Supplementary information for:

Gd(III) Complexes Intercalated into Hydroxy Double Salts as Potential MRI Contrast Agents

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Table S1: Synthesis conditions and chemical formulae for all intercalates of Ni_2Zn_3-NO_3. The interlayer spacings listed below are those of the Gd^{3+} complex intercalates; in all cases reflections can also be seen between 7.7 and 9.7 Å corresponding to nitrate and/or carbonate intercalated HDS.

ID	Molar ratio [Ni_2Zn_3-NO_3: Gd complex]	Reaction time / day (s)	Interlayer spacing / Å	Chemical formula
D1	5 : 1	7	/	$[Ni_2Zn_3(OH)_8](GdC_{14}H_{18}O_{10}N_3)_{0.09}\cdot[(NO_3)+0.5(CO_3)]_{1.82}\cdot nH_2O$
D2	2 : 1	7	/	$[Ni_2Zn_3(OH)_8](GdC_{14}H_{18}O_{10}N_3)_{0.13}\cdot[(NO_3)+0.5(CO_3)]_{1.74}\cdot nH_2O$
D3	1 : 1	7	/	$[Ni_2Zn_{2.3}(OH)_8](GdC_{14}H_{18}O_{10}N_3)_{0.08}\cdot[(NO_3)+0.5(CO_3)]_{0.44}\cdot nH_2O$
D4	1 : 5	7	14.6	$[Ni_2Zn_3(OH)_8](GdC_{14}H_{18}O_{10}N_3)_{0.21}\cdot[(NO_3)+0.5(CO_3)]_{1.58}\cdot nH_2O$
D5	5 : 1	3	14.7	$[Ni_2Zn_3(OH)_8](GdC_{14}H_{18}O_{10}N_3)_{0.05}\cdot[(NO_3)+0.5(CO_3)]_{1.90}\cdot nH_2O$
D6	2 : 1	3	14.8	$[Ni_2Zn_3(OH)_8](GdC_{14}H_{18}O_{10}N_3)_{0.06}\cdot[(NO_3)+0.5(CO_3)]_{1.88}\cdot nH_2O$
D7	1 : 1	3	14.8	$[Ni_2Zn_4(OH)_8](GdC_{14}H_{18}O_{10}N_3)_{0.07}\cdot[(NO_3)+0.5(CO_3)]_{3.86}\cdot nH_2O$
D8	1 : 5	3	14.8	$[Ni_2Zn_3(OH)_8](GdC_{14}H_{18}O_{10}N_3)_{0.50}\cdot[(NO_3)+0.5(CO_3)]_{1.00}\cdot nH_2O$
D9	5 : 1	1	14.8	$[Ni_2Zn_3(OH)_8](GdC_{14}H_{18}O_{10}N_3)_{0.04}\cdot[(NO_3)+0.5(CO_3)]_{1.92}\cdot nH_2O$
D10	2 : 1	1	14.8	$[Ni_2Zn_3(OH)_8](GdC_{14}H_{18}O_{10}N_3)_{0.07}\cdot[(NO_3)+0.5(CO_3)]_{1.86}\cdot nH_2O$
D11	1 : 1	1	14.7	$[Ni_2Zn_{2.5}(OH)_8](GdC_{14}H_{18}O_{10}N_3)_{0.05}\cdot[(NO_3)+0.5(CO_3)]_{0.9}\cdot nH_2O$
D12	1 : 5	1	14.6	$[Ni_2Zn_3(OH)_8](GdC_{14}H_{18}O_{10}N_3)_{0.17}\cdot[(NO_3)+0.5(CO_3)]_{1.66}\cdot nH_2O$
P1	5 : 1	3	14.6	$[Ni_2Zn_3(OH)_8](GdC_9H_{23}N_3O_{15}P_5)_{0.34}\cdot[(NO_3)+0.5(CO_3)]_{1.32}\cdot nH_2O$
P2	2 : 1	3	/	$[Ni_2Zn_{4.1}(OH)_8](GdC_9H_{23}N_3O_{15}P_5)_{0.06}\cdot[(NO_3)+0.5(CO_3)]_{4.08}\cdot nH_2O$
P3	1 : 1	3	/	$[Ni_2Zn_3(OH)_8](GdC_9H_{23}N_3O_{15}P_5)_{0.10}\cdot[(NO_3)+0.5(CO_3)]_{1.80}\cdot nH_2O$
P4	5 : 1	1	/	$[Ni_2Zn_{2.5}(OH)_8](GdC_9H_{23}N_3O_{15}P_5)_{0.36}\cdot[(NO_3)+0.5(CO_3)]_{0.28}\cdot nH_2O$
P5	2 : 1	1	/	$[Ni_2Zn_3(OH)_8](GdC_9H_{23}N_3O_{15}P_5)_{0.05}\cdot[(NO_3)+0.5(CO_3)]_{1.90}\cdot nH_2O$
P6	1 : 1	1	14.5	$[Ni_2Zn_3(OH)_8](GdC_9H_{23}N_3O_{15}P_5)_{0.10}\cdot[(NO_3)+0.5(CO_3)]_{1.80}\cdot nH_2O$

Table S2: Experimental conditions, X-ray diffraction data and chemical formulae of the Zn_5-Gd(DTPA) intercalates. The reaction time is 7 days in all cases.

Sample	Molar ratio Zn_5-NO_3: $[Gd(DTPA)]^{2-}$	$[Gd(DTPA)]^{2-}$ interlayer spacing / Å	NO_3^- interlayer spacing / Å	Chemical formula
ZD1	2 : 1	18.4	9.3	$[Zn_5(OH)_8](GdC_{14}H_{18}O_{10}N_3)_{0.02}\cdot[(NO_3)+0.5(CO_3)]_{1.96}\cdot nH_2O$
ZD2	1 : 1	18.6	9.6	$[Zn_5(OH)_8](GdC_{14}H_{18}O_{10}N_3)_{0.07}\cdot[(NO_3)+0.5(CO_3)]_{1.86}\cdot nH_2O$
ZD3	1 : 5	/	9.3	$[Zn_5(OH)_8](GdC_{14}H_{18}O_{10}N_3)_{0.14}\cdot[(NO_3)+0.5(CO_3)]_{1.72}\cdot nH_2O$

Table S3: Proton relaxivities of the Zn_5-Gd(DTPA) materials.

Sample	[Gd] mM	T_1 [ms]	T_2 [ms]	r_1 [$s^{-1}mM^{-1}$]	r_2 [$s^{-1}mM^{-1}$]
Zn_5-NO_3	/	2806.00	81.27		
ZD1	0.21	355.67	70.73	13.63	68.52
ZD2	0.67	151.40	49.36	9.91	30.40
ZD3	1.36	247.67	84.77	2.97	8.67

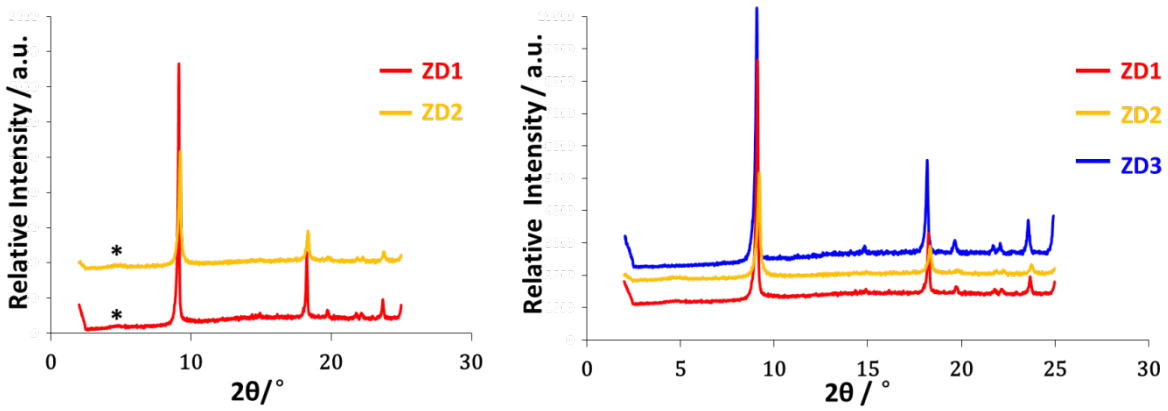

Fig. S1: X-ray diffraction patterns for the reaction products of Zn_5-NO_3 and $[Gd(DTPA)(H_2O)]^{2-}$, with intercalate reflections marked with *.

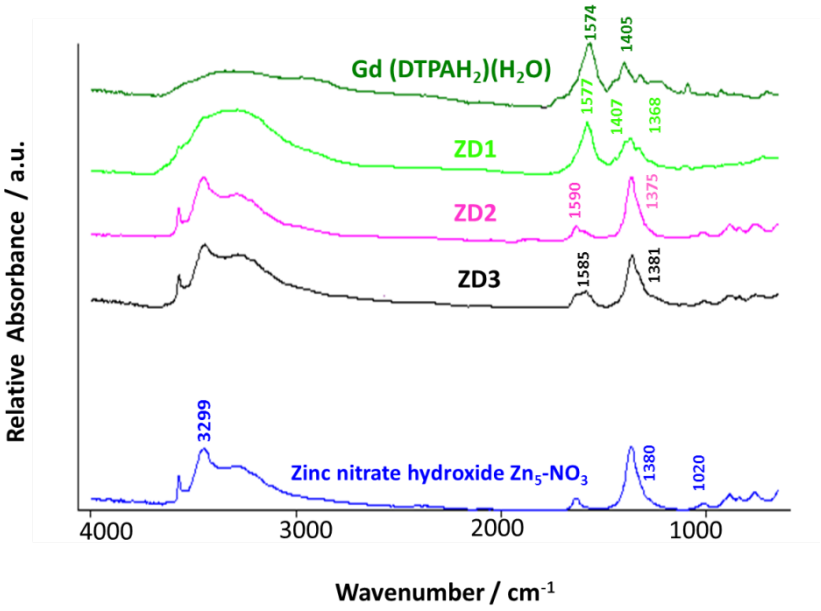

Fig. S2: IR spectra of Zn_5-NO_3 and its $[Gd(DTPA)(H_2O)]^{2-}$ intercalates.

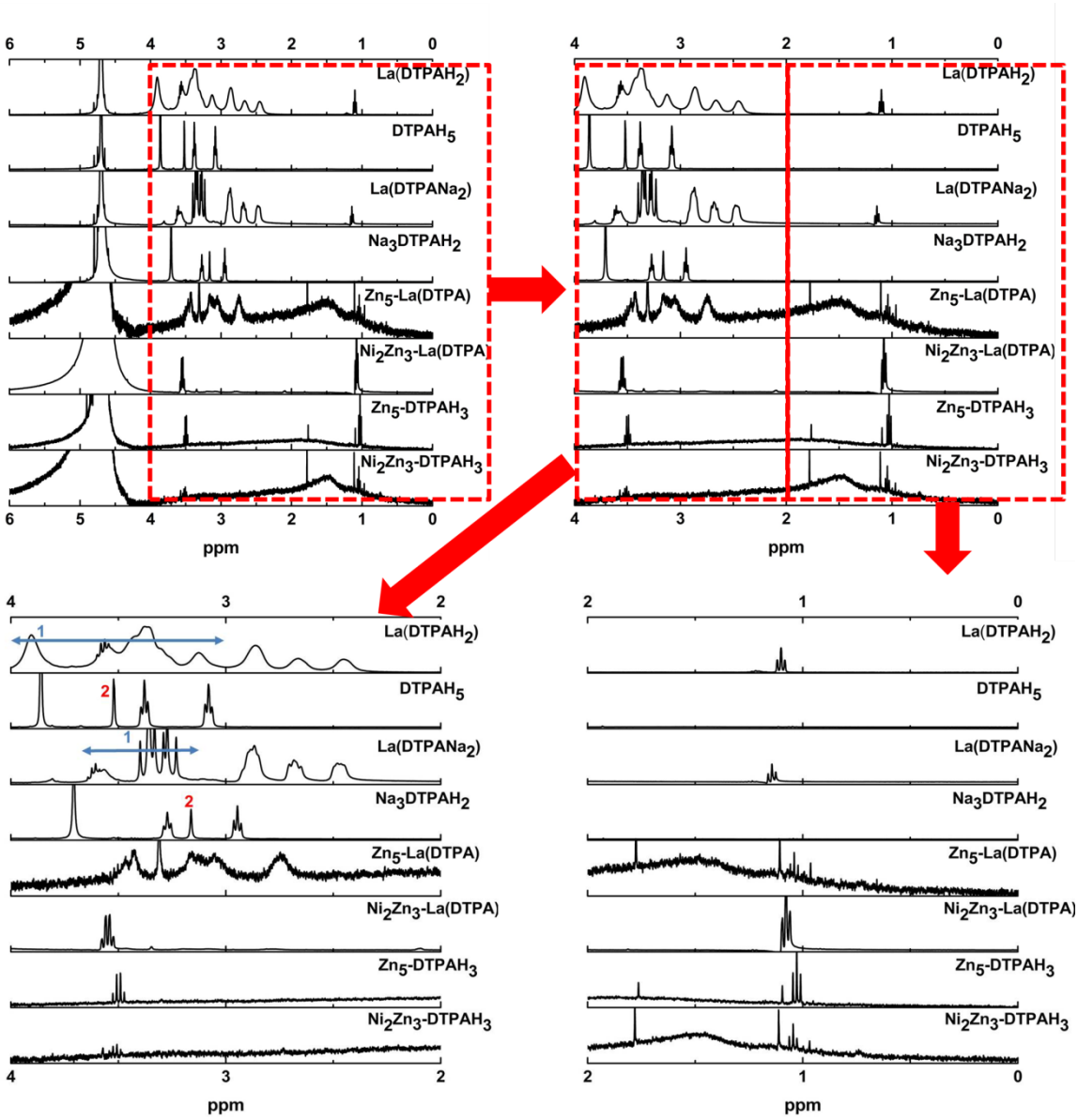

Fig. S3: ^{1}H NMR spectra (different expansions) of La(DTPAH$_2$)(H$_2$O), DTPAH$_5$, La(DTPANa$_2$), and Na$_3$DTPAH$_2$, and of [La(DTPA)(H$_2$O)]$^{2-}$, and [DTPAH$_3$]$^{2-}$ after de-intercalation from HDS hosts.

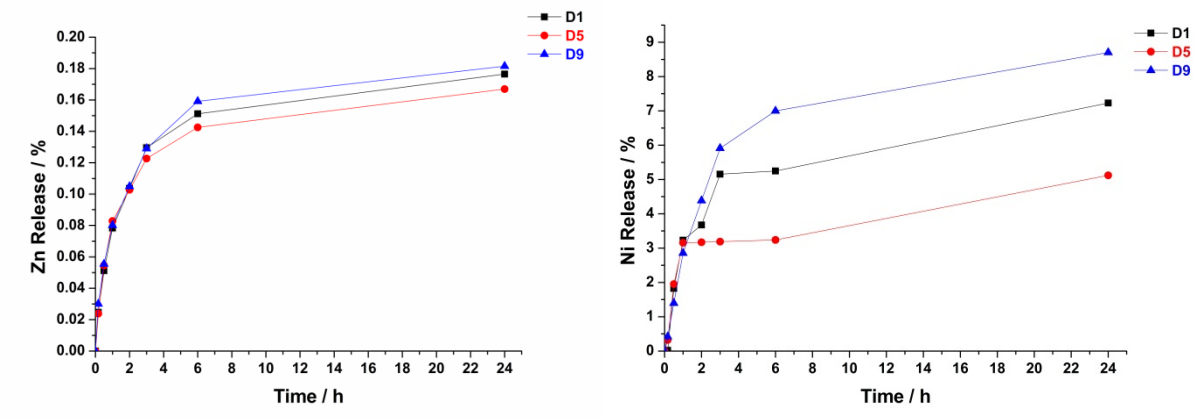

Fig. S4: Zn and Ni release profiles from selected HDSs.