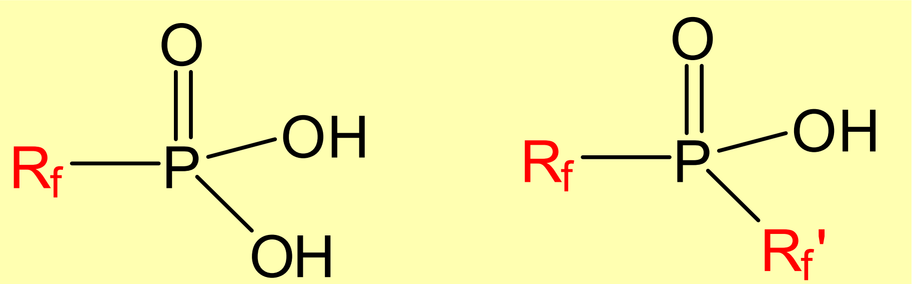
Fluoroalkyl-phosphonic-acid-based proton conductors



Stephen Creager (PI) and Darryl DesMarteau
Clemson University
and
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University of Utah

May 16, 2007

FC 20

DE-FG36-06GO16031

Overview

Timeline

- Start: April 2006
- Finish: March 2011
- Twenty percent complete

Budget

- Total project funding
  - DOE $1,500,000
  - Contractor $381,000
- Funding for FY06
  - $150,000 from DOE for April – Oct 2006
  - $150,000 from DOE for Oct 2006 – March 2007

Barriers

- Barriers
  - Thermal, air and water management.
- Targets
  - Membrane ionic conductivity > 0.10 S/cm at < 120 ^{o}C and water partial pressure of 1.5 kPa for transportation
  - Membrane ionic conductivity > 0.10 S/cm at > 120 ^{o}C for stationary

Partners

- Dr. Alex Kitaygorodskiy, Clemson
- Dr. Ashok Krishnaswami, JEOL
- Professor Klaus D. Kreuer, Max Planck Institute, Stuttgart, GE

  (all these will help with NMR studies of proton transport rates)

Objectives

Overall project objective	• Provide new electrolyte materials for use in next-generation hydrogen-fuel-cell power sources, especially for automotive transportation applications.
Specific project objectives	(1) Synthesize and characterize new proton-conducting electrolytes based on the fluoroalkylphosphonic acid functional group; and (2) Create and apply new computer models to study proton conduction in fluoroalkylphosphonic acid-based electrolytes.
Year 1 Milestones (April 2006 – March 2007)	• Synthesize and/or purify at least 10 g each of one or more small-molecule fluoroalkylphosphonic acid electrolytes. • Fabricate and validate an apparatus for measuring ionic conductivity of electrolytes at temperatures between ambient and 120 ^{o}C and relative humidities between 25 and 100 percent. • Develop classical force fields for and perform MD simulations of low molecular weight fluoroalkylphosphonic acid electrolytes using developed force field. • Develop first generation of the multi state empirical valence bond model (MS-EVB) for proton transport in fluorophosphonic acid.

Approach

Task 1.0 Synthesize new fluoroalkyl-phosphonic-acid-based electrolytes. – Small-molecule acids – Trifluorovinylether (TFVE) monomers – Tetrafluoroethylene (TFE) copolymers to give ionomer membranes	**Task 5.0** Perform computer simulations of fluoroalkylphosphonic-acid electrolytes. – Develop and validate force fields including multi-state empirical valence bond model for explicit treatment of proton transport in MD simulations. Predict proton and water transport rates.
Task 2.0 Characterize new fluoroalkyl-phosphonic-acid-based electrolytes. – Structure, purity, ion (proton) transport rates (diffusivity, conductivity)	**Task 6.0** Perform computer simulations of fluoroalkylphosphonic acid electrolyte / heterocycle/water mixtures. – As in Task 5.
Task 3.0 Demonstrate conductivity of at least 0.07 S/cm at 80% RH at ambient temperature.	**Task 7.0** Project Management and Reporting. – Deliver membrane(s) to Topic 2 awardee; periodic reports; annual reviews
Task 4.0 Demonstrate conductivity of at least 0.10 S/cm at 50% RH at 120 ^{o}C.	

Rationale: Why fluoroalkyl-phosphonic acids?

1. They are similar to phosphoric acid in allowing for **structure-diffusion-based proton hopping** without the need for excess liquid water;
2. They are **stronger acids** than phosphoric and alkylphosphonic acids which should promote proton dissociation, hopping and transport;
3. They should have **weaker adsorption** onto Pt than other phosphorous-acid-based electrolytes which should help prevent electrocatalyst poisoning and promote higher oxygen reduction activity;
4. They should provide **higher oxygen solubility** than other phosphorous-acid-based electrolytes which should also promote higher oxygen reduction activity; and
5. They should be quite **chemically and thermally stable** which will provide durability in PEM fuel-cell power sources

Electrolyte Structures

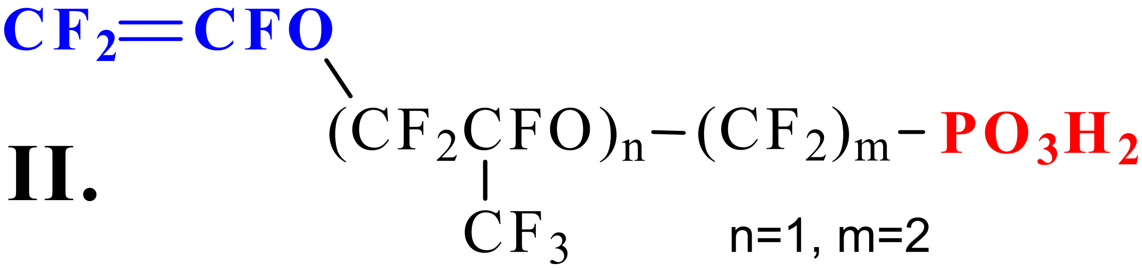
I.

$F—(CF_2)_n—PO_3H_2$

$H_2O_3P—(CF_2)_n—PO_3H_2$

Small molecules

II.

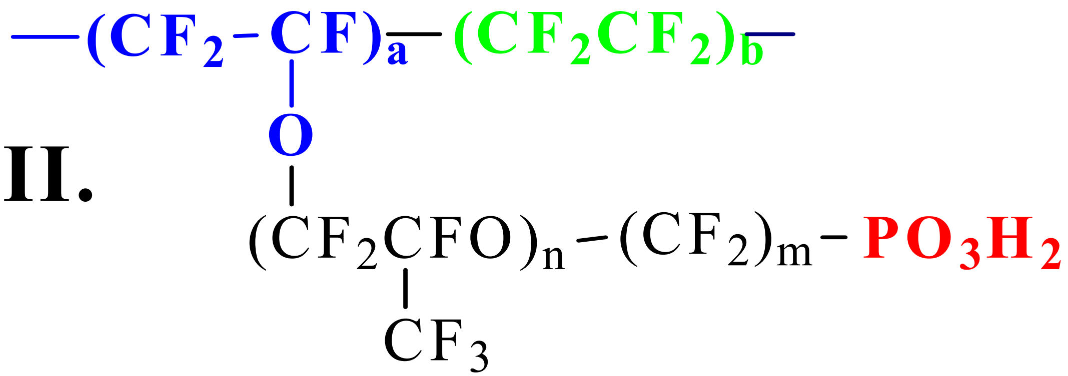


$CF_2{=}CFO—(CF_2CF(CF_3)O)_n-(CF_2)_m-PO_3H_2$

n=1, m=2

Trifluorovinylether monomers

III.



$—(CF_2-CF(O(CF_2CF(CF_3)O)_n-(CF_2)_m-PO_3H_2))_a—(CF_2CF_2)_b—$

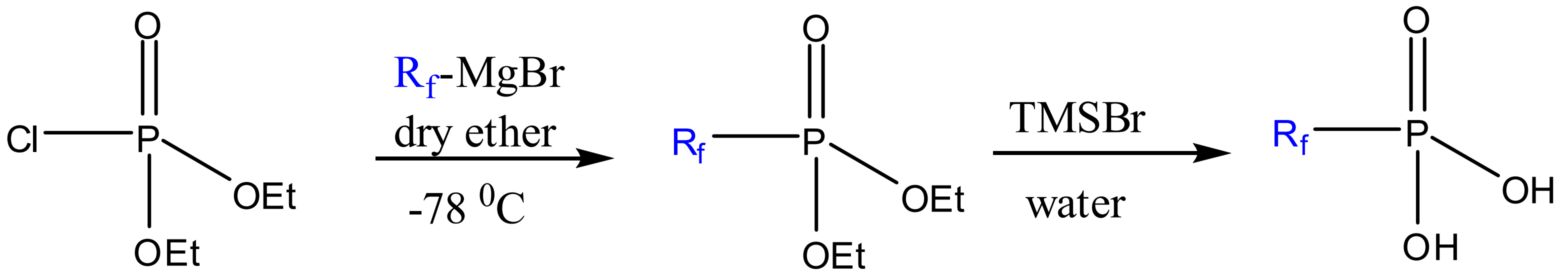
Fluoroalkylphosphonic acid ionomers

Technical Accomplishments

Synthesis & characterization of R_f-PO_3H_2 small-molecule model compounds and trifluorovinyl ether monomers

Fluoroalkylphosphonic acid synthesis

$$R_f\text{-I} + CH_3CH_2MgBr \xrightarrow[-78\ ^{0}C]{\text{dry ether}} R_f\text{-MgBr}$$



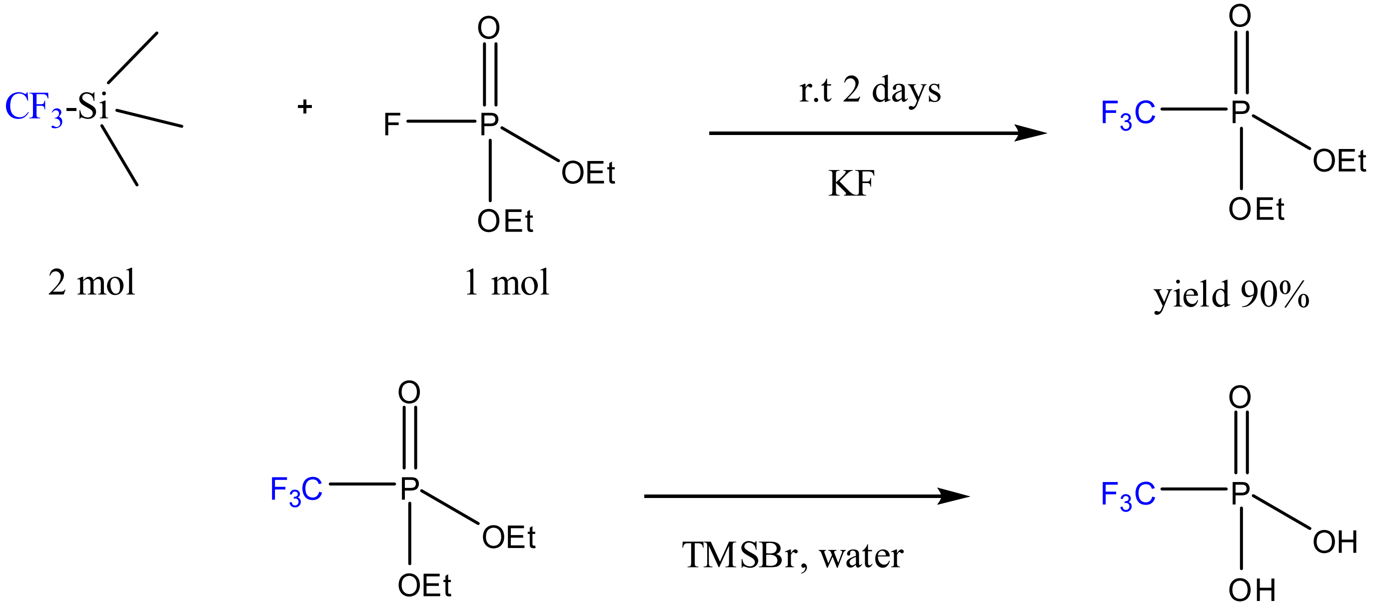
R_f-I ⟶
CF_3 --------------------gas
CF_3CF_2---------------gas
$CF_3CF_2CF_2$--------- liquid
$CF_3CF_2CF_2CF_2$----liquid

<u>Some problems with this method</u>:

- Instability of the R_f^- anion
- R_f-H formation, olefin formation

Cen, Wenbiao; Shen, Yanchang.Journal of Fluorine Chemistry (1991), 52(3), 369-75.

An improved synthesis of perfluoroalkyl-phosphonic acids

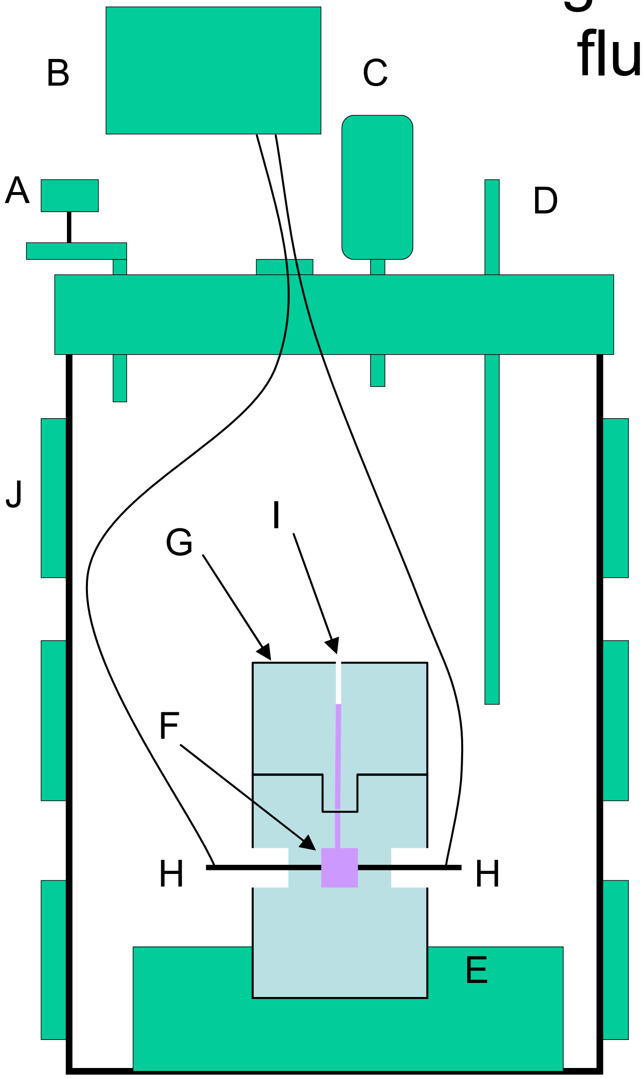


- Yields are high, all by-products are volatile and easily removed.
- Higher perfluoroalkyl homologues have not yet been synthesized via this method
- Preparations using R_f – C_2F_5, C_3F_7, C_4F_9 are in progress

Semchenko, F. M.; Eremin, O. G.; Martynov, B. I. Zhurnal Obshchei Khimii (1992), 62(2), 473-4.

Conductivity Studies

Diagram of a conductivity cell for study of liquid fluoroalkylphosphonic acid electrolytes.

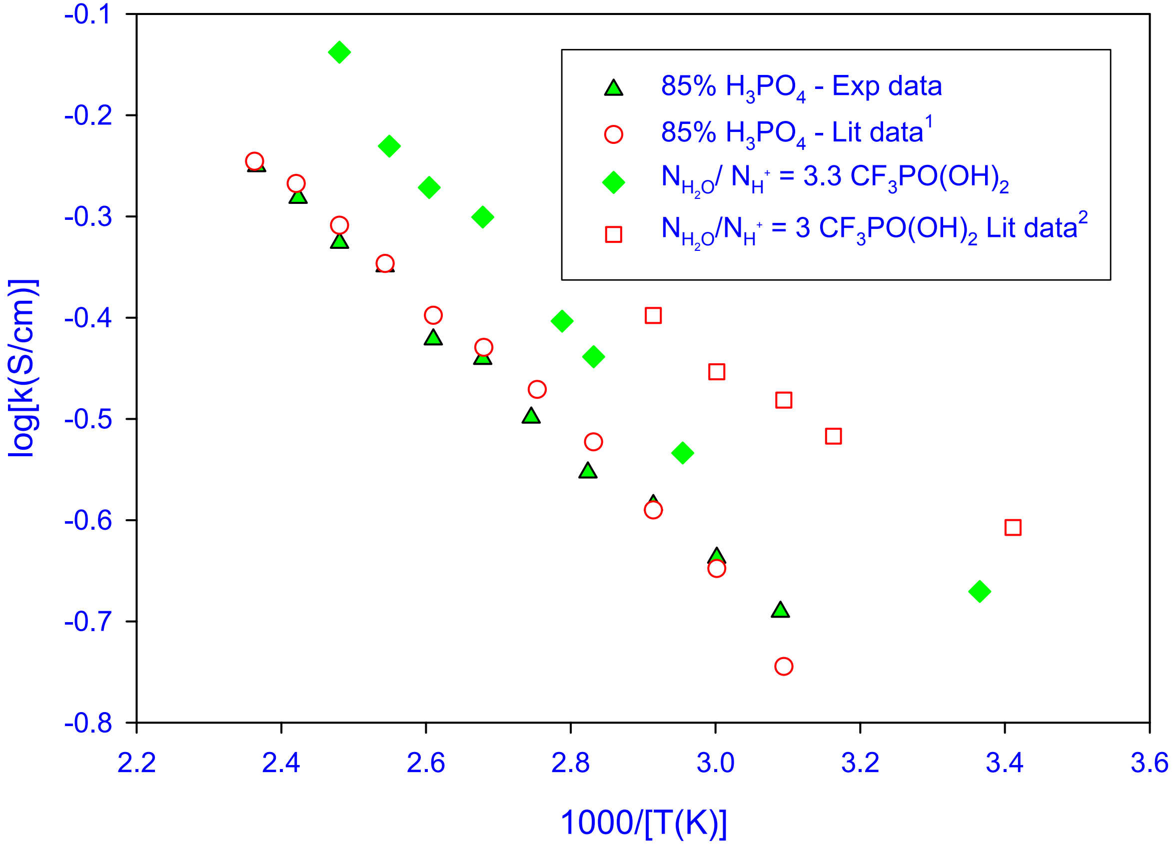


- **Cell internal volume is less than 20 μL**

Parts are as follows:

A. Vacuum / gas inlet / outlet
B. Impedance analyzer
C. Pressure transducer
D. Thermocouple
E. Cell holder
F. Liquid electrolyte (acid plus water)
G. PEEK cell body
H. Platinized platinum rod electrodes
I. Filling / pressure equalization hole (1 mm diameter)
J. Heating tape for temperature control

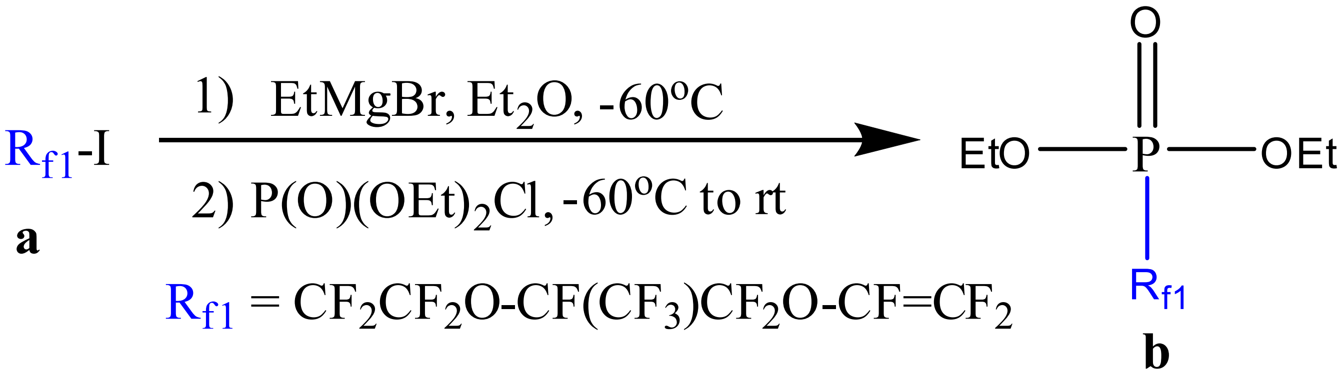
Arrhenius plots of ionic conductivity



- Trifluoromethylphosphonic acid with three waters per acid has higher conductivity than 85% phosphoric acid
- Studies using variable amounts of water, from near-anhydrous to very water-rich, are in progress.
- Studies using different fluoroalkyl groups including simple chains, difunctional compounds, and trifluorovinylether monomers, are in progress.

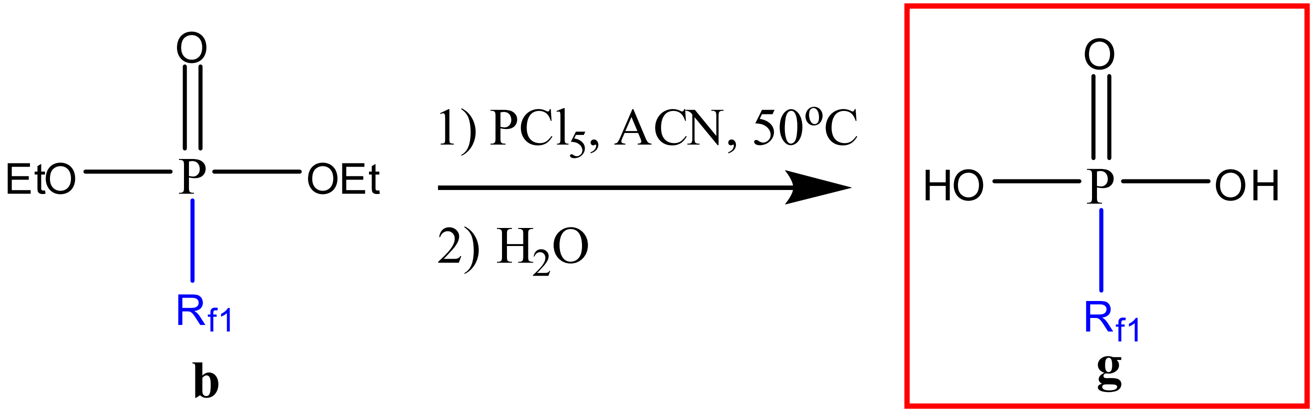
1. Chin, D.-T., Chang H. H., Journal of Applied Electrochemistry, 1989. 19: pp. 95-99
2. Razaq, M., Razaq A., Yeager E. Case Western Reserve Univ. 1989 pp 214 NTIS No. PB89178768

Synthesis of monofluoroalkylphosphonic acid trifluorovinyl ether (TFVE) monomer **g**



a **b**

$R_{f1} = CF_2CF_2O\text{-}CF(CF_3)CF_2O\text{-}CF{=}CF_2$

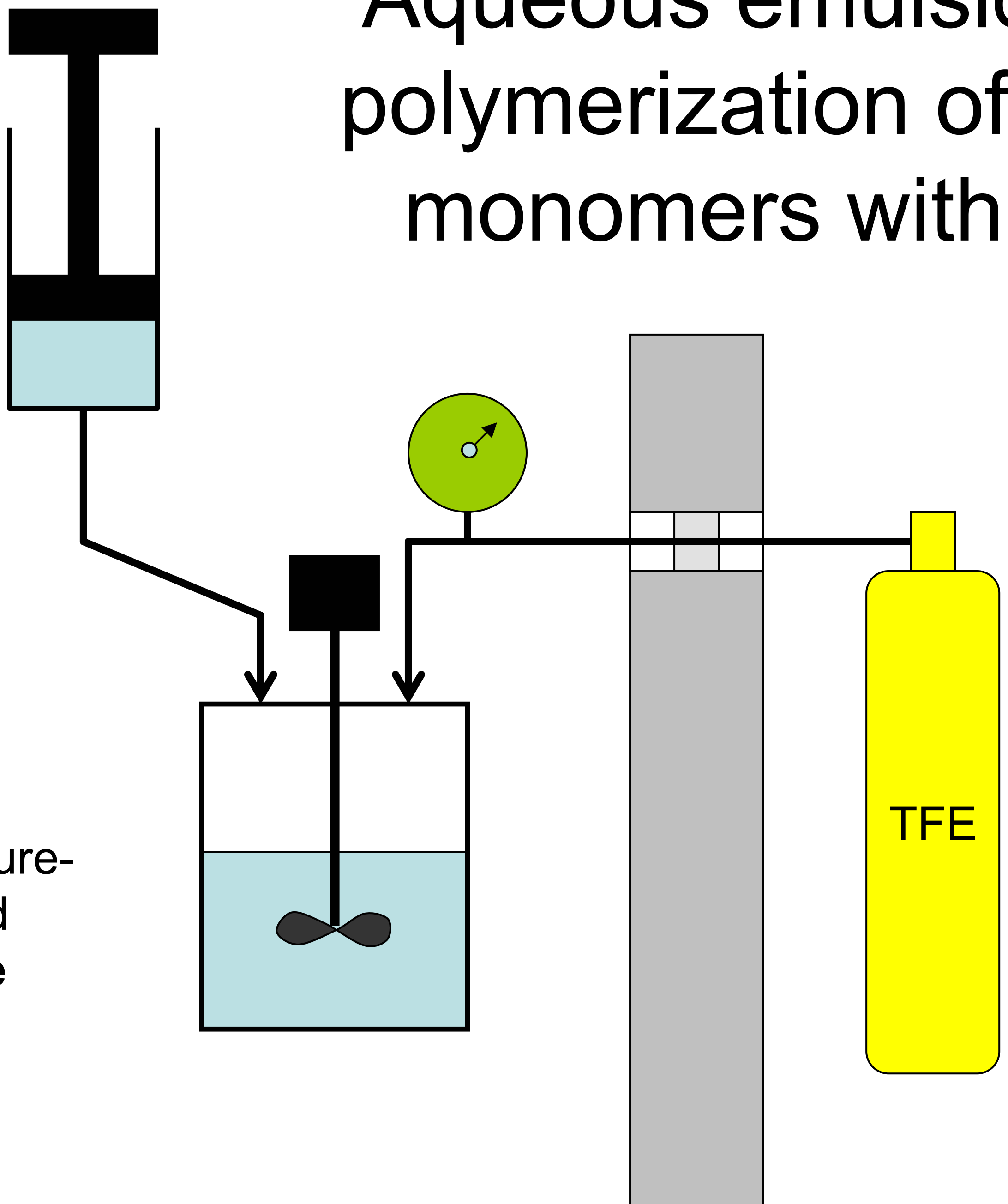


b **g**

- Monomer g was obtained in excellent yield in approximately 10 gram amount

Fluoroalkyl Phosphonic Acid Ionomer Synthesis and Characterization

Aqueous emulsion co-polymerization of TFVE monomers with TFE



Monomer feed from syringe pump

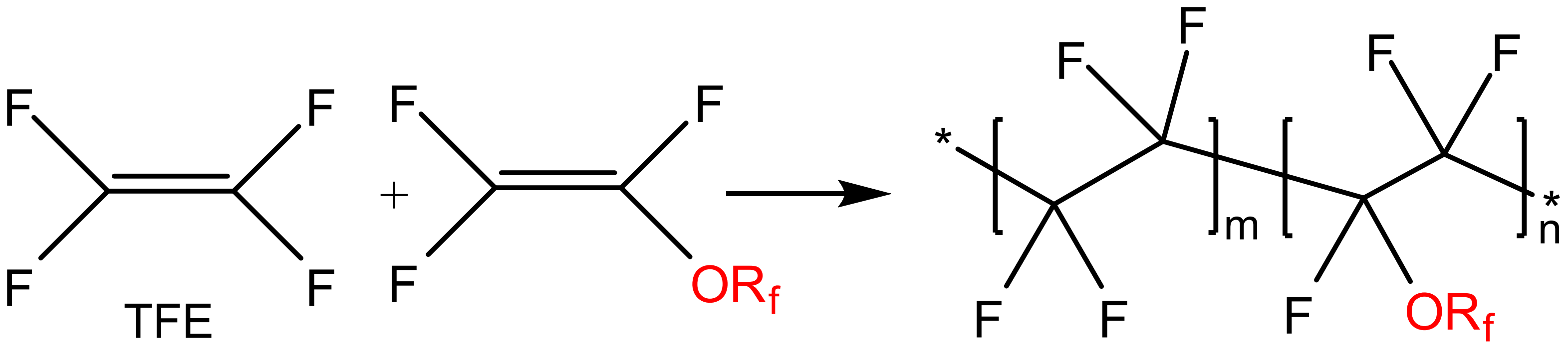
Stirred, temperature-controlled autoclave

TFE tank behind explosion-proof wall

Fluoropolymer Synthesis at Clemson

Darryl DesMarteau, Clemson Chemistry Department

Aqueous emulsion co-polymerization of TFVE monomers with TFE

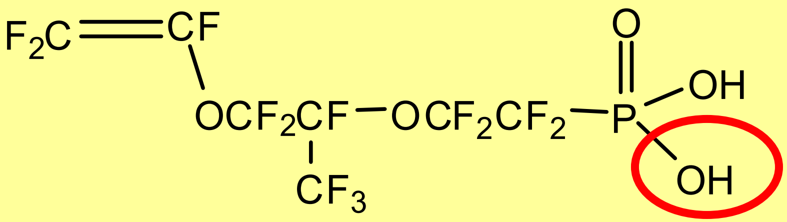


$OR_f = OCF_2CF(CF_3)OC_2F_4P(O)(ONa)_2$ (monomer g)

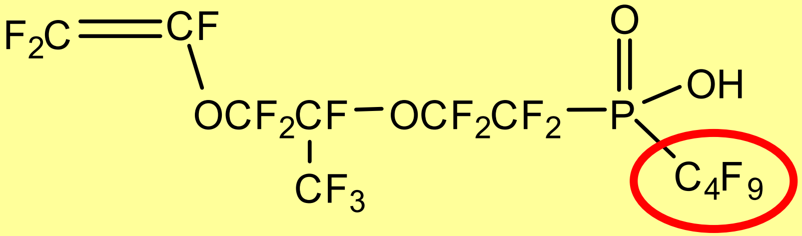
Result: Good ionomers were NOT formed.

Suspected reason: The TFVE monomer is not a good surfactant

Idea: Switch to di-fluoroalkyl-phosphonic acid monomers



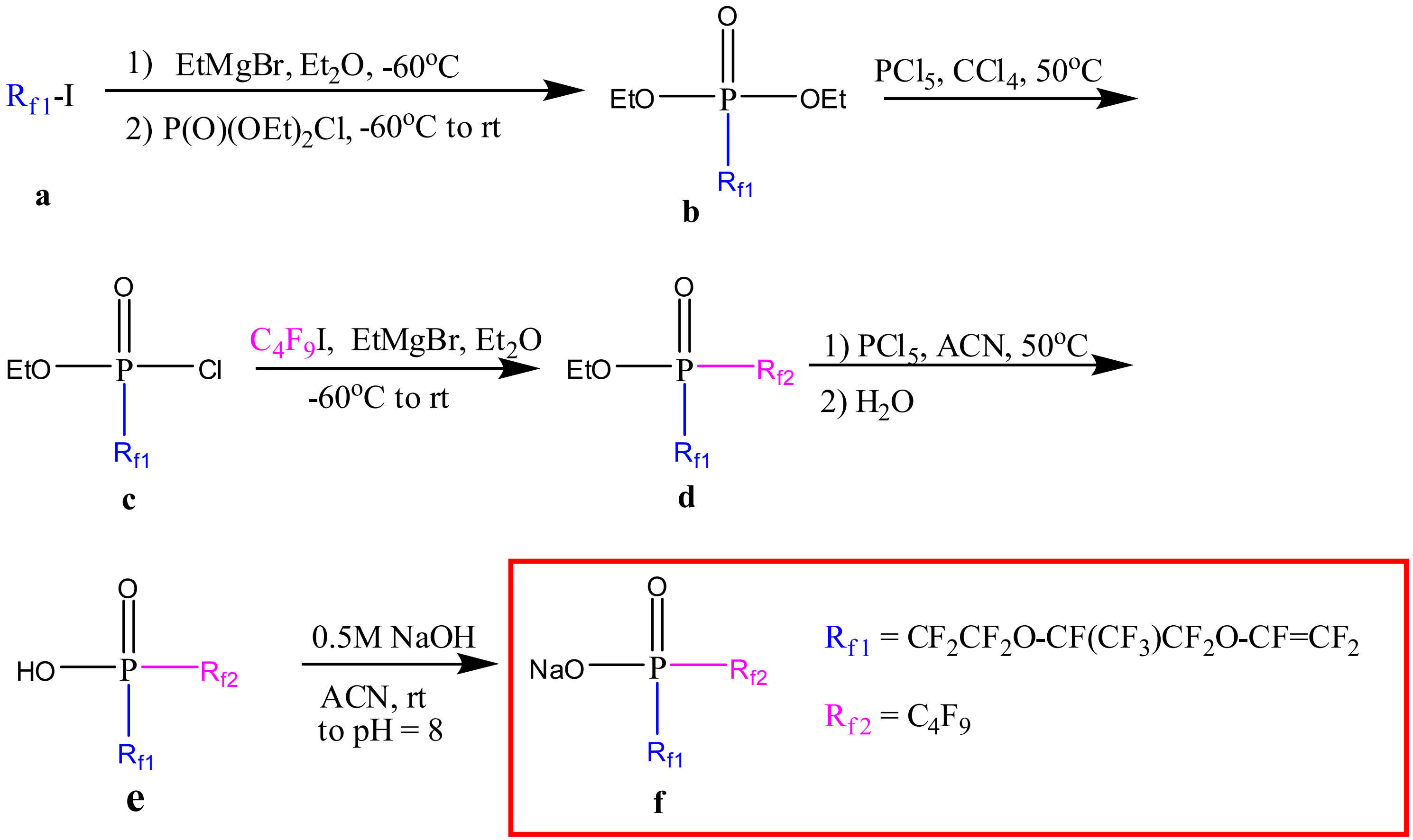
Mono-fluoroalkyl-phosphonic acid
Trifluorovinyl ether monomer



Di-fluoroalkyl-phosphonic acid
Trifluorovinyl ether monomer

- Should be better surfactant in Na^+ form than the mono-fluoroalkylphosphonic acids, therefore more likely to produce good ionomers by emulsion co-polymerization with TFE in water
- Should still be quite strong acids, proton dissociation is favored
- Should / could promote proton transport by a hopping mechanism (untested so far but in progress)

Synthesis of difluoroalkyl-phosphonic acid trifluorovinyl ether (TFVE) monomer



$R_{f1} = CF_2CF_2O\text{-}CF(CF_3)CF_2O\text{-}CF{=}CF_2$

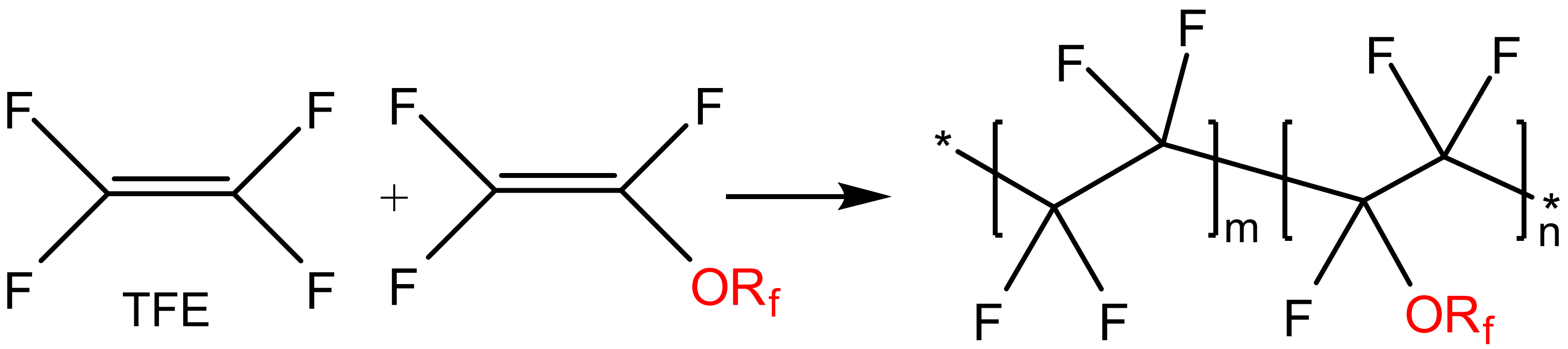
$R_{f2} = C_4F_9$

Monomer f was also obtained in 10 g amount in excellent yield

NMR shows the CMC of monomer f is approx. 4 mM….

It’s a good surfactant!

Aqueous emulsion co-polymerization of TFVE monomers with TFE

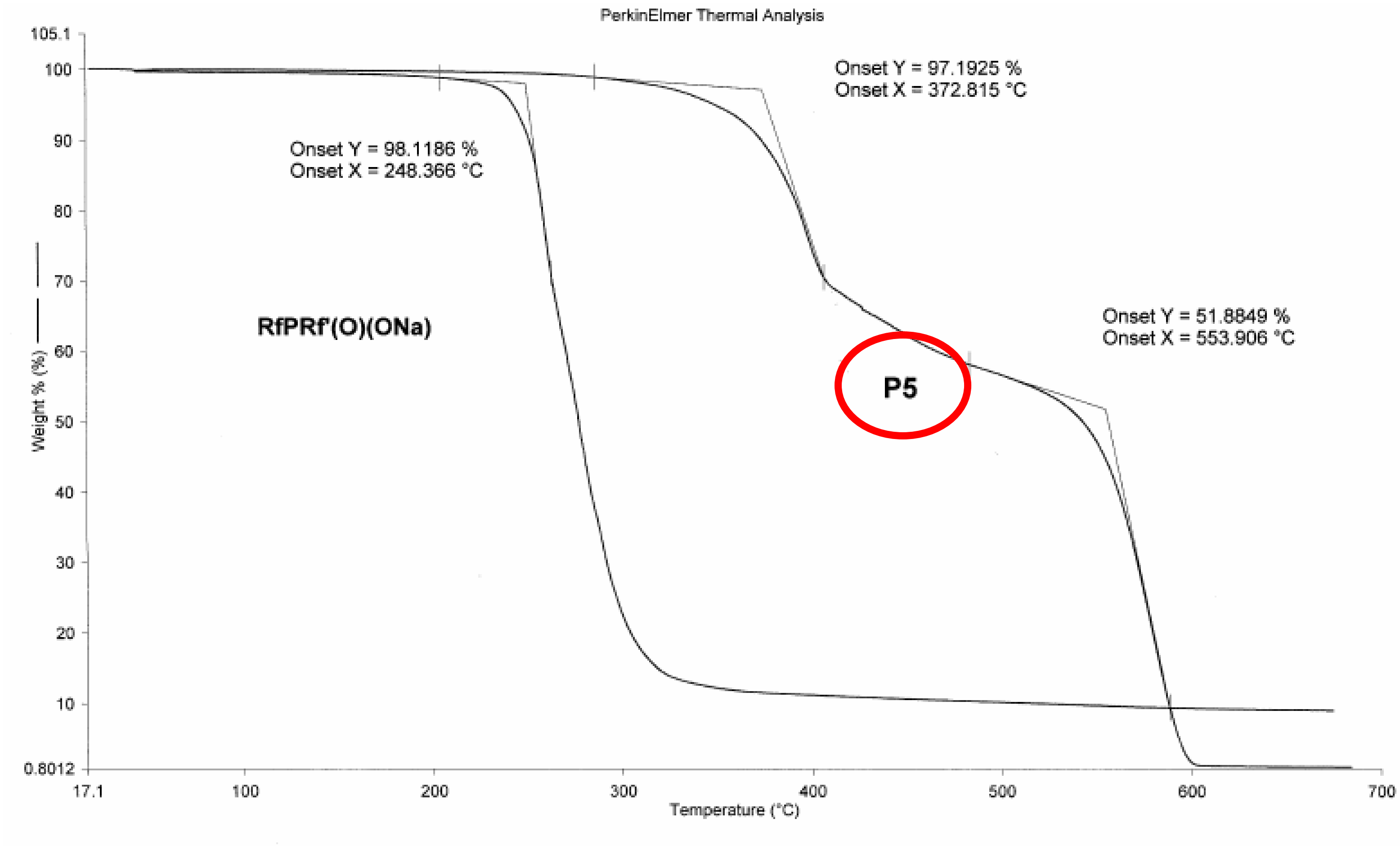


OR_f : $OCF_2CF(CF_3)OC_2F_4P(O)(ONa)C_4F_9$ (Monomer f)

Result: Good ionomers were formed!

- Co-polymer P5, EW approx. 1300 g / equiv (6 TFE / equiv)
- Sparingly soluble in multiple solvents
- Membranes have been formed by solvent casting
- Conductivity testing is in progress

TGA of the co-polymer **P5**



Co-polymer P5 shows excellent thermal stability to past 350 °C

Computer modeling studies of proton transport in fluoroalkyl phosphonic acids (FPAs)

Multiscale Simulation Methodology

Quantum chemistry calculations of fluoroalkylphosphonic-acids fragments interacting with water

Classical force field and proton hopping model (MS-EVB, Q-HOP) development

Atomistic MD Simulations of small-molecule FPA-based electrolytes. Compare D_i, λ with exp. (Clemson, MPI)

Atomistic MD simulations of fluoroalkylphosphonic acid-based ionomers

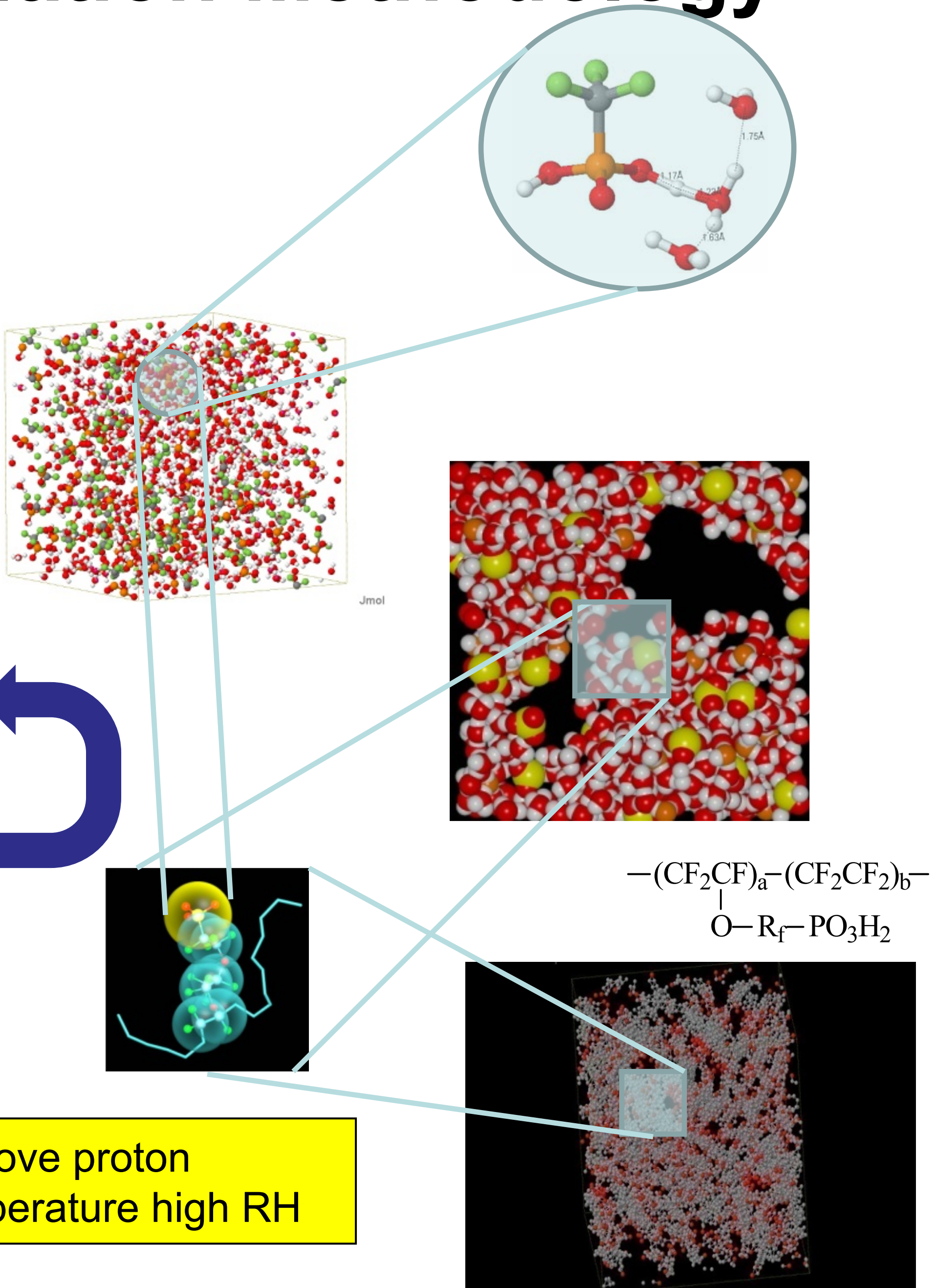
high T, low RH

Coarse-grained PEM simulations (PEM morphology)

low T, high RH

Continuum simulations (homogenized PEM transport)

Optimize membrane structure to improve proton transport at RH=20%, 120 °C and low temperature high RH

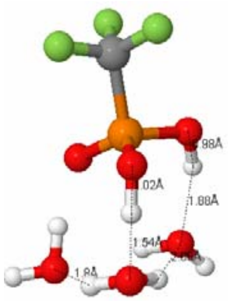


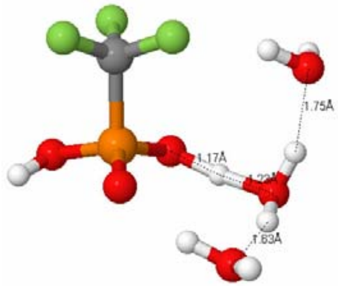
$$-(CF_2CF)_a-(CF_2CF_2)_b- \\ \quad | \\ O-R_f-PO_3H_2$$

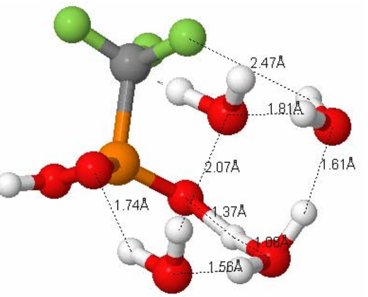
Summary of Technical Accomplishments

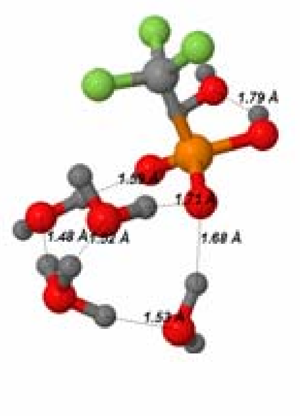
- Performed quantum chemistry studies of $CF_3PO(OH)_2$-nH_2O and $2CF_3PO(OH)_2$-nH_2O complexes (n=0-6)
- Developed many-body polarizable *classical* quantum chemistry-based force fields for simulations of FPA-based proton conductors
  - Initiated classical molecular dynamics simulations of trifluoromethylphosphonic acid/water and heptafluoropropylphosphonic acid/water solutions using developed polarizable force fields
  - Performed initial classical simulations of fluorophosphonic acid-based ionomer at high hydration using nonpolarizable force fields
- Extended the Multi-State Empirical Valence Bond (MS-EVB) model to allow efficient simulations of proton transport for *high proton concentration* conditions that are expected to be occur at low RH high temperature PEM operations
  - Implemented extended MS-EVB in the molecular dynamics simulation code
  - Initial simulations of low molecular weight FPA/water electrolytes are underway

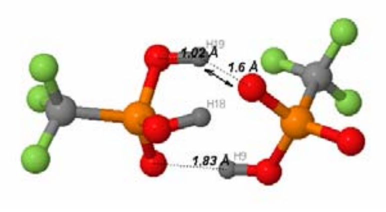
Quantum Chemistry Studies FPA/water Clusters

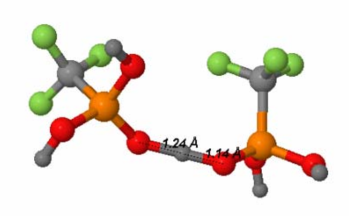


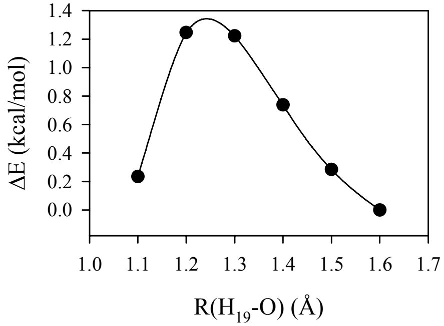


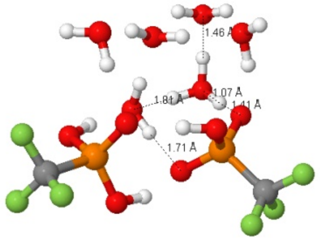












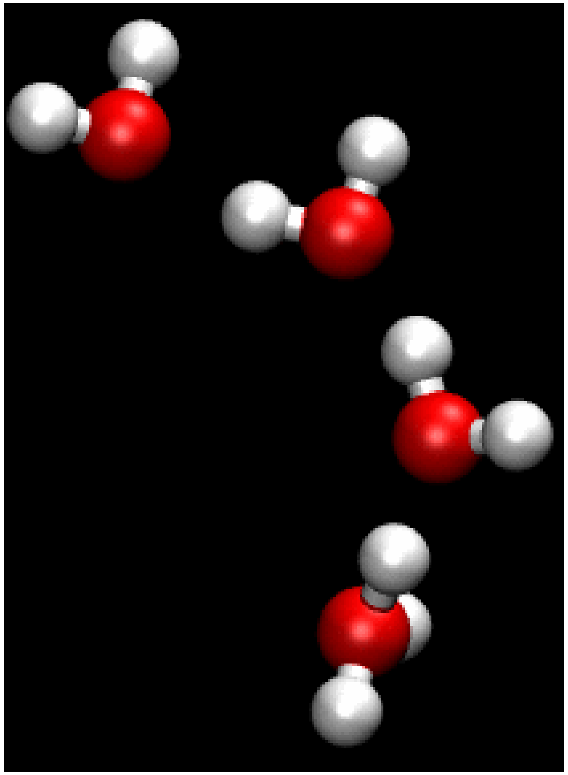
complex	Binding energy* (kcal/mol)	r(P**O-** **H**...Ow-Hw)[a] (Å)	r(PO-**H…O**$_w$-H$_w$) [a] (Å)
FPA		0.96	
FPA + H_2O	-11.0	1.0	1.67
FPA + 2 H_2O	-20.8	1.04	1.5
FPA + 3 H_2O	-31.8	***1.17***	***1.23***
FPA + 4 H_2O	-41.4	1.01	1.62
FPA + 4 H_2O	-43.2	***1.37***	***1.08***
FPA + 5 H_2O	-52.6	2nd solv. shell	
FPA + 6 H_2O	-64.7	2nd solv. shell	

*Binding energy is calculated at the mPW1PW91/aug-cc-pvDz level

- The structure of the hydrogen bonding network is very important as it significantly influences FPA protonation
- FPA + 3 H_2O: proton is shared between FPA and water; FPA + 4 H_2O: FPA becomes deprotonated
- Low energy barrier for proton transfer from FPA to the deprotonated FPA
- Energetics of the proton transfer and 2FPA-nH_2O complexes is utilized during MS-EVB model development

Jmol

Multi-State Empirical Valence Bond Model (MS-EVB)



The definition of the protonated species can change during the dynamical process.

Building on the previous work:
Schmitt and Voth, J. Phys. Chem. B 102, 5547 (1998)
Schmitt and Voth, J. Chem. Phys. 111, 9361 (1999)
Day et al, J. Chem. Phys. 117, 5839 (2002)
(Related work by Warshel, Borgis, and co-workers)

$$H_{ii} = V^{\text{intra}}_{H_3O^+} + \sum_{k}^{nH_2O} V^{\text{intra}}_{(H_2O)_k} + \sum_{k}^{nH_2O} V^{\text{inter}}_{(H_2O)_k, H_3O^+} + \sum_{k<k'}^{nH_2O} V^{\text{inter}}_{(H_2O)_{k,k'}}$$

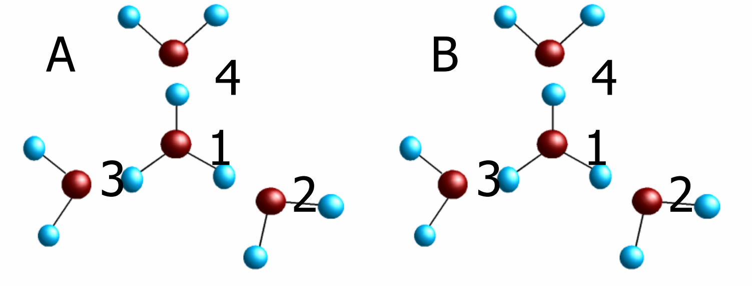
$$V_{ij} = (V_{const.} + V_{ex.}) \bullet A(R_{OO}, R_{OH})$$

$$E_0 = \sum_{ij} c_i^0 c_j^0 H_{ij}(x) \qquad F_k(x) = -\sum_{ij} c_i^0 c_j^0 \frac{\partial}{\partial x_k} H_{ij}(x)$$

$$H = \begin{bmatrix} H_{11} & V_{12} & V_{13} & V_{14} \\ V_{21} & H_{22} & V_{23} & V_{24} \\ V_{31} & V_{32} & H_{33} & V_{34} \\ V_{41} & V_{42} & V_{43} & H_{44} \end{bmatrix}$$

Challenges for Simulating Proton Transfer at Low Hydration

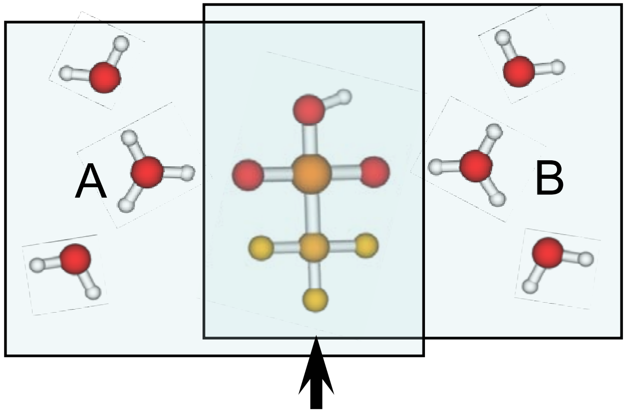
- Brute force application of MS-EVB for treatment of multiple protons lead to a big **H** matrix and is computationally expensive (CPU time scales as N^m, where N – number of states, m – number of excess protons)
- Recent improvements of MS-EVB methodology for multiple proton treatment allowed linear scaling of CPU time vs. number of excess protons for conditions when protons are often sufficiently far from each other and sparse matrix methods apply. The problem is solved using self-consistent iterative (SCI) scheme (SCI-MS-EVB).
- At low RH and high temperature multiple protons are expected to be often found in proximity of each other and SCI-MS-EVB condition breaks down.
- In order to preserve the computational savings of SCI-MS-EVB where possible, **a novel hybrid methodology has been developed** and implemented in the MD simulations code significantly reducing computational cost over the brute force solution of the **H** matrix.



A1B1, A1B2, A1B3, A1B4, A2B1 ……

16 states required to describe

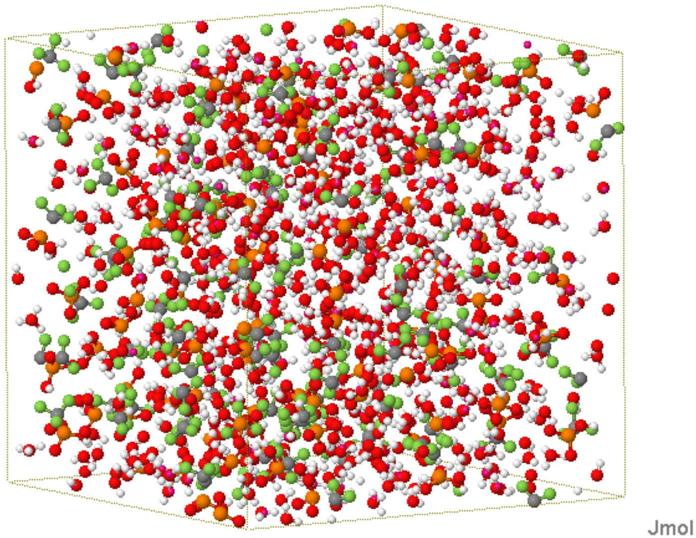
only two independent $(H_9O_4)^+$



Hybrid SCI-MS-EVB

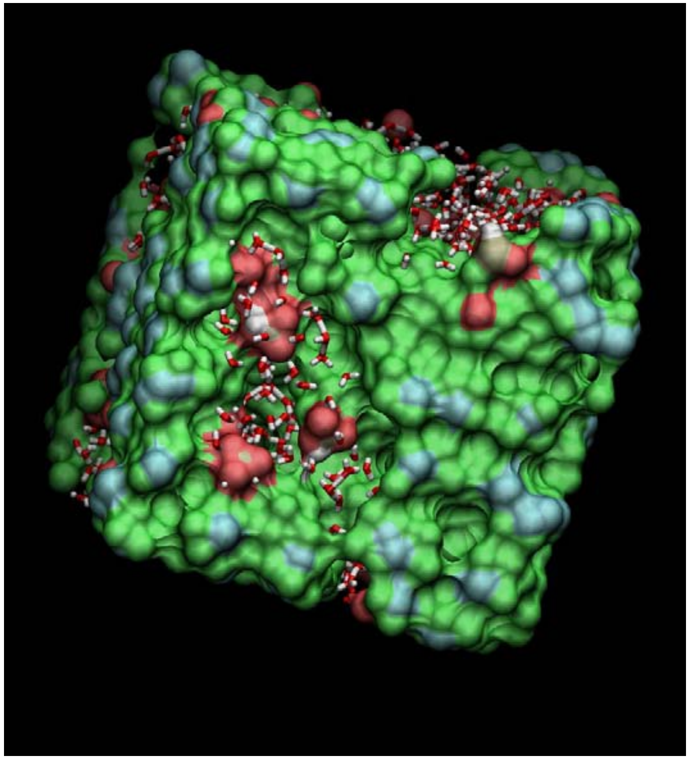
SCI-MS-EVB is described in Wang, F. and G. A. Voth (2005). Journal of Chemical Physics 122(14): 144105.

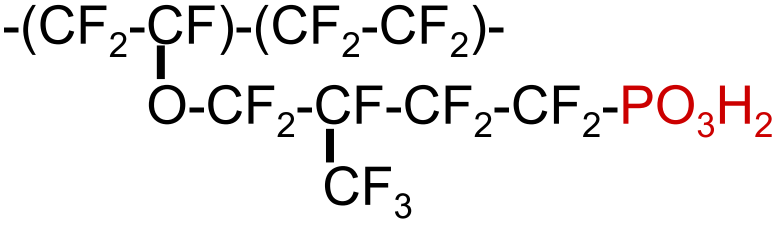
Undergoing MD simulations



Classical MD simulations are underway for the following electrolytes

- Trifluoromethyl-phosphonic acid/water and heptafluoropropyl-phosphonic acid/water using developed many-body polarizable force field
- FPA-based ionomer using nonpolarizable force field





$$\begin{array}{l}-(CF_2\text{-}\underset{|}{C}F)\text{-}(CF_2\text{-}CF_2)\text{-}\\ \qquad\quad O\text{-}CF_2\text{-}\underset{\displaystyle CF_3}{\underset{|}{C}}F\text{-}CF_2\text{-}CF_2\text{-}PO_3H_2\end{array}$$

Future Work for FY 07 and 08

- **Synthesis**: Small-molecule model compounds and monomers, and optimizing ionomer preparations.
- **Characterization**: Conductivity of electrolytes in liquid & membrane form, with variable water content. Also, PFG NMR studies of ion / molecule diffusion.
- **Computer modeling**: MD simulations of small molecule model compounds and ionomers with explicit proton hopping. Validation against PFG NMR and conductivity studies. Development of the coarse-grained model for ionomers and predicting their morphologies.

Summary

- **Objective**. Provide new electrolyte materials for use in next-generation hydrogen-fuel-cell power sources.
- **Approach**. Synthesize and characterize fluoroalkyl phosphonic acid electrolytes as small-molecule models, monomers, and ionomer membranes. Model proton conduction in the same.
- **Technical accomplishments**. Many model compounds, trifluorovinyl ether monomers, and ionomers were synthesized. Conductivity studies show initial promise. Comprehensive studies at variable water content are in progress.
- **Planned future work.** Synthesis optimization for small molecules and ionomers; conductivity studies on electrolytes with variable water content; PFG NMR studies of model compounds; computer modeling of model compounds and ionomers. Head-to-head comparison with experiments. Guidance based upon simulations results.

Additional Slides

Fluoroalkyl-phosphonic-acid-based proton conductors

Synthesis & Characterization

Steve Creager
Professor
Electrochemistry
And Carbon

Darryl DesMarteau
Professor
Fluoropolymers

Clemson University

Computer Modeling

Greg Voth
Professor
Theoretical &
Physical
Chemistry

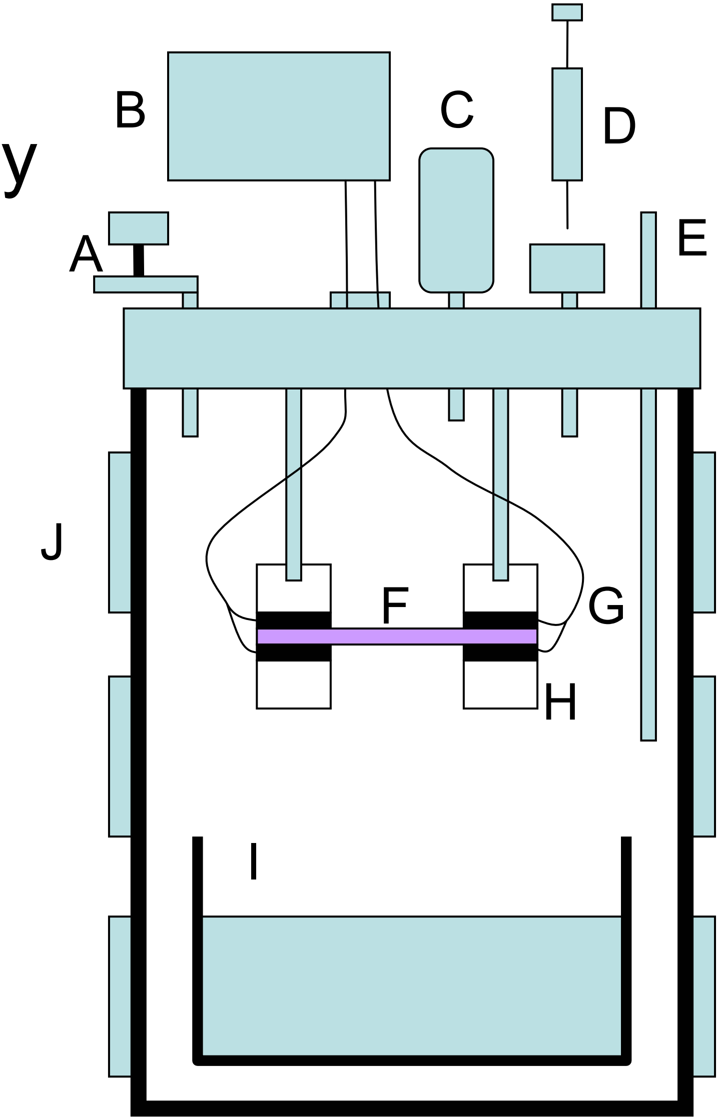
Grant Smith
Professor
Computational
Polymers

Oleg Borodin
Research
Professor
Computational
polymers

University of Utah

Characterization

Variable temperature / humidity membrane ionic conductivity



A. Vacuum / gas inlet / outlet.

B. Impedance analyzer

C. Pressure transducer

D. Water injection port and syringe

E. Thermocouple

F. Electrolyte membrane

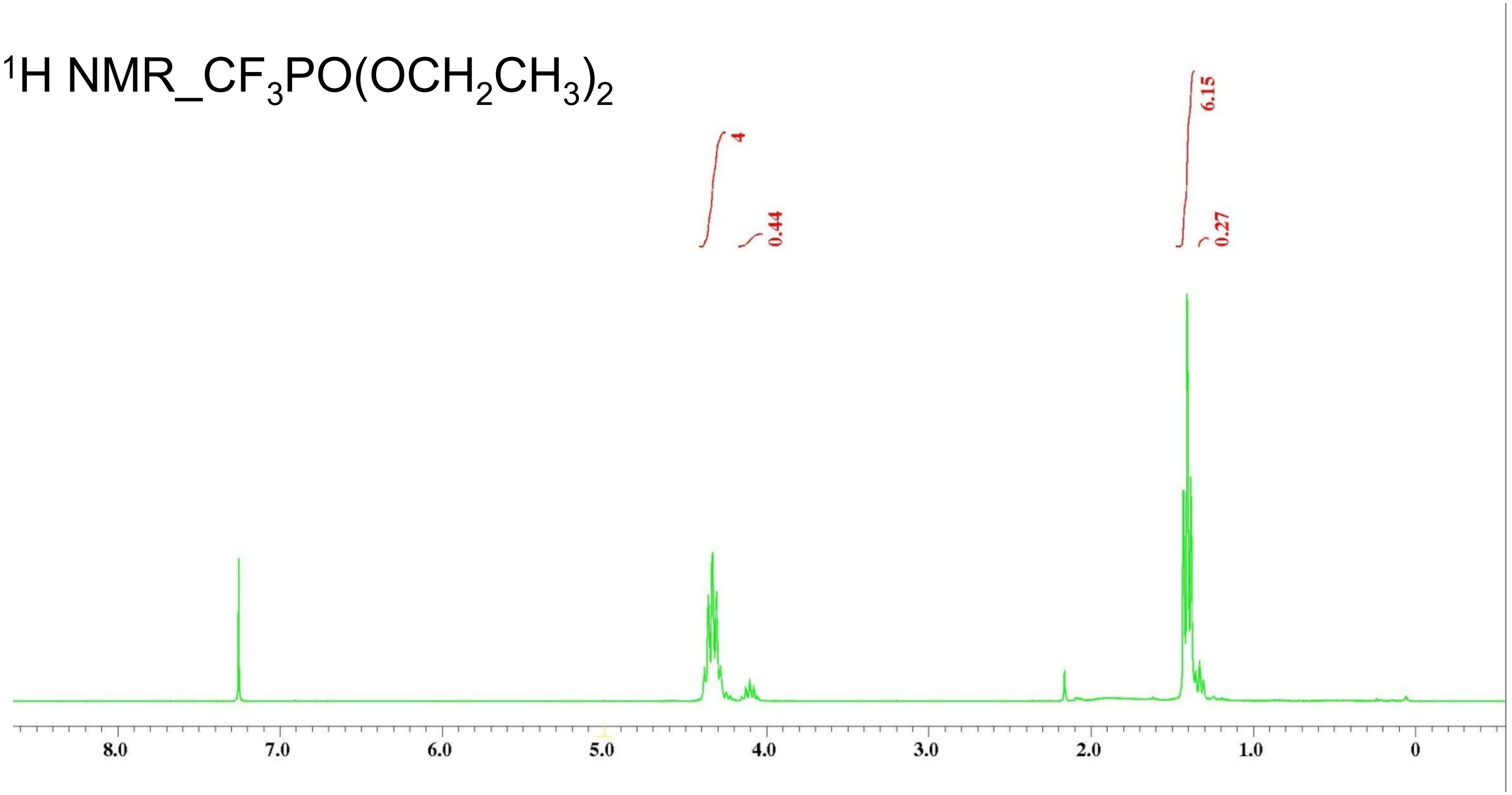
G. Dual platinized platinum foil contacts

H. PEEK open-faced conductivity cell

I. Saturated salt solution for humidity control (optional)

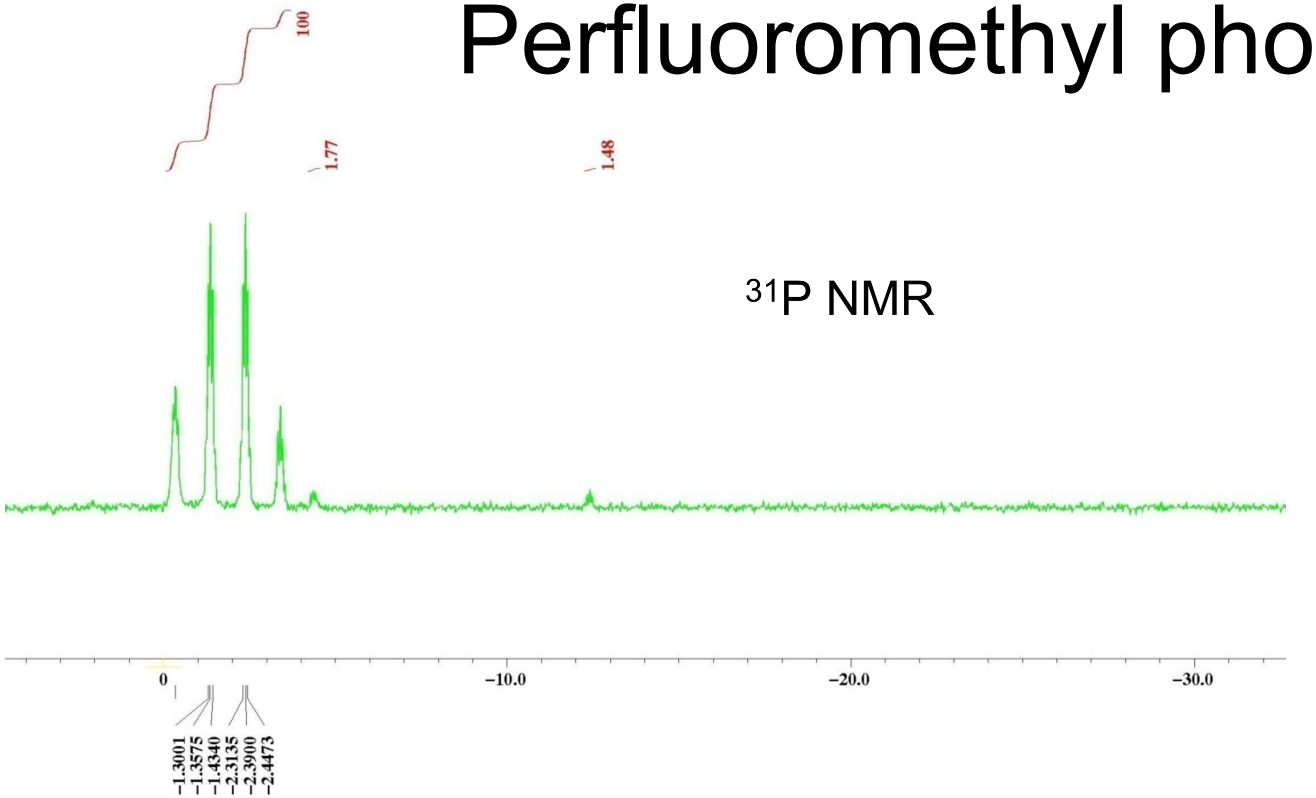
J. Heating tape for temperature control

NMR data for trifluoromethyl phosphonic acid diethyl ester

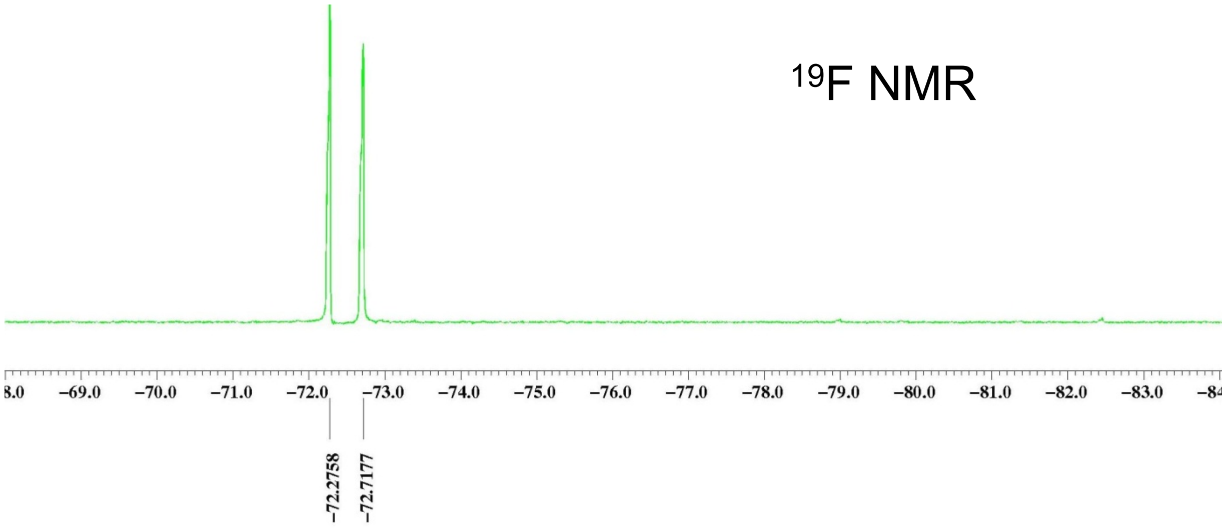


^1H NMR_$CF_3PO(OCH_2CH_3)_2$

Perfluoromethyl phosphate



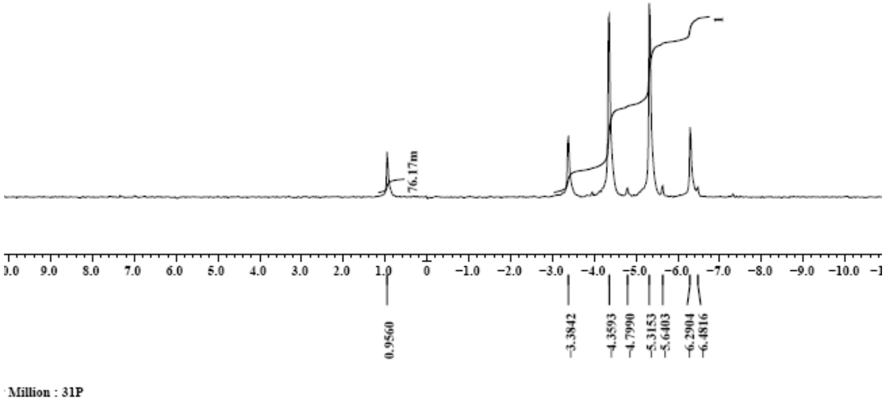
^{31}P NMR



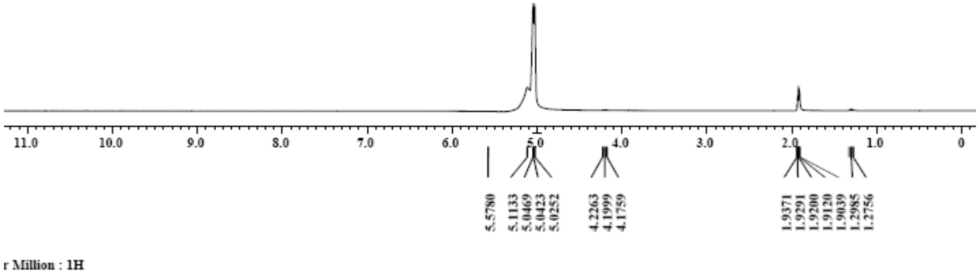
^{19}F NMR

NMR spectra of trifluoromethyl-phosphonic acid following hydrolysis

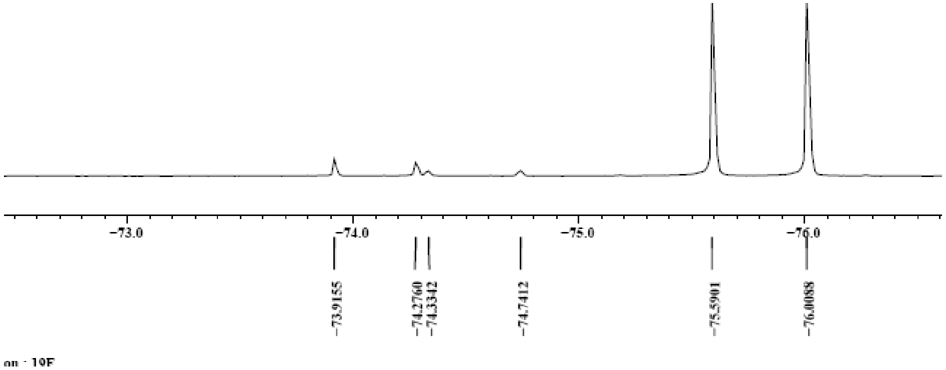
^{31}P NMR



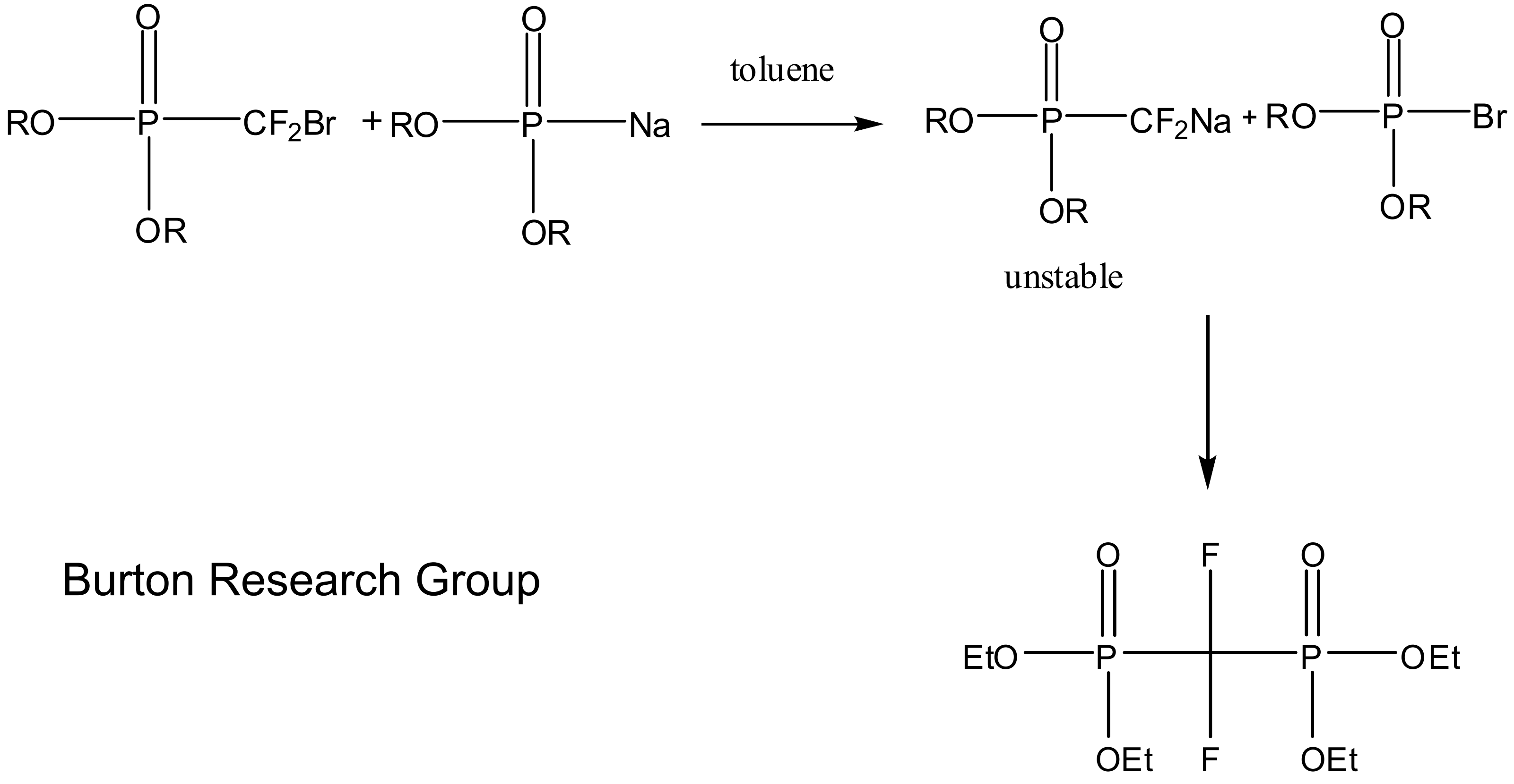
^{1}H NMR



^{19}F NMR



Synthesis of Perfluoroalkyl Bisphosphonates



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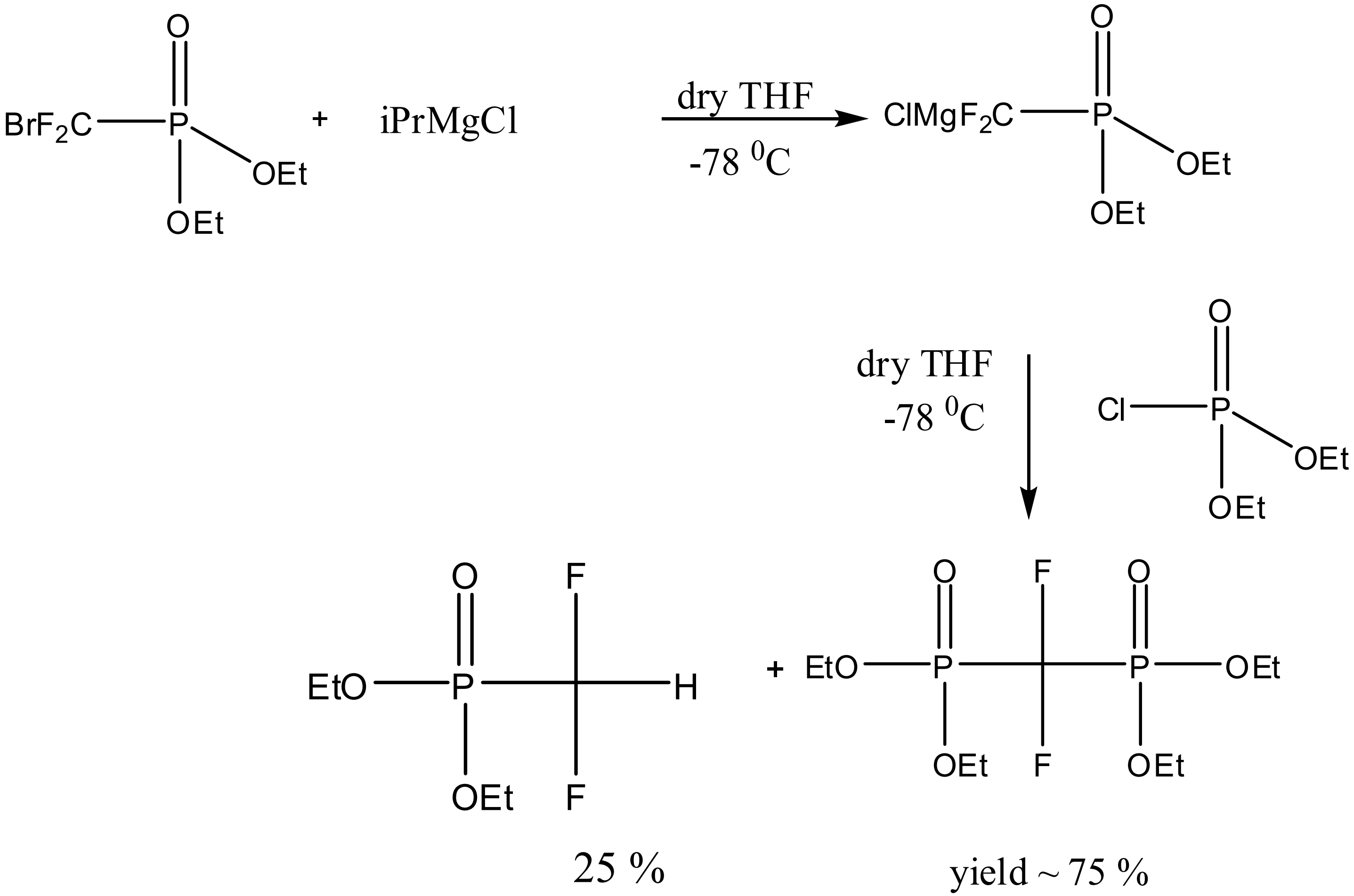
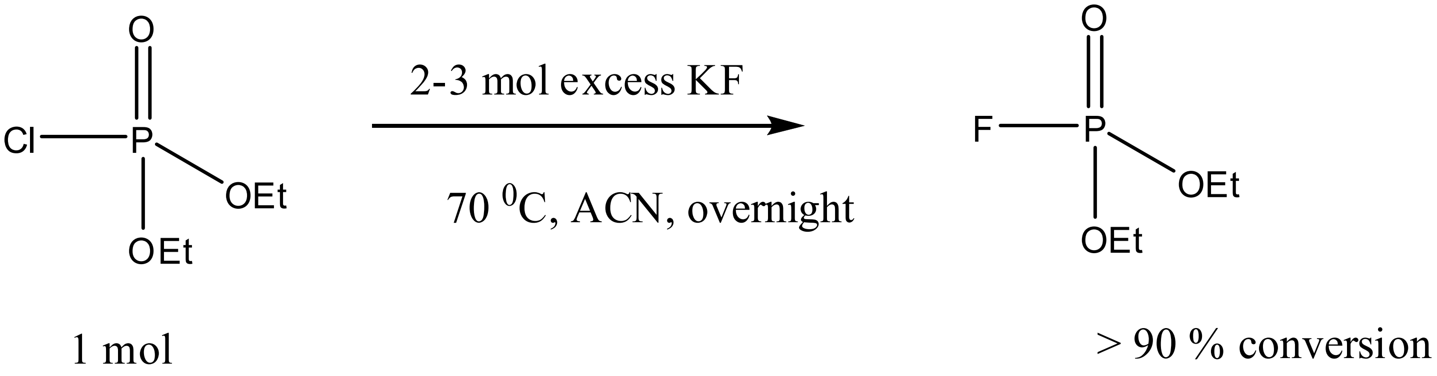
yield 47 %

Improved Synthetic Method for bis-phosphonic acids



Improved Synthetic Method for Fluorophosphate

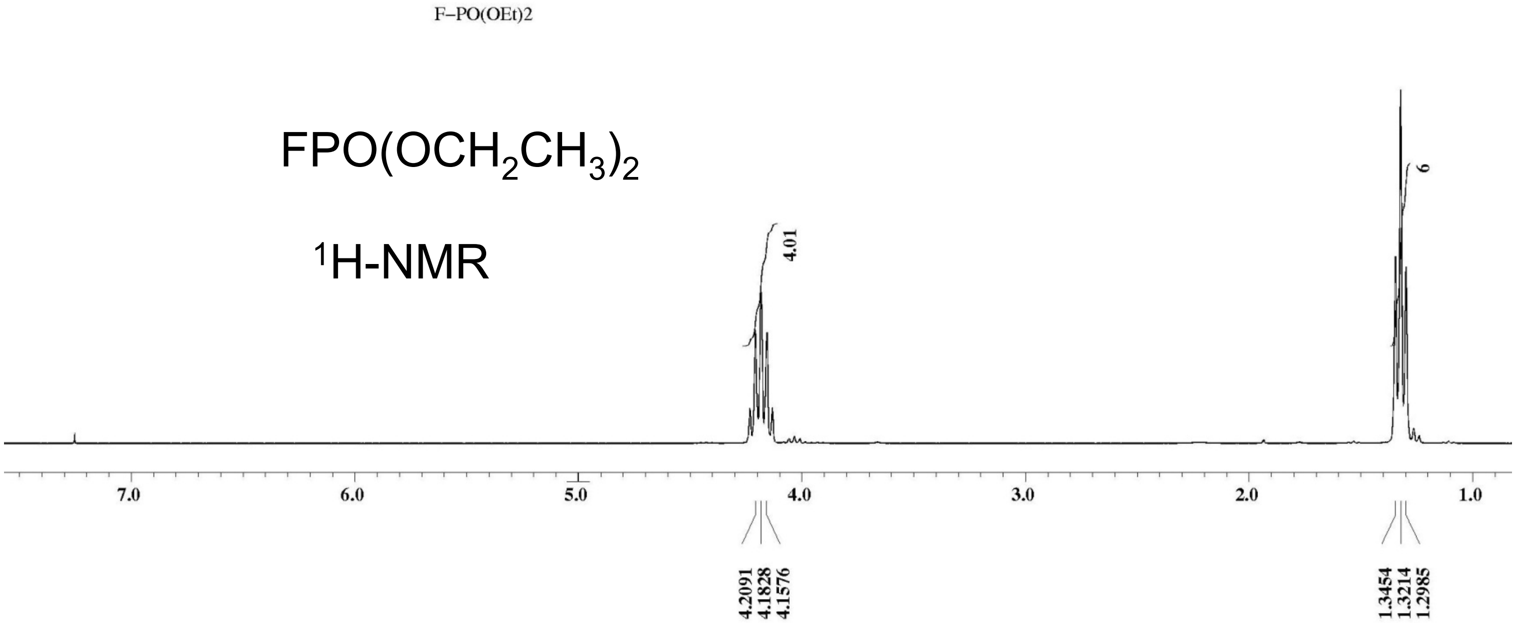


- by products can be minimized further by reaction with more excess KF

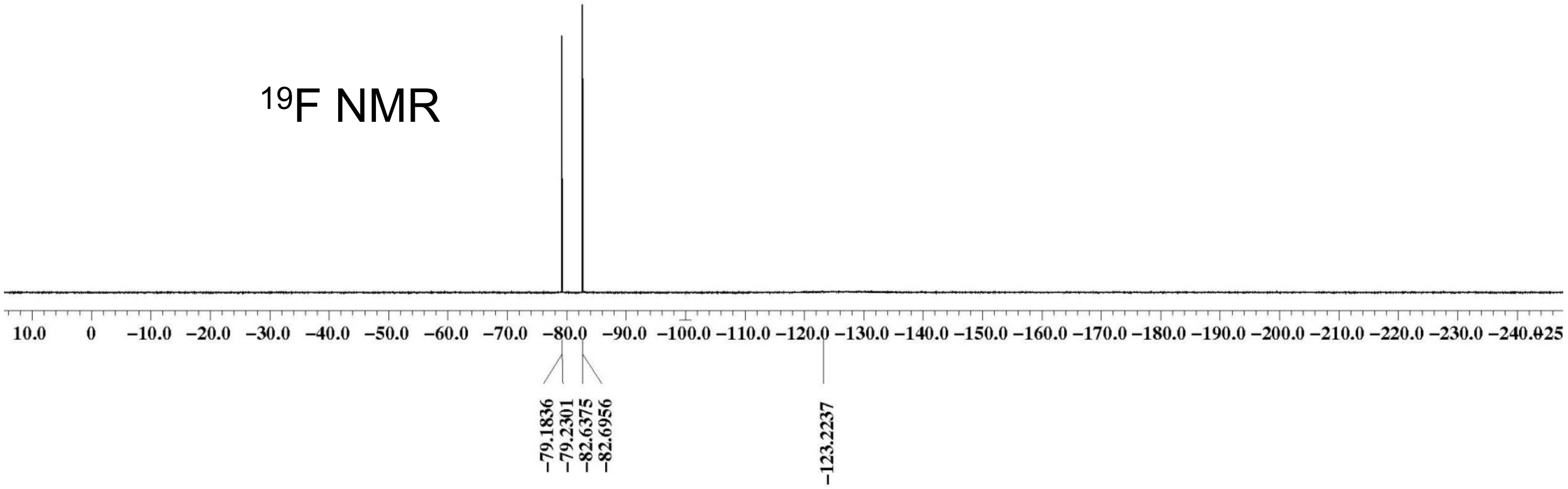
Fluorophosphate NMR Data

$FPO(OCH_2CH_3)_2$

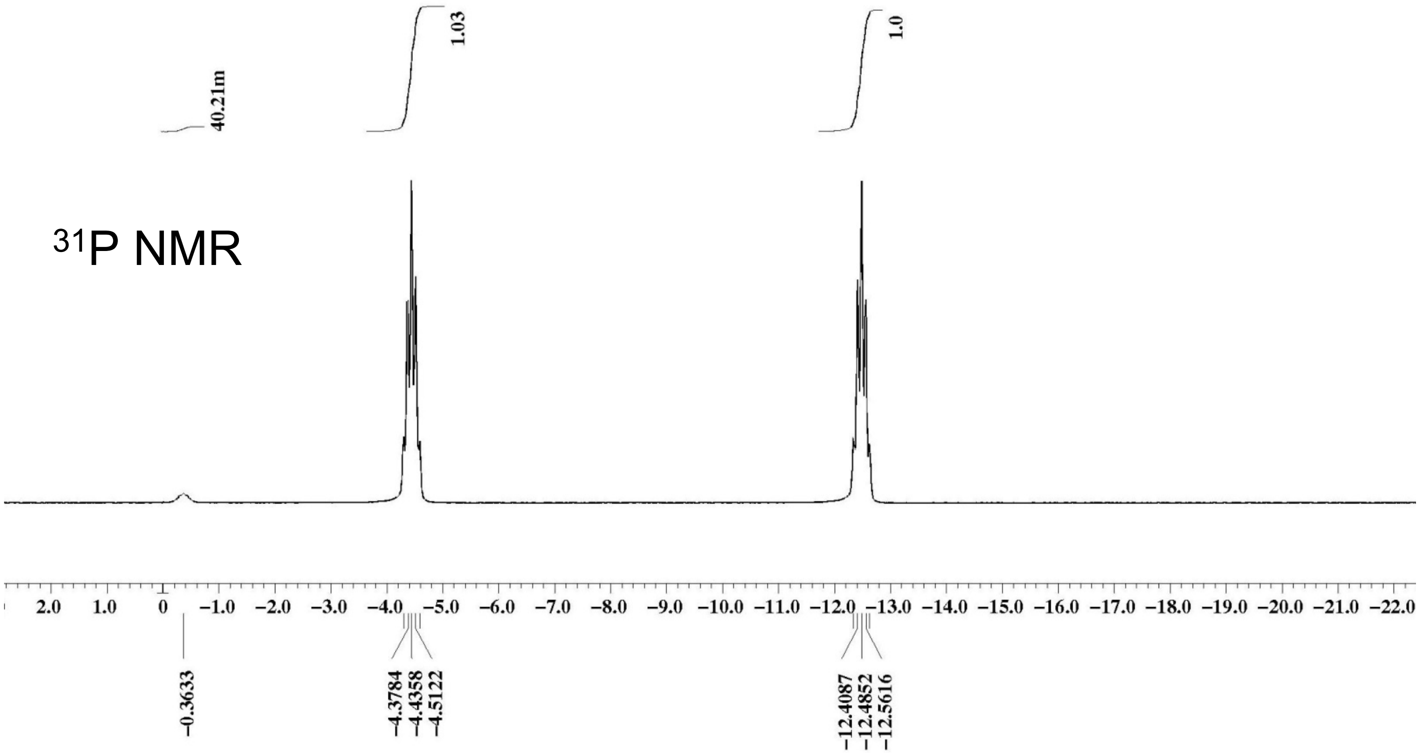
^{1}H-NMR



^{19}F NMR



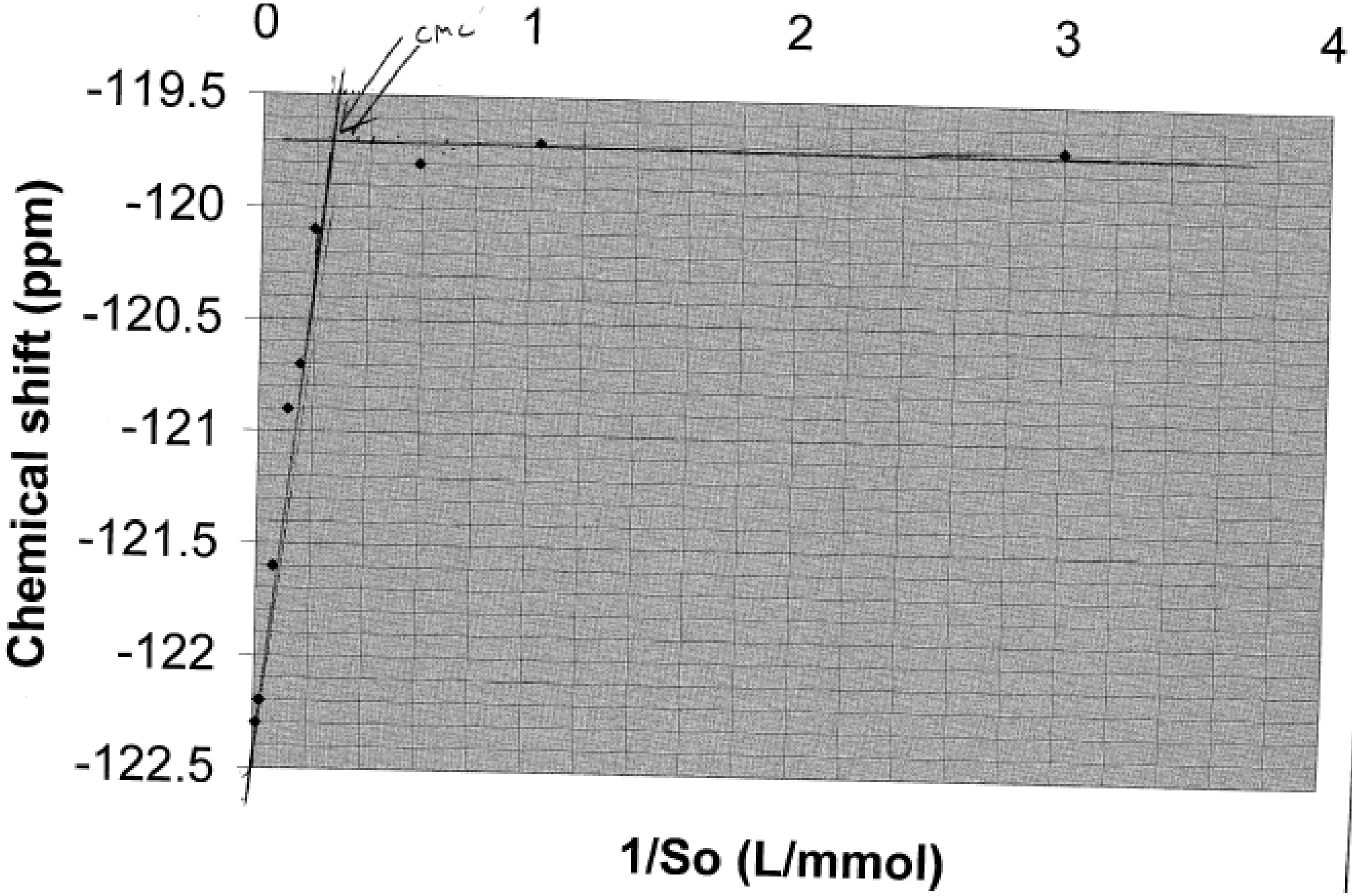
Fluorophosphate NMR Data



Surfactant character of monomer f
Chemical shift for the cis-vinyl fluorine in monomer **f** as a function of monomer concentration

Concentration (mmol/L)	**1/So (L/mmol)**	**PPM shift, cis-vinyl fluorine**
142	0.007	-122.3
59	0.0168	-122.2
43	0.0233	-122.2
16	0.0633	-121.6
9.3	0.108	-120.9
6.6	0.152	-120.7
5.1	0.197	-120.1
1.7	0.587	-119.8
0.96	1.035	-119.7
0.3	3	-119.7

Chemical shift of cis-vinyl fluorine in monomer **f** as a function of reciprocal surfactant concentration

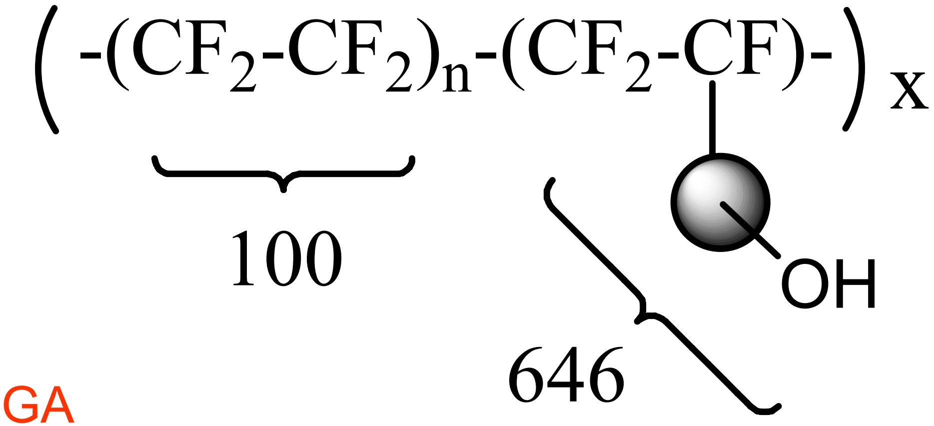


> CMC of compound **f** is 4 mmol/L.

> Compound **f** is a very good surfactant.

> Suitable for Self-Emulsifying Polymerization.

Equivalent weight of Co-polymer P5

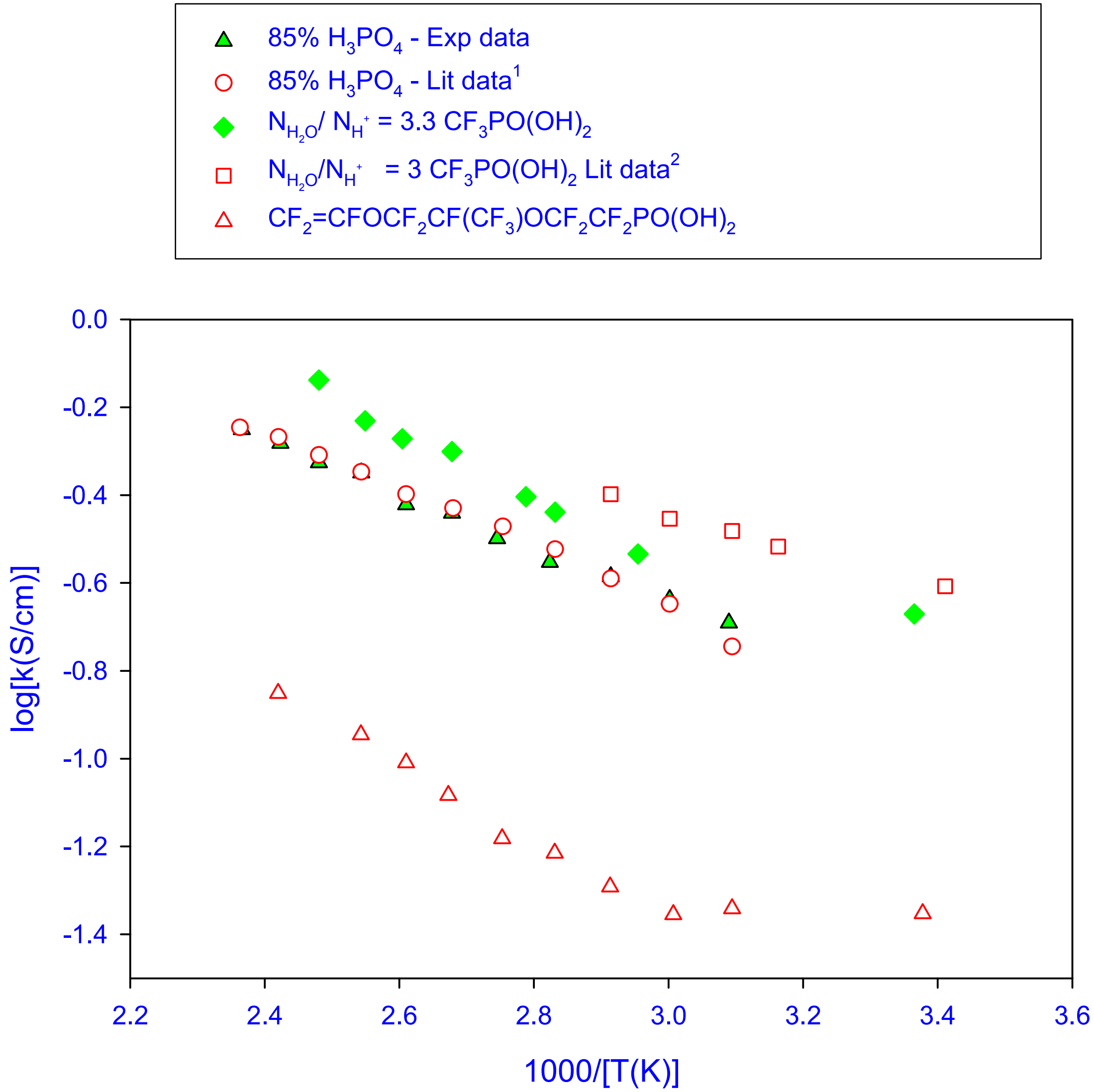


How does TGA
give EW?

From back titration: EW = 1307 g / equiv
From TGA: EW = 1290 g / equiv

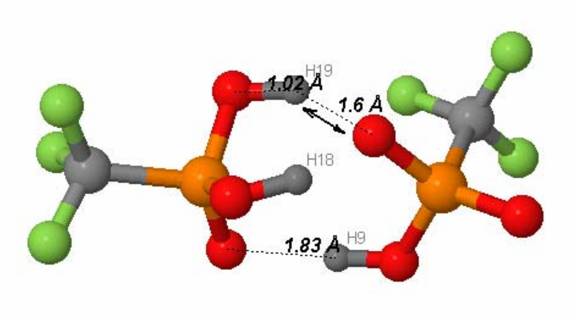
That means the *n* = (1307-646)/100 = 6

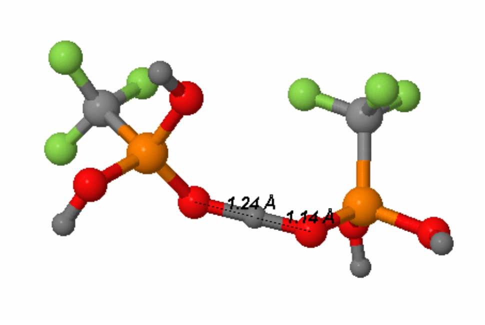
Arrhenius plots of conductivity including data for monomer g as a neat liquid

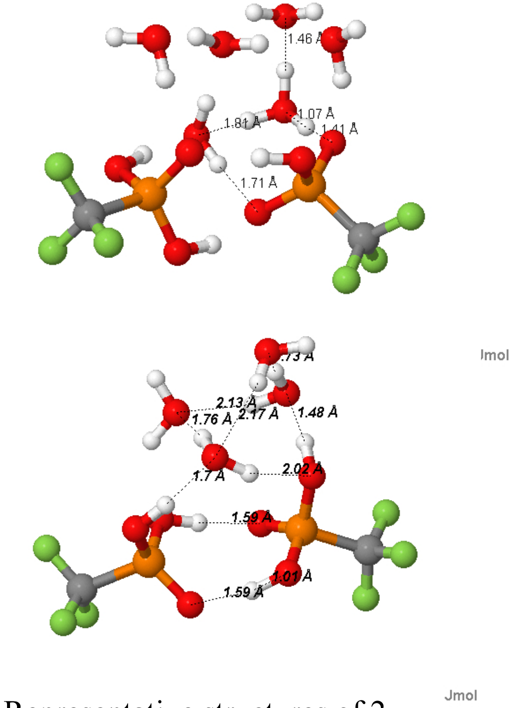


1. Chin, D.-T., Chang H. H., Journal of Applied Electrochemistry, 1989. 19: pp. 95-99
2. Razaq, M., Razaq A., Yeager E. Case Western Reserve Univ. 1989 pp 214 NTIS No. PB89178768

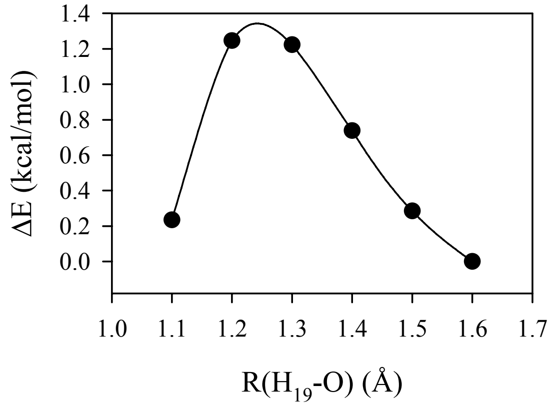
Barriers For Anhydrous Proton Transfer and Energetics of 2FPA-nH_2O Complexes

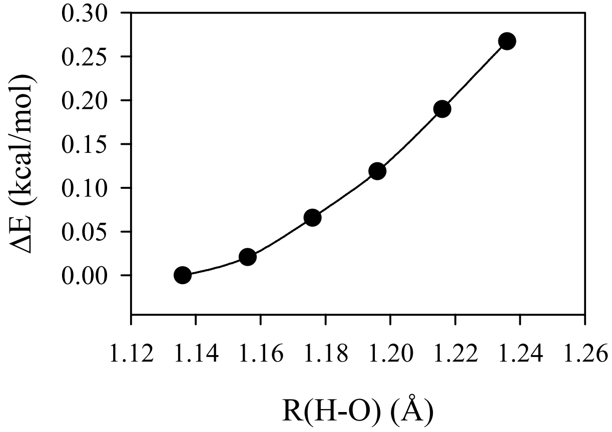






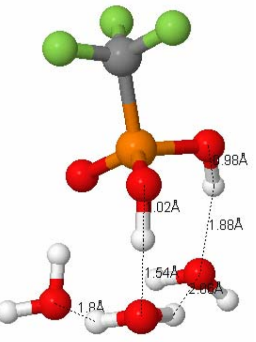
Representative structures of 2 FPA/water complexes leading to FPA protonation

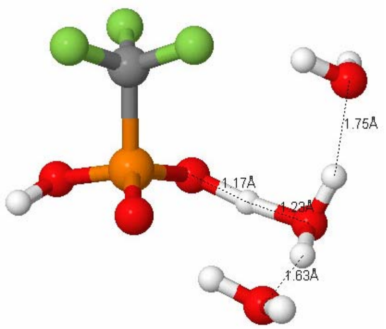


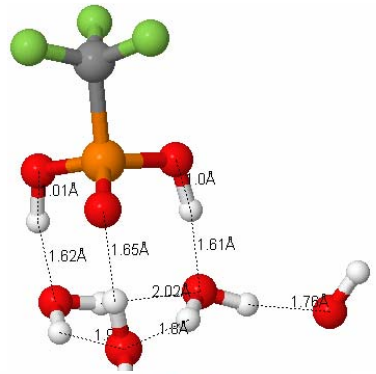


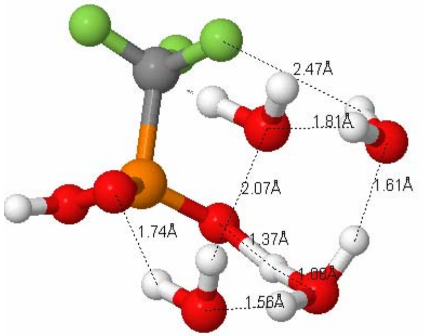
- Low energy barrier for proton transfer from FPA to the deprotonated FPA
- An excess proton is shared between two FPAs is a slightly asymmetric configuration
- Energetics of the proton transfer and 2FPA-nH_2O complexes is utilized during MS-EVB model development

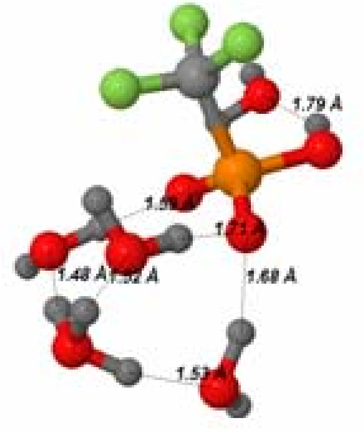
Quantum Chemistry Studies FPA-nH_2O Clusters

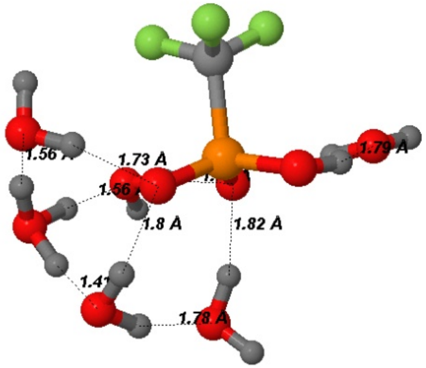












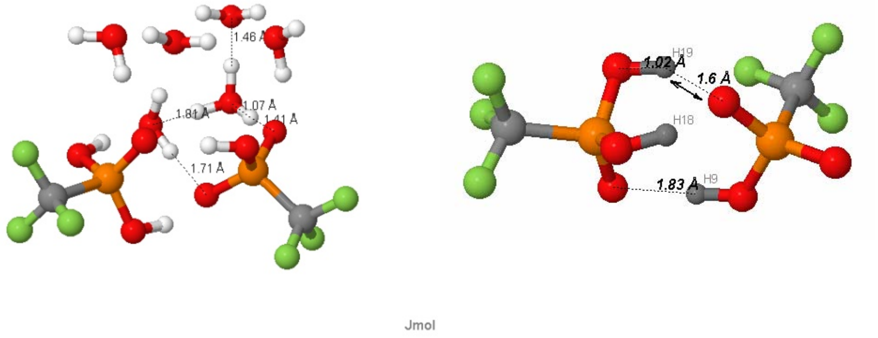
complex	mPW1PW 91/aug-cc-pvDz (kcal/mol)	r(P**O-H**...Ow-Hw)^a (Å)	r(PO-**H…O**$_w$ -H$_w$) ^{a} (Å)
FPA		0.96	
FPA + H_2O	-11.0	1.0	1.67
FPA + 2 H_2O	-20.8	1.04	1.5
FPA + 3 H_2O	-31.8	***1.17***	***1.23***
FPA + 3 H_2O	-33.8	1.02	1.54
FPA + 4 H_2O	-41.4	1.01	1.62
FPA + 4 H_2O	-43.2	***1.37***	***1.08***
FPA + 5 H_2O	-52.6	2nd solv. shell	
FPA + 6 H_2O	-64.7	2nd solv. shell	

- The structure of the hydrogen bonding network is very important as it significantly influences FPA protonation
- FPA + 3 H_2O: proton is shared between FPA and water
- FPA + 4 H_2O: FPA becomes deprotonated

PT Properties of FPA Present Special Challenges

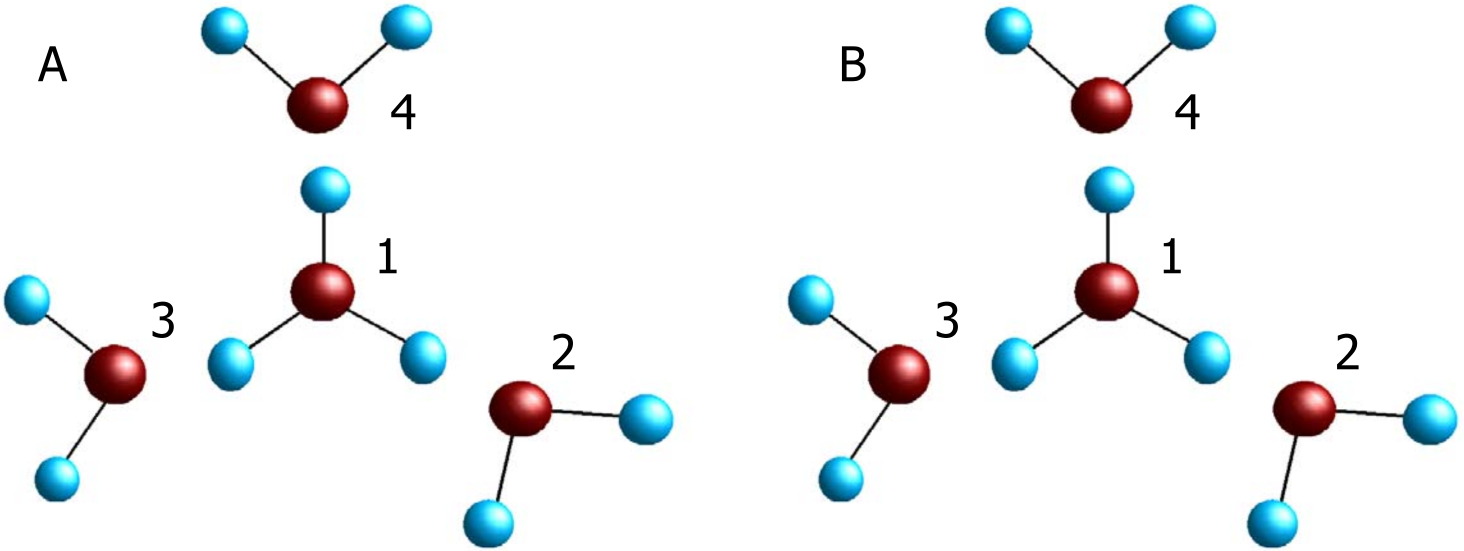
- At relevant water contents, FPA molecules are partially protonated; i.e., the acid groups themselves participate in PT.

- Multiproton MS-EVB techniques used for very wet Nafion^{TM} are not capable of modeling these phenomena



- **FPA simulations require:**
  - A protonatable FPA model
  - **Methodological advances in the multiproton MS-EVB method itself**

Many Protons: The Big Matrix Approach to Solve Multi-Proton MS-EVB Problem (THE DUMB WAY)



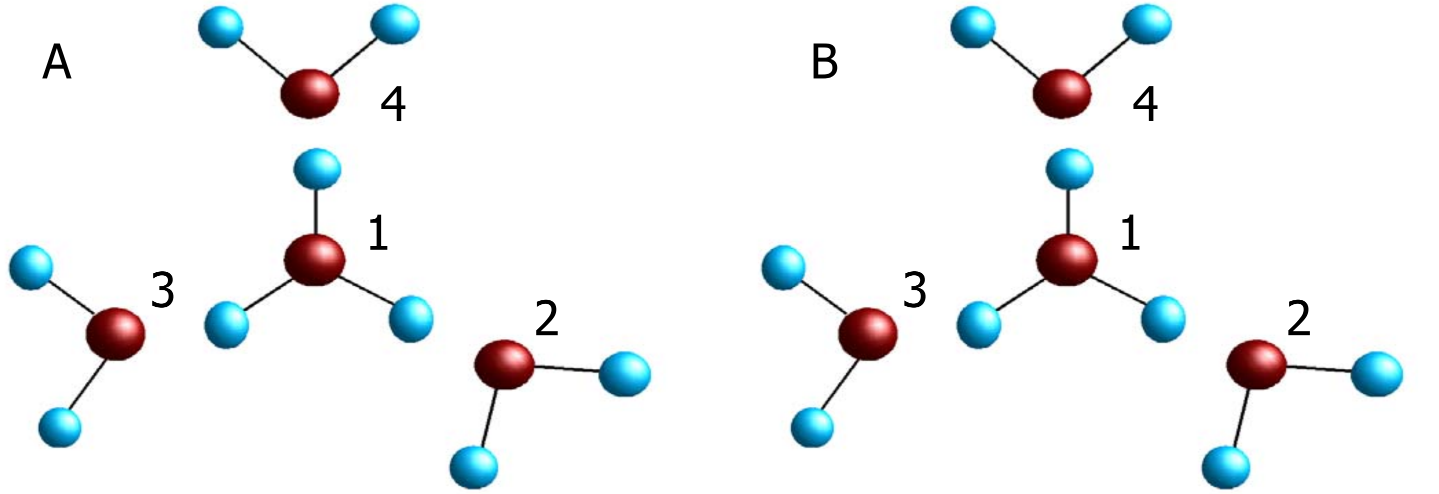
A1B1, A1B2, A1B3, A1B4, A2B1 ……

16 states required to describe

only two independent $(H_9O_4)^+$

Linear Scaling Approach

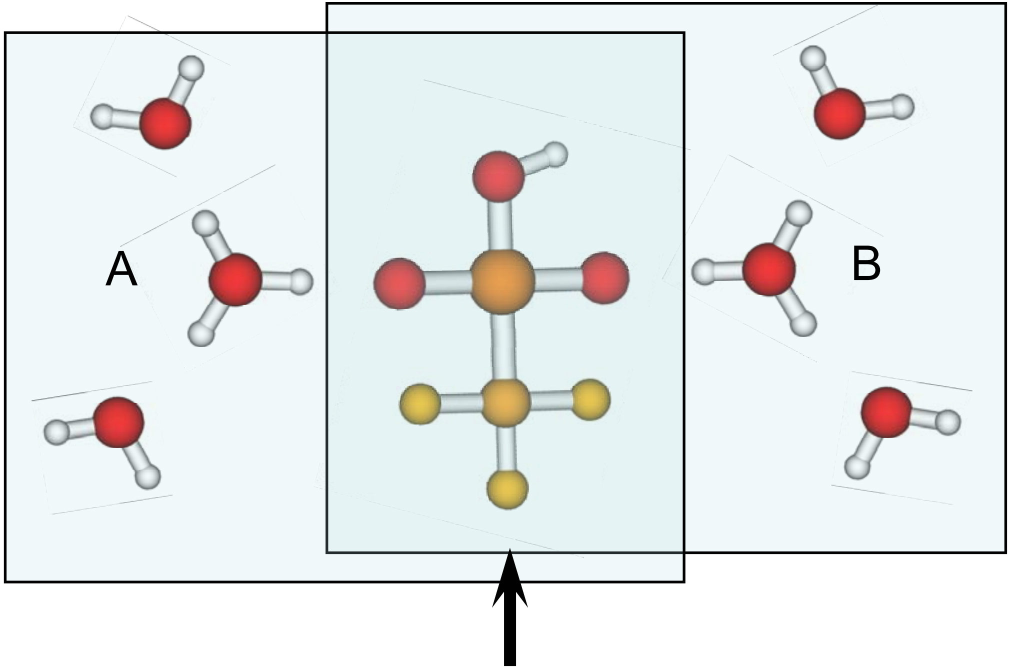
(THE GOOD WAY) Feng (Seymour) Wang



- **Each EVB center sees all other EVB centers as arrays of effective particles.**
- **Each effective particle has interaction parameters that are a linear combination of those of a pure hydronium and those of a pure water according to its local EVB vector.**
- **The coefficients of each EVB state are iterated until convergence. Sparse matrix methods.**
- **This method scales linearly in the number of excess protons and over computational nodes [F. Wang and GAV, JCP (2005)]**

The Breakdown of the SCI Approximation

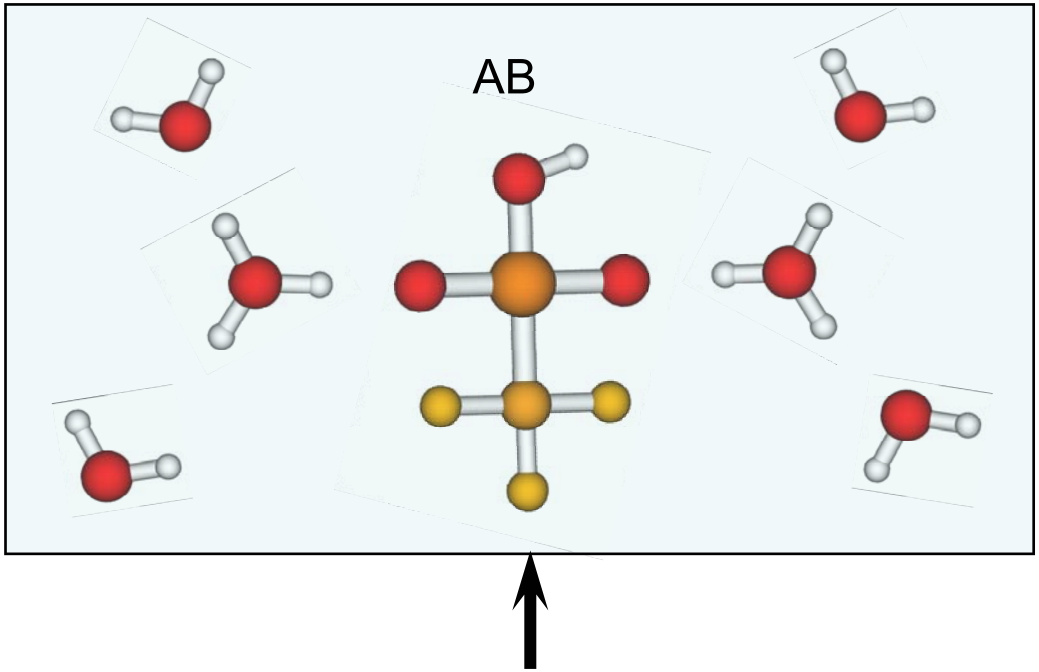
- As two excess protons come close together, the SCI approximation breaks down
  - Interactions between effective particles are less realistic
  - Overlap of complexes becomes problematic



The FPA molecule may draw multiple excess protons unacceptably close together

A Hybrid Approach

- Where the SCI approach breaks down, the Big Matrix approach becomes necessary.



A single supercomplex including both excess protons is needed

- To preserve the computational savings of SCI where possible, we've developed a novel methodology in which the Big Matrix approach is triggered dynamically where it is strictly necessary

Testing Q-HOP on imidazole

- Recently we have also implemented a simplified version of the Q-HOP model[46] into our *Lucretius* MD simulation package and have investigated proton mobility in the Im/Im$^+$/TFSI$^-$ mixtures described above utilizing an in-house developed QC-based force field with many-body polarization. In Fig. 11 we show the mean square displacement of Im and proton (estimated from TST) as well as proton mean square displacement obtained from simulations using the Q-HOP methodology with explicit proton hopping. This figure illustrates that our MD simulations yield a ratio of proton mobility to the vehicular diffusion of its carrier (Im) of 1.5 – 1.8 depending upon the method employed. Experimental measurements on the same system at somewhat lower temperature (303 K) predict that this ratio should be around 1.4. We also find that the estimated proton diffusion obtained using the TST approach differs only by 30% from that yielded by the Q-HOP MD simulations (with explicit proton hopping).

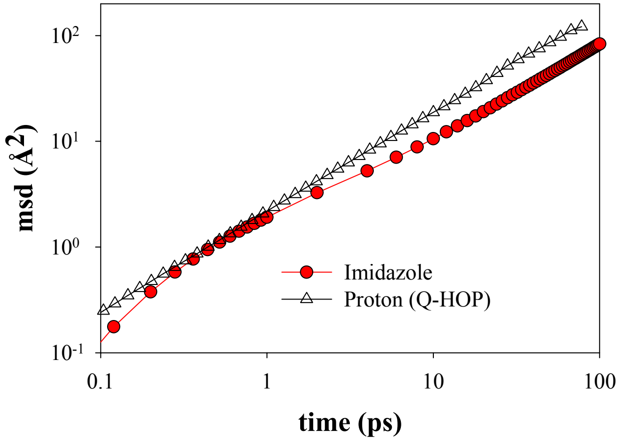


Fig. 11 Mean square displacements (msd) of proton and proton carrier (Im) obtained from simulations of Im/Im$^+$/TFSI$^-$ (60/20/20) mixture at 393 K and atmospheric pressure using classical MD and explicit proton hopping Q-HOP MD simulations.