Supporting Information for :

Optical and relaxometric properties of monometallic (Eu^{III}, Tb^{III}, Gd^{III}) and heterobimetallic (Re^{I}/Gd^{III}) systems based on a functionalized bipyridine-containing acyclic ligand

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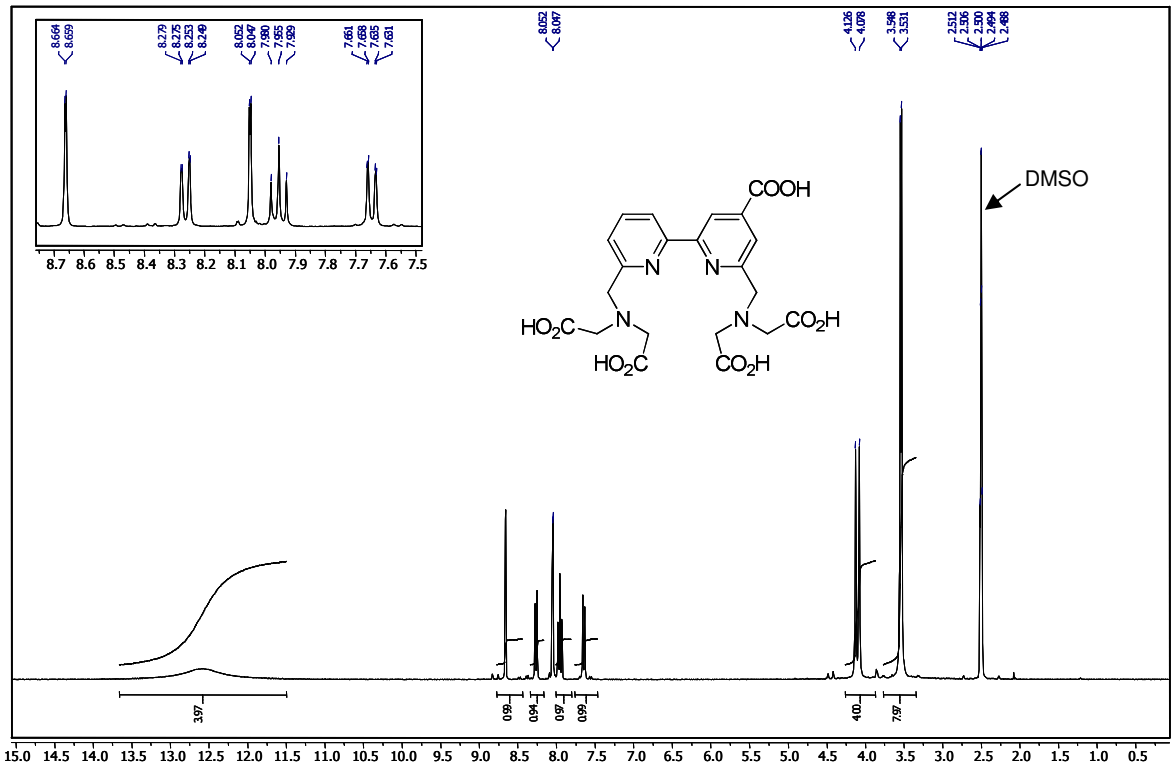
Table of contents Page



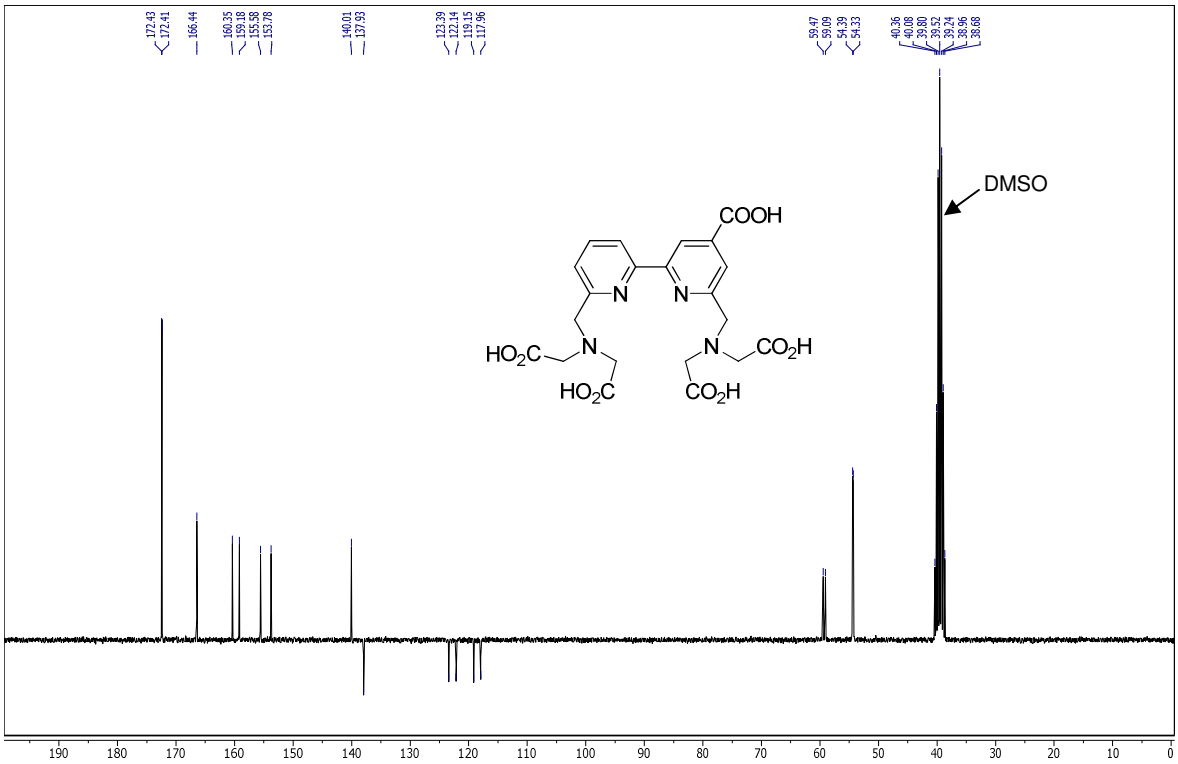


Figure S1: ^{1}H and J MOD ^{13}C NMR (300 and 75 MHz respectively; DMSO-d_6) spectra of compound **2** (H_5BPMNTA).

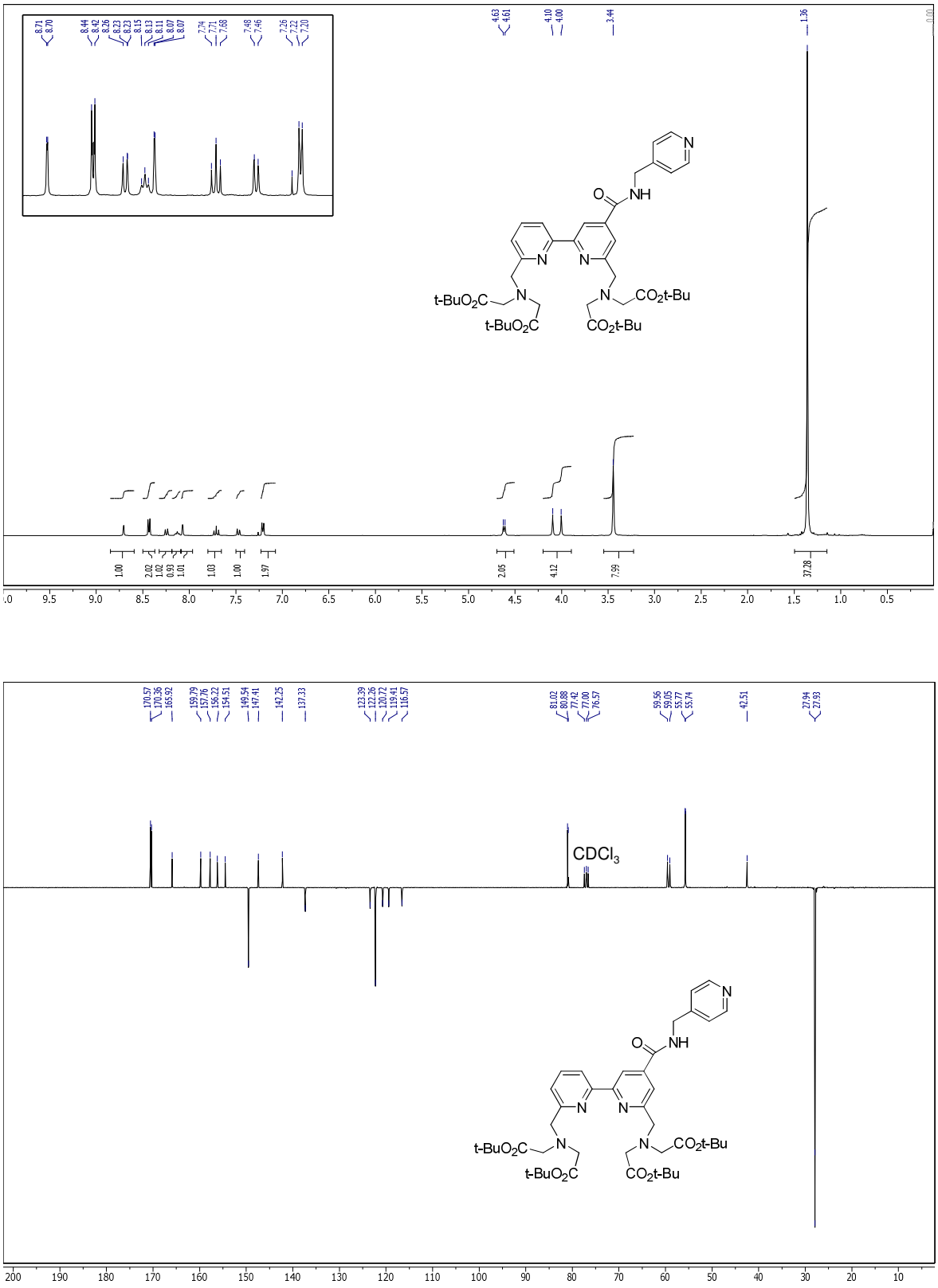
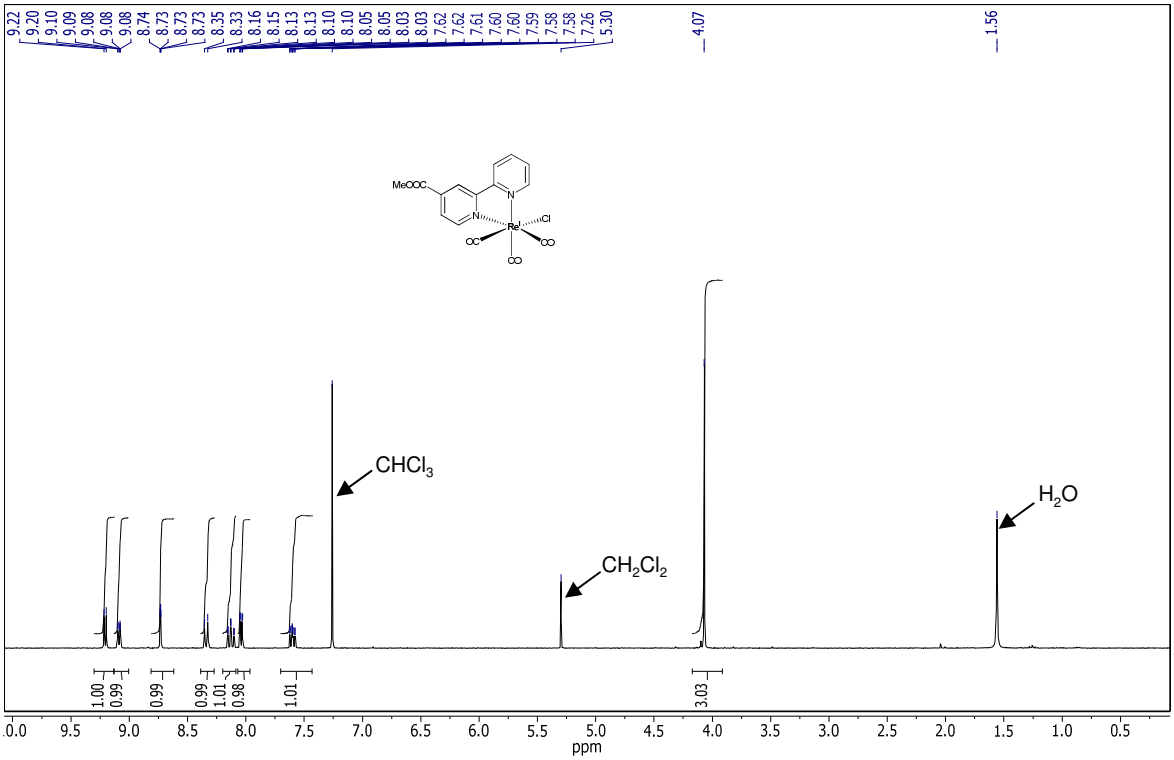


Figure S2: ^{1}H and J MOD ^{13}C NMR (300 and 75 MHz respectively; $CDCl_3$) spectra of compound **5**.



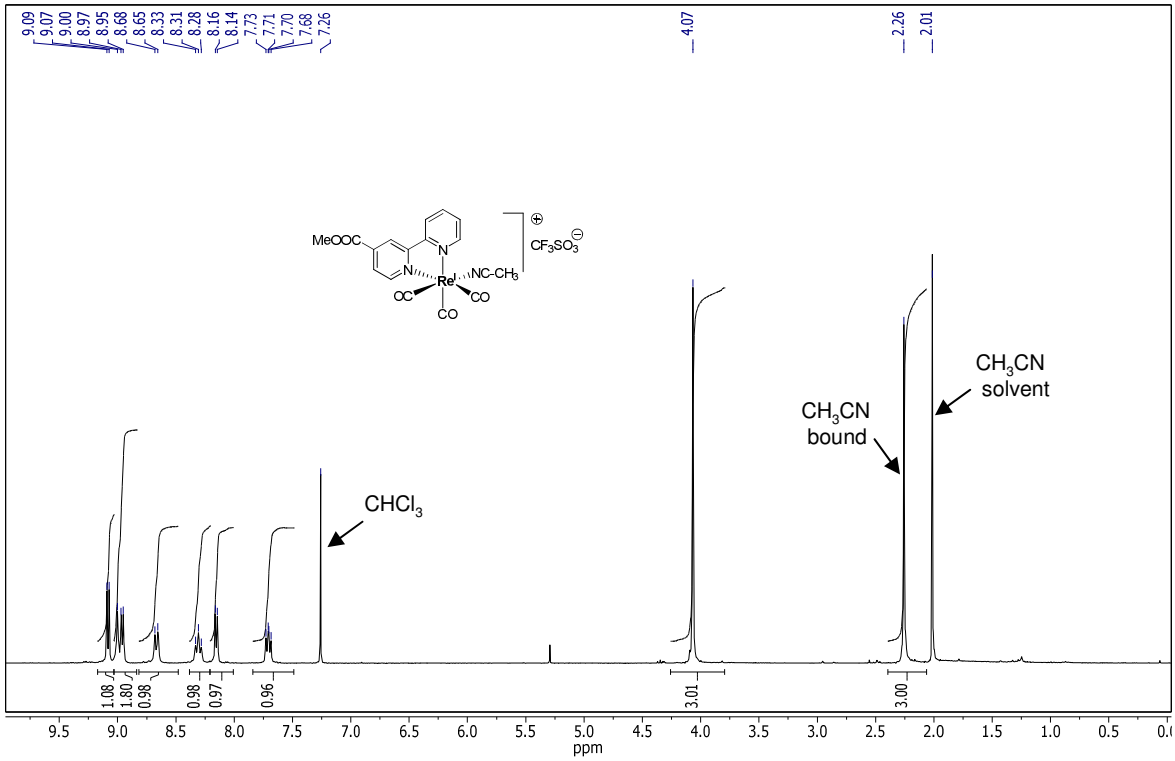


Figure S3: ^{1}H NMR (300 MHz, $CDCl_3$) spectra of compounds **9** and **10**.

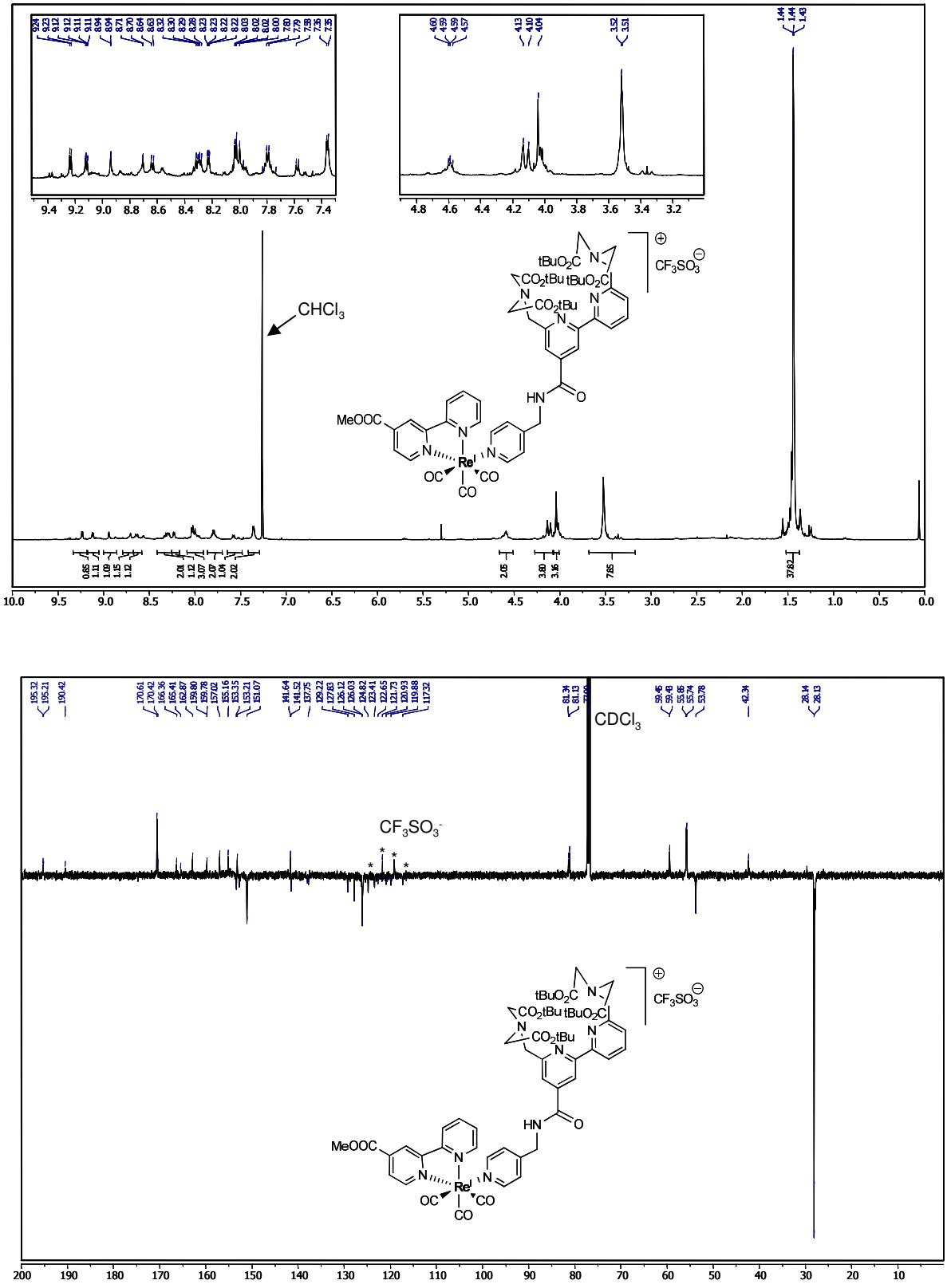
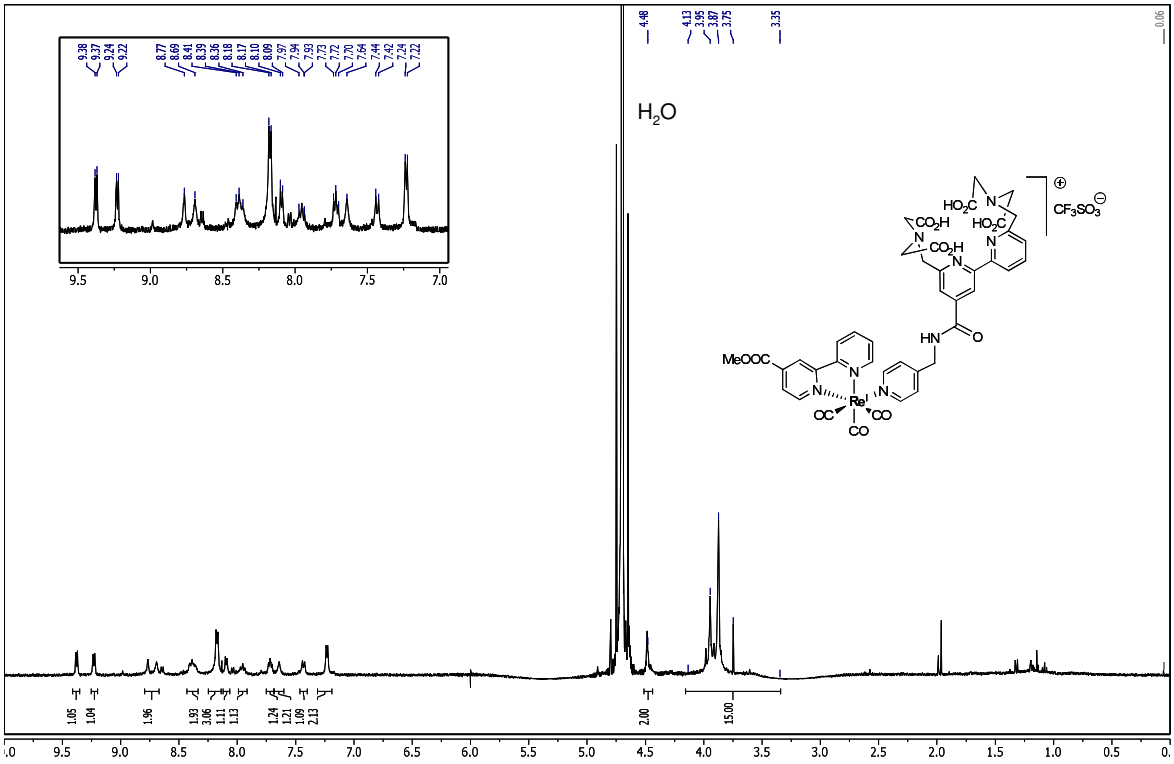


Figure S4: ^{1}H and J MOD ^{13}C NMR (300 and 125 MHz respectively; $CDCl_3$) spectra of compound **11**.



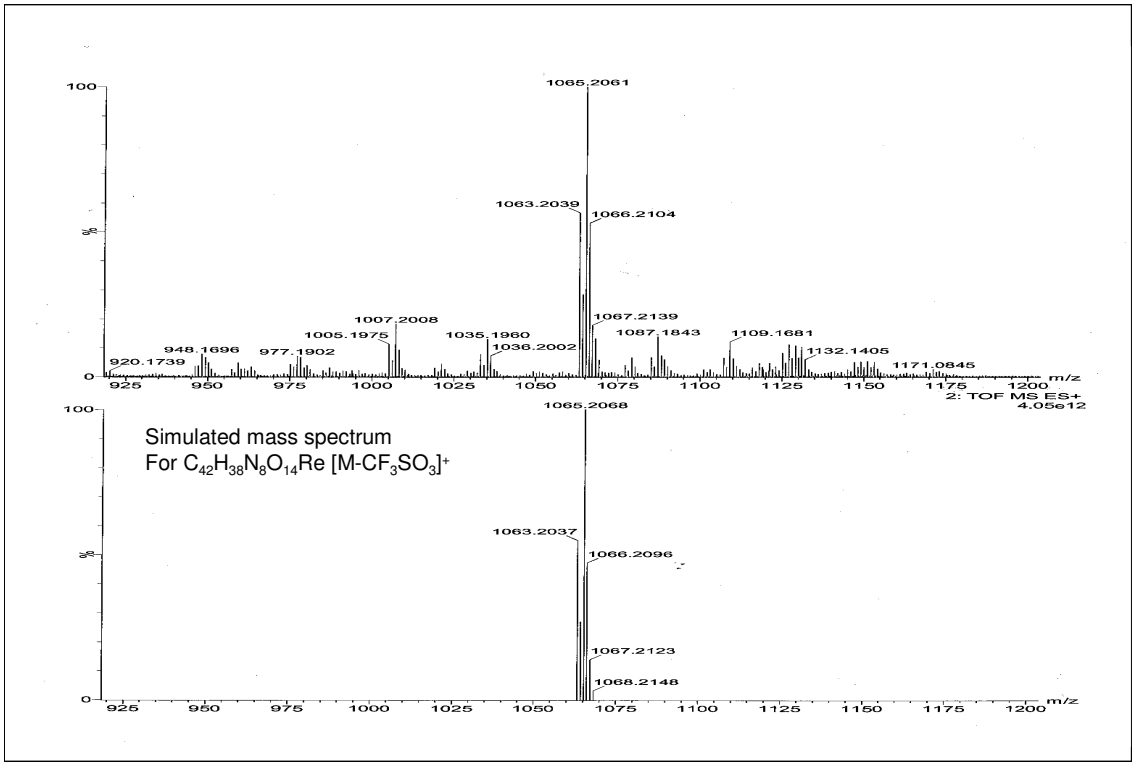
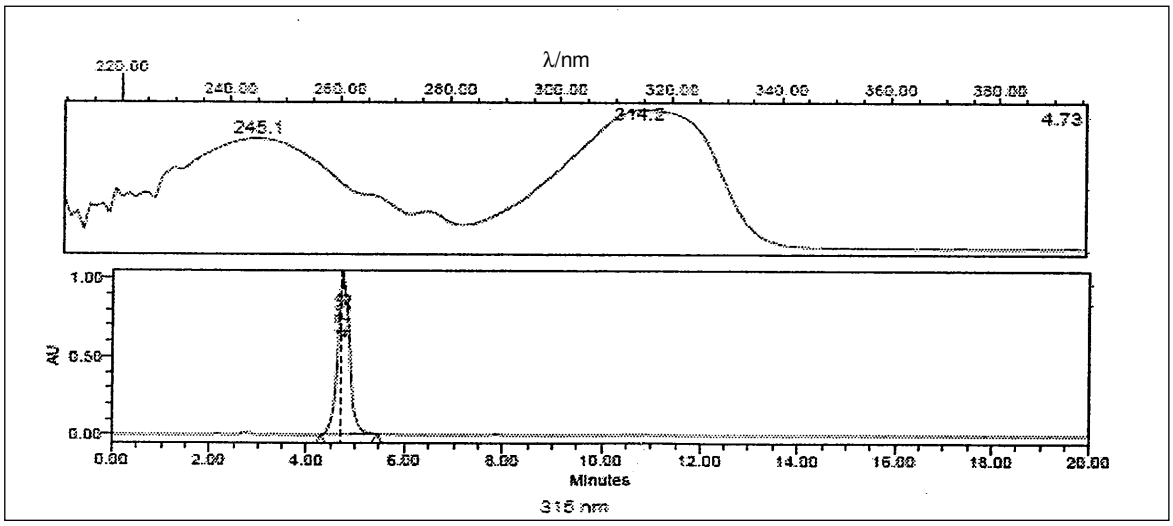


Figure S5: ^{1}H NMR (400 MHz, D_2O) and ES^{+}/HRMS spectra of compound **12**.



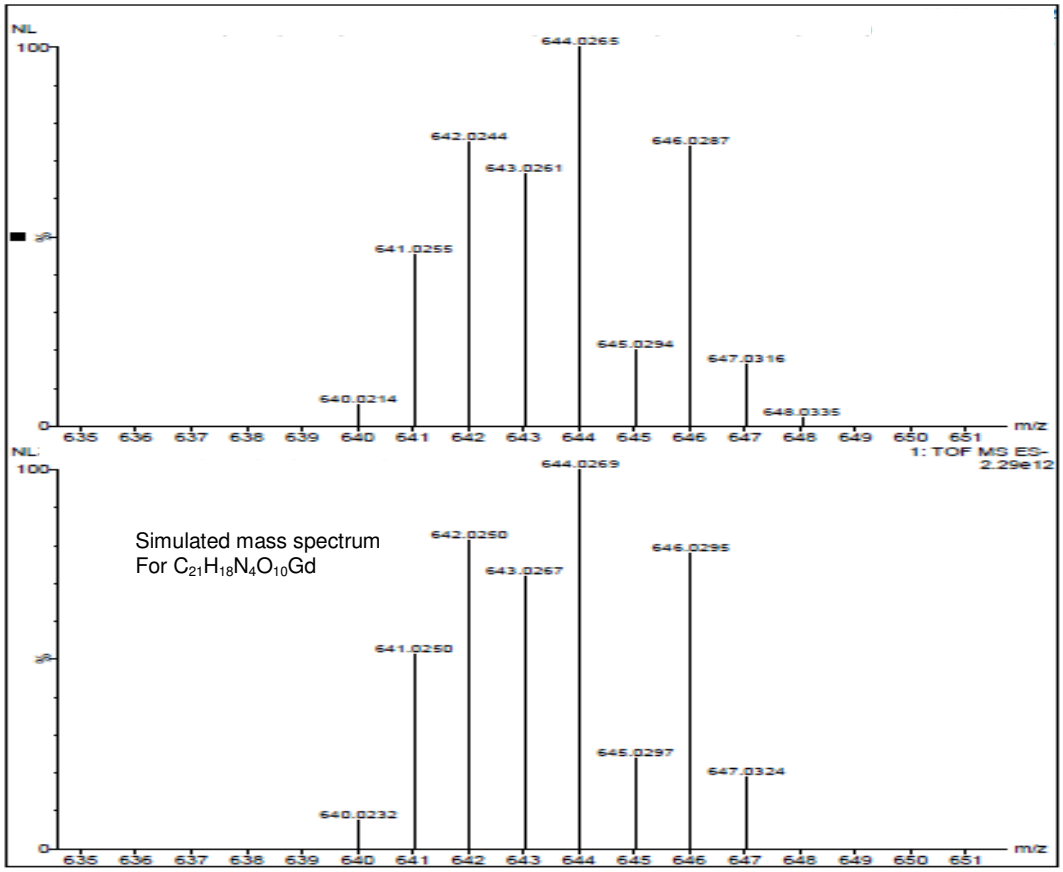


Figure S6: HPLC-UV chromatogram and ES$^-$/HRMS spectrum of Gd-BPMNTA complex (HPLC conditions are provided in the experimental part).

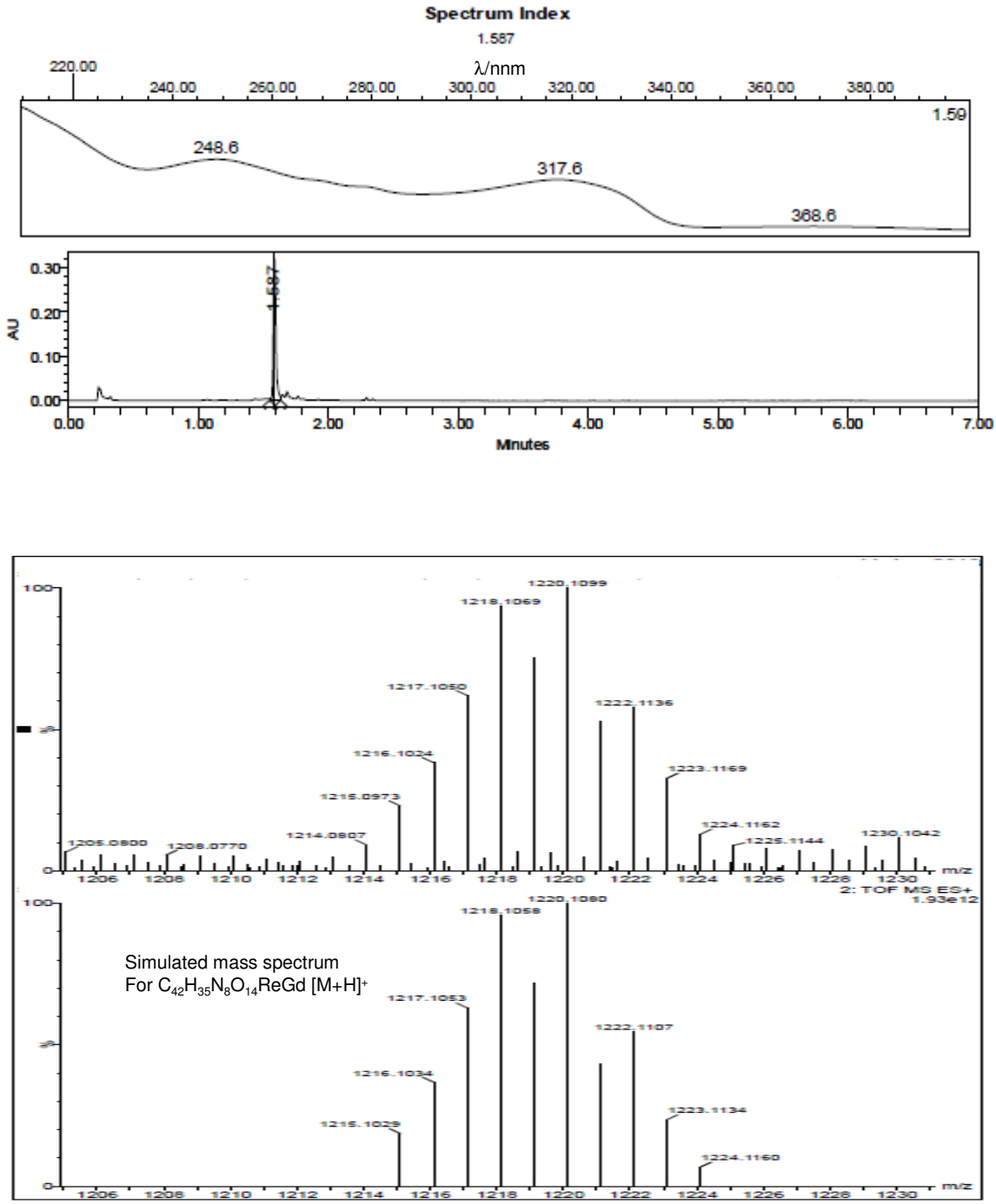


Figure S7: UPLC-UV chromatogram and ES$^+$/HRMS spectrum of dinuclear Re/Gd complex **13** (UPLC conditions are provided in the experimental part).

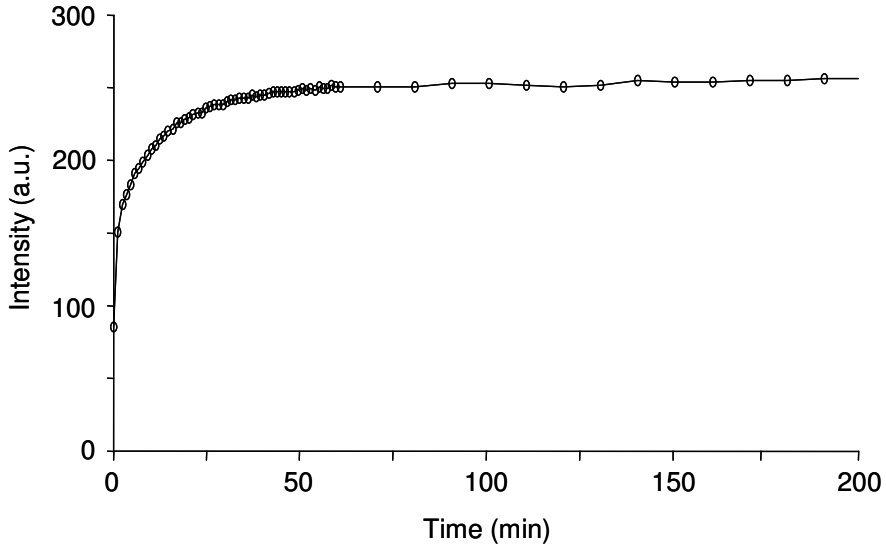


Figure S8: Plot of emission intensity of the $^5D_0 \rightarrow ^7F_2$ transition (617 nm) vs. time after mixing BPMNTA chelator (1 μM) and $EuCl_3$ (1 equiv.) in Tris buffer (pH 7.4) at room temperature.

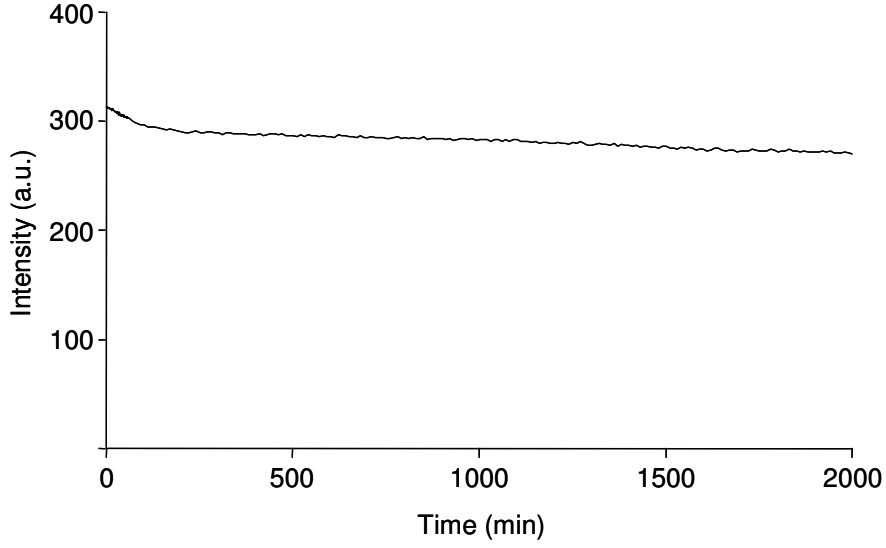


Figure S9: Plot of emission intensity of the $^5D_0 \rightarrow ^7F_2$ transition (617 nm) of Eu-BPMNTA complex (1 μM) *vs.* time in the presence of 1000 molar equivalents of EDTA in Tris buffer (pH 7.4).

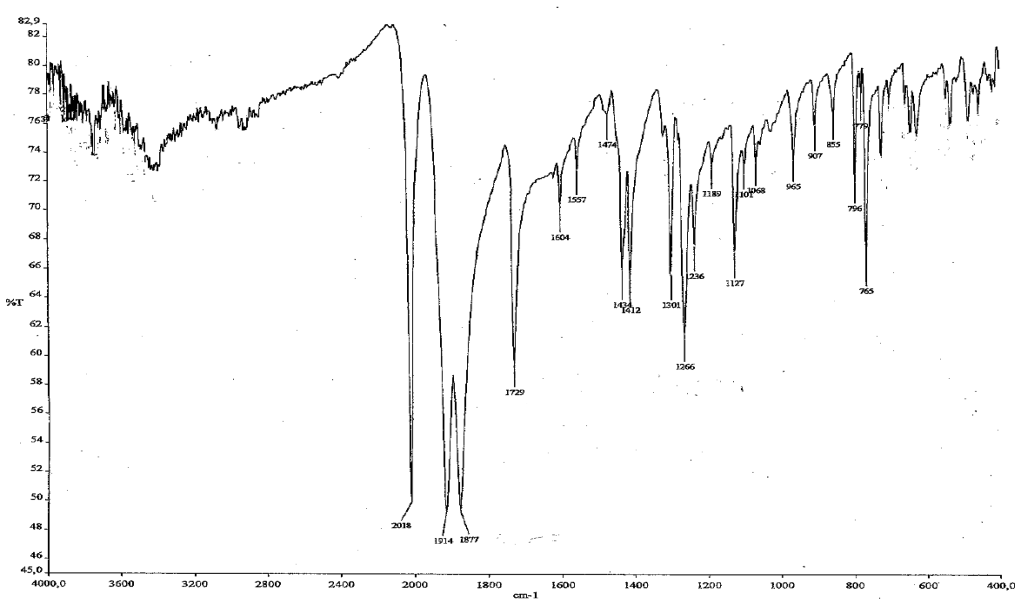


Figure S10: Infrared spectrum of Re complex **9**.

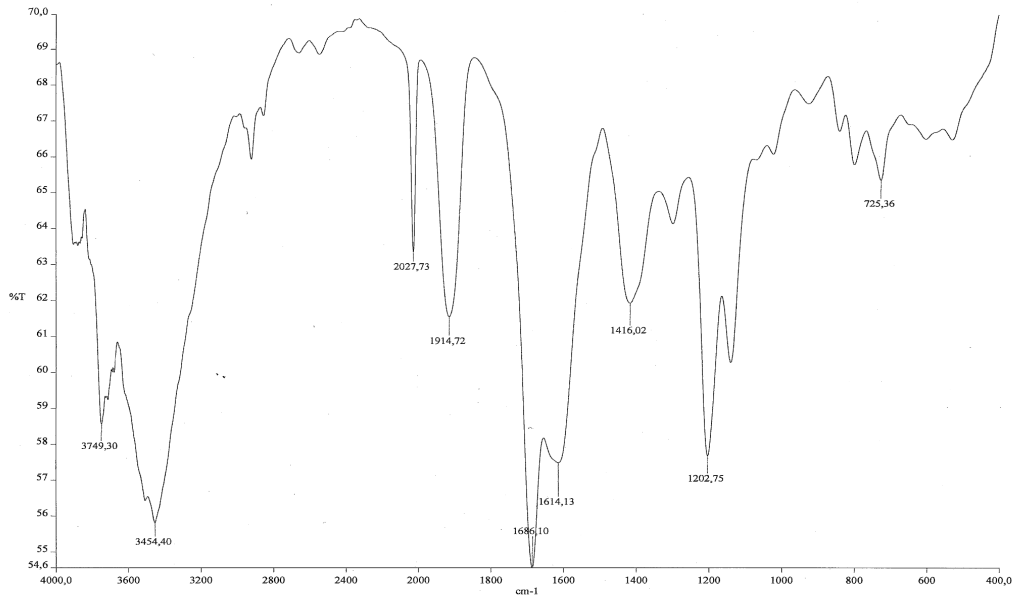


Figure S11: Infrared spectrum of dinuclear Re/Gd complex **13**.

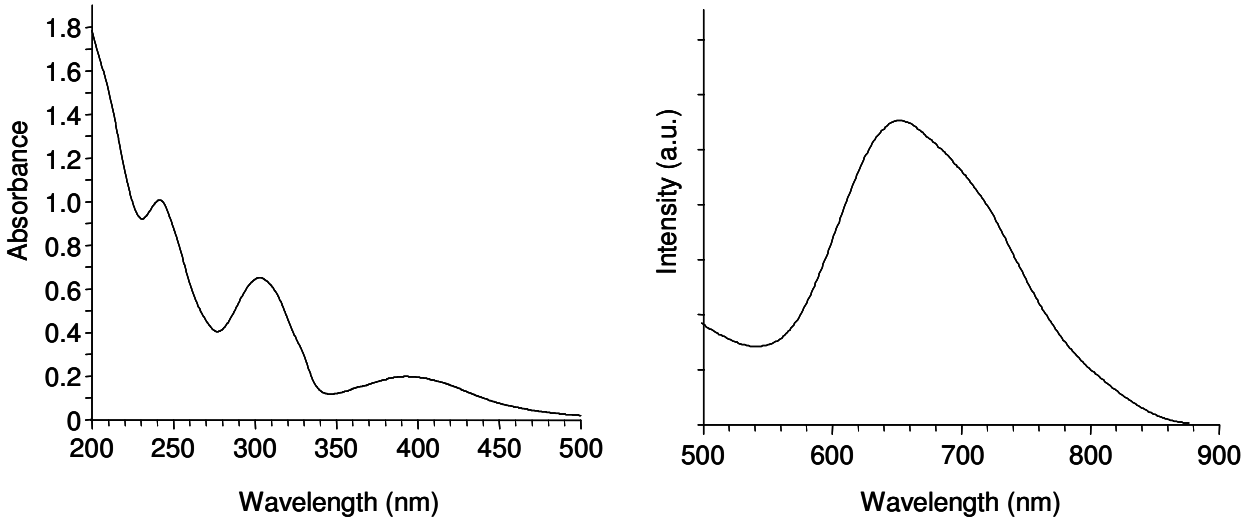


Figure S12: Absorption (left) and emission (right) spectra of compound **9** in CH_3CN.

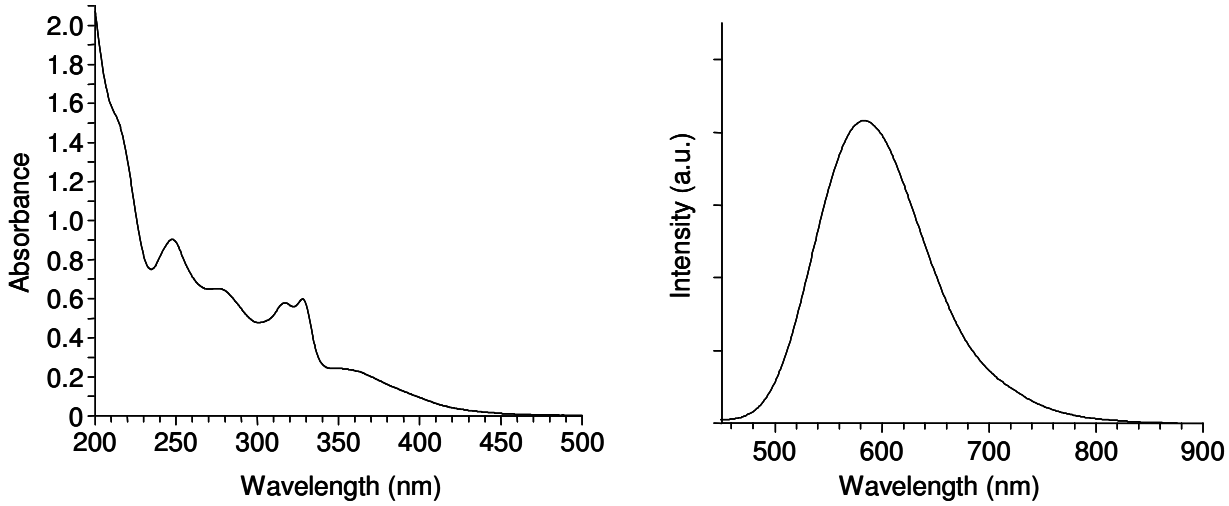


Figure S13: Absorption (left) and emission (right) spectra of compound **10** in CH_3CN.

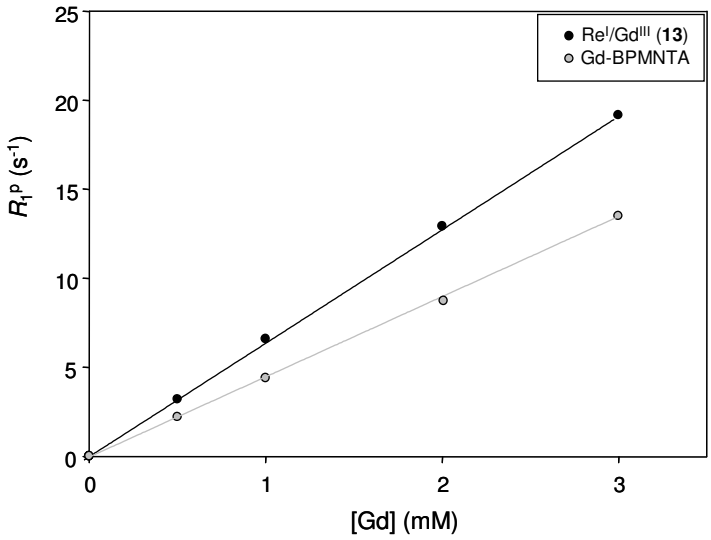


Figure S14: Plot of the paramagnetic relaxation rate, R_1^p, of Gd-BPMNTA complex and dinuclear complex **13** in water at 310 K and 20 MHz *vs.* complex concentrations (0.5 – 3 mM). $R_1^p = R_1^{obs} - R_1^{dia}$ where R_1^{obs} is the observed relaxation rate and R_1^{dia} is the relaxation rate in absence of paramagnetic center.

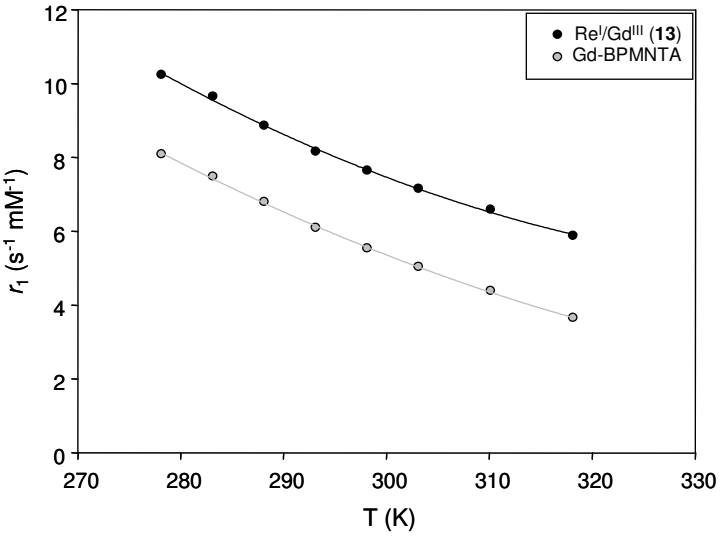


Figure S15: Temperature (278 – 318 K) dependence of the proton longitudinal relaxivity, r_1, of Gd-BPMNTA complex and dinuclear complex **13** in water at 20 MHz.

parameter	value
τ_M^{310K} [ns]	9.0 ± 3.0
$\Delta H^{\neq}$ [kJ mol^{-1}]	55.5 ± 0.7
$\Delta S^{\neq}$ [J mol^{-1} K^{-1}]	87.9 ± 0.6
$A/\hbar$ [10^6 rad s^{-1}]	-3.9 ± 0.3
B [10^{20} s^{-2}]	4.71 ± 0.85
τ_v^{298K} [ps]	1.35 ± 0.3
E_v [kJ mol^{-1}]	4.95 ± 3.5

Table S1: Parameters obtained from the theoretical fitting of the O-17 data of dinuclear Re/Gd complex **13** in water at 11.75 T.

parameter	value
τ_M^{310K} [ns]	9
τ_R^{310K} [ps]	138 ± 3.3
τ_{SO}^{310K} [ps]	87.6 ± 1.4
τ_V^{310K} [ps]	25.6 ± 1.5
r_1 (mM^{-1} s^{-1}) at 20 MHz	6.6
r_1 (mM^{-1} s^{-1}) at 60 MHz	6.0

Table S2: Relaxivity values at 20 and 60 MHz (T = 310 K) and parameters obtained from the theoretical fitting of the proton NMRD data in water at 310 K of dinuclear Re/Gd complex **13**. In the fitting procedure using the IS and OS model, some parameters were fixed: $q = 1$, $\tau_M = 9$ ns, $r_{GdH} = 0.31$ nm, $d = 0.36$ nm and $D = 2.93 \times 10^{-9}$ m^2 s^{-1}.