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Ion and Molecule Sensors Using Molecular Recognition in Luminescent, Conductive Polymers

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Research Objective

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.

Research Progress and Implications

As of June 1, 1998, we have prepared several polymers based on the incorporation of 2,2'-bipyridine into poly(phenylenevinylene) polymers. The central idea, illustrated in Figure **1**, is to prepare a pseudoconjugated, ligand-containing polymer that upon incorporating metal ions undergoes a conformational change, thus converting the initial partially conjugated polymer to a fully or near fully conjugated one. Such conjugation enhancement,along with the simultaneous electron density change caused by incorporating metal ions onto the backbone of polymers, dramatically changes the optical and conductivity properties of the polymer. These property changes are used to signal the presence of the metal ion analyte. We have developed several synthetic routes to these polymers and have demonstrated that they exhibit selective binding properties when exposed to transition metals and lanthanides. In addition, we have developed a new polymer that gives us the versatility that we need for rapid attachment of ligands that bind heavy metals, such as lead and plutonium.

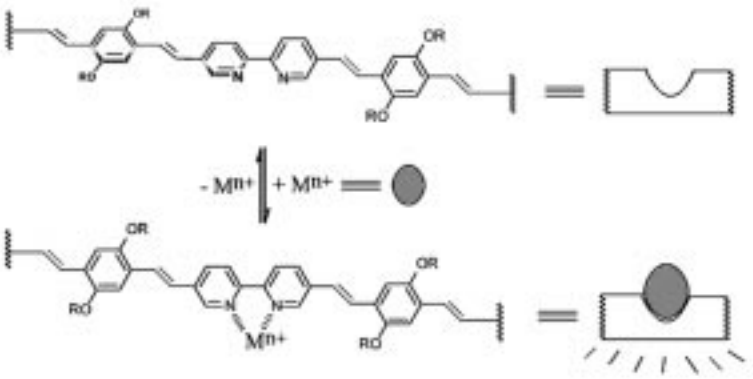

Figure 1**. Metal binding results in conformational changes in the conjugated polymers.**

This polymer has reactive ester groups that can be used to append other ligands to a pre-formed conjugated polymer backbone.

We have prepared ligands that are specific for iron, plutonium (IV), uranyl, and lead ions, which are highly suitable for incorporation as molecular recognition sites in the polymers. This work has addressed two important questions regarding the incorporation of multidentate metal-ion specific sequestering agents into sensor materials. The first question was whether it was feasible to attach such ligands (specifically, Pu(IV) sequestering ligands) to the polymer, and the second question was to what extent these ligands need to be preorganized in order to exhibit discriminate binding of metal ions. Four different Pu(IV) sequestering ligands were attached to a Merrifield resin. Extraction experiments with these materials demonstrated their high efficiency at Pu(IV) complexation as well as high selectivity over simultaneously present Fe(III) which has similar complexation behavior. It appears that the presence of tetradentate ligand groups (containing two bidentate units each) is sufficient to provide strong and selective binding of Pu(IV).

We developed photoinitiated polymerization reactions that serve to fix the poly(phenylenevinylene) polymers at well separated spots on the tip of a single optical imaging fiber. Polymer blends of the conjugated sensor polymer with either siloxane or 2-hydoxy-ethylacrylate polymers are used for this purpose. Addition of crosslinkers to the acrylate polymer makes it possible to trap the conjugated polymer within the structure of the acrylate. Crosslinking prevents swelling of the acrylate polymer in the presence of organic solvents, and thus prevents loss of the entrapped conjugated sensor polymer. We have demonstrated that the metal binding properties of polymer blends containing the conjugated polymers and either siloxane or 2-hydroxyethylacrylate polymers attached to the ends of fiber optics are very similar to those observed for polymer solutions. These results represent the achievement of a critical milestone which demonstrates that conjugated polymers in polymer blends offer a convenient and functional way in which to prepare prototype fiber optic sensors for metal ions.

Planned Activities

The following work is planned for the next year: derivatization of conjugated polymers with the new ligands that are designed specifically for actinides; the synthesis of well-defined conjugated oligomers of phenylenevinylene substituted with ligands for heavy metals; the use of pre-formed oligomers as additives in acrylate polymers for producing fiber optic sensors; functionalization of the sequestering agents that were developed for uranyl ions with the goal of providing a ligand that will make the properties of the conjugated polymers sensitive to the presence of the uranyl ion; synthesis of new ligands that make use of the stereochemical coordination properties of lead ions to produce polymer-compatible ligands that are sensitive to lead; investigations of the photoimmobilization of the oligomers and polymers on fiber optics using photo excitation of a particular region of the fiber to initiate selective binding to the fiber; testing of a prototype sensor on heavy metal and actinide groundwater contamination.

Other Access to Information

FY1997 Year-End Progress Report (14 pages with figures and references) M.R. Wasielewski

This report is available on-line at **www.chem.nwu.edu/~wasielew/Homepage.html**