

Supporting information

Measurements of the quantum yields.

1. Determination of the quantum yield of Rhodamine B in H₂O, using quinine bisulfate as the reference standard.

The quantum yield of Rhodamine B in H₂O was determined by using the primary reference standard, quinine bisulfate. Five quinine bisulfate solutions with the absorbance ranging from 0.0099 to 0.1002 at 354 nm and five Rhodamine B reference solutions with the absorbance ranging from 0.0078 to 0.082 at 354 nm were prepared. The fluorescence emission spectra of the solutions were obtained with the following conditions:

Quinine bisulfate: excitation at 354 nm (band width 1 nm), emission at 370-620 nm (band width 1 nm, 0.5 nm/step, 0.5 s integration). The slope of fluorescence intensity vs. absorbance for the five quinine bisulfate solutions, S_Q , was obtained.

Rhodamine B: excitation at 354 nm (band width 1 nm), emission at 450-710 nm (band width 1 nm, 0.5 nm/step, 0.5 s integration). The slope of fluorescence intensity vs. absorbance for the five Rhodamine B solutions, S_R , was obtained.

The quantum yield of Rodamine B in H₂O, Φ_R , was determined by the equation: $\Phi_R = \Phi_Q \times S_R/S_Q$, where Φ_Q is the quantum yield of quinine bisulfate and is equal to 0.546 at 25 °C¹.

With four repeated measurements, Φ_R was determined to be 0.250, 0.254, 0.252 and 0.247. An average value of $\Phi_R = 0.251 \pm .004$ was used in this work for the quantum yield of Rodamine B in H₂O as the secondary reference standard for measuring the quantum yield of Cm(III) in H₂O.

2. Determination of the quantum yield of Cm(III) in H₂O, using Rhodamine B in H₂O as the reference standard.

The quantum yield of Cm(III) in H₂O was determined by using the secondary reference standard, Rhodamine B in H₂O. Five Rhodamine B reference solutions with the absorbance ranging from 0.0078 to 0.082 at 396 nm and five Cm(III) H₂O solutions (0.001 M HClO₄, [Cm(III)] = 0.149, 0.447, 0.745, 1.043, and 1.490 mM) were prepared. The fluorescence emission spectra of the solutions were obtained with the following conditions:

Rhodamine B: excitation at 396 nm (band width 1 nm), emission at 500-720 nm (band width 1 nm, 0.5 nm/step, 0.5 s integration). The slope of fluorescence intensity vs. absorbance for the five Rodamine B solutions, S_R , was obtained.

Cm(III) in H₂O: excitation at 396 nm (band width 1 nm), emission at 500-650 nm (band width 1 nm, 0.5 nm/step, 0.5 s integration). The slope of fluorescence intensity vs. absorbance for the five Cm(III) H₂O solutions, S_{Cm,H_2O} was obtained. The measurements were performed at different temperatures. The measurement at 25 °C was repeated twice and the results were averaged.

The quantum yield of Cm(III) in H₂O, $\Phi_{\text{Cm,H}_2\text{O}}$, was determined by the equation: $\Phi_{\text{Cm,H}_2\text{O}} = \Phi_{\text{R}} \times S_{\text{Cm,H}_2\text{O}}/S_{\text{R}}$, where Φ_{R} is the quantum yield of Rodamine B and is equal to 0.251 at 25°C (determined in this work).

3. Determination of the quantum yield of Cm(III) in D₂O, using quinine bisulfate as the reference standard.

The quantum yield of Cm(III) in D₂O was determined by using the primary reference standard, quinine bisulfate in H₂O. Five quinine bisulfate reference solutions with the absorbance ranging from .0099 to 0.1002 at 354 nm and five Cm(III) D₂O solutions (0.001 M DClO₄, [Cm(III)] = 0.149, 0.447, 0.745, 1.043, and 1.490 mM) were prepared. Two excitation wavelengths (396 nm and 375 nm) were used for collecting the fluorescence emission spectra of these solutions, with the following conditions:

Quinine bisulfate: (1) excitation at 396 nm (band width 1 nm), emission at 350-620 nm (band width 1 nm, 0.25 nm/step, 0.5 s integration). (2) excitation at 375 nm (band width 1 nm), emission at 350-620 nm (band width 1 nm, 0.5 nm/step, 0.5 s integration). The slope of fluorescence intensity vs. absorbance for the five quinine bisulfate, S_{Q} , was obtained.

Cm(III) in D₂O: (1) excitation at 396 nm (band width 1 nm), emission at 550-650 nm (band width 1 nm, 0.25 nm/step, 0.5 s integration). (2) excitation at 375 nm (band width 1 nm), emission at 550-650 nm (band width 1 nm, 0.5 nm/step, 0.5 s integration). The slope of fluorescence intensity vs. absorbance for the five Cm(III) D₂O solutions, $S_{\text{Cm,D}_2\text{O}}$ was obtained. The measurements were performed at different temperatures. The measurement at 25 °C was repeated twice and the results were averaged.

The quantum yield of Cm(III) in D₂O, $\Phi_{\text{Cm,D}_2\text{O}}$, was determined by the equation: $\Phi_{\text{Cm,D}_2\text{O}} = \Phi_{\text{Q}} \times S_{\text{Cm,D}_2\text{O}}/S_{\text{Q}}$, where Φ_{Q} is the quantum yield of quinine bisulfate and is equal to 0.546 at 25°C¹.

References

- (1) Demas, J. N., Crosby, G. A. *J. Phys. Chem.* **1971**, 75, 991.