Modelling the Luminescence of Iridium Cyclometalated Complexes Encapsulated in Cucurbituril

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Supporting Information.

Experimental

The description of the preparation and instrumental methods were given in a previous publication. We will summarize only those experimental aspects which are directly relevant to the current study.

^{1}H NMR spectroscopy

NMR spectra (1D and 2D) were recorded on a Varian Unity plus-400 spectrometer (operating at 400 MHz for the ^{1}H nuclei. All NMR experiments were conducted at 25 °C. ^{1}H NMR spectra were referenced to tetramethylsilane (TMS) (0 ppm) at 25 °C using the residual ^{1}H signal of the respective deuterated solvent. Sodium acetate buffer solution (0.05 M, pH 4.7) in D_2O was used as solvent in

most experiments. Solid Q[10] was dissolved in deuterated sodium acetate buffer, with heating and sonication used to speed the dissolution. Aliquots of Q[10] stock solution were added into a solution to give a 1:1 molar ratio. Concentrations of species in NMR experiments were ~1 mM.

Luminescence Studies

Time-resolved luminescence

Luminescence lifetimes were determined using an Edinburgh Instruments FLS980 fluorescence spectrometer equipped with a pulsed EPLED excitation source (360 nm). Exponential Tail Fit Analysis was used to fit the emission decay, with χ^2 values and intensity residuals used to determine goodness of fit. For all fitting results reported here, χ^2 values were close to unity. All samples were prepared in the sodium acetate buffer solution and were deoxygenated by purging with argon or nitrogen. Quantum yields were measured in a deaerated sodium acetate buffer solution (pH 4.7) at 360 nm excitation wavelength, using optically dilute method with one single point measurement.[27] In the single point method, the quantum yield of the unknown (Φ) was calculated using the following equation:

$$\Phi = \Phi_R (I/I_R)(A_R/A)(\eta^2/\eta_R^2) \qquad (1)$$

Where Φ_R is the quantum yield of the reference compound; I, I_R are the integrated emission intensities of unknown and reference; A, A_R are the absorbances of unknown and reference at the excitation wavelength (λ_{ex}) ; η, η_R are the refractive indices of the solvents. A deaerated $[Ru(bpy)_3]^{2+}$ water solution (Φ_R = 0.042, λ_{ex} = 360 nm) was used as reference. Refractive index for sodium acetate buffer is 1.34.[28]

Steady-State Titrations.

Steady-state luminescence spectra were recorded on a Horiba Jobin Yvon FluoroMax-3 fluorescence spectrophotometer at room temperature unless otherwise specified. Samples were excited at 360 nm in quartz cuvettes (1 cm path length). Both Q[10] and the relevant iridium complex were dissolved in sodium acetate buffer solution (0.05 M, pH 4.7). Aliquots of Q[10] stock solution were then added to a stock solution of **Ir-X**. **Ir-X** initial concentrations and volumes, and Q[10] stock concentrations and total volume added were as follows: **Ir-CHO**: 1.0 x 10^{-5} M, 2.0 mL, Q[10] 3.4 x10^{-5} M, 720 µL; **Ir-CH$_2$NH$_2$$^+$Bu**, 7.6 x 10^{-6} M, 3 mL Q[10] 4.8 x 10^{-5} M,

390 μL; **Ir-H** 1.2 x 10^{-5} M, 2.5 mL, Q[10] 1.3 x10^{-4} M, 380 μL; **Ir-DMB** (2.6 x 10^{-6} M, 2 mL, Q[10] 2.9 x 10^{-5} M, 385 μL).

Derivation of model titration curve.

The total fluorescence of the **Ir-X** + Q[10] mixture is given by

$$F = \Phi k^a [M]_{tot}$$

where k^a is the absorption rate, Φ is the quantum yield and $[M]_{tot}$ is the total concentration of metal complex (which is fixed during the titration). Defining, $\Delta F = F - F_0$ where, F_0, is the intensity of the free complex, we have

$$\frac{\Delta F}{F_0} \approx \frac{\Phi k^a [M]_{tot}}{k_f^r k^a [M]_{tot}} = \frac{\Phi}{k_f^r}$$

where k_f^r is the radiative rate of the free complex and we have assumed that $F \gg F_0$. The expression for the quantum yield is given in the main text by

$$\Phi \approx \frac{c_1' x_1 + c_2' x_2}{f} \qquad\qquad (15a)$$

$$f = 1 + c_3 [M_f] \qquad\qquad (15b)$$

and thus we have

$$\frac{\Delta F}{F_0} \approx \frac{c_1 x_1 + c_2 x_2}{f}$$

where, $c_i k_f^r = c_i'$ (*i = 1,2*).