Europium, Uranyl, and Thorium-Phenanthroline Amide Complexes in Acetonitrile Solution: An ESI-MS and DFT Combined Investigation

Cheng-Liang Xiao,[a,b‡] Cong-Zhi Wang,[b‡] Lei Mei,[b] Xin-Rui Zhang,[b] Nathalie Wall,[c] Yu-Liang Zhao,[b] Zhi-Fang Chai,[a,b] and Wei-Qun Shi*[b]

[a] School for Radiological and Interdisciplinary Sciences (RAD-X) and Collaborative Innovation Center of Radiation Medicine of Jiangsu Higher Education Institutions, Soochow University, Suzhou 215123, China.

[b] Laboratory of Nuclear Energy Chemistry and Key Laboratory For Biomedical Effects of Nanomaterials and Nanosafety, Institute of High Energy Physics, Chinese Academy of Sciences, Beijing 100049, China.

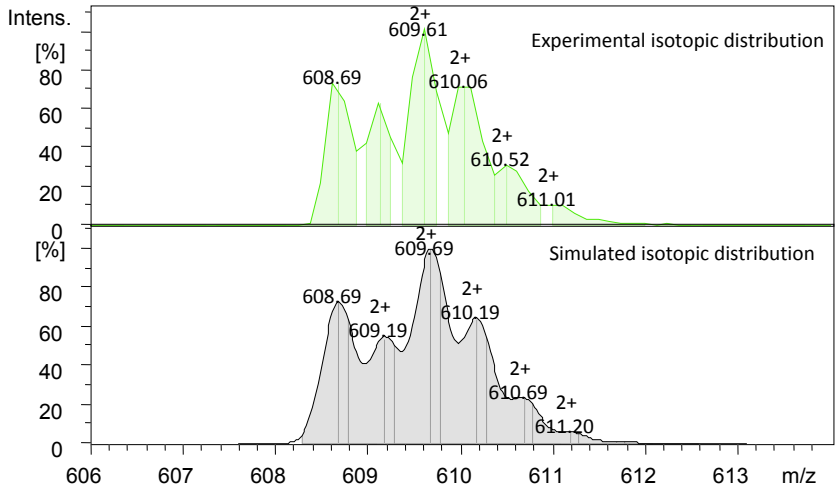
[c] Chemistry Department, Washington State University, Pullman 99164-4630, USA

*E-mail: shiwq@ihep.ac.cn

‡ These authors contributed equally to this work.

Supplementary Information

(A)



(B)

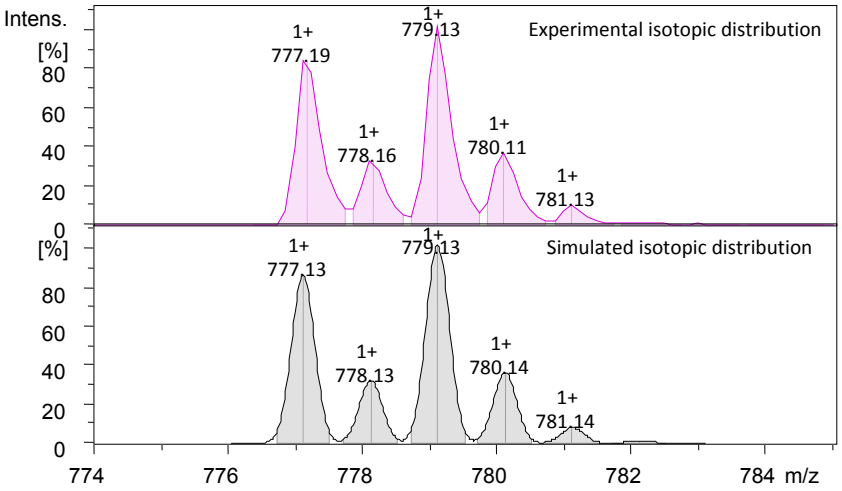


Fig. S1 Experimental and simulated isotopic distribution of *m/z* 609 (A) and 777 (B) in Eu(III) complexes.

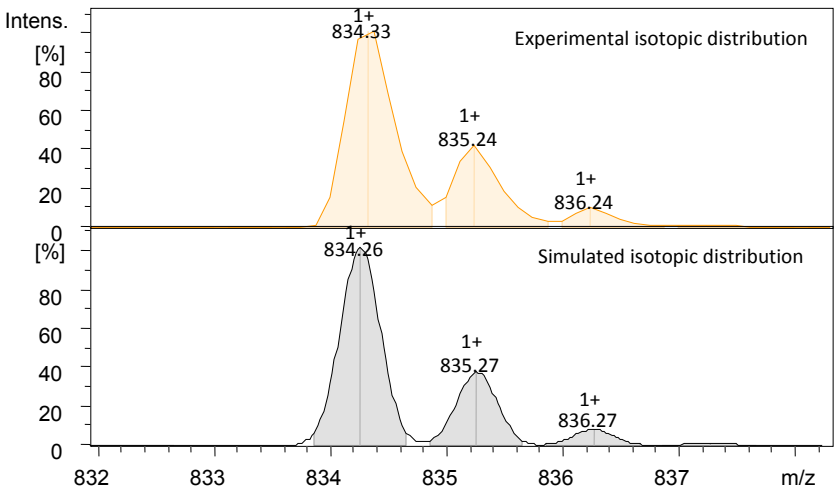


Fig. S2 Experimental and simulated isotopic distribution of *m/z* 834 in U(VI) complexes.

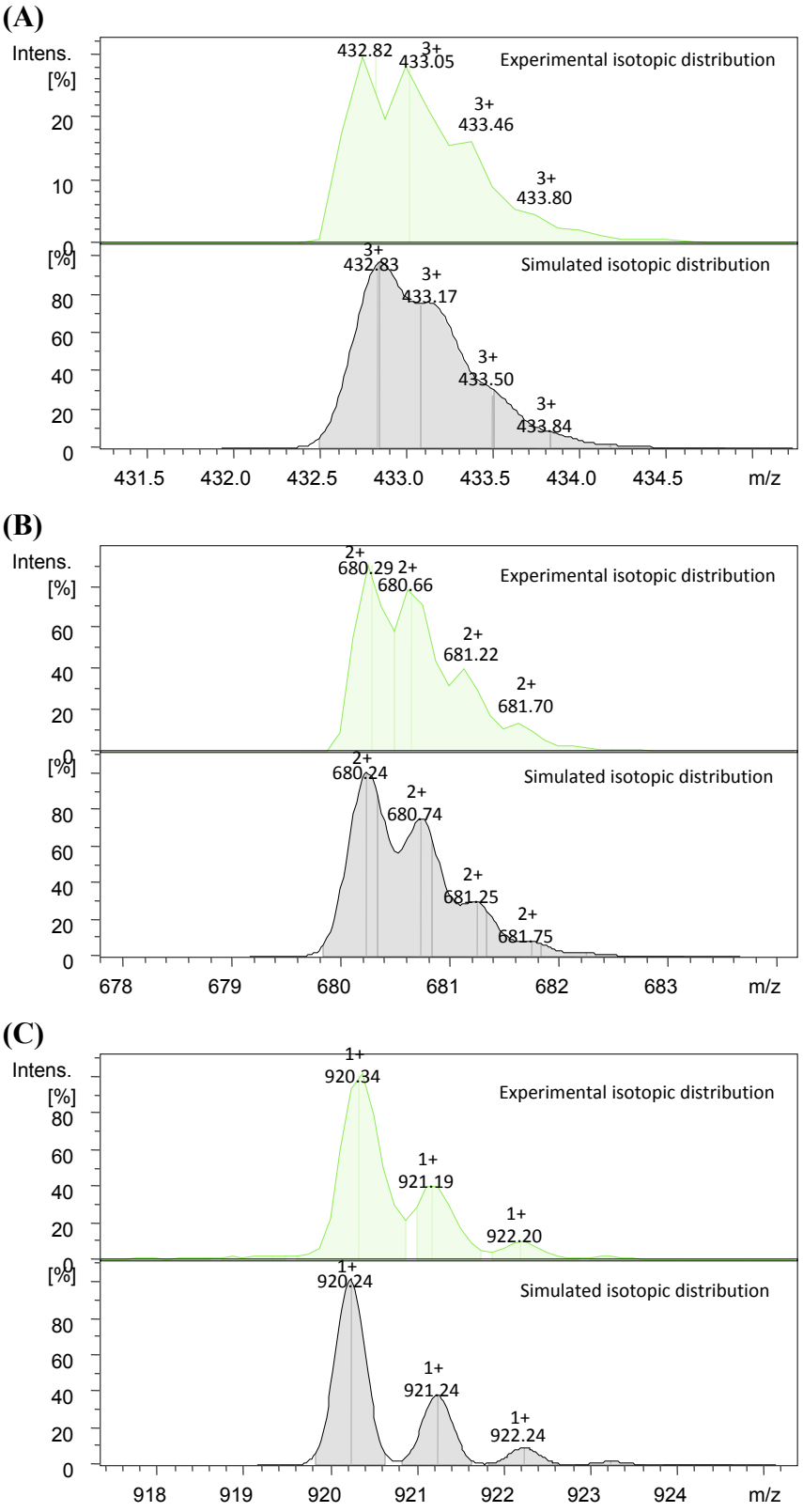


Fig. S3 Experimental and simulated isotopic distribution of *m/z* 433 (A), 680 (B) and 920 (C) in Th(IV) complexes.

Table S1 Eu(III) Complexes with Et-Tol-DAPhen Ligand Detected by ESI-MS in Acetontrile Solution

[Eu(III)]/[L] ratio	*m/z*	complexes
0	503	$[LH]^+$
0.25	609	$[EuL_2(NO_3)]^{2+}$
0.5	609	$[EuL_2(NO_3)]^{2+}$
0.75	609	$[EuL_2(NO_3)]^{2+}$
1.0	609	$[EuL_2(NO_3)]^{2+}$
1.25	777	$[EuL(NO_3)_2]^+$

Table S2 MS/MS Results of Eu(III) Complexes

complexes	CID condition	*m/z*	assignments
503	cut off: 250; amplitude: 0.90	485	$-CH_4-H_2$
		475	$-C_2H_5+2H$
		467	$-2CH_4-2H_2$
		457	$-C_3H_7-H_2$
		322	$-2C_7H_7+2H$
		307	$-2C_7H_7-CH_3+2H$
609	cut off: 150; amplitude: 1.00	579	$-2C_2H_5$
		563	$-C_7H_7$
		416	$-4C_2H_5-3C_7H_7$
		336	$-HNO_3-4C_2H_5-4C_7H_7$
777	cut off: 200; amplitude: 1.00	717	$-2C_2H_5$
		704	$-2C_2H_5-CH_3$
		686	$-C_7H_7$
		535	$-2C_2H_5-2C_7H_7$
		509	$-2C_2H_5-2C_7H_7-2N$

Table S3 U(VI) Complexes with Et-Tol-DAPhen Ligand Detected by ESI-MS in Acetontrile Solution

[U(VI)]/[L] ratio	*m/z*	complexes
0	503	$[LH]^+$
0.5	834	$[UO_2L(NO_3)]^+$
1.0	834	$[UO_2L(NO_3)]^+$
2.0	834	$[UO_2L(NO_3)]^+$

Table S4. MS/MS Results of U(VI) Complexes

complexes	CID condition	*m/z*	assignments
834	cut off: 200; amplitude: 1.00	787	$-2CH_4-CH_3$
		774	$-2C_2H_6$
		760	$-2C_2H_5-CH_4$
		742	$-C_7H_8$
		641	$-2C_7H_7-CH_3$

Table S5 Changes of the Gibbs Free Energy (kcal/mol) Including Zero-Point Energy (ZPE) and Thermal Corrections for the Reactions Concerning Eu^{3+}, UO_2^{2+} and Th^{4+} in Acetonitrile Solution

Reactions	ΔG
$[Eu(CH_3CN)_8]^{3+} + CH_3CN \rightarrow [Eu(CH_3CN)_9]^{3+}$	11.2
$[Eu(CH_3CN)_9]^{3+} + CH_3CN \rightarrow [Eu(CH_3CN)_{10}]^{3+}$	14.0
$[UO_2(CH_3CN)_5]^{2+} + CH_3CN \rightarrow [UO_2(CH_3CN)_6]^{2+}$	13.0
$[Th(CH_3CN)_9]^{4+} + CH_3CN \rightarrow [Th(CH_3CN)_{10}]^{4+}$	8.3
$[Th(CH_3CN)_{10}]^{4+} + CH_3CN \rightarrow [Th(CH_3CN)_{11}]^{4+}$	18.3
$[Th(CH_3CN)_{11}]^{4+} + CH_3CN \rightarrow [Th(CH_3CN)_{12}]^{4+}$	11.3

Table S6 Average U-N and U-O Bond Distances (Å), Wiberg Bond Indices (WBIs) of U-N and U-O Bonds, and Natural Charges on the U, N, and O Atoms in $[UO_2L(NO_3)]^+$ (L= Et-Tol-DAPhen)

Complexes	Bond Length		Wiberg Bond Index		Natural Charge		
	U-N(L)	U-O(L)	U-N(L)	U-O(L)	Q_U	$Q_{N(L)}$	$Q_{O(L)}$
$[UO_2L(NO_3)]^+$	2.644	2.417	0.386	0.511	1.439	-0.427	-0.591

Table S7 Average Electron Density (ρ), Laplacian ($\nabla^2\rho$), and Energy Density (H(r)) at U-N and U-O Bond Critical Points in $[UO_2L(NO_3)]^+$(All values in a.u.).

Bonds	ρ	$\nabla^2\rho$	H(r)
U-N(L)	0.0452	0.1264	-0.0031
U-O(L)	0.0603	0.2281	-0.0032

Table S8 Th(IV) Complexes with Et-Tol-DAPhen Ligand Detected by ESI-MS in Acetontrile Solution

[Th(IV)]/[L] ratio	*m/z*	complexes
0	503	$[LH]^+$
0.25	503, 525, 541, 680	$[LH]^+$, $[L+Na]^+$, $[L+K]^+$, $[ThL_2(NO_3)_2]^{2+}$
0.5	503, 525, 680	$[LH]^+$, [L+Na]+, $[ThL_2(NO_3)_2]^{2+}$
0.75	680	$[ThL_2(NO_3)_2]^{2+}$
1.0	680	$[ThL_2(NO_3)_2]^{2+}$
1.25	433, 680, 920	$[ThL_2(NO_3)]^{3+}$, $[ThL_2(NO_3)_2]^{2+}$, $[ThL(NO_3)_3]^+$
1.5	433, 680, 920	$[ThL_2(NO_3)]^{3+}$, $[ThL_2(NO_3)_2]^{2+}$, $[ThL(NO_3)_3]^+$
2.0	433, 680, 920	$[ThL_2(NO_3)]^{3+}$, $[ThL_2(NO_3)_2]^{2+}$, $[ThL(NO_3)_3]^+$

Table S9 MS/MS Results of Th(IV) Complexes

complexes	CID condition	*m/z*	assignments
433	cut off: 115; amplitude: 0.50	412	$-HNO_3$
		402	$-HNO_3-CH_3+2H$
		373	$-C_7H_7+2H$
680	cut off: 165; amplitude: 1.00	648	$-HNO_3$
		635	$-HNO_3-2CH_3+2H$
		612	$-HNO_3-4CH_3-CH_2$
		590	$-2C_7H_7$
		544	$-2C_7H_7-2C_2H_5-2CH_3$
920	cut off: 250; amplitude: 1.00	873	$-2CH_4-CH_3$
		846	$-2C_2H_5-CH_4$
		829	$-C_7H_7$
		800	$-C_7H_7-CH_3+H$
		737	$-2C_7H_7$
		667	$-2C_7H_7-2C_2H_5-N$
		622	$-2C_7H_7-2C_2H_5-2NO$

S1. ESI-MS experiments after solvent extraction

1 mM of Et-Tol-DAPhen in 1 mL of cyclohexanone was contacted with 1 mL of 1 M HNO_3 solution containing 1 mM of Eu(III) or U(VI) or Th(IV). After shaking for 60 min, the organic phase was separated and diluted with HPLC grade acetonitrile in 1000 times for ESI-MS measurements.

S1.1 ESI-MS of Eu(III) complexes

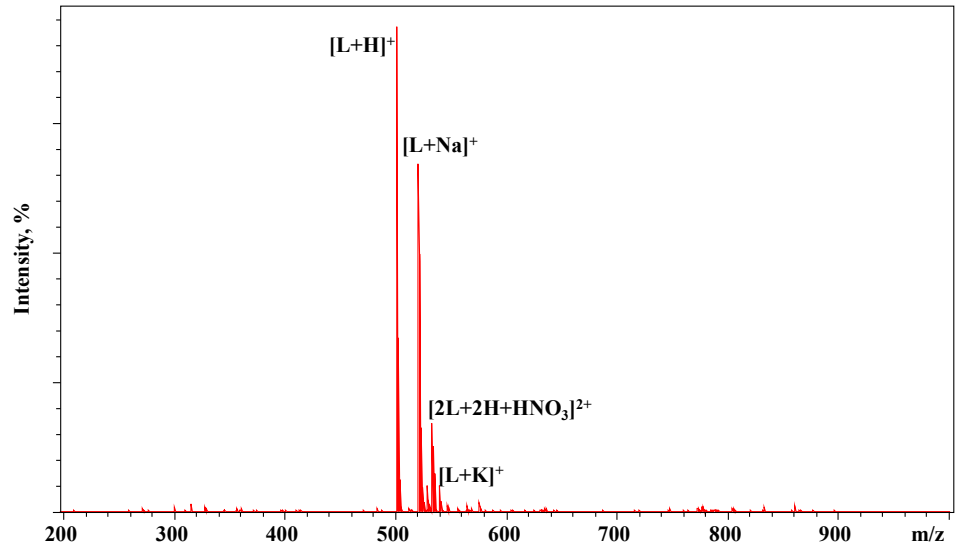


Fig. S4 ESI-MS of Eu(III) complexes after solvent extraction.

With respect to Eu(III), Et-Tol-DAPhen shows nearly no extraction as previously reported. If the ESI-MS sample of Eu(III) complex was prepared through a liquid-liquid extraction step and further diluted in acetonitrile solution, it is found that the signal of Eu(III) complex in ESI-MS was not detected from **Fig. S4**.

S1.2 ESI-MS of U(VI) complexes

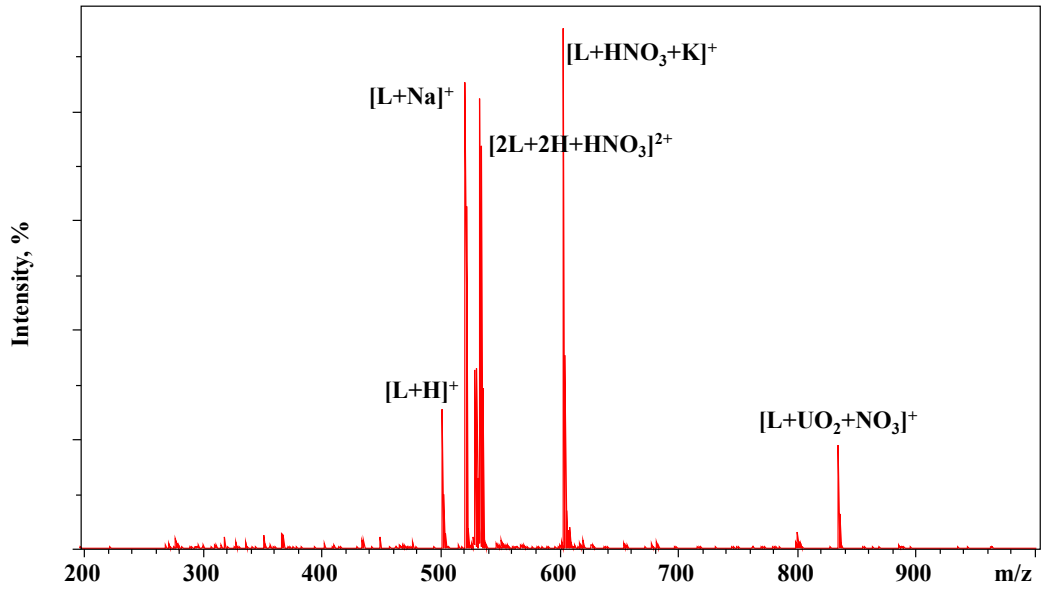


Fig. S5 ESI-MS of U(VI) complexes after solvent extraction.

ESI-MS of U(VI) complexes was shown in **Fig. S5**. The MS peaks at m/z between 502 and 525 are attributed to the hydrogen and sodium ion adducts of the ligand ($[L+H]^+$, $[L+Na]^+$), respectively. The peak at m/z 535 and 604 can be due to $[2L+2H+HNO_3]^{2+}$ and $[L+HNO_3+K]^+$, respectively. Only 1:1 U(VI) complex ($[UO_2L(NO_3)]^+$) at m/z 834 is observed in this experimental conditions, which is quite consistent with the results obtained in acetonitrile solution.

S1.3 ESI-MS of Th(IV) complexes

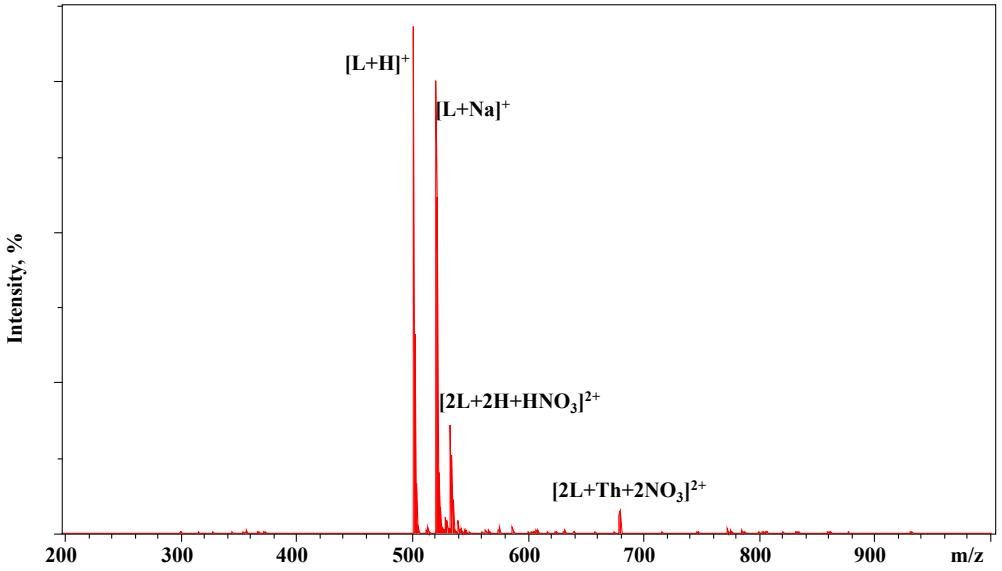


Fig. S6 ESI-MS of Th(IV) complexes after solvent extraction.

ESI-MS of Th(IV) complexes was shown in **Fig. S6**. The MS peaks at m/z between 500 and 540 are similar to those of U(VI) complexes which has no relationship with Th(IV). One Th(VI) complex observed at m/z 680 can be attributed to $[2L+Th+2NO_3]^{2+}$, which is the main species regardless of the ratio of metal-to-ligand in acetonitrile solution.