

Supporting Information

Giacomo M. Di Mauro¹, Nathaniel Z. Hardin¹, Ayyalusamy Ramamoorthy^{1,2,*}

¹Department of Chemistry, University of Michigan, Ann Arbor, MI, 48109-1055 (USA)

²Biophysics and Chemistry Department, Macromolecular Science and Engineering, and Biomedical Engineering, University of Michigan, Ann Arbor, MI, 48109-1055 (USA)

*Corresponding author:

Ayyalusamy Ramamoorthy, Email: ramamoor@umich.edu

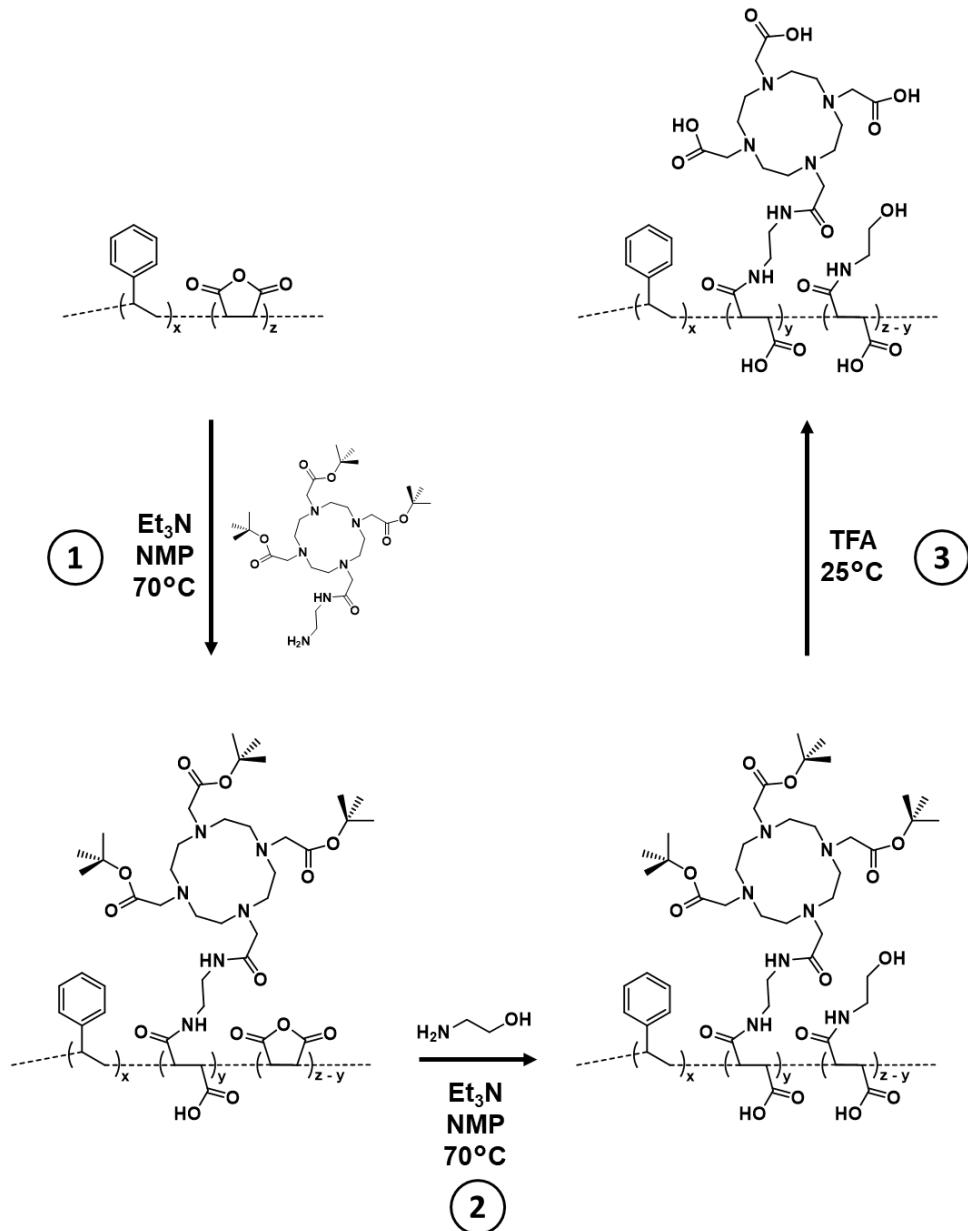


Figure S1. Reaction scheme for the synthesis of SMA-EA-DOTA: 1) The nucleophilic ring opening reaction using DOTA-t-butyl-acetate. 2) Nucleophilic ring opening reaction using ethanolamine. 3) TFA deprotection of DOTA.

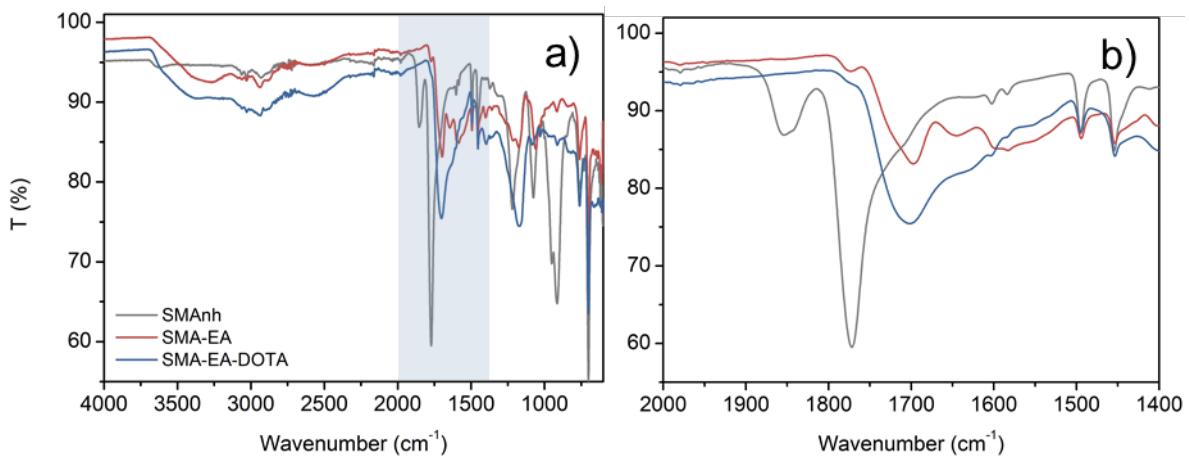


Figure S2. FT-IR spectra of copolymers. a) SMAnh, SMA-EA, and SMA-EA-DOTA; b) Expanded regions showing the C=O stretching frequency (2000-1400 cm^{-1}).

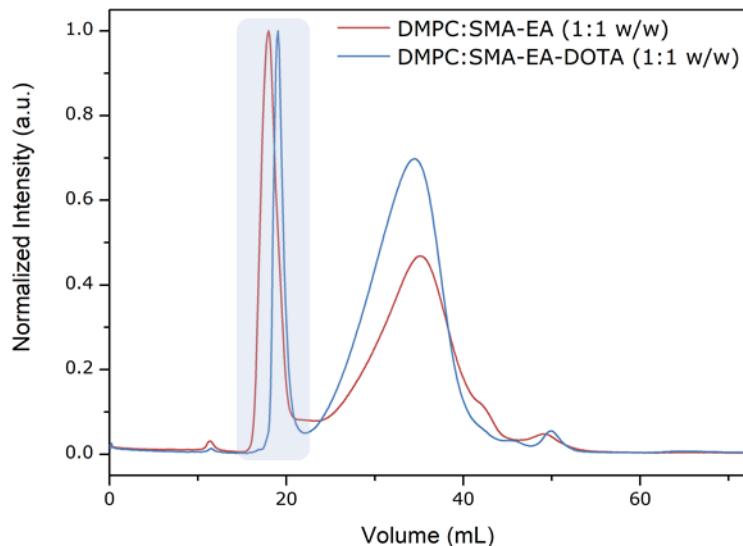


Figure S3. SEC Chromatograms of polymer-nanodiscs. 1:1 w/w DMPC: SMA-EA (red) and DMPC: SMA-EA-DOTA (blue) nanodiscs elution at room temperature.

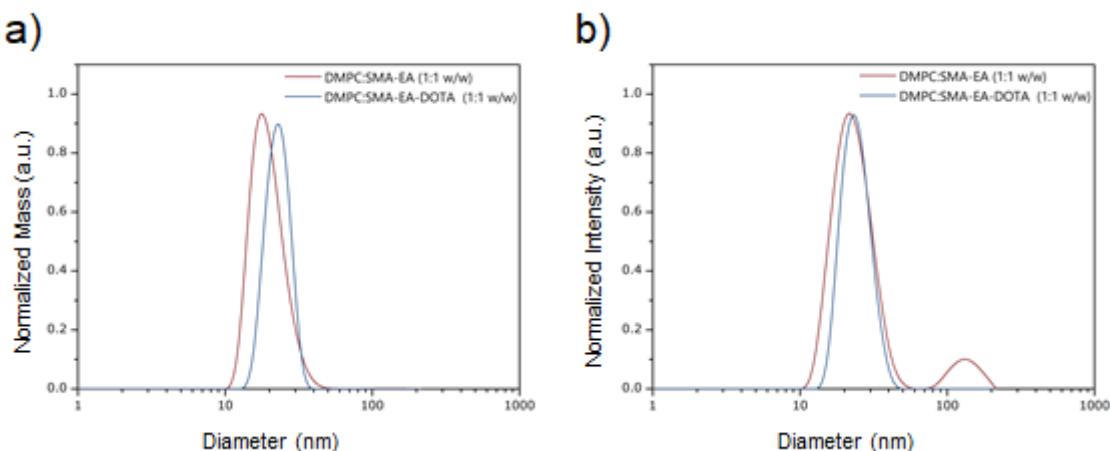


Figure S4. DLS of nanodiscs. DLS profiles of 1:1 w/w DMPC:SMA-EA (in red) and DMPC:SMA-EA-DOTA (in blue). a) The mass profiles, and b) intensity profiles. Both were obtained on samples passed through SEC.

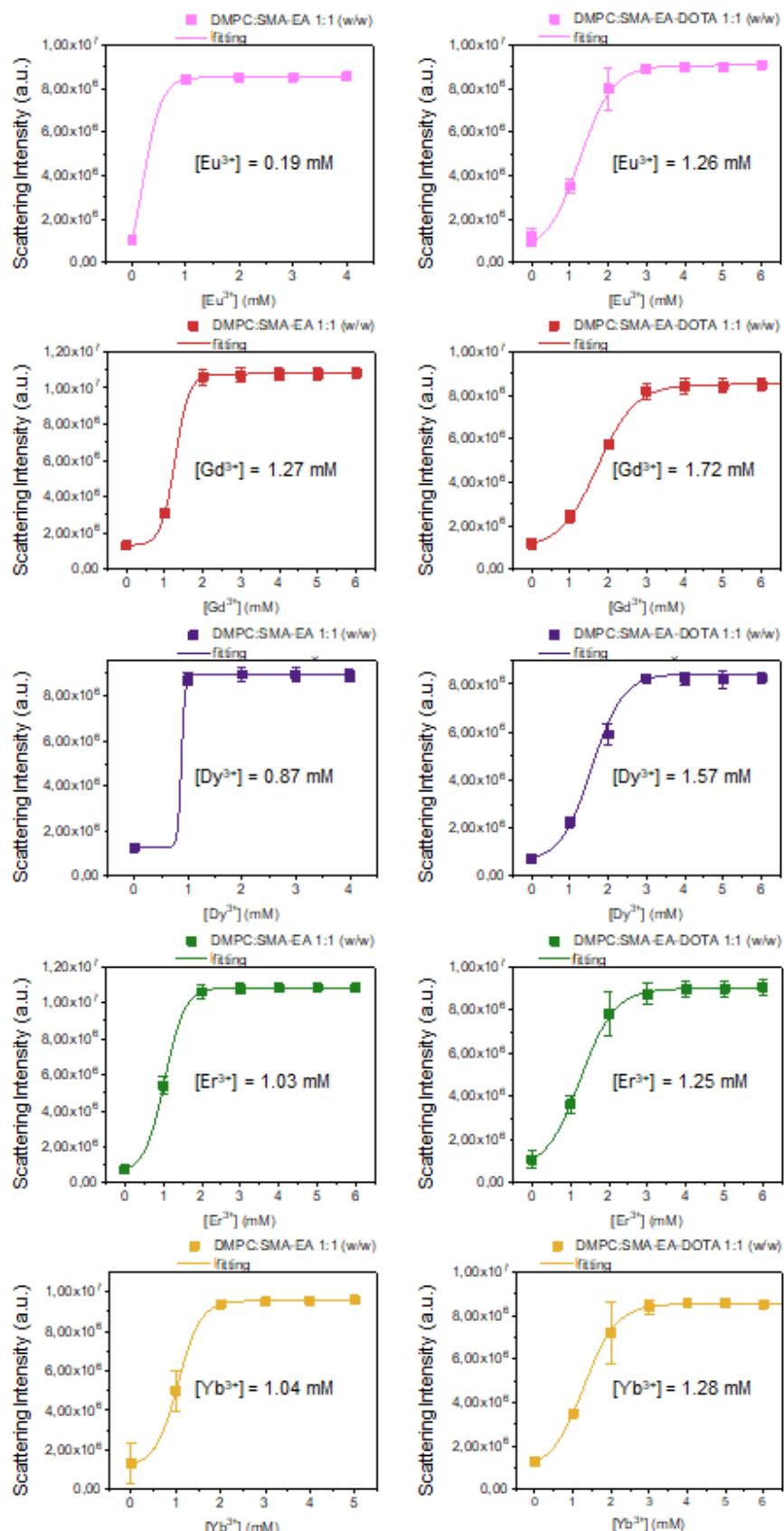


Figure S5. Static Light Scattering metal titrations. SLS traces obtained by titrating 1 mg of SMA-EA nanodiscs (left column) and SMA-EA-DOTA nanodiscs (right column) with a solution of varying metal ion concentration. The concentration values were obtained by fitting the experimental points, obtained in triplicate.

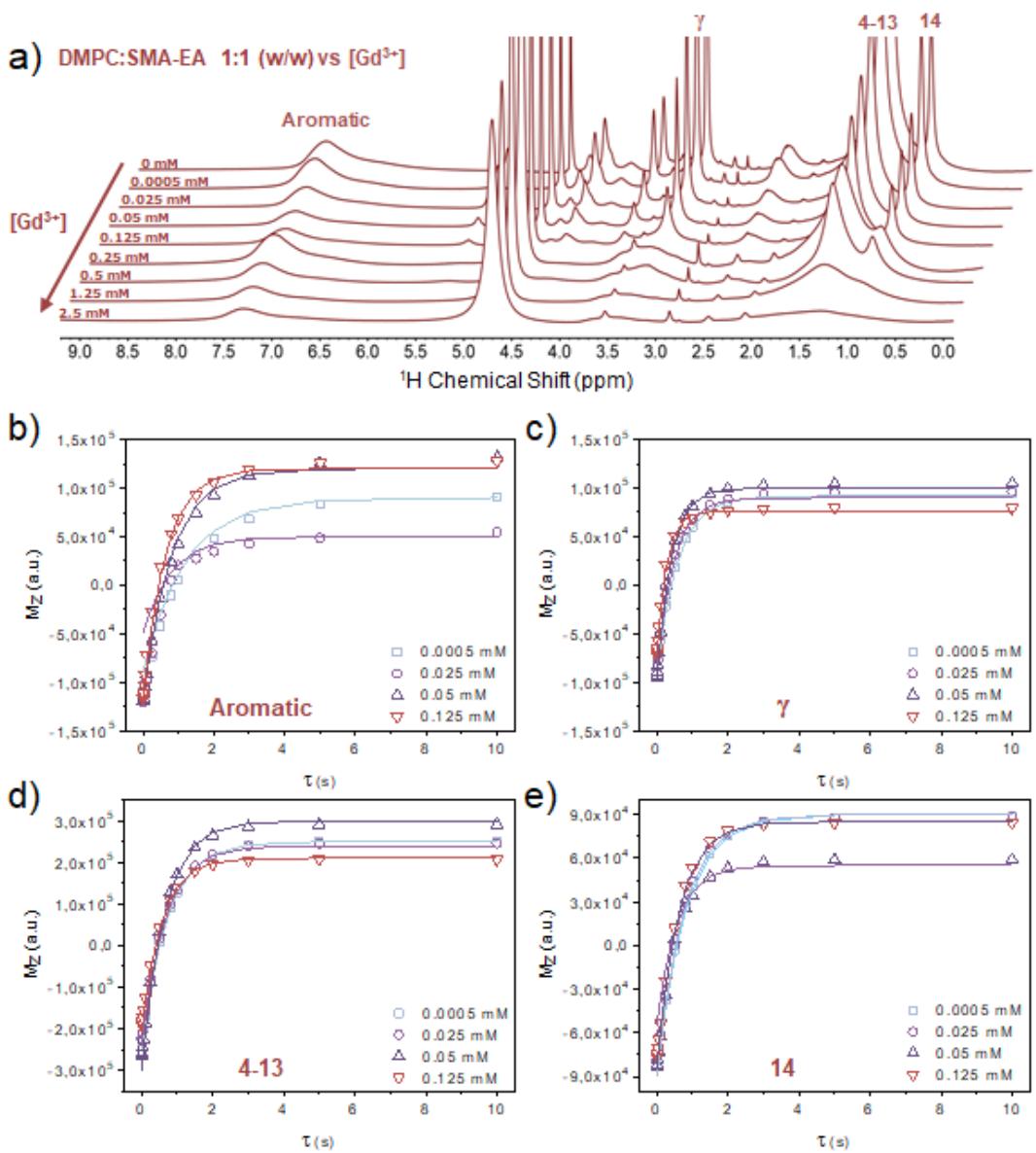


Figure S6. T_1 measurements for DMPC:SMA-EA 1:1 (w/w) macro-nanodiscs. a) the stacking of 1D ^1H -NMR spectra in the presence of different concentrations of $[Gd^{3+}]$ ions. b), c), d), and e) inversion recovery fitting plots of data for the selected ^1H peaks at various $[Gd^{3+}]$ concentrations.

$[Gd^{3+}]$ (mM)	^1H Peaks			
	Aromatic (s)	γ (s)	4-13 (s)	14 (s)
0	1.68	0.58	0.74	0.80
0.0005	1.20	0.58	0.72	0.81
0.025	0.80	0.48	0.67	0.76
0.05	0.82	0.40	0.65	0.56
0.125	0.64	0.27	0.56	0.62
0.25	N/D	N/D	N/D	N/D
0.5	N/D	N/D	N/D	N/D
1.25	N/D	N/D	N/D	N/D
2.5	N/D	N/D	N/D	N/D

Table S1. T_1 values measured from DMPC:SMA-EA 1:1 (w/w) macro-nanodiscs for varying $[Gd^{3+}]$. Values marked as N/D are data not determined due to significant line-broadening due to the presence of paramagnetic ions.

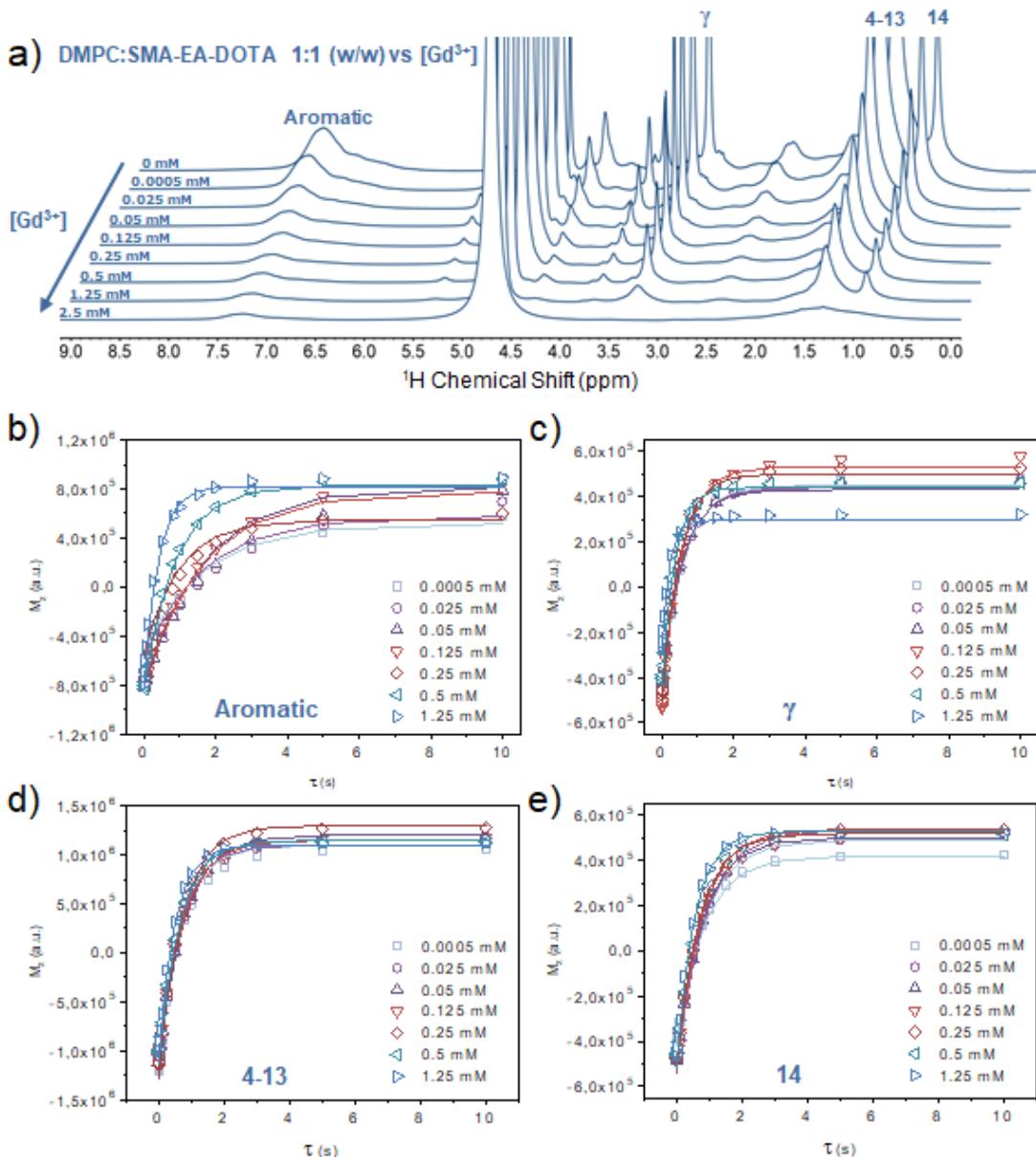


Figure S7. T₁ measurements for DMPC: SMA-EA-DOTA 1:1 (w/w) macro-nanodiscs. a) the stacking of 1D ¹H-NMR spectra in the presence of different concentrations of [Gd³⁺] ions. b), c), d), and e) inversion recovery plots for the selected ¹H peaks at various [Gd³⁺] concentrations.

[Gd ³⁺] (mM)	¹ H Peaks			
	Aromatic (s)	γ (s)	4-13 (s)	14 (s)
0	1.65	0.59	0.70	0.80
0.0005	1.70	0.60	0.70	0.85
0.025	1.70	0.58	0.67	0.83
0.05	1.70	0.56	0.77	0.87
0.125	1.70	0.53	0.72	0.79
0.25	0.97	0.49	0.70	0.76
0.5	0.89	0.35	0.65	0.70
1.25*	0.40	0.20	0.50	0.55
2.5	N/D	N/D	N/D	N/D

Table S2. T₁ values of DMPC: SMA-EA-DOTA 1:1 (w/w) macro nanodiscs for varying [Gd³⁺].

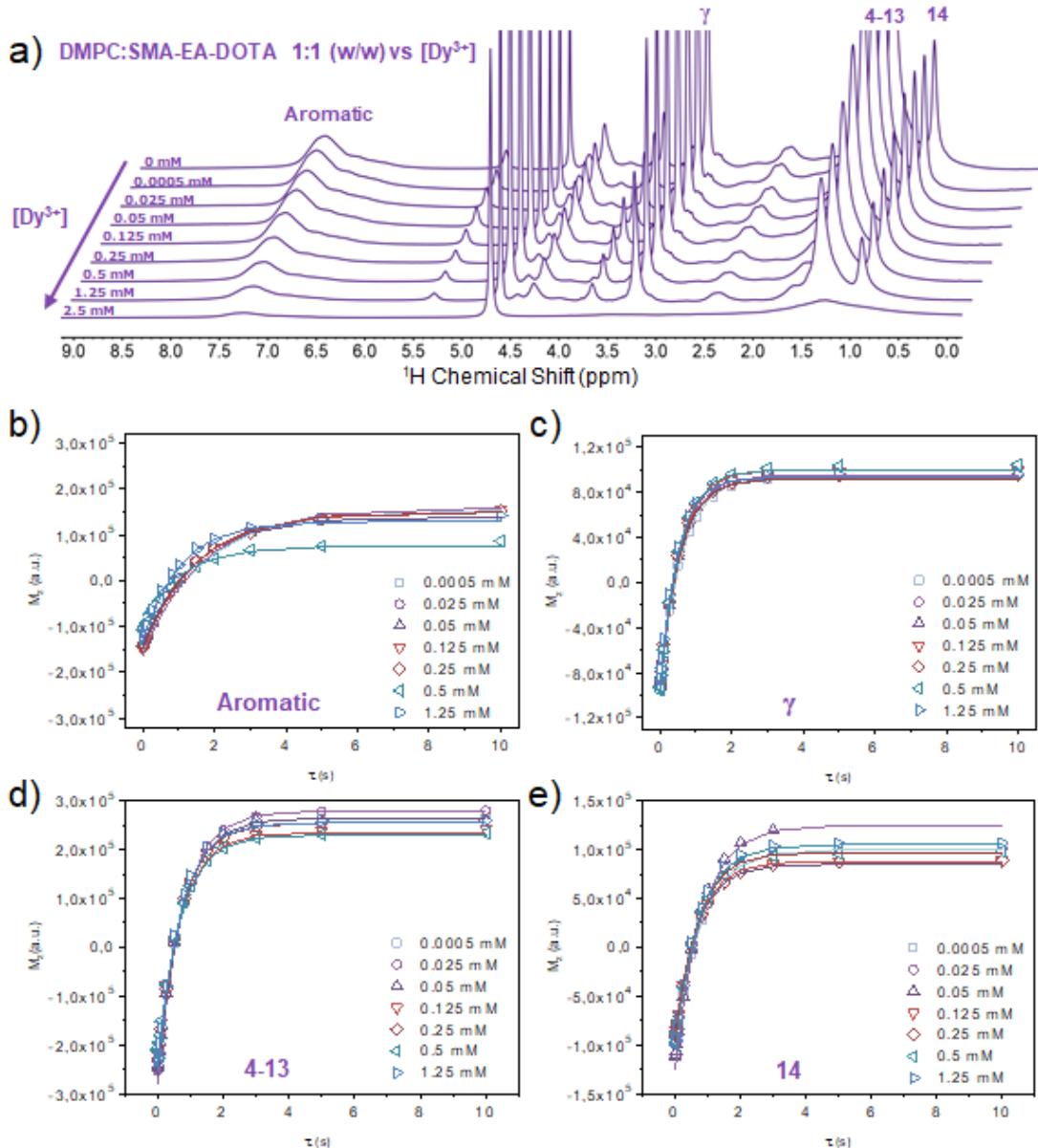


Figure S8. T_1 measurements for DMPC: SMA-EA-DOTA 1:1 (w/w) macro-nanodiscs. a) the stacking of 1D ^1H -NMR spectra in the presence of different concentrations of $[\text{Dy}^{3+}]$ ions. b), c), d), and e) inversion recovery plots for the selected ^1H peaks at various $[\text{Dy}^{3+}]$ concentrations.

$[\text{Dy}^{3+}]$ (mM)	Peaks			
	Aromatic (s)	γ (s)	4-13 (s)	14 (s)
0	1.65	0.59	0.70	0.80
0.0005	1.69	0.60	0.740	0.80
0.025	1.67	0.55	0.74	0.80
0.05	1.44	0.55	0.73	0.80
0.125	1.51	0.55	0.70	0.69
0.25	1.48	0.54	0.70	0.68
0.5	1.18	0.52	0.70	0.70
1.25	1.05	0.48	0.68	0.72
2.5	N/D	N/D	N/D	N/D

Table S3. T_1 values of DMPC: SMA-EA-DOTA 1:1 (w/w) macro nanodiscs for varying $[\text{Dy}^{3+}]$.

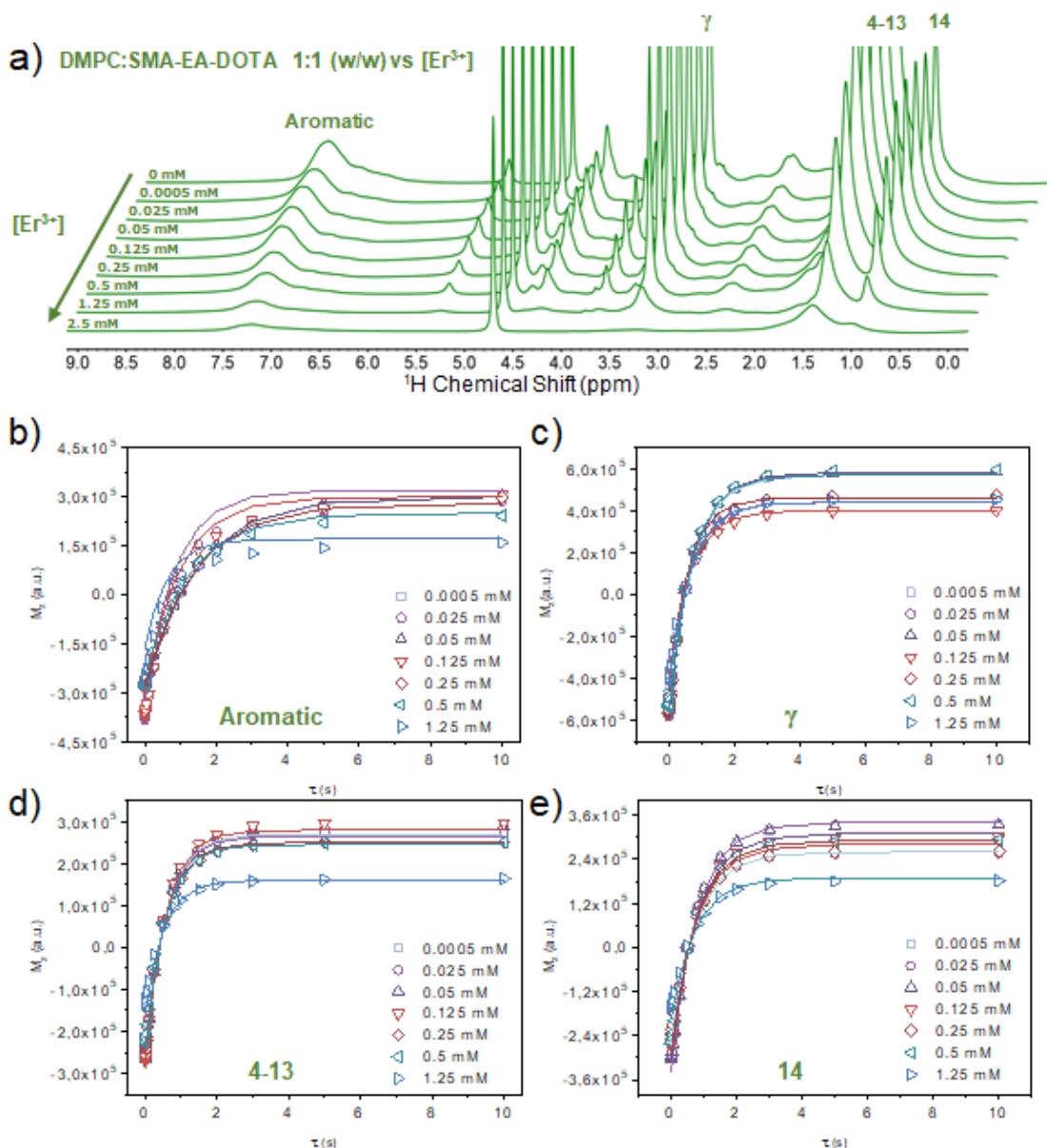


Figure S9. T₁ measurements for DMPC: SMA-EA-DOTA 1:1 (w/w) macro-nanodiscs. a) the stacking of 1D ¹H-NMR spectra in the presence of different concentrations of [Er³⁺] ions. b), c), d), and e) inversion recovery plots for the selected ¹H peaks at various [Er³⁺] concentrations.

[Er ³⁺] (mM)	Peaks			
	Aromatic (s)	γ (s)	4-13 (s)	14 (s)
0	1.65	0.59	0.70	0.80
0.0005	1.48	0.56	0.73	0.77
0.025	0.88	0.56	0.66	0.78
0.05	1.46	0.56	0.72	0.77
0.125	1.00	0.56	0.66	0.78
0.25	1.42	0.56	0.60	0.78
0.5	1.10	0.55	0.70	0.77
1.25	0.62	0.52	0.68	0.75
2.5	N/D	N/D	N/D	N/D

Table S4. T₁ values of DMPC: SMA-EA-DOTA 1:1 (w/w) macro nanodiscs for varying [Er³⁺].

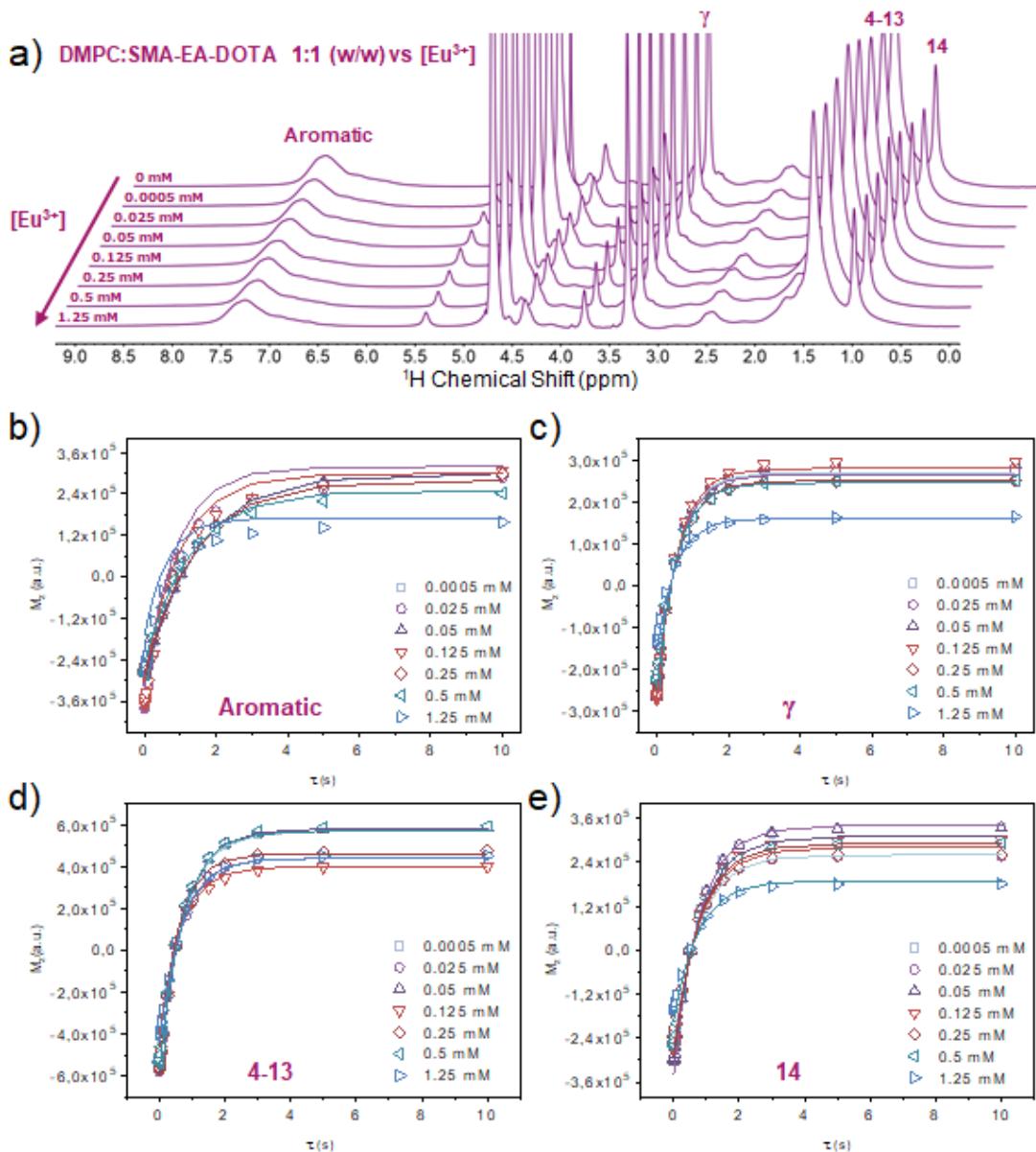


Figure S10. T₁ measurements for DMPC: SMA-EA-DOTA 1:1 (w/w) macro-nanodiscs. a) the stacking of 1D ¹H-NMR spectra in the presence of different concentrations of [Eu³⁺] ions. b), c), d), and e) inversion recovery fitting plots for the selected ¹H peaks at various [Eu³⁺] concentrations.

[Eu ³⁺] (mM)	Peaks			
	Aromatic (s)	γ (s)	4-13 (s)	14 (s)
0	1.65	0.59	0.70	0.80
0.0005	1.85	0.66	0.72	0.78
0.025	1.90	0.60	0.72	0.76
0.05	1.76	0.58	0.74	0.80
0.125	1.68	0.58	0.74	0.80
0.25	1.70	0.60	0.74	0.80
0.5	1.70	0.58	0.73	0.80
1.25	1.64	0.60	0.74	0.80
2.5	N/D	N/D	N/D	N/D

Table S5. T₁ values of DMPC: SMA-EA-DOTA 1:1 (w/w) macro nanodiscs for varying [Eu³⁺].

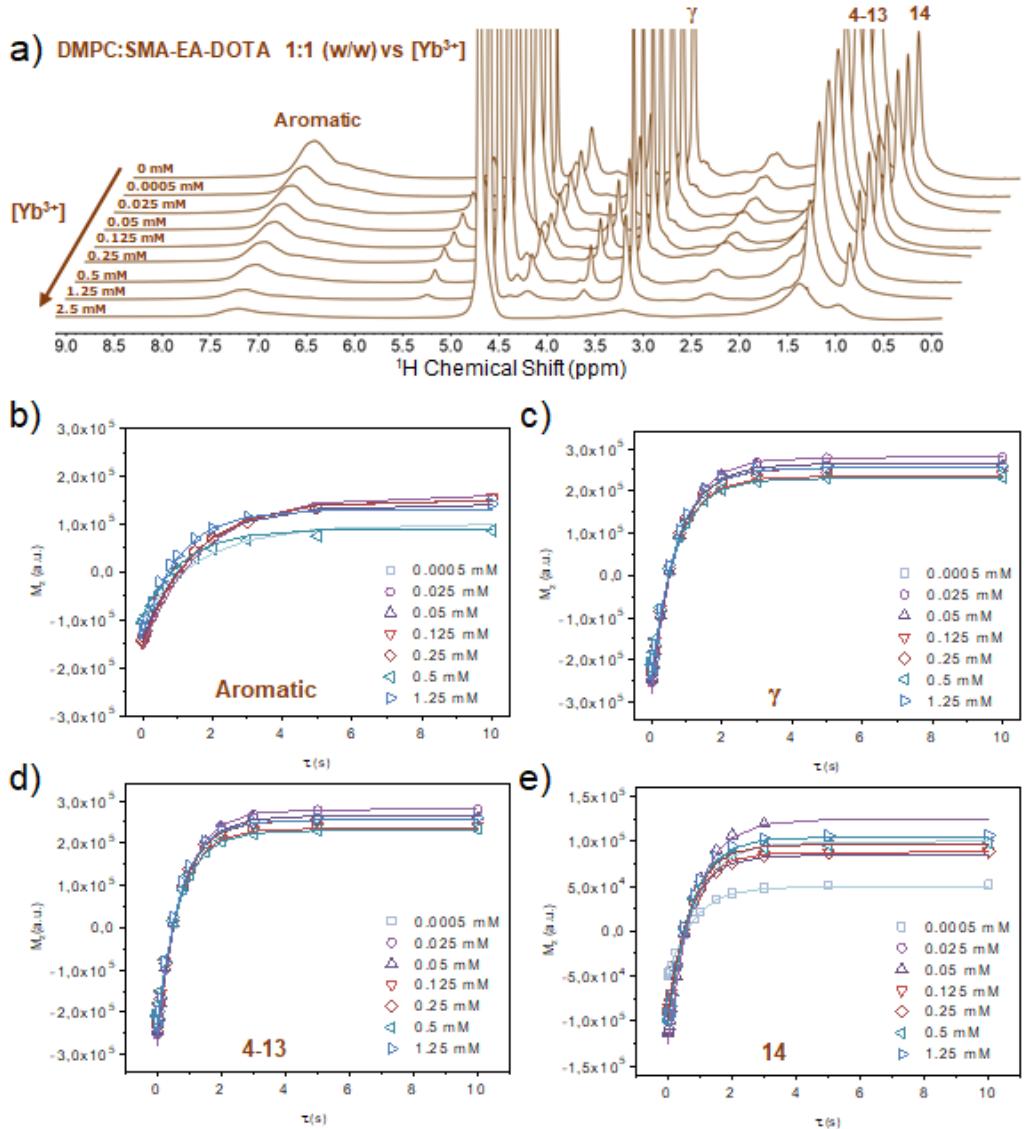


Figure S11. T_1 measurements for DMPC: SMA-EA-DOTA 1:1 (w/w) macro-nanodiscs. a) the stacking of 1D ¹H-NMR spectra in the presence of different concentrations of $[Yb^{3+}]$ ions. b), c), d), and e) inversion recovery plots for the selected ¹H peaks at various $[Yb^{3+}]$ concentrations.

$[Yb^{3+}]$ (mM)	Peaks			
	Aromatic (s)	γ (s)	4-13 (s)	14 (s)
0	1.65	0.59	0.70	0.80
0.0005	1.78	0.58	0.73	0.78
0.025	1.78	0.58	0.73	0.78
0.05	1.74	0.58	0.73	0.80
0.125	1.72	0.58	0.72	0.80
0.25	1.72	0.57	0.73	0.78
0.5	1.67	0.57	0.72	0.79
1.25	1.66	0.54	0.71	0.77
2.5	N/D	N/D	N/D	N/D

Table S6. T_1 values of DMPC: SMA-EA-DOTA 1:1 (w/w) macro nanodiscs for varying $[Yb^{3+}]$.

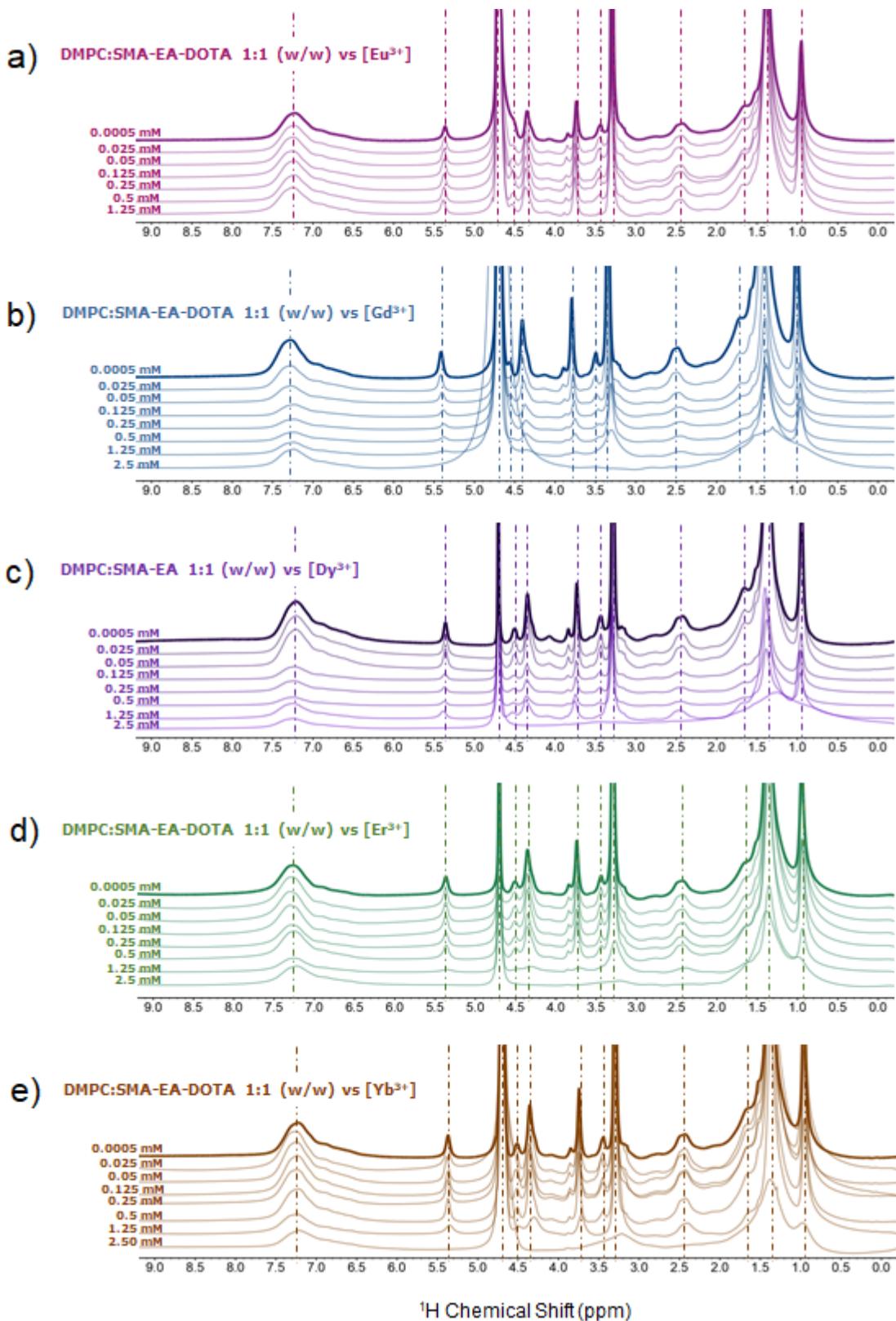


Figure S12. NMR spectra of SMA-EA-DOTA in the presence of paramagnetic metals. Stacking of 1D ¹H-NMR of DMPC: SMA-EA-DOTA 1:1 (w/w) macro-nanodiscs in the presence of different Ln³⁺ ions. Lanthanide trivalent ions such as Eu³⁺, Gd³⁺, Dy³⁺, Er³⁺, Yb³⁺ are respectively shown in a), b), c), d), and e).

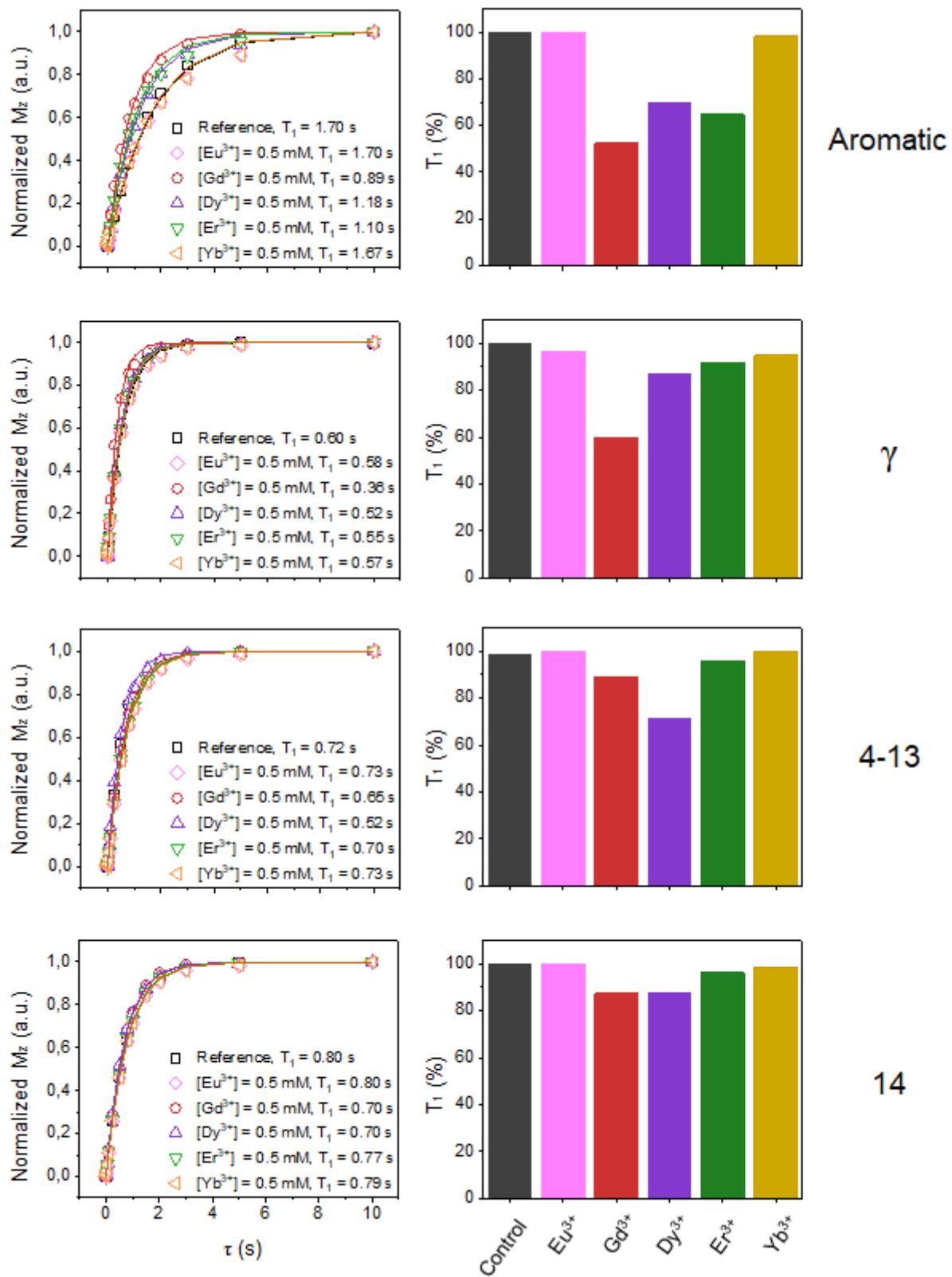


Figure S13. Normalized fitting (left panel) and normalized T_1 values (right panel) for DMPC: SMA-EA-DOTA 1:1 (w/w) macro-nanodiscs in the presence of 0.5 M Ln^{3+} . From top to bottom data relative to the aromatic, gamma, 2-13, and 14 1H peaks.