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Electronic Supplementary Information

to the paper "New Insights into the Selectivity of Four 1,10-Phenanthroline-Derived Ligands toward the Separation of Trivalent Actinides and Lanthanides: A DFT Based Comparison Study" 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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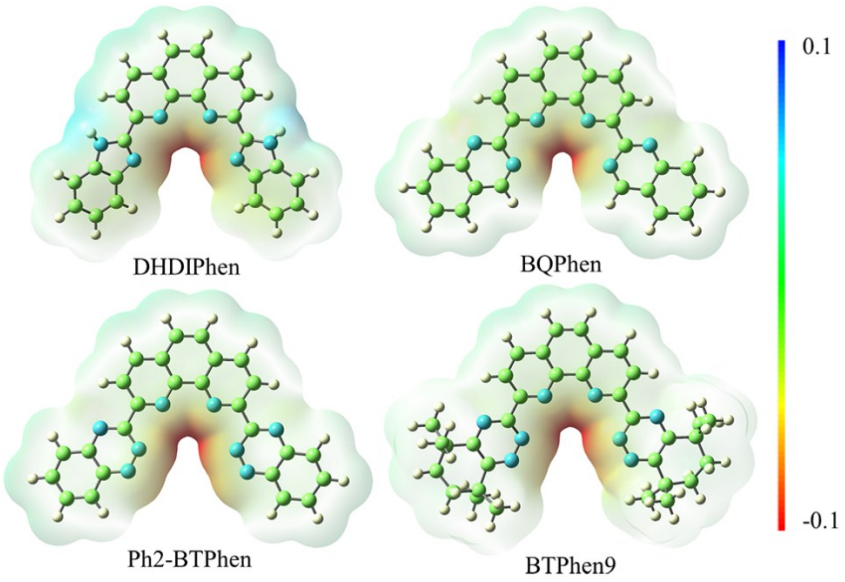

Fig. S1 The ESP maps of DHDIPhen, BQPhen, Ph2-BTPhen and $CyMe_4$-BTPhen.

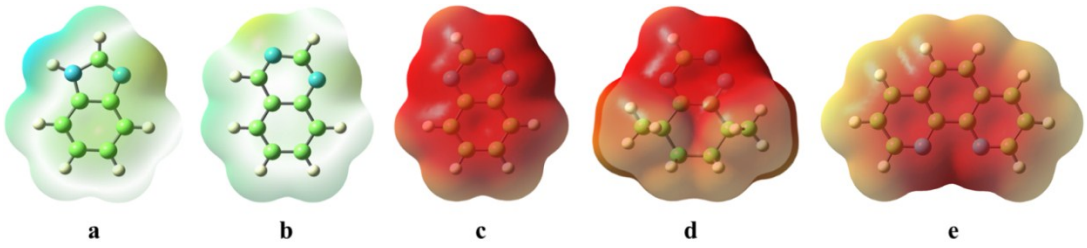

Fig. S2 The ESP maps of substituents and phenanthroline.

Table S1 Properties of Substituents and Phenanthroline.[a]

	a	b	c	d	e	H_2O	Am^{3+}(ref)[#]	Eu^{3+}(ref)[#]	H_2O(ref)[*]
IP	8.32	8.75	8.49	8.09	8.08	12.53	-	-	12.6
EA	-1.08	0.38	0.98	-0.21	0.31	-2.92	-	-	-6.4
χ	3.62	4.56	4.73	4.15	4.19	4.80	-	-	3.10
η	4.70	4.18	3.75	3.94	7.77	7.72	7.35	10.75	9.5
ESP	-1.77	-1.44	-1.60	-1.69	-2.49	-	-	-	-

[#] D. Manna and T. K. Ghanty, *Phys. Chem. Chem. Phys.*, 2012, **14**, 11060-11069.

[*] R. G. Pearson, *Inorg. Chem.*, 1988, **77**, 734-740.

[a] IP, EA, χ and η are the ionization potential, electron affinity, electronegativity and hardness, respectively in electronvolts; ESP values are the electronic potential where the matel contacts the nitrogen donor atoms (kcal/mol);

Table S2 NBO Populations of Am and Eu Atoms in Complexes.

Complexes	NBO Populations
$ML_a(NO_3)_3$	Eu: [Xe] 6s(0.17) 4f(6.37) 5d(0.73) 6p(0.01) 6d(0.06)
	Am: [Rn] 7s(0.19) 5f(6.30) 6d(1.05) 7p(0.01)
$ML_b(NO_3)_3$	Eu: [Xe] 6s(0.16) 4f(6.38) 5d(0.73) 6p(0.01) 6d(0.06)
	Am: [Rn] 7s(0.18) 5f(6.32) 6d(1.03) 7p(0.01)
$ML_c(NO_3)_3$	Eu: [Xe] 6s(0.16) 4f(6.38) 5d(0.76) 6p(0.01) 6d(0.06)
	Am: [Rn] 7s(0.18) 5f(6.29) 6d(1.10) 7p(0.01)
$ML_d(NO_3)_3$	Eu: [Xe] 6s(0.16) 4f(6.38) 5d(0.74) 6p(0.01) 6d(0.06)
	Am: [Rn] 7s(0.18) 5f(6.31) 6d(1.06) 7p(0.01)

Table S3 Contribution (%) of Metal Atoms and the Nitrogen of Ligand (N_L) and Oxygen Atoms of Nitrate Anion (O_N) to the Delocalized Canonical MOs for Complexes $ML_a(NO_3)_3$ and $ML_c(NO_3)_3$ (M=Eu, Am).

$ML_a(NO_3)_3$		**MO-82α**	**MO-160α**	**MO-161α**	**MO-180α**	**MO-182α**
	Eu	5p: 76.85	5d: 3.09	5d: 2.64	4f: 20.13	4f: 14.62
	N_L	2s: 2.07	2p: 30.10 2s: 4.58	2p: 22.72 2s: 3.83	-	-
	$O_{(N)}$	2p: 7.04	2p: 18.49	2p: 35.37	2p: 34.09	2p: 38.65
		MO-98α	**MO-177α**	**MO-178α**	**MO-196α**	**MO-198α**
	Am	6p: 70.61	6d: 3.09	6d: 4.58	5f: 11.68	5f: 7.09
	N_L	2s: 6.40	2p: 35.22 2s: 5.96	2p: 44.02 2s: 5.69	-	-
	$O_{(NO)}$	2s: 5.22	2p: 15.24	2p: 5.80	2p: 46.26	2p: 23.27
$ML_c(NO_3)_3$		**MO-84α**	**MO-166α**	**MO-167α**	**MO-186α**	**MO-188α**
	Eu	5p: 18.73	5d: 6.09	5d: 1.99	4f: 23.03	4f: 26.99
	N_L	2s: 7.84	2p: 12.63 2s: 2.56	2p: 35.14 2s: 4.29	-	-
	$O_{(N)}$	2p: 5.59	2p: 42.78	2p: 5.73	2p: 37.10	2p: 35.74
		MO-100α	**MO-181α**	**MO-182α**	**MO-202α**	**MO-204α**
	Am	6p: 16.20	6d: 5.89	5f: 2.36 6d: 3.28	5f: 1.53 6d: 2.38	5f: 12.94 6d: 1.07
	N_L	2s: 5.13	2p: 17.11 2s: 3.16	2p: 42.14 2s: 5.01	-	-
	$O_{(N)}$	2s: 5.00	2p: 14.24	2p: 4.71	2p: 28.67	2p: 42.51

Table S4 Changes of Gibbs Free Energies (ΔG, kcal/mol) for Complexation Reactions of 1:1 Metal to Ligands Ratio in Gas and Cyclohexanone Phases at the BP86/6-311G*/RECP level of Theory.

	ΔG_{gas}	ΔG_{cyc}	$\Delta\Delta G_{gas}$	$\Delta\Delta G_{cyc}$
$L_a + [M(NO_3)_2(H_2O)_4]^+ + NO_3^- \rightarrow ML_a(NO_3)_3 + 4H_2O$	-99.03/-102.75	-28.11/-30.75	-3.73	-2.64
$L_b + [M(NO_3)_2(H_2O)_4]^+ + NO_3^- \rightarrow ML_b(NO_3)_3 + 4H_2O$	-121.14/-124.78	-31.38/-34.27	-3.64	-2.89
$L_c + [M(NO_3)_2(H_2O)_4]^+ + NO_3^- \rightarrow ML_c(NO_3)_3 + 4H_2O$	-116.17/-121.65	-31.94/-35.35	-5.49	-3.41
$L_d + [M(NO_3)_2(H_2O)_4]^+ + NO_3^- \rightarrow ML_d(NO_3)_3 + 4H_2O$	-117.24/-122.03	-32.82/-36.29	-4.79	-3.47
$HL + a + [M(NO_3)_2(H_2O)_4]^+ + NO_3^- \rightarrow ML_a(NO_3)_3 + 3H_2O + H_3O^+$	-36.14/-39.87	-10.08/-12.71	-3.73	-2.64
$HL + b + [M(NO_3)_2(H_2O)_4]^+ + NO_3^- \rightarrow ML_b(NO_3)_3 + 3H_2O + H_3O^+$	-33.60/-37.24	-5.54/-8.43	-3.64	-2.89
$HL + c + [M(NO_3)_2(H_2O)_4]^+ + NO_3^- \rightarrow ML_c(NO_3)_3 + 3H_2O + H_3O^+$	-32.96/-38.44	-7.58/-10.99	-5.49	-3.41
$HL + d + [M(NO_3)_2(H_2O)_4]^+ + NO_3^- \rightarrow ML_d(NO_3)_3 + 3H_2O + H_3O^+$	-33.55/-38.34	-8.51/-12.00	-4.79	-3.47

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

Table S5 Changes of Gibbs Free Energies (ΔG, kcal/mol) for Complexation Reactions of $[M(NO_3)(H_2O)_6]^{2+}$ (M=Am, Eu) Complexes with Ligands in Gas, Aqueous, n-Octanol and Cyclohexanone Phases at the B3LYP/6-311G*/RECP level of Theory. [a]

	ΔG_{gas}	ΔG_{water}	$\Delta G_{n\text{-}oct}$	ΔG_{cyc}
$L_a + [M(NO_3)(H_2O)_6]^{2+} + 2NO_3^- \rightarrow ML_a(NO_3)_3 + 4H_2O$	-281.42/-287.30	-33.19/-37.70	-28.32/-32.74	-42.42/-46.58
$L_b + [M(NO_3)(H_2O)_6]^{2+} + 2NO_3^- \rightarrow ML_b(NO_3)_3 + 4H_2O$	-303.54/-309.33	-35.08/-39.90	-32.97/-37.78	-45.69/-50.10
$L_c + [M(NO_3)(H_2O)_6]^{2+} + 2NO_3^- \rightarrow ML_c(NO_3)_3 + 4H_2O$	-298.56/-306.20	-35.45/-41.17	-32.39/-38.01	-46.25/-51.19
$L_d + [M(NO_3)(H_2O)_6]^{2+} + 2NO_3^- \rightarrow ML_d(NO_3)_3 + 4H_2O$	-299.64/-306.58	-35.15/-40.35	-31.95/-37.19	-47.13/-52.12
$HL + a + [M(NO_3)(H_2O)_6]^{2+} + 2NO_3^- \rightarrow ML_a(NO_3)_3 + 3H_2O +$	-218.54/-224.42	-12.96/-17.47	-12.03/-16.45	-24.38/-28.54
$HL + b + [M(NO_3)(H_2O)_6]^{2+} + 2NO_3^- \rightarrow ML_b(NO_3)_3 + 3H_2O +$	-216.00/-221.79	-8.47/-13.30	-7.62/-13.73	-19.85/-24.26
$HL + c + [M(NO_3)(H_2O)_6]^{2+} + 2NO_3^- \rightarrow ML_c(NO_3)_3 + 3H_2O +$	-215.35/-222.99	-9.51/-15.23	-8.11/-12.42	-21.89/-26.82
$HL + d + [M(NO_3)(H_2O)_6]^{2+} + 2NO_3^- \rightarrow ML_d(NO_3)_3 + 3H_2O +$	-215.94/-222.88	-8.54/-13.74	-12.03/-12.44	-22.82/-27.81

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

Table S6 Differences in Gibbs Free energies (ΔΔG, kcal/mol) Between $[M(NO_3)(H_2O)_6]^{2+}$ (M=Am, Eu) Complexes with Ligands in Gas, Aqueous, n-Octanol, and Cyclohexanone Phases at the B3LYP/6-311G*/RECP Level.

	$\Delta\Delta G_{gas}$	$\Delta\Delta G_{water}$	$\Delta\Delta G_{n\text{-}oct}$	$\Delta\Delta G_{cyc}$
$L_a + [M(NO_3)(H_2O)_6]^{2+} + 2NO_3^- \rightarrow ML_a(NO_3)_3 + 4H_2O$	-5.88	-4.51	-4.42	-4.16
$L_b + [M(NO_3)(H_2O)_6]^{2+} + 2NO_3^- \rightarrow ML_b(NO_3)_3 + 4H_2O$	-5.79	-4.83	-4.80	-4.41
$L_c + [M(NO_3)(H_2O)_6]^{2+} + 2NO_3^- \rightarrow ML_c(NO_3)_3 + 4H_2O$	-7.64	-5.72	-5.62	-4.94
$L_d + [M(NO_3)(H_2O)_6]^{2+} + 2NO_3^- \rightarrow ML_d(NO_3)_3 + 4H_2O$	-6.94	-5.20	-5.24	-4.99