Electronic Supplementary Information (ESI)

Theoretical Insights into Selective Extraction of Am(III) from Cm(III) and Eu(III) with Asymmetric N-heterocyclic Ligands

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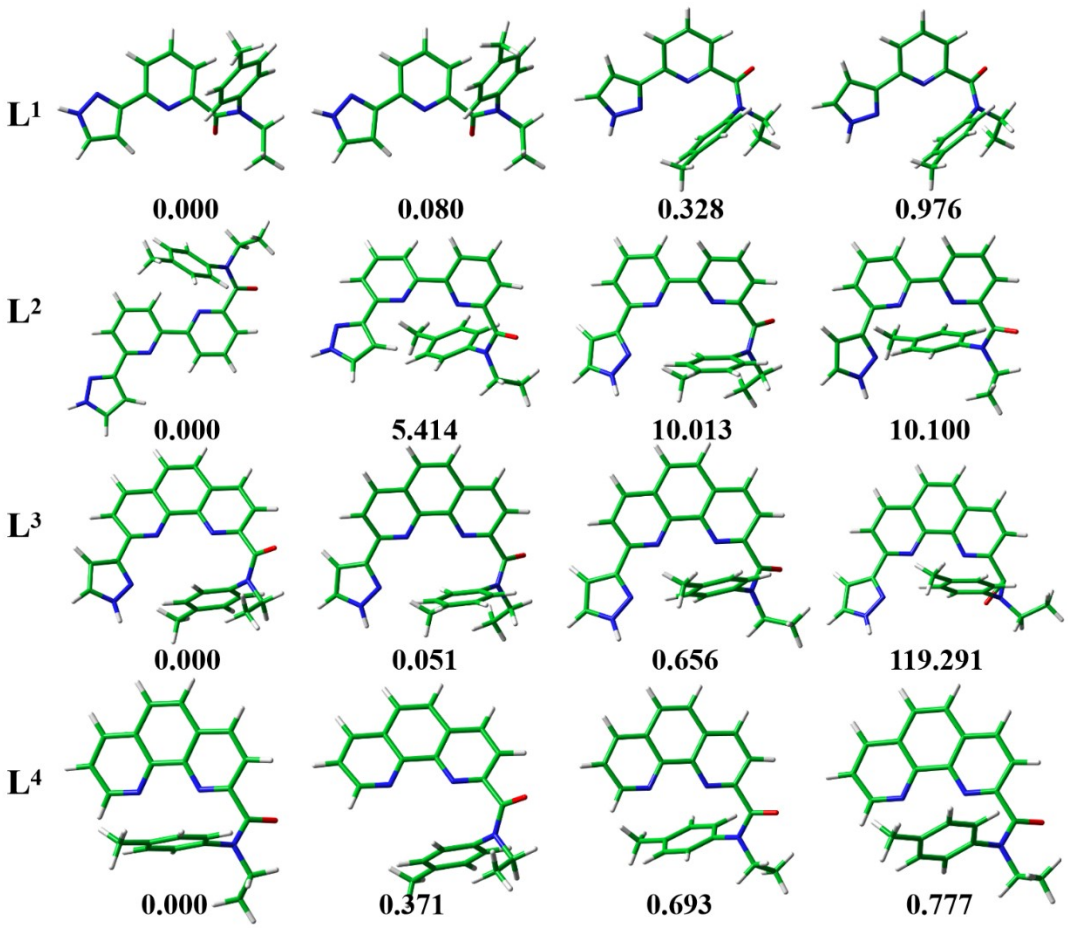

Figure S1. Optimized structures and relative energies of the isomers for L^1-L^4 ligands.

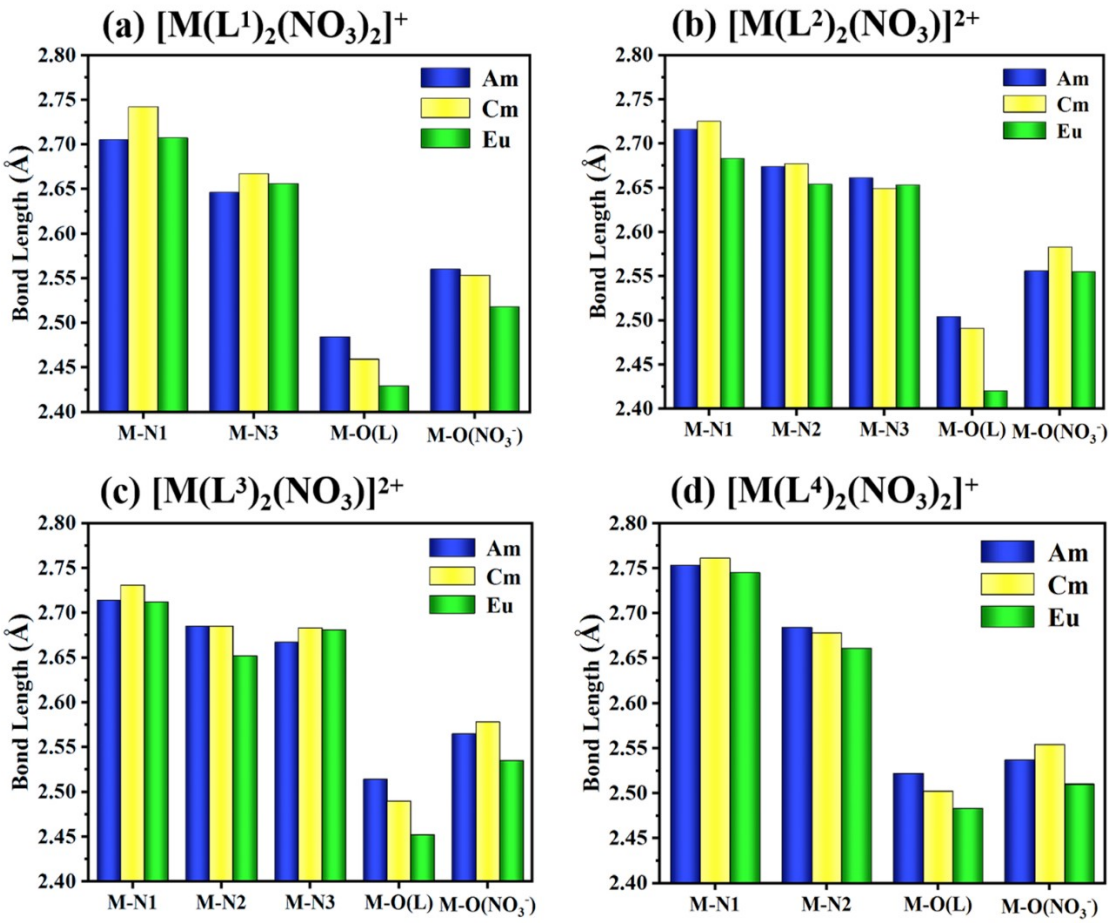

Figure S2. M−N and M−O bond lengths (Å) in 1:2 type complexes at the B3LYP/6-311G(d,p)/RECP level of theory.

Table S1. Average M−N and M−O bond lengths (Å) in the 1:1 and 1:2 type complexes with L^1—L^4 ligands at the B3LYP/6-311G(d,p)/RECP level of theory in the gas phase[a].

Species	Bond Distances					
	CN	M-N1	M-N2	M-N3	M-O	M-O(NO_3^-)
$ML^1(NO_3)_3$	9	2.682/2.672/2.641	/	2.575/2.553/2.531	2.520/2.530/2.489	2.507/2.505/2.470
$ML^2(NO_3)_3$	10	2.786/2.821/2.790	2.715/2.728/2.701	2.566/2.577/2.551	2.509/2.507/2.475	2.545/2.537/2.505
$ML^3(NO_3)_3$	10	2.766/2.806/2.774	2.696/2.714/2.687	2.598/2.597/2.572	2.554/2.524/2.495	2.536/2.536/2.504
$ML^4(NO_{3)3}$	9	2.645/2.678/2.651	2.633/2.659/2.620	/	2.528/2.520/2.493	2.513/2.501/2.468
$[M(L^1)_2(NO_3)_2]^+$	10	2.705/2.742/2.707	/	2.646/2.667/2.656	2.484/2.459/2.429	2.560/2.553/2.518
$[M(L^2)_2(NO_3)]^{2+}$	10	2.716/2.725/2.683	2.674/2.677/2.654	2.661/2.649/2.653	2.504/2.491/2.420	2.556/2.583/2.555
$[M(L^3)_2(NO_3)]^{2+}$	10	2.714/2.731/2.712	2.685/2.685/2.652	2.667/2.683/2.681	2.514/2.490/2.452	2.565/2.578/2.535
$[M(L^4)_2(NO_3)_2]^+$	10	2.753/2.761/2.745	2.684/2.678/2.661	/	2.522/2.502/2.483	2.537/2.554/2.510

[a]…/…/… represents the results obtained for the Am(III)/Cm(III)/Eu(III) complexes, respectively.

Table S2. Calculated average Wiberg bond indices of M−N and M−O bond in complexes with L^1—L^4 ligands at the B3LYP/6-311G(d,p)/RECP level of theory in the gas phase[a].

Species	M-N1	M-N2	M-N3	M-O	M-O(NO_3^-)
$ML^1(NO_3)_3$	0.418/0.415/0.376	/	0.514/0.525/0.481	0.536/0.516/0.464	0.602/0.590/0.524
$ML^2(NO_3)_3$	0.366/0.335/0.308	0.393/0.381/0.343	0.531/0.512/0.469	0.532/0.524/0.461	0.557/0.553/0.486
$ML^3(NO_3)_3$	0.375/0.339/0.313	0.407/0.387/0.348	0.504/0.498/0.455	0.491/0.511/0.446	0.565/0.553/0.488
$ML^4(NO_3)_3$	0.458/0.428/0.394	0.444/0.416/0.388	/	0.521/0.517/0.447	0.598/0.598/0.526
$[M(L^1)_2(NO_3)_2]^+$	0.415/0.376/0.351	/	0.478/0.456/0.400	0.569/0.588/0.522	0.542/0.537/0.476
$[M(L^2)_2(NO_3)]^{2+}$	0.419/0.404/0.377	0.436/0.426/0.386	0.474/0.476/0.408	0.560/0.563/0.535	0.545/0.509/0.452
$[M(L^3)_2(NO_3)]^{2+}$	0.424/0.407/0.365	0.427/0.419/0.387	0.478/0.459/0.402	0.552/0.569/0.510	0.535/0.512/0.468
$[M(L^4)_2(NO_3)_2]^+$	0.396/0.386/0.347	0.418/0.416/0.373	/	0.531/0.542/0.465	0.566/0.535/0.490

[a]…/…/… represents the results obtained for the Am(III)/Cm(III)/Eu(III) complexes, respectively.

Table S3. Calculated properties (au) at BCPs of M−N and M−O bonds for the 1:2 type complexes at the B3LYP/6-311G(d,p)/RECP level of theory [a].

Species	Bonds	ρ	$\nabla^2\rho$	H×10^{-4}
$[M(L^1)_2(NO_3)_2]^+$	M-N1	0.035/0.032/0.030	0.114/0.106/0.103	-4.5/-2.4/12.3
	M-N3	0.038/0.036/0.032	0.134/0.126/0.120	-6.7/-3.6/16.0
	M-O_L	0.046/0.048/0.045	0.199/0.206/0.199	-2.8/-1.2/17.2
	M-O(NO_3^-)	0.042/0.042/0.041	0.161/0.161/0.156	-8.3/-7.3/7.8
$[M(L^2)_2(NO_3)]^{2+}$	M-N1	0.034/0.033/0.032	0.110/0.108/0.109	-6.4/-5.4/10.3
	M-N2	0.038/0.037/0.034	0.124/0.122/0.116	-12.5/-11.3/7.7
	M-N3	0.037/0.038/0.033	0.129/0.129/0.119	-8.3/-7.5/14.1
	M-O_L	0.045/0.045/0.047	0.184/0.189/0.203	-1.6/-1.1/11.5
	M-O(NO_3^-)	0.043/0.040/0.037	0.158/0.150/0.140	-9.2/-7.7/10.3
$[M(L^3)_2(NO_3)]^{2+}$	M-N1	0.035/0.034/0.031	0.113/0.108/0.104	-10.4/-8.1/9.0
	M-N2	0.037/0.037/0.035	0.122/0.121/0.117	-14.0/-13.3/4.5
	M-N3	0.037/0.035/0.031	0.127/0.122/0.113	-6.1/-4.1/14.5
	M-O_L	0.044/0.046/0.044	0.182/0.190/0.186	-1.8/-1.4/15.6
	M-O(NO_3^-)	0.042/0.040/0.039	0.156/0.151/0.149	-8.1/-7.1/8.2
$[M(L^4)_2(NO_3)_2]^+$	M-N1	0.032/0.031/0.028	0.104/0.100/0.095	-3.1/-1.8/14.1
	M-N2	0.037/0.037/0.034	0.123/0.122/0.117	-10.7/-9.9/9.6
	M-O_L	0.042/0.044/0.040	0.177/0.182/0.172	2.1/2.2/21.4
	M-O(NO_3^-)	0.045/0.043/0.041	0.167/0.160/0.157	-11.2/-9.4/5.4

[a] …/…/… represents the results obtained for the Am(III)/Cm(III)/Eu(III) complexes, respectively.

Table S4. Changes of Gibbs free energy (ΔG, kcal/mol) and their Am/Cm and Am/Eu differences ($\Delta\Delta G$, kcal/mol) for complexation reactions of 1:1 and 1:2 type species in nitrobenzene at the B3LYP/6-311G(d,p)/RECP level of theory [a].

Reactions	ΔG	$\Delta\Delta G_{Am/Cm}/\Delta\Delta G_{Am/Eu}$
$[M(H_2O)_9]^{3+}_{aq} + L^1_{org} + 3NO_3^-{}_{aq} \rightarrow ML^1(NO_3)_{3org} + 9H_2O_{aq}$	-51.95/-51.89/-49.16	-0.06/-2.79
$[M(H_2O)_9]^{3+}_{aq} + L^2_{org} + 3NO_3^-{}_{aq} \rightarrow ML^2(NO_3)_{3org} + 9H_2O_{aq}$	-61.09/-56.45/-55.88	-4.64/-5.21
$[M(H_2O)_9]^{3+}_{aq} + L^3_{org} + 3NO_3^-{}_{aq} \rightarrow ML^3(NO_3)_{3org} + 9H_2O_{aq}$	-65.04/-64.42/-61.92	-0.62/-3.12
$[M(H_2O)_9]^{3+}_{aq} + L^4_{org} + 3NO_3^-{}_{aq} \rightarrow ML^4(NO_3)_{3org} + 9H_2O_{aq}$	-54.00/-52.36/-50.90	-1.64/-3.10
$[M(H_2O)_9]^{3+}_{aq} + 2L^1_{org} + 2NO_3^-{}_{aq} \rightarrow [M(L^1)_2(NO_3)_2]^+_{org} + 9H_2O_{aq}$	-51.08/-48.73/-46.67	-2.35/-4.41
$[M(H_2O)_9]^{3+}_{aq} + 2L^2_{org} + NO_3^-{}_{aq} \rightarrow [M(L^2)_2(NO_3)]^{2+}_{org} + 9H_2O_{aq}$	-41.43/-38.92/-40.21	-2.51/-1.22
$[M(H_2O)_9]^{3+}_{aq} + 2L^3_{org} + NO_3^-{}_{aq} \rightarrow [M(L^3)_2(NO_3)]^{2+}_{org} + 9H_2O_{aq}$	-52.51/-50.74/-50.69	-1.77/-1.82
$[M(H_2O)_9]^{3+}_{aq} + 2L^4_{org} + 2NO_3^-{}_{aq} \rightarrow [M(L^4)_2(NO_3)_2]^+_{org} + 9H_2O_{aq}$	-51.74/-48.59/-48.94	-3.15/-2.80

[a] …/…/… represents the results obtained for the Am(III)/Cm(III)/Eu(III) complexes, respectively.