Key Words

ligand

separation

extraction

phenanthroline

hydrophillic

acidity

lanthanides

actinides

complexes

coordination

Objective

1. Develop a Hydrophillic Phenanthroline-Based Ligand: The primary objective was to design and synthesize a carboxylic group-modified phenanthroline-diimide ligand that can efficiently separate Americium (Am(III)) from Lanthanides (Lns(III)) under high acidity conditions (over 1.5 M HNO3).

2. Overcome Limitations of Existing Ligands: Address the challenges associated with existing hydrophilic ligands, such as harsh preparation conditions, inferior extraction performances, limited available chemical structures, and incapability of extraction under high acidity.

3. Demonstrate Selectivity and Efficiency: Demonstrate the new ligand's superior selectivity and separation capabilities for Lns(III)/Ans(III) and Ans(III)/Ans(III) under high acidity, particularly aiming for high separation factors for Eu(III)/Am(III) and Cm/Am.

4. Utilize Crystal Engineering: Use crystal engineering approaches to create unique dimeric architectures for Eu(III) complexes, which could be the origin of the ligand's outperforming selectivity

and acid resistance.

5. Facilitate Sustainable Nuclear Fuel Cycle: Provide a greener synthetic procedure that is straightforward for mass production, ensuring high crystallinity, chemical stability, and superior extraction kinetics/performances, ultimately contributing to the sustainable development of nuclear energy by closing the nuclear fuel cycle.

Methodology

1. Ligand Synthesis:

- Synthesized the dibutyric acid functionalized phenanthroline diimide ligand (Phen-2DIBA).

- Mixed N-hydroxysuccinimide activated phenanthroline dicarboxylic precursor with 4-aminobutyric acid in dimethyl sulfoxide (DMSO) at room temperature.

- Added a catalytic amount of triethylamine and stirred overnight.

- Poured the mixture into water to quench the reaction.

- Acidified with hydrochloric acid to obtain belt-like crystals.

- Verified chemical structure using 1H and 13C NMR and HRMS.

2. Solvent Extraction Behaviors:

- Demonstrated solvent extraction behaviors by using Phen-2DIBA as the aqueous masking agent in combination with TODGA in dodecane as the organic phase.

- Conducted initial screening of acid concentration.

3. UV-Vis Absorption Spectroscopy Titrations:

- Performed titrations in 0.01 M HNO_3 with ion strength controlled by 0.1 M $NaNO_3$.

- Monitored peak shifts indicating metal-ligand interaction

4. Data Fitting with HypSpec Program

- Fitted data to derive species evolution during titration.

- Confirmed dominant species using ESI-MS.

5. 1H NMR Titrations:

- Conducted titrations using La(III) and Lu(III) ions due to their radius differences and diamagnetic nature.

- Analyzed shifts in aromatic peaks and alkyl chain peaks to confirm species formation.

6. Stability Tests:

- Monitored stability of the ligand and related species under high-acidity conditions using NMR spectroscopy over one week.

7. Coordination Mode Analysis:

- Used IR spectra and single-crystal X-ray diffraction to elucidate coordination modes.

- Observed characteristic peak shifts and complexation behavior.

8. Time-Resolved Laser Fluorescence Spectroscopy (TRLFS) Titrations:

- Conducted TRLFS titrations to confirm true coordination in the extraction process under high acidity.

- Monitored characteristic Eu(III) emission and calculated water molecules around the Eu(III) center.

9. Synthesis Procedure for Phen-2DIBA:

- Followed a straightforward, scalable synthetic procedure without using corrosive reagents.

- Achieved high crystallinity and chemical stability of the ligand.

10. Experimental Conditions:

- Used various experimental conditions, such as ligand and metal concentrations, solvents, and titration conditions, to thoroughly investigate the extraction and coordination behaviors.

Key Findings

Ligand Synthesis

Synthesis and Characterization

- Synthesized a dibutyric acid functionalized phenanthroline diimide ligand (Phen-2DIBA).

- High crystallinity and straightforward mass production confirmed by NMR and HRMS.

- Phen-2DIBA demonstrated solubility and stability in high-acidity conditions (1.5 M HNO3).

Solvent Extraction Behaviors

Extraction Performance:

- Phen-2DIBA used as an aqueous masking agent with TODGA in dodecane.

- High separation factor (SFEu/Am) of about 50 in 1.5 M HNO3.

- Unoptimized results outperformed previously reported ligands.

Coordination and Cpmplexation

UV-Vis Absorption and TRLFS Titrations

- UV-Vis absorption indicated metal-ligand interaction.

- TRLFS titrations confirmed true coordination in high-acidity conditions.

- Lifetimes of Eu(III) emission peaks increased with ligand addition, confirming 1:1 complexation.

NMR and ESI-MS Analyses

- NMR titrations with La(III) and Lu(III) confirmed 1:1 species in aqueous phase.

- Stability of ligand and metal-ligand species under high acidity confirmed by NMR spectroscopy.

Single-Crystal X-ray DIffraction

- Revealed eight-oxygen, two-nitrogen coordination architecture.

- Relatively hydrophobic environment in the bridging zone increased complex stability.

Stability Tests

Long-term Stability:

- Phen-2DIBA demonstrated stability in 1.5 M HNO3 over one week.

- High crystallinity and chemical stability confirmed by powder X-ray diffraction.

Conclusion

Summary of Achievments

- Developed a simple yet efficient carboxylic group modified hydrophilic phenanthroline-based tetradentate N,O-ligand.

- Displayed superior Lns(III)/Ans(III) and Ans(III)/Ans(III) separation capabilities under high acidity (over 1.5 M HNO3).

- Achieved high separation factors (SFEu/Am of 120 and SFCm/Am of 4.4).

- Coordination behaviors revealed a metal/ligand ratio of 1 in solution extraction process.

- Demonstrated the bifunctional role of carboxylic groups in ligand design and stability.

Implications for Future Research

- Current ligand design can inspire new functional groups and coordination modes for efficient, high-acid-tolerant ligands.

- Provides a step toward closing the nuclear fuel cycle by improving separation processes.

Relevance to Study

Efficient Ligand Design: Developed a hydrophilic phenanthroline-based ligand (Phen-2DIBA) that demonstrates high selectivity for Am(III) over Eu(III) under high acidity (1.5 M HNO3) .

Stability and Solubility: The ligand is stable and soluble in high-acidity environments, making it suitable for the harsh conditions encountered in nuclear fuel reprocessing .

High Separation Factors: Achieved high separation factors for Eu(III)/Am(III) and Cm(III)/Am(III), crucial for efficient partitioning in the nuclear fuel cycle .

Scalability and Green Synthesis: The ligand synthesis is straightforward, scalable, and environmentally friendly, which is essential for practical application in large-scale nuclear fuel reprocessing .

Coordination Behavior: Detailed analysis of coordination behavior with actinides and lanthanides provides insights into the mechanism of selectivity and stability, aiding the design of future ligands .

Versatility in Application: The ligand s performance in solvent extraction processes using TODGA as the organic phase shows its applicability in established reprocessing workflows .

Advanced Analytical Techniques: Utilized advanced techniques like UV-Vis absorption spectroscopy, TRLFS, NMR, and single-crystal X-ray diffraction to thoroughly characterize the ligand and its complexes, ensuring reliability and reproducibility of results .

Enhancement Over Existing Ligands: Demonstrated superior performance compared to existing hydrophilic ligands, highlighting the potential for improving current nuclear fuel reprocessing technologies

Acid Tolerance: The ligand s ability to function effectively in high-acid conditions is particularly relevant for handling high-level liquid waste in nuclear fuel reprocessing .

Implications for Sustainable Nuclear Energy: By improving the separation of minor actinides, this ligand contributes to the goal of closing the nuclear fuel cycle, thereby supporting the sustainable development of nuclear energy .

Critical Parameters Identified

High Importance

Chemical Stabilty

- Stability in High Acidity: The ligand (Phen-2DIBA) demonstrated stability in 1.5 M HNO3 over one week.

- Resilience in Harsh Conditions: High crystallinity and chemical stability confirmed by NMR and powder X-ray diffraction.

Radiolysis Resistance: Not Directly Addressed: The study did not explicitly test or discuss radiolysis resistance, though it is implied that the ligand's stability under high-acidity conditions may also contribute to its resistance to radiolysis.

Thermodynamics:

- High Separation Factors: Achieved high separation factors (SFEu/Am of 120 and SFCm/Am of 4.4) indicating favorable thermodynamic properties for selective binding and separation of metal ions.

- Coordination Behavior: Detailed analysis of the coordination behaviors of the ligand with Eu(III) and Am(III) suggests strong and selective binding, further indicating favorable thermodynamics.

Medium Importance

Kinetics

- Fast Extraction Kinetics: The coordination of Phen-2DIBA with Eu(III) and Am(III) reached equilibrium in about 5 minutes, demonstrating efficient forward kinetics.

Loading Capacity: Not Explicitly Discussed: The study does not provide specific data on the loading capacity of the ligand.

Operational Condition Range:

- Functionality in High Acidity: The ligand operates effectively in a high-acidity environment (1.5 M HNO3), demonstrating its ability to function under a broad range of conditions.

Low Importance

Solubilty

- Solubility in Acid: Phen-2DIBA is soluble in HNO3 with concentrations higher than 1.25 M, which is essential for its application but can be managed through solvent selection.

Dispersion Numbers: Not Discussed: The study does not address dispersion numbers

Phase Disengagament: Not Discussed: The study does not address phase disengagement directly, though the practical separation using the ligand in combination with TODGA in dodecane indicates its application in phase separation processes.