Electronic Supplementary Material (ESI) for Dalton Transactions.

Separation mechanism of Am(III) from Eu(III) by diglycolamide and nitrilotriacetamide extraction reagents using DFT calculations

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Table S1 Total energy (E^{tot}) and gibbs correaction energy (G^{corr}) of each compound

compounds	E^{tot} / hartree			G^{corr} / kJ mol^{-1}
	BP86	B3LYP	B2PLYP	BP86
H_2O	-76.5631	-76.5243	-76.5004	9.46
TMDGA	-650.4887	-650.1043	-649.9031	524.88
HMNTA	-917.5426	-916.9843	-916.7048	821.99
$Eu(H_2O)_9$	-11768.3997	-11766.7693	-11766.1498	432.93
$Eu(TMDGA)_3$ (Δ)	-13030.8572	-13028.4167	-13027.4217	1693.01
$Eu(TMDGA)_3$ (Λ)	-13030.8571	-13028.4155	-13027.4200	1693.01
$Eu(HMNTA)(H_2O)_5$ (C)	-12379.7274	-12377.6854	-12376.8861	1083.34
$Eu(HMNTA)(H_2O)_5$ (A)	-12379.7291	-12377.6879	-12376.8888	1091.80
$Am(H_2O)_9$	-32775.9113	-32772.4885	-32771.5440	431.36
$Am(TMDGA)_3$ (Δ)	-34038.3643	-34034.1328	-34032.8131	1695.82
$Am(TMDGA)_3$ (Λ)	-34038.3661	-34034.1343	-34032.8150	1695.82
$Am(HMNTA)(H_2O)_5$ (C)	-33387.2354	-33383.4041	-33382.2811	1084.66
$Am(HMNTA)(H_2O)_5$ (A)	-33387.2376	-33383.4074	-33382.2853	1092.10

Table S2 α-Orbital energies in valence region with PDOS and OP for $[Eu(TMDGA)_3]^{3+}$

MO(α)	Orbital energy / eV	PDOS(f) [%]	OP[M(f)-all] ($x10^2$)	MO(α)	Orbital energy / eV	PDOS(f) [%]	OP[M(f)-all] ($x10^2$)
102	-24.6222	0.2	0.0375	123	-22.6312	0.6	0.0873
103	-24.6105	0.1	0.0390	124	-22.6197	0.5	0.0862
104	-24.5934	0.6	0.1649	125	-22.4312	3.7	0.2616
105	-24.1523	1.2	0.0650	126	-22.4143	3.8	0.2277
106	-24.1085	13.4	0.8528	127	-22.3441	1.9	-0.0896
107	-24.0677	3.2	0.3946	128	-22.0644	2.6	0.0123
108	-24.0573	3.7	0.4700	129	-22.0290	0.1	-0.0021
109	-23.9939	2.7	0.1066	130	-22.0184	0.0	-0.0028
110	-23.9697	0.6	0.1280	131	-21.7052	92.8	0.0539
111	-23.9191	0.3	-0.0273	132	-21.6635	91.6	-0.0711
112	-23.8954	0.3	-0.0367	133	-21.6186	88.4	-0.0503
113	-23.7925	0.1	-0.0452	134	-21.6116	92.2	-0.2822
114	-23.6149	75.8	-0.4943	135	-21.2668	3.5	-0.1857
115	-23.3871	84.1	0.0284	136	-21.1680	0.2	0.0124
116	-23.2728	3.3	-0.0139	137	-21.1530	0.2	0.0144
117	-22.9781	2.3	0.2891	138	-21.1340	0.5	0.0076
118	-22.9506	3.6	0.0442	139	-21.1207	1.0	-0.0052
119	-22.8712	1.0	0.0247	140	-21.1136	1.8	-0.0200
120	-22.8663	0.6	0.1418	141	-20.5264	0.6	-0.0075
121	-22.8415	5.4	0.1599	142	-20.5114	1.0	-0.0309
122	-22.6676	0.6	0.0877	143	-20.4839	0.1	-0.0091

Table S2 cont.

MO(α)	Orbital energy / eV	PDOS(f) [%]	OP[M(f)-all] ($x10^2$)	MO(α)	Orbital energy / eV	PDOS(f) [%]	OP[M(f)-all] ($x10^2$)
144	-20.3440	0.3	-0.0365	165	-19.3353	0.0	-0.0152
145	-20.3068	1.4	-0.1821	166	-19.3217	0.3	0.1252
146	-20.2545	1.4	-0.3435	167	-19.3065	0.3	0.1779
147	-19.9636	0.1	0.0884	168	-19.2765	0.1	-0.0023
148	-19.9361	0.1	0.0430	169	-19.2417	0.8	-0.1399
149	-19.9209	0.1	-0.0454	170	-19.1998	1.3	-0.3931
150	-19.8605	0.2	-0.0221	171	-17.8319	0.0	-0.1826
151	-19.8510	0.4	-0.0400	172	-17.8079	0.0	-0.1748
152	-19.8259	0.1	0.0242	173	-17.7075	0.1	0.0669
153	-19.8153	0.3	0.0474	174	-17.6994	0.1	0.1652
154	-19.7440	0.1	0.0204	175	-17.6542	0.1	0.0903
155	-19.7397	0.1	0.0572	176	-17.6354	0.1	0.0168
156	-19.6357	0.0	-0.1191	177	-17.4496	1.0	0.8503
157	-19.6213	0.1	-0.0431	178	-17.3737	1.1	0.4701
158	-19.6047	0.2	-0.0951	179	-17.1551	0.6	0.0344
159	-19.6006	0.1	-0.1008	180	-16.0509	0.4	0.4575
160	-19.5851	0.0	0.0093	181	-15.9157	0.0	-0.1403
161	-19.5775	0.1	-0.0269	182	-15.8808	0.2	0.2117
162	-19.4545	0.7	0.2508	183	-15.8593	0.3	0.2697
163	-19.3704	0.2	0.1375	184	-15.8310	0.0	0.0109
164	-19.3680	0.3	0.2156	185(HOMO)	-15.8017	0.1	0.0270

Table S3 α-Orbital energies in valence region with PDOS and OP for $[Am(TMDGA)_3]^{3+}$

MO(α)	Orbital energy / eV	PDOS(f) [%]	OP[M(f)-all] ($x10^2$)	MO(α)	Orbital energy / eV	PDOS(f) [%]	OP[M(f)-all] ($x10^2$)
150	-21.0592	0.0	0.0186	176	-19.3032	0.8	0.1932
151	-20.5201	0.6	0.1703	177	-19.2782	1.1	0.2038
152	-20.5013	0.6	0.1335	178	-19.2559	1.0	0.2286
153	-20.4390	0.2	0.0304	179	-19.2501	0.6	0.0409
154	-20.3228	0.7	0.1252	180	-19.1854	0.4	0.0686
155	-20.3155	0.1	0.0307	181	-18.4844	74.8	0.6638
156	-20.2915	1.1	0.1782	182	-17.9187	22.6	1.2400
157	-20.0888	0.1	0.0820	183	-17.8352	0.7	0.0925
158	-19.9721	0.3	0.1012	184	-17.7579	12.0	0.5881
159	-19.9574	0.4	0.1455	185	-17.7258	2.5	0.3047
160	-19.8994	0.4	0.0900	186	-17.7054	3.1	0.2466
161	-19.8836	1.0	0.1539	187	-17.6384	3.9	0.1815
162	-19.8556	0.9	0.1529	188	-17.5889	24.3	0.4273
163	-19.8112	0.4	0.1285	189	-17.5070	12.2	1.0676
164	-19.7674	0.6	0.2159	190	-17.2558	35.4	-0.2991
165	-19.7277	0.6	0.1311	191	-17.0776	59.7	-0.9868
166	-19.6763	1.1	0.1262	192	-16.7568	88.0	-0.4193
167	-19.6224	0.6	0.1053	193	-16.5078	76.9	-1.6823
168	-19.6121	1.2	0.1806	194	-16.3415	61.6	-2.1731
169	-19.5868	0.5	0.1374	195	-16.2966	61.0	-2.4046
170	-19.5761	0.2	0.0447	196	-15.9723	9.9	-0.3730
171	-19.5549	0.3	0.0607	197	-15.8931	3.1	-0.0454
172	-19.4730	1.9	0.5338	198	-15.8675	3.4	-0.3784
173	-19.3508	1.2	0.3332	199	-15.8065	3.8	-0.4231
174	-19.3443	0.5	0.1075	200	-15.7619	4.6	-0.4180
175	-19.3293	1.3	0.1057	201(HOMO)	-15.6906	13.0	-1.1220

Table S4 α-Orbital energies in valence region with PDOS and OP for $[Eu(HMNTA)(H_2O)_5]^{3+}$

MO(α)	Orbital energy / eV	PDOS(f) [%]	OP (x10^2) M(f)-all	OP (x10^2) M(f)-NTA
72	-26.6149	1.0	0.3054	0.0110
73	-26.4832	0.2	0.0853	0.0626
74	-26.4024	1.1	0.3143	0.1105
75	-26.3760	0.7	0.2541	0.0167
76	-26.1564	0.3	0.1209	0.0204
77	-26.0914	1.2	0.2159	0.1708
78	-25.8837	37.7	0.1304	0.0870
79	-25.8778	3.8	-0.0100	-0.0320
80	-25.8010	55.6	-0.0956	-0.0948
81	-25.2402	0.3	0.0209	0.0222
82	-25.0361	2.9	0.2373	0.2396
83	-24.9406	2.1	0.1777	0.1661
84	-24.6663	19.2	0.2843	0.3190
85	-24.5588	26.4	0.2744	0.2295
86	-24.5512	57.1	-0.0027	0.0205
87	-24.3161	20.4	0.2607	0.2235
88	-24.2241	76.2	-0.0617	-0.0670
89	-23.9123	64.1	0.9683	-0.0246
90	-23.8587	47.5	0.6230	0.0843
91	-23.7512	61.5	0.3491	0.1118
92	-23.7417	15.3	0.0511	-0.1774
93	-23.6121	47.6	-0.1823	-0.4089
94	-23.5501	3.5	-0.0573	-0.0374
95	-23.4989	10.0	0.0525	0.1120
96	-23.3087	4.7	-0.2385	0.0058
97	-23.0837	11.9	-0.6574	0.0046
98	-23.0361	0.8	-0.1199	-0.0565
99	-22.9966	10.5	-0.6428	-0.0137
100	-22.9476	1.0	-0.0441	-0.0469
101	-22.6924	13.0	-1.4241	-0.0156
102	-22.5493	0.4	0.0112	0.0140
103	-22.1950	0.6	-0.0085	0.0015
104	-22.0480	0.7	-0.0108	0.0088
105	-21.6205	0.1	0.0639	0.0568
106	-21.4932	0.2	0.0081	0.0172
107	-21.4845	0.1	0.0534	0.0497
108	-21.1631	0.0	0.0685	0.0494
109	-21.1242	0.0	0.0054	0.0404
110	-21.0442	0.1	0.0035	0.0444
111	-20.9841	0.1	-0.0920	-0.0601
112	-20.9498	0.1	-0.1066	0.0372
113	-20.9062	0.1	-0.0276	0.0266
114	-20.8450	0.3	0.0960	0.0919
115	-20.7743	0.4	0.0766	0.0437
116	-20.7373	0.0	-0.3388	-0.0178
117	-20.6709	0.0	-0.0093	0.0134
118	-20.5109	0.2	0.1050	0.0681
119	-20.4436	0.2	-0.0993	-0.0176
120	-20.4328	0.0	-0.0353	0.0266
121	-20.3677	0.0	-0.0879	-0.0008
122	-20.3495	0.0	-0.0588	0.0298
123	-20.2953	0.0	-0.0161	-0.0071
124	-20.2611	0.0	0.0131	0.0360
125	-18.9457	0.1	0.2476	0.2814
126	-18.8616	0.3	0.3295	0.3122
127	-18.7993	0.4	0.1866	0.1676
128	-18.0450	0.3	0.0717	0.0726
129	-17.2501	0.0	0.0380	0.0376
130	-17.1587	0.1	0.0191	0.0354
131(HOMO)	-17.0961	0.0	0.0254	0.0428

Table S5 α-Orbital energies in valence region with PDOS and OP for $[Am(HMNTA)(H_2O)_5]^{3+}$

MO(α)	Orbital energy / eV	PDOS(f) [%]	OP (x10^2) M(f)-all	OP (x10^2) M(f)-NTA
102	-23.8029	0.2	0.0842	0.0619
103	-23.7479	0.0	0.0258	0.0197
104	-23.5942	0.0	0.0087	0.0118
105	-23.3452	0.4	0.2819	0.1285
106	-23.2608	1.4	0.3346	-0.0038
107	-23.0973	1.3	0.3517	0.0191
108	-23.0478	0.7	0.2384	0.0477
109	-23.0157	0.6	0.1234	0.0309
110	-22.9566	2.1	0.5285	-0.0164
111	-22.7474	1.6	0.4425	-0.0105
112	-22.6105	0.2	0.0916	0.0598
113	-22.2450	0.3	0.0800	0.0589
114	-22.1046	0.5	0.1118	0.1186
115	-21.6717	0.7	0.1810	0.1685
116	-21.5389	0.4	0.0990	0.0970
117	-21.4962	0.2	0.0565	0.0578
118	-21.2124	1.1	0.2073	0.1951
119	-21.1160	1.6	0.1844	0.1420
120	-21.0545	0.6	0.1684	0.1594
121	-20.9977	4.7	0.4698	0.4494
122	-20.9851	4.7	0.3649	0.2754
123	-20.9326	1.8	0.2908	0.0064
124	-20.8722	1.8	0.1707	0.1076
125	-20.8088	2.4	0.4623	0.1805
126	-20.6899	2.1	0.1737	0.1249
127	-20.6488	9.3	0.5442	0.1002
128	-20.5759	3.1	0.1320	0.0696
129	-20.491	1.8	0.1696	0.1403
130	-20.423	1.8	0.0765	0.0177
131	-20.3879	13.6	0.3959	0.1722
132	-20.3375	1.1	0.1349	0.0651
133	-20.3084	1.5	0.1369	0.0676
134	-20.3008	4.8	0.1266	0.0095
135	-20.0088	52.2	-1.0102	0.1707
136	-19.2567	42.6	1.1999	1.5598
137	-19.0716	64.9	-0.2880	0.4638
138	-19.0104	12.3	0.4301	0.6405
139	-18.8259	45	-0.1486	0.2413
140	-18.6635	46.9	-0.8383	-0.1397
141	-18.4433	88.4	-1.5480	-0.3516
142	-18.3592	71.9	-1.8365	-0.9257
143	-18.2809	56.3	-1.7157	-1.3221
144	-17.9957	42.7	-2.3823	-2.0293
145	-17.2368	3.7	-0.4598	-0.3384
146	-17.1957	2.9	-0.4876	-0.4398
147(HOMO)	-17.1198	2.1	-0.3144	-0.2971