

**Project Title:** Electroactive Materials for Anion Separation – Technetium from Nitrate

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### ***Progress Report***

#### RESEARCH OBJECTIVE

The aim of the proposed research is to use electroactive ion exchange materials to remove anionic contaminants from HLW wastes and process streams. An ion exchange process using electroactive materials sorbs contaminants selectively and then expels (elutes) them electrochemically by changing the charge balance through redox reactions in the sorbent as opposed to requiring the addition of a chemical eluent. Such processes can theoretically remove anions (e.g., pertechnetate, chromate, and perchlorate) and concentrate them in a separate product stream while adding no process chemicals. A practical implementation in HLW process facilities would be a breakthrough in the ability of DOE to economically minimize waste and prevent pollution throughout the complex. To enable this, our work focuses on manipulating specific properties of redox polymers to control the hydrophobicity and ion-pair properties pertinent to the reversibility, selectivity, stability, intercalation/de-intercalation rates, and capacity of the polymers.

#### RESEARCH PROGRESS AND IMPLICATIONS

This report summarizes work during 6/01/03 - 6/01/04 of a six-year project that began on 10/01/97. In previous years, we've shown that the polyvinylferrocene (PVF) class of polymers have two primary issues affecting their potential use as materials for removal of  $\text{TcO}_4^-$  from high level waste (HLW): 1) the oxidized polymers (i.e., ferrocenium form) are not stable under the high pH conditions (highly alkaline) that is encountered for the

wastes; 2) the slight selectivities observed are most likely due to hydration energy effects of the anions ( $\text{TcO}_4^-$  has a smaller hydration energy than  $\text{NO}_3^-$ , and therefore it will occupy hydrophobic polymers more readily than  $\text{NO}_3^-$ ). In previous studies, we have examined the effects of alkylating the cyclopentadienyl rings of the ferrocene moiety in the polymers to enhance the alkaline stability of the polymers, and have seen evidence that this does provide some improvement (we can cycle the polymer through redox in 1 M NaOH solution before the ferrocenium centers all decompose). Alkylation also provides a more hydrophobic environment which improves the selectivity of the polymer for  $\text{TcO}_4^-$ . However, preparation of alkylated PVF materials have many inherent difficulties; alkylation brings back the issue of low MW polymer since the alkyl chains tend to interfere with rapid growth of the polymer chain, hence the zwitterionic intermediates formed from vinylferrocene derivatives quench the polymerization process.

A series of iron complexes using the 4-methyl-4'-vinylbipyridyl ligand (mvbpy) has been synthesized according to published literature procedures to address the issue of pH stability. The series of synthesized iron compounds includes  $\text{Fe}(\text{mvbpy})_2(\text{CN})_2$ ,  $\text{Fe}(\text{mvbpy})(\text{m}_2\text{bpy})(\text{CN})_2$ ,  $\text{Fe}(\text{mvbpy})_2\text{Cl}_2$ ,  $\text{Fe}(\text{mvbpy})(\text{m}_2\text{bpy})\text{Cl}_2$ ,  $[\text{Fe}(\text{mvbpy})_3](\text{PF}_6)_2$  and  $[\text{Fe}(\text{mvbpy})(\text{m}_2\text{bpy})_2](\text{PF}_6)_2$  where  $\text{m}_2\text{bpy}$  is 4,4'-dimethylbipyridyl (Figure 1). The  $\text{Fe}(\text{mvbpy})(\text{m}_2\text{bpy})(\text{CN})_2$  was stable in highly alkaline solutions for days, and so most studies concentrated on this material.

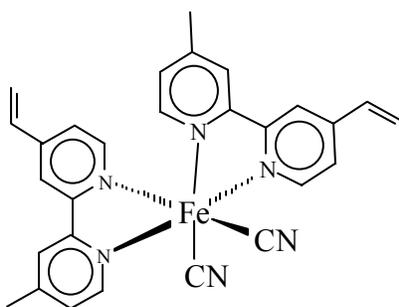


Figure 1.  $\text{Fe}(\text{mvbpy})_2(\text{CN})_2$

The mvbpy ligand was made using the Abruña method, while other bipyridyl ligands were made via Negishi cross coupling reaction; this approach allows preparation of asymmetric ligands.

A series of polymers of the following iron complexes containing the mvbpy have been successfully synthesized and spectroscopically characterized:  $[\text{Fe}(\text{mvbpy})(\text{m}_2\text{bpy})_2](\text{PF}_6)_2$ ,  $\text{Fe}(\text{mvbpy})(\text{m}_2\text{bpy})\text{Cl}_2$  and  $\text{Fe}(\text{mvbpy})(\text{m}_2\text{bpy})(\text{CN})_2$ . Also, copolymers with styrene and 4-vinylpyridine were prepared. In general, the molecular weights of the complex homopolymers and copolymers with styrene were fairly small. The molecular weights for the copolymers with  $\text{Fe}(\text{mvbpy})(\text{m}_2\text{bpy})(\text{CN})_2/4$ -vinylpyridine were as expected (Table 1).

Table 1. Weight average molecular weight for various copolymers of Fe(mvbpy)<sub>2</sub>(CN)<sub>2</sub> and 4-vinyl pyridine

Fe(mvbpy) <sub>2</sub> (CN) <sub>2</sub> /4-vinyl pyridine	Weight Average Molecular Weight (Daltons)
1:8	11,700
1:6.5	8400
1:6	10,300
1:3	2400
1:2	2800

Of particular importance was the stability of the Fe(III) complexes in base. Both Fe(mvbpy)<sub>2</sub>(CN)<sub>2</sub> and Fe(mvbpy)<sub>2</sub>Cl<sub>2</sub> were oxidized with concentrated nitric acid to the Fe (III) nitrate salts, which were then isolated as PF<sub>6</sub><sup>-</sup> salts using NH<sub>4</sub>PF<sub>6</sub>. The chloride complex decomposed in 1M NaOH aqueous/acetonitrile solution within 20 minutes, while the cyano complex underwent reduction back to the Fe (II) complex. Cyclic voltammetry of both the Fe (II) and Fe (III) cyano complexes were identical.

In order to do electrochemistry on some of the polymers, we examined quaternized pyridyl polymers to enhance the conductivity of the materials. This was accomplished using octylbromide and ethylbromide. The quaternized pyridines could be tuned for solubility in water with 50/50 mixtures of octylbromide/ethylbromide giving polymers that were partially soluble in water (octylbromide only gave water insoluble polymers and ethylbromide gave polymers completely soluble in water).

In summary, we have some new electroactive materials that are stable under high pH conditions. With the particular system we're using, we must find a better way to make the polymers more conductive. We are still looking for ways to enhance the selectivity of the polymers, and believe that the synthetic methods (e.g., Negishi or Stille Coupling) to prepare asymmetric bipyridyls will allow to arrive at the correct materials. Our prior experience with the polyvinylferrocene polymers show promise for their use as electroactive ion-exchange materials, though not for the highly alkaline radioactive wastes found at Hanford.

#### PLANNED ACTIVITIES

This is the final year of this project. During the remaining months we will work on preparing asymmetric bipyridyls that contain a polymerizable group (e.g., vinyl) on one ring and a group with selectivity for tetrahedral anions.

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INFORMATION ACCESS

*Presentation*

“Materials for Electroactive Ion-Exchange (EaIX) Separations of Perchnetate Ion,”  
M. Stender, T.L. Hubler, M. Alhoshan, W.H. Smyrl. 227<sup>th</sup> American Chemical Society  
National Meeting, March 28-April 1, 2004, Anaheim, CA.