

Water detection by “turn on” fluorescence of the quinone-containing complexes $[\text{Ru}(\text{phen})_2(1,10\text{-phenanthroline-5,6-dione})]^{2+}$ and $[\text{Ru}(\text{phenanthroline-5,6-dione})_3]^{2+}$

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Table of Contents:	Page
Materials and instrumentation	S2
NMR 2 in CD_3CN and D_2O (Fig. S1)	S3
Equilibrium constant determination	S4-5
Fluorescence water titration	S6

EXPERIMENTAL

Materials. d_3 -acetonitrile (99.8%) and deuterium oxide (99.9%) was purchased from Cambridge Isotope Laboratories and used as received. 1,10-phenanthroline-5,6-dione (phendione),¹ $[Ru(phen)_3]Cl_2$,² $[(phen)_2Ru(phendione)]Cl_2$ (**1**)³, and $[Ru(phendione)_3]Cl_2$ (**2**)⁴ were prepared according to literature methods. Reagent grade acetonitrile was dried over 3 Å molecular sieves for a period of > 72 hrs prior to use.

Instrumentation. 1H NMR spectra were recorded on a JEOL Eclipse plus 500 MHz spectrometer. Spectra were referenced to tetramethylsilane (TMS) or residual solvent peaks from the deuterated solvent. UV-visible spectra were obtained on a Hewlett-Packard HP8453A spectrometer. Fluorescence data was collected on a Horiba Jobin Yvon Fluoromax-3 fluorimeter using an Osram 150 W Xe lamp as the source.

Fluorescence Titrations. Stock solutions of 6.67 μM of **1** or **2** was prepared in acetonitrile (described above). A standard fluorescence cuvette ($l = 10$ mm) was charged with 3.00 mL of the stock solution and sealed with a rubber septum and allowed to come to equilibrium during a period of 24 hrs. After 24 hrs, an initial spectrum was taken using λ_{ex} of 450 nm and recording the I_{em} at 405 nm) Subsequently, 2 μL aliquots of water were injected through the septum and allowed to come to equilibrium after another 24 hr period, during which the ΔI eventually came to zero. An external standard of 10 μM anthracene (in ethanol) was used to correct for instrumental drift between measurements. The initial residual water concentration of the acetonitrile was determined using a standard addition plot and revealed the initial acetonitrile solution was 0.083 M (0.2 % v/v) water.

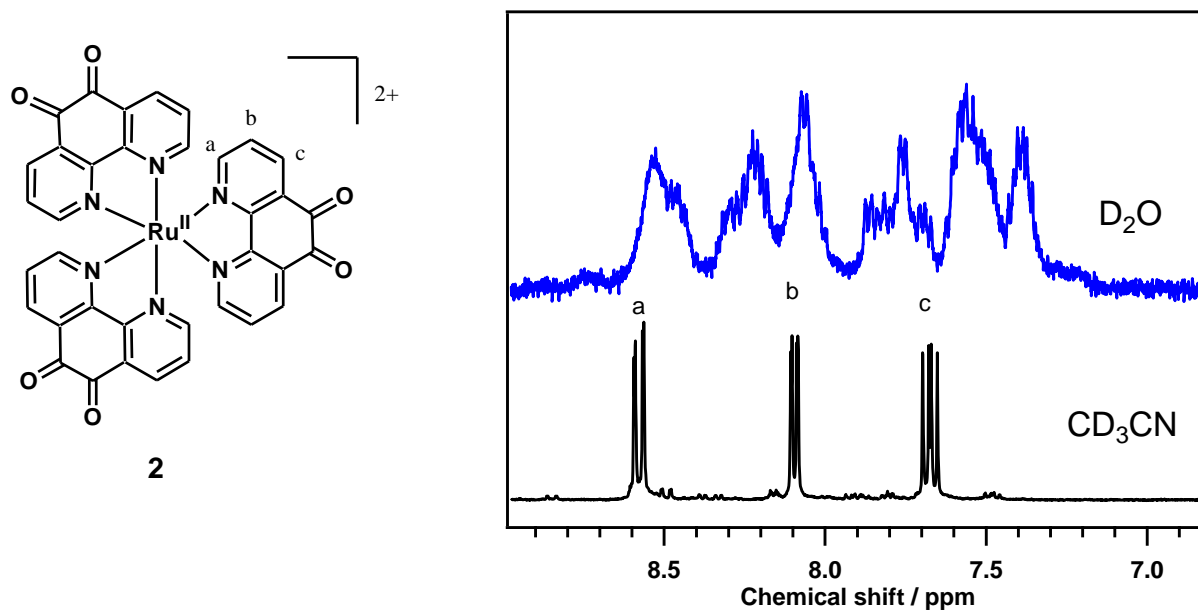
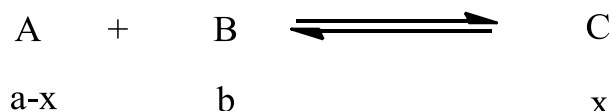


Figure S1. NMR spectra of **2** in acetonitrile (black) and water (blue). Peak assignments are given as indicated in the structure figure.

Equilibrium Constant Determination



$$(1) \quad K_{eq} = \frac{x}{b(a-x)} \quad \text{therefore } x = \frac{K_{eq}ab}{1 + K_{eq}b} \quad (2)$$

Consider the equilibrium above where A = **1**, B = water, and C = **1H₂O** and a = [**1**]_i, b = [water]_i and x = [**1H₂O**]_{eq}. The equilibrium constant can be written as in equation 1 assuming b >> x (which is true until the water concentration (b) approaches the concentration of [**1**]_i). The relationship relating fluorescence intensity to concentration is given by equation 3, where I_{em} is the fluorescence intensity, φ is the quantum yield, I₀ is the incident light intensity, k is the proportionality constant, ε is the molar absorptivity, l is the path length, and c is the concentration. The quantum yield was calculated with respect to [Ru(phen)₃]²⁺ by equation 4, where F is the integrated fluorescence intensity and A is the absorbance.⁸

Since the system is at equilibrium, we can assume that the entire sample absorbs photons and is in the excited state; however, only **1H₂O** emits. Therefore, since the ratio of **1H₂O**/**1** was found to be 0.212 in pure water (water in this case can be ignored since it is the solvent), the quantum yield was divided by 0.212, as shown in equation 5, to compensate for this equilibrium.

$$I_{em} = \phi I_0 k (1 - e^{-\epsilon lc}) \quad (3)$$

$$\text{where } \phi = \phi_{std} \left(\frac{F_{1H_2O}}{F_{std}} \right) \left(\frac{I_{0\,std}}{I_{0\,1H_2O}} \right) \left(\frac{A_{std}}{A_{1H_2O}} \right) \quad (4)$$

$$\text{and } \phi' = \phi / K_{pure\,H_2O} \quad (5)$$

Equation 3 was simplified to equation 6 when εlc < 0.05.

$$c = \frac{I_{em}}{I_0 \phi' k \epsilon l} \quad \text{when } \epsilon lc < 0.05 \quad (6)$$

Which simplifies further to equation 7 provides:

$$c = \frac{I_{em}}{\lambda_x} \quad (7)$$

where $I_0\phi'\kappa\epsilon l = \lambda_x$

And since $c = x$, combining equation 2 and 7

$$I_{em} = \frac{\lambda_x K_{eq} ab}{1 + K_{eq} b} \quad (8)$$

Therefore, by plotting intensity vs concentration of water, the slope, m , can be used to calculate the proportionality constant, λ_x , using equation 9 and the slope.

$$\begin{aligned} I_{em} &= \lambda_x K_{eq} a \cdot b + a \lambda_x \\ y &= m \quad x + b \end{aligned} \quad (9)$$

A similar derivation is obtained for complex **2**, resulting in

$$I_{em} = \frac{\lambda_x K_{eq} ab^3}{1 + K_{eq} b^3} \quad (10)$$

which can be linearized to

$$\begin{aligned} I_{em} &= \lambda_x K_{eq} a \cdot b^3 + a \lambda_x \\ y &= m \quad x + b \end{aligned} \quad (11)$$

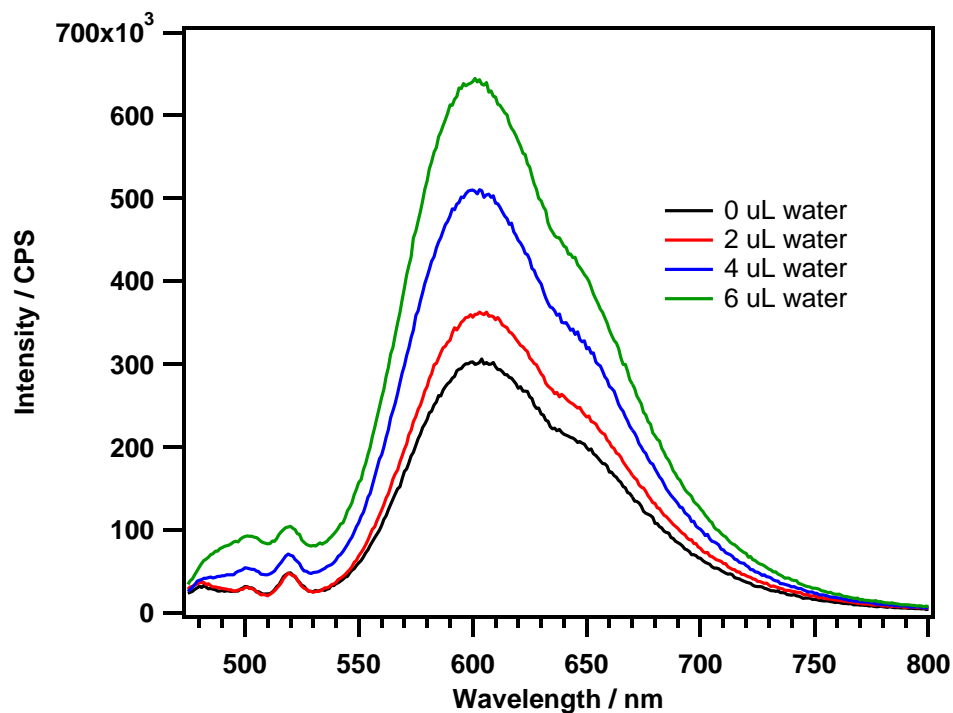


Figure S2. Standard addition titration of water into an acetonitrile solution containing 6.67 μM **1** in 3.00 mL volume of MeCN. In this run the acetonitrile had an initial water concentration of 0.116 M.

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