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Enhanced Photophysics from Self-Assembled Cyclometalated Ir(III) Complexes in Water

Michelle M. McGoorty[†], Rony S. Khnayzer,[‡] and Felix N. Castellano[†*]

†Department of Chemistry, North Carolina State University, 2620 Yarbrough Drive, Raleigh, North Carolina, 27695-8204, United States

‡Department of Natural Sciences, Lebanese American University, Chouran, Beirut 1102-2801, Lebanon

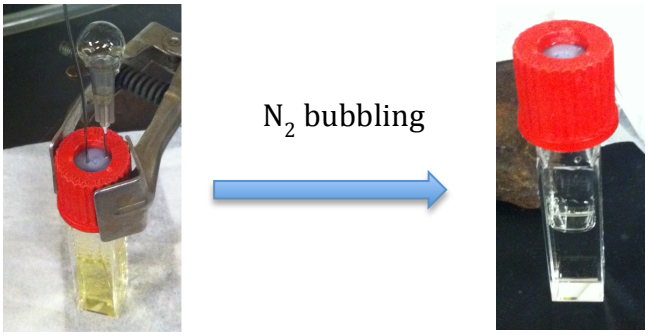


Figure S1: Removal of complex **2** from aqueous solution by slow bubbling of nitrogen.

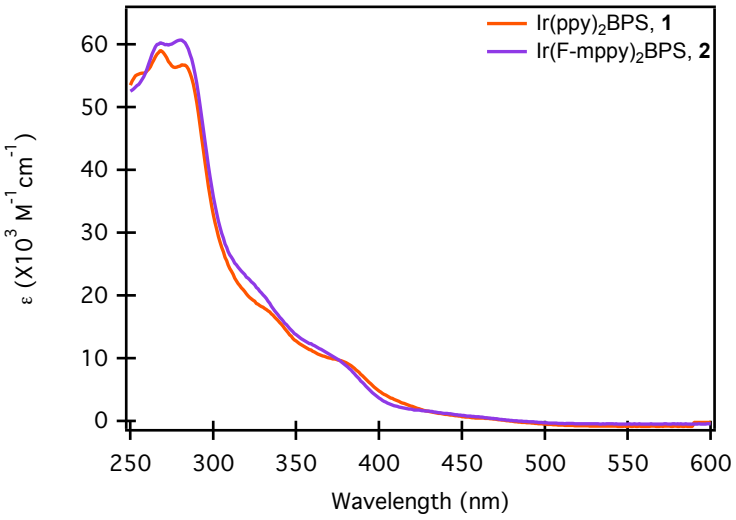


Figure S2: Absorption spectra of complexes **1** and **2** in air-equilibrated water.

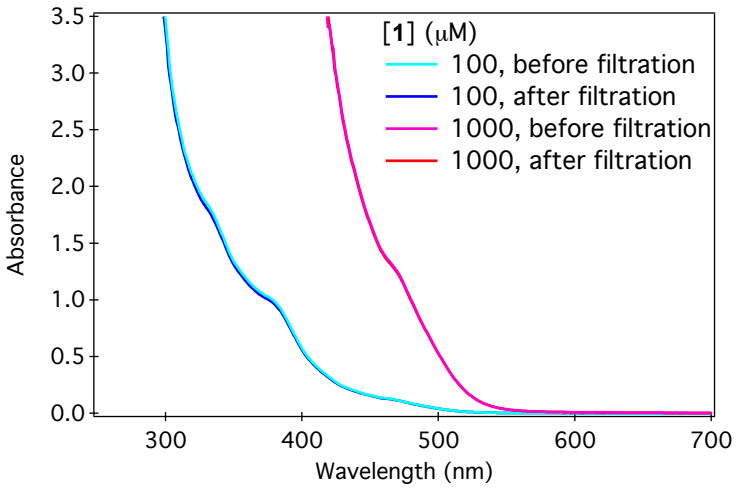


Figure S3: Absorption Spectra of **1** in water at 100 μM and 1000 μM before and after filtration using a 0.2 μm pore size cellulose acetate membrane filter.

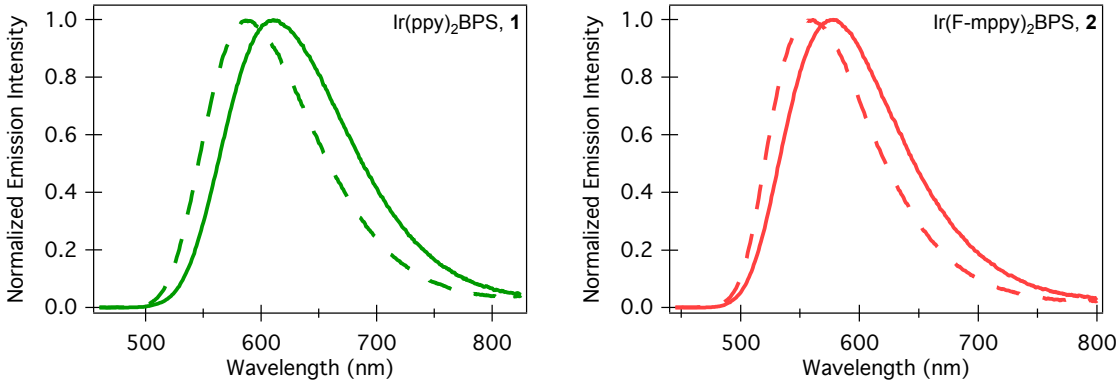


Figure S4: Emission spectra of **1** and **2** in methanol (solid line) and 5% methanol in dichloromethane (dotted line), λ_{ex} = 430 nm.

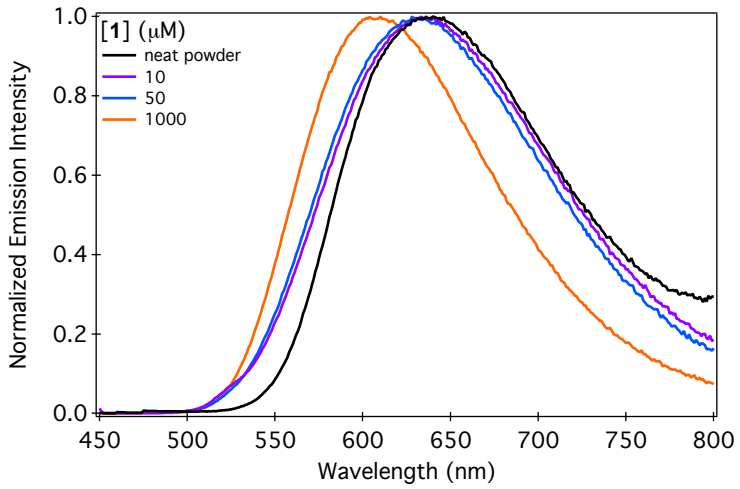


Figure S5: Comparison of neat powder emission spectra of **1** to that of the concentration-dependent solution spectra, λ_{ex} = 443 nm.

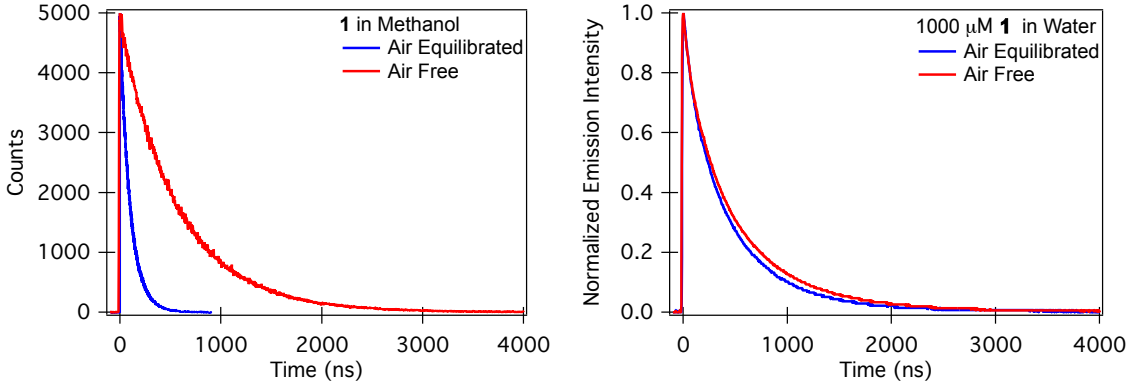
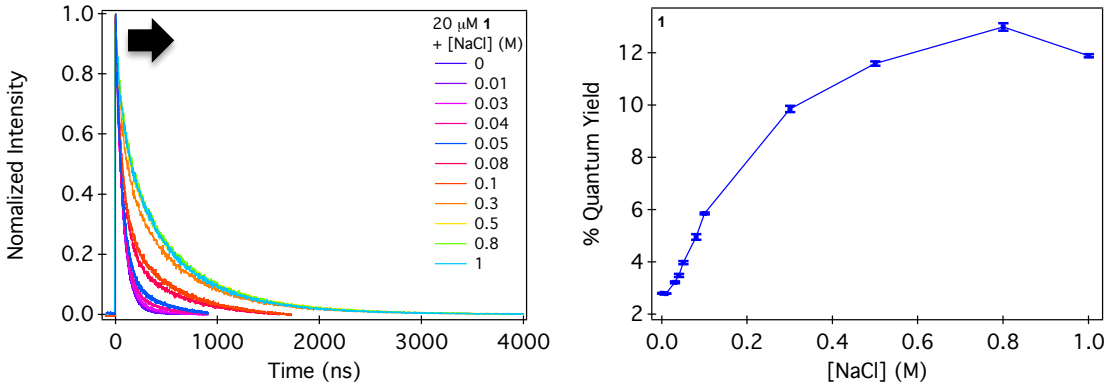


Figure S6: Time-resolved photoluminescence intensity decays of **1** in air equilibrated and air free methanol.

7a)



7b)

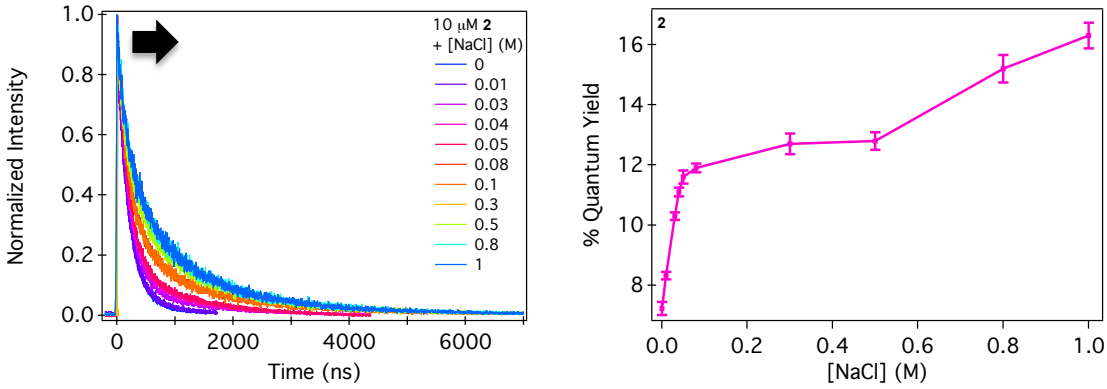


Figure S7: Changes in excited-state lifetimes and quantum yields of **1** and **2** with addition of NaCl to aqueous solutions.

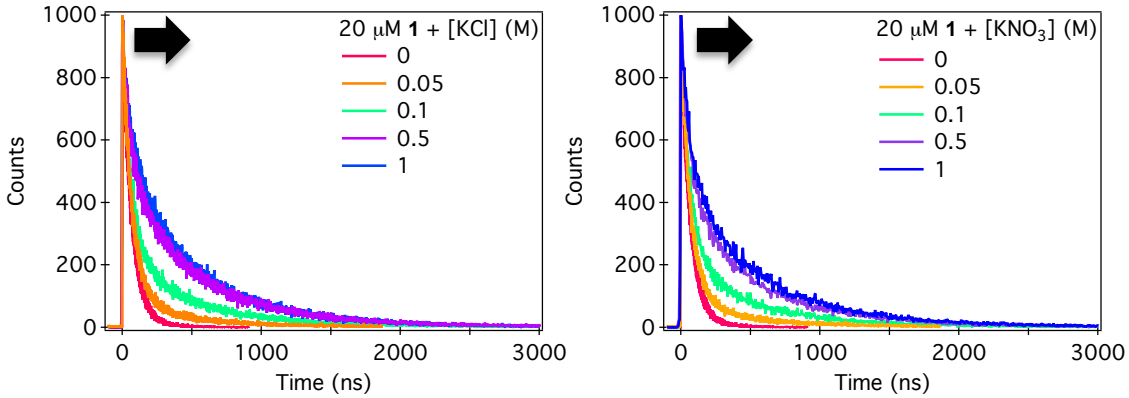
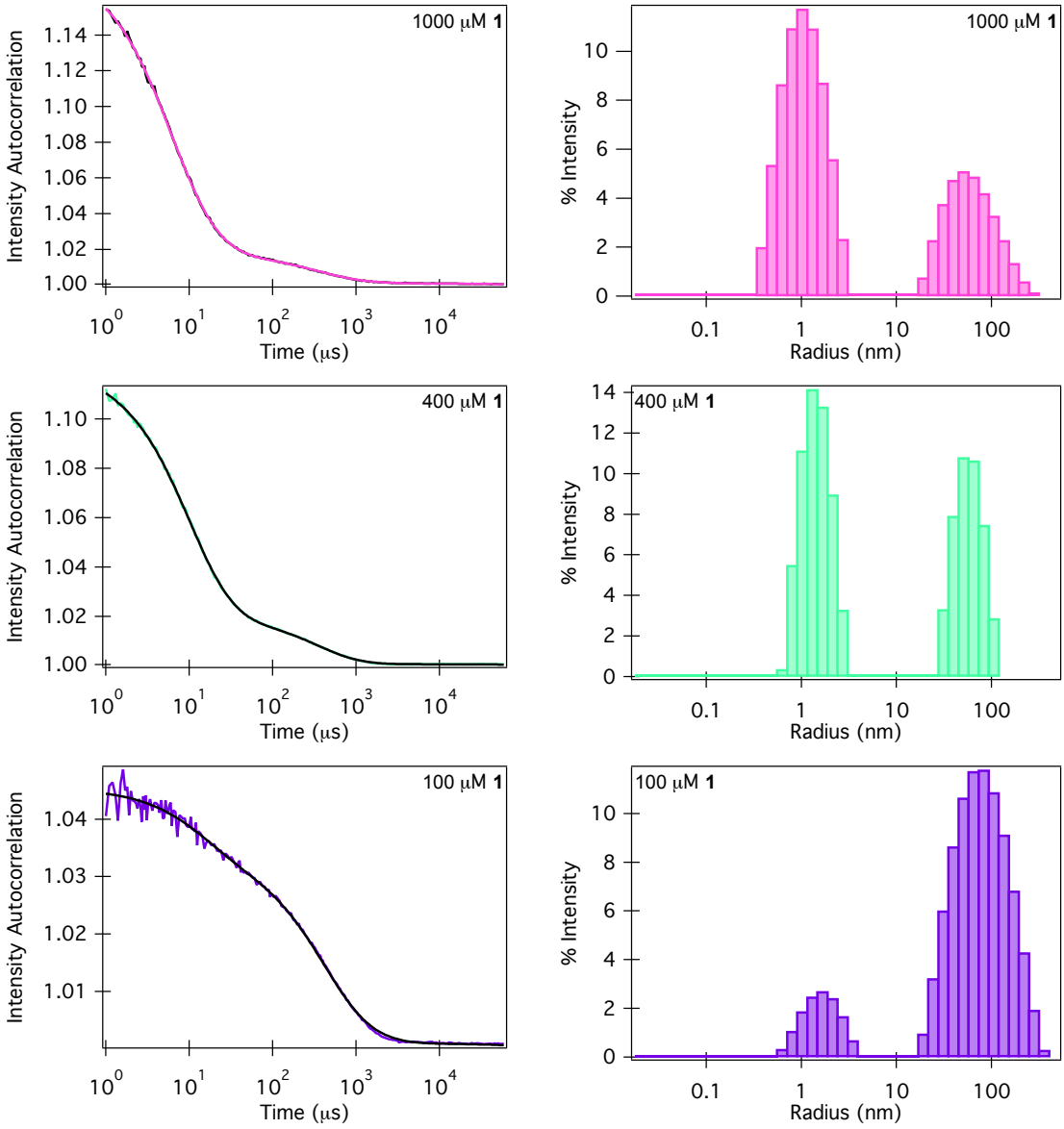


Figure S8: Changes in excited-state lifetimes of **1** with additions of KCl and KNO_3 to aqueous solution.

9a)


1000 μM 1
Intensity Autocorrelation
Time (μs)
% Intensity
Radius (nm)
400 μM 1
100 μM 1

9b)

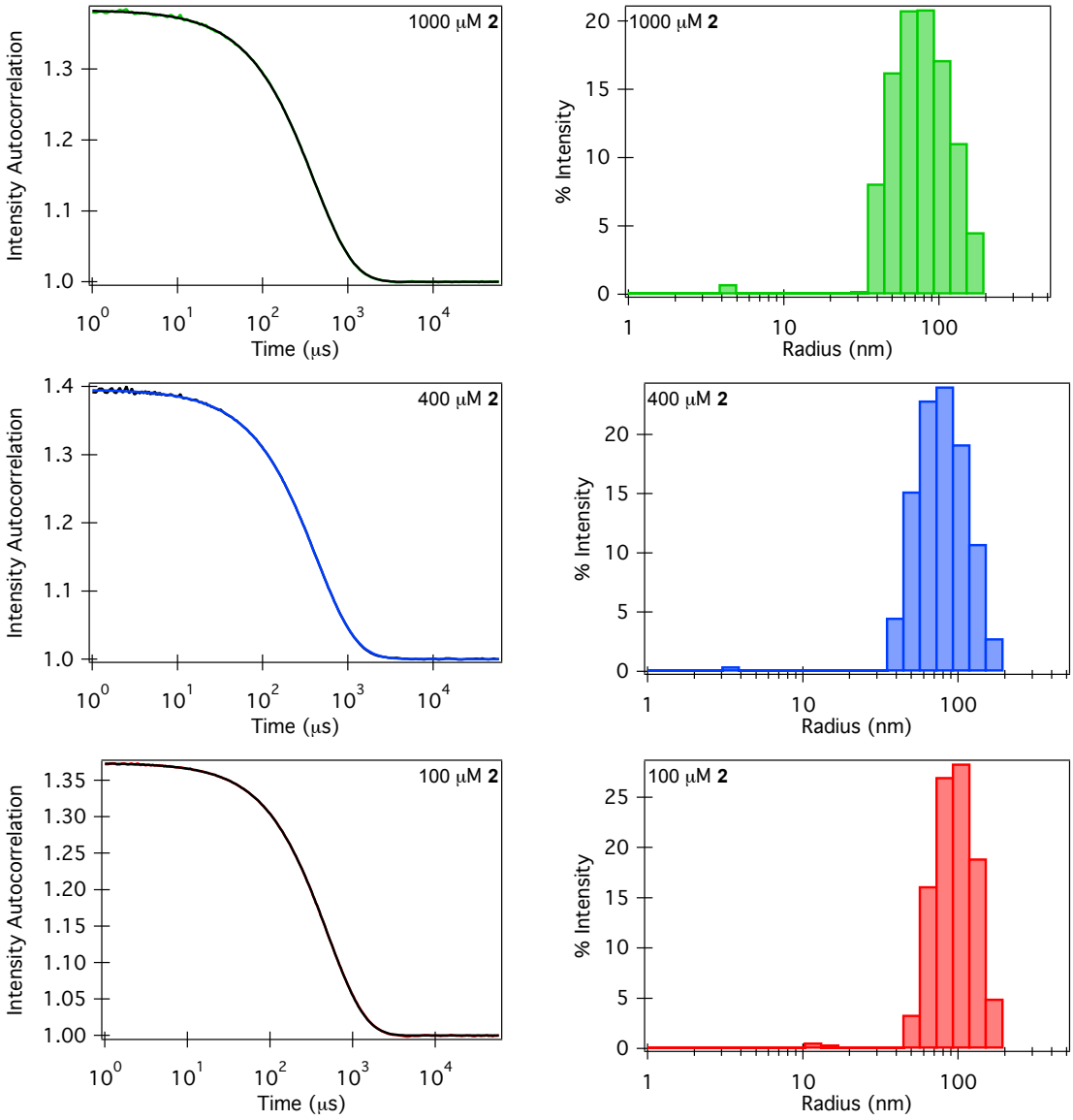
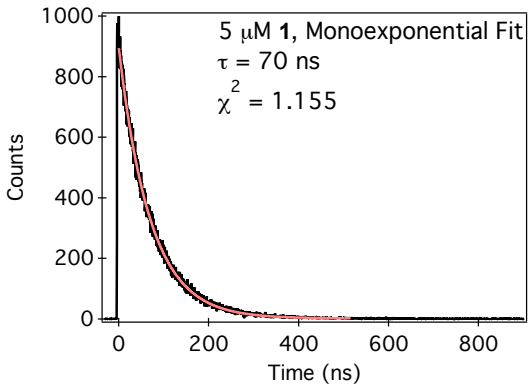
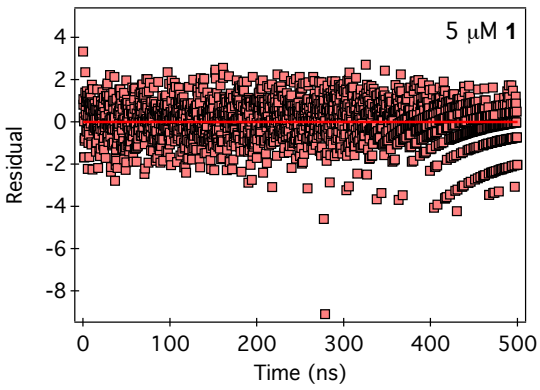
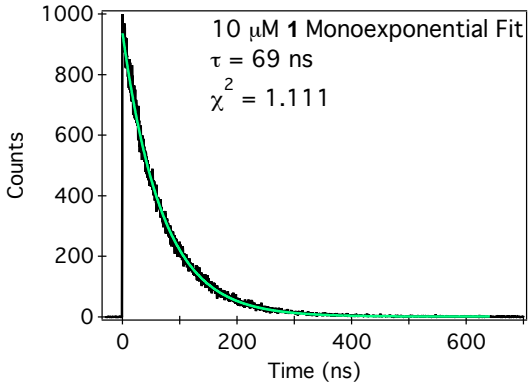


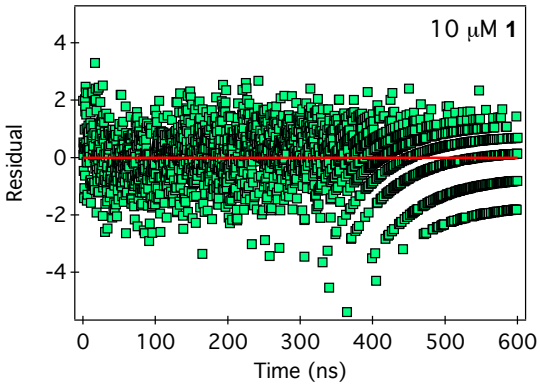
Figure S9: DLS measurements for **1** and **2** in aqueous solution at the concentrations specified in the legends. The graphs on the left side are the autocorrelation functions (color) and their regularization fits (black). The graphs on the right are the histograms calculated from the autocorrelation functions indicating particle radius and polydispersity.

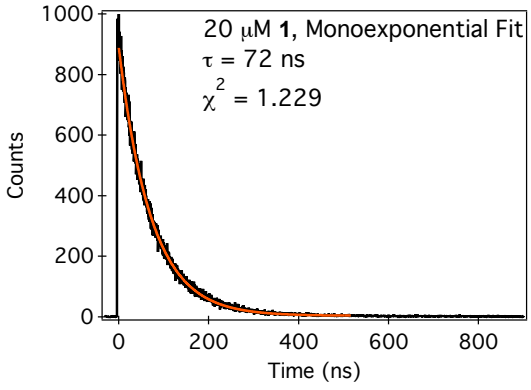
10a)

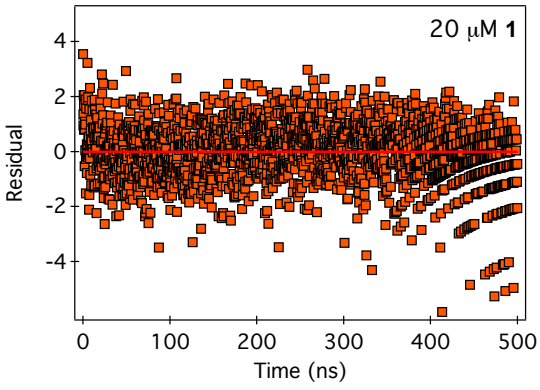

5 μM 1, Monoexponential Fit
τ = 70 ns
χ2 = 1.155
Counts
Time (ns)

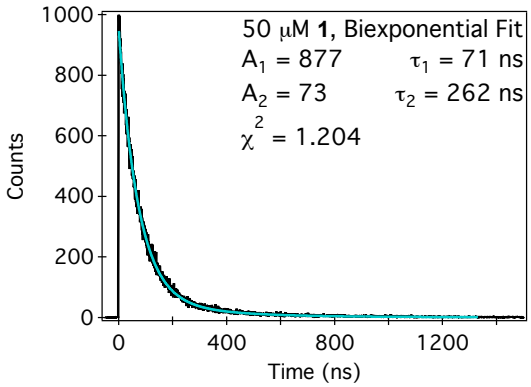

5 μM 1
Residual
Time (ns)

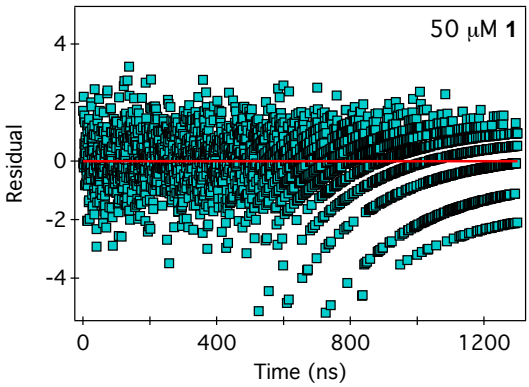

10 μM 1 Monoexponential Fit
τ = 69 ns
χ2 = 1.111
Counts
Time (ns)

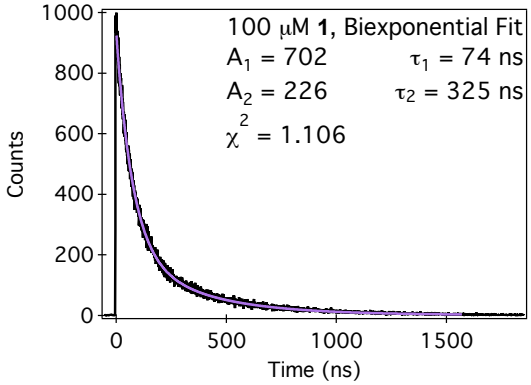

10 μM 1
Residual
Time (ns)

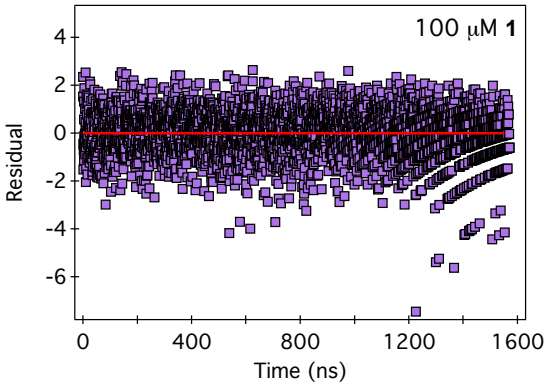

20 μM 1, Monoexponential Fit
τ = 72 ns
χ2 = 1.229
Counts
Time (ns)

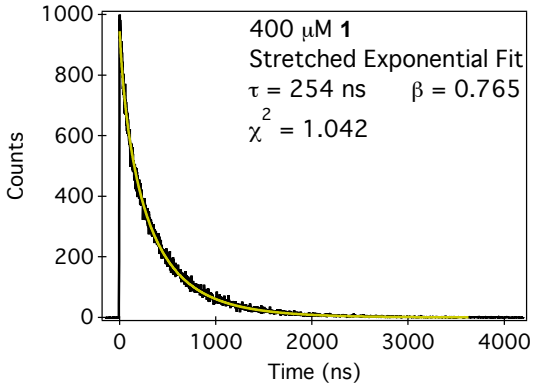

20 μM 1
Residual
Time (ns)

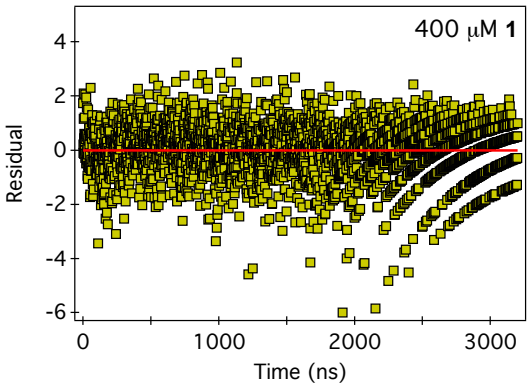

50 μM 1, Biexponential Fit
A1 = 877 τ1 = 71 ns
A2 = 73 τ2 = 262 ns
χ2 = 1.204
Counts
Time (ns)

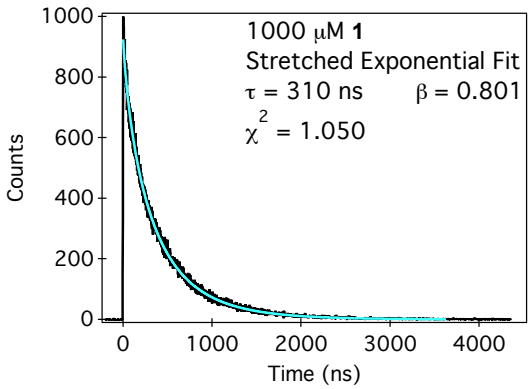

50 μM 1
Residual
Time (ns)

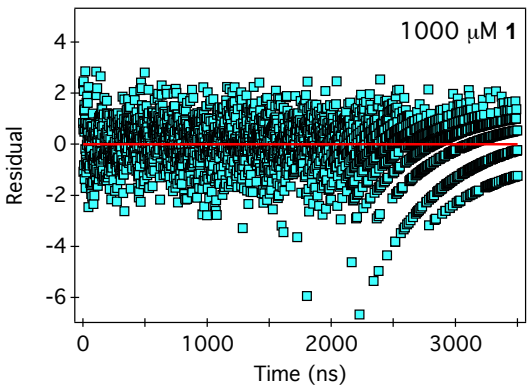

100 μM 1, Biexponential Fit
A1 = 702 τ1 = 74 ns
A2 = 226 τ2 = 325 ns
χ2 = 1.106
Counts
Time (ns)


100 μM 1
Residual
Time (ns)

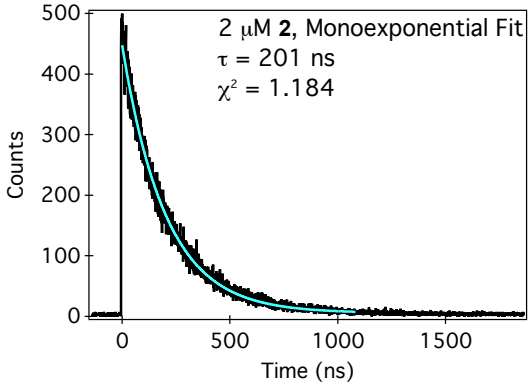

400 μM 1
Stretched Exponential Fit
τ = 254 ns β = 0.765
χ2 = 1.042
Counts
Time (ns)

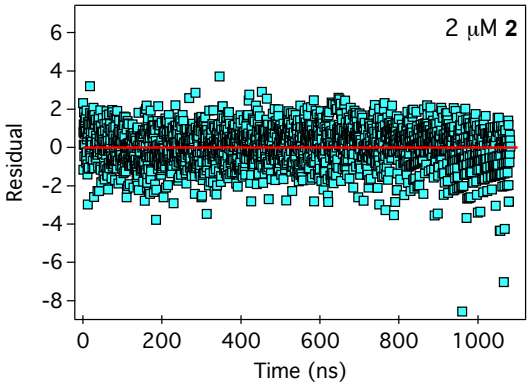

400 μM 1
Residual
Time (ns)

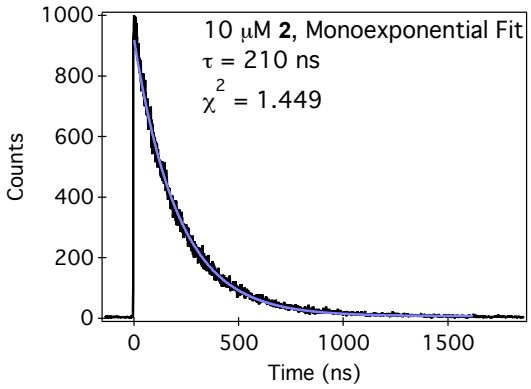

1000 μM 1
Stretched Exponential Fit
τ = 310 ns β = 0.801
χ2 = 1.050
Counts
Time (ns)

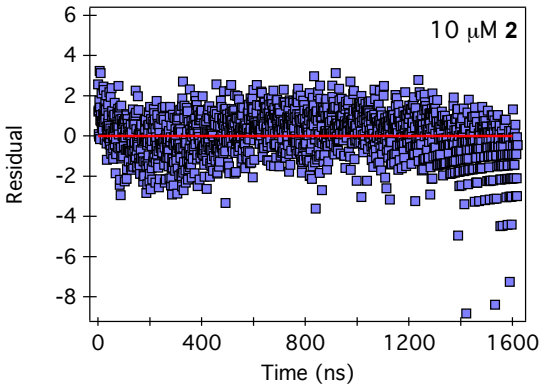

1000 μM 1
Residual
Time (ns)

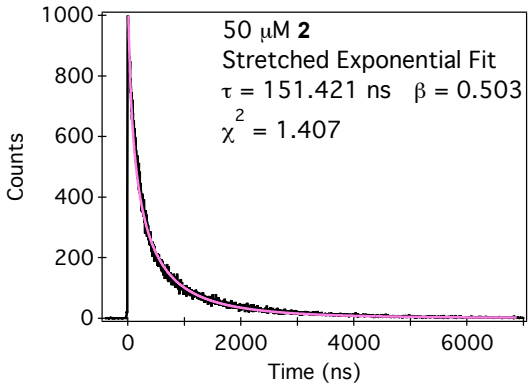
10b)

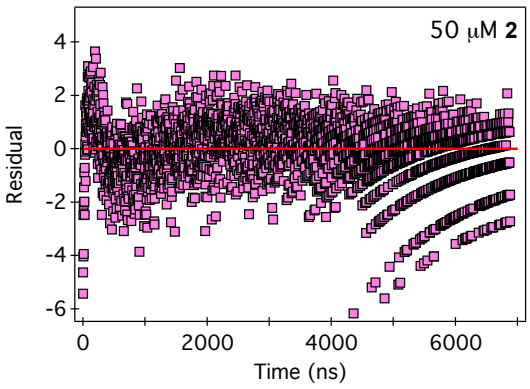

2 μM **2**, Monoexponential Fit
τ = 201 ns
χ² = 1.184
Counts
Time (ns)


2 μM **2**
Residual
Time (ns)


10 μM **2**, Monoexponential Fit
τ = 210 ns
χ² = 1.449
Counts
Time (ns)


10 μM **2**
Residual
Time (ns)


50 μM **2**
Stretched Exponential Fit
τ = 151.421 ns β = 0.503
χ² = 1.407
Counts
Time (ns)


50 μM **2**
Residual
Time (ns)

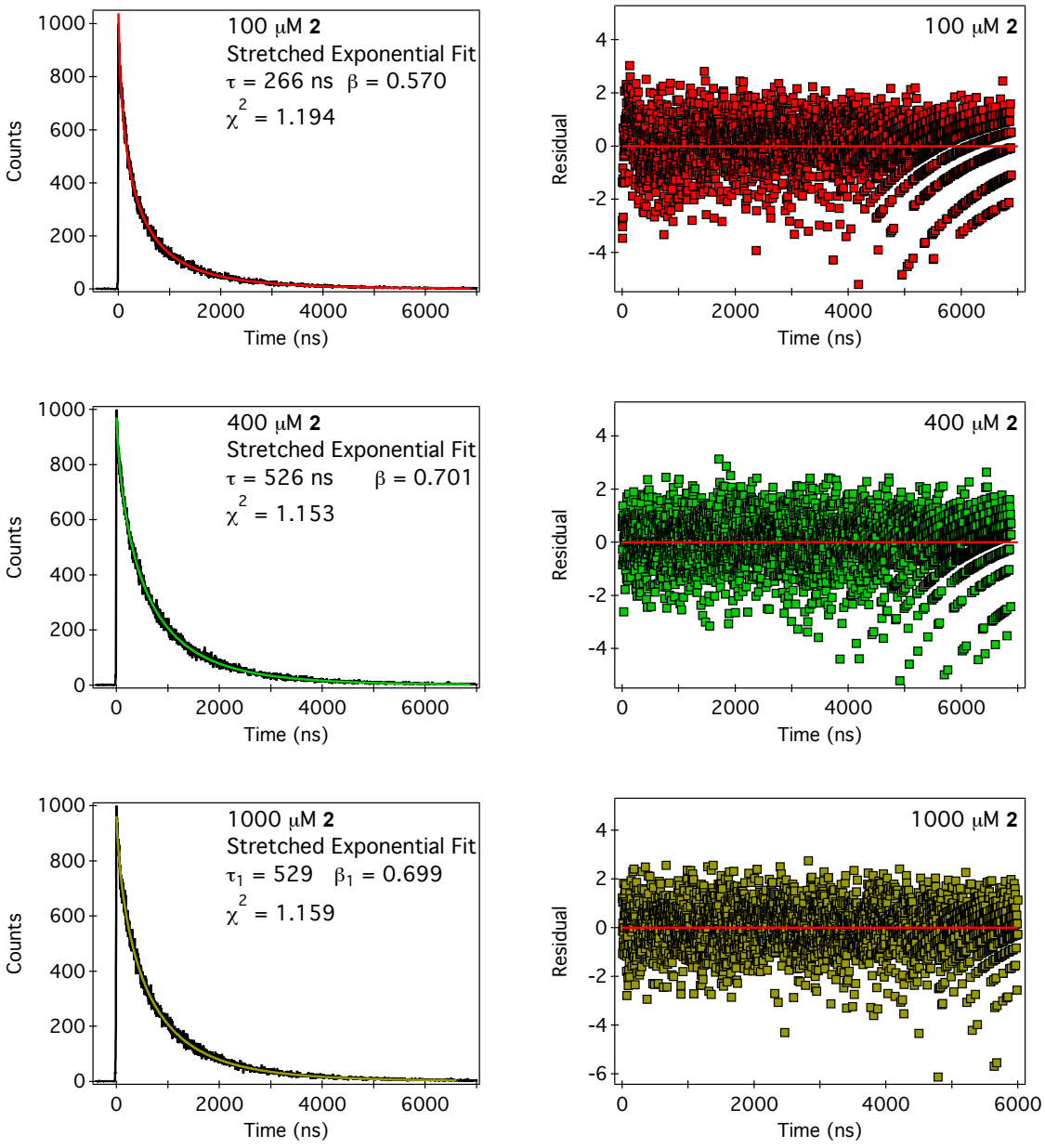


Figure S10: Time-resolved excited state decays and modeling for **1** and **2** in air-equilibrated water. The graphs on the left represent the excited state decays (black) and the fits (colored) at the concentrations and with the fitting models specified in the legends. The right graph is the residual for the chosen fitting model.

Experimental

Spectroscopy: All samples were measured in 1 cm^2 quartz cuvettes, in air-equilibrated HPLC-grade water unless otherwise indicated.

Absorption Spectra: UV-Vis spectra were recorded on a Shimadzu UV-1800 double beam spectrophotometer.

Emission Spectra: Emission spectra were recorded on an Edinborough Instruments FL/FS920 or 980 fluorometer using a 450 W Xe arc lamp as the excitation source.

Quantum Yield Measurements: Concentration-dependent quantum yields were calculated using the relative method.[1] In order to correct for any inner-filter effects at increasing concentrations, the absorbance of the reference and the sample were matched at the excitation wavelength. At high concentration, these quantum yields were checked using front-face illumination, which provided the same results. For each quantum yield measurement, this was done at two different excitation wavelengths, and those values were averaged. Air-equilibrated aqueous solutions of $[Ru(bpy)_3]Cl_2$, which has a reported quantum yield of 0.04,[2] were used as the reference.

Excited-State Intensity decays: Excited-state decays were measured on an Edinburgh Instruments Mini-Tau spectrometer, with a 405 nm picosecond laser diode as the excitation source. A band-pass filter centered at 600 nm with a 45 nm width was used to select the emission. The recorded decays were fit using Edinburgh Instruments FAST software, and the best fit was determined after considering the reduced χ^2 value of the fit as well as inspecting the residuals.

Dynamic Light Scattering: Dynamic Light Scattering (DLS) measurements were performed using a DynaPro Nanostar instrument from Wyatt Technology. All measurements were recorded at 25°C using 663 nm incident laser light. Scatter was collected at 90°. Prior to measurement, aqueous solutions were filtered using a 0.4 mm pore size filter. Each experiment contained an average of 50 measurements, and each measurement had a 5 second acquisition time. The hydrodynamic radii were calculated by Wyatt's Dynamics 7 software using the Stokes-Einstein equation.

CryoSEM: CrysoSEM was performed at the Analytical Instrument Facility (AIF) at North Carolina State University.

Mass Spectrometry: Mass spectrometry was performed by the Michigan State University Mass Spectrometry core.

Elemental Analysis: Elemental analysis was performed by Atlantic Microlab.

Synthesis

Cyclometalated chloro-bridged Ir(III) dimers were synthesized by literature procedures.[3,4] The F-mppy ligand was synthesized via the Krohnke method using literature procedures.[5] The BPS ligand was purchased from commercial sources as a mixture of isomers with respect to the position of the sulfonates. Sulfonation can occur in either the meta or the para position of each phenyl, giving three possible ligand isomers (*m-m, m-p, p-p*). The ratio of these isomers will vary by batch, giving different proton NMR signals, as well as different integrations. The use of these isomeric mixtures has been well established in the literature.[6,7,8] As it has been determined that these isomers cannot be distinguished through spectroscopic or electrochemical measurements,[9,10] commercially available isomeric ligands were used without further purification.

[Ir(ppy)$_2$BPS] (Complex 1): ^{1}H NMR (400 MHz, CD_3OD, d): 8.39-8.41 (m, 2H), 8.21 (s, 2H), 8.12-8.14 (d, 2H), 8.0-8.04 (m, 4H), 7.8-7.87 (m, 6H), 7.61-7.72 (m, 6H), 7.02-7.06 (m, 2H), 6.91-6.97(m, 4H), 6.41-6.43 (d, 2H). HR-ESI-MS (M-) *m/z* calc. 991.1236, found 991.1211. Anal. Calcd for $C_{46}H_{30}ClIrN_4Na_2O_6S_2 \bullet 4H_2O$ (as a solid, each sulfonate group retains a sodium, and the complex has a chloride counterion. This has been observed in all of the complexes described here, and has also been reported previously in the literature.[11]): C, 48.27; H, 3.35; N, 4.89. Found: C, 48.38; H, 3.45; N, 5.03.

[Ir(F-mppy)$_2$BPS] (Complex 2): ^{1}H NMR (400 MHz, CD_3OD, d): 8.41-8.44 (m, 2H), 8.25 (s, 2H), 8.00-8.07 (m, 7H), 7.87-7.92 (m, 4H), 7.66-7.76 (m, 7H), 7.36 (s, 1H), 6.78-6.83 (m, 1H), 5.95-5.98 (m, 1H), 2.04 (s, 6H) HR-ESI-MS (M-) *m/z* calc. 1055.1361, found 1055.1331. Anal. Calcd for $C_{48}H_{32}ClF_2IrN_4Na_2O_6S_2 \bullet 8H_2O$: C, 45.02; H, 3.78; N, 4.37. Found: C: 45.05% H: 3.68% N: 4.48%.

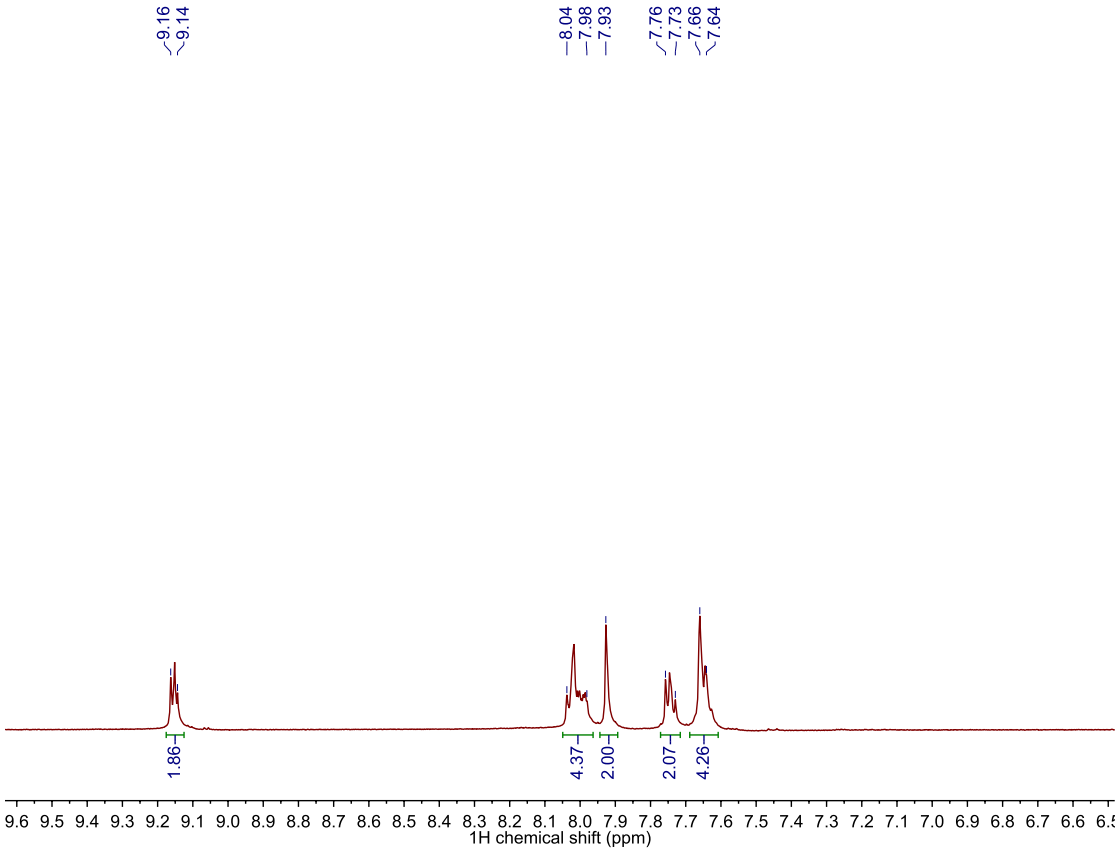


Figure S11: ^{1}H NMR of the commercially available bathophenanthrolinedisulfonic acid disodium salt hydrate (BPS) ancillary ligand starting material.

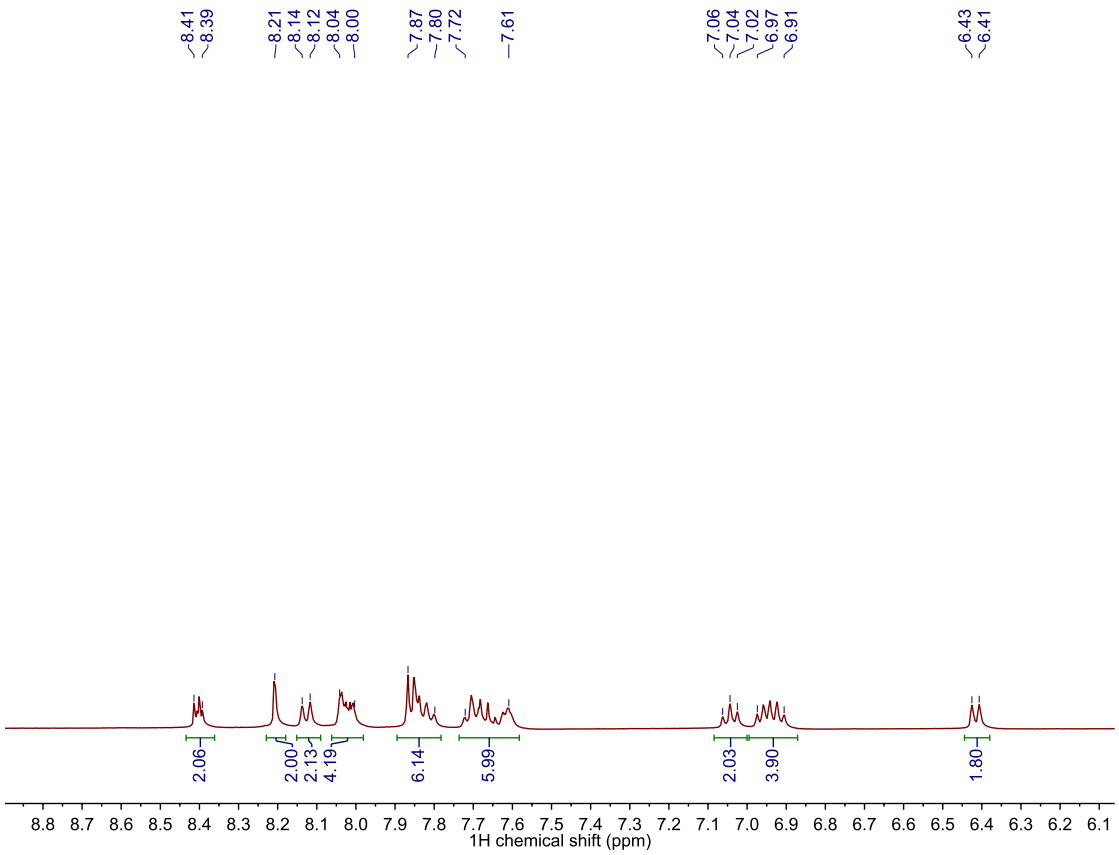


Figure S12: ^{1}H NMR of Ir(ppy)$_2$BPS, Complex **1**.

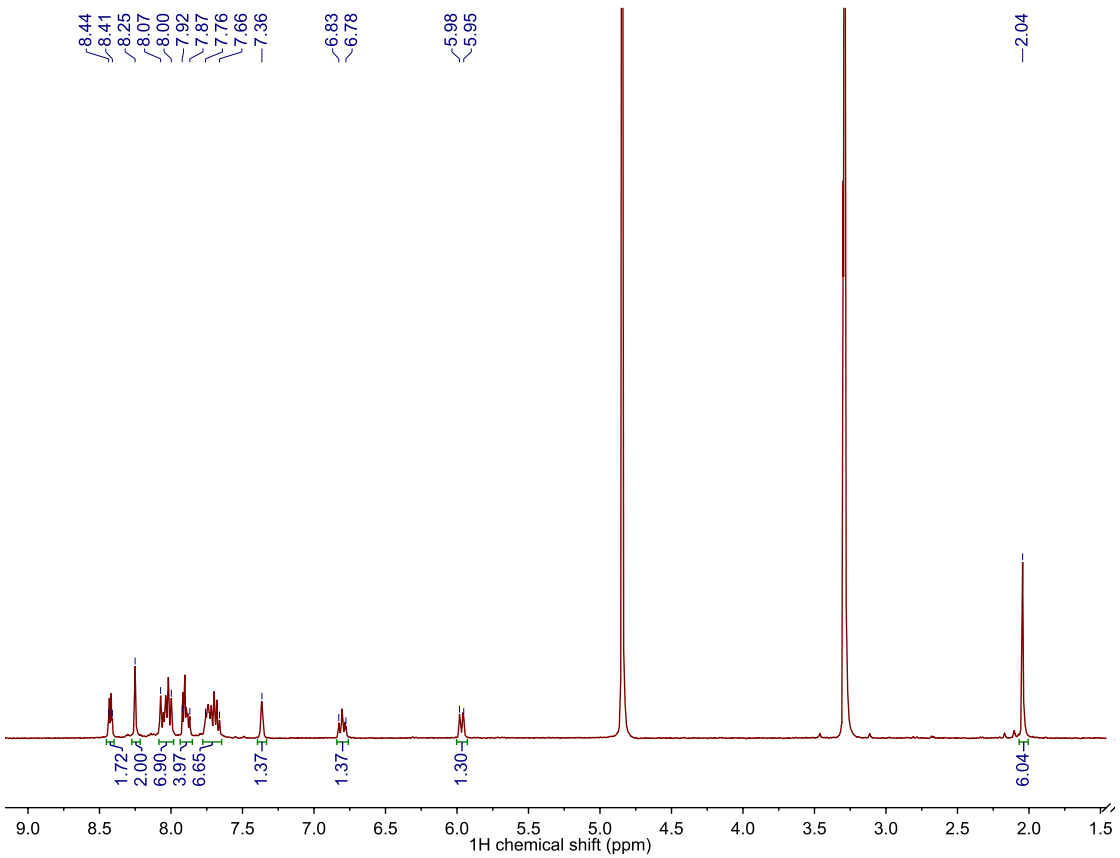


Figure S13: ^{1}H NMR of Ir(F-ppy)$_2$BPS, Complex **2**.

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