Supporting Information

# Comparison of Solution Properties of Polymethylated DOTA-like Lanthanide Complexes with Opposite Chirality of the Pendant Arms

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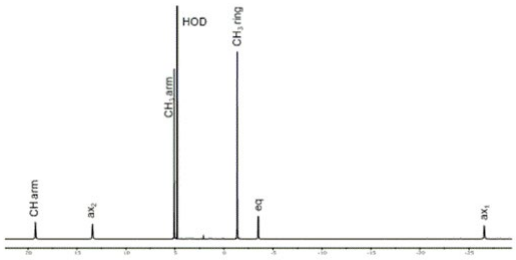
Ce-4S4R-M4DOTMA

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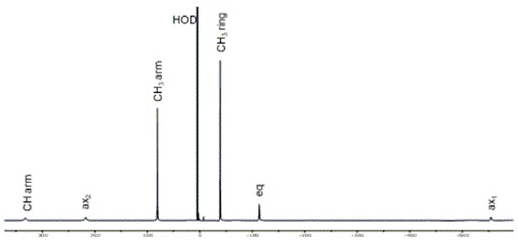


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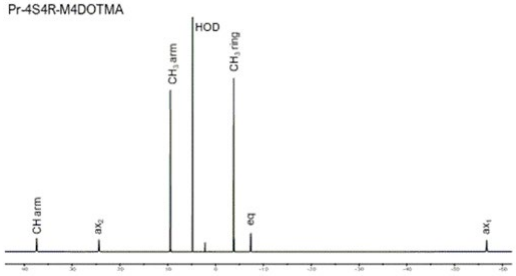


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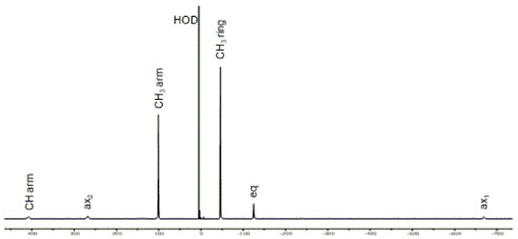


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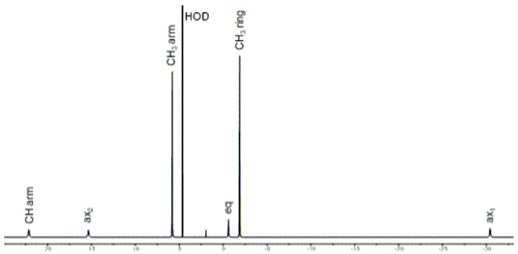
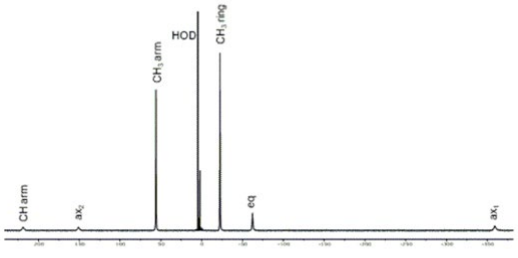



Ho-4S4R-M4DOTMA

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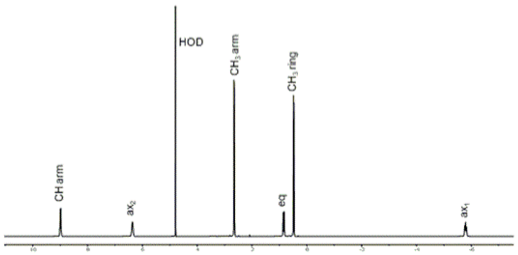
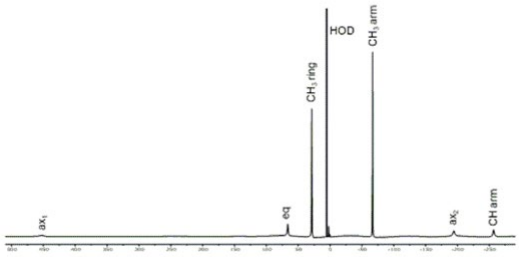
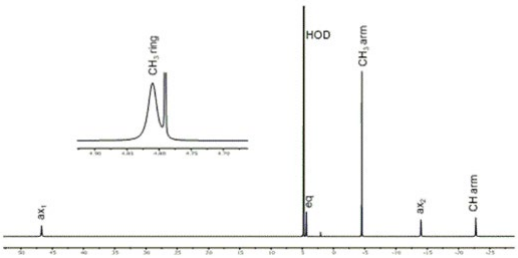



Er-4S4R-M4DOTMA




Eu-4S4R-M4DOTMA




Yb-4S4R-M4DOTMA

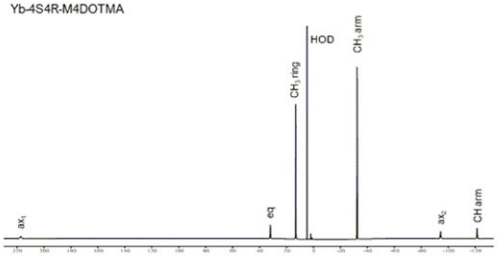


Figure S1. Proton NMR spectra of Ln-4S4R-M4DOTMA at 400 MHz and 25 ºC. Peak assignments for La- to Eu-4S4R-M4DOTMA and Lu-4S4R-M4DOTMA were based on 2D COSY. From these assignments, proton peaks for Er- to Yb-4S4R-M4DOTMA were patterned. Yb-4S4R-M4DOTMA assignments matched the proton assignments from Ranganathan, et al.[7]

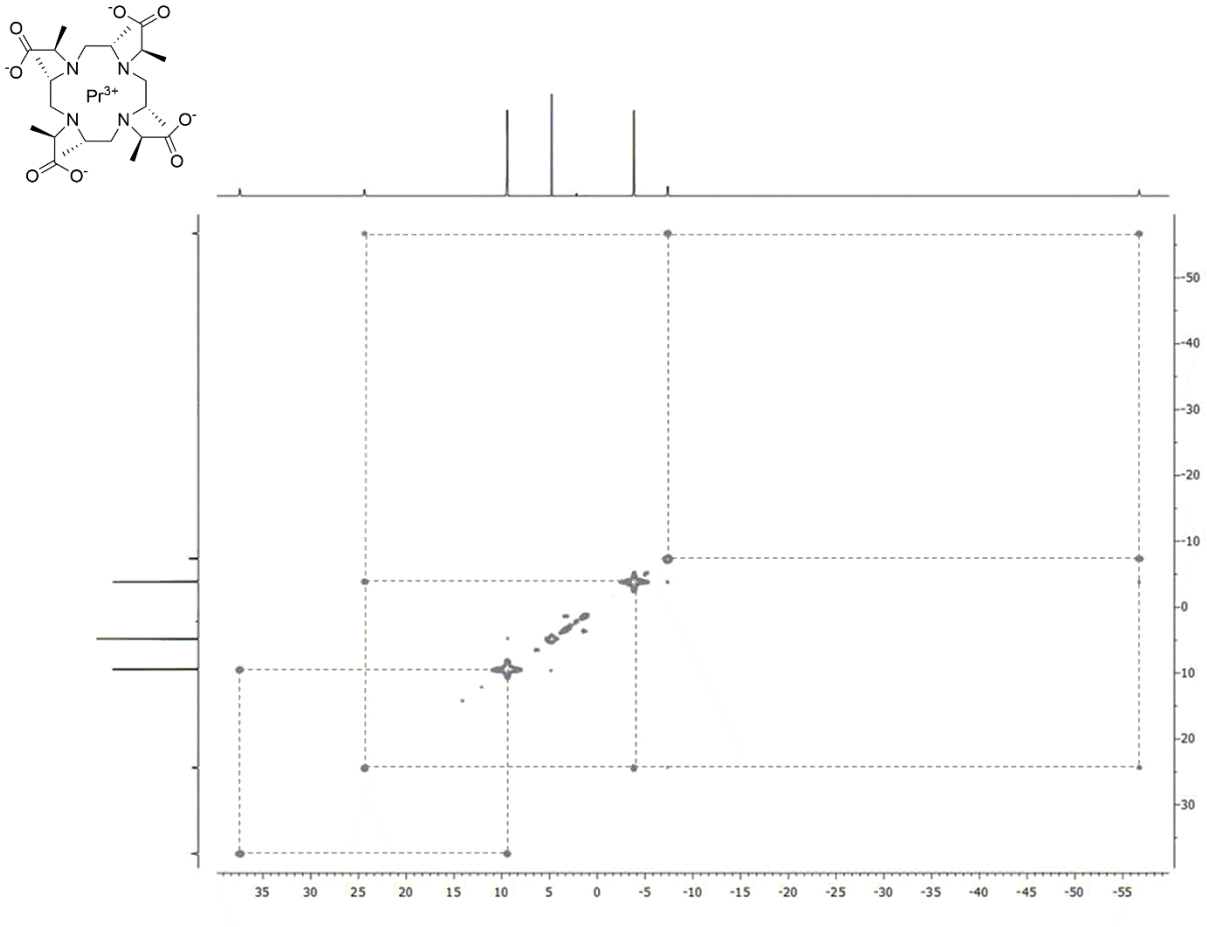



Figure S2. 2D COSY spectrum of Pr-4S4R-M4DOTMA at 400 MHz and 25 ºC.

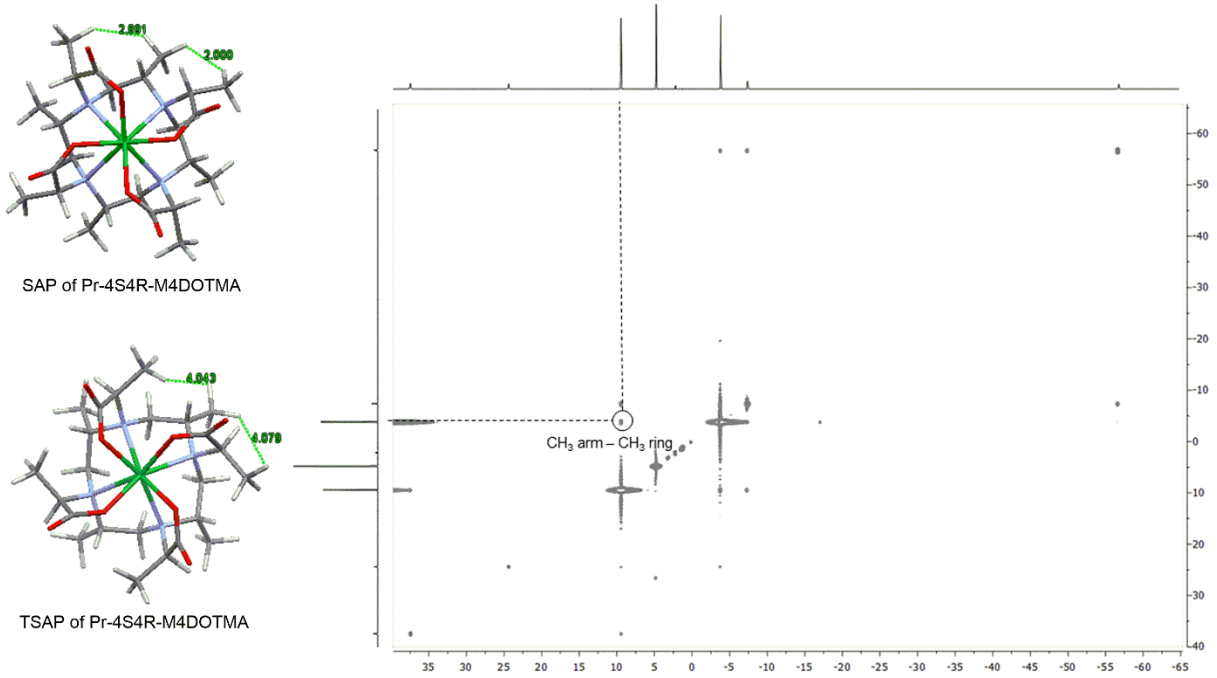



Figure S3. 2D NOESY spectrum of Pr-4S4R-M4DOTMA at 25°C and 400 MHz (mixing time = 100 ms). To the left are the optimized structures of Pr-4S4R-M4DOTMA in SAP (top) and TSAP (bottom) form.

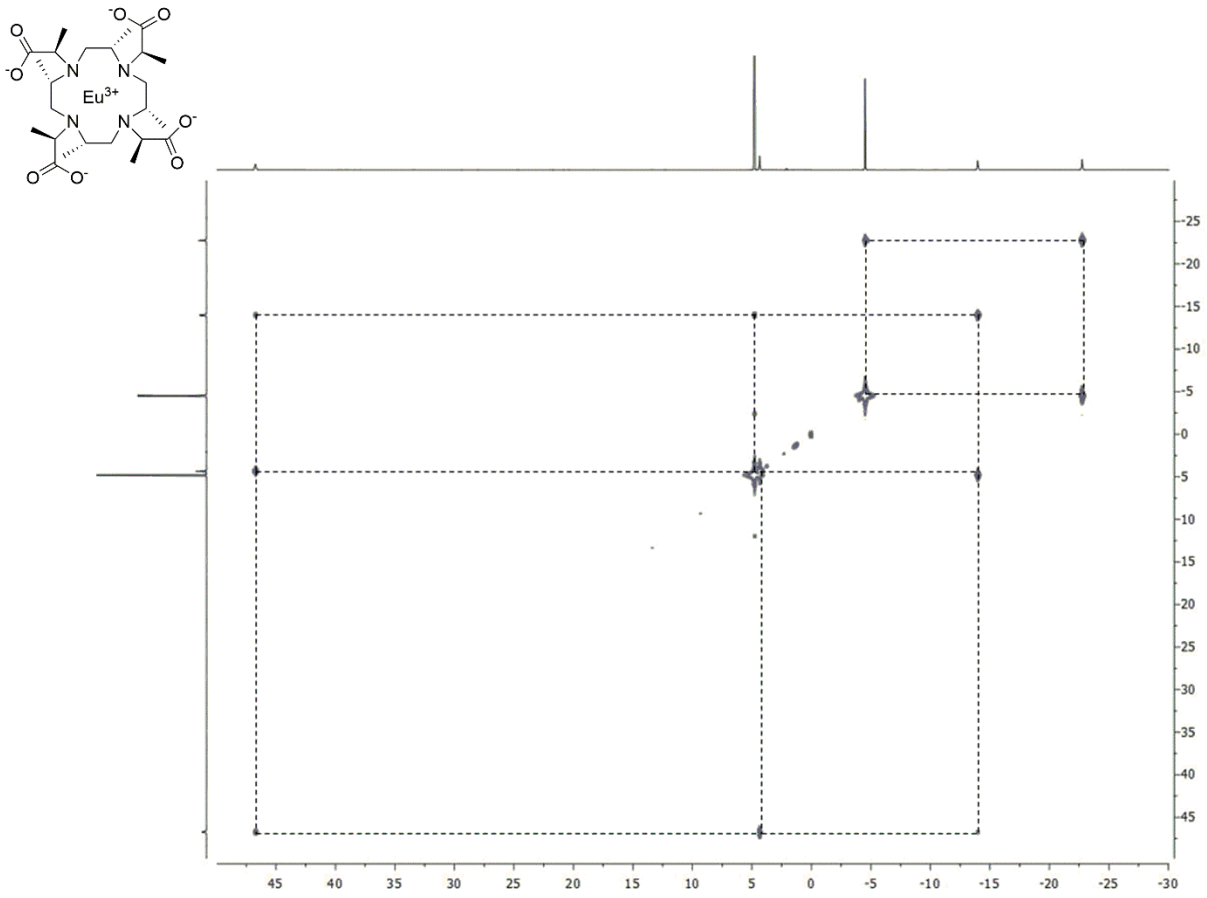



Figure S4. 2D COSY spectrum of Eu-4S4R-M4DOTMA at 400 MHz and 25 ºC.

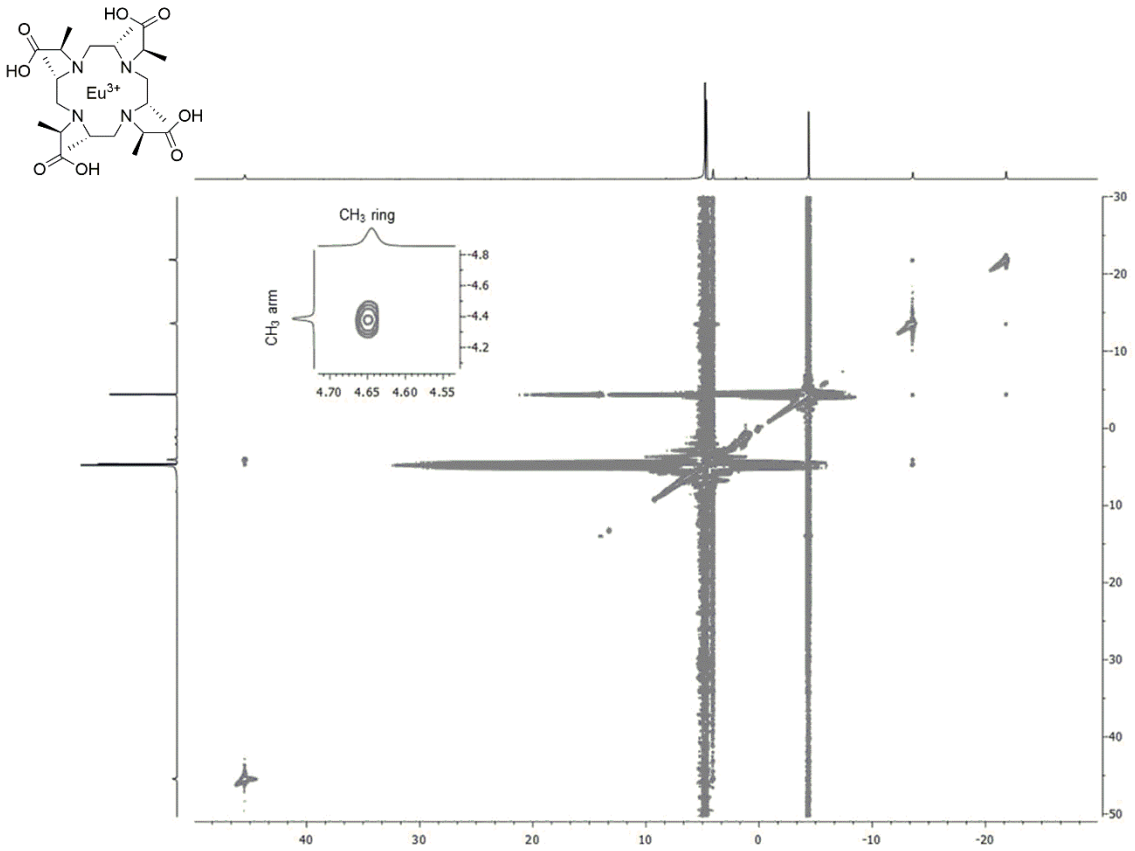
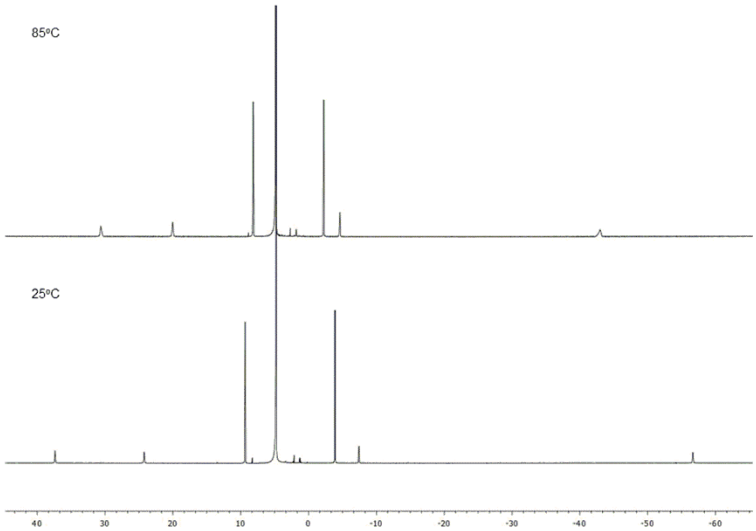
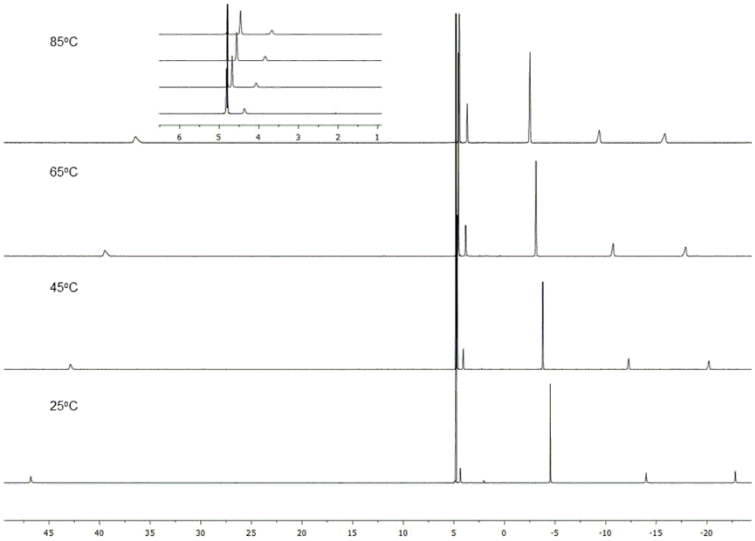



Figure S5. 2D NOESY spectrum of Eu-4S4R-M4DOTMA at 25°C and 400 MHz (mixing time = 5 ms).

a.


85ºC
25ºC
40
30
20
10
0
-10
-20
-30
-40
-50
-60

b.


85ºC
6
5
4
3
2
1
65ºC
45ºC
25ºC
45
40
35
30
25
20
15
10
5
0
-5
-10
-15
-20

c.

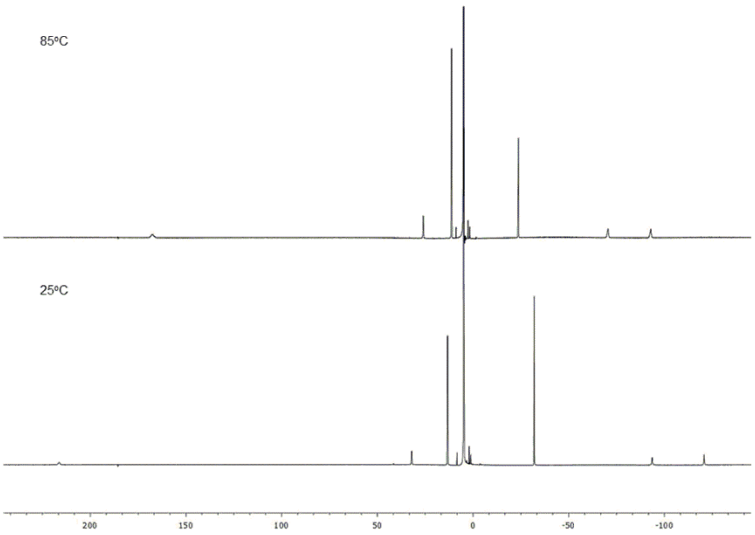

85ºC
25ºC
200
150
100
50
0
-50
-100

Figure S6. Variable temperature $^{1}H$ NMR spectra of (a) Pr-4S4R-M4DOTMA, (b) Eu-4S4R-M4DOTMA, and (c) Yb-4S4R-M4DOTMA at 400 MHz. The inset on Eu-4S4R-M4DOTMA shows a clearer view of the shift of the $CH_3$ ring protons as temperature is increased.

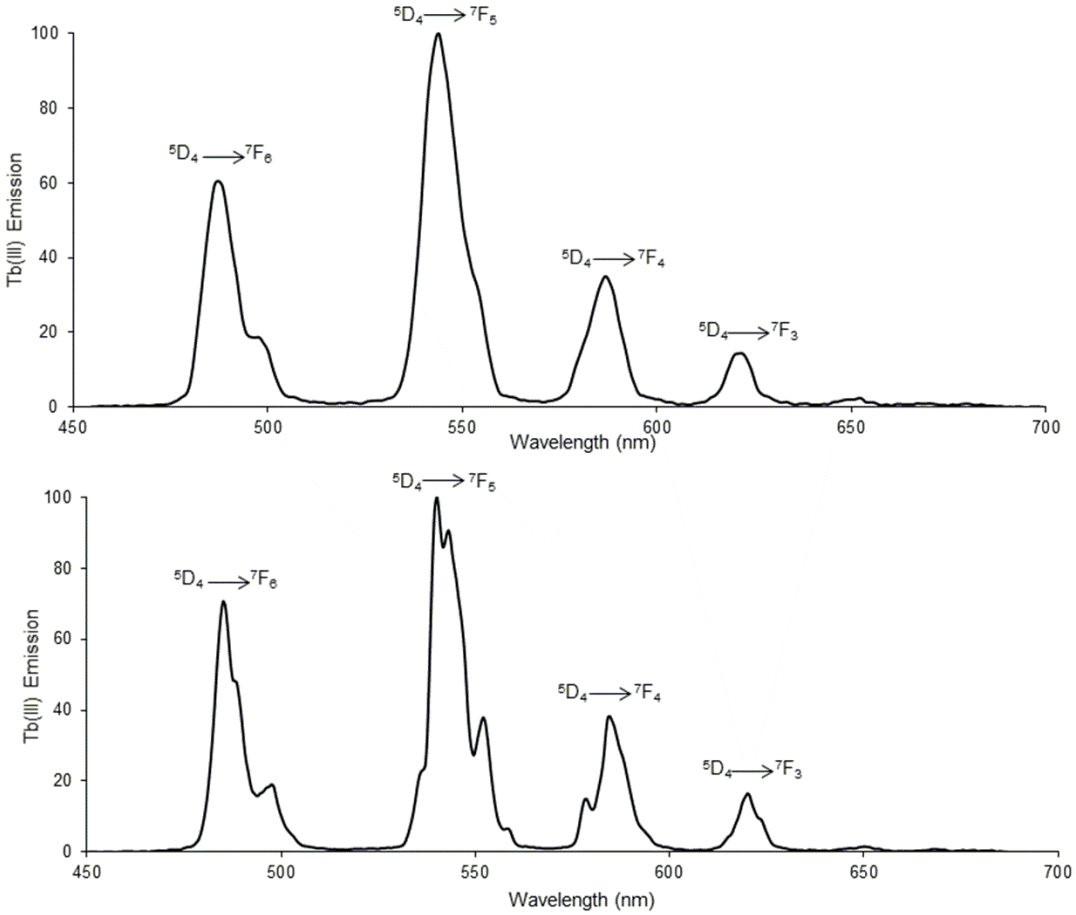



Figure S7. Normalized metal based emission spectrum of Tb-8S-M4DOTMA (top) and Tb-4S4R-M4DOTMA (bottom) with direct excitation of Tb(III) at 271 nm.

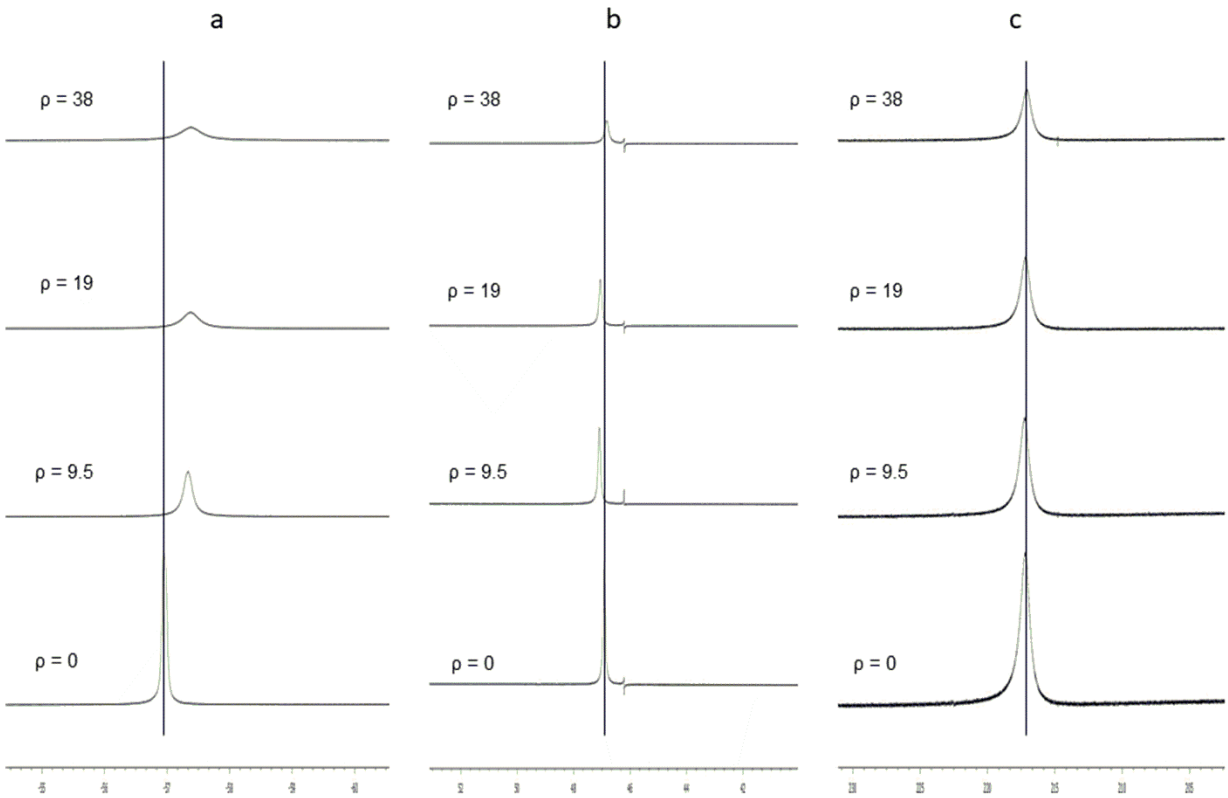



Figure S8. Proton NMR spectra showing the axial 1 protons of (a) Pr-4S4R-M4DOTMA, (b) Eu-4S4R-M4DOTMA, and (c) Yb-4S4R-M4DOTMA at increasing NaF concentrations (ρ = [NaF]/[Ln-M4DOTMA]). The vertical line guides the eye to show the change in the chemical shift as the ionic strength increases.

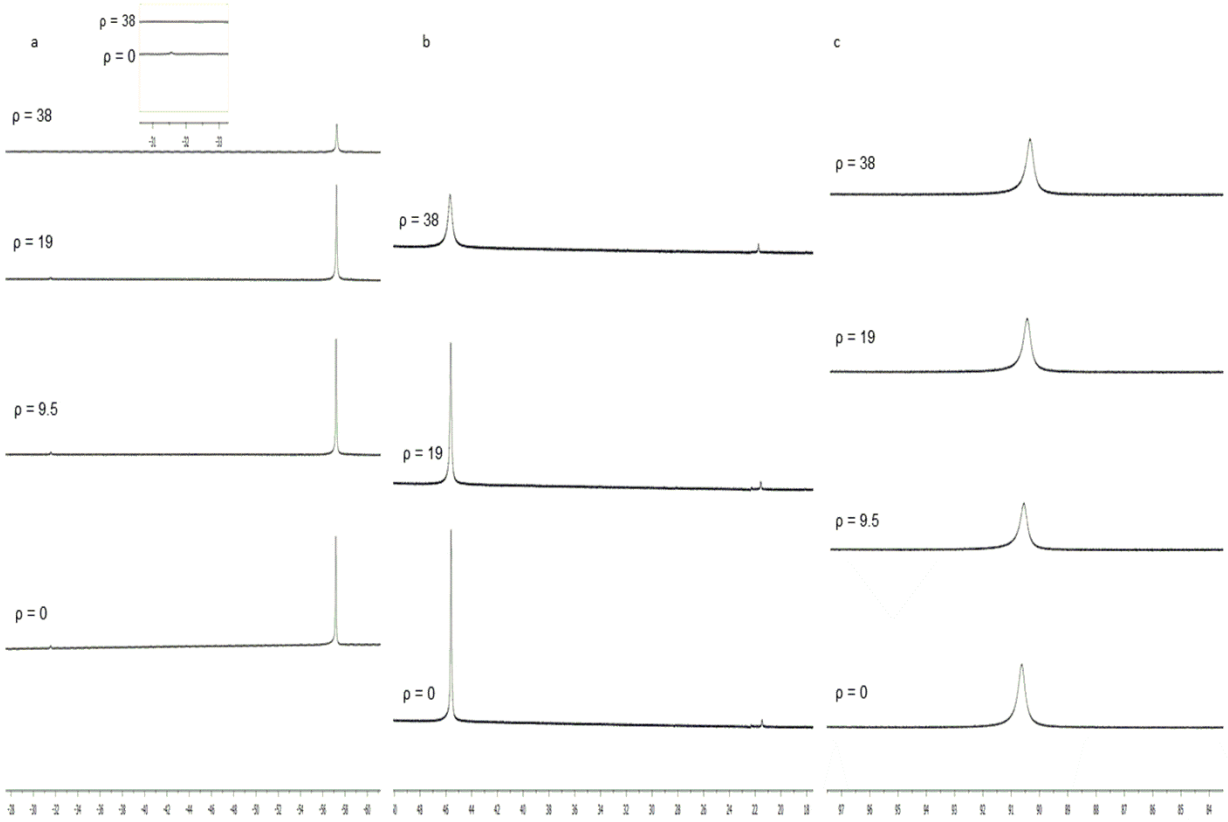



Figure S9. Proton NMR spectra showing the axial 1 protons of (a) Pr-8S-M4DOTMA, (b) Eu-8S-M4DOTMA, and (c) Yb-8S-M4DOTMA at increasing NaF concentrations (ρ = [NaF]/[Ln-M4DOTMA]). The inset shows a close-up of the axial 1 protons of the TSAP isomer of Pr-8S-M4DOTMA at ρ=0 and ρ=38.

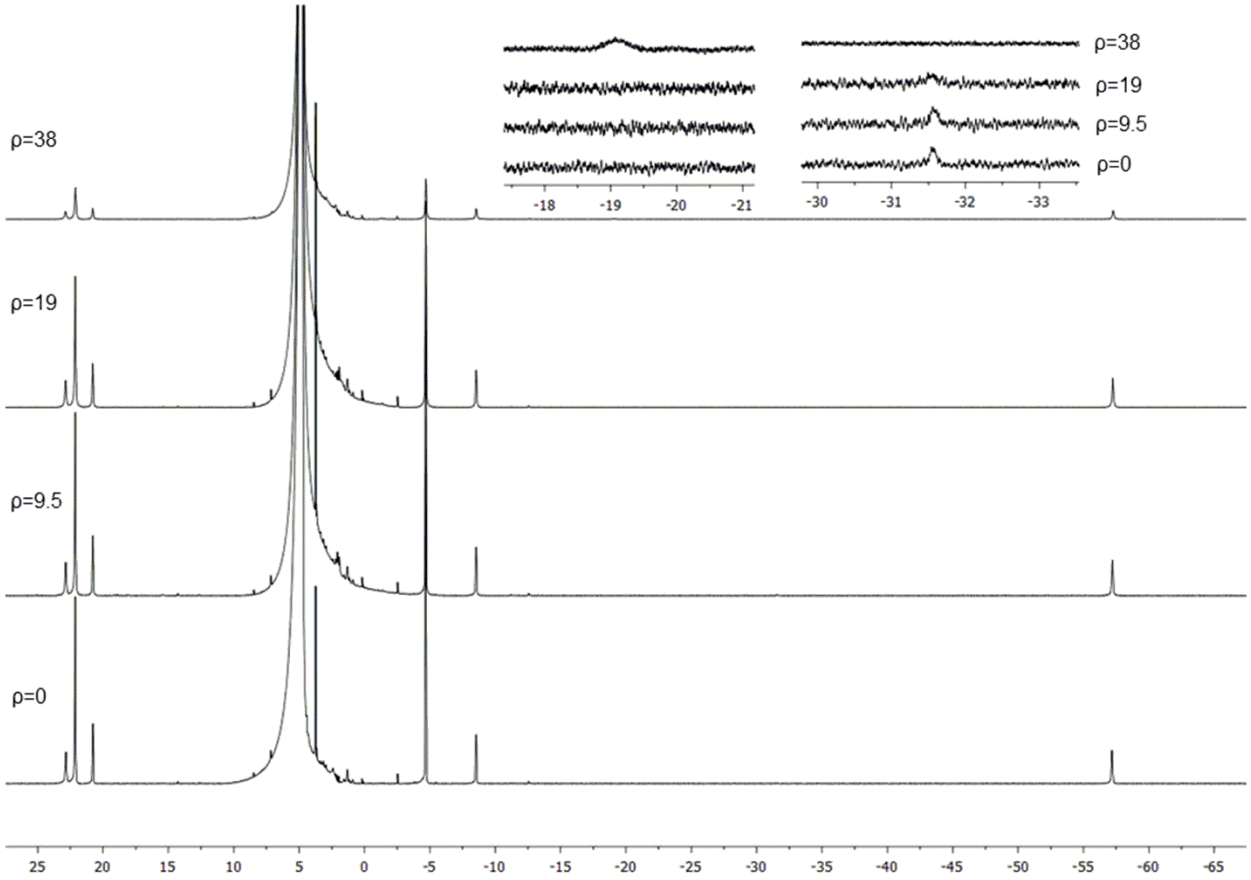



Figure S10. $^{1}$H-NMR of Pr-8S-M4DOTMA at 400 MHz and 298 K at increasing NaF concentration (ρ = [NaF]/[Ln-M4DOTMA]). The insets show the disappearance of the $ax_1$ of the SAP isomer (minor) and the appearance of a new peak at -19 ppm as the NaF concentration increases.

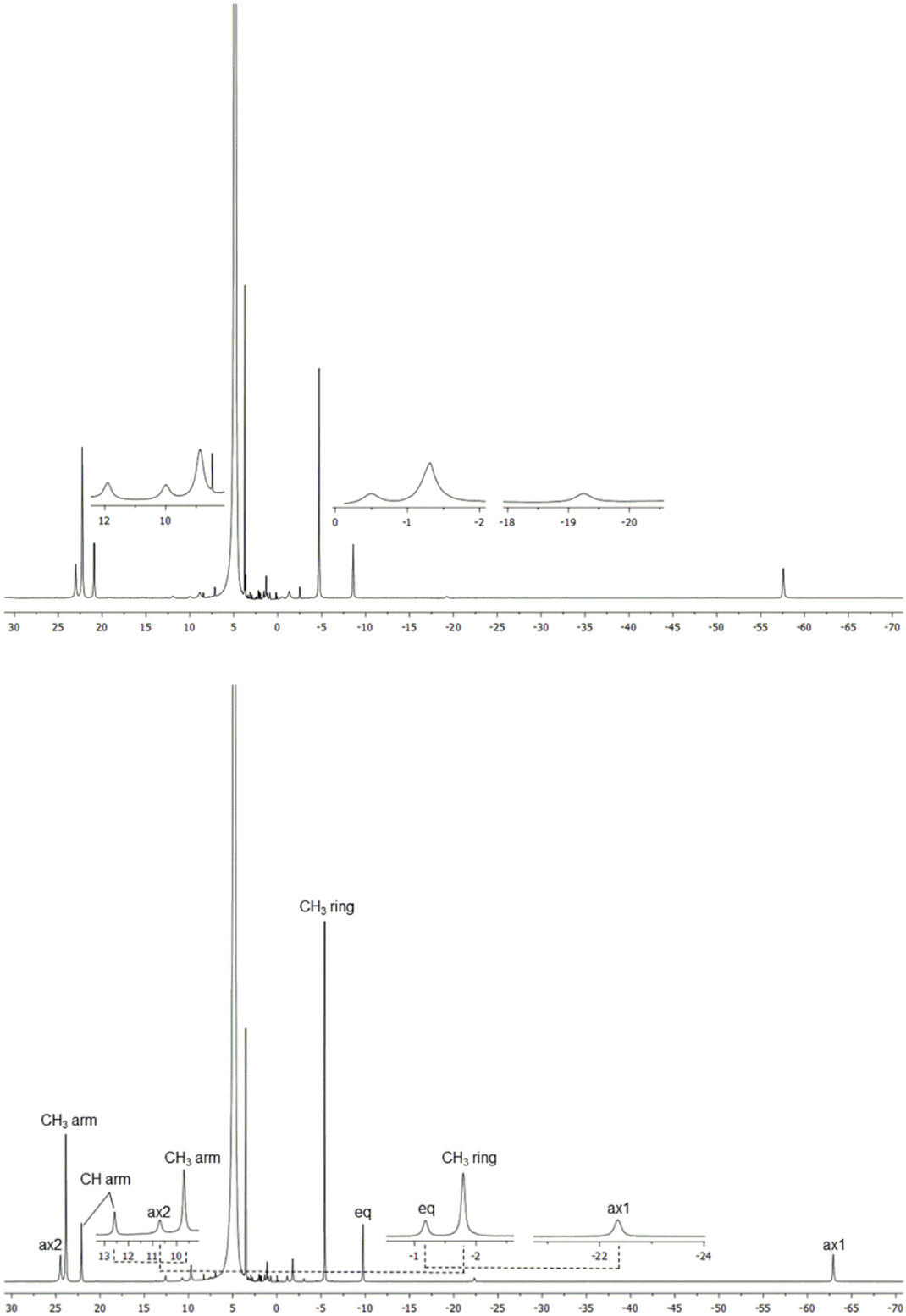



Figure S11. $^{1}$H-NMR of Pr-8S-M4DOTMA with NaF (ρ = [NaF]/[Ln-M4DOTMA] = 38) at 298 K (top) and 278 K (bottom) at 600 MHz. The dotted lines underneath the spectrum indicate the couplings

determined from 2D COSY at 278 K. The inset provides a closer view of the peaks from the minor TSAP isomer.

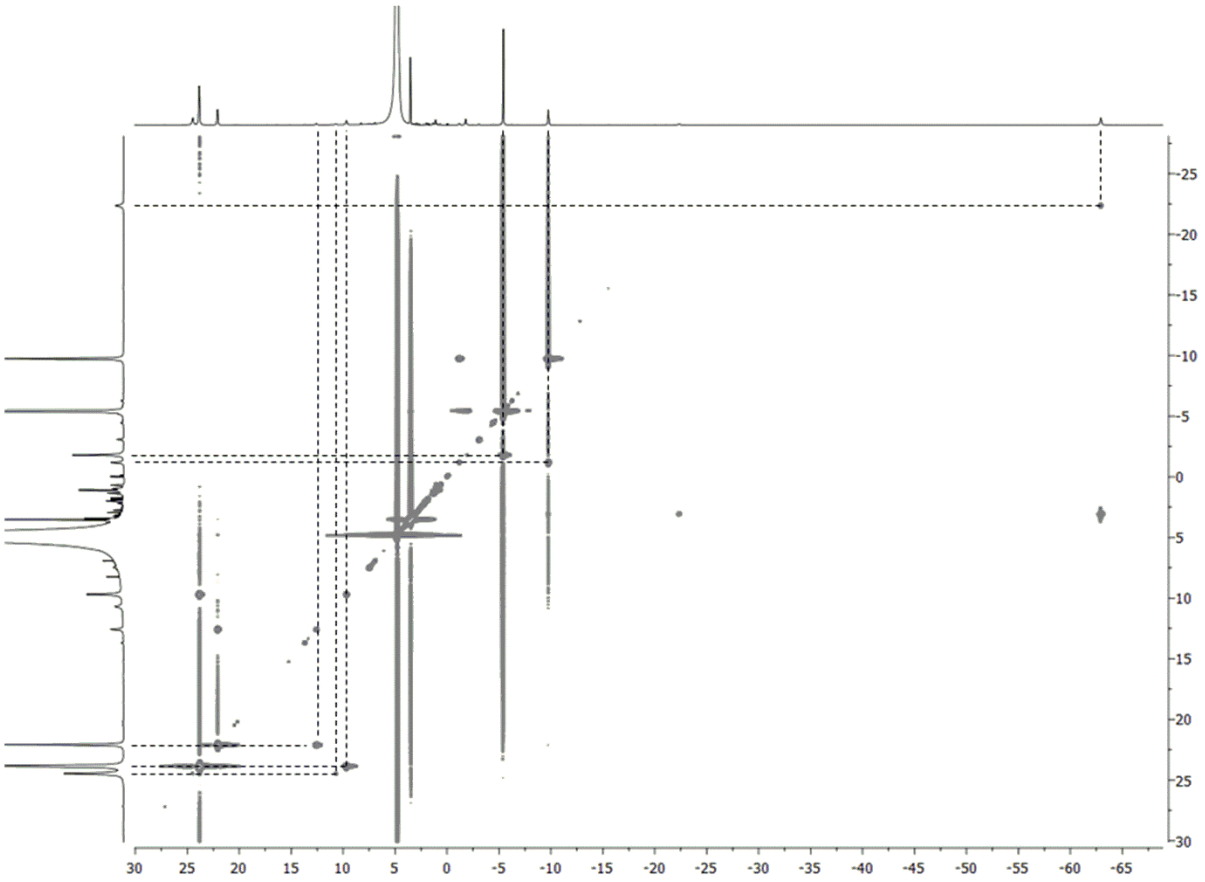



Figure S12. $^{1}$H-NMR EXSY spectrum of Pr-8S-M4DOTMA with NaF (ρ = [NaF]/[Ln-M4DOTMA] = 38) at 278 K and 600 MHz (mixing time = 25 ms). The dashed lines link two resonances that are connected by exchange cross peaks.

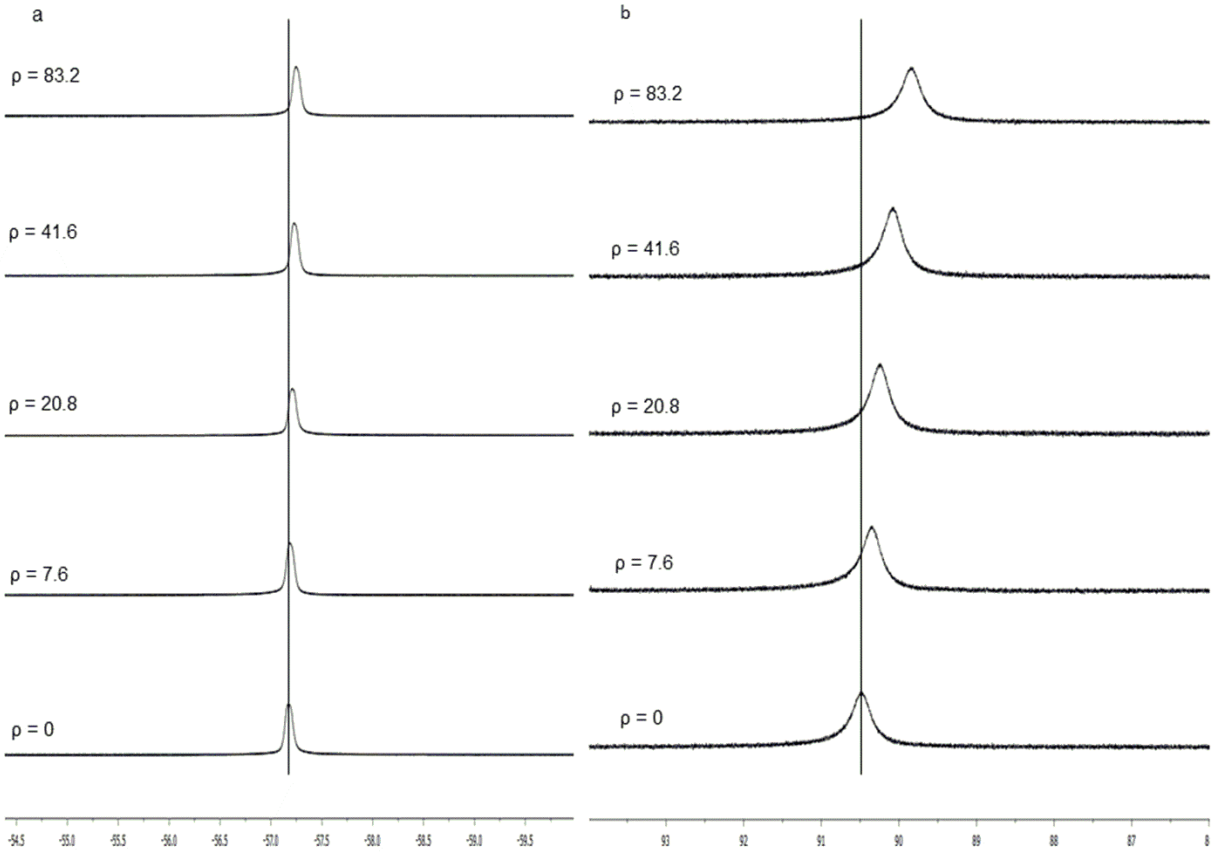



Figure S13. $^{1}$H-NMR showing the axial 1 protons of (a) Pr-8S-M4DOTMA and (b) Yb-8S-M4DOTMA at increasing NaCl concentration (ρ = [NaCl]/[Ln-8S-M4DOTMA]). The vertical line guides the eye to show the change in the chemical shift as the ionic strength increases.

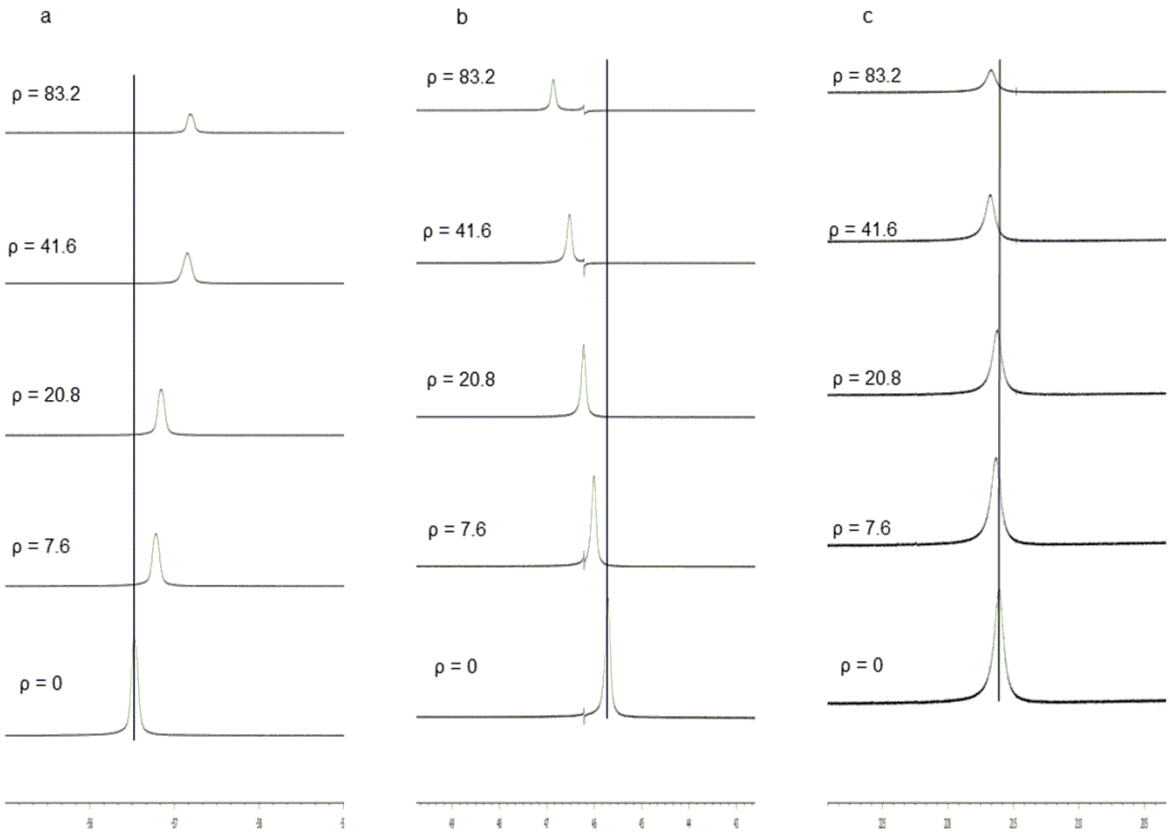



Figure S14. $^{1}$H-NMR showing the axial 1 protons of (a) Pr-4S4R-M4DOTMA, (b) Eu-4S4R-M4DOTMA, and (c) Yb-4S4R-M4DOTMA at increasing NaCl concentration (ρ = [NaCl]/[Ln-4S4R-M4DOTMA]). The vertical line guides the eye to show the change in the chemical shift as the ionic strength increases.