Electronic Supplementary Information for

Theoretical Insights into Selective Separation of Trivalent Actinide and Lanthanide by Ester and Amide Ligands based on Phenanthroline Skeleton

Cui Wang,[a,b] Qun-Yan Wu,*[b] Cong-Zhi Wang,[b] Jian-Hui Lan,[b] Chang-Ming Nie,*[a] Zhi-Fang Chai,[b,c] and Wei-Qun Shi*[b]

[a] School of Chemistry and Chemical Engineering, University of South China, Hengyang, 421001, China.

[b] Laboratory of Nuclear Energy Chemistry, Institute of High Energy Physics, Chinese Academy of Sciences, Beijing, 100049, China.

[c] Engineering Laboratory of Advanced Energy Materials, Ningbo Institute of Industrial Technology, Chinese Academy of Sciences, Ningbo, Zhejiang, 315201, China

Corresponding Authors

*E-mail: wuqy@ihep.ac.cn, niecm196132@163.com and shiwq@ihep.ac.cn.

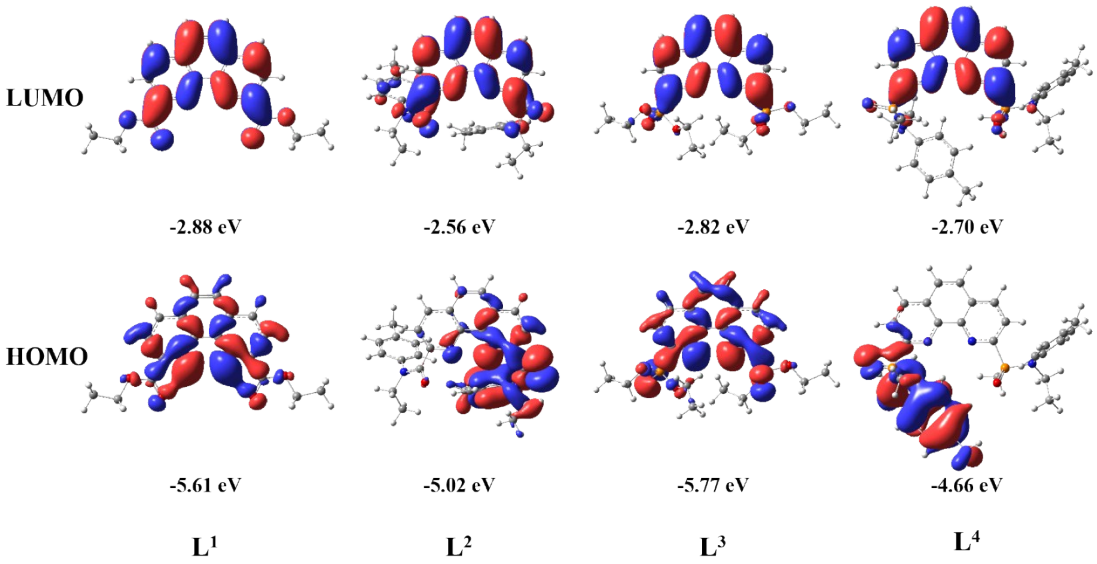

Fig. S1 The diagrams of HOMO and LUMO for the four ligands, and the corresponding MO energies (eV) obtained at the BP86/6-31G(d) level of theroy. (The isosurface value is 0.02 a.u.)

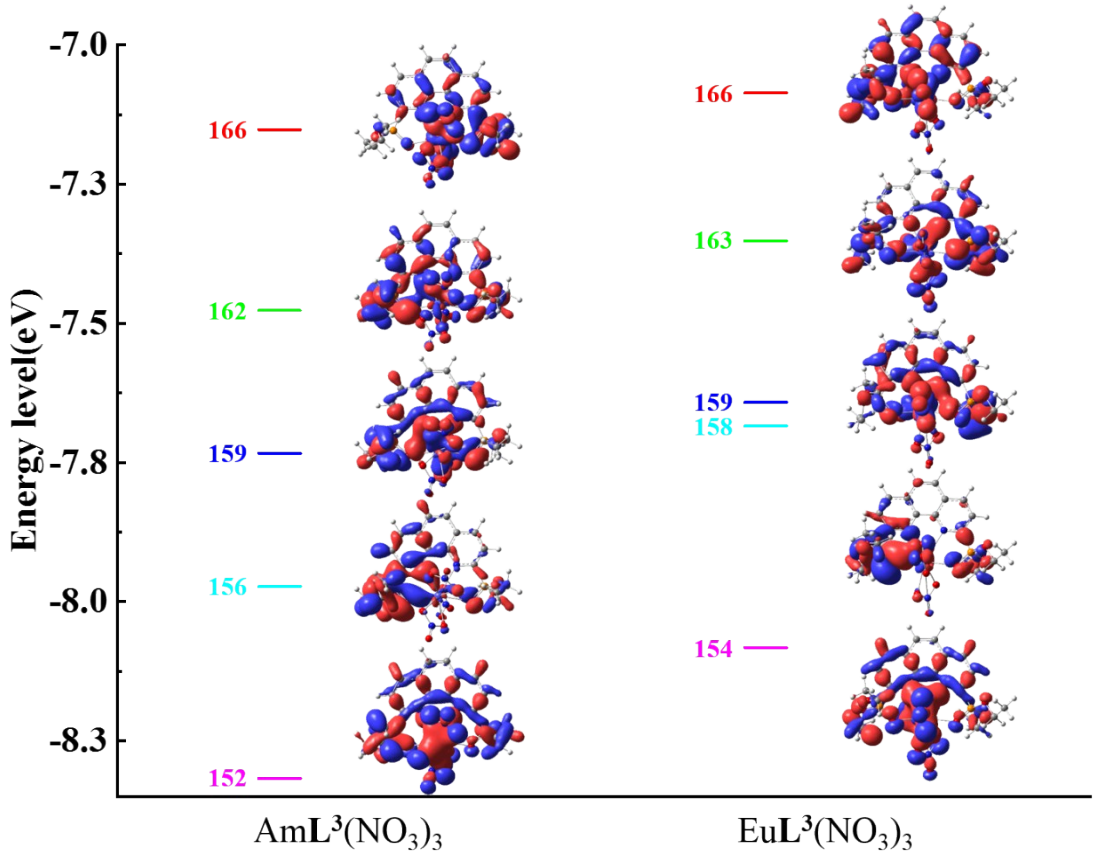

Fig. S2 Energy level (eV) of the α-spin valence MOs for the $ML^3(NO_3)_3$ complexes obtained at the BP86/6-31G(d)/RECP level of theory in the gas phase. (The isosurface value is 0.02 a.u.)

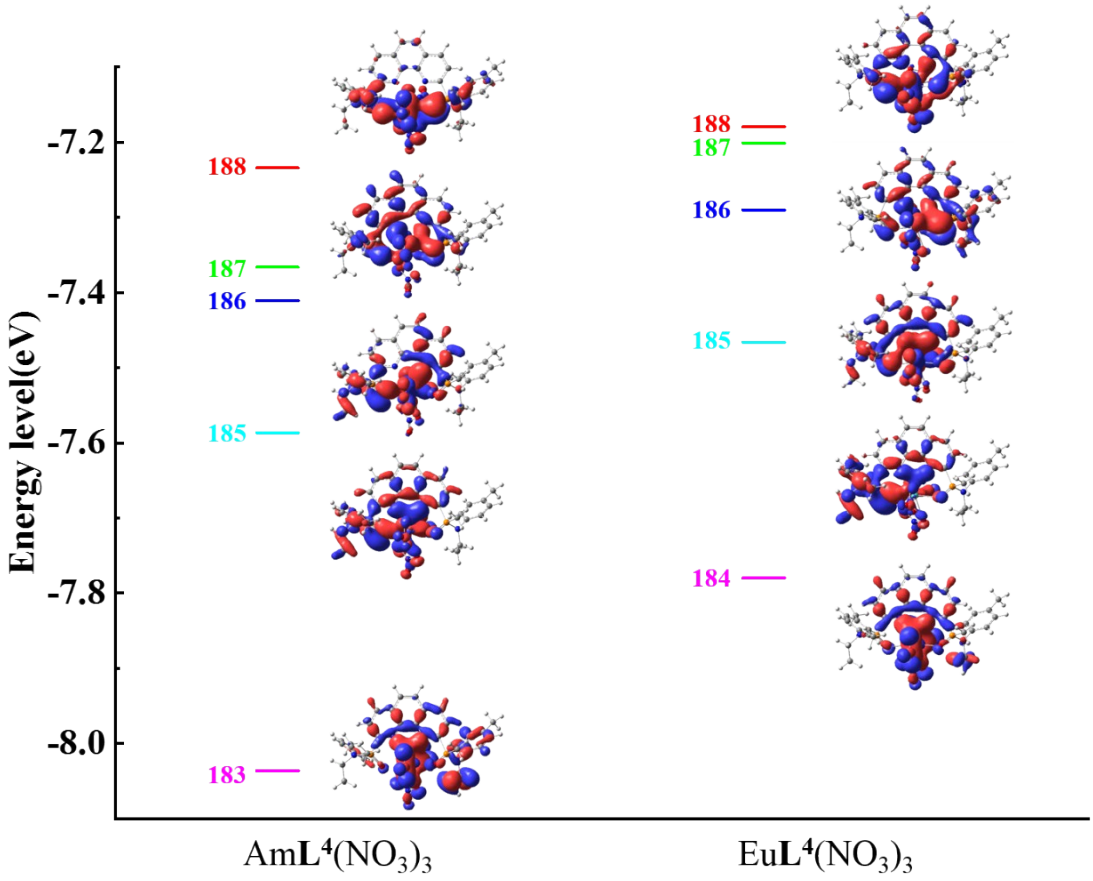

Fig. S3 Energy level (eV) of the α-spin valence MOs for the M**L**^{4}$(NO_3)_3$ complexes obtained at the BP86/6-31G(d)/RECP level of theory in the gas phase. (The isosurface value is 0.02 a.u.)

Table S1 The relative electronic energies (kcal/mol) to each ground state for the $ML^2(NO_3)_3$ (M=Am, Eu) complexes

Spin state	singlet	triplet	quintet	septet
Am$L^2(NO_3)_3$	141.14	53.64	27.85	0.00
Eu$L^2(NO_3)_3$	147.01	79.60	62.21	0.00

Table S2 The calculated S^2 of the lowest electronic state for the $ML(NO_3)_3$ (M=Am, Eu) complexes are obtained with the BP86/6-31G(d)/RECP level of theory

Complexes	S^2	S(S+1)
Am$L^1(NO_3)_3$	12.07	12.00
Eu$L^1(NO_3)_3$	12.27	12.00
Am$L^2(NO_3)_3$	12.06	12.00
Eu$L^2(NO_3)_3$	12.25	12.00
Am$L^3(NO_3)_3$	12.05	12.00
Eu$L^3(NO_3)_3$	12.25	12.00
Am$L^4(NO_3)_3$	12.05	12.00
Eu$L^4(NO_3)_3$	12.25	12.00

Table S3 Calculated average MBOs of the M-N and M-O bonds in the $[ML(NO_3)_3]$ complexes at the BP86/6-31G(d)/RECP level of theory in the gas phase

Complexes	Eu/Am-O_L	Eu/Am-N_L	Eu/Am-O_N
M$L^1(NO_3)_3$	0.220/0.288	0.168/0.229	0.307/0.389
M$L^2(NO_3)_3$	0.257/0.319	0.184/0.234	0.287/0.359
M$L^3(NO_3)_3$	0.307/0.343	0.174/0.209	0.281/0.351
M$L^4(NO_3)_3$	0.324/0.362	0.167/0.208	0.276/0.346

Table S4 Mulliken charge on the metal ions and the charge transfer from the NO_3^- [$\Delta Q(NO_3^-)$] and ligand [$\Delta Q(L)$] to the metal ion in the $ML(NO_3)_3$ complexes[a]

Complexes	Q(M)	ΔQ(M)	$\Delta Q(NO_3^-)$	ΔQ(L)
M$L^1(NO_3)_3$	1.272/1.180	1.728/1.820	0.442/0.487	0.401/0.360
M$L^2(NO_3)_3$	1.278/1.185	1.722/1.815	0.445/0.468	0.388/0.411
M$L^3(NO_3)_3$	1.240/1.102	1.760/1.898	0.442/0.462	0.434/0.511
M$L^4(NO_3)_3$	1.255/1.127	1.745/1.873	0.431/0.458	0.442/0.499

[a]…/…denotes the values of the Eu/Am complexes, respectively.

Table S5 Composition and energy level (eV) for the α-spin valence MOs of the $ML(NO_3)_3$（L^1-L^4）complexes obtained at the BP86/6-31G(d)/RECP level of theory in the gas phase

Complexes	Order	M%	s/p/d/f%	N1%	N2%	O1%	O2%	E/eV
	131	5.20	-/1.29/1.55/1.64	1.15	0.23	50.70	9.17	-7.50
	130	7.64	-/2.47/2.21/1.19	3.36	7.10	8.82	0.42	-7.56
$AmL^1(NO_3)_3$	129	4.57	-/-/2.02/0.50	0.15	0.09	9.91	55.51	-7.74
	128	8.00	-/-/4.16/2.94	31.74	20.53	0.36	1.50	-7.82
	127	7.49	-/-/5.48/-	5.89	9.96	7.25	1.69	-7.92
	131	6.65	-/2.19/2.31/0.66	2.35	1.11	13.06	1.47	-7.37
	130	4.32	-/-/1.98/0.61	0.09	1.39	50.64	4.57	-7.40
$EuL^1(NO_3)_3$	129	4.91	-/-/2.82/-	0.65	1.98	2.55	50.94	-7.58
	128	6.14	-/-/3.63/0.53	36.95	16.55	0.93	1.39	-7.61
	127	7.08	0.84/-/4.58/-	2.23	20.48	4.29	12.86	-7.67
	176	4.20	-/-/1.61/1.24	0.03	2.12	7.39	0.91	-6.93
	172	3.24	-/-/1.35/-	0.46	0.21	31.40	3.44	-7.33
$AmL^2(NO_3)_3$	171	7.38	-/2.99/2.48/-	3.92	12.73	0.09	0.22	-7.37
	169	10.08	-/-/7.51/-	6.63	11.45	0.34	0.19	-7.69
	166	7.78	6.19/-/1.05/-	4.31	3.25	0.64	0.23	-8.22
	176	3.69	-/-/1.25/0.83	0.17	2.55	8.21	0.46	-6.81
	172	2.83	-/-/0.87/-	0.57	1.11	25.29	2.84	-7.21
$EuL^2(NO_3)_3$	171	6.91	-/0.95/3.60/0.63	7.69	31.42	0.12	0.68	-7.32
	169	9.03	-/-/7.06/-	8.93	10.74	0.55	0.26	-7.49
	168	9.14	6.88/-/.81/-	8.02	6.28	0.40	0.36	-7.97
	166	4.96	-/2.03/-/0.57	1.57	3.61	5.46	0.81	-7.15
	162	3.12	-/-/1.09/-	8.40	1.11	3.85	13.21	-7.48
$AmL^3(NO_3)_3$	159	4.90	-/-/2.97/-	8.93	3.77	10.02	9.11	-7.73
	156	2.90	-/-/1.31/-	12.57	0.31	3.13	30.97	-7.97
	152	8.16	6.76/-/0.77/-	4.20	5.14	1.11	3.06	-8.32
	166	2.89	-/-/-/-	4.07	8.29	4.06	1.08	-7.09
	163	4.10	-/-/2.15/0.61	5.15	1.15	3.45	11.66	-7.35
$EuL^3(NO_3)_3$	159	3.95	-/-/2.08/-	6.18	4.23	2.58	5.38	-7.64
	158	3.18	-/-/1.67/-	0.03	1.96	55.05	3.60	-7.68
	154	7.56	5.47/0.58/1.35/-	6.48	6.71	2.94	1.12	-8.08
	188	4.45	-/1.76/2.00/-	0.18	0.08	27.14	16.01	-7.23
	187	5.97	-/-/3.32/0.81	26.30	6.11	9.01	11.17	-7.37
$AmL^4(NO_3)_3$	186	5.72	-/-/2.51/1.81	0.14	19.71	1.16	23.61	-7.41
	185	6.05	-/-/4.61/-	8.99	6.80	1.71	26.43	-7.59
	183	7.22	4.64/-/1.35/-	3.48	4.55	1.15	0.64	-8.04
	188	4.81	-/1.10/2.07/-	3.50	5.39	9.99	20.24	-7.18
	187	4.22	-/-/2.37/-	11.00	5.90	34.16	4.44	-7.20
$EuL^4(NO_3)_3$	186	5.56	-/1.26/2.63/-	8.65	16.34	3.04	10.64	-7.29
	185	3.80	-/-/3.00/-	5.12	4.01	1.47	39.10	-7.47
	184	8.89	7.11/-/2.05/-	7.31	5.31	0.78	1.30	-7.78

Table S6 Second-order perturbative estimates (E(2), kcal/mol) of donor-acceptor interactions between ligands and Am(III)/Eu(III) in the [$ML(NO_3)_3$] complexes. Only energies over 3.0 kcal/mol are presented

Complexes	donor→acceptor	Character of empty metal orbital	E(2)
$AmL^1(NO_3)_3$	N 1→ Am	s(0.22%),p(0.10%),d(99.29%),f(0.40%)	7.73
	N 2→ Am	s(0.09%),p(0.15%),d(99.30%),f(0.46%)	5.78
	O 1→ Am	s(0.09%),p(0.15%),d(99.30%),f(0.46%)	9.64
	O 2→ Am	s(1.01%),p(0.07%),d(98.59%),f(0.33%)	5.43
$EuL^1(NO_3)_3$	N 1→ Eu	s(0.43%),p(0.02%),d(99.18%),f (0.37%)	13.89
	N 2→ Eu	s(0.11%),p(0.11%),d(99.45%),f(0.33%)	5.56
	O 1→ Eu	s(0.11%),p(0.11%),d(99.45%),f(0.33%)	7.58
	O 2→ Eu	s(4.17%),p(0.03%),d(95.40%),f(0.40%)	7.87
$AmL^2(NO_3)_3$	N 1→ Am	s(0.00%),p(0.06%),d(99.67%),f(0.27%)	8.39
	N 2→ Am	s(0.08%),p(0.20%),d(99.35%),f(0.36%)	5.85
	O 1→ Am	s(1.56%),p(0.10%),d(97.94%),f(0.40%)	8.31
	O 2→ Am	s(0.08%),p(0.20%),d(99.35%),f(0.36%)	10.41
$EuL^2(NO_3)_3$	N 1→ Eu	s(1.38%),p(0.04%),d(98.31%),f(0.27%)	8.74
	N 2→ Eu	s(0.01%),p(0.16%),d(99.46%),f(0.37%)	6.52
	O 1→ Eu	s(2.79%),p(0.04%),d(97.08%),f(0.09%)	11.44
	O 2→ Eu	s(0.01%),p(0.16%),d(99.46%),f(0.37%)	7.86
$AmL^3(NO_3)_3$	N 1→ Am	s(0.13%),p(0.07%),d(99.31%),f(0.49%)	7.87
	N 2→ Am	s(0.11%),p(0.13%),d(99.31%),f(0.46%)	8.16
	O 1→ Am	s(1.66%),p(0.04%),d(97.93%),f(0.37%)	3.75
	O 2→ Am	s(1.66%),p(0.04%),d(97.93%),f(0.37%)	15.45
$EuL^3(NO_3)_3$	N 1→ Eu	s(9.37%),p(0.01%),d(90.36%),f(0.26%)	9.44
	N 2→ Eu	s(0.06%),p(0.08%),d(99.61%),f(0.25%)	8.50
	O 1→ Eu	s(0.06%),p(0.08%),d(99.61%),f(0.25%)	8.79
	O 2→ Eu	s(6.56%),p(0.02%),d(92.95%),f(0.47%)	15.68
$AmL^4(NO_3)_3$	N 1→ Am	s(0.12%),p(0.69%),d(11.01%),f(88.17%)	5.35
	N 2→ Am	s(6.7%),p(1.84%),d(38.1%),f(53.34%)	7.40
	O 1→ Am	s(6.7%),p(1.84%),d(38.1%),f(53.34%)	11.38
	O 2→ Am	s(1.08%),p(1.26%),d(15.81%),f(81.85%)	8.44
$EuL^4(NO_3)_3$	N 1→ Eu	s(1.35%),p(17.60%),d(32.87%),f(48.18%)	8.37
	N 2→ Eu	s(23.55%),p(7.62%),d(19.04%),f(49.79%)	8.76
	O 1→ Eu	s(23.55%),p(7.62%),d(19.04%),f(49.79%)	8.33
	O 2→ Eu	s(0.85%),p(2.78%),d(47.94%),f(48.43%)	9.86