Electronic Supplementary Material (ESI) for Dalton Transactions.


Supplementary data

# A benzimidazole functionalised DO3A chelator showing pH switchable coordination modes with lanthanide ions

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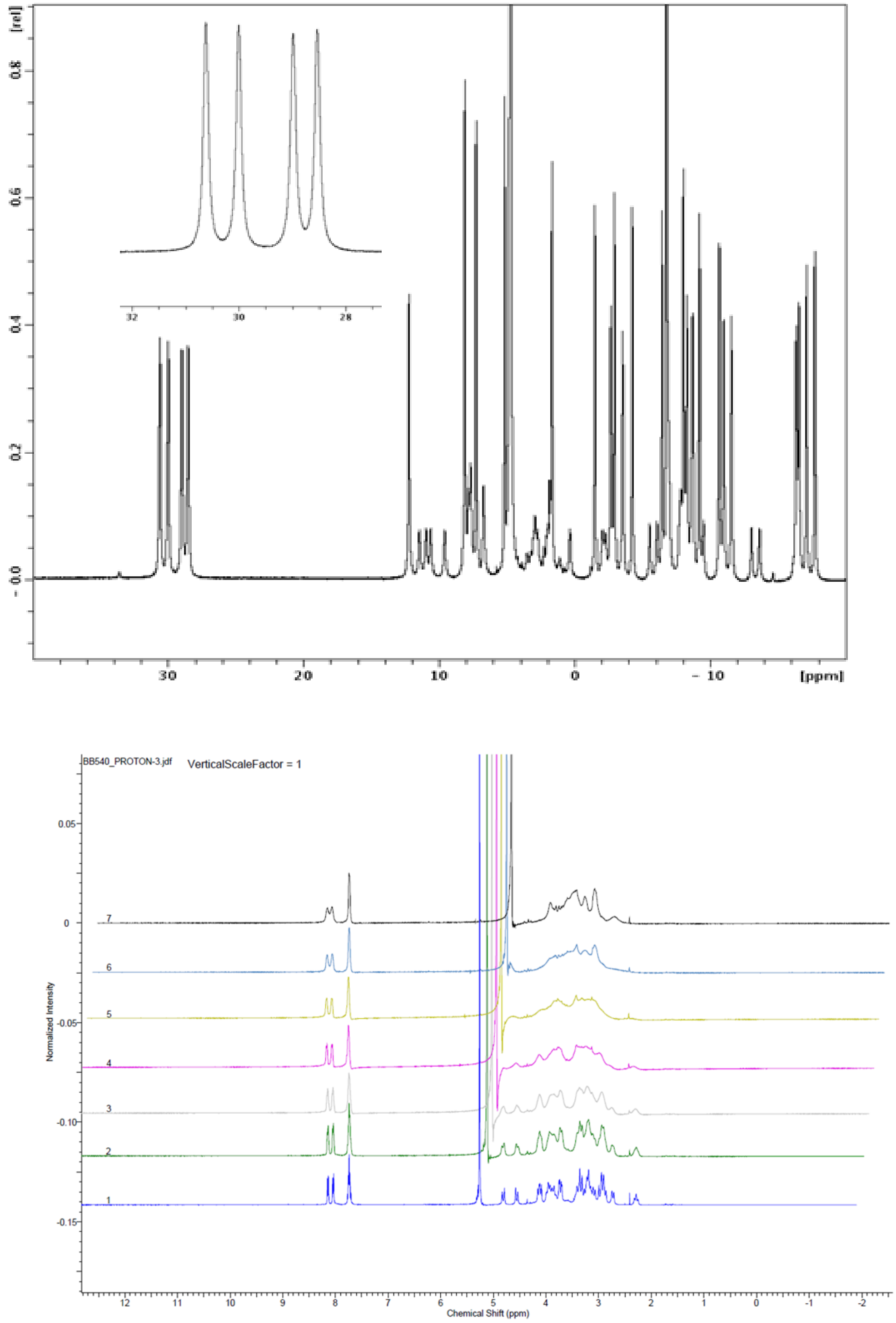



**Figure S1.** 500 MHz $^1$H NMR spectrum of (a) [Eu**2**] in $D_2O$ at room temperature and (b) [Y**2**] in $D_2O$ (variable temperature from 25°C to 85°C in 10°C increments.)

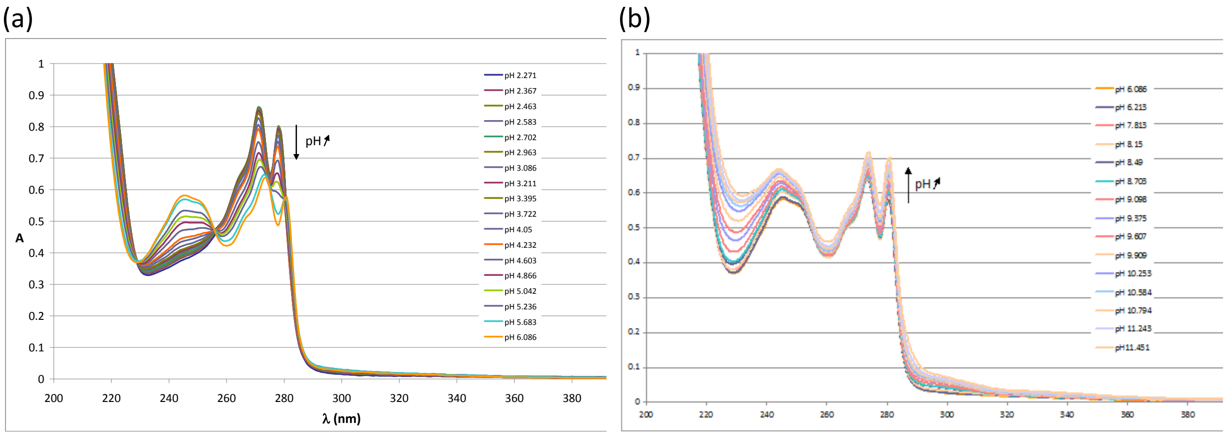



**Figure S2:** UV/vis. spectra of **2** showing spectral change with pH (a) 2<pH<6 and (b) 8<pH<12.

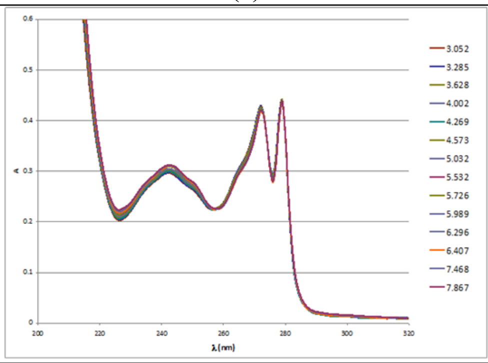
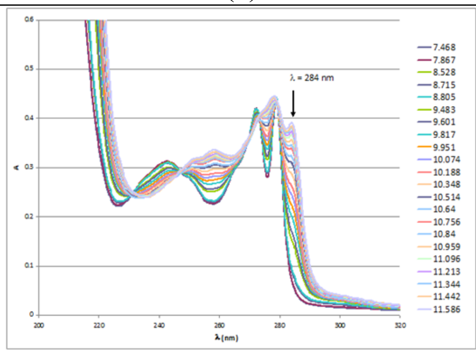
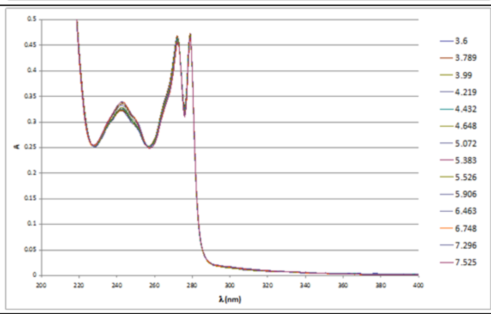
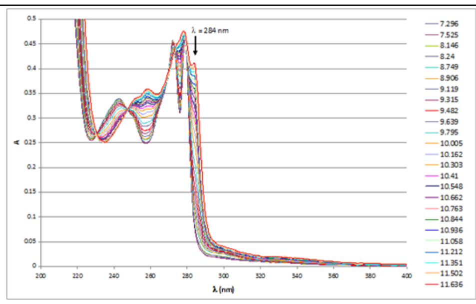
| | (a) | (b) |
|---|---|---|
| [Gd**2**] |  |  |
| [Eu**2**] |  |  |

**Figure S3:** UV/vis. spectra of [Gd**2**] and [Eu**2**] showing spectral change with pH (a) 2<pH<7.5 and (b) 7.5<pH<12.

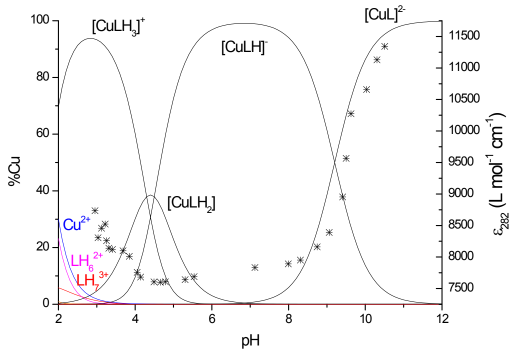
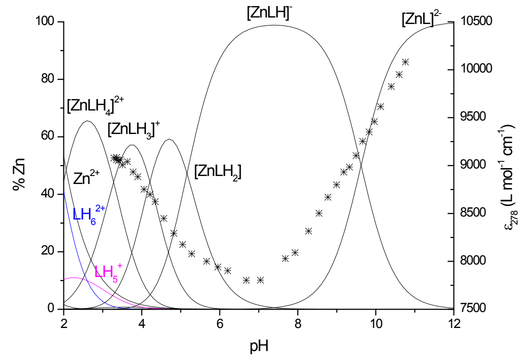
| | |
|---|---|
|  |  |
| $LH_4$ and $Cu^{2+}$ | $LH_4$ and $Zn^{2+}$ |

**Figure S4:** Speciation plots for copper(II) and zinc (II) with **2**. The variation of spectral intensity at 282 or 278 nm is shown.

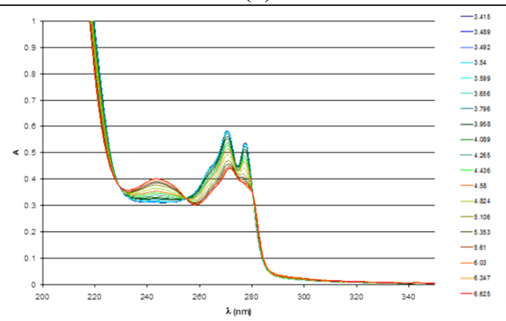
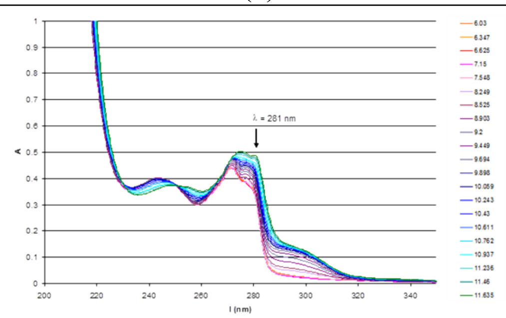
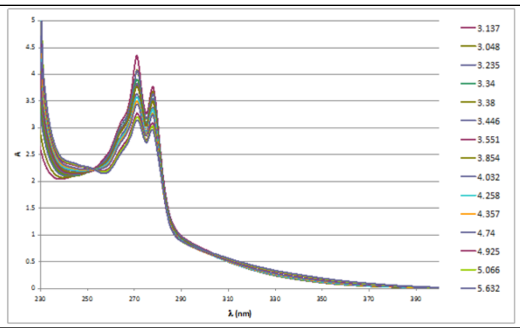
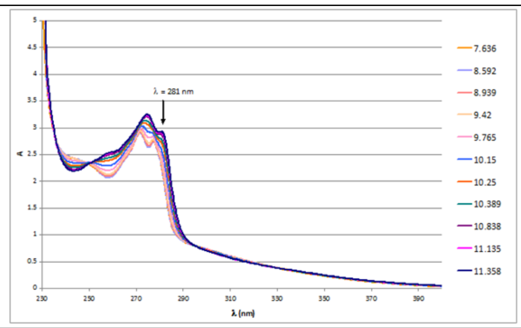
| | (a) | (b) |
|---|---|---|
| [Zn**2**] |  |  |
| [Cu**2**] |  |  |

**Figure S5:** UV/vis. spectra of [Zn**2**] and [Cu**2**] showing spectral change with pH (a) 2<pH<7.5 and (b) 7.5<pH<12.

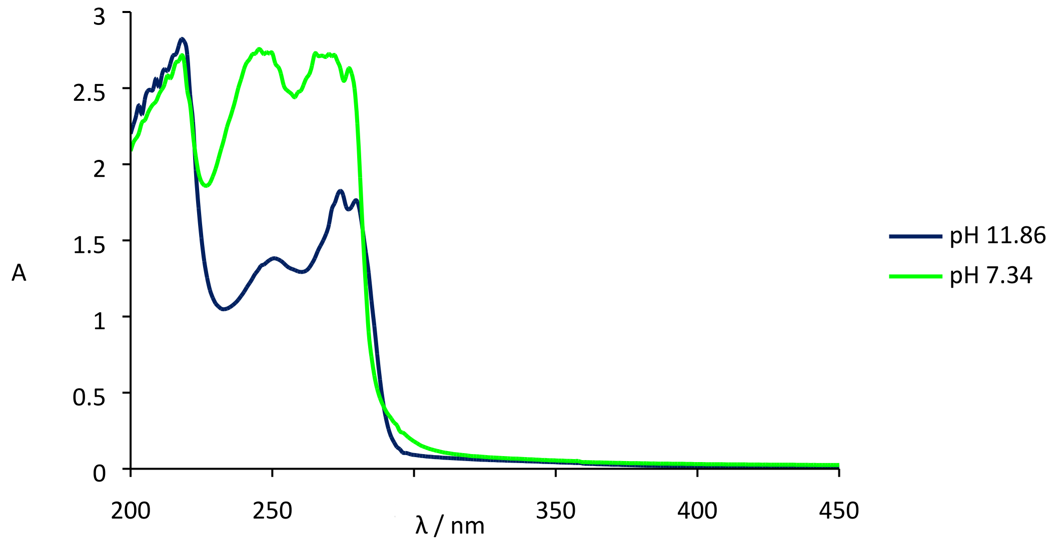



**Figure S6.** UV/Vis spectrum of [Eu**2**] above and below the $pK_a$ value of 9.28

**Table S1** Deprotonation constants of the protonated complexes

| $pK_{MLH}$ | *Cu* | *Zn* | *Gd* | *Eu* |
|---|---|---|---|---|
| $MLH_4$ = $MLH_3$ + H | - | 3.3 | - | - |
| $MLH_3$ = $MLH_2$ + H | 4.3 | 4.2 | - | - |
| $MLH_2$ = MLH + H | 4.5 | 5.2 | 3 | 4.1 |
| MLH = ML + H | 9.2 | 9.6 | 8.4 | 9.3 |

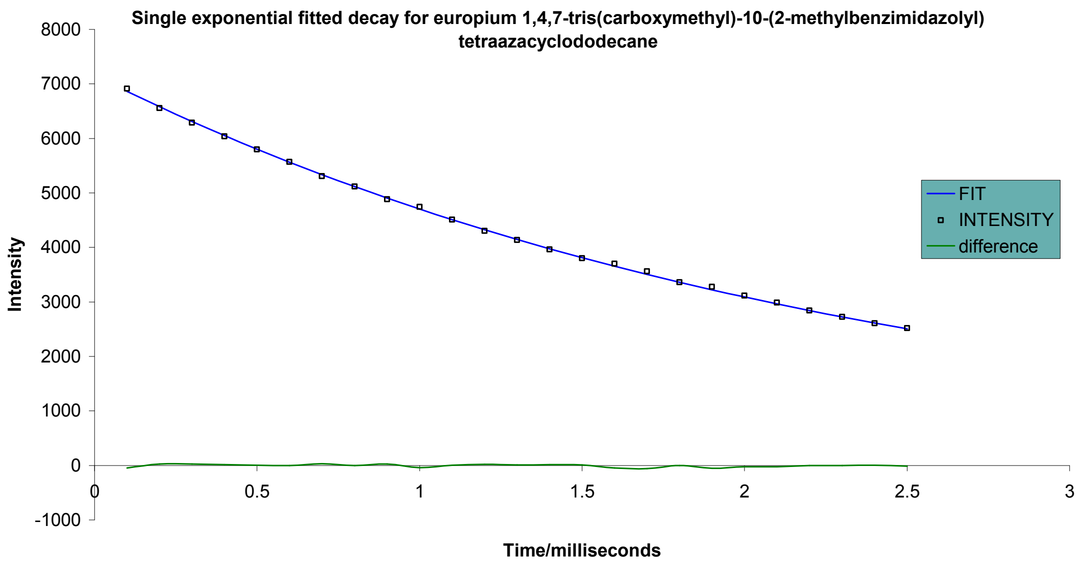



**Figure S7**. Fitted decay for the emission from [Eu**2**] in $D_2O$ ($\lambda_{exc}$ = 272 nm, $\lambda_{em}$ = 615 nm).

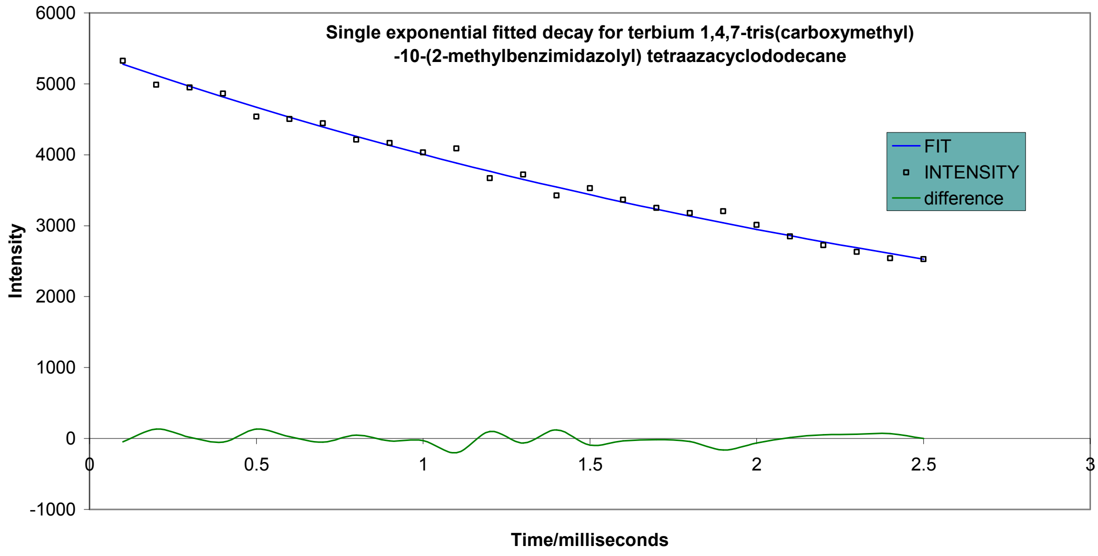



**Figure S8.** Fitted decay for the emission from [Tb**2**] in $D_2O$ ($\lambda_{exc}$ = 272 nm, $\lambda_{em}$ = 545 nm).

**Equations S1 to S3:** Calculating *q* values for europium(II), terbium(III) and ytterbium(III) complexes.

$q^{Eu} = 1.2(1/\tau H_2O - 1/\tau D_2O - 0.25)$ Eqn. S1

$q^{Tb} = 5(1/\tau H_2O - 1/\tau D_2O - 0.06)$ Eqn. S2

$q^{Yb} = 1(1/\tau H_2O - 1/\tau D_2O - 0.1)$ Eqn. S3

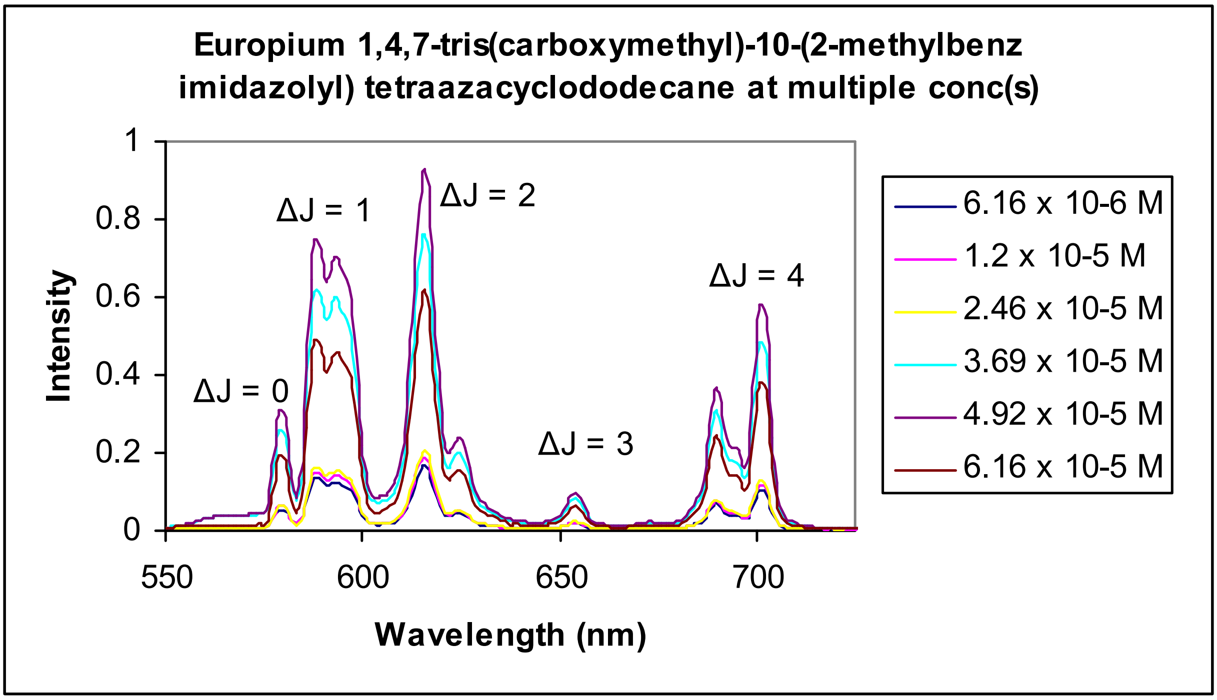



**Figure S9.** Emission spectra for [Eu**2**] at various concentrations in aqueous solution, spectra are shown uncorrected. Emission spectra were obtained using $\lambda_{exc}$ = 272 nm.

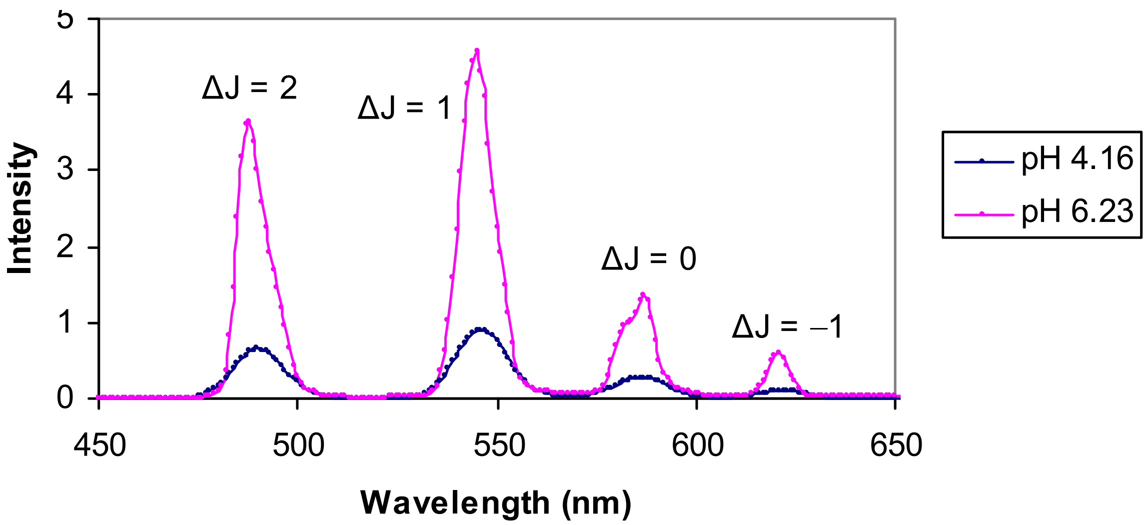



**Figure S10.** Emission spectra for [Tb**2]** in aqueous solution, spectra are shown uncorrected.

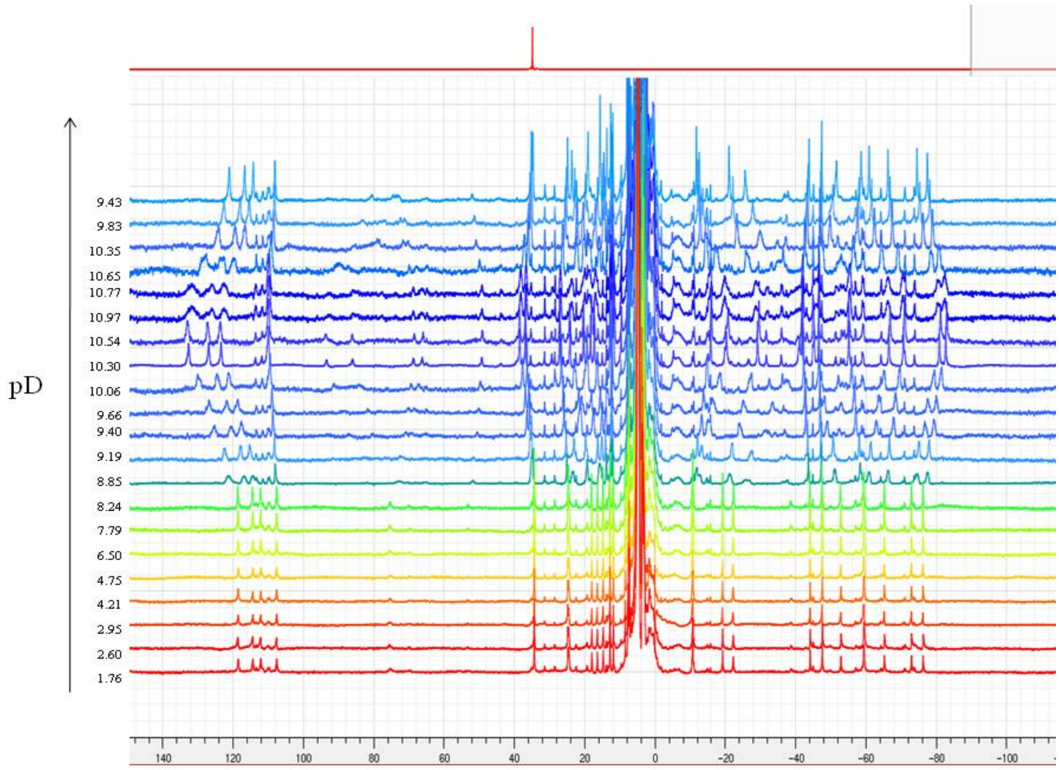



**Figure S11 .** Full stacked plot showing the pD dependence of the $^{1}$H NMR spectrum of (300 MHz) [Yb**2**] at 293K, note the irreversible behaviour as the pD is raised to pD 11, then lowered to pD 2.

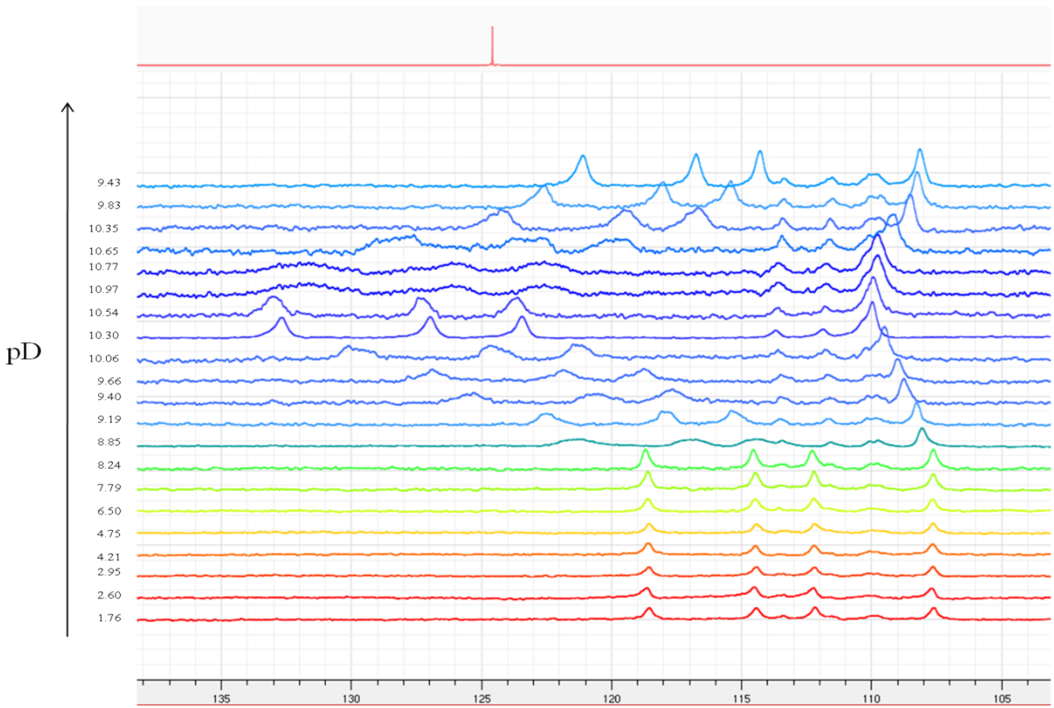



**Figure S12**. Expansion of the 130 – 100 ppm region of the spectra of [Yb**2**] showing a dependence of the axial proton resonances on the pD.

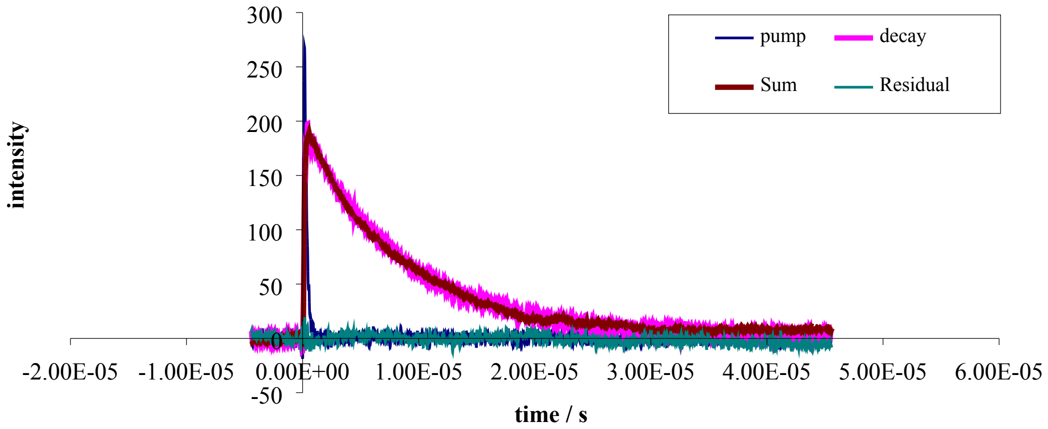



**Figure S13.** Plot of the luminescence lifetime of [Yb**2**] in $CD_3OD$.

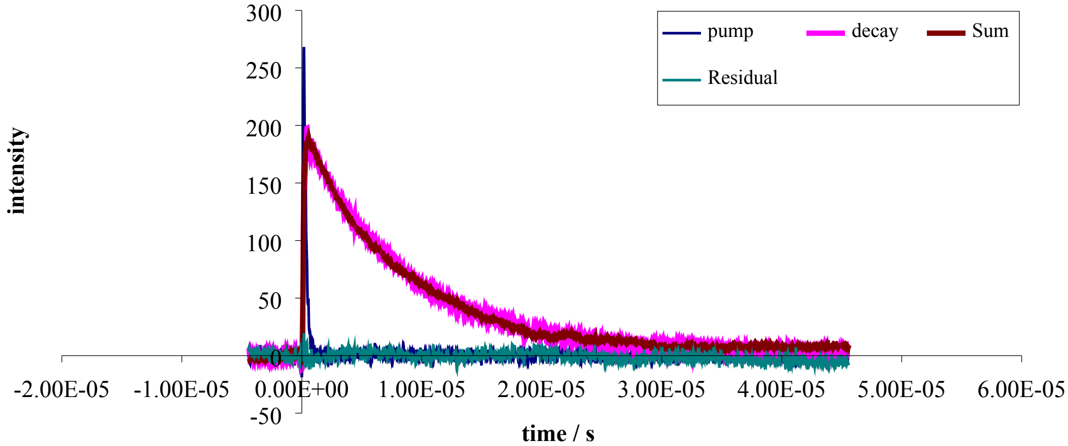



**Figure S14.** Plot of the luminescence lifetime of [Yb**2**] in $CH_3OH$.

| Solvent | Lifetime / µs |
|---|---|
| $CD_3OD$ | 6.8 |
| $CH_3OH$ | 2.3 |

**Table S2** Luminescence lifetimes of [Yb**2**] in methanol.