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Supporting Information for

Towards the Rational Design of MRI Contrast Agents: Electron spin Relaxation is Largely Unaffected by the Coordination Geometry of Gadolinium(III) DOTA-type Complexes

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Table S1. ^{1}H-NMR results for the cycle protons of [Tb(*S-RRRR*-**1**)(D_2O)]$^{-}$

T (K)	^{1}H freq. (MHz)	Signal #	T_1 (ms)	$1/T_1$ (s^{-1})
295.2	200	1	0.733	1364
295.2	200	2	0.832	1202
295.2	200	3	0.739	1353
295.2	200	4	0.799	1252
295.2	200	5	1.860	538
295.2	200	6	1.450	690
295.2	200	7	1.561	641
295.2	200	8	1.966	509
295.2	200	9	1.713	584
295.2	200	10	1.668	600
295.2	200	11	1.420	704
332.7	200	1	0.996	1004
332.7	200	2	1.266	790
332.7	200	3	1.130	885
332.7	200	4	1.099	910
332.7	200	5	2.835	353
332.7	200	6	N/A	N/A
332.7	200	7	2.391	418
332.7	200	8	2.377	421
332.7	200	9	2.587	387
332.7	200	10	2.392	418
332.7	200	11	2.165	462
295.2	400	1	0.404	2475
295.2	400	2	0.499	2004
295.2	400	3	0.442	2262
295.2	400	4	0.432	2315
295.2	400	5	1.077	929
295.2	400	6	0.907	1103
295.2	400	7	0.997	1003
295.2	400	8	0.943	1060
295.2	400	9	0.944	1059
295.2	400	10	0.926	1080
295.2	400	11	0.829	1206
332.7	400	1	0.666	1502
332.7	400	2	0.833	1200
332.7	400	3	0.730	1370
332.7	400	4	0.717	1395
332.7	400	5	1.779	562
332.7	400	6	N/A	N/A
332.7	400	7	1.598	626
332.7	400	8	1.619	618
332.7	400	9	1.642	609
332.7	400	10	1.573	636
332.7	400	11	1.426	701
295.2	500	1	0.313	3195
295.2	500	2	0.410	2439
295.2	500	3	0.340	2941
295.2	500	4	0.330	3030
295.2	500	5	0.896	1116
295.2	500	6	0.753	1328
295.2	500	7	0.762	1312
295.2	500	8	0.845	1183
295.2	500	9	0.752	1330
295.2	500	10	0.729	1372
295.2	500	11	0.672	1488
332.7	500	1	0.521	1919
332.7	500	2	0.636	1572
332.7	500	3	0.565	1770
332.7	500	4	0.559	1789
332.7	500	5	1.460	685
332.7	500	6	1.136	880
332.7	500	7	1.252	799
332.7	500	8	1.279	782
332.7	500	9	1.308	765
332.7	500	10	1.225	816
332.7	500	11	1.093	915

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Table S2. ^{1}H-NMR results for the macrocyclic protons of [Tb(*S*-*SSSS*-**1**)(D_2O)]$^{-}$

T (K)	^{1}H Freq. (MHz)	Signal #	T_1 (ms)	$1/T_1$ (s^{-1})
295.2	200	1	0.772	1295
295.2	200	2	0.698	1433
295.2	200	3	0.611	1637
295.2	200	4	0.674	1484
295.2	200	5	1.687	593
295.2	200	6	1.237	808
295.2	200	7	1.620	617
295.2	200	8	1.291	775
295.2	200	9	1.291	775
295.2	200	10	1.142	876
295.2	200	11	1.130	885
332.7	200	1	1.184	845
332.7	200	2	0.874	1144
332.7	200	3	0.890	1124
332.7	200	4	0.996	1004
332.7	200	5	2.502	400
332.7	200	6	1.885	531
332.7	200	7	2.045	489
332.7	200	8	1.877	533
332.7	200	9	1.877	533
332.7	200	10	1.745	573
332.7	200	11	1.800	556
295.2	400	1	0.509	1965
295.2	400	2	0.366	2732
295.2	400	3	0.386	2591
295.2	400	4	0.419	2387
295.2	400	5	1.095	913
295.2	400	6	0.920	1087
295.2	400	7	1.018	982
295.2	400	8	0.793	1261
295.2	400	9	0.823	1215
295.2	400	10	0.763	1311
295.2	400	11	0.803	1245

T (K)	^{1}H Freq. (MHz)	Signal #	T_1 (ms)	$1/T_1$ (s^{-1})
332.7	400	1	0.816	1225
332.7	400	2	0.602	1661
332.7	400	3	0.645	1550
332.7	400	4	0.700	1429
332.7	400	5	1.781	561
332.7	400	6	1.480	676
332.7	400	7	1.576	635
332.7	400	8	1.352	740
332.7	400	9	1.352	740
332.7	400	10	1.261	793
332.7	400	11	1.344	744
295.2	500	1	0.411	2433
295.2	500	2	0.309	3236
295.2	500	3	0.342	2924
295.2	500	4	0.350	2857
295.2	500	5	0.908	1101
295.2	500	6	0.721	1387
295.2	500	7	0.766	1305
295.2	500	8	0.605	1653
295.2	500	9	0.636	1572
295.2	500	10	0.561	1783
295.2	500	11	0.587	1704
332.7	500	1	0.695	1439
332.7	500	2	0.498	2008
332.7	500	3	0.559	1789
332.7	500	4	0.591	1692
332.7	500	5	1.466	682
332.7	500	6	1.196	836
332.7	500	7	1.265	791
332.7	500	8	1.098	911
332.7	500	9	1.060	943
332.7	500	10	0.988	1012
332.7	500	11	1.062	942

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Table S3. Analysis of the longitudinal relaxation rates of the cycle protons of [Tb(*S*-*RRRR*-**1**)(D_2O)]$^-$

^{1}H signal #	r_{TbH} (Å)	Residual $1/T_1$ (s^{-1}) [295.2 K]	Residual $1/T_1$ (s^{-1}) [332.7 K]	Residual $1/T_1$ (s^{-1}) [295.2 K, average τ_R]	Residual $1/T_1$ (s^{-1}) [332.7 K, average τ_R]
1	3.76	1173 ± 72	855 ± 20	1083 ± 58	964 ± 35
2	3.76	739 ± 72	567 ± 20	649 ± 58	677 ± 35
3	3.76	1013 ± 72	721 ± 20	923 ± 582	831 ± 35
4	3.76	1027 ± 72	744 ± 20	937 ± 58	854 ± 35
5	4.27	314 ± 59	244 ± 17	272 ± 582	295 ± 35
6	4.27	494 ± 59	404 ± 29	452 ± 58	487 ± 60
7	4.27	439 ± 59	325 ± 17	397 ± 58	376 ± 35
8	4.27	371 ± 59	318 ± 17	329 ± 58	369 ± 35
9	4.27	445 ± 59	298 ± 17	403 ± 58	349 ± 35
10	4.27	471 ± 59	334 ± 17	429 ± 58	385 ± 35
11	4.27	586 ± 59	404 ± 17	544 ± 58	455 ± 35

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Table S4. Analysis of the longitudinal relaxation rates of the cycle protons of [Tb(*S*-*SSSS*-**1**)(D_2O)]$^-$

^{1}H signal #	r_{TbH} (Å)	Residual $1/T_1$ (s^{-1}) [295.2 K]	Residual $1/T_1$ (s^{-1}) [332.7 K]	Residual $1/T_1$ (s^{-1}) [295.2 K, average τ_R]	Residual $1/T_1$ (s^{-1}) [332.7 K, average τ_R]
1	3.76	810 ± 90	647 ± 31	635 ± 80	659 ± 24
2	3.76	1379 ± 90	1082 ± 31	1204 ± 80	1094 ± 24
3	3.76	1296 ± 90	965 ± 31	1122 ± 80	977 ± 24
4	3.76	1155 ± 90	852 ± 31	980 ± 80	864 ± 24
5	4.27	362 ± 74	304 ± 26	281 ± 80	310 ± 24
6	4.27	587 ± 74	437 ± 26	506 ± 80	443 ± 24
7	4.27	461 ± 74	394 ± 26	380 ± 80	400 ± 24
8	4.27	722 ± 74	484 ± 26	641 ± 80	490 ± 24
9	4.27	680 ± 74	495 ± 26	599 ± 80	501 ± 24
10	4.27	816 ± 74	549 ± 26	734 ± 80	555 ± 24
11	4.27	771 ± 74	503 ± 26	690 ± 80	509 ± 24

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Table S5. The room temperature rotational correlation times (τ_R^{298}) of [Tb(*S*-*SSSS*-**1**)(D_2O)]$^-$ and [Tb(*S*-*RRRR*-**1**)(D_2O)]$^-$ determined using the Curie relaxation method

	Temp (K)	τ_R^{298} (ps)[a]	$\langle\Delta(1/T_1)\rangle$ (s^{-1})
Tb*S*-*SSSS*-**1**	295.2	99 ± 6	95
Tb*S*-*SSSS*-**1**	332.7	131 ± 5	34
Tb*S*-*RRRR*-**1**	295.2	109 ± 6	75
Tb*S*-*RRRR*-**1**	332.7	158 ± 6	21
Tb*S*-*SSSS*-**1**	295.2	124.2[b]	120
Tb*S*-*SSSS*-**1**	332.7		36
Tb*S*-*RRRR*-**1**	295.2		87
Tb*S*-*RRRR*-**1**	332.7		53

a) $\tau_R^{298} = 1/6D_R$, b) the average τ_R^{298} value for both complexes.

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Table S6. EPR results for [Gd(*S-RRRR*-**1**)(H_2O)]$^-$

T (K)	ΔH_{pp} (G)	B_c (G)	EPR freq. (Hz)
274.3	11.8	33853.7	9.4343 _ 10^{10}
275.2	11.0	33853.2	9.4342 _ 10^{10}
277.2	12.0	33852.2	9.4339 _ 10^{10}
278.6	12.1	33851.8	9.4338 _ 10^{10}
279.2	12.2	33851.3	9.4337 _ 10^{10}
281.2	12.4	33850.4	9.4335 _ 10^{10}
282.6	12.4	33850.0	9.4333 _ 10^{10}
283.1	12.6	33849.5	9.4333 _ 10^{10}
285.2	12.8	33848.8	9.4331 _ 10^{10}
285.6	12.7	33848.5	9.4330 _ 10^{10}
287.2	13.0	33848.2	9.4330 _ 10^{10}
288.8	13.1	33847.1	9.4327 _ 10^{10}
289.2	13.3	33847.5	9.4328 _ 10^{10}
291.0	13.4	33845.9	9.4324 _ 10^{10}
291.0	13.3	33846.1	9.4324 _ 10^{10}
292.9	13.6	33843.7	9.4318 _ 10^{10}
295.0	13.8	33843.8	9.4319 _ 10^{10}
297.3	13.9	33843.2	9.4317 _ 10^{10}
297.3	14.0	33842.9	9.4316 _ 10^{10}
300.2	14.4	33841.3	9.4312 _ 10^{10}
304.6	14.7	33839.3	9.4307 _ 10^{10}
306.8	14.8	33838.1	9.4305 _ 10^{10}
309.6	15.2	33836.9	9.4301 _ 10^{10}
312.3	15.5	33835.3	9.4297 _ 10^{10}
315.3	15.7	33833.7	9.4293 _ 10^{10}
318.5	16.0	33832.2	9.4289 _ 10^{10}
321.4	16.4	33830.5	9.4285 _ 10^{10}
324.2	16.5	33828.8	9.4281 _ 10^{10}
327.2	16.9	33827.3	9.4276 _ 10^{10}
330.4	17.2	33825.1	9.4271 _ 10^{10}
334.5	17.7	33823.1	9.4265 _ 10^{10}
337.7	18.4	33820.9	9.4260 _ 10^{10}
279.4	248.9	3410.4	9.0847 _ 10^{9}
282.6	237.0	3406.7	9.0833 _ 10^{9}
283.2	228.8	3403.3	9.0844 _ 10^{9}
287.6	230.7	3394.5	9.0842 _ 10^{9}
289.1	231.9	3391.0	9.0830 _ 10^{9}
291.8	245.1	3386.3	9.0847 _ 10^{9}
293.4	231.0	3380.7	9.0829 _ 10^{9}
294.8	240.8	3379.7	9.0845 _ 10^{9}
296.9	234.5	3373.9	9.0824 _ 10^{9}
300.3	240.9	3368.2	9.0844 _ 10^{9}
307.0	239.7	3356.1	9.0845 _ 10^{9}
314.5	242.0	3342.6	9.0845 _ 10^{9}
321.3	240.0	3330.1	9.0847 _ 10^{9}
330.5	234.5	3314.5	9.0848 _ 10^{9}
335.9	230.4	3306.0	9.0849 _ 10^{9}
343.5	221.0	3295.4	9.0850 _ 10^{9}

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Table S7. EPR results for [Gd(*S*-*SSSS*-**1**)(H_2O)]$^-$

T (K)	ΔH_{pp} (G)	B_c (G)	EPR freq. (Hz)
273.9	10.0	33855.8	$9.4355 \_ 10^{10}$
276.3	10.3	33854.6	$9.4351 \_ 10^{10}$
277.4	10.5	33854.6	$9.4350 \_ 10^{10}$
279.2	10.8	33853.8	$9.4349 \_ 10^{10}$
281.1	11.1	33853.1	$9.4347 \_ 10^{10}$
281.5	10.9	33851.5	$9.4344 \_ 10^{10}$
283.5	11.3	33853.0	$9.4344 \_ 10^{10}$
285.9	11.6	33850.3	$9.4339 \_ 10^{10}$
286.0	11.5	33851.0	$9.4340 \_ 10^{10}$
288.1	12.0	33849.7	$9.4337 \_ 10^{10}$
288.8	11.9	33849.2	$9.4335 \_ 10^{10}$
290.2	12.1	33848.9	$9.4334 \_ 10^{10}$
291.1	12.1	33848.1	$9.4332 \_ 10^{10}$
291.8	12.5	33846.7	$9.4329 \_ 10^{10}$
293.3	12.6	33847.2	$9.4330 \_ 10^{10}$
296.0	12.7	33846.2	$9.4326 \_ 10^{10}$
298.1	13.1	33845.1	$9.4324 \_ 10^{10}$
301.5	13.3	33843.6	$9.4319 \_ 10^{10}$
303.3	13.6	33842.9	$9.4317 \_ 10^{10}$
305.9	13.5	33841.9	$9.4313 \_ 10^{10}$
308.8	14.3	33840.8	$9.4310 \_ 10^{10}$
311.4	14.5	33839.3	$9.4306 \_ 10^{10}$
315.7	14.8	33837.6	$9.4301 \_ 10^{10}$
318.0	14.8	33836.7	$9.4298 \_ 10^{10}$
321.0	15.1	33835.5	$9.4295 \_ 10^{10}$
322.8	15.5	33834.8	$9.4293 \_ 10^{10}$
325.6	15.8	33833.6	$9.4289 \_ 10^{10}$
328.1	15.7	33832.3	$9.4286 \_ 10^{10}$
329.8	15.8	33832.1	$9.4284 \_ 10^{10}$
332.7	15.5	33830.7	$9.4281 \_ 10^{10}$
335.0	16.0	33829.7	$9.4278 \_ 10^{10}$
338.6	17.0	33828.6	$9.4273 \_ 10^{10}$
279.2	194.7	3364.5	$9.0841 \_ 10^{9}$
279.8	191.1	3365.7	$9.0840 \_ 10^{9}$
283.1	184.3	3364.0	$9.0838 \_ 10^{9}$
291.3	178.5	3359.4	$9.0834 \_ 10^{9}$
295.0	176.6	3361.3	$9.0832 \_ 10^{9}$
296.6	178.2	3359.7	$9.0833 \_ 10^{9}$
303.1	179.0	3359.4	$9.0830 \_ 10^{9}$
308.2	190.2	3374.9	$9.0827 \_ 10^{9}$
311.2	189.9	3363.7	$9.0830 \_ 10^{9}$
317.0	194.7	3366.6	$9.0829 \_ 10^{9}$
318.5	191.5	3375.2	$9.0829 \_ 10^{9}$
322.2	219.4	3361.9	$9.0829 \_ 10^{9}$
322.2	208.8	3365.6	$9.0829 \_ 10^{9}$
323.7	209.9	3370.0	$9.0829 \_ 10^{9}$
327.4	222.1	3363.7	$9.0829 \_ 10^{9}$
328.1	224.6	3364.1	$9.0830 \_ 10^{9}$
335.4	240.7	3366.4	$9.0830 \_ 10^{9}$
342.1	258.2	3361.4	$9.0830 \_ 10^{9}$