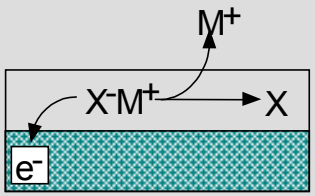
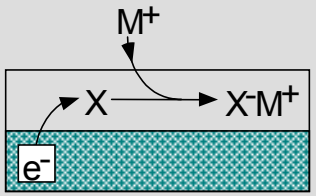
Electroactive Materials for Anion Separation-Technetium from Nitrate

TL Hubler, Pacific Northwest National Lab
WH Smryl, University of Minnesota
J McBreen, Brookhaven National Laboratory

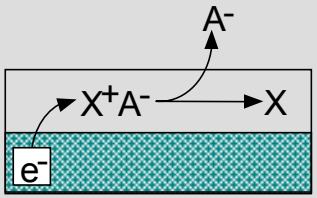
EalX/Redox Polymers



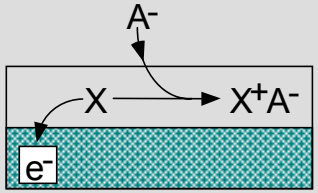
Cation Deintercalation/elution



Cation Intercalation/uptake

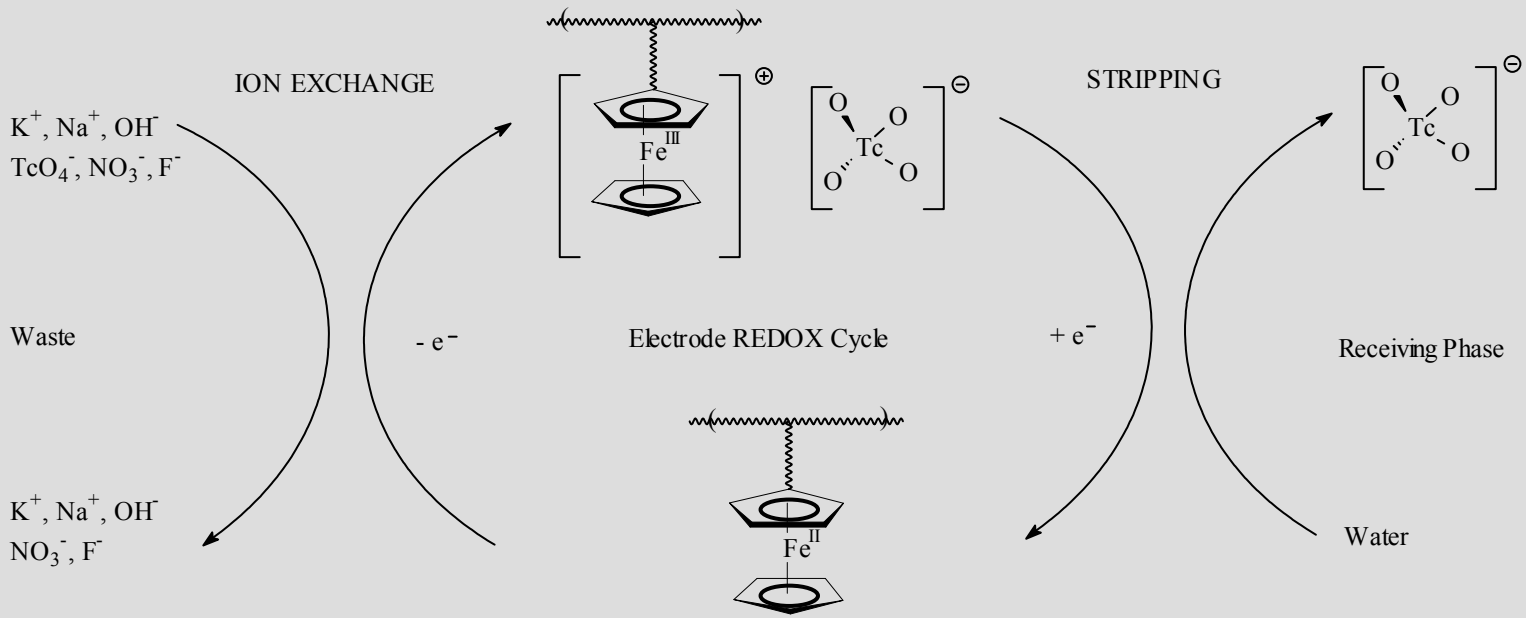


Anion Deintercalation/elution



Anion Intercalation/uptake

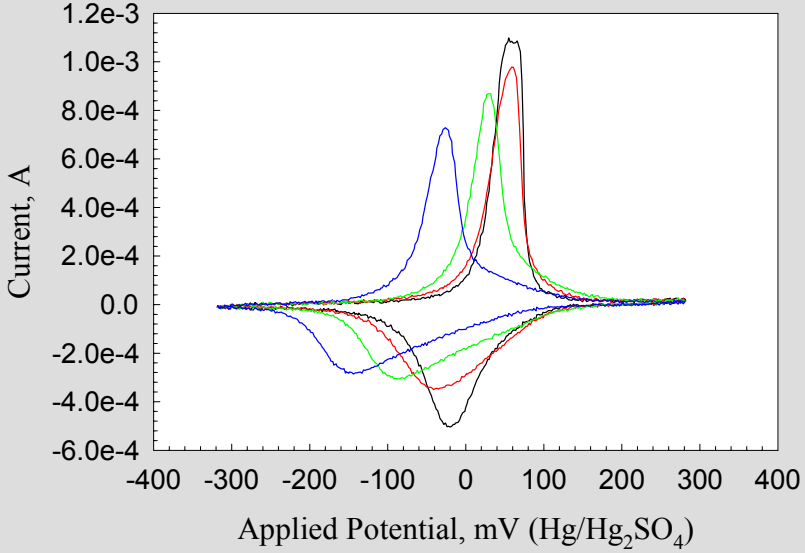
EalX Using PVF Polymers

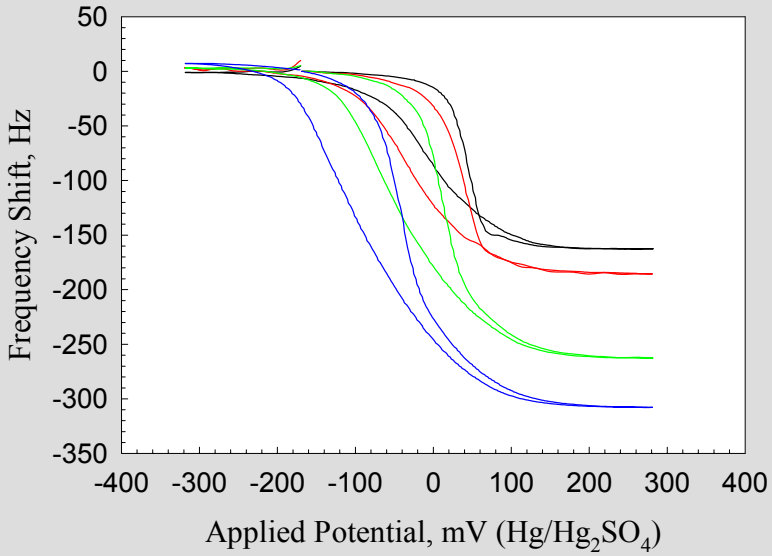


Preparation of PVF

- PVF usually prepared via bulk polymerization (usually gives higher MW polymer).
- Slow addition of AIBN (in benzene) to VF solution gives high MW PVF. Less AIBN = less intermolecular termination steps. High effective concentration of VF leads to significantly more growth of addition polymer.
- There is a significant amount of polymer branching.

PVF Selectivity

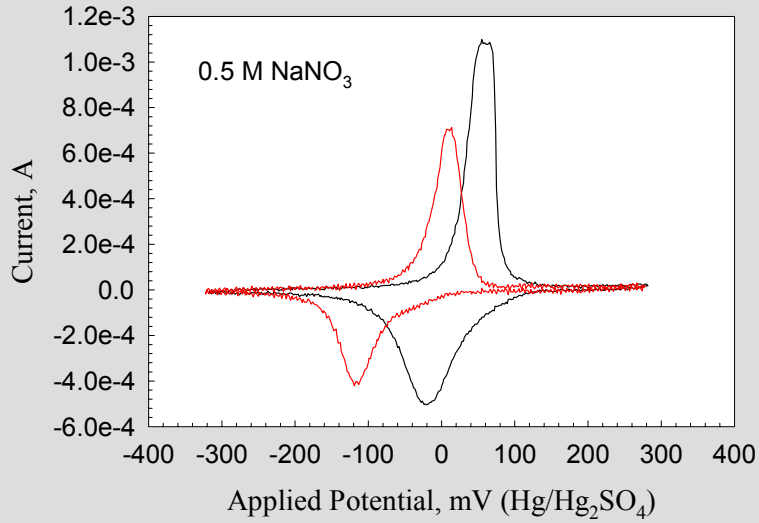


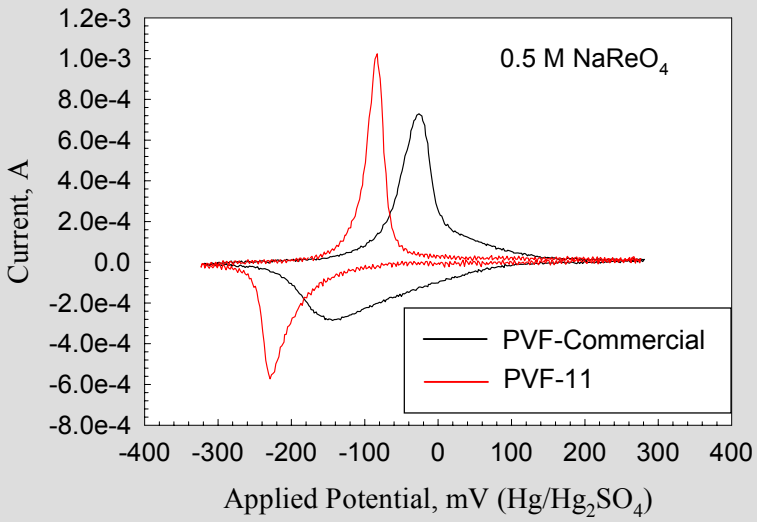


- 0.5 M $NaNO_3$
- 0.495 M $NaNO_3$ & 0.005 M $NaReO_4$
- 0.45 M $NaNO_3$ & 0.05 M $NaReO_4$
- 0.5 M $NaReO_4$

- Frequency shifts shown in (B) are proportional to mass uptake
- NO_3^- transport in the polymer is more facile than ReO_4^- transport as indicated by sharper cathodic (negative) peak in (A)
- The separation factor was determined to be 30 ± 6.

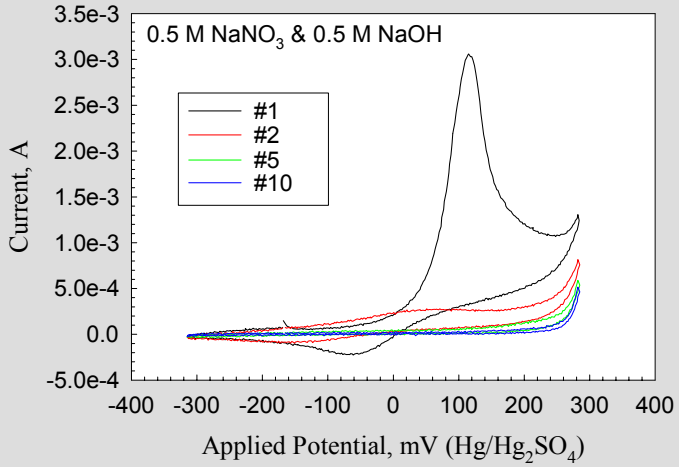
Intercalation/De-intercalation of ReO_4^-

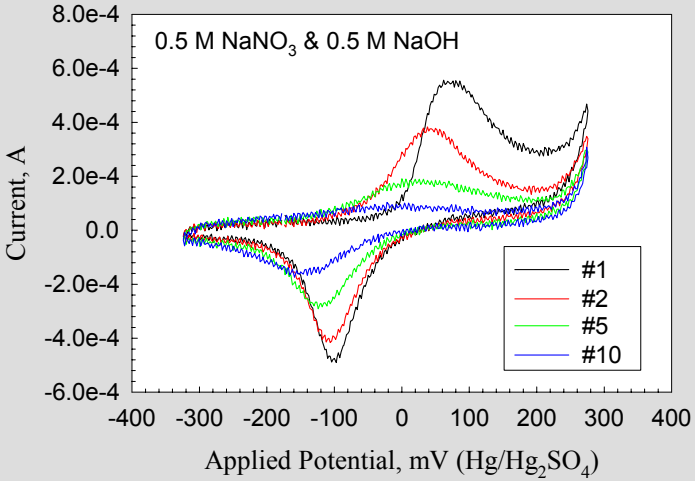




- De-intercalation of NO_3^- from alkylated PVF is more facile.
- Oxidation (intercalation) and reduction (de-intercalation) waves are shsharper for alkylated PVF in ReO_4^- solution. Alkylated PVF has a highigher void volume, hence guest anion transport is more facile.

Effect of Alkyl Group on Alkaline Stability of the Ferrocene Polymers



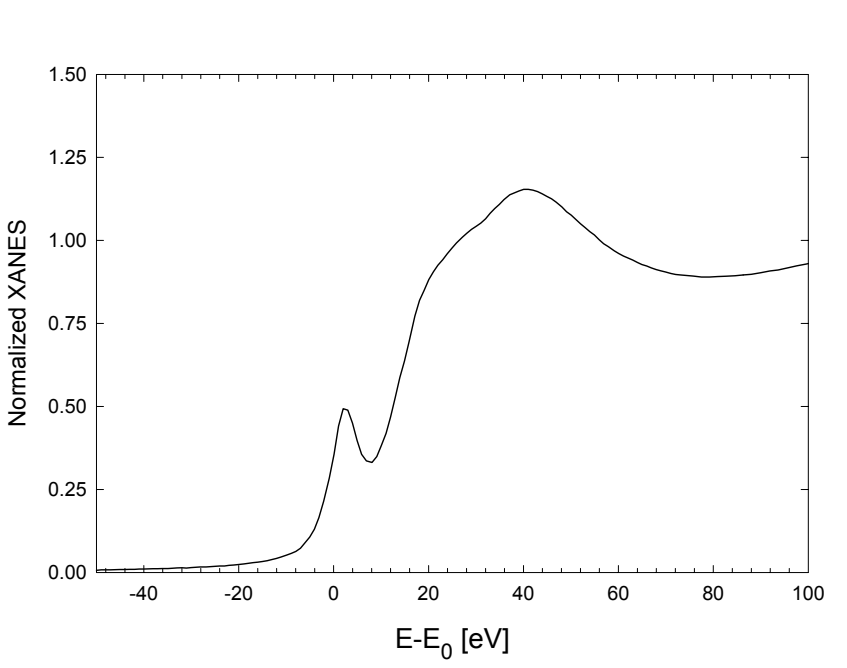


- Commercial PVF shows immediate deactivation in alkaline solution
- Alkylated PVF shows redox activity after 10 cycles. Sample is composed of of 70/30 monovinyl/divinyl groups.
- Have increased the ability to redox cycle up to 30 cycles.

Electrochemical Uptake of TcO_4^- into PVF

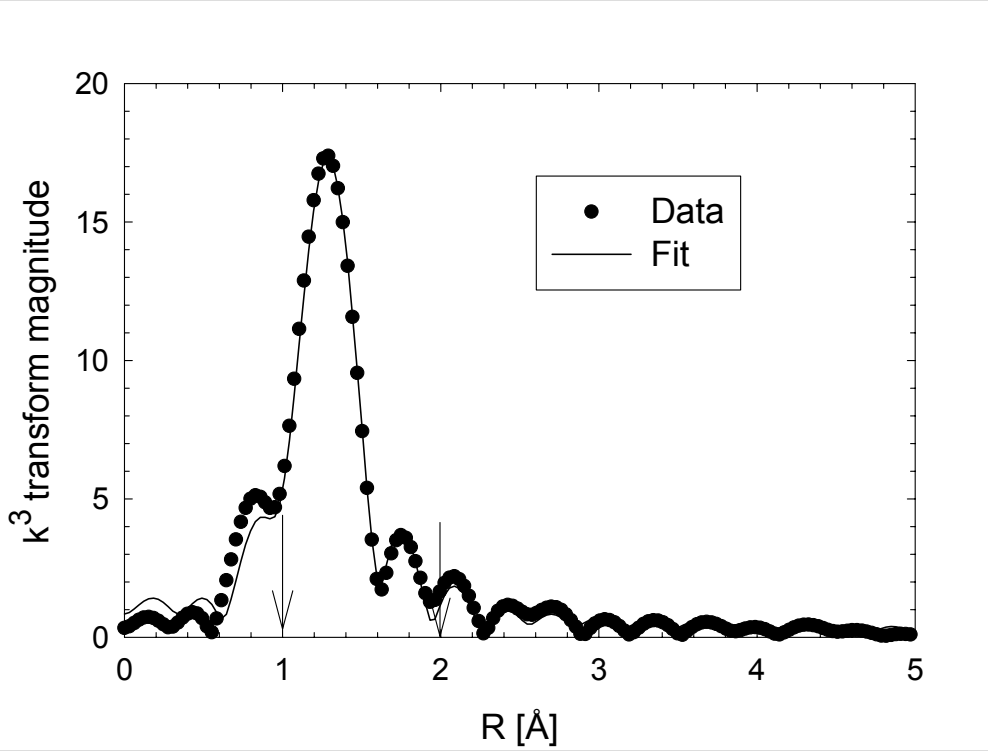
- 3 samples of PNNL prepared polymer loaded onto carbon cloth for study at BNL
- Samples prepared so that total activity of Tc-99 couldn't exceed 100 µCi (0.1 M $NaNO_3$ as supporting electrolyte)
- After electrochemical loading of samples, 3 rinse cycles were performed to removed any entrained TcO_4^- and $NaNO_3$
- Before and after analysis showed that 1.5-3.5% of theoretical available capacity was loaded with TcO_4^- ; total activity was about 0.2 µCi

XANES for PVF Loaded with TcO_4^-



The Tc K-edge XANES shows a strong pre-edge peak which arises from a 1s→4d transition (mixed with O 2p). This feature is a fingerprint of the TcO_4^- anion; and is signature of Tc in tetrahedral coordination with oxygen.

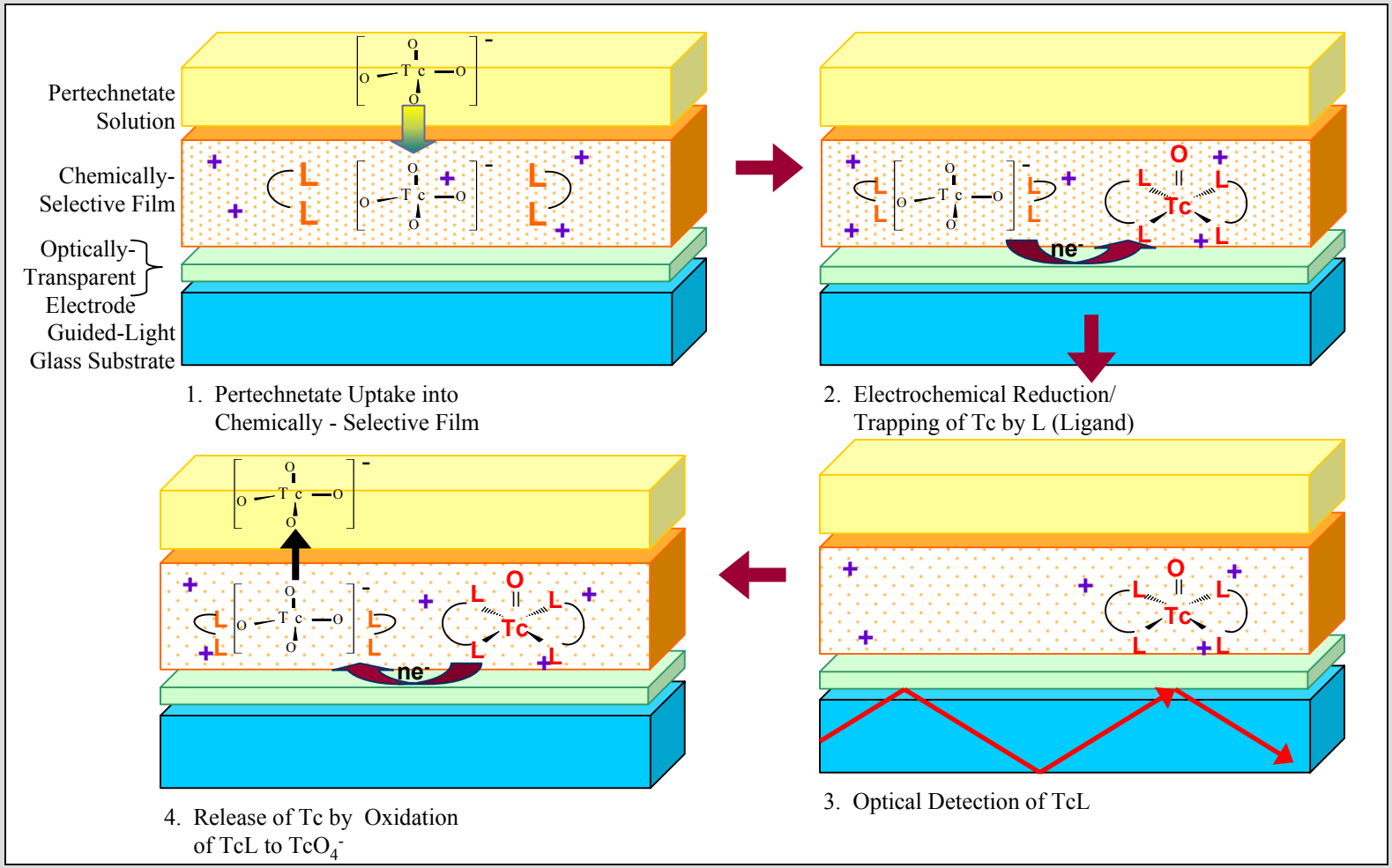
EXAFS for PVF Loaded with TcO_4^-



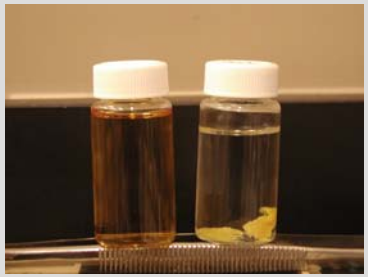
S_0^2 set at 0.95; 4.2 (3) Tc-O correlations at 1.713 (4) Å; R-factor: 0.002

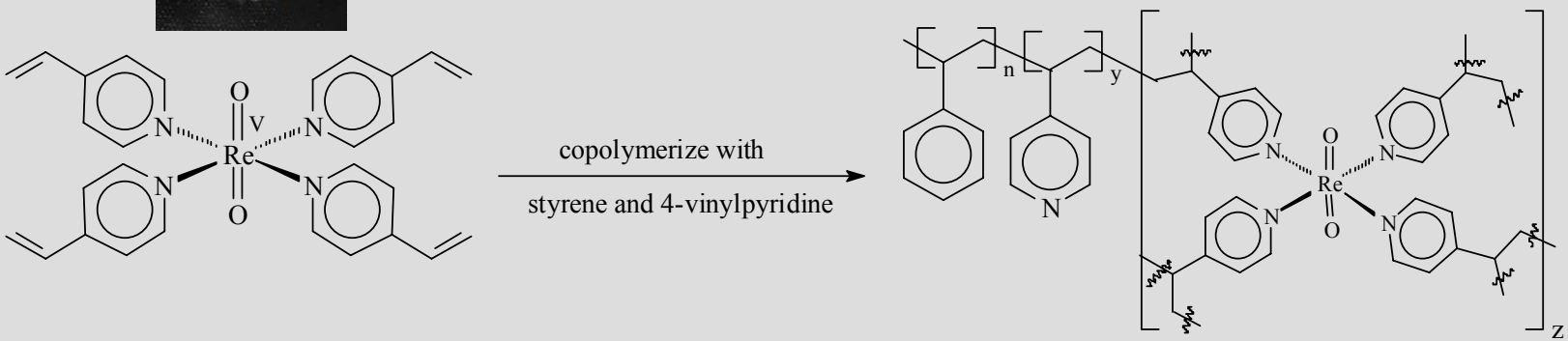
The EXAFS results clearly indicate that Tc is present as a TcO_4^- moiety in the sample. The Tc is tetrahedrally coordinated to oxygen atoms. However, no strong correlations from Tc or Fe further neighbors is visible in the EXAFS data.

Spectroelectrochemical Sensor for TcO_4^-



$Re(4\text{-}vpy)_4O_2^-$/Copolymerization

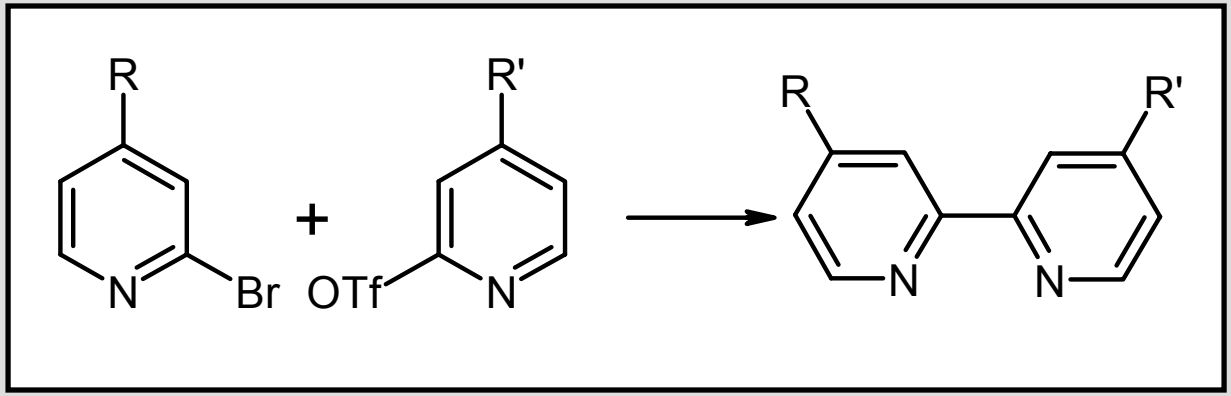




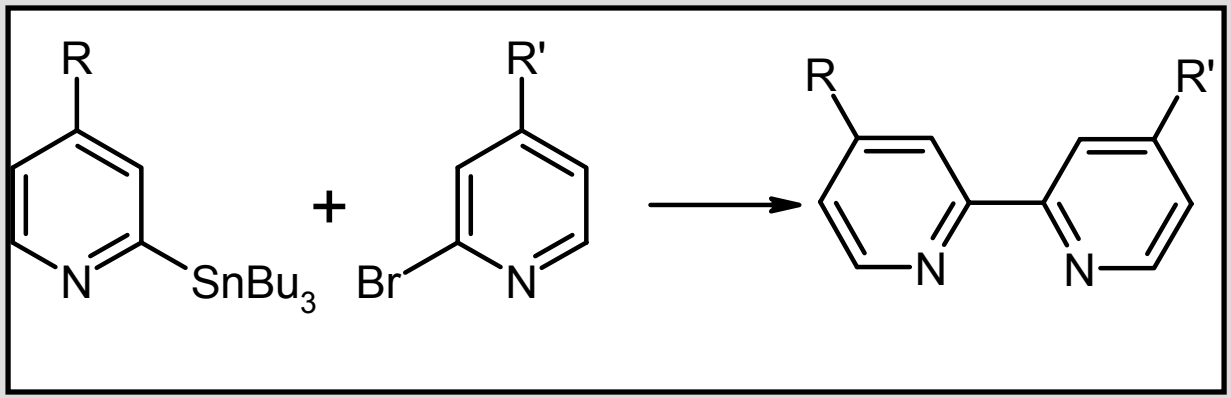
- Complexes have desired optical/electrochemical properties
- Optical characteristics of polymer are similar to monomer
- Rhenium could be driven off, forming metal templated site
- Tc complexes have also been prepared

Palladium Catalyzed Cross Coupling Reactions

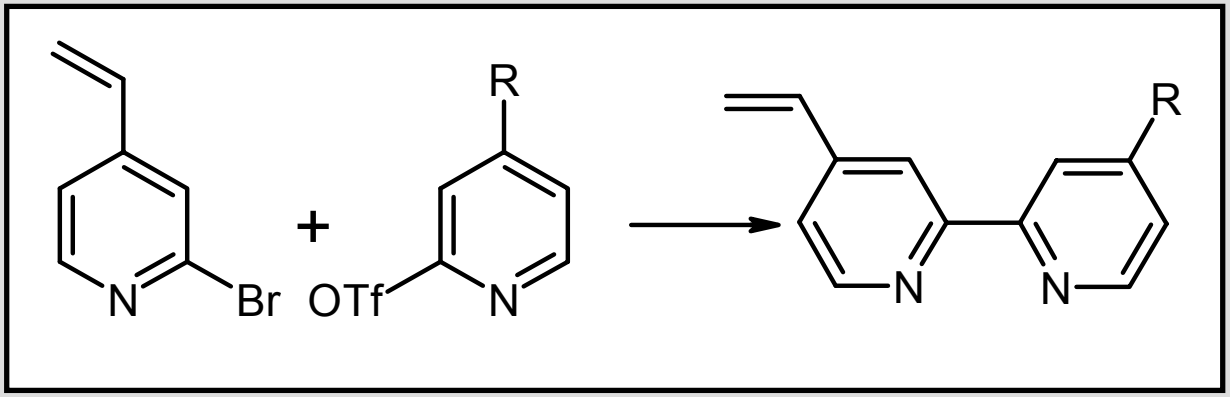
Negishi
~93-98%



Stille
~56-75%



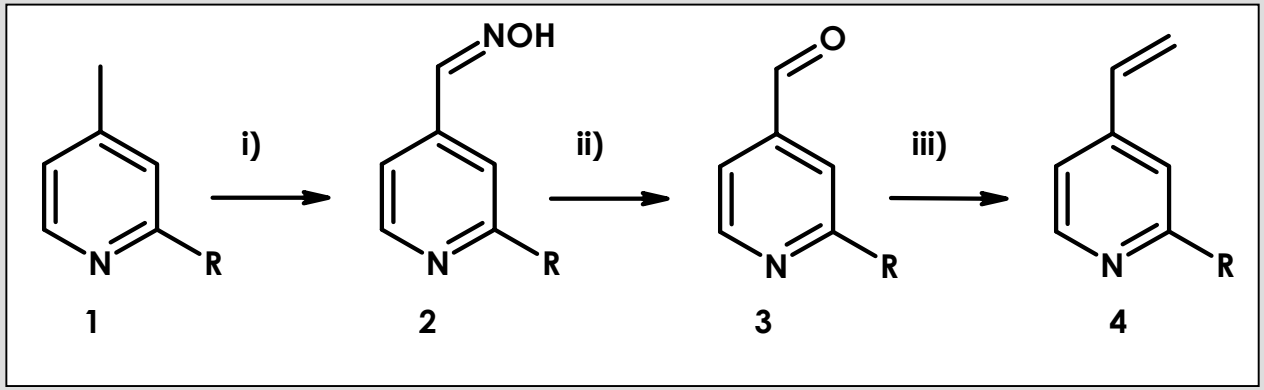
Negishi Coupling



- Instead of adding vinyl to ligand, make vinyl, then ligand
- The 2-halo-4-vinylpyridines are building blocks

Vinyl Formation

Scheme A[a]

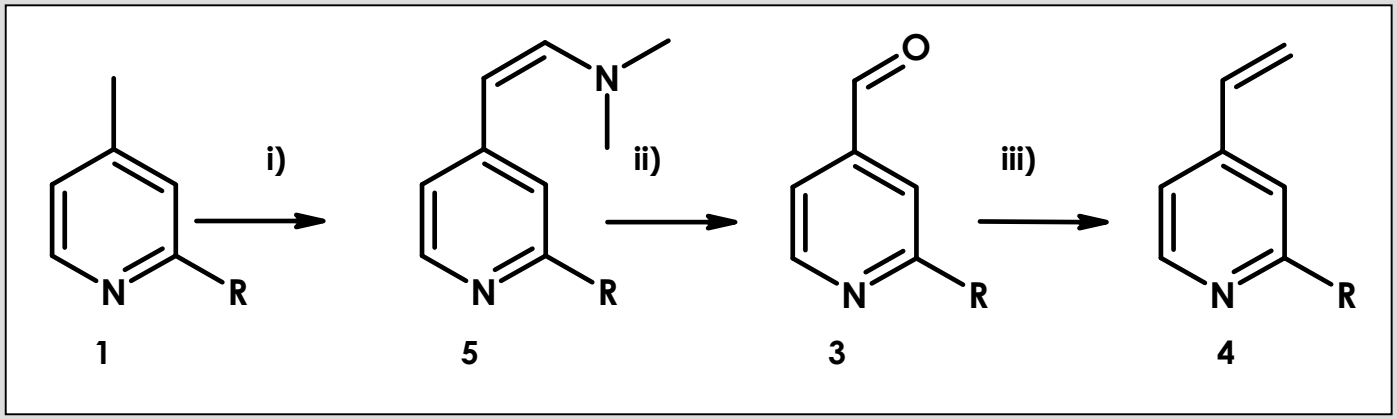


[a]**1a, 2a, 3a, 4a:** R = Br; **1b, 2b, 3b, 4b:** R = Cl; **1c, 2c, 3c, 4c.** R = Py; **i)** t-BuOK, THF, t-BuONO, -20°C or RT **ii)** Conc. HCl, CHO, 0°C **iii)** $(C_6H_5)_3PCH_3Br$, K_2CO_3, 18-crown-6, Benzene, 120°C

i. **Convert 4-methyl to 4-aldoxime**
ii. **Convert 4-aldoxime to 4-formyl**
iii. **Perform Wittig reaction on 4-formyl to form 4-vinyl**

Vinyl Formation

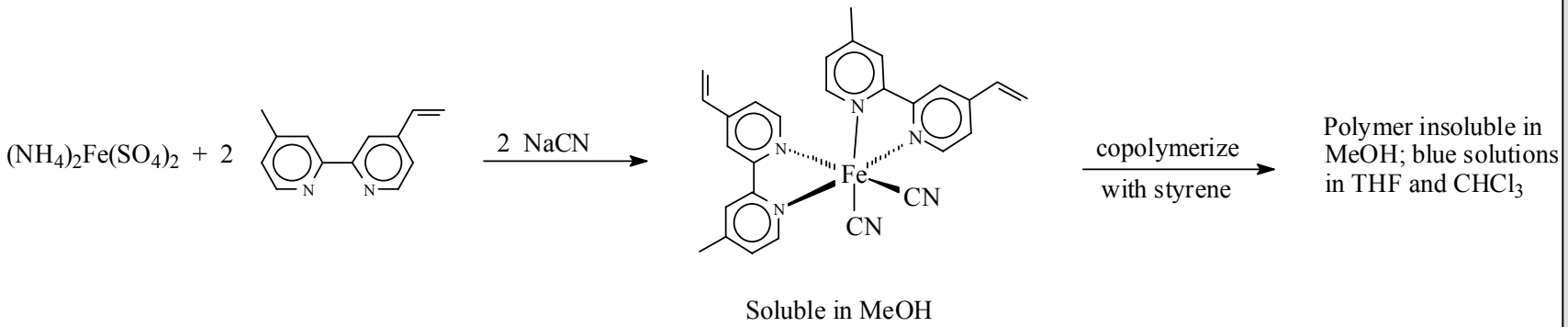
Scheme B[a]



[a]**1a, 5a, 3a, 4a:** R = Br; **1c, 5c, 3c, 4c:** R = Py; **i)** Bredereck's Reagent, DMF **ii)** $NaIO_4$, H_2O **iii)** $(C_6H_5)_3PCH_3Br$, K_2CO_3, 18-crown-6, Benzene, 120°C

i. **Convert 4-methyl to 4-dimethylaminovinyl (Bredereck's Rxn)**
ii. **Oxidize 4-dimethylaminovinyl to 4-formyl with $NaIO_4$**
iii. **Perform Wittig reaction on 4-formyl to form 4-vinyl**

New Directions for Electroactive Polymers



- Completing characterization of these polymers – look promising for as materials to deal with the pH issue for electroactive polymers
- Other ligands are phenanthroline, terpyridines, etc

Future Work

- Fe complexes which are base stable –
  - Prepare structures which have selective groups for TcO_4^- , e.g., guanidinium structure.
- Continue work with functionalizing membranes for separations; e.g., carbon nanotubes
- Potential for use of these materials for ClO_4^- removal from water. PVF polymers may still have application in this case if selective groups can be attached.

Research Teams

- Separations
  - Matthias Stender (postdoc, PNNL)
  - Scot Rassat (PNNL)
  - Prof. Kevin Gable (visiting faculty, OSU)
  - Mike Lilga (PNNL)

- UC/Sensor Project
  - Prof. William R. Heineman (UC)
  - Prof. Carl J. Seliskar (UC)
  - David J. Monk (postdoc, Tufts U.)