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

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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), $\lambda_{ex} = 430$ nm.
Figure S5: Comparison of neat powder emission spectra of 1 to that of the concentration-dependent solution spectra, $\lambda_{ex} = 443$ nm.

Figure S6: Time-resolved photoluminescence intensity decays of 1 in air equilibrated and air free methanol.
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 KNO₃ to aqueous solution.
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
\[ \tau = 70 \text{ ns} \]
\[ \chi^2 = 1.155 \]

10 µM 1, Monoexponential Fit
\[ \tau = 69 \text{ ns} \]
\[ \chi^2 = 1.111 \]

20 µM 1, Monoexponential Fit
\[ \tau = 72 \text{ ns} \]
\[ \chi^2 = 1.229 \]
50 µM 1, Biexponential Fit
\[ A_1 = 877 \quad \tau_1 = 71 \text{ ns} \]
\[ A_2 = 73 \quad \tau_2 = 262 \text{ ns} \]
\[ \chi^2 = 1.204 \]

100 µM 1, Biexponential Fit
\[ A_1 = 702 \quad \tau_1 = 74 \text{ ns} \]
\[ A_2 = 226 \quad \tau_2 = 325 \text{ ns} \]
\[ \chi^2 = 1.106 \]

400 µM 1, Stretched Exponential Fit
\[ \tau = 254 \text{ ns} \quad \beta = 0.765 \]
\[ \chi^2 = 1.042 \]

1000 µM 1, Stretched Exponential Fit
\[ \tau = 310 \text{ ns} \quad \beta = 0.801 \]
\[ \chi^2 = 1.050 \]
10b)

2 μM 2, Monoexponential Fit
\[ \tau = 201 \text{ ns} \]
\[ \chi^2 = 1.184 \]

10 μM 2, Monoexponential Fit
\[ \tau = 210 \text{ ns} \]
\[ \chi^2 = 1.449 \]

50 μM 2
Stretched Exponential Fit
\[ \tau = 151.421 \text{ ns} \]
\[ \beta = 0.503 \]
\[ \chi^2 = 1.407 \]
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.\textsuperscript{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,\textsuperscript{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 $\chi^2$ 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: CryoSEM 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. The F-mppy ligand was synthesized via the Krohnke method using literature procedures. 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. As it has been determined that these isomers cannot be distinguished through spectroscopic or electrochemical measurements, commercially available isomeric ligands were used without further purification.

**[Ir(ppy)$_2$BPS] (Complex 1):** $^1$H NMR (400 MHz, CD$_3$OD, 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$_{30}$ClIrNa$_2$O$_{6}$S$_2$•4H$_2$O (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): 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$_3$OD, 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$_2$IrN$_4$Na$_2$O$_{6}$S$_2$•8H$_2$O: 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.
References