

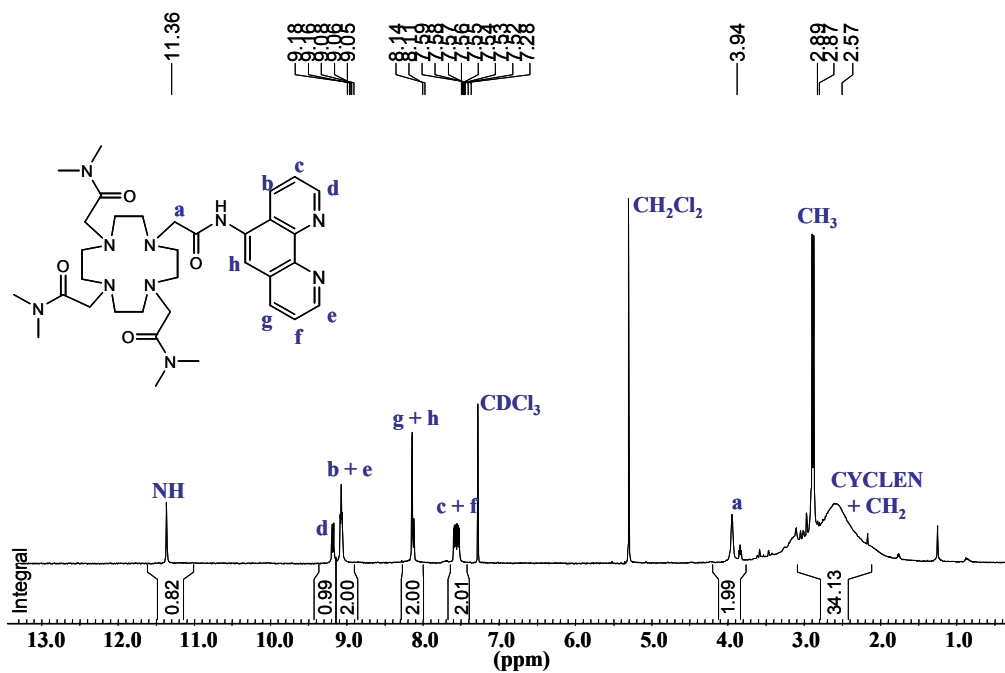
# Luminescent Sensing and Formation of Mixed *f-d* Metal Ion Complexes Between a Eu(III)-cyclen-*phen* Conjugate and Cu(II), Fe(II), and Co(II) in Buffered Aqueous Solution

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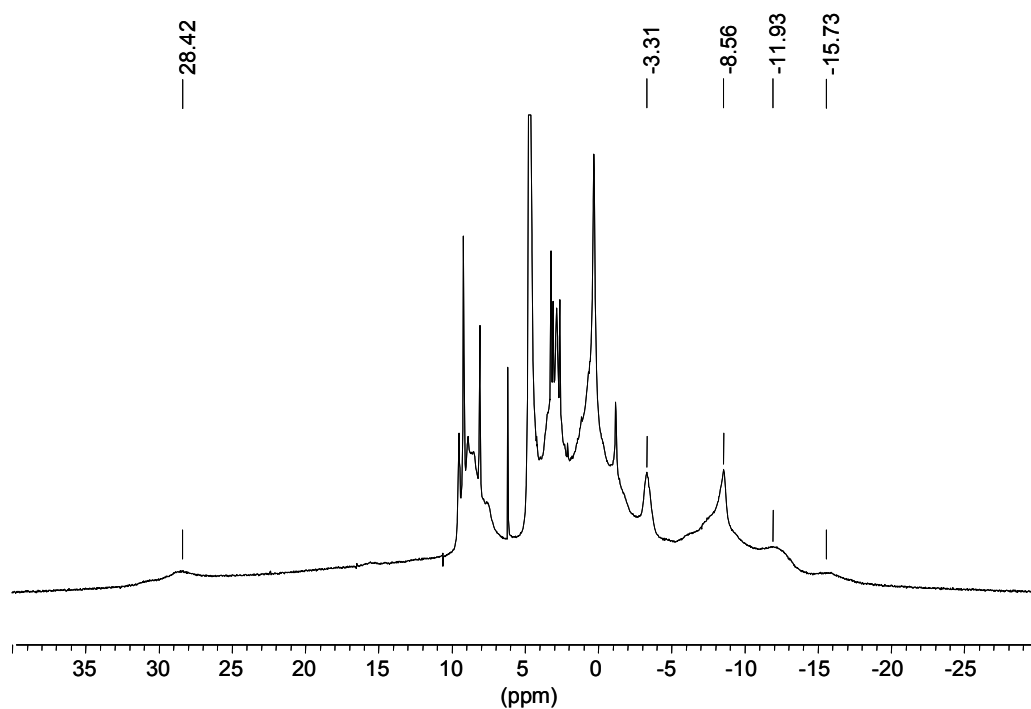
## Electronic Supporting Information

### 1. Figures

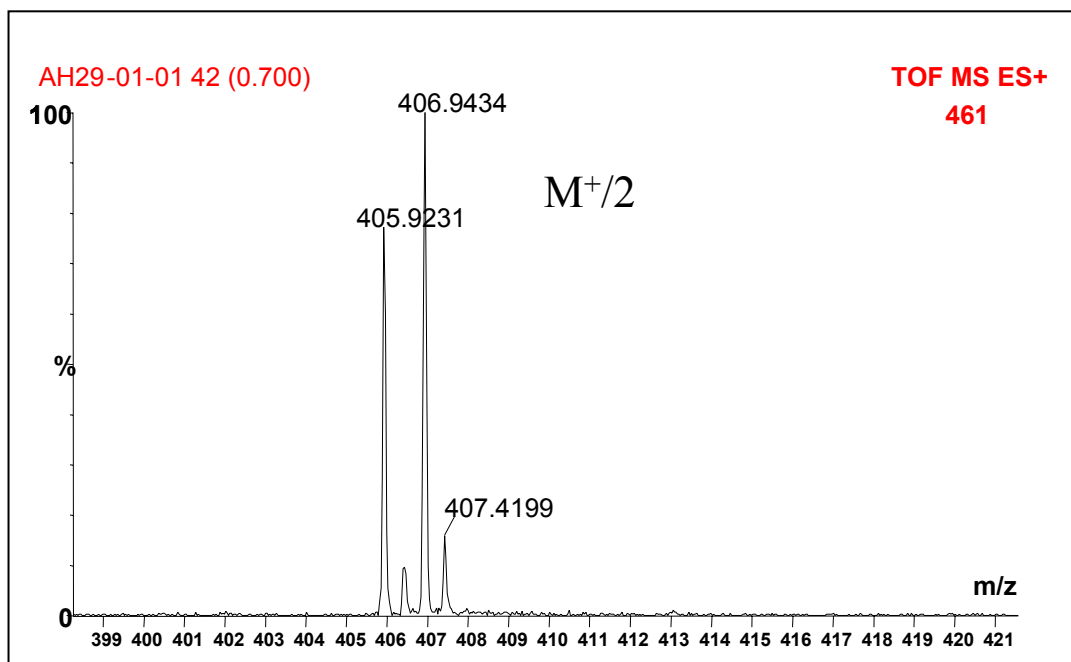
Figure S1. <sup>1</sup>H NMR spectrum of **1**, CDCl<sub>3</sub>, 400 MHz.



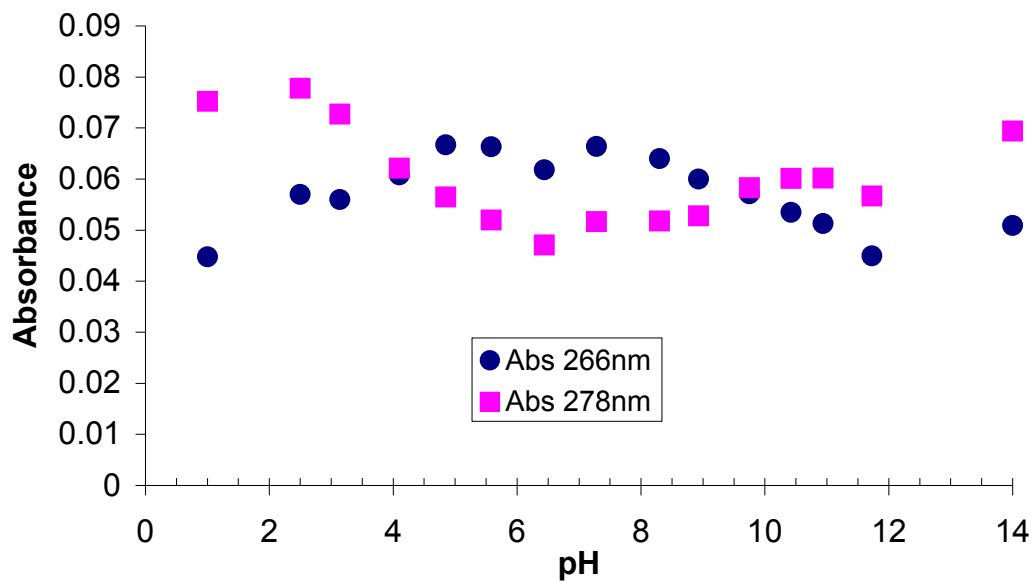
**Figure S2.**  $^1\text{H}$  NMR spectrum of **1.Eu**,  $\text{D}_2\text{O}$ , 400 MHz.



**Figure S3.** ESMS spectrum of **1.Eu**,  $\text{H}_2\text{O}$ .

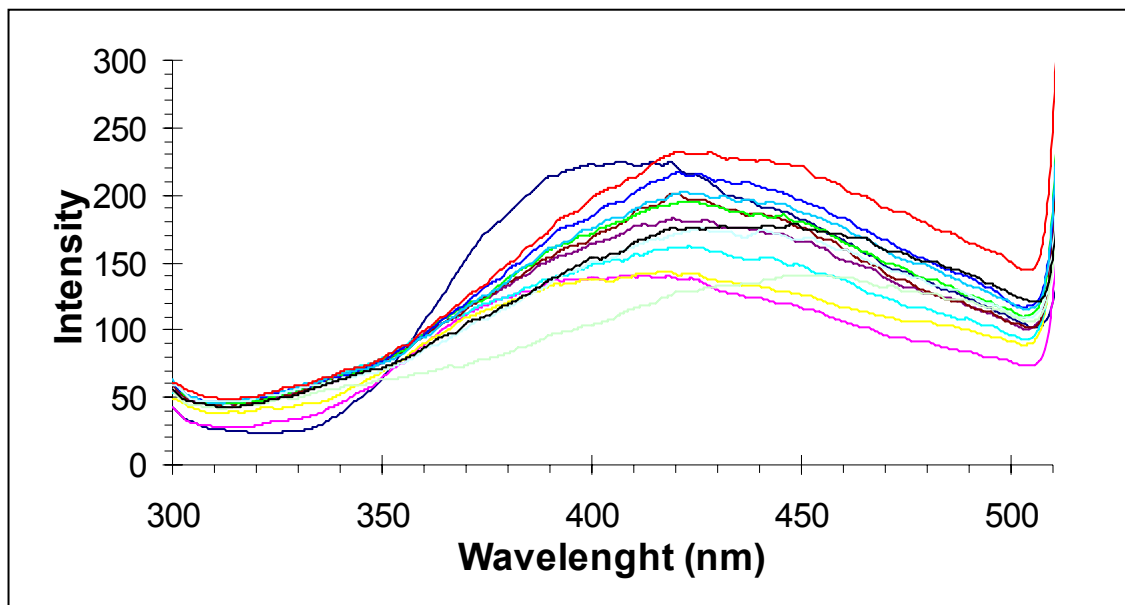


**Figure S4.** pH dependence in the absorption spectra of **1.Eu** at 266 nm (blue circles) and at 278 nm (in red).

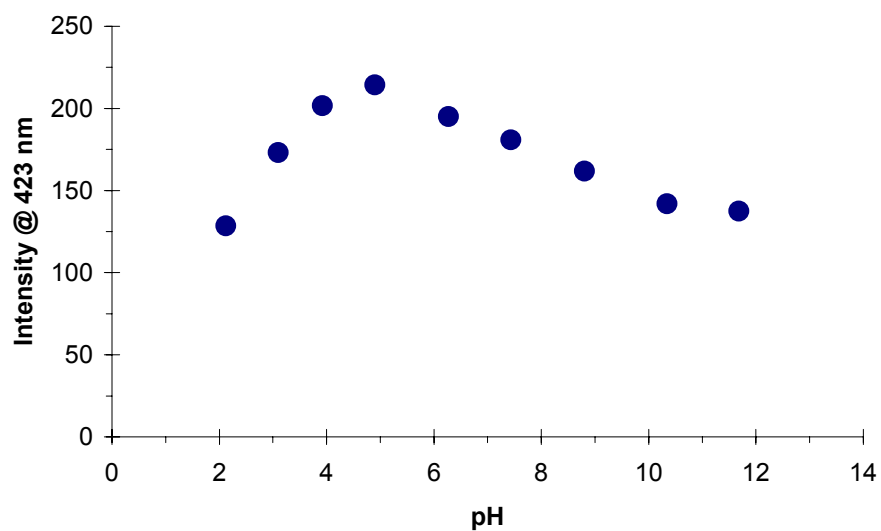


**Figure S5.** A) The changes in the fluorescence emission spectra as a function of pH. B) Changes in fluorescence emission at 423 nm as a function of pH upon excitation at 266 nm.

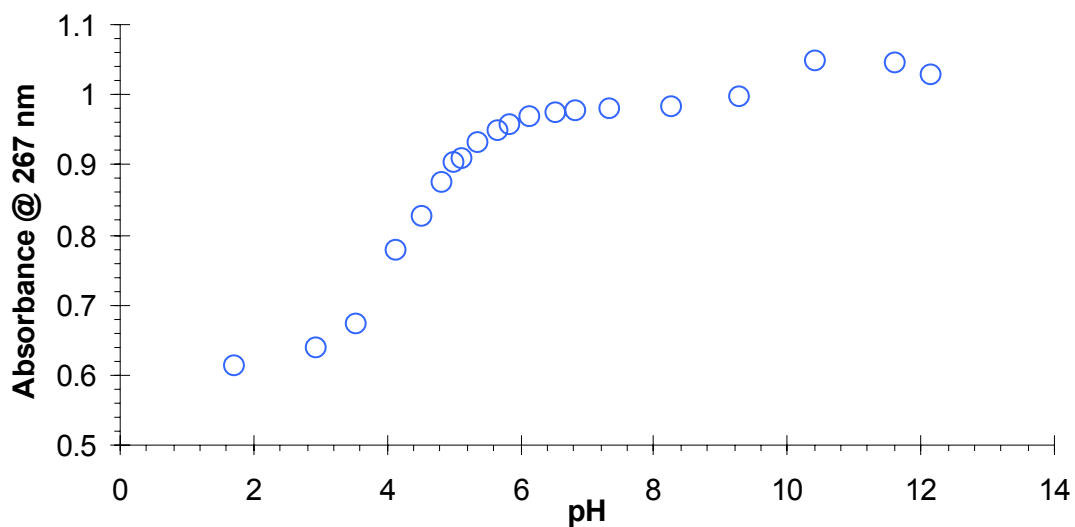
**A**



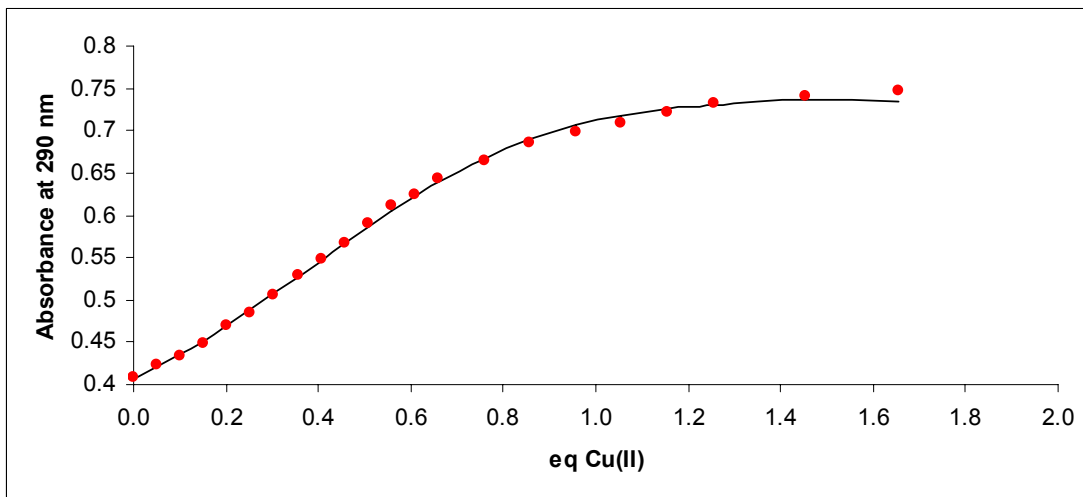
**B**



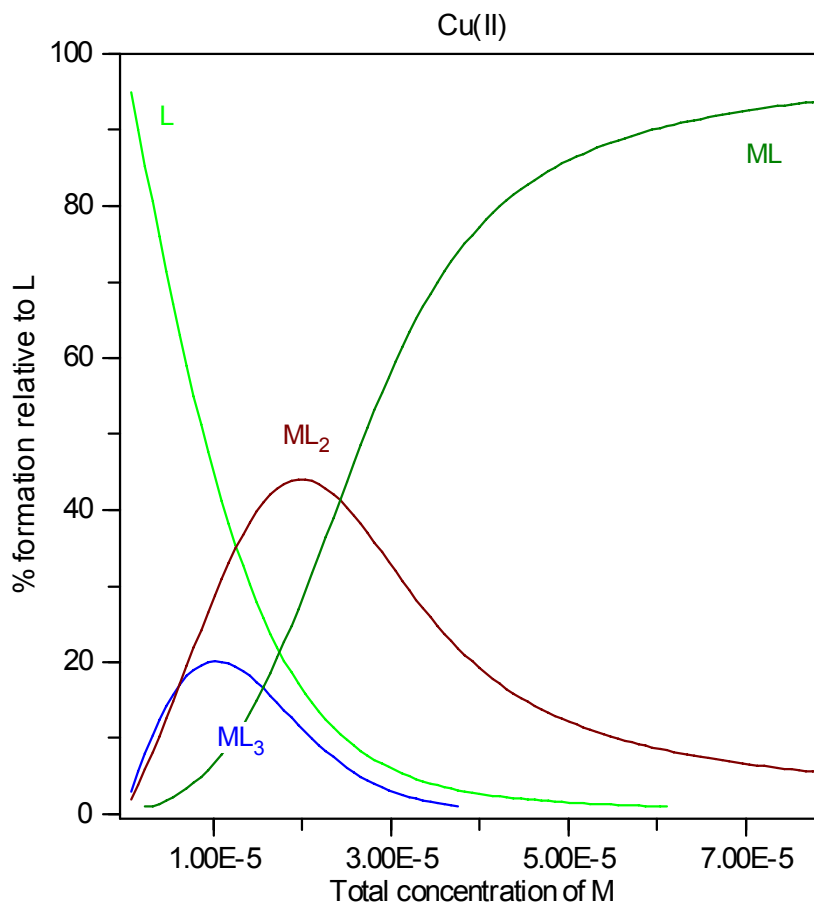
**Figure S6.** Changes in the ground state of **4** upon pH titration.



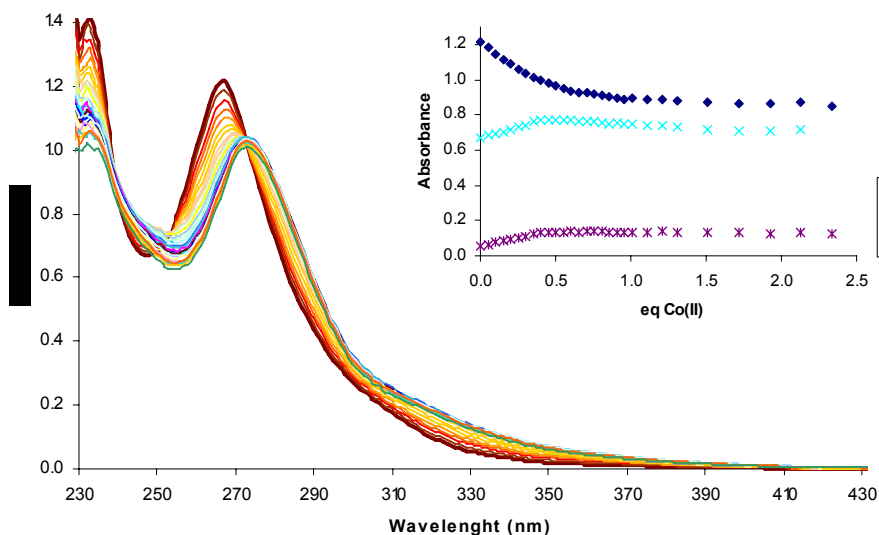
**Figure S7.** Experimental binding isotherm for the UV-visible titration of **1.Eu** with Cu(II) at pH 7.4, and the corresponding fit obtained using SPECFIT. Red circles: experimental data, black line: fit.



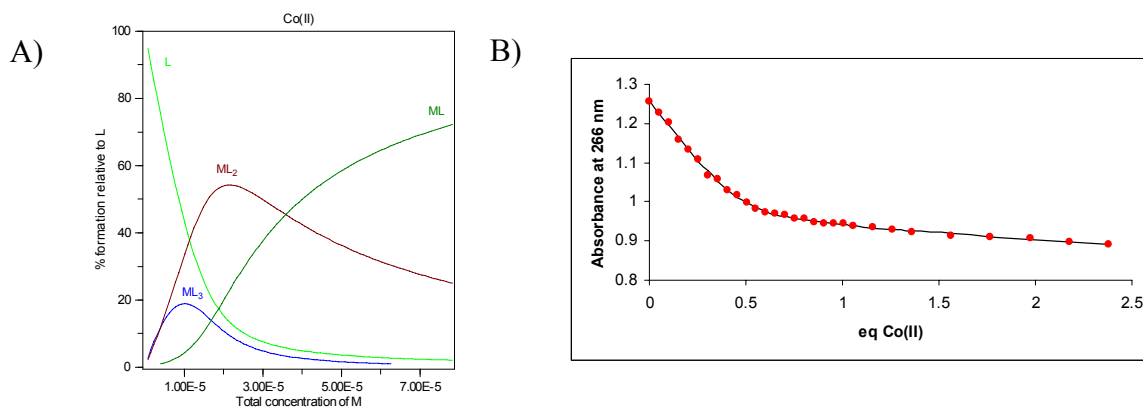
**Figure S8.** Speciation diagram for the UV-visible titration of **1.Eu** with Cu(II) at pH 7.4.



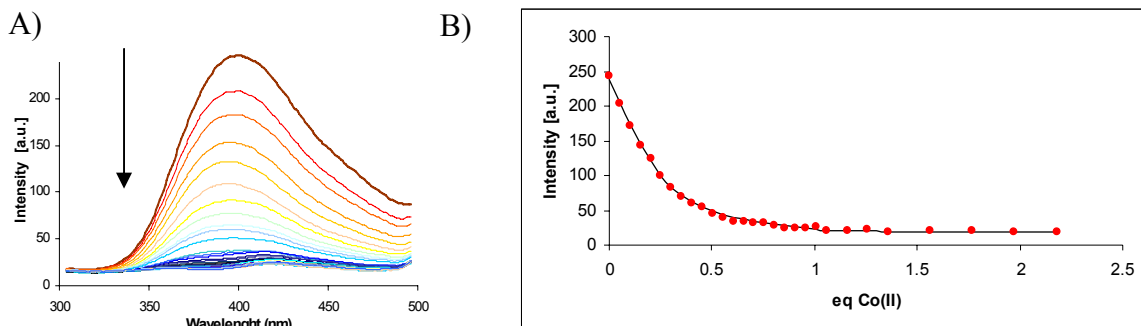
**Figure S9.** Changes in the absorption spectra of **1.Eu** upon titration with  $\text{CoCl}_2$  at pH 7.4. *Inset:* The changes observed at 247, 266 and 330 nm, respectively as a function of added equivalents of  $\text{Co(II)}$ .



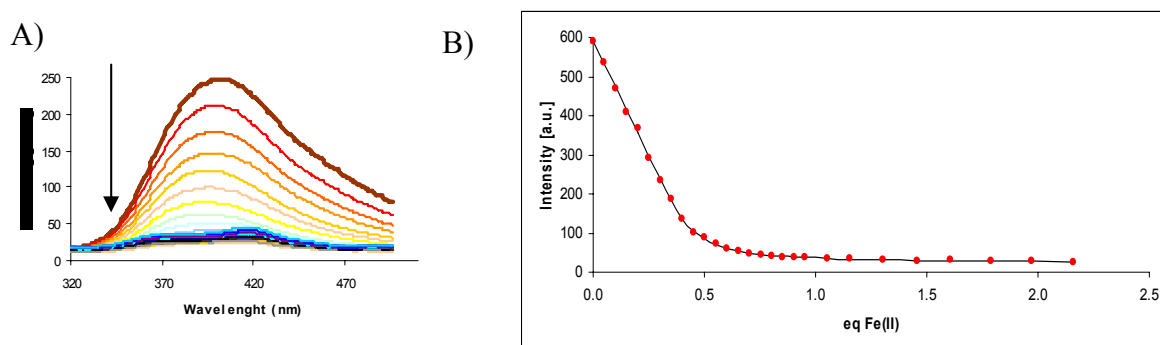
**Figure S10. A)** Speciation diagram for the UV-visible titration of **1.Eu** with  $\text{Co(II)}$  at pH 7.4. **B)** The corresponding binding isotherm and fit obtained using SPECFIT. Red circles: experimental data, black line: fit.



**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.

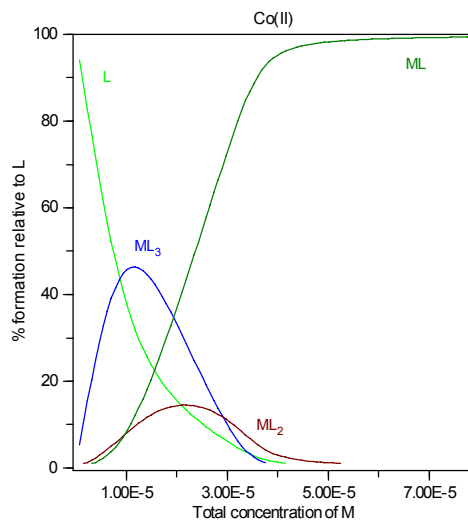


**Figure S12.** **A)** The changes in the fluorescence emission of **1.Eu** upon titration with Fe(II) at pH 7.4. **B)** The corresponding binding isotherm at 396 nm and fit obtained using SPECFIT.

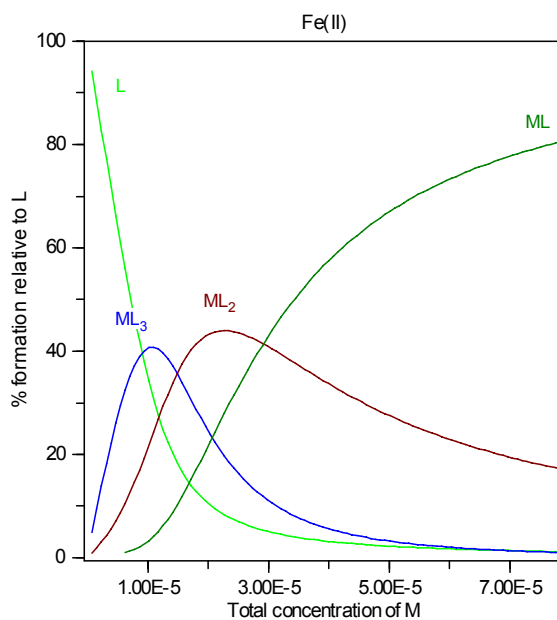




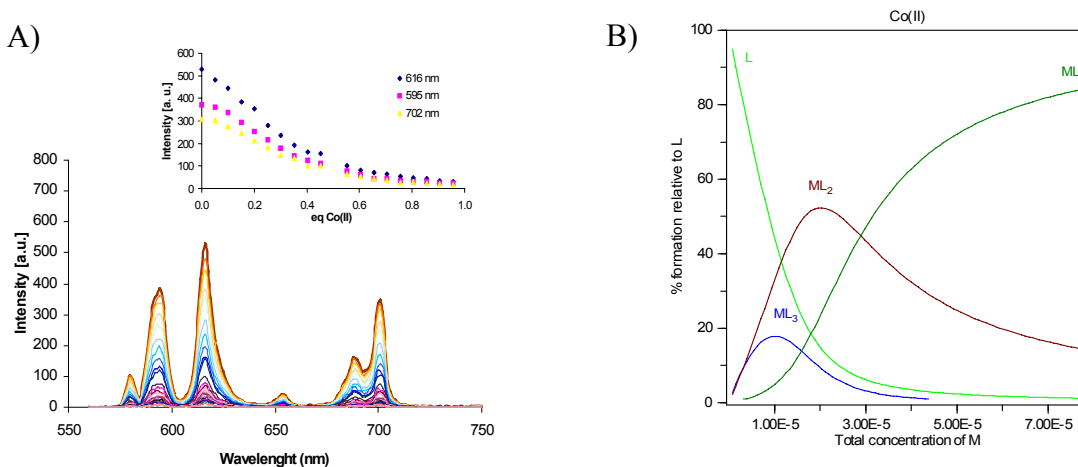
**Figure S13.** Speciation distribution for the fluorescence titration of **1.Eu** with Co(II) at pH 7.4.



**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.

pH	$1/\tau_{\text{H}_2\text{O}}$ ( $\text{ms}^{-1}$ )	$1/\tau_{\text{D}_2\text{O}}$ ( $\text{ms}^{-1}$ )	$q$ (0.5)
1.4	2.320	1.270	0.87
3.0	2.443	1.133	1.18
4.0	2.643	1.554	0.92
5.3	2.559	1.160	1.29
7.1	3.050	1.892	1.00
7.9	3.359	1.930	1.32
10.1	3.709	2.695	0.83

### General experimental for spectrophotometer titrations:

UV-Vis spectra were recorded on a Varian UV-Vis spectrophotometer. Luminescence spectra were measured on a Varian Carey Eclipse Fluorescence spectrophotometer. Titrations have been carried out by addition of aliquots of metal ions MCl<sub>2</sub> stock solutions: [CuCl<sub>2</sub>] = 1.08 mM, [FeCl<sub>2</sub>] = 0.87 mM, [CoCl<sub>2</sub>] = 0.89 mM. in a 35.8  $\mu\text{M}$  solution of the ligand **1.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.