Synthesis and characterization of luminescent lanthanide complexes for directed uptake via the mannose receptor

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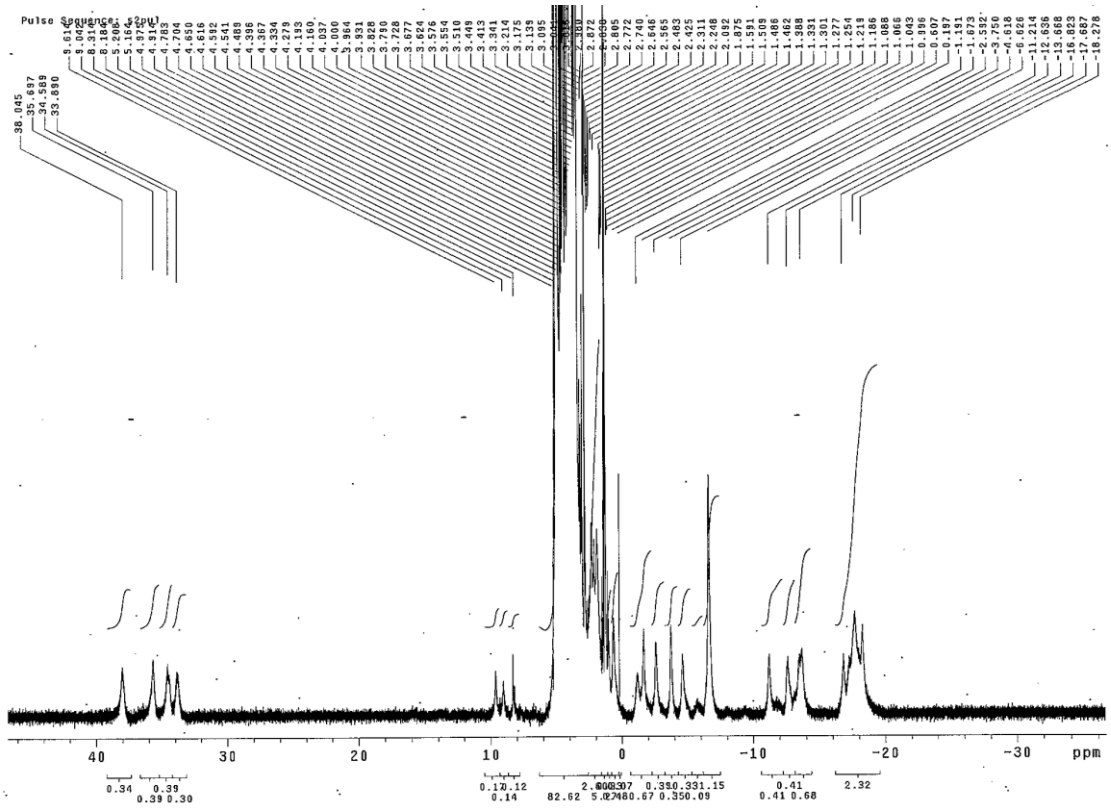
Supplementary Information

Nuclear Magnetic Resonance

NMR spectra of complexes **1** – **4** as shown in **Supplementary Figures 1** – **4** respectively, were obtained using a 300MHz NMR spectrometer in either Methanol-D_4 or Deuterium oxide.



Supplementary Figure 1: NMR spectrum of complex **1** in CD_3OD

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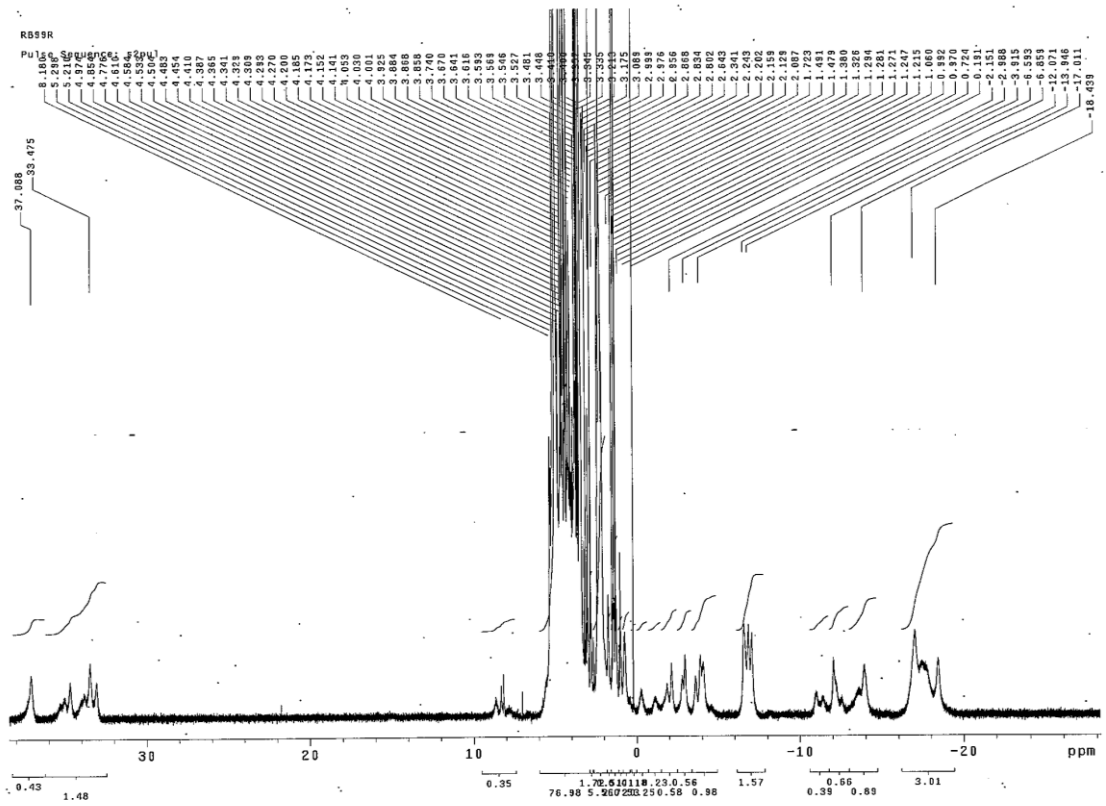
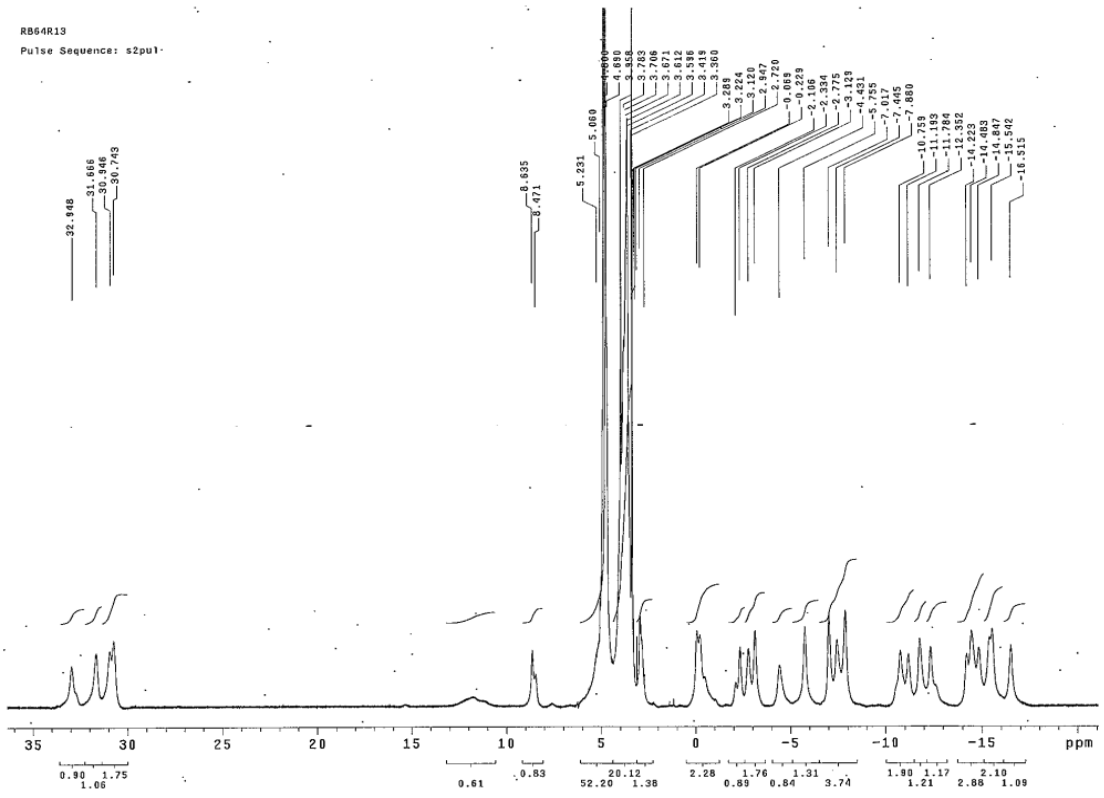
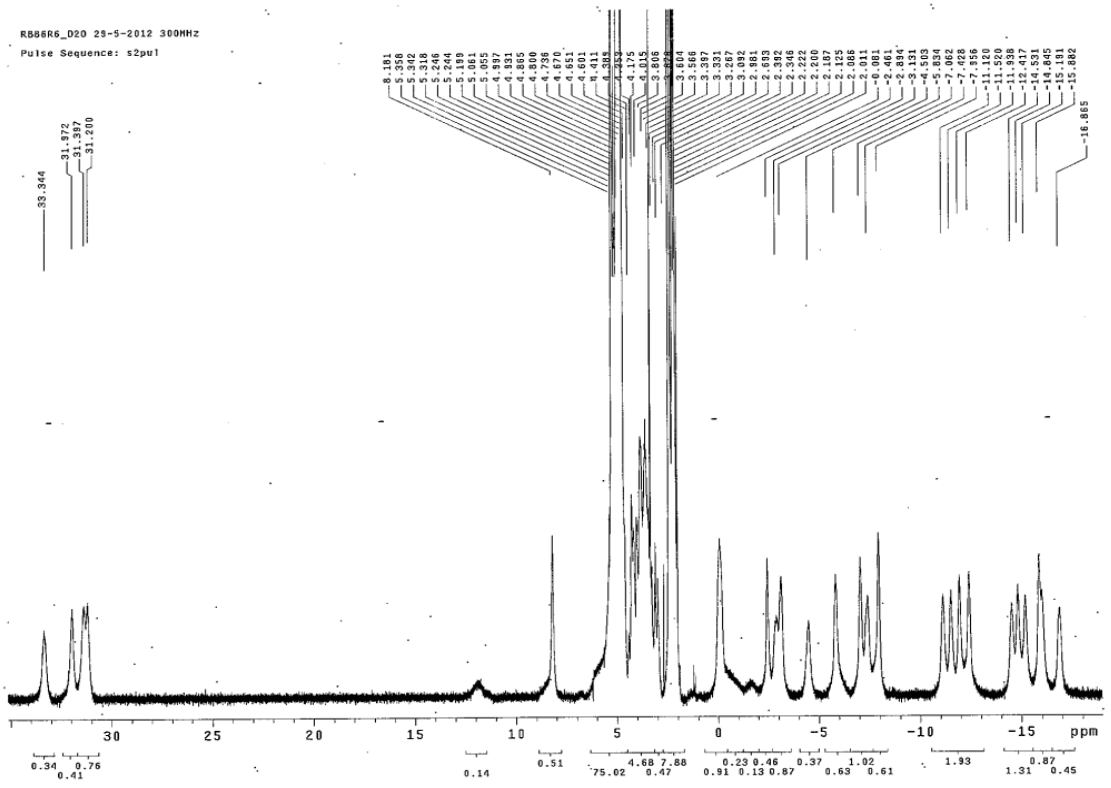


Supplementary Figure 2: NMR spectrum of complex **2** in CD_3OD



Supplementary Figure 3: NMR spectrum of complex **3** in D_2O

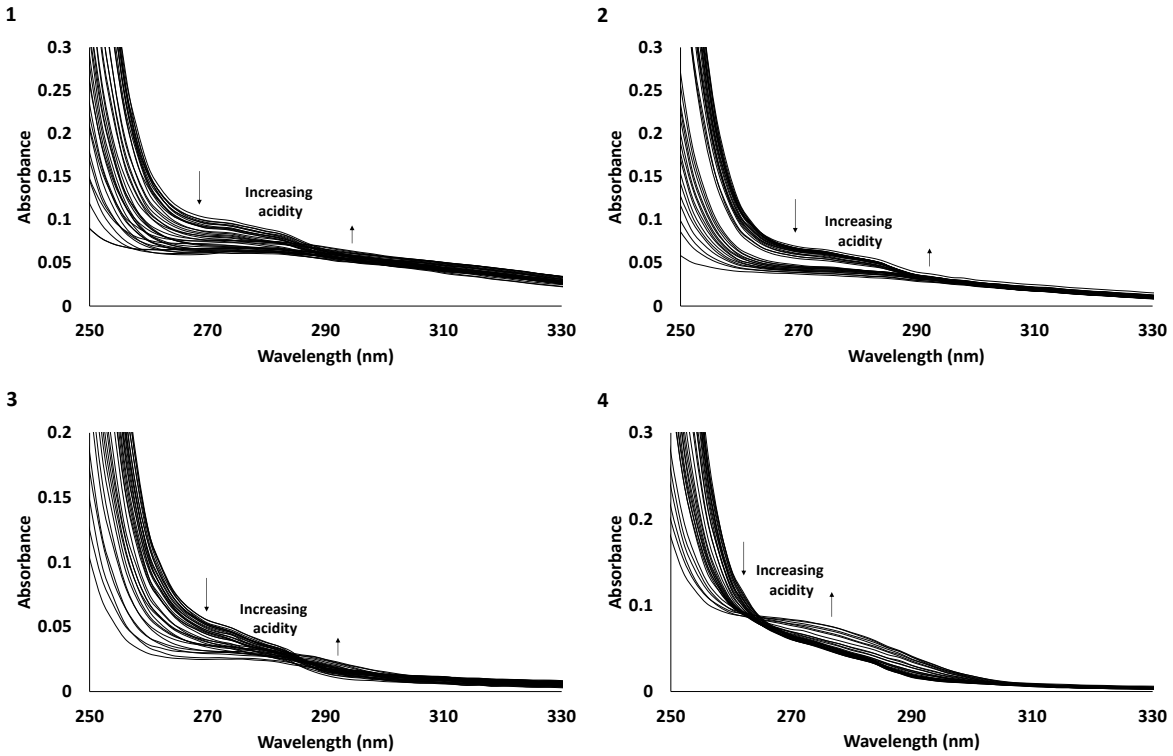


Supplementary Figure 4: NMR spectrum of complex **4** in D_2O

UV-Visible, fluorescence and phosphorescence measurements

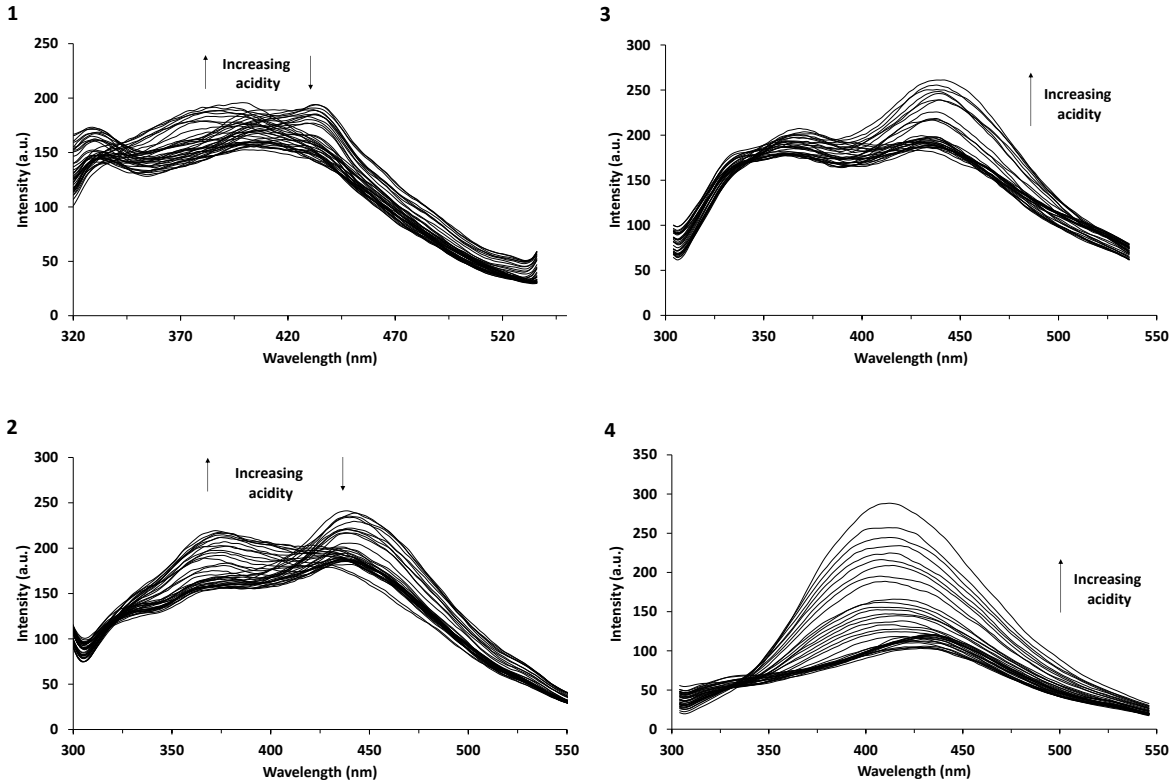
UV-Visible measurements were conducted using a Varian UV-Visible spectrophotometer. Fluorescence and phosphorescence measurements were conducted with a CaryEclipse Fluriometer. A dilute solution of the protonated complex (5 x 10^{-5} M) in water with constant ionic strength (I = 0.1 M using NaCl) was titrated against NaOH. UV-Visible absorption spectra of complexes **1 - 4** (**Supplementary Figure 5**) were recorded over the range of 200-450 nm. Using excitation at 260 nm, fluorescent measurements for complexes **1 - 4** (**Supplementary Figure 6**) were recorded over the range of 300 - 550 nm and phosphorescent measurements (**Supplementary Figure 7**) over the range of 550 - 750 nm.

UV-Visible Spectra



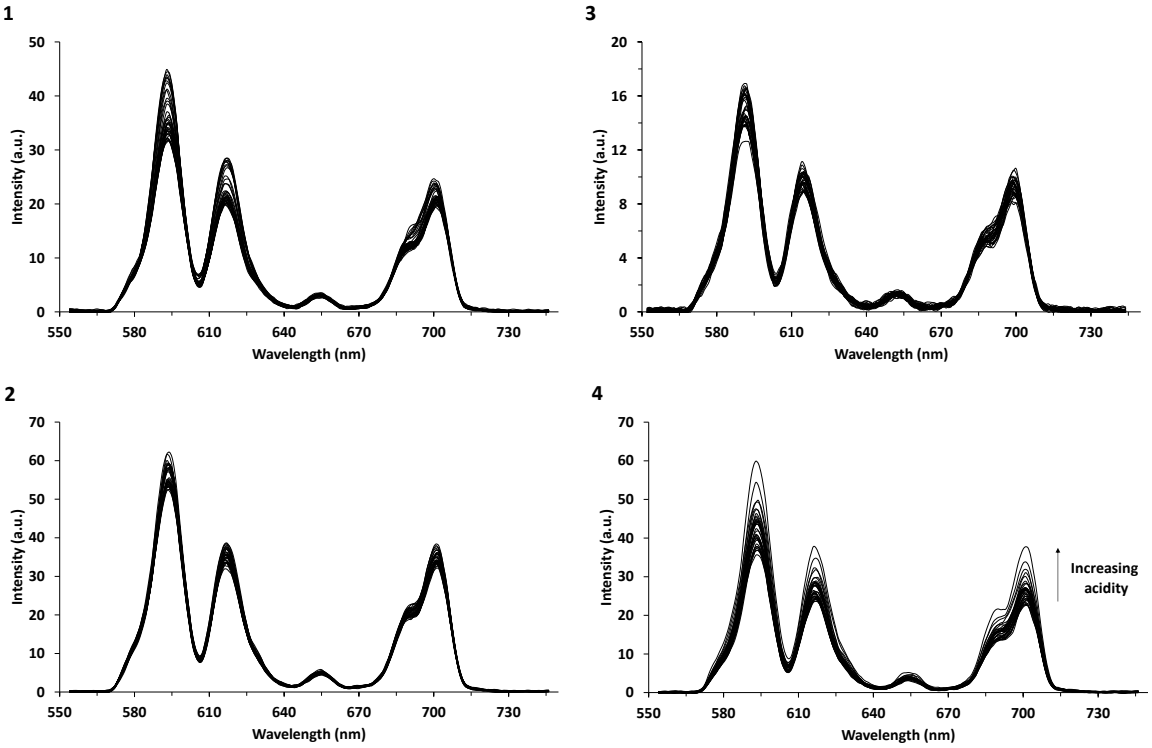
Supplementary Figure 5: UV-Visible absorption spectra of complexes **1** – **4** over the pH range of 2 - 10.

Fluorescence Spectra



Supplementary Figure 6: Fluorescence spectra of complexes **1 - 4** over the pH range of 2 - 10.

Phosphorescence Spectra



Supplementary Figure 7: Phosphorescent spectra of complexes **1** - **4** over the pH range of 2 - 10.

Lifetime measurements and Q-values at varying pH

Luminescent lifetimes of complexes **1 – 4** (**Supplementary Table 2**) were recorded with a CaryEclipse Fluriometer using the settings shown in **Supplementary Table 1**.

Excitation wavelength	Emission wavelength	Number of Flashes	Excitation slit width	Emission slit width	Delay	Gate	PMT voltage	Total Decay
260 nm	592 nm	1	10 nm	10 nm	0.1 ms	0.01 ms	High	3 ms

Supplementary Table 1: General settings employed for Europium(III) lifetime studies using a CaryEclipse Fluorimeter.

Complex	pH	τ_{H_2O} / nm	τ_{D_2O} / nm	Q-value
1	2.8	0.580	1.852	**0.97**
1	6.8	0.571	1.462	**0.84**
1	10.5	0.648	2.291	**0.88**
2	2.5	0.589	1.814	**0.93**
2	6.6	0.589	1.804	**0.94**
2	10.6	0.626	2.204	**0.93**
3	2.7	0.624	2.009	**0.88**
3	6.8	0.603	2.091	**0.97**
3	10.2	0.631	2.107	**0.89**
4	2.7	0.685	2.108	**0.75**
4	6.8	0.593	2.038	**0.99**
4	10.1	0.636	2.220	**0.90**

Supplementary Table 2: Luminescent lifetimes of complexes **1** - **4** in water and deuterium oxide at different pH.