

FINAL REPORT

U. S. Department of Energy

**SENSORS USING MOLECULAR RECOGNITION IN
LUMINESCENT, CONDUCTIVE POLYMERS**

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Executive Summary

The purpose of this project is to develop sensor technology for detecting specific heavy metal ions, such as transition metals, lead, lanthanides, and actinides in waste streams. The sensing strategy uses molecular recognition of the metal ions by polymers that change their luminescence and conductivity properties upon metal binding. Research problems that are being addressed by this project include: 1) designing molecular recognition sites that are highly selective for the metal ions of interest in the presence of a large background of other chemical species, 2) finding ways to incorporate many different selective groups into a single polymer, 3) fabricating polymer films, strips, sheets, and coatings that can be applied to other materials, such as fiber optics and surfaces, 4) developing interfaces between the polymers and substrates that can be used to produce prototype arrays of many sensor elements for rapid multi-contaminant detection and quantitation, and 5) developing multiplexed data collection techniques to rapidly process the data obtained from many polymer sensors into a chemical profile of a waste stream or waste site in real time.

We developed new sensor materials based on metal ion sensing by fluorescent polymers that change their fluorescence colors when different metals are bound. The properties of these polymers show that fiber optic technology can be used to monitor these fluorescence changes at relatively long distances from the source. This will be particularly useful for remote sensing.

We developed the first combinatorial dye synthesis leading to the identification of new metal chelators and indicators. The approach involved preparing a library of azo dyes and screening them for their metal binding response using both absorbance and fluorescence spectral changes. We were able to fully characterize and identify dozens of new structures that can be used in metal ion array sensors. In parallel work, we successfully prepared cross-reactive sensor arrays and developed training protocols that allow the arrays to identify individual compounds or components of mixtures.

We also developed synthetic methods of attaching actinide specific ligands to polymers under this project. Hydroxypyridinone (HOPO) ligands were attached to polystyrene, and in related work used to sequester plutonium. The HOPO ligands form extraordinarily strong complexes

with actinides, and solution thermodynamic parameters for uranyl(UO_2^{2+}) and Ce(IV), a model for Pu(IV), with a number of ligand systems were determined. We have identified the bis-bidentate ligand, 5-LIO-HOPO, as a good candidate for specific coordination to uranyl cations. This ligand or its variants have potential in polymeric sensor materials that target this analyte.

Research Objectives

The purpose of this project is to develop sensor technology for detecting specific heavy metal ions, such as transition metals, lead, lanthanides, and actinides in waste streams. The sensing strategy uses molecular recognition of the metal ions by polymers that change their luminescence and conductivity properties upon metal binding. Research problems that are being addressed by this project include: 1) designing molecular recognition sites that are highly selective for the metal ions of interest in the presence of a large background of other chemical species, 2) finding ways to incorporate many different selective groups into a single polymer, 3) fabricating polymer films, strips, sheets, and coatings that can be applied to other materials, such as fiber optics and surfaces, 4) developing interfaces between the polymers and substrates that can be used to produce prototype arrays of many sensor elements for rapid multi-contaminant detection and quantitation, and 5) developing multiplexed data collection techniques to rapidly process the data obtained from many polymer sensors into a chemical profile of a waste stream or waste site in real time.

Methods and Results

The effect of π -conjugation attenuation on the photophysics and exciton dynamics of two conjugated polymers **1** and **2** were examined in solution. The structures of polymers **1** and **2** have 2,2'-bipyridyl-5-vinylene units that alternate with one and three 2,5-bis(2'-ethylhexyloxy)-1,4-phenylenevinylene monomer units, respectively. The photophysics and exciton dynamics of polymers **1** and **2** were compared to those of the homopolymer, poly(2,5-bis(2'-ethylhexyloxy)-1,4-phenylenevinylene) (BEH-PPV). A series of changes in the photophysics of polymers **1** and **2** were found as a result of π -conjugation attenuation. These changes include blue shifts in absorption and emission spectra, spectral diffusion in stimulated emission, enhancement in photoluminescence quantum yields and lifetimes, and increases in photoinduced absorption intensities and lifetimes. These changes are systematically more pronounced in polymer **1** than in polymer **2**, and are correlated with π -conjugation attenuation in the polymers due to twisting of the 2,2'-bipyridine groups about the 2,2' single bond. An exciton dynamics model involving an ensemble of initial exciton states localized on oligomeric segments within the polymer with

different conjugation lengths is proposed to describe the observed differences between polymers **1** and **2** and BEH-PPV. When the electronic coupling between these segments is strong, the polymer displays characteristics that are close to those of a one-dimensional semiconductor. However, when these couplings are weakened by groups, such as the 2,2'-bipyridine that attenuate π -conjugation, the polymer displays properties of an ensemble of oligomers.

The effects of metal ion chelation to the 2,2'-bipyridine (bpy) groups on the photophysics and exciton dynamics of two conjugated polymers **1** and **2** in solution were investigated. The photophysics and exciton dynamics of metalated polymers **1** and **2** were compared to those of the metal-free polymers. The origins of ionochromic effects due the metal ion chelation were studied using both steady-state and transient optical spectroscopy, and the results indicate that both conformational flattening and participation of π electrons from the metal in the π -conjugation of the polymer backbone play important roles in metal ion binding induced red-shifts in absorption and photoluminescence spectra. The photoluminescence properties of the metalated polymers are determined by the metal ion electronic structures, where the close shell Zn^{2+} bound polymer **2** has an increased photoluminescence quantum yield and the corresponding open shell Ni^{2+} or Fe^{3+} bound polymers have quenched photoluminescence due to spin-orbit coupling. The dual character of metalated polymer **2** as a conjugated polymer and as a metal-bpy complex was investigated. In addition, the structures of metal ion binding sites were studied via X-ray absorption fine structure (XAFS) and were related to the photophysical properties of the metalated polymers.

The synthesis and characterization of metal-binding indicators with diverse optical responses on exposure to various heavy metal ions were investigated. A combinatorial approach, based on azo coupling of diazonium salts with either phenolic compounds or aromatic amines, generated a library of azo dyes. Each reaction mixture, containing the products(s) of azo coupling, was incubated with a series of solutions, each containing a different heavy metal ion. The absorbance and, in some cases, fluorescence spectra of the resulting complexes were recorded. The metal chelates showed extensive diversity in their UV-visible absorbance spectra upon binding to selected metal ions. Of the azo dyes prepared, the terdentate dyes were particularly useful, providing distinct spectral responses to three or more metal ions in a panel of seven.

We have shown that a combinatorial library synthesis approach is an efficient means to discover new indicators. Our intention was to find a rapid method to identify promising candidate materials. On the basis of our experience with these selected compounds and on literature data, we assumed that the yields of the azo dyes, generated by established methods, were moderate to good across the examples studied. Also, only the reaction mixtures displaying deep color due to the presence of the azo dyes(s) were included in further investigations with metal ions.

UV-visible absorbance spectra of the azo dyes obtained in this work showed diverse responses upon exposure to selected heavy metal ions. These and similar azo dyes could be used for metal ion determination in various optical sensors. Optical analyzers employing azo dyes usually can detect metal ions in the concentration range of about 10^{-6} - 10^{-3} M. However, novel optical sensors, based on electrochemically assisted solvent extraction, hold promise for achieving higher sensitivities. The dyes that cross-reacted with multiple metal ions could be utilized in a sensor array format to quantify these ions in mixtures by means of a computational pattern analysis method.

The screen for particular properties limits combinatorial libraries. In the present work, we have prepared previously unreported azo dyes and screened them for an optical change upon metal binding.

We have developed four new chelating hydroxypyridinone and catecholamide polystyrene supported extractants and evaluated their ability to selectively remove ppm levels of plutonium from a variety of acidic aqueous waste compositions. The hydroxypyridinone and catecholamide ligands, modeled after the metal ion binding sites found in siderophores, were derivatized to allow covalent attachment to a polymeric support. The synthesis, loading capacities and chemical stability of the new resins were determined along with the results from extraction studies evaluating their performance for the extraction of Pu(IV) and Pu(VI) from a variety of HNO₃ and NaNO₃ solutions up to 5M and in competition with Fe(III), Al(III), Zr(IV) and EDTA. The kinetics of metal ion sorption onto the resins are fast and the extraction results are compared to the commercial Chelex resin.

A rational design of uranyl sequestering agents based on 3-hydroxy-2 (1*H*)-pyridinone ligands has resulted in the first effective agents for mammalian uranyl decorporation. In this study crystal structures of uranyl complexes with four of these agents are compared and correlated with the chemical and biological properties. These hydroxypyridinone ligands bind the uranyl ion in the equator of a pentagonal prism; a solvent molecule fills the fifth coordination site. The tetradentate ligands are composed of two hydroxypyridonate groups connected by a diamine linker via amide coupling. The dihedral angles between two pyridinone ring planes in these complexes differ as the length of linear backbone changes, giving these molecules a ruffled shape. The physical parameters (such as NMR chemical shifts) of the uranyl complexes with tetradentate Me-3,2-HPOP ligands correlate with the length of the diamine linker, as does the in vivo activity. The ligands are amides of 3-hydroxy-*N*-methyl-2-(1*H*)-4-carboxypyridone. For L¹ the amine is propane amine. For the tetradentate bis-amides the linker groups are (L³) 1,3-diaminopropane, (L⁴) 1,4-diaminobutane, (L⁵) 1,5-diaminopentane.

Ligands containing the 1-methyl-3-hydroxy-2(1*H*)-pyridinone group (Me-3,2-HOPO) are powerful plutonium-(IV) sequestering agents. The Ce(IV) complexes of bidentate and tetradentate HOPO ligands have been quantitatively studied as models for this sequestration. The complexes Ce(L¹)₄, Ce(L²)₄, Ce(L³)₂, and Ce(L⁴)₂ (L¹ = Me-3,2-HOPO; L² = PR-Me-3,2-HOPO; L³ = 5LI-Me-3,2-HOPO; L⁴ = 5LIO-Me-3,2-HOPO) were prepared in THF solution from Ce(acac)₄ and the corresponding ligand. The complex Ce(L⁴)₂ was also prepared in aqueous solution by air oxidation of the Ce(III) complex [Ce(L⁴)₂]⁻. A new criterion, the shape measure *S*, has been introduced to describe and compare the geometry of such complexes. For these complexes the shape measure shows that the coordination geometry is strongly influenced by small changes in the ligand backbone or solvent. Solution thermodynamic studies determined overall formation constants (log ***b***) for Ce(L²)₄, and Ce(L³)₂, and Ce(L⁴)₂ of 40.9, 41.9, and 41.6, respectively. A thermodynamic cycle has been used to calculate these values from the corresponding formation constants of Ce(III) complexes and standard electrode potentials. From the formation constants and from the protonation constants of the ligands, extraordinarily high *pM* values for Ce(IV) are generated by these tetradentate ligands (37.5 for Ce(L³)₂ and 37.0 for Ce(L⁴)₂). The corresponding constants for Pu(IV) are expected to be substantially the same.

Relevance, Impact, and Technology Transfer

Molecule-selective sensors will prove very valuable for quantitation of hazardous materials in the vadose zone and in groundwater, and thereby provide a means to rapidly gauge the effectiveness of environmental remediation strategies at specific waste sites. It is important that sensor materials be cheap, easily manufactured, resistant to harsh chemical environments, sensitive to and selective for a variety of chemical species, physically small, and capable of modification as new needs arise. For example, detection of chloro- and nitroaromatics and their subsequent removal from the environment is important because the contamination of the soil and groundwater by small amounts of these substances can result in these substances entering the food chain with serious health consequences. The technology that will be derived from molecular sensors attached to polymers will provide a uniquely versatile method of analyzing for dozens of contaminants simultaneously. For example, although vadose zone and groundwater contamination problem abounds at sites such as Hanford, there are many sites in which the subtle interaction of a variety of contaminants makes analysis and evaluation of these sites particularly difficult.

Close interactions of the Berkeley group with the staff at LBL provides a direct pipeline to personnel whose major focus is environmental remediation of contaminants from weapons processing.

Project Productivity

All major goals of this project were accomplished.

Personnel Supported

Argonne National Laboratory:

Wighard Jaeger, Postdoctoral Fellow

Lin Chen, Staff Scientist

David Gosztola, Staff Scientist

Tufts University:

(All are partially supported)

Tarun Kumar Mandal, Postdoctoral Fellow

Senerath Palamkumbura, Postdoctoral Fellow

Caroline Schauer, Postdoctoral Fellow

Ferenc Szudorki, Postdoctoral Fellow

Myoyong Lee, Postdoctoral Fellow

Mary Elizabeth Tabacco, Postdoctoral Fellow

University of California, Berkeley:

Jide Xu, Staff Scientist

Chris Sunderland, Graduate Student

Dan Doble, Postdoctoral Fellow

Emil Radkov, Postdoctoral Fellow

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Interactions

The three groups involved in this project carried out a collaborative effort.

Transitions

Work stemming from this research is being considered by the DOE for use in heavy element extraction and removal.

Patents

None

Future Work

Work on these topics is being carried out in the Raymond and Walt labs using other funding sources. The Wasielewski group does not currently have funding to address these problems.

Literature Cited

None

Feedback

The terminal nature of these three year projects severely limits the ability of the principal investigators to build momentum that will allow serious follow-up work to progress. A method must be sought to insure that a significant fraction of available funds are targeted toward competitive renewals.

Appendices

None