Electronic Supplementary Material (ESI) for RSC Advances.

Supplementary Information

Highly selective extraction of tetravalent plutonium from complex system with novel phenylpyridine diamide ligands

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1. Synthesis routes

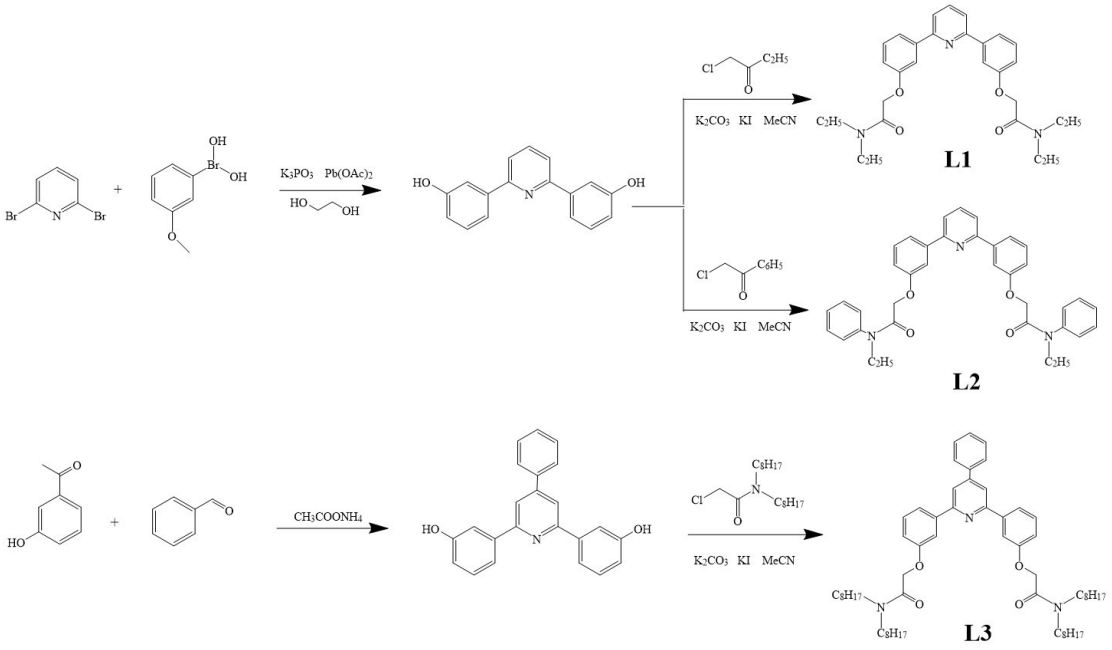


Fig. S1 Synthesis routes of **L1** (PPEA), **L2** (PEPA), and **L3** (PPOA)

L1 (PPDA) and L2 (PEPA)

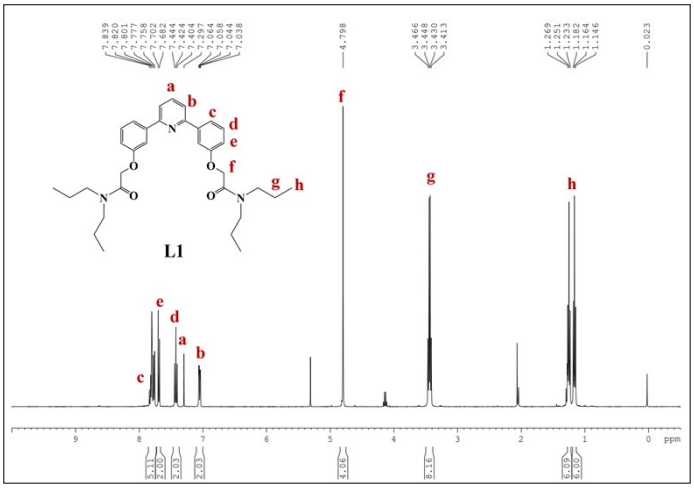
2,6-Dibromopyridine (10.39 g), dihydroxy(3-methoxyphenyl)-bromane (20 g), and potassium phosphate (27.93 g) were added to ethylene glycol (350 mL) under the protection of an Ar atmosphere. After stirring for 5 min, palladium acetate (0.057 g) was added and reacted at 80 °C for 3 h. Once the solution had cooled to 25 °C, ethyl

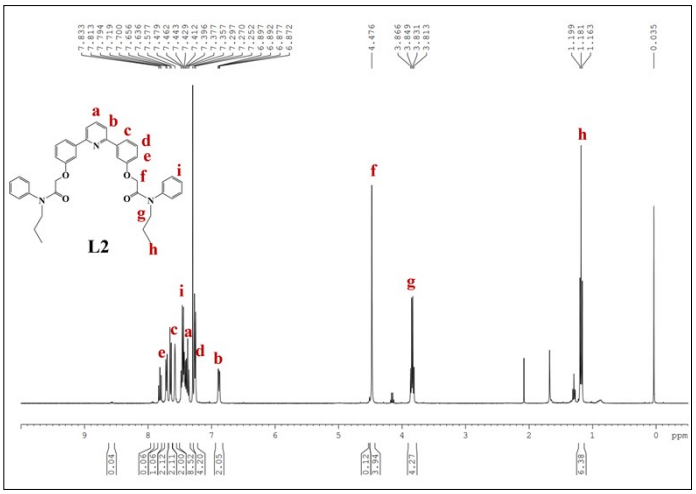
acetate (500 mL) was added. The mixture was washed three times with saturated salt water to obtain intermediate product **A**(2,6-bis(3-methoxyphenyl)pyridine). Subsequently, pyridine hydrochloride (22.5 g) was heated and melted in an Ar atmosphere, followed by the addition of compound **A** (4.6 g). The reaction was carried out at 200 °C for 16 h. Then, the reaction solution was poured into ice water and stirred thoroughly to obtain intermediate product **B**(3,3'-(pyridine-2,6-diyl)diphenol). Next, potassium carbonate (15.74 g) and potassium iodide (3.2 g) were added to acetonitrile (200 mL) with constant stirring for 15 min. Then, compound **B** (10 g) was added with continuous stirring at room temperature for 30 min, followed by the addition of chloroacetamide. The reaction was carried out at 85 °C for 16 h. Finally, after washing with saturated salt water, the organic phase was separated and purified through a column to obtain 2,2′-((pyridine-2,6-diylbis(3,1-phenylene))bis(oxy))bis(*N*,*N*-diethylacetamide) (PPEA, **L1**) and 2,2′-((pyridine-2,6-diylbis(3,1-phenylene))bis(oxy))bis(*N*-ethyl-*N*-phenylacetamide) (PEPA, **L2**).

L3 (PPOA)

Benzaldehyde (6.12 mL), 3-hydroxyacetophenone (16.33 g), and ammonium acetate (60 g) were added to glacial acetic acid (150 mL) and refluxed for 3 h. Then, the product was dissolved in ether and extracted with water (10 mL) three times. After the organic phase was removed, the product was recrystallized with an ether/petroleum ether mixture (1:1, v/v) and dried at 30 °C to obtain intermediate product **A** (3,3′-(4-phenylpyridine-2,6-diyl)diphenol). Next, potassium carbonate (15.74 g) and potassium iodide (3.2 g) were added to acetonitrile (200 mL) and stirred for 15 min. Subsequently, intermediate product **A** (13 g) was added with stirring at room temperature for 30 min, followed by the addition of chloroacetyl-di-*n*-octylamine (26 g). The reaction was carried out at 85 °C for 16 h. Finally, after washing with saturated salt water, the organic phase was separated and purified through a column to obtain 2,2′-(((4-phenylpyridine-2,6-diyl)bis(3,1-phenylene))bis(oxy))bis(*N*,*N*-dioctylacetamide) (PPOA, **L3**).

2. Characterization





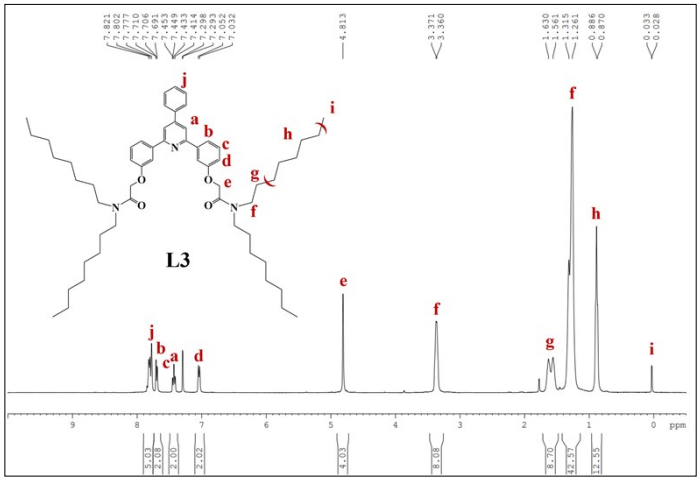


Fig. S2 ^{1}H NMR spectra of **L1** (PPEA), **L2** (PEPA), and **L3** (PPOA) in $CDCl_3$.

Characterization data: ^{1}H NMR (400 MHz, $CDCl_3$, ppm)

3. Solvent extraction

Table S1 Pu(IV) stripping efficiency of **L1** (PPEA) in 1-(trifluoromethyl)-3-nitrobenzene using five stripping agents

Stage	Stripping agent				
	0.2 M DMHAN–0.1 M MMH	0.2 M HNO_3	0.1 M EDTA–0.5 M HNO_3	0.2M $H_2C_2O_4$–0.5 M HNO_3	0.2 M AHA–0.5 M HNO_3
1	85.4%	82.3%	83.4%	77.1%	83.2%
2	73.6%	74.2%	81.2%	69.4%	81.4%
3	78.9%	77.8%	71.1%	71.4%	76.5%
Total after 3 stages	99.2%	99.0%	99.1%	98.0%	99.3%

Table S2 Pu(IV) stripping efficiency of **L3** (PPOA) in 1-(trifluoromethyl)-3-nitrobenzene using five stripping agents

Stage	Stripping agent				
	0.2 M DMHAN–0.1 M MMH	0.2 M HNO_3	0.1 M EDTA–0.5 M HNO_3	0.2M $H_2C_2O_4$–0.5 M HNO_3	0.2 M AHA–0.5 M HNO_3
1	82.5%	81.6%	77.5%	72.5%	81.8%
2	72.1%	73.5%	83.2%	65.3%	72.5%
3	80.6%	80.3%	81.9%	76.8%	80.2%
Total after 3 stages	99.1%	99.0%	99.3%	97.8%	99.0%

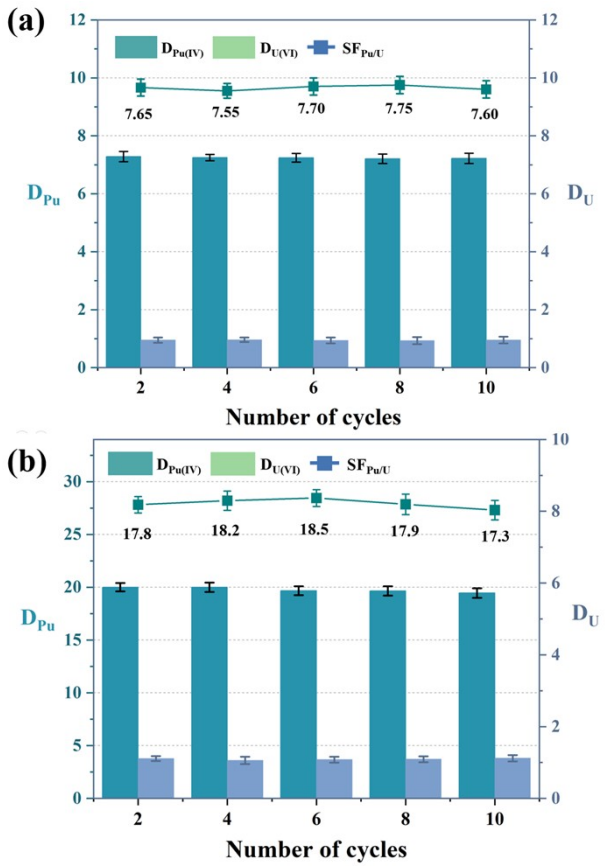


Fig. S3 Reusability of extractants (a) **L2** (PEPA) and (b) **L3** (PPOA). Organic phase: 0.05 M ligand in 1-(trifluoromethyl)-3-nitrobenzene; aqueous phase: 3 M HNO_3, 5 mg/L Pu(IV), and 1 g/L U(VI).

4. Radiation stability

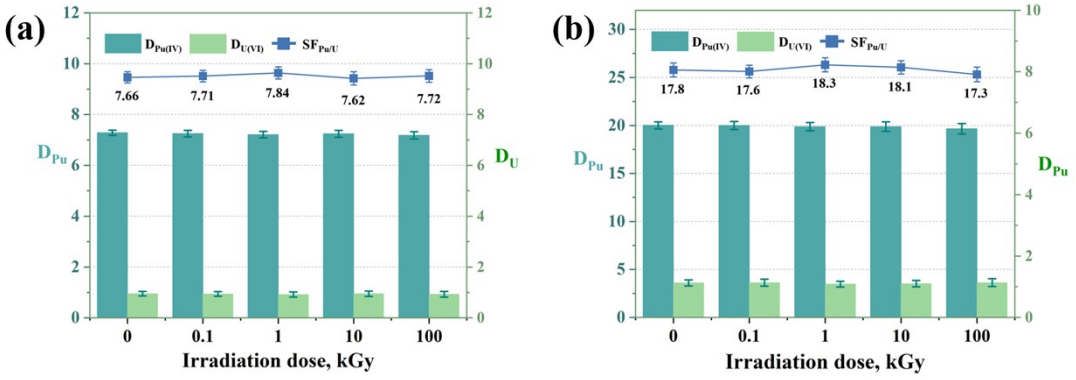


Fig. S4 Extraction of Pu(IV) and U(VI) using ligands (a) **L1** (PPEA) and (b) **L3** (PPOA) exposed to different γ radiation doses. Organic phase: 0.05 M ligand in 1-(trifluoromethyl)-3-nitrobenzene; aqueous phase: 3 M HNO_3, 5 mg/L Pu(IV), and 1 g/L U(VI).