Electronic Supplementary Material (ESI) for Dalton Transactions.


# Intramolecular sensitization of americium luminescence in solution: Shining light on short-lived forbidden 5*f* transitions

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# Supporting Information

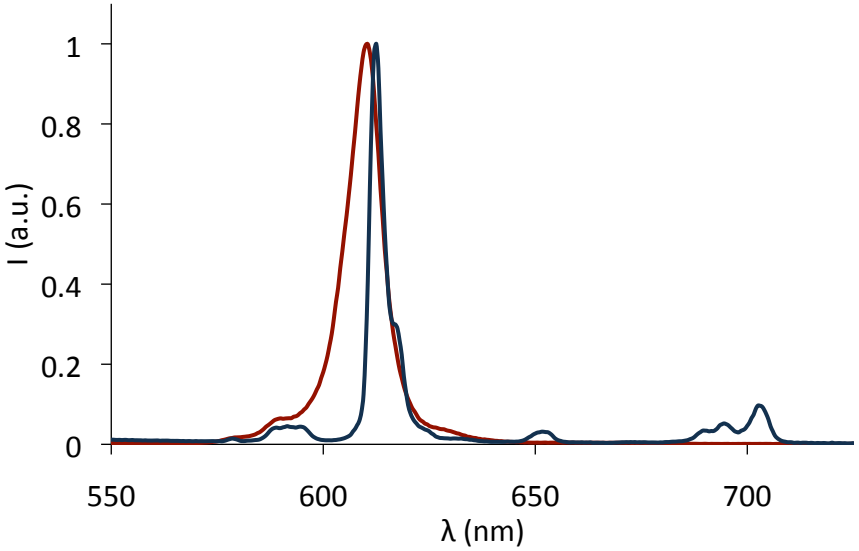


**Figure S1.** Normalized steady-state emission spectra ($\lambda_{exc}$ = 345 nm) of $Eu^{III}$ (blue) and $Cm^{III}$ (red) complexes formed in situ with **2**, in 0.1 M HEPES buffer (pH 7.4, 25°C, [$M^{III}$] = [**2**] = 10 μM).

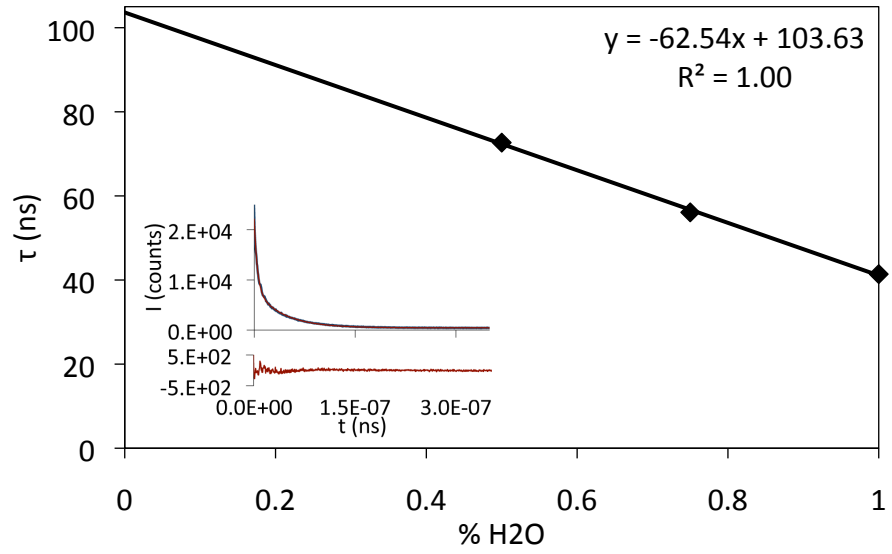


**Figure S2.** Am(III) luminescence lifetime determination as a function of %$H_2O$ content in $D_2O$:$H_2O$ mixtures for [$Am^{III}$(**1**)]$^-$ (10 μM in 0.1 M HEPES, pH 7.4, 25°C). **Inset:** Luminescence decay of [$Am^{III}$(**1**)]$^-$ (blue) in $H_2O$ with the fitted curve (red) and its residual.

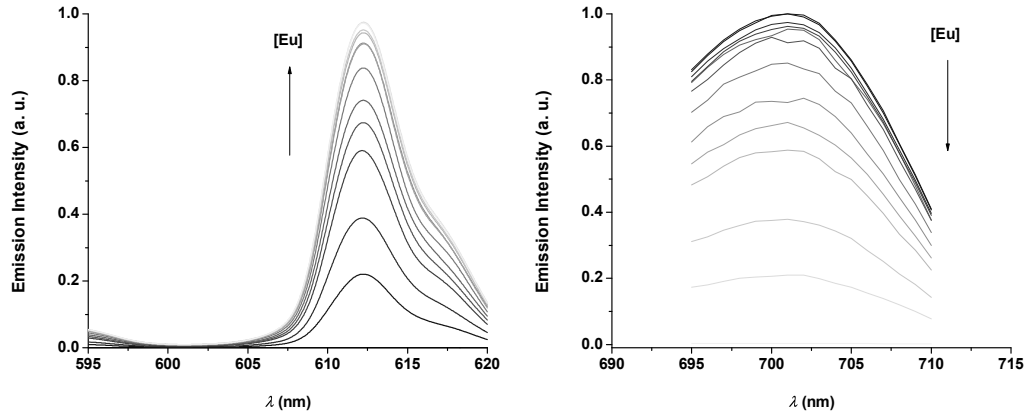


**Figure S3.** Metal competition batch titration of $[Am^{III}(\mathbf{1})]^-$ with $Eu^{III}$. Changes in normalized luminescence intensity ($\lambda_{exc}$ = 325 nm) upon addition of Eu over two emission windows, $\lambda_{em1}$ = 595–620 nm and $\lambda_{em2}$ = 695–710 nm, corresponding to the $Eu^{III}$ $^5D_0 \rightarrow {}^7F_2$ and $Am^{III}$ $^5D_1 \rightarrow {}^7F_1$ transitions, respectively.

**Table S1** Photophysical parameters for $Eu^{III}$ and $Cm^{III}$ complexes formed with ligand **2**.[a]

| | $Eu^{III}$ | $Cm^{III}$ |
|---|---|---|
| $\lambda_{max}$ (nm) | 341 | 342 |
| $\varepsilon_{max}$ ($M^{-1}cm^{-1}$) | 13,360 | 14,140 |
| $\lambda_{exc}$ (nm) | 345 | 345 |
| $\Phi_{tot}$ ($H_2O$)[b] | $2.0 \times 10^{-3}$ | $4.0 \times 10^{-1}$ |
| $\tau_{obs}$ (μs)[b] | 272 | 139 |
| $q$ | 3.4[c] | 4.2[d] |

[a]All values reported are the results of at least three independent experiments performed in aqueous buffered solutions (0.1 M HEPES, pH 7.4); [b]Uncertainties determined from the standard deviation between three independent measurements are within 10% of the given value; [c]Using equation from T. Kimura, R. Nagaishi, Y. Kato, and Z. Yoshida, *J. Alloys Compd.*, 2001, **323-324**, 164-168; [d]Using equation from T. Kimura and G. R. Choppin, *J. Alloys Compd.*, 1994, **213-214**, 313-317..

**Table S2** Deconvolution of the normalized $Am^{III}$ $^5D_1 \rightarrow {}^7F_1$ emission peak for the three ligands.[a]

| **1** | | **2** | | **3** | |
|---|---|---|---|---|---|
| peak max (nm) | peak area (%) | peak max (nm) | peak area (%) | peak max (nm) | peak area (%) |
| 689.5 | 18.3 | 688.9 | 21.8 | 687.9 | 18.6 |
| 698.3 | 38.9 | 693.2 | 29.7 | 694.7 | 32.2 |
| 702.7 | 22.7 | 698.7 | 23.2 | 699.4 | 18.7 |
| 706.5 | 20.1 | 704.5 | 25.4 | 704.6 | 30.6 |

[a]Deconvolution performed with four Lorentzian functions, best fitting the participation of four transitions between two $^5D_1$ ($\Gamma_2$, $\Gamma_5$) emitting and two $^7F_1$ ($\Gamma_2$, $\Gamma_5$) accepting levels.

**Quantum Yield Determination.** Quantum yields were determined by the optically dilute method using eq. **S1**, where *A* is the absorbance at the excitation wavelength, *I* is the intensity of the excitation light at the same wavelength, *n* is the refractive index and *D* is the integrated luminescence intensity. The subscripts '*x*' and '*r*' refer to the sample and reference respectively.

$$\frac{\Phi_x}{\Phi_r} = \frac{A_r(\lambda_r)}{A_x(\lambda_x)} \frac{I(\lambda_r)}{I(\lambda_x)} \frac{n_x^2}{n_r^2} \frac{D_x}{D_r} \qquad \textbf{(S1)}$$

For quantum yield calculations, excitation wavelengths of 325 nm (for ligand 1) or 345 nm (for ligands 2 and 3) were utilized for both the reference and sample, hence the $I(\lambda_r)/I(\lambda_x)$ term is removed. Similarly, the refractive indices term, $n_x^2/n_r^2$, was taken to be identical for the aqueous reference and sample solutions. Hence, a plot of integrated emission intensity (i.e. $D_r$) versus absorbance at 325 nm or 345 nm (i.e. $A_r(\lambda_r)$) yields a linear plot with a slope which can be equated to the reference quantum yield $\Phi r$. Quinine sulfate in 0.5 M (1.0 *N*) sulfuric acid was used as the reference ($\Phi_r$ = 0.546). By analogy, for the sample, a plot of integrated emission intensity (i.e. $D_x$) versus absorbance at 325 nm (for ligand 1) or 345 nm (for ligands 2 and 3) (i.e. $A_x(\lambda_x)$) yields a linear plot and $\Phi x$ can then be evaluated. The values reported in the manuscript are the average of three independent measurements.

**Triplet Stat Energy Determination.** The Gd(III) complexes of **2** and **3** were prepared *in situ*, to determine the ligand centered triplet excited state energies. Because the $Gd^{3+}$ ion exhibits a size and atomic weight similar to $Eu^{3+}$ but lacks an appropriately positioned electronic acceptor level, the phosphorescence of the ligand can be observed by luminescence measurements in a solid matrix (1:3 (v/v) MeOH:EtOH) at 77 K. Upon cooling to 77 K, the Gd spectra of **2** and **3** revealed intense unstructured emission bands from 450 to 600 nm, assigned to phosphorescence from the ligands $T_1$ excited states. The lowest $T_1$ state energies were estimated by spectral deconvolution of the 77 K luminescence signal into several overlapping Gaussian functions.