Theoretical Studies on the Synergistic Extraction of Am^{3+} and Eu^{3+} with CMPO-HDEHP and CMPO-HEH[EHP] Systems

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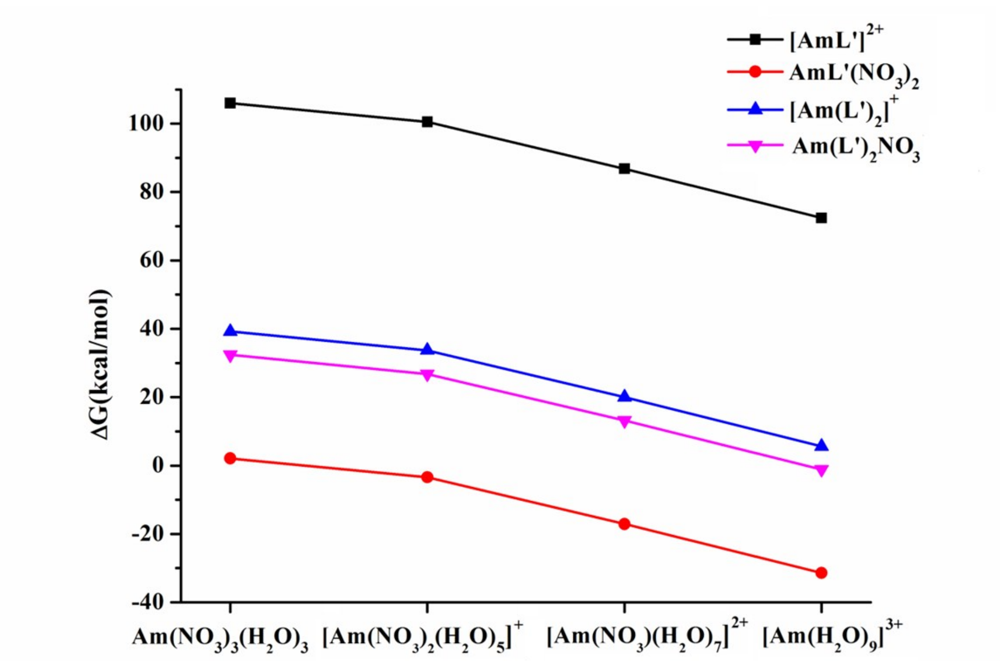
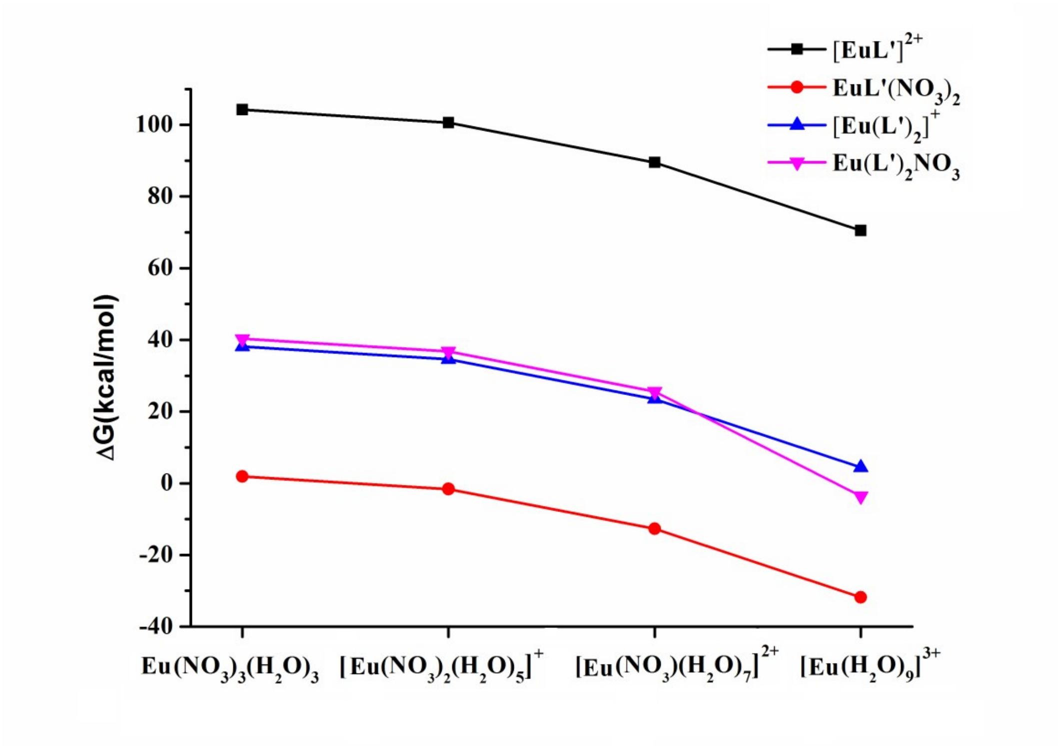
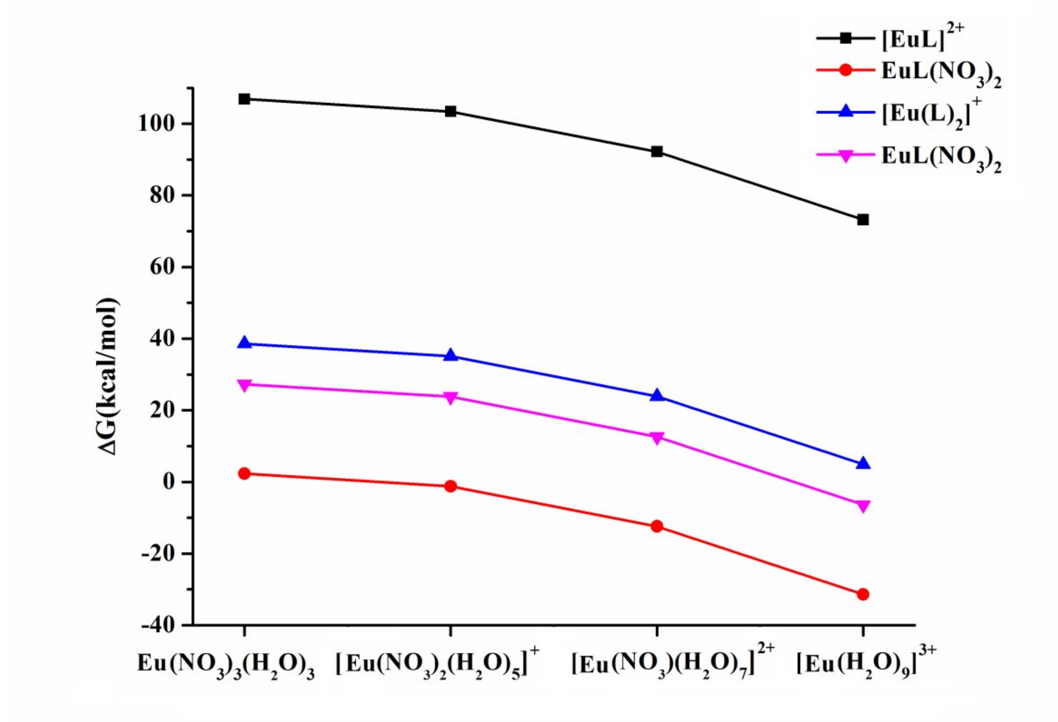
Electronic Supplementary Information



(a)



(b)



(c)

Figure S1 Changes in Gibbs free energy (ΔG, kcal/mol) for the extraction reactions starting from CN 9 Am^{3+} reactants to extraction complexes in *n*-dodecane with L'(a), and starting from CN 9 Eu^{3+} reactants with L(b) and L'(c) to extraction complexes

Table S1 Probable extraction reactions and corresponding Gibbs free energy in water and *n*-dodecane solution obtained by the B3LYP method.[a,b]

Reaction	**ΔG_{aq}**	**ΔG_{org}**
$[M(H_2O)_9]^{3+}+HL \rightarrow [ML]^{2+}+9H_2O+H^+$	10.9/14.2	73.8/84.6
$[M(H_2O)_9]^{3+}+HL' \rightarrow [ML']^{2+}+9H_2O+H^+$	10.2/30.2	71.0/73.0
$[M(H_2O)_9]^{3+}+HL+2NO_3^- \rightarrow ML(NO_3)_2+9H_2O+H^+$	-23.1/-26.7	-30.8/-28.4
$[M(H_2O)_9]^{3+}+HL'+2NO_3^- \rightarrow ML'(NO_3)_2+9H_2O+H^+$	-28.6/-27.6	-31.2/-30.9
$[M(H_2O)_9]^{3+}+2HL \rightarrow ML_2^+ +9H_2O+2H^+$	21.9/25.2	5.4/7.4
$[M(H_2O)_9]^{3+}+2HL' \rightarrow ML'_2{}^+ +9H_2O+2H^+$	28.1/26.7	5.0/6.2
$[M(H_2O)_9]^{3+}+2HL+NO_3^- \rightarrow ML_2(NO_3)+9H_2O+2H^+$	18.4/21.9	-5.8/-2.5
$[M(H_2O)_9]^{3+}+2HL'+NO_3^- \rightarrow ML'_2(NO_3)+9H_2O+2H^+$	29.4/31.8	-3.2/-0.6
$[M(NO_3)(H_2O)_7]^{2+}+HL \rightarrow [ML]^{2+}+7H_2O+NO_3^- +H^+$	29.4/28.0	92.2/98.4
$[M(NO_3)(H_2O)_7]^{2+}+HL' \rightarrow [ML']^{2+}+7H_2O+NO_3^- +H^+$	28.6/44.0	89.5/86.8
$[M(NO_3)(H_2O)_7]^{2+}+HL+NO_3^- \rightarrow ML(NO_3)_2+7H_2O+H^+$	-4.7/-12.9	-12.4/-14.6
$[M(NO_3)(H_2O)_7]^{2+}+HL'+NO_3^- \rightarrow ML'(NO_3)_2+7H_2O+H^+$	-10.2/-13.7	-12.7/-17.1
$[M(NO_3)(H_2O)_7]^{2+}+2HL \rightarrow ML_2^+ +7H_2O+NO_3^- +2H^+$	40.3/39.0	23.9/21.2
$[M(NO_3)(H_2O)_7]^{2+}+2HL' \rightarrow ML'_2{}^+ +7H_2O+NO_3^- +2H^+$	46.5/40.5	23.5/20.0
$[M(NO_3)(H_2O)_7]^{2+}+2HL \rightarrow ML_2(NO_3)+7H_2O+2H^+$	36.9/35.8	12.6/10.3
$[M(NO_3)(H_2O)_7]^{2+}+2HL' \rightarrow ML'_2(NO_3)+7H_2O+2H^+$	47.8/45.6	25.6/13.2
$[M(NO_3)_2(H_2O)_5]^{+}+HL \rightarrow [ML]^{2+}+5H_2O+2NO_3^- +H^+$	40.5/41.7	103.4/112.1
$[M(NO_3)_2(H_2O)_5]^{+}+HL' \rightarrow [ML']^{2+}+5H_2O+2NO_3^- +H^+$	39.8/57.7	100.6/100.5
$[M(NO_3)_2(H_2O)_5]^{+}+HL \rightarrow ML(NO_3)_2+5H_2O+H^+$	6.5/0.8	-1.2/-0.9
$[M(NO_3)_2(H_2O)_5]^{+}+HL' \rightarrow ML'(NO_3)_2+5H_2O+H^+$	1/-0.1	-1.6/-3.4

$[M(NO_3)_2(H_2O)_5]^+ + 2HL \rightarrow ML_2^+ + 5H_2O + 2NO_3^- + 2H^+$	51.5/52.7	35.1/34.9
$[M(NO_3)_2(H_2O)_5]^+ + 2HL' \rightarrow ML'_2{}^+ + 5H_2O + 2NO_3^- + 2H^+$	57.7/54.2	34.6/33.7
$[M(NO_3)_2(H_2O)_5]^+ + 2HL \rightarrow ML_2(NO_3) + 5H_2O + NO_3^- + 2H^+$	48.1/49.4	23.8/24.0
$[M(NO_3)_2(H_2O)_5]^+ + 2HL' \rightarrow ML'_2(NO_3) + 5H_2O + NO_3^- + 2H^+$	59.0/59.3	36.8/26.8
$M(NO_3)_3(H_2O)_3 + HL \rightarrow [ML]^{2+} + 3H_2O + 3NO_3^- + H^+$	44.0/47.2	106.9/117.6
$M(NO_3)_3(H_2O)_3 + HL' \rightarrow [ML']^{2+} + 3H_2O + 3NO_3^- + H^+$	43.3/63.2	104.2/106.0
$M(NO_3)_3(H_2O)_3 + HL \rightarrow ML(NO_3)_2 + 3H_2O + NO_3^- + H^+$	10.0/6.3	2.3/4.6
$M(NO_3)_3(H_2O)_3 + HL' \rightarrow ML'(NO_3)_2 + 3H_2O + NO_3^- + H^+$	4.5/5.4	1.9/2.1
$M(NO_3)_3(H_2O)_3 + 2HL \rightarrow ML_2^+ + 3H_2O + 3NO_3^- + 2H^+$	55.0/58.2	38.6/40.4
$M(NO_3)_3(H_2O)_3 + 2HL' \rightarrow ML'_2{}^+ + 3H_2O + 3NO_3^- + 2H^+$	61.2/59.7	38.1/39.2
$M(NO_3)_3(H_2O)_3 + 2HL \rightarrow ML_2(NO_3) + 3H_2O + 2NO_3^- + 2H^+$	51.6/55.0	27.3/29.5
$M(NO_3)_3(H_2O)_3 + 2HL' \rightarrow ML'_2(NO_3) + 3H_2O + 2NO_3^- + 2H^+$	62.5/64.8	40.3/32.4

[a] Gibbs free energy of solvation for H^+ was set to be −264.0 kcal/mol.[42,43]

[b] …/… represents the results of Eu^{3+} and Am^{3+} complexes, respectively.

[23] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, *Gaussian 09, Revision D.01,* Gaussian, Inc., Wallingford CT, 2013