# Blue-Green Emissive Cationic Iridium(III) Complexes Using Partially Saturated Strongly-Donating Guanidyl-pyridine/pyrazine Ancillary Ligands

**Kamrul Hasan,[a] Amlan K Pal,[a] Thomas Auvray,[a] Eli Zysman-Colman*[b] and Garry S Hanan*[a]**

[a]*Département de Chimie, Université de Montréal, 2900 Edouard-Montpetit, Montréal, Québec H3T-1J4, Canada. E-mail: garry.hanan@umontreal.ca; Fax: +1-514 343-2468; Tel: +1-514 343-7056*

[b]*Organic Semiconductor Centre, EaStCHEM School of Chemistry, University of St Andrews, St Andrews, Fife, UK, KY16 9ST, Fax: +44-1334 463808; Tel: +44-1334 463826; E-mail: eli.zysman-colman@st-andrews.ac.uk;*
*URL: http://www.zysman-colman.com*

## SUPPORTING INFORMATION

## Table of contents

## Materials, method and instrumentation:

***General Synthetic Procedures***. Commercial chemicals were used as supplied. All reactions were performed using standard Schlenk techniques under inert ($N_2$) atmosphere with freshly distilled anhydrous solvents obtained from a Pure MBRAUN (MB-SPS) purification system except where specifically mentioned. Flash column chromatography was performed using silica gel (Silia-P from Silicycle, 60 Å, 40-63 $\mu$m). Analytical thin layer chromatography (TLC) was performed with silica plates with aluminum backings (250 $\mu$m with indicator F-254). Compounds were visualized under UV light. $^{1}$H. $^{19}$F and $^{13}$C NMR spectra were recorded on a Brucker Avance 400 spectrometer at 400 MHz, 376 MHz and 100 MHz, respectively. The following abbreviations have been used for multiplicity assignments: "s" for singlet, "d" for doublet, "t" for triplet, "m" for multiplet and "br" for broad. Deuterated chloroform ($CDCl_3$), deuterated acetone $(CD_3)_2CO$ and deuterated actonitrile ($CD_3CN$) were used as the solvent of record. Chemical shifts are reported in part per million (ppm) relative to residual solvent protons (1.96 ppm for $CD_3CN$, 7.26 ppm for $CDCl_3$ and 2.07 for $(CD_3)_2CO$) and the carbon resonance (0.73 and 118.69 ppm for $CD_3CN$, 77.00 ppm for $CDCl_3$ and 29.34 and 205.64 for $(CD_3)_2CO$) of the solvent. Melting points (Mp's) were recorded using open-ended capillaries on a Meltemp melting point apparatus and are uncorrected. High resolution mass spectra were recorded on a quadrupole time-of-flight (ESI-Q-TOF), model MICROTOF II from Bruker in positive electrospray ionization mode at the Université de Montreal. 1,3,4,6,7,8-Hexahydro-2H-pyrimido[1,2-*a*]pyrimidine (H-hpp), 2-bromopyridine, 2-chloropyrazine, (±) BINAP, $Pd(OAc)_2$, *t*-BuOK were purchased from Aldrich and used as received. The corresponding iridium(III) dimers, $[(C\hat{}N)_2Ir(Cl)]_2$ were prepared

according to the literature, where C^N is 2-phenylpyridinato or 2-(2,4-difluorophenyl)-5-methylpyridinato.[1]

***Photophysical measurements.*** All samples were prepared in HPLC grade acetonitrile (ACN) with varying concentrations on the order of $\mu$M. Absorption spectra were recorded at RT using a Cary 500i double beam spectrophotometer. Molar absorptivity determination was verified by linear least-squares fit of values obtained from at least three independent solutions at varying concentrations with absorbance ranging from $6.88 \times 10^{-1}$ to $3.19 \times 10^{2}$ μM.

The sample solutions for the emission spectra were prepared in Ar-degassed dry ACN. Emission spectra were recorded at room temperature using a Cary Eclipse 300 fluorimeter or a Perkin Elmer LS55 fluorimeter. The samples were excited at the absorption maxima of the dominant low-energy $^{1}$MLCT band as indicated in Table **S3**. Excited state lifetimes were measured with an Edinburgh Instruments Mini Tau lifetime fluorimeter with an EPL 405 laser (exciting at 405 nm). Emission quantum yields were determined using the optically dilute method.[2] A stock solution with absorbance of ca. 0.5 was prepared and then four dilutions were prepared with dilution factors of 40, 20, 13.3 and 10 to obtain solutions with absorbances of ca. 0.013 0.025, 0.038 and 0.05, respectively. The Beer-Lambert law was found to be linear at the concentrations of the solutions. The emission spectra were then measured after the solutions were rigorously degassed with solvent-saturated argon gas (Ar) for 20 minutes prior to spectrum acquisition using septa-sealed quartz cells from Starna. For each sample, linearity between absorption and emission intensity was verified through linear regression analysis and additional measurements were acquired until the Pearson regression factor ($R^2$) for the linear fit of the data set surpassed 0.9. Individual relative quantum yield values were calculated for each solution and the values

reported represent the slope value. The equation $\Phi_s = \Phi_r(A_r/A_s)(I_s/I_r)(n_s/n_r)^2$ was used to calculate the relative quantum yield of each of the sample, where $\Phi_r$ is the absolute quantum yield of the reference, *n* is the refractive index of the solvent, *A* is the absorbance at the excitation wavelength, and *I* is the integrated area under the corrected emission curve. The subscripts s and r refer to the sample and reference, respectively. A solution of quinine sulfate in ACN ($\Phi_r$ = 0.54) was used as the external reference.[3]

***Electrochemistry measurements.*** Cyclic voltammetry (CV) measurements were performed in argon-purged purified HPLC grade acetonitrile at room temperature with a BAS CV50W multipurpose equipment interfaced to a PC or a Biologic SP-50 potentiostat. Solutions for cyclic voltammetry were prepared in ACN and degassed with ACN-saturated argon bubbling for about 20 min prior to scanning. Tetra(*n*-butyl)ammonium hexafluorophosphate ($TBAPF_6$; ca. 0.1 M in ACN) was used as the supporting electrolyte. A non-aqueous $Ag/Ag^+$ electrode (silver wire in a solution of 0.1 M $AgNO_3$ in ACN) was used as the pseudoreference electrode; a glassy-carbon electrode was used for the working electrode and a Pt electrode was used as the counter electrode. The redox potentials are reported relative to a standard calomel electrode (SCE) electrode with a ferrocenium/ferrocene ($Fc^+/Fc$) redox couple as an internal reference (0.38 V vs SCE).[4]

## Synthetic details:

1-(Pyridin-2-yl)-2,3,4,6,7,8- hexahydro-1*H*-pyrimido[1,2- *a*]pyrimidine (Guanidyl-pyridine (gpy), **L1):** The synthesis was carried out according to our recently reported protocol.[5]

**Yield:** 95%. $^1$H NMR (400 MHz, Chloroform-*d*) δ (ppm): 8.25 (ddd, *J* = 5.0, 1.9, 0.8 Hz, 1H), 7.69 – 7.66 (m, 1H), 7.50 – 7.45 (m, 1H), 6.78 (ddd, *J* = 7.1, 5.0, 1.0 Hz, 1H), 3.92 – 3.87 (m, 1H), 3.45 – 3.40 (m, 1H), 3.24 (t, *J* = 6.0 Hz, 1H), 3.20 (t, *J* = 6.4 Hz, 1H), 2.07 – 2.00 (m, 1H), 1.93 – 1.86 (m, 1H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ (ppm): 156.93, 150.13, 147.38, 136.10,

118.97, 116.97, 49.12, 48.90, 44.23, 43.87, 24.03, 23.04. The $^{1}H$ and $^{13}C$ NMR are in good agreement with previously reported result.[5]

1-(Pyrazin-2-yl)-2,3,4,6,7,8-hexahydro-1H-pyrimido[1,2-α]- pyrimidine (Guanidyl-pyrazine (gpz), **L2):** The synthesis was carried out according to our recently reported protocol.[5] **Yield:** 82 %. $^{1}H$ NMR (400 MHz, Chloroform-*d*) δ (ppm): 9.10 – 9.08 (m, 1H), 8.14 (dd, *J* = 2.8, 1.5 Hz, 1H), 7.96 (d, *J* = 2.7 Hz, 1H), 3.87 – 3.83 (m, 2H), 3.46 – 3.42 (m, 2H), 3.27 (t, *J* = 6.0 Hz, 2H), 3.23 (t, *J* = 6.3 Hz, 2H), 2.11 – 2.03 (m, 2H), 1.92 (dt, *J* = 11.7, 5.9 Hz, 2H). $^{13}C$ NMR (101 MHz, $CDCl_3$) δ (ppm): 207.35, 153.42, 149.05, 142.42, 141.03, 135.58, 49.01, 48.78, 44.05, 43.18, 31.33, 23.87, 22.91. The $^{1}H$ and $^{13}C$ NMR are in good agreement with previously reported result.[5]

***General procedure for the synthesis of [(C^N)$_2$Ir(N^N)]PF$_6$ complexes.*** Iridium dimer (0.07 mmol, 1.0 equiv.) and N^N ligand (gpy or gpz) (0.15 mmol, 2.10 equiv.) were solubilized with 20 mL of DCM/MeOH (50:50). The mixture was degassed by multiple vacuum and $N_2$ purging cycles. The suspension was heated at 50 °C for 19 h. The reaction mixture was cooled to room temperature and evaporated to dryness. The resulted solid was dissolved in minimum amount of MeOH and a solution of $NH_4PF_6$ (10 equiv., 1.0 g / 10 mL) was added drop by drop to the methanolic solution to cause the precipitation of a solid. The suspension was cooled to 0 °C for 1 h, filtered and the resulting solid was washed with cold water. The crude solid was purified by flash chromatography on silica gel using DCM to DCM/Acetone (9/1).

$[(ppy)_2Ir(gpy)]PF_6$, **1**. Light yellow solid. **Yield:** 90%. Mp: 191-192 °C. $R_f$ : 0.25 (DCM/acetone (5%) on silica. $^{1}H$ NMR (400 MHz, Acetone-$d_6$) δ (ppm): 8.71 (dd, *J* = 5.9, 1.4 Hz, 1H), 8.46 (dd, *J* = 5.9, 1.3 Hz, 1H), 8.29 – 8.25 (m, 1H), 8.22 (dd, *J* = 8.2, 1.3 Hz, 1H), 8.07 – 7.99 (m,

3H), 7.85 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.78 – 7.70 (m, 2H), 7.59 – 7.55 (m, 1H), 7.37 (ddt, *J* = 9.0, 7.1, 3.5 Hz, 2H), 7.02 (ddd, *J* = 7.1, 5.7, 1.2 Hz, 1H), 6.90 (tdd, *J* = 7.5, 6.2, 1.3 Hz, 2H), 6.75 (qd, *J* = 7.5, 1.4 Hz, 2H), 6.29 (dd, *J* = 7.5, 1.3 Hz, 1H), 6.19 (dd, *J* = 7.6, 1.2 Hz, 1H), 4.11 (dt, *J* = 14.1, 4.7 Hz, 1H), 3.54 (tdd, *J* = 12.8, 8.6, 3.7 Hz, 2H), 3.38 (dt, *J* = 12.0, 8.2 Hz, 1H), 3.34 – 3.22 (m, 2H), 3.16 (dt, *J* = 11.5, 5.3 Hz, 1H), 3.09 – 3.01 (m, 1H), 2.44 (ddt, *J* = 11.8, 8.0, 4.4 Hz, 1H), 2.33 (td, *J* = 10.5, 9.2, 5.0 Hz, 1H), 1.65 – 1.56 (m, 1H), 1.12 (dt, *J* = 13.4, 3.9 Hz, 1H). $^{13}$C NMR (101 MHz, Acetone-$d_6$) δ (ppm): 168.71, 168.66, 155.25, 153.67, 153.45, 151.33, 150.74, 150.69, 149.87, 144.99, 144.86, 140.70, 138.64, 138.41, 132.36, 129.89, 125.39, 124.34, 123.09, 122.79, 122.03, 121.90, 120.18, 119.66, 118.00, 48.96, 48.79, 48.59, 46.88, 23.15, 22.99. HR-MS (ES-Q-TOF): **[M-PF$_6$]$^+$** ($C_{34}H_{32}N_6Ir^+$) Calculated: 717.2314; Experimental: 717.2313.

[(dFMeppy)$_2$Ir(gpy)]PF$_6$, **2**. Light yellow solid. **Yield:** 82%. Mp: 184-185 °C. $R_f$ : 0.28 (DCM/acetone (5%) on silica. $^1$H NMR (400 MHz, Acetone-$d_6$) δ (ppm): 8.56 (s, 1H), 8.44 (d, *J* = 2.0 Hz, 1H), 8.35 (dd, *J* = 8.4, 1.7 Hz, 1H), 8.30 – 8.24 (m, 1H), 8.11 – 8.05 (m, 1H), 7.99 (t, *J* = 7.5 Hz, 2H), 7.78 (d, *J* = 8.4 Hz, 1H), 7.59 – 7.52 (m, 1H), 7.09 (t, *J* = 6.6 Hz, 1H), 6.59 (ddt, *J* = 11.9, 9.2, 2.2 Hz, 2H), 5.77 (dd, *J* = 8.6, 2.4 Hz, 1H), 5.60 (dd, *J* = 8.8, 2.4 Hz, 1H), 4.24 – 4.16 (m, 1H), 3.62 – 3.53 (m, 2H), 3.47 – 3.37 (m, 2H), 3.32 (dt, *J* = 10.5, 5.8 Hz, 1H), 3.21 (dt, *J* = 11.5, 4.9 Hz, 1H), 2.49 (s, 1H), 2.44 (s, 3H), 2.41 (s, 3H), 2.33 (s, 1H), 1.75 (s, 1H), 1.24 – 1.11 (m, 1H). $^{19}$F NMR (376 MHz, Acetonitrile-$d_3$) δ (ppm): -73.17, -75.03 , -111.02 – -111.38 (m), -111.41 (d, *J* = 9.1 Hz), -111.99 (t, *J* = 11.4 Hz), -113.27 – -113.81 (m). $^{13}$C NMR (101 MHz, Acetone-$d_6$) δ (ppm): 164.32, 162.08, 157.68, 154.98, 154.72, 153.63, 151.51, 150.63, 150.04, 141.27, 140.44, 140.29, 134.04, 133.78, 128.77, 123.58, 123.39, 122.85, 122.66, 122.53, 118.41, 114.34, 114.17, 98.23, 97.95, 97.70, 48.97, 48.85, 48.54, 47.16, 23.11, 17.76, 17.40. HR-MS (ES-Q-TOF): **[M-PF$_6$]$^+$** ($C_{36}H_{32}N_6IrF_4^+$) Calculated: 817.2250; Experimental: 817.2253.

$[(ppy)_2Ir(gpz)]PF_6$, **3**. Light red solid. **Yield:** 80%. Mp: 238 °C. $R_f$ : 0.32 (DCM/acetone (5%) on silica. $^1$H NMR (400 MHz, Acetonitrile-$d_3$) δ 8.76 (d, $J$ = 1.0 Hz, 1H), 8.55 – 8.51 (m, 1H), 8.28 (dd, $J$ = 5.8, 0.7 Hz, 1H), 8.15 (d, $J$ = 7.9 Hz, 1H), 8.09 (d, $J$ = 7.9 Hz, 1H), 8.01 (d, $J$ = 3.3 Hz, 1H), 8.00 – 7.94 (m, 2H), 7.80 (dd, $J$ = 7.8, 1.0 Hz, 1H), 7.71 (dd, $J$ = 7.8, 1.1 Hz, 1H), 7.42 (dd, $J$ = 3.3, 1.0 Hz, 1H), 7.30 (ddd, $J$ = 7.4, 5.9, 1.4 Hz, 1H), 7.24 (ddd, $J$ = 7.3, 5.9, 1.5 Hz, 1H), 6.99 – 6.90 (m, 2H), 6.79 (tt, $J$ = 7.5, 1.3 Hz, 2H), 6.24 – 6.20 (m, 1H), 6.15 – 6.10 (m, 1H), 3.95 (ddd, $J$ = 14.2, 5.9, 3.5 Hz, 1H), 3.49 – 3.37 (m, 2H), 3.30 – 3.24 (m, 1H), 3.23 – 3.15 (m, 1H), 3.14 – 3.01 (m, 2H), 2.93 – 2.85 (m, 1H), 2.34 (tdt, $J$ = 11.6, 8.1, 4.1 Hz, 1H), 2.26 – 2.19 (m, 1H), 1.60 – 1.50 (m, 1H), 1.08 (ddq, $J$ = 13.1, 5.9, 3.4 Hz, 1H). $^{13}$C NMR (101 MHz, Acetonitrile-$d$3) δ (ppm): 168.31, 168.07, 152.71, 152.51, 151.10, 150.97, 150.61, 150.25, 145.13, 144.72, 142.31, 141.42, 140.99, 138.87, 138.61, 132.33, 132.17, 130.11, 130.02, 125.45, 124.43, 123.30, 122.92, 122.34, 122.26, 120.41, 119.84, 48.89, 48.70, 48.03, 46.96, 22.99, 22.81. HR-MS (ES-Q-TOF): $\mathbf{[M\text{-}PF_6]^+}$ ($C_{33}H_{31}N_7Ir^+$) Calculated: 718.2266; Experimental: 718.2245.

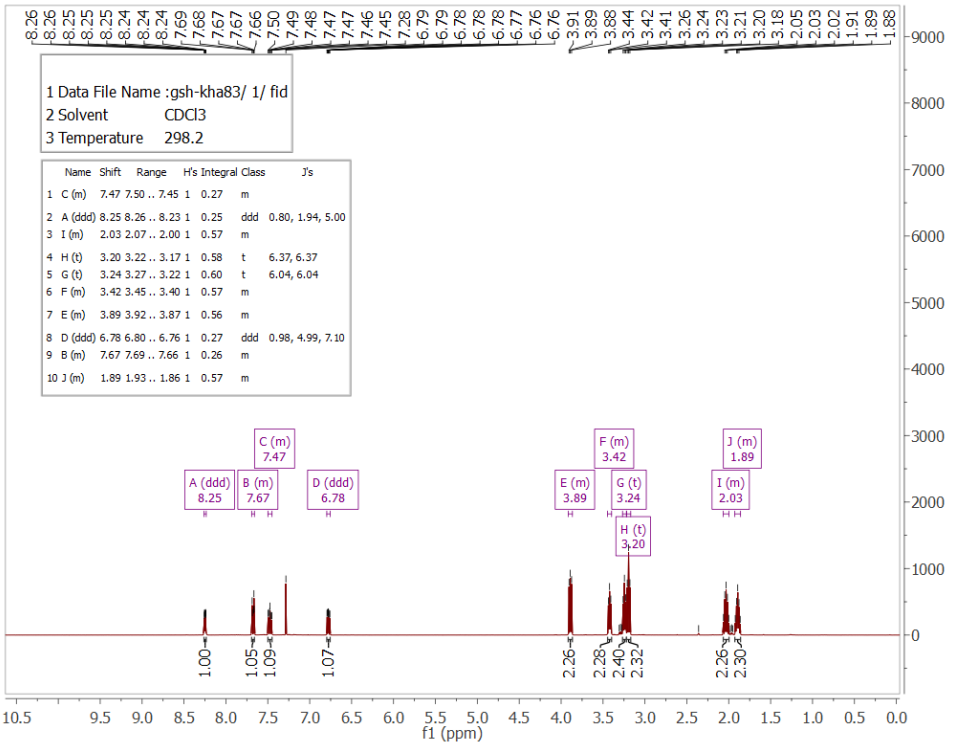


Figure **S1**. $^{1}$H NMR spectrum of **Guanidyl-pyridine**, **gpy** in $CDCl_3$

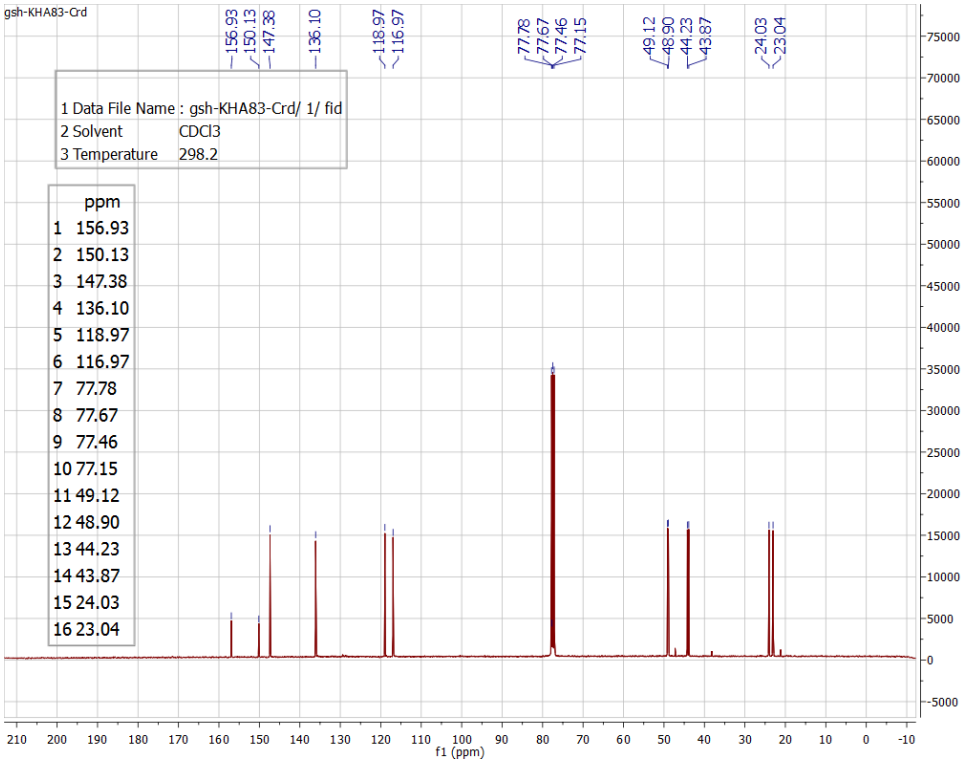


Figure **S2**. $^{13}$C NMR spectrum of **Guanidyl-pyridine**, **gpy** in $CDCl_3$

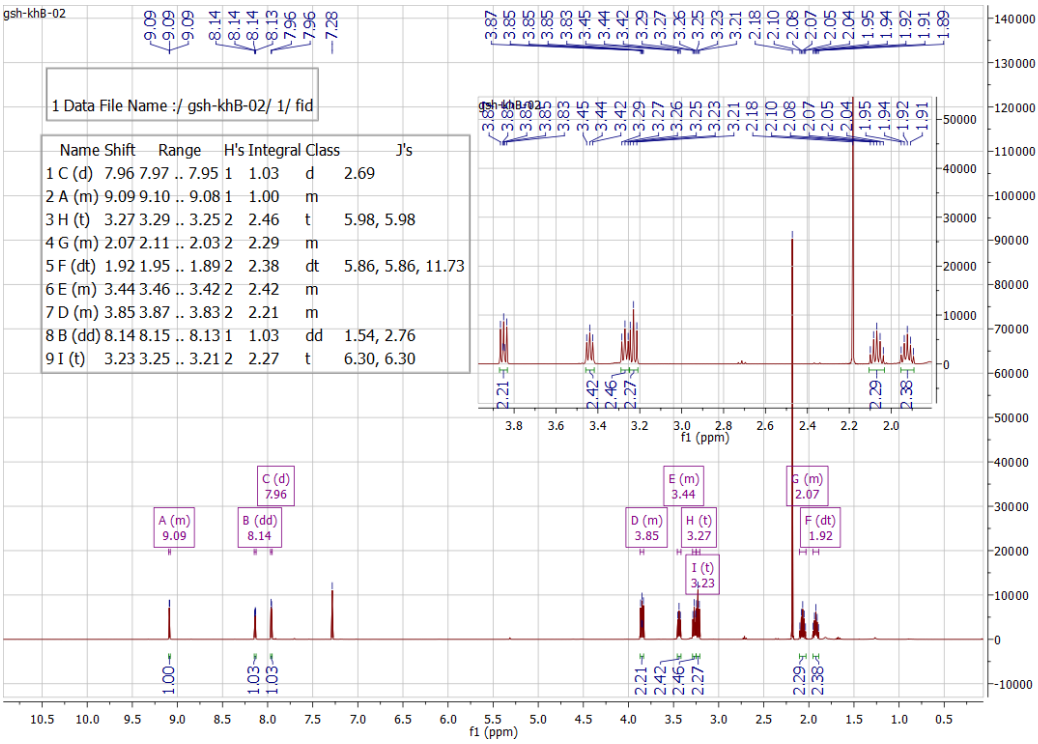


Figure **S3**. $^{1}$H NMR spectrum of **Guanidyl-pyrazine**, **gpz** in $CDCl_3$

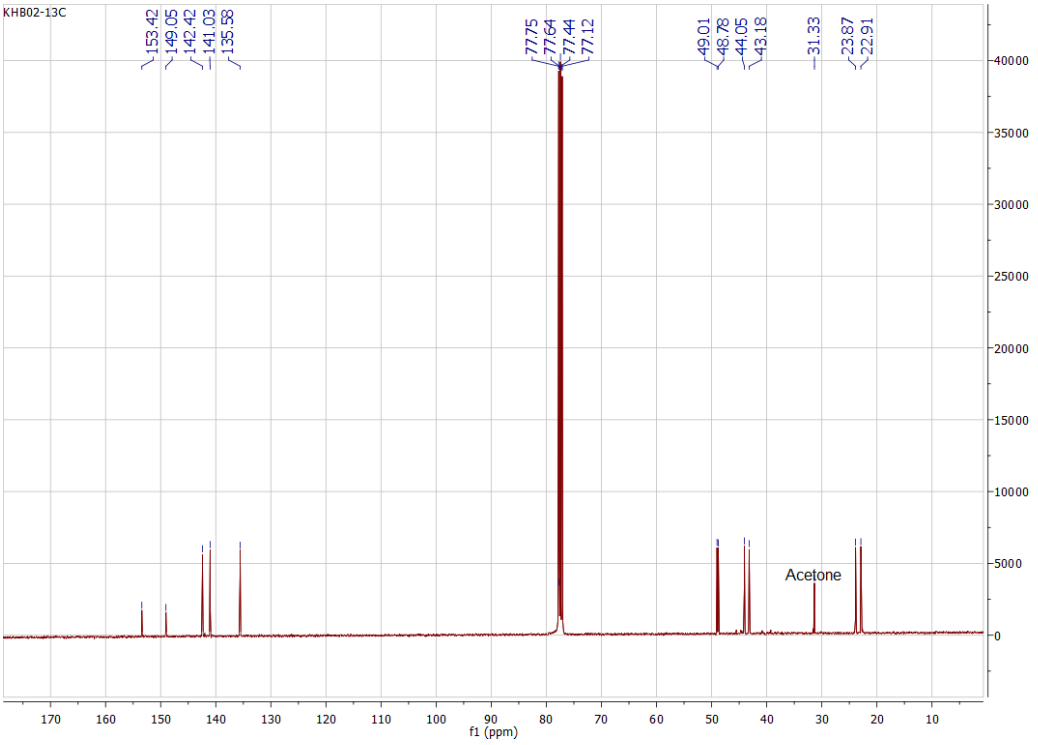


Figure **S4**. $^{13}$C NMR spectrum of **Guanidyl-pyrazine**, **gpz** in $CDCl_3$

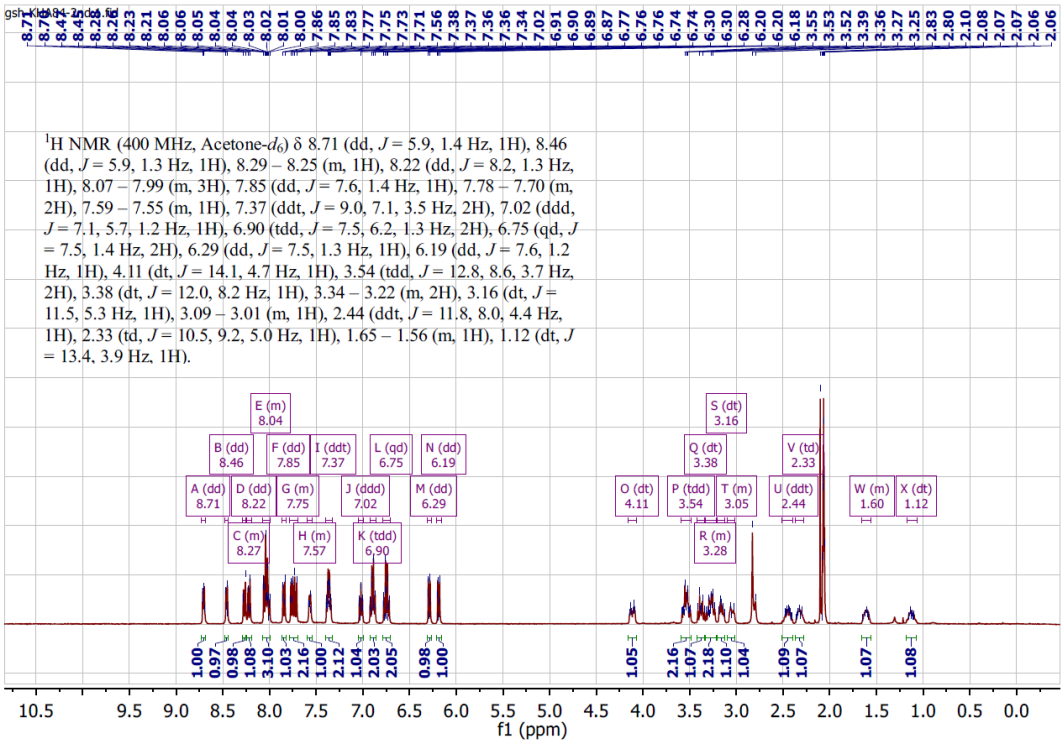


Figure **S5**. $^1$H NMR spectrum of **[(ppy)$_2$Ir(gpy)]PF$_6$, 1** in Acetone-$d_6$

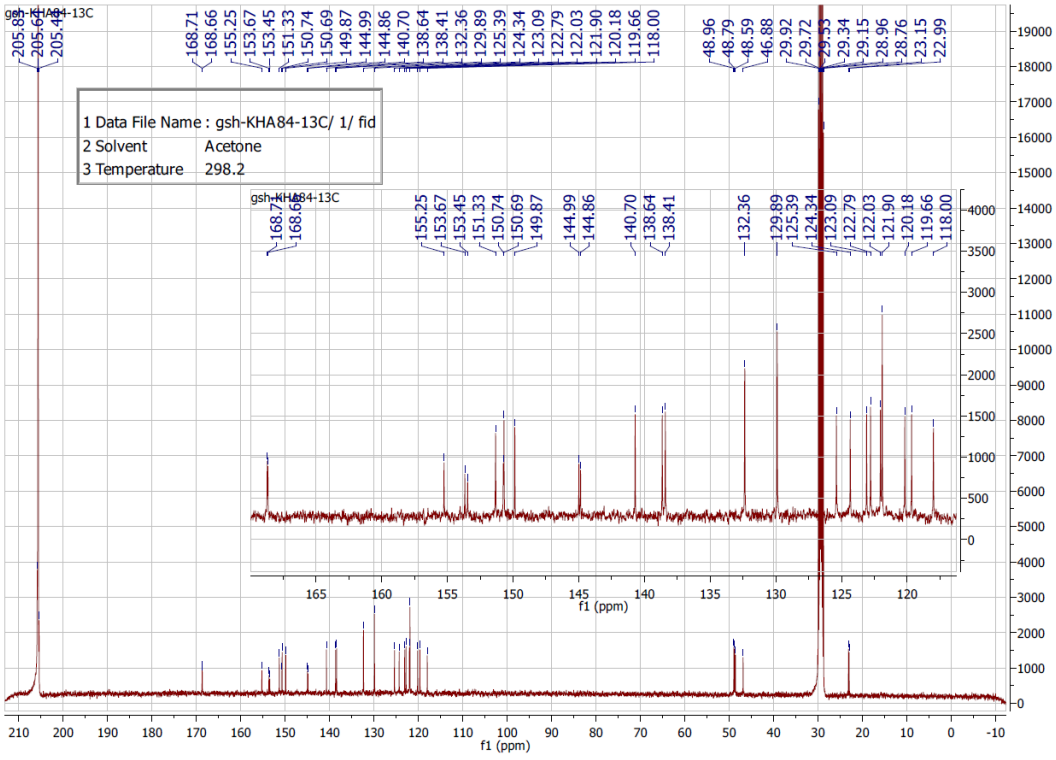


Figure **S6**. $^{13}$C NMR spectrum of **[(ppy)$_2$Ir(gpy)]PF$_6$, 1** in Acetone-$d_6$

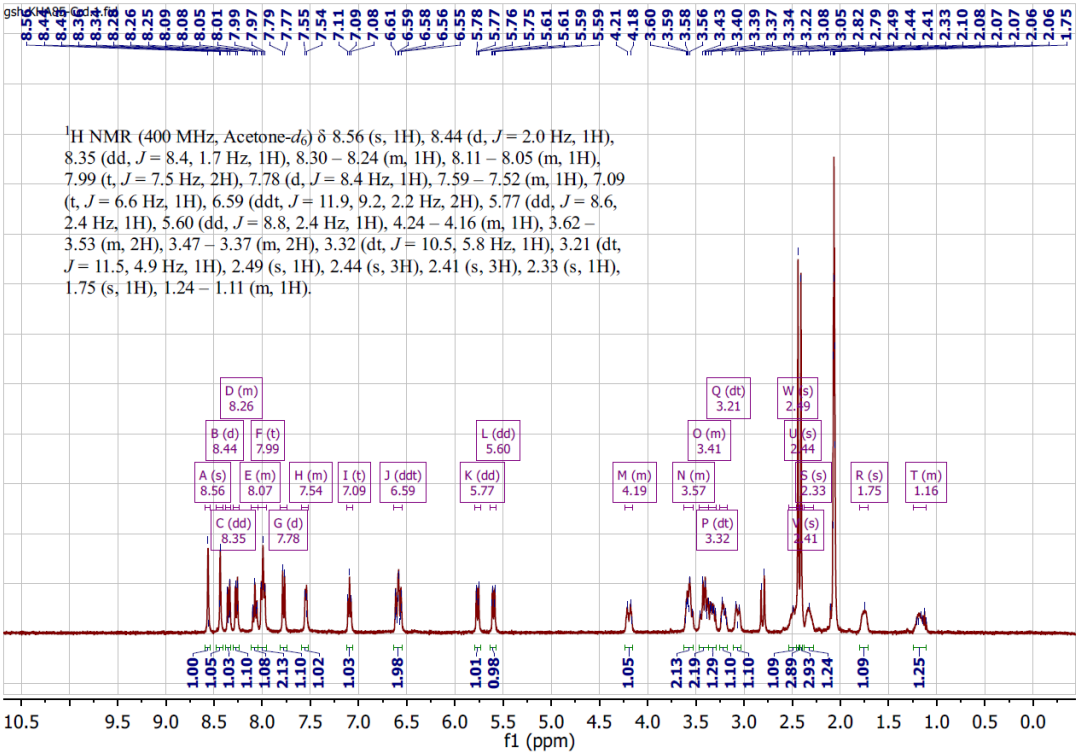


Figure **S7**. $^1$H NMR spectrum of **[(dFMeppy)$_2$Ir(gpy)]PF$_6$**, **2** in Acetone-$d_6$

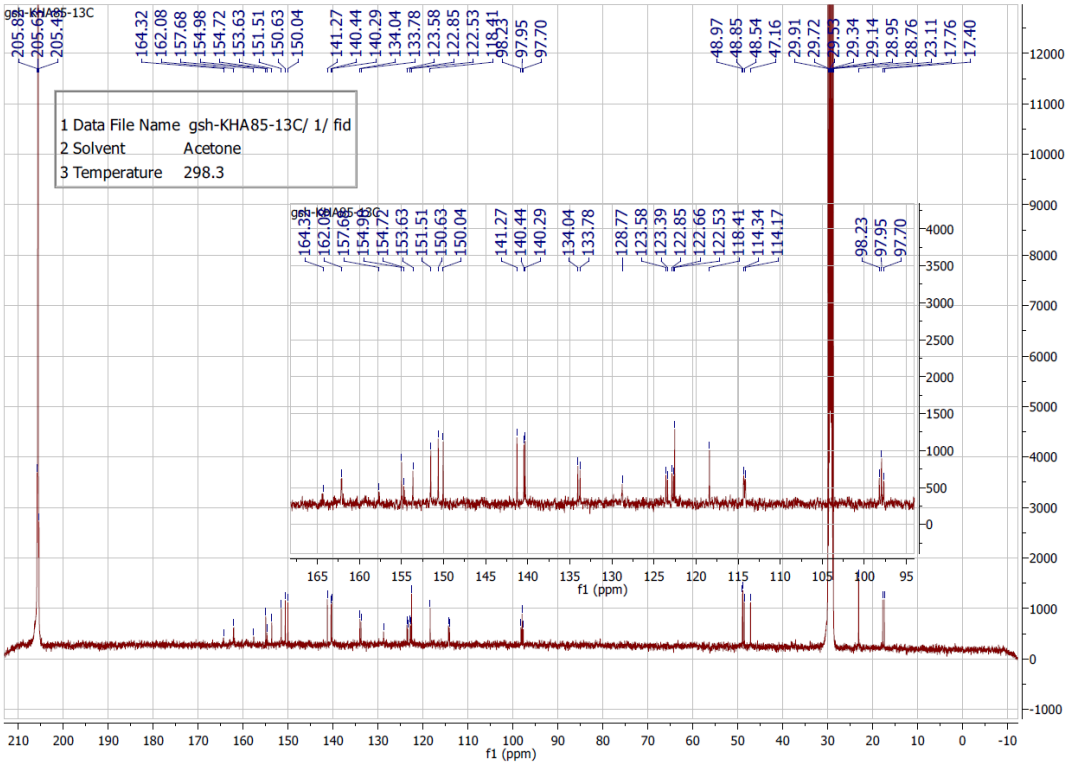


Figure **S8**. $^{13}$C NMR spectrum of **[(dFMeppy)$_2$Ir(gpy)]PF$_6$**, **2** in Acetone-$d_6$

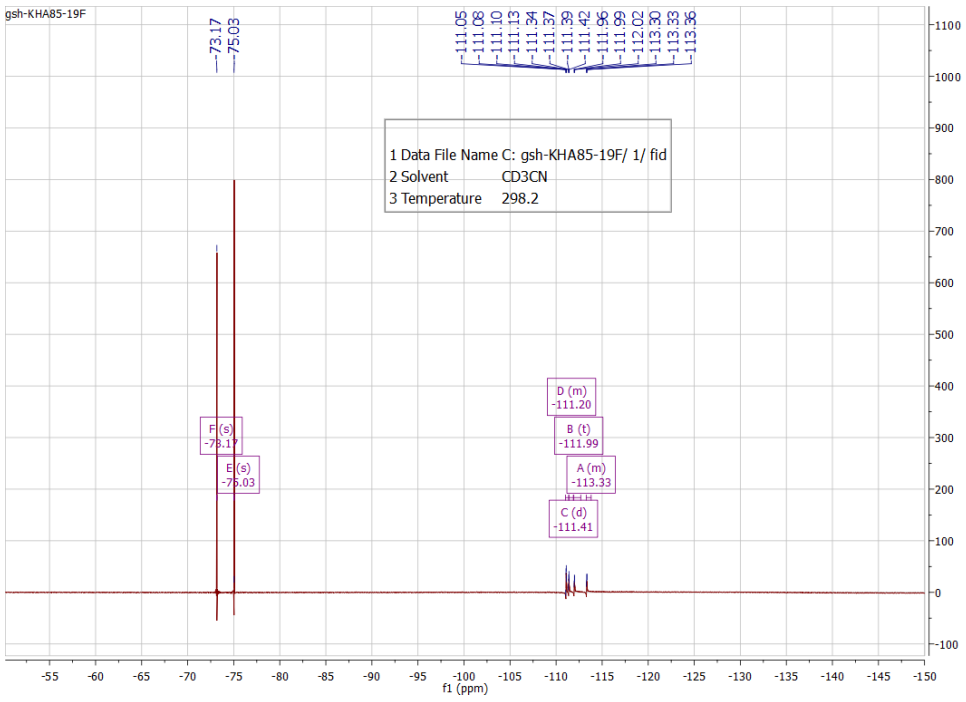


Figure **S9**. $^{19}$F NMR spectrum of **[(dFMeppy)$_2$Ir(gpy)]PF$_6$**, **2** in Acetonitrile-$d_3$

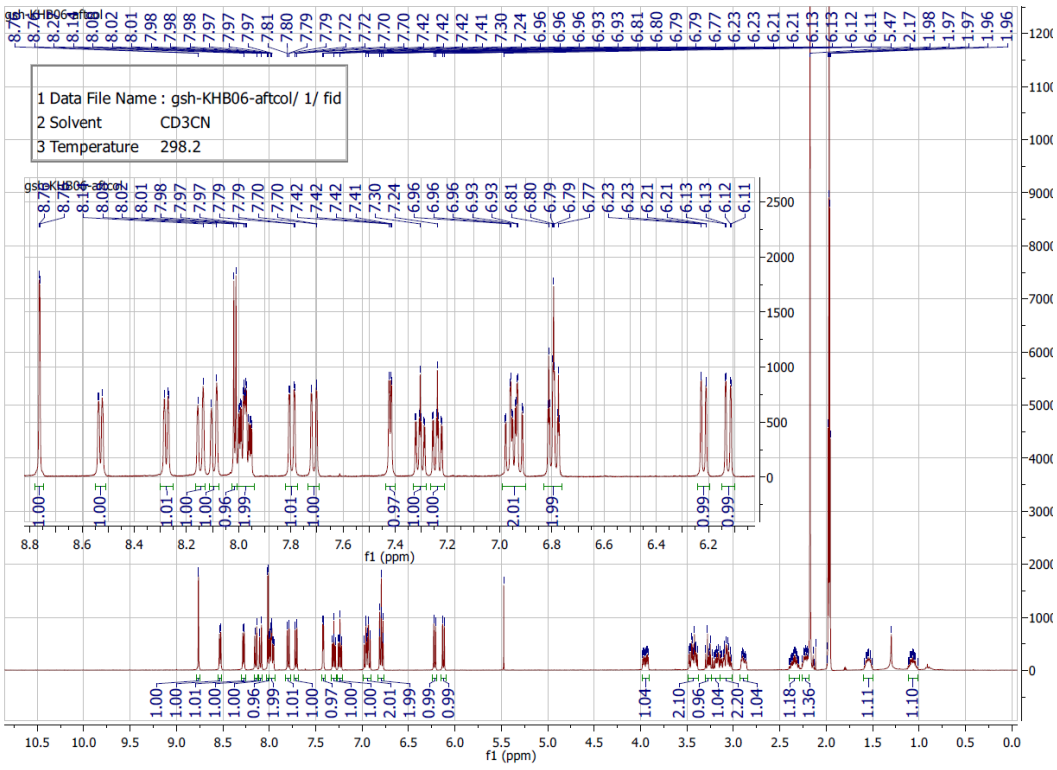


Figure **S10**. $^{1}$H NMR spectrum of **[(ppy)$_2$Ir(gpz)]PF$_6$**, **3** in Acetonitrile-$d_3$

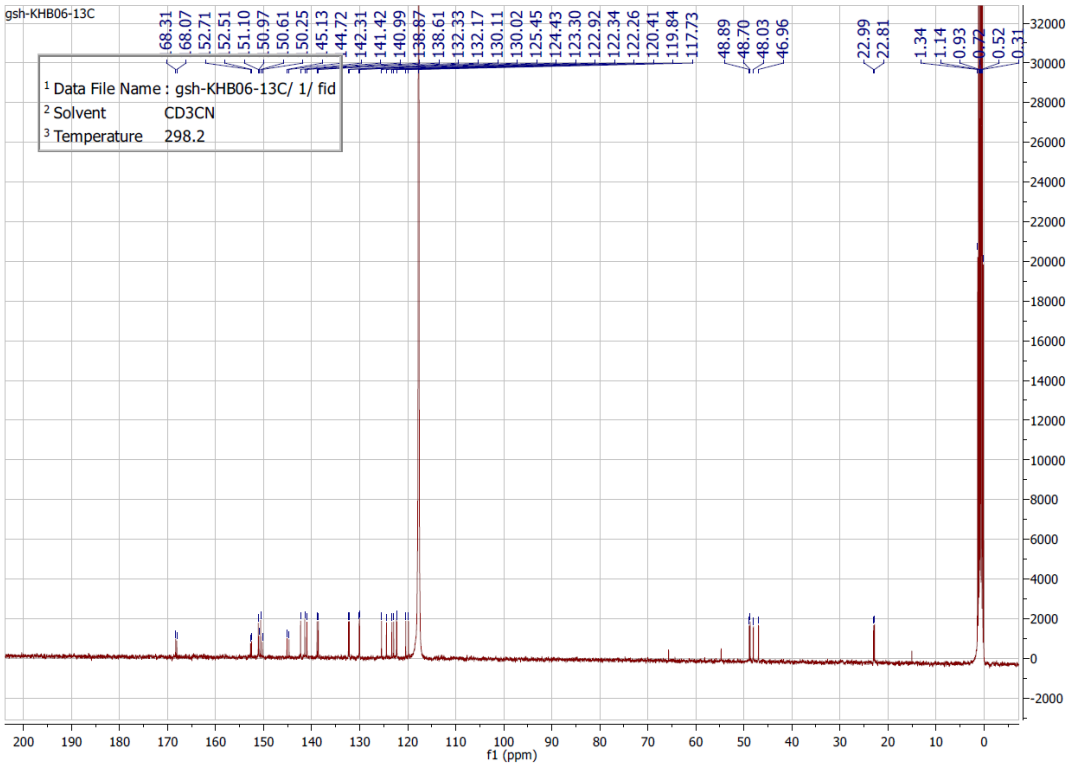


Figure **S11**. $^{13}$C NMR spectrum of **[(ppy)$_2$Ir(gpz)]PF$_6$, 3** in Acetonitrile-$d_3$

**Crystallographic Section**

X-ray crystallographic data were collected from a single crystal sample, which was mounted on a loop fiber. Data were collected using a Bruker Venture diffractometer equipped with a Photon 100 CMOS Detector, a Helios MX optics and a Kappa goniometer and a Gallium Liquid Metal Jet Source (λ = 1.34139 Å) at 100(2) K. The crystal-to-detector distance was 4.0 cm, and the data collection was carried out in 1024 x 1024 pixel mode. The initial unit cell parameters were determined by a least-squares fit of the angular setting of strong reflections, collected by a 110.0 degree scan in 110 frames over three different parts of the reciprocal space.

The diffraction quality of the best-available crystal was checked, revealing poor diffraction with a large amount of diffuse scattering. Data collection, cell refinement and data reduction were done using APEX2[6] and SAINT.[7] Absorption corrections were applied using SADABS.[8]

Structures were solved by direct methods using SHELXS2012 and refined on $F^2$ by full-matrix least squares using SHELXL2012.[9] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined isotropic on calculated positions using a riding model. For compound **3** the highest difference peak is 3.23 Å far from Ir-atom and the deepest hole is 5.29 Å from H-atom. In addition, in **3** four more peaks with density around 2.88-1.81 e/Å$^3$ were present essentially due to the quality of the crystal employed, which was the best available.

**Table S1**. Crystallographic data for complex **3·$CH_2Cl_2$**.

| **Compound** | **3·$CH_2Cl_2$** |
|---|---|
| CCDC Number | 1015124 |
| Formula | $[C_{33}H_{31}N_7Ir][PF_6]\cdot CH_2Cl_2$ |
| *Mw* (g/mol); $d_{calcd.}$(g/cm$^3$) | 947.74; 1.830 |
| *T* (K); F(000) | 100(2); 3728 |
| Crystal System | Orthorhombic |
| Space Group | Pbca |
| Unit Cell: | |
| *a* (Å) | 10.9180(12) |
| *b* (Å) | 16.0878(17) |
| *c* (Å) | 39.160(4) |
| $\alpha$ (°) | 90 |
| $\beta$ (°) | 90 |
| $\gamma$ (°) | 90 |
| *V* (Å$^3$); Z | 6878.4(13); 8 |
| $\theta$ range (°); completeness | 4.78-60.04; 0.991 |
| $R_{fle}$:collec./indep.; $R_{int}$ | 110188/6939; 0.0740 |
| $\mu$ (mm$^{-1}$) | 6.855 |
| R1(F); wR(F$^2$); GoF(F$^2$)[a] | 0.0787; 0.1875; 1.241 |
| Residual electron density | 3.23; -5.29 |

[a]R1(F) based on observed reflections with I>2σ(I) for complex **3**; wR(F$^2$) and GoF(F$^2$) based on all data.

**Table S2**. Comparison of observed and calculated bond distances and angles of complex **3**.

| Complex | Bond Length | | | Angle | | |
|---|---|---|---|---|---|---|
| **3** | | Obs. (X-ray) | Calc. (DFT) | | Obs. (X-ray) | Calc. (DFT) |
| | $Ir1\text{-}N1_{ppy}$ | 2.068(8) | 2.08625 | $C1_{ppy}\text{-}Ir1\text{-}N1_{ppy}$ | 80.6(4) | 79.885 |
| | $Ir1\text{-}N2_{ppy}$ | 2.041(8) | 2.08940 | $C12_{ppy}\text{-}Ir1\text{-}N2_{ppy}$ | 80.8(4) | 79.987 |
| | $Ir1\text{-}N3_{gpz}$ | 2.152(8) | 2.23670 | $N3_{gpz}\text{-}Ir1\text{-}N7_{gpz}$ | 83.8(3) | 81.916 |
| | $Ir1\text{-}N7_{gpz}$ | 2.135(9) | 2.24302 | | | |
| | $Ir1\text{-}C1_{ppy}$ | 1.998(11) | 2.02302 | | | |
| | $Ir1\text{-}C12_{ppy}$ | 2.012(9) | 2.02099 | | | |

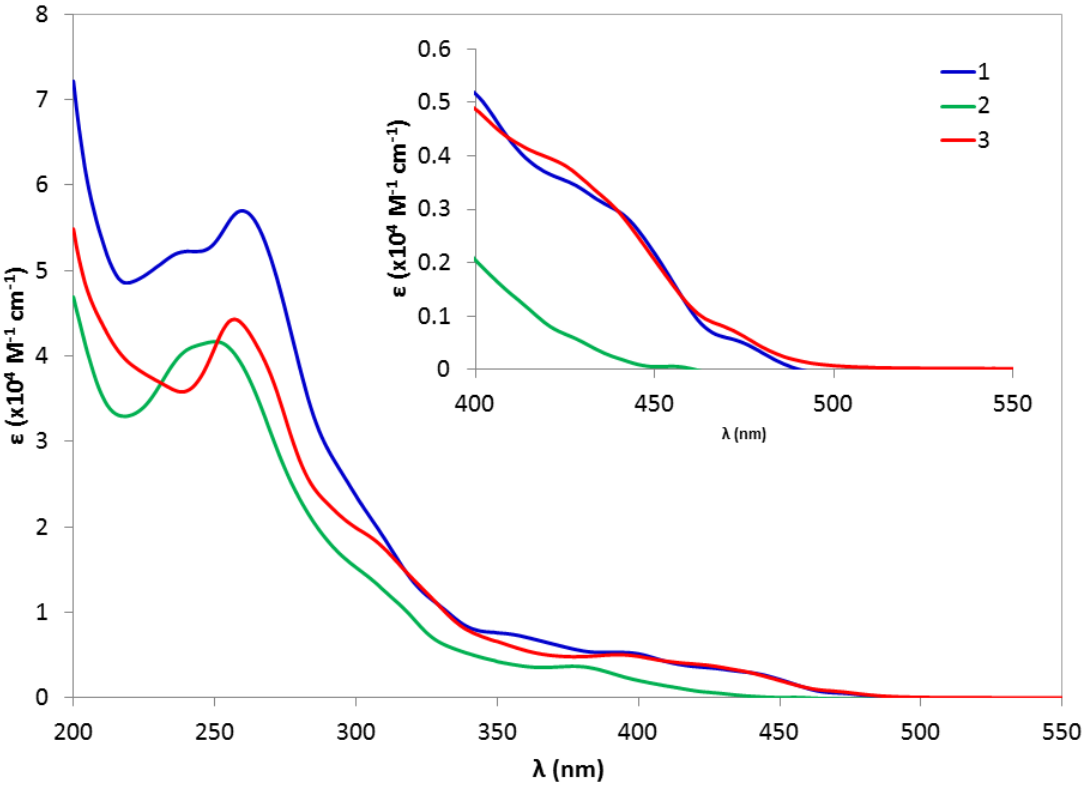


Figure **S12**. UV-vis absorption spectra of complexes **1-3** in acetonitrile at 298 K. Inset: Zoomed at lower energy transitions.

**Table S3**: Molar absorptivity data of complexes **1-3** in acetonitrile at 298 K.

| Complex | $\lambda_{abs}$ /nm ($\varepsilon$ /$10^4$ $M^{-1}cm^{-1}$) | $E_{HOMO}$/eV (TD-DFT) | $E_{LUMO}$/eV (TD-DFT) | $\lvert E_{LUMO}-E_{HOMO}\rvert$/eV (conversion in nm in parenthesis) (TD-DFT) |
|---|---|---|---|---|
| **1** | 241 (5.22); 260 (5.70); 360 (0.71); 403 (0.49); 445 (0.26); 477 (0.043) | -5.32 | -1.6 | 3.72 (333 nm) |
| **2** | 256 (4.06); 383 (2.16); 461 (0.003) | -5.66 | -1.75 | 3.91 (317 nm) |
| **3** | 257 (4.33); 311 (1.72); 402 (0.48); 443 (0.27); 477 (0.054) | -5.43 | -2.12 | 3.31 (374 nm) |

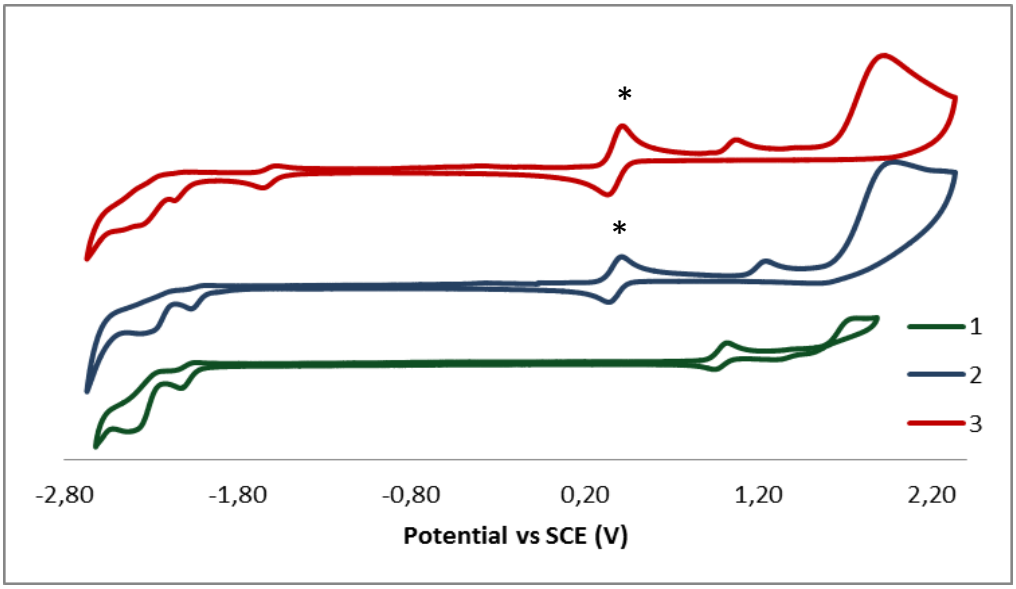


Figure **S13**. Cyclic voltammograms of complexes **1**-**3** in deaerated acetonitrile at 298 K using 0.1 M ($n$-$Bu_4NPF_6$) at the scan rate of 100 mV/s. The waves marqued with an * correspond to the Fc+/Fc redox couple.

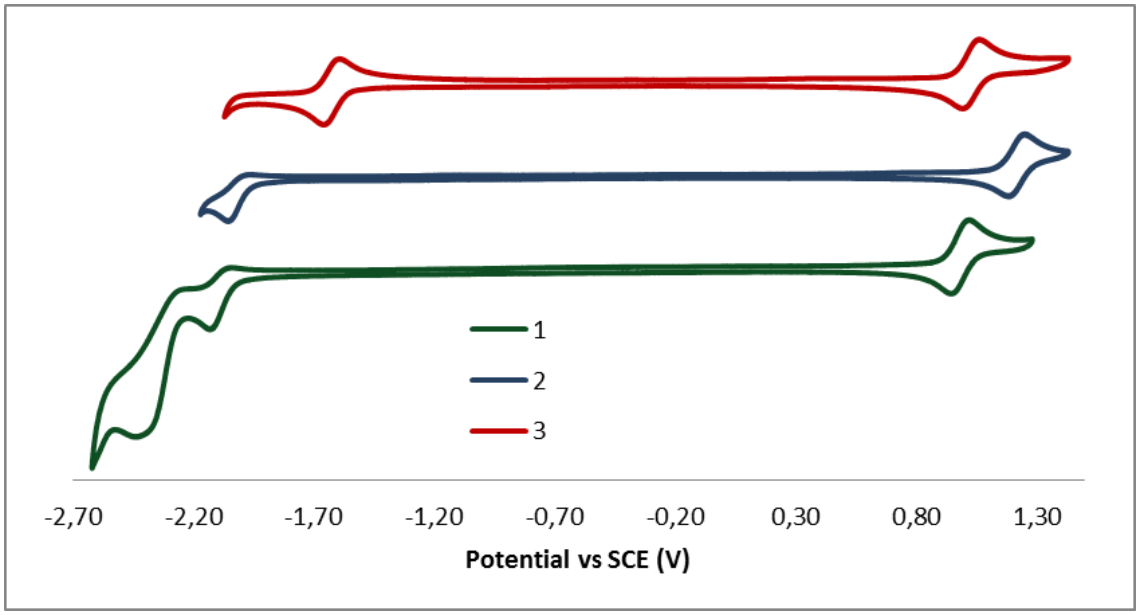


Figure **S14**. Cyclic voltammograms of complexes **1**-**3** up to 1st redox potential in deaerated acetonitrile at 298 K using 0.1 M ($n$-$Bu_4NPF_6$) at the scan rate of 100 mV/s.

**Table S4**: Electrochemical data of complexes **1-3** in degassed acetonitrile at 298 K.[a]

| Complex | $E^{1}_{1/2}{}^{ox}$ /V (ΔEp) | $E^{2}_{pa}{}^{ox}$/ V | $E^{3}_{pa}{}^{ox}$/ V | $E^{1}_{1/2}{}^{red}$ /V (ΔEp) | $E^{2}_{pc}{}^{red}$/ V | Δ$E$/ V | $E_{HOMO}$/e V | $E_{LUMO}$/e V | $\lvert E_{LUMO}-E_{HOMO}\rvert$/e V |
|---|---|---|---|---|---|---|---|---|---|
| **1** | 0.99 (88) | 1.35 | 1.72 | -2.13 | -2.40 | 3.12 | -5.32 | -1.6 | 3.72 |
| **2** | 1.21 (72) | 1.66 | 1.95 | -2.12 | -2.35 | 3.31 | -5.66 | -1.75 | 3.91 |
| **3** | 1.04 (82) | 1.43 | 1.78 | -1.60 (95) | -2.32 (131)[b] | 2.72 | -5.43 | -2.12 | 3.31 |

[a]CV traces recorded in ACN solution with 0.1 M ($n$-$Bu_4N$)$PF_6$ at 298 K at 50 $mVs^{-1}$. Values are in V vs. SCE ($Fc/Fc^+$ vs. SCE = 0.38 V).[19] $\Delta E = \Delta E_{redox}$; $\Delta E_p$ in mV = $|E_{pa} - E_{pc}|$, where $E_{pa}$ = anodic peak potential and $E_{pc}$ = cathodic peak potential; $E_{1/2} = (E_{pa} + E_{pc})/2$ and result from one-electron processes. A non-aqueous $Ag/Ag^+$ electrode (silver wire in a solution of 0.1 M $AgNO_3$ in ACN) was used as the pseudoreference electrode; a glassy-carbon electrode was used for the working electrode and a Pt electrode was used as the counter electrode. $E_{pa}$ reported for oxidation peak potentials and $E_{pc}$ reported for reduction peak potentials.[b] $E^{2}_{1/2}{}^{red}$ for second reduction.

## DFT Calculations:

### Computational details:

All calculations were performed with the Gaussian03[10] suite of programs employing the DFT method, the Becke three-parameter hybrid functional,[11] and Lee-Yang-Parr's gradient-corrected correlation functional (B3LYP).[12] Singlet ground state geometry optimizations for $[\mathbf{1}]^{1+}$, $[\mathbf{2}]^{1+}$ and $[\mathbf{3}]^{1+}$ were carried out at the (R)B3LYP level in the gas phase, using the crystallographic structure of **3** as starting point. All elements except Ir were assigned to the 6-31G(d,p) basis set.[13] The double-ζ quality LANL2DZ ECP basis set[14] with an effective core potential and one additional f-type polarization was employed for the Ir-atom. Vertical electronic excitations based on (R)B3LYP-optimized geometries were computed for $[\mathbf{1}]^{1+}$, $[\mathbf{2}]^{1+}$ and $[\mathbf{3}]^{1+}$ using the TD-DFT formalism[15a,b] in acetonitrile using conductor-like polarizable continuum model (CPCM).[16a-c] Vibrational frequency calculations were performed to ensure that the optimized geometries represent the local minima and there are only positive eigenvalues. The electronic distribution and localization of the singlet excited states were visualized using the electron density difference maps (ED-DMs).[17] *Gausssum 2.2* and *Chemissian* were employed to visualize the absorption spectra (simulated with Gaussian distribution with a full-width at half maximum (fwhm) set to 3000 $cm^{-1}$) and to calculate the fractional contributions of various groups to each molecular orbital. All calculated Kohn-Sham orbitals were visualized with ChemCraft.[18]

**Table S5**. Selected transitions from TD-DFT calculations of $[\mathbf{1}]^{1+}$ in the singlet ground state (b3lyp/LanL2DZ(f)[Ir]6-31G**[C,H,N], CPCM ($CH_3CN$)).

| Energy (eV) | λ/nm | λ/nm (εx$10^4$ $M^{-1}cm^{-1}$) [expt.] | Oscillator strength | Major transition(s) | Character |
|---|---|---|---|---|---|
| 5.04 | 246 | 241 (5.22) | 0.211 | H->L+7 (19%), H->L+8 (47%) | [ppy(π) to gpy(π∗) + ppy(π) to ppy(π∗)] (major) + [Ir(dπ) to ppy(π*) and gpy(π*)] (minor) |
| 4.77 | 260 | 260 (5.70) | 0.224 | H-6 -> L+2 (30%), H-2 -> L+5 (12%), H -> L+6 (12%) | [ppy(π) to gpy(π∗) + ppy(π) to ppy(π∗) + gpy(π) to gpy(π∗)] (major) + [Ir(dπ) to ppy(π*) and gpy(π*)] (minor) |
| 3.78 | 328 | 360 (0.71) | 0.0787 | H-3 -> L (33%), H-2 -> L (40%), H-1 -> L+1 (10%) | [ppy(π) to ppy(π∗)] (major) + [Ir(dπ) to ppy(π*)] (minor) |
| 2.97 | 417 | 403 (0.49) | 0.0455 | H -> L (93%) | [ppy(π) to ppy(π∗)] (major) + [Ir(dπ) to ppy(π*)] (minor) |

**Table S6**. Selected transitions from TD-DFT calculations of $[\mathbf{2}]^{1+}$ in the singlet ground state (b3lyp/LanL2DZ(f)[Ir]6-31G**[C,H,N,F], CPCM ($CH_3CN$)).

| Energy (eV) | λ/nm | λ/nm (εx$10^4$ $M^{-1}cm^{-1}$) [expt.] | Oscillator strength | Major transition(s) | Character |
|---|---|---|---|---|---|
| 4.79 | 259 | 256 (4.06) | 0.217 | H-2 -> L+4 (32%) | [dFMeppy(π) to dFMeppy(π∗)] (major) + [dFMeppy (π) to gpy(π∗) + gpy(n/π) to gpy(π*) + gpy(n/π) to dFMeppy (π*)] (minor) |
| 3.15 | 394 | 383 (2.16) | 0.040 | H -> L (93%) | [dFMeppy (π) to dFMeppy (π∗) + Ir(dπ) to dFMeppy (π*)] (major) + [gpy(n/π) to dFMeppy (π*)] (minor) |

**Table S7**. Selected transitions from TD-DFT calculations of $[\mathbf{3}]^{1+}$ in the singlet ground state (b3lyp/LanL2DZ(f)[Ir]6-31G**[C,H,N], CPCM ($CH_3CN$)).

| Energy (eV) | λ/nm | λ/nm (εx$10^4$ $M^{-1}cm^{-1}$) [expt.] | Oscillator strength | Major transition(s) | Character |
|---|---|---|---|---|---|
| 4.75 | 261 | 257 (4.33) | 0.171 | H-3 -> L+5 (16%), H-2 -> L+5 (23%) | [ppy(π) to ppy(π*)] (major) + [Ir(dπ) to ppy(π*)] (minor) |
| 3.85 | 322 | 311 (1.72) | 0.074 | H-3 -> L+1 (33%), H-2 -> L+1 (43%) | [ppy(π) to ppy(π*)] (major) + [Ir(dπ) to ppy(π*)] (minor) |
| 3.02 | 410 | 402 (0.48) | 0.048 | H -> L+1 (94%) | [ppy(π) to ppy(π*)] + [Ir(dπ) to ppy(π*)] (almost equal contributions) |
| 2.60 | 476 | 443 (0.27) | 0.005 | H -> L (98%) | [ppy(π) to gpz(π*)] + [Ir(dπ) to gpz(π*)] (almost equal contributions) |

**Table S8**. MO composition of $[\mathbf{1}]^{1+}$ in Singlet (*S*=0) Ground State (b3lyp/LanL2DZ(f)[Ir]6-31G**[C,H,N]).

| MO | Energy (eV) | Composition | | |
|---|---|---|---|---|
| | | Ir | ppy | gpy |
| LUMO+5 | -0.79 | 2 | 28 | 71 |
| LUMO+4 | -0.96 | 1 | 78 | 21 |
| LUMO+3 | -1.04 | 3 | 88 | 10 |
| LUMO+2 | -1.36 | 2 | 8 | 90 |
| LUMO+1 | -1.52 | 4 | 90 | 7 |
| **LUMO** | **-1.6** | **4** | **95** | **1** |
| **HOMO** | **-5.32** | **42** | **47** | **11** |
| HOMO-1 | -5.94 | 44 | 25 | 31 |
| HOMO-2 | -6.09 | 14 | 80 | 6 |
| HOMO-3 | -6.2 | 43 | 50 | 7 |
| HOMO-4 | -6.42 | 18 | 76 | 6 |
| HOMO-5 | -6.52 | 2 | 94 | 5 |

**Table S9**. MO composition of $[\mathbf{2}]^{1+}$ in Singlet (*S*=0) Ground State (b3lyp/LanL2DZ(f)[Ir]6-31G**[C,H,N,F]).

| MO | Energy (eV) | Composition | | |
|---|---|---|---|---|
| | | Ir | dFMeppy | gpy |
| LUMO+5 | -0.86 | 2 | 37 | 61 |
| LUMO+4 | -1.02 | 1 | 74 | 26 |
| LUMO+3 | -1.09 | 2 | 85 | 13 |
| LUMO+2 | -1.47 | 2 | 5 | 93 |
| LUMO+1 | -1.68 | 4 | 93 | 3 |
| **LUMO** | **-1.75** | **4** | **95** | **1** |
| **HOMO** | **-5.66** | **40** | **43** | **18** |
| HOMO-1 | -6.15 | 29 | 51 | 20 |
| HOMO-2 | -6.29 | 6 | 76 | 18 |
| HOMO-3 | -6.35 | 28 | 67 | 5 |
| HOMO-4 | -6.57 | 45 | 39 | 16 |
| HOMO-5 | -6.77 | 2 | 95 | 3 |

**Table S10**. MO composition of $[\mathbf{3}]^{1+}$ in Singlet (*S*=0) Ground State (b3lyp/LanL2DZ(f)[Ir]6-31G**[C,H,N]).

| MO | Energy (eV) | Composition | | |
|---|---|---|---|---|
| | | Ir | ppy | gpz |
| LUMO+5 | -0.94 | 2 | 88 | 10 |
| LUMO+4 | -1.07 | 2 | 91 | 7 |
| LUMO+3 | -1.22 | 0 | 17 | 83 |
| LUMO+2 | -1.56 | 4 | 94 | 1 |
| LUMO+1 | -1.65 | 4 | 95 | 1 |
| **LUMO** | -2.12 | **2** | **1** | **96** |
| **HOMO** | -5.43 | **41** | **49** | **10** |
| HOMO-1 | -6.03 | 42 | 28 | 30 |
| HOMO-2 | -6.16 | 7 | 86 | 7 |
| HOMO-3 | -6.31 | 38 | 57 | 5 |
| HOMO-4 | -6.49 | 31 | 63 | 6 |
| HOMO-5 | -6.58 | 3 | 94 | 4 |

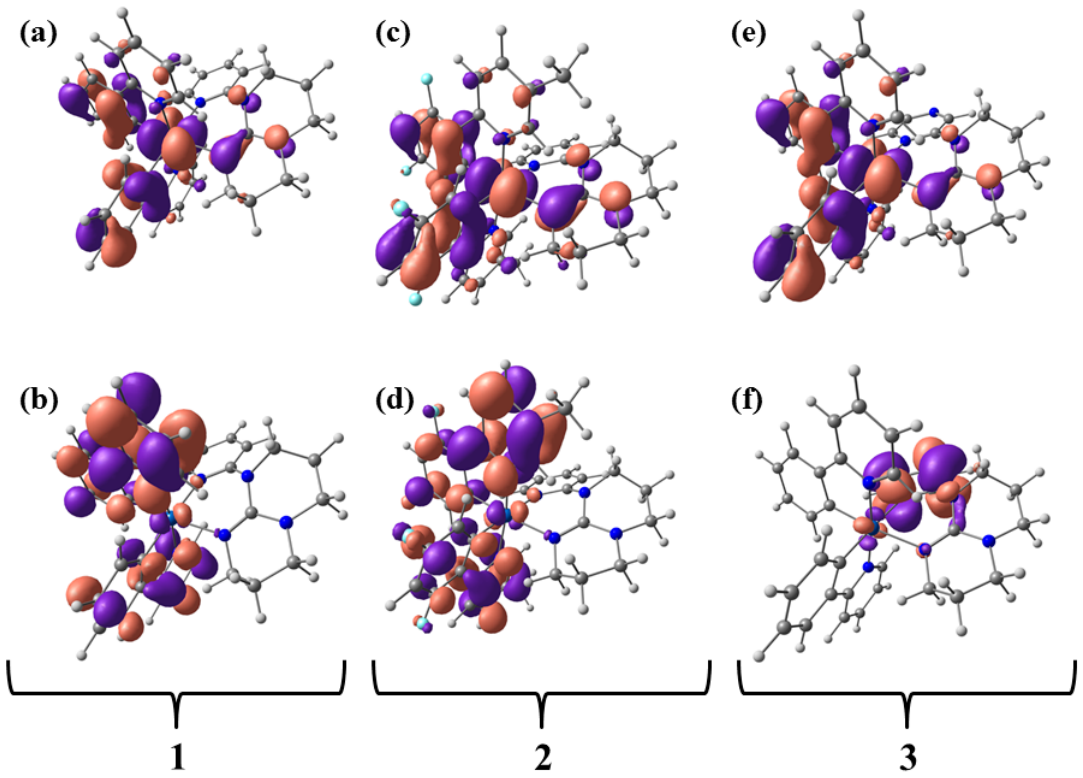


**Figure S15**: Kohn-Sham MO sketches of (a) HOMO and (b) LUMO of complex **1**, (c) HOMO and (d) LUMO of complex **2**, (e) HOMO and (f) LUMO of complex **3**.

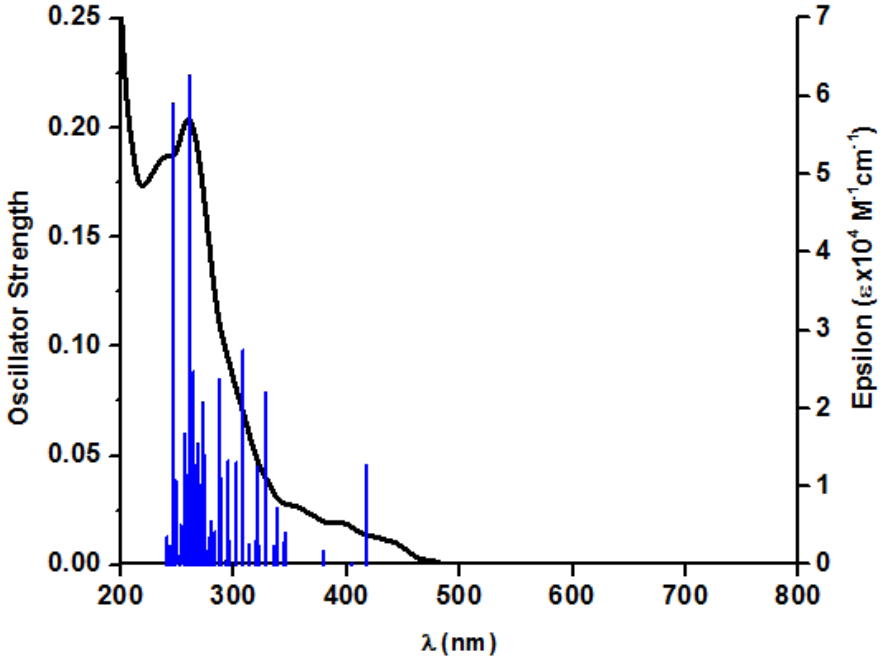


Figure **S16**. Overlay of experimental absorption spectra of the complex **1** in acetonitrile with its predicted transitions and oscillator strength, calculated by TD-DFT.

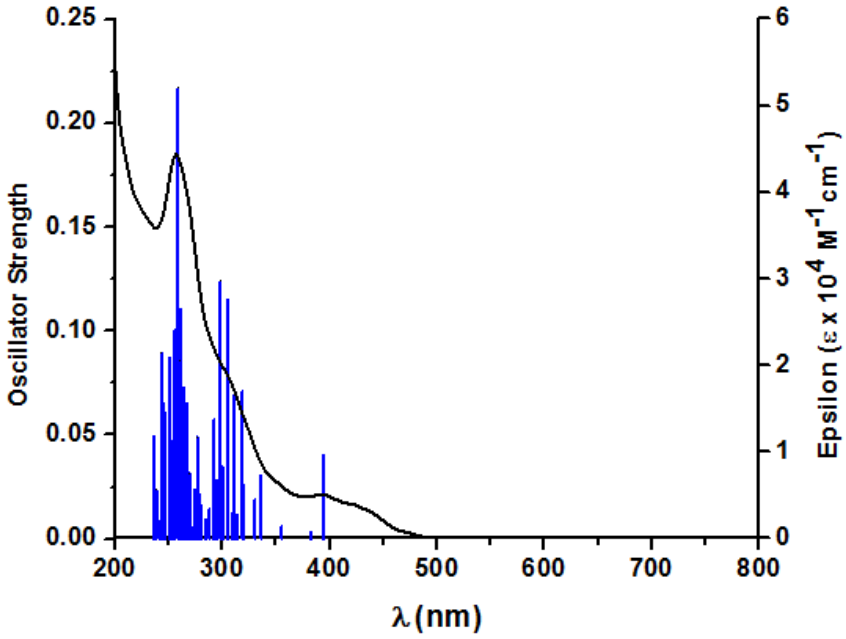


Figure **S17**. Overlay of experimental absorption spectra of the complex **2** in acetonitrile with its predicted transitions and oscillator strength, calculated by TD-DFT.

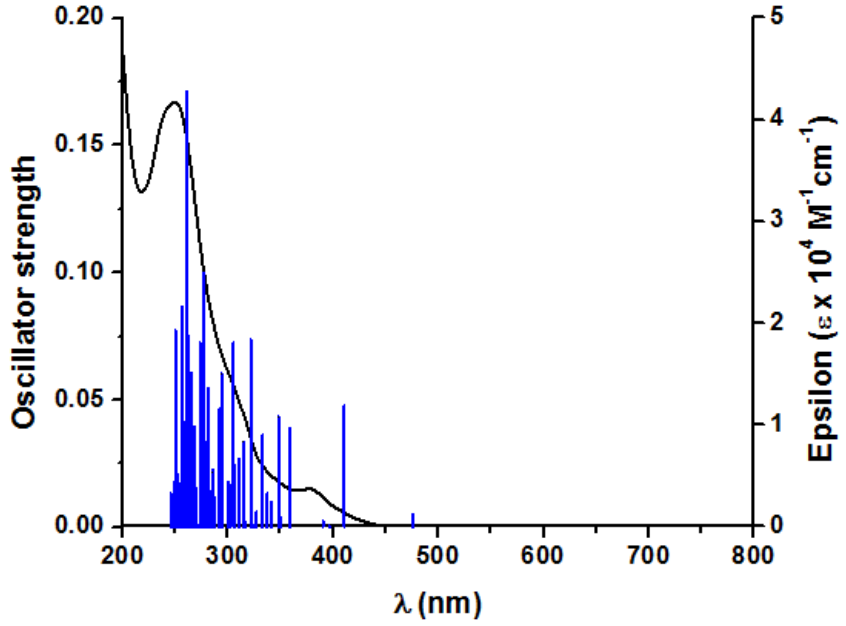


Figure **S18**. Overlay of experimental absorption spectra of the complex **3** in acetonitrile with its predicted transitions and oscillator strength, calculated by TD-DFT.

**Table S11**. Optimized atomic coordinates obtained from DFT calculations of [**1**]$^{1+}$

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 77 | 0 | 0.427957 | 0.020918 | 0.029433 |
| 2 | 7 | 0 | 1.243746 | -1.357537 | 1.369877 |
| 3 | 7 | 0 | -0.155222 | 1.420505 | -1.403852 |
| 4 | 7 | 0 | -0.974006 | 0.994594 | 1.493708 |
| 5 | 7 | 0 | -2.906429 | 0.275958 | 0.275083 |
| 6 | 7 | 0 | -1.299812 | -1.383197 | -0.194681 |
| 7 | 6 | 0 | 0.878532 | -1.502827 | 2.659514 |
| 8 | 1 | 0 | 0.077560 | -0.860335 | 3.001216 |
| 9 | 6 | 0 | 1.481998 | -2.412285 | 3.513835 |
| 10 | 1 | 0 | 1.152653 | -2.485623 | 4.543963 |
| 11 | 6 | 0 | 2.511927 | -3.213883 | 3.012123 |
| 12 | 1 | 0 | 3.014925 | -3.932689 | 3.651288 |
| 13 | 6 | 0 | 2.880045 | -3.083313 | 1.681349 |
| 14 | 1 | 0 | 3.669240 | -3.700935 | 1.270540 |
| 15 | 6 | 0 | 2.233327 | -2.151770 | 0.853235 |
| 16 | 6 | 0 | 2.496744 | -1.947357 | -0.568821 |
| 17 | 6 | 0 | 3.441950 | -2.695265 | -1.293940 |
| 18 | 1 | 0 | 4.044763 | -3.453725 | -0.802931 |
| 19 | 6 | 0 | 3.614978 | -2.469212 | -2.653221 |
| 20 | 1 | 0 | 4.346036 | -3.043405 | -3.213300 |
| 21 | 6 | 0 | 2.840302 | -1.493426 | -3.290454 |
| 22 | 1 | 0 | 2.974149 | -1.309778 | -4.353283 |
| 23 | 6 | 0 | 1.902753 | -0.747540 | -2.573899 |
| 24 | 1 | 0 | 1.329982 | 0.009657 | -3.099652 |
| 25 | 6 | 0 | 2.943735 | 1.394416 | 1.188602 |
| 26 | 1 | 0 | 3.140688 | 0.499796 | 1.771938 |
| 27 | 6 | 0 | 3.796135 | 2.491760 | 1.336464 |
| 28 | 1 | 0 | 4.633135 | 2.433660 | 2.027330 |
| 29 | 6 | 0 | 3.585338 | 3.661949 | 0.599861 |
| 30 | 1 | 0 | 4.248008 | 4.513202 | 0.718481 |
| 31 | 6 | 0 | 2.524616 | 3.721872 | -0.296351 |
| 32 | 1 | 0 | 2.371179 | 4.628627 | -0.874319 |
| 33 | 6 | 0 | 1.667841 | 2.618496 | -0.449909 |
| 34 | 6 | 0 | 0.567155 | 2.582699 | -1.409687 |
| 35 | 6 | 0 | 0.246366 | 3.595019 | -2.328773 |
| 36 | 1 | 0 | 0.815926 | 4.516356 | -2.325370 |
| 37 | 6 | 0 | -0.773854 | 3.408943 | -3.249206 |
| 38 | 1 | 0 | -1.014602 | 4.189160 | -3.964440 |

| | | | | | |
|---|---|---|---|---|---|
| 39 | 6 | 0 | -1.471191 | 2.196424 | -3.255278 |
| 40 | 1 | 0 | -2.256078 | 1.994912 | -3.975507 |
| 41 | 6 | 0 | -1.128466 | 1.235149 | -2.317232 |
| 42 | 1 | 0 | -1.620807 | 0.272152 | -2.285210 |
| 43 | 6 | 0 | -0.441095 | 1.679292 | 2.532066 |
| 44 | 1 | 0 | 0.641421 | 1.731201 | 2.542894 |
| 45 | 6 | 0 | -1.199123 | 2.302854 | 3.510021 |
| 46 | 1 | 0 | -0.710595 | 2.851803 | 4.306717 |
| 47 | 6 | 0 | -2.586783 | 2.191687 | 3.433185 |
| 48 | 1 | 0 | -3.227055 | 2.637635 | 4.187732 |
| 49 | 6 | 0 | -3.146159 | 1.484120 | 2.378650 |
| 50 | 1 | 0 | -4.220060 | 1.366104 | 2.325076 |
| 51 | 6 | 0 | -2.316920 | 0.906422 | 1.398601 |
| 52 | 6 | 0 | -4.212695 | 0.777232 | -0.189428 |
| 53 | 1 | 0 | -4.175806 | 0.860241 | -1.282226 |
| 54 | 1 | 0 | -4.357274 | 1.783824 | 0.199682 |
| 55 | 6 | 0 | -5.308298 | -0.193223 | 0.234501 |
| 56 | 1 | 0 | -5.309497 | -0.297365 | 1.324057 |
| 57 | 1 | 0 | -6.299388 | 0.162185 | -0.062363 |
| 58 | 6 | 0 | -5.018071 | -1.532449 | -0.439284 |
| 59 | 1 | 0 | -5.432712 | -2.368303 | 0.139161 |
| 60 | 1 | 0 | -5.500844 | -1.559697 | -1.424617 |
| 61 | 6 | 0 | -2.550222 | -1.005342 | -0.184599 |
| 62 | 7 | 0 | -3.582869 | -1.771290 | -0.664198 |
| 63 | 6 | 0 | -3.335972 | -3.009050 | -1.425855 |
| 64 | 1 | 0 | -3.943257 | -2.971006 | -2.338997 |
| 65 | 1 | 0 | -3.705770 | -3.854360 | -0.829907 |
| 66 | 6 | 0 | -1.861230 | -3.196629 | -1.750071 |
| 67 | 1 | 0 | -1.677449 | -4.238445 | -2.028367 |
| 68 | 1 | 0 | -1.562817 | -2.573032 | -2.599780 |
| 69 | 6 | 0 | -1.047418 | -2.793553 | -0.525237 |
| 70 | 1 | 0 | 0.017856 | -2.913918 | -0.710684 |
| 71 | 1 | 0 | -1.311872 | -3.430583 | 0.331202 |
| 72 | 6 | 0 | 1.702312 | -0.951774 | -1.199722 |
| 73 | 6 | 0 | 1.851074 | 1.430363 | 0.307590 |

---

**Table S12**. Optimized atomic coordinates obtained from DFT calculations of [**2**]$^{1+}$

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 77 | 0 | -0.173675 | -0.042646 | -0.066024 |
| 2 | 7 | 0 | -1.142935 | -1.833257 | -0.536058 |
| 3 | 7 | 0 | 0.557638 | 1.829178 | 0.497523 |
| 4 | 7 | 0 | 1.137915 | 0.023891 | -1.876887 |
| 5 | 7 | 0 | 3.130738 | -0.164000 | -0.564656 |
| 6 | 7 | 0 | 1.500078 | -1.286959 | 0.715915 |
| 7 | 6 | 0 | -0.870860 | -2.597583 | -1.614118 |
| 8 | 1 | 0 | -0.065597 | -2.249437 | -2.249072 |
| 9 | 6 | 0 | -1.559424 | -3.763213 | -1.930610 |
| 10 | 6 | 0 | -2.588644 | -4.139263 | -1.053988 |
| 11 | 1 | 0 | -3.169013 | -5.036571 | -1.251130 |
| 12 | 6 | 0 | -2.868633 | -3.376633 | 0.067983 |
| 13 | 1 | 0 | -3.654216 | -3.668842 | 0.748328 |
| 14 | 6 | 0 | -2.130178 | -2.210034 | 0.334451 |
| 15 | 6 | 0 | -2.279198 | -1.324909 | 1.486698 |
| 16 | 6 | 0 | -3.191514 | -1.507971 | 2.539916 |
| 17 | 9 | 0 | -4.045038 | -2.557652 | 2.526364 |
| 18 | 6 | 0 | -3.268515 | -0.653984 | 3.626389 |
| 19 | 1 | 0 | -3.983696 | -0.820801 | 4.421637 |
| 20 | 6 | 0 | -2.389287 | 0.424244 | 3.642200 |
| 21 | 9 | 0 | -2.439161 | 1.270695 | 4.684483 |
| 22 | 6 | 0 | -1.466690 | 0.661406 | 2.628552 |
| 23 | 1 | 0 | -0.830788 | 1.534077 | 2.713722 |
| 24 | 6 | 0 | -2.709295 | 0.743890 | -1.613341 |
| 25 | 1 | 0 | -2.979893 | -0.301145 | -1.710837 |
| 26 | 6 | 0 | -3.537452 | 1.694582 | -2.204563 |
| 27 | 9 | 0 | -4.623086 | 1.279934 | -2.877972 |
| 28 | 6 | 0 | -3.285339 | 3.060424 | -2.134764 |
| 29 | 1 | 0 | -3.937441 | 3.787227 | -2.602046 |
| 30 | 6 | 0 | -2.160756 | 3.455251 | -1.428865 |
| 31 | 9 | 0 | -1.918423 | 4.784289 | -1.361170 |
| 32 | 6 | 0 | -1.291571 | 2.545646 | -0.805296 |
| 33 | 6 | 0 | -0.127298 | 2.903072 | 0.000629 |
| 34 | 6 | 0 | 0.298914 | 4.201028 | 0.334513 |
| 35 | 1 | 0 | -0.234416 | 5.050121 | -0.065901 |
| 36 | 6 | 0 | 1.376294 | 4.383439 | 1.185557 |
| 37 | 1 | 0 | 1.690792 | 5.390724 | 1.445073 |
| 38 | 6 | 0 | 2.048416 | 3.277264 | 1.728780 |

| | | | | | |
|---|---|---|---|---|---|
| 39 | 6 | 0 | 1.591862 | 2.022744 | 1.341025 |
| 40 | 1 | 0 | 2.050582 | 1.120568 | 1.726424 |
| 41 | 6 | 0 | 0.548514 | 0.171289 | -3.086261 |
| 42 | 1 | 0 | -0.531511 | 0.254395 | -3.064118 |
| 43 | 6 | 0 | 1.249150 | 0.239751 | -4.279034 |
| 44 | 6 | 0 | 2.637404 | 0.119806 | -4.229579 |
| 45 | 1 | 0 | 3.234140 | 0.142557 | -5.135944 |
| 46 | 6 | 0 | 3.253583 | -0.049158 | -2.998102 |
| 47 | 1 | 0 | 4.326358 | -0.176922 | -2.953062 |
| 48 | 6 | 0 | 2.482447 | -0.077691 | -1.820374 |
| 49 | 6 | 0 | 4.496338 | 0.379988 | -0.453389 |
| 50 | 1 | 0 | 4.565673 | 0.929417 | 0.492597 |
| 51 | 1 | 0 | 4.649174 | 1.104190 | -1.252140 |
| 52 | 6 | 0 | 5.501323 | -0.765228 | -0.477729 |
| 53 | 1 | 0 | 5.396476 | -1.330948 | -1.408605 |
| 54 | 1 | 0 | 6.531310 | -0.399905 | -0.430394 |
| 55 | 6 | 0 | 5.212485 | -1.652089 | 0.732267 |
| 56 | 1 | 0 | 5.516408 | -2.690579 | 0.547565 |
| 57 | 1 | 0 | 5.795115 | -1.300268 | 1.593002 |
| 58 | 6 | 0 | 2.760582 | -1.070429 | 0.447174 |
| 59 | 7 | 0 | 3.798555 | -1.633089 | 1.145316 |
| 60 | 6 | 0 | 3.571171 | -2.386033 | 2.392145 |
| 61 | 1 | 0 | 4.281735 | -2.018856 | 3.142999 |
| 62 | 1 | 0 | 3.818339 | -3.439728 | 2.205023 |
| 63 | 6 | 0 | 2.136168 | -2.258649 | 2.879748 |
| 64 | 1 | 0 | 1.927997 | -3.042418 | 3.613788 |
| 65 | 1 | 0 | 1.974522 | -1.294686 | 3.374240 |
| 66 | 6 | 0 | 1.210277 | -2.365484 | 1.673248 |
| 67 | 1 | 0 | 0.168111 | -2.280266 | 1.973071 |
| 68 | 1 | 0 | 1.336694 | -3.341868 | 1.184030 |
| 69 | 6 | 0 | -1.394285 | -0.206779 | 1.533330 |
| 70 | 6 | 0 | -1.568083 | 1.151285 | -0.911665 |
| 71 | 6 | 0 | 3.197398 | 3.433107 | 2.691912 |
| 72 | 1 | 0 | 4.011578 | 4.017709 | 2.249827 |
| 73 | 1 | 0 | 2.881944 | 3.957812 | 3.600170 |
| 74 | 1 | 0 | 3.602649 | 2.463504 | 2.994878 |
| 75 | 6 | 0 | -1.214535 | -4.569964 | -3.155808 |
| 76 | 1 | 0 | -0.943237 | -5.597195 | -2.889704 |
| 77 | 1 | 0 | -2.066491 | -4.628641 | -3.841799 |
| 78 | 1 | 0 | -0.374873 | -4.132098 | -3.702125 |
| 79 | 1 | 0 | 0.717404 | 0.378143 | -5.213237 |

---

**Table S13**. Optimized atomic coordinates obtained from DFT calculations of **[3]**$^{1+}$

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 77 | 0 | 0.428448 | 0.016672 | 0.029639 |
| 2 | 7 | 0 | 1.207289 | -1.398527 | 1.354855 |
| 3 | 7 | 0 | -0.111758 | 1.448571 | -1.388208 |
| 4 | 7 | 0 | -0.962720 | 0.990854 | 1.485128 |
| 5 | 7 | 0 | -2.916024 | 0.309505 | 0.270653 |
| 6 | 7 | 0 | -1.325585 | -1.354209 | -0.244587 |
| 7 | 6 | 0 | 0.827009 | -1.558553 | 2.638478 |
| 8 | 1 | 0 | 0.031225 | -0.910942 | 2.982960 |
| 9 | 6 | 0 | 1.408636 | -2.489463 | 3.484530 |
| 10 | 1 | 0 | 1.067931 | -2.573974 | 4.510062 |
| 11 | 6 | 0 | 2.432340 | -3.297560 | 2.980228 |
| 12 | 1 | 0 | 2.918830 | -4.033080 | 3.613061 |
| 13 | 6 | 0 | 2.815918 | -3.151407 | 1.655418 |
| 14 | 1 | 0 | 3.601009 | -3.773239 | 1.243157 |
| 15 | 6 | 0 | 2.191004 | -2.197911 | 0.835661 |
| 16 | 6 | 0 | 2.473423 | -1.973201 | -0.579699 |
| 17 | 6 | 0 | 3.415745 | -2.722320 | -1.307077 |
| 18 | 1 | 0 | 4.001767 | -3.497883 | -0.822648 |
| 19 | 6 | 0 | 3.607746 | -2.475241 | -2.660254 |
| 20 | 1 | 0 | 4.336759 | -3.050451 | -3.221876 |
| 21 | 6 | 0 | 2.854861 | -1.477583 | -3.289234 |
| 22 | 1 | 0 | 3.003352 | -1.277805 | -4.347127 |
| 23 | 6 | 0 | 1.919986 | -0.730218 | -2.570333 |
| 24 | 1 | 0 | 1.364203 | 0.043946 | -3.089302 |
| 25 | 6 | 0 | 2.946212 | 1.330932 | 1.251963 |
| 26 | 1 | 0 | 3.115728 | 0.426756 | 1.829014 |
| 27 | 6 | 0 | 3.815753 | 2.411040 | 1.427438 |
| 28 | 1 | 0 | 4.638163 | 2.330456 | 2.133288 |
| 29 | 6 | 0 | 3.640539 | 3.592121 | 0.699309 |
| 30 | 1 | 0 | 4.316346 | 4.429603 | 0.839379 |
| 31 | 6 | 0 | 2.597633 | 3.681639 | -0.215317 |
| 32 | 1 | 0 | 2.471151 | 4.597472 | -0.785311 |
| 33 | 6 | 0 | 1.723371 | 2.596351 | -0.396379 |
| 34 | 6 | 0 | 0.636097 | 2.594178 | -1.372379 |
| 35 | 6 | 0 | 0.348232 | 3.623104 | -2.283706 |
| 36 | 1 | 0 | 0.937996 | 4.531410 | -2.264468 |
| 37 | 6 | 0 | -0.667111 | 3.470082 | -3.215755 |
| 38 | 1 | 0 | -0.883035 | 4.263288 | -3.924551 |

| | | | | | |
|---|---|---|---|---|---|
| 39 | 6 | 0 | -1.393228 | 2.274770 | -3.241189 |
| 40 | 1 | 0 | -2.176741 | 2.100492 | -3.969924 |
| 41 | 6 | 0 | -1.081520 | 1.295244 | -2.311432 |
| 42 | 1 | 0 | -1.595967 | 0.343288 | -2.293028 |
| 43 | 6 | 0 | -0.452370 | 1.674071 | 2.533306 |
| 44 | 1 | 0 | 0.628763 | 1.731339 | 2.586212 |
| 45 | 6 | 0 | -1.266083 | 2.287426 | 3.474008 |
| 46 | 1 | 0 | -0.838120 | 2.847284 | 4.300195 |
| 47 | 6 | 0 | -3.103662 | 1.522617 | 2.383400 |
| 48 | 1 | 0 | -4.184458 | 1.434022 | 2.352801 |
| 49 | 6 | 0 | -2.304286 | 0.923913 | 1.381535 |
| 50 | 6 | 0 | -4.226409 | 0.826994 | -0.169576 |
| 51 | 1 | 0 | -4.202950 | 0.919362 | -1.261781 |
| 52 | 1 | 0 | -4.357954 | 1.831351 | 0.230304 |
| 53 | 6 | 0 | -5.321118 | -0.139682 | 0.262827 |
| 54 | 1 | 0 | -5.307576 | -0.250508 | 1.351619 |
| 55 | 1 | 0 | -6.313539 | 0.225333 | -0.016881 |
| 56 | 6 | 0 | -5.049979 | -1.475993 | -0.425536 |
| 57 | 1 | 0 | -5.454714 | -2.313658 | 0.156963 |
| 58 | 1 | 0 | -5.552737 | -1.496063 | -1.400729 |
| 59 | 6 | 0 | -2.573387 | -0.970175 | -0.211794 |
| 60 | 7 | 0 | -3.620092 | -1.719794 | -0.683306 |
| 61 | 6 | 0 | -3.394690 | -2.953598 | -1.458412 |
| 62 | 1 | 0 | -4.022880 | -2.906851 | -2.356664 |
| 63 | 1 | 0 | -3.752595 | -3.802148 | -0.859974 |
| 64 | 6 | 0 | -1.928534 | -3.140644 | -1.818032 |
| 65 | 1 | 0 | -1.754242 | -4.178609 | -2.115849 |
| 66 | 1 | 0 | -1.647829 | -2.505302 | -2.665167 |
| 67 | 6 | 0 | -1.085212 | -2.760024 | -0.606317 |
| 68 | 1 | 0 | -0.024915 | -2.878314 | -0.819350 |
| 69 | 1 | 0 | -1.330272 | -3.410628 | 0.245455 |
| 70 | 6 | 0 | 1.701674 | -0.955346 | -1.202622 |
| 71 | 6 | 0 | 1.872251 | 1.396880 | 0.350649 |
| 72 | 7 | 0 | -2.600860 | 2.198701 | 3.407707 |

---

**References:**


1 M. Nonoyama, *Bull. Chem. Soc. Jpn.***1974**, *47*, 767.

2 Crosby, G. A.; Demas, J. N. *J. Phys. Chem.* **1971**, *75*, 991.

3 W. H. Melhuish, *J. Phys. Chem*., **1961**, *65*, 229–235.

4 V. V. Pavlishchuk and A. W. Addison, *Inorg. Chim. Acta* **2000**, *298*, 97.

5 A. K. Pal, S. Nag, J. G. Ferreina, V. Brochery, G. L. Ganga, A. Santora, S. Serroni, S. Campagna and G. S. Hanan, *Inorg. Chem*., **2014**, *53*, 1679-1689.

6 *APEX2 (2013); Bruker Molecular Analysis Research Tool.* Bruker AXS Inc., Madison, WI 53719-1173.

7 (a) SAINT (2013) V8.34A; Integration Software for Single Crystal Data. Bruker AXS Inc., Madison, WI 53719-1173. (b) SAINT (2013) V8.34A; Integration Software for Single Crystal Data. Bruker AXS Inc., Madison, WI 53719-1173.

8 Sheldrick, G. M. (1996). *SADABS*, Bruker Area Detector Absorption Corrections. Bruker AXS Inc., Madison, WI 53719-1173.

9 *SHELXTL (2012) version 6.14*; Bruker Analytical X-ray Systems Inc., Madison, WI 53719-1173.

10 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, T. J. Vreven, K. N. Kudin, J. C. Burant, J. M. S. Millam, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Startmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y.Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, J. M. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Cliffors, J. B. Cioslowski, G. Liu, A. Liashenko, I. Piskorz, L. M. R. Komaromi, D. J. Fox, T. Keith, M. A. Al–Laham, C. Y. Peng, A. Manayakkara, M. Challacombe, P. M. W. Gill, B. G. Johnson, W.

Chen, M. W. Wong, C. Gonzalez, J. A. Pople, *Gaussian 2003, Revision C.02; Gaussian Inc.:Pittsburgh PA,* **2003**.

11 A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648.

12 C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B: Condens. Matter* **1988**, *37*, 785.

13 A. D. McLean, G. S. Chandler, *J. Chem. Phys.* **1980**, *72*, 5639.

14 P. J. Hay, W. R. Wadt, *J. Chem. Phys.* **1985**, *82*, 270.

15 a) M. E. Casida, C. Jamorski, K. C. Casida, D. R. Salahub, *J. Chem. Phys.* **1998**, *108*, 4439; b) R. E. Stratmann, G. E. Scuseria, M. J. J. Frisch, *Chem. Phys.* **1998**, *109*, 8218.

16 a) M. Cossi, N. Rega, G. Scalmani, V. Barone, *J. Comput. Chem.* **2003**, *24*, 669; b) M. Cossi, V. Barone, *J. Chem. Phys.* **2001**, *115*, 4708; c) V. Barone, M. Cossi, *J. Phys. Chem. A* **1998**, *102*, 1995.

17 W. R. Browne, N. M. O'Boyle, J. J. McGarvey, J. G. Vos, *Chem. Soc. Rev.* **2005**, *34*, 641.

18 D. A. Zhurko, G. A. Zhurko, *ChemCraft 1.5*; Plimus: San Diego, CA. Available at http://www.chemcraftprog.com.

19 V. V. Pavlishchuk and A. W. Addison, *Inorg. Chim. Acta,* **2000**, *298*, 97.