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Theoretical unraveling the separation of Am(III)/Eu(III): Insights from mixed N, O-donor ligands with variations of central heterocyclic moieties

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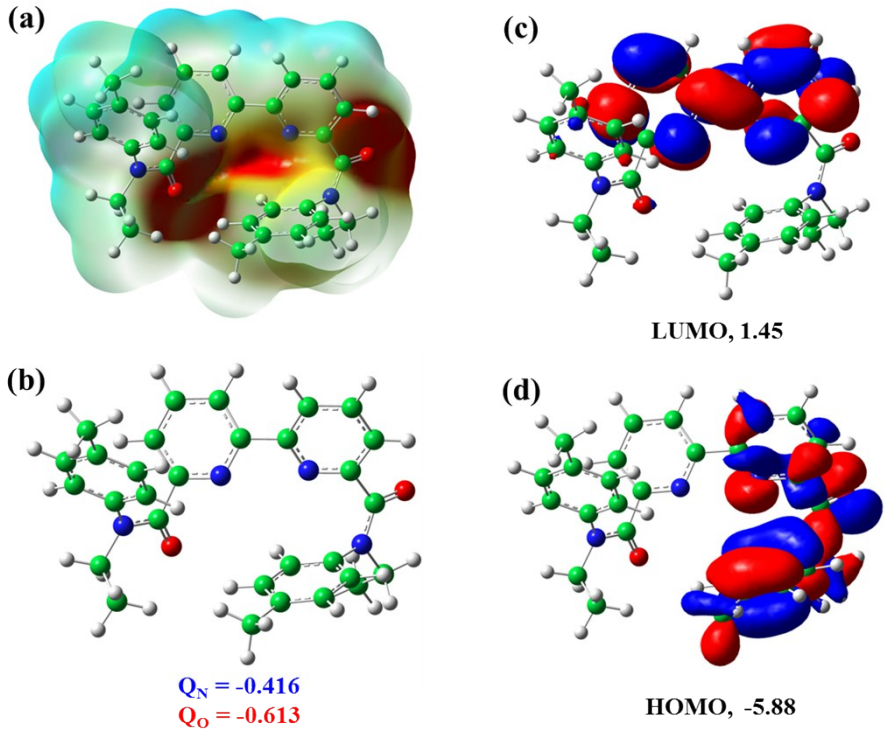

Fig. S1 The maps of ESP (a), the natural charges of oxygen and nitrogen atom (b), LUMO (c) and HOMO (d) of ligand $\mathbf{L_b}$ with *cis*-conformation at the B3LYP/6-31G(d) level of theory.

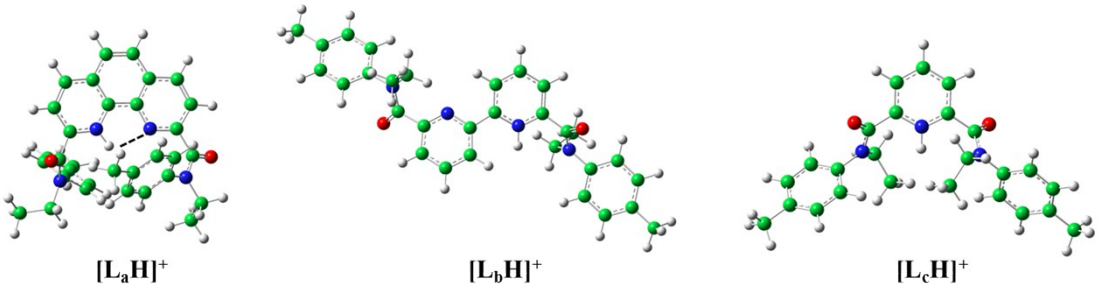

Fig. S2 Structures of the protonated forms of the three ligands at the B3LYP/6-31G(d) level of theory in the gas phase.

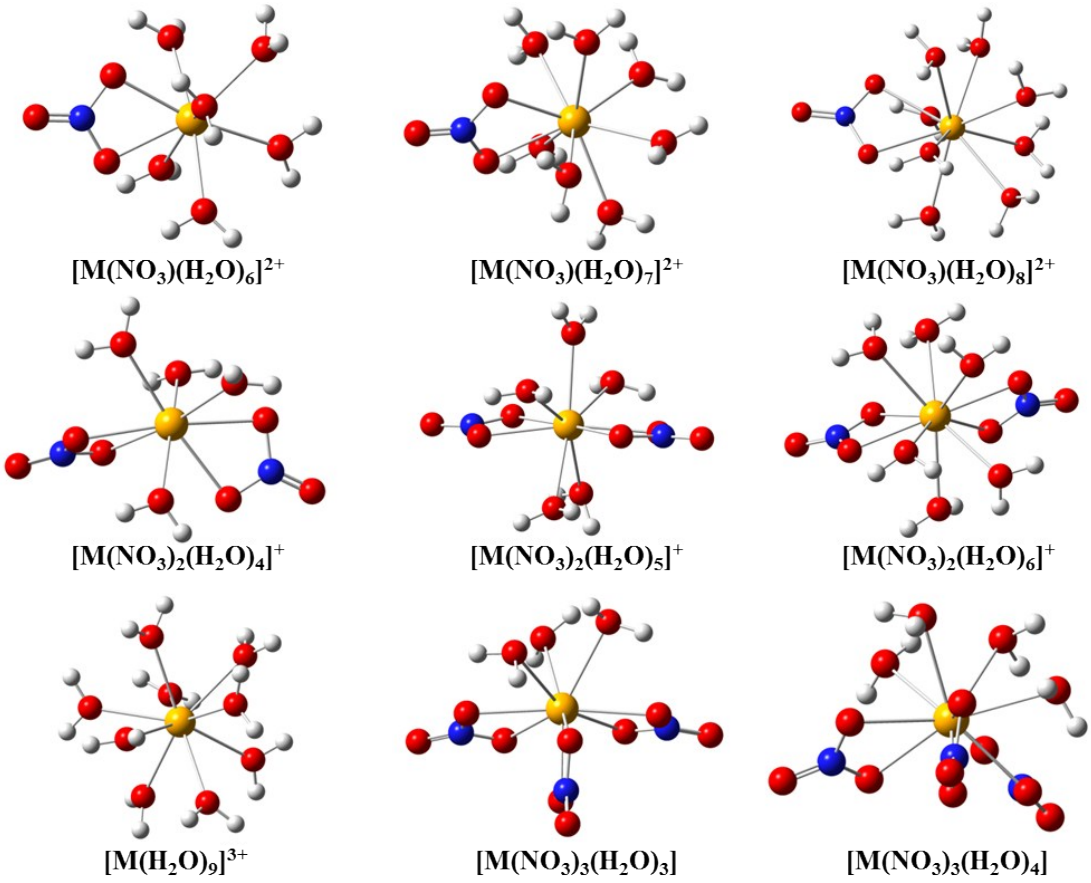

Fig. S3 Structures of the Am(III) and Eu(III) hydrates and nitrate hydrates at the B3LYP/6-31G(d)/RECP level of theory in the gas phase.

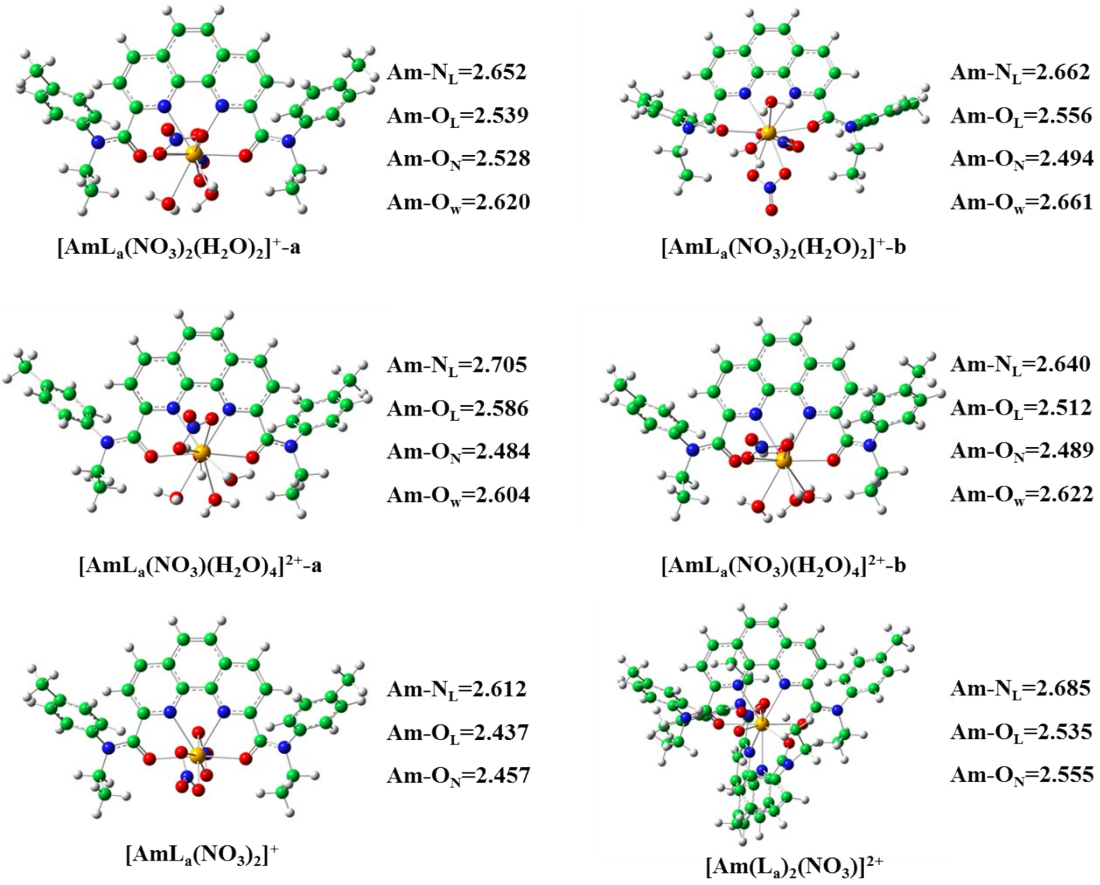

Fig. S4 The optimized structures of the Am-complexes at the B3LYP/6-31G(d)/RECP level of theory in the gas phase. And the corresponding bond lengths (Å) are presented. H, C, N, O and Am atoms are represented by white, green, blue, red and orange spheres, respectively.

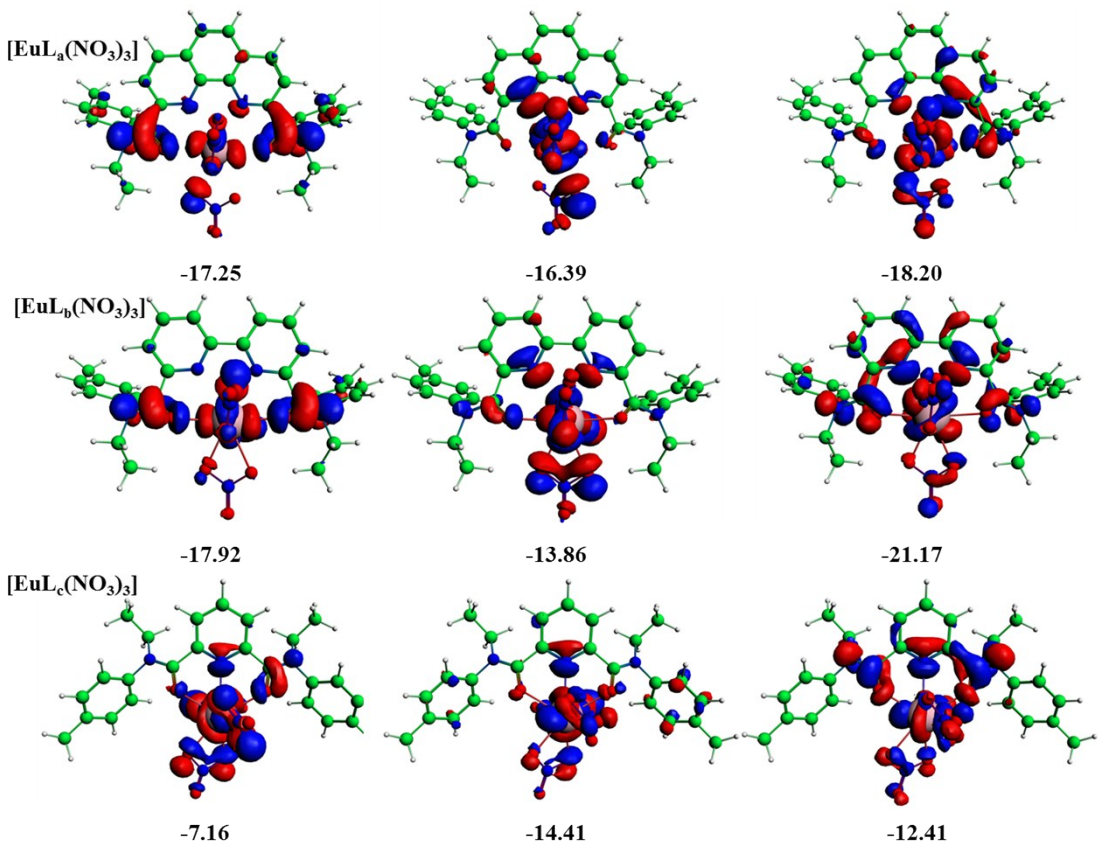

Fig. S5 Natural orbitals for the chemical valence (NOCV) with the larger contribution to the orbital interaction energy for the complexes [EuL$(NO_3)_3$]. The corresponding orbital interaction energy (kcal/mol) contribution for each NOCV pair is also presented.

Table S1. The relative electronic energies (kcal/mol) to each ground state for the $[M(H_2O)_9]^{3+}$ and $ML_a(NO_3)_3$ (M=Am, Eu) complexes.

Spin state	$[Am(H_2O)_9]^{3+}$	$[AmL_a(NO_3)_3]$	$[Eu(H_2O)_9]^{3+}$	$[EuL_a(NO_3)_3]$
septet	0.00	0.00	0.00	0.00
quintet	39.96	52.19	55.86	59.07
triplet	90.32	73.49	87.33	94.64
singlet	106.91	101.51	139.69	141.59

Table S2. Average M-N and M-O bond lengths (Å) in the $[ML_a(NO_3)_3]$ (M=Am, Eu) complexes in the gas phase using B3LYP functional and four basis sets.

Complexes	Bond length	6-31G*	6-31+G**	6-311G**	6-311+G**
$[AmL_a(NO_3)_3]$	Am-N_L	2.734	2.725	2.733	2.723
	Am-O_L	2.550	2.535	2.547	2.537
	Am-O_N	2.525	2.544	2.538	2.548
$[EuL_a(NO_3)_3]$	Eu-N_L	2.737	2.719	2.730	2.722
	Eu-O_L	2.512	2.498	2.510	2.505
	Eu-O_N	2.489	2.508	2.503	2.512

Table S3. Total bonding energy (kcal/mol), Pauli, electrostatic and orbital interactions obtained from energy decomposition analysis at the BP86/TZP level of theory.

complexes	ΔE_{int}	ΔE_{pauli}	ΔE_{orb}	ΔE_{es}	$\%\Delta E_{orb}$	$\%\Delta E_{es}$
$[AmL_a(NO_3)_3]$	-1289.44	214.78	-496.87	-1007.35	33.03	66.97
$[AmL_b(NO_3)_3]$	-1286.36	214.64	-502.19	-998.81	33.46	66.54
$[AmL_c(NO_3)_3]$	-1291.98	228.58	-473.61	-1046.97	31.15	68.85
$[EuL_a(NO_3)_3]$	-1311.02	182.24	-514.00	-979.26	34.42	65.58
$[EuL_b(NO_3)_3]$	-1311.19	182.90	-517.87	-976.23	34.66	65.34
$[EuL_c(NO_3)_3]$	-1310.17	196.66	-506.52	-1000.32	33.61	66.39

Table S4. Second-order perturbative estimates (E(2), kcal/mol) of donor-acceptor interactions in the NBO basis between N-ligands and Am(III)/Eu(III). Only energies above 7.0 kcal/mol are represented.

complexes	donor→acceptor[a]	Character of empty metal orbital	E(2)
$[AmL_a(NO_3)_3]$	N_L→Am	p(4%), d(83%), f(13%)	13.28
	N_L→Am	p(39%), d(32%), f(29%)	16.88
	O_L→Am	s(2%), d(91%), f(6%)	8.44
	O_L→Am	s(2%), d(91%), f(6%)	8.14
$[EuL_a(NO_3)_3]$	N_L→ Eu	d(96%), f(3%)	18.38
	N_L→ Eu	p(3%), d(96%)	9.72
	N_L→ Eu	p(27%), d(72%)	9.83
	O_L→ Eu	s(11%), d(87%), f(2%)	11.91
	O_L→ Eu	s(11%), d(87%), f(2%)	9.65
$[AmL_b(NO_3)_3]$	N_L→Am	p(1%), d(83%), f(16%)	7.10
	N_L→Am	p(4%), d(78%), f(18%)	13.12
	N_L→Am	p(27%), d(34%), f(39%)	15.13
	O_L→Am	s(2%), p(1%), d(92%), f(5%)	9.10
	O_L→Am	s(2%), p(1%), d(92%), f(5%)	9.63
$[EuL_b(NO_3)_3]$	N_L→Eu	s(68%), d(25%), f(7%)	12.46
	N_L→ Eu	p(2%), d(78%), f(18%)	14.23
	N_L→ Eu	p(53%), d(22%), f(25%)	10.92
	O_L→ Eu	s(10%), p(2%), d(89%)	12.75
	O_L→ Eu	s(10%), p(2%), d(89%)	10.43
$[AmL_c(NO_3)_3]$	N_L→Am	p(14%), d(76%), f(11%)	11.27
	O_L→Am	p(54%), d(37%), f(9%)	9.59
	O_L→Am	p(3%), d(91%), f(6%)	8.04
$[EuL_c(NO_3)_3]$	N_L→Eu	s(14%), d(76%), f(10%)	17.24
	N_L→ Eu	s(1%), p(82%), d(15%), f(2%)	10.88
	O_L→ Eu	p(27%), d(66%), f(3%)	16.63
	O_L→ Eu	p(51%), d(23%), f(25%)	8.67

[a]The donor is the lone pair of O/N.

Table S5. Changes of Gibbs free energy (ΔG, kcal/mol) for the reactions of Am(III) hydrates and nitrate hydrates with ligand L_a in aqueous (ΔGaq.) and cyclohexanone (ΔGcyc.) phase at the B3LYP/6-311G(d,p)/RECP level of theory.

Reactions	ΔGaq.	ΔGcyc.
(1)$[Am(H_2O)_9]^{3+} + L_a + 3NO_3^- = [AmL_a(NO_3)_3] + 9H_2O$	-50.79	-49.77
(2)$[Am(NO_3)(H_2O)_8]^{2+} + L_a + 2NO_3^- = [AmL_a(NO_3)_3] + 8H_2O$	-42.65	-41.64
(3)$[Am(NO_3)(H_2O)_7]^{2+} + L_a + 2NO_3^- = [AmL_a(NO_3)_3] + 7H_2O$	-39.73	-38.72
(4)$[Am(NO_3)(H_2O)_6]^{2+} + L_a + 2NO_3^- = [AmL_a(NO_3)_3] + 6H_2O$	-38.42	-37.41
(5)$[Am(NO_3)_2(H_2O)_6]^{+} + L_a + NO_3^- = [AmL_a(NO_3)_3] + 6H_2O$	-28.43	-27.42
(6)$[Am(NO_3)_2(H_2O)_5]^{+} + L_a + NO_3^- = [AmL_a(NO_3)_3] + 5H_2O$	-27.37	-26.35
(7)$[Am(NO_3)_2(H_2O)_4]^{+} + L_a + NO_3^- = [AmL_a(NO_3)_3] + 4H_2O$	-27.94	-26.93
(8)$[Am(NO_3)_3(H_2O)_4] + L_a = [AmL_a(NO_3)_3] + 4H_2O$	-23.46	-22.45
(9)$[Am(NO_3)_3(H_2O)_3] + L_a = [AmL_a(NO_3)_3] + 3H_2O$	-20.04	-19.02

Table S6. Changes of Gibbs free energy (ΔG, kcal/mol) for the reactions of Am(III) hydrates and nitrate hydrates with ligand L_a in aqueous (ΔGaq.) and cyclohexanone (ΔGcyc.) phase at the B3LYP/6-311G(d,p)/RECP level of theory.

Reactions	ΔGaq.	ΔGcyc.
(1)$[Am(NO_3)(H_2O)_8]^{2+} + L_a + 2NO_3^- = [AmL_a(NO_3)_3] + 8H_2O$	-42.65	-41.64
(2)$[Am(NO_3)(H_2O)_8]^{2+} + L_a + NO_3^- = [AmL_a(NO_3)_2(H_2O)_2]^{+}$-a + $6H_2O$	-31.18	-29.35
(3)$[Am(NO_3)(H_2O)_8]^{2+} + L_a + NO_3^- = [AmL_a(NO_3)_2(H_2O)_2]^{+}$-b + $6H_2O$	-28.42	-26.53
(4)$[Am(NO_3)(H_2O)_8]^{2+} + L_a = [AmL_a(NO_3)(H_2O)_4]^{2+}$-a + $4H_2O$	-16.39	-10.23
(5)$[Am(NO_3)(H_2O)_8]^{2+} + L_a = [AmL_a(NO_3)(H_2O)_4]^{2+}$-b + $4H_2O$	-20.64	-14.36
(6)$[Am(NO_3)(H_2O)_8]^{2+} + L_a + NO_3^- = [AmL_a(NO_3)_2]^{+} + 8H_2O$	-36.08	-34.32
(7)$[Am(NO_3)(H_2O)_8]^{2+} + 2L_a = [Am(L_a)_2(NO_3)]^{2+} + 8H_2O$	-33.36	-29.87

Table S7. Changes of Gibbs free energy (ΔG, kcal/mol) for the reactions of the Am(III) hydrates and nitrate hydrates with ligand L_a in aqueous and cyclohexanone phase with 6-311G(d,p) basis set using M06-2X and BLYP method, respectively.

Reactions	Method	Aqueous		Cyclohexanone	
		$\Delta G_{aq.}$	$\Delta\Delta G/SF_{Am/Eu}$	$\Delta G_{cyc.}$	$\Delta\Delta G/SF_{Am/Eu}$
$[M(NO_3)(H_2O)_8]^{2+}+L_a+2NO_3^- = [ML_a(NO_3)_3]+8H_2O$	M06-2X	-38.99/-36.62	-2.37/54.73	-37.98/-37.07	-0.91/4.65
$[M(NO_3)(H_2O)_8]^{2+}+L_b+2NO_3^- = [ML_b(NO_3)_3]+8H_2O$		-43.56/-41.49	-2.07/32.97	-42.39/-40.37	-2.03/30.82
$[M(NO_3)(H_2O)_8]^{2+}+L_c+2NO_3^- = [ML_c(NO_3)_3]+8H_2O$		-19.36/-17.43	-1.93/26.03	-17.96/-16.12	-1.84/22.36
$[M(NO_3)(H_2O)_8]^{2+}+L_a+2NO_3^- = [ML_a(NO_3)_3]+8H_2O$	BLYP	-43.36/-41.33	-2.04/31.34	-42.38/-40.40	-1.98/28.32
$[M(NO_3)(H_2O)_8]^{2+}+L_b+2NO_3^- = [ML_b(NO_3)_3]+8H_2O$		-43.76/-41.94	-1.82/21.62	-42.66/-40.88	-1.77/19.87
$[M(NO_3)(H_2O)_8]^{2+}+L_c+2NO_3^- = [ML_c(NO_3)_3]+8H_2O$		-34.07/-32.24	-1.83/21.99	-32.83/-31.07	-1.76/19.53