Supplementary Information (SI) for New Journal of Chemistry.
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The Extraction and Separation Performance of Two Amidic Acid Ligands toward Actinides

Synthesis and Characterization

Under an argon atmosphere, 36.05 g of diglycolic anhydride (0.3 mol) was weighed into a three-necked flask and dissolved in 400 mL of anhydrous THF. The system temperature was controlled below 10°C using an ice-water bath, and 50 g of bis(2-ethylhexyl)amine (0.2 mol) was added dropwise. After the addition was complete, the reaction was allowed to proceed at room temperature for 24 hours. Completion of the reaction was monitored by thin-layer chromatography (TLC). After the reaction, the solvent was removed by rotary evaporation. The residue was dissolved in 500 mL of dichloromethane and washed three times with 500 mL of saturated NaCl solution. The organic phase was dried over anhydrous $MgSO_4$, filtered, and concentrated by rotary evaporation to remove the solvent. The target compound, HDEHDGA, was obtained by further solvent removal under vacuum.

Under an argon atmosphere, 17 g of 4-methylmorpholine-2,6-dione (0.13 mol) was weighed into a three-necked flask and dissolved in 400 mL of anhydrous THF. The system temperature was controlled below 10°C using an ice-water bath, and 21.57 g of bis(2-ethylhexyl)amine (0.08 mol) was added dropwise. After the addition was complete, the reaction was allowed to proceed at room temperature for 24 hours. Completion of the reaction was monitored by thin-layer chromatography (TLC). After the reaction, the solvent was removed by rotary evaporation. The residue was dissolved in 700 mL of dichloromethane and washed three times with 700 mL of saturated NaCl solution. The organic phase was dried over anhydrous $MgSO_4$, filtered, and concentrated by rotary evaporation to remove the solvent. The target compound, HDEHNDGA, was obtained by further solvent removal under vacuum.

All synthesized products were analyzed by ^1H nuclear magnetic resonance (^1H NMR) spectroscopy and FTIR spectroscopy analysis. The ^1H NMR spectra and FTIR spectroscopy are shown in **Fig. S2**, and the HPLC spectra are provided in the appendix.

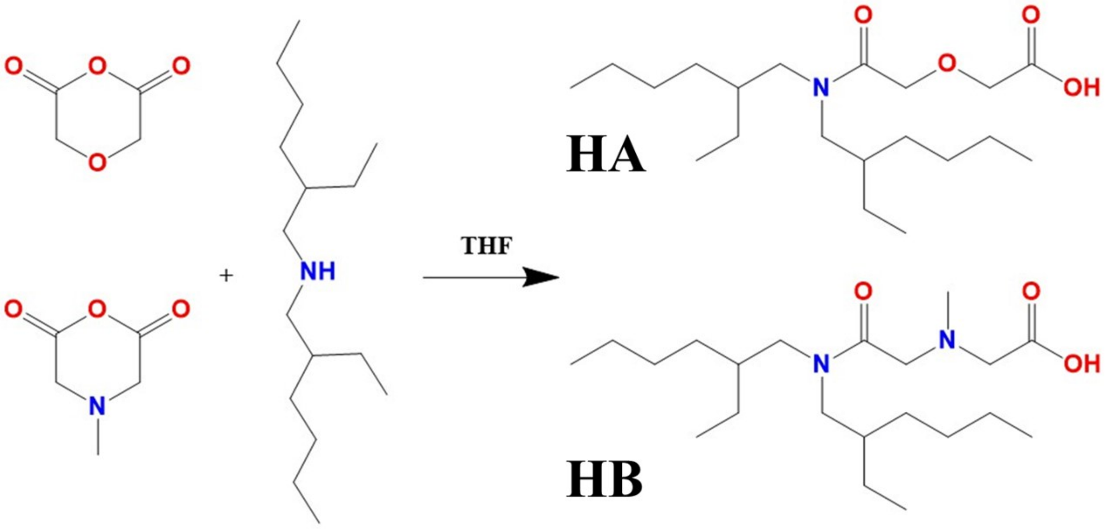

Fig S1 The synthesis of HA and HB

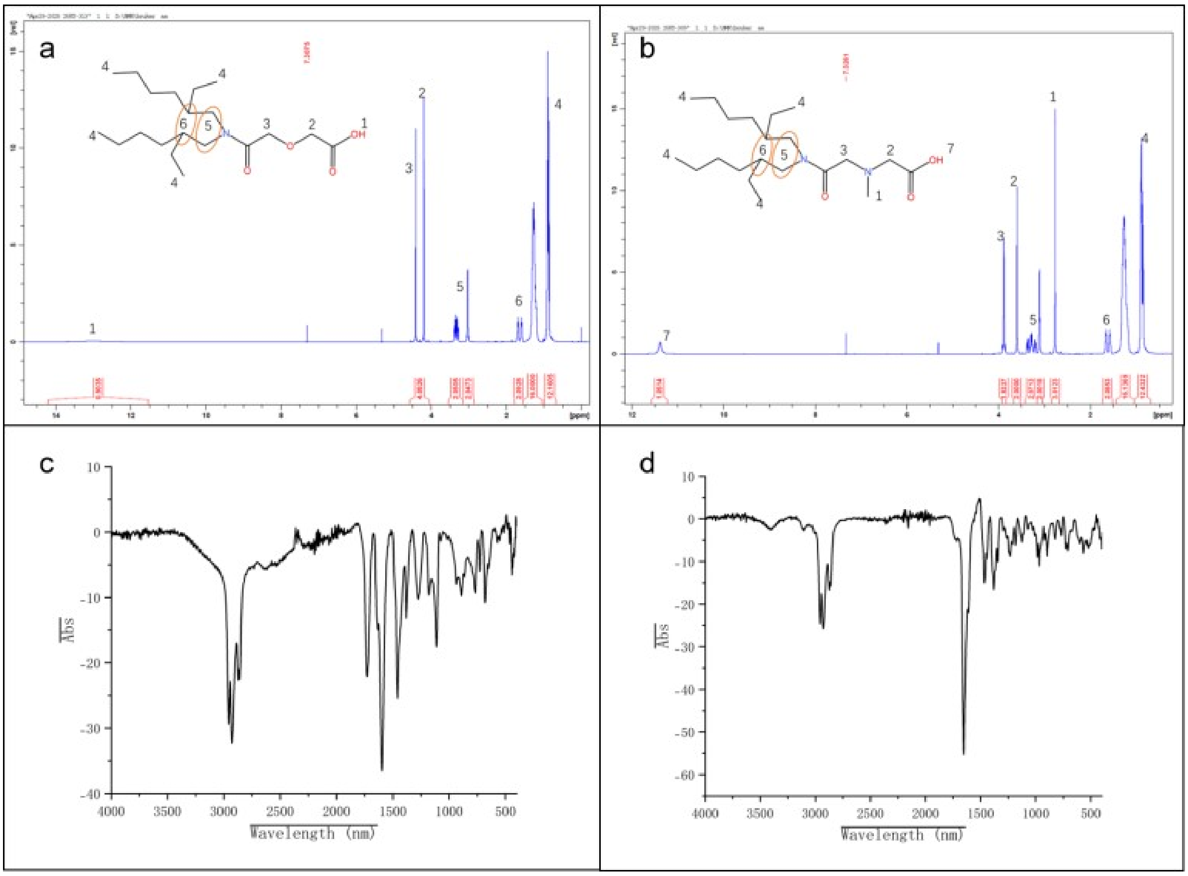

Fig S2 1H NMR spectroscopy of ligand a) HDEHDGA and b) HDEHNDGA; FTIR spectroscopy of ligand c) HDEHDGA and d) HDEHNDGA.

The purification of Pu(IV)

The oxidation state of Pu was adjusted to the Pu(IV) state using a trace amount of high-concentration $NaNO_2$. For purification, Pu(IV) was extracted from the 1 M HNO_3 aqueous phase with 0.5 M TTA dissolved in xylene, the loaded organic phase was then stripped with 8 M HNO_3.

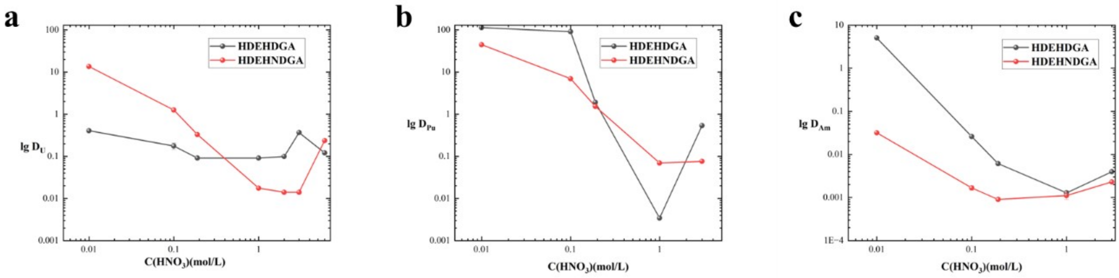

Fig S3 The extraction capabilities of the two ligands for U(VI), Pu(IV) and Am(III)

Derivation of Equation 10

First, taking the logarithm of Equation 8 yields[1]:

$$lgK_{ex} = lg(D_M \cdot \frac{[H^+]^n}{[HA]_{(o)}^n} \cdot \frac{1}{[NO_3^-]^{[m-n]}})$$

This expression can be simplified according to the logarithmic operation rules to:

$$\mathrm{lg}K_{ex} = lg\left(D_M\right) + lg\frac{[H^+]^n}{[HA]_{(o)}^n} + \mathrm{lg}\frac{1}{[NO_3^-]^{[m-n]}}$$

$$= lg\left(D_M\right) + lg\,[H^+]^n - \mathrm{lg}\ [HA]_{(o)}^n - \mathrm{lg}\,[NO_3^-]^{[m-n]}$$

$$= \mathrm{lg}\left(D_M\right) - (\mathrm{m-n})\mathrm{lg}\left([NO_3^-]\right) - n\mathrm{lg}\left([HA]\right) + n\mathrm{lg}\left([H^+]\right)$$

Rearranging the terms gives:

$$lgK_{ex} = \mathrm{lg}\left(D_M\right) - (\mathrm{m-n})\mathrm{lg}\left([NO_3^-]\right) - n\mathrm{lg}\left([HA]\right) + n\mathrm{lg}\left([H^+]\right)\#(10)$$

and：

$$\mathrm{lg}\left(D_M\right) = \mathrm{lg}\left(K_{ex}\right) + (\mathrm{m-n})\mathrm{lg}\left([NO_3^-]\right) + n\mathrm{lg}\left([HA]\right) - n\mathrm{lg}\left([H^+]\right)\#(S1)$$

Table S1 Topological parameters (a.u.) at the bond critical points (BCPs) of the complexes from QTAIM analysis at the theory level of B3LYP/ ECP60MWB/6-311G(d,p).

Complex	Bond	ρ	$\nabla^2\rho$	$H(r)$ (10^{-2})
HA	Pu-O_{amide1}	0.059	0.283	-0.124
	Pu-O_{amide2}	0.064	0.289	-0.343
	Pu-$O_{nitrate1}$	0.051	0.190	-0.183
	Pu-$O_{nitrate2}$	0.055	0.207	-0.264
	Pu-$O_{nitrate3}$	0.049	0.185	-0.133
	Pu-$O_{nitrate4}$	0.060	0.226	-0.378
HB	Pu-O_{amide1}	0.058	0.233	-0.253
	Pu-O_{amide2}	0.080	0.373	-0.930
	Pu-$O_{nitrate1}$	0.055	0.213	-0.223
	Pu-$O_{nitrate2}$	0.056	0.228	-0.207
	Pu-$O_{nitrate3}$	0.048	0.188	-0.104
	Pu-$O_{nitrate4}$	0.060	0.228	-0.349

O_{amide1} and O_{amide2} refer to the coordinating amide carbonyl oxygen atoms from the two respective ligands in the 2:1 extraction complex. $O_{nitrate1}$ to $O_{nitrate4}$ represent the four coordinating oxygen atoms originating from the two bidentate nitrate ions in the inner coordination sphere.

Table S2 The molecular orbitals energy of the free ligands（eV）

Ligand	HOMO	LUMO	$\Delta Gap_{Homo\text{-}LUMO}$
HA	-6.46	-0.37	6.09
HB	-6.33	-0.26	6.07

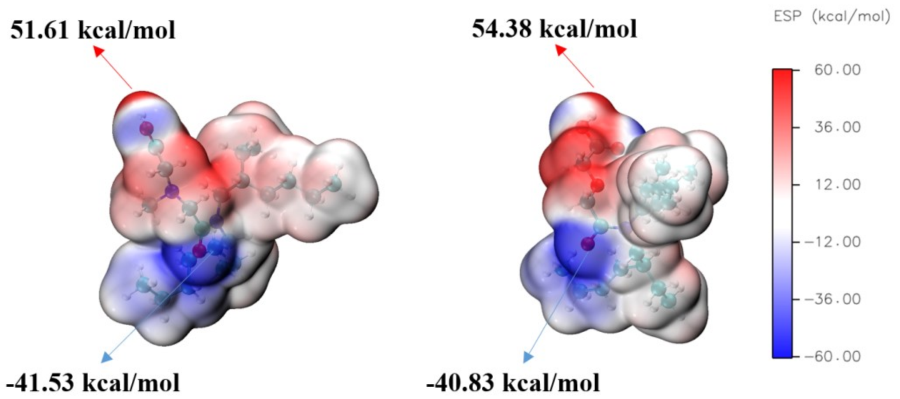

Fig. S4 The ESP map of the free ligands (left: HB; right: HA)

References

1. Dhawa A, Ravi J, Puspalata R, et al. New Journal of Chemistry, 2024, 48(1): 281-299. DOI:10.1039/D3NJ02840B.