Supporting Information

Synthesis and Characterization of N-2-Aryl-1,2,3-Triazole Based Iridium Complexes as Photocatalysts with Tuneable Photoredox Potential

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I. General Methods and materials:

All of the reactions dealing with air and/or moisture-sensitive reactions were carried out under an atmosphere of nitrogen using oven/flame-dried glassware and standard syringe/septa techniques. Unless otherwise noted, all commercial reagents and solvents were obtained from the commercial provider and used without further purification. \( ^1 \)H NMR and \( ^{13} \)C NMR spectra were recorded on Varian 600 MHz or Agilent 400 MHz spectrometer. Chemical shifts were reported relative to internal tetramethylsilane (\( \delta 0.00 \) ppm) or CD\(_{3}\)CN (\( \delta 1.94 \) ppm) for \( ^1 \)H NMR and CD\(_{3}\)CN (\( \delta 1.39 \) ppm) for \( ^{13} \)C NMR. Flash column chromatography was performed on 230-430 mesh silica gel. Analytical thin layer chromatography was performed with precoated glass baked plates (250μ) and visualized by UV lamp. ESI-MS were recorded on Thermo Scientific Q-exactive spectrometer.

The UV-Vis spectra were obtained with a Shimadzu UV-1800 UV spectrophotometer in 10 mm path length quartz cuvettes with \( 1 \times 10^{-5} \)M Iridium complex solutions in freshly distilled acetonitrile (ACN). The fluorescence spectra were obtained in 10 mm path length quartz cuvettes using Shimadzu RF-5301 PC spectrofluorophotometer with \( 1 \times 10^{-5} \)M Iridium complex solutions in ACN.

The fluorescence quantum yields of iridium complexes (\( \Phi_x \)) were calculated based on equation (1) using Ru(bpy)_3(PF_6)_2 in ACN (\( \Phi = 0.094 \))\(^1\) as a standard. All the samples were tested with \( 1 \times 10^{-5} \)M ACN solutions under argon protection.

\[ \Phi_x = \frac{n_x^2}{n_{std}^2} \cdot \frac{1 - 10^{-Abs_x}}{1 - 10^{-Abs_{std}}} \cdot \frac{I_x}{I_{std}} \cdot \Phi_{std} \]  

\( \Phi \) is the quantum yield, \( I \) is integrated emission intensity, \( Abs \) is the absorption at the excitation wavelength (370nm), and \( n \) is the refractive index of pure solvents (\( n_x = n_{std} \) in this case); ‘std’ stands for reference standard samples, ‘x’ stands for samples.

The excited-state lifetime were measured on a Horiba Fluorolog-3 spectrofluorometer with a NanoLED-370nm as the light source. The samples were prepared in ACN (\( 1 \times 10^{-5} \)M solutions) and tested in 10 mm path length quartz cuvettes. A highly diluted colloidal silica solution (0.01% dilution of LUDOX AS-40 colloidal silica using deionized water) was used to get the prompt spectra. All samples were tested under same conditions.

The cyclic voltammetry measurements were conducted on a WaveNow USB potentiostat in a three-compartment cell at 0.1 V/s scan rate using 1 mM Iridium complex solutions in freshly distilled acetonitrile with 0.1 M tetrabutylammonium hexafluorophosphate as the supporting electrolyte. \(^2\) A platinum wire was used as the working electrode and a folded

platinum plate was used as the counter electrode. A silver wire was used as the quasi-reference electrode. Potentials were calibrated using Fc+/Fc redox couple (0.40V in ACN) after each experiment and reported vs. SCE.

The N-2-aryl triazoles were synthesized according to the literature reported previously. The photocatalytic reactions were performed under same conditions as previous literature reports.

**General procedure for the preparation of [(pta)$_2$Ir($\mu$-Cl)]$_2$:**

![Reaction Scheme]

The preparation [(pta)$_2$Ir($\mu$-Cl)]$_2$ is adapted from literature report. The pta ligand 1 (2.5 mmol), IrCl$_3$·xH$_2$O (353 mg, 1 mmol) in 32 mL 2-ethoxyethanol/water (3:1) was refluxed at 140 °C under nitrogen or argon atmosphere for 24 h. After cooled to room temperature, the yellow precipitate was isolated by filtration and washed with water and ethanol and allowed to air dry. The yellow solid was used for the next step without further purification. Yields of the $\mu$-dichloro-bridged iridium(III) dimer 2 are ranged from 53% to 95% (2a: 63%, 2b: 92%, 2c: 53%, 2d: 78%, 2e: 87%, 2f: 89%, 2g: 95%).

**Procedure for the preparation of N-1b:**

![Reaction Scheme]

The procedure is adapted from literature report. The $\mu$-dichloro-bridged iridium(III) dimer 2b (424 mg, 0.3 mmol), sodium carbonate (350 mg, 3.3 mmol) and the N$^\N$ ligand 2-picolinamide (96 mg, 0.78 mmol) was suspended in 22 mL 2-ethoxyethanol. The reaction mixture was stirred at 140 °C for 20 h under nitrogen atmosphere. After the reaction was cooled to room temperature, 150 mL ethyl acetate was added. The solution

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was extracted with water three times. The organic layer was dried over Na$_2$SO$_4$ and concentrated under reduced pressure. The solid was then purified by flash chromatography on silica gel using ethyl acetate and recrystallized from ether / hexane to yield N-1b in 75% yield.

**General procedure for the preparation of [(pta)$_2$Ir(ppy)]PF$_6$**:  

![Diagram of [(pta)$_2$Ir(ppy)]PF$_6$]

The μ-dichloro-bridged iridium(III) dimer 2 (0.15 mmol) and the N^N ligand 2,2’-bispyridine (58 mg, 0.375 mmol) was suspended in 10 mL 1,2-ethanediol. The reaction mixture was stirred at 120 °C for 20 h under nitrogen or argon atmosphere. After the reaction was cooled to room temperature, 150 mL distilled water was added. The solution was extracted with ethyl ether three times to remove the excess bpy. Ammonium hexafluorophosphate solution (1 g in 10 mL water) was added to the aqueous layer to yield a yellow precipitate. The solution was then heated at 70 °C for 10 min. After cooled to room temperature, the yellow precipitate was filtrated and further purified by flash chromatography on silica gel using 10% DCM / acetone eluent. After the column, the solid was re-dissolved in minimum amount of methanol and precipitated again using NH$_4$PF$_6$ (1 g in 10 mL water). The yellow precipitate was filtered and washed with water and then recrystallized from minimum amount of hot acetonitrile for further experiments.

**General procedure for the preparation of [(pta)$_2$Ir(tapy)]PF$_6$**:  

![Diagram of [(pta)$_2$Ir(tapy)]PF$_6$]

The μ-dichloro-bridged iridium(III) dimer 2 (0.15 mmol) and the N^N ligand tapy (83 mg, 0.375 mmol) was suspended in 10 mL 1,2-ethanediol. The reaction mixture was stirred at 120 °C for 20 h under nitrogen or argon atmosphere. After the reaction was cooled to room temperature, 150 mL distilled water was added, followed by ammonium

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hexafluorophosphate solution (1 g in 10 mL water) to yield a yellow precipitate. The precipitate was filtered and further purified by flash chromatography on silica gel using 10% acetone/DCM eluent. After the column, the solid was re-dissolved in minimum amount of methanol and precipitated again using \( \text{NH}_4\text{PF}_6 \) (1 g in 10 mL water). The precipitate was filtered and washed with water and then recrystallized from minimum amount of hot acetonitrile for further experiments.
II. Compounds Characterization

C-1a: Yellow Solid (79% yield). $^1$H NMR (400 MHz, CD$_3$CN): δ 8.58 (d, $J = 8.2$ Hz, 2H), 8.22-8.16 (m, 4H), 7.88 (dd, $J = 8.1$, 1.5 Hz, 4H), 7.84 (s, 2H), 7.80 (dd, $J = 8.0$, 1.2 Hz, 2H), 7.57 (ddd, $J = 7.6$, 5.5, 1.1 Hz, 2H), 7.51-7.45 (m, 6H), 7.19 (td, $J = 7.7$, 1.1 Hz, 2H), 7.00 (td, $J = 7.5$, 1.3 Hz, 2H), 6.52 (dd, $J = 7.5$, 1.2 Hz, 2H); $^{13}$C NMR (100 MHz, CD$_3$CN): δ 157.57, 152.88, 150.26, 142.34, 141.07, 133.72, 132.51, 130.81, 130.64, 130.26, 129.65, 129.57, 129.44, 127.01, 125.64, 125.24, 115.46. ESI-MS calculated for [C$_{38}$H$_{28}$IrN$_8$]$: 789.2066$, found: 789.2047.

C-1b: Yellow Solid (85% yield). $^1$H NMR (400 MHz, CD$_3$CN): δ 8.57 (d, $J = 8.2$ Hz, 2H), 8.24-8.18 (m, 4H), 7.88-7.83 (m, 6H), 7.80 (s, 2H), 7.59 (ddd, $J = 7.6$, 5.5, 1.3 Hz, 2H), 7.51-7.43 (m, 6H), 6.98 (td, $J = 8.8$, 2.6 Hz, 2H), 6.22 (dd, $J = 8.8$, 2.6 Hz, 2H); $^{13}$C NMR (100 MHz, CD$_3$CN): δ 163.01 (d, $J = 248.1$ Hz), 157.48, 153.12, 150.33, 141.32, 138.90, 133.39 (d, $J = 6.0$ Hz), 132.66, 130.86, 130.25, 129.55, 129.48, 127.05, 125.71, 120.13 (d, $J = 20.4$ Hz), 117.23 (d, $J = 9.2$ Hz), 112.05 (d, $J = 14.6$ Hz); $^{19}$F NMR (376 MHz, CD$_3$CN): δ -73.84 (d, $J = 706.8$ Hz, 6F), -114.80 (m, 2F). ESI-MS calculated for [C$_{38}$H$_{26}$F$_2$IrN$_8$]: 825.1878, found: 825.1861.

C-1c
C-1c: Yellow Solid (68% yield). \(^1\)H NMR (400 MHz, CD\(_3\)CN): \(\delta\) 8.55 (d, \(J = 8.2\) Hz, 2H), 8.23-8.18 (m, 4H), 7.38 (dd, \(J = 8.1, 1.6\) Hz, 4H), 7.75 (d, \(J = 9.1\) Hz, 2H), 7.74 (s, 2H), 7.58 (dd, \(J = 7.7, 5.5, 1.2\) Hz, 2H), 7.50-7.41 (m, 6H), 6.77 (dd, \(J = 8.8, 2.6\) Hz, 2H), 5.91 (d, \(J = 2.6\) Hz, 2H), 3.63 (s, 6H); \(^{13}\)C NMR (100 MHz, CD\(_3\)CN): \(\delta\) 160.70, 157.54, 153.00, 149.67, 141.05, 136.24, 132.81, 131.68, 130.66, 130.24, 129.67, 129.42, 126.91, 125.56, 118.95, 116.72, 109.51, 55.96. ESI-MS calculated for \([C_{40}H_{32}IrN_8O_2]^+\): 849.2277, found: 849.2262.

C-1d: Synthesized from one-Pot sequential reactions without isolating the \(\mu\)-dichloro-bridged iridium(III) dimer. Yellow Solid (62% yield over two steps). \(^1\)H NMR (400 MHz, CD\(_3\)CN): \(\delta\) 8.56 (d, \(J = 8.1\) Hz, 2H), 8.24-8.17 (m, 4H), 7.91-7.86 (m, 4H), 7.84 (dd, \(J = 8.8, 4.8\) Hz, 2H), 7.76 (s, 2H), 7.59 (dd, \(J = 7.7, 5.5, 1.2\) Hz, 2H), 7.26-7.20 (m, 4H), 6.98 (td, \(J = 8.8, 2.7\) Hz, 2H), 6.21 (dd, \(J = 8.8, 2.6\) Hz, 2H); \(^{13}\)C NMR (100 MHz, CD\(_3\)CN): \(\delta\) 164.49 (d, \(J = 246.0\) Hz), 163.03 (d, \(J = 248.1\) Hz), 157.47, 153.13, 149.44, 141.34, 138.83, 133.35 (d, \(J = 6.0\) Hz), 132.53, 129.55, 129.29 (d, \(J = 8.5\) Hz), 126.00 (d, \(J = 2.9\) Hz), 125.70, 120.13 (d, \(J = 20.5\) Hz), 117.20 (d, \(J = 22.1\) Hz), 117.24 (d, \(J = 9.2\) Hz), 112.02 (d, \(J = 24.7\) Hz); \(^{19}\)F NMR (376 MHz, CD\(_3\)CN): -73.92 (d, \(J = 706.0\) Hz, 6F), -113.59 (m, 2F), -114.77 (m, 2F). ESI-MS calculated for \([C_{38}H_{24}F_4IrN_8]^+\): 861.1689, found: 861.1670.

C-1e: Yellow Solid (55% yield). \(^1\)H NMR (400 MHz, CD\(_3\)CN): \(\delta\) 8.56 (d, \(J = 8.1\) Hz, 2H), 8.23-8.18 (m, 4H), 7.89-7.84 (m, 4H), 7.74 (d, \(J = 8.7\) Hz, 2H), 7.71 (s, 2H), 7.58 (dd, \(J = 7.7, 5.5, 1.2\) Hz, 2H), 7.25-7.19 (m, 4H), 6.76 (dd, \(J = 8.8, 2.6\) Hz, 2H), 5.90 (d, \(J = 2.6\) Hz, 2H), 3.63 (s, 6H); \(^{13}\)C NMR (100 MHz, CD\(_3\)CN): \(\delta\) 164.36 (d, \(J = 246.0\) Hz), 160.72, 157.53, 152.98, 148.78, 141.08, 136.19, 132.77, 131.55, 129.42, 129.12 (d, \(J = \))
8.4 Hz), 126.19 (d, J = 3.0 Hz), 125.57, 118.99, 117.16 (d, J = 22.0 Hz), 116.72, 109.47, 55.96; 19F NMR (376 MHz, CD$_3$CN): -73.84 (d, J = 706.2 Hz, 6F), -113.93 (m, 2F). ESI-MS calculated for [C$_{40}$H$_{30}$F$_2$IrN$_8$O$_2$]$^+$: 885.2089, found: 885.2078.

C-1f: Yellow Solid (56% yield). 1H NMR (400 MHz, CD$_3$CN): δ 8.56 (d, J = 8.1 Hz, 2H), 8.23-8.17 (m, 4H), 7.83-7.77 (m, 6H), 7.69 (s, 2H), 7.58 (ddd, J = 7.7, 5.5, 1.2 Hz, 2H), 7.04-7.00 (m, 4H), 6.97 (td, J = 8.8, 2.7 Hz, 2H), 6.19 (dd, J = 8.8, 2.6 Hz, 2H), 3.82 (s, 6H); 13C NMR (100 MHz, CD$_3$CN): δ 162.89 (d, J = 247.6 Hz), 162.00, 157.47, 153.09, 150.30, 141.28, 138.98, 133.29 (d, J = 6.0 Hz), 131.96, 129.53, 128.57, 125.68, 121.90, 120.06 (d, J = 20.4 Hz), 117.02 (d, J = 9.1 Hz), 115.62, 111.91 (d, J = 24.5 Hz), 56.21; 19F NMR (376 MHz, CD$_3$CN): -73.87 (d, J = 705.7 Hz, 6F), -115.13 (m, 2F). ESI-MS calculated for [C$_{40}$H$_{30}$F$_2$IrN$_8$O$_2$]$^+$: 885.2089, found: 885.2076.

C-1g: Yellow Solid (38% yield). 1H NMR (400 MHz, CD$_3$CN): δ 8.55 (d, J = 8.1 Hz, 2H), 8.22-8.17 (m, 4H), 7.79-7.75 (m, 4H), 7.72 (d, J = 8.7 Hz, 2H), 7.64 (s, 2H), 7.59-7.56 (m, 2H), 7.03-6.99 (m, 4H), 6.76 (dd, J = 8.8, 2.6 Hz, 2H), 5.89 (d, J = 2.6 Hz, 2H), 3.82 (s, 6H), 3.62 (s, 6H); 13C NMR (100 MHz, CD$_3$CN): δ 161.84, 160.55, 157.53, 152.96, 149.65, 141.00, 136.34, 132.70, 130.96, 129.39, 128.41, 125.54, 122.11, 118.96, 116.51, 115.59, 109.37, 56.19, 55.94. ESI-MS calculated for [C$_{42}$H$_{36}$IrN$_8$O$_2$]$^+$: 909.2489, found: 909.2478.
**C-2:** Yellow Solid (40% yield). $^1$H NMR (600 MHz, CD$_3$CN): $\delta$ 8.42 (d, $J = 8.4$ Hz, 1H), 8.26 (td, $J = 8.0$, 1.6 Hz, 1H), 8.09-8.07 (m, 2H), 8.05 (s, 1H), 7.95 (ddd, $J = 4.6$, 3.2, 1.6 Hz, 2H), 7.90-7.88 (m, 3H), 7.82-7.80 (m, 3H), 7.73 (dd, $J = 5.8$, 0.7 Hz, 1H), 7.54-7.49 (m, 4H), 7.10-7.04 (m, 4H), 6.93 (ddt, $J = 14.5$, 7.3, 1.3 Hz, 2H), 6.28 (dd, $J = 21.6$, 7.7 Hz, 2H); $^{13}$C NMR (150 MHz, CD$_3$CN): $\delta$ 168.48, 167.95, 153.69, 150.90, 150.83, 150.18, 149.39, 148.19, 145.52, 145.21, 145.19, 143.13, 140.05, 139.98, 136.93, 132.94, 132.38, 131.81, 131.47, 131.03, 130.42, 128.56, 127.76, 127.61, 126.00, 125.74, 124.78, 124.67, 124.12, 123.92, 121.01, 120.97, 115.87. ESI-MS calculated for [C$_{35}$H$_{26}$IrN$_6$]$^+$: 723.1843, found: 723.1858.

**C-3a:** Light yellow Solid (85% yield). $^1$H NMR (400 MHz, CD$_3$CN): $\delta$ 8.46 (d, $J = 8.4$ Hz, 1H), 8.33 (ddd, $J = 8.4$, 7.6, 1.6 Hz, 1H), 8.25 (s, 1H), 8.13 (s, 1H), 8.01-7.97 (m, 4H), 7.92-7.90 (m, 4H), 7.82 (d, $J = 7.9$ Hz, 2H), 7.58-7.44 (m, 10H), 7.26-7.19 (m, 2H), 7.02 (ddt, $J = 10.6$, 7.5, 1.3 Hz, 2H), 6.52 (dd, $J = 7.6$, 5.1 Hz, 2H); $^{13}$C NMR (100 MHz, CD$_3$CN): $\delta$ 153.49, 151.48, 150.37, 150.20, 149.76, 143.74, 142.50, 142.24, 138.52, 134.05, 133.56, 133.35, 131.88, 130.91, 130.88, 130.51, 130.35, 130.33, 129.64, 129.59, 129.56, 129.26, 128.57, 127.72, 127.69, 127.47, 127.02, 126.98, 125.79, 125.56, 124.70, 115.77, 115.59, 115.37. ESI-MS calculated for [C$_{41}$H$_{30}$IrN$_{10}$]$^+$: 855.2284, found: 855.2269.
**C-3b**: Light yellow Solid (71% yield). $^1$H NMR (400 MHz, CD$_3$CN): $\delta$ 8.46 (ddd, $J = 8.4, 1.2, 0.8$ Hz, 1H), 8.34 (ddd, $J = 8.4, 7.6, 1.6$ Hz, 1H), 8.32 (s, 1H), 8.10 (s, 1H), 8.03-7.99 (m, 3H), 7.95 (s, 1H), 7.91-7.88 (m, 4H), 7.86 (dd, $J = 8.8, 4.9$ Hz, 2H), 7.59-7.44 (m, 10H), 7.02 (tdd, $J = 8.8, 6.0, 2.7$ Hz, 2H), 6.23 (ddd, $J = 8.8, 4.3, 2.6$ Hz, 2H); $^{13}$C NMR (100 MHz, CD$_3$CN): $\delta$ 162.80 (d, $J = 248.1$ Hz), 162.64 (d, $J = 247.9$ Hz), 153.59, 151.71, 150.44, 149.61, 144.02, 139.10, 139.08, 138.80, 133.45 (d, $J = 3.6$ Hz), 131.95, 130.94 (d, $J = 2.1$ Hz), 130.55, 130.33, 130.31, 130.26, 130.19, 129.48, 129.45, 128.49, 127.71, 127.54, 127.34, 127.28, 127.06, 127.02, 120.56 (d, $J = 21.0$ Hz), 120.12 (d, $J = 21.1$ Hz), 117.36 (d, $J = 9.3$ Hz), 117.05 (d, $J = 9.3$ Hz), 115.84, 112.57 (d, $J = 19.4$ Hz), 112.32 (d, $J = 19.4$ Hz); $^{19}$F NMR (376 MHz, CD$_3$CN): -73.92 (d, $J = 705.9$ Hz, 6F), -114.50 (m, 1F), -115.05 (m, 1F). ESI-MS calculated for [C$_{41}$H$_{28}$F$_2$IrN$_{10}$]$: 891.2096$, found: 891.2083.

**C-3c**: Light yellow Solid (44% yield). $^1$H NMR (400 MHz, CD$_3$CN): $\delta$ 8.45 (dd, $J = 8.3, 0.6$ Hz, 1H), 8.33 (td, $J = 8.0, 1.5$ Hz, 1H), 8.29 (s, 1H), 8.06-8.00 (m, 3H), 8.05 (s, 1H), 7.90 (s, 1H), 7.90-7.87 (m, 4H), 7.76 (d, $J = 8.7$ Hz, 2H), 7.59-7.42 (m, 10H), 6.80 (ddd, $J = 8.7, 6.2, 2.6$ Hz, 2H), 5.91 (dd, $J = 2.2$ Hz, 2H), 3.64 (2s, 6H); $^{13}$C NMR (100 MHz, CD$_3$CN): $\delta$ 160.58, 160.30, 153.47, 151.58, 149.76, 149.71, 149.60, 143.76, 138.54, 136.40, 136.08, 132.50, 132.46, 131.90, 130.74, 130.72, 130.52, 130.31, 130.29, 129.78, 129.66, 129.63, 128.57, 127.72, 127.43, 126.92, 126.88, 126.83, 119.37, 118.81, 116.86, 116.56, 115.74, 110.01, 109.82, 56.02, 55.97. ESI-MS calculated for [C$_{43}$H$_{34}$IrN$_{10}$O$_2$]$^+$: 915.2495, found: 915.2481.
III. ORTEP Drawing of the Crystal Structures

ORTEP Drawing of the Crystal Structures for complex N-1

Figure 1. Perspective view of the molecular structure of Ir(N$_3$C$_{14}$H$_9$F)$_2$(C$_6$H$_5$N$_2$O) with the atom labeling scheme. The thermal ellipsoids are scaled to 30% probability. CCDC number: 1012360
Figure 1. Perspective view of the molecular structure of \([\text{Ir(bpy)}(\text{C}_{14}\text{H}_{8}\text{N}_{3}\text{F}_{2})_{2}]\text{PF}_6\) with the atom labeling scheme. The thermal ellipsoids are scaled to enclose 30% probability. CCDC number: 1010939
IV. UV-Vis Spectra and Fluorescence Spectra
No normalized Absorption

Normalized Emission Intensity

wavelength (nm)

Normalized Absorption

Normalized Emission Intensity

wavelength (nm)
V. Cyclic Voltammetry

\[ E (V) \]

\[ I (\mu A) \]

![Diagram of cyclic voltammetry for S1 and S2](image-url)
I(µA)

E (V)

C-1a

C-1b

S24
I(µA)

E (V)

C-1e

C-1f

I(µA)

E (V)
I(μA) vs E (V)

C-3a

C-3b
VI. Excited-state lifetime

All the samples are tested under same conditions as described above (Section I). The sample solutions were degassed with nitrogen bubbles for 20 mins, capped with rubber septum and sealed with Parafilm, followed by protection with nitrogen using freeze/thaw techniques prior to the measurement. For parallel comparison, we tested two literature reported samples under our conditions: [(ppy)$_2$Ir(dtbbpy)]PF$_6$ (experimental: 175 ns, literature: 557 ns) and Ru(bpy)$_3$(PF$_6$)$_2$ (experimental: 382 ns, literature: 1100 ns). Complexes C-3a, C-3b and C-3c were fitted with two exponentials while all the other complexes were fitted with one exponential using DAS6.

\[ [(ppy)_2Ir(dtbbpy)]PF_6 \]

![Graph](image.png)

Calculated using 1 exponential

The initial parameters are:

- Shift Value = 0 ch; 0 sec
- Shift Limit = 40 ch; 1.75583E-08 sec
- T1 Estimate = 299.4264 ch; 1.314355E-07 sec

A Free
B1 Free

- Prompt and decay LO = 193 ch; 8.471879E-08 sec
- Prompt and decay HI = 2695 ch; 1.18299E-06 sec

Background on prompt = 1 (manual)
Time calibration = 4.389575E-10 sec/ch

The fitted parameters are:
Hi reduced to: 2655 ch

SHIFT = 0.503097 ch; 2.208382E-10 sec S.Dev = 1.189053E-11 sec
T1 = 397.7953 ch; 1.746152E-07 sec S.Dev = 2.967923E-10 sec
A = 14.67546 S.Dev = 0.1670179
B1 = 0.3065412 [100.00 Rel.Ampl][1.00 Alpha] S.Dev = 3.783242E-04
Average Life Time = 1.746152E-07 sec
CHISQ = 1.017701 [2459 degrees of freedom]

Ru(bpy)$_3$(PF$_6$)$_2$

Calculated using 1 exponential

The initial parameters are:

Shift Value = 0 ch; 0 sec
Shift Limit = 40 ch; 3.51166E-08 sec
T1 Estimate = 307.987 ch; 2.703864E-07 sec
A Free
B1 Free

Prompt and decay LO = 85 ch; 7.462277E-08 sec
Prompt and decay HI = 2703 ch; 2.373004E-06 sec

Background on prompt = 1 (manual)
Time calibration = 8.77915E-10 sec/ch

The fitted parameters are:

Hi reduced to: 2663 ch

SHIFT = 0.3908297 ch; 3.431153E-10 sec S.Dev = 2.258932E-11 sec
T1 = 434.98 ch; 3.818755E-07 sec S.Dev = 8.897758E-10 sec
A = 97.82068 S.Dev = 0.3045523
B1 = 0.470622 [100.00 Rel.Ampl][1.00 Alpha] S.Dev = 6.445636E-04
Average Life Time = 3.818755E-07 sec
CHISQ = 1.06252      [ 2575 degrees of freedom ]

C-1a

Calculated using 1 exponential

The initial parameters are:

Shift Value = 0        ch; 0              sec
Shift Limit = 40       ch; 3.51166E-08    sec
T1 Estimate = 292.838  ch; 2.570869E-07   sec
A Free
B1 Free

Prompt and decay LO = 57     ch; 5.004115E-08   sec
Prompt and decay HI = 2647   ch; 2.323841E-06   sec

Background on prompt = 1 (manual)
Time calibration = 8.77915E-10 sec/ch

The fitted parameters are:

Hi reduced to: 2607 ch

SHIFT = 0.5974014     ch; 5.244676E-10 sec  S.Dev = 1.119862E-11 sec
T1   = 302.9154      ch; 2.65934E-07  sec  S.Dev = 3.112539E-10 sec
A    = 41.43258     S.Dev = 0.2173026
B1   = 0.5112242     [ 100.00 Rel.Ampl][ 1.00 Alpha] S.Dev = 4.446301E-04
Average Life Time = 2.65934E-07   sec
CHISQ = 1.099121      [ 2547 degrees of freedom ]
Calculated using 1 exponential

The initial parameters are:

- Shift Value = 0  ch;  0  sec
- Shift Limit = 40  ch;  3.51166E-08  sec
- T1 Estimate = 372.2305  ch;  3.267867E-07  sec

A Free
B1 Free

- Prompt and decay LO = 37  ch;  3.248285E-08  sec
- Prompt and decay HI = 2671  ch;  2.344911E-06  sec

Background on prompt = 1 (manual)
Time calibration = 8.77915E-10 sec/ch

The fitted parameters are:

Hi reduced to: 2631 ch

- SHIFT = 0.5086936  ch;  4.465898E-10  sec  S.Dev = 1.235969E-11  sec
- T1 = 407.7457  ch;  3.57966E-07  sec  S.Dev = 4.258433E-10  sec
- A = 47.75816  S.Dev = 0.2819181
- B1 = 0.4984699  [ 100.00 Rel.Ampl] [ 1.00 Alpha]  S.Dev = 3.910421E-04

Average Life Time = 3.57966E-07  sec

CHISQ = 1.135972  [ 2591 degrees of freedom ]

Chi Sq. = 1.135972
C-1c

Calculated using 1 exponential

The initial parameters are:

- Shift Value = 0    ch; 0        sec
- Shift Limit = 40   ch; 4.389575E-09 sec
- T1 Estimate = 169.1614 ch; 1.856367E-08 sec
- A Free
- B1 Free

Prompt and decay LO = 812    ch; 8.910837E-08 sec
Prompt and decay HI = 2683   ch; 2.944307E-07 sec

Background on prompt = 1 (manual)
Time calibration = 1.097394E-10 sec/ch

The fitted parameters are:

Hi reduced to: 2643 ch

- SHIFT = 0.453698    ch; 4.978853E-11 sec S.Dev = 8.439614E-12 sec
- T1 = 275.3003      ch; 3.021128E-08 sec S.Dev = 9.846059E-11 sec
- A = 37.60783       S.Dev = 0.2243803
- B1 = 8.788235E-02  [ 100.00 Rel.Ampl][ 1.00 Alpha] S.Dev = 2.024839E-04
- Average Life Time = 3.021128E-08 sec
- CHISQ = 0.933201    [ 1828 degrees of freedom ]

Chi Sq. = 0.933201
C-1d

Chi.Sq. = 1.131363

Calculated using 1 exponential

The initial parameters are:

- Shift Value = 0  ch; 0  sec
- Shift Limit = 40  ch; 3.51166E-08  sec
- T1 Estimate = 287.6757 ch; 2.52548E-07  sec

A Free
B1 Free

- Prompt and decay LO = 69  ch; 6.05761E-08  sec
- Prompt and decay HI = 2687  ch; 2.35895E-06  sec

Background on prompt = 1  (manual)
Time calibration = 8.77915E-10 sec/ch

The fitted parameters are:

- Hi reduced to: 2647 ch

SHIFT = 0.4703841  ch; 4.12957E-10  sec  S.Dev = 1.27369E-11  sec
T1   = 308.0277  ch; 2.70422E-07  sec  S.Dev = 3.39540E-10  sec
A    = 52.95856  S.Dev = 0.2339391
B1   = 0.5000985  [ 100.00 Rel.Ampl] [ 1.00 Alpha] S.Dev = 4.39496E-04
Average Life Time = 2.70422E-07  sec
CHISQ = 1.131363  [ 2575 degrees of freedom ]
Calculated using 1 exponential

The initial parameters are:

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shift Value</td>
<td>0 ch; 0 sec</td>
</tr>
<tr>
<td>Shift Limit</td>
<td>40 ch; 4.389575E-09 sec</td>
</tr>
<tr>
<td>T1 Estimate</td>
<td>269.9332 ch; 2.96223E-08 sec</td>
</tr>
<tr>
<td>Prompt and decay LO</td>
<td>817 ch; 8.965706E-08 sec</td>
</tr>
<tr>
<td>Prompt and decay HI</td>
<td>2727 ch; 2.992593E-07 sec</td>
</tr>
<tr>
<td>Background on prompt</td>
<td>1 (manual)</td>
</tr>
<tr>
<td>Time calibration</td>
<td>1.097394E-10 sec/ch</td>
</tr>
</tbody>
</table>

The fitted parameters are:

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hi reduced to:</td>
<td>2687 ch</td>
</tr>
<tr>
<td>SHIFT</td>
<td>9.247364E-03 ch; 1.0148E-12 sec S.Dev = 9.412315E-12 sec</td>
</tr>
<tr>
<td>T1</td>
<td>288.3633 ch; 3.164481E-08 sec S.Dev = 1.262334E-10 sec</td>
</tr>
<tr>
<td>A</td>
<td>56.06471 S.Dev = 0.260014</td>
</tr>
<tr>
<td>B1</td>
<td>8.461874E-02 [ 100.00 Rel.Ampl][ 1.00 Alpha] S.Dev = 2.07085E-04</td>
</tr>
<tr>
<td>Average Life Time</td>
<td>3.164481E-08 sec</td>
</tr>
<tr>
<td>CHISQ</td>
<td>0.9649003 [ 1867 degrees of freedom ]</td>
</tr>
</tbody>
</table>
The initial parameters are:

- Shift Value = 0 (ch; 0 sec)
- Shift Limit = 40 (ch; 1.75583E-08 sec)
- T1 Estimate = 297.8851 (ch; 1.307589E-07 sec)

A Free
B1 Free

Prompt and decay LO = 201 (ch; 8.823045E-08 sec)
Prompt and decay HI = 2675 (ch; 1.174211E-06 sec)

Background on prompt = 1 (manual)
Time calibration = 4.389575E-10 sec/ch

The fitted parameters are:

Hi reduced to: 2635 ch

- SHIFT = 0.3860314 (ch; 1.694514E-10 sec) S.Dev = 8.379197E-12 sec
- T1 = 390.7628 (ch; 1.715283E-07 sec) S.Dev = 2.22235E-10 sec
- A = 82.85342 S.Dev = 0.3409277
- B1 = 0.2904978 [100.00 Rel.Ampl][1.00 Alpha] S.Dev = 2.399315E-04

Average Life Time = 1.715283E-07 sec
CHISQ = 1.082008 [2431 degrees of freedom]
C-1g

The initial parameters are:
- Shift Value = 0 ch; 0 sec
- Shift Limit = 40 ch; 4.389575E-09 sec
- T1 Estimate = 117.7722 ch; 1.292425E-08 sec
- A Free
- B1 Free

Prompt and decay LO = 835 ch; 9.163237E-08 sec
Prompt and decay HI = 2659 ch; 2.91797E-07 sec

Background on prompt = 1 (manual)
Time calibration = 1.097394E-10 sec/ch

The fitted parameters are:
- Hi reduced to: 2619 ch
- SHIFT = -1.511307 ch; -1.658498E-10 sec S.Dev = 1.129568E-11 sec
- T1 = 164.2944 ch; 1.802956E-08 sec S.Dev = 8.000964E-11 sec
- A = 43.13564 S.Dev = 0.1962022
- B1 = 0.1359902 [100.00 Rel.Ampl][1.00 Alpha] S.Dev = 4.017249E-04
- Average Life Time = 1.802956E-08 sec
- CHISQ = 1.046326 [1781 degrees of freedom]
Calculated using 1 exponential

The initial parameters are:

- **Shift Value** = 0 ch; 0 sec
- **Shift Limit** = 40 ch; 8.77915E-09 sec
- **T1 Estimate** = 387.4972 ch; 8.504739E-08 sec

A Free
B1 Free

- **Prompt and decay LO** = 409 ch; 8.976681E-08 sec
- **Prompt and decay HI** = 2691 ch; 5.906173E-07 sec

Background on prompt = 1 (manual)
Time calibration = 2.194787E-10 sec/ch

The fitted parameters are:

Hi reduced to: 2651 ch

- **SHIFT** = 0.3212092 ch; 7.049859E-11 sec S.Dev = 9.764486E-12 sec
- **T1** = 501.614 ch; 1.100936E-07 sec S.Dev = 3.117276E-10 sec
- **A** = 84.2297 S.Dev = 0.392129
- **B1** = 0.1542881 [ 100.00 Rel.Ampl] [ 1.00 Alpha] S.Dev = 2.143631E-04

Average Life Time = 1.100936E-07 sec
CHISQ = 1.018662 [ 2239 degrees of freedom ]
Calculated using 2 exponentials

The initial parameters are:

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shift Value</td>
<td>0 ch; 0 sec</td>
</tr>
<tr>
<td>Shift Limit</td>
<td>40 ch; 1.755E-08 sec</td>
</tr>
<tr>
<td>T1 Estimate</td>
<td>150.4275 ch; 6.603E-08 sec</td>
</tr>
<tr>
<td>T2 Estimate</td>
<td>601.7099 ch; 2.641E-07 sec</td>
</tr>
<tr>
<td>A Free</td>
<td></td>
</tr>
<tr>
<td>B1 Free</td>
<td></td>
</tr>
<tr>
<td>B2 Free</td>
<td></td>
</tr>
</tbody>
</table>

Prompt and decay LO = 205 ch; 8.998E-08 sec
Prompt and decay HI = 3518 ch; 1.544E-06 sec

Background on prompt = 1 (manual)
Time calibration = 4.389E-10 sec/ch

The fitted parameters are:

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hi reduced to</td>
<td>3478 ch</td>
</tr>
<tr>
<td>SHIFT</td>
<td>9.356E-02 ch; 4.107E-11 sec</td>
</tr>
<tr>
<td>T1</td>
<td>6.639E-01 ch; 2.914E-09 sec</td>
</tr>
<tr>
<td>T2</td>
<td>516.154E-01 ch; 2.265E-07 sec</td>
</tr>
<tr>
<td>A</td>
<td>77.17587</td>
</tr>
<tr>
<td>B1</td>
<td>0.2414948 [2.24 Rel.Ampl]; 0.64 Alpha]</td>
</tr>
<tr>
<td>B2</td>
<td>0.135377 [97.76 Rel.Ampl]; 0.36 Alpha]</td>
</tr>
<tr>
<td>Average Life Time</td>
<td>8.325E-08 sec</td>
</tr>
</tbody>
</table>
| CHISQ                   | 1.143413 [3268 degrees of freedom ]
C-3b

Calculated using 2 exponentials

The initial parameters are:

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shift Value</td>
<td>0</td>
</tr>
<tr>
<td>Shift Limit</td>
<td>40</td>
</tr>
<tr>
<td>T1 Estimate</td>
<td>106.7029 ch; 9.367609E-08 sec</td>
</tr>
<tr>
<td>T2 Estimate</td>
<td>426.8117 ch; 3.747044E-07 sec</td>
</tr>
<tr>
<td>A Free</td>
<td></td>
</tr>
<tr>
<td>B1 Free</td>
<td></td>
</tr>
<tr>
<td>B2 Free</td>
<td></td>
</tr>
</tbody>
</table>

Prompt and decay LO = 2 ch; 1.75583E-09 sec
Prompt and decay HI = 4096 ch; 3.59594E-06 sec
Background on prompt = 1 (manual)
Time calibration = 8.77915E-10 sec/ch

The fitted parameters are:

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hi reduced to:</td>
<td>4056 ch</td>
</tr>
<tr>
<td>SHIFT</td>
<td>0.1195633 ch; 1.049664E-10 sec</td>
</tr>
<tr>
<td>T1</td>
<td>3.303561 ch; 2.900246E-09 sec</td>
</tr>
<tr>
<td>T2</td>
<td>438.8091 ch; 3.852371E-07 sec</td>
</tr>
<tr>
<td>A</td>
<td>129.7937</td>
</tr>
<tr>
<td>B1</td>
<td>0.3673247 [ 1.13 Rel.Ampl] [ 0.60 Alpha] S.Dev = 1.066362E-02</td>
</tr>
<tr>
<td>B2</td>
<td>0.2421349 [ 98.87 Rel.Ampl] [ 0.40 Alpha] S.Dev = 5.042904E-04</td>
</tr>
<tr>
<td>Average Life Time</td>
<td>1.548005E-07 sec</td>
</tr>
<tr>
<td>CHISQ</td>
<td>1.035399               [ 4050 degrees of freedom ]</td>
</tr>
</tbody>
</table>
The initial parameters are:

- **Shift Value**: 0 ch; 0 sec
- **Shift Limit**: 40 ch; 8.77915E-09 sec
- **T1 Estimate**: 321.9654 ch; 7.066456E-08 sec
- **T2 Estimate**: 1287.861 ch; 2.826582E-07 sec

- **A Free**
- **B1 Free**
- **B2 Free**

**Prompt and decay LO**: 381 ch; 8.36214E-08 sec
**Prompt and decay HI**: 3401 ch; 7.464472E-07 sec

**Background on prompt**: 1 (manual)
**Time calibration**: 2.194787E-10 sec/ch

The fitted parameters are:

- **Hi reduced to**: 3361 ch
- **SHIFT**: -0.1458581 ch; -3.201274E-11 sec S.Dev = 1.377985E-11 sec
- **T1**: 10.5551 ch; 2.31662E-09 sec S.Dev = 1.14752E-10 sec
- **T2**: 540.5867 ch; 1.186473E-07 sec S.Dev = 7.761685E-10 sec
- **A**: 103.4928 S.Dev = 0.2637861
- **B2**: 3.844109E-02 [96.87 Rel.Ampl][0.38 Alpha] S.Dev = 1.240731E-04

**Average Life Time**: 4.615849E-08 sec
CHISQ = 1.074417 [2975 degrees of freedom]
VII. NMR spectra

C-1a