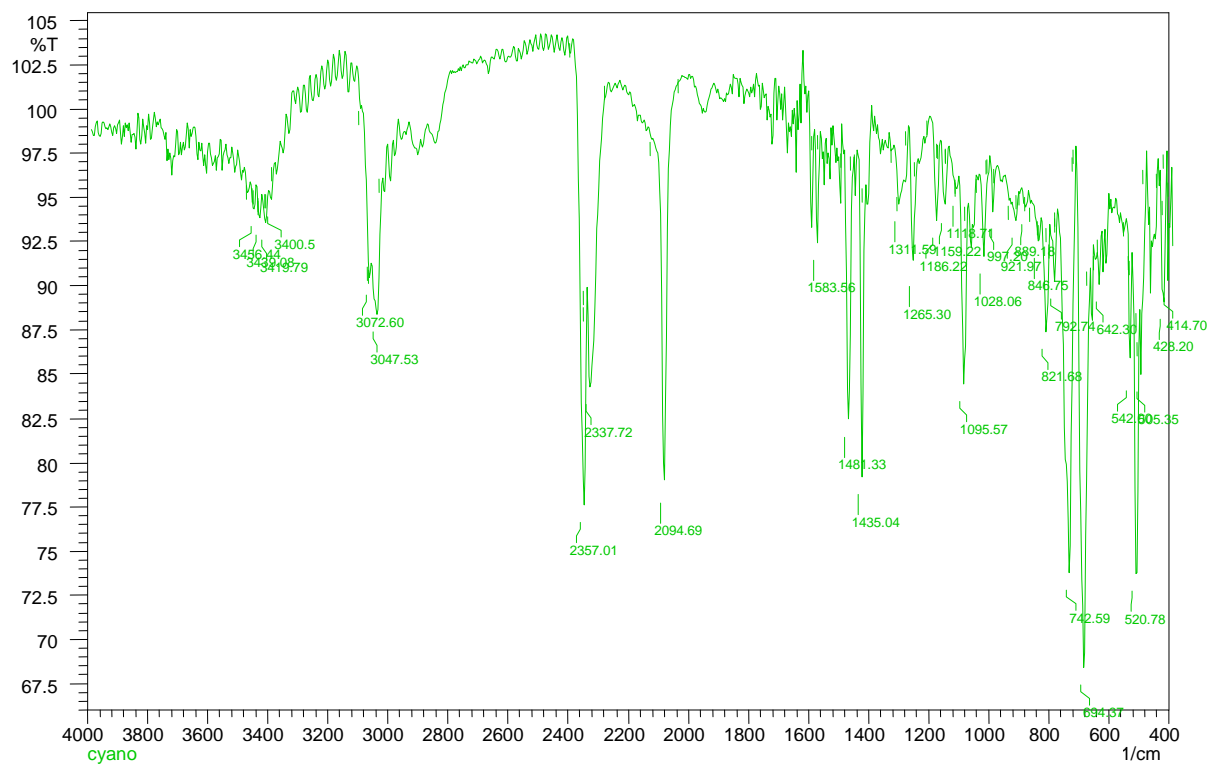


Fig. S11 FTIR spectra of the complex **2a** (IR band observed at 2094cm⁻¹ shows the stretching frequency for Ir-H)

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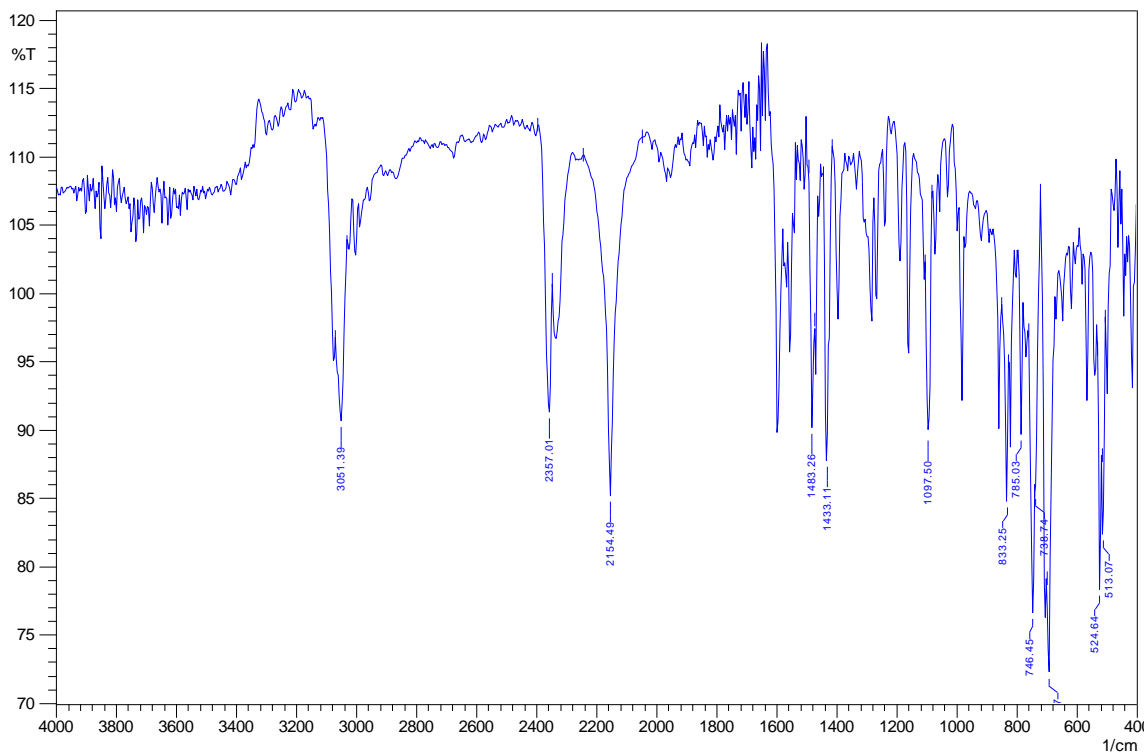
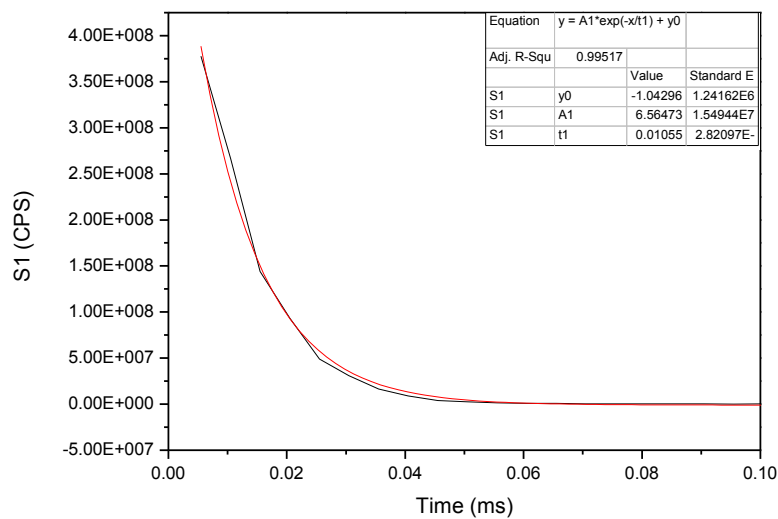
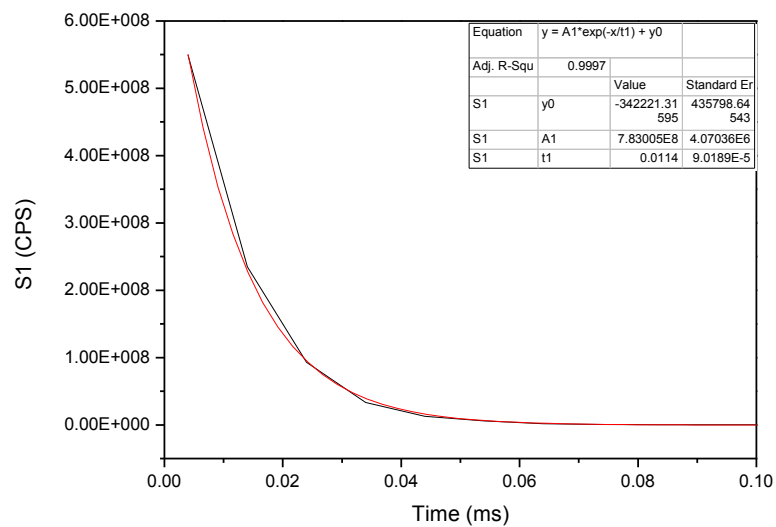


Fig. S12 FTIR spectra of the complex **2b** (IR band observed at 2154cm^{-1} shows the stretching frequency for Ir-H)



A



B

Fig. S13 Luminescent life-time decay curve in thin-film of **2a** [shown in (A)] and **2b** [shown in (B)] (black, raw data and red, single exponential fitting)

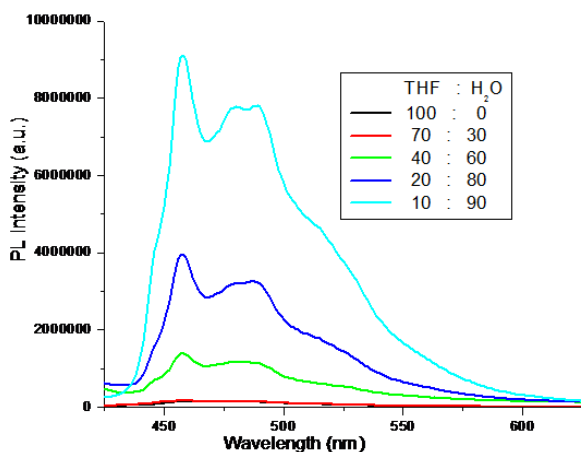


Fig. S14 PL emission spectra show gradual enhancement of emission intensity of **2b** with increasing concentration of water into the solution of THF (462nm, 482nm).

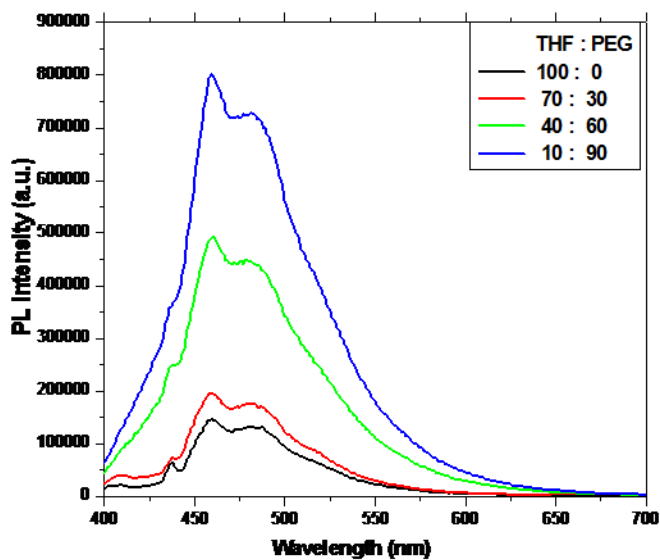
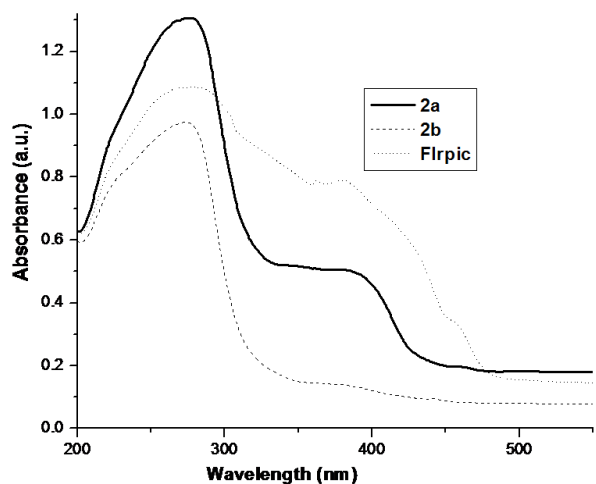
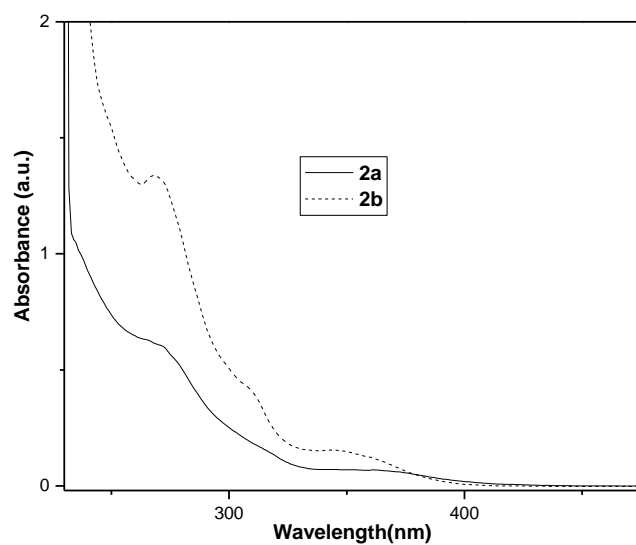


Fig. S15 PL emission spectra showing gradual enhancement of emission intensity of **2b** with increasing concentration of PEG into the solution of THF (460nm, 482nm).



A



B

Fig. S16 Absorbance spectrum (A) for the solid state complexes of **2a** (274nm, 386nm, 461nm), **2b** (273nm, 378nm, 445nm) and Flrpic (376nm, 382nm, 458nm); (B) for the solution state complexes **2a** (271nm, 314nm and 364nm) and **2b** (269nm, 308nm and 348nm) (in 10^{-4} M DCM).

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Table S1 Crystal data and structure refinement for **2b**.

Empirical formula	C ₄₇ H ₃₆ ClF ₂ IrNP ₂
Formula weight	942.38
Temperature	100K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	<i>Pna</i> 2 ₁
Unit cell dimensions	a = 32.2085(4) Å; b = 12.2682(1) Å; c = 9.6830(1) Å $\alpha = \beta = \gamma = 90^\circ$
Volume	3826.14 Å ³
Z	4
Density (calculated)	1.636 Mg/m ³
Absorption coefficient	3.692 mm ⁻¹
F(000)	1868
Crystal size	0.2 × 0.2 × 0.1 mm ³
Theta range for data collection	2.45 to 37.03°
Index ranges	0 ≤ h ≤ 54; 0 ≤ k ≤ 20; 0 ≤ l ≤ 16
Reflections collected	10162
Independent reflections	9908 [R(int) = 2.23%]
Completeness to theta	40.08°, 98.9%
Absorption correction	SADABS
Max. and min. transmission	0.709 and 0.5255
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	10162/1/487
Goodness-of-fit on F ²	1.062
Final R indices [I > 2σ(I)]	R1 = 0.0223, wR2 = 0.0617
R indices (all data)	R1 = 0.0233, wR2 = 0.0622
Largest diff. peak and hole	1.932, -2567 e.Å ⁻³

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Table S2 Selected Bond lengths [Å] and angles [°] for **2b**

Ir1- C19	1.998(3)
Ir1 - N1	2.160(2)
Ir1- P1	2.3199(6)
Ir1 - P2	2.3278(6)
Ir1 - Cl1	2.4641(7)
C19 Ir1 N1	78.99(10)
C19 Ir1 P1	91.25(8)
N1 Ir1 P1	95.37(6)
C19 Ir1 P2	95.38(8)
N1 Ir1 P2	91.68(6)
P1 Ir1 P2	171.13(2)
C19 Ir1 Cl1	176.97(8)
N1 Ir1 Cl1	98.14(7)
P1 Ir1 Cl1	88.04(2)
P2 Ir1 Cl1	85.63(2)

References

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