Theoretically unraveling the separation of trivalent Am and Eu ions by phosphine oxide ligands with different central heterocyclic moieties

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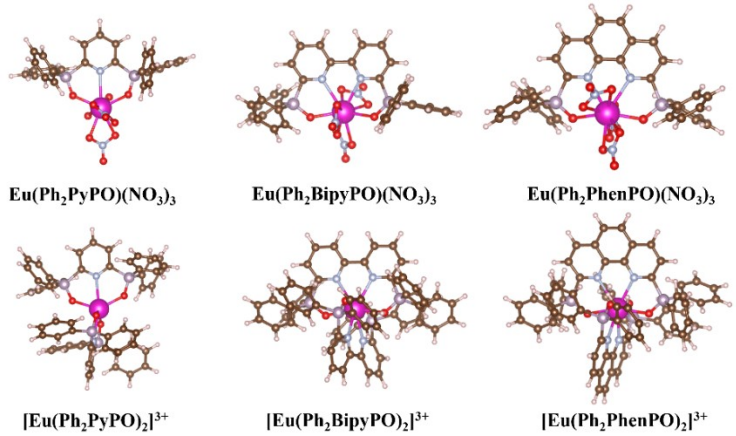

Figure S1 Optimized structures of the studied $EuL(NO_3)_3$, $[Eu(L)_2]^{3+}$ complexes with L=Ph_2PyPO, $Ph_2BipyPO$, and $Ph_2PhenPO$, respectively.

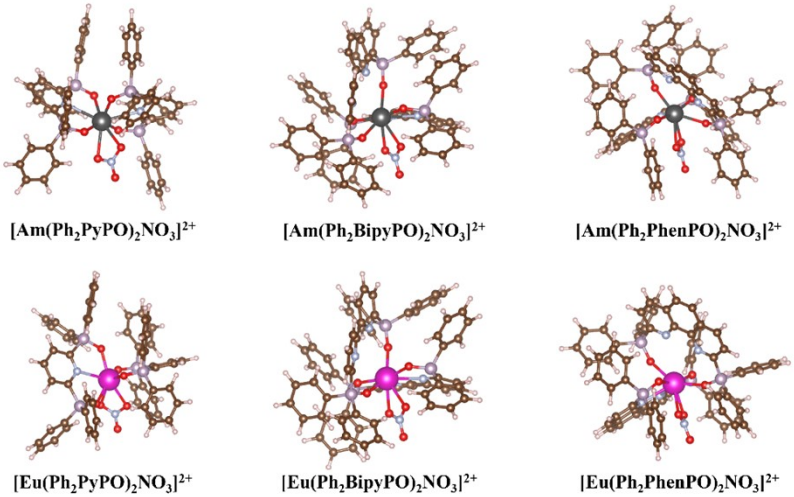

Figure S2 Optimized structures of the studied $[Am(L)_2NO_3]^{2+}$ and $[Eu(L)_2NO_3]^{2+}$ complexes with L=Ph_2PyPO, $Ph_2BipyPO$, and $Ph_2PhenPO$, respectively.

Table S1. Average M-O and M-N bond length (Å) in $[ML_2NO_3]^{2+}$ complexes, optimized at the B3LYP/6-311g(d)//RECP level of theory. [a]

Complex	Bond length	
	M-N	$M\text{-}O_{P=O}$
$[M(Ph_2PyPO)_2(NO_3)]^{2+}$	2.856/2.820	2.410/2.360
$[M(Ph_2BipyPO)_2(NO_3)]^{2+}$	2.760/2.709 (3.690/3.892)	2.426/2.364
$[M(Ph_2PhenPO)_2(NO_3)]^{2+}$	2.790/2.715 (3.370/3.624)	2.439/2.379

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

Table S2. The Mayer bond orders of M-N and $M\text{-}O_{P=O}$ bonds in $[ML_2(NO_3)]^{2+}$ complexes. [a]

Complex	M-N	$M\text{-}O_{P=O}$
$[M(Ph_2BipyPO)_2(NO_3)]^{2+}$	0.172/0.162 (0.088/0.037)	0.301/0.314
$[M(Ph_2PhenPO)_2(NO_3)]^{2+}$	0.171/0.175 (0.106/0.054)	0.279/0.307

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

Table S3. The Wiberg bond indices of M-N and M-OP=O bonds in the studied metal complexes.[a]

Complex	M-N	$M\text{-}O_{P=O}$
$M(Ph_2PyPO)(NO_3)_3$	0.167/0.155	0.311/0.332
WBI(Am-N/O)- WBI(Eu-N/O)	0.012	-0.021
$M(Ph_2BipyPO)(NO_3)_3$	0.198/0.195	0.325/0.338
WBI(Am-N/O)- WBI(Eu-N/O)	0.003	-0.013
$M(Ph_2PhenPO)(NO_3)_3$	0.194/0.188	0.334/0.345
WBI(Am-N/O)- WBI(Eu-N/O)	0.006	-0.011
$[M(Ph_2PyPO)_2]^{3+}$	0.386/0.341	0.737/0.797
WBI(Am-N/O)- WBI(Eu-N/O)	0.045	-0.060
$[M(Ph_2BipyPO)_2]^{3+}$	0.435/0.414	0.758/0.784
WBI(Am-N/O)- WBI(Eu-N/O)	0.021	-0.026
$[M(Ph_2PhenPO)_2]^{3+}$	0.410/0.408	0.746/0.769
WBI(Am-N/O)- WBI(Eu-N/O)	0.002	-0.023

[a].../... represents results of Am- and Eu-complexes, respectively.

Table S4. Changes in Gibbs free energy (ΔG, kcal/mol) for the extraction reactions with Ph_2PyPO (L^a), $Ph_2BipyPO$ (L^b) and $Ph_2PhenPO$ (L^c) in aqueous-nitrobenzene with $[M(H_2O)_9]^{3+}$ at the B3LYP/6-311G(2df,p) level of theory.[a]

Reactions	ΔG_{aq}(kcal/mol)	$\Delta\Delta G$(kcal/mol)
$[M(H_2O)_9]^{3+}_{aq} + 3NO_3^-{}_{aq} + L^a{}_{nitro} \rightarrow ML^a(NO_3)_{3,\,nitro} + 9H_2O_{aq}$	-85.03/-51.71	-33.32
$[M(H_2O)_9]^{3+}_{aq} + 3NO_3^-{}_{aq} + L^b{}_{nitro} \rightarrow ML^b(NO_3)_{3,\,nitro} + 9H_2O_{aq}$	-67.52/-37.15	-30.37
$[M(H_2O)_9]^{3+}_{aq} + 3NO_3^-{}_{aq} + L^c{}_{nitro} \rightarrow ML^c(NO_3)_{3,\,nitro} + 9H_2O_{aq}$	-59.24/-31.50	-27.74
$[M(H_2O)_9]^{3+}_{aq} + 2L^a{}_{nitro} \rightarrow [M(L^a)_2]^{3+}{}_{nitro} + 9H_2O_{aq}$	-75.05/-38.28	-36.77
$[M(H_2O)_9]^{3+}_{aq} + 2L^b{}_{nitro} \rightarrow [M(L^b)_2]^{3+}{}_{nitro} + 9H_2O_{aq}$	-76.74/-48.26	-28.49
$[M(H_2O)_9]^{3+}_{aq} + 2L^c{}_{nitro} \rightarrow [M(L^c)_2]^{3+}{}_{nitro} + 9H_2O_{aq}$	-72.29/-44.11	-28.17
$[M(H_2O)_9]^{3+}_{aq} + 2L^a{}_{nitro} + NO_3^-{}_{aq} \rightarrow [M(L^a)_2(NO_3)]^{2+}{}_{nitro} + 9H_2O_{aq}$	-78.50/-49.89	-28.61
$[M(H_2O)_9]^{3+}_{aq} + 2L^b{}_{nitro} + NO_3^-{}_{aq} \rightarrow [M(L^b)_2(NO_3)]^{2+}{}_{nitro} + 9H_2O_{aq}$	-69.21/-38.97	-30.25
$[M(H_2O)_9]^{3+}_{aq} + 2L^c{}_{nitro} + NO_3^-{}_{aq} \rightarrow [M(L^c)_2(NO_3)]^{2+}{}_{nitro} + 9H_2O_{aq}$	-67.33/-43.36	-23.97

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