Luminescent Sensing and Formation of Mixed $f$-$d$ Metal Ion Complexes Between a Eu(III)-cyclen-phen Conjugate and Cu(II), Fe(II), and Co(II) in Buffered Aqueous Solution

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Electronic Supporting Information

1. Figures

Figure S1. $^1$H NMR spectrum of 1, CDCl$_3$, 400 MHz.
Figure S2. $^1$H NMR spectrum of 1.Eu, D$_2$O, 400 MHz.

Figure S3. ESMS spectrum of 1.Eu, H$_2$O.
**Figure S4.** pH dependence in the absorption spectra of **1.Eu** at 266 nm (blue circles) and at 278 nm (in red).
Figure S5. A) The changes in the fluorescence emission spectra as a function of pH. B) Changes in fluorescence emission at 423 nm as a function of pH upon excitation at 266 nm.
Figure S6. Changes in the ground state of 4 upon pH titration.

Figure S7. Experimental binding isotherm for the UV-visible titration of 1.Eu with Cu(II) at pH 7.4, and the corresponding fit obtained using SPECFIT. Red circles: experimental data, black line: fit.
Figure S8. Speciation diagram for the UV-visible titration of 1.Eu with Cu(II) at pH 7.4.
Figure S9. Changes in the absorption spectra of 1.Eu upon titration with CoCl₂ at pH 7.4. Inset: The changes observed at 247, 266 and 330 nm, respectively as a function of added equivalents of Co(II).

![Absorption spectra and inset](image)

Figure S10. A) Speciation diagram for the UV-visible titration of 1.Eu with Co(II) at pH 7.4. B) The corresponding binding isotherm and fit obtained using SPECFIT. Red circles: experimental data, black line: fit.

![Speciation diagram and binding isotherm](image)
**Figure S11.** **A)** The changes in the fluorescence emission of 1.Eu upon titration with Co(II) at pH 7.4. **B)** The corresponding binding isotherm at 396 nm and fit obtained using SPECFIT.

![Graph A](image1.png) ![Graph B](image2.png)

**Figure S12.** **A)** The changes in the fluorescence emission of 1.Eu upon titration with Fe(II) at pH 7.4. **B)** The corresponding binding isotherm at 396 nm and fit obtained using SPECFIT.

![Graph A](image3.png) ![Graph B](image4.png)
Figure S13. Speciation distribution for the fluorescence titration of 1.Eu with Co(II) at pH 7.4.

Figure S14. Speciation distribution for the fluorescence titration of 1.Eu with Fe(II) at pH 7.4.
Figure S15. **A)** The changes in the Eu(III) emission upon titration with Co(II). *Inset:* the changes in the 595, 616 and 702 nm transitions as a function of added Co(II). **B)** The speciation distribution diagram for the same titration, generated from the results obtained by fitting the changes in the Eu(III) emission using SPECFIT.
2. Tables

**Table S1.** Determination of metal-bound water molecules at different pHs.

<table>
<thead>
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<th>pH</th>
<th>(1/\tau_{\text{H}_2\text{O}}) (ms(^{-1}))</th>
<th>(1/\tau_{\text{D}_2\text{O}}) (ms(^{-1}))</th>
<th>(q) (0.5)</th>
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<td>1.32</td>
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<tr>
<td>10.1</td>
<td>3.709</td>
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</table>

**General experimental for spectrophotometer titrations:**

UV-Vis spectra were recorded on a Varian UV-Vis spectrophotometer. Luminescence spectra were measured on a Varian Cary Eclipse Fluorescence spectrophotometer. Titrations have been carried out by addition of aliquots of metal ions MCl\(_2\) stock solutions: \([\text{CuCl}_2] = 1.08\) mM, \([\text{FeCl}_2] = 0.87\) mM, \([\text{CoCl}_2] = 0.89\) mM, in a 35.8 uM solution of the ligand **Eu** in water at pH 7.4, buffered with 0.1 M HEPES and 0.1 M tetrabutylammonium chloride solution to maintain constant ionic strength.