SUPPORTING INFORMATION

Synthesis, structural, photophysical and electrochemical studies of various *d*-metal complexes of btp [2,6-bis(1,2,3-triazol-4-yl)pyridine] ligands that give rise to the formation of metallo-supramolecular gels

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^{1}H NMR spectraof ligands and complexes

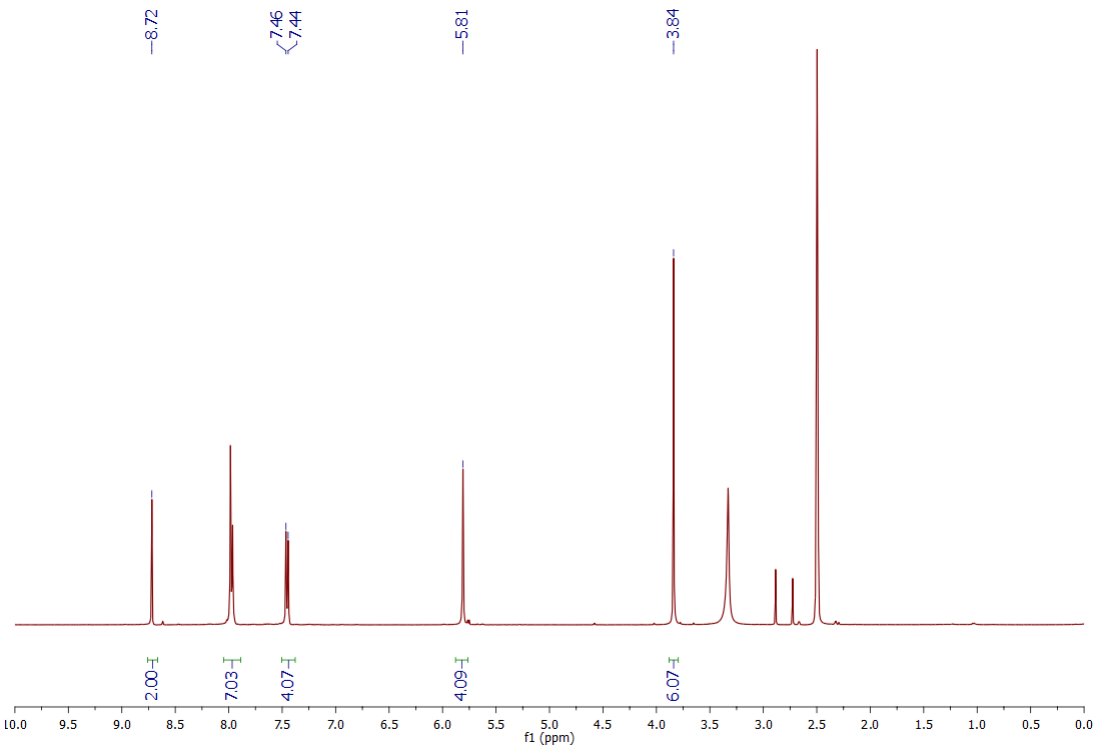

Fig. S1 ^{1}H NMR (400 MHz, DMSO-d_6) spectrum of ligand **1**.

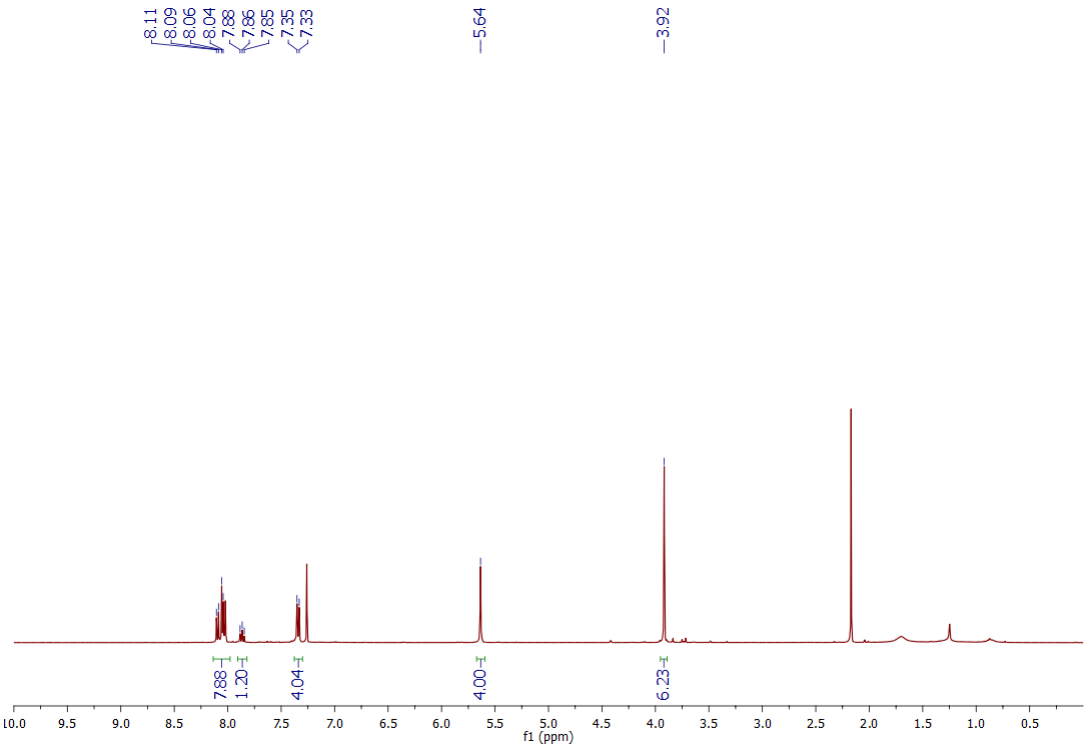

Fig. S2 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of ligand **1**.

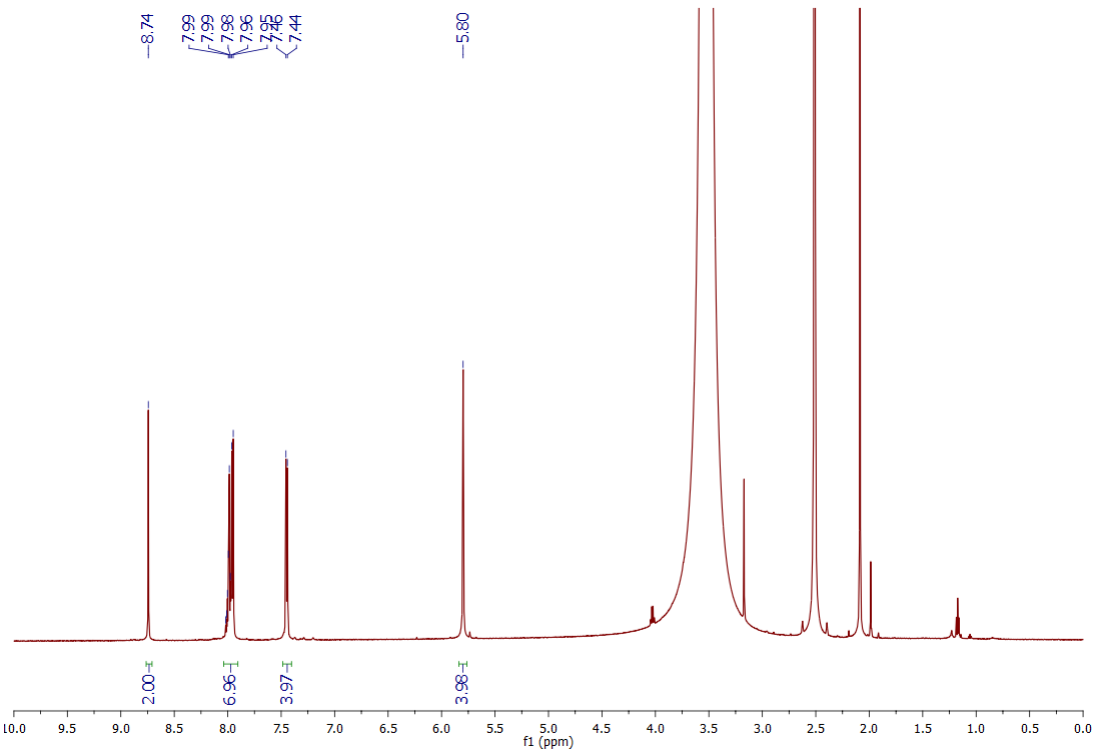

Fig. S3 ^{1}H NMR (600 MHz, DMSO-d_6) spectrum of ligand **2**.

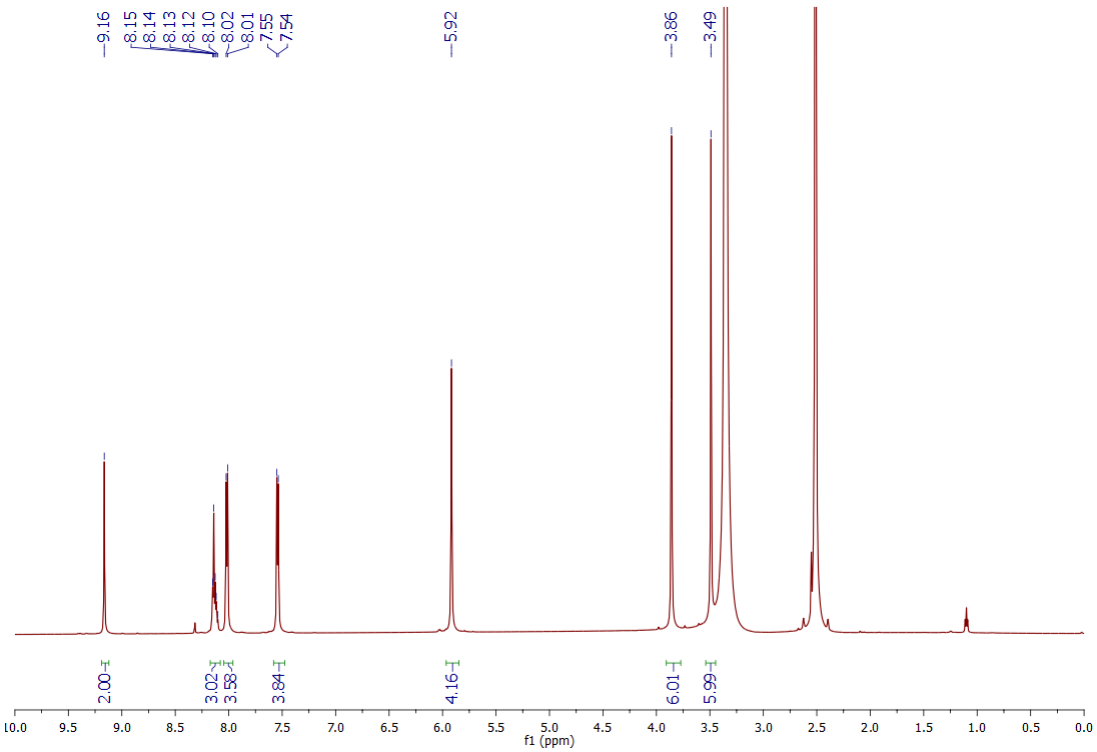

Fig. S4 ^{1}H NMR (600 MHz, DMSO-d_6) spectrum of [Ru·**1**Cl$_2$(DMSO)].

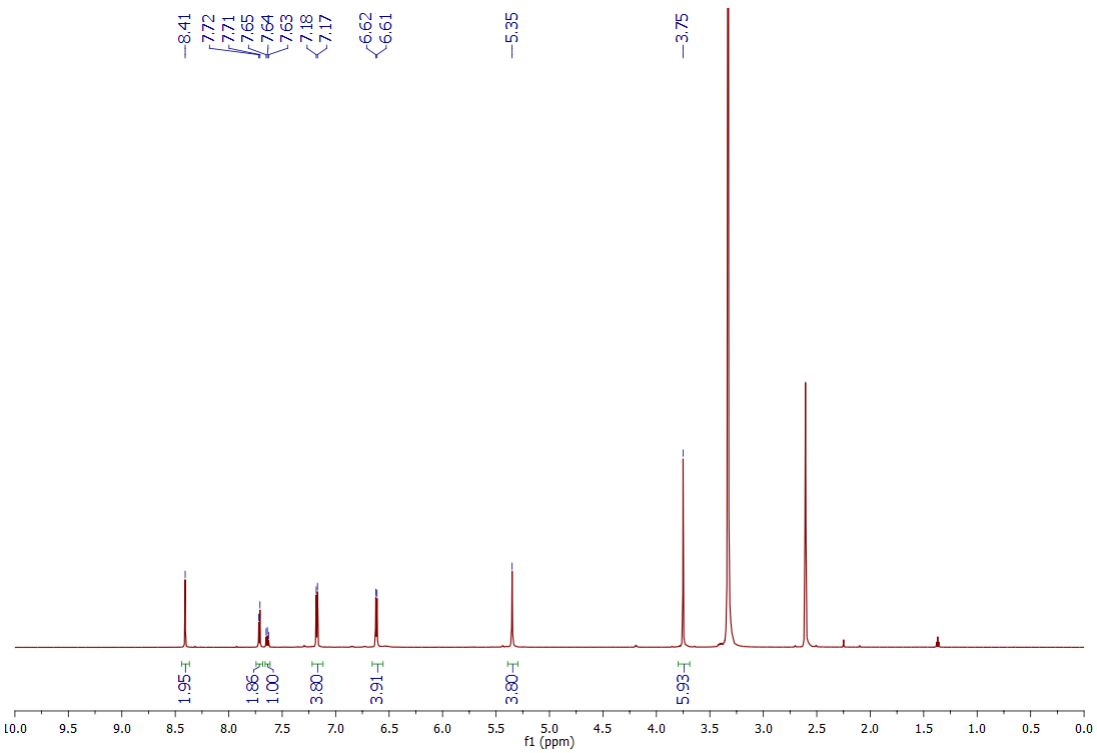

Fig. S5 ^{1}H NMR (600 MHz, DMSO-d_6) spectrum of [Ru·**1**$_2$](PF$_6$)$_2$

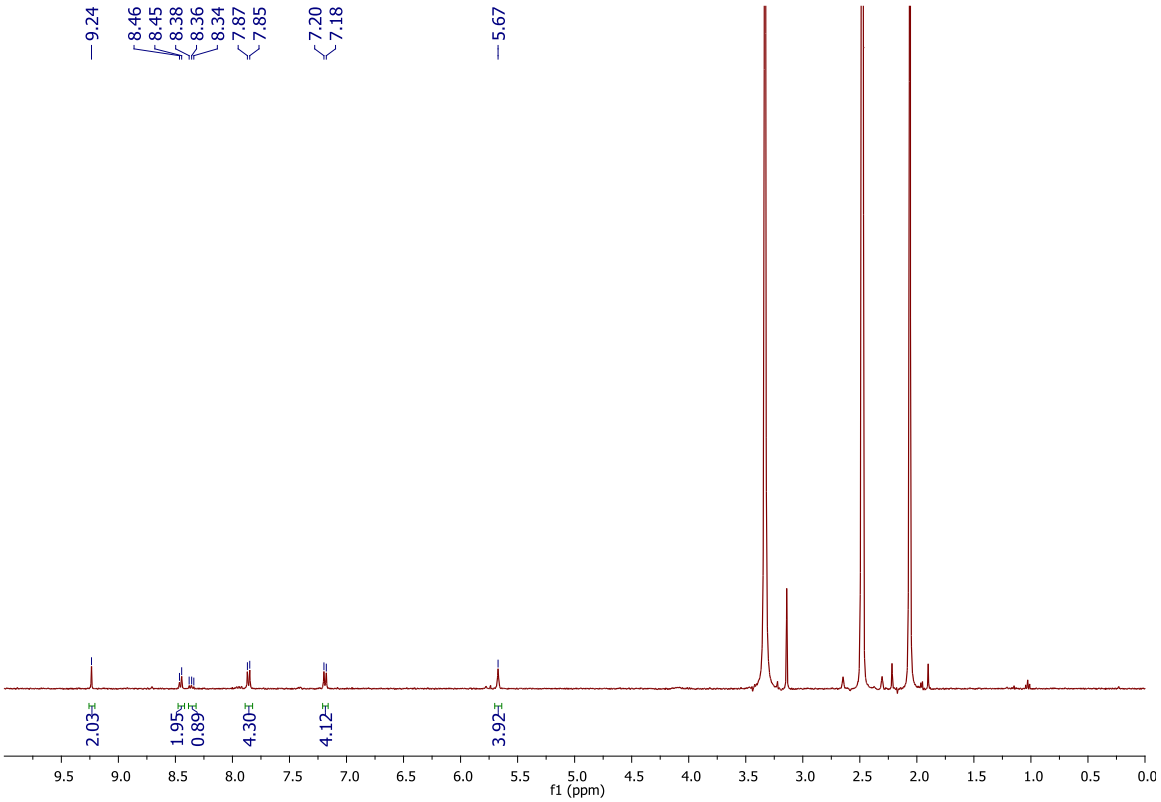

Fig. S6 ^{1}H NMR (400 MHz, DMSO-d_6) spectrum of [Ru·**2**$_2$](PF$_6$)$_2$.

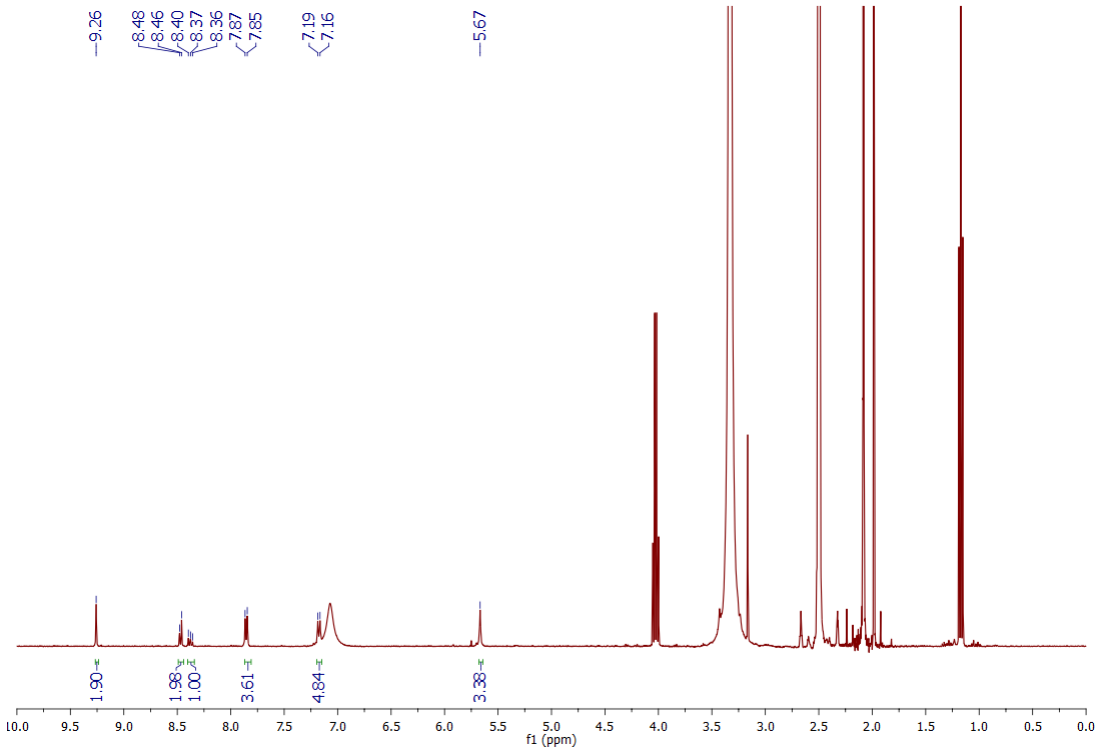

Fig. S7 ^{1}H NMR (400 MHz, DMSO-d_6) spectrum of dried gel containing [Ru·**2**$_2$]$^{2+}$.

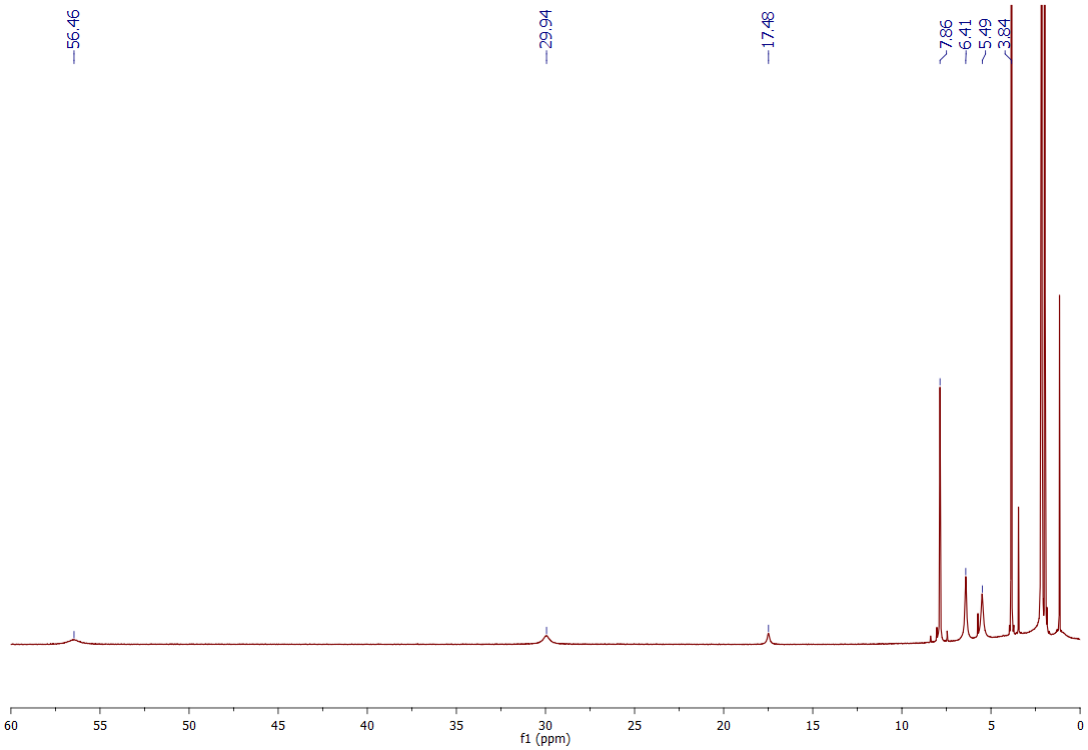

Fig. S8 ^{1}H NMR (600 MHz, CD_3CN) spectrum of paramagnetic complex [Ni·**1**$_2$]$(PF_6)_2$

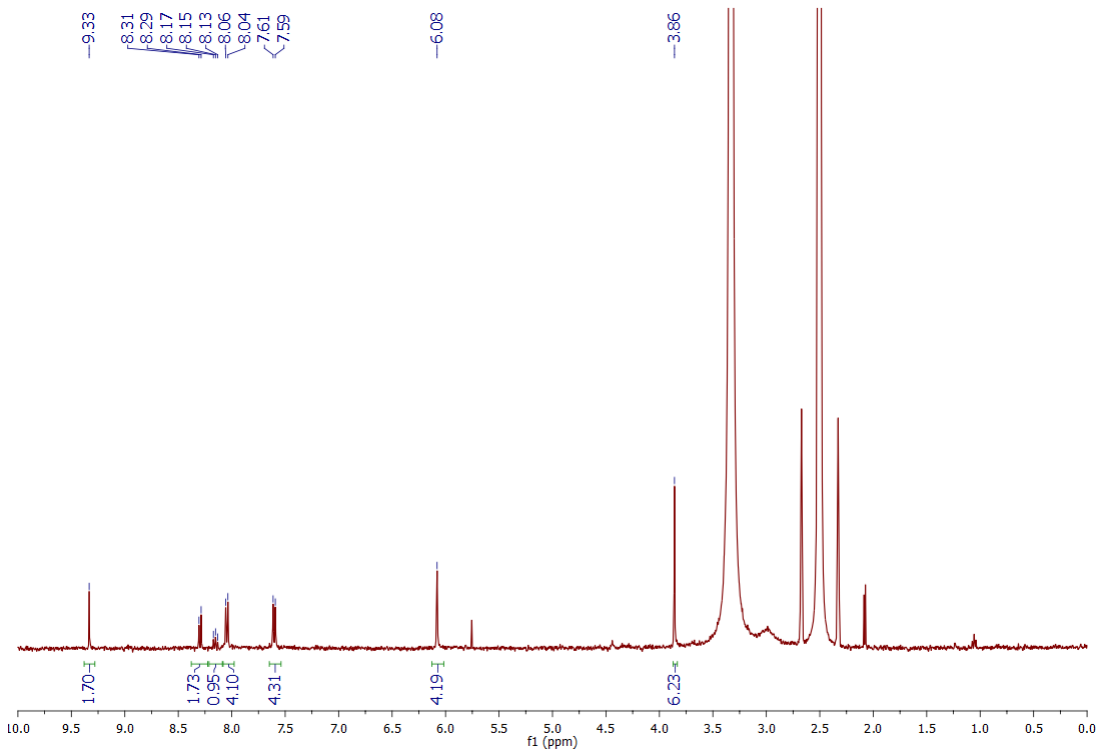

Fig. S9 ^{1}H NMR (400 MHz, DMSO-d_6) spectrum of [Ir·**1**Cl_3].

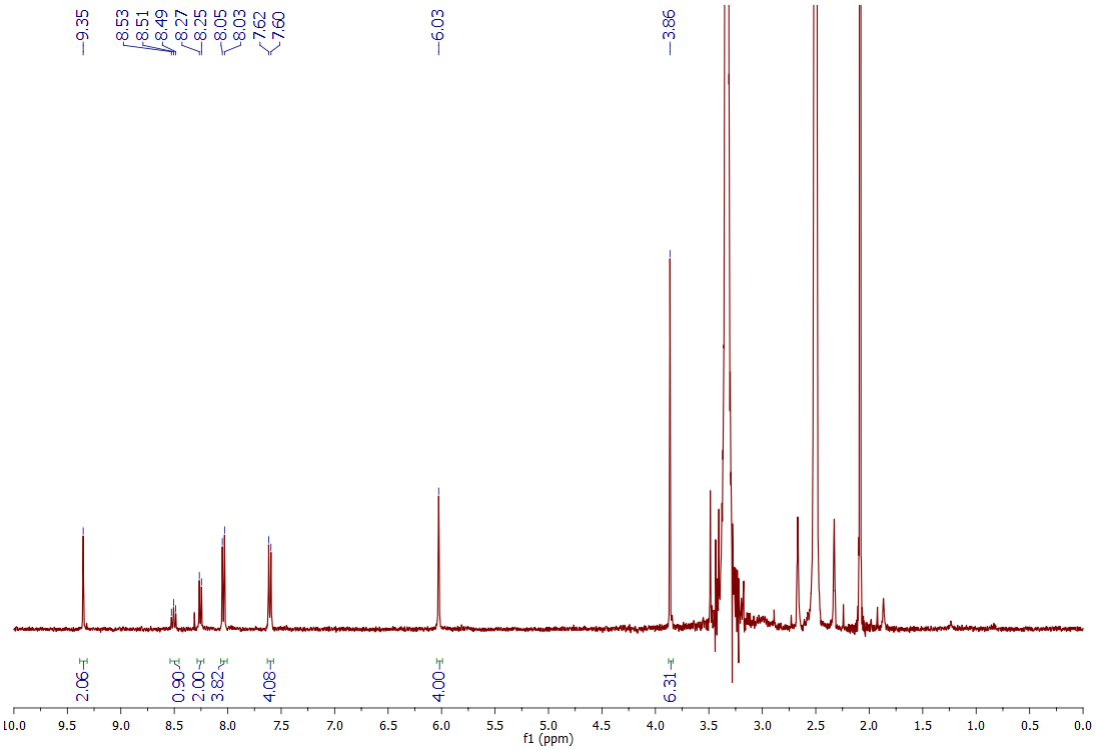

Fig. S10 ^{1}H NMR (400 MHz, DMSO-d_6) spectrum of [Pt·**1**Cl]Cl

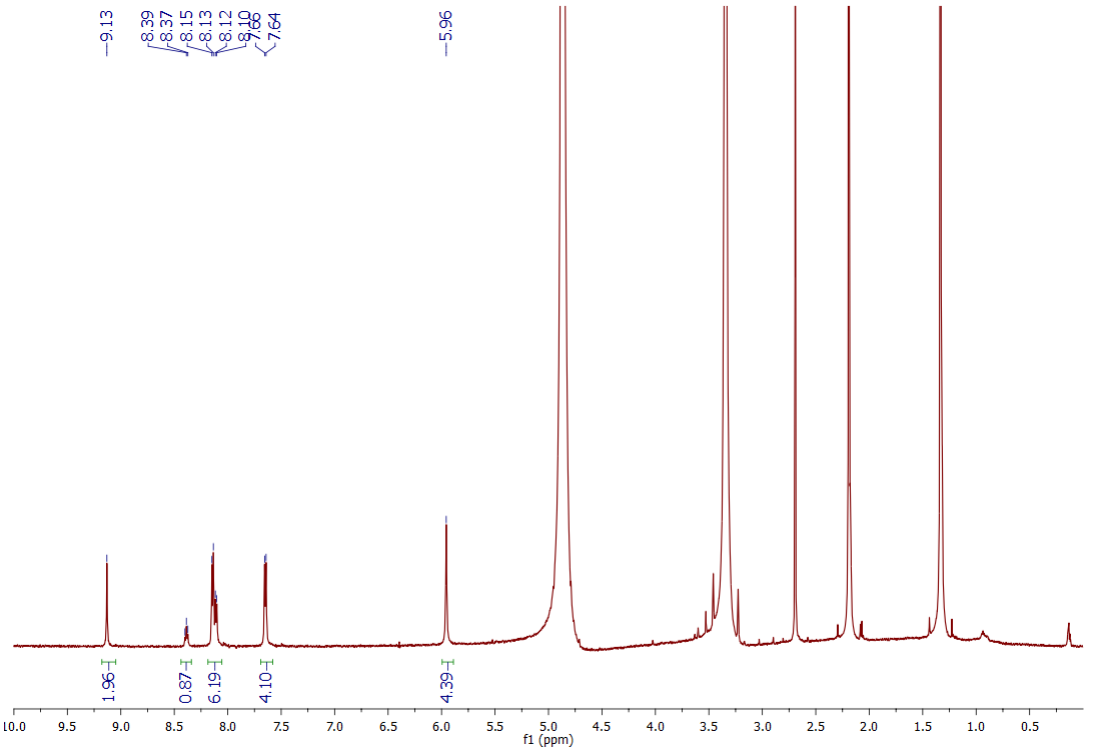

Fig. S11 ^{1}H NMR (600 MHz, CD_3OD) spectrum of [Pt·**2**Cl]Cl

Mass spectrometry of complexes

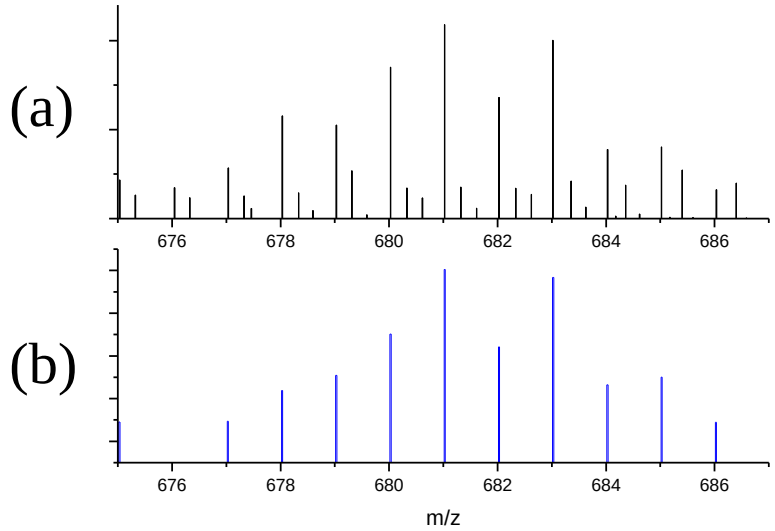

Fig. S12 (a) Experimental and (b) calculated HRMS isotopic pattern distribution for [Ru·**1**Cl_2(DMSO)]. HRMS (*m/z*) (MALDI+): Calculated for $C_{27}H_{23}N_7O_4Cl_2Ru^+$ *m/z* = 681.0232 $[M-(DMSO)]^+$. Found *m/z* = 681.0213.

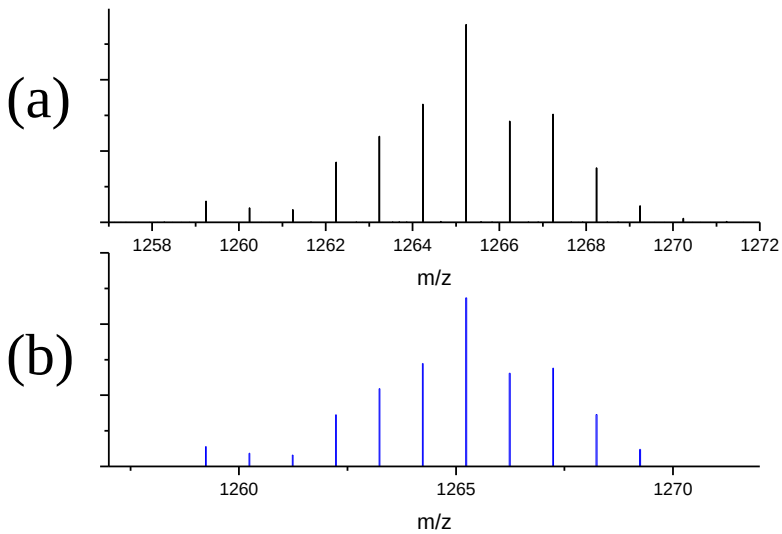

Fig. S13 (a) Experimental and (b) calculated HRMS isotopic pattern distribution for.$[Ru·\mathbf{1}_2]^{2+}$ HRMS (*m/z*) (MALDI): Calculated for $C_{54}H_{46}N_{14}O_8F_6PRu^+$ *m/z* = 1265.2308 $[M-PF_6]^+$. Found *m/z* = 1265.2323.

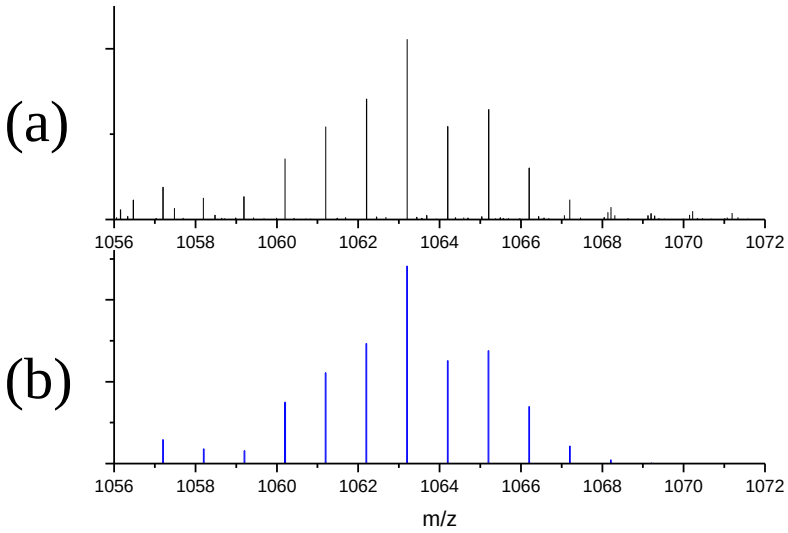

Fig. S14 (a) Experimental and (b) calculated HRMS isotopic pattern distribution for $[Ru{\cdot}\mathbf{2}_2]^{2+}$. HRMS (*m/z*) (MALDI): Calculated for $C_{50}H_{37}N_{14}O_8Ru^+$ *m/z* = 1063.1962 $[M-2(PF_6)-H]^+$. Found *m/z* = 1063.1998.

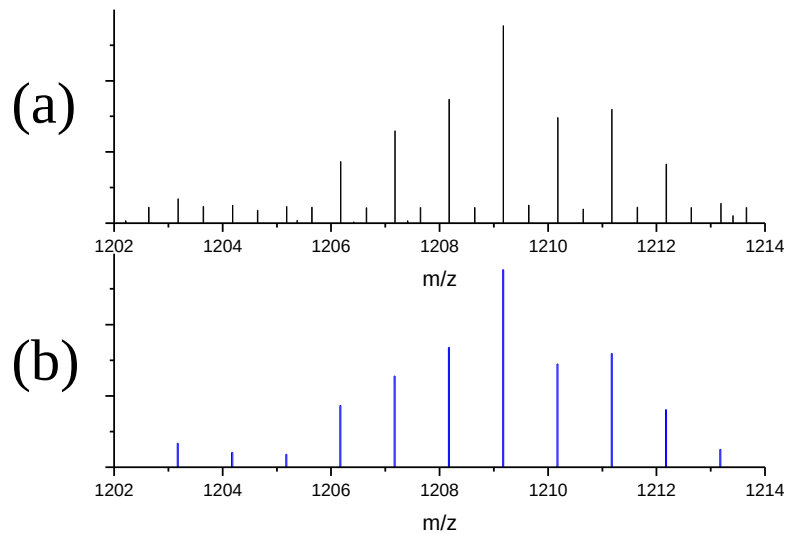

Fig. S15 (a) Calculated and (b) theoretical HRMS isotopic pattern distribution for gel of $[Ru{\cdot}\mathbf{2}_2]^{2+}$.Calculated for $C_{50}H_{38}N_{14}O_8RuPF_6^+$ $[M-Cl]^+$ *m/z* = 1209.1682. Found *m/z* = 1209.1732.

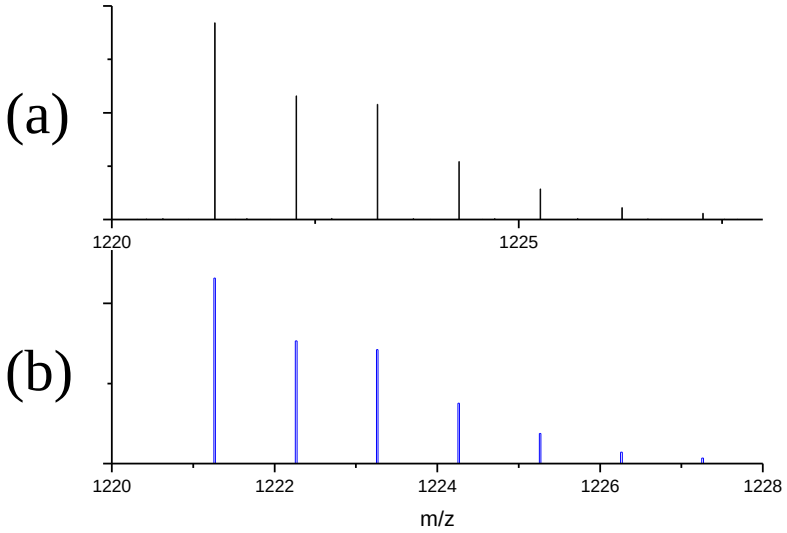

Fig S16 (a) Experimental and (b) calculated HRMS isotopic pattern distribution for $[Ni{\cdot}\mathbf{1}_2]^{2+}$. HRMS (*m/z*) (MALDI+): Calculated for $C_{54}H_{46}N_{14}O_8NiF_6P^+$ *m/z* = 1221.2618. Found *m/z* = 1221.2644

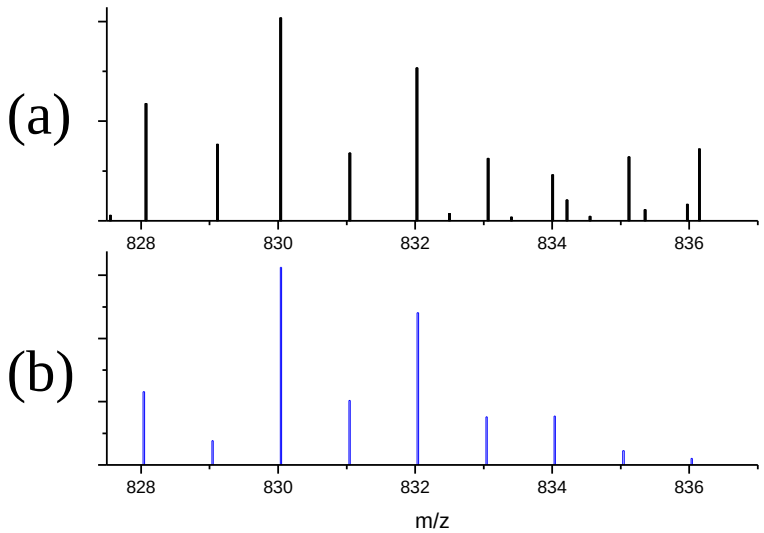

Fig S17 (a) Experimental and (b) calculated HRMS isotopic pattern distribution for $[Ir{\cdot}\mathbf{1}Cl_3]$. HRMS (*m/z*) (ESI+): Calculated for $C_{27}H_{23}N_7O_4Cl_3IrNa^+$ *m/z* = 830.0404 $[M+Na]^+$. Found *m/z* = 830.0373.

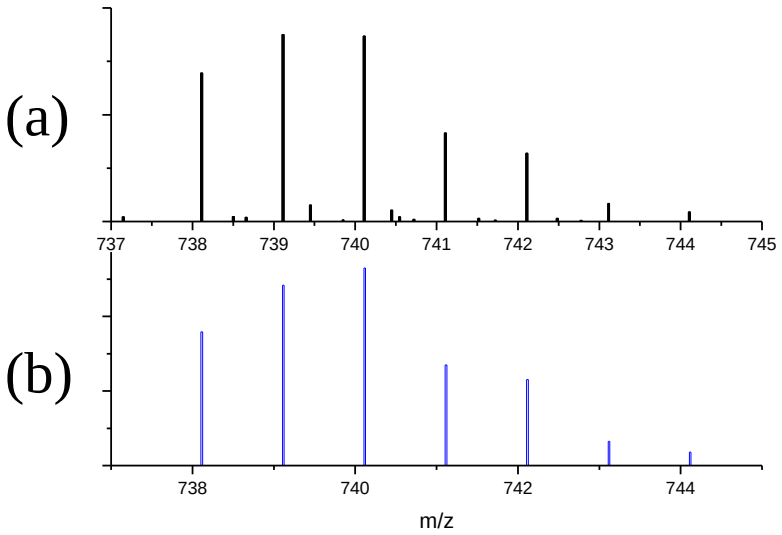

Fig S18 (a) Experimental and (b) calculated HRMS isotopic pattern distribution for [Pt·**1**Cl]Cl. HRMS (*m/z*) (ESI+): Calculated for $C_{27}H_{23}N_7O_4ClPt^+$ *m/z* = 739.1148 $[M]^+$. Found *m/z* = 739.1143

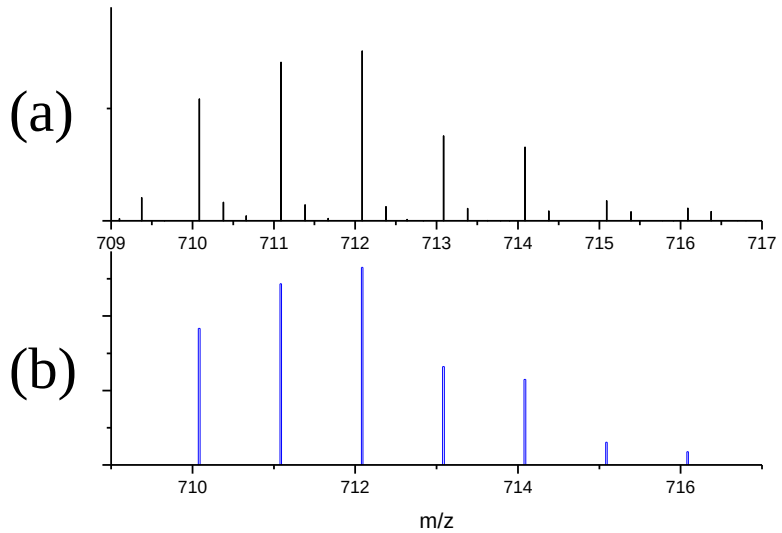

Fig S19 (a) Experimental and (b) calculated HRMS isotopic pattern distribution for [Pt·**2**Cl]Cl. HRMS (MALDI−): Calculated for $C_{25}H_{19}N_7O_4ClPt^-$ *m/z* = 711.0835 $[M-Cl]^-$. Found *m/z* = 711.0859.

X-RAY and refinement details

Special refinement details for the crystal structures:

1: The structure contained no solvent and no disorder. All non-H atoms were made anisotropic

[Ru·2$_2$](PF$_6$)Cl·CH$_3$CN·0.5H$_2$O·1.25EtOH·0.5Et$_2$O: The structure contained a half occupancy Et$_2$O, a half occupancy CH$_3$CN, a full occupancy ethanol where the methyl group was disordered over two sites (0.75:0.25), a half occupancy CH$_3$CN which shares the same site with a 0.25 occupancy water, and finally there is also a 0.25 occupancy ethanol giving a total solvent count of CH$_3$CN·0.5H$_2$O·1.25EtOH·0.5Et$_2$O. The main residue also contains disorder in one of the carboxylic acid arms where the COOH group is split over 2 sites (0.6:0.4). The atoms were best modelled isotropic and split as attempts to model these as anisotropic/split or anisotropic/non-split gave unsatisfactory refinements.

[Ni·1$_2$](PF$_6$)Cl:CH$_3$CN·H$_2$O: The structure contained one full occupancy CH$_3$CN and one full occupancy H$_2$O. One of the ester arms in the main residue was disordered over two sites (0.6:0.4) and again it was best to model the groups as spilt and isotropic rather than anisotropic.

[Ir·1Cl$_3$]·0.25HOCH$_2$CH$_2$OH·0.25H$_2$O: The structure contains 0.25 ethylene glycol and 0.25 water molecules. Both were refined as isotropic. One of the ester arms in the main residue was disordered over two sites (0.5:0.5) and again it was best to model the groups as spilt and isotropic rather than anisotropic.

Ligand 1

```
Bond precision:      C-C = 0.0039 A              Wavelength=0.71073
Cell:          a=6.3501(13)    b=12.965(3)     c=14.859(3)
               alpha=92.45(    beta=101.17(    gamma=100.30(3)
              3)              3)
Temperatu      108 K
re:
                      Calculated                      Reported
Volume                1177.0(5)                       1176.9(4)
Space group           P -1                            P-1
Hall group            -P 1                            ?
Moiety formula        C27 H23 N7 O4                   ?
Sum formula           C27 H23 N7 O4                   C27 H23 N7 O4
Mr                    509.52                          509.52
Dx,g cm-3             1.438                           1.438
Z                     2                               2
Mu (mm-1)             0.101                           0.101
F000                  532.0                           532.0
F000'                 532.22
h,k,lmax              7,15,17                         7,15,17
Nref                  4154                            3981
Tmin,Tmax             0.982,0.990                     0.801,1.000
Tmin'                 0.941
Correction method= MULTI-SCAN
Data completeness= 0.958        Theta(max)= 25.000
R(reflections)= 0.0639( 3614)      wR2(reflections)= 0.1304( 3981)
S = 1.214              Npar= 345
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Alert level B

PLAT029_ALERT_3_B _diffrn_measured_fraction_theta_full Low 0.958

Alert level G

PLAT154_ALERT_1_G The su's on the Cell Angles are Equal ..... 0.03000 Deg.

0 **ALERT level A** = Most likely a serious problem - resolve or explain
1 **ALERT level B** = A potentially serious problem, consider carefully
0 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
1 **ALERT level G** = General information/check it is not something unexpected

1 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
0 ALERT type 2 Indicator that the structure model may be wrong or deficient
1 ALERT type 3 Indicator that the structure quality may be low
0 ALERT type 4 Improvement, methodology, query or suggestion
0 ALERT type 5 Informative message, check

PLATON version of 30/05/2011; check.def file version of 24/05/2011

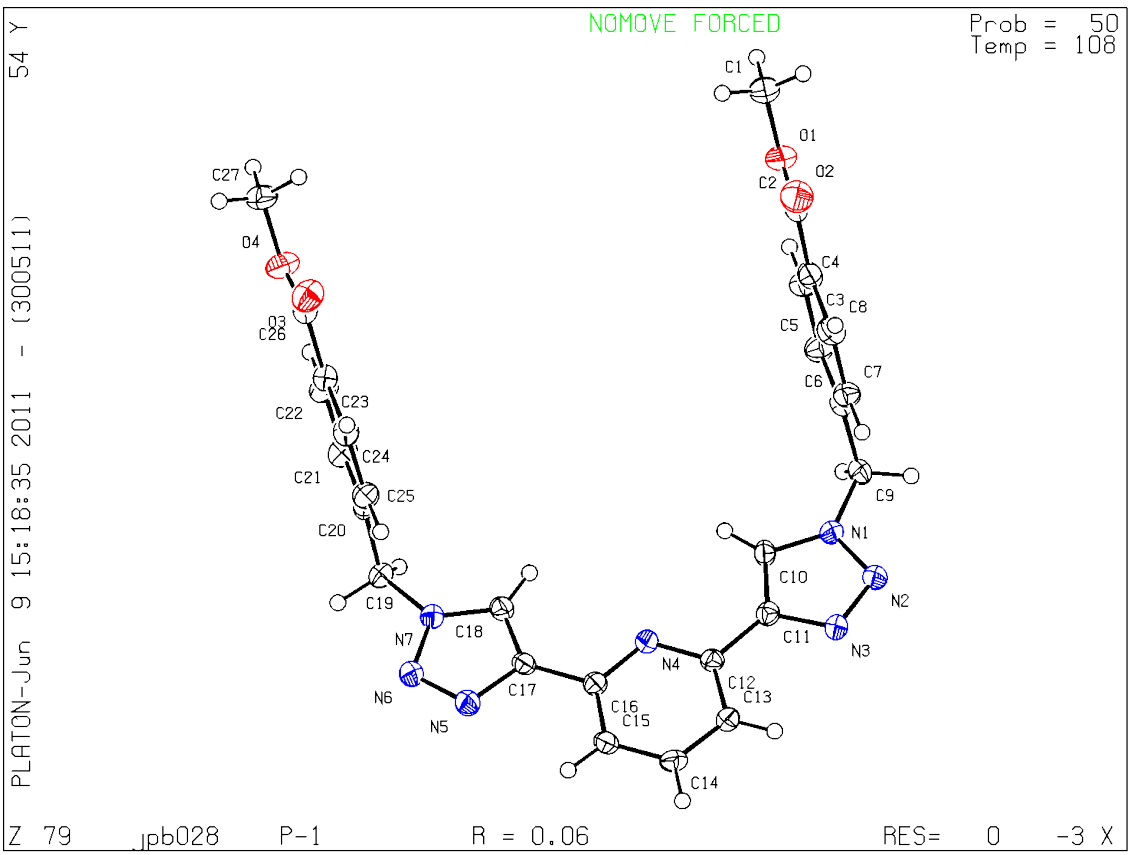

Fig. S20 Ellipsoid plot of the X-ray crystal structure of ligand **1**

Table S1. Hydrogen bonding in the packing structure of **1**

D-H···A	d(D-H)	d(H···A)	d(D···A)	∠(DHA)
C(19)-H(19B)···N(5)	0.990	2.583	3.545(3)	164.1
C(9)-H(9A)···N(3)	0.990	2.606	3.572(3)	165.3
C(9)-H(9B)···N(6)	0.990	2.541	3.497(3)	162.2
C(13)-H(13)···N(3)	0.949	2.633	3.532(3)	158.1

Ru(II) complex [Ru·2_2]PF_6Cl

Bond precision: C-C = 0.0083 A Wavelength=0.71073
Cell: a=12.235(2) b=17.491(4) c=17.627(4)
alpha=105.76 beta=105.52 gamma=93.49(3)

```
            (3)             (3)
   Temperatu
re:            108 K
                     Calculated                          Reported
   Volume            3461.6(15)                          3461.4(12)
   Space group       P -1                                P-1
   Hall group        -P 1                                ?
                     2(C50  H38  N14  O8  Ru), 2(F6
   Moiety formula    P), C4  H10  O, 2(C2  H6  O), C2    ?
                     H4 N O0
   Sum formula       C113 H109 Cl2 F12 N30 O20.50        C56.50  H54.50  Cl  F6  N15
                     P2 Ru2                              O10.25 P Ru
   Mr                2778.29                             1389.14
   Dx,g cm-3         1.333                               1.333
   Z                 1                                   2
   Mu (mm-1)         0.367                               0.367
   F000              1421.0                              1421.0
   F000'             1419.68
   h,k,lmax          14,20,20                            14,20,20
   Nref              12192                               11674
   Tmin,Tmax         0.857,0.922                         0.659,1.000
   Tmin'             0.857
   Correction method= MULTI-SCAN
   Data completeness= 0.958        Theta(max)= 25.000
   R(reflections)= 0.0705( 11286)     wR2(reflections)=        0.2138(
                                    11674)
   S = 1.103             Npar= 873
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Alert level B

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PLAT201_ALERT_2_B Isotropic non-H Atoms in Main Residue(s) 3
PLAT220_ALERT_2_B Large Non-Solvent C Ueq(max)/Ueq(min) ... 4.1 Ratio
PLAT230_ALERT_2_B Hirshfeld Test Diff for O41 -- C41 .. 9.3 su
PLAT230_ALERT_2_B Hirshfeld Test Diff for C41 -- C42 .. 10.0 su
PLAT420_ALERT_2_B D-H Without Acceptor >O111 - >H11X ... ?

Alert level C

PLAT077_ALERT_4_C Unitcell contains non-integer number of atoms .. ?
PLAT202_ALERT_3_C Isotropic non-H Atoms in Anion/Solvent 1
PLAT214_ALERT_2_C Atom C200 (Anion/Solvent) ADP max/min Ratio 4.3 oblat
PLAT222_ALERT_3_C Large Non-Solvent H Uiso(max)/Uiso(min) .. 4.5 Ratio
PLAT230_ALERT_2_C Hirshfeld Test Diff for C42 -- C43 .. 5.8 su
PLAT234_ALERT_4_C Large Hirshfeld Difference C2 -- C3 .. 0.16 Ang.
PLAT244_ALERT_4_C Low 'Solvent' Ueq as Compared to Neighbors of P1
PLAT244_ALERT_4_C Low 'Solvent' Ueq as Compared to Neighbors of C91
PLAT342_ALERT_3_C Low Bond Precision on C-C Bonds ..... 0.0083 Ang
PLAT413_ALERT_2_C Short Inter XH3 .. XHn H3 .. H20B .. 2.14 Ang.
PLAT414_ALERT_2_C Short Intra D-H..H-X H7 .. H2X .. 1.97 Ang.
PLAT480_ALERT_4_C Long H...A H-Bond Reported H11X .. O100 .. 2.62 Ang.
PLAT721_ALERT_1_C Bond Calc 0.93000, Rep 0.91570 Dev... 0.01 Ang.
O500 -H50X 1.555 1.555 # 119
PLAT772_ALERT_2_C Suspect O-H Bond in CIF: O200 -- H201 .. 1.35 Ang.

Alert level G

PLAT002_ALERT_2_G Number of Distance or Angle Restraints on AtSite 3
PLAT005_ALERT_5_G No _iucr_refine_instructions_details in the CIF ?
PLAT007_ALERT_5_G Note: Number of Unrefined Donor-H Atoms 12
PLAT045_ALERT_1_G Calculated and Reported Z Differ by ..... 0.50 Ratio
PLAT072_ALERT_2_G SHELXL First Parameter in WGHT Unusually Large. 0.13

PLAT083_ALERT_2_G SHELXL Second Parameter in WGHT Unusually Large. 9.93
PLAT152_ALERT_1_G The Supplied and Calc. Volume s.u. Differ by ... 3 Units
PLAT154_ALERT_1_G The su's on the Cell Angles are Equal ..... 0.03000 Deg.
PLAT242_ALERT_2_G Check Low Ueq as Compared to Neighbors for C111
PLAT244_ALERT_4_G Low 'Solvent' Ueq as Compared to Neighbors of C80
PLAT301_ALERT_3_G Note: Main Residue Disorder ..... 4 %
PLAT302_ALERT_4_G Note: Anion/Solvent Disorder ..... 44 %
PLAT860_ALERT_3_G Note: Number of Least-Squares Restraints 2

0 **ALERT level A** = Most likely a serious problem - resolve or explain
6 **ALERT level B** = A potentially serious problem, consider carefully
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4 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
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6 ALERT type 3 Indicator that the structure quality may be low
7 ALERT type 4 Improvement, methodology, query or suggestion
2 ALERT type 5 Informative message, check

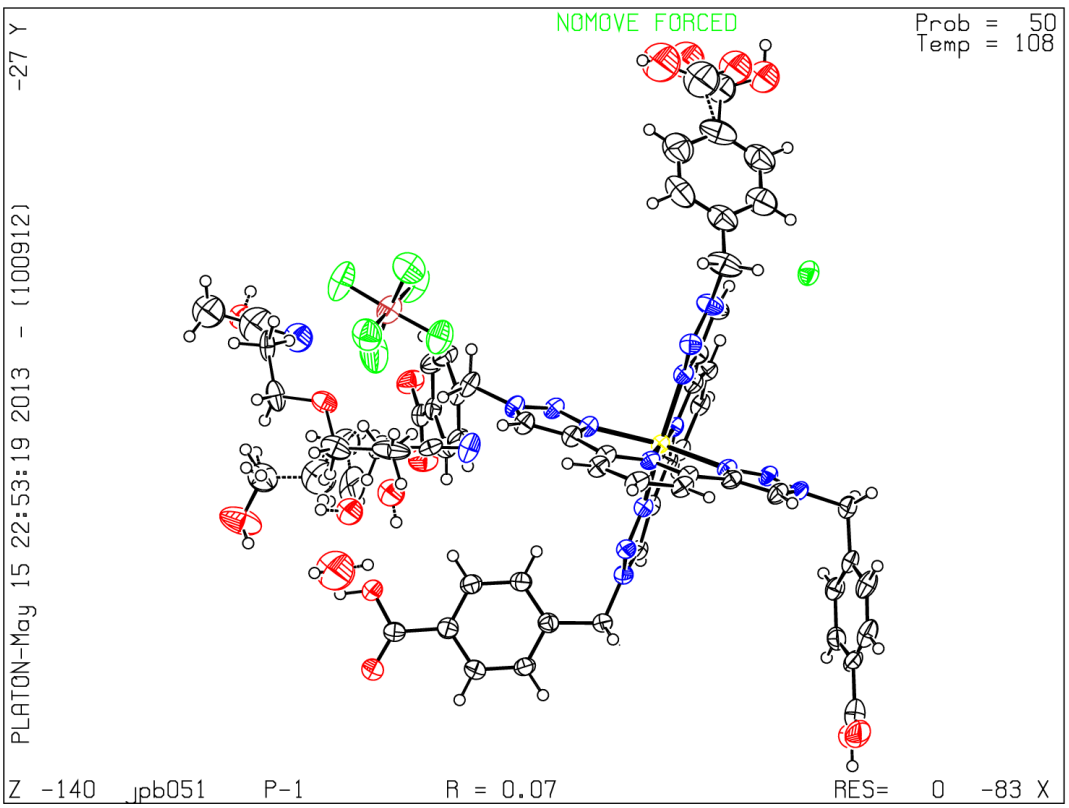

Fig. S21 Ellipsoid plot of the X-ray crystal structure of [Ru·**2**$_2$]PF_6Cl

Ru(II) complex of [Ru·1_2]$^{2+}$

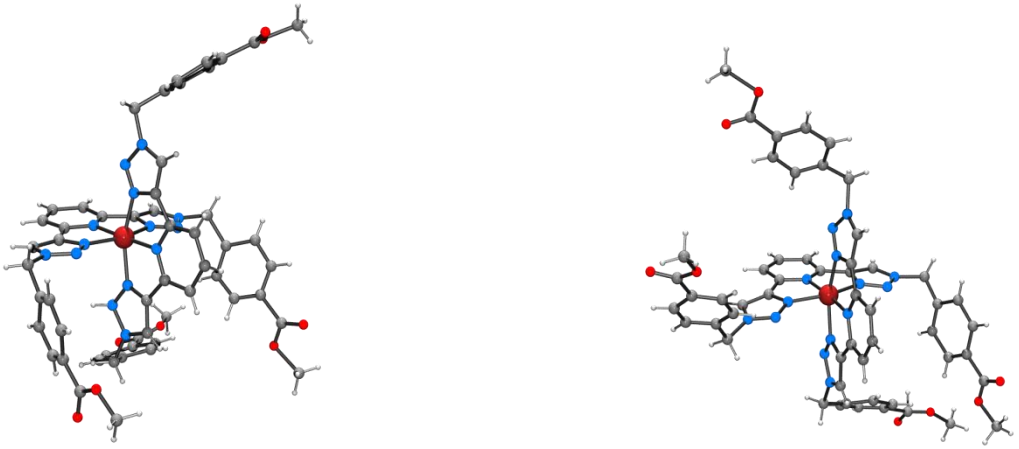

Fig. S22 Ball and stick models of the two independent molecules in the unit cell of $[Ru{\cdot}\mathbf{1}_2]^{2+}$. Data could not be refined sufficiently for detailed analysis, but the distorted octahedral geometry is clear and analogous to the geometry of $[Ru{\cdot}\mathbf{2}_2]PF_6Cl$.

Ni(II) complex $[Ni{\cdot}\mathbf{1}_2]PF_6Cl$

Bond precision: C-C = 0.0045 A Wavelength=1.54178

Cell: a=14.4083(10) b=14.8238(11) c=16.2001(12)
alpha=108.541(3) beta=91.506(3) gamma=115.862(3)

Temperature: 108 K

	Calculated	Reported
Volume	2896.2(4)	2896.2(4)
Space group	P -1	P-1
Hall group	-P 1	?
Moiety formula	C54 H46 N14 Ni O8, F6 P, C2 H3 N, Cl, H2 O	?
Sum formula	C56 H51 Cl F6 N15 Ni O9 P	C56 H51 Cl F6 N15 Ni O9 P
Mr	1317.23	1317.25
Dx,g cm-3	1.510	1.510
Z	2	2
Mu (mm-1)	1.952	1.952
F000	1356.0	1356.0
F000'	1355.74	
h,k,lmax	16,17,18	16,16,18
Nref	9473	8995
Tmin,Tmax	0.558,0.761	0.558,0.753
Tmin'	0.472	

Correction method= MULTI-SCAN
Data completeness= 0.950 Theta(max)= 63.490
R(reflections)= 0.0497(8484) wR2(reflections)= 0.1274(8995)
S = 1.039 Npar= 801

Alert level B

PLAT029_ALERT_3_B _diffrn_measured_fraction_theta_full Low 0.950
PLAT201_ALERT_2_B Isotropic non-H Atoms in Main Residue(s) 4
PLAT220_ALERT_2_B Large Non-Solvent C Ueq(max)/Ueq(min) ... 4.3 Ratio

Alert level C

THETM01_ALERT_3_C The value of sine(theta_max)/wavelength is less than 0.590
Calculated sin(theta_max)/wavelength = 0.5804
PLAT220_ALERT_2_C Large Non-Solvent O Ueq(max)/Ueq(min) ... 3.3 Ratio

PLAT222_ALERT_3_C Large Non-Solvent H Uiso(max)/Uiso(min) .. 4.7 Ratio
PLAT242_ALERT_2_C Check Low Ueq as Compared to Neighbors for C42
PLAT244_ALERT_4_C Low 'Solvent' Ueq as Compared to Neighbors of P1
PLAT244_ALERT_4_C Low 'Solvent' Ueq as Compared to Neighbors of C100
PLAT250_ALERT_2_C Large U3/U1 Ratio for Average U(i,j) Tensor 3.4

Alert level G

PLAT005_ALERT_5_G No _iucr_refine_instructions_details in the CIF ? Do !
PLAT007_ALERT_5_G Note: Number of Unrefined Donor-H Atoms 2
PLAT154_ALERT_1_G The su's on the Cell Angles are Equal ..... 0.00300 Deg.
PLAT231_ALERT_4_G Hirshfeld Test (Solvent) P1 -- F6 .. 6.0 su
PLAT301_ALERT_3_G Note: Main Residue Disorder ..... 5 %
PLAT710_ALERT_4_G Delete 1-2-3 or 2-3-4 Linear Torsion Angle ... # 15
N44 -NI1 -N4 -C16 23.80 1.10 1.555 1.555 1.555 1.555
And 3 other PLAT710 Alerts
More ...
PLAT779_ALERT_4_G Suspect or Irrelevant (Bond) Angle in CIF .... # 226
C66 -C63 -C166 1.555 1.555 1.555 32.90 Deg.

0 **ALERT level A** = Most likely a serious problem - resolve or explain
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7 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
10 **ALERT level G** = General information/check it is not something unexpected

1 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
5 ALERT type 2 Indicator that the structure model may be wrong or deficient
4 ALERT type 3 Indicator that the structure quality may be low
8 ALERT type 4 Improvement, methodology, query or suggestion
2 ALERT type 5 Informative message, check

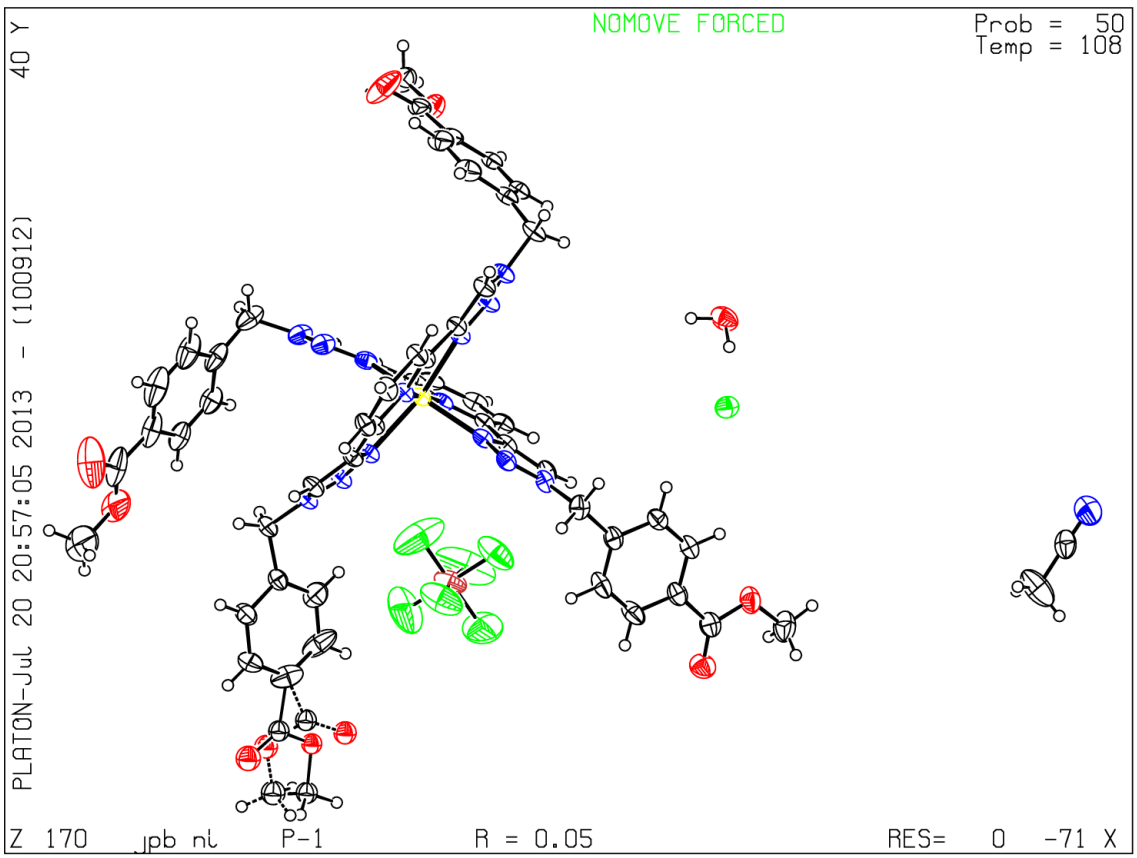

Fig. S23 Ellipsoid plot of the X-ray crystal structure of $[Ni{\cdot}\mathbf{1}_2]PF_6Cl$

Table S2 Hydrogen bonds for [Ni·$\mathbf{1}_2$]PF_6Cl [Å and °].

D-H···A	d(D-H)	d(H···A)	d(D···A)	∠(DHA)
O(100)-H(10X)···Cl(1)	0.978	2.2273	3.193(2)	169.3
O(100)-H(10Y)···Cl(1)	0.921	2.3105	3.221(3)	169.6
C(10)-H(10A) ··Cl(1)	0.950	2.7042	3.434(3)	134.1
C(9)-H(9B) ··N(100)	0.990	2.721	3.687(4)	165.0
C(58)-H(58A) ··N(100)	0.950	2.626	3.357(6)	134.2
C(18)-H(18A) ··O(44)	0.950	2.129	2.993(6)	150.7
C(50)-H(50A) ··F(1)	0.950	2.509	3.295(3)	140.2
C(50)-H(50A) ··F(2)	`0.950	2.346	3.277(3)	166.3

Ir(III) complex [Ir·1Cl_3]

```
Bond precision:      C-C = 0.0135 A                Wavelength=1.54178
Cell:          a=15.4149(18)   b=14.1809(19)   c=15.627(2)
               alpha=90        beta=105.781(9) gamma=90
Temperature:   100 K
                     Calculated                    Reported
Volume               3287.3(7)                     3287.2(7)
Space group          P 21/c                        P2(1)/c
Hall group           -P 2ybc                       ?
Moiety formula       4(C27 H23 Cl3 Ir N7 O4), C2 H8 O3   ?
Sum formula          C110 H100 Cl12 Ir4 N28 O19    C27.50 H25 Cl3 Ir N7 O4.75
Mr                   3312.46                       828.10
Dx,g cm-3            1.673                         1.673
Z                    1                             4
Mu (mm-1)            10.497                        10.497
F000                 1620.0                        1620.0
F000'                1609.06
h,k,lmax             18,16,18                      18,16,18
Nref                 5756                          5490
Tmin,Tmax            0.720,0.900                   0.498,0.753
Tmin'                0.626
Correction method= MULTI-SCAN
Data completeness= 0.954        Theta(max)= 66.160
R(reflections)= 0.0470( 4690)      wR2(reflections)= 0.1304( 5490)
S = 1.072              Npar= 400
```

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level B

PLAT029_ALERT_3_B _diffrn_measured_fraction_theta_full Low 0.954

Alert level C

PLAT094_ALERT_2_C Ratio of Maximum / Minimum Residual Density 3.81
PLAT220_ALERT_2_C Large Non-Solvent C Ueq(max)/Ueq(min) ... 3.1 Ratio

PLAT234_ALERT_4_C Large Hirshfeld Difference C22 -- C23 .. 0.24 Ang.
PLAT241_ALERT_2_C Check High Ueq as Compared to Neighbors for C24
PLAT242_ALERT_2_C Check Low Ueq as Compared to Neighbors for C2
PLAT242_ALERT_2_C Check Low Ueq as Compared to Neighbors for C20
PLAT342_ALERT_3_C Low Bond Precision on C-C Bonds ..... 0.0135 Ang.

Alert level G

PLAT002_ALERT_2_G Number of Distance or Angle Restraints on AtSite 7
PLAT005_ALERT_5_G No _iucr_refine_instructions_details in the CIF ? Do !
PLAT007_ALERT_5_G Note: Number of Unrefined Donor-H Atoms 5
PLAT045_ALERT_1_G Calculated and Reported Z Differ by ..... 0.25 Ratio
PLAT083_ALERT_2_G SHELXL Second Parameter in WGHT Unusually Large. 10.77
PLAT242_ALERT_2_G Check Low Ueq as Compared to Neighbors for O4
PLAT242_ALERT_2_G Check Low Ueq as Compared to Neighbors for C126
PLAT244_ALERT_4_G Low 'Solvent' Ueq as Compared to Neighbors of C100
PLAT301_ALERT_3_G Note: Main Residue Disorder ..... 10 %
PLAT302_ALERT_4_G Note: Anion/Solvent Disorder ..... 100 %
PLAT710_ALERT_4_G Delete 1-2-3 or 2-3-4 Linear Torsion Angle ... # 19
CL2 -IR1 -N4 -C16 32.00 3.00 1.555 1.555 1.555 1.555
PLAT710_ALERT_4_G Delete 1-2-3 or 2-3-4 Linear Torsion Angle ... # 24
CL2 -IR1 -N4 -C12 -145.00 2.00 1.555 1.555 1.555 1.555
PLAT779_ALERT_4_G Suspect or Irrelevant (Bond) Angle in CIF .... # 114
C26 -C23 -C126 1.555 1.555 1.555 25.80 Deg.
PLAT811_ALERT_5_G No ADDSYM Analysis: Too Many Excluded Atoms .... ! Info
PLAT860_ALERT_3_G Note: Number of Least-Squares Restraints 5

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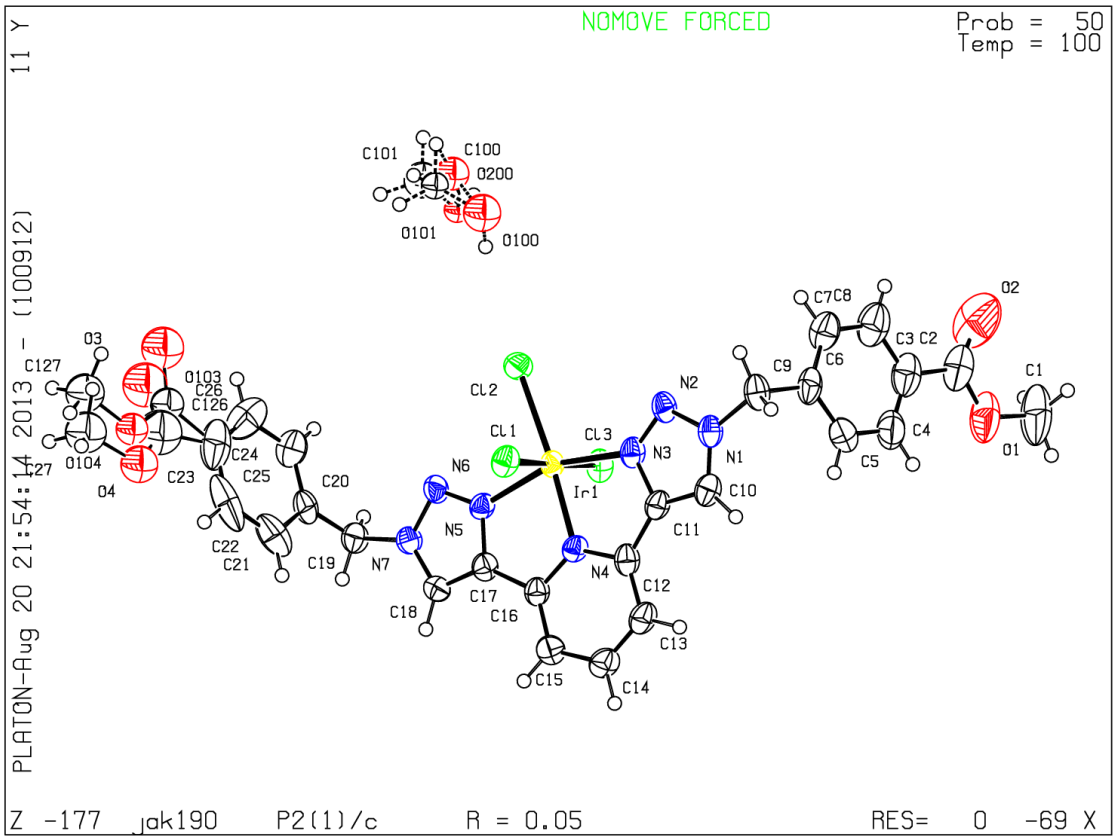

Fig. S24 Ellipsoid plot of the X-ray crystal structure of [Ir·**1**Cl_3].

Microscopy of gels

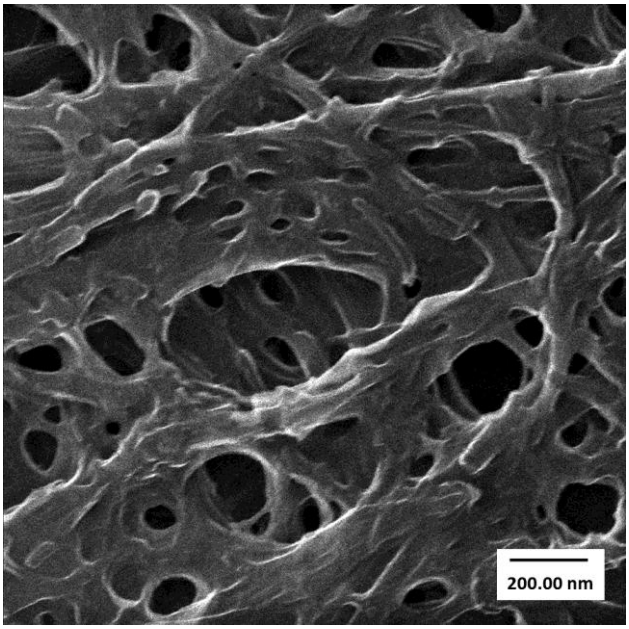

Fig. S25 HIM image of Ru(II) metallogel

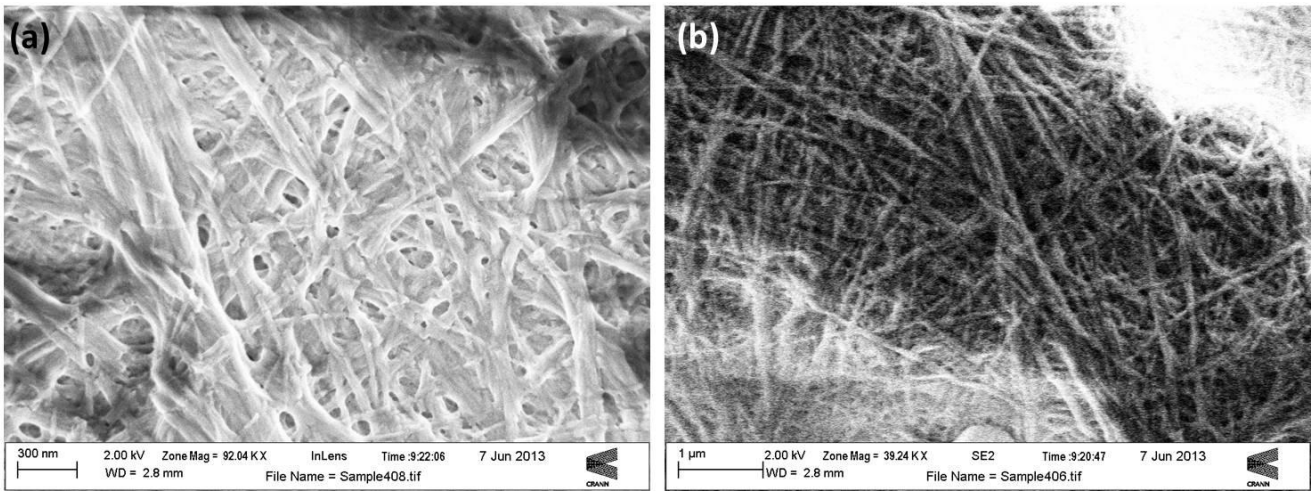

Fig. S26 SEM images of Ru(II) metallogel

Spectroscopy

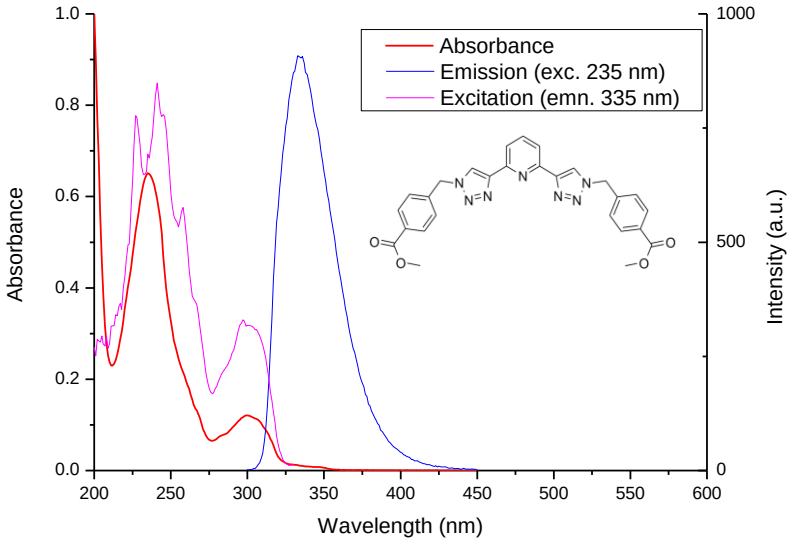

Fig. S27 UV-Vis absorbance (red), emission (blue) and excitation (magenta) spectra for ligand **1** in CH_3CN.

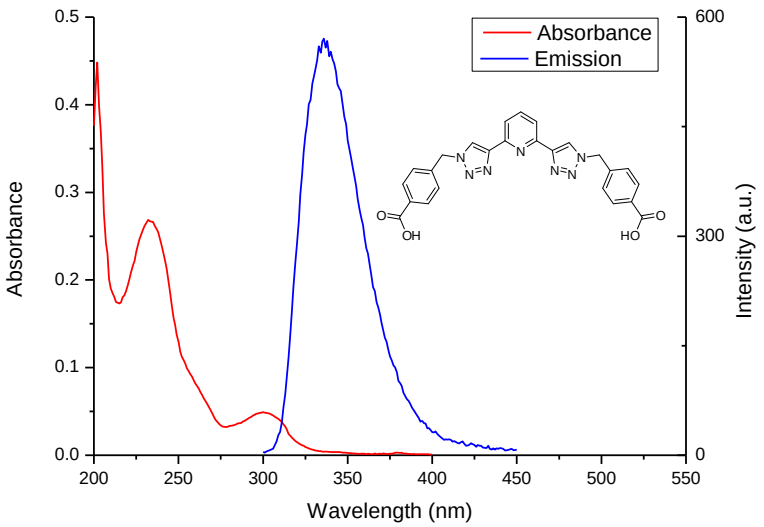

Fig. S28 UV-Vis absorbance (red) and emission (blue) spectra for ligand **2** in CH_3CN.

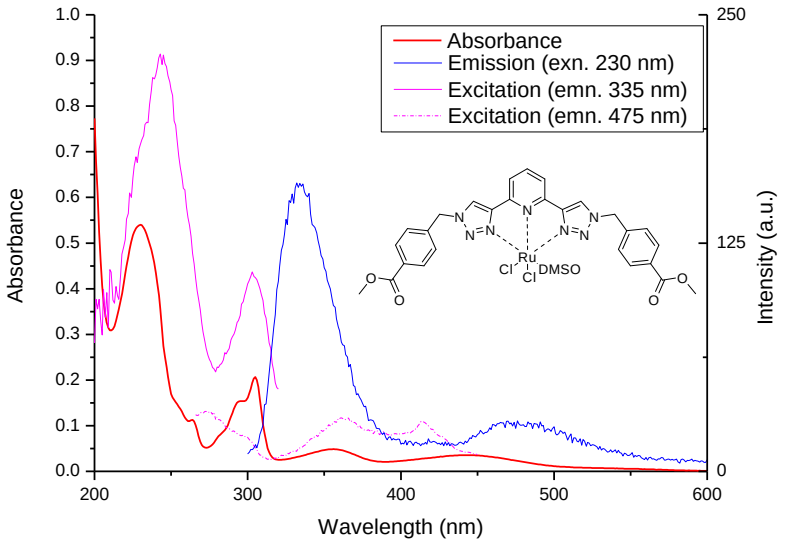

Fig. S29 UV-Vis absorbance (red), emission (blue) and excitation (magenta) spectra for [Ru·**1**Cl_2(DMSO)] in CH_3CN.

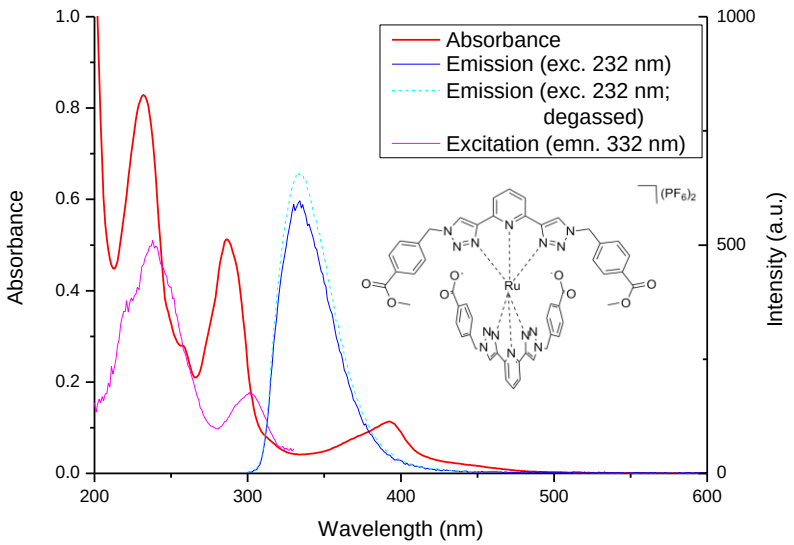

Fig. S30 UV-Vis absorbance (red), emission (blue) and excitation (magenta) spectra for [Ru·$\mathbf{1}_2$]$(PF_6)_2$ in CH_3CN.

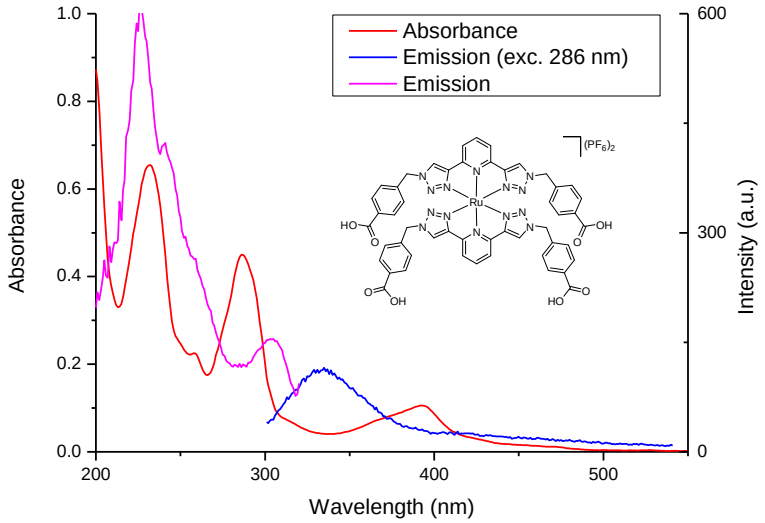

Fig. S31 UV-Vis absorbance (red), emission (blue) and excitation (magenta) spectra for $[Ru{\cdot}\mathbf{2}_2](PF_6)_2$ in CH_3CN.

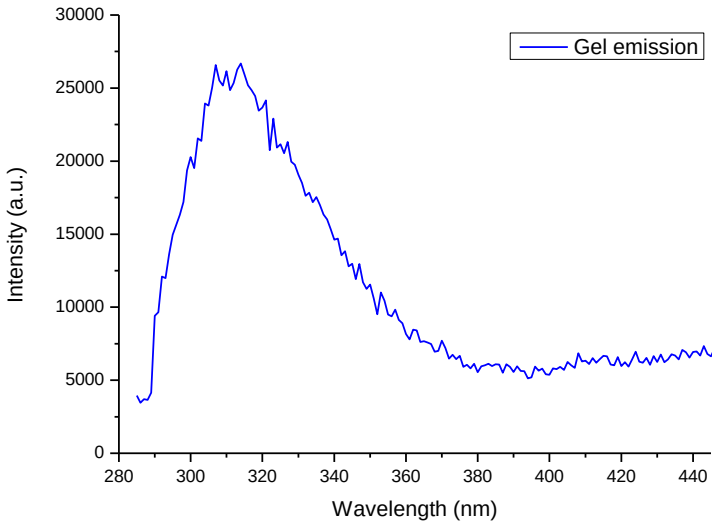

Fig. S32 Emission spectrum from gel of $[Ru{\cdot}\mathbf{2}_2]^{2+}$ immobilised on quartz slide at room temperature.

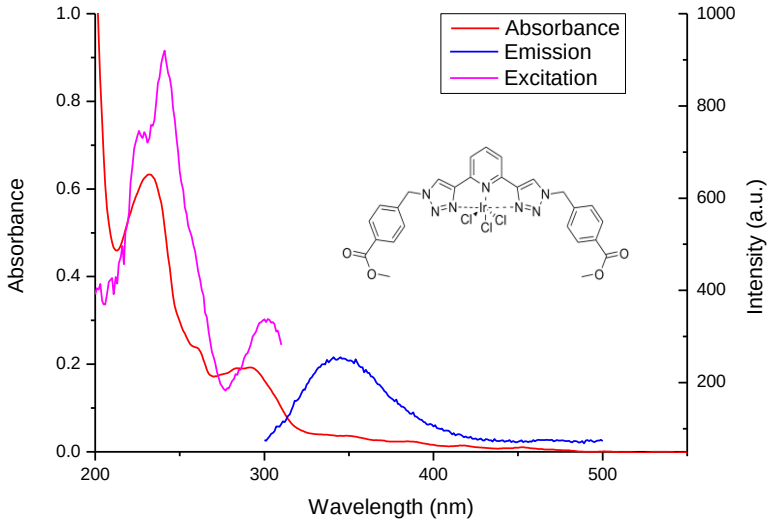

Fig. S33 UV-Vis absorbance (red), emission (blue) and excitation (magenta) spectra for [Ir·**1**Cl_3] in CH_3CN.

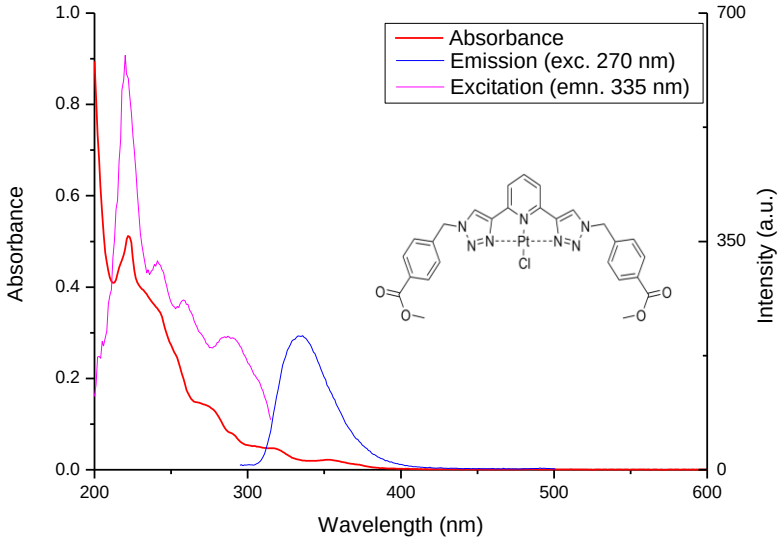

Fig. S34 UV-Vis absorbance (red), emission (blue) and excitation (magenta) spectra for [Pt·**1**Cl]Cl in CH_3CN.

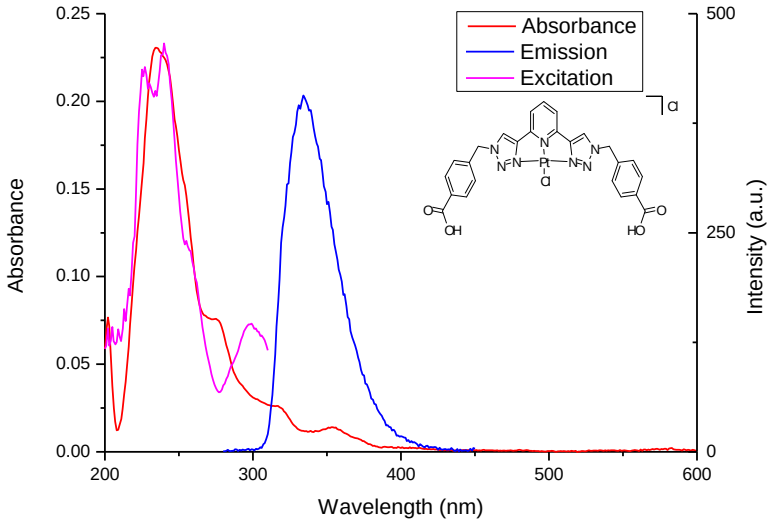

Fig. S35 UV-Vis absorbance (red), emission (blue) and excitation (magenta) spectra for [Pt·**2**Cl]Cl in CH_3CN.

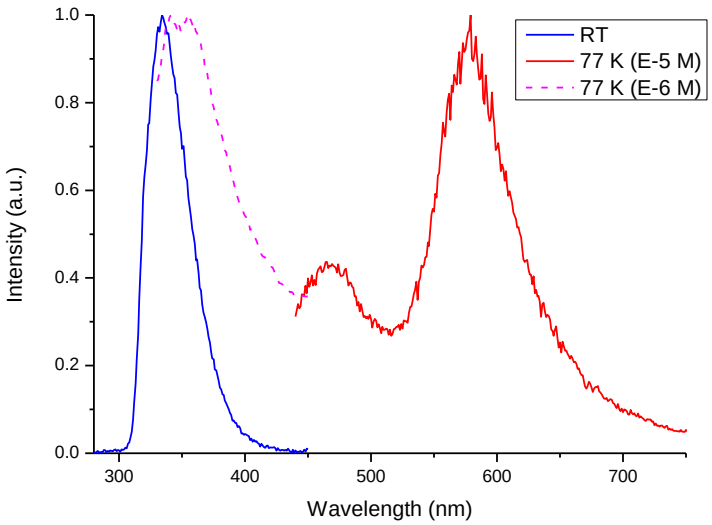

Fig. S36 Emission spectra of [Pt·**2**Cl]Cl at room temperature (blue) and 77 K (red).

Electrochemistry

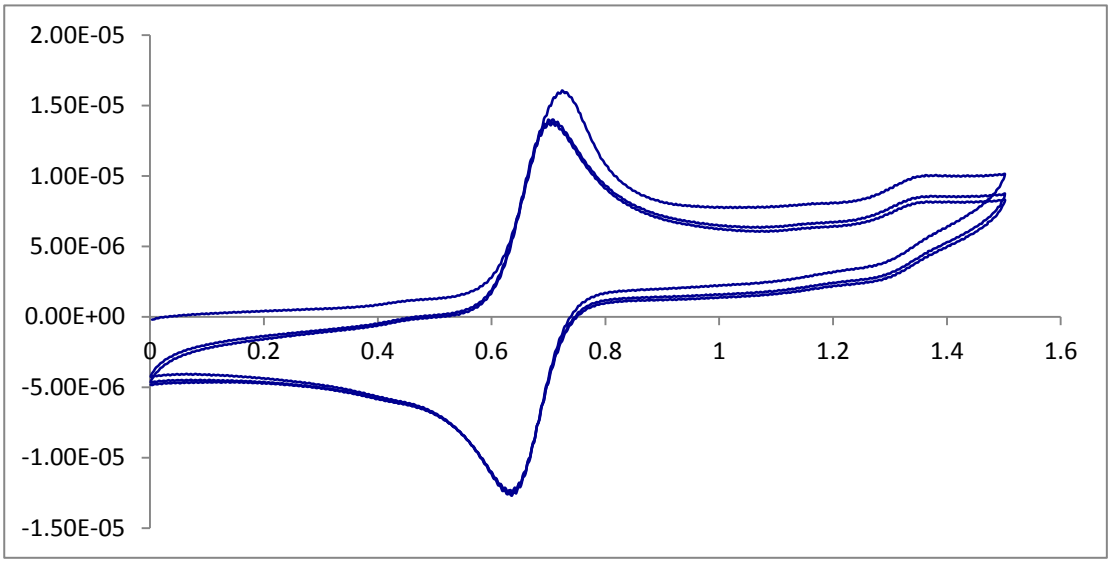

Fig. S37 CV of [Ru·**1**Cl_2(DMSO)] in CH_3CN. $E_{1/2}$ = +0.75 V (ΔE_p = 55 mV), referenced to $[Ru(bpy)_3]^{2+}/[Ru(bpy)_3]^{3+}$, $E_{1/2}$ = +1.39 V (ΔE_p = 55 mV)

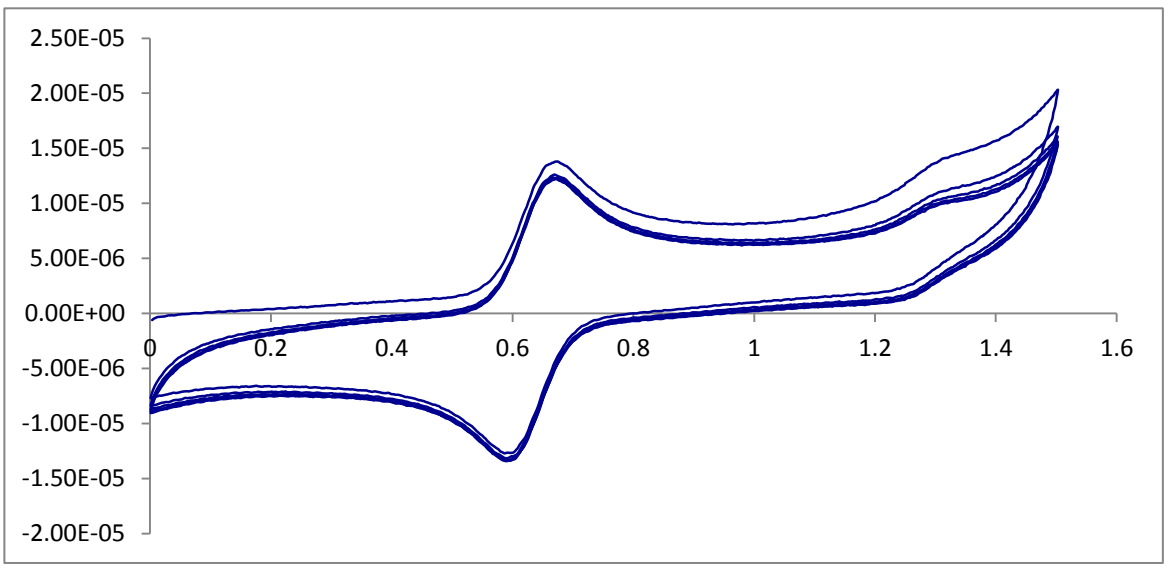

Fig. S38 CV of [Ru·**1**Cl_2(DMSO)] in CH_3NO_2. $E_{1/2}$ = +0.75 V (ΔEp = 58 mV), referenced to $Ru(bpy)_3^{2+/3+}$, $E_{1/2}$ = 1.39 V (ΔEp = 55 mV)

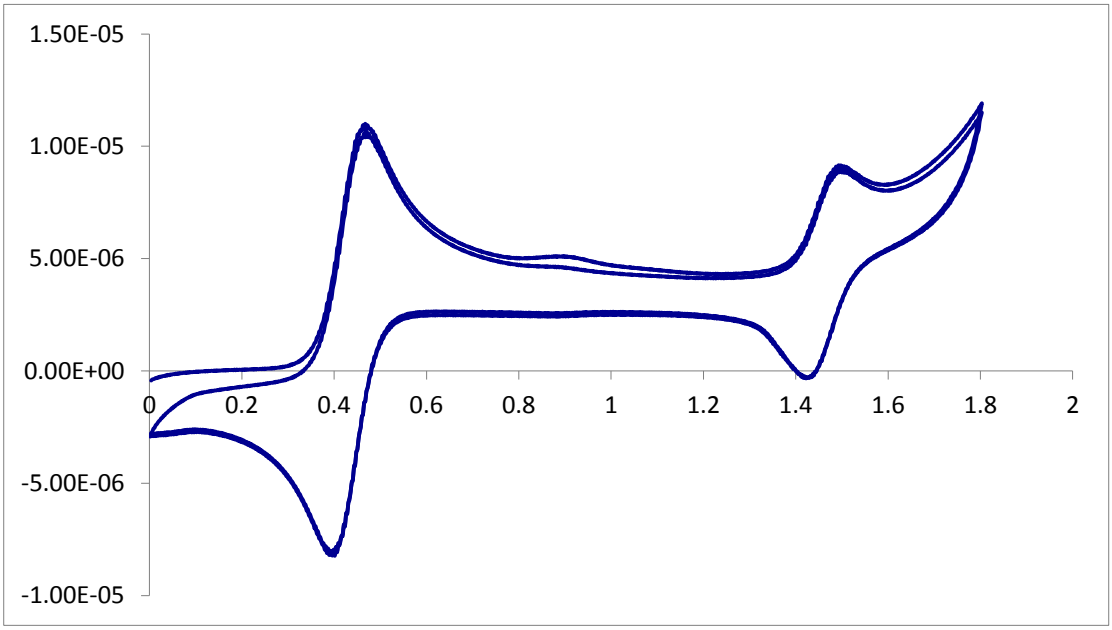

Fig. S39 CV of [Ru·**1**$_2$](PF$_6$)$_2$ in CH$_3$CN. $E_{1/2}$ = +1.43 V (ΔE_p = 70 mV), referenced to Fc$^+$/Fc, $E_{1/2}$ = +0.41 V (ΔE_p = 72 mV)

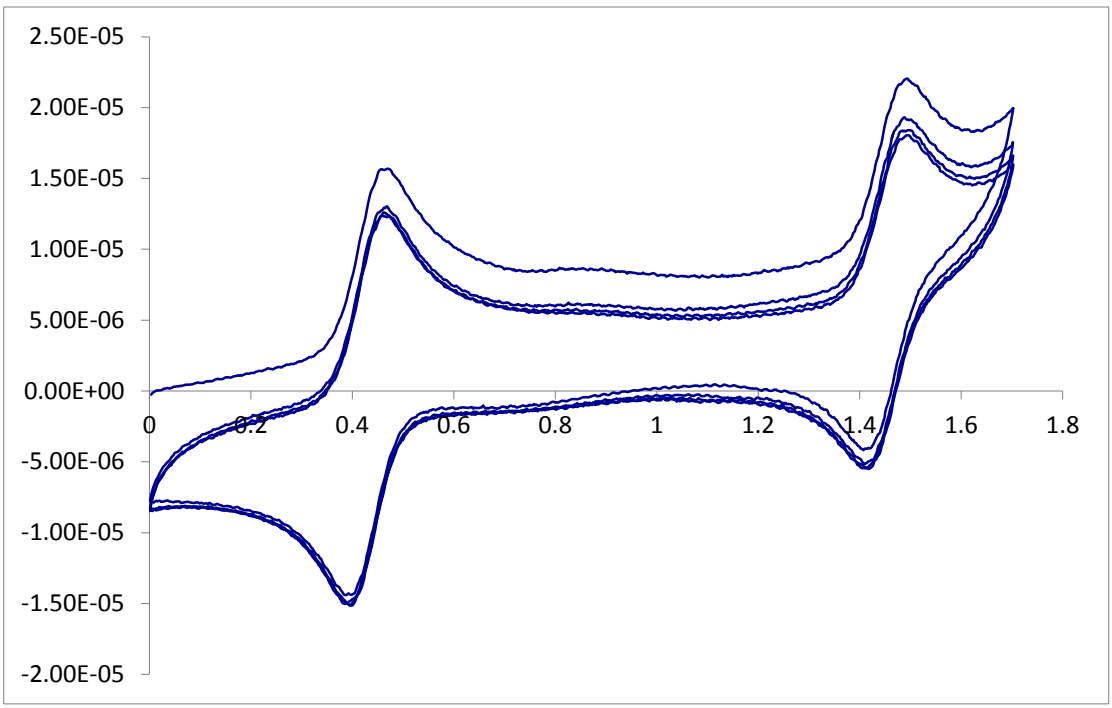

Fig. S40 CV of [Ru·**2**$_2$](PF$_6$)$_2$ in CH$_3$CN. $E_{1/2}$ = +1.43 V (ΔE_p = 60 mV), referenced to Fc$^+$/Fc, $E_{1/2}$ = +0.41 V (ΔE_p = 72 mV)