

Salophen Sol-Gel Hybrid Material for the Aqueous Sensing of Actinyl Ions

Jaclynn L. Unangst¹, Tina M. Nenoff², Timothy J. Boyle², Leo J. Small², Stanley Chou² and Mikael Nilsson¹

Ph.D. Candidate in Materials Science at The University of California, Irvine¹

Department of Chemical Engineering and Materials Science

Advisors: Professor Mikael Nilsson and Kenneth J. Shea

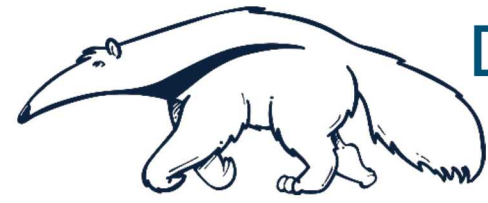
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Sandia National Laboratories²

Manager: Carlos J. Gutierrez

Mentor: Tina M. Nenoff

Department: 01874



UC Irvine

Abstract

In this study we utilized a nonsymmetrical salophen Schiff base with triethoxysilyl functionality to make a sol-gel-based thin film sensor for UV-Vis detection of the actinyl ions: UO_2^{2+} , NpO_2^{2+} , and $\text{PuO}_2^{2+/3+}$ in aqueous solutions at pH 5. Different formulations of the sol-gel were tested as sensors including the addition of a PNIPAm template and 1,4-bis(triethoxysilyl)benzene monomer to increase porosity and sensing capability of the salophen ligand. The initial performance of the sensors show that Sensor 2, with added template and monomer, has the best response rate after 30 seconds with improvement after 30 minutes.

Introduction: Sensing Actinides with Salophen

Sensing of radioactive materials is very important for national security, human and environmental safety and ensuring a safe and reliable future for nuclear energy. The development of an optical sensor designed for aqueous uptake of uranium, neptunium and plutonium allows for the rapid determination of these radioactive actinyl ions through a color change in the sensor that can be detected with UV-Vis spectroscopy. For a salophen Schiff base sensor, Fig. 1, this is due to the change in structure upon chelation to these ions. Schiff bases have been utilized as ligands for solvent extraction of U and Np ions¹, but to make a solid sensor, chemical modification is required to attach the ligand to a substrate. The salophen can be altered with a 3-(triethoxysilyl)propyl tether for covalent anchoring to a borosilicate glass substrate while still maintaining rotational freedom required for chelation² Fig 2A. Other agents such as the bridged polysilsesquioxane, 1,4-bis(triethoxysilyl)benzene ((Ph)BPS), Fig. 1, and the template polymer, poly(N-isopropylacrylamide) (PNIPAm), are added to the sensor solution to increase film porosity and facilitate ion transport³⁻⁴ for a fast, transparent, actinyl ion thin film sensor.

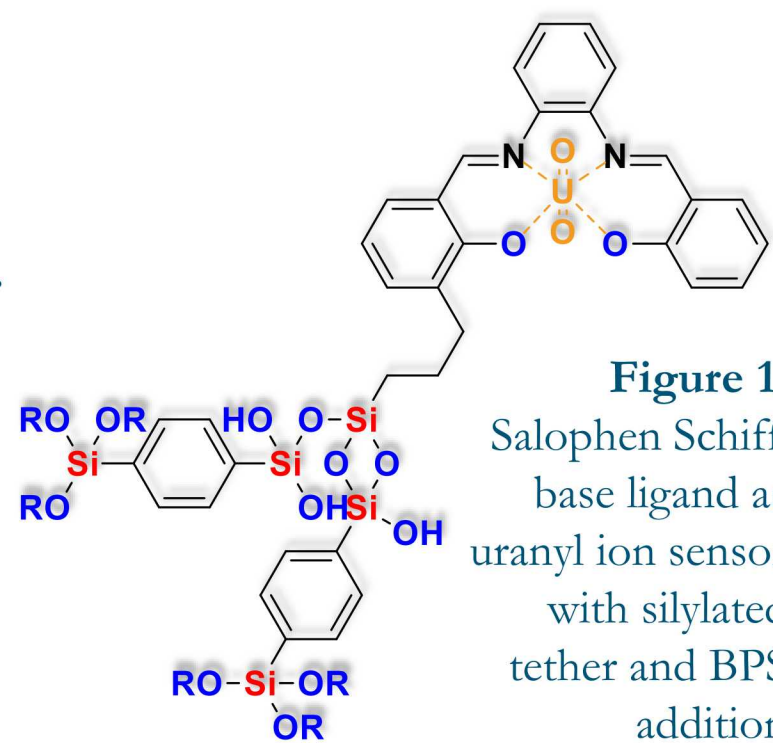


Figure 1. Salophen Schiff base ligand as uranyl ion sensor with silylated tether and BPS addition

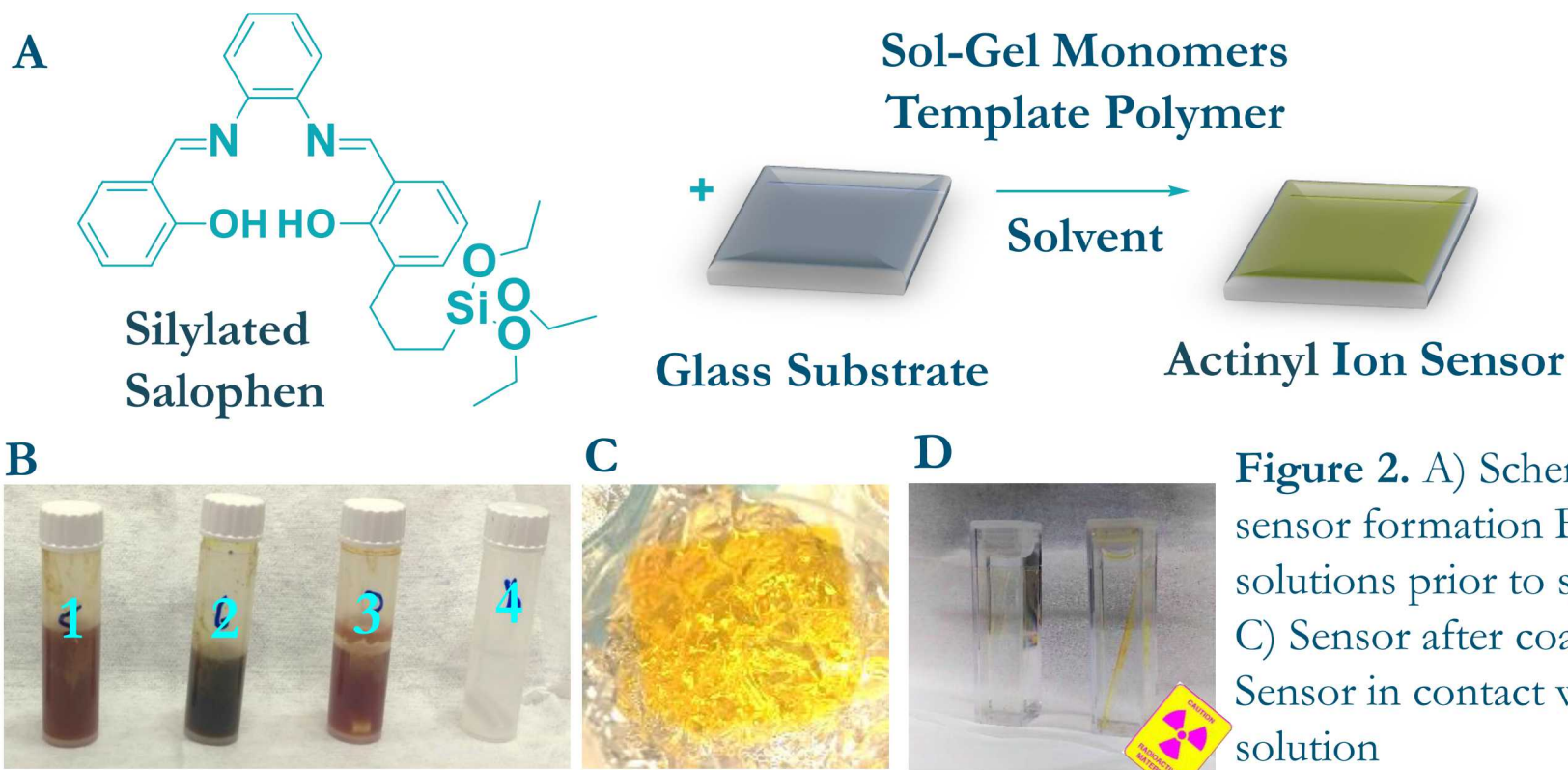


Figure 2. A) Schematic of sensor formation B) Sensor solutions prior to spin coating C) Sensor after coating D) Sensor in contact with UO_2^{2+} solution

Preliminary Results: UV-Vis of UO_2^{2+} Sensing

The actinide sensors were tested with the uranyl solution with data points taken at 30 seconds, 5 minutes and 30 minutes to determine initial response rate. The absorbance data below shows the response of Sensor 2 containing the salophen ligand, (Ph)BPS monomer and templated with the PNIPAm polymer. The salophen and (Ph)BPS peaks are below 375 nm and decrease with contact time. The other sensors (response not shown) did not show appreciable change even after 30 minutes.

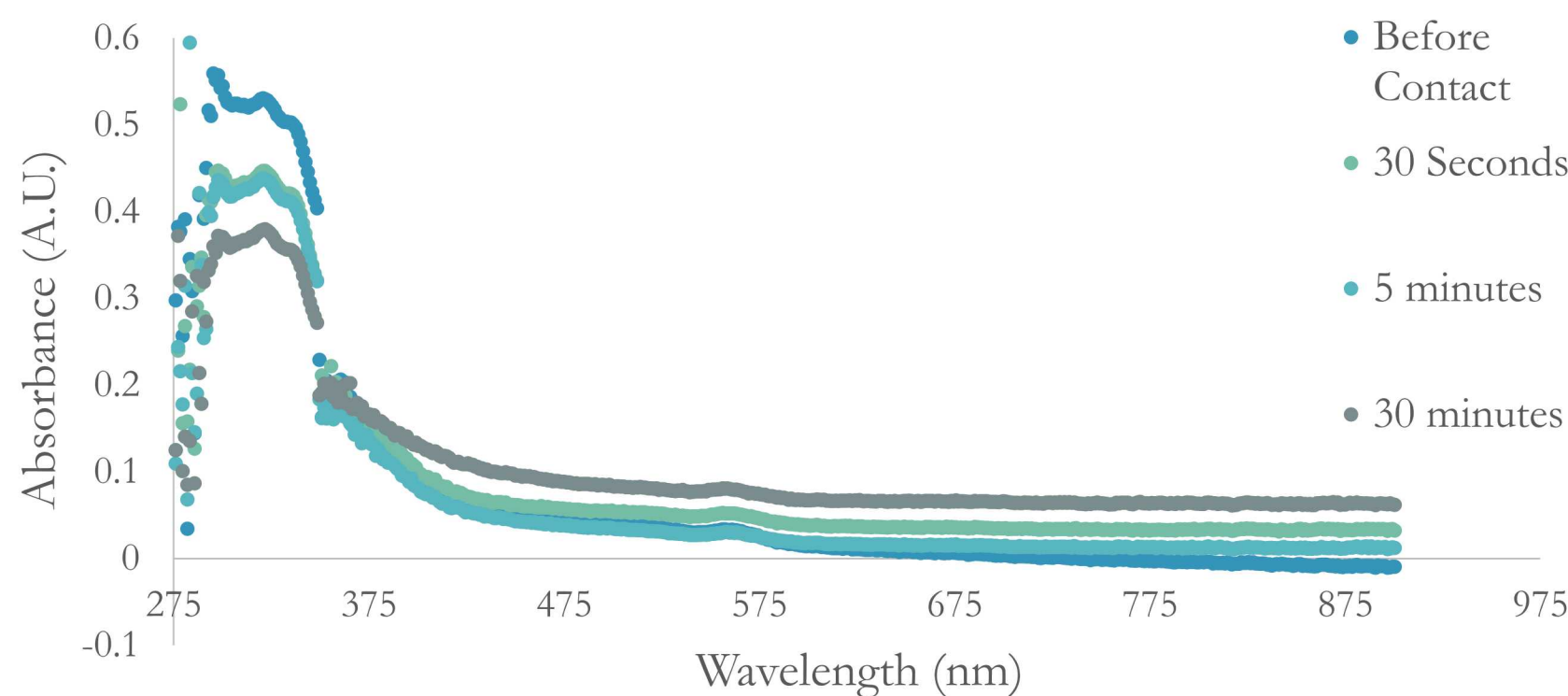


Figure 3. Performance of Sensor 2 at 1 mM UO_2^{2+} during 30 minutes of agitation

Discussion: Porosity Agents Aid Salophen Sensor

The initial data shows that Sensor 2 has the best response to the uranyl ion at 1 mM concentration at pH 5 in terms of the decreasing salophen peak at <375 nm. It is challenging to determine the exact salophen response as there is overlap from the (Ph)BPS functionality and possibly any remaining PNIPAm. In addition, a shift to a higher visible wavelength (~ 460 nm) is expected upon chelation of the salophen with the actinyl ions, and this response is not readily apparent. Further analysis through adding more samples and controls for error, adding more time points, and allowing for more time to anneal the sensor and remove the PNIPAm template prior to testing is planned. It should be noted that coating the substrate with only nonsymmetrical salophen is possible, but there is no ion response.

Conclusion & Future Work

Sensor 2 containing salophen, (Ph)BPS and PNIPAm template shows potential as a hybrid material thin film sensor for the uranyl ions. Beyond full determination and optimization of sensor performance, attempts at coating through spray deposition and determining the sensor impedance and radiolytic degradation are also of interest.

Methods: Formulating a Sensor Solution

The nonsymmetrical salophen Schiff base ligand is synthesized through a five-step procedure completed previously². The development of the Schiff base sol-gel solution for sensing is described in Table 1 and lists the composition of the thin film solutions, Fig. 2B, prior to spin coating on 9x35 mm borosilicate glass slides, Fig. 2C, and annealing at 70°C for 1 hour.

Thin Film	Salophen Ligand	TEOS	(Ph) BPS	PNIPAm	Catalyst 2 M HCl	Solvent	H ₂ O	Conditions
1	30 mg	30 mg	X	80 mg	50 uL	1 mL Acetone, 1 mL EtOH	40 uL	Solutions stirred at room temperature for 16 hrs
2	30 mg	X	30 mg	80 mg	50 uL	1 mL Acetone, 1 mL EtOH	40 uL	
3	60 mg	X	X	80 mg	50 uL	1 mL Acetone, 1 mL EtOH	40 uL	
4	X	X	30 mg	80 mg	50 uL	1 mL Acetone, 1 mL EtOH	40 uL	

Table 1. Composition and preparation of sensor solutions prior to spin coating on substrate

The aged sensors are then washed with DI water and contacted with the aqueous 1 mM uranyl solution in 2% HNO_3 at pH 5 for up to 30 minutes on a rotator before UV-Vis analysis of the thin film-coated glass slide.