Electronic Supplementary Information for

Enhancing of Am^{3+}/Cm^{3+} separation ability by weakening binding affinity of N donor atom: A comparative theoretical study of N, O combined extractants

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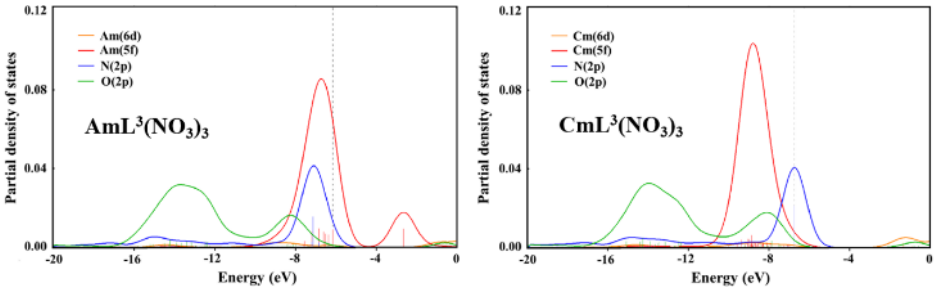

Figure S1. Partial density-of-state (PDOS) analysis of $ML^3(NO_3)_3$. The Am/Cm d, f and N/O p orbitals plotted as an orange, red, blue and dark green curve, respectively.

Table S1. The Wiberg bond indicies (WBIs) of M-N and M-O bonds.[a]

Complex	$M\text{-}N_{WBI}$	$M\text{-}O_{WBI}$
$ML^1(NO_3)_3$	0.445/0.432	0.524/0.531
$ML^2(NO_3)_3$	0.315/0.307	0.696/0.701
$ML^3(NO_3)_3$	0.157/0.092	0.636/0.657
$[M(L^1)_2NO_3]^{2+}$	0.504/0.476	0.680/0.669
$[M(L^2)_2NO_3]^{2+}$	0.378/0.371	0.763/0.754

[a] ../.. represents the results of M=Am and M=Cm, respectively.

Table S2. Changes of Gibbs free energies (kcal/mol) for extraction reactions of 1 : 1 and 1:2 metal to ligand ratios in cyclohexanone at the B3LYP/6-311G(d,p)/RECP level of theory.[a]

Reaction	ΔG	$\Delta\Delta G$
$[M(H_2O)_9]^{3+}_{aq}+L^1_{,org}+3NO_3^-_{,aq}\rightarrow ML^1(NO_3)_{3,org}+9H_2O_{aq}$	-203.31/-197.43	-5.88
$[M(H_2O)_9]^{3+}_{aq}+L^2_{,org}+3NO_3^-_{,aq}\rightarrow ML^2(NO_3)_{3,org}+9H_2O_{aq}$	-211.09/-205.06	-6.03
$[M(H_2O)_9]^{3+}_{aq}+L^3_{,org}+3NO_3^-_{,aq}\rightarrow ML^3(NO_3)_{3,org}+9H_2O_{aq}$	-210.80/-203.18	-7.63
$[M(NO_3)(H_2O)_7]^{2+}_{aq}+L^1_{,org}+2NO_3^-_{,aq}\rightarrow ML^1(NO_3)_{3,org}+7H_2O_{aq}$	-128.44/-125.19	-3.26
$[M(NO_3)(H_2O)_7]^{2+}_{aq}+L^2_{,org}+2NO_3^-_{,aq}\rightarrow ML^2(NO_3)_{3,org}+7H_2O_{aq}$	-136.23/-132.82	-3.41
$[M(NO_3)(H_2O)_7]^{2+}_{aq}+L^3_{,org}+2NO_3^-_{,aq}\rightarrow ML^3(NO_3)_{3,org}+7H_2O_{aq}$	-135.94/-130.93	-5.01
$[M(H_2O)_9]^{3+}_{aq}+2L^1_{,org}+NO_3^-_{,aq}\rightarrow[M(L^1)_2NO_3]^{2+}_{,org}+9H_2O_{aq}$	-67.84/-61.40	-6.43
$[M(H_2O)_9]^{3+}_{aq}+2L^2_{,org}+NO_3^-_{,aq}\rightarrow[M(L^2)_2NO_3]^{2+}_{,org}+9H_2O_{aq}$	-79.35/-72.77	-6.59
$[M(H_2O)_9]^{3+}_{aq}+2L^2_{,org}+NO_3^-_{,aq}\rightarrow[M(L^{3'})_2NO_3]^{2+}_{,org}+9H_2O_{aq}$	-93.15/-86.23	-6.92
$[M(NO_3)(H_2O)_7]^{2+}_{aq}+2L^1_{,org}\rightarrow[M(L^1)_2NO_3]^{2+}_{,org}+7H_2O_{aq}$	7.03/10.84	-3.81

$[M(NO_3)(H_2O)_7]^{2+}_{aq}+2L^{2}_{,org}\rightarrow[M(L^{2})_2NO_3]^{2+}_{,org}+7H_2O_{aq}$	-4.49/-0.52	-3.97
$[M(NO_3)(H_2O)_7]^{2+}_{aq}+2L^{3'}_{,org}\rightarrow[M(L^{3'})_2NO_3]^{2+}_{,org}+7H_2O_{aq}$	-18.28/-13.98	-4.30

[a]. ./. .represents the results of M=Am and M=Cm, respectively.

Table S3. Changes of Gibbs free energies (kcal/mol) for extraction reactions of 1 : 1 and 1:2 metal to ligand ratios in nitrobenzene at the B3LYP/6-311+G(2df,p)/RECP level of theory.[a]

Reactions	ΔG	$\Delta\Delta G$
$[M(H_2O)_9]^{3+}_{aq}+L^{1}_{,org}+3NO_3^{-}_{,aq}\rightarrow ML^{1}(NO_3)_{3,org}+9H_2O_{aq}$	-21.76/-15.62	-6.14
$[M(H_2O)_9]^{3+}_{aq}+L^{2}_{,org}+3NO_3^{-}_{,aq}\rightarrow ML^{2}(NO_3)_{3,org}+9H_2O_{aq}$	-30.49/-24.15	-6.34
$[M(H_2O)_9]^{3+}_{aq}+L^{3}_{,org}+3NO_3^{-}_{,aq}\rightarrow ML^{3}(NO_3)_{3,org}+9H_2O_{aq}$	-29.11/-22.46	-6.65
$[M(NO_3)(H_2O)_7]^{2+}_{aq}+L^{1}_{,org}+2NO_3^{-}_{,aq}\rightarrow ML^{1}(NO_3)_{3,org}+7H_2O_{aq}$	-11.35/-8.00	-3.35
$[M(NO_3)(H_2O)_7]^{2+}_{aq}+L^{2}_{,org}+2NO_3^{-}_{,aq}\rightarrow ML^{2}(NO_3)_{3,org}+7H_2O_{aq}$	-20.08/-16.53	-3.55
$[M(NO_3)(H_2O)_7]^{2+}_{aq}+L^{3}_{,org}+2NO_3^{-}_{,aq}\rightarrow ML^{3}(NO_3)_{3,org}+7H_2O_{aq}$	-18.70/-14.83	-3.87
$[M(H_2O)_9]^{3+}_{aq}+2L^{1}_{,org}+NO_3^{-}_{,aq}\rightarrow[ML^{1}_2(NO_3)]^{2+}_{,org}+9H_2O_{aq}$	-27.51/-25.98	-1.53
$[M(H_2O)_9]^{3+}_{aq}+2L^{2}_{,org}+NO_3^{-}_{,aq}\rightarrow[ML^{2}_2(NO_3)]^{2+}_{,org}+9H_2O_{aq}$	-44.40/-37.57	-6.83
$[M(H_2O)_9]^{3+}_{aq}+2L^{2}_{,org}+NO_3^{-}_{,aq}\rightarrow[ML^{3'}_2(NO_3)]^{2+}_{,org}+9H_2O_{aq}$	-56.34/-49.32	-7.02
$[M(NO_3)(H_2O)_7]^{2+}_{aq}+2L^{1}_{,org}\rightarrow[ML^{1}_2(NO_3)]^{2+}_{,org}+7H_2O_{aq}$	-17.10/-18.35	1.25
$[M(NO_3)(H_2O)_7]^{2+}_{aq}+2L^{2}_{,org}\rightarrow[ML^{2}_2(NO_3)]^{2+}_{,org}+7H_2O_{aq}$	-33.98/-29.94	-4.04
$[M(NO_3)(H_2O)_7]^{2+}_{aq}+2L^{3'}_{,org}\rightarrow[ML^{3'}_2(NO_3)]^{2+}_{,org}+7H_2O_{aq}$	-45.93/-41.70	-4.23

[a]. ./. .represents the results of M=Am and M=Cm, respectively.

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