Supporting Information for:

New polyaminocarboxylate macrocycles containing phenolate binding units: synthesis, luminescent and relaxometric properties of their lanthanide complexes

Morgane Enel,[a,b] Nadine Leygue,[a,b] Stéphane Balayssac,[a,b] Sophie Laurent,[c,d] Chantal Galaup,*[a,b] Luce Vander Elst*[c,d] and Claude Picard*[a,b]

[a]CNRS; Laboratoire de Synthèse et Physico-Chimie de Molécules d'Intérêt Biologique, SPCMIB, UMR-5068; 118 Route de Narbonne, F-31062 Toulouse cedex 9, France.

[b]Université de Toulouse; UPS, Laboratoire de Synthèse et Physico-Chimie de Molécules d'Intérêt Biologique, SPCMIB; 118 route de Narbonne, F-31062 Toulouse cedex 9, France.

[c]NMR and Molecular Imaging Laboratory, Department of General, Organic and Biomedical Chemistry, University of Mons, 23 Place du Parc, B-7000 Mons, Belgium.

[d]Center for Microscopy and Molecular Imaging (CMMI), Rue Adrienne Bolland, 8, B-6041 Gosselies, Belgium

E-mail: galaup@chimie.ups-tlse.fr (CG), luce.vanderelst@umons.ac.be (LVE), picard@chimie.ups-tlse.fr (CP),

Table of contents Page

DOSY experiments

In 2D DOSY ^{1}H NMR experiments, the acquisition parameters were as follows: 32K data points, acquisition time 2.04 s, spectral width 16 ppm, number of scans 16, relaxation delay 2 s, pulse field gradient length 1.5 ms and recovery delay 3 ms, diffusion time 100 ms and LED 50 ms. The spoiler gradients were 0.6 ms long with a field strength of -9.26 and -7.12 $G.cm^{-1}$. Forty experiments were recorded with gradient intensity linearly sampled from 5 to 95%. The gradient system was calibrated to 54.1 $G.cm^{-1}$ at maximum intensity. Data were then processed using Gifa 5.2 software with the inverse Laplace Transform method using the Maximum Entropy (MaxEnt) algorithm. The processing parameters were 2048 points along the Laplace spectrum diffusion axis and 20000 MaxEnt iterations. The inverse Laplace Transform was computed only on the columns presenting a signal 32 times greater than the noise level of the experiment. DOSY spectra are presented with chemical shifts on the horizontal axis and diffusion coefficients expressed in $\mu m^2.s^{-1}$ on the vertical axis. Experiment was analyzed with the NMRnotebook software (NMRTEC).

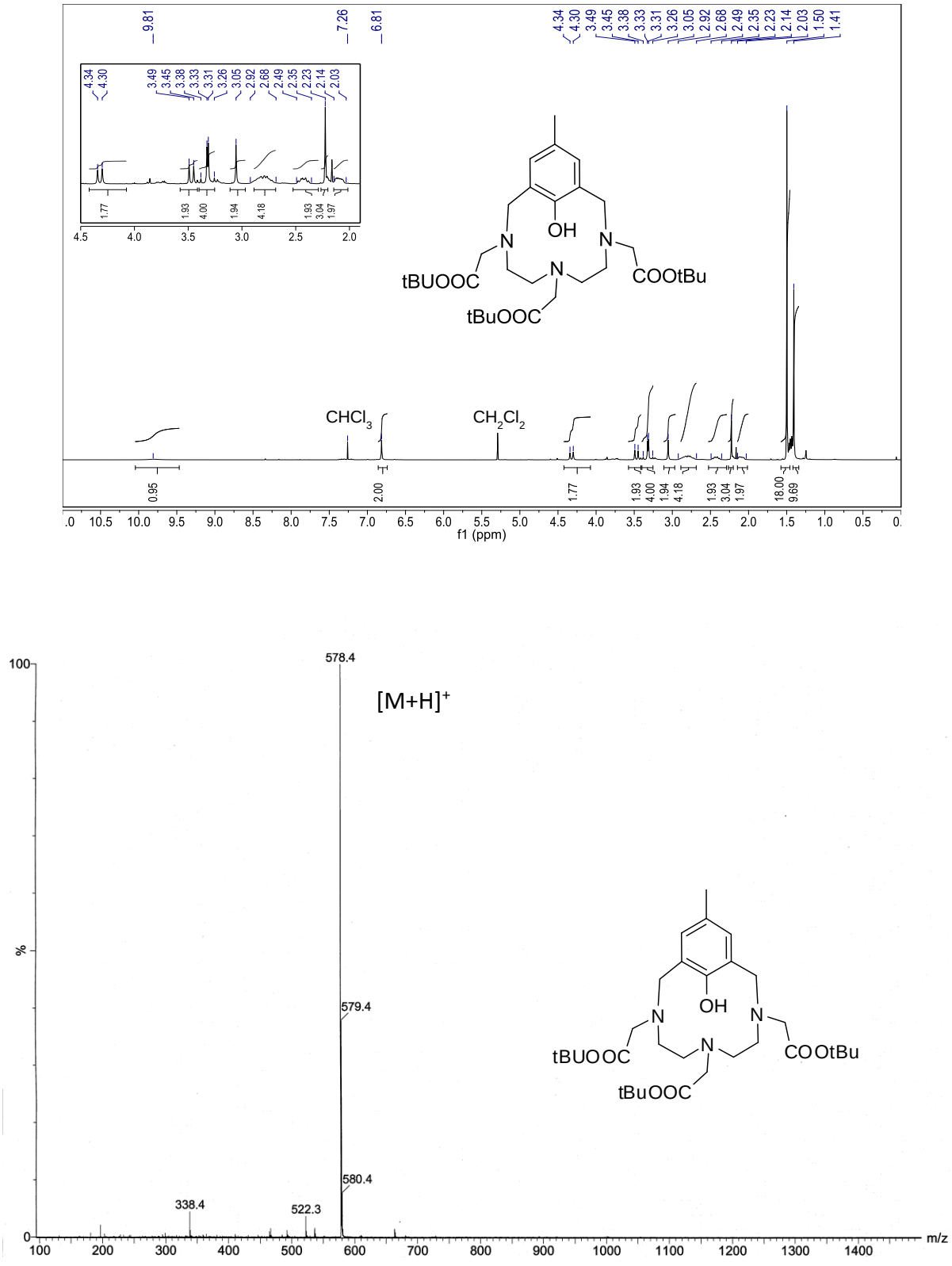
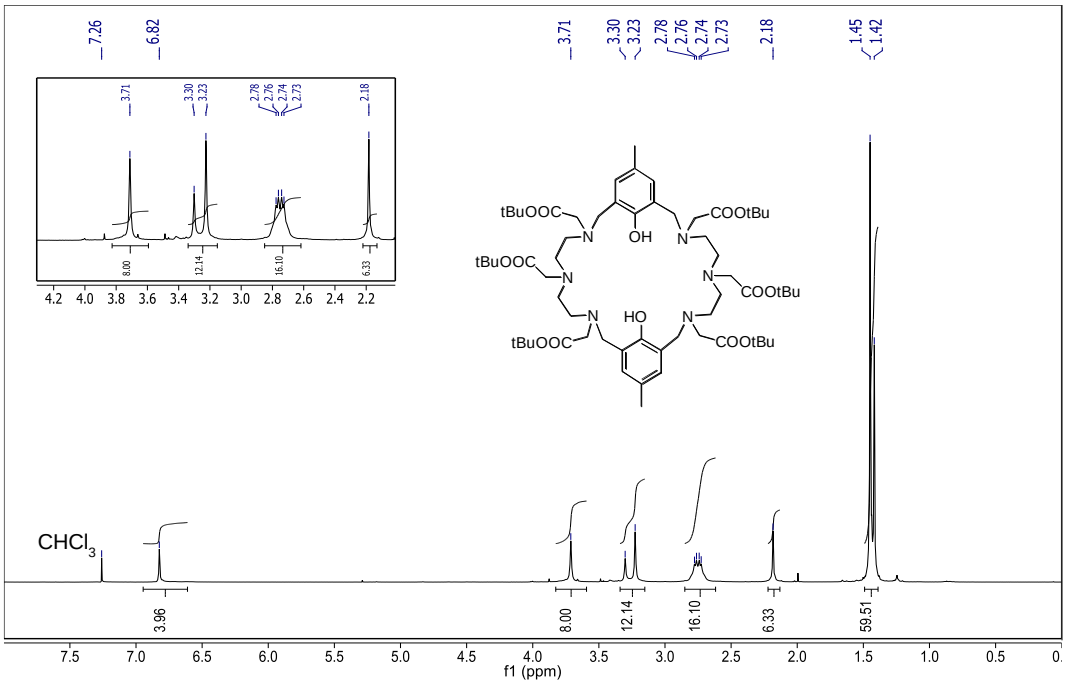


Figure S1: ^{1}H NMR (300 MHz, $CDCl_3$) and ES^{+}/MS spectra of compound **3**



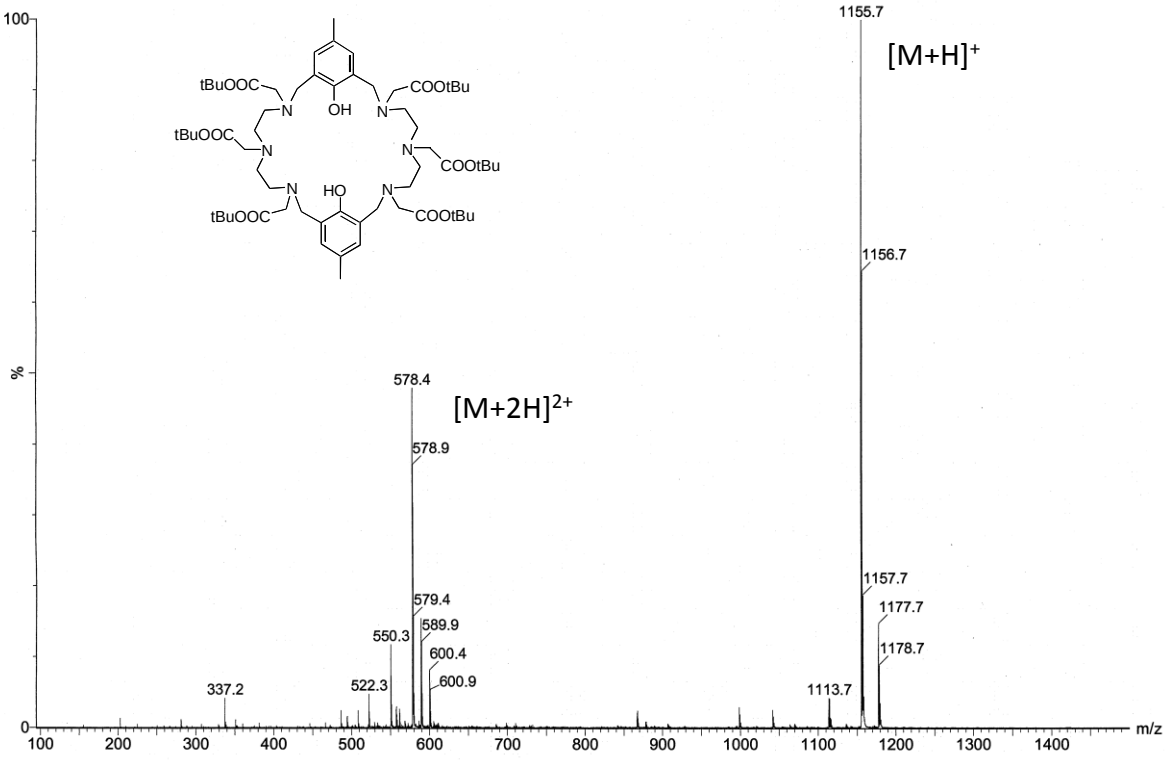
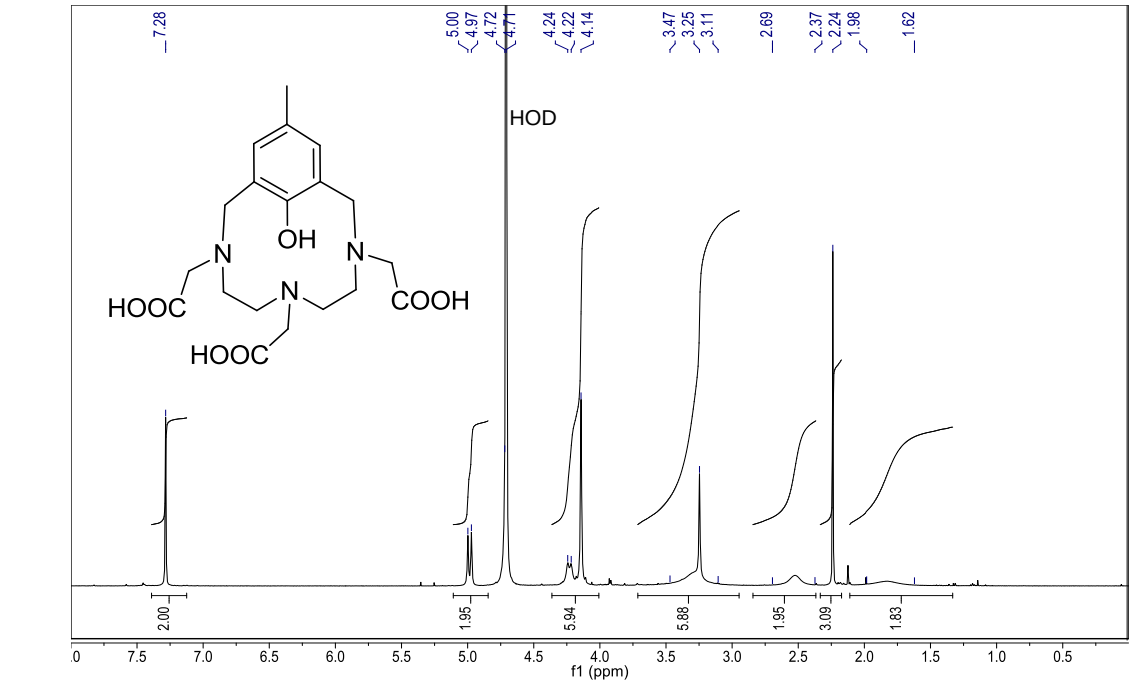


Figure S2: ^{1}H NMR (300 MHz, $CDCl_3$) and ES^{+}/MS spectra of compound **4**



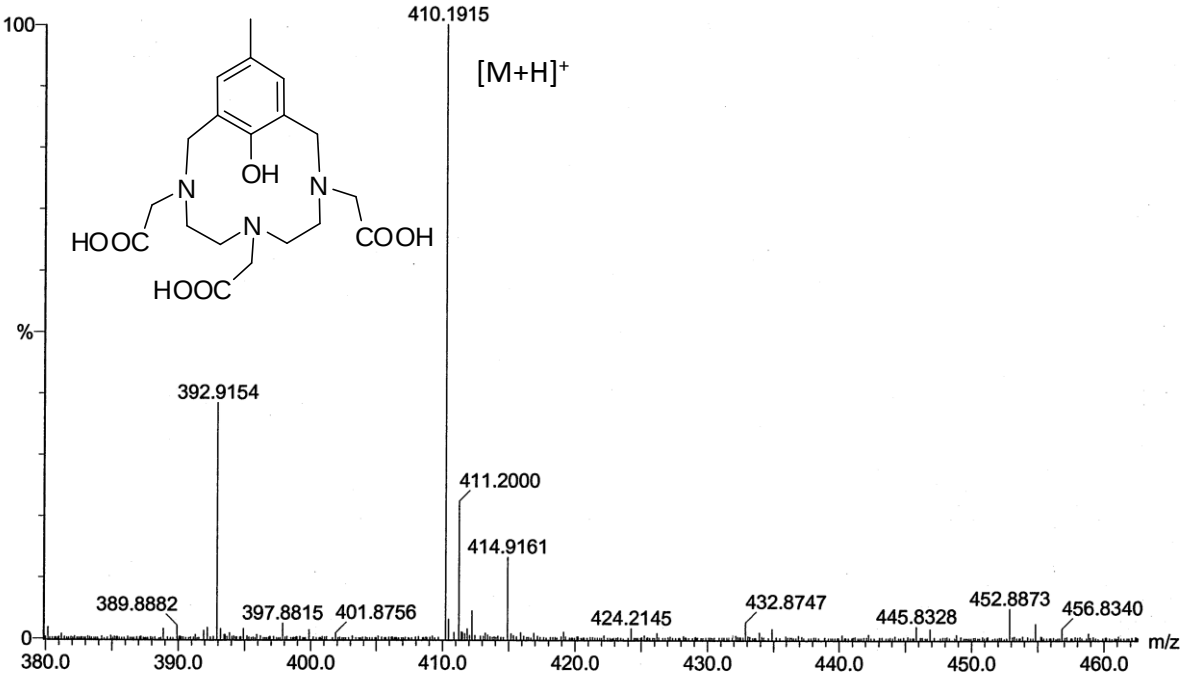
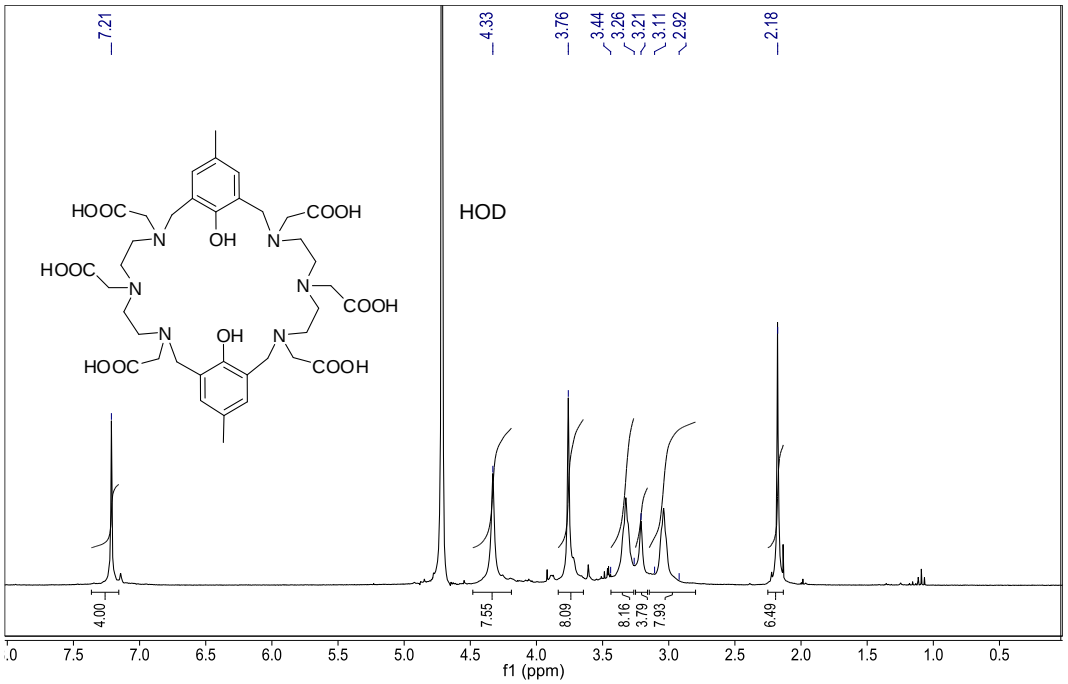


Figure S3: ^{1}H NMR (500 MHz, D_2O) and ES^{+}/HRMS spectra of ligand H_4L^1



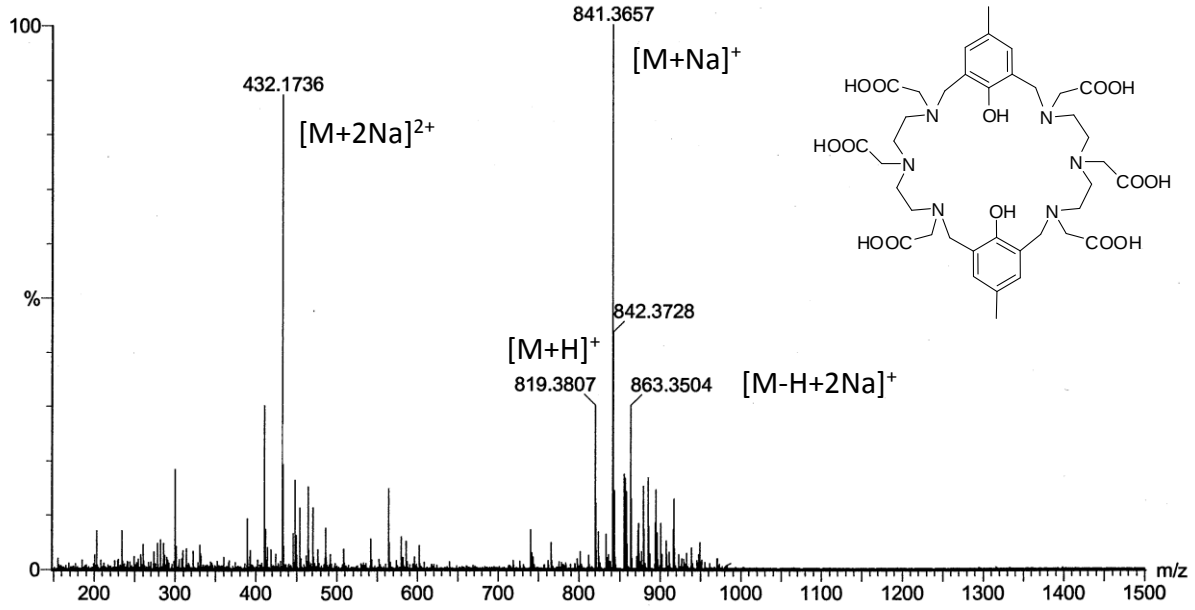


Figure S4: ^{1}H NMR (300 MHz, D_2O) and ES^{+}/HRMS spectra of ligand H_8L^2

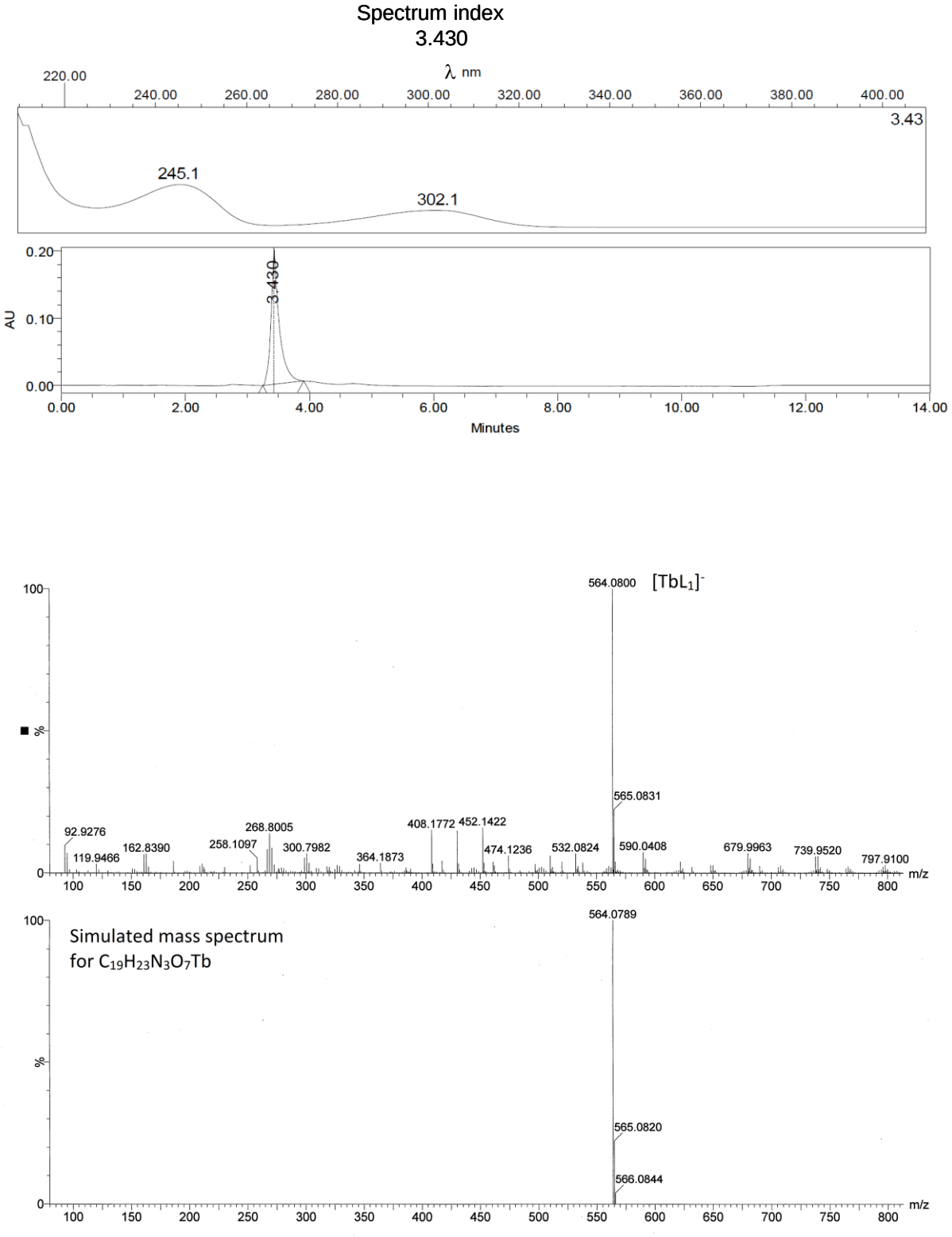


Figure S5: HILIC-UPLC chromatogram (UV-Vis detection) and ES$^-$/HRMS spectrum (measured and calculated pattern) of **[**TbL^1]Na complex (HILIC-UPLC conditions are provided in the experimental part).

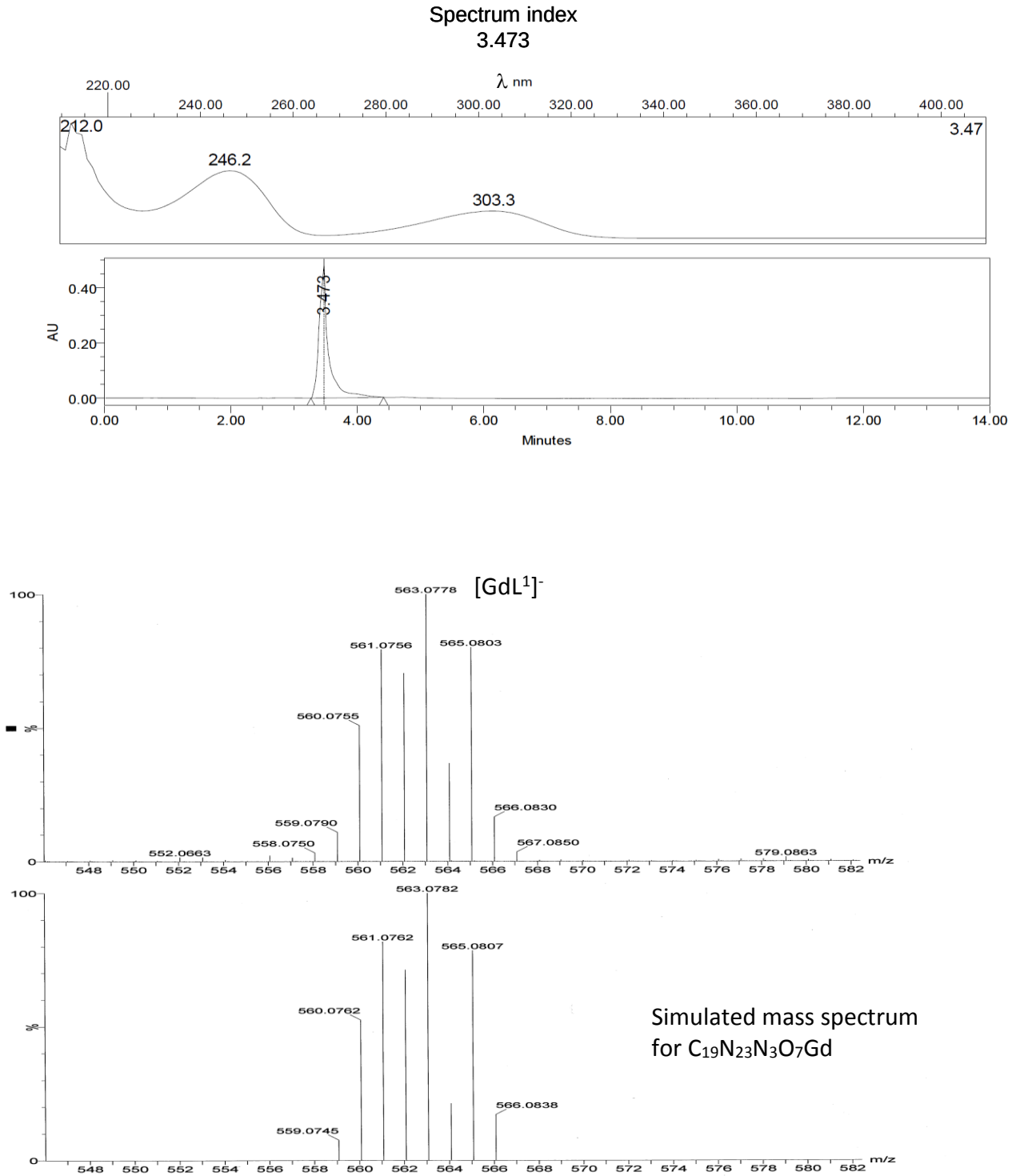


Figure S6: HILIC-UPLC chromatogram (UV-Vis detection) and ES$^-$/HRMS spectrum (measured and calculated pattern) of **[**GdL^1]Na complex (HILIC-UPLC conditions are provided in the experimental part).

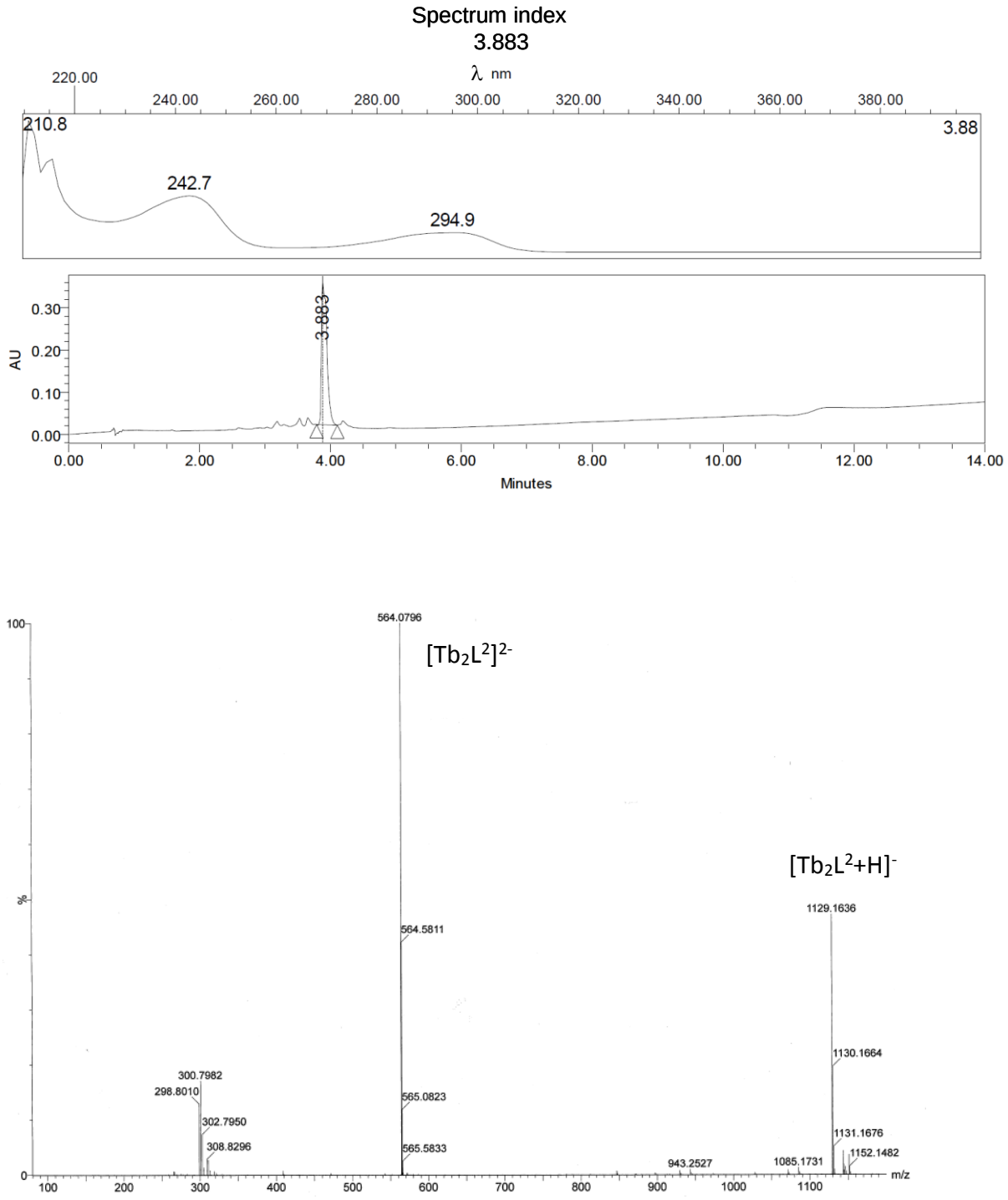


Figure S7: HILIC-UPLC chromatogram (UV-Vis detection) and ES$^-$/HRMS spectrum of $[Tb_2L^2]Na_2$ complex (HILIC-UPLC conditions are provided in the experimental part).

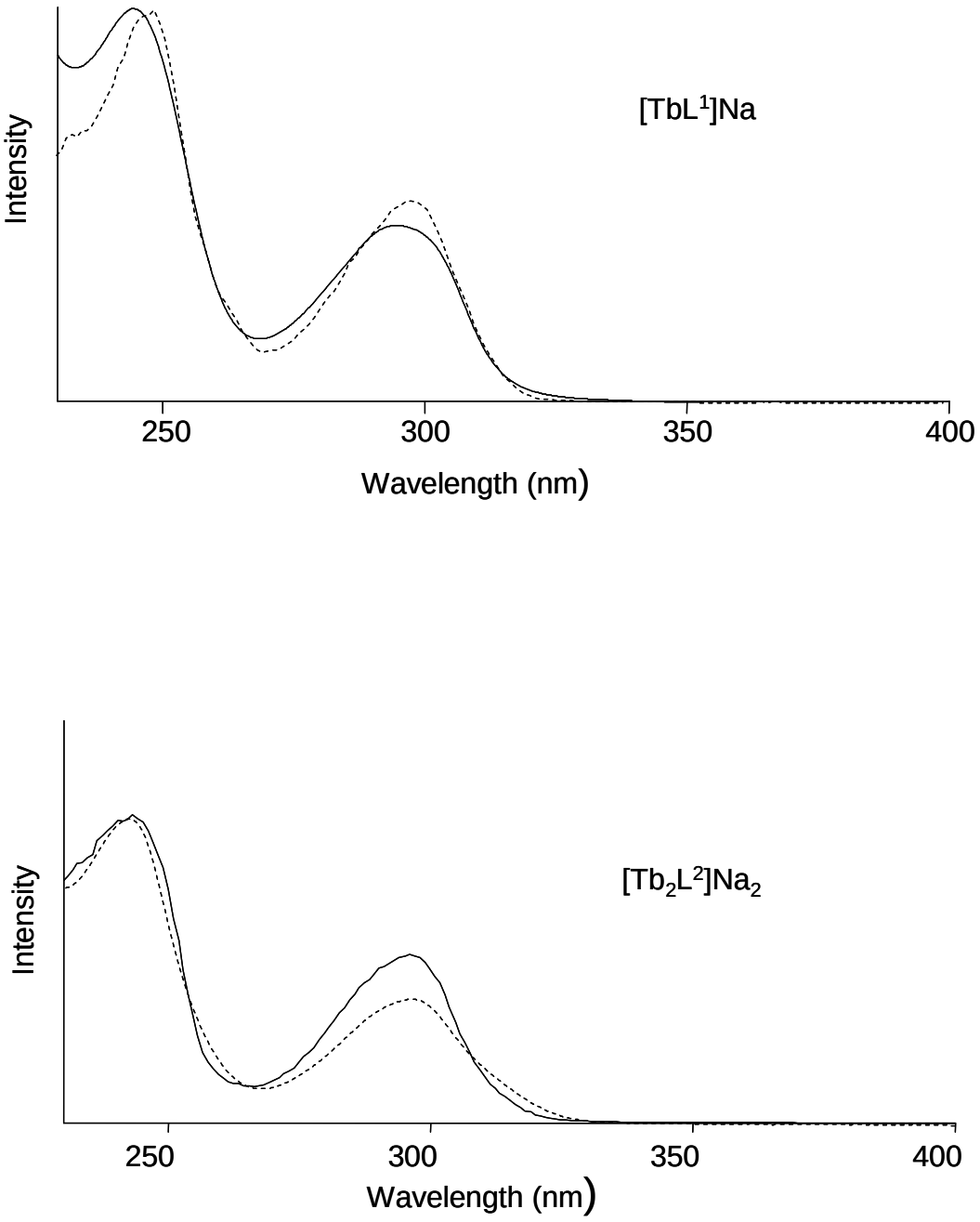


Figure S8: Normalized absorption (—) and corrected excitation (---, λ_{em} = 545 nm) spectra of $[TbL^1]Na$ and $[Tb_2L^2]Na_2$ complexes in Tris buffer (pH 7.4).

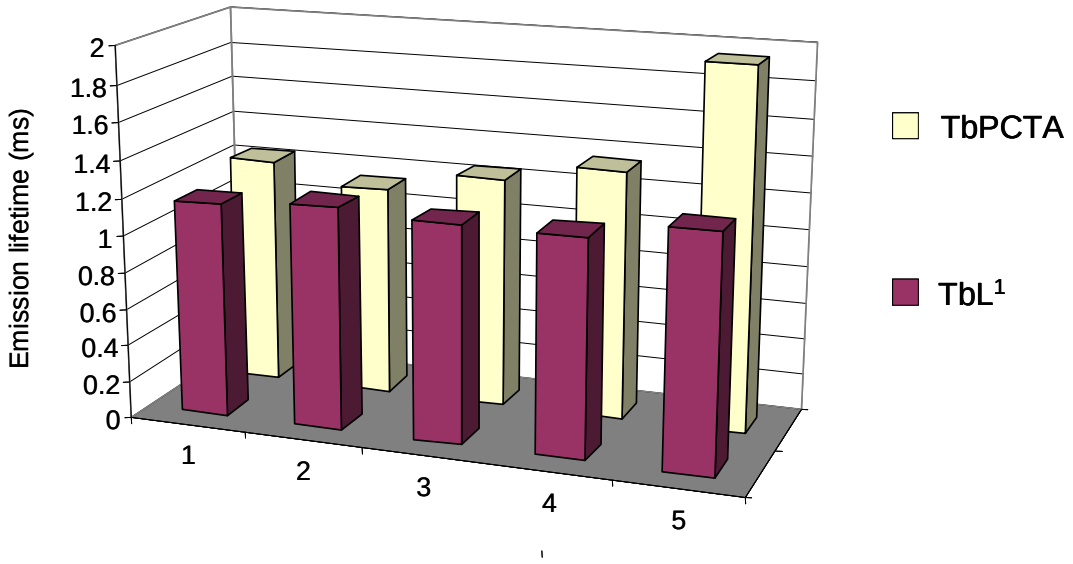


Figure S9: Effects of added anions on the emission lifetimes in [TbL^1]Na and TbPCTA complexes.

(1) [[TbL^1]Na] or [TbPCTA] = 0.05 mM at pH 7.4 (Tris buffer 50 mM), (2) with phosphate (1.1 mM), (3) with lactate (2.3 mM), (4) with carbonate (26 mM) and (5) with fluoride (0.1M).

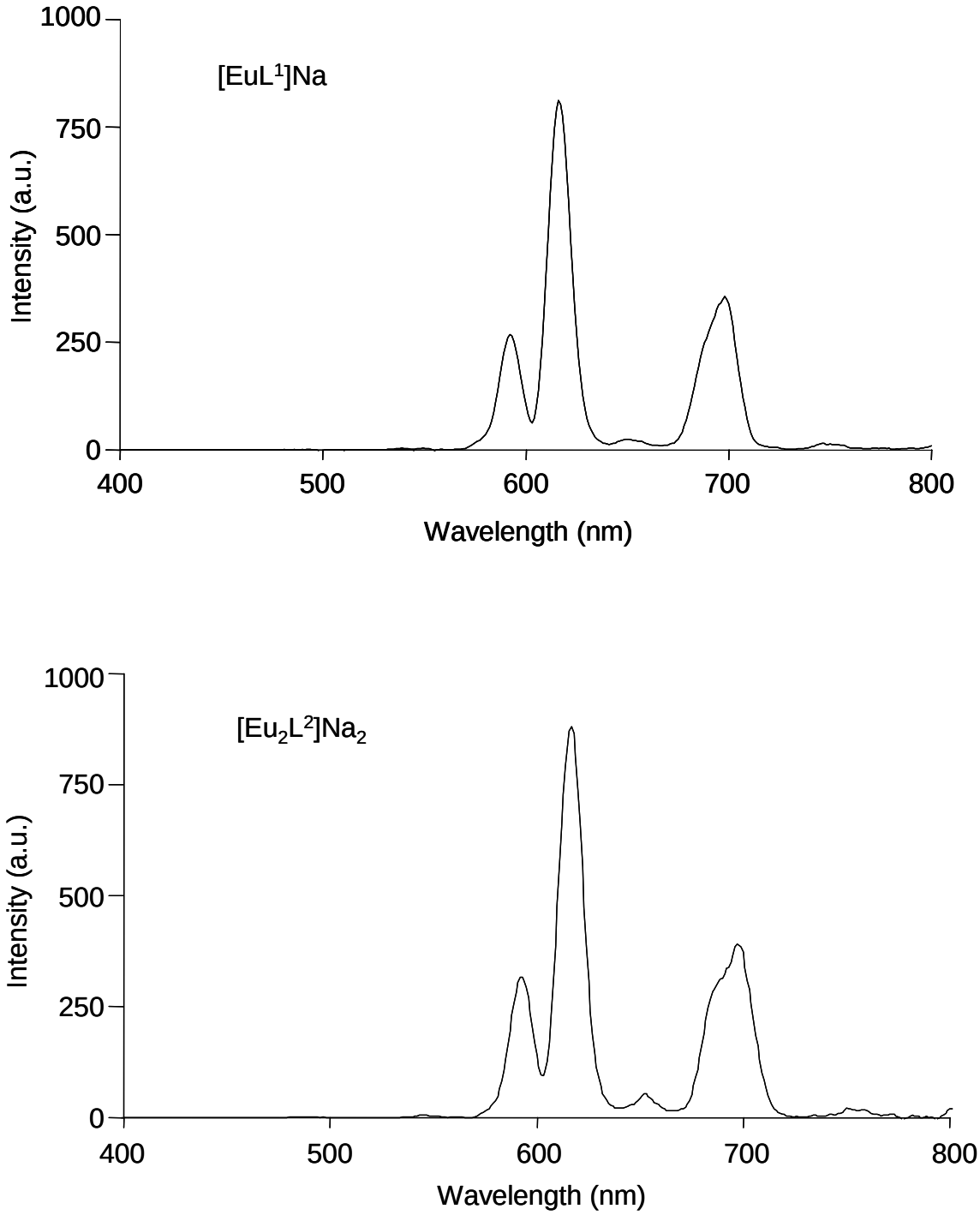


Figure S10: Corrected emission spectra of $[EuL^1]Na$ and $[Eu_2L^2]Na_2$ complexes in Tris buffer (pH 7.4) under excitation at 296 nm at 298 K. Excitation and emission band-passes 20 and 10 nm respectively, delay time 0.1 ms and gate time 1 ms.

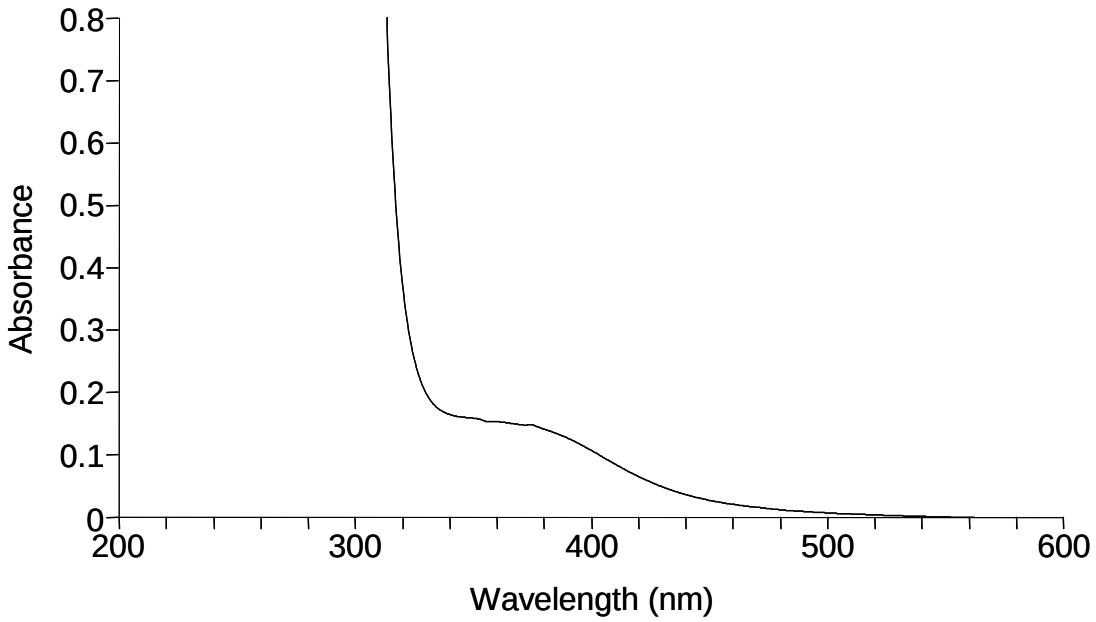


Figure S11: Absorption spectrum of $[Eu_2L^2]Na_2$ showing the LMCT absorption band at 360 nm in Tris buffer (pH 7.4) at 298 K.

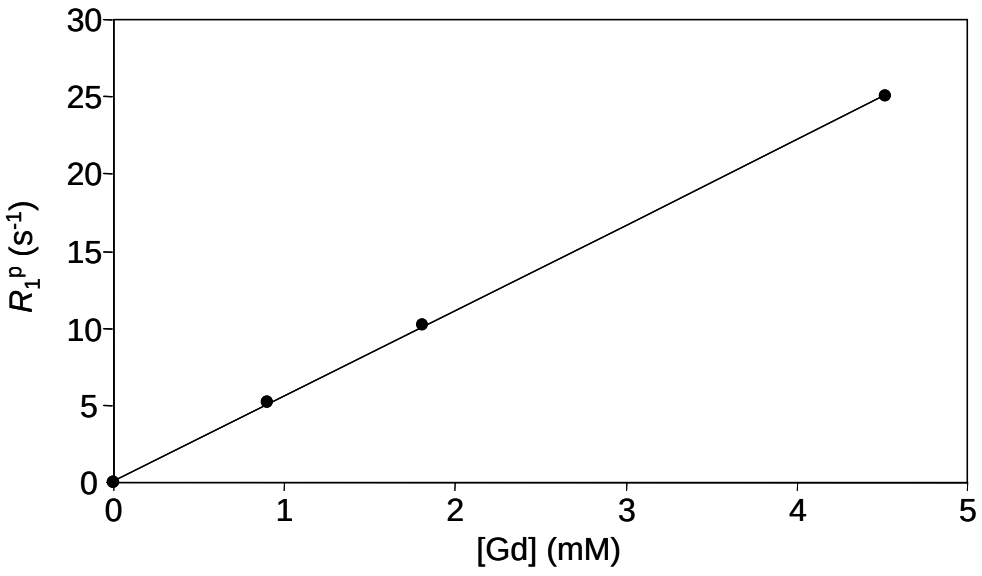


Figure S12: Plot of paramagnetic relaxation rate, R_1^p, of $[GdL^1]Na$ complex in water at 310 K and 20 MHz vs complex concentrations. $R_1^p = R_1^{obs} - R_1^{dia}$ where R_1^{obs} is the observed relaxation rate and R_1^{dia} is the relaxation rate in absence of paramagnetic center.

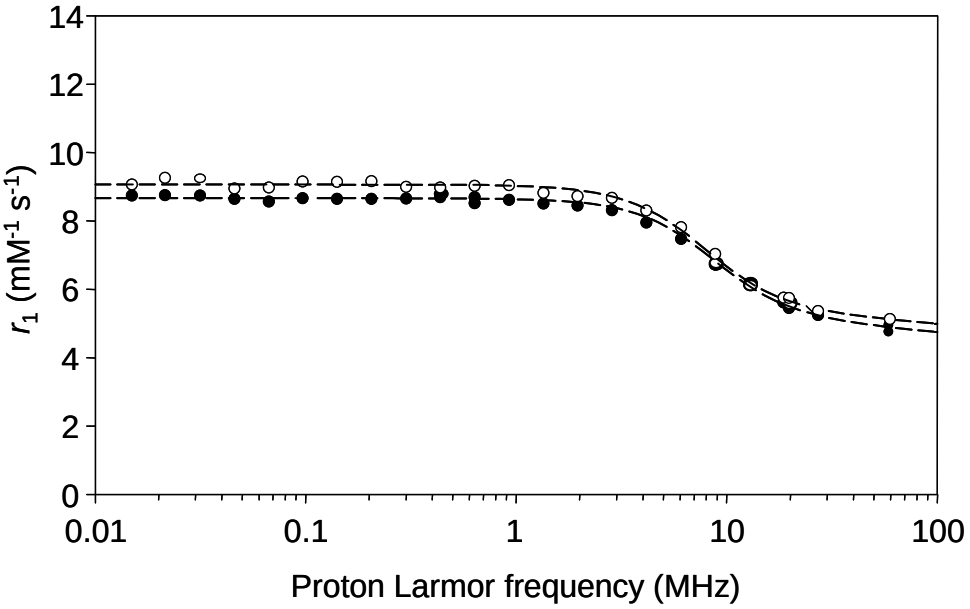


Figure S13: ^{1}H NMRD relaxivity profiles of [GdL^{1}]Na complex for two different concentrations 0.904 mM (open circles) and 1.807 mM (closed circles) at 310 K.