Supporting Information

Synthesis, Photophysical, and Relaxivity Study of a New *d-f* Heterometallic Trinuclear Complex as a Potential Bimodal Imaging Probe for MRI and Optical Imaging

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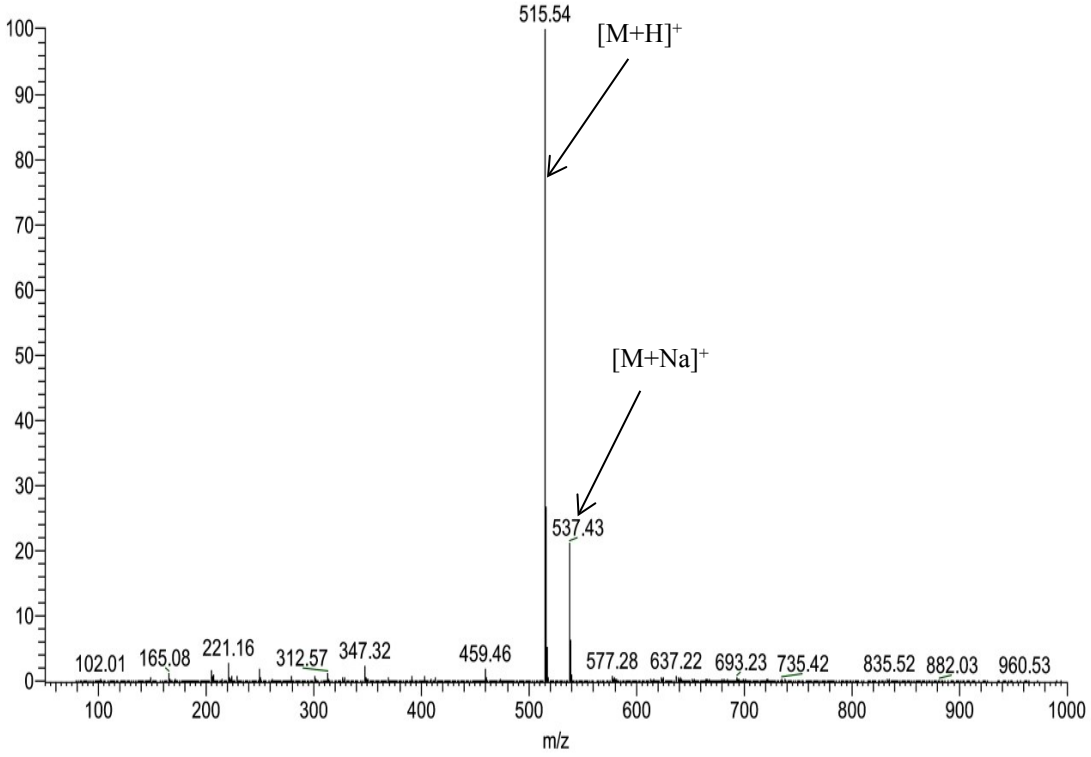


Figure S1. ESI mass spectrum of **1**.

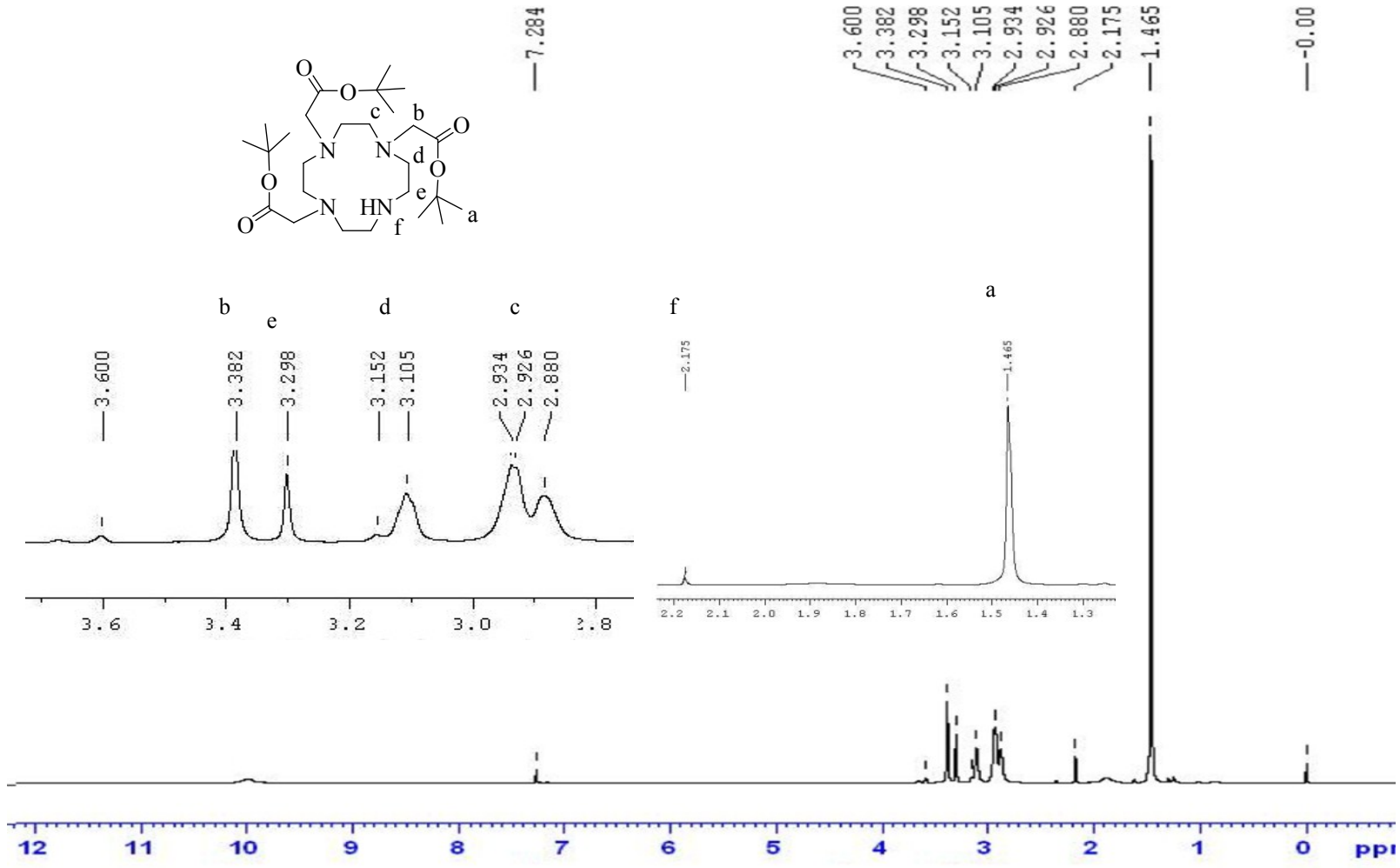
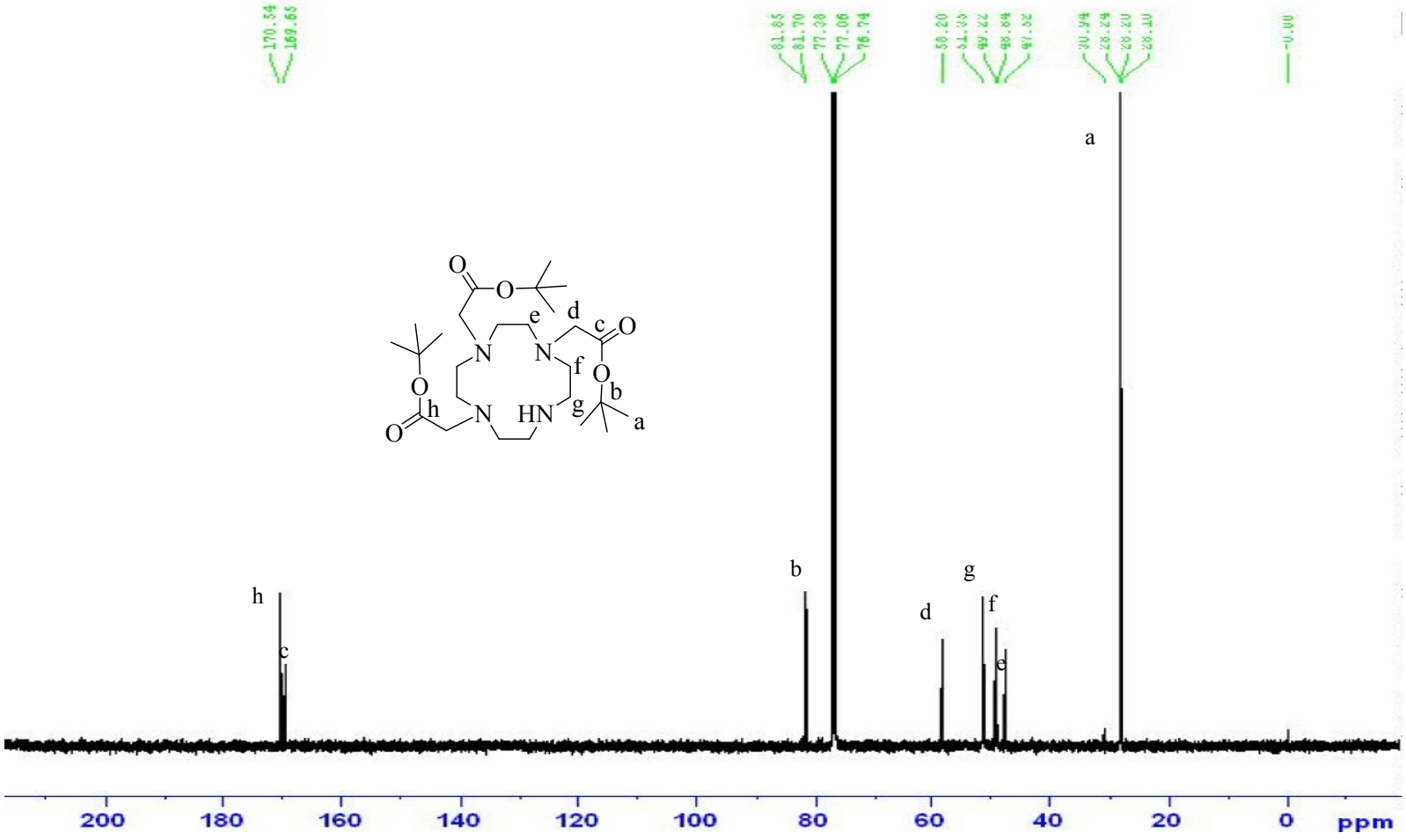


Figure S2. 400 MHz ^{1}H NMR spectrum of **1** in $CDCl_3$ at 25 ºC.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81.85
81.70
77.38
77.06
76.74
58.20
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49.22
46.84
47.52
30.94
28.24
28.20
28.10
0.00
a
b
c
d
e
f
g
h
O
O
N
N
HN
200
180
160
140
120
100
80
60
40
20
0
ppm

Figure S3. 100 MHz ^{13}C NMR spectrum of **1** in $CDCl_3$ at 25 ºC.

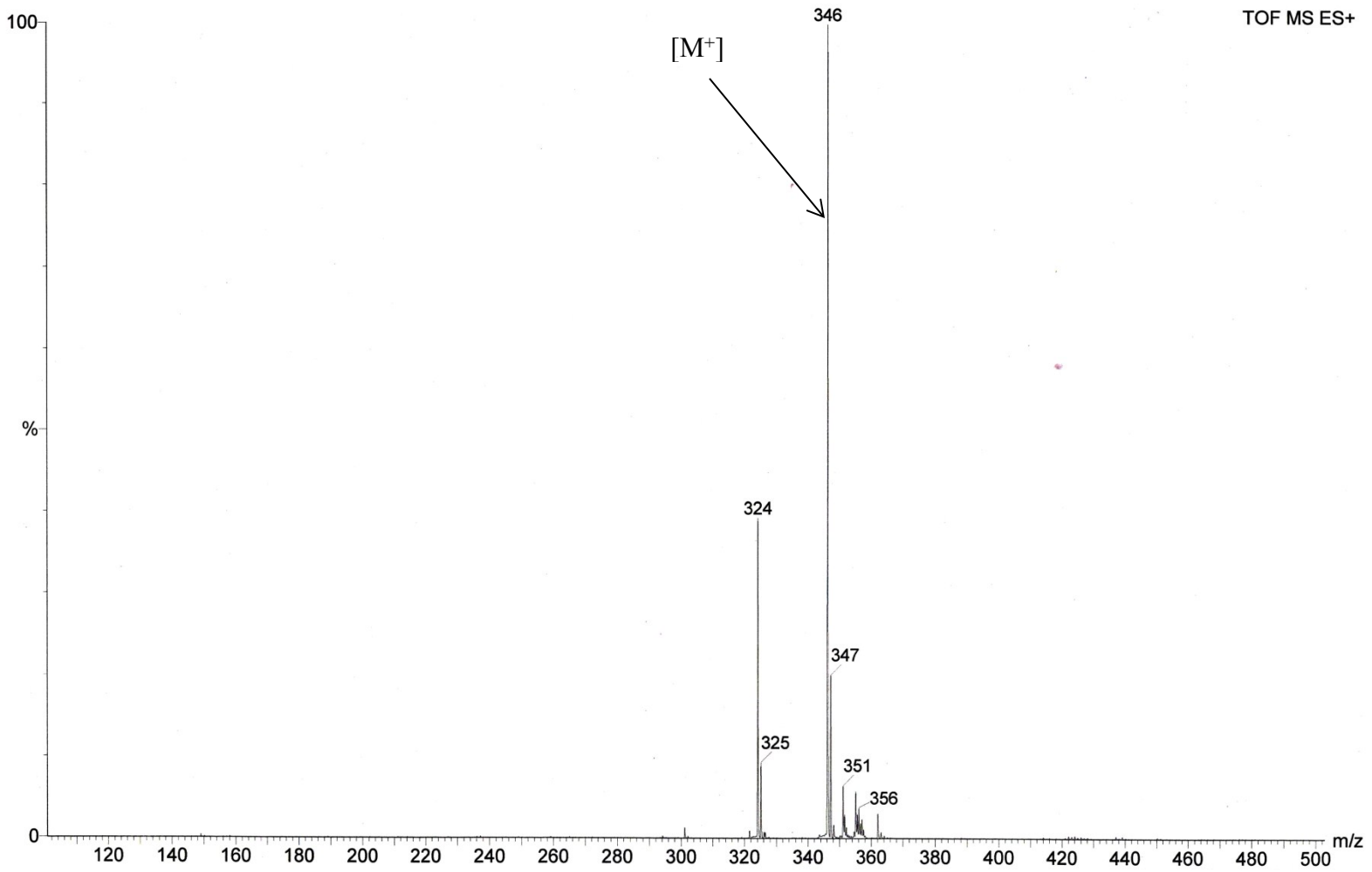


Figure S4. ESI-TOF mass spectrum of **2**.

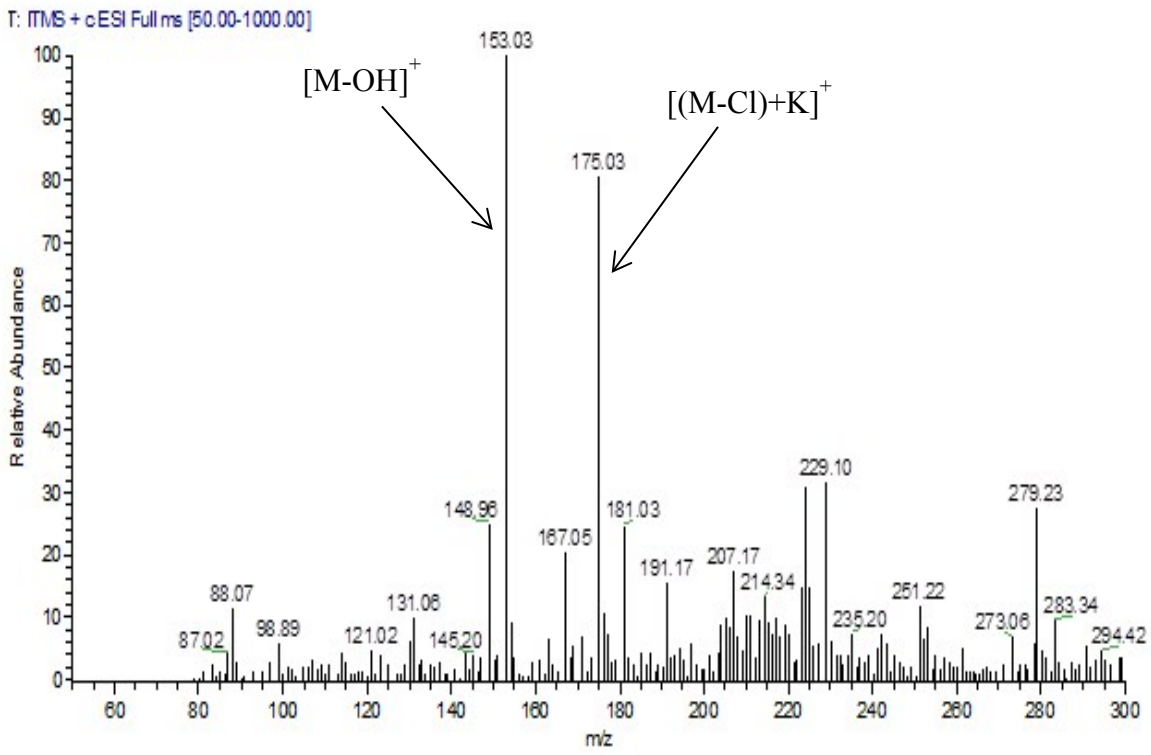


Figure S5. ESI mass spectrum of **3**.

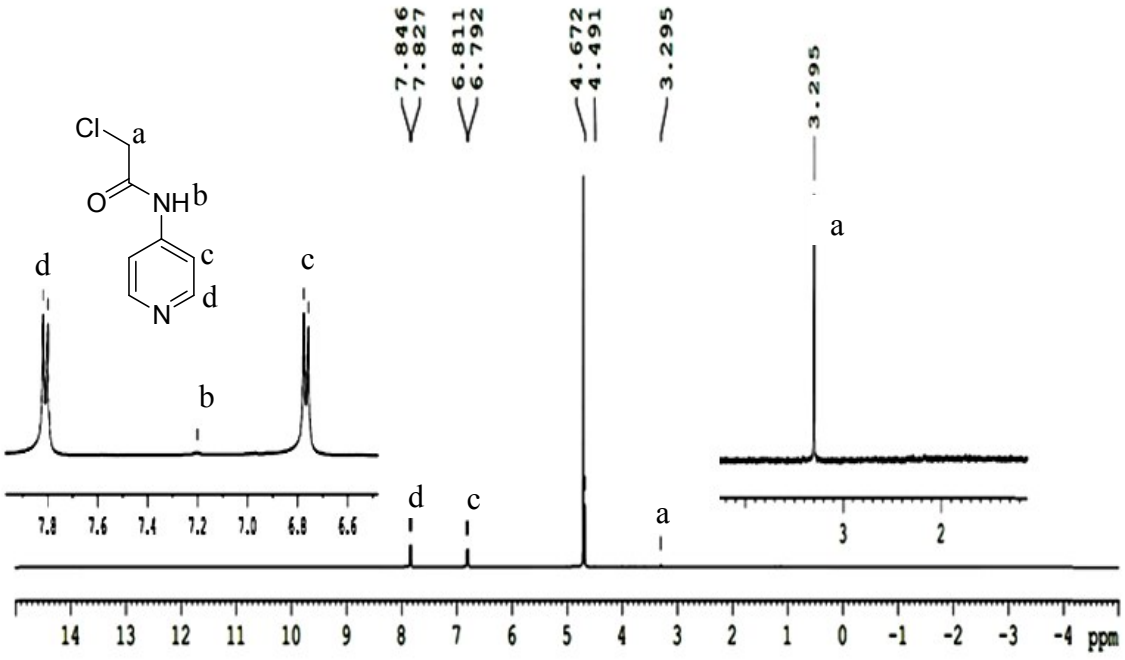


Figure S6. 400 MHz ^{1}H NMR spectrum of **3** in D_2O at 25 °C.

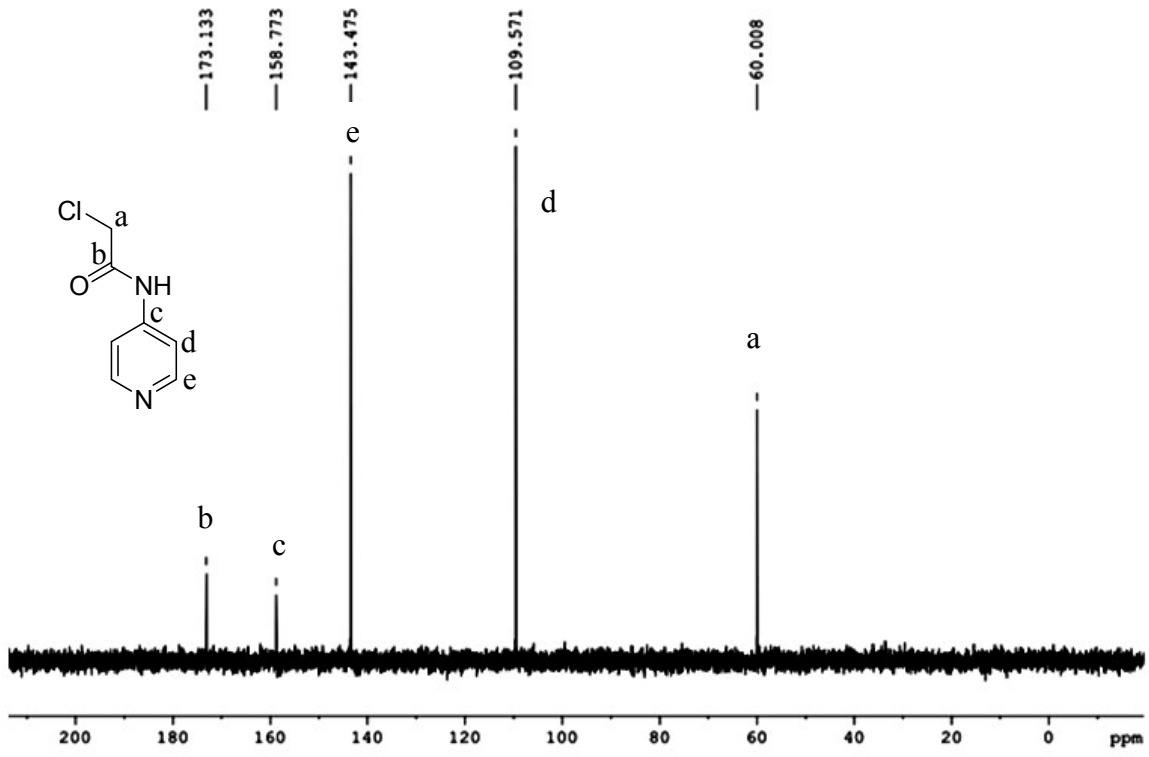


Figure S7. 100 MHz ^{13}C NMR spectrum of **3** in D_2O at 25 °C.

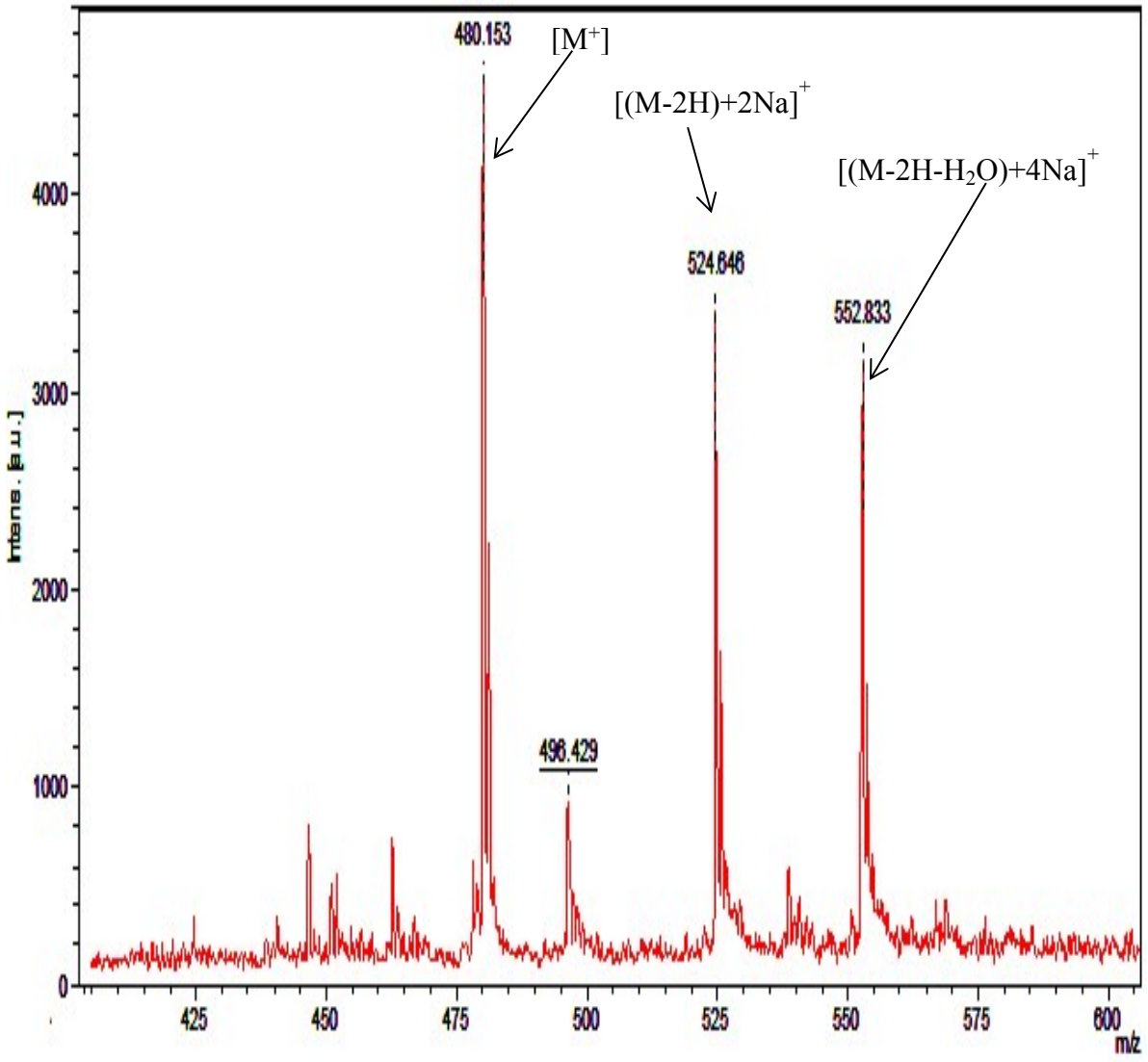


Figure S8. MALDI-TOF mass spectrum of **4**.

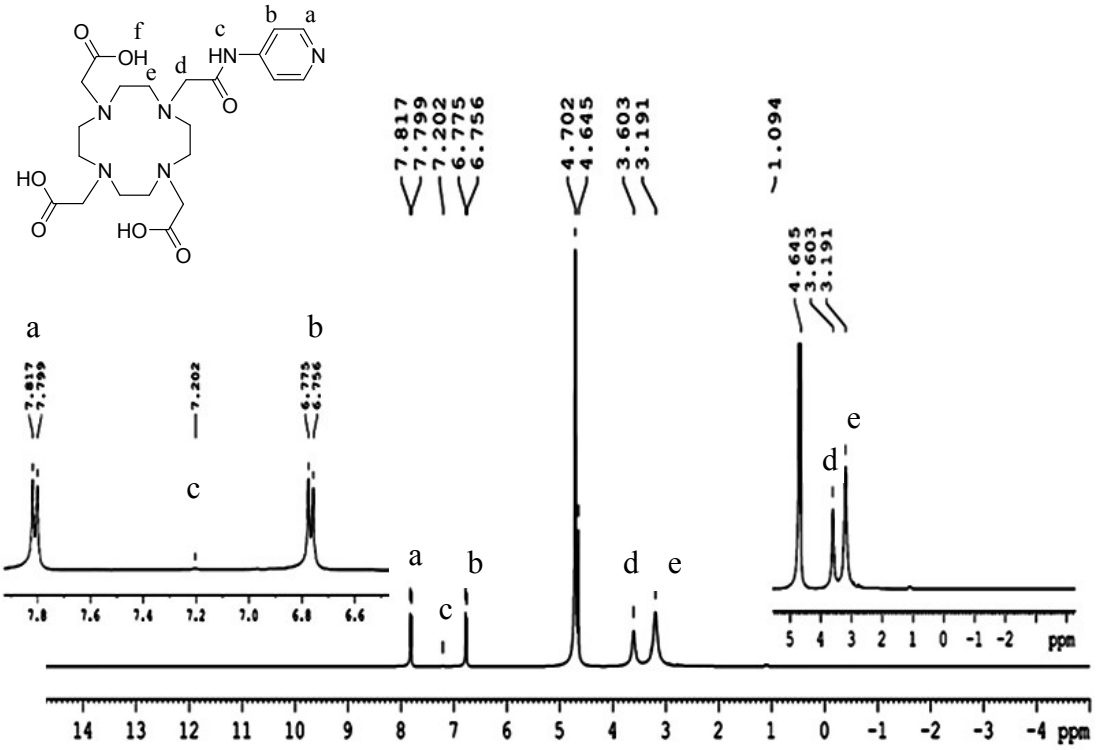


Figure S9. 400 MHz ^{1}H NMR spectrum of **4** in D_2O at 25 °C.

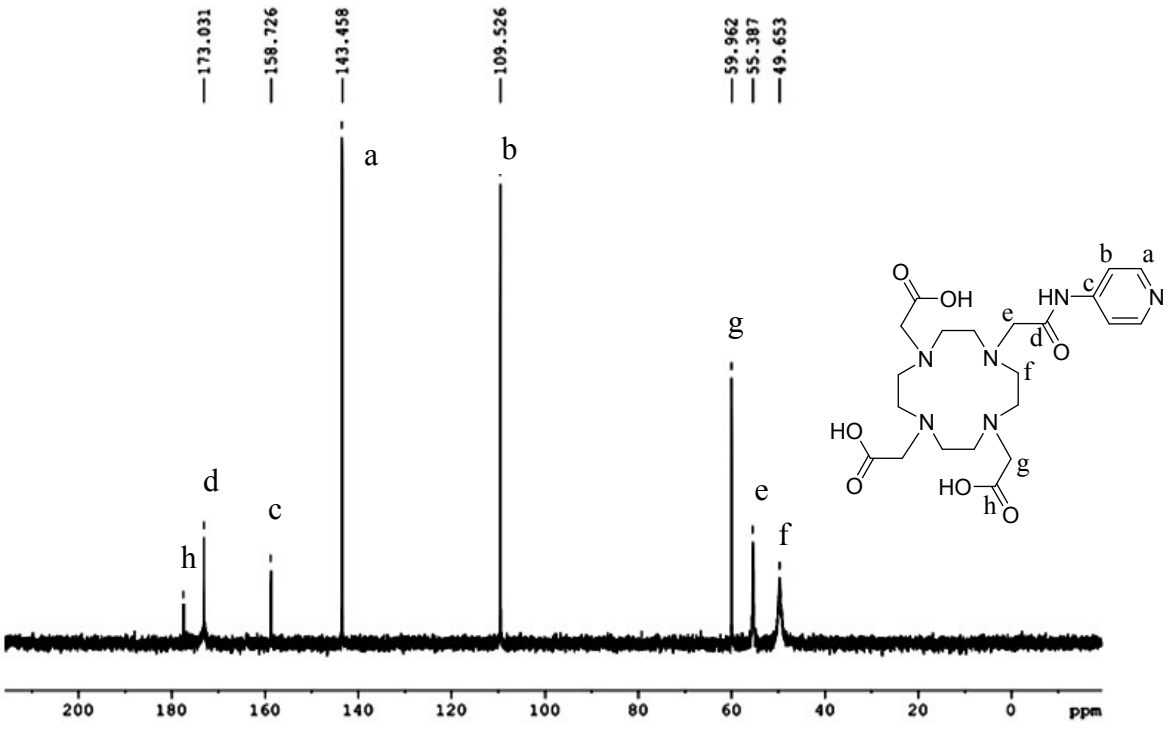


Figure S10. 100 MHz ^{13}C NMR spectrum of **4** in D_2O at 25 °C.

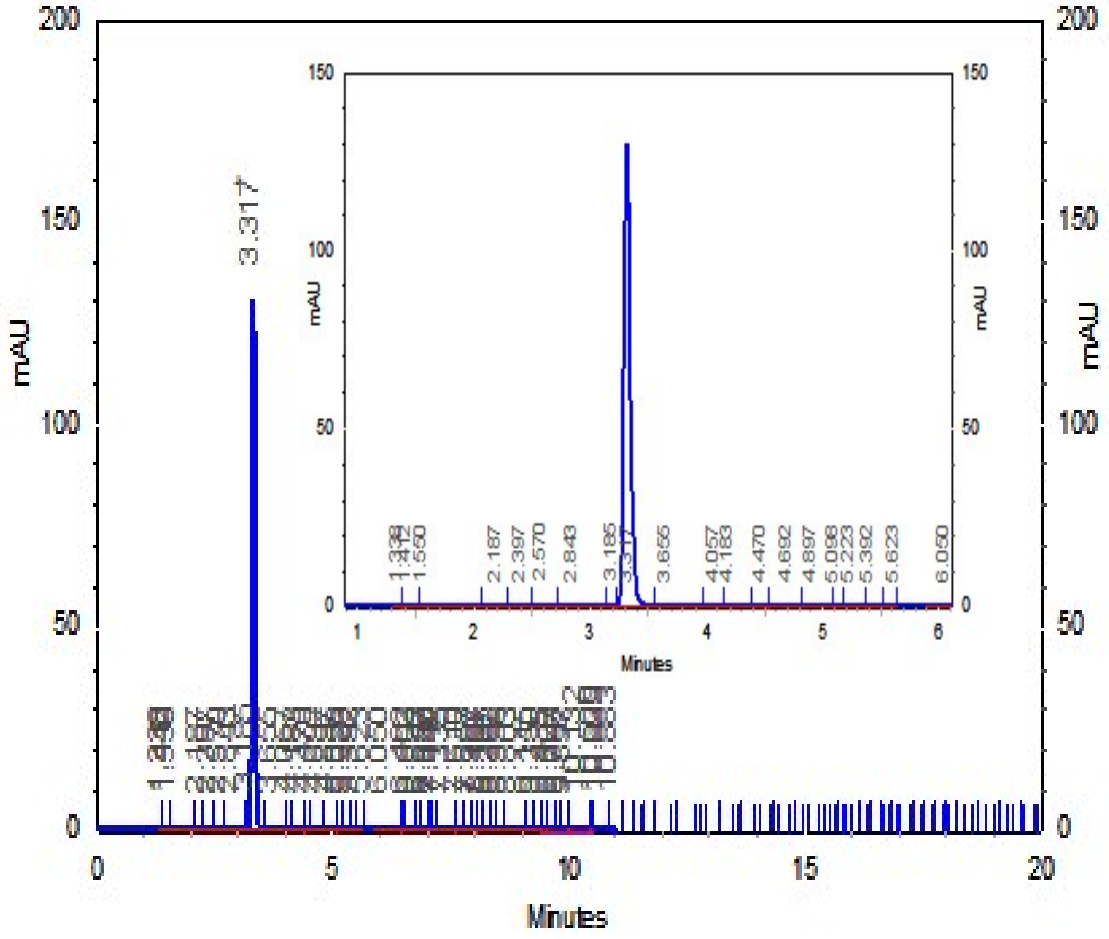

200
150
100
50
0
mAU
3.317
0
5
10
15
20
Minutes
150
100
50
0
mAU
1.338
1.412
1.550
2.187
2.397
2.570
2.843
3.185
3.317
3.655
4.057
4.183
4.470
4.692
4.897
5.098
5.223
5.392
5.623
6.050
1
2
3
4
5
6
Minutes

Figure S11. High performance liquid chromatogram of **4** (t_R = 3.31 min). inset: expansion of chromatogram of **4**.

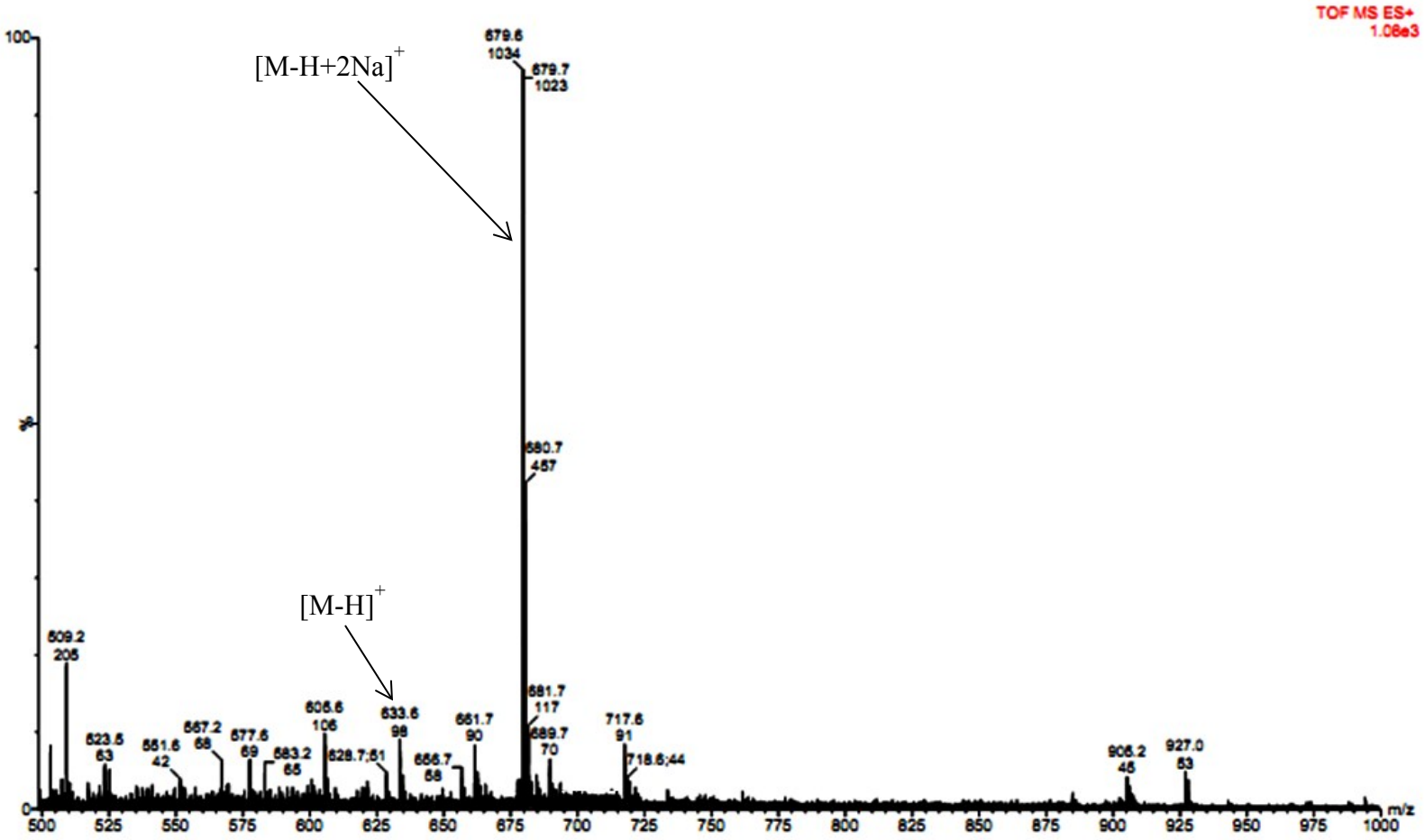

TOF MS ES+
1.06e3
100
%
0
[M-H+2Na]+
[M-H]+
679.6
1034
679.7
1023
680.7
457
681.7
117
689.7
70
509.2
205
523.5
63
551.6
42
557.2
68
577.6
69
583.2
65
606.6
106
628.7;51
633.6
99
656.7
58
661.7
90
717.6
91
718.6;44
906.2
45
927.0
53
500
525
550
575
600
625
650
675
700
725
750
775
800
825
850
875
900
925
950
975
1000
m/z

Figure S12. ESI-TOF mass spectrum of [Gd(DOTA-AMpy)H_2O] (**5**).

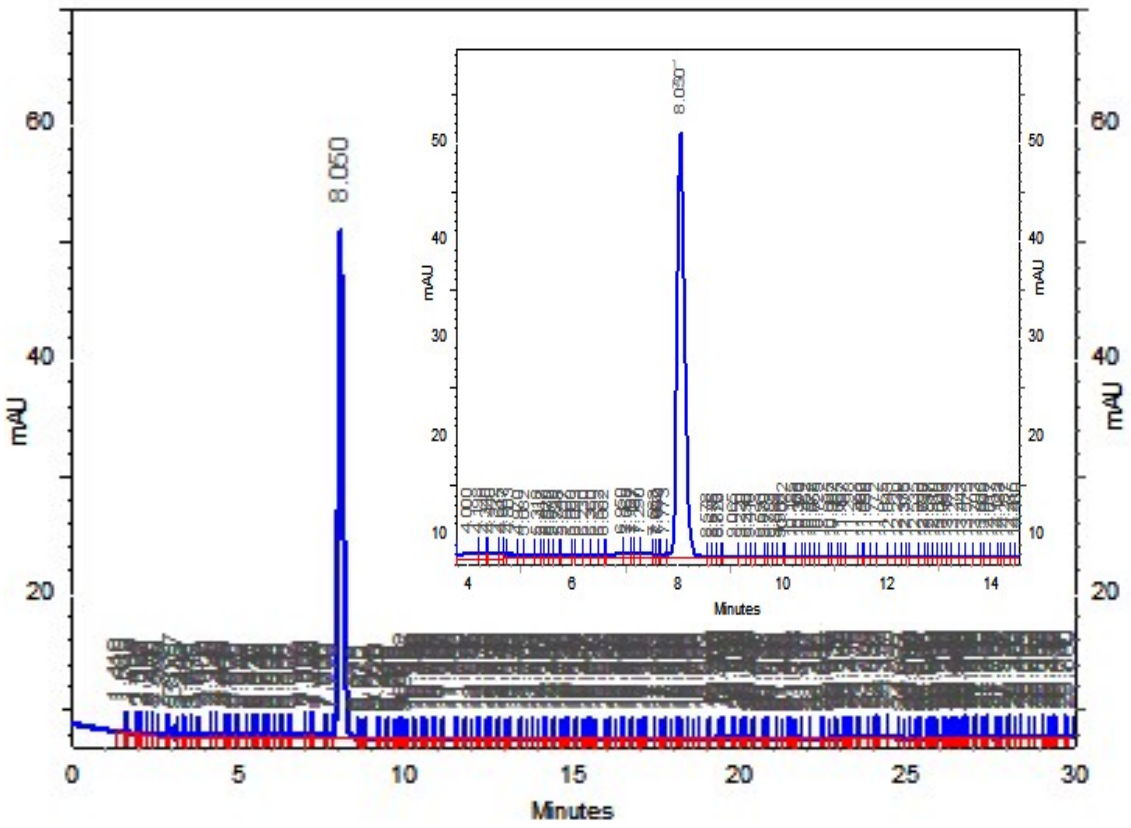

8.050
mAU
Minutes
8.050
mAU
Minutes

Figure S13. High performance liquid chromatogram of $[Ru(bpy)_2\{Gd(DOTA\text{-}AMpy)(H_2O)\}_2]\text{-}Cl_2$ (**7**) (t_R = 8.05 min); inset: expansion of the chromatogram.

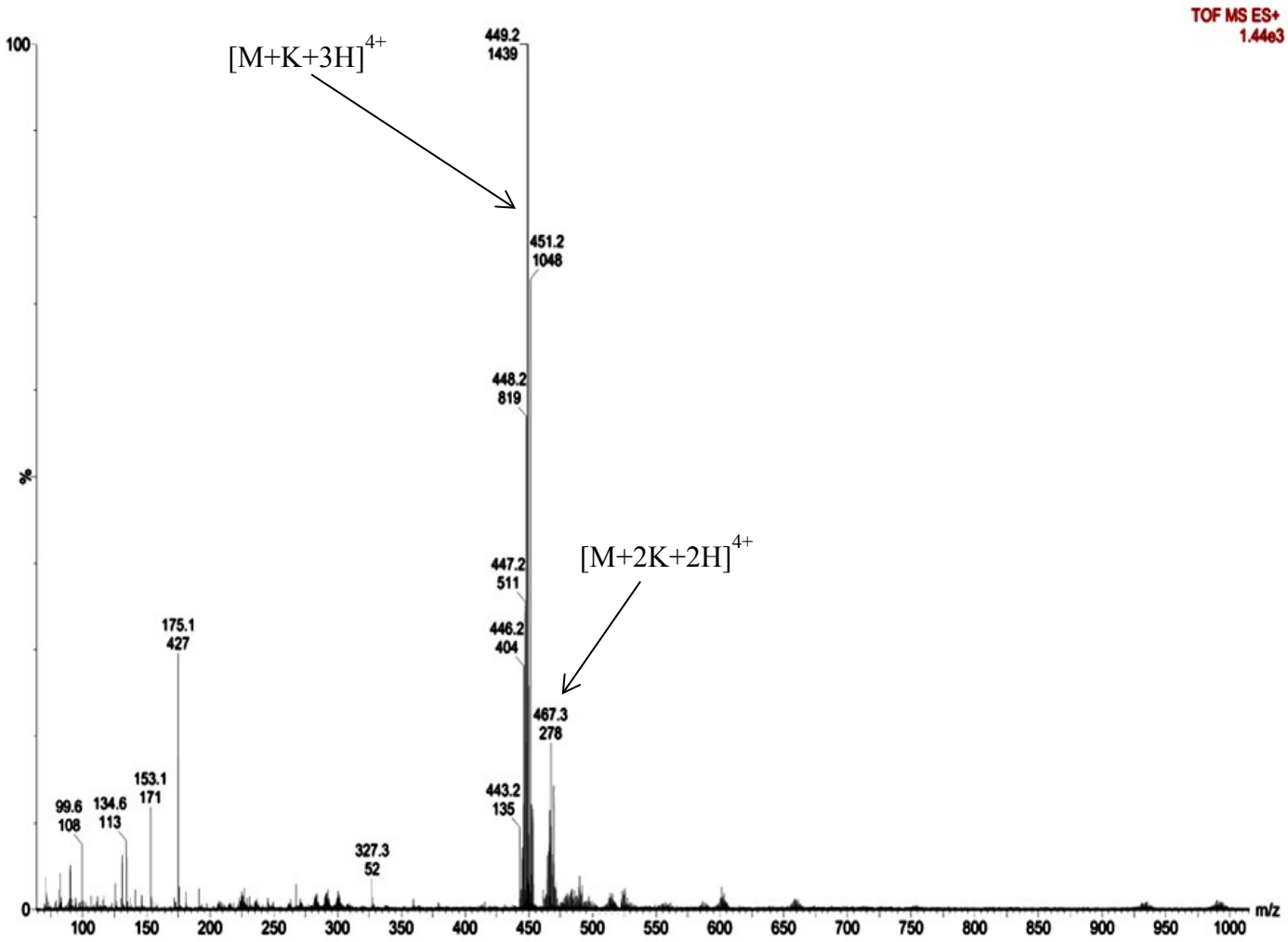


Figure S14. ESI-TOF mass spectrum of $[Ru(bpy)_2\{Gd(DOTA\text{-}AMpy)(H_2O)\}_2]Cl_2$ (**7**).

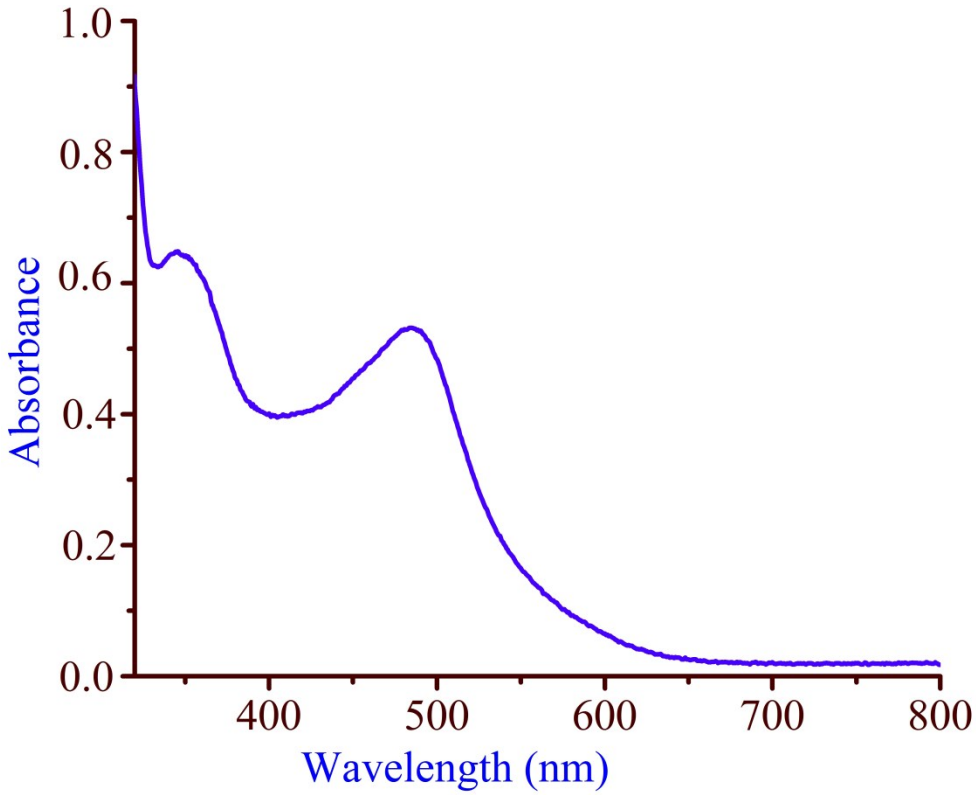


Figure S15. Electronic absorption spectrum of $[Ru(bpy)_2\{Gd(DOTA\text{-}AMpy)(H_2O)\}_2]Cl_2$ (**7**) in 0.1 M Tris-HCl buffer, pH = 7.4 at 25 °C.

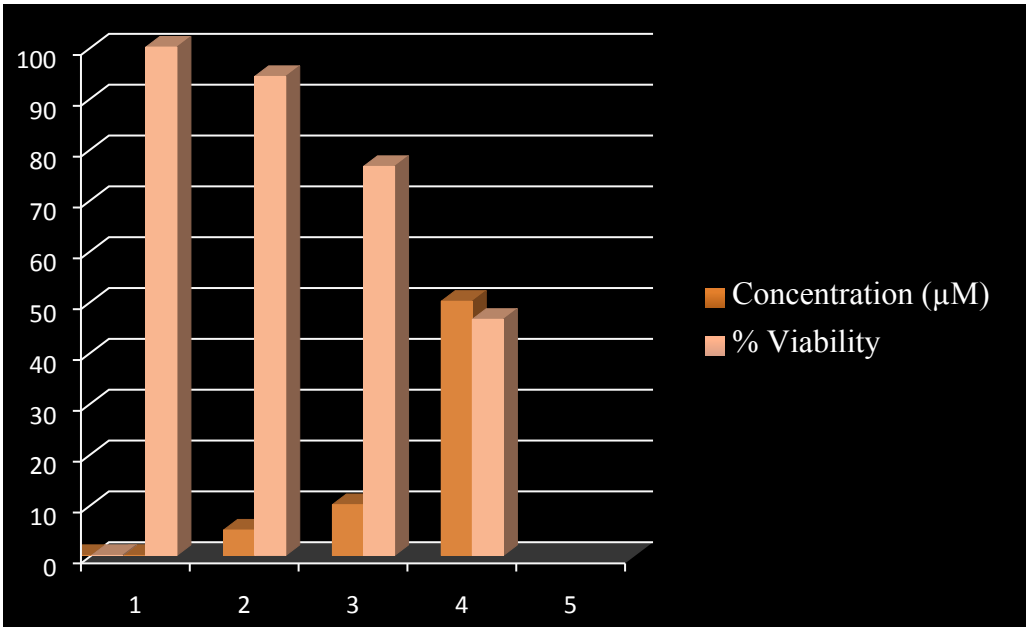
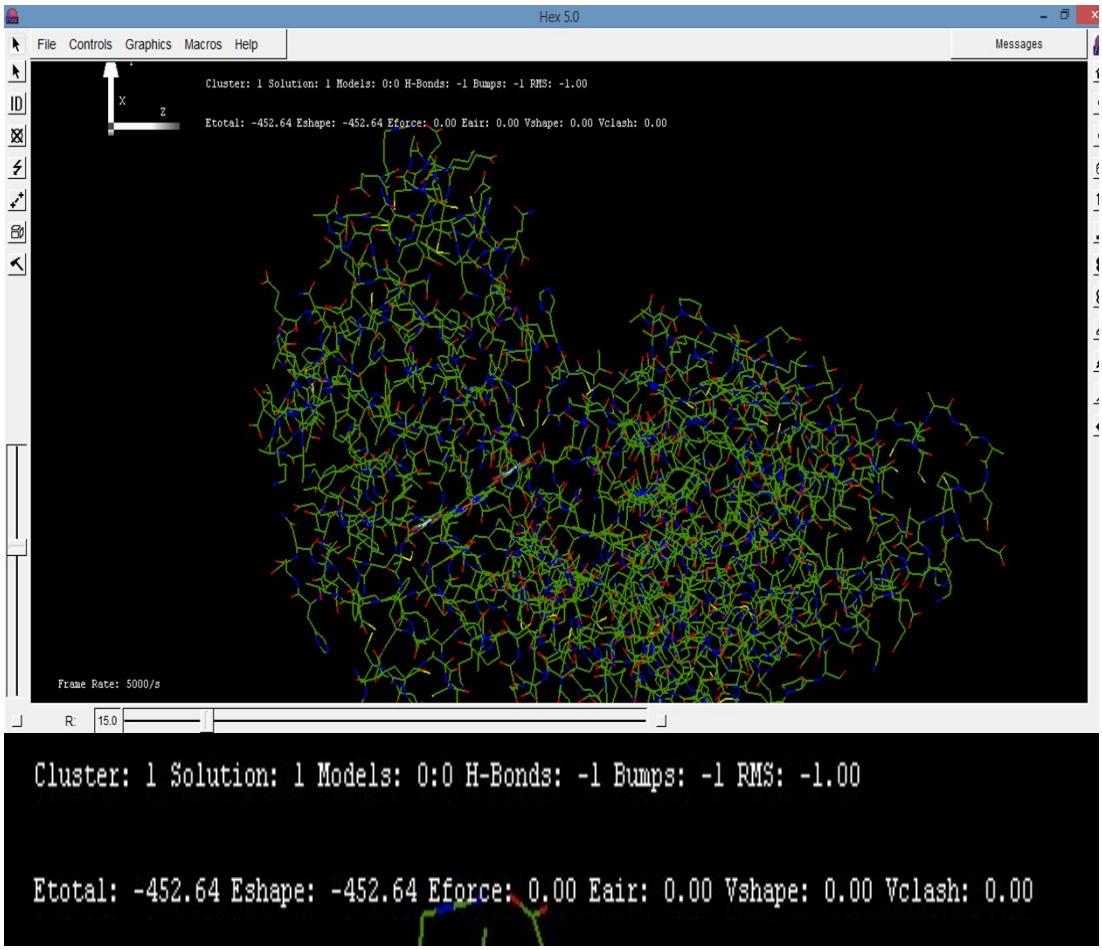


Figure S16. Concentration versus viability plot of incubated HeLa cells with varying concentration of $[Ru(bpy)_2\{Gd(DOTA\text{-}AMpy)(H_2O)\}_2]Cl_2$ (**7**) for 24 h at 37 ºC: (1) control, (2) 5 μM, (3) 10 μM, and (4) 50 μM.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Etotal: -452.64 Eshape: -452.64 Eforce: 0.00 Eair: 0.00 Vshape: 0.00 Vclash: 0.00
Frame Rate: 5000/s
R: 15.0
Cluster: 1 Solution: 1 Models: 0:0 H-Bonds: -1 Bumps: -1 RMS: -1.00
Etotal: -452.64 Eshape: -452.64 Eforce: 0.00 Eair: 0.00 Vshape: 0.00 Vclash: 0.00

Figure S17. Molecular docked model of $[Ru(bpy)_2\{Gd(DOTA\text{-}AMpy)(H_2O)\}_2]Cl_2$ (**7**) with human serum albumin.

Table S1. Electronic Absorption Spectral Data of $[Ru(bpy)_2\{Gd(DOTA\text{-}AMpy)(H_2O)\}_2]Cl_2$ (7) in 0.1 M Tris-HCl Buffer, pH = 7.4 at 25 °C (6×10^{-5} M)

λ_{max} (nm)	ε ($dm^3\ mol^{-1}\ cm^{-1}$)	Assignment[a]
274	15,833	LC ($\pi \rightarrow \pi^*$)
341	10,333	Ru^{II} MC ($d \rightarrow d$)
480	9,000	^{1}MLCT ($d \rightarrow \pi^*$)

[a] *Inorg. Chem*., 2011, **50**, 10005-10014.

Table S2. Intercalation of $[Ru(bpy)_2\{Gd(DOTA\text{-}AMpy)(H_2O)\}_2]Cl_2$ (7) with DNA (PDB ID: 1BNA; Q-Site Finder) and Preferential Binding Site from the Docked Structure

DNA (PDB ID: 1BNA)		binding site of complex **7**	distance (Å)	type of bonding	docking energy (kcal/mol)
sequence A	*position*				
CGCGAATTCGCG	G4′	O	3.81	hydrogen	5236
CGCGAATTCGCG	C3′	O	4.05	hydrogen	

62	ATOM	62	C5'	DG A	4	22.714	17.625	18.753	1.00 37.89	C
63	ATOM	63	C4'	DG A	4	21.393	16.960	18.505	1.00 53.00	C
64	ATOM	64	O4'	DG A	4	20.353	17.952	18.496	1.00 38.79	O
65	ATOM	65	C3'	DG A	4	21.264	16.229	17.176	1.00 56.72	C
66	ATOM	66	O3'	DG A	4	20.284	15.214	17.238	1.00 64.12	O
67	ATOM	67	C2'	DG A	4	20.793	17.368	16.288	1.00 40.81	C
68	ATOM	68	C1'	DG A	4	19.716	17.901	17.218	1.00 30.52	C
69	ATOM	69	N9	DG A	4	19.305	19.281	16.869	1.00 28.53	N
70	ATOM	70	C8	DG A	4	20.017	20.263	16.232	1.00 27.82	C
71	ATOM	71	N7	DG A	4	19.313	21.394	16.077	1.00 28.01	N

42	ATOM	42	O5'	DC A	3	24.260	24.246	19.327	1.00 35.42	O
43	ATOM	43	C5'	DC A	3	24.584	23.285	20.335	1.00 45.75	C
44	ATOM	44	C4'	DC A	3	23.523	22.233	20.245	1.00 43.02	C
45	ATOM	45	O4'	DC A	3	22.256	22.844	20.453	1.00 36.85	O
46	ATOM	46	C3'	DC A	3	23.424	21.557	18.903	1.00 40.14	C
47	ATOM	47	O3'	DC A	3	24.121	20.309	18.928	1.00 49.62	O
48	ATOM	48	C2'	DC A	3	21.930	21.406	18.661	1.00 53.79	C
49	ATOM	49	C1'	DC A	3	21.278	21.966	19.909	1.00 22.18	C

Table S3. Molecular Docking Data of HSA (PDB ID: 1h9z; Q-Site Finder) and Preferential Binding Site of $[Ru(bpy)_2\{Gd(DOTA\text{-}AMpy)(H_2O)\}_2]Cl_2$ (7) from Docked Structure

Human Serum Albumin (PDB ID: 1h9z)		Binding site of complex **7**	Distance (Å)	Type of Bonding	Docking Energy (kcal/mol)
Residue	*Position*				
ARG 197	NH2	O	3.04	Hydrogen	-452.64
SER 193	OG	O	2.75	Hydrogen	
SER 193	OG	O	2.84	Hydrogen	

2100	ATOM	1554	C	ARG A 197	29.093	2.924	17.241	1.00	59.10	C
2101	ATOM	1555	O	ARG A 197	29.297	1.903	16.578	1.00	60.16	O
2102	ATOM	1556	CB	ARG A 197	29.589	2.844	19.699	1.00	60.94	C
2103	ATOM	1557	CG	ARG A 197	30.663	2.968	20.785	1.00	66.35	C
2104	ATOM	1558	CD	ARG A 197	30.303	2.185	22.048	1.00	70.70	C
2105	ATOM	1559	NE	ARG A 197	29.358	2.888	22.917	1.00	75.30	N
2106	ATOM	1560	CZ	ARG A 197	29.714	3.686	23.925	1.00	77.79	C
2107	ATOM	1561	NH1	ARG A 197	31.001	3.887	24.199	1.00	80.28	N
2108	ATOM	1562	NH2	ARG A 197	28.784	4.282	24.666	1.00	77.73	N
2109	ATOM	1563	N	LEU A 198	28.050	3.724	17.048	1.00	58.46	N
2110	ATOM	1564	CA	LEU A 198	27.027	3.455	16.043	1.00	57.05	C

2068	ATOM	1522	OG	SER A 192	30.977	12.477	21.028	1.00	49.68	O
2069	ATOM	1523	N	SER A 193	29.493	9.463	22.482	1.00	47.30	N
2070	ATOM	1524	CA	SER A 193	30.043	8.119	22.553	1.00	48.70	C
2071	ATOM	1525	C	SER A 193	29.169	7.134	21.770	1.00	48.45	C
2072	ATOM	1526	O	SER A 193	29.682	6.271	21.054	1.00	47.94	O
2073	ATOM	1527	CB	SER A 193	30.141	7.682	24.016	1.00	50.03	C
2074	ATOM	1528	OG	SER A 193	30.764	6.416	24.131	1.00	53.90	O
2075	ATOM	1529	N	ALA A 194	27.851	7.263	21.912	1.00	48.06	N
2076	ATOM	1530	CA	ALA A 194	26.921	6.378	21.212	1.00	48.06	C
2077	ATOM	1531	C	ALA A 194	27.000	6.544	19.690	1.00	48.01	C
2078	ATOM	1532	O	ALA A 194	27.021	5.560	18.950	1.00	47.26	O
2079	ATOM	1533	CB	ALA A 194	25.494	6.629	21.694	1.00	48.35	C
2080	ATOM	1534	N	LYS A 195	27.042	7.784	19.221	1.00	49.03	N
2081	ATOM	1535	CA	LYS A 195	27.136	8.025	17.788	1.00	51.73	C

2068	ATOM	1522	OG	SER A 192	30.977	12.477	21.028	1.00	49.68	O
2069	ATOM	1523	N	SER A 193	29.493	9.463	22.482	1.00	47.30	N
2070	ATOM	1524	CA	SER A 193	30.043	8.119	22.553	1.00	48.70	C
2071	ATOM	1525	C	SER A 193	29.169	7.134	21.770	1.00	48.45	C
2072	ATOM	1526	O	SER A 193	29.682	6.271	21.054	1.00	47.94	O
2073	ATOM	1527	CB	SER A 193	30.141	7.682	24.016	1.00	50.03	C
2074	ATOM	1528	OG	SER A 193	30.764	6.416	24.131	1.00	53.90	O
2075	ATOM	1529	N	ALA A 194	27.851	7.263	21.912	1.00	48.06	N
2076	ATOM	1530	CA	ALA A 194	26.921	6.378	21.212	1.00	48.06	C
2077	ATOM	1531	C	ALA A 194	27.000	6.544	19.690	1.00	48.01	C
2078	ATOM	1532	O	ALA A 194	27.021	5.560	18.950	1.00	47.26	O
2079	ATOM	1533	CB	ALA A 194	25.494	6.629	21.694	1.00	48.35	C
2080	ATOM	1534	N	LYS A 195	27.042	7.784	19.221	1.00	49.03	N
2081	ATOM	1535	CA	LYS A 195	27.136	8.025	17.788	1.00	51.73	C