**Supporting Information**

# Highly Selective Detection of $H^+$ and $OH^-$ with a Single Emissive Iridium(III) Complex: A Mild Approach to Conversion of Non-AIEE to AIEE Complex

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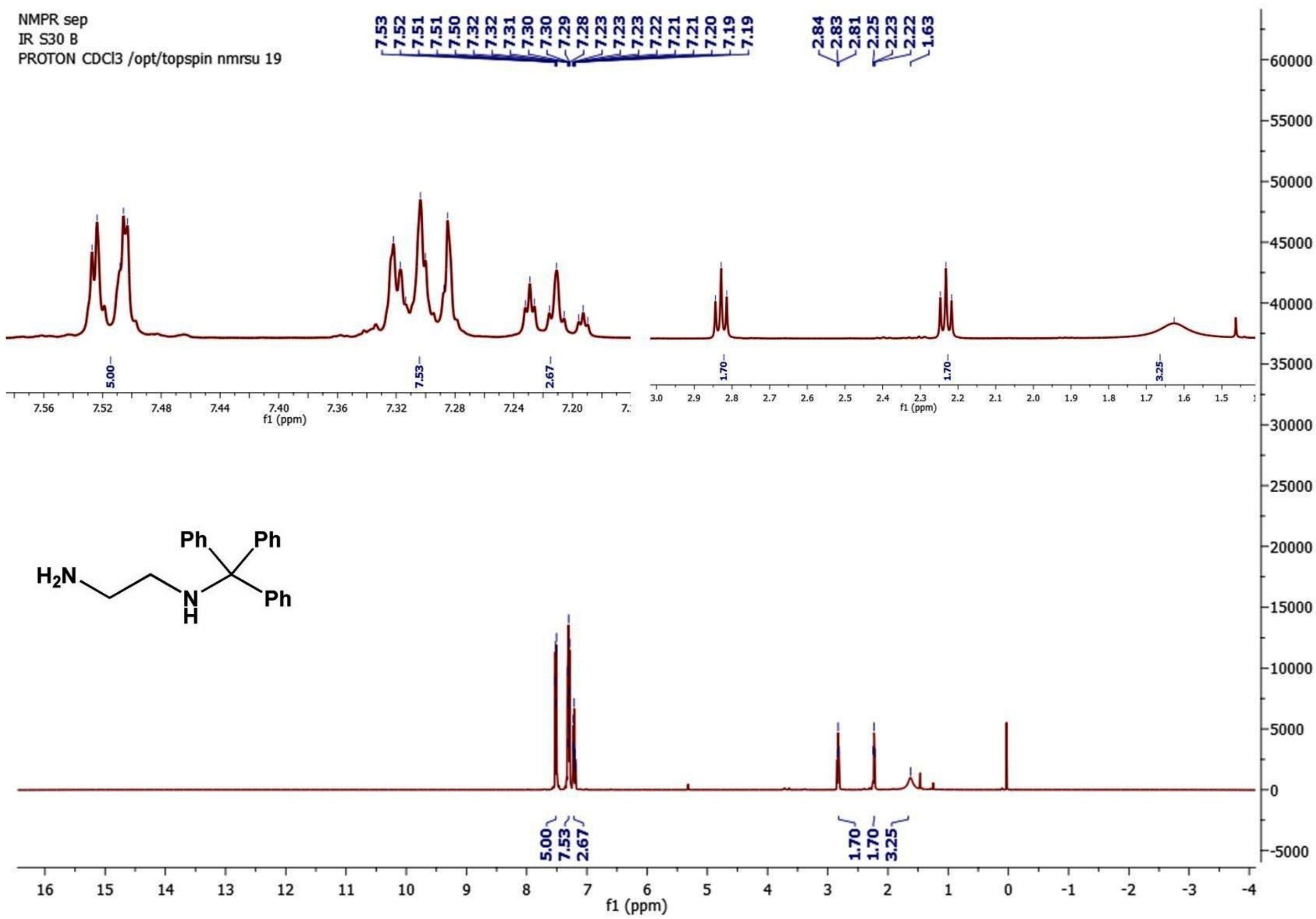
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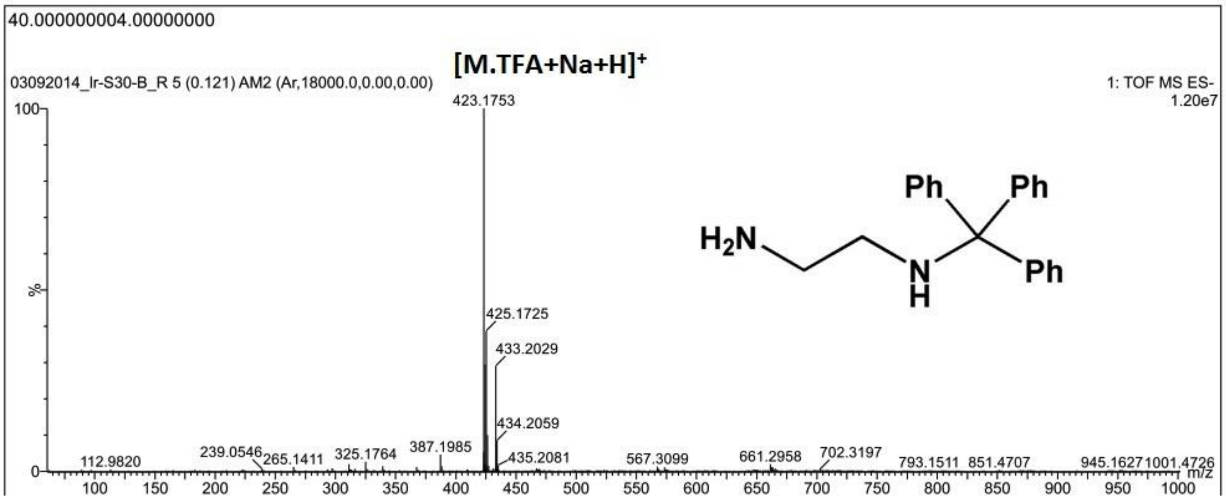
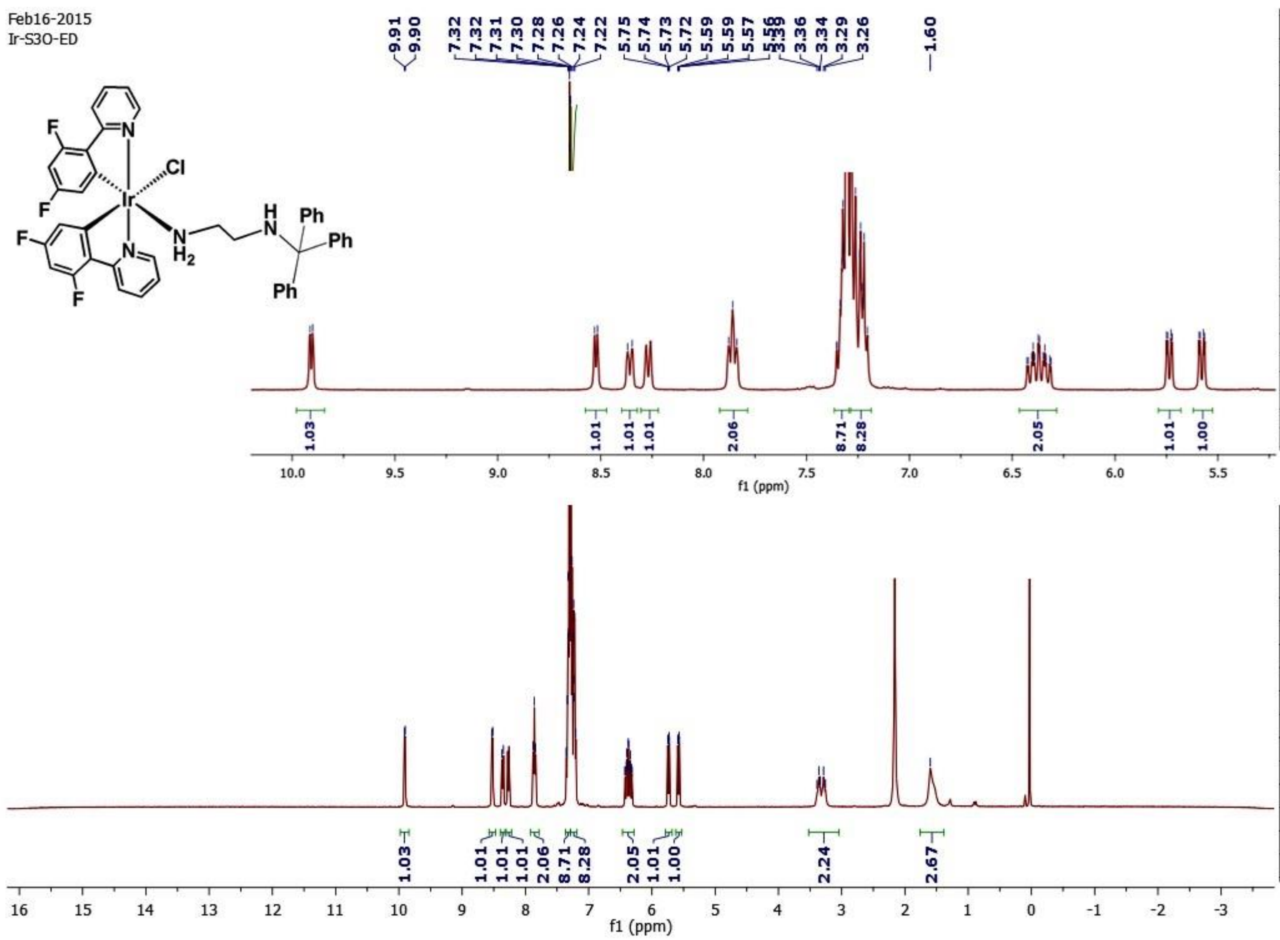
IR S30 B
PROTON CDCl3 /opt/topspin nmrsu 19
7.53 7.52 7.51 7.51 7.50 7.32 7.32 7.31 7.30 7.29 7.28 7.23 7.23 7.23 7.22 7.21 7.21 7.20 7.19 7.19
2.84 2.83 2.81 2.25 2.23 2.22 1.63
5.00 7.53 2.67
1.70 1.70 3.25
f1 (ppm)
Ph Ph H2N N H Ph

a




b

**Figure S1.** (a) $^{1}$H NMR spectra of ligand in $CDCl_3$ (b) HRMS data of the ligand.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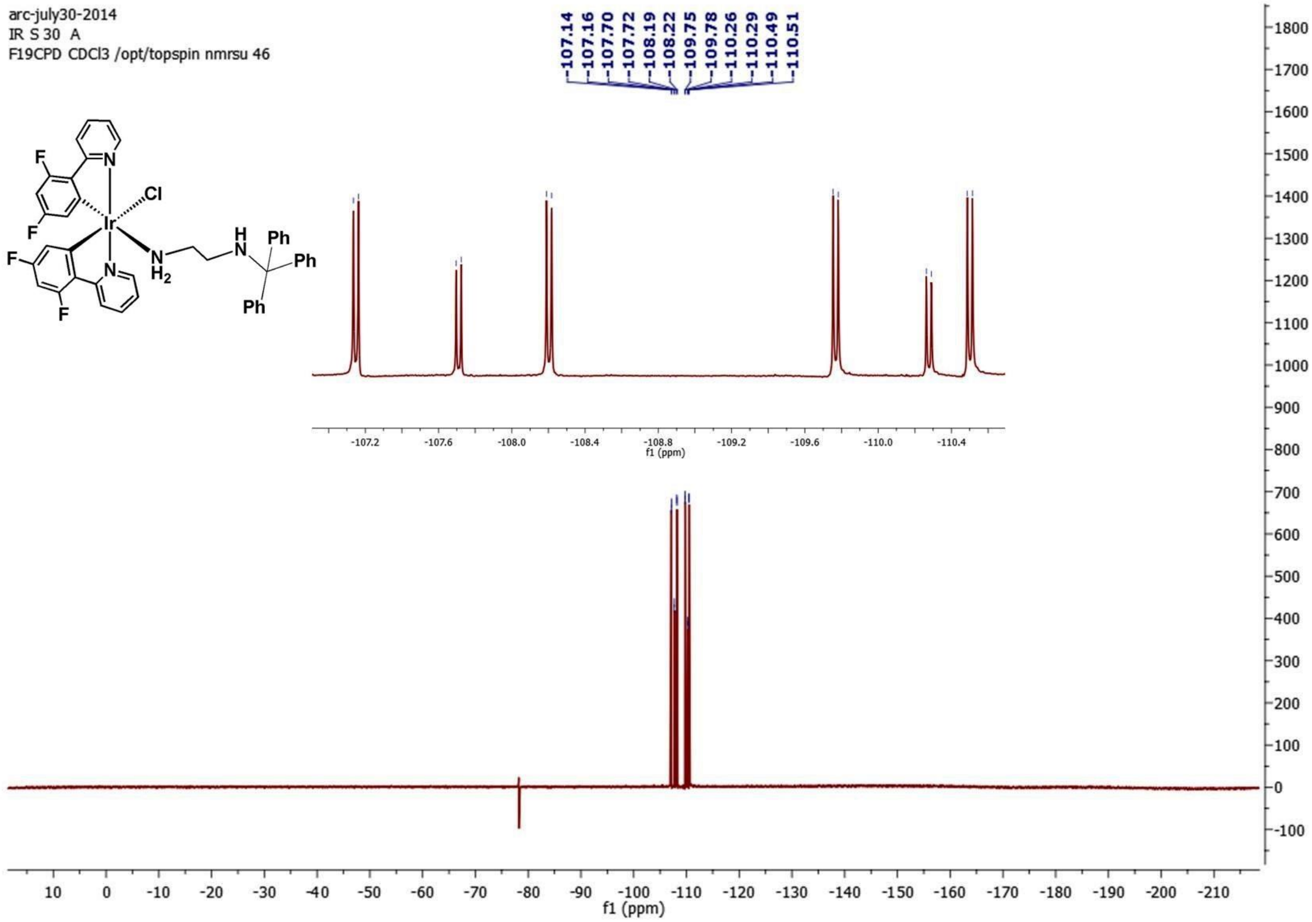
Ir-S3O-ED
F
N
Cl
Ir
F
F
N
H
Ph
Ph
N
H2
F
Ph
9.91
9.90
7.32
7.32
7.31
7.30
7.28
7.26
7.24
7.22
5.75
5.74
5.73
5.72
5.59
5.59
5.57
5.56
3.39
3.36
3.34
3.29
3.26
1.60
f1 (ppm)
f1 (ppm)

a


arc-july30-2014
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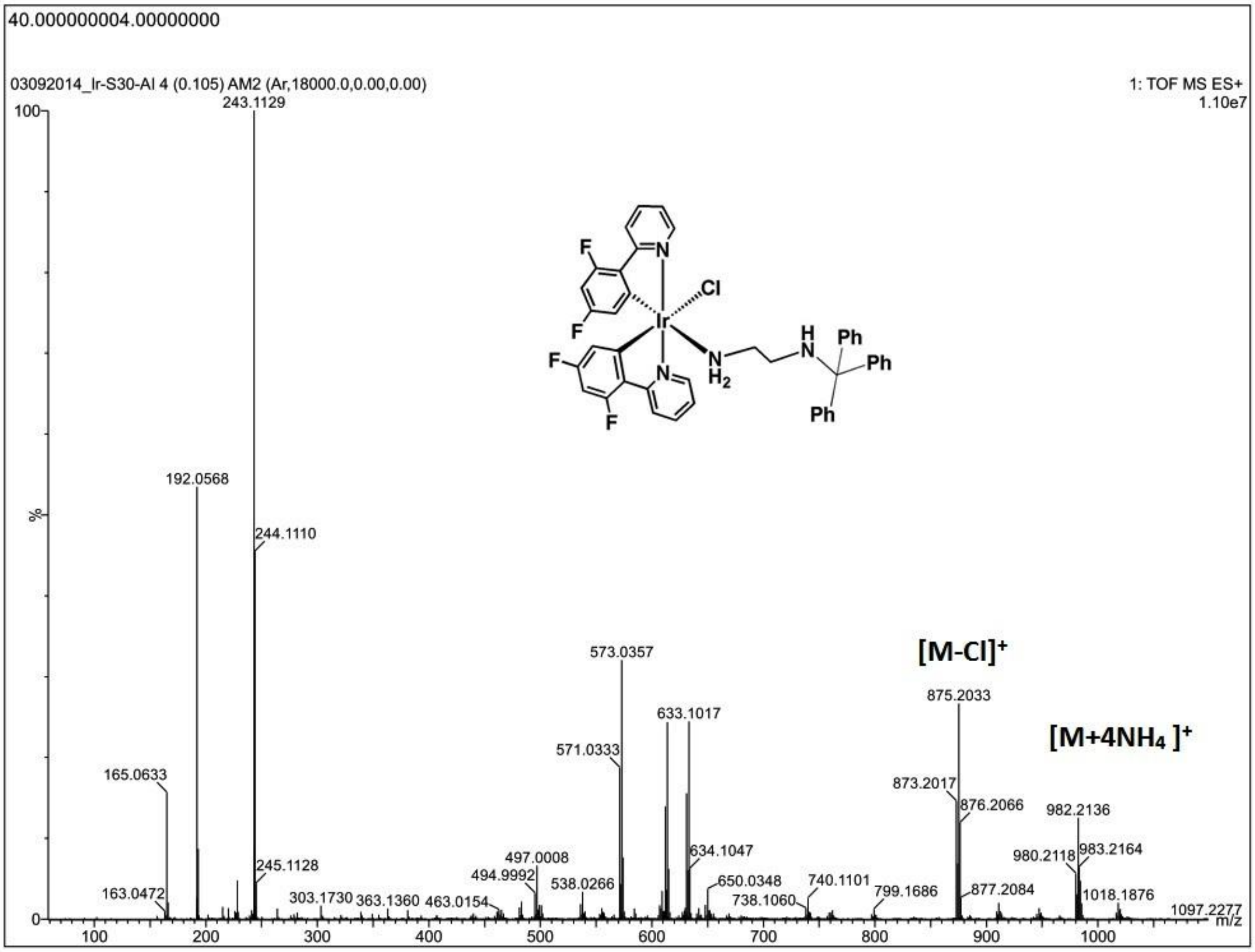
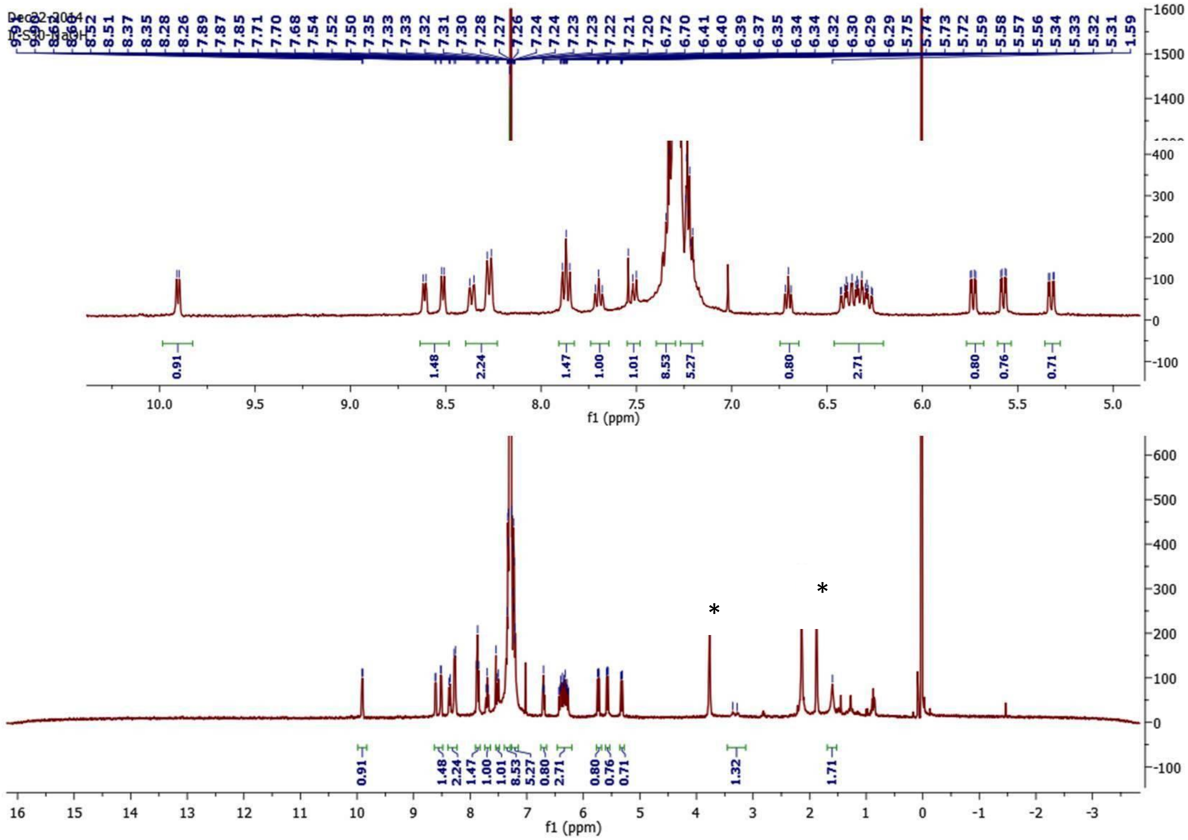
F19CPD CDCl3 /opt/topspin nmrsu 46
-107.14
-107.16
-107.70
-107.72
-108.19
-108.22
-109.75
-109.78
-110.26
-110.29
-110.49
-110.51
F
N
Cl
Ir
N
H
Ph
Ph
Ph
$H_2$
f1 (ppm)
f1 (ppm)

b




c

**Figure S2.** (a) [1]H NMR spectra of **1** in $CDCl_3$; (b) [19]F NMR spectra of **1** in $CDCl_3$ (c) HRMS data of **1**.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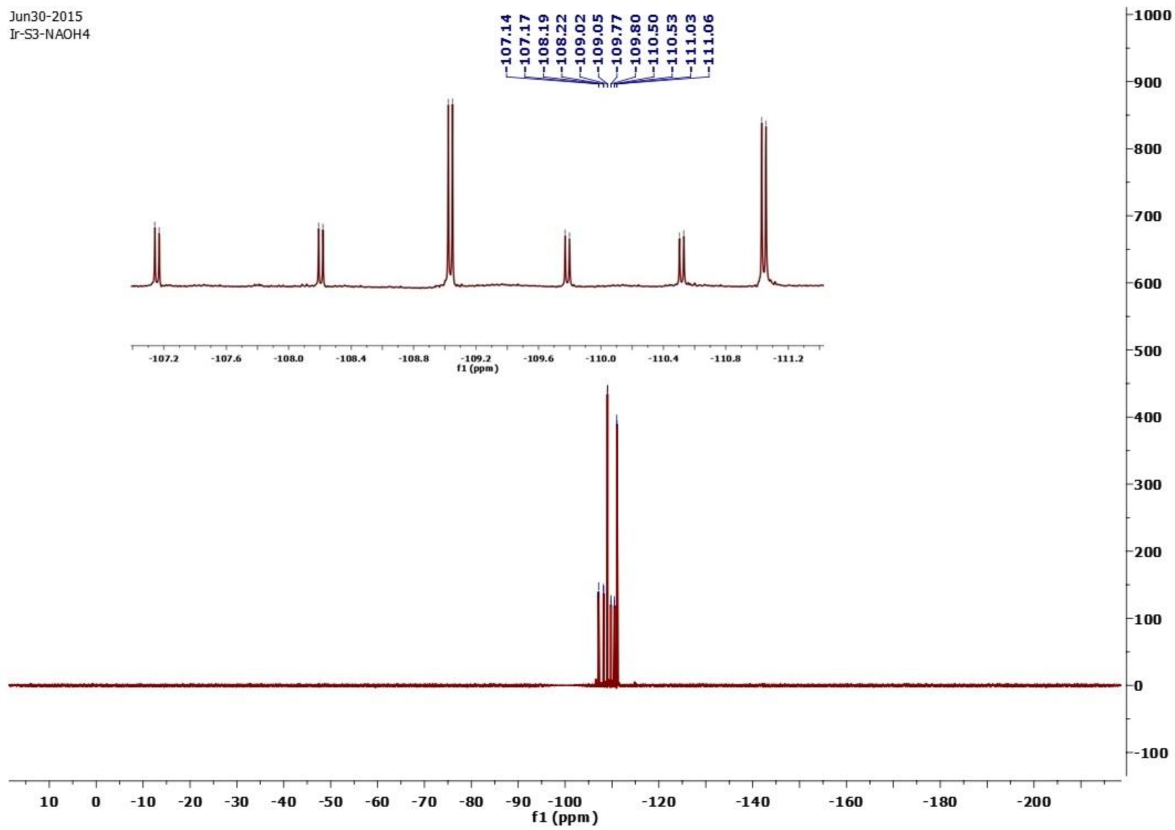
0.91
1.48
2.24
1.47
1.00
1.01
8.53
5.27
0.80
2.71
0.80
0.76
0.71
1.32
1.71
*
*
f1 (ppm)

a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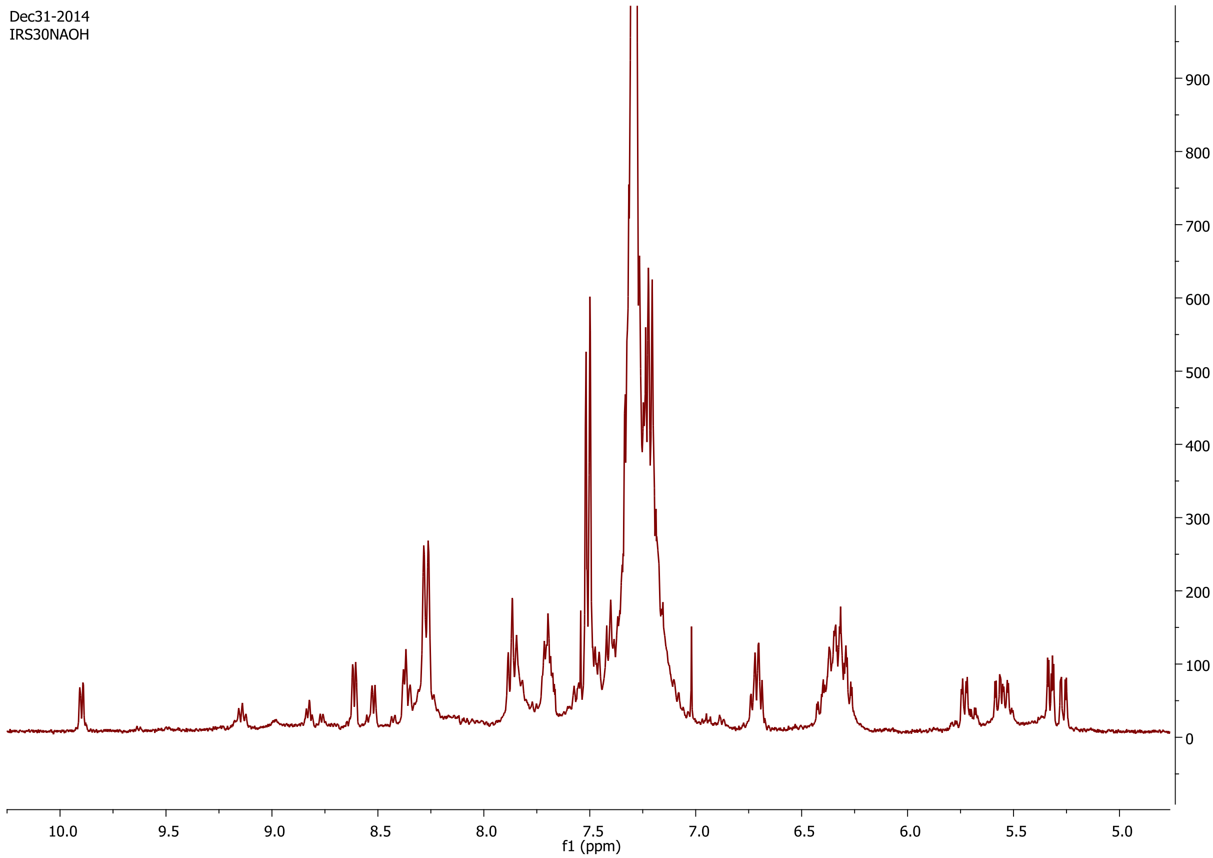
-108.19
-108.22
-109.02
-109.05
-109.77
-109.80
-110.50
-110.53
-111.03
-111.06
f1 (ppm)
f1 (ppm)

b



Dec31-2014
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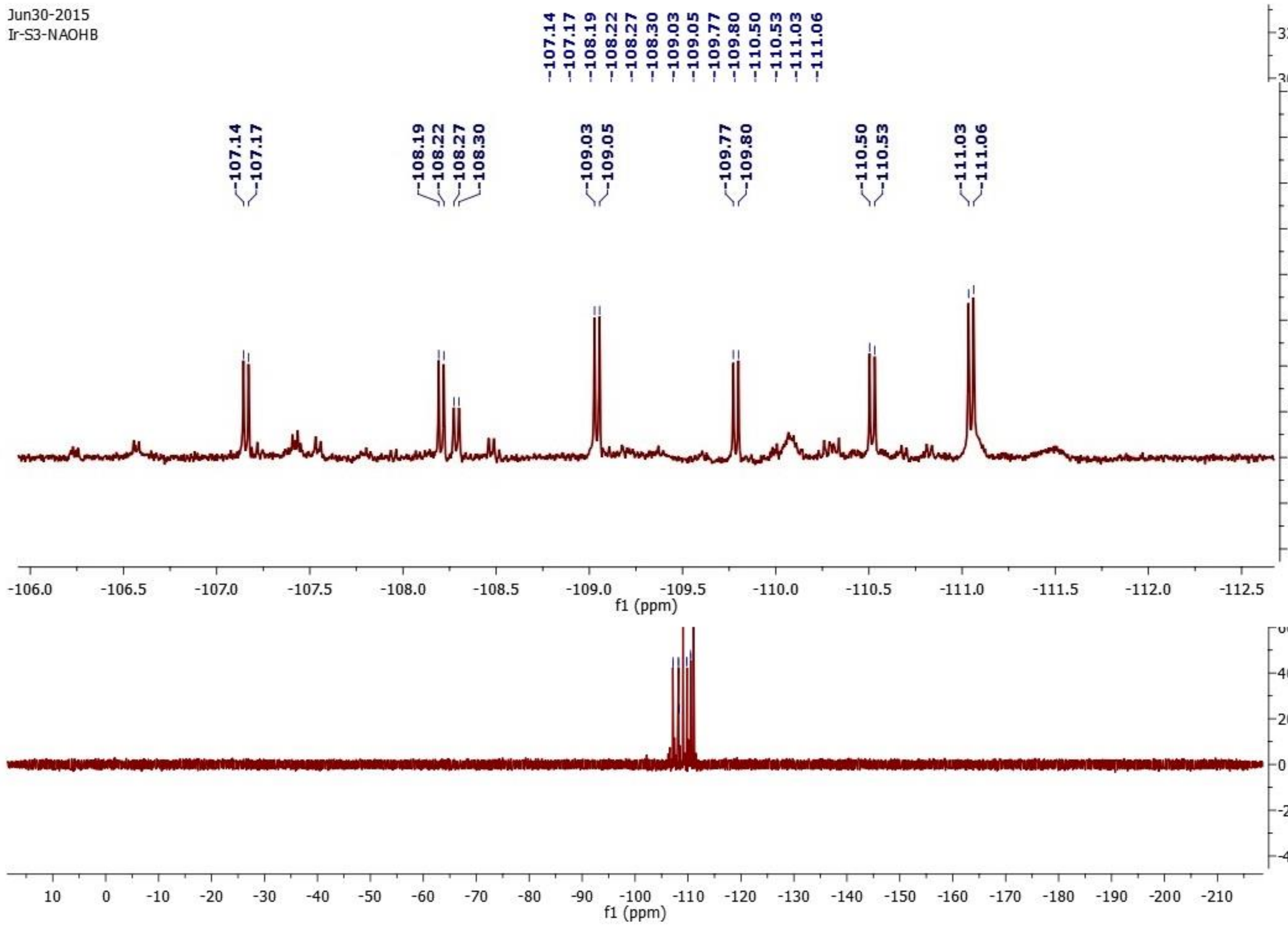
900
800
700
600
500
400
300
200
100
0
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
f1 (ppm)


c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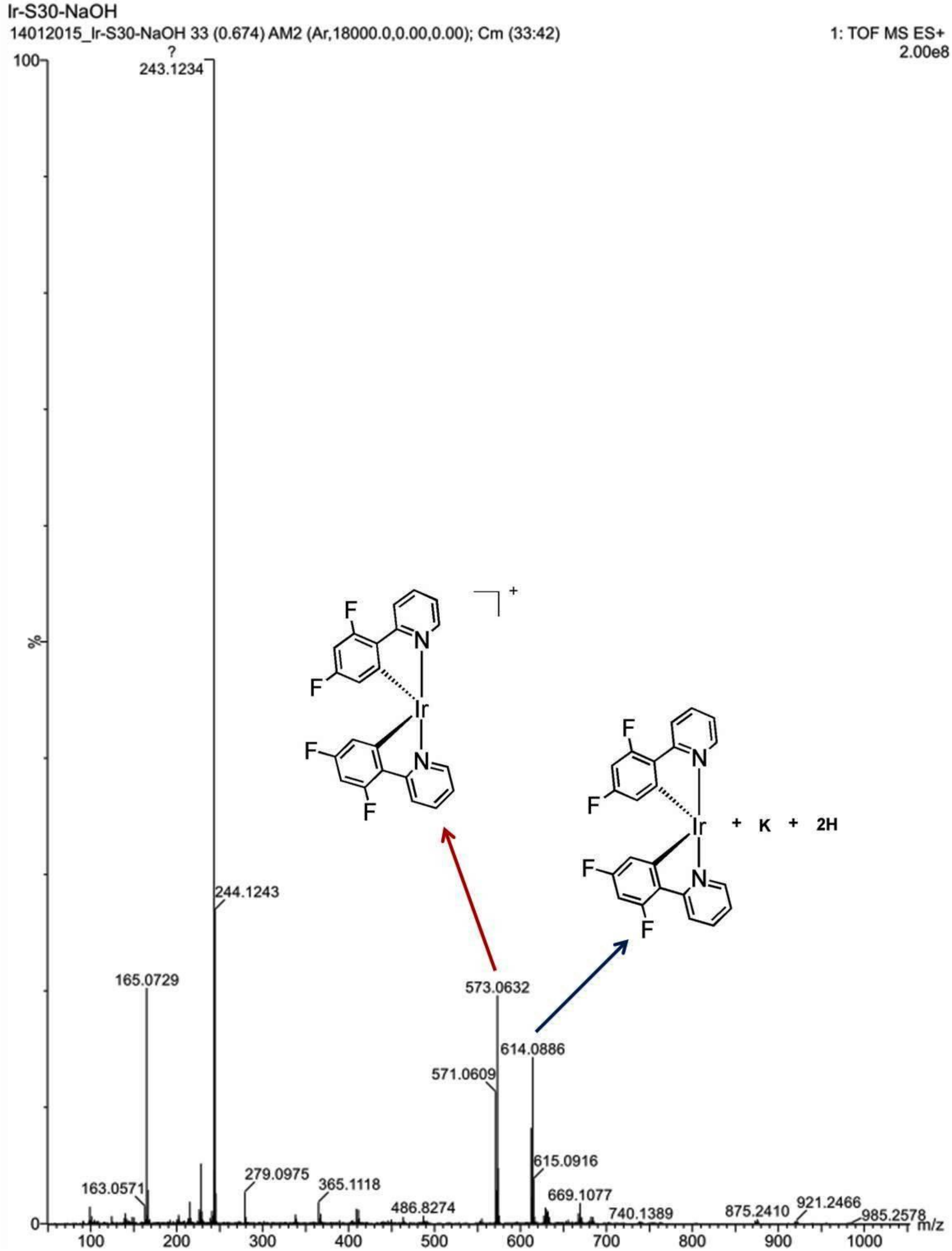
-107.17
-108.19
-108.22
-108.27
-108.30
-109.03
-109.05
-109.77
-109.80
-110.50
-110.53
-111.03
-111.06
f1 (ppm)
f1 (ppm)

d



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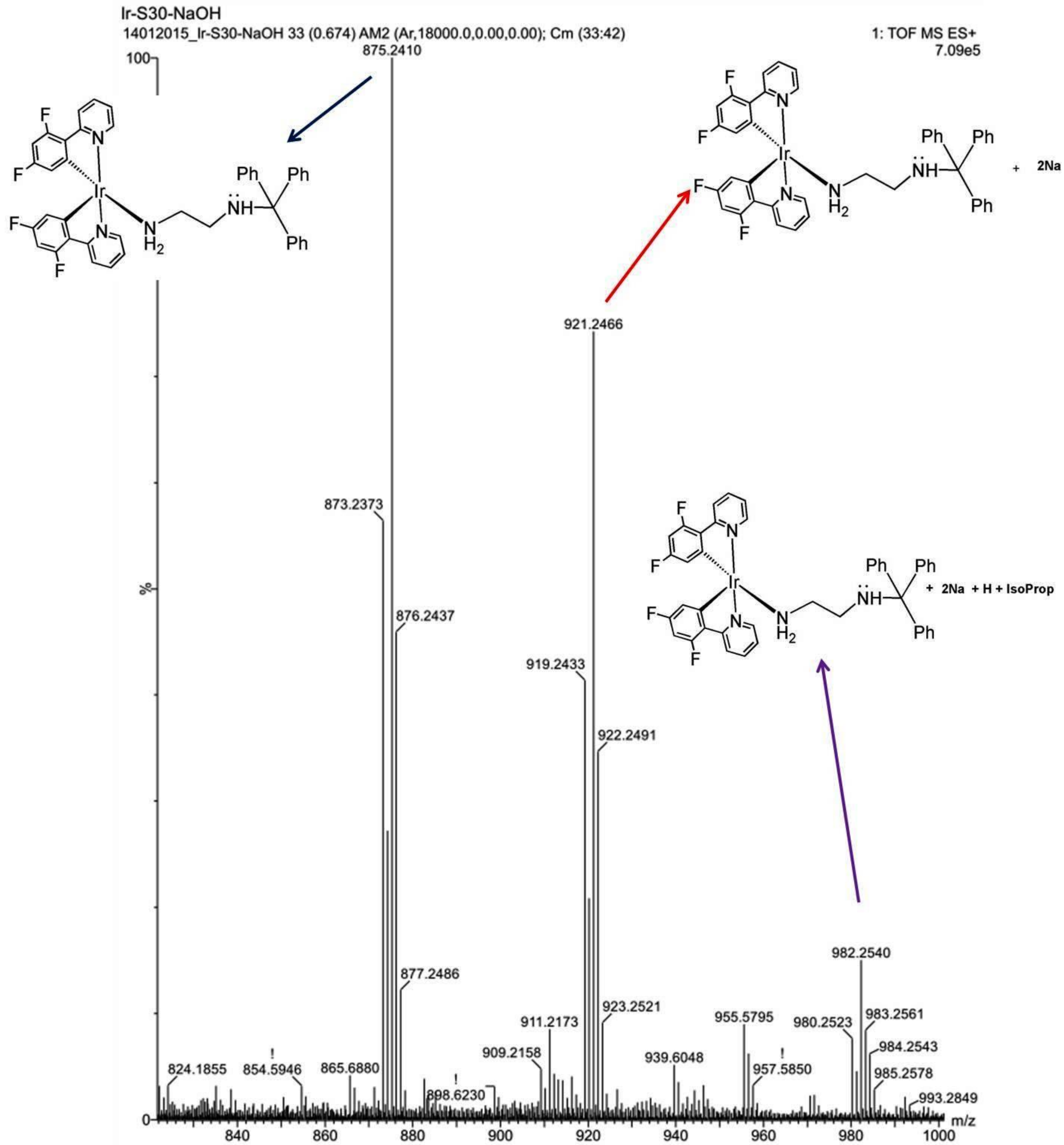
14012015_Ir-S30-NaOH 33 (0.674) AM2 (Ar,18000.0,0.00,0.00); Cm (33:42)
1: TOF MS ES+
2.00e8
100
%
0
?
243.1234
244.1243
165.0729
163.0571
279.0975
365.1118
486.8274
573.0632
571.0609
614.0886
615.0916
669.1077
740.1389
875.2410
921.2466
985.2578
100
200
300
400
500
600
700
800
900
1000
m/z
F
F
N
Ir
F
N
F
+
F
F
N
Ir
F
N
F
+ K + 2H

e


Ir-S30-NaOH
14012015_Ir-S30-NaOH 33 (0.674) AM2 (Ar,18000.0,0.00,0.00); Cm (33:42)
1: TOF MS ES+
7.09e5
875.2410
921.2466
873.2373
876.2437
919.2433
922.2491
982.2540
877.2486
923.2521
911.2173
955.5795
980.2523
983.2561
984.2543
909.2158
939.6048
824.1855
854.5946
865.6880
957.5850
985.2578
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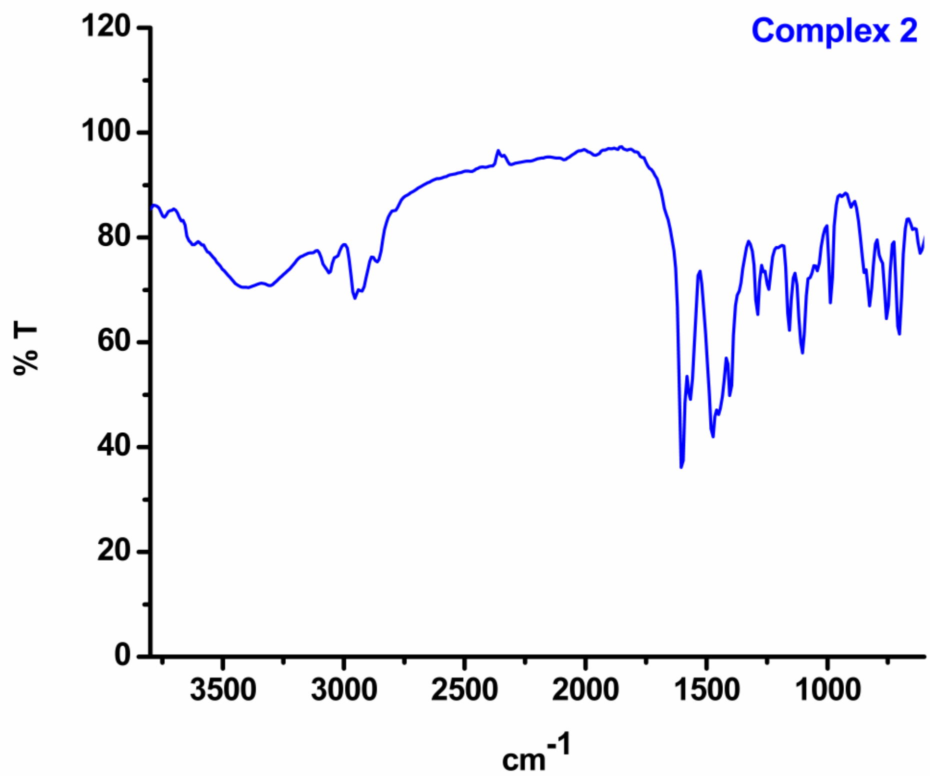
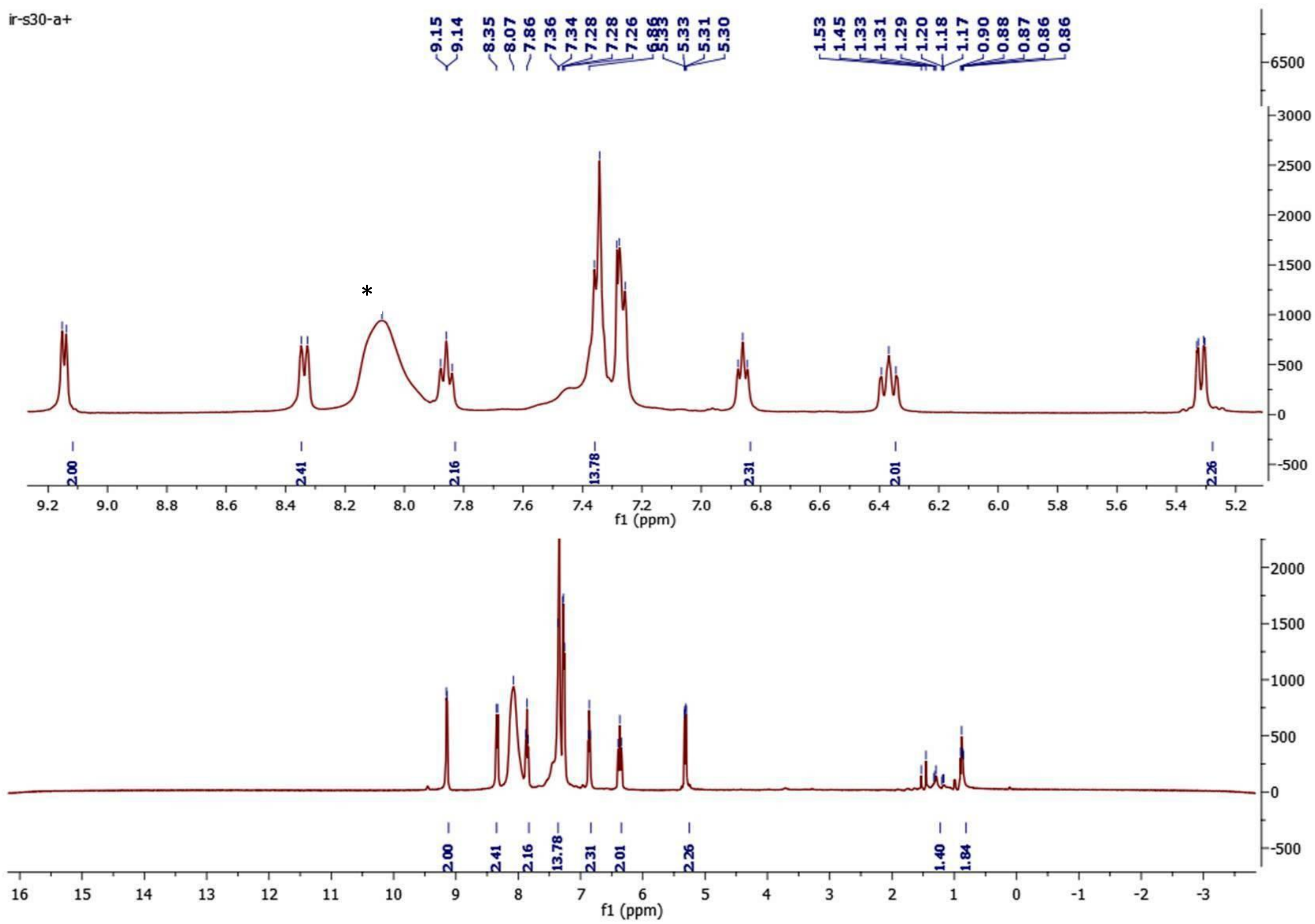
993.2849
+ 2Na
+ 2Na + H + IsoProp
Ph
NH
N
H2
Ir
F
%
m/z

f




g

**Figure S3.** (a) $^{1}$H NMR spectra of purified **2** in $CDCl_3$; (b) $^{19}$F NMR spectra of purified **2** in $CDCl_3$; (c) $^{1}$H NMR spectra of **1** after addition of 1M NaOH; (d) $^{19}$F NMR spectra of **1** after addition of 1M NaOH (top: extended; bottom: full); (e) HRMS data of **2**; (f) Expansion of HRMS data of the **2**; (g) IR spectra of **2** showing –OH stretching frequency at 3421$cm^{-1}$


ir-s30-a+
9.15
9.14
8.35
8.07
7.86
7.36
7.34
7.28
7.28
7.26
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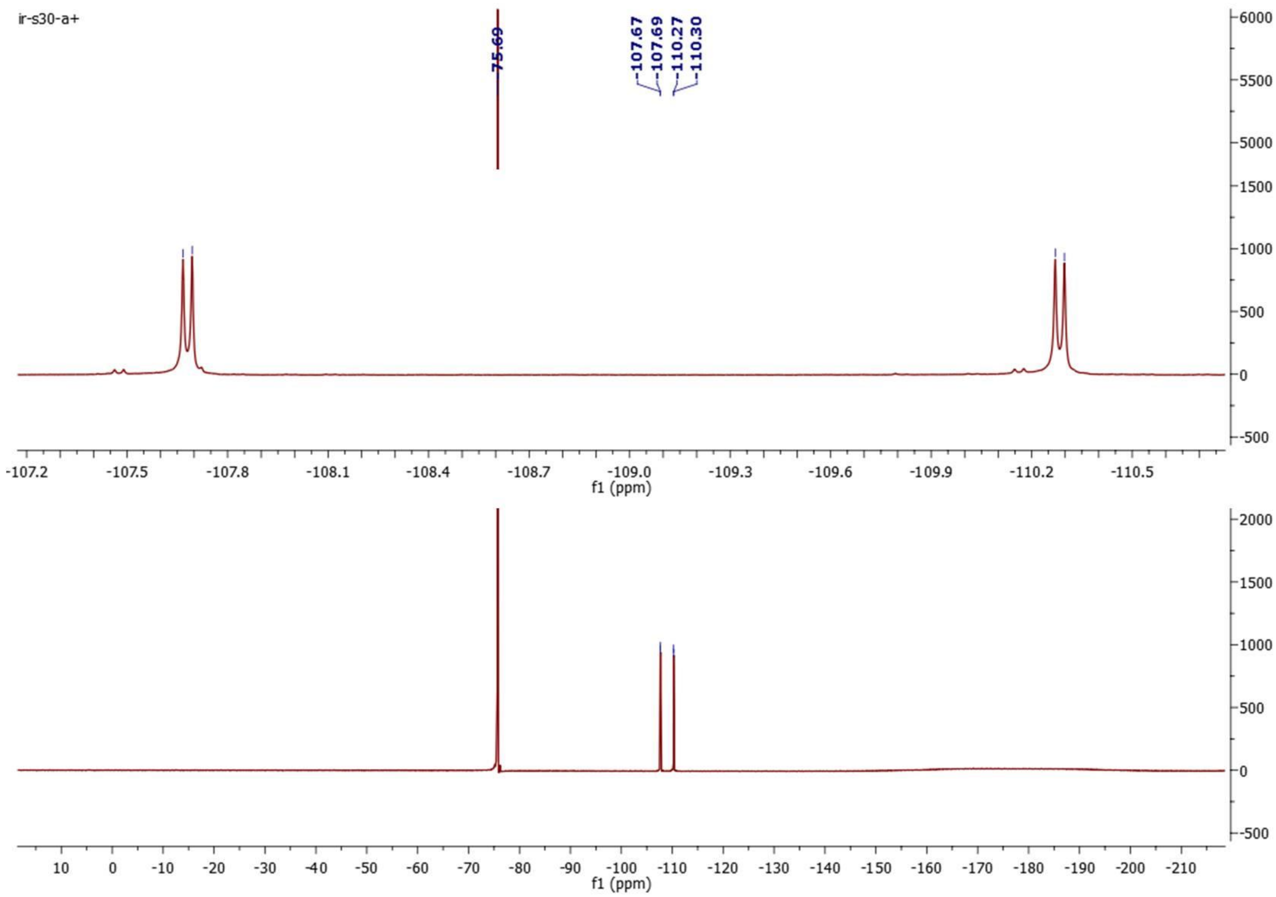
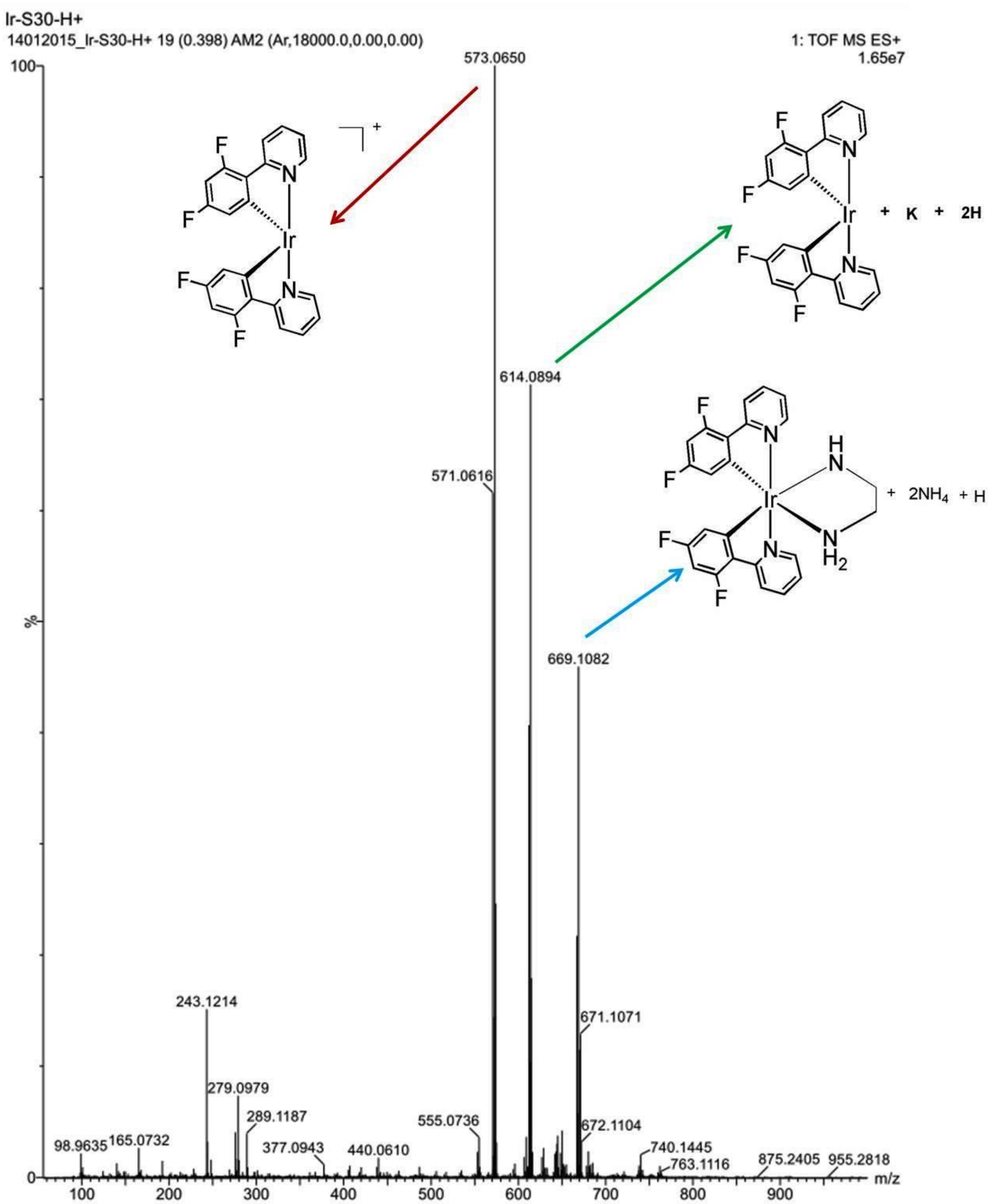
5.33
5.33
5.31
5.30
1.53
1.45
1.33
1.31
1.29
1.20
1.18
1.17
0.90
0.88
0.87
0.86
0.86
*
2.00
2.41
2.16
13.78
2.31
2.01
2.26
1.40
1.84
f1 (ppm)
f1 (ppm)

a




b



Ir-S30-H+
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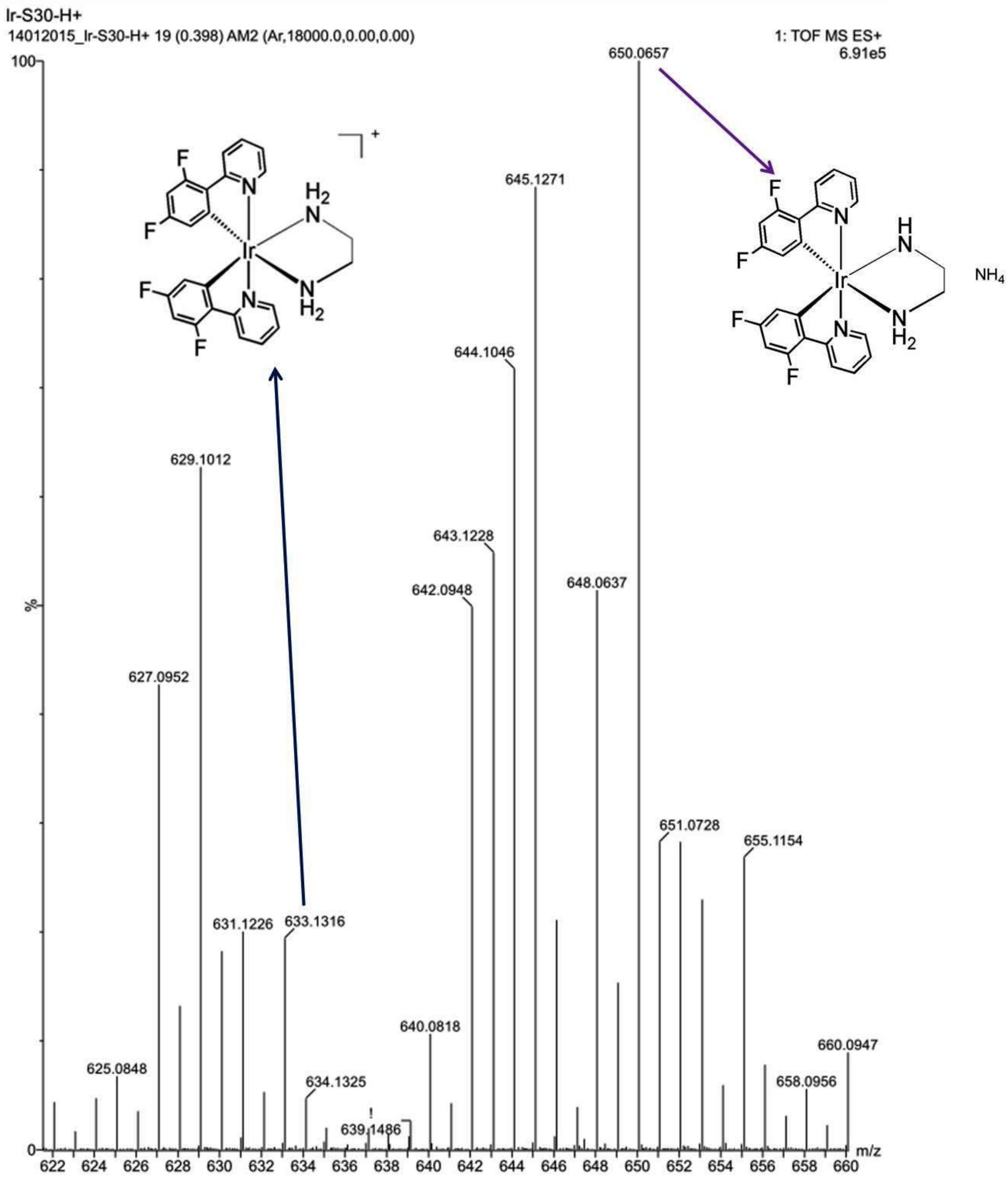
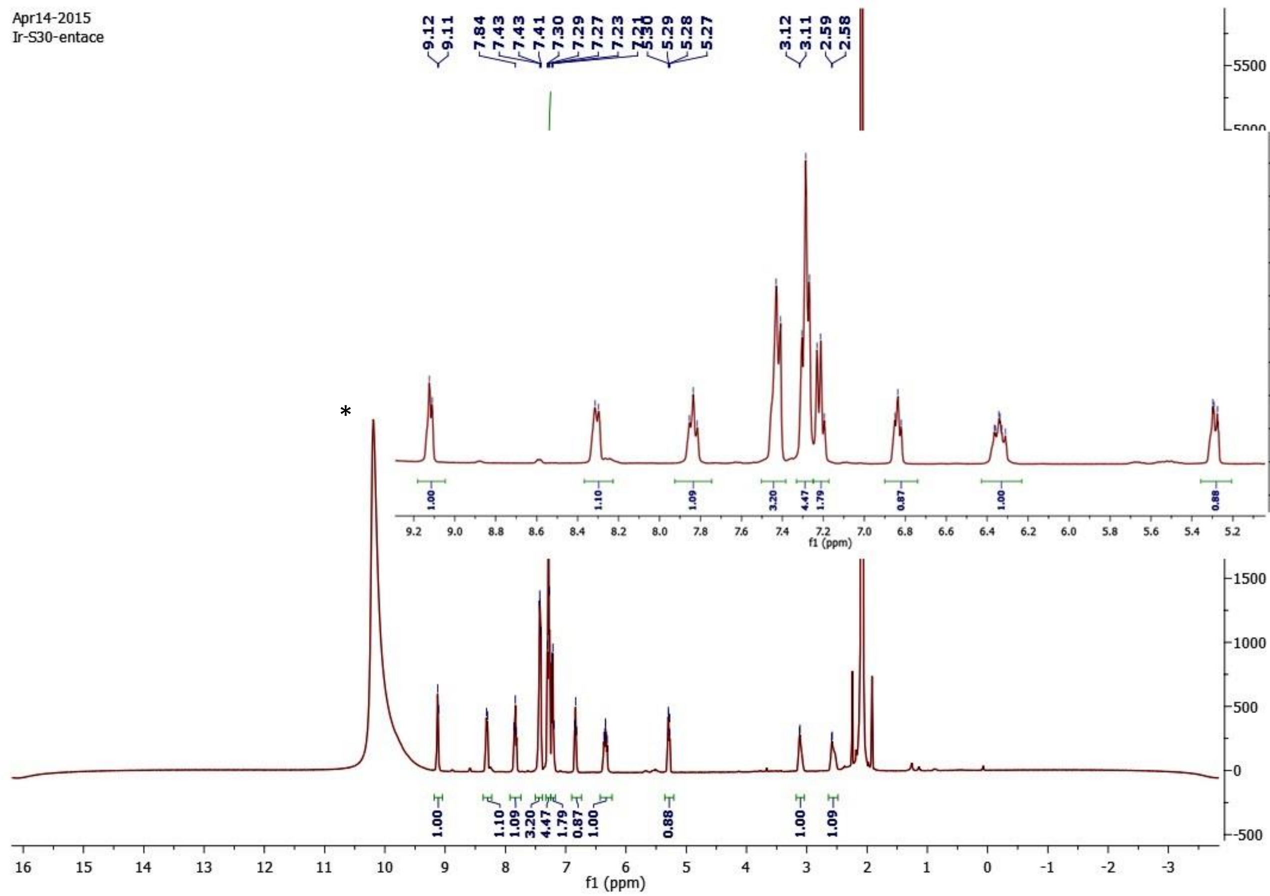
1.65e7
573.0650
614.0894
571.0616
669.1082
243.1214
671.1071
279.0979
289.1187
555.0736
672.1104
98.9635
165.0732
377.0943
440.0610
740.1445
763.1116
875.2405
955.2818
%
m/z
+ K + 2H
+ 2NH4 + H


c

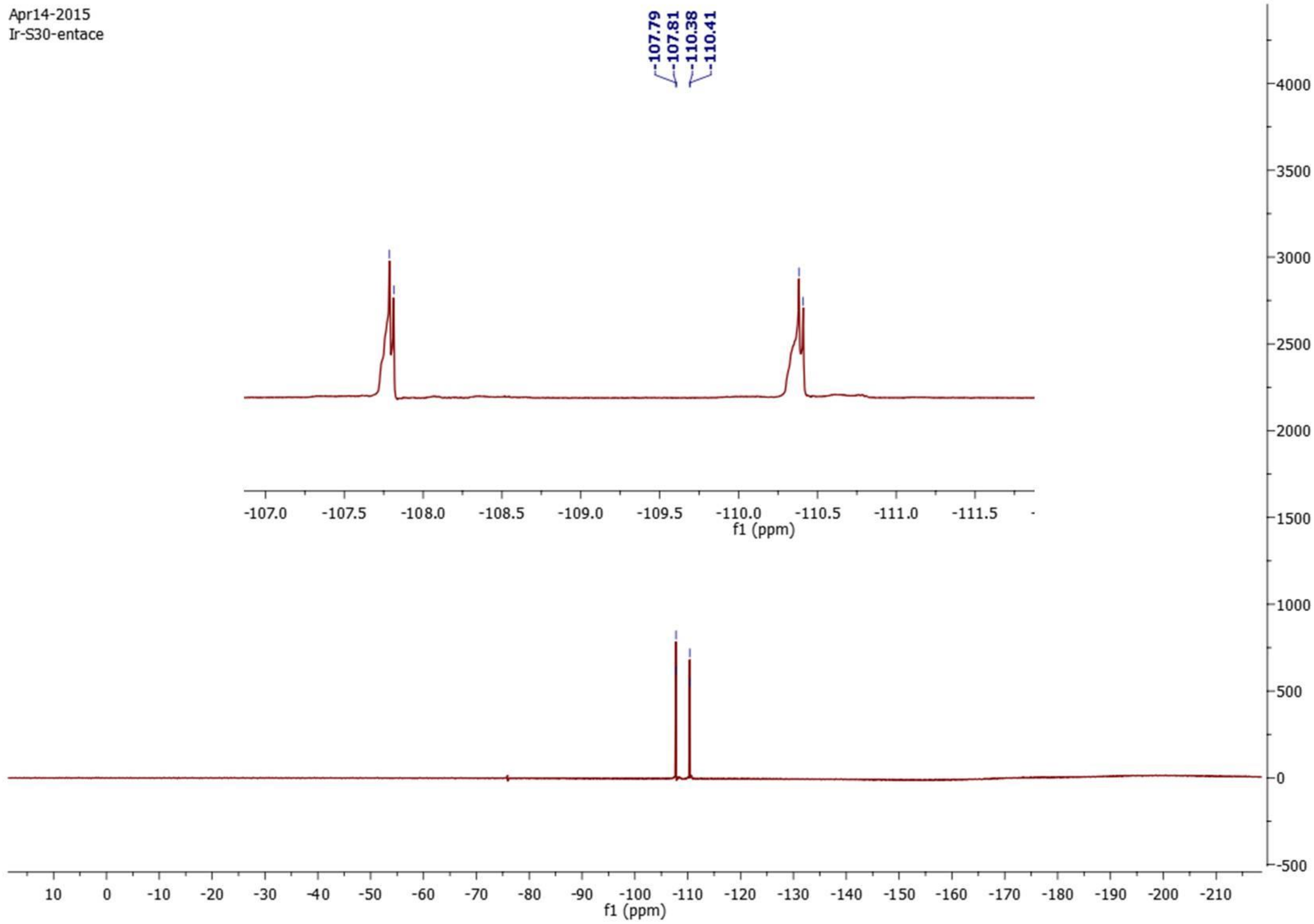



d

**Figure S4.** (a) [1]H NMR spectra of **3** in $CDCl_3$ (* TFA, acid proton signal in [1]H NMR); (b) [19]F NMR spectra of **3** in $CDCl_3$ (c) HRMS data of **3** (d) Expansion of HRMS data of the **3**.




a




b

**Figure S5.** (a) $^{1}$H NMR spectra of **1** in $CDCl_3$ after addition of AcOH (*AcOH, acid proton signal in $^{1}$H NMR) ; (b) $^{19}$F NMR spectra of **1** in $CDCl_3$ after addition of AcOH

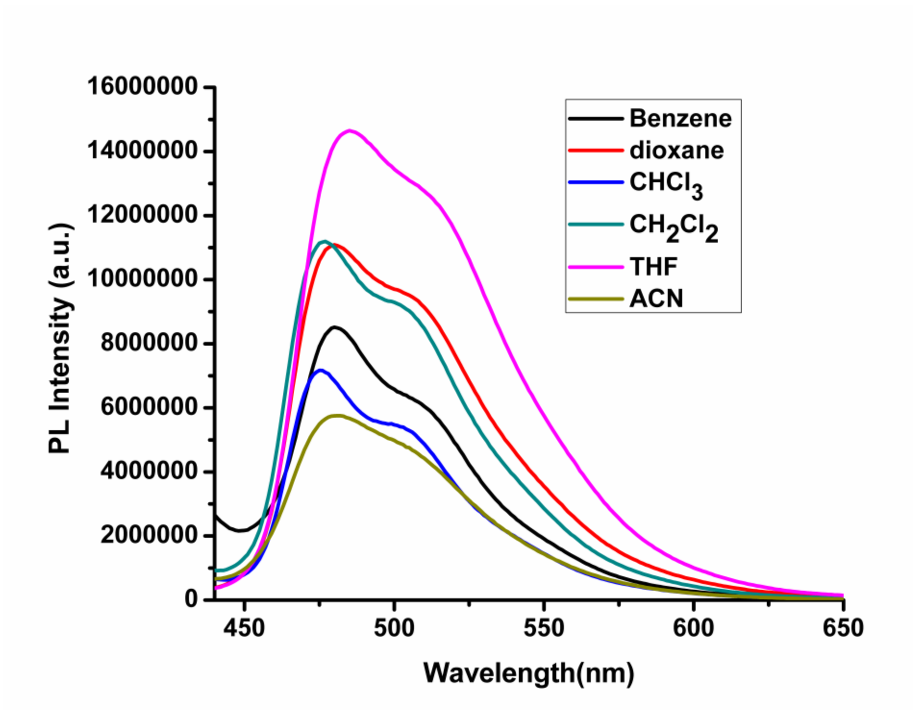



**Figure S6.** Emission spectra of **1** in different solvents keeping concentration same, [c]=1x10$^{-5}$

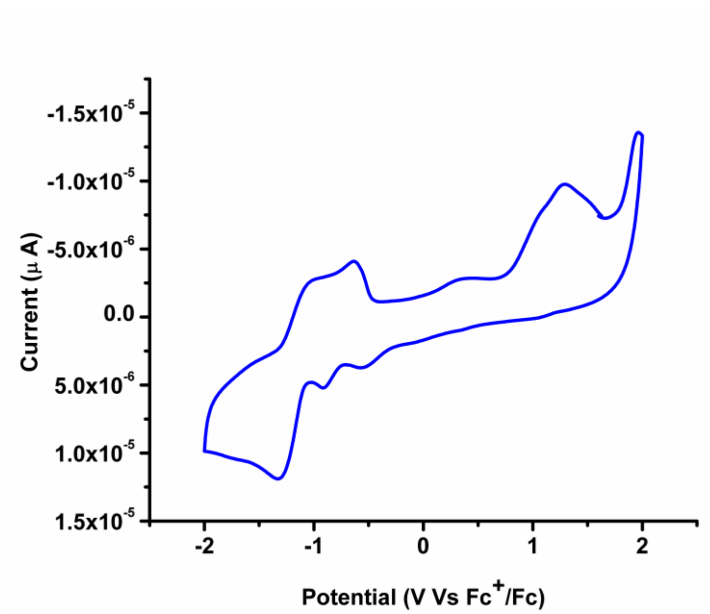



**Figure S7.** Cyclic voltammogram of **1**, recorded in ACN at a scan rate of 0.05 V s$^{-1}$

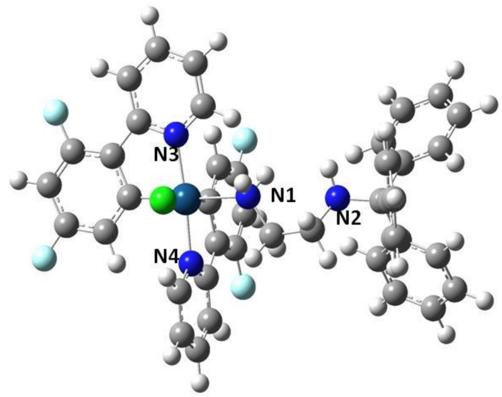



**Figure S8.** Optimized structure of **1**, (using Gaussian 09 program suite) in DCM solvent.

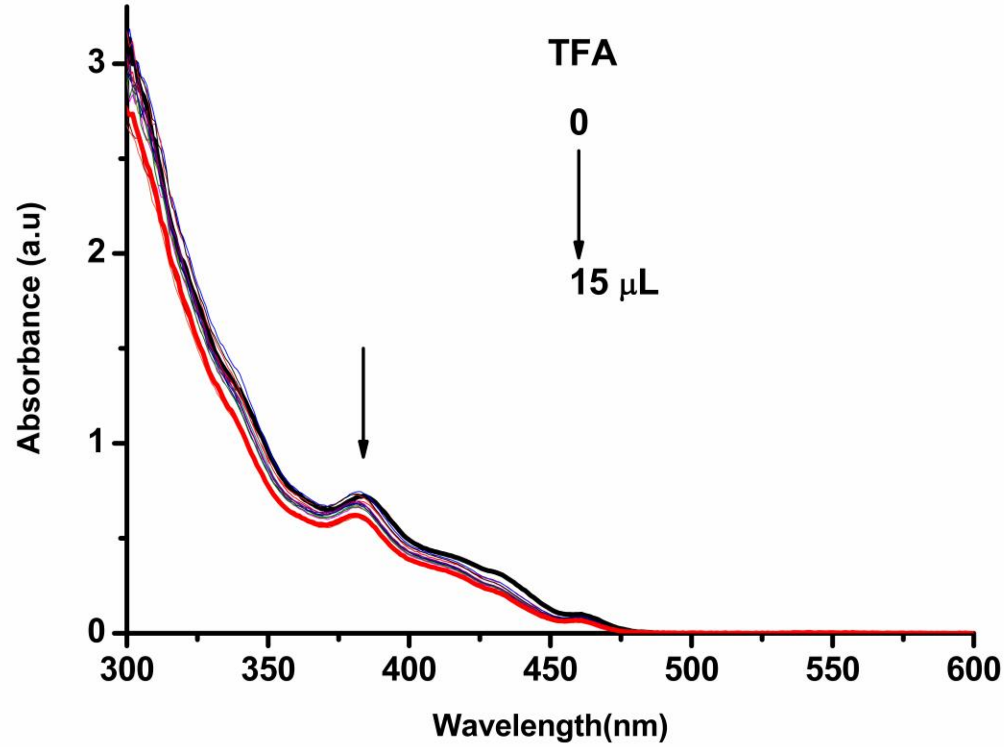



**Figure S9.** Absorbance spectra of **1** with increasing concentration of TFA (0-15 μL) with [c] =$1x10^{-5}$

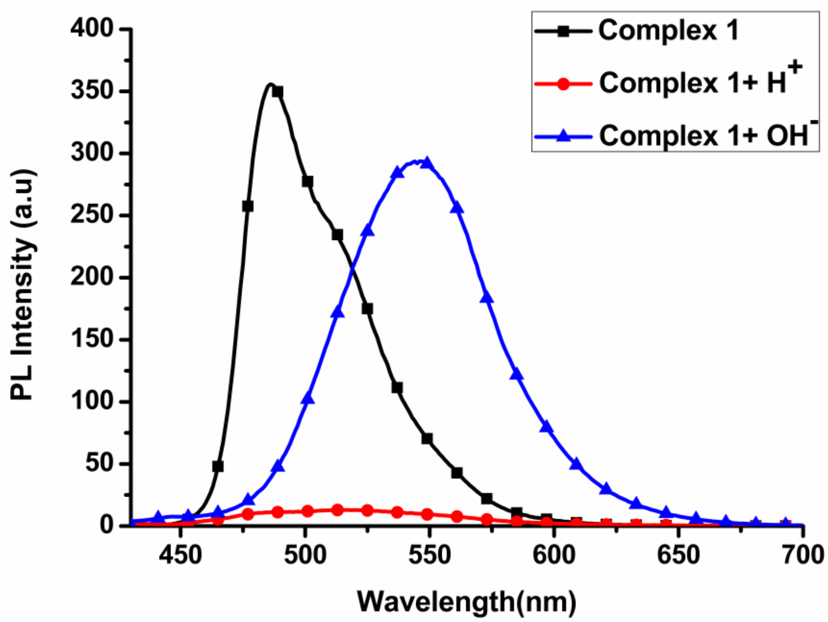



**Figure S10.** Emission spectra of **1** in DCM , DCM+ TFA and THF+ 1M NaOH in water (1:9,v/v)

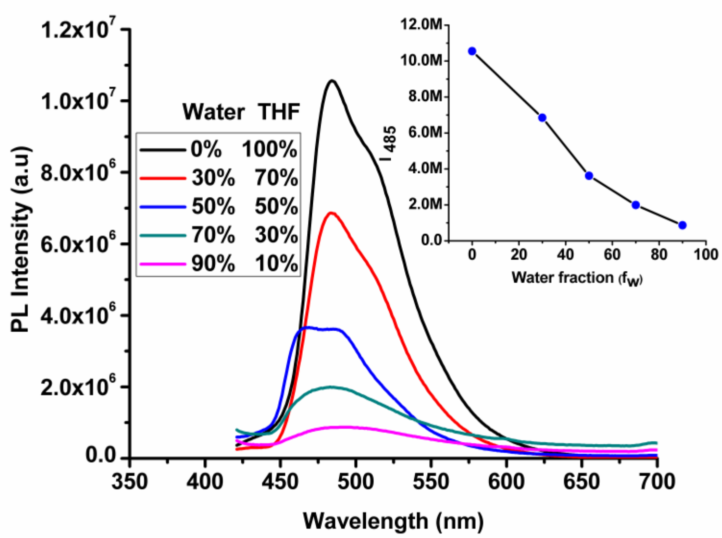



**Figure S11.** Emission spectra of **1** in presence of different water fraction (0 - 90%).

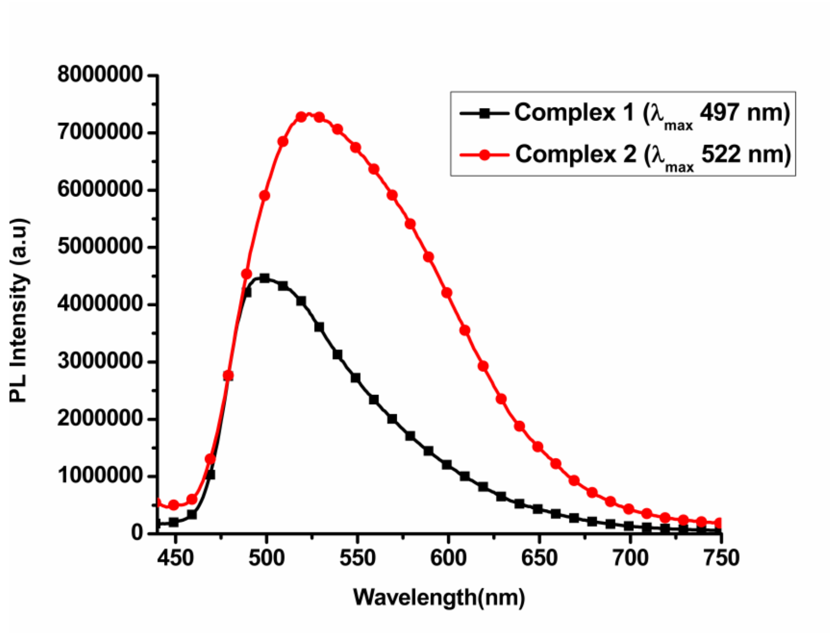
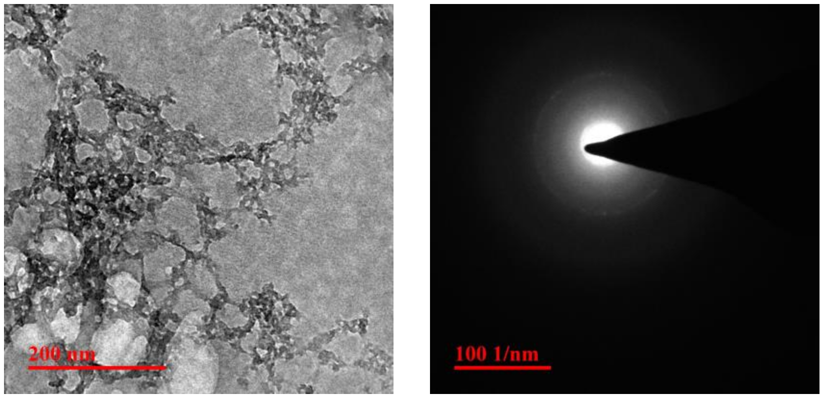
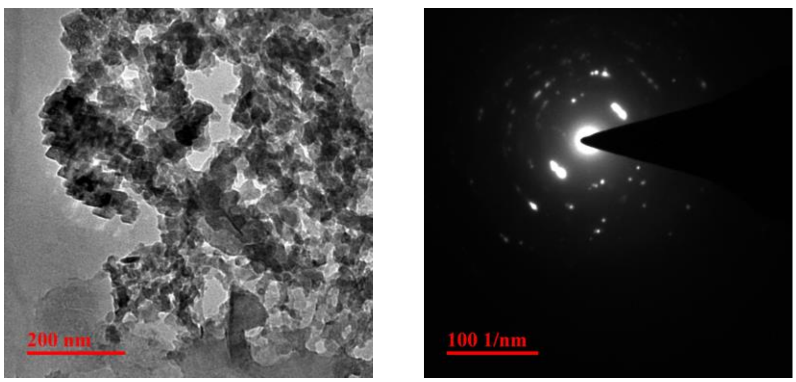



**Figure S12.** Thin film emission of **1** and **2**

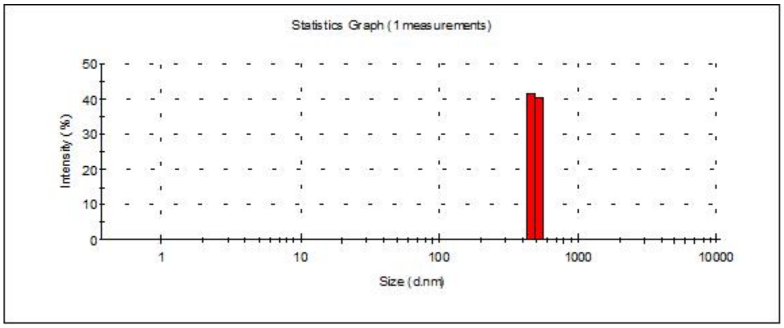



a

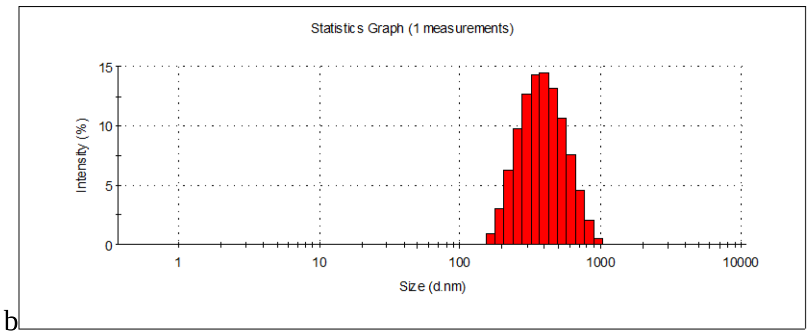



b

**Figure S13.** TEM images and ED patterns of **2** (a) amorphous nano aggregates at $f_w$= 40% and (b) crystalline aggregate at $f_w$= 90%

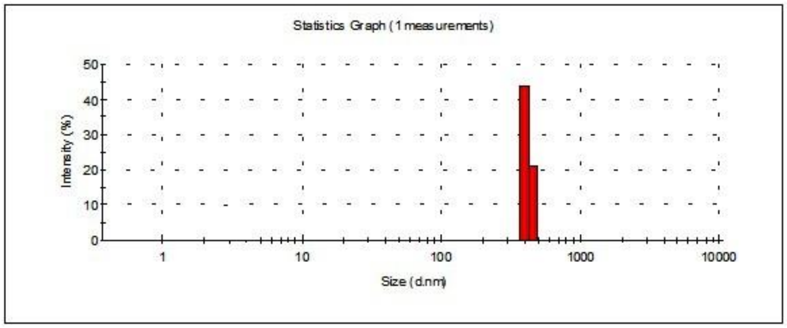



a

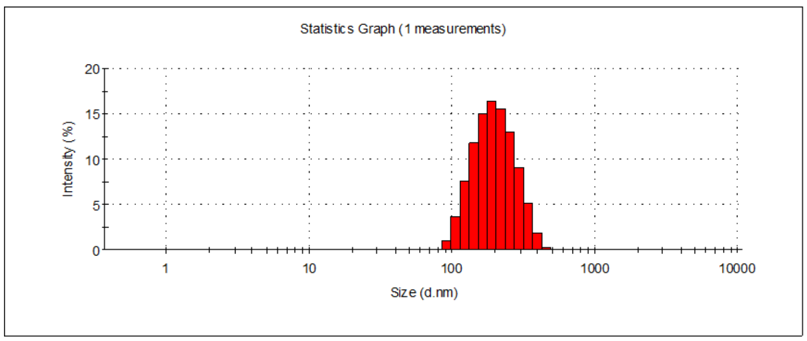
b 


b

**Figure S14.** (a,b) Size distribution graph for **1** in presence of different 1M NaOH fractions (a) at 50% , (b) at 90%




a




b

**Figure S15.** Size distribution graph for **1** in presence of different water fractions (a) at 50%, (b) at 90%

**Table S1.** Crystal data and structure refinement for **1**

| | |
|---|---|
| Empirical formula | C43 H34 Cl F4 Ir N4 |
| Formula weight | 910.41 |
| Temperature (K) | 100 K |
| Crystal system | Triclinic |
| Space group | P -1 |
| Unit cell dimensions | a=11.2477(14) Å<br>b=11.5288(18) Å<br>c=16.682(2) Å<br>α = 103.532(7), β = 93.738(7) (4) γ = 94.584(6) |
| Volume (Å3) | 2088.6(5) |
| Z | 2 |
| Density (Mg/m3) | 1.448 |
| Absorption coefficient ($mm^{-1}$) | 3.311 |
| F(000) | 900.0 |

**Table S2**. Selected Bond lengths [Å] and angles [°] for **1**

| Bond distances (Å) | **Complex 1** |
|---|---|
| Ir1- C33 | 2.020 (8) |
| Ir1- C22 | 2.019 (9) |
| Ir1-Cl1 | 2.485 (2) |
| Ir1-N3 | 2.052 (7) |
| Ir1-N4 | 2.049 (7) |
| Ir1-N1 | 2.193 (7) |
| | |
| **Bond angles (°)** | |
| N4 Ir1 Cl1 | 87.8 (2) |
| N3 Ir1 Cl1 | 96.5 (2) |
| N1 Ir1 Cl1 | 87.2 (2) |
| N3 Ir1 C22 | 80.4 (3) |
| N4 Ir 1N3 | 172.4 (2) |
| N1 Ir1 C33 | 176.8 (2) |

**Table S3** Photophysical properties of **1, 2** and **3**

| **Complex** | **UV-Vis absorption[a] nm, (ε x $10^4$, $M^{-1}cm^{-1}$)** | **PL[a] ($\lambda_{emi}$) (nm)** | **τ (μs)[b]** | **QY[c]** | **QY[d]** |
|---|---|---|---|---|---|
| **1 (solution)** | 262 (5.0), 331(1.2) 388(0.52), 436(0.32),468(0.10) | 485 | 1.3 | 3.0 | |
| **1 (Solid)** | | 497 | | | 3.08 |
| **2 (solution)** | 256(4.42), 383(0.64), 433(0.28),464(0.14) | 507 | | 2.5 | |
| **2 (solid)** | | 522 | | | 3.40 |
| **3 (solution)** | 262(3.50), 329(0.50), 435(0.16), 468(0.08) | 507 | | 0 | |
| **3 (Solid)** | | 510 | | | 0 |

[a] Spectra were recorded in degassed dichloromethane (DCM) at room temperature with ε x $10^4$, $M^{-1}cm^{-1}$; [b] Life time data recorded in DCM with [c]=1 x $10^{-4}$ M ; [c]solid state quantum yield for **1-3** were calculated using integerating sphere. [d]quantum yields for the two complexes were measured in degassed DCM against quinine sulfate in 1.0 N sulfuric acid as reference (QY = 0.546).

**Table S4**. Comparison of some selected structural parameters (i.e., bond distances and bond angles) for the complex 1 obtained from experiment (i.e., X-ray study) and theoretical calculation.

| Structural parameters | Specific bond/angle | Exp. value (Å) | Theoretical value (Å) |
|---|---|---|---|
| Bond Length | Ir-Cl | 2.485 (2) | 2.53 |
| | Ir-N1 | 2.193 (7) | 2.23 |
| | Ir-N3 | 2.054 (7) | 2.04 |
| | Ir-C33 | 2.020 (8) | 1.99 |
| | Ir-N4 | 2.049 (7) | 2.04 |
| | Ir-C22 | 2.019 (9) | 1.99 |
| Bond angle | ∠C33IrN4 | 80.9° (3) | 80.63° |
| | ∠C22IrN3 | 80.4° (3) | 80.62° |
| | ∠C22IrN4 | 95.6° (3) | 96.05° |
| | ∠N1IrN3 | 90.5° (3) | 90.50° |
| | ∠N1IrCl | 87.2° (2) | 87.08° |
| | ∠C22IrC33 | 90.7° (3) | 87.40° |
| | ∠N3IrC33 | 92.7° (3) | 94.03° |
| | ∠N3IrCl | 96.5° (2) | 96.03° |
| | ∠C33IrCl | 92.7° (2) | 94.33° |
| | ∠N4IrN1 | 95.9° (3) | 94.96° |
| | ∠N1IrC22 | 89.7° (3) | 91.04° |

**Detection limit calculation** [1,2]

To determine the Signal/Noise ratio, the emission intensity of both complexes without $H^+/OH^-$ was measured by 10 times and the standard deviation of blank measurements was determined.
The detection limit is then calculated with the following equation.
**Detection limit = 3σ/m;** where σ is the standard deviation of blank measurements, m is the slope between the plot of PL intensity versus sample concentration.

References :

1. Yang, Mi-H.; Thirupathi, P.; Lee, K.-H.; *Org. Lett*. **2011**, *13***,** 5028.

2. Kaur, . S.; Bhalla, V.; Vij, V.; Kumar, M. ; *J. Mater. Chem. C* **2014**, *2*, 3936.