

Stable Mn²⁺, Cu²⁺ and Ln³⁺ complexes with cyclen-based ligands functionalized with picolinate pendant arms. Unexpected self-aggregation of the La³⁺ complex in solution †

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Electronic Supporting Information

Figure S1: Titration curves of the dodpa^{2-} ligand alone (black) and in presence of one equivalent of Mn^{2+} (magenta) and Cu^{2+} (blue) ($[\text{dodpa}^{2-}] = 2.0 \text{ mM}$, $V_{\text{tot}} = 8.0 \text{ cm}^3$, $t = 25^\circ \text{C}$ and $I = 0.15 \text{ M NaCl}$).

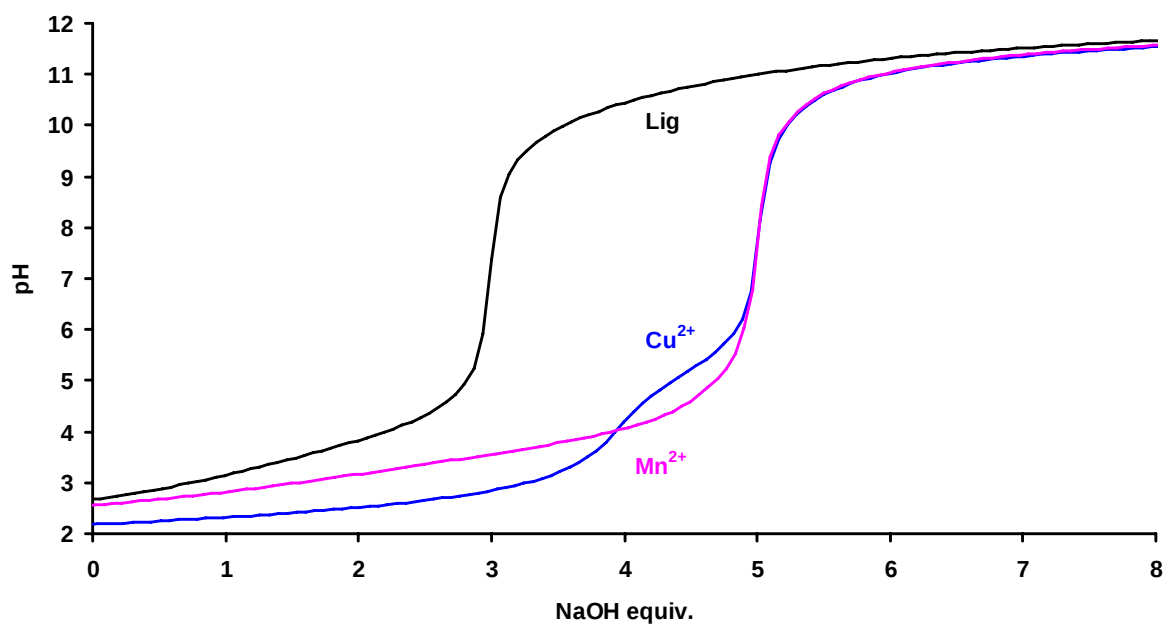


Figure S2: Titration curves of the Medodpa^{2-} ligand alone (black) and in presence of one equivalent of Mn^{2+} (magenta) and Cu^{2+} (blue) ($[\text{Medodpa}] = 2.0 \text{ mM}$, $V_{\text{tot}} = 8.0 \text{ cm}^3$, $t = 25^\circ \text{C}$ and $I = 0.15 \text{ M NaCl}$).

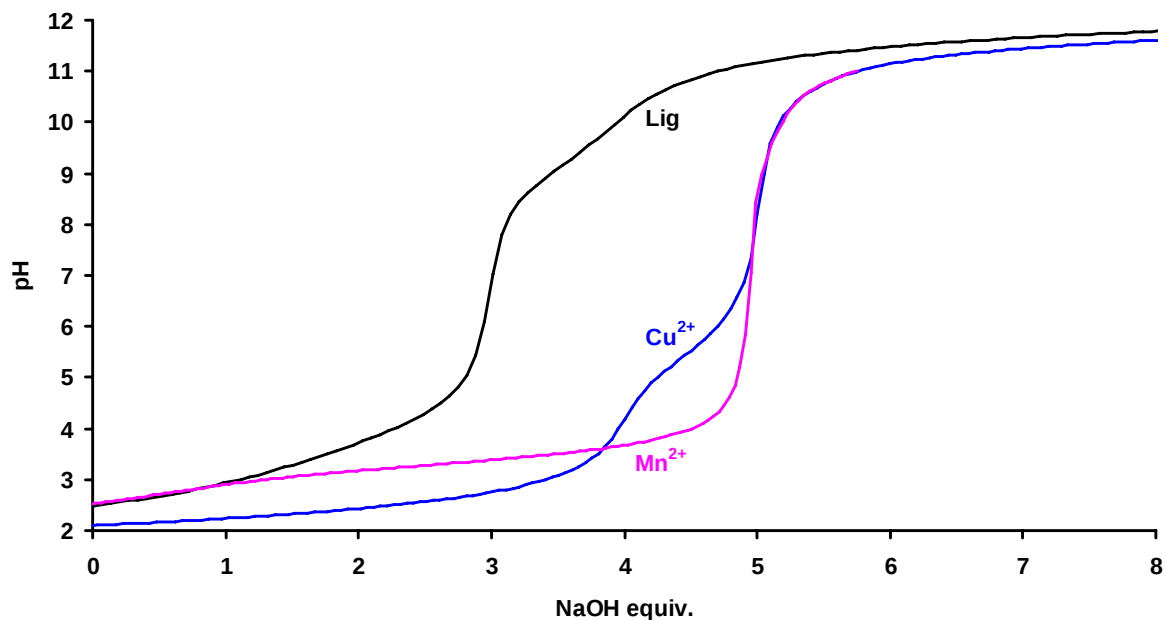


Figure S3: The species distribution curves calculated with the use of stability constants obtained by pH-potentiometry and the ^1H -relaxometric profile for the obtained for $[\text{Mn}(\text{dodpa})]$ as a function of pH ($[\text{dodpa}^{2-}] = [\text{Mn}^{2+}] = 2.5 \text{ mM}$, $t = 25^\circ\text{C}$, $I = 0.15 \text{ M NaCl}$, $B = 20 \text{ MHz}$).

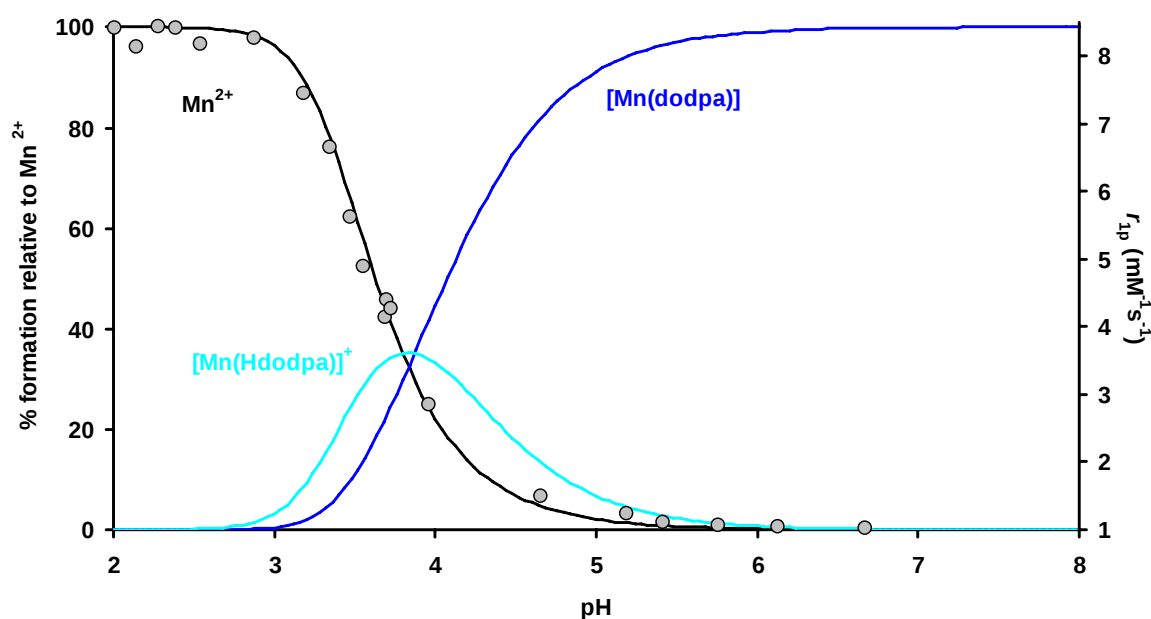


Figure S4: Species distribution diagrams for the $\text{Mn}^{2+}:\text{dodpa}^{2-}$ and $\text{Mn}^{2+}:\text{Medodpa}^{2-}$ (1:1) systems (10^{-3} M) calculated using the constants reported in Table 1 obtained potentiometrically.

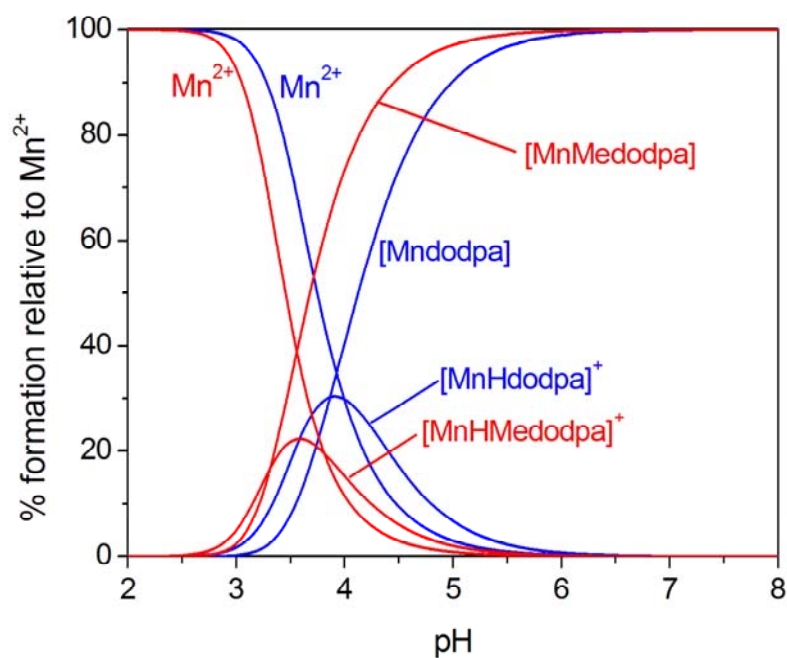


Figure S5: The structure of the bimp⁵⁻ ligand.

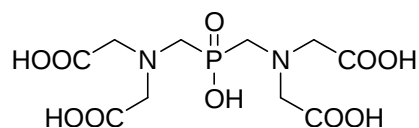


Figure S6: Absorption spectra of the Cu²⁺–dodpa²⁻ system (batch samples) as a function of c_{H+} recorded in the range of c_{H+} = 0.01591-0.7148 (I=1.0 M NaCl; [Cu²⁺]=2.216 mM, [dodpa²⁻]=2.269 mM, l=1 cm, 25 °C).

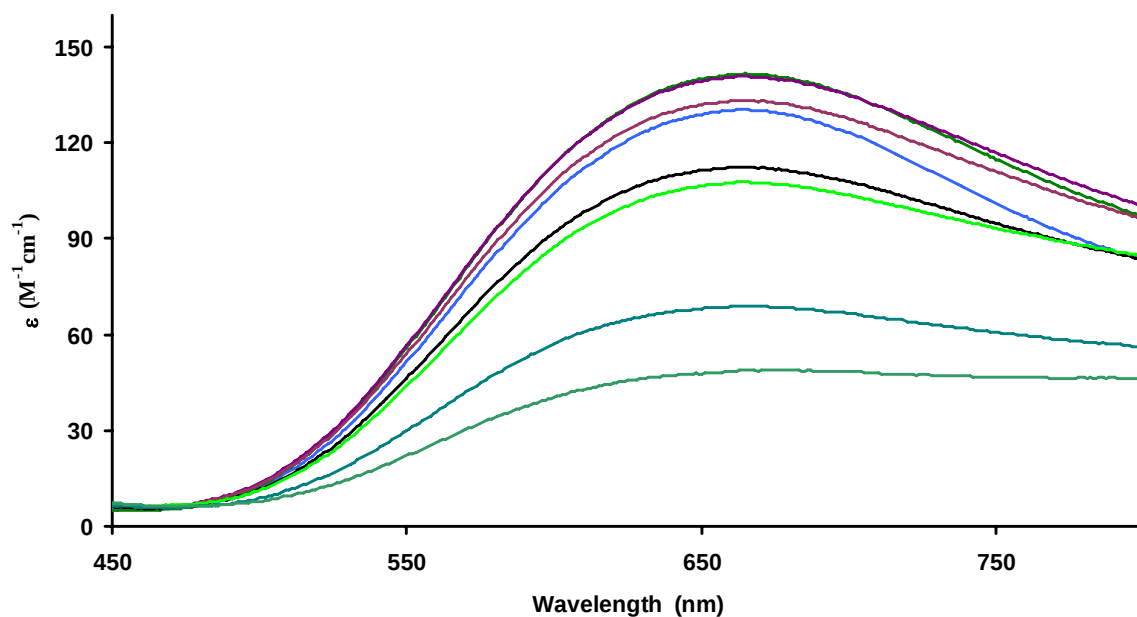


Figure S7: Absorption spectra of the Cu²⁺–Medodpa²⁻ system as a function of –log c_{H+} recorded in the range of –log c_{H+}=1.85-8.26 (I=0.15 M NaCl; [Cu²⁺]=[Medodpa²⁻]=1.438 mM, l=1 cm, 25 °C).

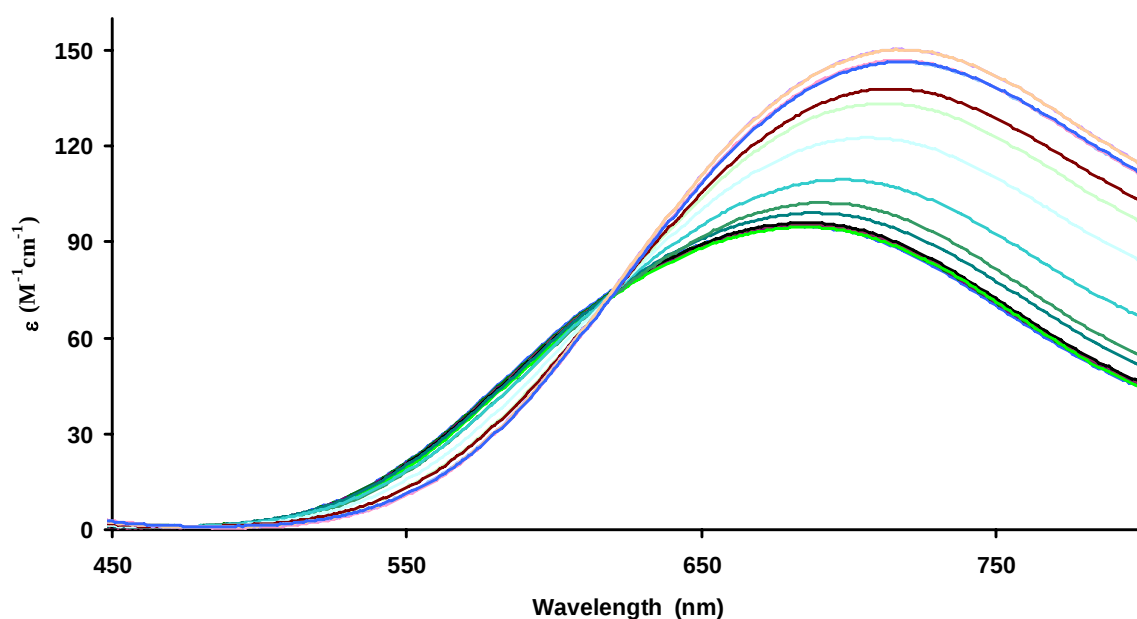


Figure S8: Absorption spectra of the Cu^{2+} – dodpa^{2-} – bimp^{5-} – H^+ -system as a function of c_{bimp} recorded in the range of $c_{\text{bimp}}=2.052$ -50.05 mM ($I=0.15$ M NaCl, $[\text{Cu}^{2+}]=1.99$ mM, $[\text{dodpa}^{2-}]=2.02$ mM, $l=1$ cm, 25°C).

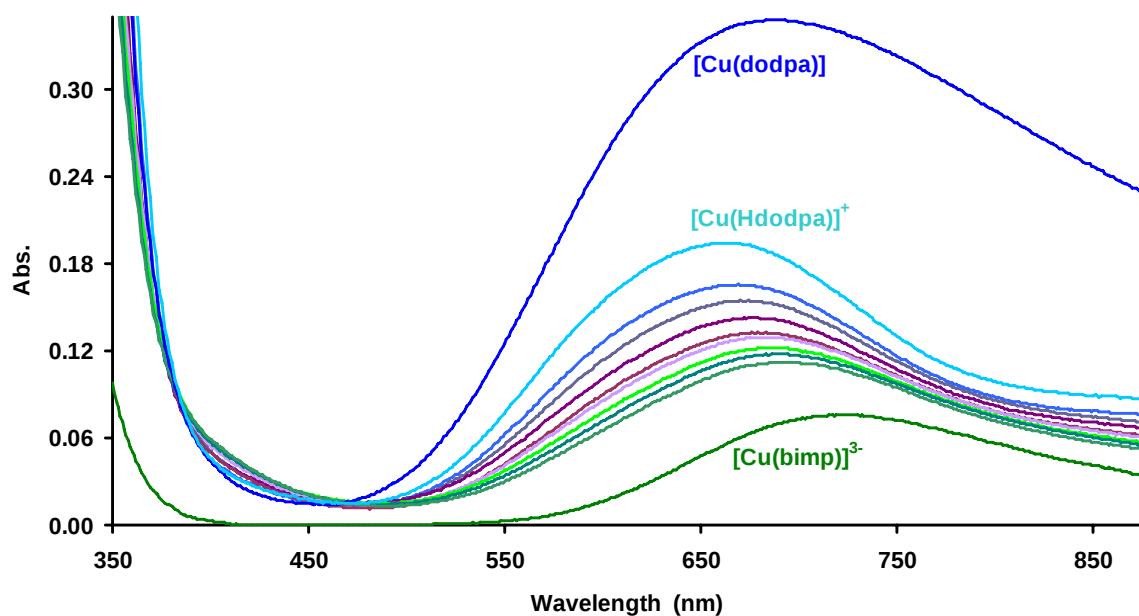


Figure S9: Absorption spectra of the Cu^{2+} –Medodpa $^{2-}$ –bimp $^{5-}$ – H^+ –system as a function of c_{bimp} recorded in the range of $c_{\text{bimp}}=2.002$ –80.28 mM ($I=0.15$ M NaCl; $[\text{Cu}^{2+}]=[\text{Medodpa}^{2-}]=2.00$ mM, $l=1$ cm, 25°C).

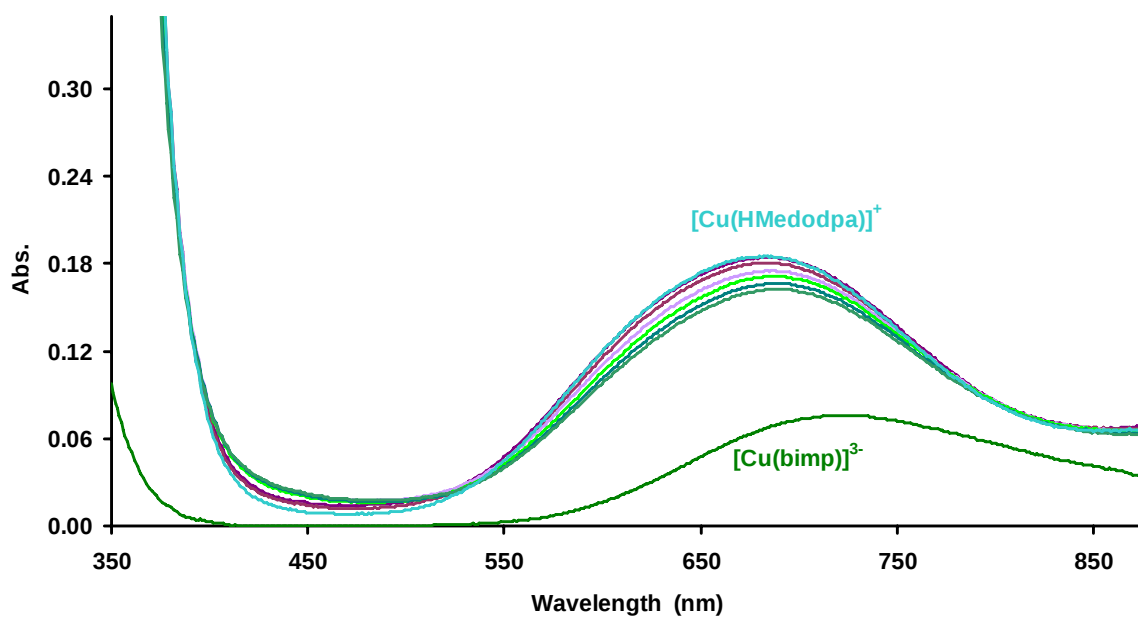


Figure S10: Relaxivity (0.47 T) as a function of time recorded for the sample prepared by mixing 1.00 mM Gd^{3+} and 1.05 mM dodpa $^{2-}$ at pH=5.45 set by using 50 mM NMP buffer ($I=0.15$ M NaCl, 25°C). The dotted line indicate the relaxivity of the $[\text{Gd}(\text{dodpa})]^\ddagger$ at the equilibrium in the given sample.

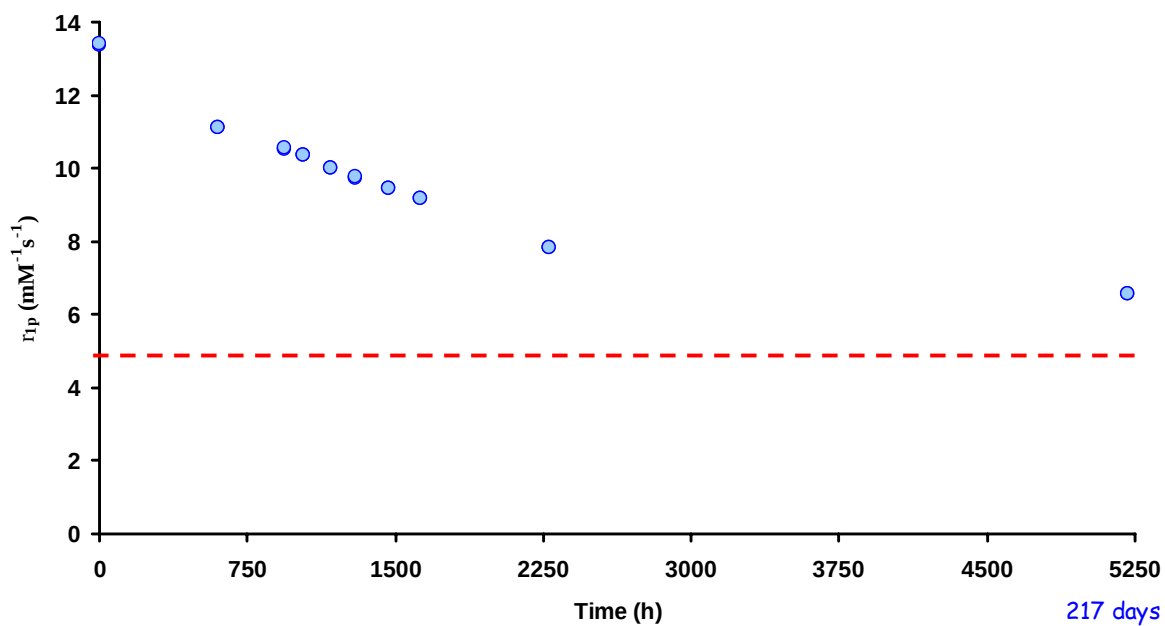


Figure S11: ^1H NMR spectra (500 MHz) of the $[\text{Lu}(\text{dodpa})]^+$ (top) and $[\text{La}(\text{dodpa})]^+$ (bottom) recorded in D_2O solution at 298 K (pD $\sim$ 7.0)

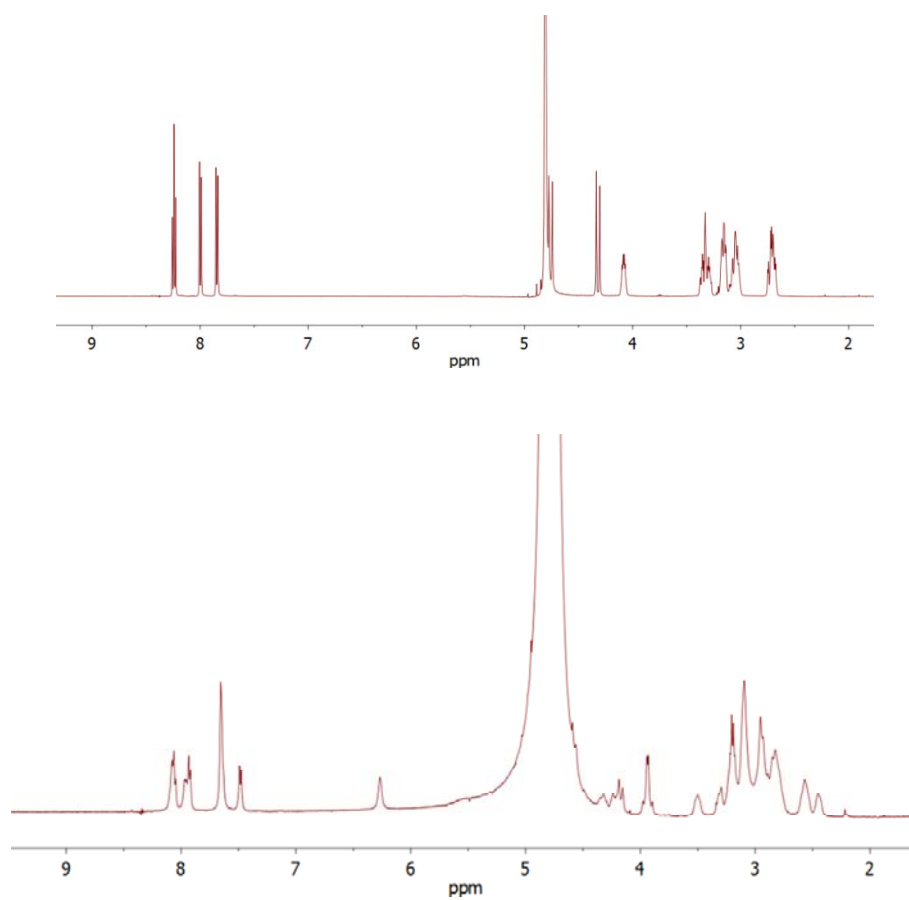


Figure S12: ESI⁺-MS recorded in aqueous solution for the [La(dodpa)]⁺ complex.

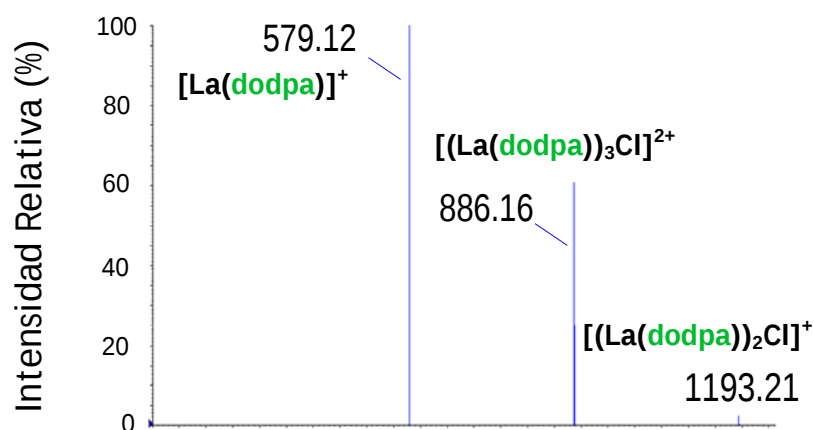


Table S1. Cartesian coordinates (Å) of [La₃(dodpa)₃(H₂O)₃]³⁺ optimized at the HF/3-21G level.

Center Number	Atomic Number	Coordinates (Angstroms)		
		X	Y	Z
1	57	1.766027	3.284821	0.065314
2	57	2.020679	-3.144321	0.036826
3	57	-3.830316	-0.155106	-0.016163
4	8	2.399875	-1.077772	1.527190
5	8	1.828024	0.779911	0.431985
6	8	4.109609	2.385471	0.177598
7	8	4.961665	0.361493	-0.392427
8	8	-0.209998	-1.902532	0.405175
9	8	-2.178749	-1.611852	1.433813
10	8	-0.056511	-4.643946	-0.244541
11	8	-2.104799	-4.086363	-1.049636
12	8	-4.115213	2.352623	-0.060766
13	8	-2.715385	4.032988	-0.668107
14	8	-1.614125	1.076774	0.316590
15	8	-0.343505	2.552863	1.408894
16	8	0.022246	2.039146	-1.442531
17	8	1.824459	-0.997386	-1.407604
18	8	-2.002153	-1.361705	-1.410224
19	7	2.282665	2.273338	2.605977
20	7	2.008120	5.093513	2.252395
21	7	3.492283	5.361006	-0.331637
22	7	1.415848	4.816497	-2.399278
23	7	-0.132867	5.274725	0.148033
24	7	3.079452	2.610312	-2.248642
25	7	0.701467	-3.322263	2.500111
26	7	3.284025	-4.485361	2.208729
27	7	4.688728	-2.554386	0.407265
28	7	2.959525	-5.655997	-0.537055
29	7	3.744181	-3.396358	-2.317368
30	7	0.992037	-3.658411	-2.486686
31	7	-3.256472	0.883335	2.460920
32	7	-5.574705	-0.731670	2.114565
33	7	-6.458979	0.393176	-0.522531
34	7	-4.939965	-1.285513	-2.474564
35	7	-4.672967	-2.782421	0.129069
36	7	-3.704272	1.189480	-2.397256
37	6	2.159557	0.150360	1.486373
38	6	2.254981	0.947985	2.745396
39	6	2.424758	1.134652	5.101012
40	6	2.479343	2.502992	4.949711

41	6	2.425646	3.046195	3.670266
42	6	2.671176	4.515953	3.454275
43	6	2.790394	6.299853	1.841349
44	6	3.978514	5.899749	0.968587
45	6	3.040666	6.428457	-1.256313
46	6	2.496031	5.844653	-2.556630
47	6	0.040357	5.399787	-2.333748
48	6	-0.281600	6.156165	-1.045977
49	6	-0.205851	6.047941	1.426221
50	6	0.575413	5.395507	2.573277
51	6	1.502267	3.899352	-3.571979
52	6	2.694984	2.974255	-3.468918
53	6	3.362463	2.512941	-4.589407
54	6	4.428771	1.643963	-4.424542
55	6	4.801129	1.257136	-3.148700
56	6	4.105097	1.777684	-2.081341
57	6	4.451177	1.456539	-0.638261
58	6	2.327344	0.334911	3.971640
59	6	-0.985439	-1.996288	1.408507
60	6	-0.413781	-2.607576	2.647860
61	6	-1.028034	-2.443284	3.865688
62	6	-0.453770	-3.037395	4.978388
63	6	0.684517	-3.797945	4.817717
64	6	1.230154	-3.938107	3.548207
65	6	2.362653	-4.896733	3.302304
66	6	4.216697	-3.434492	2.730940
67	6	5.270002	-2.964773	1.722083
68	6	5.634885	-2.803914	-0.718512
69	6	4.947770	-2.548706	-2.054374
70	6	4.063908	-4.826967	-2.614783
71	6	4.172483	-5.734545	-1.393447
72	6	3.107664	-6.461493	0.708954
73	6	3.981073	-5.710394	1.713928
74	6	3.034406	-2.830078	-3.498190
75	6	1.637670	-3.390868	-3.619546
76	6	1.027267	-3.597508	-4.845656
77	6	-0.276764	-4.059800	-4.880352
78	6	-0.945934	-4.300775	-3.691225
79	6	-0.262247	-4.103571	-2.514724
80	6	-0.881724	-4.327671	-1.153491
81	6	-3.419819	3.043810	-0.885146
82	6	-3.443779	2.492167	-2.299764
83	6	-3.209833	3.272516	-3.408941
84	6	-3.285067	2.673792	-4.657084
85	6	-3.565134	1.321458	-4.748530
86	6	-3.763445	0.595411	-3.585293
87	6	-4.042326	-0.888513	-3.600258
88	6	-6.302166	-0.723375	-2.743732
89	6	-7.160792	-0.469228	-1.506519
90	6	-7.220778	0.542114	0.749141
91	6	-6.991346	-0.679101	1.640482
92	6	-5.130537	-2.102219	2.527265
93	6	-5.280261	-3.173722	1.440499
94	6	-5.451716	-3.319481	-1.025358
95	6	-4.930838	-2.776528	-2.356049
96	6	-5.437537	0.190968	3.275218
97	6	-4.034934	0.686274	3.513819
98	6	-3.616017	1.037923	4.791388
99	6	-2.386276	1.638814	4.951551
100	6	-1.604995	1.885866	3.832817
101	6	-2.077897	1.486886	2.606596
102	6	-1.284725	1.732673	1.362187
103	1	2.474366	0.695884	6.076723
104	1	2.582570	3.145425	5.800104
105	1	3.741100	4.625499	3.331323
106	1	2.390952	5.077287	4.340971
107	1	3.135536	6.843032	2.716809
108	1	2.150612	6.963964	1.290598

109	1	2.296674	7.018568	-0.755978
110	1	3.864254	7.092742	-1.507614
111	1	3.320459	5.367930	-3.068489
112	1	2.144546	6.651721	-3.194697
113	1	-0.662427	4.584444	-2.400950
114	1	-0.123804	6.063282	-3.181323
115	1	0.353006	7.018257	-0.930919
116	1	-1.304453	6.508837	-1.123577
117	1	-1.238229	6.147639	1.743603
118	1	0.160368	7.046918	1.244405
119	1	0.522935	6.057896	3.435594
120	1	0.105825	4.459951	2.828460
121	1	0.601848	3.305739	-3.612745
122	1	1.553590	4.462936	-4.500031
123	1	3.067766	2.837690	-5.566261
124	1	4.968638	1.289420	-5.279391
125	1	5.624834	0.600653	-2.970236
126	1	2.302160	-0.729950	4.037789
127	1	-1.919571	-1.861470	3.936872
128	1	-0.894904	-2.921874	5.947472
129	1	1.137612	-4.291587	5.652738
130	1	1.910934	-5.841377	3.028680
131	1	2.921291	-5.061129	4.219088
132	1	4.735997	-3.808499	3.611545
133	1	3.608855	-2.593583	3.021848
134	1	5.810856	-2.137373	2.167831
135	1	5.992542	-3.747874	1.547265
136	1	6.012897	-3.809444	-0.647180
137	1	6.480634	-2.127781	-0.651485
138	1	4.621459	-1.521472	-2.041098
139	1	5.672300	-2.675261	-2.857419
140	1	4.984579	-4.890141	-3.189935
141	1	3.270452	-5.213016	-3.239682
142	1	5.024331	-5.473141	-0.795550
143	1	4.324160	-6.753232	-1.741995
144	1	3.588524	-3.024837	-4.412974
145	1	2.972801	-1.762485	-3.359354
146	1	1.565215	-3.410196	-5.752124
147	1	-0.759443	-4.236010	-5.820375
148	1	-1.953171	-4.657298	-3.668493
149	1	-3.018789	4.316775	-3.287446
150	1	-3.147126	3.254492	-5.546992
151	1	-3.646229	0.842815	-5.702688
152	1	-4.474982	-1.171355	-4.556576
153	1	-3.104250	-1.404859	-3.477949
154	1	-6.167404	0.223384	-3.246571
155	1	-6.842404	-1.375844	-3.425440
156	1	-7.426159	-1.390387	-1.021769
157	1	-8.086678	-0.001169	-1.831493
158	1	-8.283440	0.651888	0.554231
159	1	-6.877623	1.446579	1.229567
160	1	-7.673457	-0.659990	2.486451
161	1	-7.203442	-1.570576	1.078162
162	1	-5.697577	-2.426268	3.398126
163	1	-4.091441	-2.024378	2.800126
164	1	-4.819288	-4.083149	1.809057
165	1	-6.324025	-3.399086	1.280962
166	1	-6.489370	-3.073746	-0.882388
167	1	-5.378227	-4.402324	-1.062120
168	1	-3.911638	-3.113236	-2.459003
169	1	-5.510518	-3.217616	-3.164746
170	1	-6.041162	1.068392	3.084372
171	1	-5.827266	-0.278484	4.173696
172	1	-4.253227	0.858098	5.632867
173	1	-2.047017	1.924780	5.926286
174	1	-0.655034	2.365442	3.907163
175	1	4.226698	4.814402	-0.758021
176	1	-0.923303	4.636760	0.126648

177	1	2.155240	-5.986876	-1.051570
178	1	4.536920	-1.550444	0.424428
179	1	3.554971	-7.427382	0.493551
180	1	2.117861	-6.635365	1.105756
181	1	4.901479	-5.422309	1.240885
182	1	4.237637	-6.362098	2.544875
183	1	4.621046	6.762022	0.815265
184	1	4.565074	5.124622	1.440200
185	1	-6.289253	1.307818	-0.916661
186	1	-3.740991	-3.178180	0.074929
187	1	-2.174426	-2.324582	-1.469535
188	1	-1.205619	-1.294327	-0.831732
189	1	-0.407966	2.193894	-2.287712
190	1	-0.606934	1.567214	-0.827483
191	1	1.806535	-0.212893	-0.787745
192	1	1.131684	-0.911185	-2.071187

Table S2. Cartesian coordinates (Å) of [Lu(dodpa)]⁺ optimized at the TPSSh/6-31G(d) level.

Center Number	Atomic Number	Coordinates (Angstroms)		
		X	Y	Z
1	71	0.000000	0.000000	0.086985
2	7	-1.000720	1.930353	1.529200
3	6	0.000000	2.457369	2.501138
4	6	1.437540	2.301315	2.005008
5	6	2.023663	-0.017742	2.793830
6	6	2.209589	-1.439601	2.257948
7	7	1.000720	-1.930353	1.529200
8	6	0.000000	-2.457369	2.501138
9	6	-1.437540	-2.301315	2.005008
10	6	-2.023663	0.017742	2.793830
11	6	-2.209589	1.439601	2.257948
12	6	-1.392589	2.978260	0.537613
13	6	1.392589	-2.978260	0.537613
14	1	-0.126065	1.902115	3.436178
15	1	-0.199914	3.513095	2.733750
16	1	1.590104	2.874901	1.086464
17	1	2.126486	2.692557	2.767261
18	1	1.185950	0.026718	3.498505
19	1	2.925171	0.283606	3.346868
20	1	3.048170	-1.442680	1.554864
21	1	2.471175	-2.122900	3.078516
22	1	0.126065	-1.902115	3.436178
23	1	0.199914	-3.513095	2.733750
24	1	-1.590104	-2.874901	1.086464
25	1	-2.126486	-2.692557	2.767261
26	1	-1.185950	-0.026718	3.498505
27	1	-2.925171	-0.283606	3.346868
28	1	-3.048170	1.442680	1.554864
29	1	-2.471175	2.122900	3.078516
30	1	-1.950266	3.791815	1.024769
31	1	-0.471668	3.402464	0.120685
32	1	1.950266	-3.791815	1.024769
33	1	0.471668	-3.402464	0.120685
34	6	-2.203503	2.365572	-0.591621
35	6	-3.174194	3.040765	-1.332635
36	6	-3.826266	2.353273	-2.364923
37	1	-3.416015	4.076239	-1.114414
38	6	-2.536301	0.407123	-1.836032
39	6	-3.515755	1.015509	-2.620202
40	1	-4.580901	2.861972	-2.957203
41	1	-4.004152	0.437486	-3.396611
42	6	2.203503	-2.365572	-0.591621
43	6	3.174194	-3.040765	-1.332635

44	6	2.536301	-0.407123	-1.836032
45	6	3.826266	-2.353273	-2.364923
46	1	3.416015	-4.076239	-1.114414
47	6	3.515755	-1.015509	-2.620202
48	1	4.580901	-2.861972	-2.957203
49	1	4.004152	-0.437486	-3.396611
50	7	1.906070	-1.082240	-0.856470
51	7	-1.906070	1.082240	-0.856470
52	6	-2.113233	-1.052445	-1.990786
53	8	-1.121558	-1.390164	-1.193610
54	8	-2.705791	-1.766958	-2.784316
55	6	2.113233	1.052445	-1.990786
56	8	2.705791	1.766958	-2.784316
57	8	1.121558	1.390164	-1.193610
58	7	1.733297	0.887926	1.664441
59	7	-1.733297	-0.887926	1.664441
60	1	2.542430	0.890229	1.039585
61	1	-2.542430	-0.890229	1.039585
