# Terpyridine-Based Extracting Agents for High-Level Nuclear Waste Treatment

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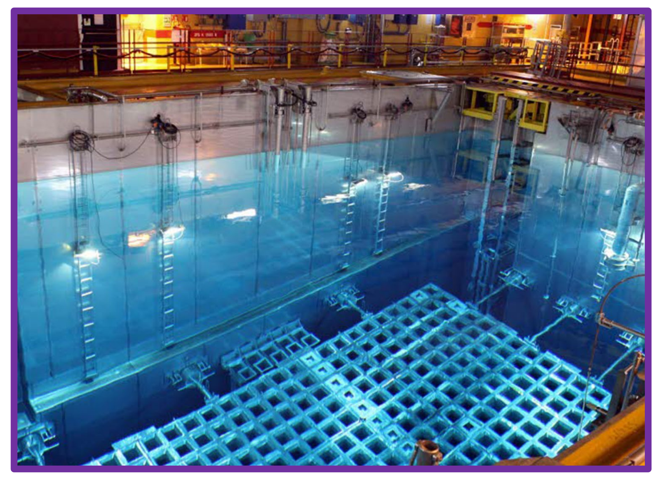
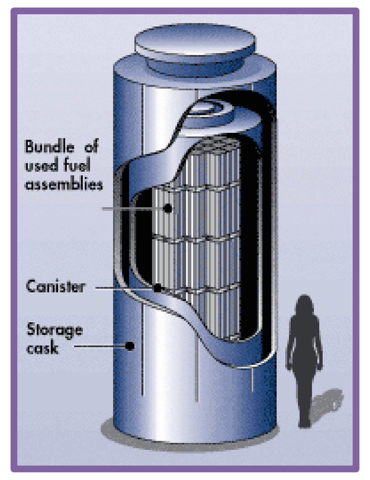
## THE WASTE ISSUE

- Nuclear power generates 18.2% US electricity and contributes 10% to global energy production[1]
- Spent reactor fuel rods are removed and cooled in water producing radioactive water[2]
- Radioactive material is transferred to "dry casks" made of stainless steel and concrete for safer storage and kept onsite[3]
- No national repository for commercial waste, creating a need for more reprocessing techniques[3]






*A spent fuel cooling pool (left) [2] and dry cask storage container (right) [3]*

## PROBLEM STATEMENT

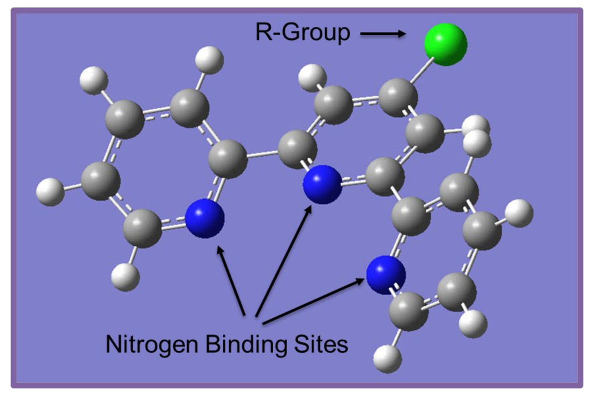
- Research potential extracting agents for extraction of usable actinide material from nuclear waste (molecular reprocessing)
- Optimize physical and thermodynamic properties by using computational software
- Compare metrics across all extracting agent simulations and give appropriate recommendations for future research

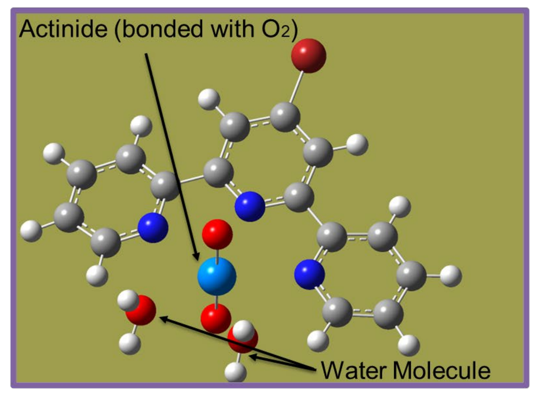
## REQUIREMENTS

| # | Description |
|---|---|
| 1 | Thermodynamic analysis of the reaction should be obtained to produce a quantifiable change in free energy (in kJ/mol). |
| 2 | Each ligand should have a distinct difference in the reaction energy required for each actinide (at least 200 kJ/mol). |
| 3 | The geometry (actinide and bonding agent distance in Angstroms, dihedral angles of benzene rings) of the ligand should be mathematically optimized. |
| 4 | The electronic effects of the R-Group on Terpyridine result in a dipole moment above 4 debyes when unbonded. |
| 5 | All reaction simulations should be defined in a practical, real-life environment. This means that both the ligands and actinides are submerged in water. |
| 6 | Cost and feasibility of production analysis of each ligand studied should be obtained via research. |
| 7 | A moving model (digitally animated or physical) should be created for use in academic presentations. |

## TERPYRIDINE

- TERPY (2,2':6',2"-terpyridine) is a tridentate heterocyclic ligand in coordination chemistry[4]
- Binding sites that form a "pincer" formation around metals and actinides[5]
- TERPY bonds with the actinide compound, separates it from water molecules[6]
- **Interchangeable R-groups** alter electronic effects that impact the molecule's bonding behaviors



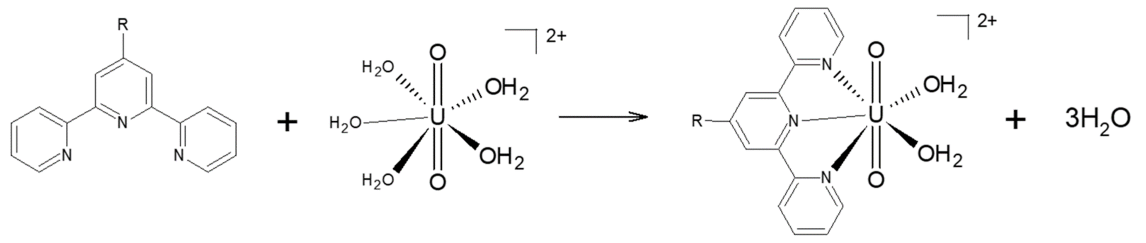

*Depictions of Terpyridine agent by itself and when bound to Actinide complex*

## SIMULATION PROCESS

- Gaussian 16 (a computational chemistry software) used to predict TERPY-actinide chelation reactions[7]
- Program utilizes computational chemistry and quantum mechanics to simulate reactions at the molecular level and provides data on atomic distances, energy levels, dipole moments, etc.

## ANALYSIS METRICS

- 11 TERPY variants simulated with U, Np and Pu
- Each TERPY variant was compared to unalerted TERPY-H, the control extracting agent
- Four assessment criteria:
  - Physical distance between actinide and nitrogen coordination sites (smaller distances indicate stronger attraction)
  - Change in Gibbs Free Energy (ΔG) of reaction (lower ΔG indicate greater reaction efficiency, larger ΔG gaps between actinides indicate greater potential for selectivity)
  - Dihedral angles between benzene rings (small angle variations during reaction indicates greater efficiency)
  - Dipole moment of the extracting agent (higher moments predict greater intermolecular attraction)

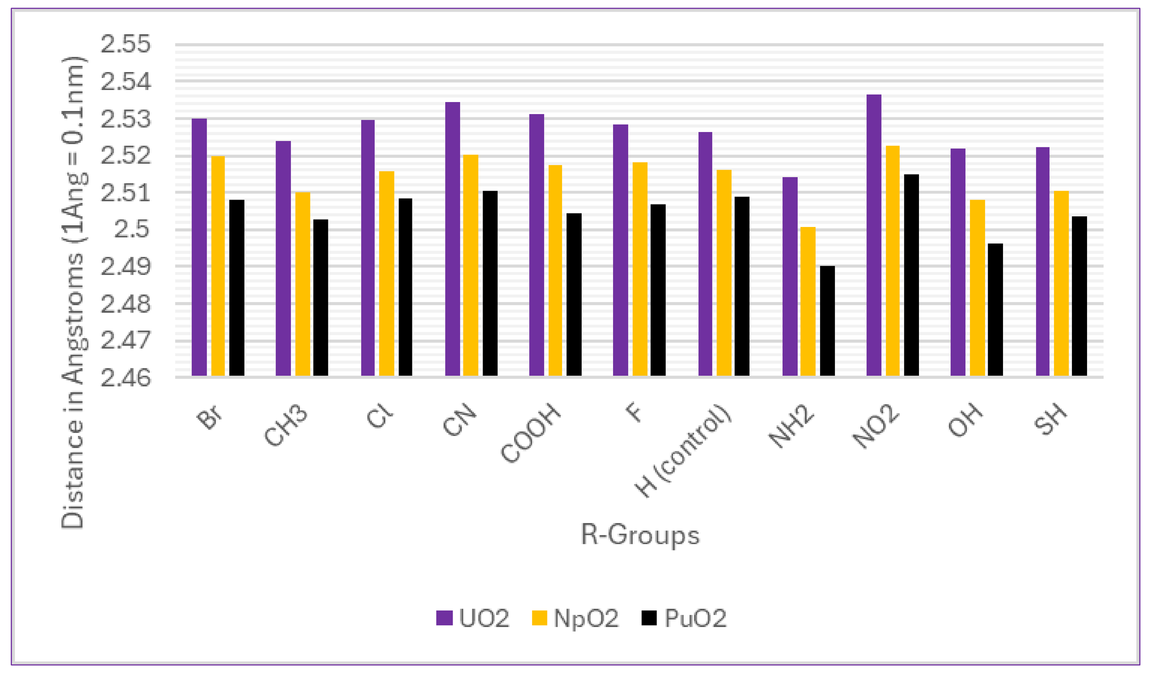



$$L + AnO_2(H_2O)_5 \Rightarrow AnO_2(L)(H_2O)_2 + 3H_2O$$

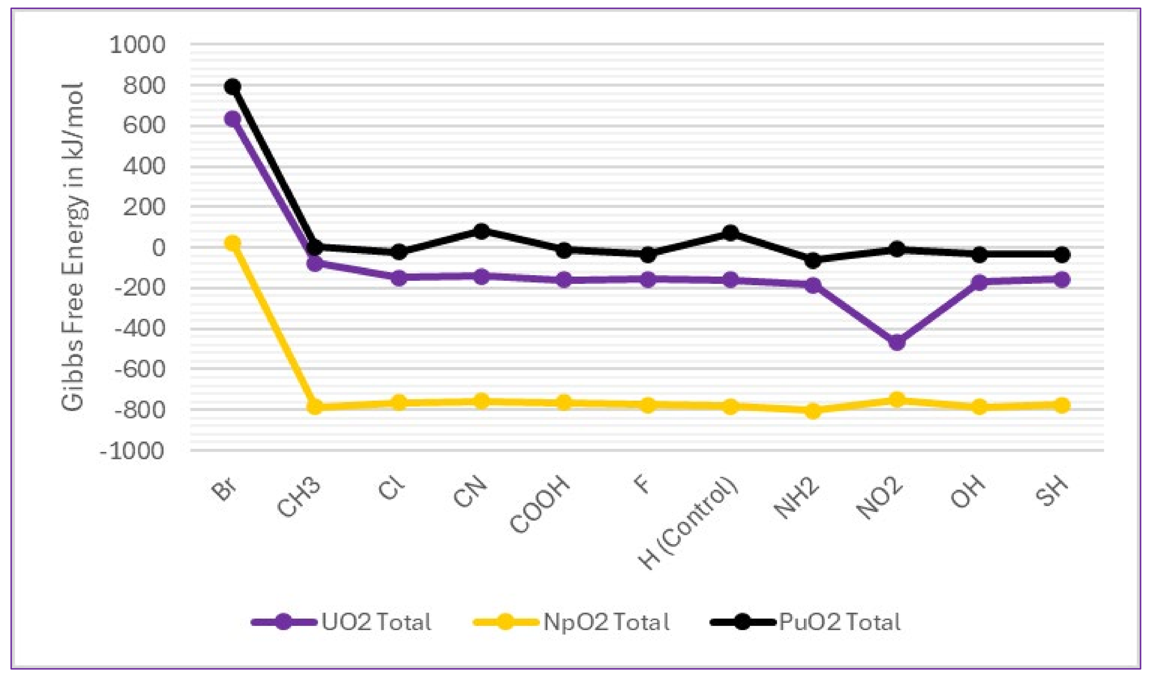
*A diagram depicting the chelation reaction between TERPY and the actinide uranium, paired with the chemical equation[6]*

## RESULTS

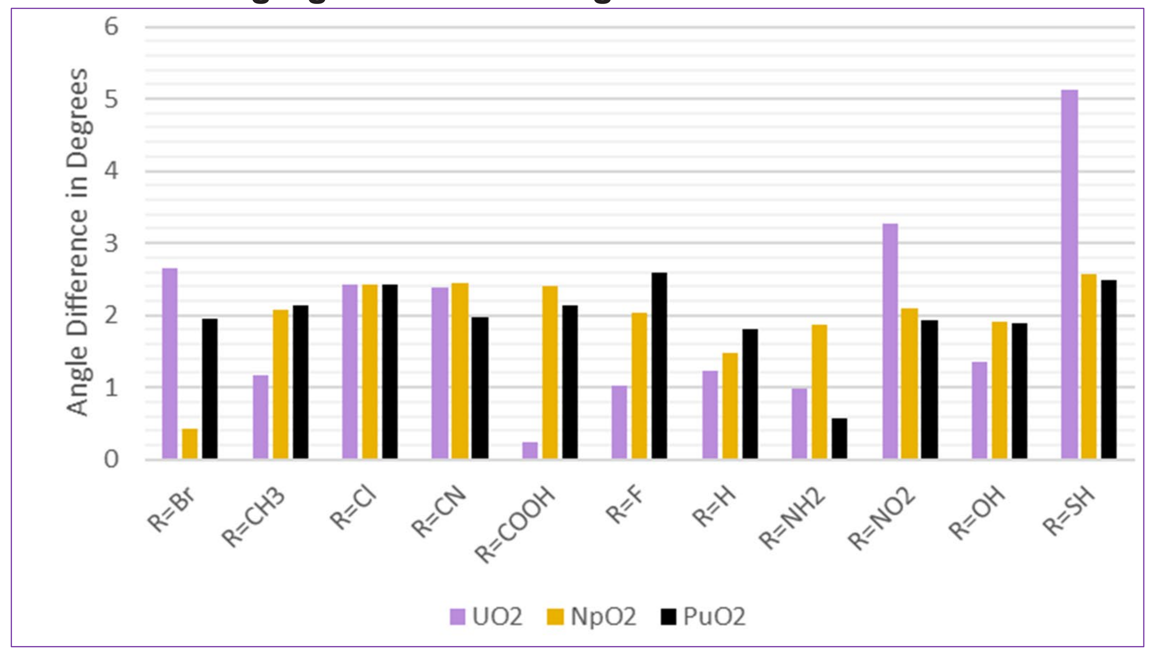
**Distance Between Extracting Agent Bonding Positions and Actinide Molecules**



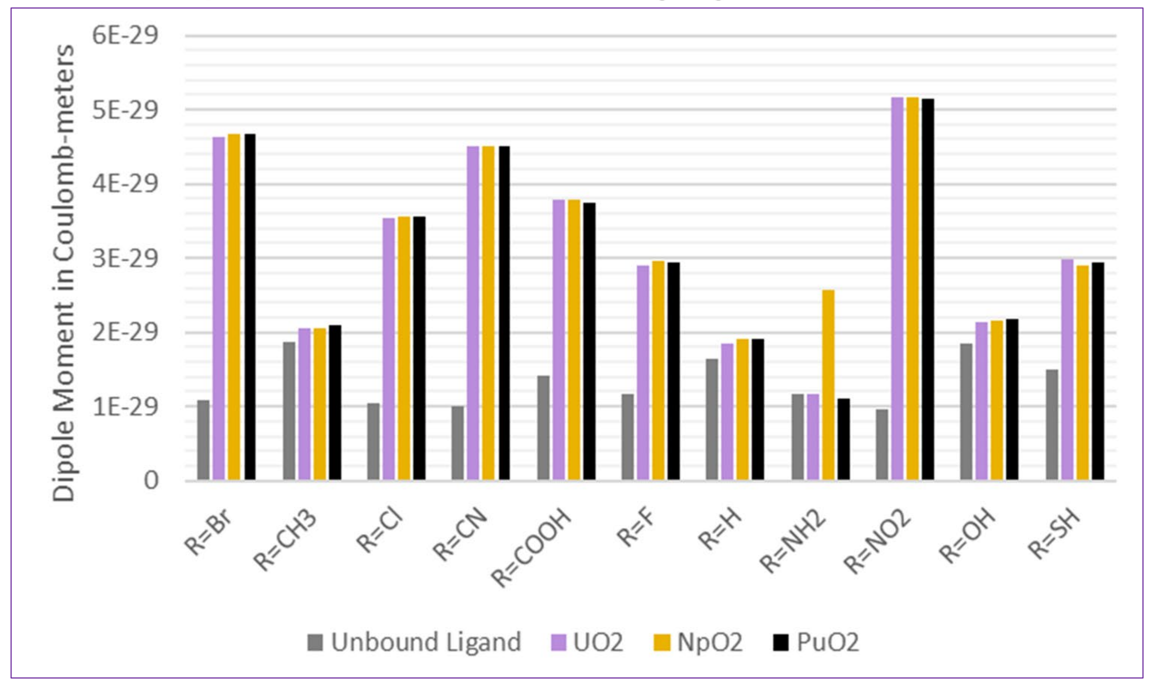

**Free Energy Change of Extracting Agent-Actinide Binding Process**




**Extracting Agent Dihedral Angles when Bound to Actinide**




**Dipole Moments of Extracting Agent Complexes**




## SUMMARY AND CONCLUSIONS

- Four TERPY variations considered as/more effective than standard terpyridine: $NH_2$, OH, $CH_3$, SH
  - Each showed low ΔG, shorter bond lengths, and minimized changes in dihedral angles
- Np selectivity is adequate, but selectivity between U and Pu may not be
- TERPY-$NO_2$ also notable for its free energy selectivity
- Overall, evidence supports the use of terpyridine-based extracting agents for actinides, but requires physical experimentation

## FUTURE WORK

Further cost analysis against current remediation options (PUREX, CSEX, etc.) is necessary to see if this implementation in industry is viable. Testing with other aqueous solutions, such as molten salts[8], is also advised, as nuclear reactors in operation diversify from PWRs.

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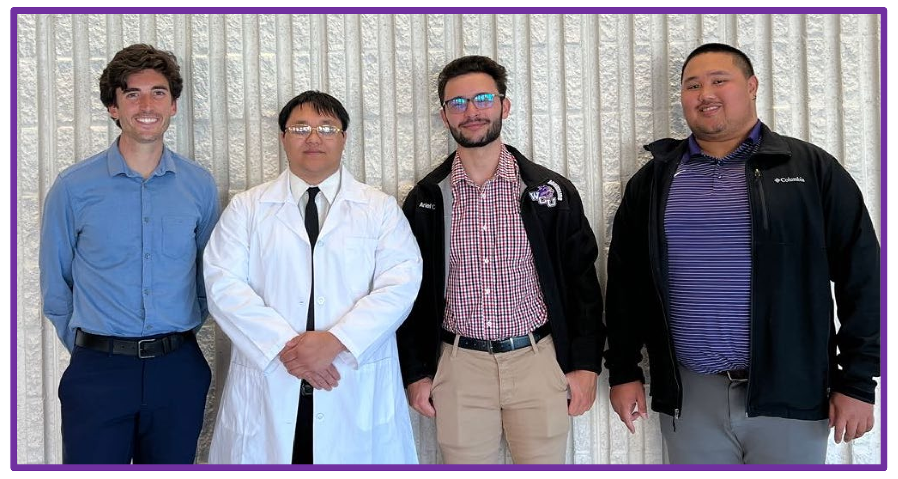
- Collaborator: Hayden Privette, BS Mathematics and BS Chemistry



*WCU Radiochemistry Team*

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