Electronic Supplementary Information

to the paper "Theoretical Insights into the Separation of Am(III) over Eu(III) with PhenBHPPA" by Han Wu, Qun-Yan Wu, Cong-Zhi Wang, Jian-Hui Lan, Zhi-Rong Liu, Zhi-Fang Chai and Wei-Qun Shi

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Table S1 The average ρ and $\nabla^2\rho$ values of the M-N_L and M-O_L BCPs in the Eu and Am complexes with PhenBHPPA.

Species	$[ML]^{3+}$	$[ML(NO_3)]^{2+}$	$[ML(H_2O)_3]^{3+}$	$[ML(NO_3)(H_2O)_2]^{2+}$	$[ML(NO_3)_2]^{+}$	$ML(NO_3)_3$
$\rho_{M\text{-}N_L}$	0.047/0.051	0.039/0.043	0.027/0.033	0.030/0.035	0.027/0.031	0.026/0.029
$\nabla^2\rho_{M\text{-}N_L}$	0.158/0.167	0.134/0.143	0.090/0.097	0.101/0.116	0.084/0.098	0.089/0.098
$\rho_{M\text{-}O_L}$	0.069/0.073	0.052/0.054	0.036/0.045	0.044/0.047	0.036/0.039	0.034/0.036
$\nabla^2\rho_{M\text{-}O_L}$	0.299/0.315	0.223/0.229	0.142/0.179	0.185/0.196	0.151/0.155	0.137/0.142

[a] …/… represent the results of Eu and Am complexes, respectively.

Table S2 Contribution (%) of metal atom and the nitrogen (N_L) and oxygen atoms of ligand (O_L), and the oxygen atoms of nitrate anion (O_N) to the delocalized canonical MOs for complexes $[EuL(NO_3)_2]^+$ and $[AmL(NO_3)_2]^+$.

	261	254	253	243	240	225
Eu	4f: 78.69	4f: 10.74	4f:31.55	4f:1.45	4f:1.01	5d:1.32
N_L	-	-	-	2p:33.67	2p:15.35	2p:28.59
$O_{(NO_3^-)}$	2p:9.22	2p:21.27	2p:31.02	2p:26.73	2p:38.41	2p:11.74
O_L	2p:1.05	2p:10.00	-	-	2p:9.22	-
	279	272	271	249	244	240
Am	5f: 72.01 6d:1.45	5f: 15.93 6d:1.15	5f: 17.43 6d:1.06	5f:3.12	5f:6.71	6d:2.80
N_L	-	-	-	2p:26.74	2p:37.52	2p:29.26
$O_{(NO_3^-)}$	2p:12.57	2p: 52.68	2p:40.57	2p: 15.63	2p:12.74	2p:3.94
O_L	-	2p:1.10	-	-	2p:1.08	-

Table S3 Changes of Gibbs free energies (kcal/mol) for complexation reactions of Am^{3+} and Eu^{3+} complexes with PhenBHPPA ligand in the gas phase, aqueous, n-octanol and cyclohexanone phases at the B3LYP/6-31G*/RECP Level of Theory.[a]

Reactions	ΔG_{gas}	ΔG_{aq}	$\Delta G_{n\text{-}oct}$	ΔG_{cyc}
$[M(NO_3)(H_2O)_6]^{2+} + L \rightarrow [ML(NO_3)]^{2+} + 6H_2O$	**-66.39/-71.48**	**-13.32/-18.52**	**-4.20/-8.40**	**-11.58/-16.04**
$[M(NO_3)(H_2O)_6]^{2+} + L \rightarrow [ML(H_2O)_3]^{3+} + 3H_2O + NO_3^-$	**133.55/128.07**	**4.43/-2.44**	**26.82/20.05**	**14.33/-7.31**
$[M(NO_3)(H_2O)_6]^{2+} + L \rightarrow [ML(NO_3)(H_2O)_2]^{2+} + 4H_2O$	**-74.79/-79.32**	**-14.21/-19.89**	**-3.91/-8.07**	**-12.47-17.29**
$[M(NO_3)(H_2O)_6]^{2+} + L + NO_3^- \rightarrow [ML(NO_3)_2]^{+} + 6H_2O$	**-210.74/-217.17**	**-21.47-28.33**	**-18.39/-24.09**	**-23.68/-29.83**
$[M(NO_3)(H_2O)_6]^{2+} + 2NO_3^- + L \rightarrow ML(NO_3)_3 + 6H_2O$	**-277.62/-286.85**	**-17.25/-27.13**	**-14.12/-14.42**	**-18.80/-21.48**
$[M(NO_3)_2(H_2O)_3]^{+} + L \rightarrow [ML(NO_3)]^{2+} + NO_3^- + 3H_2O$	**106.23/105.25**	**-4.38/-5. 21**	**4.73/4.92**	**-2.65/-2.72**
$[M(NO_3)_2(H_2O)_3]^{+} + L \rightarrow [ML(H_2O)_3]^{3+} + 2NO_3^-$	**306.17/304.81**	**13.37/10.88**	**35.76/33.37**	**23.26/20.63**
$[M(NO_3)_2(H_2O)_3]^{+} + L \rightarrow [ML(NO_3)(H_2O)_2]^{2+} + H_2O + NO_3^-$	**97.83/56.00**	**-5.28/-6.57**	**5.03/5.25**	**-3.54/-3.97**
$[M(NO_3)_2(H_2O)_3]^{+} + L \rightarrow [ML(NO_3)_2]^{+} + 3H_2O$	**-38.12/-40.43**	**-12.53/-15.01**	**-9.45/-10.77**	**-14.75/-16.51**
$[M(NO_3)_2(H_2O)_3]^{+} + NO_3^- + L \rightarrow ML(NO_3)_3 + 3H_2O$	**-105.00/-110.11**	**-8.31/-13.81**	**-5.19/-1.11**	**-9.86/-8.17**
$M(NO_3)_3(H_2O)_4 + L \rightarrow [ML(NO_3)]^{2+} + 2NO_3^- + 4H_2O$	**234.86/225.18**	**7.25/-0.73**	**16.37/17.60**	**8.99/9.96**
$M(NO_3)_3(H_2O)_4 + L \rightarrow [ML(H_2O)_3]^{3+} + H_2O + 3NO_3^-$	**434.80/435.83**	**25.00/23.55**	**47.39/46.04**	**34. 90/33.31**
$M(NO_3)_3(H_2O)_4 + L \rightarrow [ML(NO_3)(H_2O)_2]^{2+} + 2H_2O + 2NO_3^-$	**226.46/228.44**	**6.35/6.11**	**16.66/17.92**	**8.09/8.71**
$M(NO_3)_3(H_2O)_4 + L \rightarrow [ML(NO_3)_2]^{+} + NO_3^- + 4H_2O$	**90.52/90.59**	**-0.90/-2.33**	**2.18/1.91**	**-3.11/-3.83**
$M(NO_3)_3(H_2O)_4 + L \rightarrow ML(NO_3)_3 + 4H_2O$	**23.63/20.91**	**3.32/-1.14**	**6.44/11.57**	**1.77/4.51**
$[M(NO_3)_2(H_2O)_4]^{+} + L \rightarrow [ML(NO_3)]^{2+} + NO_3^- + 4H_2O$	**121.09/120.21**	**2.26/2.04**	**11.37/12.71**	**4.00 /4.53**
$[M(NO_3)_2(H_2O)_4]^{+} + L \rightarrow [ML(H_2O)_3]^{3+} + 2NO_3^- + H_2O$	**321.02/319.77**	**20.01/18.12**	**42.40/40.61**	**29.90/27.87**
$[M(NO_3)_2(H_2O)_4]^{+} + L \rightarrow [ML(NO_3)(H_2O)_2]^{2+} + 2H_2O + NO_3^-$	**112.68/112.37**	**1.36/0.68**	**11.67/12.49**	**3.10/3.28**

$[M(NO_3)_2(H_2O)_4]^+ + L \rightarrow [ML(NO_3)_2]^+ + 4H_2O$	**-23.26/-25.48**	**-5.89/-7.77**	**-2.81/-3.53**	**-8.11/-9.27**
$[M(NO_3)_2(H_2O)_4]^+ + NO_3^- + L \rightarrow ML(NO_3)_3 + 4H_2O$	**-90.15/-95.16**	**-1.67/-6.57**	**-1.45/6.14**	**-3.22/-0.92**
$M(NO_3)_3(H_2O)_3 + L \rightarrow [ML(NO_3)]^{2+} + 2NO_3^- + 3H_2O$	**232.16/232.81**	**8.16/9.30**	**17.28/19.43**	**9.90/11.79**
$M(NO_3)_3(H_2O)_3 + L \rightarrow [ML(H_2O)_3]^{3+} + 3NO_3^-$	**432.10/432.37**	**25.91/25.38**	**48.30/17.33**	**35.81/35.14**
$M(NO_3)_3(H_2O)_3 + L \rightarrow [ML(NO_3)(H_2O)_2]^{2+} + H_2O + 2NO_3^-$	**223.76/224.98**	**7.26/7.94**	**17.57/19.75**	**9.00/10.54**
$M(NO_3)_3(H_2O)_3 + L \rightarrow [ML(NO_3)_2]^+ + NO_3^- + 3H_2O$	**87.81/87.13**	**0.01/-0.51**	**3.09/3.73**	**-2.20/-2.00**
$M(NO_3)_3(H_2O)_3 + L \rightarrow ML(NO_3)_3 + 3H_2O$	**20.93/17.45**	**4.23/0.69**	**7.35/13.40**	**2.68/6.34**
$[M(H_2O)_9]^{3+} + NO_3^- + L \rightarrow [ML(NO_3)]^{2+} + 9H_2O$	**-314.36/-308.93**	**-32.05/-28.86**	**-22.94/-18.73**	**-30.31/-26.37**
$[M(H_2O)_9]^{3+} + L \rightarrow [ML(H_2O)_3]^{3+} + 6H_2O$	**-114.42/-109.37**	**-14.30/-12.78**	**8.09/9.71**	**-4.41/-3.03**
$[M(H_2O)_9]^{3+} + L + NO_3^- \rightarrow [ML(NO_3)(H_2O)_2]^{2+} + 7H_2O$	**-322.76/-316.76**	**-32.95/-30.22**	**-22.64/-18.41**	**-31.21/-27.62**
$[M(H_2O)_9]^{3+} + L + 2NO_3^- \rightarrow [ML(NO_3)_2]^+ + 9H_2O$	**-458.71/-454.61**	**-40.20/-38.67**	**-37.12/-34.43**	**-42.42/-40.17**
$[M(H_2O)_9]^{3+} + L + 3NO_3^- \rightarrow ML(NO_3)_3 + 9H_2O$	**-525.59/-524.29**	**-35.98/-37.47**	**-32.86/-24.76**	**-61.72/-31.82**

[a]…/… denotes Gibbs free energies for Eu amd Am complexes.

Table S4 Differences in the Gibbs free energies (kcal/mol) of formation and extraction of the PhenBHPPA complexes with of Am^{3+} and Eu^{3+} in gas, aqueous, n-octanol, and cyclohexanone phases at the B3LYP/6-31G*/RECP Level.

Reactions	$\Delta\Delta G_{gas}$	$\Delta\Delta G_{aq}$	$\Delta\Delta G_{n\text{-}oct}$	$\Delta\Delta G_{cyc}$
$[M(NO_3)_2(H_2O)_3]^+ + L \rightarrow [ML(NO_3)]^{2+} + NO_3^- + 3H_2O$	-0.98	-0.83	0.19	-0.07
$[M(NO_3)_2(H_2O)_3]^+ + L \rightarrow [ML(H_2O)_3]^{3+} + 2NO_3^-$	-1.36	-2.49	-2.39	-2.39
$[M(NO_3)_2(H_2O)_3]^+ + L \rightarrow [ML(NO_3)(H_2O)_2]^{2+} + H_2O + NO_3^-$	-4.183	-1.29	0.22	-0.43
$[M(NO_3)_2(H_2O)_3]^+ + L \rightarrow [ML(NO_3)_2]^+ + 3H_2O$	-2.31	-2.48	-1.32	-1.76
$[M(NO_3)_2(H_2O)_3]^+ + NO_3^- + L \rightarrow ML(NO_3)_3 + 3H_2O$	-5.11	-5.50	4.08	1.69
$[M(NO_3)_2(H_2O)_4]^+ + L \rightarrow [ML(NO_3)]^{2+} + NO_3^- + 4H_2O$	-0.88	-0.22	1.34	0.53

$[M(NO_3)_2(H_2O)_4]^+ + L \rightarrow [ML(H_2O)_3]^{3+} + 2NO_3^- + H_2O$	-1.25	-1.89	-1.79	-2.03
$[M(NO_3)_2(H_2O)_4]^+ + L \rightarrow [ML(NO_3)(H_2O)_2]^{2+} + 2H_2O + NO_3^-$	-0.31	-0.68	0.82	0.18
$[M(NO_3)_2(H_2O)_4]^+ + L \rightarrow [ML(NO_3)_2]^+ + 4H_2O$	-2.22	-1.88	-0.72	-1.16
$[M(NO_3)_2(H_2O)_4]^+ + NO_3^- + L \rightarrow ML(NO_3)_3 + 4H_2O$	-5.01	-4.90	7.59	2.30
$M(NO_3)_3(H_2O)_3 + L \rightarrow [ML(NO_3)]^{2+} + 2NO_3^- + 3H_2O$	0.65	1.14	2.15	1.89
$M(NO_3)_3(H_2O)_3 + L \rightarrow [ML(H_2O)_3]^{3+} + 3NO_3^-$	0.27	-0.53	-30.97	-0.67
$M(NO_3)_3(H_2O)_3 + L \rightarrow [ML(NO_3)(H_2O)_2]^{2+} + H_2O + 2NO_3^-$	1.22	0.68	2.18	1.54
$M(NO_3)_3(H_2O)_3 + L \rightarrow [ML(NO_3)_2]^+ + NO_3^- + 3H_2O$	-0.68	-0.52	0.64	-0.20
$M(NO_3)_3(H_2O)_3 + L \rightarrow ML(NO_3)_3 + 3H_2O$	-3.48	-3.54	6.05	3.66
$[M(H_2O)_9]^{3+} + NO_3^- + L \rightarrow [ML(NO_3)]^{2+} + 9H_2O$	5.43	3.19	4.21	3.94
$[M(H_2O)_9]^{3+} + L \rightarrow [ML(H_2O)_3]^{3+} + 6H_2O$	5.05	1.52	1.62	1.38
$[M(H_2O)_9]^{3+} + L + NO_3^- \rightarrow [ML(NO_3)(H_2O)_2]^{2+} + 7H_2O$	6.00	2.73	4.23	3.59
$[M(H_2O)_9]^{3+} + L + 2NO_3^- \rightarrow [ML(NO_3)_2]^+ + 9H_2O$	4.10	1.53	2.69	2.25
$[M(H_2O)_9]^{3+} + L + 3NO_3^- \rightarrow ML(NO_3)_3 + 9H_2O$	1.30	1.49	8.10	29.9

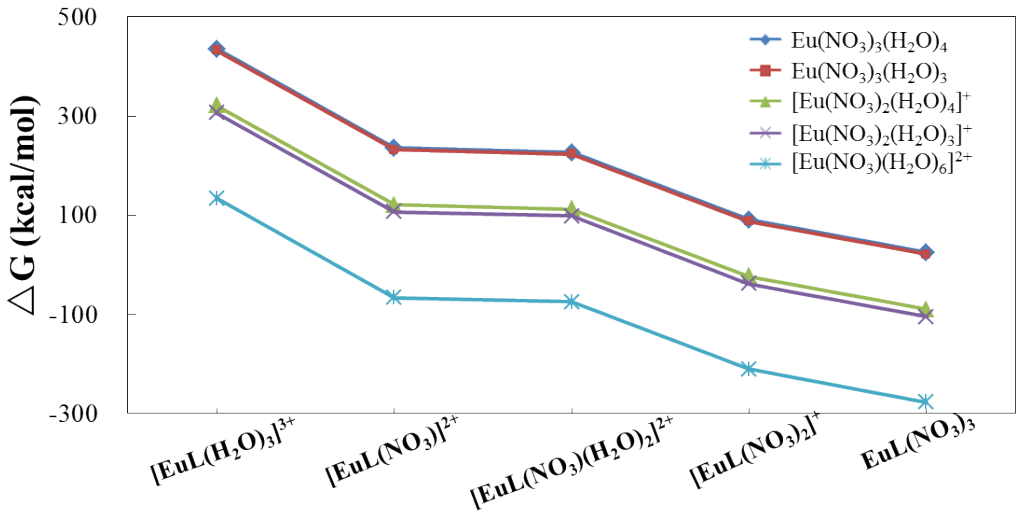

Fig. S1 Changes of Gibbs free energy (ΔG, kcal/mol) for 25 complexing reactions from five different Eu(III) starting reactants to five different products in the gas phase.

Complete Gaussian 09 reference (Reference 37)

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