Sandia National Laboratories

SAND2018-9464PE

Salophen Schiff Base Sol-Gel Hybrid Material for the Aqueous Sequestration of Actinyl Ions

NSSC

PRESENTED BY

Jaclynn Unangst

PhD Candidate, University of California, Irvine
Department of Chemical Engineering and Materials Science
Advisors: Professor Mikael Nilsson and Professor Kenneth J. Shea

Hongwu Xu Team Meeting - 28th August, 2018

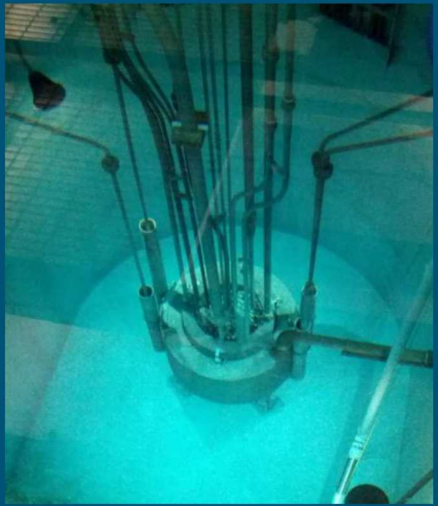
Sandia National Laboratories is a multimission laboratory managed and operated by National Technology & Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.

SAND No.

Nuclear Program at the University of California, Irvine

UC Irvine

UCI Campus TRIGA Reactor



Graduate Summer Internship at Sandia National Lab

June – August 2018

Nanoscale Sciences Department

Manager: Dr. Carlos Gutierrez

Senior Scientist Mentor: Dr. Tina Nenoff

Project: Actinide Sensors

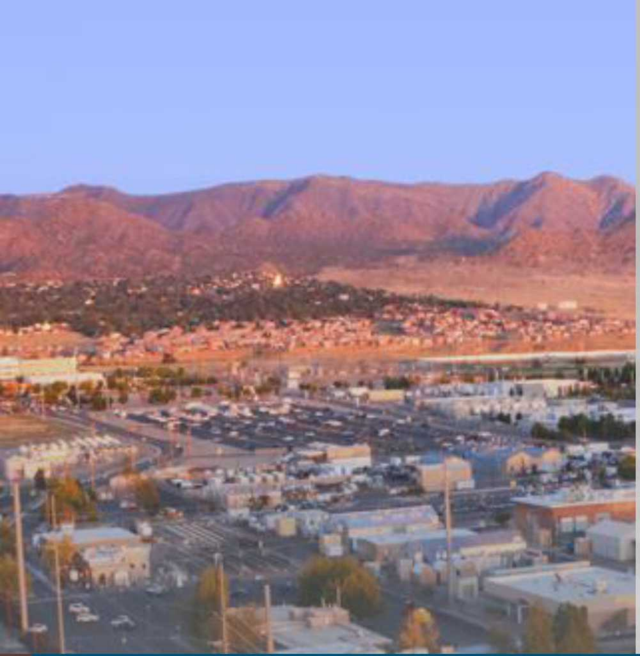
Today's Presentation

PhD thesis work conducted at UCI

- **Develop of nonsymmetrical ligand for actinyl ion uptake as a hybrid material**
  - Incorporate ligand into silica sol-gel hybrid material
  - Test hybrid material for uptake of actinyl ions including U and Np
- **Develop bridged polysilsesquioxane (BPS) hybrid material with ligand for enhanced hybrid material performance under radiolytic conditions**

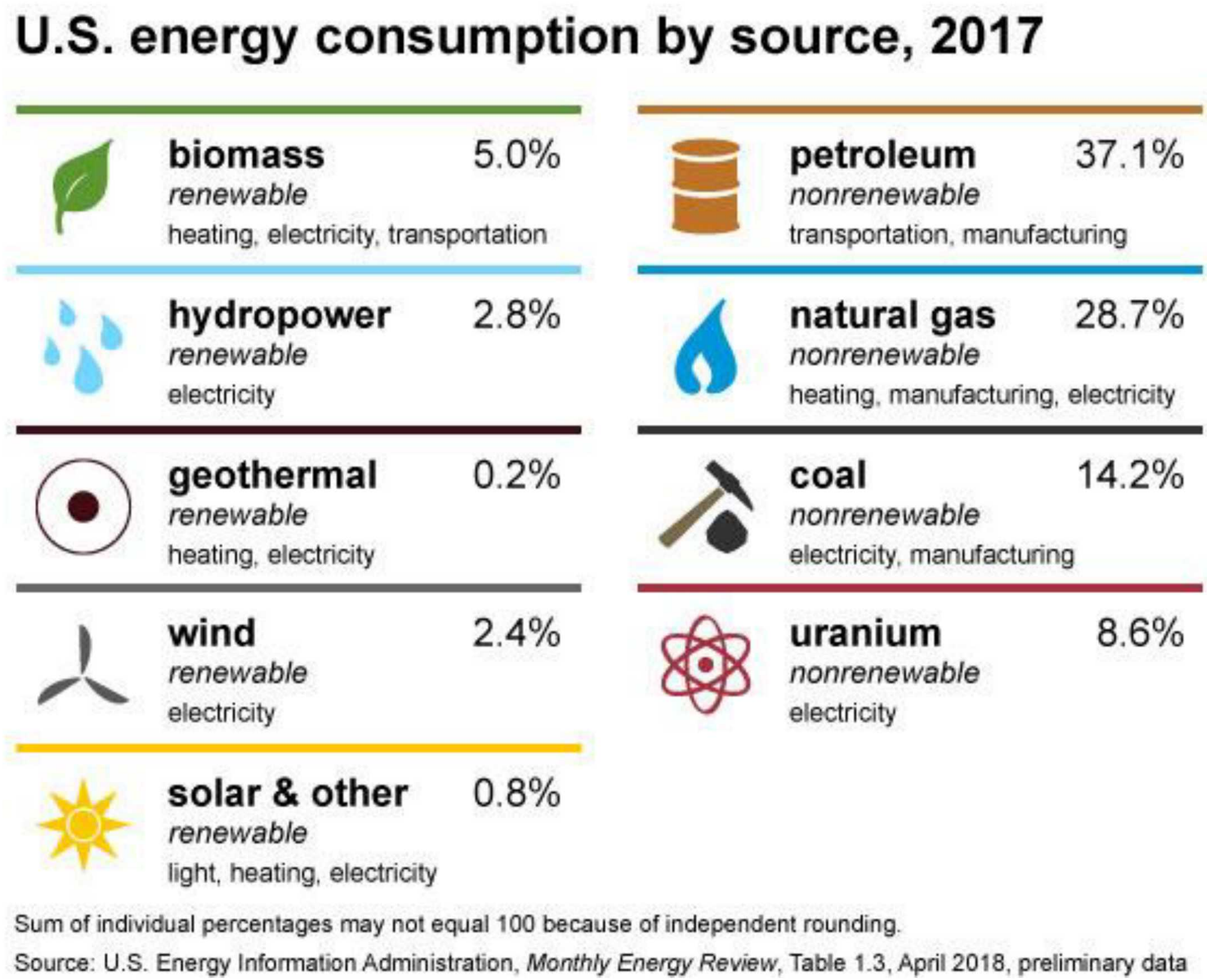
PhD thesis work conducted at SNL

- **Formulate ligand into optical sensor for the detection of actinyl ions in aqueous solutions using UV-Vis, FTIR and Impedance analysis**



Designing a Hybrid Material for Actinyl Ion Uptake

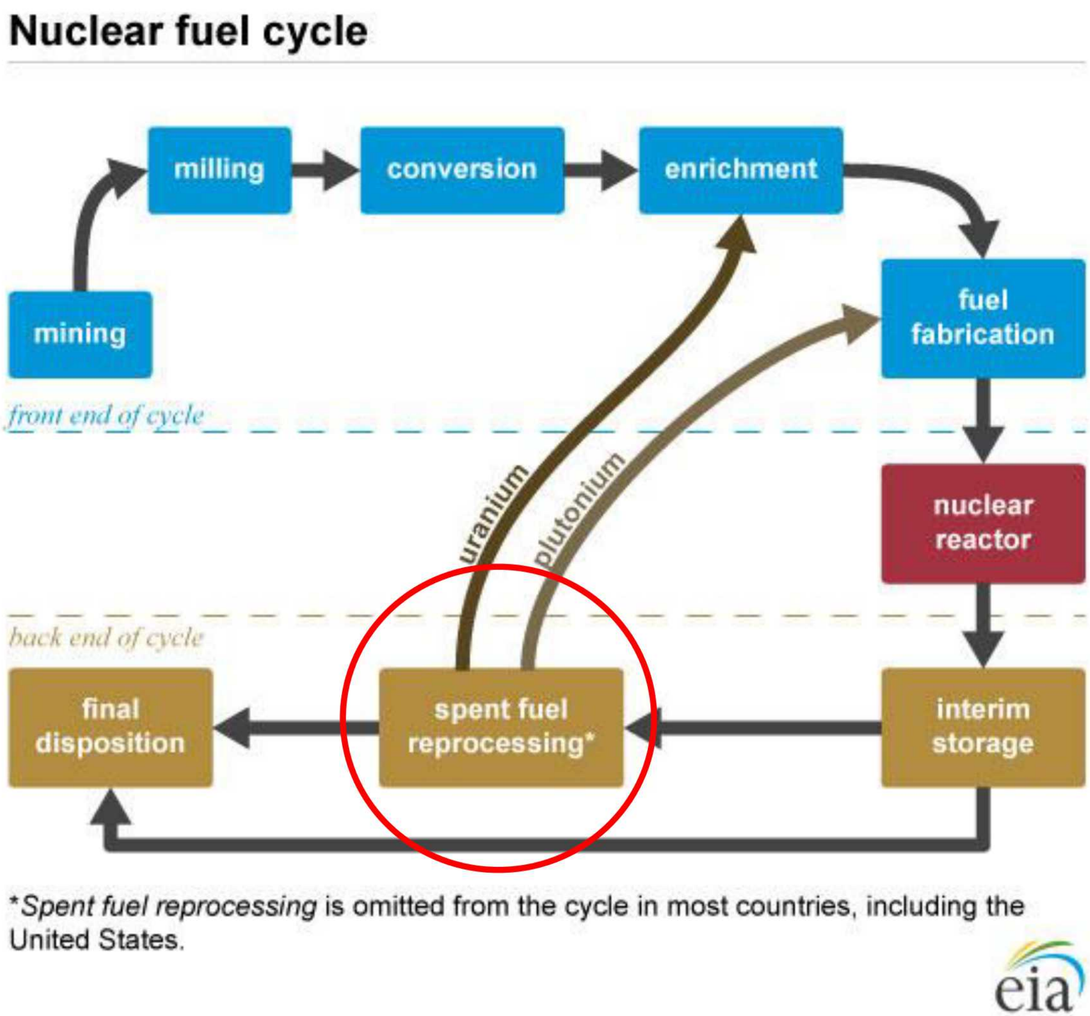
Although nonrenewable, nuclear has the potential to sustain a green energy future



The Nuclear Research of Nilsson Group at UCI

- **Solvent extraction** of actinides and lanthanides for reprocessing of spent nuclear fuel
  - Experimentation with novel ligands, synergistic effects, MD simulation, on-line monitoring and centrifugal contactors
- **Resin and sensor** development for actinides and lanthanides
- **Radiolysis** of solvent extraction components
- **Medical isotopes** utilizing radioactive lanthanides
- **Radiation detectors** for beta and gamma particles

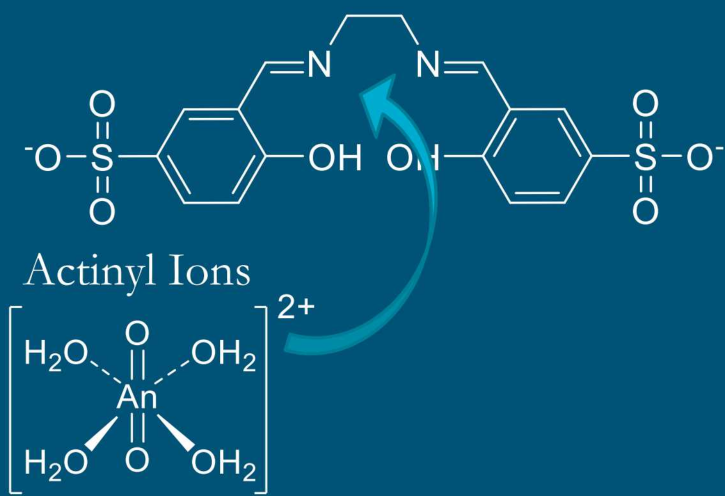
Mission: Separate fission products in SNF from fissile actinides to be reused as fuel



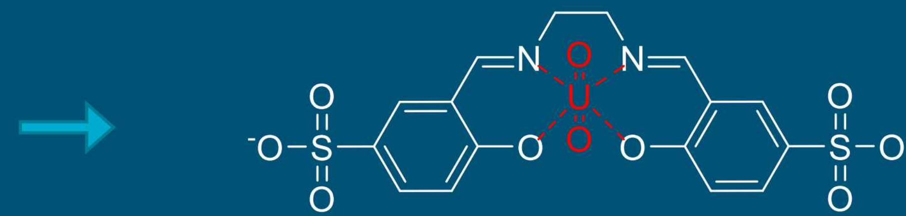
Schiff Base Ligand as Aqueous Holdback Reagent: **Solvent Extraction of Actinides**

Sulfonated Salen Schiff Base

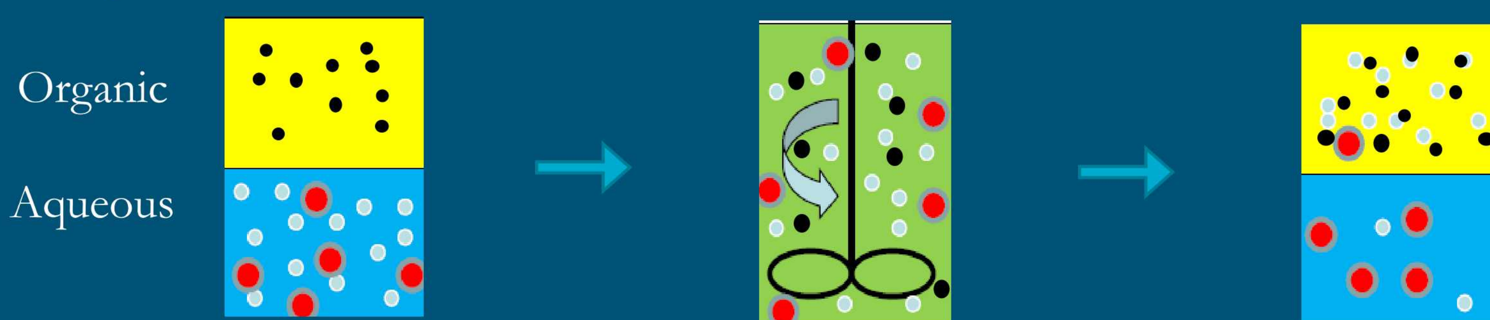
Sulfonated Salen Schiff Base Post Extraction of UO_2^{2+}



An = U, Np, Pu, Am

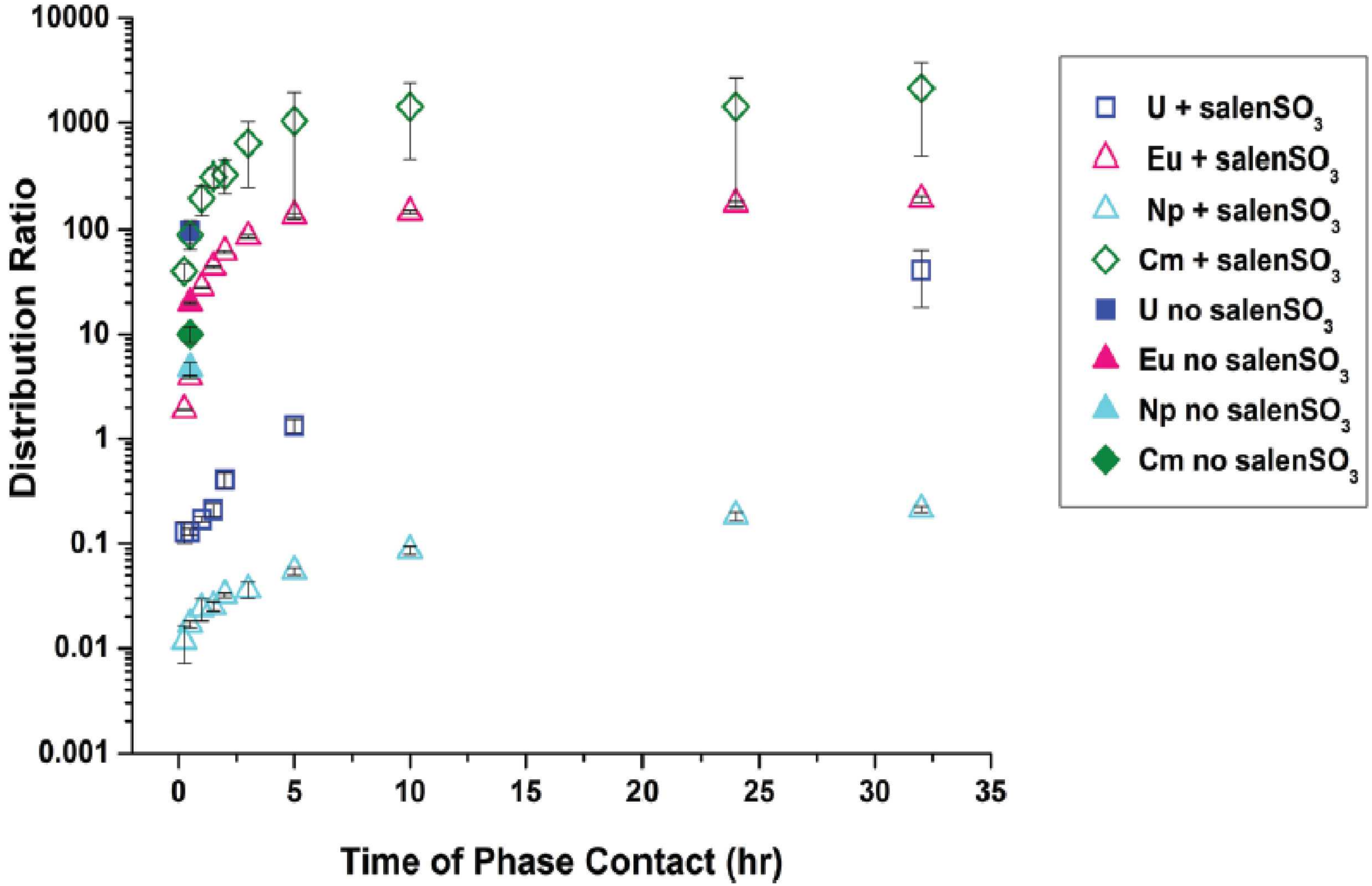


- Chelator in organic phase
- Schiff Base + UO_2^{2+} Ions
- Fission Products



Hawkins, C. H. *et al. Dalton Trans.*, 2016, 45, 15415–15426

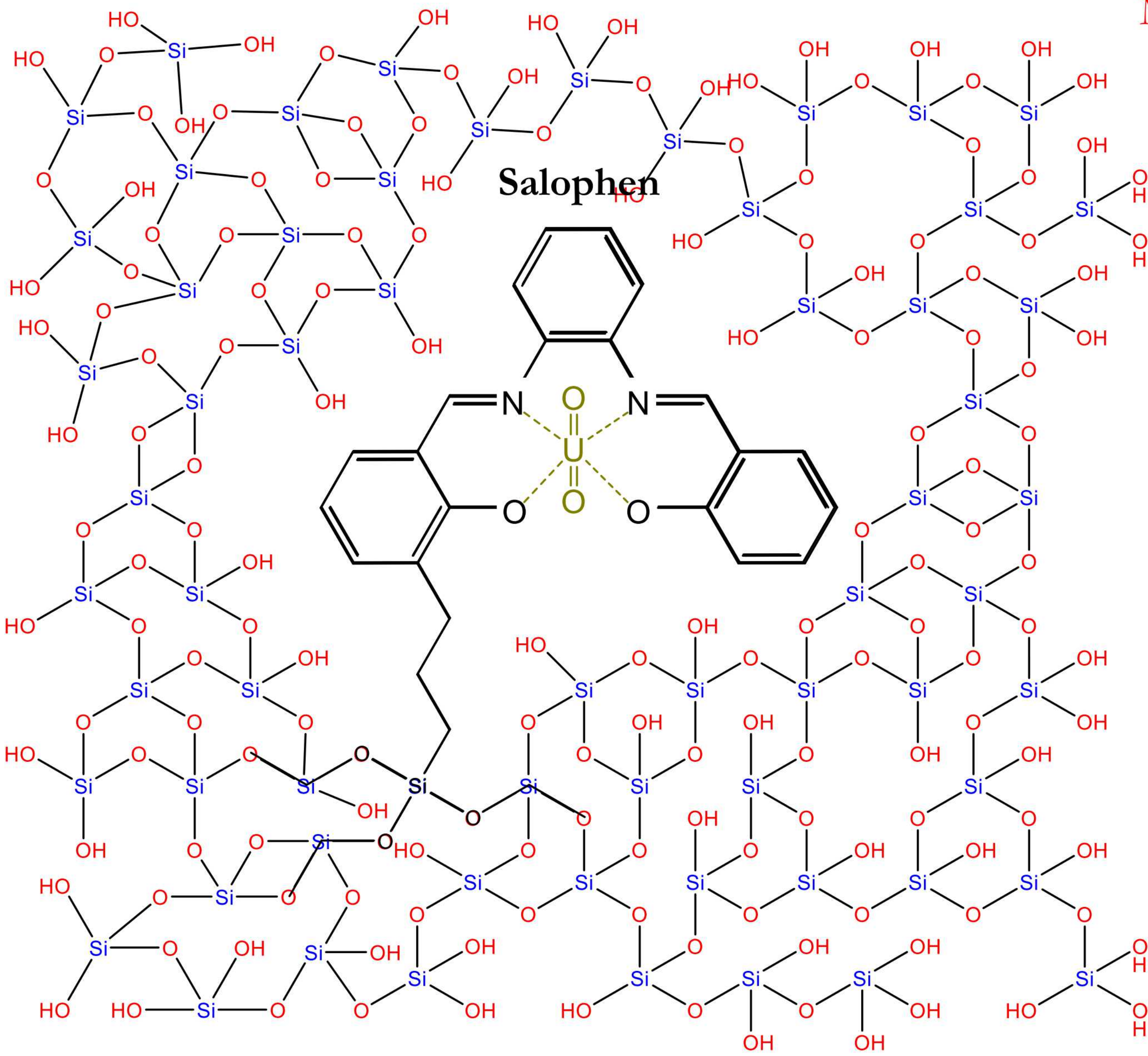
Schiff Base Ligand Selectivity for Linear Dioxo Actinides



Solvent extraction of actinide (V/VI) species of U and Np verses lanthanide and actinide (III) species in aqueous solution in the presence of aqueous Schiff base ligand holdback reagent

Hawkins, C. H. *et al.* *Dalton Trans.*, 2016, 45, 15415–15426

Schiff Base Ligand as Solid Support Material: Aqueous Sequestration of Actinides



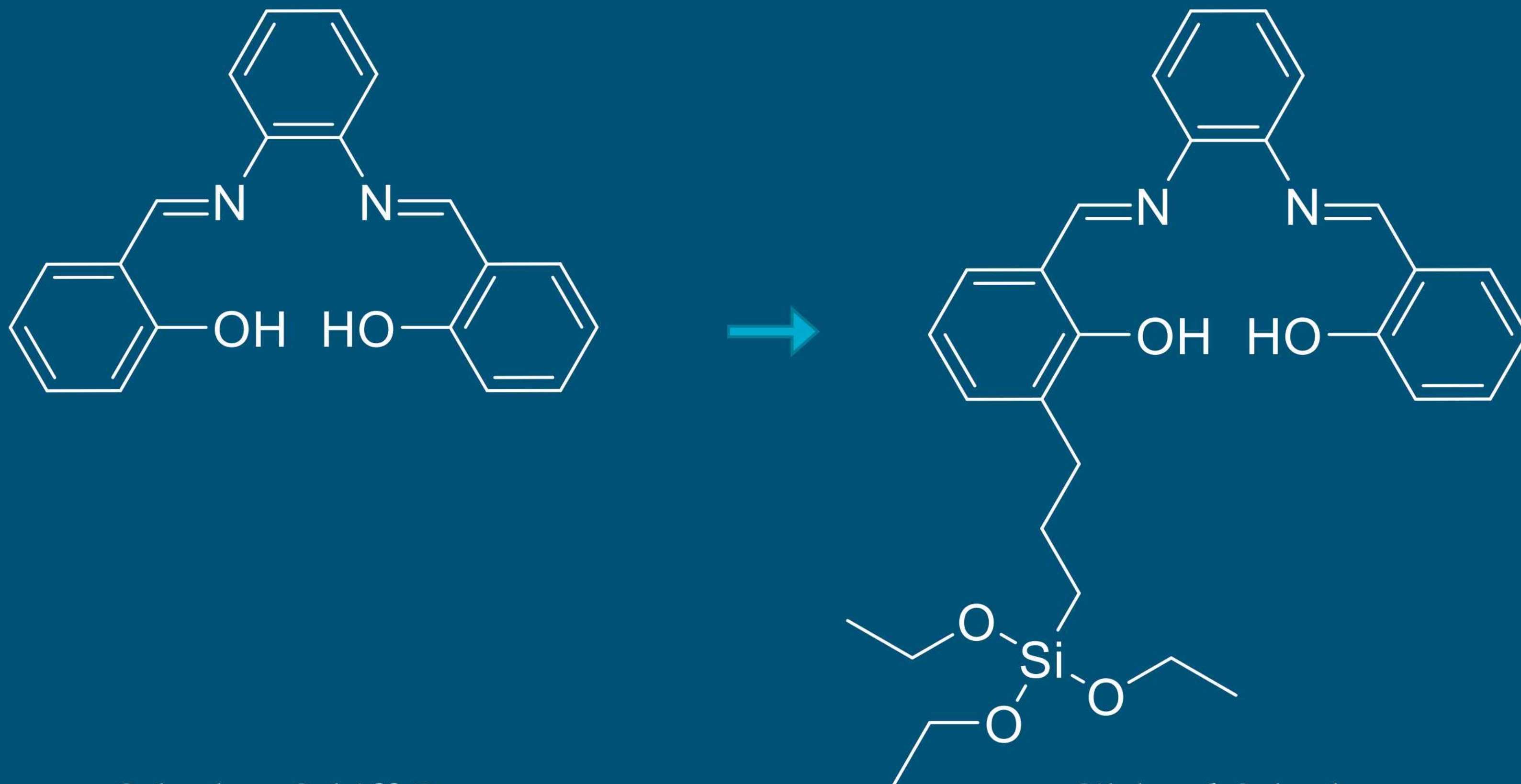
Motivation for Solid Support:

- Minimize solvent waste as a column filtration system
- Eliminate solubility issues
- Recyclable
- Other applications: contamination relief system and seawater sequestrant of uranium

Motivation for Silica

- Mechanically strong, amorphous network
- Tunable particle size, surface area, porosity and chemical functionality
- Processed as colloids, resins, gels, and transparent thin films

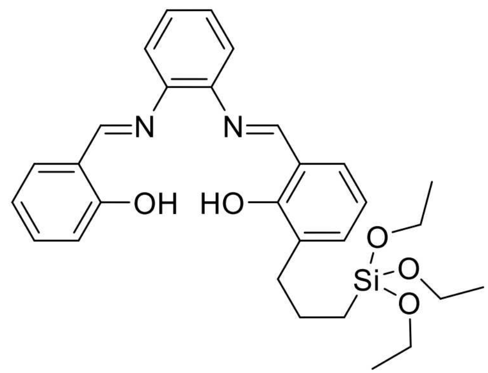
Development of Salophen Schiff Base Ligand for Actinyl Ion Uptake in Adsorbent Material: A tethered salophen



Salophen Schiff Base

Silylated Salophen

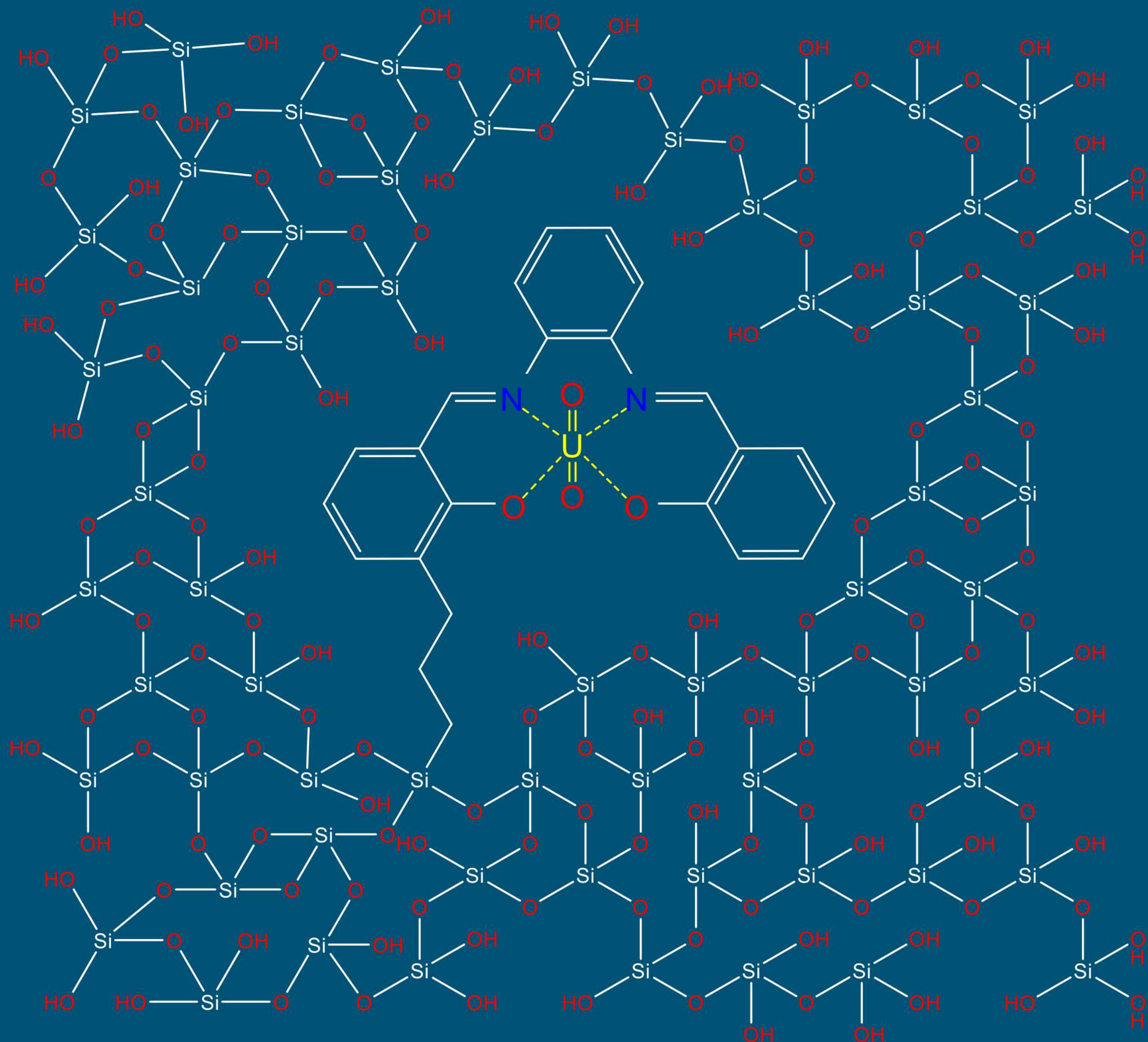
Silylated Salophen Synthesis Scheme



Protocol: Five-step synthesis utilizing sonication

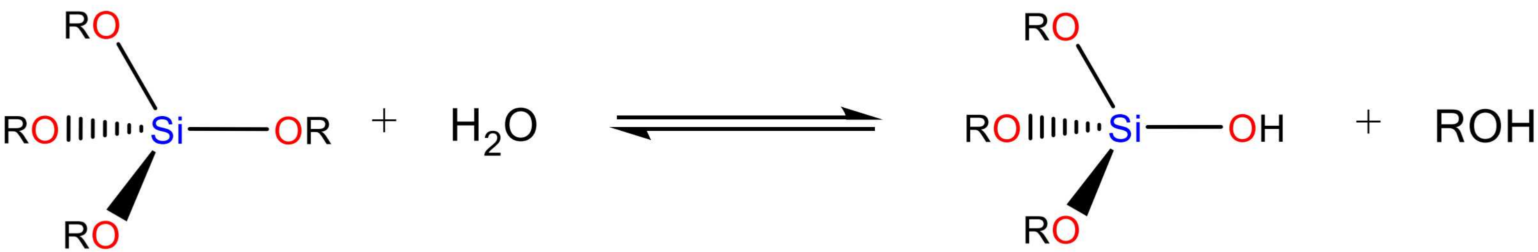
Characterization: ^{1}H and ^{13}C NMR, and ESI-MS

Salophen Hybrid Sorbent Material: Sequestration of Actinides

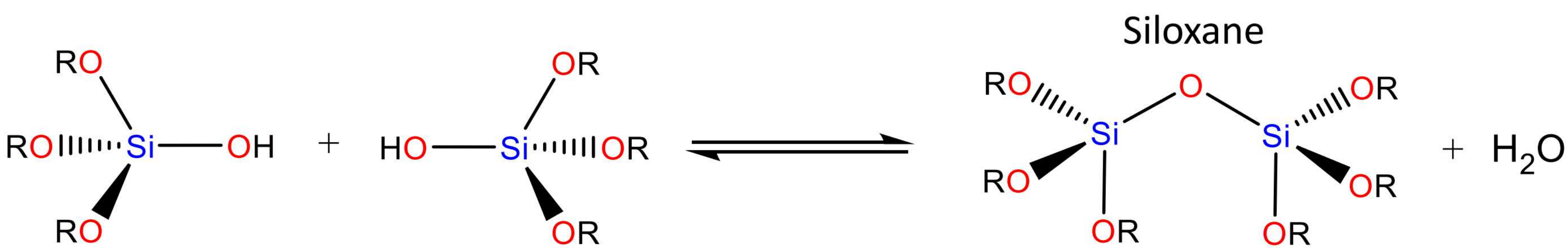


Silica Sol-gel Synthesis Scheme

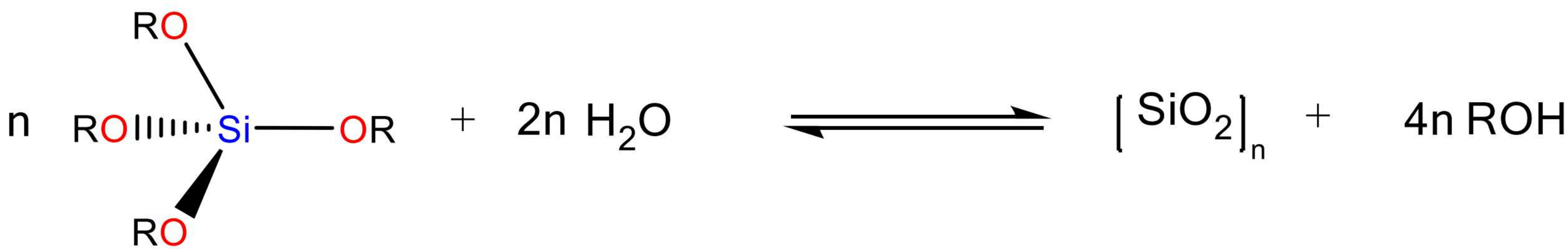
Hydrolysis



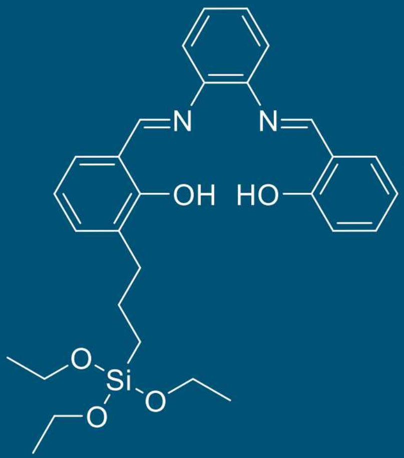
Condensation

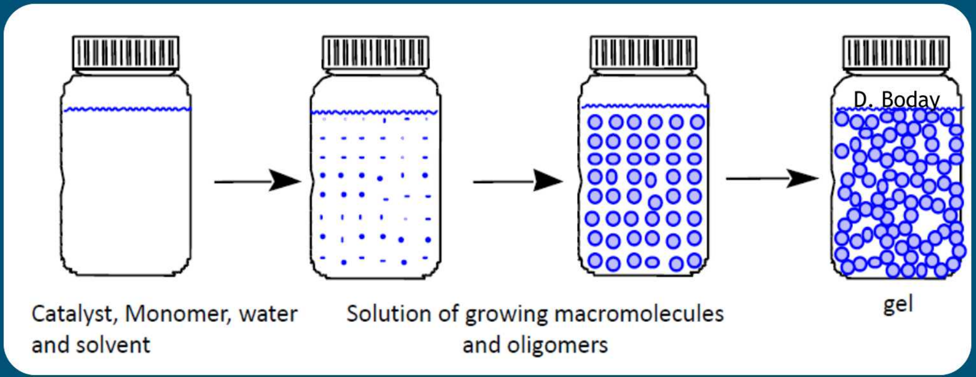


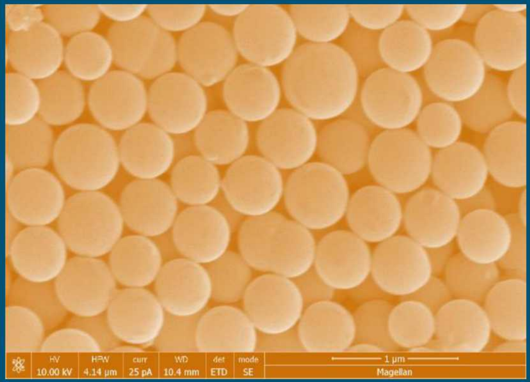
Net Reaction



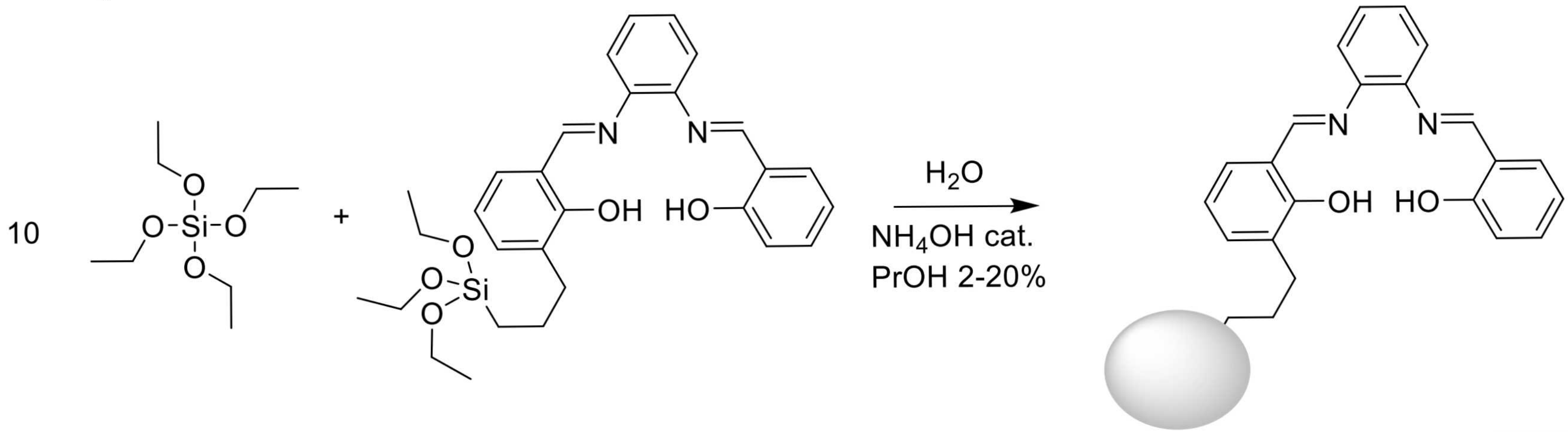
Sol-Gel Synthesis of Hybrid Material: Co-Condensation Approach





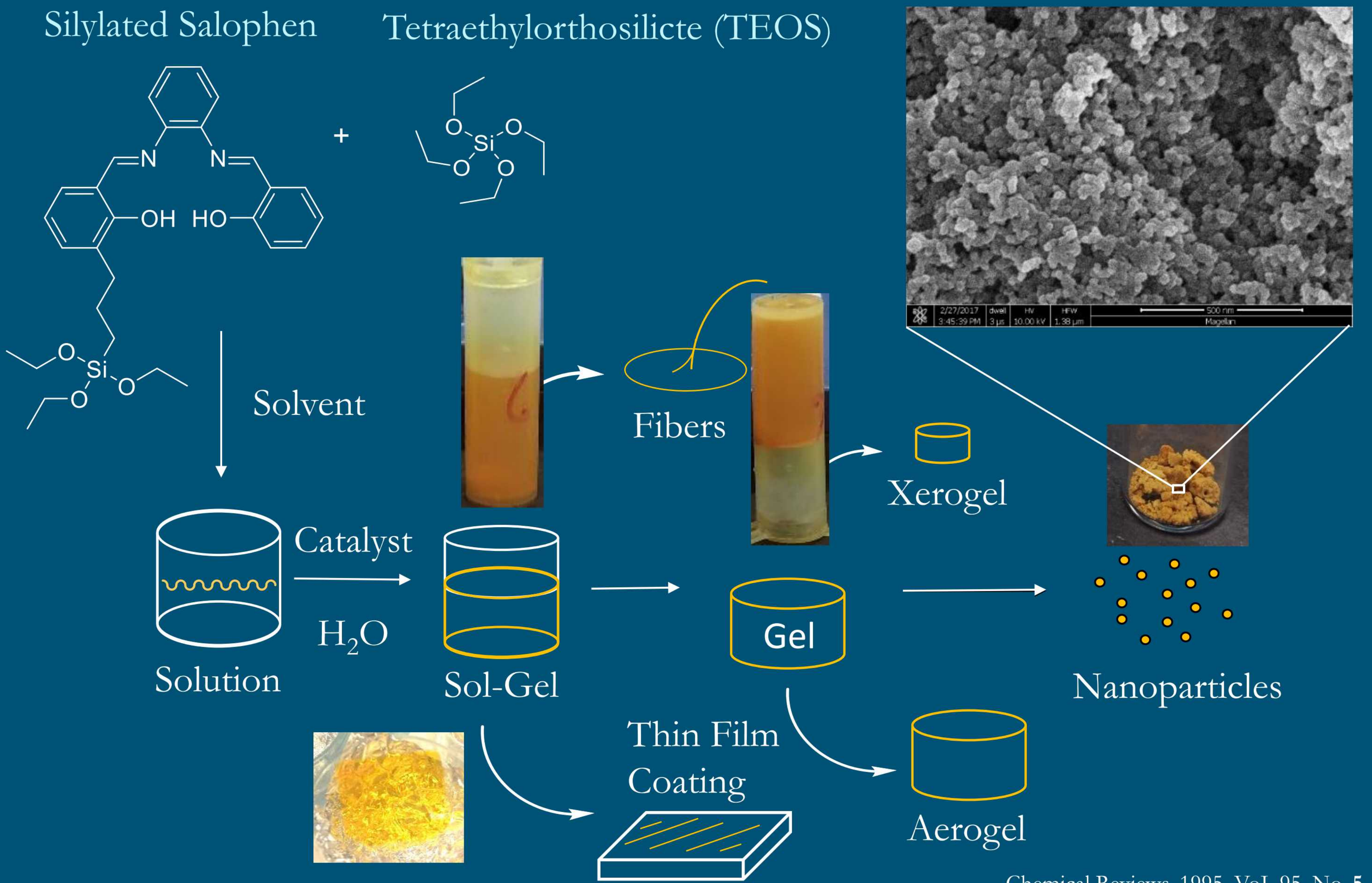


Hybrid Material Formulation



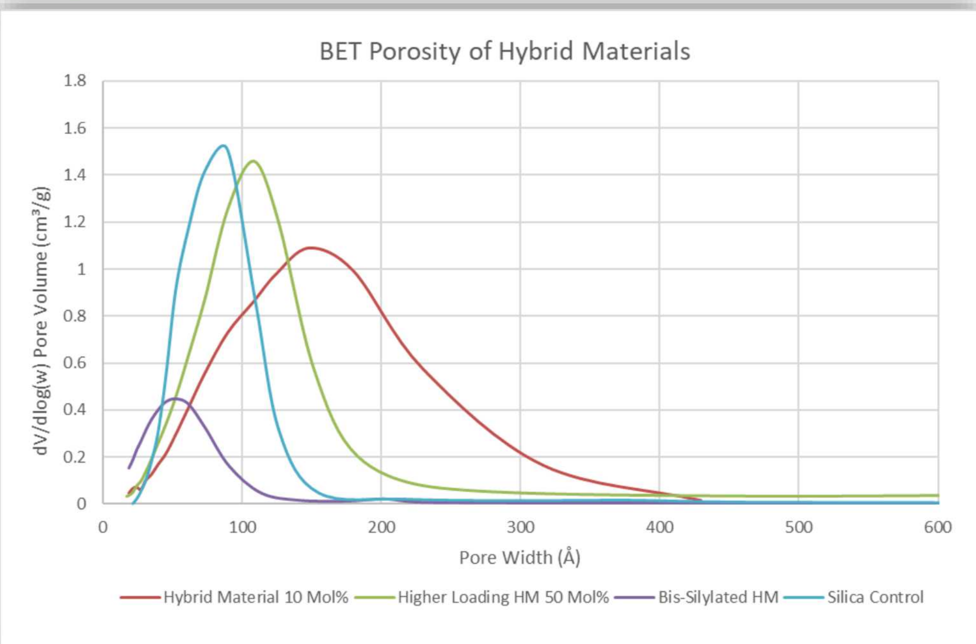
Sample	TEOS Monomer	Ligand Monomer	pNIPAm Template	H_20	NH_3 (aq) Catalyst	Propanol and Acetone Co-solvents
Hybrid Material	2 mmol	0.2 mmol	12 wt %	150 mmol	1.5 M	2 vol %
High Loading Hybrid Material	2 mmol	1.1 mmol	12 wt %	150 mmol	1.5 M	2 vol %
Bis-Silylated Hybrid Material	2 mmol	0.2 mmol	12 wt %	150 mmol	1.5 M	2 vol%
Silica Blank 1	2 mmol	0	12 wt %	150 mmol	1.5 M	2 vol %
Silica Blank 2	2 mmol	0	0	150 mmol	1.5 M	2 vol %

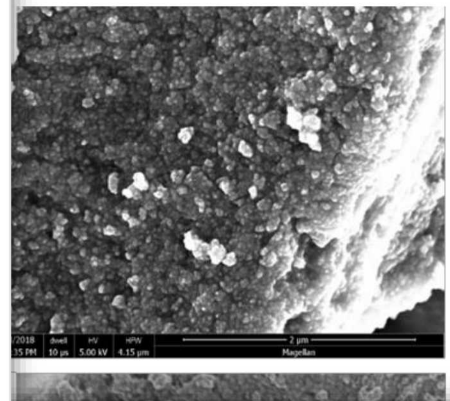
Processing of Hybrid Material as Sol-Gels

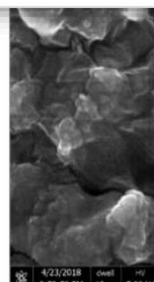


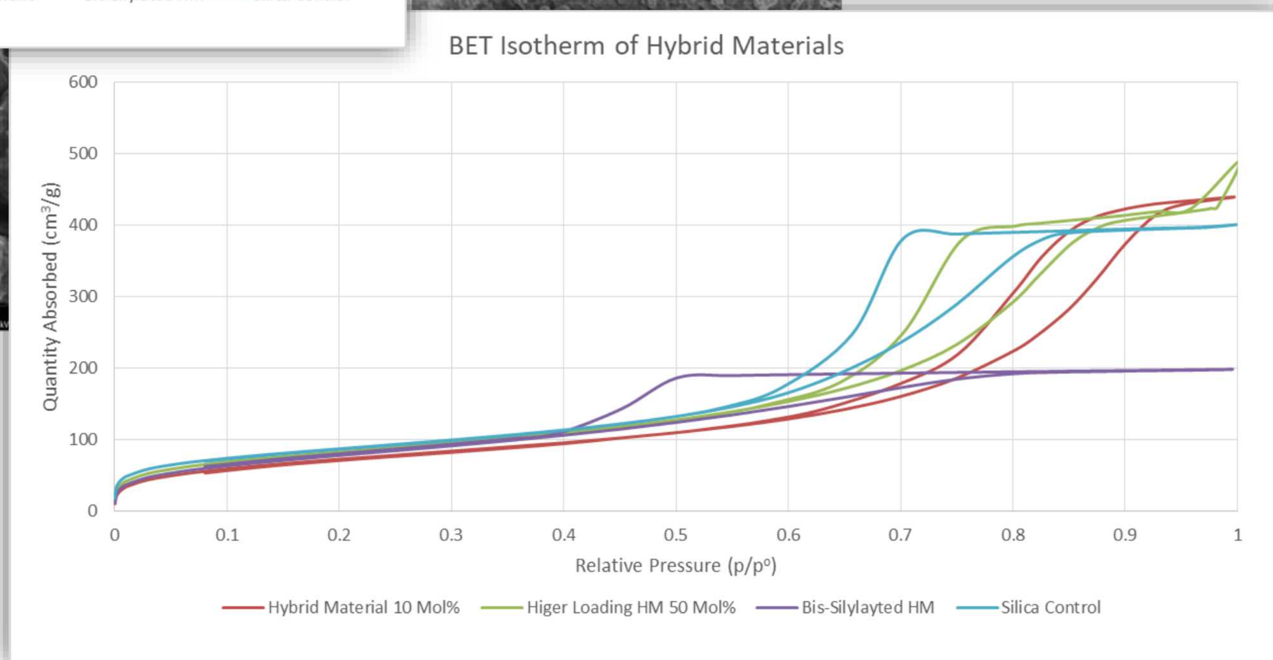
Chemical Reviews, 1995, VoI. 95, No. **5**

Structure and Morphology of Hybrid Material Gels

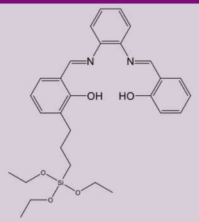
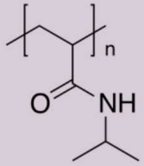
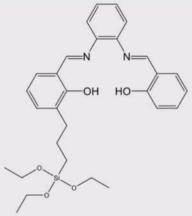
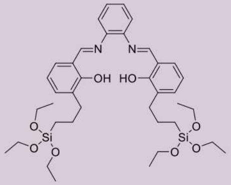
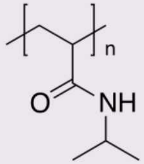








Testing of Hybrid Material Gels for Uranyl Ion Uptake

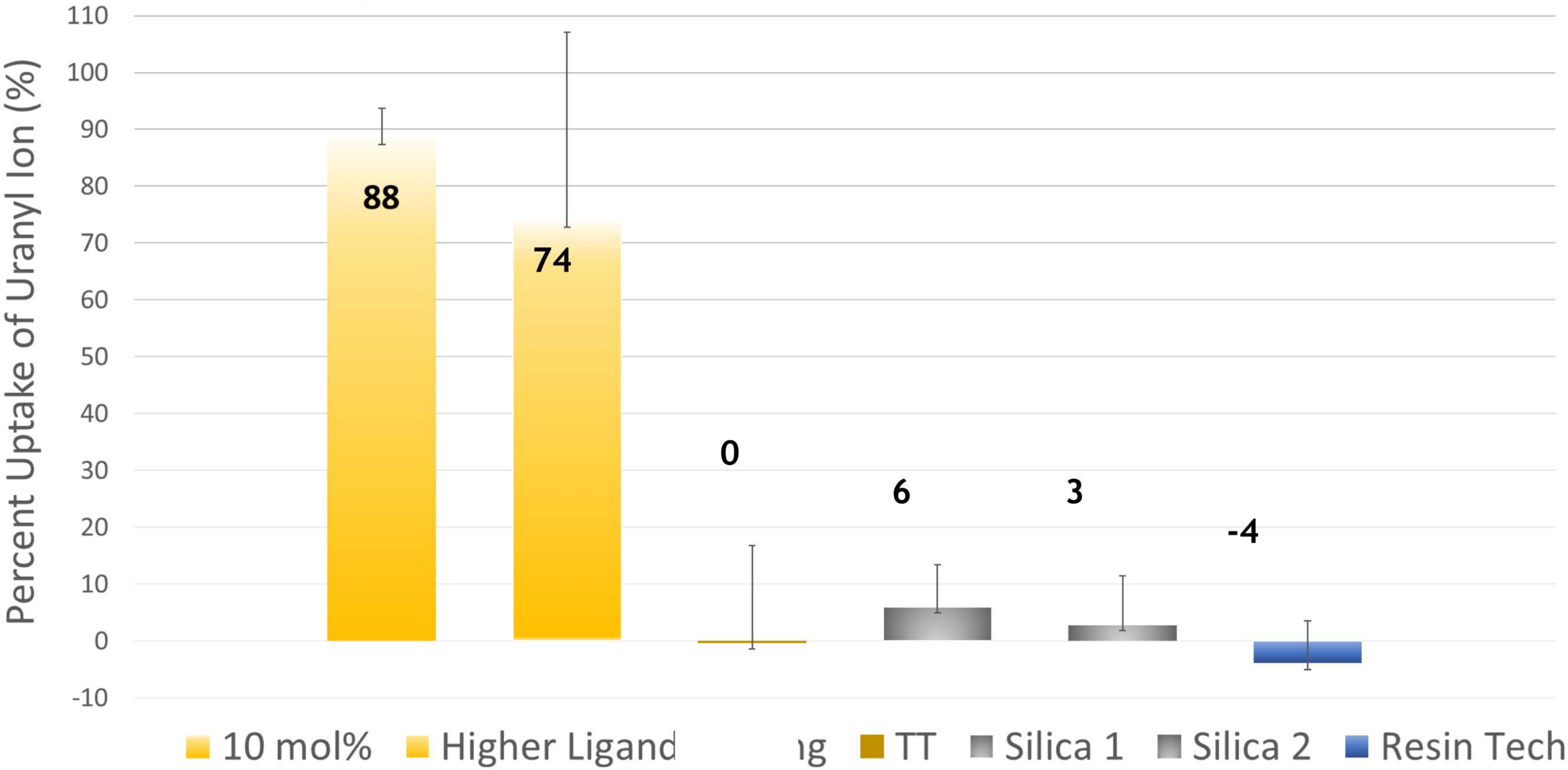
Sample	Ligand	Percent Ligand (Theoret.)	Ligand Incorporation Method	Porosity Agent	BET Surface Area Porosity
Hybrid Material		10	Co-Condensation		267 m^2/g 15 nm
Hybrid Material: Higher Loading		50	Co-Condensation	No	300 m^2/g 11 nm
Hybrid Material: Bis-Silylated Salophen		10	Co-Condensation	No	290 m^2/g 5 nm
Silica Control	X	0	X		310 m^2/g 9 nm

Testing of Hybrid Material Gels: Batch Uptake of Uranyl Ion in Solution

Samples are contacted with 0.1 mM uranyl ion solution for 24 hrs at pH 5, then analyzed with ICP-MS

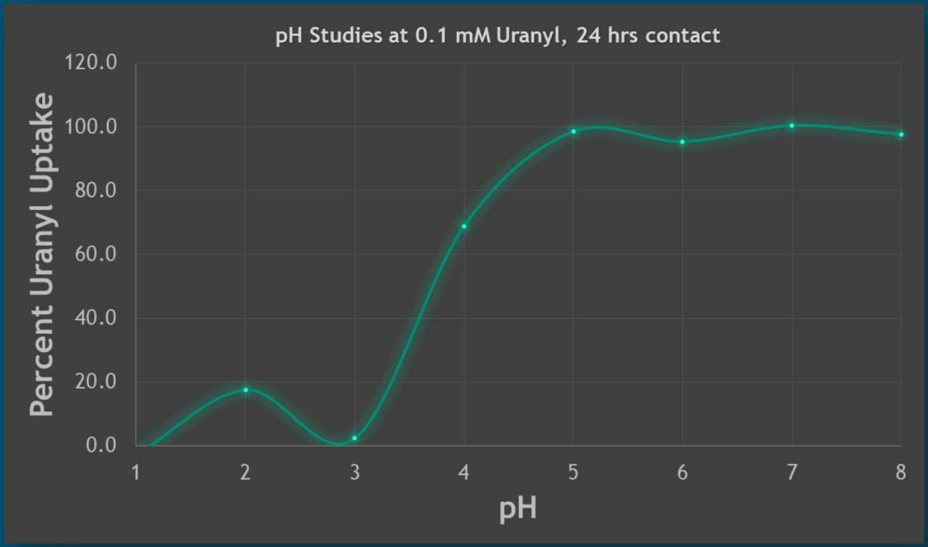
Hybrid Material

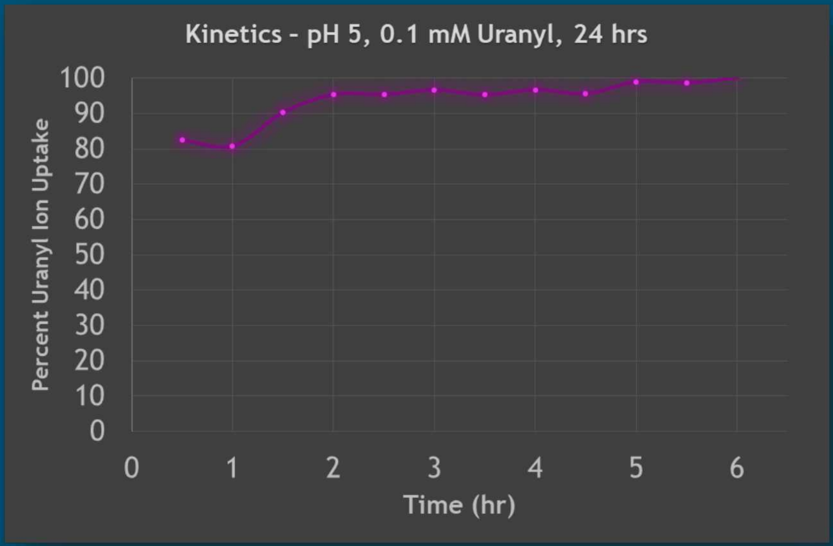
Silica Control

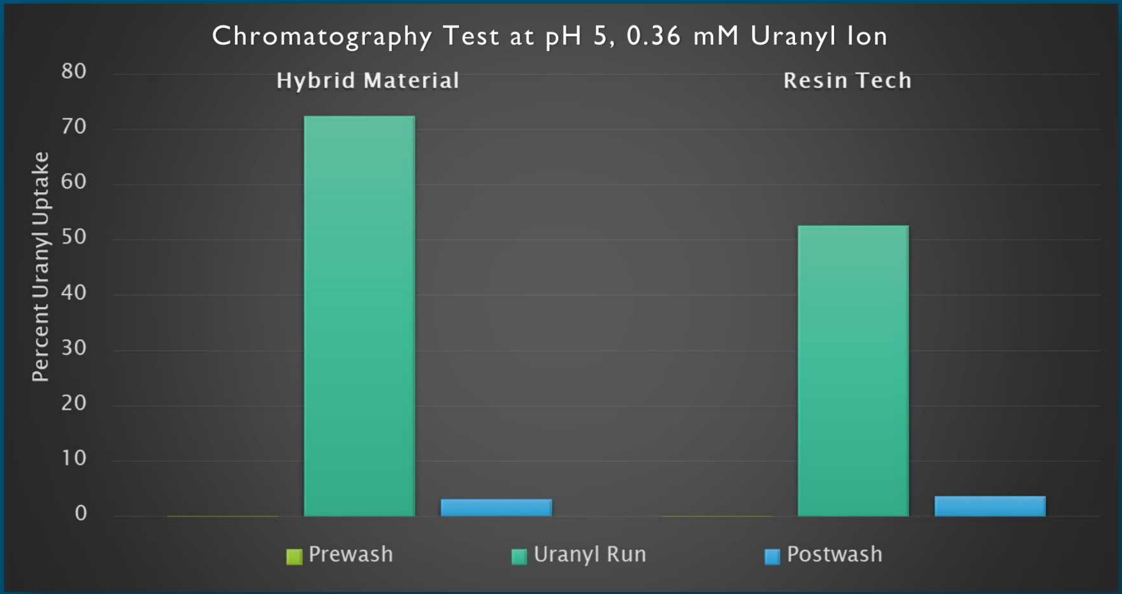


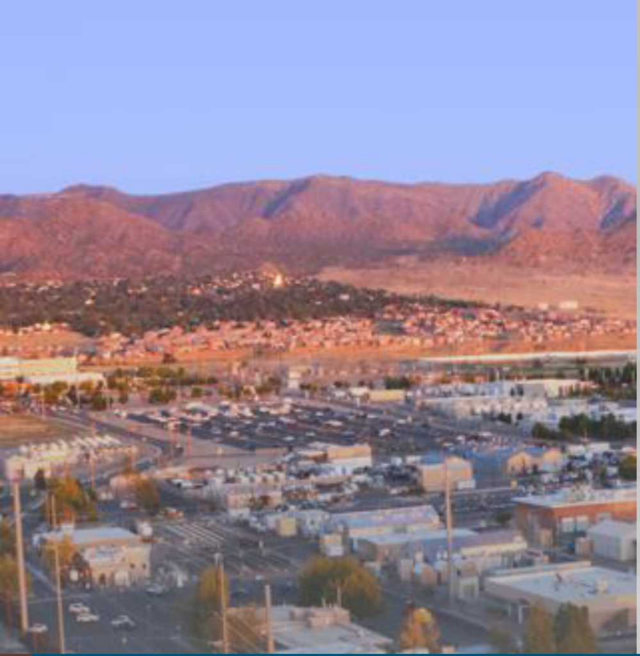
Manuscript in Preparation for Publication

Performance of Hybrid Material: pH, Kinetics, Column Chromatography





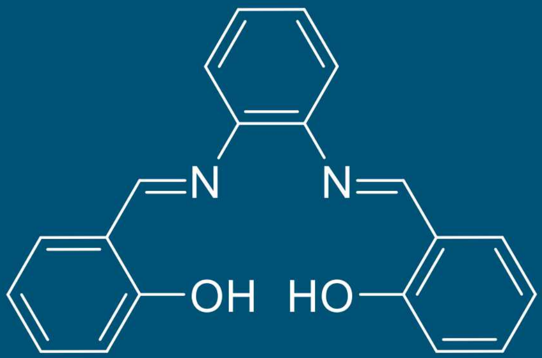




Designing an Enhanced Hybrid Material for the Sequestration of Actinyl Ions under Radiolytic Conditions

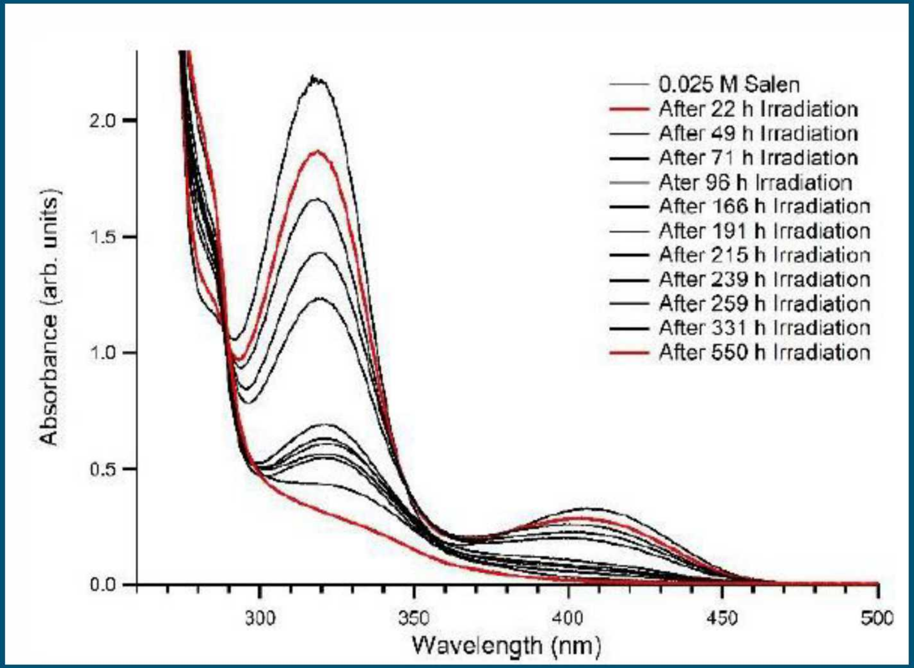
Radiolysis of the Salophen Schiff Base

Under ionizing radiation, organic ligands, including Schiff bases, degrade this includes during reprocessing/solvent extraction of SNF



This has been studied under various radiolytic conditions and analyzed through

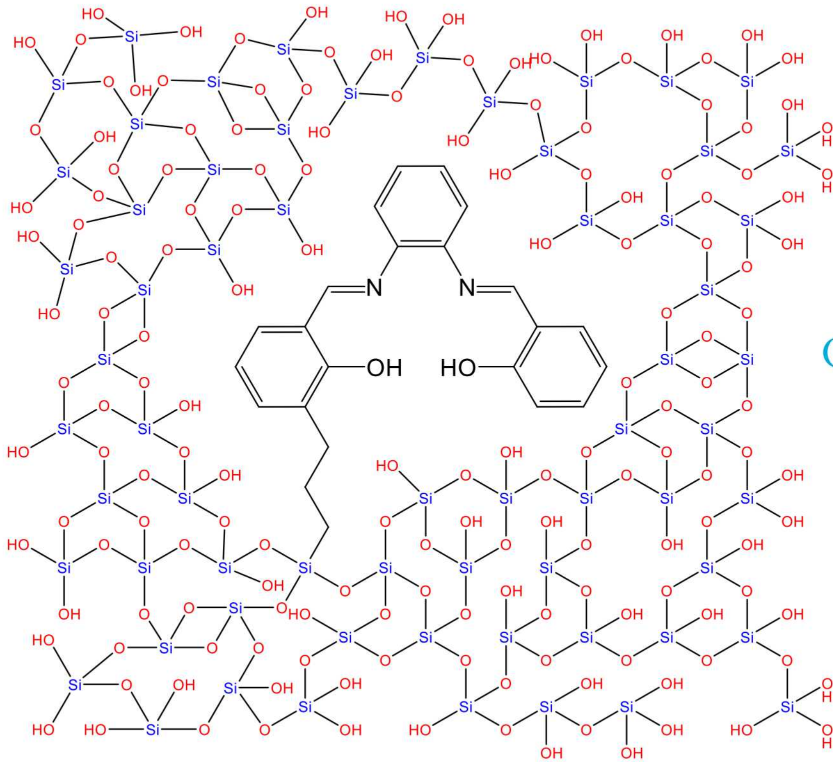
- Absorption Spectroscopy
- ESI-MS
- NMR to determine degradation products



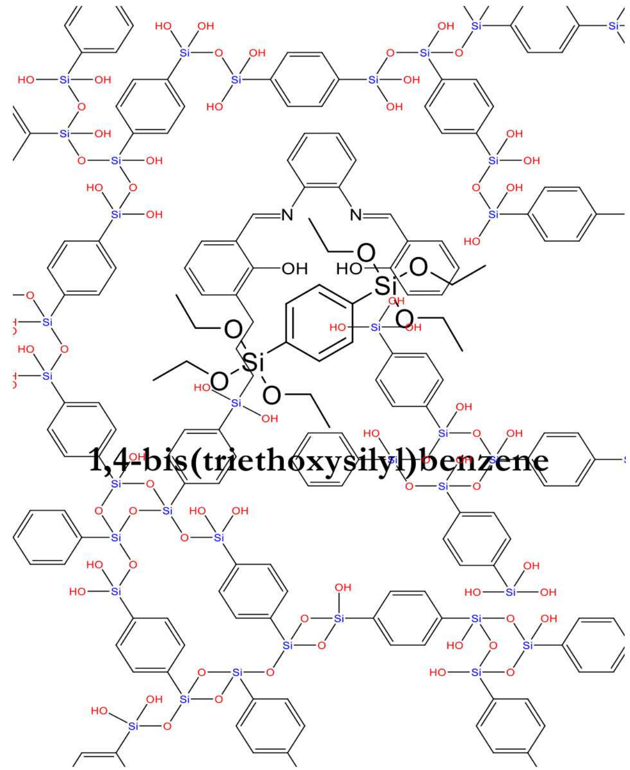
CG Bustillos - 2018 - escholarship.org

Potential to Delay Radiolysis of Salophen in Hybrid Materials
Enhance Properties with Bridged Polysilsesquioxanes (BPS) Addition

Solid support material may act as radiation shield to delay the degradation of salophen while chelating actinyl ions in SNF, may also increase number of cycles salophen can be used



Or



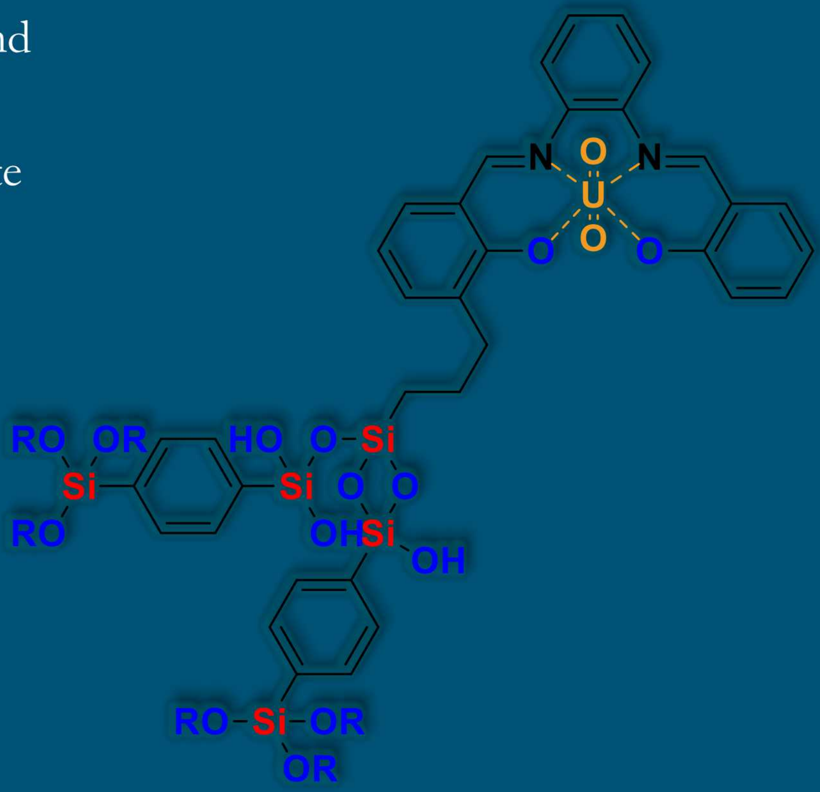
Samples have been irradiated at GIF (Gamma Irradiation Facility) at SNL at:

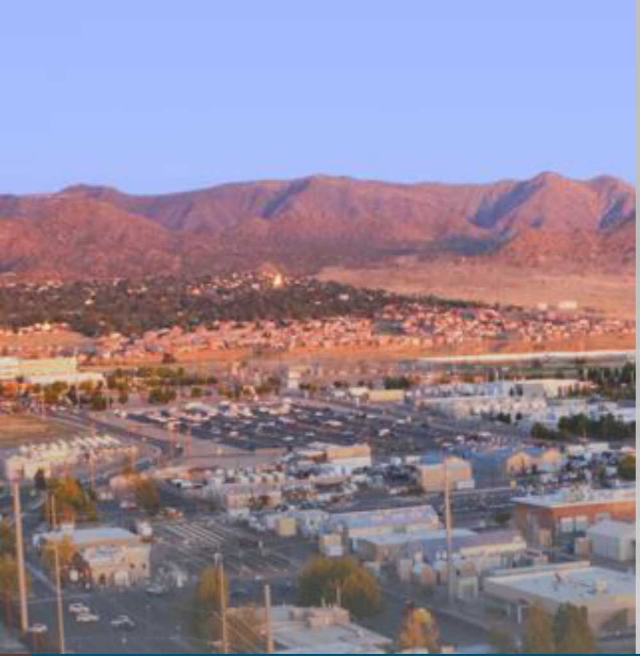
1.3 rads/sec, for 3 days

705.5 rads/sec for 23 min/37 sec

Next Steps in Solid-Support Development

- Analyze batch uptake and performance of BPS Salophen Hybrid Material compared to Silica Salophen Hybrid Material
- Analyze GIF products with NMR to determine degradation level of salophen and support material
- Determine if GIF products can still chelate uranium as an adsorbent material

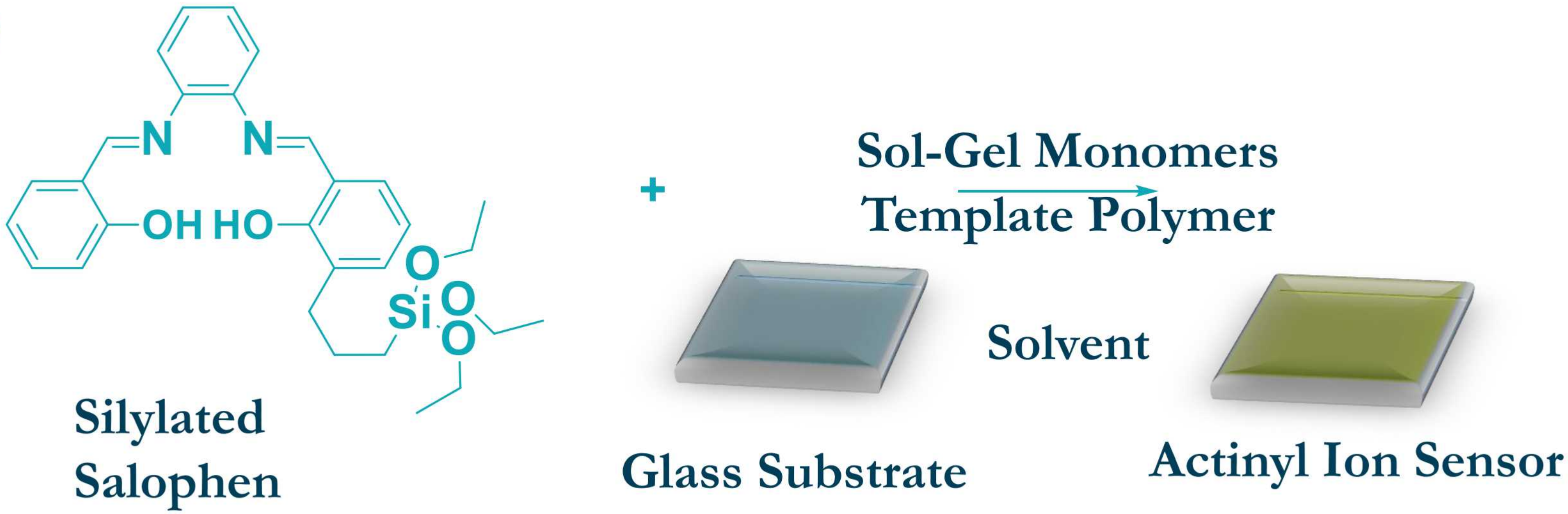




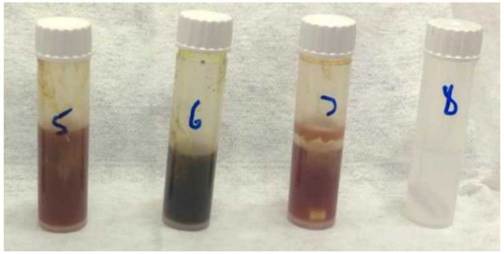
Salophen Schiff Base as a Thin Film Sensor for Actinyl Ions in Aqueous Solution

Salophen Schiff Base as Thin Film Sensor

A)

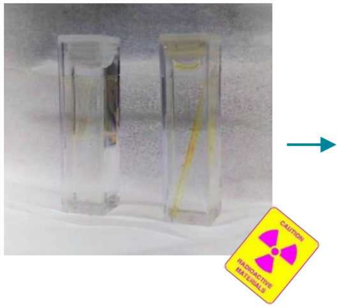


B)

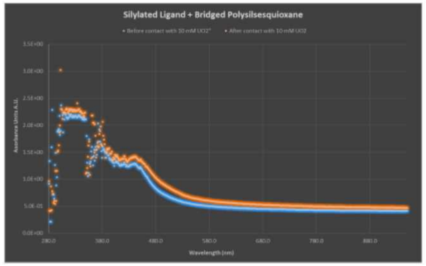


C)

D)

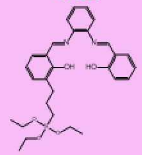
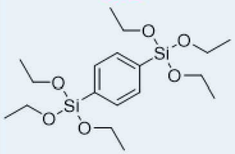
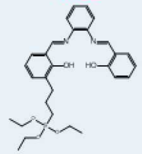
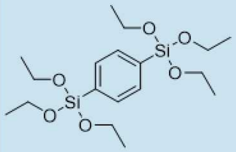
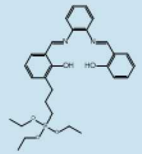
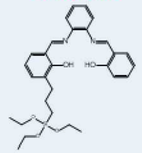
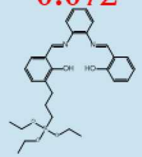


E)

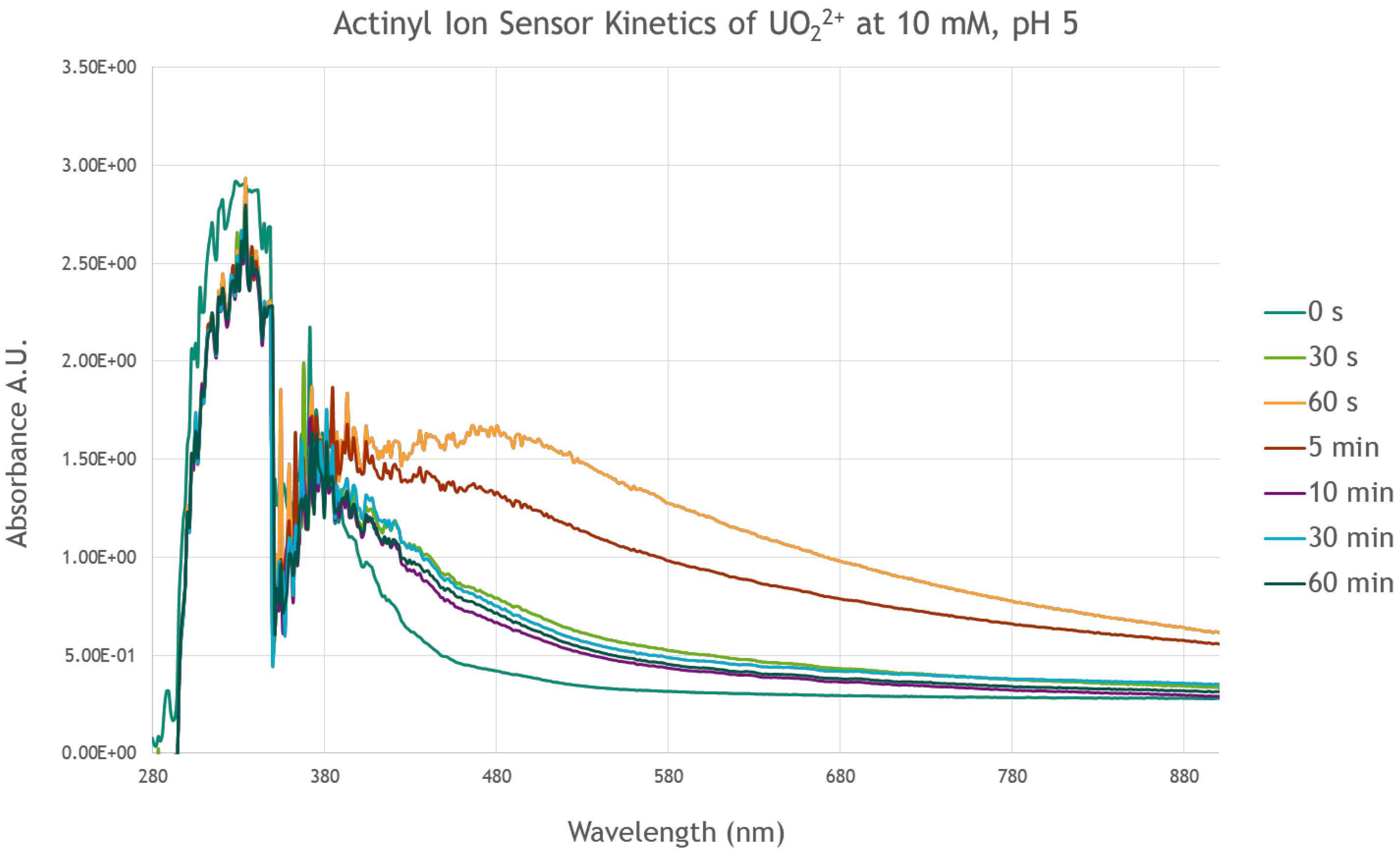


A) Schematic of sensor formation B) Sensor solutions prior to spin coating, dip coating or electrospray deposition C) Sensor after coating on glass substrate D) Sensor in contact with UO_2^{2+} solution E) UV-Vis of solid sensor

Formulating Salophen as Clear Optical Sensor

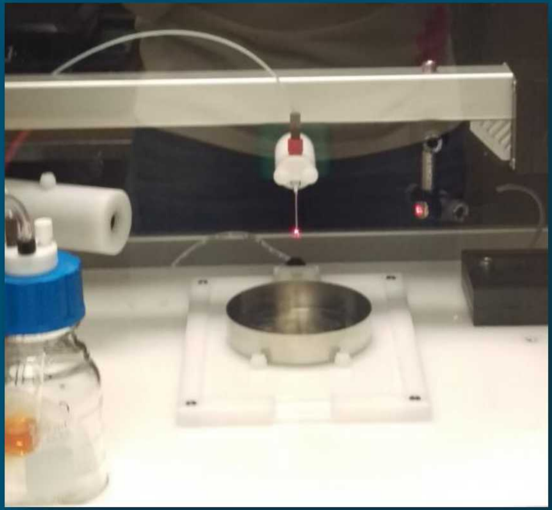
Sample	Ph BPS (g)	Ligand (g)	PNIPAm (g)	Catalyst	Co-solvent	H2O
1 L + PNIPAm + Acetone	X	0.1 	0.5 	X	1 mL Acetone	X
2 L + Acetone + BPS	0.5 	0.1 	X	2 N HCl 10 uL	1 mL Acetone	360 uL
3 L + Acetone + BPS	0.5 	0.1 	X	2 M NH4OH 10 uL	1 mL Acetone	360 uL
4 Ligand Only	X	0.072 	X	X	1 mL Acetone	X
5 Ligand for Spray Deposition	X	0.072 	X	X	2 mL Acetone 5 mL EtOH	X

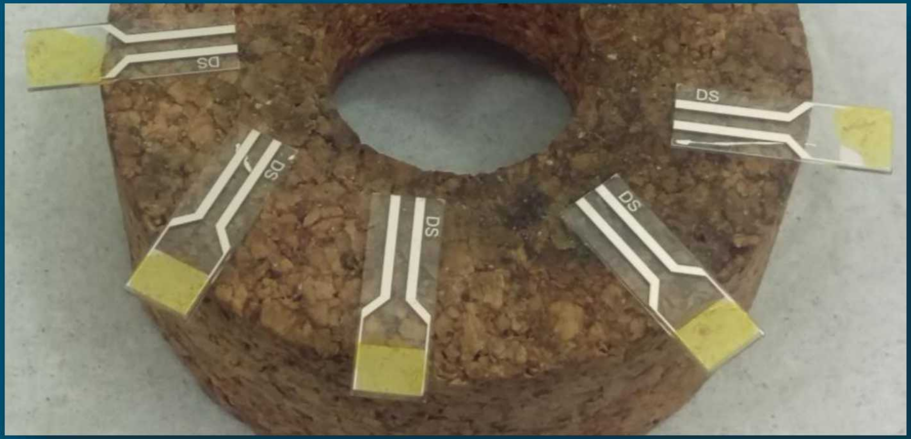
Performance of Optical Thin Film Sensor: Absorption Spectroscopy of Formulation 1 through Dip Coating and RT heat-age



Current Work with Sol-Gel Sensor

- Kinetics with error analysis
- Concentration testing: detection range and limit
- Recycling of thin film sensor
- Confirmation of uranyl chelation with FTIR and Impedance testing - SNL
- Developing deposition method with Electrospray Deposition - SNL





Overall Conclusions

- Salophen Schiff bases can maintain their functionality of actinyl ion chelators in an adsorbent material if incorporated in a nonsymmetrical manner during a co-condensation sol-gel polymerization
- PNIPAm can be used as porosity template agent for silica sol-gels to increase porosity and ion transport
- Salophen Schiff base can be made into an optical sensor for actinyl ions with the aid of a PNIPAm porosity agent and added functionality of a 3-(triethoxysilyl)propyl substituent
- It remains to be determined if 1,4-bis(triethoxysilyl)benzene will aid in the delay of radiolytic degradation of salophen Schiff base chelator and how it performs as an adsorbent material in comparison to silica sol-gels

Acknowledgements

- Professor Nilsson and Professor Shea
- Nilsson Research Group, UCI
- Shea Research Group, UCI
- Sandia National Lab
  - Dr. Tina Nenoff and Dr. Leo Small
- Los Alamos National Lab
  - Dr. Hongwu Xu and Team

Thank you for your attention!